PHOSPHORUS SORPTION OF SOILS OF SOUTHERN GUINEA SAVANNA ZONE OF NIGER STATE

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DEDICATION

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This research work is dedicated to my beloved wife and children.

CERTIFICATION

This is to certify that this thesis is an original work undertaken by Samuel K. Odega and has been prepared in accordance with the regulations governing the preparation and presentation of thesis in the Federal University of Technology, Minna.

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ABSTRACT

Topsoils (0-20 cm) and subsoils (20-45) of Basement complex and sedimentary materials were studied for their phosphorus sorption characteristics and related to some selected soil properties. A total of 24 samples were examined from Upland and Lowland soils of these lithological formations located in Niger State. Soil properties studied include pH, organic carbon, cation exchange capacity (CEC), particle size, available and total P and total N.

Results showed that besides the clay content of the soils which were generally higher in the subsoil, the sand content, pH, organic matter, CEC, available P and total P and N were lower in the subsoil of both the basement complex soils and the soils derived from sedimentary rock. On the other hand the values of the silt content of the soils produced no consistent trend. The values of P and N in relation to the organic matter content in this study is in agreement with earlier observations that most of soil plant nutrients reside in the organic fraction. In addition, low to very low values of the soil properties studied were recorded in the soils. However, the soils derived from sedimentary sand stones had higher values of both total and available P, while the lower values of organic carbon and clay content were recorded for these soils compared to the basement complex soils.

Statistical treatment of the results revealed the absence of any significant difference between the values of the different soil properties in top and subsoils or lowland and upland of the formations studied. Similarly no significant difference were observed between the values of the different soil properties in top and subsoils or upland and lowland and some selected factors.

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It was also observed that the presence of added phosphorus, Cu, Zn, pH and time greatly influence the amount of P sorbed.

Significant difference shown by some physical and chemical properties of the soils formed on the basement materials and sedimentary parent material showed that parent materials have strong influence on soil formation in Nigerian Guinea Savanna. Lack of significant difference in some chemical properties of the soils show that as the soils get older they start to lose some of their geological attributes.

CHAPTER ONE

INTRODUCTION

The major challenge for agricultural research in tropical Africa is to enable farmers to produce enough food for a rapidly growing population, while sustaining the natural resource base so that future food production will not be curtailed.

In Nigeria, the rainfall pattern in the moist Savanna ecological zone is distinctly seasonal, with wet season often alternating with a prolonged dry season which may last between five and eight months. The climatic zone therefore remains dry for longer period than it is often thought. This feature often limits the ability of the zone to adequately support production of crops and livestock all the year round.

Until recently, enough arable land was available for cultivation and so traditionally, farmers in the tropics could solve the problem of any food shortage or shortage in the production of other agricultural products by abandoning farm **(and** which lost its productivity rapidly under continuous cultivation to revert to natural vegetation and regain its fertility during fallow periods lasting for 5 to 20 years or more. The restorative power of the fallow is linked to the regrowth of deep rooted trees and shrubs and other vegetation that recycle plant nutrient and build up soil organic matter. The farmer will then return to earlier fallow ready to be exploited again or more often to virgin lands, thus avoiding a permanent degradation of soil fertility while keeping food production at a sustainable level. However, since there are not enough arable farmlands or forest to clear easily due not only to increased deforestation for agricultural purpose but also to population pressure and other socio-economic pressure, the other option the farmers had

was to reduce the fallow period and intensify the cultivation of the already impoverished marginal farmlands that are now fragmented by poor land tenure system.

In the Guinea Savanna area of West Africa and in Nigeria in particular, soils are often highly leached and acids, and suffer multiple deficiencies of nutrients. Because of the low fertility status of most of the soils, productivity is quite low. Furthermore, environmental factors, such as the length of the dry season and erratic rainfall can have positive or negative interactions with nutrient elements which complicate the situation considerably. Poor fertiliser practices can further exacerbate the problem. Because the crop is often weakened by these adverse factors, attacks by opportunistic pathogens usually ensue. Thus at a given site a particular crop may be suffering from a number of nutrient deficiencies, complicated interaction with other controllable or uncontrollable factors.

Phosphorus is one of the essential micro-nutrient elements required by crops. It is the second most limiting soil nutrient for crops and plays an important role in dry matter production as evidenced by its primary role in energy mediated reactions (Bawman and Moir (1993). In the highly weathered soils of the tropics P deficiency is a common phenomenon (Fageria and Filho 1987) and it is one of the major limiting factors for crop production in the tropics.

When P fertilisers are applied to the soils, various products are formed. These products are less soluble than the added fertilisers and the nutrients are therefore less available to plants. This phenomenon has been defined as "P sorption or fixation" (Fox and Kamprath, 1970). The fixation capacity of a soil P is a measure of the amount of P needed to satisfy the fixation sites and provide excess for plant uptake.

The efficiency of applied phosphorus remains one of the biggest problems in crop production in the humid tropics. The availability of the applied phosphorus is controlled by the sorption and desorption characteristics of the soils. Although the use of P sorption isotherm for determining P fertiliser practices have been advocated for West African soils (JUO and Fox 1977, Mokwunye 1977.) very limited information exist on sorption characteristics of soils of the Nigerian moist Savanna. Soils of the Nigerian moist Savanna are derived principally from either the basement complex or sedimentary sand stone parent materials with soils formed on basement complex being richer than soils on sand stone because of its higher nutrient reserves and clay content (Eweazor et al 1989).

Assessing a soils capacity to supply nutrients without fertilisation is an important component of research for efficient use of plant nutrients supplied through fertiliser application. However, soil testing as a research tool for fertiliser recommendations has received some level of attention especially in rice cultivation in Nigeria. The calibration of different soils tests with yield responses covering deficiency to sufficiency range is needed to fix critical limits of various nutrients in the soils and plant tissues for the Nigerian moist Savanna. However, rather than the total amount or available phosphorus, the capacity of soil to retain or release phosphorus to the surrounding soil solution is engaging the attention of soil scientists all over the world.

While some detailed studies have been carried out on some Nigerian soils especially in South Western Nigeria but very little attention has been directed at obtaining data on the sorption characteristics of phosphorus for major soil types in Guinea Savanna zone of Nigeria.

This project was planned:

1. To determine some of the physicochemical properties of some soils formed on Basement complex and sedimentary mineral in the Southern Guinea Savanna zone of Nigeria.

- 2. To determine the total and available P in the soils.
- 3. To determine the sorption characteristics of these soils.
- 4. To relate the sorption parameters to the physicochemical properties of the soil.

CHAPTER TWO

LITERATURE REVIEW

2.1 Total and Available Phosphorus

Phosphorus in soil consists of organic and inorganic forms. The total amount of phosphorus in south western Nigerian soils seems to be influenced by parent rock, vegetation and, cropping history. Enwezor and Moore (1966), Adepetu (1970), and Adepetu and Corey (1975) showed that total phosphorus content of South Western Nigerian soil are higher in the rainforest than Savanna grassland. However, forest soils of Basement complex have higher total P than forest on sedimentary material (Uzu et al 1995). Various workers have reported fairly similar ranges of total phosphorus values for South Western Nigerian surface soils, despite differences in methods of determination. Adepetu (1970) reported a range varying from 170 ppm-P on a cropped land in the savannah grassland near Ogbomosho, to 710 ppm-P at a bush fallow site in the rainforest, Ado Ekiti (Uzu et al 1975) reported 217 to 638 ppm-P in the basement complex soil and 191 to 243 in sedimentary rock soils. Also Omotoso 1971 reported a range of 288 to 1172 ppm total P in cocoa soil of South Western Nigeria.

Organic phosphorus accounts for about 20 to 50% of the total P in soils. For savanna soils values that range from 20 to 40% have been reported with most figures varying between 20 to 25%. High values 30 to 54% have however been reported for forest soils (Olaitan and Lombin, 1985). Total P has been shown to be very low throughout Northern Nigeria than in the South, the values varying from 40 to 600 ppm with the mean of 100 ppm (Anon, 1964). Organic P constitutes a significant part of the total P in the plough layer of the South Western Nigerian soils. This has been found to range from 20 to 70% of total P by Omotoso (1971) and 36 to 79% by Adepetu and Corey (1975).

For soils throughout Nigeria, Enwezor and Moore (1966) found a range of 17 to 72%. According to Adepetu (1970) total soil P contained 47% organic P in forest soils and 57% in Savanna soils. In an Iwo soil series of South Western Nigeria, about 25% of the organic P fraction was mineralised during two cropping periods on the field, resulting in a release of about three times as much P as was taken up by maize during the period (Adepetu and Corey, 1977). It was also observed that the P mineralised during cropping in the green house correlated with P uptake make maize crop much better than the inorganic P extraction procedure, indicating the importance of organic P as a predictor of P availability in soils of South Western Nigeria under shifting cultivation. Therefore, attempts to evaluate the amount of available P in soil, for purpose of P-fertiliser recommendation, in soils with considerably high organic matter contents, such as newly cleared fallow land should also take into consideration the contribution from organic phosphorus. This is of special importance in peasant agriculture of South Western Nigeria, in which shifting cultivation still prevail.

2.1.1 Available phosphorus

Availability of phosphorus to plant in Nigerian soils is determined by the forms in which the P exists in soils. Some earlier workers have reported that the magnitude of occurrence of various inorganic-P fractions in Nigerian soils follow the order: occluded-P, iron-P, aluminium-P, calcium-P (Bates and Baker, 1960; Enwezor and Moor, 1966; Uzu 1973). However, the work of Adepetu and Corey (1975)a showed that the order of inorganic-P fractions in South Western Nigerian soils was Fe-P 49%; Occluded-P, 26%, Al-P, 20% and Ca-P, 5%. All the studies agree however that most of soil inorganic-P (native and applied) are found associated with Fe and Al minerals. Adepetu and Corey reported that most of the mineralised P as well as any added P (fertiliser) was

converted to Fe-P and Al-P. Also Udo and Uzu (1972) showed that over 80% of the added P was recovered as Fe-P and Al-P.

Bray No 1 as well as P uptake bay crop correlate significantly with both Fe-P and Al-P (Adepetu and Corey, 1975; Udo and Uzu 1972). Therefore these P fractions are regarded as readily available forms of soil-P in South Western Nigeria soils. These studies also suggest that Al-P is more readily available to crops than Fe-P. In a subsequent study, Udo and Ogunwale (1977) suggested that a high proportion of P claimed to be precipitated as Al-P and Fe-P by earlier workers are infact largely sorbed on surfaces collides or particles of Al and Fe. Udo and Uzu (1972) have earlier suggested that inorganic P in amorphous association with Al or Fe may be more readily available than the crystallised forms.

Phosphorus applied to soils in Nigeria show varying availability to plants because of the difference in the P-fixing power of the soils (Udo and Uzu, 1972); Adepetu 1981; Juo and Fox 1977; Adepetu and Dada 1977). The extent of P-fixation in the soils determine to a large extent, the P-fertilisation requirement for optimum crop performance in South Western Nigerian soils (Anyaduba and Adepetu, 1983). This probably explains why although soils in South Western Nigeria have widespread response to P-fertiliser application, a study by Adepetu and Adeyemo (unpublished 1979) showed that some soils indicated to be P-deficient by chemical extractants showed no crop response Therefore, available-P values as determined by chemical to fertilisation. extractants may sometimes not be sufficient to determine what must be done to remedy P-deficiency that may be predicted by the results of the chemical The interpretation of the available-P values in terms of extractants. fertilisation requirements, in the face of the established critical plant requirements, may require a knowledge of quantity/intensity relationship ie P-buffering capacity or fixing capacity of the soils.

The ability of soil to sorb or fix applied phosphorus has been sued by several workers to characterise south western Nigerian soils (Sobulo 1970, Udo and Uzu, 1972; Adepetu and Dada 1977; Ataga and Omoti, 1978; Fox and Kang, 1978; Adepetu 1981). It is clear from these studies that the adsorption capacity of south Western Nigerian soils are generally less than 600 ppm P and rank low to medium compared to the high P-fixing volcanic as tropical Hawaiian soils that have 2,500-3,000 ppm P-fixing capacity. From the works of Adepetu, (1981), Adepetu and Dada (1977), and Ataga and Omoti, (1978), it was apparent that the relatively sandy savannah soils of south western Nigeria (mostly psametic ustherthent; Apomu series) have lower P-sorption capacity than the more clayey forest soils.

Based on the pioneering work of Beckwith (1965) in Australia, some workers have attempted to determine the amount of **P-fertilisation** requirements of south western Nigerian soil from sorption isotherms, at standard soil solution concentration of 0.2 ppm P (Fox and Kang, 1978; Sobulo, 1977; Atuga and Omoti 1978). This use of 0.2 ppm P as the universal critical soil solution-P seems to be of no practical value or justifiable applicability in Nigerian soils or for that matter soils generally. For according to Adepetu (1975)O and Adepetu (1981), the equilibrium soil solution P concentration, to which the soil could be fertilised to achieve optimum crop yield, varies greatly with soil type and plant species. Also Adepetu and Anyaduba (1983) showed that in five soils studied, optimum yield of cowpea was obtained with an initial soil solution P concentration that varied between 0.12 and 0.27 ppm. The critical solution P concentration was found to be inversely related to the clay content and the P sorption capacity of the soils.

While Enwezor (1979) has suggested about 50% saturation of the Padsorption maximum of the acid south eastern Nigerian soils in order to

achieve optimum yield, the work of Anyaduba and Adepetu (1983) indicated that the higher the P-fixing capacity of the soil, the lower the percentage of this capacity that need to be satisfied with fertilisation in order to achieve an optimum crop yield in south western Nigerian soils. Further study is necessary to determine the percentage saturation appropriate for different Psorption capacity in order to achieve optimum crop yield.

A critical factor in determining the amount of P reaching the root surface is the quantity of P in soil solution which determines the diffusion coefficient of P in the soil. In turn, the amount of PO sorbed by the soil (capacity factor) describes the ability of the soil to replenish solution P (Intensity factor) during plant growth. Phosphate sorption which involves the use of the capacity/intensity approach has been successfully used to predict the P requirement of several crops under different soil conditions (Jones and Benson 1975, Mokwunye 1977, Enwezor 1977).

In the determination of whether or not a soil is deficient in P, it is traditional to concentrate on only the extractable P which is consequently used to determine plant requirement for P. However, in the determination of extractable PO in mineralisation studies, allowance should be made for that portion of the mineralised P that would be absorbed by the soil mineral fraction. This is also true of P fertilisation work in crop production whereby only a small fraction of the added P fertiliser is made available to the growing crop. Fox <u>et al</u> (1973) suggest that P sorption isotherms could be an effective technique for determining P fertiliser rate for crops on soils with both high and low capacities to sorb P since the critical equilibrium solution P for maximum growth, though varies among different crops appears constant for a particular plant growth on soils of different P buffering capacities.

2.2 Soil Test Method for Available P

A number of P extraction methods exist, all of which have some merits and limitations. World wide the most common methods are probably the alkaline bicarbonate extract of Olsen <u>et al</u> (1954) and ammonium fluoride extract (Bray and Kurtz, 1945) with various modifications. The value of these extractants relies on correlation studies that establish the relationship between extract and crops response.

Bray No. 1 extraction for available P determination has been found the most suitable procedure for soil of South Western Nigeria (Bromfield, 1969; Sobulo 1970; Adetunji 1974; Agboola and Corey 1973; Adepetu and Corey 1975; Agboola and Sobulo 1981). Therefore Bray No. 1-P represents the P availability index in these soils.

Soil status of available-P in south-western Nigeria has been documented, summarised and evaluated by Adepetu (1970), Agboola and Corey (1976), Adepetu et al (1970), Adepetu <u>et al</u> 1981, Agboola and Shobulo 1981, Adeoye, (1986) and Sobulo 1982. The summary of all these and other works have been provided in a recent publication of Adepetu (1986).

Though there is considerable importance attached to the use of soil test methods to monitor crop response to applied nutrients and in making fertiliser recommendations, remarkably there is very little information available on soil test methods for soils in the North-eastern Nigeria In his comparison of five different methods for the best approximation of organic P levels in soils of the major ecological zones of Northern Nigeria, Ipinmidun (1973) found Legg and Black ignition method, Mehta <u>et al</u> extraction method and Harrap method (sodium EDTA) as most suitable and reliable. The author, however, recommended Legg and Black ignition method over the other two methods for routine analysis of the soils in the area due to inconvenience and the speed

of the ignition method. Recent studies have also shown that the evaluation of method based on Olsen extractant (sodium bicarbonate 8.5) may be suitable for some of the soils of the savanna areas where soil pH varies between 6.0 and 8.0

2.3 Factors Affecting Phosphorus Availability

The availability of inorganic phosphorus is largely determined by factors such as soil pH, soluble iron, aluminium and manganese containing minerals, available calcium and calcium minerals, amount and decomposition of organic matter and activities of microorganism. The first four factors are interrelated because their effects are largely dependent upon soil pH.

2.3.1 pH and phosphate ions

The availability of phosphorus to plants is determined to no small degree by the ionic form of this element. The ionic form in turn is determined by the pH of the solution in which the ion is found. Thus, in highly acid solutions only the $H_2PO_4^{-1}$ ions are present. If the pH is increased, first the $HPO_4^{2^-}$ ions and finally $PO_4^{3^-}$ ions dominate.

 $H_2PO_4^- = H_2O + HPO_4^2 = H_2O + PO_4^{3-}$

At intermediate pH levels of two of the phosphate ions may be present simultaneously. Thus, in solution at pH 6 both $H_2PO_4^{2-}$ and HPO_4^{2-} ions are found.

In general, the $H_2PQ_4^{2^-}$ ion is considered somewhat more available to plant than $HPQ_4^{2^-}$ ion. In soils however, this relationship is complicated by the presence or absence of other compounds or ions. For example the presence of soluble iron and aluminium under very acidic conditions or calcium at high pH values, will markedly affect the availability of phosphorus. Clearly, therefore, the effect of soil pH on phosphorus availability is determined in no small degree by the various cations present.

2.3.2 Precipitation by iron aluminium and manganese ions

If the same degree of acidity should exist in a normal mineral soil, however, quite different results would be expected. Some soluble ion, aluminium and manganese are usually found in strongly acid mineral soils. Reactions with the $H_2PO_4^-$ ion would immediately occur, rendering the phosphorus insoluble and also unavailable for the plant growth.

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The chemical reaction occurring between the soluble iron and aluminium and the $H_2PO_4^-$ ions probably results in the hydroxy phosphate. This may be represented as follows:

> Al^{3+} + $H_2PO_4^-$ + $H_2O \Rightarrow 2H^+$ + $Al(OH)_2H_2PO_4$ (Soluble) (Insoluble)

2.3.3 Fixation by hydrous oxides

It should be emphasised that the $H_2PO_4^-$ ion reacts not only with the soluble iron, aluminium and manganese but also with insoluble hydrous oxides of these elements, such as limonite and goethite. The actual quantity of phosphorus fixed by these minerals in acid soils quite likely exceeds that due to chemical precipitation by the soluble iron, aluminium and manganese cations.

The compounds formed as a result of fixation by iron and aluminium oxides are likely to be hydroxy phosphates, just as in the case of chemical precipitation. Their formation can be illustrated by means of the following equation if the hydrous oxide of aluminium is represented as aluminium hydroxide



By means of this and similar reactions the formation of several basic phosphate minerals containing either iron or aluminium or both is thought to occur. Since several such compounds are possible, fixation of phosphorus by this mechanism probably takes place over a relatively wide pH range. Also the large quantities of hydrous iron and aluminium oxides present in most soils make possible the fixation of tremendous total amounts of phosphorus by this means.

Thus as both of the equations above show, the acid condition which would make possible the presence of the readily available $H_2PO_4^-$ ion in mineral soils at the same time results in conditions conducive to the vigorous fixation or precipitation of the phosphorus by iron, aluminium and manganese compounds.

2.3.4 Fixation by silicate clays

A third means of fixation of phosphorus under moderately acid conditions involves silicate minerals such as kaolinite, montmorillonite, and illite. Although there is some doubt about the actual mechanism involved, the overall effect is essentially the same as when phosphorus is fixed by simpler iron and aluminium compounds. Some scientists visualise the fixation of phosphorus by silicate minerals as a surface $H_2PO_4^{-1}$ ions. Other investigators have evidence that aluminium and iron ions are removed from edges of the silicate crystals forming hydroxy phosphates of the same general formula as those already discussed. This type of reaction might be expressed as follows:

[A1] +
$$H_2PO_4$$
 + $2H_2O \Rightarrow 2H^{\dagger}$ + $Al(OH)_2H_2PO_4$
(in silicate crystal) (insoluble)

Thus even though phosphate react with different ions and compounds in acid soils, apparently the same insoluble iron and aluminium compounds are formed in each case. Major differences from soil to soil are probably due to differences in rate of phosphate precipitation and in the surface area of the phosphates once the reaction has occurred. 2.3.5 Influence of soil organisms and organic matter on the availability of inorganic phosphorus

In addition to pH and related factors organic matter and micro-organism strikingly affect inorganic phosphorus availability. Just as was the case with nitrogen, the rapid decomposition of organic matter and consequent high microbial population results in the temporary tying up of inorganic phosphates in microbial tissue.

Products of organic decay such as organic acids and humus are thought to be effective in forming complexes with iron and aluminium. This engagement of iron and aluminium reduces inorganic phosphate fixation to a remarkable degree. The ability of humus and lignin to reduce phosphate affixation were effective in releasing phosphorus after it had been fixed as basic iron phosphate. Thus organic decomposition product undoubtedly play an important role in organic phosphorus availability.

2.4 Sorption Reactions

Sorption is defined as a general term used to encompass the process of adsorption, absorption, desorption, ion exchange, ion exclusion, ion retardation, chemisorption and dialysis. It is one of the most important chemical processes in soil. It affects the fate and mobility of nutrients and contaminants in soils and water greatly. It also affects the electrostatic properties of suspended particles and colloids. The electrostatic properties affect coagulation and settling (Stumm 1992; Sparks 1995). Unfortunately, some scientists still use the term adsorption rather than sorption even when they have not definitively ruled out the possibility of precipitation and diffusion phenomena.

Adsorption can be defined as the accumulation of substance or material at an interface between the solid surface and the bathing solution. It determines the quality of plant nutrients, metals, radio nuclide, pesticides and other organic chemicals that are retained on soil surfaces. Therefore it is one

of the primary processes that affect transport of nutrients and contaminants in soils. As the amount of a metal cation or anion sorbed on a surface (surface coverage) increases to a higher surface coverage a surface precipitate can form. When the precipitate consists of chemical species derived from both the aqueous solution and dissolution of the mineral, it is referred to as a co-precipitate

There is a continuum between surface complexation (adsorption) and surface precipitation. At low surface coverage, surface complexation tends to dominate. As surface coverage increases nucleation occurs and results ion the formation of distinct entities or aggregates on the surface. As surface loading increases further, surface precipitation becomes the dominant mechanism. Diffusion of molecules or ions through crystalline solids is extremely slow at 25°C so that the term solid diffusion should greatly be interpreted to mean transfer through micropores faults or interfaces of the solid rather than through the lattice itself (Mc Bride 1994).

2.5 Desorption

The release of adsorbed species is often referred to as desorption. While most studies in environmental soil chemistry have focused on the adsorption or sorption of ion and molecules on soils, the desorption process is also extremely important. This is particularly true for soils that are already contaminated. To predict the fate and mobility of contaminants in such soils and to develop sound and cost-effective remediation strategies, information on desorption is required. For example, if it is found that the contaminant is bound strongly to the soil and little if any desorption occurs, or if the desorption process is extremely slow, movement into ground water may not be a problem. However, depending on the use of the soil, the "persistence" of the contaminant in the soil may present a problem for

homesite construction of crop production. On the other hand, if desorption is effected easily the contaminant could become mobile and contaminate water supplies. However, its ease of desorption could be an advantage in using remediation techniques such as leaching to decontaminate the soil. Without question, a great need in sorption research is more research on desorption phenomena.

It is often observed that desorption is a more difficult process than adsorption and that not all of the adsorbate is desorbed ie. the reactions appear to be irreversible. Such apparent irreversibility is commonly referred to as hysteresis or non singularity. In such cases the adsorption and desorption isotherm corresponding to the forward and backward reactions would not coincide (Verburg and Baveys 1994). Such hysteresis is often observed in both organic chemical and metal reactions with natural materials. There are a number of reasons that "non-real hysteresis" may be observed, including artifacts related to experimental conditions such as failure to attain an adsorption equilibrium (Sparks 1989) and to pre-wash the sorbant (to remove fine particles, etc) before initiation of sorption and subsequent desorption studies, and chemical and microbial transformation that occur during a particular experiment.

However, it appears that "real hysteresis" can occur and this is affected dramatically by the type of absorbant especially humic substances and the time over which the adsorption process has occurred.

2.6 Sorption Model and Kinetics of Sorption Reaction

The scientific literature is replete with investigations or various aspects of adsorption and desorption of plant nutrients, metals, radio-nuclides and organic chemicals. Many of these studies have used microscopic approaches such as adsorption isotherms, empirical and semi-empirical equations (eg. Freundlick Langmiir) and surface complexation modes (eg. constant capacitance, triple layer) to describe desorption. While these investigations have been useful, no real mechanistic information about sorbate retention/release can be gleaned.

It should be recognised that adsorption isotherm are purely descriptions of microscopic data and do not definitely prove a reaction mechanism. For example the conformity of experimental adsorption data to a particular isotherm does not indicate this is a unique description of the experimental data and that only adsorption is operational. Thus one cannot differentiate between desorption and other sorption processes such as surface precipitation, and surface diffusion using an adsorption isotherm even though this has been done in the soil chemistry literature.

Surface complexation model are chemical models that are based on molecular descriptions of the electrical double layer using equilibrium derived desorption data (Goldberg 1972). Thus no mechanistic information on sorption can be obtained. Surface complexation models often describe sorption data over a broad range of experimental conditions such as varying pH and ionic strengths and have been used widely to describe metal cation and anion sorption reaction on oxide clays and soils and organic ligand and competitive sorption reactions on oxides. However, surface complexation model employ an array of adjustable parameters to fit experimental data and it has been shown that often sorption data will equally well fit a number of the models (eg Westall and Hoihl, 1980).

Another major disadvantage of the surface complexation models and of most equilibrium-based model, is that three dimensional surface complexes are not accounted for or differentiated. An exception is the research of Farley <u>et al.</u> (1985) and James and Healey (1972), who considered surface precipitation

in successfully modelling sorption of hydrolysable metal ion. Infact Farley <u>et</u> <u>al</u> (1985) include prescription in a thermodynamic sorption model that is a surface complextion model. Arguably, one of the major needs in modelling sorption on soils and natural materials is to include surface precipitation and other non-adsorption phenomena as part of the model description and prediction. This is particularly important as recent research is definitely showing that multinuclear surface species occur on an array of natural surface at low surface coverage and over rapid time scales (Fendorf <u>et al</u> 1994a, O Day et al 1994a and b, Papelis and Hayes 1996; Scheidegger et al 1996a, b, c and d).

To ascertain precise sorption/release mechanism one must employ approaches that yield atomic/molecular information. Such information can be obtained using spectroscopic/microscopic techniques. The rate of sorption/desorption reactions also provide significant information on possible mechanism. Thus a knowledge of the kinetic and mechanism of sorption/release reactions is imperative in predicting the fate and mobility speciation and risk assessments of ions and molecules in soil and aqueous environments.

Accordingly, this critical view will focus on past and future research on non equilibrium aspects of sorption/desorption and the confirmation of reaction mechanism using insitu atomic/molecular resolution surface technique.

Without question microscopic sorption phenomena are exceedingly important in soils. However, most soils are seldom ever at equilibrium. Moreover, while equilibrium sorption data can be used to propose reaction mechanisms definitive mechanism cannot be obtained and time dependent or kinetic data are not determined.

Many soil chemical processes are time dependent. To fully understand the dynamic interactions with soils of metals, radio nulides pesticides

industrial chemicals sludge and manures and fertilisers and to predict their fate with time a knowledge of the kinetic of these reactions is important. Certainly an important factor is controlling the rate of many soil chemical sorption reactions in the type and quality of soils components. For example ion exchange adsorption reaction are usually more rapid on clay minerals such as kaolinite and mica. This is attributed to the readily available sites for desorption on kaolinite compared with the multiple types of sites on vermiculite and micas. External planner, edge and interlayer sites exists on the surfaces of vermiculate and micas with some of the latter partially or totally collapsed. High rates of reaction are often observed for external sites, intermediate rates on edge sites and low rates on inter-layer sites (Jardime and Sparks 1984).

The type of surface complex ie. outersphere versus innersphere (monodentate vs. bidentate) also affect the rate and reversibility of sorption reactions. Oversphere complexation is usually rapid and reversible, whereas innershpere complexation is slower and may appear to be irreversible (Sparks 1995).

The kinetics of metal and organic sorption reactions on soils and soil components are often characterised by a rapid, followed by a slow reaction. The rapid reaction is most probably ascribable to chemical reaction and film diffusion processes. For example, sorption reactions of certain metal cations such as Cu^{2t} and oxy anions such as boratte, arsenate, molybdate, selenite, selenate and chromate on goethite occur on millisecond time-scale as measured by pressure jumpo relaxation (Zhang and Sparks 1989, 1990, Grossl et al 1994). Sorption of metal on humic is also rapid. Half live for Pb^{2t}, Cu^{2t} and Zn^{2t} sorption on peat ranged from 5 to 15 sec. (Benzl et al 1976) film diffusion was assumed to be rate limiting step.

The slow sorption reaction occurring overtime scales of days and longer has been attributed to diffusion into microscope of inorganic minerals and humic components sites of lower reactivity, and surface precipitation (Sparks 1996a and b). However, the mechanism is not clearly understood and the absence of high vacuums) surface spectroscopic/microscopic techniques.

2.7 Phosphorus Adsorption Isotherm

The relationship between the amount of P adsorbed per unit mass of soil and the equilibrium P concentration bathing the soil at a constant temperature has been described by several adsorption isotherms. The main motivation for describing adsorption curves were to identify the soil constituents involved in adsorption, predict the amount of fertiliser needs of soils to meet the demand of plant uptake for an optimum yield (Fox and Kamprath 1970, Fox and Kang 1978, Kalages et al 1988), study the nature of adsorption process (Barrow 1984, 1987).

Although the use of P-sorption isotherms for determining P fertiliser requirements and for establishing P fertilisation practices has been advocated for West African soils (Mokwunye 1977, Ayodele <u>et al</u> 1984), there is a dearth of information on the sorption characteristics of major soils of Nigerian moist savanna.

CHAPTER THREE

EXPERIMENTAL

3.1 Geographical Zone of Soil Samples Studied

The Savanna region shows considerable differences, and forms belt related to climate and soils. It is characterised by grass vegetation either tall or short, annual or perennial and by varying amounts of trees though the trees are always sparse enough to allow light to reach the ground and give a grass cover and in some types of savanna are both small and very scattered.

The project area lies between latitude 8° and 11°20'N longitude 4°30' and 7°4'E with the land area of 7,424,400 million hectares covering 8% of the total land area of the country. About 85% of the land is arable which also represents about 6 million hectares of land.

The climate of the area is of a typical middle belt. It experiences distinct dry and wet seasons. The wet season lasts for about 200 days and starts from April. The average rainfall is 1227 mm with July and September recording the highest rain of 226.3 mm and 248.8 mm respectively. The weather at this time is humid with potential evapotransportation of 1350 mm. The cold harmattan winds usher in the dry season which gradually becomes hot between March and May just before the rain sets in.

With seasonal variations, the atmospheric temperature is relatively constant over the study area. The maximum temperature is relatively constant over the study area. The maximum temperature which does not exceed 38°C is between March and April. The lowest temperature occurs usually in December and January. Thus the study area is blessed with moderate climatic condition throughout the year.

The whole area lies in natural vegetation known as the southern Guinea Savanna. This zone is characterised predominantly by grassland with scattered tall trees and shrubs. Due to population concentration of this zone human activities have profoundly modified local vegetation of the study area. The local vegetation shows high growing grasses which have been shortened in many places by seasonal bush burning.

The sedimentary locations consist of level to gently sloping plains with occasionally flat topped hills capped with iron stones. The elevation of the plains is about 150 m above sea level. The slope is between 1 and 3% with no major stream in the area but the area is drained by tributaries of the River Niger. The basement complex consist of an area of rocks and valleys. Occasionally small steep mesas rise between 20 to 25 m above the well drained gently sloping lands between valley. The scenery is fairly uniform since the lithology and rock structure are not greatly variable.

The geology and soils of the area consist of soils of two lithological formations (Basement Complex and Sedimentary Soils). The sedimentary soils comprise coarse sands or sandy clays with essentially horizontal beds of weakly cemented clays, silt, stones and sandstones. The soil in the area is made up of upland soils and depositional soils. The upland soils overlive thick sandstone, and the major part consist of gently undulating plains with very deep soils. Most soils were classified as ferrisols which normally occupy the high elevation, of the terrain and at lower levels (steep slopes) pass into ferruginous topical soils which in the valleys are replaced by weakly developed soils or depositional and hydromorphic soils. Soils in depositional areas are weakly developed alluviums or hydromorphic soils.

3.2 Soil Investigation

Soils from two major lithological formations, basement complex and sedimentary soils were used for this study. Six different locations with

homogeneous soils properties were chosen for this investigation. A total number of twenty-four soil samples were taken from these locations. These include Minna, Suleja and Abuja for Basement Complex and Bida, Mokwa and Enagi for Sedimentary soils. In each location bulk soil samples were collected from 0-20 cm (top soil) and 20-45 cm subsoil for both upland and lowland. 3.2.1 Laboratory studies

The soil samples were air-dried under shade and ground to pass through a 2 mm sieve. For organic carbon and total Nitrogen determination the samples were further sieved to pass through a 0.5 mm sieve and then kept in labelled polythene bags from where portions for the different experiments were taken.

3.2.2 Soil pH determination (electronic method)

pH is defined as the negative logarithm of the hydrogen ion concentration.

$$pH = -log[H^{\dagger}]$$

pH is perhaps the most commonly measured soil characteristics. It is certainly the most widely used criterion for judging whether a soil is acidic or alkaline pH however changes with temperature.

pH can be measured calorimetrically or electrometrically. Calorimetric measurement is the least expensive, however it is subject to interferences by water, colour turbidity, colloidal matter, high saline content, oxidant and redundant. For these reasons calorimetric method should be used only when an estimate of pH is needed or spot or location. The electronic method was used in the present determination.

Materials and Reagents

pH meter [model Kent Eil 7045/46[15 VA]] Beakers (50 cm³), mettler, balance, deionised distilled water.

0.01 mol/dm³ CaCl₂

Prepared by dissolving 1.10g $CaCl_2$ salt with deionised distilled water in a 1 dm³ volumetric flask and the solution was made up to mark. Standard Buffer Solution (pH₄ and pH₉)

Each tablet of pH_4 and pH_9 was ground and dissolved in 100 cm³ volumetric flask and made up to mark.

Procedure

10g of soil was weighed into 100 cm³ beaker. 25 cm³ of water was added and allowed to stand for 30 minutes, stirring with a glass rod at interval.

The pH meter was standardised with buffer solution of pH_4 and pH_9 . Then the solution was transferred into a 100 cm³ beaker and the electrodes were immersed in the solution. The electrodes were rinsed with distilled water after each determination. The measurements were repeated using 1:2 soil calcium chloride solution suspension.

3.2.3 Particle size determination (hydrometer method)

Apparatus

1. Multimix machine with baffled "milk shake" cups.

- Glass cylinder of approximately one litre capacity for soil suspension during setting.
- 3. Special hydrometer for measuring the density of soil suspension.
- 4. Thermometer for measuring temperature of the suspension.
- 5. A 2 mm sieve.

Reagent

Sodium hexametaphosphate dispersing agent (Calgon 5%), prepared by dissolving 50g of the salt in 1000 cm^3 of distilled water.

Procedure

50g of soil was weighed and transferred to a "milk shake" mix cup. 50 cm³ of sodium hexametaphosphate was added along with 1000 cm³ of distilled

water. This was mixed with a stirring rod and the samples were allowed to settle for 30 minutes. The soil suspension was stirred for 15 minutes with the multimix machine and the suspension was transferred from the cup to the glass cylinder. With the hydrometer in the suspension distilled water was added to lower line and the volume became 1130 cm³. Upper line 1250 cm³ was used when 100g were used and the hydrometer was removed.

The top of the cylinder was covered with the hand and inverted several times until all the soils was in the suspension. The cylinder was then placed on a flat surface and the time was noted. Soil hydrometer was immediately placed into the suspension. The hydrometer was slided slowly into the suspension until hydrometer was floated. After the cylinder had settled down, the first reading of the hydrometer was taken at 40 seconds, the hydrometer was removed and the temperature of the suspension was recorded with a thermometer. After the first hydrometer reading, the suspension stood for three hours and the second reading was recorded. The temperature of the suspension was also recorded. The first reading measured the percentage of silt and clay in the suspension.

Results were corrected to a temperature of 68°F. For every degree rise about 68°F, 0.2 was added to hydrometer reading before computation and for below 68°F, 0.2 was subtracted from the hydrometer reading.

The fraction of sand, silt and clay were then calculated using the following equation

 $C = R - R_L + (0.36T)$

where

C = corrected hydrometer reading R = hydrometer sampling reading R_L = Hydrometer blank solution reading

3.2.4 Organic Carbon/matter determination by the Wakley-Black method (Olsen, 1965

The method was used to measure the active and decomposable organic matter in the soil. The carbon present in the soil residues and humus is oxidised but the carbon present as graphite and charcoal is not oxidised. Apparatus

Burette 25 cm³, automatic pipette and Erlenmeyer flask 250 cm³. <u>Reagents</u>

<u>0.5 mol/dm³K₂Cr₂O₂:</u>

24g of $K_2 Cr_2 O_7$ was weighed approximately in a 500 cm³ volumetric flask and made up to mark with water.

$0.5 \text{ mol/dm}^3 \text{ FeSO}_4$:

140g of anhydrous $FeSO_4$ was weighed accurately into 1000 cm³ volumetric flask and made up to 900 cm³ with water, 15 cm³ of concentrated H_2SO_4 was added and made up to 1000 cm³ with water.

Concentrated H₁SO₄ (98% V/V)

Barium Diphenylamine Sulphonate (0.16%)

Procedure

1g of soil sample was weighed into a conical flask. 10 cm³ of 0.5 mol/dm³ $K_2Cr_2O_7$ was measured into the sample and swirled properly to mix with the dichromate solution. 20 cm³ of concentrated H_2SO_4 was added to the mixture and mixed properly. It was then allowed to cool. 100 cm³ of distilled water was then added. 5 to 6 drops of barium diphenylamine sulphonate indicator was added. The resulting mixture was titrated with 0.5 mol/dm³ FeSO₄ to a dark-green end-point. A blank titration was also carried out. 3.2.5 Determination of exchangeable acidity by KCl extraction method

Reagents

Distilled water

1 mol/dm³ KCl:

Prepared by dissolving 37.28g of the salt in 500 cm³ volumetric flask and making it up to mark with water.

0.1 mol/dm³ NaOH:

Prepared by dissolving 4g of the salt in 100 cm³ volumetric flask and making up to mark with water.

Phenolphthalein Indicator

Procedure

5g soil was weighed into different conical flasks and 100 cm³ of KCl solution was added into each flask, stoppered and secured properly on the mechanical shaker and left to shake for one hour. Each was filled into a 100 cm³ volumetric flask and made up to mark using the 1 mol/dm³ KCl solution. Titration for H⁴ and Al³⁺

100 cm³ of distilled water was poured into a 250 cm³ standard volumetric flask. 25 cm³ portion of the KCl extract was added using 25 cm³ pipette. Five drops of phenolphthalein indicator were added and titrated to a permanent pink using 0.1 mol/dm³ NaOH solution.

The pink end point was destroyed with drops of 0.1 mol/dm³ HCl and 10 cm^3 of NaF which is complexing agent for Al was added. With some samples, the colour reverted back to pink indicating the presence of Al. This was further titrated with 0.05 mol/dm³ HCl to colourless for exchange Al.

The amount of base used is equal to the amount of acidity $(H^{\dagger} \text{ and } Al^{J^{\dagger}})$ was expressed in millimole, mmol) per kg. soil using the formula

M x
$$v_2$$
 x $\frac{100}{20}$ x $\frac{1000}{S}$

where

M = concentration in mol/dm³ V = volume of NaOH used S = original mass of soil
3.2.6 Determination of exchangeable bases K^{\dagger} , Na^{\dagger} , $Ca^{2\dagger}$ and $Mg^{2\dagger}$ <u>Reagents</u>

0.02 mol/dm³ of Na-EDTA:

Prepared by dissolving 7.44g of the salt in 1000 cm³ volumetric flask and making up to the mark with distilled water.

1.0 mol/dm³ Ammonium Acetate:

Prepared by dissolving 64g of the salt in 1000 cm³ volumetric flask and making it up to mark with distilled water.

5 cm³ NH₄Cl/NaOH Buffer Solution:

Prepared by dissolving 7.5g NH_4Cl in 142 cm³ NH_4OH , and diluting to 250 cm³ with distilled water in volumetric flask.

procedure

5g of the 2mm mesh sieved air-dried soil samples were weighed and transferred into milk shake bottles. 100 cm^3 of 1 mol/dm^3 Ammonium acetate (neutral) solution was added to each of the different samples and were shaken on a mechanical shaker for 1 hour. Filtration was continued unit 100 cm³ of each leachate was obtained.

 25 cm^3 of NaH₄Cl/NH₄OH buffer solution was added to 50 cm^3 distilled water in a 250 cm³ conical flask. 20 cm^3 of each of the soil sample extracts was added into each of the conical flask, about 5-6 drops of Erichrome Black T indicator was added and these solutions were each titrated with 0.02 mol/dm³ disodium salt of EDTA until a bright blue end point was obtained.

This titration was a measure of total Ca^{2+} and Mg^{2+} in the sample solution, and these ions were calculated in mol. Kg^{-1} soil by using the following expression:

 $M \times V_2 \times \frac{100}{20} \times \frac{1000}{S}$

where

 $M = \text{concentration of EDTA in mol/dm}^{3}$ V = volume of EDAT used S = mass of soil sample used $Meg Ca^{2t}/Mg^{2t} \text{ soil } = A$ $Meg Ca^{2t}/100g \text{ soil } = B$ $\therefore Mg^{2t}/100g \text{ soil } = A - B$ = C

Cation Exchange Capacity (CEC)

CEC was determined by summation of the exchangeable bases (Na^{\dagger}, K^{\dagger}, Ca^{2t} and Mg^{2t}) and exchangeable acidity (Al^{3t} and H^{\dagger}).

Percentage Base Saturation

Base saturation was calculated by dividing the total exchangeable metallic cations by cation exchange capacity (CEC).

3.2.7 Available P determination by Bray No. 1 method Bray and Kurtz, 1945 Apparatus

Volumetric Flask (1000 cm³)

Polythene Bottles

Mechanical Shaker

Centrifuge

Reagents

1 mol/dm³ Ammonium Fluoride (NH4F):

Prepared by dissolving 37g of ammonium fluoride (NH_4F) with distilled water in a 1 dm³ volumetric flask and the solution was made up to mark. <u>0.5 mol/dm³ HCl</u>:

Prepared by diluting 21.5 cm³ Conc.HCl to 500 cm³ with distilled water under fume cupboard.

Extracting Solution

Prepared by adding 15 cm³ of 1 mol/dm³ NH_4F and 25 cm³ of 0.5 mol/dm³ HCl to 460 cm³ of distilled water.

Stanous Chloride (SnCl₂·2H₂O) Stock Solution:

This was prepared by dissolving 10g Stanous chloride in 25 cm³ of conc. HCl. The solution was then stored in a dark polythene bottle in a refrigerator.

Ammonium Molybdate (NH₄)₆MO₇O₇₄ · 4H₂O:

Prepared by dissolving 15g of ammonium molybdate in 350 cm³ of 10 mol/dm³ HCl in 1 dm³ volumetric flask. It was cooled to room temperature and diluted to 1 dm³ with distilled water.

Stanous Chloride (SnCl₂·2H₂O) dilute Solution:

1 cm³ of SnCl₂ stock solution was measured and mixed with 333 cm³ of distilled water. Fresh solution was made every 2 hours as needed.

1g of air-dried sample (2mm sieved) was weighed into a 15 cm³ centrifuge tube and 7 cm³ of the extracting solution was added and left to shake for 1 minute on a mechanical shaker. The suspension was centrifuged at 2,000 rpm for 15 minutes. 2 cm³ of the clear supernatant solution was measured into a 20 cm³ test tube. 5 cm³ distilled water and 2 cm³ of ammonium molybdate solution were added. The content was mixed properly and 1 cm³ of SnCl₂·2H₂O dilute solution was added and mixed again.

After 5 minutes but not later than 20 minutes, the percentage transmittance was measured on the electrophotometer at 660 mµ wavelength. **S**tandard curve within the range of 0-1 µg P/cm³ (or ppm P) was prepared. The optical density (OD) of standard solution was plotted against the µg P/cm³ (or ppm P) was plotted and the content of extractable P in soil was calculated. **3.2.8 Total phosphorus in soil (extraction by perchloric acid digestion method)** Reagent

Perchloric aid (HClO₄) 72%

Procedure

2g of 100 mesh soil was approximately weighed into 300 cm³ conical flask and 30 cm³ of perchloric acid (HClO₄) was added.

The mixture was digested at 130°C in a fume cupboard until the solution appeared colourless with a slight increase in temperature.

As digestion was completed, white fumes of HClO_4 appeared and silica became white (note taken to dryness). The flask was removed and cooled sufficiently to avoid spattering. 50 cm³ of water was added and the resulting solution was filtered through filter paper into a 250 cm³ volumetric flask. The flask and residue were washed into the main solution and brought to mark.

Standard curve within the range of $0-1 \ \mu g \ P/cm^3$ (or ppm P) was prepared. Optical density (OD) of standard solution against the $\mu g \ P/cm^3$ (or ppm P) was plotted and the content of extractable P in soil was calculated. 3.2.9 Total nitrogen in soil (micro-Kjeldahl method)

Apparatus

Macro-Kjeldahl digestion Distillation Apparatus

Macro-Kjeldahl flasks 500 cm³ and 750 cm³

Reagents

Kjeldahl Tablet

<u>10 mol/dm³ NaOH Solution:</u>

420g of sodium hydroxide pellets was weighed in a heavy walled (1 dm³) pyrex flask. 500 cm³ of distilled water was added and the flask was swirled until the alkali was dissolved. The solution was cooled with a stopper in the neck of the flask to prevent absorption of the atmospheric CO_2 and was allowed to stand for several days to allow any Na_1CO_3 present to settle. The clear supernatant liquid was siphoned into a large pyrex bottle which contained about 1 dm³ of CO_2 -free water and was marked to indicate a volume of 5 dm³. The solution was made up to 5 dm³ by adding CO_2 -free water. The bottle was swirled vigorously to mix the contents and the neck was fitted with some arrangement which permitted the alkali to be stored and dispensed with protection from atmospheric CO_2 .

Mixed Boric Acid-indicator Solution:

80g of Boric acid was dissolved in $3,800 \text{ cm}^3$ of distilled deionised water by heating on a hot plate of low heat. The solution was cooled and 80 cm^3 of the mixed indicator was then added (separately by dissolving 0.099g of Bromocresol green and 0.066g of methyl red in 100 cm³ of 95% ethanol). 0.1 mol/dm³ NaOH was added through a burette until the solution became reddish purple in colour (pH 5.0). The solution was diluted to 4 dm³ with distilled water and was mixed thoroughly before use.

Procedure

5g of air-dried soil sample (0.5 mm sieved) was weighed to a dry 500cm³ macro-Kajeldahl flask. 20 cm³ of distilled water was added. The flask was swirled for a minute and then allowed to stand for 30 minutes. One tablet of mercury catalyst was added and 30 cm³ of Conc. H_2SO_4 through an automatic pipette. The flask was cautiously heated at low heat on the digestion stand. The heat was increased until the digest was cleared after the water had been removed and frothing had ceased. The flask was allowed to cool and about 100 cm³ of distilled water was added slowly to the flask. The digest was carefully transferred into another clean macro-Kjeldahl flask (750 cm³). All sand particle were retained in the original digestion flask because sand can cause severe bumping during Kjeldahl distillation. The sand residue was washed four times with 50 cm³ of distilled water and the aliquot was transferred into the same flask. 50 cm³ H₁BO₁ indicator solution was added

into a 500 cm³ Erlenmeyer flask which was then placed under the condenser of the distillation apparatus. The end of the condenser was about 4 cm above the surface of the H_1BO_1 solution.

The 750 cm³ Kjeldahl flask was attached to the distillation apparatus. The funnel stop cork of the distillation flask was opened and about 50 cm³ of 10 mol/dm³ NaOH was poured through it. The condenser was kept cool (below 30° C) and a sufficient cold water was allowed to flow through and the heat was regulated to minimise frothing and also to prevent suck-back. 150 cm³ distillate was collected and the distillation was stopped. The NH₄N in the distillate was determined by titrating with 0.01M standard HCl (or H₂SO₄) using a 25 cm³ burette graduated at 0.1 cm³ intervals. The colour change at the end point was from green to pink. The percentage N content in soil was calculated

Formula:
$$\frac{\% \text{ Total N} = (T_s - T_b) 0.014 \times 0.01 \times D \times 100}{W \times L}$$

where

3.3 Sorption Studies

3.3.1 Concentration dependent absorption

Apparatus

Standard volumetric flask (1000 cm^3)

Standard volumetric flask (250 cm³)

Centrifuge

Shaker

Reagent

1000 mg/dm³ PO₄⁻³ Solution:

Prepared by dissolving 4.39g of the KH_2PO_4 with extracting solution (CaCl₂ solution) in a 1000 cm³ volumetric flask and diluting to mark with more water.

 0.5 cm^3 , 1.25 cm^3 , 2.5 cm^3 and 5 cm^3 of stock solution were each pipetted into 250 cm³ volumetric flask and made up to mark with CaCl₂ solution to give 0, 2, 6, 10 and 20 mg/dm³ PO₄⁻³ solution.

Procedure

20 cm³ of each of the dilute P standard solution was added to 1g of separate soil samples and shaken on a reciprocating shaker at 30°C for 2 hours at the end of which period the mixture was filtered through a Whatman No.41 filter paper. The residue was left on the filter paper overnight to allow the proper drainage of the filtrate. The filtrate was then collected in a second polypropylene bottle. 2 to 3 drops of toluene was added to the filtrate in order to arrest microbial growth. P remaining in the solution was determined by molybdate blue method (Murphy and Ricley 1962). The difference between the added P and solution P was taken as the sorbed P which is also the amount of P lost from the solution during the shaking.

Calculation for extractable P

ppm P in solution x $\frac{10}{2}$ x $\frac{7}{1}$

3.3.2 pH dependent adsorption

Apparatus

Standard volumetric flask (100 cm³) pH meter (model Kent Eil 7045/46 (15 VA) Beakers (50 cm³) Mettler Balance

Reagent

100 mg/dm³ KH₂ PO₄ Solution:

Prepared by dissolving 4.39g of the salt with extracting solution $(0.01 \text{ mol/dm}^3\text{CaCl}_2)$ in 1000 cm³ standard volumetric flask and diluting to mark with the same solution.

0.01 mol/dm³ CaCl²:

Prepared by dissolving $1.11g \text{ CaCl}_2$ in 1000 cm³ volumetric flask with distilled deionised water and diluted to mark.

Procedure

 20 cm^3 of PO₄³⁻ solution was added to 1g of soil sample. The pH of the suspension was then adjusted to the required pH value of 4, 6, 7.5 and 8.5 using either 1 mol/dm³ HCl or NaOH. The mixture was then shaken on a reciprocating shaker at 30°C for 2 hours at the end of which period the mixture was filtered through a Whatman No.41 filter paper. The residue was left on the filter paper overnight to allow for proper drainage. The filtrate was then collected in a second polypropylene bottle. 2 to 3 drops of Toluene was added to the filtrate to arrest microbial growth. P remaining in the solution was determined by molybdate blue method (Murphy and Riley, 1962). The solution P was taken as the sorbed P which is also the amount of P lost from the solution during the shaking.

3.3.3 Time dependent

1g soil sample was weighed into 50 cm³ polypropylene bottle 10 cm³ portion of 0.01 mol/dm³ CaCl₂ solution which serve as extracting solution was added to the soil in each bottle followed by 20 cm³ of 100 mg/dm³ as (KH_2PO_4) working solution. A few drops of toluene were added to suppress microbial growth. The bottles were stoppered and shaken on the reciprocating shaker for 5, 30, 60, 100 and 120 minutes. At the end of every shaking time, the

suspension was filtered into a second 50 cm³ polypropylene bottle and P remaining in the solution was determined by Molybdate blue method (Murphy and Riley, 1962). The difference between added P and solution P was taken as the sorbed P which is also the amount of P lost from the solution during the shaking.

CHAPTER FOUR

RESULTS, DISCUSSIONS AND CONCLUSIONS

4.1 The Physicochemical Characteristics of the Soils

The physicochemical characteristics which were determined in the basement complex and sedimentary soils of southern Guinea Savanna include soil particle size, pH, organic carbon content, cation exchange capacity (CEC). available P, total P and total N (Table 1).

4.1.1 Soil pH

The pH in $(CaCl_2)$ values for topsoils and subsoils of basement complex ranged from 4.70 to 6.51 and 4.28 to 5.64 with mean values of 5.49 and 4.84 respectively. The mean values indicate weakly acid to very weakly acid reactions respectively. Those of the sedimentary materials ranged from 4.95 to 5.34 and 4.25 to 5.34 with mean values of 4.95 and 4.58 respectively. Mean values indicate very weakly acid for both top and subsoils. These results corroborate the findings of Klinkenberg and Higgins (1968), in their study of Nigerian Savanna region. It has been observed by Ezenwa, (1988) that the type of vegetation is likely to have a significant influence on soil reactions. It is quite interesting to note also that the subsoils are generally more acidic than the topsoils. These observations could be due to the fact that since hydrogen ion (H⁺) is a mobile ion, it is possible that the leaching effect must have carried it from the topsoils to the subsoils.

The low pH in the soil derived from sedimentary rock might be due to the more acidic nature of the parent material.

4.1.2 Particle size distribution

The particle size distribution for top and subsoils of basement complex showed that the percentage clay ranged from 10.12 to 24.40 and from 14.48 to

24.00 with mean values of 13.94 and 18.53 respectively. The percentage silt ranged from 1.52 to 15.52 and from 4.56 to 15.18 with mean values of 8.09 and 9.13 respectively. For the sedimentary soils, the values ranged from 8.60% to 16.00% topsoil and from 8.60% to 21.40% subsoil with mean values of 11.97% and 14.30% respectively. The percentage silt ranged from 3.32 to 10.43 and from 1.78 to 16.56 with mean values of 6.32 and 7.95 respectively. The results showed that sedimentary soils predominantly contain more sand particles than those of the basement complex. This could be attributed to the nature of the parent materials of sedimentary rock, Nupe sandstone which contain high percentage quartz. This suggestion is in line with the observation of Young (1976) that grain size of a parent material was the main determinant of soil texture.

4.1.3 Organic carbon

The percentage organic carbon content of top and subsoils of basement complex ranged from 0.44 to 0.75 and 0.37 to 0.81 with mean values of 0.70 and 0.65 respectively. Those of the sedimentary sandstones ranged from 0.43 to 0.75 with mean values of 0.63 for the topsoil and 0.43 to 0.63 with a mean value of 0.54 for subsoil. It is observed that organic carbon content of the basement complex soils are higher than those of the sedimentary sandstones. The same observation was reported by Yisa (1998) for soils of the same area. The organic carbon content of soils as reported by Ezenwa (1985) is higher in soils derived from basement complex than those of the sedimentary sandstones. The low organic carbon contents of soils as earlier mentioned may be attributed to occasional destruction of the leaf litter by wild fires. Besides, it could be due to rapid humification. According to Ojanuga (1971) low organic matter contents of tropical soils were due to rapid humification and also due to the low polymerisation of humic compounds into stable

compounds that are commonly accumulated as complexes with soil clays. The report further indicated that high annual rainfall of more than 1250 mm and the permeable horizons of those well drained soil hampered the polymerisation of humic compounds by transporting them downwards as rapidly as they were formed.

4.1.4 Total nitrogen

The total nitrogen contents of top and subsoils of basement complex ranged from 0.32% to 0.63% and from 0.30% to 0.58% with mean values of 0.55% and 0.47% respectively. In the sedimentary soils the total nitrogen contents ranged from 0.32% to 0.63% and from 0.31% to 0.62% with mean values of 0.55% and 0.41% respectively.

The total nitrogen of these lithological sites were very low. This is not unconnected with the corresponding low organic matter contents in these areas of study. This is in agreement with the findings of Jones (1973) who studied 295 well drained soils of the Savanna region of West Africa and observed that total nitrogen ranged from 0.08% to 0.29% with a mean value of 0.05% and concluded that Savanna soils were generally low in total nitrogen, N. He attributed this low nitrogen content to the predominantly sandy nature of the soils and relatively low rainfall in the region. Besides, nitrogen is highly mobile and it is therefore expected that the sandy nature of these soils would further aggravate the problem.

4.1.5 Cation exchange capacity (CEC)

The cation exchange capacity (CEC) of top and subsoils of the basement complex ranged from 19.80 to 41.80 and 17.80 to 41.60 mmol/kg with mean values of 31.90 and 29.70 mmol/kg respectively. The cation exchange capacity (CEC) of the sedimentary soils ranged from 20.60 to 44.80 mmol/kg and 17.00 mmol/kg to 40.00 mmol/kg with mean value of 33.57 mmol/kg and 29.27 mmol/kg respectively. The cation exchange capacity (CEC) in the study area is generally low. This could be due to low values of organic carbon and the low values and type of clay in the study area.

4.1.6 Total phosphorus

The total phosphorus, P, contents of top and subsoils of the basement complex ranged from 13.13 to 20.13 mg/dm³ and from 10.15 to 17.50 mg/dm³ respectively. The total phosphorus contents of soils derived from sedimentary rock ranged from 16.28 to 25.73 mg/dm³ and from 13.83 to 30.98 mg/dm³ with mean values of 21.58 and 18.58 mg/dm³ respectively.

The total phosphorus, P, contents of soils of the study area were quite low. This agrees with Ipimidium (1972) who reported that soils of Savanna region of Nigeria have very low value. Furthermore, Anon (1964) reported that total P in Savanna soils of Nigeria are very low.

4.1.7 Available phosphorus

The available phosphorus contents of top and subsoils of the basement complex ranged from 10.50 to 17.33 mg/dm³ and from 10.50 to 11.55 mg/dm³ with mean values of 12.84 and 10.84 mg/dm³ respectively. While the available phosphorus, P, of soils derived from sedimentary soils ranged from 10.50 to 17.50 mg/dm³ and from 9.63 to 15.40 mg/dm³ with mean values of 13.91 mg/dm³ and 11.87 mg/dm³ respectively.

Generally, the available phosphorus contents of soils of the study area were very low. This is not unusual because the total phosphorus in the study area were quite low which is in line with Ipimidium (1972) who reported that soils of Savanna region of Nigeria have very low values of P. It was further observed that soils of sedimentary rock, Nupe sandstones have higher values of available P, than soils of the basement complex. This also could be due to the low organic carbon contents of the study areas and the shallow nature of most of the basement complex soils as reported by Ezenwa (1986).

4.1.8 General Trend

Beside clay content of the soils which were generally higher in the subsoil, sand content, pH, organic carbon, CEC available P, total P and total N were lower in the subsoil of both the basement complex soils and the soils derived from sedimentary rocks. On the other hand the values of the silt content of these soils did not show any consistent trend. The values of P and N in relation to the organic matter content is in agreement with the observation that most of the plant nutrients in soil reside in the organic matter fractions.

4.2 Inter-Relationship of the Soil Properties for the Study Areas

The results of the soil analysis and coefficients of correlation (r) of soil properties and analysis of variance (ANOVA) of the soils of the study areas are presented in appropriate tables. The data are subdivided into soil types according to geological formations.

4.2.1 Inter-relationship of the soil properties for the basement complex <u>Upland Topsoil</u>

The coefficient of correlation (r) shows that there were no significant correlation in most comparisons except cation exchange capacity and total nitrogen which correlated negatively and significantly (P<0.10) with pH and organic carbon respectively (Table 5).

Upland Subsoil

pH and total P, pH and clay, and total P and clay correlated positively with each other and significantly at 0.1 and 0.05 probability levels respectively (Table 6). Comparison with other soil properties showed that there were no significant correlations.

Lowland Topsoil

Table 7, shows the coefficient of correlation of soil properties of the lowland topsoil of the basement complex. No significant relationships were

observed in most comparisons. There were however, a significant positive correlation between total P and clay at 0.05 probability level.

Lowland Subsoil

No significant correlations were observed in most comparisons for lowland subsoil of the basement complex with the exception of total P and clay, and total N and organic carbon that correlated significantly at 0.05 and 0.10 respectively as shown in Table 8.

4.2.2 Inter-relationship of the soil properties for the sedimentary rocks <u>Upland_Topsoil</u>

The coefficient of correlation (r) shows that no significant relationship were observed in most comparisons of the soil properties of the upland soil of sedimentary rocks, as shown in Table 9. However, there were significant positive correlations between cation exchange capacity (CEC) and pH at P<0.05 probability level. Conversely, there were significant negative correlation between available P and organic carbon and differed at P<0.05.

Upland Subsoil

Table 10, shows the coefficient of correlation of soil properties of the upland soils of the sedimentary rocks indicating significant negative correlation between cation exchange capacity (CEC) and pH and between available P and clay at 1.0 and 0.05 respectively. Comparison with the other soil properties showed that there were no significant correlations observed in most comparisons.

Lowland Topsoil

Comparison between clay and pH and between total P and clay showed significant negative correlation at P<0.05 and 1.0 respectively, for the lowland soils of the sedimentary rocks. Conversely, significant positive correlation were observed between total P and pH at P<1.0. Most values for the lowland topsoil did not produce any significant correlation (Table 11).

Lowland Subsoil

No significant correlations were observed in most comparisons for the subsoil of the sedimentary rocks. However, significant negative relationship were observed between pH and clay at 1.0. Conversely, the coefficient of correlation showed significant positive correlation between total P and organic carbon at 0.05 (Table 12).

4.2.3 Analysis of variance (ANOVA) for basement complex

The analysis of variance (ANOVA) for upland topsoil and subsoil and the soil characteristics are presented in Table 13. pH (H_2O) of the basement complex were generally low falling within a range of 5.50-6.22). The highest pH (H_2O) was from topsoil (Upland) while the lowest was from the subsoil (Upland). The difference of mean value was not significant at P<0.05. This observation is also true of clay, organic carbon, cation exchange capacity (CEC), total P and total N.

For the lowland topsoil and subsoils, and the soil characteristics of the basement complex, the pH (H_2O) also was generally low, ranging from 5.68-5.87 The highest pH (H_2O) value was from the **topsoil** (lowland). The difference of mean value was equally not significant at P<0.05. A similar pattern was observed in clay organic carbon (OC), cation exchange capacity (CEC), total P, available P and total N.

4.2.4 Analysis of variance (ANOVA) for sedimentary rock

The pH (H_2O) of the sedimentary rock were generally low ranging from 5.55-6.39 of the analysis of variance (ANOVA) for the Upland (topsoil) and subsoil and the soil characteristics. Here, pH (H_2O) Upland topsoil was highest while the lowest was from pH (H_2O) upland subsoil. The mean value was not significantly different at P<0.05. Other comparisons of clay, cation exchange capacity (CEC), total P, available P and total N showed similar pattern.

However, marked significant difference was observed in organic carbon content between topsoil and subsoil (upland) and between subsoil (upland) and topsoil/subsoil (lowland). The highest organic carbon was from the upland topsoil while the lowest was from the upland subsoil and differed significantly at P<0.05 (Table 14). No significant difference was observed between the values of the soil properties in both topsoil and subsoil (lowland).

4.3 Sorption Studies

4.3.1 Langmuir and Freundlich parameters

In order to obtain the sorption characteristics of the soil with regards to the effect of selected factors such as pH, time, zn^{2+} , Cu^{2+} and PO_4^{-3-} concentration, a fit of the adsorption data to the Langmuir and Freundlich equations (Bohn et al 1985) was attempted. The linear form of the conventional Langmuir equation was used

$$c/x/m = \frac{1}{Kb} + \frac{c}{b}$$

where c is the equilibrium concentration of P in equilibrium solution, x/m is the amount of P adsorbed per unit mass of soil, b is the Langmuir adsorption maximum and K is related to the bonding energy (or affinity parameter) between the solute and sorption sites. The plot of c/x/m against c gave a scatter from which the best straight line was obtained. the slope of the regression line gave a value of 1/b while K was obtained from the ratio slop/intercept. The values of these parameters are given in Tables 15a and 15b. The Freundlich equation used was in the form

$y = Kc^{1/n}$

where y is the amount of P sorbed per unit mass of soil, c, is as previously defined and n and K are constants that are characteristics of a given soil. K is related to the total sorption capacity of the soil and n to the surface

available for sorption; the smaller the surface the greater is its value. Taking logarithm of both sides of the equation gives the linear form

 $\log y = \log K + (1/n) \log c$

The plot of log y against log c are shown in the appropriate figure above. The linear plot produced slopes from which the value of n for each soil was calculated. The intercept gave the value of log K from which K was obtained. The values of K and n Table (15A and 15B) afforded a means of comparing the sorbing tendencies of the soils (Elrashidi and O'Conner 1982). **4.3.2 Effect of added P on P sorption**

Adsorption isotherms were obtained by plotting the amount of P sorbed after the interaction with $PO_4^{3^-}$ against the equilibrium concentration c. The curves show a gradual rise in P sorbed with increase in the amount of added P until it becomes fairly constant (Fig. 1 & 2). When the data were plotted according to the Langmuir equations, linear curves were obtained for the topsoil and subsoil indicating a satisfactory agreement with the theoretically derived equation. Similar results were also reported by Weaver et al (1975) and Syres et al (1973). According to the latter the existence of adsorption isotherm may be common in soils and they indicate population of adsorption at low equilibrium concentrations having higher affinity for P than those associated with adsorption at higher equilibrium concentration.

In Tables 15a and 15b are shown Langmuir and Frendlich constants derived from the curves. It was observed that the sorption capacities as shown in the tables were not significantly correlated with most of the soil properties. (syres et al, 1971; Udo and Uzu 1972) except for organic matter and clay content.

For basement complex, the same pattern was observed for both the upland and lowland. The values were generally low when compared to those obtained by Rhodes (1975) for some West Indian soils. The low values probably indicate underestimation of P adsorption capacities of the soils when computation was confined to only the lower curve.

4.3.3 Effect of zn²⁺on P sorption

Fig 9 and 10 are the isotherms obtained by plotting the amount of P adsorbed after interaction with zn^{2+} against the equilibrium concentration. The curves showed that the P adsorbed increases with increase in the amount of zn^{2+} added. At later circumstances the curves begin to slow down. Further addition had no effect on the P adsorbed. On plotting the data according to Langmuir equation, linear curves were obtained indicating a satisfactory agreement with the theoretically derived equations.

Langmuir and Freundlich constants derived from the curves are shown in Tables 15a and 15b. No significant relationships were observed between the interaction of P with zn^{2t} and the two sorption coefficient. The conclusion however, should not be extrapolated to include soils with a larger amount of the soil properties.

4.3.4 Effect of time on P sorption

The amount of phosphate P sorbed increased with increased in time and remained fairly stable after some time. After this period the rate of sorption slowed down. Sapek (1975) ascribed the fast step to a rapid diffusion of ions from the solution to external soil surfaces and the slow step to the diffusion of ions into pores of inner soil surfaces. It could also be said that the sorbing site on the soil mineral could have been satisfied thus leading to the gradual movement of surface sorbed P into the inter layer of clay minerals.

Fig 5 and 6 show the P sorption as a function of time for the topsoil and subsoil respectively. Two main steps of P sorption could be recognised from these curves, an initial rapid reaction which occurs within a few minutes and the slow reaction. These two steps correspond to two types of P kinetic

sorption curves in soils of low P status whereby the labile portion is converted to the non labile pool. In soils with high P sorption ability the rapid reaction could be completed within a short time.

The bonding energy constants from graphical estimates for both Langmuir and Freundlich equations are given in Tables 15a and 15b. The values obtained in the data did not produce any significant correlation between the soil properties and the two sorption parameters. The reason for this observation is not readily available.

4.3.5 Effect of Cu²⁺ on P sorption

Sorption isotherm were obtained by plotting the amount of P sorbed after the interaction with Cu^{2t} ion, against the equilibrium concentration, c. It was observed that the sorption of P increased with increase in the concentration of Cu^{2t} ion. The curve increases gradually until a certain point where it begins to become fairly constant indicating that the sorbing sites would have been satisfied. Plotting the data according to the Langmuir and Freundlich equations, linear curves were obtained. This shows a satisfactory agreement with theoretically derived equation.

4.3.6 Effect of pH on P sorption

The amount of P sorbed under different pH values was observed to decrease with increase in pH and remained fairly stable after sometime. This was observed when the adsorption isotherm were obtained by plotting the amount of P sorbed against the equilibrium concentration. According to Parfitt (1978) in addition to some sites of permanent positive charge, kaolinite has sites of pH dependent charge at crystal edge where Al(OH)H₂O group are exposed; at low pH, such groups become positively charged and more phosphorus are sorbed.

In general, it was observed that the sorption parameters did not correlate significantly with the soil properties. The reason for these observations was not readily available.

4.4 Summary and Conclusion

Soils of basement complex and sedimentary origin in Niger State in the Southern Guinea Savanna Zone of Nigeria were studied with the main objective of determining the physicochemical properties in relation to phosphorus sorption.

a. A systematic and intensive augering in the two lithological study locations in order to ensure homogeneity of soil properties for detail study of the soil.

b. A study of physical and chemical characteristics of the soils.

c. Sorption characteristics of the soils.

The results of the study showed that sedimentary rock soils had higher organic carbon, total nitrogen, available phosphorus, cation exchange capacity, total phosphorus than the basement complex soils. The results also showed that besides the clay content of the soils which were generally higher in the subsoils the sand content, pH, organic matter, CEC, available P and total P and N were lower in the subsoil of both the basement complex soils and the soils derived from sedimentary rock. On the other hand the values of silt content of the soils produced on consistent trend. The values of P and N in relation to the organic matter content in this study is in agreement with earlier observations that most of plant nutrients reside in the organic matter fraction. In addition low to very low values of the soils properties studied were recorded in the soils. However, the soils derived from sedimentary sand stones had higher values of both total P and available P, while lower values of organic carbon and clay content were recorded for these soils compared to the basement complex soils.

P sorption could also be recognised from the adsorption curves, an initial rapid reaction, followed by a slow reaction. This behaviour is

compatible with reactions of soils of low P status whereby P kinetics adsorption curves reflect the different rates of conversion from liable to nonliable pool. The variation in the sorption indices of these soils were also reflected in both their adsorption maxima, 'b' and their bonding energy 'K' constants for both Freundlich and Langmuir equations.

Statistical treatment of the results revealed the absence of any significant difference between the values of the different soil properties in top and subsoils or lowland and upland of the formations studied. Similarly, no significant difference were observed between the values of the different soil properties in top and subsoils or upland and lowland and some selected factors. The presence of added P, Cu, Zn pH and increase in shaking time greatly influenced the amount of P sorbed.

Significant difference shown by some physical and chemical properties of the soils formed on the basement materials and sedimentary parent material showed that parent materials have strong influence on soil formation in Nigeria Guinea Savanna. Lack of significant difference in some chemical properties of the soils however shows that as the soils get older they start to lose some of their geological attributes.

Although no significant relationships were observed between the parameters and the soil properties in both lithological formations, the use of P sorption isotherms as the basic characteristics for classifying these savanna soils is still recommended for an efficient and economic use of P fertiliser in crop production.

Depth (cm)	рН (H ₂ O)	pH CaCl ₂	Sand (%)	Silt (%)	Clay (%)	Organic Carbon %	CEC mmol/kg	Available mg/dm ^j	Total P mg/dm ³	Total N (%)	C/N
				ΒA	SEM	ENT CO	MPLE	Х			
0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 Highest	6.30 5.36 5.34 5.29 6.80 6.20 6.22 5.90 6.08 5.08 5.08 5.63 5.50 6.80	5.68 4.76 4.23 6.51 5.64 5.52 5.16 5.50 4.40 5.05 4.87 6.51	83.38 78.38 82.38 73.38 74.08 71.00 72.08 60.76 79.52 70.08 76.39 80.38 83.38	3.78 6.78 6.20 12.14 1.52 8.60 15.52 15.18 10.36 7.52 11.13 4.56	12.48 14.84 11.42 14.48 24.40 20.40 12.40 24.00 10.12 22.40 12.48 15.06 24.40	0.85 0.81 0.75 0.72 0.84 0.80 0.79 0.76 0.54 0.49 0.42 0.37 0.85	41.80 30.00 19.80 17.80 23.60 23.40 40.20 41.60 34.60 31.00 31.40 29.40 41.80	$ \begin{array}{r} 11.55\\10.50\\12.25\\10.50\\12.25\\10.50\\14.36\\11.55\\14.35\\10.50\\12.25\\11.55\\14.36\end{array} $	$17.15 \\10.15 \\13.13 \\14.92 \\20.13 \\15.05 \\20.13 \\17.50 \\16.28 \\14.35 \\20.13 \\15.05 \\15.05 \\$	0.48 0.32 0.63 0.58 0.32 0.30 0.63 0.63 0.62 0.56 0.63 0.48 0.63	1.77 2.53 .19 1.24 2.63 2.67 1.25 1.31 0.87 0.88 0.67 0.77 2.67
Lowest	5.08	4.23	60.76	1.52	10.12	0.37	17.80	10.50	10.15	0.30	0.67

1 .

Table 1a: Chemical Properties of Some Soils Formed from Basement Complex and Sedimentary Soils of Niger State (Upland)

Depth (cm)	рН (Н ₂ О)	pH CaCl ₂	Sand (%)	Silt (%)	Clay (%)	Organic Carbon %	CEC mmol/kg	Available mg/dm ⁾	Total P mg/dm ³	Total N (%)	C/N
				S	EDIM	ſENTRY	SOIL				
0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45	7.29 5.50 5.86 5.83 5.75 5.50 5.74 5.82 5.63 5.50 5.82 5.38 5.38	5.34 4.95 4.90 4.47 4.45 4.25 4.76 4.32 4.96 4.80 5.26 4.66	85.38 71.08 79.39 88.38 85.52 82.08 88.08 88.08 73.38 74.52 73.52 62.38	3.78 7.52 7.19 1.73 4.36 7.38 3.32 3.32 8.78 11.12 10.48 16.56	10.84 21.40 13.42 9.84 10.12 10.54 8.60 8.60 12.84 14.36 16.00 21.06	0.75 0.60 0.64 0.55 0.68 0.59 0.54 0.46 0.72 0.63 0.44 0.43 0.75	41.80 30.80 24.20 27.40 35.00 28.40 20.60 17.00 35.00 32.60 44.80 40.00	10.50 9.63 12.25 10.50 15.40 12.60 17.33 15.40 12.60 11.55 15.40 11.55	25.73 13.83 20.13 30.98 22.75 18.90 24.50 19.60 20.08 13.13 16.28 15.05 20.08	0.63 0.62 0.60 0.56 0.32 0.31 0.62 0.32 0.63 0.32 0.48 0.32	1.19 0.07 1.07 0.98 2.13 1.90 0.89 1.44 1.14 1.97 0.92 1.25
Lowest	5.38	4.25	62.38	1.78	8.78	0.73	20.60	20.60	13.13	0.83	0.87

Table 1b: Chemical Properties of Some Soils Formed from Basement Complex and Sedimentary Soils of Niger State (Upland)

Depth (cm)	рН (Н ₂ О)	pH CaCl ₂	Sand (%)	Silt (%)	Clay (%)	Organic Carbon %	CEC mmol/kg	Available mg/dm ³	Total P mg∕dm ³	Total N (%)	C/N
				ΒA	SEMEN	T COM TOPSOILS	M P L E X				
Total Mean Highest Lowest	36.36 6.06 6.80 5.34	32.29 5.49 6.51 4.70-	467.83 77.97 83.38 72.08	48.51 8.09 15.52 1.52	83.66 13.94 24.40 10.12	4.19 0.70 0.75 0.44	191.40 31.90 41.80 19.80	77.01 12.84 17.33 10.50	106.95 17.83 20.13 13.13	3.31 0.55 0.63 0.32	1.27 1.27 1.19 1.38
					5	SUBSOILS					
Total Mean Highest Lowest	33.33 5.56 6.20 5.08	20.06 4.84 5.69 4.23	433.98 72.33 80.35 60.76	54.78 9.13 15.18 4.56	111.18 18.53 24.00 14.48	3.95 0.65 0.81 0.37	178.20 29.70 41.60 17.80	65.05 10.84 11.55 10.50	87.02 14.50 17.50 10.15	2.82 0.47 0.58 0.30	1.29 1.38 1.40 1.23

* *

Table 2a: Mean Values of properties of Top and Subsoils of basement complex and sedimentary sandstones

Depth (cm)	рН (Н ₂ О)	pH CaCl ₂	Sand (%)	Silt (%)	Clay (%)	Organic Carbon %	CEC mmol/kg	Available mg/dm ³	Total P mg∕dm ³	Total N (%)	C/N
	SEDIMENTARY SANDSTONES TOPSOILS										
Total Mean Highest Lowest	36.29 6.05 7.29 5.63	29.67 4.95 5.34 4.95	490.27 81.71 88.08 75.52	37.91 6.32 10.48 3.32	71.82 11.97 16.00 8.60	3.77 0.63 0.75 0.43	201.40 33.57 44.80 20.60	83.48 13.91 17.50 10.50	129.47 21.58 25.73 16.28	3.28 0.55 0.63 0.32	1.15 1.15 1.19 1.34
					S	SUBSOILS					
Total Mean Highest Lowest	33.53 5.59 5.83 5.83	27.45 4.58 5.34 4.25	466.52 77.75 88.38 62.38	47.68 7.95 16.56 1.78	85.80 14.30 21.40 8.60	3.26 0.54 0.63 0.43	175.60 29.27 40.00 17.80	71.23 11.87 15.40 9.63	111.49 18.58 30.98 13.83	2.45 0.41 0.62 0.31	1.33 1.32 1.02 1.39

* *

Table 2b: Mean Values of properties of Top and Subsoils of basement complex and sedimentary sandstones

Depth	рН	pH	Sand	Silt	Clay	Organic	CEC	Available	Total P	Total N	C/N
(cm)	(Н ₂ О)	CaCl ₂	(%)	(%)	(%)	Carbon %	mmol/kg	mg/dm	mg/dm ³	(%)	
BASEMENT COMPLEX											
0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45	5.84 5.29 5.15 5.06 5.82 5.81 6.12 5.88 5.90 5.00 5.15 5.20	5.25 4.56 4.03 6.31 5.42 5.22 5.01 5.30 4.20 4.95 4.47	81.25 78.30 82.18 73.12 74.08 71.00 70.15 60.56 79.52 70.00 75.18 80.18	$\begin{array}{c} 3.58\\ 6.66\\ 6.00\\ 12.14\\ 1.33\\ 3.40\\ 15.22\\ 15.14\\ 10.16\\ 7.31\\ 11.00\\ 4.16\end{array}$	15.17 15.04 11.82 14.74 24.67 25.60 14.63 24.30 11.68 22.69 13.82 15.66	0.65 0.61 0.58 0.52 0.64 0.70 0.71 0.72 0.51 0.49 0.40 0.37	41.60 30.00 19.20 17.10 23.20 23.00 40.20 41.30 34.20 31.00 31.10 29.00	11.25 10.00 12.15 10.25 12.05 10.20 14.16 11.30 14.25 10.15 12.00 11.15	$\begin{array}{c} 17.00\\ 10.00\\ 13.10\\ 14.42\\ 20.10\\ 15.00\\ 20.00\\ 17.50\\ 16.20\\ 14.30\\ 20.03\\ 15.00\\ \end{array}$	0.45 0.31 0.63 0.55 0.32 0.30 0.59 0.58 0.61 0.56 0.63 0.45	1.44 1.97 0.92 0.95 0.50 2.33 1.20 1.24 0.84 0.88 0.63 0.82
Highest	6.12	6.31 .	82.18	15.22	24.67	0.72	41.60	14.25	20.10	0.63	1.97
Lowest	5.00	4.03	60.75	1.33	11.68	0.37	17.10	10.00	10.00	0.30	0.50

Table 3a: Chemical Properties of Some Soils Formed from Basement Complex and Sedimentary Soils of Niger State (Lowland)

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Depth (cm)	рН (Н ₂ О)	pH CaCl ₂	Sand (%)	Silt (%)	Clay (%)	Organic Carbon %	CEC mmol/kg	Available mg/dm [']	Total P mg/dm ^j	Total N (%)	C/N
	_			S	EDIM	IENTRY	SOIL				
0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 0-20 20-45 0-20	$7.15 \\ 5.10 \\ 5.26 \\ 5.13 \\ 5.50 \\ 5.25 \\ 5.90 \\ 5.62 \\ 5.61 \\ 5.50 \\ 5.62 \\ $	5.14 4.70 4.60 4.13 4.30 4.28 4.52 4.06 4.95 4.60 5.00	85.38 70.08 79.19 88.21 85.52 82.00 88.00 88.00 87.00 78.08 74.12 73.22	3.78 7.42 7.19 1.68 4.06 7.18 3.31 3.39 8.58 11.02 10.28	10.84 22.50 13.62 10.11 10.42 10.82 8.69 9.61 13.34 14.86 16.50	0.75 0.58 0.62 0.50 0.62 0.55 0.54 0.45 0.70 0.60 0.42	40.80 30.60 24.10 27.20 35.00 28.00 20.24 17.00 35.00 31.60 44.60	10.40 9.60 12.00 10.25 15.20 12.50 17.13 15.40 12.60 11.50 15.40	25.70 13.80 20.13 30.92 22.70 18.50 24.05 19.30 20.00 13.03 16.08	0.63 0.61 0.60 0.54 0.31 0.29 0.63 0.31 0.62 0.31 0.46	1.19 0.95 1.03 0.93 2.00 1.90 0.86 1.45 1.13 1.94 0.91
20-45	5.38	4.47	62.18	16.56	21.26	0.41	40.00	11.50	15.00	0.31	1.32
Highest	7.15	5.14	88.21	16.56	22.50	0.75	44.60	15.40	30.92	0.63	1.94
Lowest	5.10	4.06	62.18	1.68	8.69	0.41	17.00	9.60	13.03	0.29	0.86

Table 3b Chemical Properties of Some Soils Formed from Basement Complex and Sedimentary Soils of Niger State (Lowland)

Depth (cm)	рН (Н ₂ О)	pH CaCl ₂	Sand (%)	Silt (%)	Clay (%)	Organic Carbon %	CEC mmol/kg	Available mg/dm ³	Total P mg/dm ^ĵ	Total N (%)	C/N
	BASEMENT COMPLEX (LOWLAND - TOPSOILS)										
Total Mean Highest Lowest	33.90 5.66 6.12 5.15	31.56 5.26 6.31 4.02	460.92 76.82 82.18 60.56	47.29 7.88 15.22 1.33	91.79 15.30 24.67 11.68	3.49 0.58 0.71 0.40	189.50 31.58 41.60 19.20	75.85 12.64 20.10 13.10	106.70 17.78 20.10 13.10	3.23 0.54 0.63 0.32	5.53 0.92 1.44 0.50
					LOWLA	ND - SUBSC	DILS				
Total Mean Highest Lowest	33.33 5.56 6.80 5.08	29.06 4.84 5.64 4.23	433.98 72.33 80.38 60.76	49.78 8.30 15.52 3.60	111.54 18.59 24.00 14.84	3.95 0.66 0.81 0.37	171.40 28.57 41.30 17.10	65.03 11.51 11.30 10.00	86.22 14.37 17.50 10.00	2.75 0.46 0.58 0.30	8.19 1.37 2.33 0.82

Table 4a: Mean Values of properties of Top and Subsoils of basement complex and sedimentary soils

* *

Depth (cm)	рН (Н ₂ О)	pH CaCl ₂	Sand (%)	Silt (%)	Clay (%)	Organic Carbon %	CEC mmol/kg	Available ^p mg/dm ⁹	Total P mg/dm ³	Total N (%)	C/N
	SEDIMENTARY SANDSTONES (LOWLAND - TOPSOILS)										
Total Mean Highest Lowest	35.04 5.84 7.15 5.26	28.51 4.75 5.14 5.30	489.99 81.57 88.00 73.22	37.20 6.20 10.28 3.31	73.41 12.24 13.62 9.61	3.65 0.61 0.75 0.42	199.74 33.29 44.60 20.24	82.73 13.79 17.13 10.40	128.58 21.43 25.70 16.08	3.25 0.54 0.63 0.31	7.12 1.19 2.00 0.86
					LOWLA	ND - SUBS	DILS				
Total Mean Highest Lowest	31.98 5.33 5.62 5.10	26.24 4.37 4.70 4.06	463.59 77.27 88.21 62.31	47.25 7.88 16.56 1.68	89.16 14.86 22.50 9.16	3.09 0.52 0.60 0.41	174.40 29.07 40.00 17.00	70.75 11.79 15.40 9.60	110.55 18.43 30.92 13.03	2.37 0.40 0.54 0.29	8.49 1.42 1.94 0.93

Table 4b: Mean Values of properties of Top and Subsoils of basement complex and sedimentary soils

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Table 5: Upland Topsoil Basemet - Correlation Matrix

	<u>рН</u>	<u>Clay</u>	<u>OC</u>	CEC	<u>TotP</u>	AvaP	TotN
pН	-						
Clay	0.02						
OC	0.83	-0.54	-				
CEC	-0.99**	0.13	-0.90	-			
TotP	0.40	0.52	-0.18	-0.26	-		
AvaP	-0.24	0.92	-0.74	0.36	0.79	-	
TotN	-0.74	0.65	-0.99**	0.83	0.32	0.83	-

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*Significant (P<0.05); ** Significant (P<0.1)

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2	-

Table 6: Upland Subsoil Basement Complex - Correlation Matrix

	рH	Clay	<u>OC</u>	CEC	TotP	<u>AvaP</u>	TotN
рH	-						
Clay	0.99*	-					
OC	0.72	0.634	-				
CEC	-0.76	0.83	-0.90	_			
TotP	1.00**	1.00**	0.65	-0.81	-		
AvaP	-0.55	-0.45	-0.98	-0.12	-0.48	-	
TotN	-0.90	-0.84	-0.95	0.40	-0.86	0.86	-

*

*Significant (P<0.05); ** Significant (P<0.10)

Table 7: Upland Topsoil Basement Complex - Correlation Matrix

	рH	Clay	<u>OC</u>	CEC	TotP	AvaP	TotN
pH	-						
Clay	0.71	-					
OC	0.29	-0.47	-				
CEC	0.96	0.87	-0.02	-			
TotP	0.75	1.00**	-0.41	0.90	-		
AvaP	0.95	0.44	0.58	0.82	0.50	-	
TotN	0.66	-0.07	0.91	0.43	0.006	0.87	-

-

*Significant (P<0.05); ** Significant (P<0.10)

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Table 8: Upland Subsoil Basement Complex - Correlation Matrix

	<u>рН</u>	Clay	<u>OC</u>	CEC	TotP	<u>AvaP</u>	TotN
рH	-						
Clay	0.96	-					
OC	0.27	0.53	_				
CEC	0.99	0.90	0.11	-			
TotP	0.96	1.00*	0.54	0.89			
AvaP	0.76	0.55	-0.42	0.86	0.54	-	
TotN	0.18	0.45	1.00**	0.02	0.046	0.50	-

*Significant (P<0.05); ** Significant (P<0.10)

Table 9: Upland Topsoil Sedimentary Rock - Correlation Matrix

	<u>рН</u>	Clay	<u>OC</u>	CEC	TotP	AvaP	TotN
pН	-						
Clay	-0.32	-					
OC	0.78	0.33	-				
CEC	1.00*	0.26	0.82	-			
TotP	0.91	-0.69	0.46	0.88	-		
AvaP	0.70	-0.33	-1.00^{*}	0.82	0.46	-	
TotN	0.44	0.71	1.90	0.50	0.03	0.90	-

*Significant (P<0.05); ** Significant (P<0.10)

Table 10: Upland Subsoil Sedimentary Rock Complex - Correlation Matrix

	рH	Clay	<u>OC</u>	CEC	TotP	AvaP	TotN
рH	-						
Clay	-0.35	-					
OC	0.96	-0.07	-				
CEC	-1.00**	0.42	0.94	-			
TotP	0.92	0.69	-0.77	-0.95	-	×	
AvaP	0.35	-1.00*	-0.08	-0.42	0.70		
TotN	-0.03	0.95	-0.25	0.11	0.43	0.95	-

*Significant (P<0.05); ** Significant (P<0.10)
	рH	Clay	<u>OC</u>	TotP	AvaP	TotN	CEC
pН	-	5					
Clay	-1.00*	-					
OC	0.32	-0.34	-				
TotP	0.99**	-0.99**	0.47	-			
AvaP	0.55	-0.53	-0.61	0.41	-		
TotN	0.84	-0.85	0.79	0.91	0.010	-	
CEC	0.94	0.85	-0.79	-0.91	-0.00	-1.00*	-

Table 11: Lowland (Topsoil) Sedimentary Rock - Correlation Matrix

*Significant (P<0.05); ** Significant (P<0.10)

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Table 12: Lowland (Subsoil) Sedimentary Rock - Correlation Matrix

	рH	Clay	<u>OC</u>	CEC	TotP	AvaP	TotN
рH	-						
Clay	-0.99*	-					
OC	0.71	0.63	-				
CEC	-0.88	0.93	0.29	-			
TotP	0.73	-0.66	1.00*	-0.33	-		
AvaP	0.30	-0.40	-0.47	0.71	0.43	-	
TotN	0.52	-0.42	0.97	-0.06	0.96	0.67	-

*Significant (P<0.05); ** Significant (P<0.10)

	Upla	ınd	Lowland			
	Topsoil	Subsoil	Topsoil	Subsoil+SEM		
pH(NS)	6.22±0.53	5.50±0.06	5.87±0.04	5.68±0.15 ⁸ ±0.28		
Clay(NS)	11.27±0.81	15.43±3.18	12.67±2.17	13.17±4.00 ⁸ ±2.79		
OC(NS)	0.72±0.02	0.61±0.01	0.54±0.06	0.48±0.04 ⁸ ±0.04		
CE S (NS)	37.27±2.27	30.60±1.22	29.87±7.54	28.13±6.65 ^a ±5.19		
TotP(NS)	22.85±1.63	15.29±1.82	20.30±2.37	21.88±4.74 ^a ±2.97		
AvaP(NS)	12.83±1.42	11.26±1.82 ^å	14.99±1.48 ^a	12.48±1.48 ⁸ ±1.3		
TotN(NS)	0.53±0.10	0.42±0.10 ^a	0.57±0.04 ⁸	0.40±0.08 ⁸ ±0.08		

Table 13: Analysis of variance (ANOVA) of the soil properties for basement complex

NS - means not significantly different from each other (P<0.05)

Table 14: Analysis of variance (ANOVA) of the soil properties for Sedimentary rock

	Upla	and	1	Lowland
	Topsoil	Subsoil	Topsoil	Subsoil + SEM
pH(NS)	6.39±0.21	5.55±0.34	5.73±0.26ª	$5.56\pm0.18^{a}\pm0.25$
Clay(NS)	15.79±4.38	19.21±2.26	12.10±0.34ª	$17.85 \pm 3.08^{a} \pm 2.91$
OC(NS)	0.74±0.10	0.70±0.10	0.65±0.11ª	$0.61\pm0.12^2 \pm 0.11$
CE (NS)	33.33±5.27	29.80±0.76	30.47±5.91	$29.60\pm6.87^{8}\pm5.26$
TotP(NS)	-17.85±1.17	13.18±1.53	17.78±2.33 ⁸	$15.82\pm0.84^{a}\pm1.56$
AvaP(NS)	12.71±0.84	10.50±0.06	12.93±0.70 ^a	$11.20\pm0.35^{a}\pm0.58$
TotN(NS)	0.56±0.16 ^ª	0.39 ± 0.08^{a}	0.63±0.01 ⁸	$0.55\pm0.03^{8}\pm0.09$

NS means Not Significantly different from each other (P<0.05)

			Upland Lo					vland	
		Langmuir Freundlich Langmuir		Freundlich					
Factor	Soil type	$(dm^{\frac{K}{j}}/mg)$. <u>b</u> (mg/kg)	(dm ^j /kg)	k (mg/kg)	(dm ^j /mg)	b (mg/kg)	$n (dm^{j}/kg)$	k (mg/kg
Time	Topsoil	1	25	8.33	3.63	1.25	20	8.34	3.60
	Subsoil	0.38	33.33	11	3.60	0.36	25	7.70	3.63
Zn ⁺² ion	Topsoil	2	12.50	4.55	3.78	4.00	25	14.29	3.60
	Subsoil	-2.33	14.29	5.00	3.74	6.00	16.67	9.09	3.56
Cu ²⁺ ion	Topsoil	-2.33	14.29	8.33	3.63	0.38	33.33	12.50	3.60
	Subsoil	-3.50	14.29	12.50	3.60	0	20	14.29	3.60
рН	Topsoil	3.50	14.29	6.67	3.63	6.00	16.67	8.33	3.63
	Subsoil	-7.00	14.20	10.00	3.60	3.50	14.24	8.33	3.32
PO4 ³ ion	Topsoil	2	25	11.11	3.56	0	16.67	10.00	3.65
Concentration	Subsoil	0	16 . 67	12.50	3.56	4	25	25.00	3.63

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Table 15A: Sorption Parameters of Soils of Basement Complex as Influenced by Selected Factors

			Upl	and		Lowland				
		Langmuir		Freundlich		Lang	Langmuir		Freundlich	
Factor	Soil type	K (dm ³ /mg)	(mg/kg)	<u>n</u> (dm ³ /kg)	k (mg/kg)	<u>K</u> (dm ³ /mg)	(mg/kg)	(dm ³ /kg)	(mg/kg)	
Time	Topsoil	0.36	25	0.06	3.67	6	16.67	8.33	3.67	
	Subsoil	0.80	25	6.67	3.63	0.25	33.33	7.69	3.63	
Zn^{+2} ion	Topsoil	1.75	14.29	5.56	3.71	1.75	14.30	7.14	3.71	
	Subsoil	4.00	12.50	8.33	3.60	-2.33	14.29	6.25	3.67	
Cu ²⁺ ion	Topsoil	0.00	16.67	6.67	3.67	0	16.70	6.25	3.67	
	Subsoil	0.60	14.29	9.10	3.60	-3.00	16.67	10	3.60	
рH	Topsoil	1.75	14.29	5.88	3.71	3.50	14.29	6.25	3.67	
	Subsoil	-3.50	14.29	6.67	3.67	-3.50	14.29	6.67	3.63	
PO ₄ ³ ion	Topsoil	6.00	16.67	14.29	3.53	1.50	33.33	12.50	3.60	
Concentration	Subsoil	6.80	16.47	10.00	3.60	6.00	16.67	12.50	3.60	

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Table 15B: Sorption Parameters of Soils of Sedimentary Rock as Influenced by Selected Factors

Table	e 16:	Basement	Complex	(Upland) -	- C	orrelation	coefficient Soil	Properties
and	Sorp	tion Parame	eters			*		

Parameters	pН	Clay	<u>OC</u>	CEC	TotP	AvaP	TotN
b	0.0109	-0.0109	0.0109	0.0109	0.0109	0.0109	0.0109
n	-0.4354	-0.4354	-0.4354	0.4354	0.4354	-0.4354	-0.4354
K	0.4595	0.4595	0.4595	0.4595	0.4595	0.4595	0.4595
k	0.0911	0.0911	0.0911	0.0911	0.0911	0.0911	0.0911

Not Significant at P<0.05 and P<0.10

Table 17: Correlation Coefficient of Soil Properties and Sorption Parameters Basement Complex (Lowland)

Parameters	pH	Clay	<u>OC</u>	CEC	TotP	AvaP	TotN
K	0.1617	-0.1617	0.1617	-0.1617	0.1617	0.1617	0.1617
b	0.0109	-0.0109	0.0109	-0.0109	0.0109	0.0109	0.0109
k	0.2711	-0.4197	0.4197	-0.4194	0.4194	0.4194	0.4194
n	-0.2189	0.2189	-0.2189	0.2099	-0.2189	-0.2189	-0.2189

Not Significant at P<0.05 and P<0.10

and the Pa	and the Parameters										
Function	рH	Clay	<u>OC</u>	CEC	TotP	AvaP	TotN				
b	0.0109	-0.0109	0.0109	-0.0109	0.0109	0.0109	0.0109				
n	-0.4354	-0.4354	-0.4354	0.4354	0.4354	-0.4354	-0.4354				
K	0.4595	0.4595	0.4595	-0.4595	0.4595	0.4595	0.4595				
k	0.0911	0.0911	0.0911	-0.0911	0.0911	0.0911	0.0911				
		(

Table 18: Basement Complex (Upland) - Correlation of the Functions

Correlates significantly (P<0.....) No significant correlation

Table 19: Corrlation Coefficient of Soil Properties and Parameters Sedimentry Rocks (Lowland)

<u>Parameters</u>	pH	Clay	<u>OC</u>	CEC	TotP	AvaP	TotN
К	0.4709	-0.4709	0.4709	0.4709	0.4709	0.4708	0.4709
b	0.3600	-0.3600	0.3600	0.3600	0.3600	0.3600	0.3600
k	0.5220	-0.5220	0.5220	0.5220	0.5220	0.5220	0.5220
n	-0.2240	0.2240	-0.2240	-0.2240	-0.2240	0.2240	-0.2240

Not significant at P<0.05 and P<0.10

Table 20: Correlation Coefficient of Soil Properties and Parameters Sedimentary Rock (Upland)

Parameters	рH	Clay	OC	CEC	TotP	AvaP	TotN
K	0.0918	-0.0918	0.0918	0.0918	0.0918	0.0918	0.0918
b	0.0989	-0.0989	0.0989	0.0989	0.0989	0.0989	0.0989
k	0.3499	-0.3499	0.3499	0.3499	0.3499	0.3499	0.3499
n	-0.2296	0.2404	-0.2404	-0.2404	-0.2404	-0.2404	-0.2404
(a)							

Not Sinificant P<0.05 and P<0.10



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Fig.5:Effect of shaking time on P-adsorption (Topsoll)



Shaking Time(mins)

Fig6Effect of shaking time on P-adsorption (Subsoil)

















Fig.18:Effect of pH on P-adsorption (Subsoil)



Fig.16: Effect of copper ion on P-adsorption (Subsoil)



Fig.15:Effect of copper ion on P-adsorption (Topsoil)



Fig.3: Effect of concentration on Padsorption (Topsoil)



Fig.4: Effect of concentration on P-adsorption (Subsail)



















Equil. Conc.(C)1 Fig.19:Effect of pH on P-adsorption (Topsoil)

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