PHOSPHATE RETENTION AND THE EFFECTS OF RETAINED PHOSPHATE ON THE pH, CEC, AEC AND ZPC OF SOILS WITH HIGH CONTENTS OF VARIABLE CHARGE SOIL MINERALS FROM TANGA, TANZANIA

BY

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A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT FOR THE DEGREE OF MASTER OF SCIENCE (AGRICULTURE) OF THE SOKOINE UNIVERSITY OF AGRICULTURE, MOROGORO, TANZANIA

1993

ABSTRACT

A laboratory study was undertaken to investigate on the phosphate retention and the effects of retained phosphate on the pH, CEC, AEC and ZPC of three soils, namely Rhodic Kandiustox, Rhodic Haplustox and Typic Haplustox from Tanga, Tanzania.

These highly weathered and leached soils have high contents of variable charge soil colloids (VCS) dominated by kaolinite and iron and aluminium oxides and hydrous oxides, with low to very low pH (< 5.5), low CEC (< 10 c.mole/kg soil) and aluminium saturation between 15 to 25%.

The phosphate retention capacities of the soils ranged from 1000-1400 mg P/kg in the order Rhodic Kandiustox < Rhodic Haplustox < Typic Haplustox. There were high and positive correlations between the amounts of phosphate retained and the contents of iron and aluminium oxides and the 1:1 layer silicates. The phosphate adsorption data did not conform to the linear transformations of the Langmuir and Freundlich equation models.

Additions of up to 1600 mg P/kg to the soils significantly increased the pH of the Rhodic Kandiustox, Typic Haplustox and Rhodic Haplustox by 0.1, 0.4 and 0.05 pH units, and the CEC by 103%, 66% and 61%, respectively.

Phosphate retention by the soils at 1600 mg P/kg soil reduced the AEC and lowered the ZPC of the Rhodic Kandiustox, Rhodic Haplustox andTypic Haplustox by 1.S0, 1.10 and 0.55 pH units, respectively. The effects of added and retained phosphate on the pH, CEC, AEC and ZPC of the soils could be attributed mostly to the charge reversal through specific ligand exchange reactions between the phosphate ions and the aquo and hydroxo groups on the VCS colloids.

The resultant increases in pH and CEC with phosphate retention appears to be very small in relation to the large amounts of phosphate added to the soils. However, the amounts of P fertilizers required to effect such changes in pH and CEC could be minimized if the P fertilizer materials are banded.

DECLARATION

I, RUFINI HASSAN ASSENGA, do hereby declare to the Senate of Sokoine the University of Agriculture that this dissertation is my original work and that it has never been submitted for a degree in any other University.

Signature 

Date 18/10/93

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ACKNOWLEDGEMENTS

I am most grateful to Drs. J.P. Mrema and M. Kilasara for their ever available counsel, guidance and overall supervision throughout the course of this study.

My sincere thanks goes to the Sokoine University of Agriculture (SUA) and the Norwegian Agency for International Co-operation (NORAD) for their joint financial support which enabled me to pursue the course.

Special thanks should also go to the Director, Co-ordinator of Soils and other member of staff of the National Soil Service Project - Mlingano, Tanga for their assistance, and material support during my field work. I would also like to thank the Lecturers and other members of staff of the Department of Soil Science of the Sokoine University of Agriculture for their invaluable assistance during this study.

I gratefully acknowledge the understanding, patience and constant encouragement I received from my wife Dafrosa, my child Gloria and all members of my family.

Many people and institutions were instrumental to the successful completion of this work. Since it is not possible to mention all by names, I wish to extend to them my sincere acknowledgements.

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1. INTRODUCTION

The soil orders Oxisol, Ultisol and Alfisol cover about 52% of the Tanzania total land area (Hathout, 1983; de Pauw, 1984) and 57.5% of the tropical total land area (Dudal, 1976; Sanchez and Salinas, 1981). The soils are formed under hot and humid climatic conditions and are highly weathered and leached (Herbillon, 1980). The clay fraction of the soils is dominated by 1:1 layer silicates and crystalline and/or amorphous oxides and hydrous oxides (sesquioxides) of iron and aluminium. Minerals commonly found in the above mentioned three soil orders are kaolinite, ferrihydrite, goethite, haematite, gibbsite and to a lesser extent manganese, titanium, anatase, tin, rutile and ilmenite (Sanchez, 1976; Herbillon, 1980; Parfitt, 1980).

The physico-chemical properties of the three soil orders are very much influenced by the surface charge present on the dominant minerals. The OH^- groups on the basal, planar and broken edge of the minerals have amphoteric surface charge characteristic which vary with changes in solution properties, namely pH, electrolyte concentration, nature of cation and/or anion and solvent used (Bowden et al., 1980). Due to changes or variations of surface charge with changes in solution properties, the highly weathered soils are also

known by the names "pH-dependent Soils" (Parfitt, 1978; Uehara and Gillman, 1981) or "Variable Charge Soils" (VCS) (Sanchez, 1976; Parfitt, 1980; Fox, 1980; Uehara and Gillman, 1981). The later name, however, is the most commonly used one and it distinguishes the VCS from the permanently or constant surface charge soils. The VCS are also known as "Low Activity Clays" (LAC) (Juo, 1980) because they are considered to be old, inactive and infertile. Due to high intensities of weathering and leaching the clay fractions have very few weatherable minerals left that can maintain the fertility status of the soils.

In Tanzania, the Oxisols, Ultisols and Alfisols (variable charge soils/low activity clays) are under crop production, both cash and food crops. For many years traditional systems of agriculture, for example, shifting cultivation has been practiced on the VCS/ LAC. Fertility status of the soils under the traditional agricultural systems could be maintained by the relatively high organic matter contents through shifting and fallowing the land. However, with increased population and demand for more arable land the traditional agricultural systems had to be abandoned and be replaced by intensive and continuous farming systems that could not ensure sustainable production on the soils.

The VCS generally have low inherent fertility status due to the fact that the soils often have low pH value (< pH 5.5) at field conditions. Low pH values lead to problems of aluminium and manganese toxicity, deficiencies of calcium and magnesium, high rates of leaching of potassium and high retention capacities for phosphate, sulphate and molybdenum (Fox, 1980; Nyambo, 1986). These problems coupled with soil fertility exhaustion through intensive and continuous farming and low input of soil amendments have attributed to impoverishment of the VCS and lower their productivity.

In order to make the VCS more productive research for better farming methods and management of the soils has gained increased importance, especially in the recent years. A lot of research has been conducted on the tropical VCS, especially in the developed countries in relation to surface charge characteristics, anion and cation retention capacity and the effects of addition of organic and inorganic soil amendments on the physico-chemical properties of the VCS.

Phosphate retention characteristics of the VCS and the effects of retained phosphate on the physico-chemical properties of the VCS are some of the fields of soil fertility which have been mostly researched in many tropical countries. However, for Tanzania, only very little

has been done in relation to these studies.

This study aimed at investigating on the phosphate retention capacity of Rhodic Kandiustox, Rhodic Haplustox and Typic Haplustox soils from Tanga, Tanzania. The study also aimed at investigating on the effects of retained phosphate by the soils on the pH, cation exchange capacity (CEC), anion exchange capacity (AEC), zero point of charge (ZPC) of the soils and implications of the results obtained from the study on soil fertility and management of the soils.

2. LITERATURE REVIEW

Soil fertility as a measure of the potential use of land for agricultural production is a function of the physical, biological and chemical properties of the soil. The most important soil chemical properties which influence plant growth are pH, cation and anion exchange capacity, organic matter content and types and amount of clay minerals present in the soil. Most of the soil properties, being either physical, chemical or biological are influenced by the surface charge predominant on the soil colloids (Uehara and Gillman, 1981). A lot of studies have been done on different soils in relation to charge characteristics and the factors which affect the type and magnitude of charge on the soil colloids (Van Raij and Peech, 1972; Parfitt, 1978; Barrow, 1985; Anne Lewis-Russ, 1991).

2.1 Charge Development in Soils

Soil is a dynamic body and is constantly receiving or loosing and/ or redistributing various organic and inorganic materials through various processes. Since the soil materials are constituted by charged ions, addition or removal of the charged materials into or from the soil affect the state of balance of the charges present on the soil colloids.

The origin of the charges in soils is due to imbalances of the oppositely charged ions present in the soil minerals when these minerals undergo chemical decomposition and/ or recombination. Soil mineral constituents carry both positive and negative charged ions and the net charge present on a soil mineral could be expressed by the charge balance equation proposed by Sposito (1989) as follows:

$$Qp + Qn + Qs + Qos + Qd = 0 \qquad (1)$$

where Qp, Qn, Qs, Qos and Qd is the permanent charge, net proton charge, inner-sphere complex charge, outer-sphere complex charge and dissociated charge (diffuse layer charge) components, respectively. The type of charge predominant on the various charged soil components depend on soil solution properties, mainly pH and ionic strength (Sposito, 1981; 1989; and Anne Lewis-Russ, 1991).

Due to the charge imbalances in soils two types of charge are known to exist in soils, namely the permanent (constant) surface charge and the variable (pH-dependent) charge. The former arises from isomorphous substitution of cation(s) of lower or higher positive charge by another cation (Bohn et al., 1979; Uehara and Gilman, 1981; Anne Lewis-Russ, 1991). For example, aluminium (Al^{3+}) is known to be substituted for silica (Si^{4+}) in the tetrahedral

layers, and magnesium (Mg^{2+}) and iron (Fe^{2+}) may be substituted for Al^{3+} in octahedral layers during the process of clay minerals formation (common in the phyllosilicates and zeolite). This results into a structural permanent in-built net negative charge in soils (White and Zelazny, 1986). Since the charge developed from isomorphous substitution is permanent and internally built, changes in solution properties will decrease the surface potential of the minerals as a result of increased positive or negative charge density in the solution and in the diffuse double layer. Hence the presence of net negative charge in soils lead to adsorption of counter ions (cations) into the diffuse electric double layer to balance the charge (Uehara and Gillman, 1981).

Variable surface charge, also known as pH-dependent surface charge refers to surface charge that changes in magnitude and sign with variations in solution/electrolyte properties, especially pH and ionic strength (Wada and Okamura, 1983; Barrow, 1985; Anne Lewis-Russ, 1991). The effects of the above solution properties on the surface charge of soils could be represented by the following equations according to Uehara and Gillman (1981):

$$\sigma_0 = (2n\epsilon kT/\pi)^{\frac{1}{2}} \operatorname{Sinh}(ze/2kT)\phi \qquad (2)$$

$$\sigma_0 = (2n\epsilon kT/\pi)^{\frac{1}{2}} \operatorname{Sinh}\ 1.15\ Z(pH_0 - pH) \qquad (3)$$

where, σ_0 n, ϵ, z, e, k, T, ϕ, pHo and pH is surface charge

density (esu/cm2), ionic concentration (ion/ml), dielectric constant ($esu^2/dyne.cm^2$), ionic valence, ionic charge, Boltzman constant (ergs/degree), absolute temperature (^0K), surface charge potential (esu) net zero point of charge and pH of the electrolyte, respectively. Equation (2) and (3) shows that by varying the above listed soil solution properties the surface charge of the the soil minerals could be altered. pH is governed by the proportion of OH^- and H^+ ions, commonly reffered to as potential determining ions (Bleeker and Sageman, 1990; Anne Lewis-Russ, 1991; Anderson and Sposito, 1992).

Variable charge minerals, for example, the oxides and hydroxides (oxyhydroxides) of iron and aluminium have charge deficits or excess charge at different pH values. The broken edges of 1:1 clay minerals also have exposed OH^- and/or H^+ ions, which at appropriate pH and ionic strength, undergo deprotonation or protonation by interacting with other potential determining ions in the equilibrating solution. These two phenomena may result into the alteration of the sign and magnitude of net charge on the soil colloids (Bowden et al., 1985; Barrow, 1985; Anderson and Sposito, 1992). For example, it has been reported by Barrow (1985) that when an oxide or hydroxide of iron or aluminium is placed in aqueous solution, unsatisfied charges on the minerals are compensated for by coordinating

with water molecules that dissociate into H^+ and OH^- and the net effect could be either a net positive surface charge, that is:

$$[solid]\text{-}OH + H^+ \rightleftharpoons [solid]\text{-}OH_2^+ \quad (4)$$

or a net negative surface charge:

$$[solid]\text{-}OH + OH^- \rightleftharpoons [solid]\text{-}O^- + H_2O. \quad (5)$$

It has been explained by Sanchez (1976) that the types of charge present on a soil colloid could be estimated by measuring the pH of the given soil in a dilute electrolyte (for example 1 M KCl solution) and in distilled water. The sign of the difference in pH measured in the two solutions ($\Delta pH = pH(KCl)-pH(H_2O)$) is the estimate of the net charge present on the soil colloids.

Most soils have both permanent and variable charge minerals. However, the type of charge predominant on a given soil depends on the relative proportion of the two types of minerals present in the soil, the prevailing pH and ionic strength (Uehara and Gilman, 1981; Anne Lewis-Russ, 1991). The type and amount of charge present on a soil has a significant importance as it bears some relationships to the fertility level of the soil. Permanently charged soils have net negative charge (net CEC), whereas the variable surface charge soils have net positive charge (net AEC) at normal soil pH values. The

permanently charged soils are considered to have a higher fertility status compared to the variable charge soils because they can hold substantial amounts of cations which constitute the largest portion of the plant nutrients.

2.2 Mineralogical Constituents of the Variable Charge Soils

Soils derive most of their physical and chemical properties from their mineralogical constituents. Soil properties such as texture, colour, specific surface, surface charge density, soil pH and water holding capacity are function of the type and amounts of mineral species present in a given soil (Uehara and Gillman, 1981). Under favourable conditions of moisture and temperature as it is common in the tropics, rocks and primary minerals undergo fast degradation to form secondary minerals (Bohn et al., 1979; Buol et al., 1980). The principal secondary minerals are the 2:1 layer silicates (for example montimorillonite, vermiculite and illite) and the 2:2 layer silicates (for example the chlorite). At an advanced stage of weathering the secondary minerals are degraded further through the loss of silica and bases by leaching resulting in the formation of 1:1 layer silicates, (kaolinite), oxides and hydroxides of iron (goethite and haematite) and aluminium (gibbsite and bohmite) and traces of other metal oxides like the ilmenite, magnetite, maghemite, rutile, anatase

(Sanchez, 1976; Herbillon, 1980). The 1:1 layer silicates, the oxides and hydroxides of metals particularly those of iron and aluminium and aluminosilicates form the largest part of the mineralogical components of the VCS (Sanchez, 1976; Parfitt, 1978; Uehara and Gillman, 1981).

2.3 Mechanism of Ion Retention by Soils and Pure Materials

Several theories and models have been developed over the years past to describe the mechanism of retention/ adsorption and desorption of organic and inorganic materials on pure materials and soils. The most commonly known models today are the two layer (Gouy-Chapman) model, the constant capacitance model, the triple layer model, the four layer (Stern variable surface charge-variable surface potential) model and the one-pK model (van Raij and Peech, 1972; Stumm et al., 1980; Davis and Leckie, 1978; Bowden et al., 1980; van Riemsdijk, 1986). In this study only the two layer and four layer models will be discussed.

2.3.1 Gouy-Chapman Double layer Model

The model assumes that the surface charge on a colloidal materials is balanced by the charge in solution, which is distributed between two layers (van Raij and Peech, 1972). The charge in the layer closer to the charged surface, composed by adsorbed ions is called the Stern layer and is

represented by the value σ_1, where σ is surface charge density. The charge in the other layer of ions (diffuse layer) is represented by the value σ_2. The total charge of both layers, therefore is represented by:

$$\sigma_0 = \sigma_1 + \sigma_2 \qquad (6)$$

The major setback of this model over the other models is that it cannot adequately describe realistically the relationships between the surface charge and the surface potential. This shortcoming arises from the fact that the model assumes that ions behaves like point charges and can approach the charged surface without any limitations (van Raij and Peech, 1972; Barrow, 1985). It has been proven that there is amaximum distance of approach between various ions and adsorbing materials beyond which repulsion can occur (Van Raij and Peech, 1972).

2.3.2 The Stern VSC-VSP Model

The model assumes that the various known ions are adsorbed in four different surface layers depending on the nature of the ions (Bowden *et al.*, 1980; Barrow, 1985; Sabine, 1992). The four layers/ planes starting from the surface of adsorbent towards the bulk solution are designated as o, a, b and d, respectively (Sabine, 1992). Protons, hydroxyl ions and strongly adsorbed oxyanions and metals are assumed

to form an inner-sphere surface complexes and they are placed in the o-plane (Sabine, 1992 Anne Lewis-Russ, 1991). Strongly adsorbed ions like phosphate are placed in an a-plane a short distance away from the o-plane. The major cations and anions are assumed to form outer-sphere surface complexes and are placed in the b-plane. The d-plane is assumed to indicate the beginning of the diffuse double layer.

The Stern VSC-VSP model is considered to more efficient and comprehensive in describing adsorption reactions than the other models because it has got similar assumptions like those of the mechanistic model which are built in a series of five succesive equations (Bowden et al., 1977; Barrow, 1985; Sabine, 1992). The model consider adsorption reactions to be a multiple series of complex reactions rather than simple-single reactions as considered by other models. So in order to able to describe adsorption reactions the factors which adsorption reactions must be considere in an intergrated form (Barrow, 1985).

2.4 Phosphate Retention by Variable Charge Soil Colloids

Many studies have been conducted in the recent years in relation to P retention capacity and characteristics of the VCS and on the factors influencing the P retention capacities of the soils. Reasons for the enormous studies

have been prompted by soil fertility and management problems, especially soil acidity, low cation exchange capacity and high P fixation. Phosphate adsorption studies done in Tanzania and elsewhere have shown that the oxyhydroxides of iron and aluminium are largely responsible for high P fixation capacity in soils (Uriyo et al., 1978; Parfitt, 1978; LeMare, 1981; Mrema, 1988).

The amount of P retained by the VCS has been found to depend on a number of factors, among them are equilibrium P concentration, soil:solution ratio, length of equilibration period, ionic strength, solution pH and temperature (Parfitt, 1978; Beek and Van Riemsdijk, 1979; LeMare, 1981; Boligar, 1985; Mrema, 1988). According to these authors Al^{3+} and Fe^{3+} have high capacities to fix P in acid soils. Similarly the crystalline and amorphous oxyhydroxides (Al^{3+} and Fe^{3+} oxides and hydroxides) and the amorphous aluminosilicates (allophane and imogolite) have also been found to have high capacity to fix P, the main reason being due to their high contents of iron and aluminium.

The P retention capacity of the VCS components has been suggested by Fox et al. (1971) and LeMare (1981) to follow the order amorphous aluminosilicates > amorphous oxyhydroxides > crystalline oxyhydroxides > 1:1 layer

silicates > 2:1 and 2:2 layer silicates. The reason for the above trend of P retention by the soil minerals has been attributed to increased specific attraction corresponding to the higher charge density and high specific surface of the VCS colloids (Uehara and Gillman, 1981).

2.4.1 Mechanism of Phosphate Retention by Variable Charge Soil Colloids

The mechanism of P retention by soils and synthetic materials are considered to involve exchange reactions, exchange-precipitation reactions and dissolution-precipitation reactions (Rajan and Perrott, 1975; Ryden and Syers, 1977; Parfitt, 1978; Bohn et al., 1979; LeMare, 1981).

2.4.1.1 Exchange Reaction Mechanism

Phosphate ions are considered to displace/ exchange with other negatively charged ions mainly the non-specifically retained anions (chlorides, nitrate and sulphate) and organic matter functional groups that are held adjacent to the surfaces of the soil colloids (Parfitt, 1978; Beek and Van Riemsidjik, 1979; Bohn et al., 1979). This type of ion retention is described as "non-specific anion retention mechanism" and the anions retained by this mechanism are termed "low affinity" or "indifferent ions" (Bowden et al., 1980; Singh and Uehara, 1986; Anne Lewis-Russ, 1991) or

dissociated charge complexes (Sposito, 1981). This type of P retention mechanism is thought to occur at low equilibrium P concentrations (Parfitt, 1978; Beek and Van Riemsdijk, 1979). The P held by this mechanism depend on electrostatic force alone and it can be exchanged with other anions. This reaction mechanism is important especially in the replenishment of the labile P of the soil solution.

2.4.1.2 Exchange-Precipitation Reaction Mechanism

Variable charge soil colloids have functional groups, mainly OH^- groups on the planar, basal and edge surfaces of the oxyhydroxides and also on the broken edges of 2:1 and 1:1 layer silicates (Rajan and Perrott, 1975; Bohn *et al.*, 1979). At pH values above or below the zero point of charge of the minerals, the hydroxyl groups become deprotonated and protonated, respectively hence the exchange reaction between OH^- and phosphate ion species. The phosphate ions react with the protonated groups on the oxyhydroxides of iron and aluminium to form very stable and insoluble precipitates (Parfitt, 1978; Beek and Van Riemsdijk, 1979). The protonation-precipitation reaction could be represented by the following equations (Holford and Gleeson, 1976):

$$Al^{3+} + 6H_2O \rightleftharpoons [Al(OH)_6]^{+} + 6H^{+} \qquad (7)$$

$$Al(OH)_6^{3+} + 6H_2PO_4^- \rightleftharpoons Al(OH).(H_2PO_4)_5 + 24H_2) \quad (8)$$

This type of phosphate adsorption mechanism is termed "specific ligand exchange mechanism" or "chemisorption" (Bohn et al., 1979; LeMare, 1981; Harter and Smith, 1981). The adsorbed ions are termed "high affinity specific ions" and are retained in the Stern layer (Singh and Uehara, 1986). Specifically retained ions are held by Van der Waal forces and can be adsorbed on colloidal surfaces irrespective of their type of charge (Uehara and Gillman, 1981; Barrow, 1985; Anne Lewis-Russ, 1991). Adsorption of the ions may lead to charge reversal on the colloidal surfaces (Lyklema, 1984).

Specific adsorption of P in soils has also been found to be enhanced by the presence of divalent or trivalent cations, low pH and high ionic strength (Wann and Uehara, 1978; Smith and Sanchez, 1980; Lyklema, 1984). Specific P adsorption in soils is considered to be very important as it can lead to increases in soil pH and CEC (Wann and Uehara, 1978; Parker et al., 1979; Uehara and Gillman, 1981; Sposito, 1981; Anne Lewis-Russ, 1991). Exchange-precipitation and crystallization reactions are considered to be the major processes responsible for phosphate retention by variable charge soils.

2.4.1.3 Dissolution-Precipitation Reaction Mechanism

At very high equilibrium phosphate concentrations, phosphate ions can penetrate into the inner layers of the clay minerals, disrupting the structural bonds which link the metal ions and hydroxyl groups in the minerals (Rajan and Fox, 1975; Juo and Fox, 1977; Bohn et al., 1979). The probable reaction mechanism is thought to take place in the following manner (Rajan and Watkinson, 1976):

$$\begin{matrix} Al \\ OH \\ Al \end{matrix} + H_2PO_4^- \rightleftharpoons [Al\text{-}H_2PO_4]^{1/2-} + [Al\text{-}OH]^{1/2} \qquad (9)$$

Dissolution reactions are also thought to involve the displacement of structural silicates followed by precipitation of aluminium phosphate (Bohn et al., 1979) and the reactions could be represented by the following equations:

$$Al_2Si_2O_5(OH)_2 \rightleftharpoons Al(OH)_2^+ + Si_2O_5^{2-} \qquad (10)$$

$$2Al(OH)_2^+ + 2H_2PO_4^- \rightleftharpoons 2Al(OH)_2.H_2PO_4 \qquad (11)$$

Dissolution reactions are assumed to play a minor role in phosphate fixation in soils because rarely soils become saturated with phosphate ions except around the phosphate fertilizer bands and the soil-root zones where high concentrations of phosphate may occur through banding of

phosphate fertilizers (Lindsay, 1979; Harter and Smith, 1981).

2.4.2 Phosphate Adsorption Equation Models

Different types of models have been developed in the study of adsorption of inorganic materials in pure and soil materials. The models used today could be classified into two broad groups. One group represents the equilibrium type of chemical reactions while the other represents the kinetic/ time-dependent type of reactions (Selim, 1992). The equilibrium models assume adsorption reactions to be instantaneous in nature and apparent equilibrium may occur in relatively short time (Selim, 1992). The Langmuir single and two-layer surface models, the Frenndlich and Temkin models are examples of the equilibrium types of adsorption models (Selim, 1992).

The kinetic models assume adsorption reactions to be slow and the amount of adsorbate adsorbed by an adsorbent to be a function of time (Selim, 1992). Most commonly used kinetic models are of first-order reaction and may be linear of or non linear and/or reversible or irreversible (Selim, 1992). Recently, other models have evolved, resulting such model as the combination of equilibrium and kinetic models, and the consecutive and concurrent multireaction models (Selim, 1992). The mechanistic model

(Barrow, 1983) is one of the most commonly used kinetic model for the description of adsorption reactions (Bowden et al. 1977; Selim, 1992, Barrow, 1985).

2.4.2.1 The Langmuir Equation Model

This is the most commonly used equation among the above mentionedequation models because it gives a theoretical adsorption maxima, unlike the other models (Bache and Williams, 1971). The equation is also preferred because of its simplistic form, and can be transformed into a linear form and linear regression can be used to give a better fit of the data and estimate of the adsorption coefficients (Barrow, 1978).

The equation has the general form:

$$X = kCb/1+kC \qquad (12)$$

and its linear transformed form as:

$$C/X = 1/kb + C/b \qquad (13)$$

where X, C, b and k are the amount of ion adsorbed, equilibrium concentration of the ion, ion adsorption maxima and rate/ affinity of adsorption/ desorption (bonding energy), respectively. A plot of C/X versus C should give a straight line if the data conform to the adsorption equation, with 1/b and 1/kb as slope and constant, respectively. Most of the studies using the linear form of the equation have found the plots to be curved and the affinity values to be variable, rather than constant

(Muljadi et al. 1966; Bowden et al., 1977; Parfitt, 1978; Holford, 1982; Mrema, 1988).

The isotherms have been found to have a linear portion at low ionic concentrations and curved portion at high ionic concentrations (Parfitt, 1978; Holford, 1982; Mrema, 1988). The curved nature of the isotherms is attributed to the fact that the Langmuir equation model holds true only at limited ionic concentration range (Barrow, 1978). Non-conformity of the phosphate adsorption data to the Langmuir equation model has also been attributed to the presence of multiple adsorption sites with differing affinites (Muljadi et al., 1966; Bache and Williams, 1971) and lateral interactions between the adsorbed ions themselves (Harter and Smith, 1981).

The curved nature of the isotherms is also attributed to changes in surface charge brought about by changes in ionic concentration and pH as postulated by the mechanistic equation model (Bowden et al., 1977; 1980). Therefore, propositions for modification of the Langmuir equation were initiated, and one of the modification was proposed by Gunary (1970) which changed the equation to the form:

$$C/X = A+BC+DC^{1/2} \qquad (14)$$

where A, B, and D are coefficients and the term C accounts for the overlooked assumption, that is, adsorption affinity

decreases with increasing adsorption. Muljadi *et al*. (1966), Holford (1982) and Rajan and Perrot (1975) suggested further modifications which could account for the presence of two or more adsorption sites with varying affinities. The equation suggested has the form:-

$$x = a_1 \, xm_1 \, C/(1+a_1C) + a_2x_2C/1+a_2C) + n \qquad (15)$$

where the subscripts 1, 2 n, represent the multiple adsorption surfaces.

2.4.2.2 The Freundlich Equation Model

According to Fitter and Sutton (1975) the equation has the general form:

$$x = a \, c^{1/n} \qquad (16)$$

and the linear transformed form as:

$$\log x = 1/n \log c + \log a. \qquad (17)$$

where x, c and 1/n are the amount of ion adsorbed, ionic equilibrium concentration and coefficient for ion adsorption affinity, respectively. A plot of log x versus log c should give a straight line if the data conforms to the equation. The ion affinity term decreases exponentially with increasing surface coverage, and this is one of the reasons for the better fit of the equation over the Langmuir equation. The equation could also be modified to account for labile (native) phosphate concentration. This modification give the equation the form:

$$x = a \, c^{1/n} - Q \qquad (18)$$

where Q is the labile ionic concentration (Fitter and Sutton, 1975). Although the Freundlich equation has been described as a better alternative to the Langmuir equation model, non-conformity of the equation is not an exception. Barrow and Shaw (1975) have reported non-conformity of P adsorption data to the equation. According to these authors the observed no conformity of adsorption data to the equation has been attributed to the logarithmic transformations which give unproportional weighting on the adsorption data, especialy at low concentrations.

2.4.2.3 The Temkin Equation Model

The equation has been used less extensively compared to the other two equations, mainly due to the fact that it does not give a theoretical adsorption maxima. The equation has the general form:

$$X = \alpha T \beta \ln C. \qquad (19)$$

where X, C and T are the amount of ion adsorbed, equilibrium ionic concentration and labile (native) ionic concentration, respectively and α and β are coefficients. A plot of X versus ln C should give a straight line.

It is assumed that the affinity coefficient decreases linearly with increasing surface coverage of the adsorbent (White and Taylor, 1977).

2.4.2.4 The Mechanistic Model

The model was developed by Barrow (1983). The model is considered to be superior over the other models mentioned above because it has been proved to be more successful in describing the diverse effects of ionic concentration, pH, time, temperature and other factors known to affect the adsorption of inorganic materials soils and related materials (Boweden et al., 1980; Barrow, 1984). The efficiency of the model lies on the assumptions it has on adsorption reactions. The model assume that:

(i) Adsorbing surfaces to be heterogenous and electrostatic potential develops when charged ions are adsorbed onto the surface.

(ii) Adsorbent and adsorbate are charged materials and repulsion between them can occur.

(iii) Adsorbed ions are not infinitional, rather finite and there is maximum distance the ions can approach the adsorbing surface, beyond which repulsion can occur.

(iv) There is an initial adsorption reaction followed by a diffusive penetration of the ions into the adsorbent.

(v) There is feedback effects on potential a adsorption increases.

These assumptions have been built in five series of

equations which their presentation here is beyond the scope of this study.

2.4.3. Phosphate Adsorption Isotherms

Many of the studies on phosphate and other anions adsorption by soils and synthetic materials have shown non-conformity of P adsorption data to the equation models presented in this study (Muljadi et al., 1966; Rajan and Perrott, 1975; Ryden et al., 1977; Bowden et al., 1977; Barrow, 1978; Holford, 1982). The reasons for the non-conformity to the equations have been attributed to the assumptions underlying the equations (Barrow, 1978). Some of the assumptions underlying some of the models assume that the surface charge and the rate of adsorption and/or desorption of the adsorbent do not change with increasing concentration of the adsorbed materials (Barrow, 1978; Bowden et al.,1977; Bowden, 1980).

Several factors, apart from nature of adsorbent are known to affect adsorption reactions. These factors include: temperature, equilibrating period, solid:solution ratio, method of shaking, type and concentration of supporting electrolyte, presence of accompaning specifically retained cation or anion and pH of the electrolyte (Barrow and Shaw, 1975; Barrow, 1978; Bowden, 1980; Parfitt, 1980). All the above factors may effect the surface charge and the rate of

adsorption of cations and anions onto soils and synthetic materials. The adsorption of phosphate by soils, for example, make the surface charge more negative and the affinity of soil colloids for the anion decreases with increase in P concentration and pH as well as decrease in ionic concentration (Mekaru and Uehara, 1972; Sawhney, 1974; Wann and Uehara, 1978; Uehara and Gillman, 1981). In attempt to fit into and interpret phosphate adsorption data Muljadi et al. (1966), Syers et al. (1977) have suggested the partitioning of the adsorption isotherms into two or more regions in order to get meaningful interpretation of adsorption data. Using the Langmuir equation model as an example, it has been suggested to divide the isotherm into three regions. The first region cover the linear portion close to the x-axis, at low equilibrium P concentrations. The mechanisms of P adsorption in this region has been postulated to involve specific and non-specific exchange reactions, and the adsorbing surface has low affinity for P and the adsorption process is partly reversible (Beek and Van Riemsdijk 1979; Bowden et al., 1980).

The second region was suggested to cover the convex portion to the y-axis and the main reaction mechanisms involved are specific ligand exchange together with precipitation reactions (Holford and Gleeson, 1976; Harter and Smith,

1981; Barrow, 1985). Phosphate adsorption affinity in this region is much higher than in the first region.

The third region is thought to involve dissolution-precipitation reactions and covers the steep and almost parallel to the y-axis portion of the isotherm (Rajan and Fox, 1974; Rajan and Watkinson, 1976).

2.5 Effects of Phosphate Retention on the pH and Cation Exchange Capacity (CEC) of the VCS Soils

pH and cation exchange capacity are very important soil properties which give a reflection of the fertility status of a soil. Variable charge soils are characterized by low pH values (< 5.5) and low CEC (<10 c.mole/kg) except for the Andepts which may have higher CEC value >30 c.mole/kg soil (Sanchez, 1976; Parfitt, 1980). Low pH values lead to problems of aluminium and manganese toxicity, high P-fixation capacity and unfavourable conditions for microbial activities (Bohn et al., 1979; Nyambo, 1986). Since most of the plant nutrients are available as exchangeable cations, low CEC implies low nutrient supply to plants.

The conventional methods used for raising the fertility status of soils include the use of organic manures (Sanchez, 1976; Gillman, 1985; Mnkeni and MacKenzie, 1985), inorganic P fertilizers (Sanchez and Smith, 1980; Nyambo, 1986) and acid/ base correcting liming materials (Kamprath,

1970). Use of either of the above materials will depend very much on the economic and technical benefits.

It is not well known which among the three methods of raising fertility status of a soil is more appropriate to the VCS. It is known that the VCS have very high buffering capacity (Uehara and Gillman, 1981; Ma and Tikahashi, 1991) and it is argued that it would be more appropriate and easier to manipulate the surface charge of VSC soils through additons or retention of high charge density anions, for example the phosphate fertilizers rather than liming the soils with $CaCO_3$ and related materials (Sanchez and Smith, 1980; Sanchez and Uehara, 1980; Uehara and Gillman, 1981; Ma and Tikahashi, 1991).

Lime ($CaCO_3$) and other related materials are conventionally used as soil amendments aiming at raising pH, CEC and reduce P fixation. There has been doubts as to whether liming with $CaCO_3$ can significantly increase the pH, CEC and P availability of the VCS. For example, Uehara and Sanchez (1980) and Uehara and Gillman (1981) have reported insignificant increases in pH, CEC and P availability as result of liming the VCS with $CaCO_3$. Other studies (Chen *et al.*, 1973) have showed a significant increases in pH, CEC and available P, while similar studies (Frissen *et al.*, 1980) have shown no effects at all. The reasons for the lack of response could be explained by the following

equations showing the reaction of $CaCO_3$ in the soil (Uehara and Gillman, 1981):

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad (20)$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad (21)$$

$$M\text{-}OH]^+ + OH^- \rightleftharpoons M\text{-}O]^0 + H_2O \quad (22)$$

The hydroxyl ions liberated from the dissociation of $CaCo_3$ would be expected to raise the pH of the soil. However, for VCS with net positive charge the OH^- ions liberated would be used to neutralize the positive charge on the VCS and increases in pH would only be expected when all the positive charges on the VCS have been neutralized. Depending on the effectiveness of the liming materials and soil conditions, very large amounts of lime would be required in order to bring about a significant increase in pH and CEC, which may prove to be uneconomical.

Addition of organic matter to VCS have been reported to have positive effects on the chemical and physical properties of low fertility status soils (Sanchez, 1976; Gillman, 1985; Mnkeni and MacKenzie, 1985; Bleeker and Sageman, 1990). Organic matter has varied negatively charged radicals (acts as ion exchanger) which can be exchanged with positively charged ions in the soil, thus resulting increase in CEC. Organic matter is also considered to undergo chelation with metal ions, especially

polyvalent cations such as Al^{3+} and Fe^{3+}, thus increasing P availabilty (MacKenzie and Mnkeni, 1985).

The possibilities of using organic matter on a large scale farming with an aim of raising and CEC of the VCS is considered to be limited due to the reason that very large amounts of organic matter would have to be added into the soils in order to effect such changes. Further, organic matter is quickly decomposed and oxidized under tropical conditions and such an attempt would have very short-lived effects (Uehara and Gillman, 1981). It has therefore, been suggested that the use of high charge density anions like the silicate and phosphate could be more appropriate materials in raising the pH and CEC of the VCS (Hingston et al., 1967; Mekaru and Uehara, 1972; Sawhney, 1974; Wann and Uehara, 1978; Uehara and Sanchez, 1980; Uehara and Gillman, 1981; Smith and Sanchez, 1980; Ma and Tikahashi, 1991). The increase in pH and CEC observed in VCS when treated with phosphate and/ or silicate is considered to be due to the lowering of zero point of charge of the soils (Hingston et al., 1974; Wann and Uehara, 1978) and neutralization of positive charges and charge reversal due to accumulation of more negative charges (Fey and Le Roux, 1976; Fox and Searle, 1978; Uehara and Gillman, 1981). The probable reaction mechanism between P and the VCS has been suggested by Fox and Searle (1978) and Rajan (1978) to involve the

deprotonation of the exposed OH- groups at low pH values. Phosphate react with the positively charged surface groups by displacing the octahedrally co-ordinated water molecules (aquo group), thus resulting into the reduction of the surface charge from net positive charge to neutral. At higher pH values, further P retention lead to the protonation of the variable charge surface groups and therefore phosphate displaces the hydroxyl groups (hydroxo groups) thus resulting to surface charge reversal from neutral to net negative charge. These reactions are thought to take place when there is specific liqand exchange reactions, where HPO_4^{2-} displaces the hydroxyl groups. Accordingly, the surface become more negatively charged and the equilibrium pH thus increases. The increase in net negative charge lead to the development of an electrostatic potential and counter ions (cations) are adsorbed to balance the excess negative charge, hence the observed increase in CEC.

Studying the effects of P retention by ferruginous tropical soils, Mekaru and Uehara (1972) obtained an increase in CEC of about 0.8 c.mole/kg soil when the soils were equilibrated with 1 mMole P at pH 7.0. An increase in CEC of about 370% has been reported by Juo and Maduakor (1974) when Nigerian Ultisols were equilibrated with 10 moles P/kg soil. Further, Sawhney (1974) obtained an increase in CEC

between 11% to 88% when Connecti-cut soils were equilibrated with amounts of P equivalent to 10 moles P/kg soil. Sawhney observed that the increase in CEC varied with soil pH. For example, about 800 mg P/kg soil were required to produce a 1 c.mole/kg soil increase in CEC at pH 5.0 compared to 400 mg P/kg soil at pH 7.0, respectively. Schalascha and his co-workers (1974) obtained an increase in CEC of about 81 c.moles/kg soil when Chilean Andosol soil samples were equilibrated with P (as KH_2PO_4) solutions ranging in concentration from 10 to 4165 mMole P/kg soil. Although the pH and electrolyte concentration used in the equilibration were not mentioned, however, an average increase in CEC of about 50-60% was reported for each 10 mMole P/kg soil. Sanchez (1976) obtained almost an equal increase in CEC of about 0.7 c.mole/kg soil compared to those reported by Mekaru and Uehara (1972) and Sawhney (1974) when variable charge soils were equilibrated with 10 mMole P/kg soil. Wann and Uehara (1978) reported a higher value increase in CEC (NH_4OAc, pH 7.0) of about 3.8 c.mole/kg soil when an Oxisols was treated with 50 mMole P/kg soil as $(NH_4)_2HPO_4$ at pH above the ZPC of the soils. Other studies by Garcia-Miragaya (1984) obtained an increase in CEC of about 16% for each mMole P retained by Venezuelan Ultisols.

Similar studies by Mrema (1988) showed increases in CEC and pH (in bracket) of about 9.5 c.mole (0.5), 7.0 c.mole (0.2), 4.5 c.mole (0.3) and 3.0 c.mole (0.1) when Paleustalf, Vitrandept Tropohumult and Pallustert soils from Tanzania were equilibrated with 2000 mg P/kg soil respectively.

It shows from the above studies that in order to get a substantial increase in CEC and pH, large amounts of phosphate have to be added into the soils. Theoretical or predicted increases in CEC for a variety of soils and range of P concentrations according to Sanchez and Uehara (1980) indicates that on average the increases in CEC generally lies between 0.1 to 0.2 c.mole/kg soil for each 1mMole P added to the soils. For example, the 51 c.mole/kg soil increase in CEC obtained by Schalascha et al. (1974) when volcanic ash soils were treated with 4165 mMole P/kg soil was very small compared to the amount of P added. Similarly very high amounts of P (20,000 mg P/kg soil) had to be applied to Japanese, Australian, Brazilian and New Zealand soils in order to get significant increase in CEC (Fey and LeRoux, 1976).

The amounts of P used in the above studies were very high, however, such high levels of P up to 10 mMole P/kg soil) have been reported to exist around dissolving P fertilizer

granules when the fertilizer is banded on the soil (Harter and Smith, 1981). It could therefore be said that if the recommended rates of P fertilizers (which are only few kg $P.ha^{-1}$.) are banded, a relatively high P concentration would be expected in the fertilizer bands. This could result into a significant increases in pH and CEC.

It has been suggested by Lutz et al. (1966) and Sanchez and Uehara (1980) therefore, that when initial large amounts of P are applied to VCS soils by broadicasting (amendment application) to saturate the P fixing sites followed by annual or seasonal small amount applications by banding (maintanance application) a long term positive effects on the chemical and physical properties of the soils could be obtained.

It is well known today that increases in pH and CEC in soils is mostly pronounced in VCS colloids and the increases in CEC and pH are highest in Andosols, followed by Oxisols, Ultisols and Alfisols, respectively (Sanchez and Uehara, 1980; Gillman and Fox, 1980). According to the above mentioned authors, the reasons for the above trend of increases in pH and CEC in the different soils are considered to be attributed to differences in specific surface and surface charge density of the soil colloids.

Minerals with higher specific surfaces, for example, the amorphous aluminosilicates give higher increases in pH and CEC compared to any other variable charge colloids when they are equilibrated with phosphate solutions (Uehara and Gillman, 1981). Higher increases in CEC and pH are also obtained when the VCS soils are equilibrated with cations and anions of higher charge density, higher ionic concentrations and at higher pH values (Wann and Uehara, 1978; Smith and Sanchez, 1980; Barrow, 1985).

2.6 Effects of Phosphate Retention on the Anion Exchange Capacity (AEC) of the VCS Colloids

Most soils have both permanent and variable surface charge and hence substantial amounts of cations and anions can be retained by the soils. The majority of the soils have larger amounts of negative charge (CEC) compared to positive charge (AEC) at pH values close to neutral.

Variable charge soils and organic matter have substantial amounts of positively charged sites on their colloidal surfaces at pH values below 5.5 (Hingston *et al.*, 1967; Parfitt, 1978; 1980). The positively charged sites arise from protonation of hydroxyl (OH^-) groups present on the surfaces of the VCS colloids and on the broken edges of 1:1 and 2:1 clay minerals (Bohn *et al.*, 1979; Bowden *et al.*, 1980; Parfitt, 1980; Wada and Kawabata, 1991). Exchangeable

anions, for example, NO_3^- and Cl^- are held on the positively charged sites by electrostatic forces (non-specific adsorption mechanism) and are normally found in the diffuse double layer. The higher the capacity of a soil to adsorb the non-specifically retained ions the higher is its anion exchange capacity (AEC).

Anion exchange capacity of soils depend also on the pH and ionic strength of the equilibrating solution. Several workers (Gebhardt and Coleman, 1974; Singh and Kanehiro, 1969) have observed a negative correlation between pH and AEC. At pH values below the zero point of charge of the VCS, the hydroxyl groups present on the surfaces of the soil colloids are protonated and acquire a net positive charge. In order to balance the positive charges, non-specifically retained anions are adsorbed into the diffuse layer, thus resulting in increase in AEC. Whereas the retention of non-specific retained anions increases the AEC of VCS, specifically retained anions like phosphate decreases the AEC (Sanchez, 1976; Uehara and Gillman, 1981; Barrow, 1985). At higher pH values, the surface of the soil colloids become more negatively charged and the non-specifically retained anions are repelled, hence decrease in AEC.

Generally VCS colloids, especially the aluminosilicates have higher capacities to retain exchangeable anions compare to other VCS colloids. For example, a comparison of the relative proportion of AEC to CEC (in bracket) of some soil minerals extracted from Kenyan soils were found to be as follows: montimorillonite 1 (118), vermiculite 0 (85), illite 3 (19), halloysite 15 (81), kaolinite 2 (4), gibbsite 5 (5), goethite 4 (4), allophane 15 (51) and peat 6 (136) c.mole/kg soil (Sanchez, 1976). It has also been found by Carrasco (1972) and Van Raij and Peech (1972) that most Ultisols, Oxisols and Alfisols have AEC values less than 1 c.mole/kg clay, whereas Andosols have AEC values more than 7.0 c.mole/kg clay.

Although there is scanty literature about the capacities of different soils to retain exchangeable anions, it can be said that the AEC of many soils is very low except for some soils rich in amorphous aluminosilicates and organic matter. Most of the factors likely to affect the CEC of the soils will also affect the AEC of the soils, and in particular the variable charge soils.

2.7 Effect of Phosphate Retention on the Zero Point of Charge (ZPC) of the VCS Colloids

Soil is composed of both organic and inorganic compounds and attains maximum stability when the sum of the positive and negative charged ions constituting the organic and

inorganic compounds are equal or balanced. The charge balance equation proposed by Sposito (1981; 1989) (Equation 1) implies that charged ions (positive and negative ions) interact with similar ions in the soil solution and redistribution or exchange reactions takes place untill an equilibrium is established. The attainment of equilibrium, however, is a function of number of solution properties, pH and ionic strength being the most important (Parker et al., 1979; Sposito, 1981; Barrow, 1985). For example, Barrow (1985) reported that when a pure iron oxide mineral is suspended in water and the pH of the water raised or lowered by the addition of varying amounts of dilute base or acid, a point will be reached whereby the net charge on the surface of the mineral will be zero. The pH value at which the net surface charge of the mineral is zero due to presence of equal amounts of positive and negative charges is termed "zero point of charge" (ZPC/ pH_0) (Parks, 1967; Parker et al., 1979; Payman et al., 1979; Sposito, 1981; Boligar, 1985; Barrow, 1985; Anne Lewis-Russ, 1991).

Zero point of charge is regarded as a useful parameter in the study of ion (anion) adsorption mechanisms by soils and pure materials, purity of synthetic materials and measurement of surface charge of soils and pure materials (Van Raij and Peech, 1972; Galler et al., 1976; Keng and Uehara, 1974; Stoop, 1980).

Zero point of charge could also be applied in the characterization and classification of soils, pure minerals, and geological materials in relation to their surface (Parks, 1967; Uehara and Gillman, 1981; Anne Lewis-Russ, 1991). Permanently charged soils generally are said to have ZPC values lower than their natural pH value, whereas the VCS have ZPC values higher than their natural pH values. Zero point of charge values less than pH 3.5 are considered to be a rough prediction for soils dominated by 2:1 clay minerals, whereas ZPC values above pH 3.5 predicts the domination of variable surface charge materials (Gallez et al., 1976; Stoop, 1980).

Zero point of charge has also been used in the characterization and classification of the different soil orders, their intensities of weathering, their mineralogical composition and organic matter content (Stoop, 1980; Uehara and Gillman, 1981; Gillman, 1985). For example the average ZPC values for Oxisols, Ultisols and Alfisols from Hawaii, Brazil and Nigeria were found to be 6.0-6.5, 4.0 and 3.5, respectively (Keng and Uehara, 1973; Juo, 1981). The approximate ZPC value for some pure minerals SiO_2, TiO_2, MnO_2, Fe_2O_3 and Al_2O_3 is 2.0, 4.5, 4.0, 6.5-8.0 and 7.5-9.5, respectively (Parks, 1965; Parfitt, 1980; Greenland and Mott, 1978). Although ZPC of the

different soil minerals may vary (not constant) depending on their purity and hydration state, most soil minerals and synthetic materials have characteristic fixed ZPC value at a given set of conditions and solution properties (Gazell et al.,1976; Stoop, 1980). The presence of small amounts of permanently charged materials or organic matter deposited on the surfaces of pure haematite, for example, is considered to lower the ZPC of the mineral significantly (Uehara and Gillman, 1981). Permanently charged materials and organic matter act as impurities and therefore, lower the ZPC of the pure minerals. Specifically retained anions like phosphate and silicate are said to have similar effects on the ZPC of the VCS as do organic matter (Hingston et al., 1967; Wann and Uehara, 1978; Uehara and Gillman, 1981; Stoop, 1980; Gillman, 1985).

Application of 1500 mg P/kg soil to Oxisols has been reported to have lowered ZPC of the soils from pH 5.0 to pH 3.5 (Wann and Uehara, 1978). In another study (Gillman, 1985) reported a decrease in ZPC of about one pH unit for each 100 mg P/kg added to the tropical Queensland VCS. Many of the studies have shown that specifically retained anions lowers ZPC of soils, however, the extent of lowering of the ZPC depends on the initial soil pH, ionic strength

and amount of variable charge minerals present in the soil (Wann and Uehara, 1978; Stoop, 1980; Bleeker and Sageman, 1990).

3. MATERIALS AND METHODS

3.1 Site Selection and Soil Sampling

Soils from Tanga region were selected for the study. The soil samples for the study were collected from selected sites at Marikitanda, Mlesa and Mlingano villages in Muheza district. The sites from which the soil samples were taken were selected on the basis of the soils' low pH values (<5.5), low CEC (<10 c.mole/kg) and high aluminium saturation percentage (>15%). These soils are characteristically dominated by low activity clays/ variable charge minerals/ colloids.

One soil profile was opened at each site and the profiles were located on the crests of the land catenary sequence. The profiles were described and sampled according to the procedures developed by FAO (1970). Soil classification was done following the procedures developed by FAO (1988) and Soil Survey Staff (1990). Soon after sampling, the soil samples were air-dried, sieved through 2 mm sieve and stored in plastic bags. Routine soil analysis were undertaken for the samples collected from all the horizons of the three profiles, but the studies in relation to P adsorption capacity, pH, cation exchange capacity (CEC), anion exchange capacity (AEC) and zero point of charge

(ZPC) were restricted to the subsoils (oxic horizon) samples that appears to have the highest aluminium saturation percentage. The restriction of the core studies to the subsoil samples was aimed at avoiding the effects of any revious P fertilization on the soils as well as the influence of organic matter on the surface charge characteristics of the soils.

3.2 Routine Soil Analysis

Particle size distribution of the soils were determined by the pipette method (Day, 1965) and the textural classes were allocated to each soil sample using the USDA textural triangle. Soil pH was determined in distilled water and in 1 M KCl in soil:solution ratio of 1:2.5 (Peech, 1965). The net charge on the soil colloids was taken as the difference between the pH determined in 1 M KCl and in distilled water $\Delta pH = pH(KCl - pH(H_2O)]$ (Mekaru and Uehara, 1972; Sanchez, 1976). Organic carbon was determined by the Walkley and Black wet oxidation method (Allison, 1965) and the total nitrogen by the semi micro-Kjeldahl distillation method (Bremner, 1965). Bray-1 P was determined by the Bray and Kurtz No. 1 (Watanabe and Olsen, 1965). Exchangeable acidity was determined by 1 M KCl at the pH of the soil (Peech, 1965). Cation exchange capacity (CEC) was determined by the neutral (pH 7.0)

NH_4OAc. saturation method (Peech, 1965) and the effective cation exchange capacity (ECEC) was taken as the summation of the exchangeable bases plus exchangeable acidity (Sanchez, 1976). Exchangeable bases were determined from the neutral NH_4OAc. extracts by atomic absorption spectrophotometer (Chapman, 1965). Free iron and aluminium oxides were determined by the citrate-dithionite-bicarbonate (CDB) method (Mehra and Jackson, 1960). Qualitative mineralogical analysis was determined by x-ray diffraction technique (Whittig, 1965). Qualitative mineralogical analysis was carried out on whole soil samples due to lack of appropriate mineralogical analysis equipment. The amount of soil sample required for the core studies was obtained by grinding a 2 mm sieved soil sample such that the entire sample passes through a 100 mesh sieve. As far as the routine soil analysis is concernd all the determinations were carried out in duplicate.

3.3 Phosphate Retention by the Soils

The amounts of phosphate (P) retained by the soils were determined following the procedure outlined by Fox and Kamprath (1970) and Fox *et al.*, (1971). Four gramme oven dry equivalent soil samples were weighed into duplicate eleven 100 ml centrifuge tubes and 40 ml of 0.01 M $CaCl_2$ solution containing different levels of P equivalent to 0,

50, 100, 200, 400, 600, 800, 1000, 1200, 1600 and 2000 mg P/kg as KH_2PO_4 were added into the tubes. Three drops of toulene were added into each tube to arrest microbial activities. The tubes were shaken for two hours continuously on an end-to-end shaker and left to equilibrate at room temperature for 48 hours with half hour shaking interval after every 6 hours. At the end of the equilibrating period the suspensions were immediately centrifuged. The amounts of P in the supernatant solutions were determined colourimetrically following the ammonium molybdate-ascorbic acid method (Murphy and Riley, 1962; Watanabe and Olsen, 1965). The amounts of P retained were taken as the differences between the amounts of added P and the amount of P in the supernatants. The P retention data obtained were plotted according to the Langmuir and Freundlich equations. The P adsorption maxima and bonding energies were estimated by simple regression analysis.

3.4 Determination of the Effect of Phosphate Retention on the pH, CEC and AEC of the Soils

The determination of the effects of P retention on pH, cation and anion exchange capacities involved two major steps:

3.4.1 Equilibration of the Soils with Phosphate Solutions

Four gramme oven dry equivalent soil samples were weighed into duplicate six-100 ml centrifuge tubes and 40 ml of 0.01 M $CaCl_2$ solution containing different levels of P equivalent to 0, 100, 400, 800, 1200 and 1600 mg P/kg as KH_2PO_4 were added into the tubes. Three drops of toulene were added into the tubes and shaken for two hours continously on an end-to-end shaker and left to equilibrate at room temperature for 48 hours with 1/2 hours shaking interval after every 6 hours. At the end of the equilibrating period the pH of the suspensions were immediately determined. pH adjustment was not done for the reasons that the pH of the three soil samples were not very much different from each other, the equilibrating solution ($CaCl_2$) could act as a buffering agent and pH adjustment could lead to charge reversal on the VSC colloids.

Immediately after pH determinations the samples were centrifuged. The amount of P in the supernatant solution were determined colourimetrically following the ammonium molybdate-ascorbic acid method (Watanabeand Olsen, 1965). The amount of P retained by each sample was taken as the difference between the amount of added P and the amount of

P in the corresponding supernatant.

3.4.2 Cation and Anion Retention by Saturation Method

The cation and anion exchange capacities of the P-treated soil samples were determined following the procedure outlined by Schalascha *et al*. (1974) with some modifications. The residues left in the centrifuge tubes in 3.4.1 after centrifuging were washed four times with 25 ml portions of ethanol to remove excess KH_2PO_4. In the samples thus washed, CEC and AEC was determined by saturating the soils with 1 M KCl by washing three times with 30 ml of the 1 M KCl solution buffered at pH 5 with dilute solutions of triethanolamine (TEA) and para-nitrophenol. The residues in the centrifuge tubes were then washed three times with 30 ml of 1:1 methanol-water solution until no chloride could be detected in the supernatant solutions. Potassium was then displaced by washing three times with 30 ml of 1M NH_4NO_3 solution. Potassium (K^+) andChloride (Cl^-) ions were determined in the combined three washings, the former by flame photometer and the latter by ion selectrode meter model "Radiometer ion 83 meter, Copenhagen". The values of K^+ and Cl^- thus determined were taken to represent the CEC and AEC of the soils, respectively. Modifications which were made with respect to the Schalascha *et al*. (1974) method

include the use of four gramme soil samples instead of three gramme, pH of the washing solutions adjusted to pH 5.0 and 48 hours equilibration instead of 24 hour.

3.5 Determination of the Effect of Phosphate Retention on the Zero Point of Charge (ZPC) of the Soils

The determination of the effects of P retention on ZPC of the soils involved two major stps:

3.5.1 Equilibration of the Soils with Phosphate Solutions

Into each of the one hundred and twenty-100 ml centrifuge tubes prepared, a four-gramme oven dry equivalent soil sample and 40 ml of 0.01 M $CaCl_2$ solution were added into each of the hundred and twenty-100 ml centrifuge tubes prepared for the study. The tubes were grouped into six sets, each comprising of twenty of them. To the first set no phosphate was added while to the remaining five, different levels of P equivalent to 100, 400, 800, 1200, 1600 mg P/kg were added in solution form. Three drops of toulene were added into each tube. The suspensions were hence allowed to equilibrate for 48 hours with occassional shaking as in section 3.4.1 At the end of the equilibration period the samples were centrifuged.

Two samples from each of the five sets were randomly selected for the determination of P content in the supernatant solutions in order to find out the amount of P retained by the soils. The supernatant solutions in the rest of tubes were discarded.

3.5.2 Determination of the Efects of the Retained Phosphate on ZPC of the Soils

ZPC determinations followed the method outlined by Van Raij and Peech (1972) and Uehara and Gillman (1981). Water or acid treatment was not done to avoid irreversible changes in the nature of charge sites on the surface (Stoop, 1980; Manrique, 1985). After centrifugation (3.5.1) the 20 tubes of each set were arranged into two rows each with 10 centrifuge tubes. The tubes in each of the first and second rows were treated with 10 ml of 0.02 M and 0.2 M $CaCl_2$, respectively. The middle tubes in each of the rows had nothing added to them and were designated as "zero". An increasing amounts of 0.5, 1.0, 2.0, 3.0 and 4.0 ml of 0.1 M HCl (equivalent to 1.25, 2.5, 5.0, 7.5, and 10.0 c.Mole H^+/kg soil) were added into the tubes on the left of zero and similarly 0.5, 1.0, 2.0, and 3.0 ml of 0.1 M NaOH (equivalent to 1.25, 2.5, 5.0, and 7.5 C.Mole OH^-/kg soil) were added to the tubes on the right of the zero. Distilled water was added into each tube to

bring the total volume of the solution to 20 ml. The tubes were then allowed to equilibrate for 96 hours with occasional shaking. At the end of the equilibrating period the pH in each tube was immediately determined. The results for each level of P added were plotted on one graph as c.mole H^+/OH^- added to the soils versus the equilibrium pH of the suspensions. The point of intersection for the 0.02 M and 0.2 M curves for each of the graphs drawn was taken as ZPC value of the soils at a given soil and at a particular level of added P.

It is important to note, however, where reproducible results were not obtained from individual duplicates, extra repetition were performed to get consistent results. This was the case especially with the determination of the CEC, AEC and ZPC. Also where the ZPC titration curves did not form a well defined crossing point, the ZPC values were obtained by extrapolation from the centre of the region of overlapping.

4. RESULTS AND DISCUSSION

4.1 Physico-chemical Characteristics of the Soils

Based on the physico-chemical properties of the soils and the profile descriptions (Table 1, 2, 3 and Appendices 1a to 3b) the Mlingano soil was classified as a Rhodic Ferralsol (FAO, 1988) or Rhodic Kandiustox (Soil Survey Staff, 1990). The Mlesa and Marikitanda soils were classified as Haplic Ferralsol (FAO, 1988) or Rhodic Haplustox and Typic Haplustox (Soil Survey Staff. 1990), respectively. In the remaining part of the text the Mlingano, Mlesa and Marikitanda soils will be referred to as Rhodic Kandiustox, Rhodic Haplustox and Typic Haplustox, respectively.

The physico-chemical properties of the topsoils and subsoil horizons of the soils under study are presented on Table 2, 3 and Appendix 1b, 2b and 3b. Results for the selected subsoil-oxic horizons to which the core study was confined are presented on Table 1. Since the core study was restricted to soil samples from the oxic horizons (pg. 38-39) the presentation and discussion of the results are concentrated more on the topsoil oxic horizons.

Table 1: The physico-chemical properties of the soils studied

Soil property	Soil great group, horizon and depth in cm					
	Rhodic Kandiustox		Rhodic Haplustox		Typic Haplustox	
	Ap	Oxic	Ap	Oxic	Ap	Oxic
	0-13	70-142	0-10	36-68	0-20	95-142
Clay content (%)	45	60	40	41	38	52
pH-H_2O	6.1	4.8	4.7	4.8	5.5	5.2
pH-KCl	5.0	4.0	4.2	4.2	4.9	4.5
ΔpH	-0.11	- 0.8	- 0.5	-0.6	-0.6	-0.7
Organic carbon (%)	1.90	0.55	2.51	1.08	3.70	1.04
Total nitrogen (%)	0.17	0.07	0.21	0.08	0.36	0.12
Bray-1 P (mgP/kg)	2	trace	1	1	2	2
CEC (c.molc/kg)	7.14	4.60	6.88	5.11	11.90	7.50
ECEC (c.molc/kg)	1.96	2.08	2.08	1.54	3.79	3.64
Exch. Al^{3+} "	0.01	1.14	0.47	0.56	0	0.09
Exch. bases "	1.32	0.84	1.33	0.82	3.66	2.41
Base saturation (%)	18	18	19	16	30	35
Al. saturation (%)	0	25	7	19	0	15

The clay content of the Ap horizons varied from 38% to 45% while that of the oxic horizons ranged from 41% to 60%. In the Ap horizons the clay content followed the order Rhodic Kandiustox > Rhodic Haplustox > Typic Haplustox while in the oxic horizons the trend was Rhodic Kandiustox > Typic Haplustox > Rhodic Haplustox. The clay content of the Rhodic Kandiustox and Typic Haplustox profiles increased with soil depth and their texture varied from sandy clay in the Ap horizons to clayey in the corresponding oxic horizons (Appendeces 1b and 3b). The clay content for the Rhodic Haplustox did not show much variations with increasing soil depth and the textural class as sandy clay throughout the profile (Appendix 2b).

The pH (H_2O) of the three soil profiles was strongly acid to very strongly acid (Ilaco, 1985) and the Ap horizons pH values ranged from 4.7 to 6.1 while those for the subsoil and oxic horizons varied from 4.8 to 5.2. The soil acidity for the three profiles varied in the order Rhodic Haplustox > Typic Haplustox > Rhodic Kandiustox in the Ap horizons, and Rhodic Haplustox = Rhodic Kandiustox > Typic Haplustox, in the oxic horizons, respectively. The pH of the three soils, notably that of the oxic horizons indicates that the soils were highly weathered and leached

and could likely be dominated by variable charge soil minerals.

The net charge on the soil colloids measured by ΔpH = (pH(KCl) - pH(H_2O)) (Sanchez, 1976; Uehara and Gillman, 1981) were all negative and their corresponding values were in the order Rhodic Kandiustox > Rhodic Haplustox > Typic Haplustox in the Ap horizons and Rhodic Haplustox > Typic Haplustox > Rhodic Kandiustox in the oxic horizons (Table 1). These results indicates that the three soils could have both variable charge and constant (permanent) charge due to the fact that the clay fraction of the soils studied contain kaolinite and oxyhydroxides of iron and aluminium (Table 3), minerals which characteristically contain variable charges (Sanchez, 1976; Uehara and Gillman, 1981). Further, Uehara and Gillman (1981) noted that ΔpH values ranging from positive to negative (less than -0.5) imply the presence of dominant amounts of variable charge minerals whereas negative ΔpH values above (-0.5) imply the presence of both permanent charge and variable charge minerals. The ΔpH values of the three soils ranged from (-0.11) to (-0.6) in the Ap horizons and from (-0.6) to (-0.8) in the oxic horizons, indicating the presence of both variable and permanent charge soil colloids in the soils studied.

Organic carbon content of the profiles were medium to very high (1.90 to 3.70) in the Ap horizons and very low to low (0.55 to 1.08) in the subsoil and oxic horizons (Ilaco, 1985). The organic carbon content of the three profiles decreased with increasing depth and the values followed the order Typic Haplustox > Rhodic Haplustox > Rhodic Kandiustox (Table 1 and Appendix 1b, 2b and 3b). The high organic carbon contents in the topsoils could be attributed to the fact that the soils were under permanent crops, namely sisal, tea and different food crops. The oxic horizons had low organic matter contents, a phenomenon typical to the Oxisols and Ultisols under climatic conditons favourable for high oxidation rates of organic matter, especially in the tropics (Smith and Sanchez, 1980; Uehara and Gillman, 1981).

The total nitrogen contents of the three profiles ranged from 0.17 to 0.36% in the Ap horizons and 0.07 to 0.12% in the subsoil and oxic horizons (Table 1). These values were correlated to the organic carbon contents and followed the same trend as those for the organic carbon contents.

The Bray-1 P of the three profiles were very low, both in the Ap and subsoil and oxic horizons. The P content ranged from trace to 2 mg/kg. The low P content could probably be

attributed to the inherent low P content of the soils and lack of P fertilization. Other reasons could include the high P retention capacities and affinity of the VCS minerals present in the soils. The highly weathered Oxisols and Ultisols are well known for their high P retention capacities hence the soils often have problems of P deficiencies for the normal growth of most crops (Parfitt, 1978; 1980; LeMare, 1981; Nyambo, 1986).

The CEC of the Ap and subsoil and oxic horizons of the three profiles (Table 1 and Appendix 1b-3b) were low to very low (4.60 to 11.90) according to the criteria established by Ilaco (1985). The values followed the order Typic Haplustox > Rhodic Haplustox > Rhodic Kandiustox. The CEC values particularly those of the oxic horizons corresponded to the low organic matter contents of the soils (Table 1). The low CEC values of the three soils is an indication of the low magnitude of net negative charge on the soil colloids. The CEC values of the three soils fall in the range typically characteristic as those observed in highly weathered Oxisols and Ultisols studied elsewhere (Sanchez, 1976; Soil Survey Staff, 1990). The ECEC values were lower than the minimum ECEC value (4.0 c.mole/kg) suggested by Sanchez (1976) as prerequisite for proper growth of many crops.

The percentage base saturation (PBS) of the three profiles were very low (16% to 35%) and did not vary appreciably with the soil depth. The PBS values for the three profiles followed the order Typic Haplustox > Rhodic Haplustox > Rhodic Kandiustox. The base status of the soils substantiate further the fact that the soils are highly weathered and leached and only very few weatherable minerals have been left in the clay fraction of the soils.

The exchange complexes of the three soils were dominated by aluminium and hydrogen indicating that the soils have substantial amounts of positive charges. The percentage aluminium saturation (expressed as the percentage of exchangeable aluminium over the CEC) was highest in the oxic horizons (15% to 25%) and followed the order Rhodic Kandiustox > Rhodic Haplustox > Typic Haplustox. The results indicate further that the three soils were dominated by VCS minerals, a typical characteristic of the Oxisols (Uehara and Gillman, 1981).

The CDB-extractable iron and aluminium values (Table 2) indicate that the three soils have higher contents of iron oxides than aluminium oxides. The Typic Haplustox has the highest content of iron and aluminium oxides while the Rhodic Kandiustox had the lowest values.

Table 2: Citrate–dithionite–bicarbonate (CDB) extractable iron and aluminium (%)

Soil great group	Fe	Fe_2O_3	Al	Al_2O_3
Rhodic Kandiustox	6.8	9.7	0.2	0.4
Rhodic Haplustox	10.6	15.2	1.1	2.1
Typic Haplustox	9.4	13.4	0.8	1.5

Table 3: Qualitative x-ray mineralogy composition of the soils

Soil great group	Mineralogical composition								
	Qua.	feld.	kaol.	gibb.	goet.	haem.	verm.	ilm.	rut.
Rhodic Kandiustox	xxxx	xxx	xxxx	xx	xxx	xx	x	x	x
Rhodic Haplustox	xxxx	x	xxxx	xxx	xxx	xxx	xxx	xx	xx
Typic Haplustox	xxxx	x	xxxx	xxx	xxx	xxx	xxx	xx	x

Normative constituent composition of the soils studied.
xxxx = 40 - 60%
xxx = 20 - 40%
xx = 10 - 20%
X = < - 10%.

Quar; feld; kaol; gibb; goet; haem; verm; ilm. and rut. stand for quartz, feldspar, kaolinite, gibbsite, goethite, haematite, vermiculite, ilmenite and rutile, respectively.

The mineralogical analysis indicates the presence of kaolinite, gibbsite, haematite goethite vermiculite and feldspars (Table 3). However, kaolinite and quartz are the dominant clay mineral indicating that the soils are highly weathered and that further weathering would result in increased formation of iron and aluminium oxides (Bohn et al., 1979; Buol et al., 1980).

From the above physico-chemical soil properties it can be inferred that the three soils are highly weathered and leached. Both the three soils fall in the same soil order and do not differ very much from one another despite the big difference in terms of climate under which the soils were formed. The soils have higher proportions of VCS minerals than permanent charge minerals. The fertility status of the three soils is very low and this could be attributed to the high contents of the variable charge minerals and the low pH.

4.2 Phosphate Retention by the Soils

The phosphate (P) retention capacities of the three soils are presented in Table 4, 5 and Fig. 1a, 1b and 1c. The P retention capacities of the three soils was determined at the native pH-H_2O of the soils, ranging between 4.8 to 5.2 (Table 1). The relationships between the amount of P

added, the amounts of P retained by the soils and the equilibrium P concentration were highly correlated (Table 4, 5). The amounts of P retained by the soils and the equilibrium P concentration increased with the increasing levels of the added and retained P, whereas the rate of P retention decreased with the levels of added and retained P. The results are similar to those reported by Rajan (1975), Parfitt (1977), White and Taylor (1977), Beek and Van Riemsdijk (1979), Gama (1979) and Mrema (1988).

At low levels of added and retained P and hence low equilibrium P concentrations the VCS colloids have many sites for P retention occupied by non-specifically retained anions, like the Cl^-, NO_3^- and SO_4^{2-} (Bohn at al., 1979). The non-specically retained anions are exchanged by phosphate and the phosphate ions are retained in the diffuse double layer (Gebarhardt and Coleman, 1974; Parfitt, 1977, Bohn et al., 1979). As more P was added and retained by the VCS colloids, the strongly bound aquo and hydroxo ligands on the planar, basal and edge surfaces of the VCS minerals were assumed to have been specifically exchanged by phosphate ions. Phosphate held by the specific exchange reaction mechanism is said to be fixed (Bohn et al., 1979) because it is held very strongly in the Stern layer to the extent that it is very slowly

Table 4: Phosphate retention by the soils according to the linear transformed Langmuir equation

Soil type	P-retention parameters		P-added (mgP/kg) 0	50	100	200	400	600	800	1000	1200	1600	2000
Rhodic Kandiustox	P-retained (x)	(mgP/kg)	0	49.7	98.8	194	387	512	645	801	870	980	1164
	P-retaubed (%)	-	0	99	99	97	97	85	81	80	72	61	58
	Equilibrium P (c)	(mgP/1)	0	0.03	0.12	0.58	1.30	8.80	15.25	19.87	33.00	62.00	83.60
	c/x	(kg/1)	0	0.68	1.20	3.00	3.30	17.0	24.00	25.00	38.00	63.00	72.00
	P-adsorption maxima (b)	(mgP/kg)											1091
	Bonding energy (k)	(1/mgP)											4.10.
	Correlation Coeff.(r)												0.98xxx
Rhodic Haplustox	P-retained (x)	(mgP/kg)	-0.1	49.8	99.5	197	395	589	780	874	1000	1280	1340
	P-retained (%)	(mgP/kg)	-0	99	99	98	98	98	98	87	83	80	67
	Equilibrium P (c)	(mgP/1)	-0.01	0.02	0.05	0.34	0.50	1.12	2.00	12.60	19.35	32.00	66.00
	(c/x)	(kg/1)	-	0.46	0.50	1.70	1.20	1.90	2.50	14.00	20.00	25.00	49.00
	P-adsorption maxima (b)	(mgP/kg)											1325
	Bonding energy(k)	(1/mgP)											1.82
	Correlation Coeff.(r)												0.99xxx
Typic Haplustox	P-retained (x)	(mgP/kg)	-0.03	49.8	96.0	190	377	560	730	830	992	1228	1475
	P-retained (%)		0	99	96	95	94	93	91	83	82	77	74
	Equilibrium P (c)	(mgP/e)	-0.05	0.02	0.40	0.97	2.30	3.97	7.00	17.00	21.00	37.00	52.50
	(c/x)	(kg/1)	-	0.30	4.20	5.00	6.10	7.00	9.60	20.00	21.00	30.00	36.00
	P-adsorption maxima (b)	(mgP/kg)											1392
	Bonding energy (k)	(1/mgP)											4.80
	Correlation Coeff.(r)												0.97xxx

XXX = Significant at P = 0.01; df = 11 - 2 = 9.

Table 5: Phosphate retention by the soils according to the linear transformed Freundlich equation

Soil type	P-retention Parameters		P-added (mgP/kg) 0	50	100	200	400	600	800	1000	1200	1600	2000
Rhodic Kandiustox	P-retained (x)	(mgP/kg)	0	49.7	98.8	194	387	512	645	801	870	980	1164
	P-retained (%)		0	99	99	97	97	85	81	80	72	61	58
	Equilibrium P (c)	(mgP/l)	0	0.03	0.12	0.58	1.30	8.80	15.25	19.87	33.00	62.00	83.60
	- log(x)	(mgP/kg)	-	1.70	1.99	2.29	2.59	2.71	2.81	2.90	2.94	2.99	3.06
	- log(c)	(mgP/l)	-	-1.47	-0.92	-0.24	0.11	0.94	1.18	1.30	1.52	1.79	1.92
	P-adsorption maxima(a)	(mgP/kg)											$8.9x10^5$
	Bonding energy (1/n)	(1/mgP)											2.53
	Correlation Coeff. (r)												0.99xxx
Rhodic Haplustox	P-retained (x)	(mgP/kg)	-0.5	49.8	99.5	197	395	589	780	874	1000	1280	1340
	P-retained (%)		0	99	99	98	98	97	97	87	83	80	67
	Equilibrium P (c)	(mgP/l)	-0.01	0.02	0.05	0.34	0.50	1.12	2.00	12.60	19.35	32.00	66.00
	log x	(mgP/kg)	-	1.69	2.00	2.30	2.60	2.77	2.89	2.94	3.00	3.11	3.13
	log c	(mgP/l)	-	-1.84	-1.30	-0.47	-0.30	0.05	0.30	1.10	1.28	1.50	1.82
	P-adsorption maxima(a)	(mgP/kg)											$6.7x10^5$
	Bonding energy (1/n)	(e/mgP)											2.30
	Correlation Coeff.(r)												0.95xxx
Typic Haplustox	P-retained (x)	(mgP/kg)	-0.30	4.98	96.0	190	377	560	730	830	992	1228	1475
	P-retained (%)		0	99	96	95	94	93	91	83	82	77	74
	Equilibrium P (c)	(mgP/l)	-0.05	0.02	0.40	0.97	2.30	3.97	7.00	17.00	21.00	37.20	52.50
	log x	(mgP/kg)	-	1.70	1.98	2.28	2.58	2.75	2.86	2.92	3.00	3.09	3.17
	log c	(mgP/l)	-	-1.82	-0.40	-0.01	0.36	0.60	0.84	1.23	1.32	1.57	1.72
	P-adsorption maxima(a)	(mgP/kg)											$1.1x10^5$
	Bonding energy (1/n)	(1/mgP)											2.12
	Correlation Coeff.(r)												0.98xxx

XXX = Significant at P = 0.01; df = 11 - 2 = 9.

exchangeable under normal soil conditions (White and Taylor, 1977; Parfitt, 1977; Beek and Van Riemsdijk, 1979; Bohn et al., 1979).

Specific ligand exchange reaction mechanism between P and aquo and hydroxo groups lead to charge reversal from net positive charge to net negative charge, hence increases in soil pH and CEC (Sawhney, 1974, Wann and Uehara, 1978; Sposito, 1981; Uehara and). This phenomena lead to decrease in the rate of P retention with increasing levels of added P as a result of repulsion among the already adsorbed P ions (Bowden et al., 1980; Barrow, 1985). Decrease in the rate of P retention is also attributed to saturation of the retention sites as more P is added and retained by the soils. These two phenomena are the principle causes for the observed increases in equilibrium P concentration with increasing levels of added P in this study and other similar studies.

4.2.1 Phosphate Adsorption Capacity of the Soils

The P adsorption capacities (P adsorption maxima) obtained from regression analysis of the data according to the linear transformation of the Langmuir equation (Table 4) were very high, ranging from 1100-1400 mg P/kg (Fox, 1980). The P adsorption maxima values followed the order

Typic Haplustox > Rhodic Haplustox > Rhodic Kandiustox. The high P retention capacities of the soils were attributed to the high contents of VCS minerals, namely the iron and aluminium oxides and kaolinite. The results are in conformity with other results reported for Oxisols and Ultisols (Gama, 1979; Fox, 1980; LeMare, 1981; Juo, 1981). The P retention capacity of the VCS minerals has been suggested to follow the order amorphous oxyhydroxides > crystalline oxyhdroxides > 1:1 layer silicates (Fox et al., 1971; LeMare, 1981).

The Rhodic Haplustox, however, did not retained the highest amount of P as expected compared to the rest of the soils. This is quite contrary to earlier observations (Table 2) taking into account its relatively higher Fe^{3+} and Al^{3+} oxides content. This could be explained by other factors such as the crystallinity of the different mineralogical constituents of the soils. Crystallinity in soils is a function of soil type and/or stage of weathering. Poorly crystallized soil minerals (for example amorphous oxides) have high specific surfaces with many adsorption sites compared with a well crystallized mineral (Bohn et al., 1979; Gillman, 1981).

The bonding energy (P affinity) values from regression analysis of the P adsorption data (Table 4) did not show a defined relationships to the factors largely responsible for high P retention by VCS minerals. This could be attributed to the non-conformity of the assumptions underlying the Langmuir equation at different levels of P retention. Several workers (Barrow, 1978; Bowden et al., 1980; Holford, 1982) have disqualified the Langmuir adsorption affinity parameter as it does not give meaningful results that could be used to describe phosphate adsorption reactions.

4.2.2 Phosphate Adsorption Isotherms

Plots of the P adsorption data versus the equilibrium P concentration according to the linear transformation of the Langmuir equation (Fig. 1a, 1b) were curved (L-type), and the isotherms were close to each other, almost parallel to the x-axis at equilibrium P concentrations below 10 mg P/l. The isotherms were concave to the x-axis at equilibrium P above 10 mg P/l.

The curved nature of the isotherms indicate that the data did not conform to the Langmuir equation. The reasons behind could be due to the assumptions underlying the applicability of the Langmuir equation. The assumptions

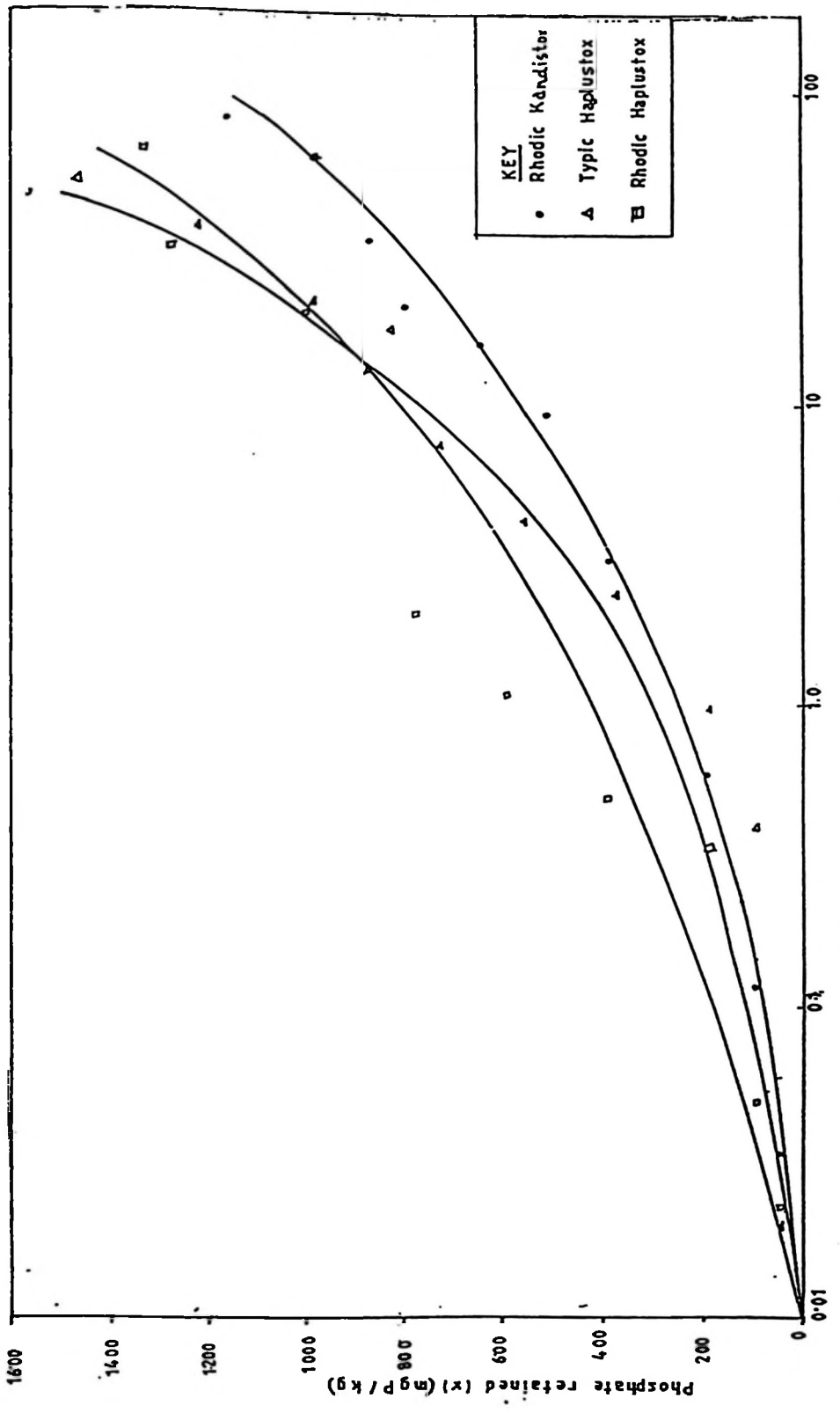


Fig. 1(a): Plots of phosphate retention data according to the Langmuir equation

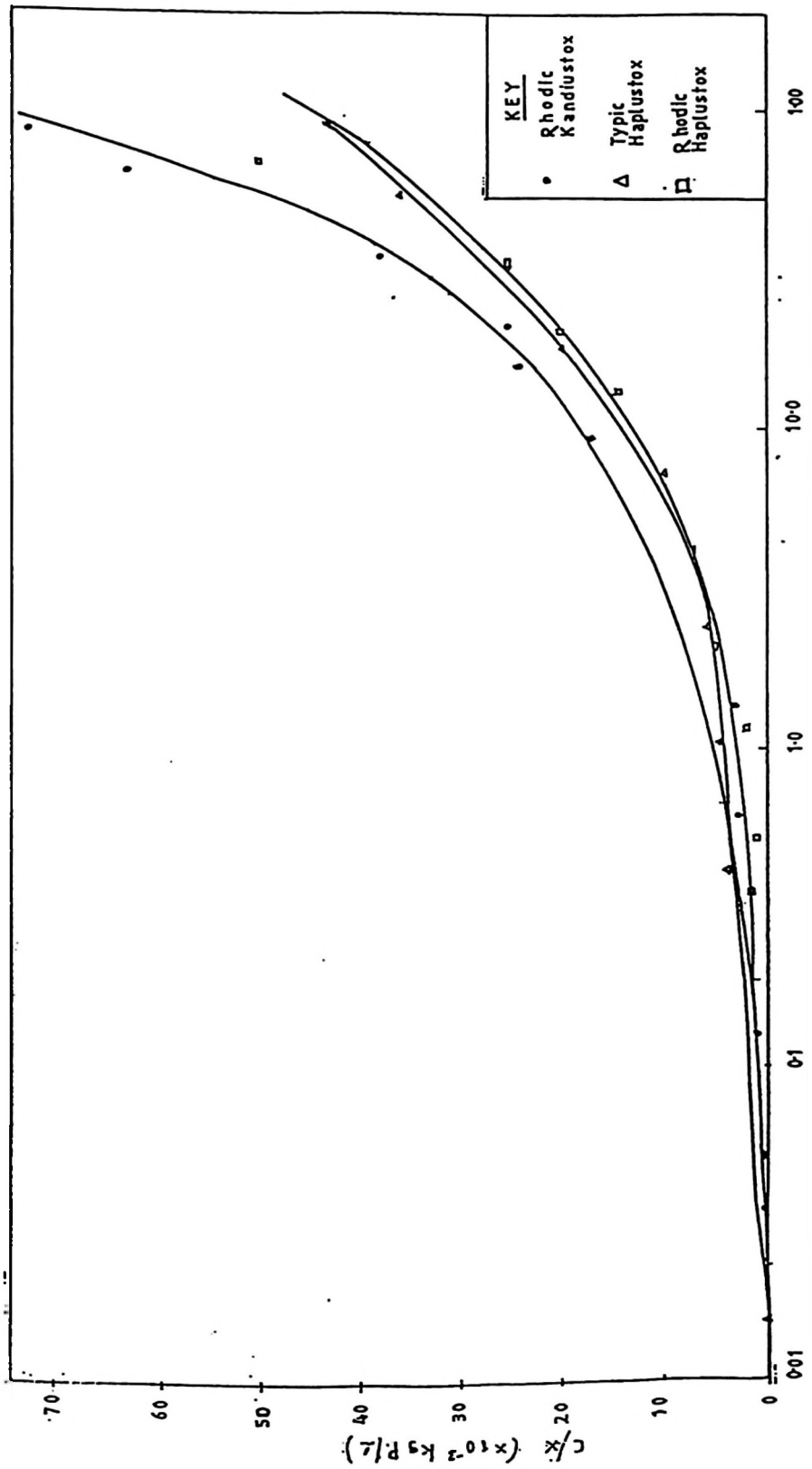


Fig.(1 b). Plots of phosphate retention data according to the linear transformed Langmuir equation

are said to overlook many factors which affect P retention by soils, like changes in pH, ionic strengh, temperature, equilibration period, soil solution ratio and the presence of other anions (Barrow, 1978; Bowden et al., 1980). Although the correlation coefficient values between the amounts of P retained and the equilibrium P concentrations were very high, (Table 4) the data did not conform to the equation. The results agree with the suggestions of Harter and Smith (1981) and Olsen and Khasawneh (1980) that high correlation coefficient values do not necessarily mean a goodness-of-fit of the adsorption data to the Langmuir equation. Non-conformity of P adsorption data to the Langmuir equation has also been reported by Rajan and Perrott (1975), White and Taylor (1977). Olsen and Khasawneh (1980) and Holford (1982).

The curved nature of the isotherms is also thought to be attributed to the presence of multiple adsorption sites with differing adsorbing affinities (Bache and Williams, 1971; Holford, 1982), lateral interactions between the adsorbed P-ions (Harter and Smith, 1981) and different P adsorption mechanisms at different equilibrium P concentrations (Rajan and Perrott, 1975; Ryden et al., 1977; Rajan and Watkinson, 1976; Parfitt, 1977; Beek and

Van Riemsdijk, 1979). It has been suggested. therefore that the use of two surface modified Langmuir equation model (Muljadi et al., 1966; Holford, 1982) or more than two surfaces equation model (Barrow, 1978; Bowden et al., 1980), other models like the kinetic models (Barrow and Shaw, 1975) and the Freundlich equation model (Fitter and Sutton, 1975; Holford, 1982) as a better alternatives to the simple Langmuir equation.

For the soils studied, the Langmuir plots hold true at equilibrium P concentrations below 10 mg P/l as the isotherms were linear. This is in accordance to the observations made by Barrow (1978) that the Langmuir equation might hold true at limited range of equilibrium concentrations less than 1.0 mg P/l. Therefore in order for the isotherms to be useful in describing P adsorption, it has been suggested that the isotherms be divided into two or more regions, each region representing a different P retention mechanisms (Muljadi et al., 1966: Syers et al., 1977). According to these authors the linear portion probably represents reaction mechanisms related to the non-specific exchange reaction mechanism. At equilibrium P concentrations between 1-40 mg P/l and >40 mg P/l the probable reaction mechanisms are specific ligand exchange and precipitation reactions and dissolution reactions in

addition to specific and precipitation reactions, corresponding to region II and III, repectively (Fig. 1a, 1b). In regions II and III, therefore the assumptions underlying the Langmuir equation do not hold true (Rajan and Watkinson, 1976; Barrow, 1978).

The P adsorption isotherms for the three soils were similar and close to each other indicating similar mechanism of P adsorption. This could be due to the similarities in the soils properties, that is the physico-chemical properties (Table 1, 2). This is also revealed by the small differences in the P adsorption capacities of the soils.

Plots of the P adsorption data according to the linear transformation of the Freundlich equation did not give straight line (Fig. 1c). The non-conformity of the data to the Freundlich equation could be attributed to the complex reaction mechanisms which could likely be affected by many factors. This appears to be the case since a number of authors (Rajan and Perrott, 1977; Parfitt, 1978; Holford 1980) have thus demonstrated.

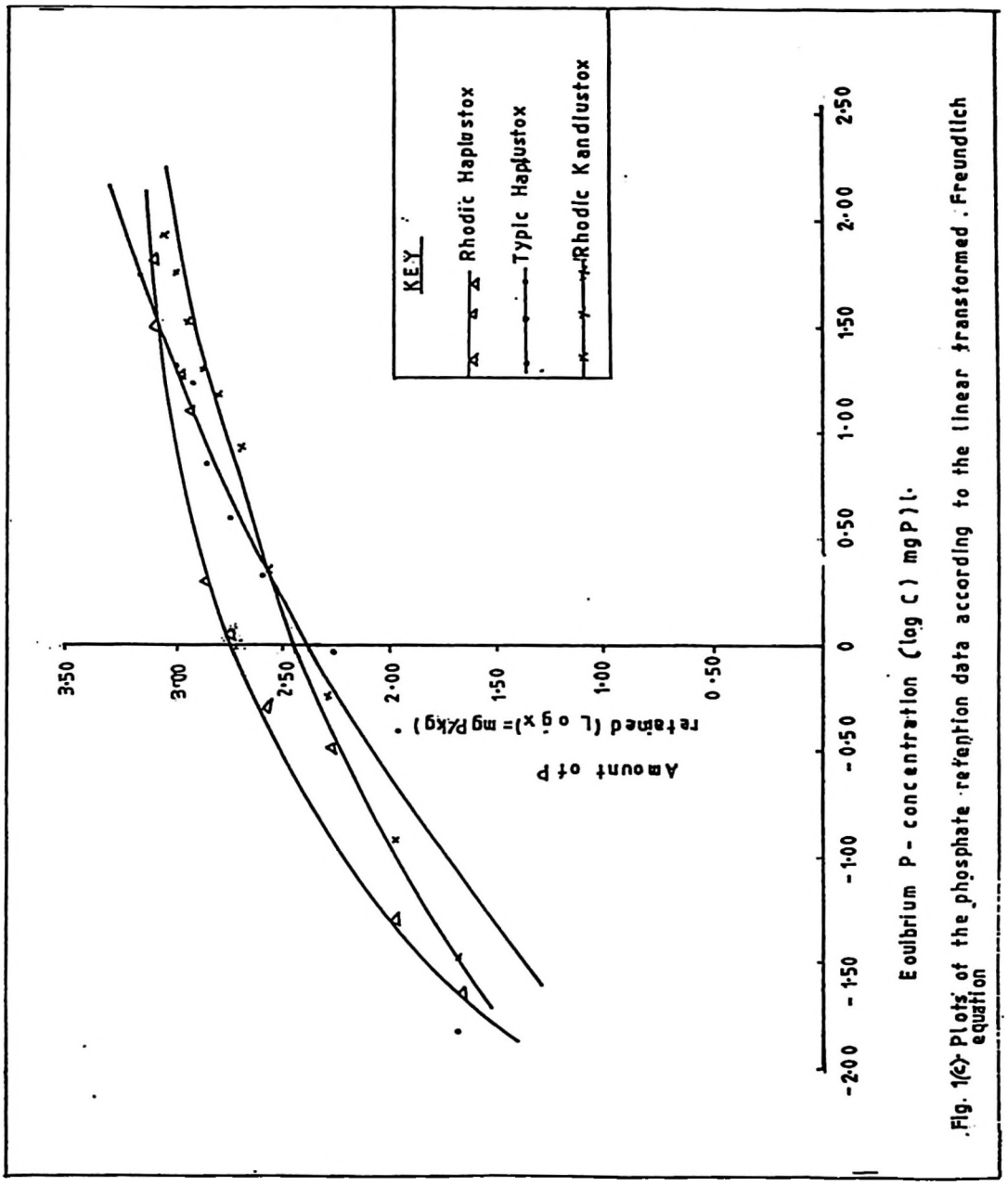


Fig. 1(c) Plots of the phosphate retention data according to the linear transformed Freundlich equation

The correlation coefficient values were very high for both the soils, however, the P adsorption maxima and P affinity values did not give a defined correlation with the factors known to influence P retention by the VCS minerals (Table 5). However, the Langmuir P adsorption maxima and bonding energy values were closer and comperable to the values obtained from other studies with similar soils (Fox, 1980; LeMare, 1981). These results the views of other authors (Barrow and Shaw, 1975; Barrow, 1978) that the Langmuir equation model could somehow give a better picture of P adsorption characteristics by soils than the other mentioned models.

4.3 Effect of Phosphate Retained on the pH of the Soils

The effects of P addition and retention on the pH of the soils are presented in Table 6. Addition and retention of increasing amounts of P increased the pH of the soils at all levels of the added P in the case of Rhodic Kandiustox and Rhodic Haplustox. The Typic Haplustox, however, has the highest increases in pH at 400 mg/kg of the added P. In the former two soils there was a gradual increase in pH at all levels of the added P beyond 400 mg P/kg. The corresponding pH values were 0.10, 0.41 and 0.06 for the Rhodic Kandiustox Rhodic Haplustox and Typic Haplustox, respectively.

Table 6: Effect of added and phosphate on the pH of the soils

Soil great group	Amount of phosphate added (mg P/kg) Equilibrium pH						Correlation	
	0	100	400	800	1200	1600	ΔpH	coefficient (r)
Rhodic Kandiustox	4.33	4.34	4.39	4.40	4.41	4.43	0.10	0.94***
Rhodic Haplustox	4.30	4.39	4.39	4.53	4.67	4.71	0.41	0.98***
Typic Haplustox	4.74	4.78	4.84	4.82	4.81	4.80	0.05	0.44

*** = significant at P = 0.01: (df = 6-2).

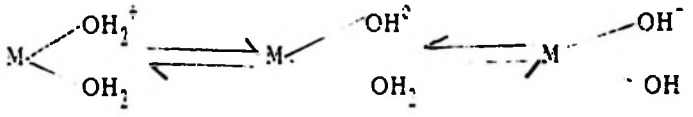
From these results it appears as if addition of P beyond 1600 mg P/kg could have resulted further increases in pH in the case of the Rhodic Kandiustox and Rhodic Haplustox. In these two soils, the increase in pH were highly correlated to the amounts of added and retained P, as opposed to the Typic Haplustox which showed a low correlation (Table 6).

The increases in pH for the three soils were attributed to the presence of iron and aluminium oxyhydroxides and kaolinite. The high contents of the VCS corresponded well with the Rhodic Haplustox which gave the highest increases in pH (Table 6). However, it was also expected for the Typic Haplustox to give a higher pH increases than the Rhodic Kandiustox because of the relatively higher iron and aluminium oxides. This deviation might have been attributed to the relative proportions of the aquo and hydroxo groups that were replaced by phosphate. According to Uehara and Gilman, (1981) it would be expected that higher increases in pH could be obtained in soils with higher proportions of hydroxo groups on the exchange sites than aquo groups (Uehara and Gillman, 1981). The deviation of the results between the Typic Haplustox and the Rhodic Kandiustox could also be attribtured to differences in the dissociation of the phosphate ions at the different pH

values of the soils. At higher pH values the dissociation of H_2PO_4 could also be higher, and this could produce protons that might have neutralized the OH^- groups produced in the ligand exchange reactions. The dissociation of H_2PO_4 could be shown by the following equation (Bohn et al., 1979):

$$H_2PO_4 \rightleftharpoons H_2PO_4^{1-} \rightleftharpoons HPO_4^{2-} \rightleftharpoons PO_4^{3-} \qquad (23)$$

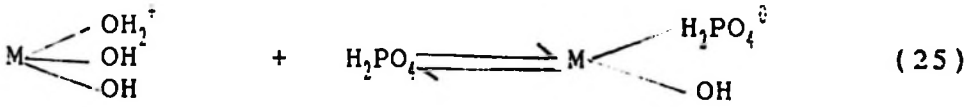
The dissociation of H_2PO_4 takes place between pH values 1-2, 4-6 and 9-11, respectively. The low pH values of the soils could have also resulted from the deprotonation of the aquo and hydroxo groups present on the VCS colloids, thus creating more sites for P retention. The deprotonation reaction could be summarized by the following equation model (Barrow, 1985):



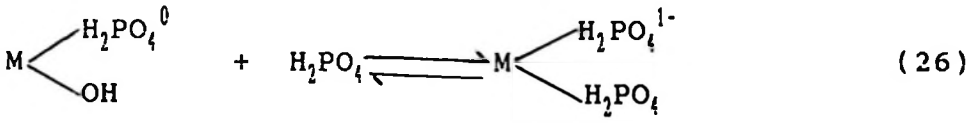
(24)

were M is a metal oxide.

Phosphate ions would be retained on the deprotonated surfaces through specific ligand exchange mechanisms, whereby the aquo groups are exchanged by phosphate ions as shown by the following equation (Rajan, 1976; Fox and Searle, 1978):



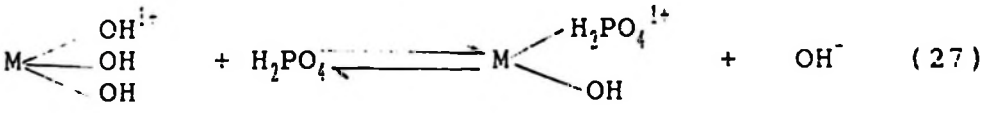
(25)



(26)

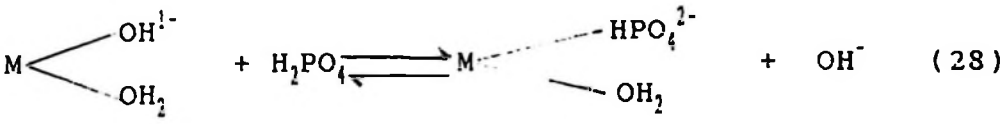
Phosphate could also be retained on the deprotonated surfaces through specific ligand reactions whereby hydroxo groups are exchanged for phosphate ions according to the following equation (Rajan, 1976; Fox and Searle, 1978; Uehara and Gillman, 1981):

(a)



(27)

(b):



(28)

The results on P retention obtained in the study were similar to those reported by Rajan and Fox (1975), Rajan and Perrott (1975), Wann and Uehara (1978), Uehara and Gillman (1981) and Mrema (1988).

Based on the results obtained in this study, about 3200 kg $P.ha^{-1}$. (equivalent to 1600 mg P/kg.) would be required to increase the pH of the Rhodic Kandiustox, Rhodic Haplustox and Typic Haplustox by 0.1, 0.4 and 0.06 pH units, respectively. This rate of P applications appears unbelievably high from the practical point of view particularly when one assumes a broadcast type of application. However, if the P fertilizer is banded, as it is commonly done for a number of crops, such levels of P would easily be attained and probably exceeded if one would determine the amount of P applied per unit surface area / soil volume of the spots fertilized by P.

4.4 Effects of Phosphate Retention on the CEC and AEC of the Soils

The effects of P retention on the CEC and AEC of the soils are shown in Table 7. Additions and retention of increasing amounts of P to the soils increased the CEC of the Rhodic Kandiustox, Typic Haplustox and Rhodic Haplustox by 103%, 66% and 61%, respectively. These increases in CEC of the three soils were equivalent to 0.08, 0.08 and 0.076 (an average of 0.08 c.mole/mMole P. kg soil) The minor differences in the increases in CEC among the three soils indicate that there was very little or no difference among the soils with respect to the

Table 7: Effects of added and retained phosphate on CEC and AEC of the soils

Soil great group	Amount of P Added	Amount of P Retained	CEC	AEC	Net charge[1]	ΔCEC/ΔP[2] Added	ΔCEC/ΔP[2] Retained
	mg P/kg)		(c.moles/kg)			(10^{-2} c.mole/mMole P)	
Rhodic Kandiustox	0	0	4.27	0.15	-4.12		
	100	96	4.30	0.15	-4.15		
	400	392	4.60	0.13	-4.47		
	800	648	5.50	0.11	-5.39		
	1200	900	6.72	0.11	-6.61		
	1600	993	8.42	0.10	-8.37	8	13
Rhodic Haplustox	0	-0.2	7.51	0.30	-7.21		
	100	97	7.59	0.22	-7.37		
	400	375	8.02	0.14	-7.88		
	800	742	8.77	0.12	-8.65		
	1200	980	10.17	0.11	-10.06		
	1600	1235	11.65	0.07	-11.58	8	11
Typic Haplustox	0	- 0.3	5.84	0.18	-5.56		
	100	98	5.93	0.16	-5.77		
	400	380	6.29	0.11	-6.18		
	800	792	7.16	0.10	-7.06		
	1200	996	8.36	0.11	-8.25		
	1600	1305	9.61	0.09	-9.25	7.6	9

1 = CEC - AEC

2 = Increase in Net charge between the lowest and highest level of added and retained P over the highest level of added and retained P.

reactions that influence the charge characteristics upon P application. This may probably be due to the fact that both the mineralogical composition and surface charge characteristics did not appreciably vary from one soil to another since they are in the same soil order.

The results obtained in the study are similar and close to those reported by Mekaru and Uehara (1972), Sawhney (1974), Schalascha et al. (1974); Sanchez (1976), Wann and Uehara (1978) and Mrema (1988). The increases in CEC obtained in the study could be attributed to non-specific P retention mechanisms whereby P exchange with other anions like the NO_3^- and Cl^- and SO_4^{2-}. This reaction is especially important for the retention of cations which have specific affinity for P. for example the Ca^{2+} and other divalent and trivalent cations (Bohn et al., 1979; Uehara and Gillman, 1981).

The increases in CEC could also be attributed to specific ligand exchange reactions (Eq. 28 to 31) between the phosphate ions and the aquo $(Al-H_2O)^+$ and hydroxo $(Al-O)^0$ groups from the exposed surfaces and broken edges of iron and aluminium oxides and hydroxides and the layer silicates (Rajan, 1976; Rajan and Watkinson, 1978; Fox and Searle, 1978; Sanchez and Uehara, 1980; Uehara and

Gillman, 1981; Mrema, 1988). The specific displacement of aquo and hydroxo groups by phosphate ions resulted in increases in the net negative charge on the soil colloids (Uehara and Gillman, 1981). In order to neutralize the negative charges on VCS colloids resulting from specific phosphate retention, more cations are adsorbed into the diffuse double layer, hence the observed increases in CEC ofthe soils (Sposito, 1981; Uehara and Gillman, 1981; Anne Lewis-Russ, 1991)

The AEC of the three soils before P additions were generally very low (< 0.3 c.mole/kg) (Table 7). The low AEC of the soils was expected taking into account that the pH of the soils was well above the ZPC and the corresponding delta pH values were negatively high (Table 1 and 8). The low AEC of the soils could most likely be attributed to the presence of both permanent and variable charge minerals in the soils, buffering effects of organic radicals and the high pH (5.0) of the soil solution used in the estimation of the AEC and CEC of the soils. The AEC values of the three soils at zero-P treatment were close to those reported for Oxisols and Ultisols of less than 1 c.mole/kg (Carrasco, 1972; Van Raij and Peech, 1973).

The AEC of the three soils decreased with the increasing amounts of added and retained P. The decrease in AEC of the three soils were very small, less than 0.1 c.mole/kg soil and did not give a well defined trend in relation to the amounts of added and retained P. The unproportional decrease in AEC in relation to the amounts of added and retained phoshate could be explained by the fact that organic and inorganic functional groups on the exposed surfaces of VCS minerals hold the H^+ and OH^- ions very strongly to the extent that it sometimes becomes difficult for other anions and cations to exchange with the H^+ and/or OH^- groups on the soil colloids (Wada and Kawabata, 1991). Also according to Uehara and Gillman (1981) some positively charged sites in soils are not easily accessible as they may be hidden in the mass of the layer silicates and the phosphate ions in the equilibrating solution may not scavenge easily through the layers and neutralize the positive charge. This could also lead to the underestimation of the AEC. It is also known that the retention of P by soil colloids is a very complex reaction mechanism which may involve many reactions operating simultaneously and some of the reactions could be affected by some of the physico-chemical properties of the equilibrating solutions (Van Raij and Peech, 1972). Therefore, some of the postulated reaction mechanisms of

P with VCS may not take place as expected. This could eventually affect the expected AEC changes upon P adsorption.

The net surface charge on the soil colloids obtained as differences between the CEC and AEC were negative for all the three soils (Table 7). The net charge on the soil colloids were in the order Typic Haplustox > Rhodic Haplustox > Rhodic Kandiustox at all levels of added P. This trend is in accordance with the pH values of the soils studied (Table 1), substantiating further that the soils have both permanent and variable charge minerals.

4.5 Effects of Phosphate Retention on the Zero Point Charge of the Soils

The effect of P additions and retention by the soils are presented on Table 8, Fig. 2 and Appendix 5 to 7. Addition and retention of different amounts of P lowered the ZPC of the Rhodic Kandiustox, Rhodic Haplustox and Typic Haplustox from pH values 4.5, 3.4 and 4.1 to pH 2.7, 3.3 and 3.0, respectively. The extent of lowering ZPC of the soils were highly correlated to the amounts of added and retained P. The ZPC values for the three soils at zero P treatment were within the range of ZPC of 4-6 that has

Table 8: Effects of added phosphate on the zero point of charge (ZPC) of the soils

Soil great group	Phosphate added (mg P/kg) ZPC						ΔZPC (0-1600 mgP)	Correlation coefficient (r)
	0	100	400	800	1200	1600		
Rhodic Kandiustox	4.5	3.8	3.7	3.2	3.0	2.7	-1.8	0.94 ***
Rhodic Haplustox	4.1	3.7	3.6	3.3	3.1	3.0	-1.1	0.95 ***
Typic Haplustox	3.9	3.7	3.6	3.5	3.4	3.3	-0.6	0.96 ***

*** significant at P= 0.01; (df = 6-2).
(-) Imply that ZPC was lowered.

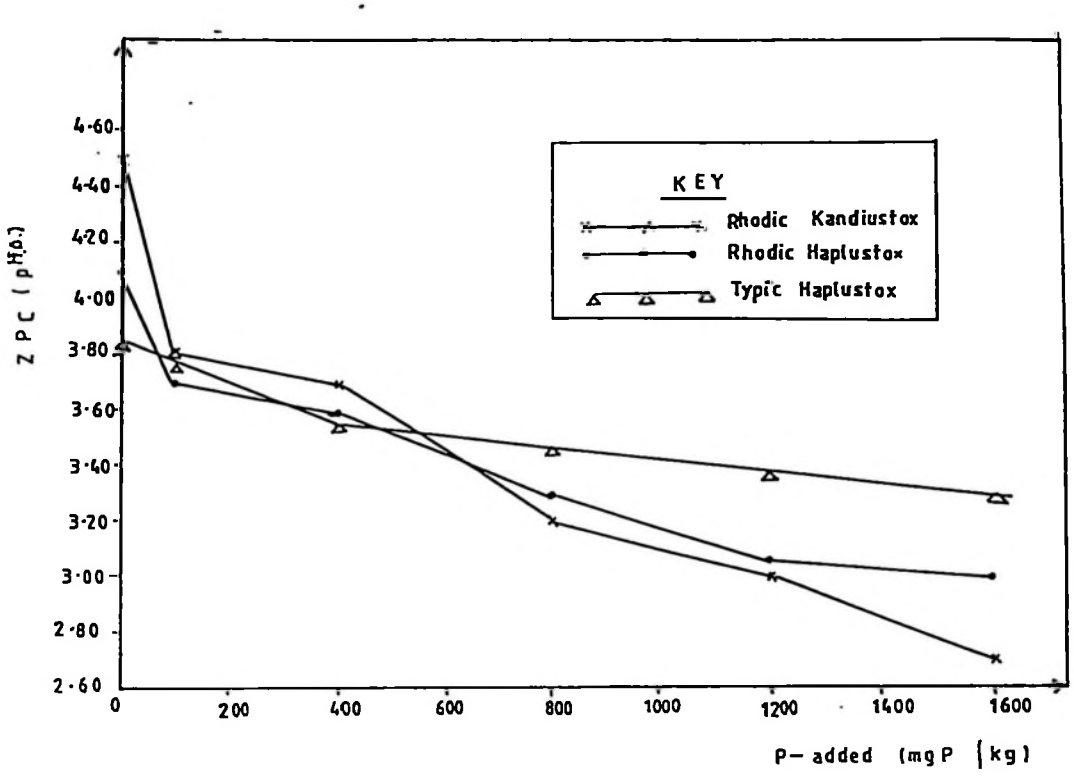


Fig. 2: Effect of different levels of added P on the P^{H}_{o} of the soils

been reported by Van Raij and Peech (1972), Keng and Uehara (1973) and Wann and Uehara (1978) for similar soils, namely Oxisols and Ultisols.

The effects of added and retained P on the ZPC of the soils were attributed to specific ligand exchange reaction mechanisms whereby the aquo and hydroxo groups present on the iron and aluminium oxyhydroxides and on the broken edges of the layer silicates are exchanged by the phosphate ions. The displacement of the aquo and hydroxo groups by phosphate ions resulted in charge reversal from net positive to negative charge and decrease in pH of the suspensions so as to balance the net charge on the soil colloids (Breesma and Lyklema, 1973; Hingston et al., 1974; Wann and Uehara. 1978; Stoop, 1980; Sanchez and Uehara, 1980; Uehara and Gillman, 1981; Anne Lewis-Russ. 1991).

The extent of lowering of the ZPC among the three soils was highest in the Rhodic Kandiustox and lowest in the Typic Haplustox. This corresponded to the lower contents of iron and aluminium oxides in the Rhodic Kandiustox compared to the Typic Haplustox (Table 2). These observations agree with the views of Wann and Uehara, (1978), Greenland and Mott (1978), Stoop (1980), Uehara

and Gillman (1981) and Gillman (1985) that presence of organic and inorganic variable charge materials, for example the iron and aluminium oxides increases the ZPC of soils, whereas permanently charged materials and organic and inorganic anions, for example, PO_4^{3-}, SiO_4^{4-} and organic radicals lowers the ZPC of soils. The ZPC of the Fe_2O_3 and Al_2O_3, for example were approximated to be 6.5 to S.0 and 7.5 to 9.5, respectively (Parks, 1965, Greenland and Mott, 1978). However, their influences on soil ZPC values will also depend on the relative proportion and weighting effects of other permanently charged materials.

The zero point of charge values of the three soils at zero P treatment were above 3.5, indicating that the soils were dominated by variable charge materials. The ZPC value of 3.5 is the minimum value suggested by Parks (1965) and Uehara and Gillman (1981) for soils dominated by VCS minerals and maximum values for soils dominated by permanent charge soil mineral colloids.

The titration curves for the determination of the ZPC of the soils (Appendix 5b, 6b and 7b) were similar and closely similar to those reported by other workers (Van Raij and Peech, 1972; Wann and Uehara, 1978) for similar soils. The resemblance of the curves of the studied soils

is an indication that the three soils had almost similar properties and the mechanisms of lowering ZPC in the soils were also similar. The titration curves for the three soils were influenced by the pH and ionic concentration of the equilibrating solutions (Appendix 5a, 6a and 7a). These are some of the factors known to influence the charge on the soil colloids (Bowden et al., 1980; Wann and Uehara, 1978; Uehara and Gillman, 1981; Anne Lewis-Russ, 1991).

4.6 Management Implications of the Results Obtained from the Study

The results obtained in the study indicate that the soils are highly weathered and leached, dominated by variable charge minerals in the clay fraction particularly kaolinite and iron and aluminium oxides and hydrous oxides (Table 1, 2 and 3).

The three soils have low fertility status attributed to low soil acidity, low base saturation and high P fixation (Table 1 and Appendix 1b, 2b and 3b). Addition of P to the soils proved to have some positive effects on the fertility status of the soils. It inhanced the soil pH by a maximum of 0.1 pH unit. Concerning the CEC, considerable increases (55 to 103%) were recorded.

The surface charge characteristics of soils are of central importance in soil management because the majority of the reactions that controls nutrients availability and many of the soil physical properties are dependent upon the physico-chemical processes that take place at the soil particle surfaces. Soil pH is an important chemical property as it determines the surface charge of the soil colloids. Therefore, the correct manipulation of the soil pH is crucial for the proper management of such soils.

The VCS are known to have high net positive surface charge density at low pH values and therefore, large amounts of P would be required to counteract the high buffering effects of such soils and bring a reasonable increases in pH and CEC. However, the actual amounts of P required to raise the pH and CEC of the soils could be reduced substantially if the P fertilizer is banded rather than broadcasted. There is substantial evidence that band application of P fertilizers is superior to broadcasting (Sleight et al., 1984; Russell, 1988). Banding is considered to reduce the soil-fertilizer contact, hence limiting the extent of P fixation by the soil colloids. Banding places the fertilizer closer to the roots, and shorten the diffuson pathway of the P ions to the plant roots.

Banding of P fertilizers also reduces the actual amounts of fertilizer required per hectare since the fertilizer granules near the roots dissolves and can result into P concentrations of about 4 to 4.5 moles/kg soil (Lindsay and Stephenson, 1959).

Though expensive, applications of high rates of P fertilizers to the high P fixing soils could have some advantages because of the high residual effects of P fertilizers. A high initial P application to the high P fixing soils (amendment application) followed by seasonal small doses (maintance application) have been proved to support a good continuous crop yields for a number of years (Fox and Kamprath, 1970; Sanchez and Uehara. 1980; Uehara and Gillman, 1981).

Adoption of the above mentioned management stratergies for soils with high P fixation capacities and low fertility status like the VCS could be more successful if the use of lime ($CaCO_3$), calcium silicate ($CaSiO_4$) and/or organic matter are also included in the management packages. When modest amounts of $CaCO_3$ and P fertilizers are used together to lower the exchangeable aluminium and increase the negative charge on the soil colloids the combined effects of the two materials would be even higher and relatively

less expensive than when used separately (Smith and Sanchez, 1980; Ma and Takahashi, 1991). This kind of management stratergy has been the basis for successful agriculture in Hawaii and Brazil where Oxisols are dominant (Uehara and Gillman, 1981). Results would be even more superior if $CaSiO_4$ rather than $CaCO_3$ is used together with P fertilizers, because the silicate group has a stronger effect on the surface charge of VCS than PO_4 and can reduce P retention by displacing PO_4^{3-} from the retention sites (Ma and Takahashi, 1991). The effects would also be enhanced if organic matter is applied together with P fertilizers (Sanchez, 1976; Gillman, 1985). Organic radicals have similar effects like the silicate ions on the surface charge of the VCS and could therefore reduce P retention.

5. SUMMARY AND CONCLUSIONS

Highly weathered soils from Tanga, Tanzania were selected for the study of phosphate retention and the effects of added and retained P on the pH, CEC, AEC and ZPC of the soils. The three soils from Mlingano, Mlesa and Marikitanda, Muheza district were classified as Rhodic Kandiustox, Rhodic Haplustox and Typic Haplustox, respectively based on the profile descriptions and the physico-chemical properties of the soils.

The three soils have very high P retention capacities ranging from 1000-1400 mg P/kg. The high P retention capacities of the soils were attributed to the high contents of the variable charge mineral colloids, namely iron and aluminium oxides and hydrous oxides and kaolinite present in the soils.

The amounts of P retained by the soils and the equilibrium P concentrations increased with the levels of added and retained P, while the rate of P retention decreased with the increasing levels of added and retained P. These phenomena indicate that the VCS colloids have many sites for P retention and the retention sites become gradually saturated with P as more P is added into the soils. Gradual saturation of the retention sites through non-

specific and specific reaction mechanism resulted in the neutralization of the positive charges and surface charge reversal from positive to negative. Further addition of P led to repulsion among the phosphate ions, decreased affinity of the colloid surface for P and therefore, increased the soil solution P concentrations.

The P adsorption data did not conform to the Langmuir and Frendlich equation models. The probable reasons for the non-conformity could be that the assumptions underlying the equations could not encompass all the factors and mechanisms affecting P retention by the soils. The equations could be useful for phosphate data interpretation only at P concentrations below 10 mg P/l.

The isotherms for the three soils were similar and close to each other. The phenomena indicate that similar P retention mechanisms were operating in the three soils and the P retention characteristics of the three soils were similar because the soils had more or less a similar mineralogical composition and their physico-chemical properties were not much different from each other. The Langmuir equation model was taken as a better equation to the Freundlich equation model because the P adsorption maxima values were more realistic and comperable to other

results obtained for soils similar to the soils used in this study.

The addition and retention of P by the soils increased their pH values by units less than 0.4. The increases in pH of the soils were attributed to specific ligand exchange mechanisms, whereby phosphate exchanges with the aquo and hydroxo groups present on the surfaces of iron and aluminium oxides and hydrous oxides and on the basal, planar and broken edges of the layer silicates, particularly kaolinite.

The Rhodic Haplustox gave the highest increases in pH due to its higher contents in the VCS colloids and lower pH values. The lowest pH increase obtained for the Typic Haplustox was attributed to its higher initial pH value (4.70) and possibly due to the presence of lower proportions of the hydroxo group on the VCS colloids compared to the aquo groups.

Additions and retention of P by the soils considerably increased their CEC and decreased their AEC to a lesser extent. The increases in CEC and decreases in AEC of the soils were attributed to non-specific and specific exchange reaction mechanisms between phosphate and the

aquo and hydroxo groups and other anions present on the soil colloids. The increase in CEC of the three soils were on average equal to 0.08 c.mole/mMole P. The Rhodic Kandiustox gave the highest increases in CEC probably because of its lower initial CEC and organic matter contents. The Rhodic Haplustox gave the smallest increase in CEC. This could be to its lower initial pH value.

The additions and retention of P by the soils significantly lowered their ZPC values. The effects of P on the ZPC of the soils were also thought to be attributed to the specific exchange reaction mechanisms between phosphate ions and the VCS colloids. The lower ZPC values of the Rhodic Kandiustox were attributed to its relatively low contents of the VCS mineral colloids namely iron and aluminium oxides compared to the other soils. The higher ZPC values of the Typic Haplustox were related to the higher contents of these minerals.

The result obtained from the study indicate that the three soils from Tanga have very low fertility status and therefore, need careful soil fertility management and conservation practices so as to make them more sustainable for crop production. The low fertility status of the soils was attributed to low pH values, low CEC, high contents of

VCS minerals and high P retention capacities. The fertility status of the soils could, therefore, be raised by manipulating the surface charge of the soil colloids through applications of adequate amounts of P fertilizers to quench the fixation/ retention sites (amendment P application) and increase the net negative charge on the soil colloids.

The amounts of P fertilizers required to amend the soils could be reduced substantially if the P fertilizers are banded. It is suggested therefore, that the costs which would be incurred to amend the soils through P fertilizers application could also be minimized substantially if other soil amendments such as organic matter and liming materials like $CaCO_3$ and $CaSiO_4$ are used together with P fertilizers.

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APPENDICES

Appendix 1a: Soil profile description no. 1

Location: Mlingano Agricultural Research Institute. Muheza district.

Landform: Broad ridge crest in dissected peneplain.

Parent material: Gneiss.

Relief: Rolling to undulating.

Slope: 1%.

Type of slope: Linear.

Lenght of slope: About 1 km.

Position on the slope: Ridge crest.

Altitude: 183 m.

Vegetation: Different species of trees, shrubs (Lantana Camara) grasses (Hyperrhenia rufa).

Land use: Sisal plantation with grasses under growth.

Brief description of the soils: Very deep well drained, dark red, strongly acid. clayey topsoil over clayey subsoil.

Classification: Rhodic Ferralsol (FAO, 1988) or Rhodic Kandiustox (Soil Survey Staff, 1990).

Authors: Banzi, F., Kimaro, R. and Assenga, R.H.

Date: 8 April, 1992.

Appendix 1(a) continued

Ap

0-13 cm: dark reddish brown (5YR 3/3, moist); clay: moderate, fine subangular blocky structure: friable when moist; slightly sticky and slightly plastic when wet; many fine and common medium pores; many fine: few medium and coarse roots; clear wavy boundary,

BA

13-28 cm: dark reddish brown (2.5 YR 3/4, moist): clay: moderate and medium subangular blocky structure: friable when moist; slightly sticky and slightly plastic when wet: many common fine; few medium pores; common fine, few medium roots: clear and smooth boundary,

Bu1

28-70 cm: dark reddish brown (2.5 YR 3/4, moist): clay: moderate and medium subangular blocky structure: friable when moist; slightly sticky and slightly plastic when wet: many common and fine; few medium pores; common fine and few medium roots; clear and smooth boundary,

Bu2

70-102 cm: dark red (2.5 YR 3/6, moist): clay; moderate fine subangular blocky structure; very friable when moist; slightly sticky and plastic when wet; common fine and few medium pores: common fine roots; diffuse smooth boundary.

Bu3

142-170 cm: dark red (2.5 YR 3/6. moist); clay: moderate fine subangular blocky structure; very friable when moist; slightly sticky and slightly plastic when wet; many fine and few medium pores; common fine roots.

Appendix 1b: The physico-chemical properties for the Rhodic Kandiustox

Soil charact.	Horizon Depth(cm)	Ap 0-13	BA 13-28	Bu1 28-70	Bu2 70-102	Bu3 102-170
Texture:						
Clay	%	45	55	56	60	58
Silt	"	4	2	4	4	4
V. fine sand	"	4	4	4	4	5
Fine sand	"	13	11	10	10	11
Medium sand	"	17	13	11	11	12
Coarse sand	"	15	12	11	9	9
V. coarse sand	"	2	3	4	2	1
Texture class		s. clay	s. clay	clay	clay	clay
pH-H_2O		5.1	5.2	5.1	4.8	4.8
pH- KCl		4.0	4.3	4.1	4.0	4.1
pH-$CaCl_2$		5.2	4.4	4.1	4.0	4.1
Organic carbon	%	1.90	1.03	0.53	0.56	0.52
Total nitrogen	%	0.17	0.10	0.06	0.07	0.08
C/N ratio		11	10	9	8	9
Available P (mg/kg)		1.8	1.3	1.0	trace	trace
CEC (NH_4OAc. (c.mole/kg)		7.14	3.70	3.68	4.60	4.40
-Calcium	"	0.57	0.35	0.38	0.60	0.43
-Magnesium	"	0.38	0.20	0.14	0.12	0.13
-Potassium	"	0.26	0.08	0.08	0.04	0.05
-Sodium	"	0.11	0.03	0.02	0.03	0.03
Exch. acid.	"	0.07	0.52	0.91	1.24	1.21
Exch. Al3+	"	0.01	0.32	0.71	1.14	1.08
Hydrogen	"	0.06	0.2	0.20	0.10	0.13
Effective CEC	"	1.96	1.18	1.53	2.08	2.00
Base saturation	%	18	16	15	18	15
Al3+ saturation	%	0	9	19	25	23

Appendix 2a: Soil profile description no. 2

Location: Mlesa village - Muheza, district.

Landform: Summits of mountain block.

Parent material: Gneiss.

Relief: Hilly to mountain.

Slope: 38%.

Position on slope: Middle slope, facing south-wards.

Length of slope: 500 m.

Altitude: 890 m.

Natural vegetation: trees of different species, banana, sugar cane and varied food crops.

Land use: Intensive mixed cropping.

Brief description of the soils: Deep, well drained, dark reddish brown, strongly acid, sandy clay topsoil over reddish-yellow clayey subsoil.

Classification: Haplic Ferralsol (FAO, 1988) or Rhodic Haplustox (Soil Survey Staff, 1990).

Authors: F. Banzi, F. Kimaro, R. and Assenga, R.H.

Date: 5 April, 1992.

Appendix 2(a) continued

Ap

0-10 cm: dark brown (7.5 YR 3.5/4, moist); sandy clay; moderate, medium and fine subangular blocky structure; friable when moist; slightly sticky and slightl plastic when wet; very many fine, medium and coarse pores; many very fine and medium; few coarse roots; gradual and smooth boundary,

AB

10-35 cm: dark reddish brown (3.5YR 3/6, moist); sandy clay; moderate, medium subangular blocky structure; friable when moist; slightly sticky and slightly plastic when wet: many fine and medium, few coarse pores; many fine and few medium and coarse roots; gradual and smooth boundary,

Bws1

36-68 cm: reddish brown (5 YR 3/4, moist); clay; moderate, medium and coarse subangular blocky structure: very friable when moist; slightly sticky and slightly plastic when wet: many medium and fine pores; few medium and coarse roots; gradual and smooth boundary

Bws2

69-135 cm: yellowish red (5 YR 5/8, moist); clay; moderate, coarse subangular blocky structure; very weak when moist; slightly sticky and slightly plastic when wet; many fine pores; very few fine roots; clear and smooth boundary.

Appendix 2b: The physico-chemical properties for the Rhodic Haplustox

Soil characteristic	Horizon Depth (cm)	Ap 0-10	AB 10-35	Bws1 36-68	Bws2 69-135
Texture:					
Clay	%	40	39	41	41
Silt	"	14	14	12	14
V. fine sand	"	6	7	7	6
Fine sand	"	12	12	14	12
Medium sand	"	11	12	12	11
Coarse sand	"	10	12	11	10
V. coarse sand	"	7	4	3	6
Texture class		s. clay	s. clay	s. clay	s. clay
pH $-H_2O$		4.7	4.8	4.8	4.8
pH -KCl	"	4.2	4.1	4.2	4.2
pH $-CaCl_2$	"	4.0	4.0	4.0	4.0
Organic carbon	%	2.51	1.81	1.22	1.08
Total nitrogen	%	0.21	0.13	0.10	0.08
C/N ratio		12	14	12	13
Available P (mg/kg)		1	2	1.3	0.7
CEC (NH_4OAc.(c.mole/kg)		6.88	5.79	4.73	5.11
Exch. calcium (c.mol/kg)		0.63	0.35	0.46	0.58
Magnesium	"	0.17	0.14	0.15	0.13
Potassium	"	0.38	0.32	0.30	0.08
Sodium	"	0.15	0.15	0.12	0.03
Exch. acidity:	"	0.75	1.16	1.12	0.72
" Aluminium	"	0.47	0.93	0.88	0.56
" Hydrogen	"	0.28	0.23	0.24	0.16
Effective CEC	"	2.08	2.12	2.15	1.54
Base saturation	%	19	16	22	16
Al^{3+} saturation.	"	7	16	19	11

Appendix 3a: Soil profile description no. 3

Location: Marikitanda village -Muheza district.

Landform: Mountain summit.

Parent material: Gneiss.

Relief: Hilly to mountain.

Slope: 40-50%.

Length of slope: 450 m, facing south-east.

Type of slope: Linear.

Position on slope; Middle slope.

Altitude: 920 m.

Vegetation: Trees and grasses of different species.

Landuse: Tea plantation

Brief description of the soils: Very deep, well drained, strongly acidic, sandy clay topsoil over clayey subsoil.

Classification: Haplic Ferralsol (FAO, 1988) or Typic Haplustox (Soil Survey Staff, 1990).

Authors: Banzi, F., Kimaro, R. and Assenga, R.H.

Date: 6 April, 1992.

Appendix 3(a) continued

Ap

0-20 cm: dark reddish brown (5YR 2.5/2, moist); sandy clay; moderate, medium to fine subangular blocky structure slightly hard when dry; friable when moist; slightly sticky and slightly plastic when wet; many fine, common medium and few coarse pores; common fine few medium and few coarse roots; clear and smooth boundary,

AB

20-56cm: dark reddish bkrown (5YR 3/3, moist); sandy clay: weak, medium subangular blocky structure; friable when moist; sticky and plastic when wet; many fine, few medium, and few coarse pores; many fine, few medium and coarse roots; clear smooth boundary,

Bws1

60-85 cm: yellowish red (3.5 YR 4/6, moist); clay; weak and fine subangular blocky; very friable when moist; slightly sticky and slightly plastic when wet, many very fine and few medium pores; many very fine, few medium and few coarse roots; gradual and smooth boundary,

Bws2

85-103 cm: yellowish red (3.5 YR 4/6, moist); clay; weak, medium and fine subangular blocky structure: very friable when moist; sticky and plastic when wet; few medium and many

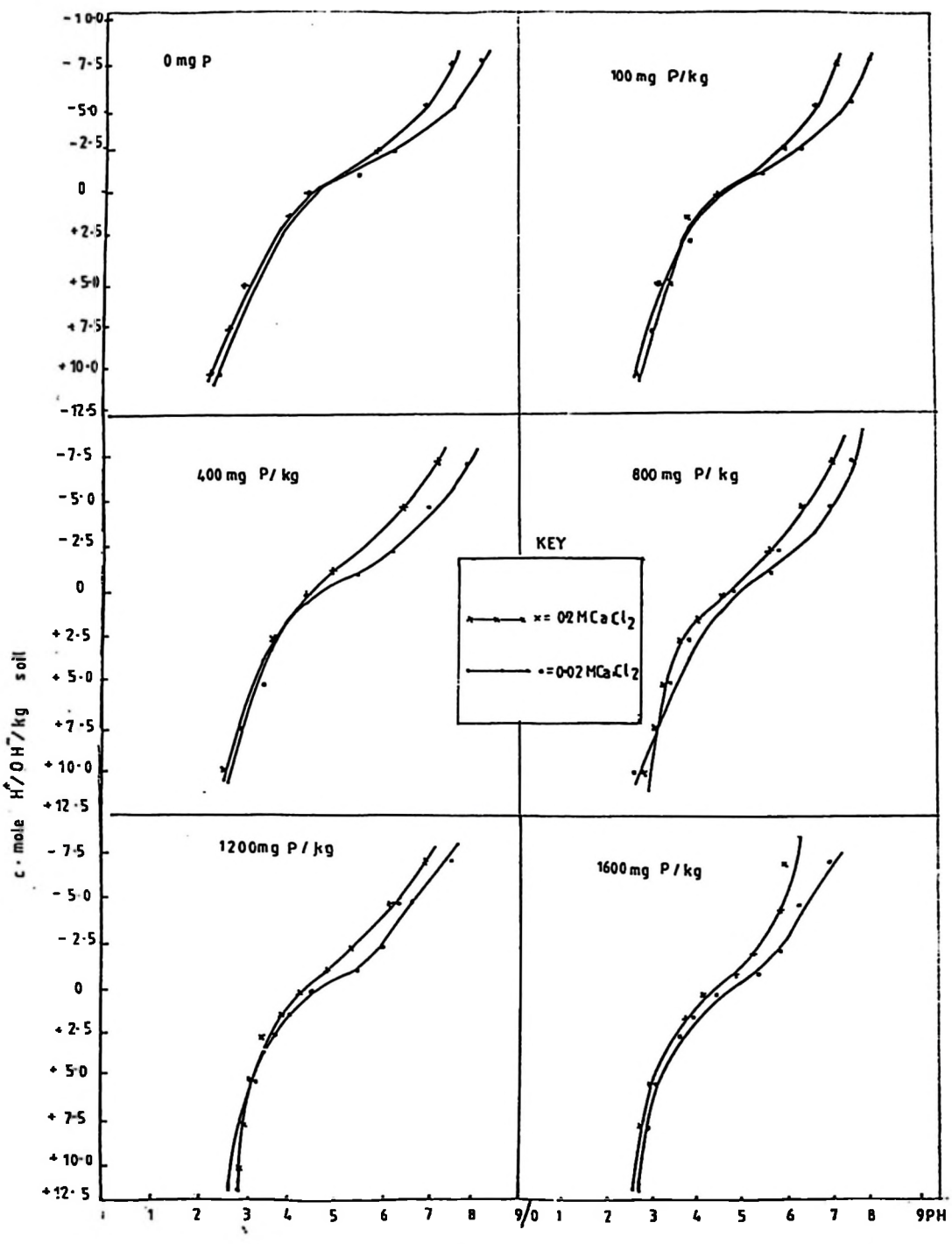
very fine pores; common, very fine roots; gradual and smooth boundary.

Appendix 3b: The physico-chemical properties for the Typic Haplustox

Soil character.	Horizon Depth (cm)	Ap 0-20	AB 20-56	Bws1 60-94	Bws2 66-103
Texture :					
Clay	%	38	50	52	56
Silt	"	15	14	13	10
V. fine sand	"	6	5	5	6
Fine sand	"	12	9	9	9
Medium sand	"	11	7	8	10
Coarse sand	"	12	9	8	8
V. coarse sand	"	6	5	5	1
Texture class	"	s. clay	clay	clay	clay
pH- H_2O		5.5	5.2	5.2	5.8
pH -KCl		4.9	4.3	4.5	4.6
pH- $CaCl_2$		4.9	4.4	4.5	4.2
Organic carbon	%	3.70	1.17	1.04	0.71
Total nitrogen	"	0.36	0.15	0.12	0.08
C/N ratio		10	8	9	9
Available P (mg/kg)		2.0	1.5	1.7	2
CEC (NH_4OAc. (c.mole/kg)		11.9	8.21	7.50	3.36
Exch. calcium	"	2.24	1.46	2.55	0.48
-Magnesium	"	0.88	0.27	0.70	0.15
-Potassium	"	0.33	0.07	0.09	0.02
-Sodium	"	0.21	0.08	0.07	0.05
Exch. acid.	"	0.13	0.31	0.23	1.12
-Aluminium	"	0	0.18	0.09	0.8
-Hydrogen	"	0.13	0.16	0.14	0.32
Effective CEC	"	3.79	2.12	3.64	1.80
Base saturation	%	30	23	35	13
Al^{3+} saturation	%	0	2	1	15

Appendix 4a: Data for the zero point charge for the Rhodic Kandiustox at different levels of added phosphate, pH and ionic concentration

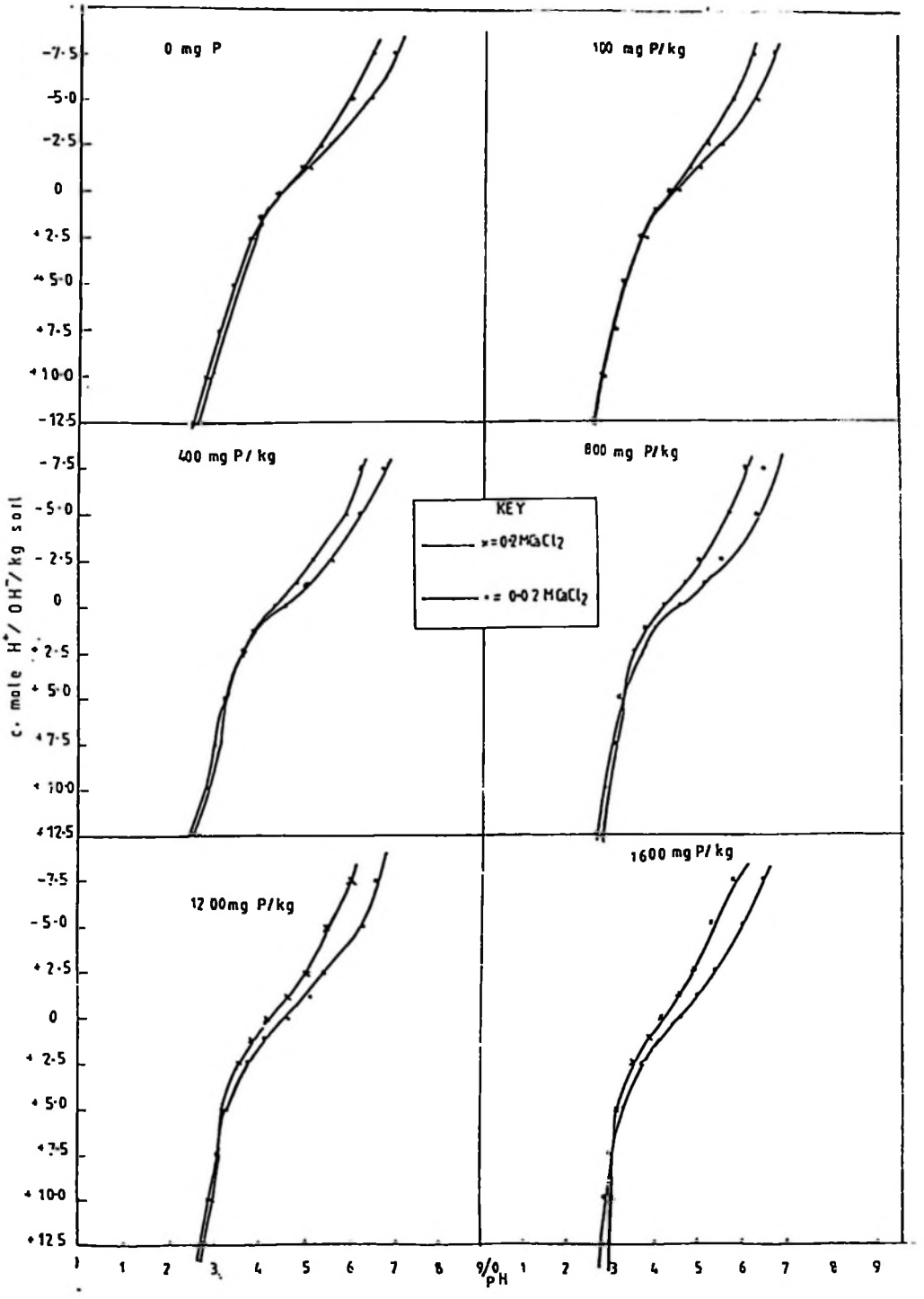
P added (mg/kg)	$CaCl_2$ (moles)	H^+/OH^- added (c.Mole/kg soil) 10.0	7.5	5.0	2.5	1.25	0	1.25	2.5	5.0	7.5
		pH									
0	0.02	2.31	2.68	3.06	3.74	4.04	4.42	5.57	6.30	7.63	8.25
	0.20	2.48	2.76	3.12	3.74	3.79	4.47	5.43	5.92	6.95	7.53
100	0.02	2.61	2.96	3.18	3.86	3.97	4.55	5.52	6.28	7.39	7.84
	0.20	2.62	2.98	3.42	3.68	3.90	5.53	5.40	5.87	6.62	7.07
400	0.02	2.63	2.90	3.13	3.88	3.92	4.46	5.50	6.27	7.05	7.96
	0.20	2.58	2.96	3.43	3.64	3.96	4.26	4.98	5.42	6.51	7.20
800	0.02	2.71	3.13	3.38	3.78	3.96	4.77	5.60	5.79	6.94	7.40
	0.20	2.82	2.98	3.23	3.63	3.98	4.50	5.14	5.57	6.26	6.89
1200	0.02	2.68	2.90	3.20	3.70	3.99	4.53	5.54	6.07	6.39	7.56
	0.20	2.88	2.92	3.22	3.40	3.76	4.25	4.80	5.35	6.23	6.95
1600	0.02	2.70	2.88	3.08	3.48	3.94	4.42	5.28	5.78	6.25	6.86
	0.20	2.57	2.69	2.97	3.20	3.73	4.13	4.80	5.22	5.83	5.91



Appindix 4b : Effect of different levels of added P on the ZPc of the Rhodic Kandiustox

Appendix 5a: Data for the zero point charge for the Rhodic Haplustox at different levels of added phosphate, pH and ionic concentration

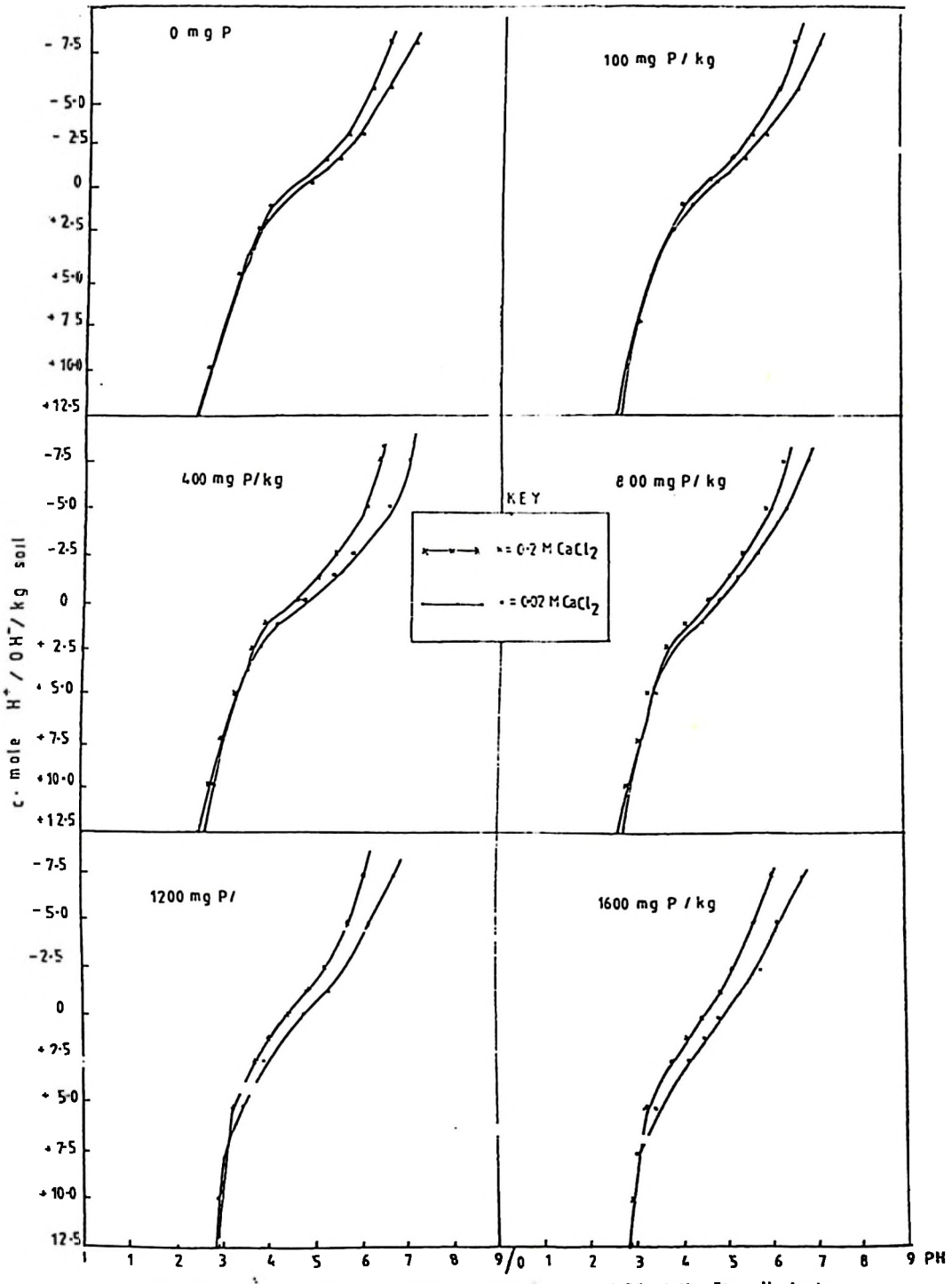
P added (mg/kg)	$CaCl_2$ (moles)	H^+/OH^- added (c.Mole/kg soil) 10.0	7.5	5.0	2.5	1.25	0	1.25	25	5.0	7.5
		pH									
0	0.02	2.70	2.99	3.41	3.73	3.91	4.32	5.04	5.43	6.34	6.80
	0.20	2.75	3.05	3.32	3.75	3.74	4.27	4.85	5.22	5.86	6.36
100	0.02	2.79	2.98	3.25	3.75	3.93	4.52	5.07	5.48	6.36	6.77
	0.20	2.78	3.07	3.30	3.64	3.92	4.27	4.86	5.13	5.84	6.25
400	0.02	2.86	3.00	3.27	3.66	3.85	4.50	4.97	5.50	6.11	6.66
	0.20	2.80	2.99	3.21	3.56	3.86	4.26	4.84	5.05	5.79	6.15
800	0.02	2.88	3.02	3.27	3.70	4.01	4.59	5.11	5.55	6.35	6.18
	0.20	2.83	3.08	3.15	3.50	3.76	4.24	4.69	5.03	5.62	6.14
1200	0.02	2.88	3.07	3.29	3.74	4.09	4.60	5.06	5.33	6.20	6.50
	0.20	2.89	3.07	3.19	3.58	3.85	4.20	4.63	5.00	5.40	5.98
1600	0.02	2.90	3.08	3.33	3.72	4.13	4.66	5.04	5.38	6.00	6.48
	0.20	2.91	2.96	3.18	3.55	3.89	4.21	4.62	4.94	5.33	5.86



Appendix 5b: Effect of different levels of added P on the Z PC the Rhodic Haplustox

Appendix 6a: Data for the zero point charge for the Typic Haplustox at different levels of added phosphate, pH and ionic concentration

P added (mg/kg)	$CaCl_2$ (moles)	H^+/OH^- added (c.Mole/kg soil)									
		10.0	7.5	5.0	2.5	1.25	0	1.25	2.5	5.0	7.5
		pH									
0	0.02	2.68	3.28	3.29	3.78	4.10	4.77	5.38	5.83	6.52	7.05
	0.20	2.65	2.92	3.28	3.72	3.98	4.60	5.10	5.64	6.12	6.48
100	0.02	2.73	3.00	3.28	3.82	4.16	4.70	5.36	5.80	6.53	6.99
	0.20	2.78	2.97	3.21	3.69	3.88	4.58	5.05	5.52	6.10	6.39
400	0.02	2.76	3.01	3.32	3.82	4.20	4.70	5.35	5.77	6.56	6.98
	0.20	2.80	3.00	3.23	3.65	3.88	4.60	5.00	5.40	6.05	6.35
800	0.02	2.92	3.05	3.36	3.85	4.40	4.76	5.22	5.67	6.30	6.80
	0.20	2.83	3.00	3.22	3.66	3.98	4.52	4.96	5.32	5.82	6.24
1200	0.02	2.87	3.09	3.41	3.93	4.44	4.79	5.33	5.62	6.23	6.76
	0.20	2.84	3.01	3.22	3.71	4.03	4.50	4.93	5.28	5.76	6.12
1600	0.02	2.92	3.14	3.44	4.14	4.40	4.78	5.39	5.61	6.12	6.71
	0.20	2.87	3.01	3.23	3.78	4.10	4.42	4.89	5.14	5.64	6.05



Appendix 6b: Effect of different levels of added P on the ZPC of the Typic Haplustox