HETEROVALENT CATION EXCHANGE EQUILIBRIA IN TWO SAVANNA SOILS

BY

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A thesis submitted to the Postgraduate School, Ahmadu Bello University, Zaria in "partial" fulfillment of the requirements for the Degree of Master of Science (Soil science).

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DECLARATION

I hereby declare that the content of this thesis is a record of my research work. The subject matter herein has not been presented in any previous publications for a higher degree.

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CERTIFICATION

This thesis entitled: HETEROVALENT CATION EXCHANGE EQUILIBRIA IN TWO SAVANNA SOILS by Yakubu Samuel, meets the regulations governing the award of the degree of Master of Science of the Ahmadu Bello University, Zaria and is approved for its contribution to scientific knowledge and literary presentation.

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DEDICATION

I dedicate this work to my mother, Late Mrs. Awasen Akwan Yakubu and my father Mr. Yakubu Gbanja Madaki for their love and moral upbringing from childhood.

ABSTRACT

Cation exchange equilibira involving K , Ca and Mg were studied in two representative savanna soils. The study examined Ca-K and Mg–K exchange equilibria with a view to establishing their preferential retention of the cations in savanna soils. Soil samples were collected at two depth ranges (0-15cm) and (15-30cm) from Zaria and Mokwa respectively. A solution of constant chloride salts concentration (0.1M) containing variable concentrations of K, Ca and Mg was prepared. The K concentration of the solution was prepared to vary from 0 to 200 mmol L^{-1} while the Ca and Mg solution were made to vary from 100 to 0 mmol L^{-1} in each case. The Ca and Mg equivalents of the Ca-K and Mg-K mixtures were made to increase from 0 to 1 while the equivalent fractions of K were made to decrease from 1 to 0 in the mixtures. For the Mokwa soil, the total adsorbed metal charge (Q_i) for Ca – K exchange was 22% greater than the total adsorbed metal charge (Q_i) for Mg-K exchange, thus indicating some preference for $CaCl^+$ over $MgCl^+$ by the surface exchange sites. This was, however, in contrast to the relative consistent total adsorbed metal charge (Q_i) for both Ca-K and Mg-K exchange in Zaria soil. Several cation exchange models were used to describe the Ca-K and Mg-K exchange equilibira. The exchange models tested in the study were the Kerr selectivity coefficient (K_k), Vanselow selectivity coefficient (K_v), Gapon selectivity coefficient (K_G), Gaines and Thomas selectivity coefficient (K_{GT}), Davies selectivity coefficient (K_D) and the thermodynamic exchange constant (K_{ex}).The trends in selectivity coefficients as a function of exchanger phase composition for Ca-K exchange were similar to Mg-K exchange. All selectivity coefficients determined for Mg-K and Ca-K for

the soils were far greater than 1 at all exchanger phase composition, suggesting a preference for K to either Ca or Mg by the soils. The Ca-K and Mg-K exchange isotherms were thus compared with the thermodynamic non-preference isotherm (TNI) line by plotting the charge fractions of adsorbed K versus the charge fraction of K in soil solution in the soil solution. The result indicated that the experimental points were below the TNI line for both Zaria and Mokwa, clearly suggesting non-preference for either Ca or Mg in the presence of K. The K preference by the soil can be explained by the relatively high hydration shell of Ca and Mg as compared to K that tends to limit the rate of diffusion of Ca and Mg from the soil solution to the surface exchange sites as compared to K. The thermodynamic exchange constant K_{ex} for the surface soil fron Zaria was 7.98 while the subsurface soil was 7.81, but K_{ex} decreased sharply to 3.12 and 4.60 for the surface and subsurface soil respectively for Mokwa. The negative values of ΔG_{ex} determined for Ca-K and Mg-K exchange seemed to lend additional credence to the notion that K was strongly preferred to Ca and Mg by the soils. The selectivity for K in the Zaria soil was stronger than the Mokwa soil apparently because of differences in mineralogical composition.

TABLE OF CONTENTS

		Page
Title page……		i
Declaration ……		ii
Certification page……		iii
Acknowledgement ……..		iv
Dedication……		v
Abstract……		vi
Table of contents……		viii
List of Tables……..		x
List of figures ……		xi
1.	**Introduction**……..	1
2.	Literature Review…….	3
2.1	Distribution of major soil classes in the savanna	3
2.2	Clay mineralogy of soils…….	6
2.3	Origin of charge in soil……..	8
2.4	Cation Exchange Equilibra in soils…….	10
2.4.1	Selectivity of Cation in soil Exchange Equilibria …	13
2.4.2	Modelling cation exchange Equilibria …….	15
3.	**MATERIALS AND METHODS**……..	20
3.1	Site information ……..	20
3.2	Routine soil analysis …….	22
3.2.1	Particle size analysis…….	22
3.2.2	Organic Carbon…….	22
3.2.3	Exchangeable cations …….	23
3.2.4	Soil pH …….	24
3.2.5	Cation Exchange Capacity…….	24
3.2.6	Exchangeable Acidity …….	25
3.3	Determination of Ca-K and Mg-K exchange equilibria	25
3.4	Modelling the Ca-K and Mg –K exchange equilibria	27
3.4.1	Kerr Selectivity Coefficient (K_K) …….	28
3.4.2	Vanselow Selectivity coefficient (K_v)…….	29
3.4.3	Gapon Selectivity coefficient (K_G)…….	30
3.4.4	Gaines and Thomas selectivity Coefficient (K_{GT})……	32
3.4.5	Davies selectivity coefficient (K_D)……..	32
3.4.6	Thermodynamic exchange constant (K_{ex})……..	33

3.5 Cation adsorption isotherms …… 36

4. **RESULTS AND DISCUSSION** …… 38

4.1 Adsorbed Metal Charge …… 38

TABLE OF CONTENTS

Page

4.2 Cation Selectivity Coefficients …… 41

4.3 Cation Adsorption isotherms…….. 43

4.4 Thermodynamic Exchange constant (K_{ex}) and the change in free Energy (ΔG_{ex}) of Exchange…… 51

4.5 Implications for K-fixation and plant Nutrition…… 62

5 SUMMARY AND CONCLUSIONS…….. 67

6 REFERENCES…… 72

LIST OF TABLES

Table		Page
1.	The relative distribution of major Soil types in the West Africa Savanna	4
2.	Solution of K-Ca and K-Mg mixtures of constant Cl^- concentration at 200 mmol.	26
3.	The K and Mg concentration in equilibrium soil solution and the surface excesses of the cations in the soils from Zaria and Mokwa	39
4.	The K and Ca concentration in equilibrium soil solution and the surface excesses of the cations in the soils from Zaria and Mokwa	40
5.	The mole fraction and the selectivity Coefficients of KX-MgX_2 exchange of surface and subsurface layers of Typic Haplustalf from Zaria and a ustult from Mokwa	44
6.	The mole fraction and the selectivity coefficients of KX –CaX_2 exchange of surface and subsurface layers of Typic Haplustalf from Zaria and a ustult from Mokwa	45
7.	The vanselow selectivity coefficient (K_v), rational activity coefficients and the thermodynamic equilibrium exchange constant as a function of the equivalent fractions of Mg^{2+} (E_{Mg}) on the exchange complex for KX- MgX_2 exchange on a surface (0-15cm) and a subsurface on a (15-30cm) of Typic Haplustalf from Zaria and a ustult from Mokwa	54
8.	The vanselow selectivity coefficient (K_v), rational activity coefficients and the thermodynamic equilibrium exchange constant as a function of the equivalent fractions of Ca^{2+} (E_{Ca}) on the exchange complex for KX- CaX_2 binary exchange on a surface (0-15cm) and subsurface (15-30cm)of Typic Haplustalf from Zaria and a ustult from Mokwa	55

9. The thermodynamic equilibrium constants and Gibbs free Energy (ΔG_{ex}) of Mg-K and Ca-K exchange for two savanna soils from Zaria and Mokwa. 61

LIST OF FIGURES

Figure		pages
1.	The Mg and Ca Adsorption isotherms of AP and Bt horizons of an Alfisol from Zaria	46
2.	The Mg and Ca Adsorption isotherms of AP and Bt horizon of the Mokwa Soil	47
3.	The K adsorption isotherms of AP and Bt horizons of the Zaria soil	48
4.	The K Adsorption isotherms of AP and Bt horizons of the Mokwa soil	49
5.	A plot of ln K_v with equivalent fractions of Adsorbed K(E_k) in the two soils used for the study	52
6.	The relationship of rational activity coefficients (f) with K Saturation or the equivalent K fractions (E_k) in the exchanger surface of the Zaria soil	56
7.	The relationship of rational activity coefficients (f) with K saturation or the equivalent K fractions (E_k) in the exchanger surface of the Mokwa soil	57
8.	Plots of the K_G for Mg-K and Ca-K exchange as a function of equivalent fraction of adsorbed K (E_K) in the Zaria and Mokwa soils	65

CHAPTER ONE

INTRODUCTION

The knowledge of the quantitative relationship between ions in solution and those on the exchange complex is of paramount interest to soil and environmental scientists. Such a relationship allows the prediction and control of cation release by soils into soil solution and aquatic environment (Sposito, 1989; Essington, 2004; Sparks, 2003).

Soil colloids exhibit a net negative charge that attracts and retains cations that are readily exchangeable with other cations. The amount of this negative charge in a soil is called the cation exchange capacity (CEC) and is often expressed as centimole charge per kilogram of soil.

Savanna soils are known to be acid to slightly acid with pH ranging from 5.0 to 6.5. The predominant soils are Alfisols/Ultisols, inceptisols and localized vertisols. Alfisols have high base saturation and are less leached as compared to Ultisols. They are both low in organic matter and cation exchange capacity (Jones and Wild, 1975). The low cation exchange capacity of savanna soil is attributed to the dominance of kaolinitic clays and low organic matter content (Jones, 1973).

The low exchange capacities of savanna soils have implications for soil management. Nutrients applied as cations such as ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}) are loosely held and are readily leached (Jones and Wild, 1975). Furthermore, the low CEC of the soil

and its dependence on pH will assume increasing importance as demands for nutrient cations become intense with the introduction of improved crop varieties, and with increasing application of nitrogenous and phosphatic fertilizers (Jones and Wild, 1975). Consequently, managing the soil CEC is a task and challenge to the resourcefulness of soil scientists in the region. At low pH, nutrient cation applications are not likely to have any beneficial effect because of rapid leaching in the absence of cation exchange sites to retain or adsorb them.

In a soil testing programme cation exchange capacity is one of the most important soil chemical parameters determined. Regretfully, very little attention has been paid to cation exchange equilibria and the preferential retention of certain cations in savanna soils. Understanding preferential retention of cations by soils is extremely important in formulating guidelines for fertilizer applications to avoid leaching and displacement of certain nutrient cations, and the excessive retention of others, thus creating cationic imbalance in soil

The objectives of this study were to:

(i) determine K-Ca and K-Mg exchange equilibria in two savanna soils of Nigeria.

(ii) evaluate competing models for describing cation exchange equilibria in soils.

CHAPTER TWO

LITERATURE REVIEW

2.1 Distribution of Major Soil Classes in the Savanna

The soils of West African Savanna can be divided into about ten main classes according to D'Hoore (1964) Soil Map for Africa. However, the Nigeria savanna is dominated by one major soil class described as the Ferruginous Tropical Soil with some Ferralitic Soils and pockets of inceptisol and vertisols within the Northeast (Table 1).

The ferruginuous soils are formed on quartz-rich parent materials, mostly on the crystalline rocks of the basement complex, on granite and many sedimentary deposits (d'Hoore, 1964). The soils are formed in areas having marked wet and dry seasons, and are characterized by the downward movement of clay within the profile; a process that tends to produce a sandy surface soil, rather low in organic matter and base exchange capacity, and a compact subsoil where the clay has accumulated. The deposit of free iron oxides in the profile in form of mottles, concretions or a ferruginous hardpan is also a characteristic feature of the soils (Jones and Wild, 1975; Agbenin, 2003). However, the soils are usually fairly shallow and most profiles are less than 150cm deep (Jones and Wild, 1975). Kaolinite is the predominant clay fraction present, sometimes with small amount of illite,

Table 1. The relative distribution of major soil types in the West Africa Savanna based on the soil map of Africa (D'Hoore, 1964)

SOIL CLASSES	% Distribution
Ferruginous formed on sandy parent material, crystalline acid rocks, undifferentiated parent material and weakly developed ferruginous soil.	58.3
Ferallitic soils formed on rock debris and on Ferruginous crusts	10.1
Hydromorphic soils	5.1
Brown and Reddish – Brown soils and Eutrophic Brown soils	7.0
Vertisols	1.9
Others	17.6

but montmorillonite is virtually absent (Jones and Wild, 1975; Ojanuga, 1979). In the surface horizon clay contents are low but very variable (0-25%), depending on parent material. Cation exchange capacities, vary from 1-10 cmol/kg and depending on soil clay content and organic matter (Jones, 1973).

The ferralitic soils are mostly found in the forest zone of West Africa, but are abundant in the savanna of Nigeria but their occurrence under 760mm mean annual rainfall with a seven-month dry season is somewhat anomalous (Jones and Wild, 1975). It may be associated with acid parent material that is permeable and deficient of weatherable minerals. The soils are much better suited to forestry and tree crops than to annual crops (Jones and Wild, 1975). However, the ferrilitic soils within the savanna region are not as leached as those occurring under a higher rainfall (Jones and Wild, 1975). D'Hoore (1964) described the more sandy ferralitic soils developed on loose sandy sediments as among the poorest soils in Africa, and many of them have cation exchange capacity less than 1 cmol kg^{-1} in the topsoil as reported for a number of profiles found in the derived savanna of eastern Nigeria. The physical properties of these soils, are, however, very good (Jones and Wild, 1975; Kowal and Kassam, 1978).

The savanna inceptisols are mostly the eutrophic brown soils as described by Jones and Wild, 1975. They have a limited distribution in the savanna because they occur only in base-rich parent material such as basalt and basic gneiss. The soils are shallow with fairly high organic matter content, high base status and good surface structural properties. The soils are usually young, and are probably formed on surfaces of parent materials exposed by erosion. They can change to ferruginuous soils on well-drained sites and into vertisols where drainage is severely restricted (Jones and Wild, 1975). The nutrient status of the soils are relatively high as compared with most other savanna soils. Weatherable minerals are quite high in the soil. In some cases, plant roots can extend to partly decomposing or decaying parent material or rock. There are, however, deficiencies of phosphate and potassium (Kaloga, 1970), probably reflecting the inherent mineral composition of the parent material.

The vertisols are characterized by dark-coloured, cracking clays of low permeability and poor internal drainage. The soils are formed from either calcareous rocks rich in ferromagnesian minerals or in depressions enriched by constituents coming from surrounding higher land (D'Hoore, 1964).

Klinkenberg and Higgins (1968) reported that Nigerian vertisols contain about 68% clay with high montmorillonite content. Although weatherable minerals are quite high, and the exchange complex is adequately saturated with cations, vertisols have poor nutrient status. The phosphate and potassium contents of the parent materials tend to be low, so that total and available phosphate and potassium in the soil are not radically different from other savanna soils.

2.2 Clay Mineralogy of Soils

Although some literature is available on the clay mineralogy of soils in the forest regions of Nigeria (Ojanuga, 1971, 1973, Okusani, 1972, Gallez et al., 1975), there is no such literature in respect of soils in the Nigeria tropical savannas. Rather the clay mineralogy of the soils of the savannas is inferred by soils classification, especially in Northern Nigeria (Jones and Wild, 1975).

The clay mineralogy of soils from the moist southern guinea savanna and sub-humid northern guinea savanna has been studied (Ojanuga, 1979). All the soils occur on basement complex. Kaolinite is the dominant clay mineral in all the well-drained soils, a property shared by the other well-drained soils of the humid tropical forests. In poorly drained soils, montmorillonite may form in significant amounts in addition to kaolinite. Quartz also occurs in the clay fraction of all the soils (Ojanuga, 1979). Kaolinization is the dominant clay forming process under good soil drainage. The kaolinization process is mostly favoured

by the marked leaching rainfall and mineralogical composition of the soil or parent material.

Because most savanna soils are weathered tropical ferruginous soils classified in soil taxonomy as either Alfisols or Ultisols, the clay mineralogy is typically kaolinitic, having low cation exchange and buffer capacities (Jones and Wild, 1975, Kowal and Kassam, 1978). The implications of the low cation exchange and buffer capacities of the soils are that OM can decline quite rapidly under continuous cultivation, followed by extensive leaching of basic cations and the development of acidity.

2.3 Origin of Charge in Soil

The two properties accounting for the reactivity of soil are surface area and surface charge. Surface area is a consequence of particle size and shape of clay in the soil as well as its organic matter content. Charge development in soils arises as a result of isomorphic substitution and ionization of functional groups on the surface of colloidal materials that make up the soil (Bohn et al 1985). These two mechanisms give rise to permanent and pH-dependent charges of soils respectively.

Permanent charge arises from isomorphic substitution of one ion substituting for another ion of similar size within a crystal lattice. The substituting ion may have an equal, greater or lower charge than the ion for which it substitutes. In layer silicate structures, cations may substitute for coordinating cation in either the tetrahedral or the octahedral sheets. If a cation of lower valence substitutes for one of higher valence, such as Mg^{2+} for Al^{3+} or Al^{3+} for

Si^{4+}, it creates a charge deficit in the mineral structure that is essentially independent of pH. This charge is called permanent charge in soils (Guenzi 1974).

The charge of some soil particles often varies with the pH at which the charge is measured. Positive charge develops at low pH, and excess negative charge develops at high pH. The total charge of a soil is the sum of its negative and positive charges (Bohn et al., 1985). The pH dependent charge comes from the loss of H^+ from several functional groups in the soil colloids. The functional groups include hydroxyl (-OH) in the surfaces of aluminosilicate clay minerals, carboxylic (-COOH), phenolic ($-C_6 H_4OH$) and amine ($-NH_2$) in organic matter. The charge that results from such groups is regulated by pH of the ambient solution (Marcano and McBride, 1989).

Savanna soils, except for vertisols, exhibit variable charge characteristics. Positive charge develops most at low pH or acidic conditions, and negative charge develops under alkaline condition or high pH. The surface charge is created by the adsorption of H^+ or OH^- onto the surface. The net charge being determined by that ion, which is adsorbed in excess. An acid soil makes an excess of H^+ to be adsorbed resulting in positive charge, whereas an alkaline soil adsorbs excess of OH^- resulting in negative charge (Gillman and Uehara, 1981).

Illustrating with Fe and Al oxides, electrical charge can develop on the surfaces of Fe and Al oxides as a result of protonation and deprotonation of the surface hydroxyl groups (Van Raij and Peach, 1972; Gast 1977 and Sposito 1984). In aqueous systems, oxides are hydroxylated and a charge on the hydroxylated surfaces develops through amphoteric dissociation of the surface hydroxyl groups or by association of proton ions. Consequently, H^+ and OH^- ions

are generally called the potential determining ions. The protonation of Fe and Al oxides leaves a net positive and deprotonation leaves a net negative charge hence the charge that developes in Fe and Al oxides can be rationalized as follows depending on the pH of the system (Sposito, 1984);

$$S - OH\ (s) + H^{+}\ (aq) \longleftrightarrow SOH_2^{+}\ \text{(Surface protonation)} \qquad 2.1$$

$$S - OH\ (s) \longleftrightarrow SO^{-}(s) + H^{+} \quad \text{(Surface deprotonation)} \qquad 2.2$$

$$S - OH_2^{+}\ (s) \longleftrightarrow S\text{-}OH^{0} + H^{+} \quad \text{(PZC = no net charge)} \qquad 2.3$$

There, however, exists a pH value where the oxide surfaces carry no net charge, which is generally referred to as the point of zero charge (PZC). When the ambient pH of the aqueous environment falls below the PZC, positive charge develops on the surface while at pH values above the PZC, negative charge develops on the surface due to deprotonation. The processes involved in charge development are represented by equation 2.1 – 2.3.

2.4 Cation Exchange Equilibra in Soils

Cation exchange reaction provides an index of the movement metals in the soil. It's understanding is necessary to predict nutrient dynamics in soil and transport as well as buffering of protons (Ludwig and Kolbl, 2003). It is important in determining nutrient imbalance in the soil (Bohn et al 1985). Potassium exchange reactions with each of the cations Ca, Mg or Na on clay minerals and soils have been investigated intensively (Bolt, 1979; Spark and Huang, 1985). Irrigation water especially sewage effluents and brackish waters, may contain considerable quantities of Na, K, Ca and Mg. These cations undergo simultaneous exchange reactions with each other on soil surfaces. The possible

reactions involving K-Ca-Mg, K-Na-Ca, and K-Na-Mg in soil and the study of their effect on K distribution between the solution and the solid phases is extremely important in plant nutrition.

The adsorbed cations on the exchange complex cannot be leached out easily, but they can be replaced by other cations in solution through simple mass action because of ionic competition for negative sites. This ionic competition exists because there are large numbers of ions present. Factors that control cation exchange in soils include the relative concentration of the ions involved, the number of charges on the ion and the speed of movement or activity of the ion.

The greater the number of charges an ion carries, the more efficient it is in replacing others on the exchange complex. The speed of movement of an ion is essentially a function of its size. The replaceability series of some of the common cations in soils is in the order Al > Ca > Mg > K > Na; and the ionic exchange is on a chemical equivalent basis (Bohn et al. 1985).

Goulding and Talibudeen, (1980) examined the free energy of exchange in five aluminosilicate minerals chosen as representatives of groups of aluminosilicates commonly occurring in soils. They were muscovite mica, illite, vermiculite, montmorillonite and kaolinite. The free energies of exchange indicated that all of the minerals selectively adsorbed K^+, selectivity decreasing in the order mica> vermiculite= illite> kaolinite > montmorillonite. Except for kaolinite, the order of selectivity was similar to that suggested by Talibudeen, (1971), based on $K^+ — Ca^{2+}$ exchange in soils, and that by Assa (1976a,b) who

examined K^+ Ca^{2+} exchange on a similar site of minerals using Gapon's constant. Kaolinite is usually considered to have a very low preference for K^+, if not actually preferring Ca^{2+}, but the kaolinite examined by Goulding and Talibudeen (1980) had an extremely high K^+ preference. A reason for this high preference was partly due to impurities of illite in the kaolinite. Talibudeen and Goulding, (1983a,b) showed that virtually no kaolinite or montmorillonite was virtually free of micaceous impurities and that all the cation-exchange properties of kaolinites can be explained by inherent 2:1 mineral impurities.

Integral and differential entropy values of the five minerals studied by Goulding and Talibudeen, (1980) were consistent with Hutcheon's (1966) view of the importance of lattice expansion and contraction on cation exchange reactions. X-ray diffraction evidence by Plancon et al. (1979) had suggested that montmorillonite surfaces rearrange and reorder before collapsing when the mineral is subjected to wetting and drying cycles following K^+ Ca^{2+} exchange. On this basis, Goulding and Talibudeen (1980) suggested three physical mechanisms that contribute to entropy changes during Ca^{2+} K^+ exchange in clays: (1) in the solid phase, replacing Ca^{2+} by K^+ realigns the aluminosilicate layers in the 001 direction such that the hexagonal holes in adjacent sheets can accommodate K^+ ions as suggested by Jackson (1963), resulting in a negative entropy change; (2) in the solid phase again, replacing Ca^{2+} by K^+ increases the randomness of distribution of exchangeable cations, resulting in a positive entropy change; (3) in the solution phase, replacing K^+ by Ca^{2+} increases the structural order of water molecules, decreasing the entropy of the system. The fact that all the expanded 2:1 minerals examined exhibited negative entropy changes during Ca^{2+} K^+ exchange, whereas muscovite mica, a collapsed 2:1 mineral, exhibited a positive entropy change, suggested that the solid-phase effects (1) and (2) dominated.

2.4.1 Selectivity of Cation in Soils

Cation exchange equilibria have been studied extensively for a variety of soils (Galindo and Bingham, 1977). Prediction of the effect of irrigation water on

soil solution composition is dependent on the cation exchange process and the selectivity that a soil complex has for a particular ion (Suarez and Zahow, 1989).

Suarez and Zahow, (1989) reported that for Ca-Mg exchange selectivity in a montmorillonite clay, Ca was preferred over Mg in Cl^-, $S0_4^{2-}$ and $Cl0_4^-$ solution. Their findings did not corroborate report of Ca-Mg exchange isotherms on a bentonite clay that Ca^{2+} and Mg^{2+} have equal preference and that apparent Ca preference in Cl media is due to preferential adsorption of $CaCl^+$ over $Mgcl^+$

Hunsaker and Pratt, (1971) reported a preference for Ca in Ca–Mg exchange equilibria in an allophane and a Dystrandept soil. Gessa (1970) concluded that the pH–dependant sites had a marked preference for divalent over monovalent cations in heterovalent cation exchange systems. In homovalent cation exchange equilibria, the selectivity for K over Na was in accord with the concept that in homovalent system, the preferentially adsorbed ion is usually the ion with the smaller hydrated radius (Galindo and Bingham, 1977). For heterovalent cation exchange equilibria, there was a marked selectivity for the divalent cation over K, which was expected on the basis of valence consideration (Galindo and Bingham, 1977). El Swaify and Swindde, (1970) observed the same trend studying a Na-Ca exchange in a soil from Hawaii. Comparable experiments with Ca-Mg revealed consistent selectivity for Ca. Regardless of the treatment, soils exhibited a distinct selectivity for Ca over Mg. This preference is expected on the basis of hydrated radius of ions (Galindo and Bingham, 1977). Hunsaker and Pratt, (1977) suggested that soils containing amorphous materials have ion exchange sites with a strong preference for Ca

over Mg when compared with other mineral exchange materials. The K_{ex} values were lower for the Mg-K series than for the Ca-Mg exchange data indicating a higher preference for Ca than for Mg.

Van Bladel and Gheyi, (1975) showed from adsorption isotherms that calcareous soils have a strong affinity for Ca over Na ions. The exchange affinity for Ca ions varied with soil organic matter content (Gheyi and Van Bladel, 1975). The exchange isotherms of Ca^{2+} by Mg^{2+} on several soils and the montmorillonite clay indicated preference of Ca over Mg ions. However, Clark (1996) and Hunsaker and Pratt (1971) noted slight preference for Ca over Mg by montmorillonite.

Udo, (1978) reported that the exchange of Ca^{2+} for K^{+} was accompanied by a decrease in free energy and enthalpy of the system. Negative values of ΔG^{o} and ΔH^{o} for K-Ca exchange were reported by Deist and Talibudeen (1967) and Hutcheon (1966) for various clays and soils, suggesting a stronger binding of K^{+} over Ca^{2+} due partly to the presence of specific K- adsorption sites on the kaolinitic clay minerals, and partly to the small hydrated ion volume of K ions. These factors probably outweigh the effect of the higher charge carried by the Ca ions. In the Mg$\longrightarrow$Ca system, the exchange of Ca for Mg was accompanied by an increase in free energy and enthalpy (Udo 1978). This preference of the clay for Ca over Mg was also shown to hold for montmorillonite clay. However, Sala et al (1991) reported the non preference of Ca^{2+} over Mg^{2+} in a Gilat soil with a relatively high CEC and Nordiya soil with low CEC. These results were in good agreement with the published data for other soils from the same geographical

area (Levy et al, 1972) and for soils with low organic matter contents (Sala et al 1991). Fletcher et al. (1984) and Haghnia pratt (1988) found that when Ca was preferred over Mg, the selectivity coefficient was often correlated with the organic matter content of the soil. Consequently, the lack of preference of Ca over Mg ion in soils from semi-arid regions that are low in organic matter is expected (Sala et al 1991). A preference for K over Ca plus Mg was however, shown for both soils (Sala et al 1991).

2.4.2 Modelling Cation Exchange Equilibria

Cation exchanger is assumed to possess a constant exchange capacity. Most equations used to model cation exchange reactions are based on the law of mass action with an assumption of the activity coefficient of the adsorbed ions (Keith Goulding, 1983). For exchange reactions the mass action equation is of the form.

$$S - A_x + XB^{y+} \rightleftharpoons S\text{-}B_x + YA^{x+} \quad (1)$$

where

A and B are cations

x and y are valencies of cation A and B respectively.

S is soil.

The reaction coefficient of equation 1 based on the law of mass action can be written as:

$$K_M = (S\text{-}B_x)\,(A^{x+})^y / (B^{y+})^x\,(S\text{-}A_x) \quad (2)$$

where

K_M = mass action constant

X and y are valencies of cations A and B respectively.

The major problem in all exchange equations is how to determine activity of adsorbed (exchangeable) cations. Kerr and Vanselow hypothesized the soil to be an ideal solution that obeys Raoult's law, which states that the partial pressure of a solvent is proportional to its mole fraction. In that case the activity of adsorbed ion can be equated to its mole fraction. This leads to Kerr – Vanselow equation given as.

$$K_{Kv} = \frac{[S\text{-}B_x]\,[A^{x+}]^y\,[S\text{-}A_x +\ _xB]^{y-x}}{[S\text{-}A_x]\,[B^{y+}]^{1/x}} \qquad (3)$$

All terms are defined as in equation (2) above.

The equations used for cation exchange reactions in soils are either empirical or semi empirical and their use is based on the law of mass action. All the equations attempt to provide a relatively uniform exchange coefficient over a wide range of exchanger phase composition (Essington, 2004). Because the activities of exchangeable cations cannot be calculated or measured precisely, different authors have made different assumptions for estimating the activities of exchangeable ion, thereby leading to several cation exchange formulations.

The Debye-Huckell and Davies equations can be used to estimate the activities of ions in solution. The modified Debye-Huckell equation can be used to estimate the activity of ions with an ionic strength of up to 0.1. The equation can be written as:

$$-\log Y_i = Az_i^2 (\mu)^{1/2} \,/\, 1 + Ba_i\mu^{1/2} \qquad (4)$$

where

Y_i is the individual ion activity coefficient

Z is the valency of the ion

U is the ionic strength of the ion

a_i is the individual ion size parameter for the ion)

The ionic strength (μ) is given by

$$\mu = \tfrac{1}{2} \sum C_i Z_i \qquad (5)$$

where

C_i is the concentration of the ion in solution in molarity

Z_i is the charge or valency of each ion.

Davies equation is normally used in cases with higher ionic strength of the soil solution with a view to accounting for ion complexes. The Davies equation can be written as:

$$-\log Y_i = O.512Z_i^2 \left[\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.3\,\mu \right]$$

All the terms in the equation are as defined in equation (5).

The stoichiometric cation exchange reaction in soil can be formulated thermodynamically in two ways. According to Sposito and Mattigod (1977), the

two formulations have come mainly from two arbitrary conventions for indexing the reaction between the exchangeable cation and the atomic portion of the solute exchanger.

If the cations are designed to react in molar amounts, then the exchange reaction may be written as follows:-

$$nMX_m + {}_MN^{n+} = nM^{m+} + {}_MNX_n \qquad (7)$$

where M and N are metal cations of charges m^+ and n^+, respectively, and the anionic part of the exchanger, X, is taken to have charge -1. Equation(7) represents the Vanselow's approach (Sposito and Mattigod, 1977). If the cations are designated instead to react in equivalents, the exchange reaction takes the form.

$$nM_{1/m}X + MN^{n+} = nM^{m+} + nN_{1/n}X \qquad (8)$$

Equation (8) represents the Gapon convention (Sposito and Mattigod, 1977), both the Vanselow and the Gapon conventions satisfy requirements of conservation of mass and charge in the exchange reaction.

The Gapon and Vanselow selectivity (K_G and K_V) for equation 7 and 8 can be written as:

$$K_{GX} = \frac{(M^{m+})^n (N_{1/n}X)^{nm}}{(N^{n+})^m (M_{1/m}X)^{mn}} \qquad (9)$$

$$K_{VX} = \frac{(M^{m+})^n (NX_n)^m}{(N^{n+})^m (MX_m)^n} \qquad (10)$$

Equations 9 and 10 are the thermodynamic exchange constants for equations (8) and (7), respectively (Babcock, 1963, Sposito and Mattigod, 1977). The conventional Gapon selectivity coefficient, K_G is obtained from Eq. (10) by considering the quantity $(K_{GX})^{1/mn}$ and by assuming that solute activities are equal to molar concentration and that exchanger activities are equal to equivalent fractions (Bolt, 1967).

Therefore,

$$K_G = \frac{[M^{m+}]^{1/m} EN_{1/n}X}{[N^{n+}]^{1/n} EM_{1/m}X} \quad (\text{moles/liter})^{1/m-1/n} \qquad (11)$$

where [ ] denotes a molar concentration and E is an equivalent fraction. Equation (11) is only thermodynamically meaningful if the activity coefficients for the solute and the exchanger species are both equal to unity. Hence K_G and $(K_{GX})^{1/mn}$ will be numerically identical. By the same reasoning Eq. (10) can produce the Vanselow selectivity coefficient, K_V:

$$K_V = \frac{[M^{m+}]^{1/m} X^{1/n} NX_n}{} \qquad (12)$$

$$[N^{n+}]^{1/n}\ X^{1/m}\ MX_m$$

where X denotes a mole fraction in the exchanger phase.

CHAPTER THREE

MATERIALS AND METHODS

3.1 SITE INFORMATION

The soils studied were collected from Zaria and Mokwa in the Northern Guinea savanna ecological zones of Nigeria. Zaria lies in the "High plain of Hausaland" that ranges in elevation from 625-853m (Ologe, 1971) on latitude 11^{o} 11'N and longitude, 7^{o} 38'E while Mokwa lies on latitude 9^{o} 18'N and longitude 5^{o} 05'. The soil samples were obtained at 01-15cm (Ap) and 15-30 cm (B).

The climate of Zaria and Mokwa as a whole has a marked seasonality because of two contrasting air masses moving across the area, a dry continental air mass often referred to as "harmattan" from the north east and a humid maritime air mass.

During the period of November to March, Zaria and Mokwa are almost dry and during the period of December to February, the areas are exposed to harmattan wind, which brings in fine dust to the area. The mean annual rainfall at Zaria is about 1087mm while Mokwa has a mean annual rainfall of 1123mm. Mokwa has, however, a short dry season during the month of August, two thirds or more of the total annual rainfall occurring in the four months of May, June, July and September.

Zaria area lies within the Northern Guinea Savanna characterized by woodland vegetation with grass under layers, while Mokwa area is in the Southern Guinea Savanna zone. The present vegetation in Zaria has been modified greatly owing to human disturbance. Actually, the present vegetation derives its existence largely to land use over a long period of time.

The land under fallow usually carries a vegetation of open shrub woodland in varying stages of re-growth. However, the constant bush burning, grazing and cutting down of trees for firewood offers little chance for woodland to approach its climax status. Only trees of economic value are left undisturbed. Such trees include *Parkia clappertoniana, Mangifera indica, Vitex doniona, Afzelia africana, Daniellia oliveri* and T*amarindus indica* (Higgins, 1963). Mokwa's vegetation is dominated by *Daniellia, Afzalia Detarium* woodland in addition to grasses comprising mainly of *Adropogan gayanus*.

Mc Curry (1973) and Wright and Mc Curry (1969) have given some account of the geology of Zaria area. According to them, apart from the superficial deposits, rocks of Precambrian to early Paleozoic age underlie the entire Zaria area. The rocks are comprised of both metamorphic and igneous rocks termed the basement complex because of their intricate pattern.

Some account of the geology of Mokwa indicates that the area is underlain by cretaceous sediments, which overlay the basement complex in the Niger trough. Two distinct geological series have been delineated for Mokwa area. The upper, consisting of fine-grained sandstones and siltstone and the lower consisting of soft coarse grained sandstone.

3.2 Routine Soil Analysis

The soil samples collected were spread out to dry and sieved through a 2.0 mm sieve. The soil analysis carried out on the <2mm soil samples were: Particle size analysis, organic carbon, exchangeable cations and exchange acidity, cation exchange capacity and pH.

3.2.1 Particle size analysis

Particle size analysis was determined by the procedure described by (Gee and Bauder, 1986). 50g of <2mm sieved soil were weighed into a 250ml plastic beaker to which 10ml of sodium hexametaphosphate (calgon) solution and water were added and stirred with a glass rod and left to stand for 30 minutes with occasional stirring. The suspension was transferred into a plastic bottle and was shaken in a mechanical shaker for 10 minutes.

The suspension was transferred to a 1000-ml graduated cylinder and made to volume with water. The suspension was vigorously mixed using a plunger. Sand, silt and clay were determined with the Bouyoucos hydrometer. The hydrometer readings were taken at time intervals of 40 seconds and 2 hours (Gee and Bauder, 1986).

3.2.2 Organic Carbon

Organic Carbon was determined using the method described by Walkley Black (Nelson and Sommer, 1982). This method involves the oxidation of the soil organic matter with potassium dichromate ($K_2Cr_20_7$) using concentrated sulphuric acid to hasten the oxidation. One gram of finely grounded soil samples was

weighed into a 250ml conical flask to which 5 ml of $1NK_2Cr_20_7$ solution as added using a pipette. The mixture was swirled to disperse the soil and 10 ml of concentrated sulphuric acid were rapidly added from a measuring cylinder and it was swirled for 1 minute again. The mixture was allowed to stand on an asbestors sheet for 30 minutes to cool down. 100 ml of distilled water was added to the flask. The resulting solution was titrated with $0.5NFeSO_4$ solution using orthophenanthroline as indicator. A blank determination containing all reagents but without soil was prepared through the same procedure. The percentage of organic carbon was calculated by the procedure described by Nelson and Sommers (1982).

3.2.3 Exchangeable cations

The exchangeable cations (Na, K, Mg and Ca) were determined by extraction with 1N NH_4OAc solution as described by Rhoades (1982). Briefly, 1g of <2mm sieved soil was weighed into a 50ml centrifuge tubes, 20 ml of IN NH_4OA_C solution buffered at pH 7.0 were added. The tubes were shaken for 30 minutes. The suspension was filtered through a whatman filter paper No.2 into a 250ml flask. The supernatant solution was preserved for determination of Ca, Mg, K and Na. Potassium and Na were determined by flame photometry, while Ca and Mg were determined by atomic absorption spectrophotometry.

3.2.4 Soil pH

The pH of the soil was determined in H_2O at soil:H_2O ratio of 1:2.5 and in 0.01M $CaCl_2$ solution at soil:solution ratio of 1:2.5. In each case, 10 g soil were weighed into plastic beaker to which 25ml of distilled water or 0.01M $CaCl_2$ solution were added and stirred several times at interval during the next 30 minutes. The soil suspension was allowed to stand for another 30 minutes undisturbed. The pH readings were taken by immersing the pH electrode into the soil but was not allowed to touch the bottom of the beaker. The pH was recorded after 30 seconds.

3.2.5 Cation Exchange Capacity

The cation exchange capacity was determined by ammonium saturation method as described by Rhoades (1982). 10g of <2mm sieved soil sample were weighed into a 100 ml plastic beaker to which 40ml of IN NH_4OAc acetate solution were added and stirred with a glass rod and left overnight. The soil was filtered with light suction using a 55 mm Buchner funnel. The leachate was tested if it was Ca free with few drops of IN NH_4Cl solution 10% ammonium oxalate and dilute NH_4OH solution.

The soil was leached repeatedly with IN NH_4Cl solution discarding the leachates. The soil was washed with 100-200 ml ethanol until it was Cl^-free. Chloride was tested in the leachate with 0.IN $AgN0_3$ solution. White precipitate on addition to that solution indicates the presence of Cl^- whereas absence of precipitate indicated that the soil was free of Cl^-. The NH_4^+ ion retained by the soil was determined by steam distillation as described by Keeney and Nelson

(1982). The cation exchange capacity was calculated as the increase of NH_4^+ ions retained by the soil.

3.2.6 Exchangeable Acidity

The KCl – extractable acidity (hydrogen and aluminium) was determined by leaching soil sample with IN KCl solution. 10g of soil were repeated by leaching with 1N KCl solution into 100 ml volumetric flask by adding a small portion of the aliquots for 2 hours. The Al^{3+} and H^+ displaced by K^+ were determined by titrating the leachate with 0.IN NaOH solution to a pink end point. A full description of the procedure is given in Thomas (1982) and Agbenin (1995).

3.3 Determination of Ca-K and Mg-K exchange equilibria

Solutions used in the cation exchange reactions were prepared from chloride salts. A solution of constant chloride salts concentration (0.1M) containing variable concentrations of K, Ca and Mg was prepared. The K concentration of the solution was prepared to vary from 0 to 200 $mmoL^{-1}$ while the Ca and Mg solution were made to vary from 100 to 0 $mmoL^{-1}$. The Ca and Mg equivalents of the Ca-K and Mg-K mixtures were made to increase from 0 to 1 while the equivalent fractions of K was made to decrease from 1 to 0 in the mixtures. Table 2 gives the composition of the Ca-K and Mg-K mixtures used in the exchange experiments.

The experimental reactions were carried out as follows. 2g of <2mm sieved soils were weighed into a pre-weighed centrifuge tubes. The weight of the tubes and the soils were determined. 20ml of the solutions containing variable amounts of K, Ca and Mg were added to the soils and the suspensions were left to stand for 20 hours after which the soil suspensions were shaken for 30 minutes, centrifuged and the supernatant solutions discarded. Another 20ml of the solutions containing variable

Table 2. Solution of K-Ca and K-Mg mixtures of constant Cl^- concentration at 200 mmol.

K-Ca mixtures			K-Mg mixtures		
K	Ca	Cl_T	K	Mg	Cl_T

Flask No:	----------mmol L^{-1}----------					
F_1	0	100	200	0	100	200
F_2	10	95	200	10	95	200
F_3	20	90	200	20	90	200
F_4	40	80	200	40	80	200
F_5	80	60	200	80	60	200
F_6	160	20	200	160	20	200
F_7	200	0	200	200	0	200

concentrations of K, Ca and Mg were added, shaken for 30 minutes, centrifuged and the supernatant solutions were discarded. This was repeated the third time, but at this time the supernatant solutions were saved for the determination of K, Ca and Mg. The centrifuge tubes and the soils were re-weighed to determine the amount of entrained solutions. The soils were washed with 80% (V/V) ethanol solution by adding 20ml at a time to the soils. This was shaken for 5 minutes, centrifuged and the solutions were discarded. The washing was done continuously with the ethanol solution until the soils in the centrifuge tubes were free of Cl^- and this was tested by adding few drops of 0.1N $AgNO_3$ to the supernatant solution.

The adsorbed K, Ca and Mg were displaced with 1N NH_4OAc buffered at pH 7.0 and this was done by adding 30ml of the solution, shaken for 30 minutes, centrifuged and decanted into storage vials. This was repeated three times, and the supernatant solutions were saved into the same vials that were later made up to 100ml by adding the extracting solution. Potassium, Ca and Mg in the extracts were determined. Atomic absorption spectrophotometry was used for the chemical analysis of Ca and Mg while flame photometry was used for the chemical analysis of K.

3.4 Modeling the Ca-K and Mg-K Exchange Reactions

A binary cation exchange reaction of Mg-K or Ca-K exchange can be written simply as:

$$CaX_2 + 2K^+ = 2KX + Ca^{2+} \qquad [1]$$

$$MgX_2 + 2K^+ = 2KX + Mg^{2+} \quad [2]$$

where X is the exchanger surface. The Ca^{2+}, K^+ and Mg^{2+} exchange selectivity or preference by the exchanger surface can be conveniently described by mass action coefficient or selectivity coefficient. The equilibrium constants for Ca-K and Mg-K exchange reactions described above can be written as Eq. [3] and [4] respectively.

$$K_{ex}\,[Ca\text{-}K] = \frac{[KX]^2\,[Ca^{2+}]}{[CaX_2)\,[K^+]^2} \quad [3]$$

$$K_{ex}\,[Mg\text{-}K] = \frac{[KX]^2\,[Mg^{2+}]}{[MgX_2]\,[K^+]^2} \quad [4]$$

where brackets or parentheses denote activities of cations, and X represents the exchanger phase considered to have one negative charge, and Ca^{2+}, K^+ and Mg^{2+} denote solution species. Because of the difficulty of measuring the activities of adsorbed cationic species: KX, CaX_2 and MgX_2, a selectivity coefficient can be employed to describe the Ca-K and Mg-K exchange reaction. The different cation selectivity coefficients are simply the various propositions to measure the activity of adsorbed cation species. The following cation selectivity coefficients were determined for Ca-K and Mg-K exchange reactions in the two savanna soils studied.

3.4.1 Kerr Selectivity coefficient (K_k)

The Kerr selectivity coefficient assumes that the exchange phase comprises of two discrete solid phases (KX and CaX_2 or KX and MgX_2) or as a uniform mixture of exchangeable cations described as a solid-solution composed of (K, Mg)X or (K, Ca)X. For the sake of simplicity, the Kerr selectivity coefficient can be written for Ca-K and Mg-K exchange reactions as:

$$K_k\,[Ca\text{-}K] = \frac{N^2_k([CaX_2] + [KX])\,(Ca^{2+})}{[N_{Ca}]\,[K^+]^2} \quad [5]$$

$$K_k\,[Mg\text{-}K] = \frac{N^2_k([MgX_2] + [KX])\,[Mg^{2+}]}{[N_{Mg}]\,[K^+]^2} \quad [6]$$

where N_{Ca}, N_{Mg} and N_k are the mole fractions of adsorbed Ca, Mg and K by the exchanger phase. The mole fractions of the adsorbed cation species were computed as:

$$N_{Ca} = \frac{CaX_2}{CaX_2 + KX} \quad [7]$$

$$N_{Mg} = \frac{MgX_2}{MgX_2 + KX} \quad [8]$$

$$N_k = \frac{KX}{CaX_2 + KX} \quad [9]$$

$$N_k = \frac{KX}{MgX_2 + KX} \quad [10]$$

Originally, Kerr equated active masses of MgX_2 and CaX_2 as the concentration of the adsorbed cations before the concept of mole fractions was introduced.

3.4.2 Vanselow Selectivity Coefficient (K_v)

The Vanselow selectivity coefficient is derived from the assumption that the concentration of adsorbed ions can be equated to the active masses. Thus Vanselow produced a true thermodynamic approach to defining the activity of a component in solid-solution by its mole fraction. Hence for Ca-K and Mg-K exchange reactions, K_v was calculated from our data by means of Eq. (11) and 12) respectively (Essignton, 2004).

$$K_v\ (Ca\text{-}K) = \frac{N^2_K(Ca^{2+})}{N_{Ca}(K^+)^2} \quad [11]$$

$$K_v\ (Mg\text{-}K) = \frac{N^2_K(Mg^{2+})}{N_{Mg}(K^+)^2} \quad [12]$$

All terms in Eq. (11) and (12) have been previously defined.

3.4.3 Gapon selectivity coefficient (K_G)

This empirical equation commonly used to describe non-symmetrical cation exchange was also computed in this study. Employing the Gapon equation for Ca-K and Mg-K exchange, the Gapon convention for the two exchange reactions can be written as follows:

$$Ca_{½}X + K^{+} = KX + ½Ca^{2+} \quad [13]$$

$$Mg_{½}X + K^{+} = KX + ½Mg^{2+} \quad [14]$$

Thus, K_G can be calculated by employing Eq. 15 and 16 below:

$$K_G \text{ (Ca-K)} = \frac{[KX][Ca^{2+}]^{½}}{[CaX_{½}][K^{+}]} \quad (15)$$

$$K_G \text{ (Mg-K)} = \frac{[KX][Mg^{2+}]^{½}}{[MgX_{½}][K^{+}]} \quad (16)$$

The exchangeable cations are expressed in $molkg^{-1}$, and the concentrations of cations in solution in $molL^{-1}$. The version of the equation employing aqueous ion activities and equivalent fraction of adsorbed cations was used in this study to model Ca-K and Mg-K exchange reactions in the soil. Hence K_G can be re-written for the exchange reactions as:

$$K_G \text{ (Ca-K)} = \frac{E_K(Ca^{2+}]^{½}}{E_{Ca}[K^{+}]} \quad (17)$$

$$K_G \text{ (Mg-K)} = \frac{E_K[Mg^{2+}]^{½}}{E_{Mg}(K^{+})} \quad (18)$$

where E_{Ca}. E_{Mg} and E_K are the equivalent fractions of adsorbed Ca^{2+}, Mg^{2+} and K^{+} respectively. The equivalent fractions of adsorbed Ca^{2+}, Mg^{2+} and K^{+} were calculated by means of Eq. (19) to 22):

$$E_{ca} = \frac{2[CaX_2]}{2[CaX_2] + [KX]} \quad (19)$$

$$E_{Mg} = \frac{2[MgX_2]}{2[MgX_2] + [KX]} \quad (20)$$

$$E_K = \frac{[KX]}{} \quad (21)$$

$$E_K = \frac{[KX]}{2[CaX_2] + [KX]} \quad (22)$$

$$E_K = \frac{[KX]}{2[MgX_2] + [KX]}$$

where [ ] denotes concentration expressed in mol kg^{-1}. The K_G values calculated in this study were based on Eq. [17] and [18].

3.4.4 Gaines and Thomas Selectivity Coefficient (K_{GT})

This model is similar to the Vanselow's selectivity coefficient, but its difference lies in the definition of a reference state of an adsorbed ion to the exchanger phase. The reference state, as defined by Gaines and Thomas, is a mono-ion solid in equilibrium with an infinitely dilute solution of that ion such that the activity of the ion in solution is unity and the rational activity coefficient *(f)*, as shall be shown later, is also equal to unity. The relevance of the equation lies in this definition of a reference state of an adsorbed ion that allows for explicit determination of actual exchange equilibrium constant. The computed K_{GT} for Ca-K and Mg-K exchange reactions was done by employing Eq [23] and [24] (Essington, 2004).

$$K_{GT(Ca\text{-}K)} = \frac{E^2_K(Ca^{2+})}{E_{Ca}(K^+)^2} \quad [23]$$

$$K_{GT(Mg\text{-}K)} = \frac{E^2_K(Mg^{2+})}{E_{mg}(K^+)^2} \quad [24]$$

3.4.5 Davies Selectivity Coefficient (K_D)

Davies (1950) and Davies Dible (1950) derived this selectivity coefficient by assuming that the exchange surface is made up of a number of negative point charges. Based on Ca-K and Mg-K exchange reactions determined in this study, the Davies selectivity coefficient was computed as:

$$K_{D\ (Ca\text{-}K)} = \frac{N^2_K(Ca^{2+})}{\{N_{Ca}(q_K N_K + q_{Ca}N_{Ca})\}(K^+)^2} \quad [25]$$

$$K_{D\ (Mg\text{-}K)} = \frac{N^2_K(Mg^{2+})}{\{N_{Mg}(q_K N_K + q_{Mg}N_{Mg})\}(K^+)^2} \quad [26]$$

where the values of q_K q_{Ca} and q_{Mg} depend on the number of nearest neighbours associated with the adsorbed cation. The q values were determined by Eq. [27] below:

$$q_i = \frac{(n_i Z_i - 2_{Zi} + 2)}{n_i} \quad [27]$$

where Z_i is the valence of ion (i) and n_i is the number of nearest neighbours. There are several versions of the Davies equation based on the assumption of the number of nearest neighbours. In this study, we have adopted the assumption of Krisnarmorthy and Overstreet (1950) that n = 4, representing a square array of surface charges, hence the calculation of K_D was simplified to Eq. [28] and [29]:

$$K_{D,\ n\text{-}4\ (Ca\text{-}K)} = \frac{N^2_K(Ca^{2+})}{\{N_{Ca}(N_k + 1.5Nc_a)\}(K^+)^2} \quad [28]$$

$$K_{D,\ n\text{-}4\ (K\text{-}Mg)} = \frac{N^2_K(Mg^{2+})}{N_{Mg(}N_K + 1.5N_{Mg})\}(K^+)^2} \quad [29]$$

3.4.6 Thermodynamic exchange constant (K_{ex})

For Ca-K and Mg-K exchange reactions described in Eq. (1) and (2), the true thermodynamic equilibrium constants were described in Eq. (3) and (4). The activities of the soluble species can be determined by multiplying activity coefficients with their molar concentrations in solution: $(Ca^{2+}) = y_{ca}{}^{2+}\ [Ca^{2+}]$; $(Mg^{2+}) = y_{Mg}{}^{2+}\ [Mg^{2+}]$; $(K^+) = y_k{}^+[K^+]$, where y is the single ion activity coefficient, determined from the Davies equation given by Sposito (1989) as:

$$\log y_i = 0.512 Z_i^2 \left[\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.3\mu \right] \qquad [30]$$

where Z_i is the valence of ion and μ is the ionic strength of the soil solution. But for an adsorbed ion, it is not possible to determine its activity in the exchanger phase. In ion exchange reaction, it is commonly assumed that the exchanger phase is a solid-solution (Sposito, 1989; Essington, 2004), hence the mole fraction of K^+, Mg^{2+} and Ca^{2+} in the exchanger phase can be related to exchange phase activity. Thus $(CaX_2) = f_{Ca}N_{Ca}$ $(MgX_2) = f_{Mg}N_{Mg}$ and (KX) = Nk, where N_{Ca}, N_{Mg} and N_K are mole fractions (see Eq. [7] – [10] respectively, and f_{Ca}, f_{Mg} and f_K are the rational activity coefficients. Thus, substituting the expressions for (CaX_2), (MgX_2), (KX) into Eq. (3) and (4) yielded the thermodynamic exchange constants for Ca-K and Mg-K exchange reactions as follows:

$$K_{ex}\ (Ca\text{-}K) = \frac{f_k^2 N_k \gamma_{Ca}^{2+} [Ca^{2+}]}{f_{Ca} N_{Ca} \gamma_{K^+}^2 (K^+)^2} \qquad [31]$$

$$K_{ex}\ (Mg\text{-}K) = \frac{f_k^2 N_k \gamma_{Mg}^{2+} [Mg^{2+}]}{f_{Mg} N_{Mg} \gamma_{k^+}^2 [K^+]^2} \qquad [32]$$

It should be noted that Eq. (31) and (32) are closely related to the Vanselow selectivity coefficients (see Eq. [11] and [12] if $f_k = f_{Ca} = 1$ and $f_k = f_{Mg} = 1$. Because the values of f_K, f_{Ca}, f_{Mg} are usually less than unity, that is to say,

the exchangeable ions do not form iSdeal mixture at the exchanger surface, the relations between K_{ex} and K_v can be written as:

$$K_{ex}{}_{(Ca\text{-}K)} = \{(f^2_K)\, I f_{Ca})\}K_v \quad (33)$$

$$K_{ex}{}_{(Ca\text{-}K)} = \{(f^2_K)\, I f_{Mg})\}K_v \quad (34)$$

Furthermore, because K_{ex} is a true thermodynamic exchange constant for the exchange reactions considered in this study, it is not expected to vary extensively with exchanger phase composition. The rational activity coefficients f_k, f_{Ca}, f_{Mg} were computed by employing Eq. (35)-(37) (Sposito, 1981; Essington, 2004):

$$\ln f_K = {}_{m/4}(E^2_{Ca}) \quad (35)$$

$$\ln f_{Ca} = {}_{m/2}(I\text{-}E_{Ca})^2 = {}_{m/2}\, E^2_k \quad (36)$$

$$\ln f_{Mg} = {}_{m/2}(I\text{-}E_{Mg})^2 = {}_{m/2}\, E^2_k \quad (37)$$

Where E_{Ca}, E_{Mg} and E_K are the equivalent fractions of adsorbed Ca^{2+}, Mg^{2+} and K^+ respectively as previously defined in Eq. (19)-(21). The quantity ${}_m$ in Eq. (35)-(37) can be determined by fitting $\ln K_V$ as a function of E_{Ca} and E_{Mg}. Although the relations between $\ln K_v$ and E_{Ca} or E_{Mg} were best described by a power series equation in our study, a truncated form of the equation in which $\ln K_v$ is expressed as a linear function of E_{ca} and E_{Mg} was adopted as suggested by Sposito (1981, 1989) and Essington (2004).

$$\ln K_{v\,(Ca\text{-}K)} = b + m\, E_{Ca} \quad (38)$$

$$\ln K_{v\,(Mg\text{-}K)} = b + m\, E_{Mg} \quad (39)$$

Where b and m are the intercept and slope of the linear regression expression respectively.

We also computed the free energy of the exchange reactions (ΔG_{ex}), assuming standard temperature (T) and pressure (P) to be T = 298 ^oK and P = 0.01Mpa, the relationship between the equilibrium exchange constant and ΔG_{ex} can be written as:

$$\Delta G_{ex} = -RT \ln K_{ex} \quad (40)$$

where R is the universal gas constant (8.314 JK^{-1} mol^{-1})

3.5 Cation adsorption isotherms

Cation exchange isotherms were determined by plotting the charge fraction of the cation in solution against the charge fractions of the adsorbed cation (Sposito, 1989). For KX-MgX_2 and KX-CaX_2 exchange reaction studied, the equivalent fractions of adsorbed Ca^{2+}, Mg^{2+} and K^+ were calculated with Eq. (19) through (21). The equivalent fractions of Ca^{2+}, Mg^{2+} and K^+ in solution were computed with Eq. (41) through (44) as follows:

$$E_{Ca(aq)} = \frac{2[Ca^{2+}]}{2[Ca^{2+}] + [K^+]} \quad (41)$$

$$E_{Mg(aq)} = \frac{2[Mg^{2+}]}{2[Mg^{2+}] + [K^+]} \quad (42)$$

$$E_{k(aq)\,(K\text{-}Ca)} = \frac{[K^+]}{2[Ca^{2+}] + [K^+]} \quad (43)$$

$$E_{k(aq)\,(K\text{-}Mg)} = \frac{[K^+]}{2[Mg^{2+}] + [K^+]} \quad (44)$$

where [ ] denotes molar concentration in solution. For MgX_2 – KX and CaX_2- KX exchange reactions, the selectivity or preference can be determined by a plot of the equivalent fraction of adsorbed Mg^{2+} or Ca^{2+} versus the equivalent fraction of Mg^{2+} or Ca^{2+} in solution (Sposito, 1989; Sparks, 2003). The exchange isotherm, thus, obtained was compared with the thermodynamic non-preference line on the cation isotherm diagram. The thermodynamic non-preference isotherm line was theoretically derived, based on the condition that K_v (Vanselow selectivity coefficient) = 1, in which case, the exchanger surface has no preference either for Ca^{2+}, Mg^{2+} or K^+. The thermodynamic non-preference isotherm (TNI) line for K^+ ($E_{k/exch}$) as a function of ionic strength was computed with Eq. (45) given by Essington (2004):

$$E_{K(exch)} = \{1 + 1/\Gamma\mu[3/E^2_{K(ca)} - 4/E_{K(aq)} + I]\}^{-0.5} \quad (45)$$

Where $\Gamma = \gamma_k^2 \left| \gamma_{ca} \right.$ and γ is single ion activity coefficient determined by means

of Eq. (30), μ is ionic strength computed from the concentration of Ca^{2+} and K^+ for Ca-K exchange or Mg^{2+} and K^+ for Mg-K exchange and the associated anion in solution. The ionic strength (u) was computed as $u = 3[Ca^{2+}] + (K^+]$ for Ca-K exchange or $\mu = 3[Mg^{2+}] + [K^+]$ for Mg-K exchange (Essington (2004). Similarly, the thermodynamic non-preference isotherm (TNI) line for Ca^{2+} ($E_{Ca(exch)}$ or Mg^{2+}

($E_{Mg(exch)}$ as a function of ionic strength was computed with Eq. (46) given by Sposito (1989).

$$E_{divalent(exch)} = I - \{rN_t[I - E_{div(aq)}]^2 / [E_{div(aq)} + A[I - E_{div(aq)}^2]\}^{-0.5} \quad [46]$$

Where N_t is sum of cations in solution while $E_{div(aq)}$ is the equivalent fraction of the divalent cation (Ca^{2+} or Mg^{2+} in our study) in the solution phase.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1. Adsorbed Metal Charge

The total adsorbed metal charge (Q_i) calculated as the summation of the surface excesses of the cations for MgX_2-KX exchange (Table 3) and CaX_2-KX exchange (Table 4) was less than CEC of the soils. It seems that the higher CEC than Q_i in the soil was probably a consequence of pH dependent charges as CEC was determined by the 1.0 M NH_4-acetate buffered at pH 7.0 that was far greater than the natural pH of the soils (Table 2). Thus, the effective CEC of the soils is unlikely to differ significantly from Q_i. The Q_i values for KX-MgX_2 exchange (Table 3) and KX-CaX_2 exchange (Table 4) were actually in a narrow range, and did not increase or decrease consistently as exchangeable Mg or Ca increased in both the surface and subsurface soils. Jensen (1973) reported relatively consistent Q_i for K-Ca exchange in bentonite clay, consistent with the results of this study.

The fact that Q_i did not increase consistently with increasing exchangeable Mg and Ca suggested that the colloidal surfaces did not show any preference for adsorption of ion pairs such as $CaCl^+$ and $MgCl^+$ in the exchange reactions as observed by Sposito (1983 a, b) who reported that $MgCl^+$ and $CaCl^+$ significantly influenced Na-Ca and Na-Mg exchange reactions in montmorillonite. Actually, Sposito (1983a) found that $CaCl^+$ and $MgCl^+$ accounted for 50 % and 30 % of exchangeable Ca and Mg respectively in montmorillonite. Preference for

Ca or Mg by soil colloids has been attributed to the preference for $CaCl^+$ and $MgCl^+$. However, for the Mokwa soil, Q_i for K-Ca exchange was 22 % greater than Q_i for K-Mg exchange, thus indicating some preference for $CaCl^+$

Table 3. The K and Mg concentration in equilibrium soil solution and the surface excesses of the cations in the soils from Zaria and Mokwa

Equilibrium concentration in solution			Surface excess of the cations		
	K	Mg	q_K	q_{Mg}	Q_i
	mmol L^{-1}		mmol kg^{-1}		
ZARIA					
0-15 cm	2.00	97.4	2.30	58.8	61.1
	3.40	94.5	3.20	50.2	53.4
	12.5	94.2	9.60	47.2	56.8
	19.9	86.0	11.2	43.6	57.8
	26.6	80.8	15.2	40.4	55.5
	80.5	75.3	32.5	20.4	52.9
	182.4	37.1	56.2	7.74	63.9
15-30 cm	1.20	98.1	2.10	62.4	64.3
	4.70	95.4	5.50	57.1	62.2
	10.4	93.1	9.60	55.6	65.2
	15.9	87.8	12.7	50.3	63.0
	37.1	68.8	19.2	37.1	56.3
	71.7	52.9	35.4	25.6	61.0
	136.7	15.6	47.0	4.30	51.3
MOKWA					
0-15 cm	1.40	113.0	1.50	58.4	59.9
	10.9	108.4	6.20	54.3	60.6
	13.5	106.3	7.00	51.3	58.2
	26.2	102.7	10.5	47.0	57.5
	43.3	91.5	17.5	40.9	58.4
	51.3	38.4	38.5	25.2	63.6

	104.3	12.8	50.4	5.20	55.6
15-30 cm	1.40	104.8	1.40	48.3	49.7
	12.6	101.3	6.90	48.9	55.8
	18.2	99.3	9.60	46.5	56.2
	25.1	88.2	11.8	35.0	46.8
	41.0	72.9	12.7	29.6	42.3
	145.8	47.3	41.5	13.1	54.6
	181.5	12.4	44.2	3.60	47.9

Qi = sum of surface excess of K (q_K) and Mg (q_{Mg}).

Table 4. The K and Ca concentration in equilibrium soil solution and the surface excesses of the cations in the soils from Zaria and Mokwa

	Equilibrium concentration in solution cations		Surface excess of the		
	K	Ca	q_K	q_{Ca}	Q_i
	---------- mmol L^{-1}----------		---------- mol kg^{-1} ----------		
			ZARIA		
0-15 cm	0.60	81.7	1.60	59.0	60.6
	4.20	76.3	6.50	52.0	58.5
	8.70	73.3	7.10	48.9	56.0
	18.9	62.0	12.7	42.5	53.8
	25.7	46.4	22.3	41.1	63.4
	54.5	38.1	44.2	18.8	63.0
	125.3	17.9	47.3	5.70	53.0
15-30 cm	0.60	80.3	2.00	94.3	96.3

	5.00	78.5	6.50	92.7	99.2
	9.10	75.7	9.60	91.5	101.1
	16.9	67.1	16.2	76.6	92.7
	39.9	49.0	37.7	55.5	93.1
	54.1	37.4	64.8	20.4	85.2
	110.8	19.8	82.1	6.60	88.7
			MOKWA		
0-15 cm	1.10	61.7	1.10	61.5	62.6
	9.30	57.0	8.10	54.8	62.9
	13.8	55.3	11.1	51.6	62.7
	22.6	50.0	12.5	49.6	62.1
	31.7	37.4	19.2	42.6	61.9
	42.5	25.6	31.2	26.4	57.6
	104.5	10.4	53.5	7.40	60.9
15-30 cm	1.00	59.2	1.90	71.5	73.4
	8.70	58.3	9.30	68.7	76.4
	9.90	56.5	9.60	67.1	78.3
	18.6	51.4	14.4	52.5	66.9
	32.6	37.0	25.6	42.8	68.4
	60.6	28.5	45.2	22.1	67.3
	112.7	23.2	61.5	8.10	69.6

Qi = sum of surface excess of K (q_K) and Ca (q_{Ca}).

over $MgCl^+$. This is in contrast to the relatively consistent Q_i for both Ca-K and Mg-K exchange in the Zaria soil. It is possible that slight differences in mineralogical composition of the soils from the two locations would be responsible for this trend.

A possible reason for higher Q_i for the Ca-K exchange than Mg-K exchange in the Mokwa soil might be H displacement in the variable charge component of the CEC (Suarez and Zahow, 1989). The higher Q_i for Ca-K than Q_i for Mg-K in the Mokwa soil is consistent with the observation of Jensen and Babcock (1973) who reported increasing Q_i with increasing Ca saturation in K-Ca in a Yolo loam soil. These results may be evidence of specific affinity for Ca relative to Mg due probably to Ca-specific sites in OM (Suarez and Zahow, 1989). Because of the relatively high ionic strength (u = 0.15 $\pm$ 0.03) of the exchange medium, it was expected that Q_i would increase with increasing Ca or Mg saturation as reported by Suarez and Zahow (1989), though in montmorillonitic clay, rather than the relatively consistent Q_i with increasing Ca and Mg saturation (Tables 3 and 4). It is quite unreasonable comparing results obtained from pure clay with natural soil because of the heterogeneity of exchange sites in the latter.

4.2 Cation Selectivity Coefficients

A number of factors affect cation selectivity coefficients determined for soils. These include the methods used to calculate ionic activity, whether by Debye-Huckell equation or by Davies equation; differences in experimental methods that might introduce hysteresis in the exchange reactions; the surface charge density and the location of the charge deficit in the silicate structure, and contamination by OM. Thus, in evaluating and interpreting the selectivity coefficients discussed in this study, these factors were taken into consideration.

The various selectivity coefficients as a function of exchanger phase composition are given in Table 5 for K-Mg exchange and Table 6 for K-Ca exchange. In general, the selectivity coefficients varied with exchanger phase composition as no single selectivity coefficients was relatively consistent throughout the exchanger phase composition. However, in the surface soil, K_V for K-Mg exchange was nearly constant at N_{Mg} from 0.121 to 0.796, while K_G was relatively consistent across a wide range of the exchanger phase composition for

both the Zaria and Mokwa soils, but declined at low N_{Mg} (Table 5). The K_D and K_{GT} followed the same trend as K_V in the surface soil from Zaria. In the Mokwa soil, K_V was relatively constant over a much narrower range of exchanger composition as compared to Zaria, whereas K_G was relatively consistent over a wide range of exchanger phase composition as were K_D and K_{GT} (Table 5). In the sub-surface layer, the selectivity coefficients as a function of the exchanger phase composition varied much more widely than the selectivity coefficients in the surface layer for both Zaria and Mokwa. The K_V was only constant at a much narrower range of exchanger phase composition in the sub-surface than surface soils. However, K_G and K_D showed relative consistency over a wider range of exchanger phase composition in the sub-surface than surface layers in the Zaria soil. In Mokwa, the selectivity coefficients were only consistent at $N_{Mg} > 0.769$.

The trends in selectivity coefficients as a function of exchanger phase composition for Ca-K exchange (Table 6) were similar to Mg-K exchange. All selectivity coefficients determined for Mg-K for the soils either from Zaria or Mokwa were > 1 at all exchanger phase composition (Table 5), suggesting a preference for K to Mg by the soils. Similarly, all selectivity coefficients for Ca-K exchange were >1 at all exchanger phase composition (Table 6), whereas at Mokwa, K_G and K_{GT} were < 1 at N_{Ca} equal to or less than 0.459 at the surface layer.

In the subsurface layer, K_{GT} was < 1.0 at N_{ca} equal to or greater than 0.326. Thus all selectivity coefficients were greater than unity in a wide range of the exchanger composition thus indicating a preference for K to Ca. The high K selectivity of these soils over a wide range of K equivalent or mole fractions has been reported for a number of soils and clay minerals. Feigenbaum et al. (1991) concluded, from their binary and ternary exchange experiments, the preference

of K to Ca and Ca + Mg in calcareous montmorillonitic soils. In kaolinitic soils from Western Nigeria, Udo (1978) showed K selectivity over Ca or Mg consistent with the results of Jensen (1973) and Levy et al. (1988).

4.3 Cation Adsorption Isotherms

To further elucidate the preference for the mono-divalent exchange systems in the study, plots of the charge fraction of the adsorbed Ca and Mg: $E_{Ca(\text{exch.})}$ and $E_{Mg(\text{exch.})}$ versus the charge fraction of Ca and Mg in aqueous solution: $E_{Ca(\text{aq.})}$, $E_{Mg(\text{aq.})}$ were made to produce the cation adsorption isotherms. The cation exchange isotherms were thus compared with the thermodynamic non-preference isotherm (TNI) line theoretically generated by means of Eq. 46 (Sposito, 1989). The plots of $E_{Ca(\text{exch})}$ and $E_{Mg(\text{exch})}$ versus $E_{Ca(\text{aq})}$ and $E_{Mg(\text{aq})}$ respectively, indicated that the experimental points were below the TNI line for both Zaria (Fig. 1) and Mokwa (Fig. 2), clearly suggesting non-preference for Ca and Mg in the presence of K. Similarly, the plots of $E_{K(\text{exch.})}$ versus $E_{K(\text{aq.})}$ for the Zaria soil indicated that all the experimental points were above the TNI line (Fig. 3). However, in the Mokwa soils, the experimental points were above TNI line at $E_{K(\text{aq.})} < 0.4$, whereas at $E_{K(\text{aq.})} > 0.4$, the experimental points fell below the TNI line (Fig. 4).

Table 5. The mole fraction and the selectivity coefficients of $KX\text{-}MgX_2$ exchange of surface and sub-surface layers of Typic Haplustalf from Zaria and a Ustult from Mokwa

Mole fractions		Selectivity coefficients				
N_{Mg}	N_K	K_K	K_V	K_G	K_{GT}	$K_{D(n=4)}$
			ZARIA			
0-15 cm						
0.962	0.038	26.32	28.57	2.72	7.25	19.23
0.941	0.059	19.61	23.80	2.51	6.10	16.13

0.831	0.169	12.99	16.39	2.22	4.48	11.63
0.796	0.204	7.94	9.90	1.76	2.75	7.04
0.727	0.273	7.63	9.52	1.81	2.76	6.99
0.385	0.615	3.92	8.93	2.39	3.22	7.46
0.121	0.879	1.91	5.52	3.38	2.46	5.21
15-30 cm						
0.968	0.032	55.56	55.56	3.83	14.49	38.46
0.912	0.088	27.03	29.41	1.54	7.81	20.41
0.852	0.148	16.39	17.24	2.25	4.67	12.20
0.799	0.201	12.82	14.08	2.09	3.89	10.00
0.658	0.342	6.06	6.94	1.63	2.10	5.24
0.420	0.580	5.10	6.41	1.96	2.26	5.32
0.084	0.916	2.88	6.25	4.31	2.29	5.99

MOKWA

0-15 cm						
0.975	0.025	23.26	29.41	2.73	7.35	19.61
0.896	0.104	6.90	9.35	1.62	2.47	6.45
0.880	0.120	5.85	8.40	1.54	2.33	5.81
0.817	0.183	3.55	5.24	1.27	1.44	3.72
0.700	0.300	3.57	4.88	1.32	1.43	3.61
0.567	0.604	2.80	2.61	1.29	0.94	2.18
0.171	0.906	1.36	1.99	2.30	0.91	1.89
15 –30 cm						
0.972	0.028	25.00	35.71	3.00	23.80	10.42
0.877	0.123	6.76	8.77	1.59	6.13	2.34
0.829	0.171	6.33	8.26	1.58	5.85	2.26
0.769	0.231	5.10	7.63	1.57	5.50	2.04
0.700	0.300	2.92	4.31	1.24	3.20	1.22
0.239	0.761	1.92	4.13	2.08	3.69	5.29
0.076	0.924	1.61	3.25	3.27	3.13	23.81

N_k = mole fraction of adsorbed K; N_{Mg} = mole fraction of adsorbed Mg; K_K = Kerr selectivity coefficient; K_V = Vanselow coefficient; K_G = Gapon constant; K_{GT} = Gaines and Thomas selectivity coefficient; K_D = Davies selectivity coefficient

Table 6. The mole fraction and the selectivity coefficients of KX-CaX_2 exchange of a surface (0-15 cm) and subsurface (15-30 cm) layers of a Typic Haplustalf from Zaria and a Ustult from Mokwa

Mole fractions		Selectivity coefficients				
N_{Ca}	N_K	K_K	K_V	K_G	K_{GT}	$K_{D(n=4)}$

ZARIA

0-15 cm

0.973	0.027	166.7	142.9	6.02	35.71	90.91
0.881	0.119	58.82	52.63	3.88	14.29	37.03
0.880	0.120	12.99	11.91	1.83	3.15	8.20
0.764	0.236	10.99	9.90	1.80	2.81	7.19
0.656	0.344	14.93	9.71	1.93	2.94	7.35
0.396	0.605	11.62	9.17	2.41	3.28	7.63
0.197	0.893	3.51	6.45	3.88	2.92	6.14

15-30 cm

0.979	0.021	142.9	71.43	4.33	18.52	50.00
0.934	0.066	22.72	11.91	1.90	3.07	8.06
0.905	0.095	14.08	7.14	1.40	1.88	4.93
0.826	0.174	12.66	6.71	1.43	1.84	4.76
0.596	0.404	12.20	6.49	1.65	2.04	5.03
0.239	0.761	5.44	5.92	2.49	2.39	5.29
0.075	0.925	2.01	3.53	3.44	1.64	3.40

MOKWA

0-15 cm

0.983	0.017	20.41	12.50	1.78	3.15	8.33
0.871	0.129	15.38	9.71	1.67	2.58	6.76
0.824	0.176	13.16	8.55	1.61	2.34	6.00
0.798	0.202	6.45	3.88	1.10	1.08	2.77
0.689	0.311	7.69	4.02	1.21	1.19	2.99
0.459	0.541	3.04	1.74	0.97	0.60	1.41
0.121	0.879	1.28	1.05	1.47	0.47	0.99

15-30 cm

0.978	0.022	50.00	22.73	2.40	5.71	15.15
0.879	0.121	19.23	10.10	1.69	2.67	6.99
0.877	0.123	15.63	7.75	1.49	2.07	5.37
0.784	0.216	11.49	6.80	1.47	1.90	4.88
0.626	0.374	11.62	5.95	1.54	1.83	4.52
0.326	0.672	2.68	2.05	1.25	0.78	1.76
0.135	0.865	1.14	1.94	1.89	0.85	1.82

N_k = mole fraction of adsorbed K; N_{Mg} = mole fraction of adsorbed Mg; K_K = Kerr selectivity coefficient; K_V = Vanselow coefficient; K_G = Gapon constant; K_{GT} = Gaines and Thomas selectivity coefficient; K_D = Davies selectivity coefficient

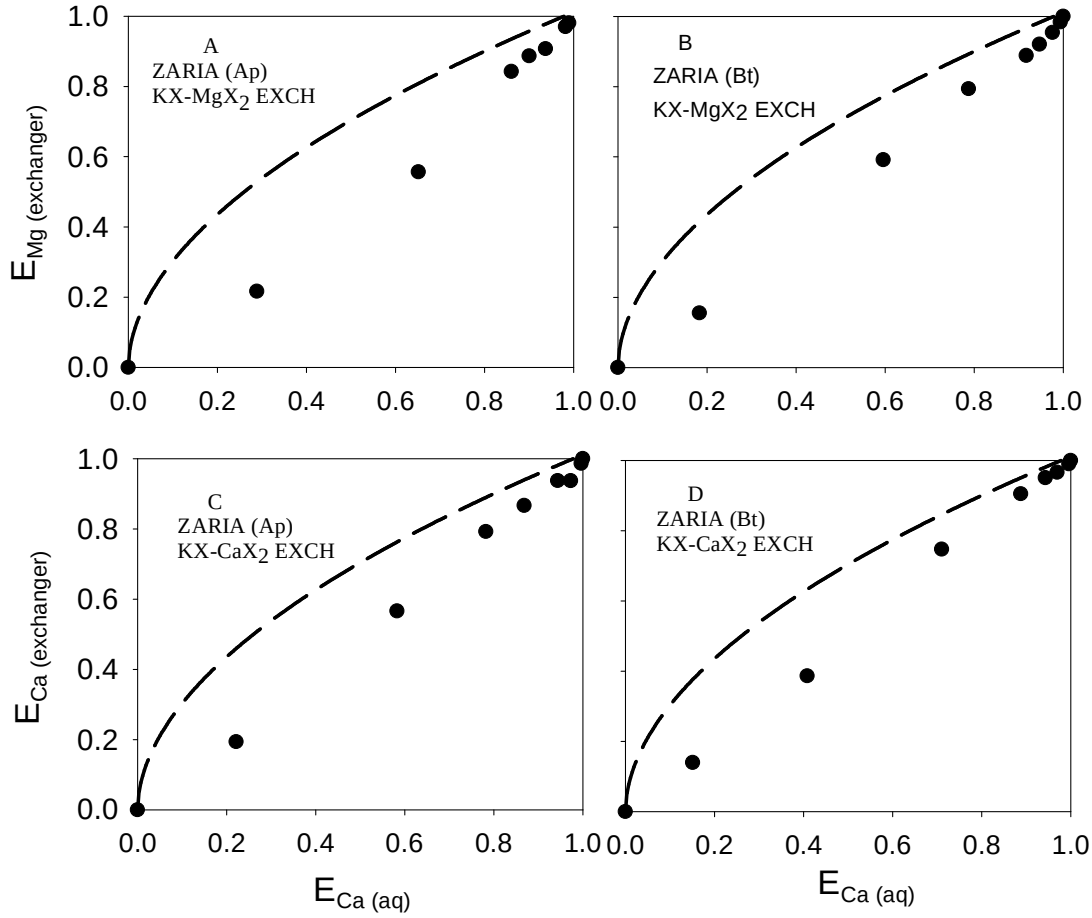


Figure 1. The Mg and Ca adsorption isotherms of Ap and Bt horizons of an Alfisol from Zaria. The dashed line is the thermodynamic non-preference isotherm line.

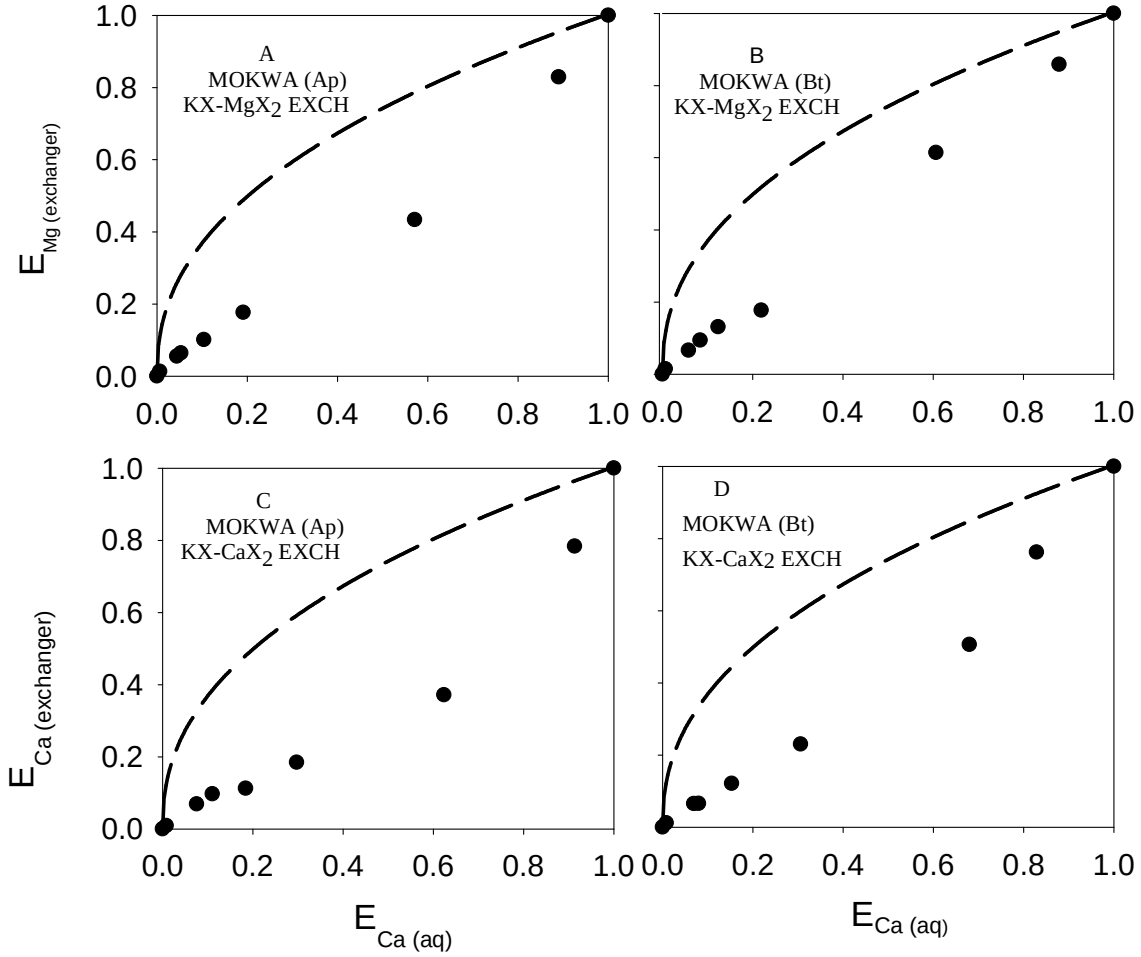


Figure 2. The Mg and Ca adsorption isotherms of Ap and Bt horizons of the Mokwa soil. The dashed line is the thermodynamic non-preference line.

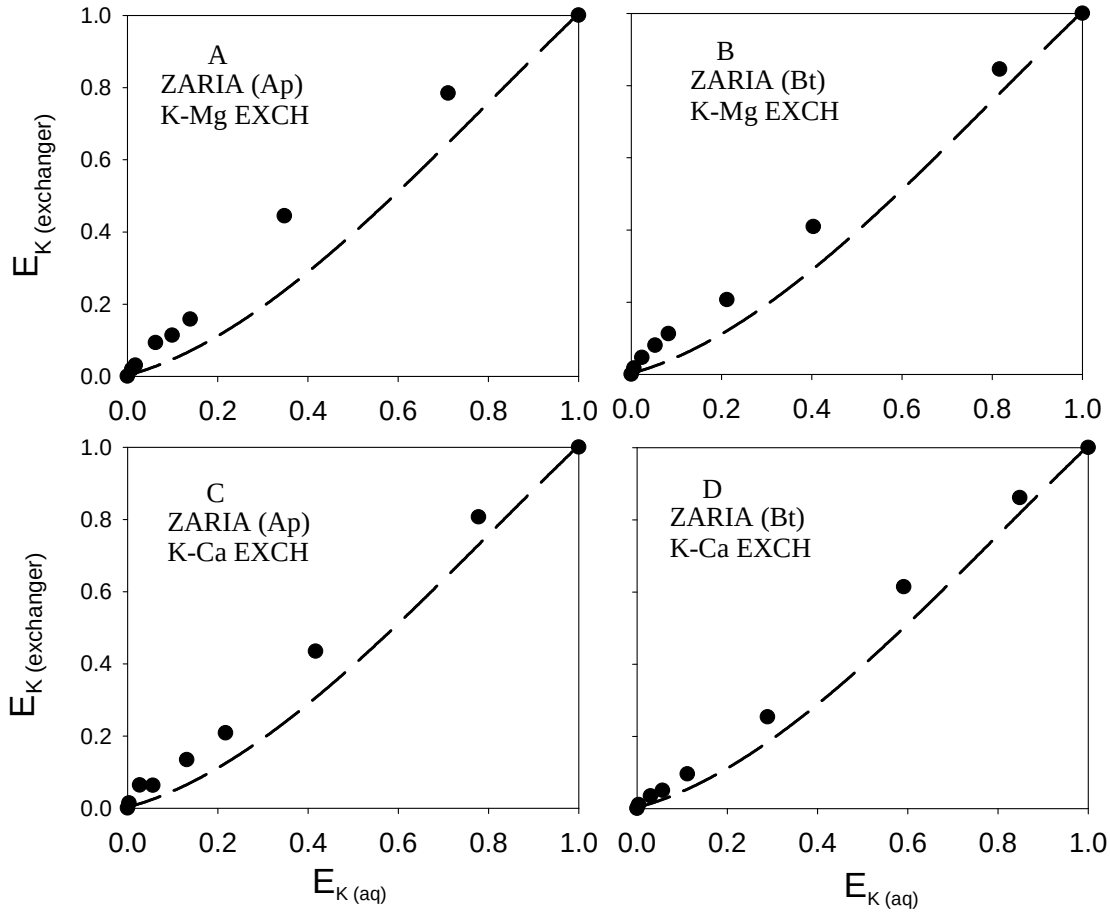


Figure 3. The K adsorption isotherms of Ap and Bt horizons of the Zaria soil. The dashed line is the thermodynamic non-preference line

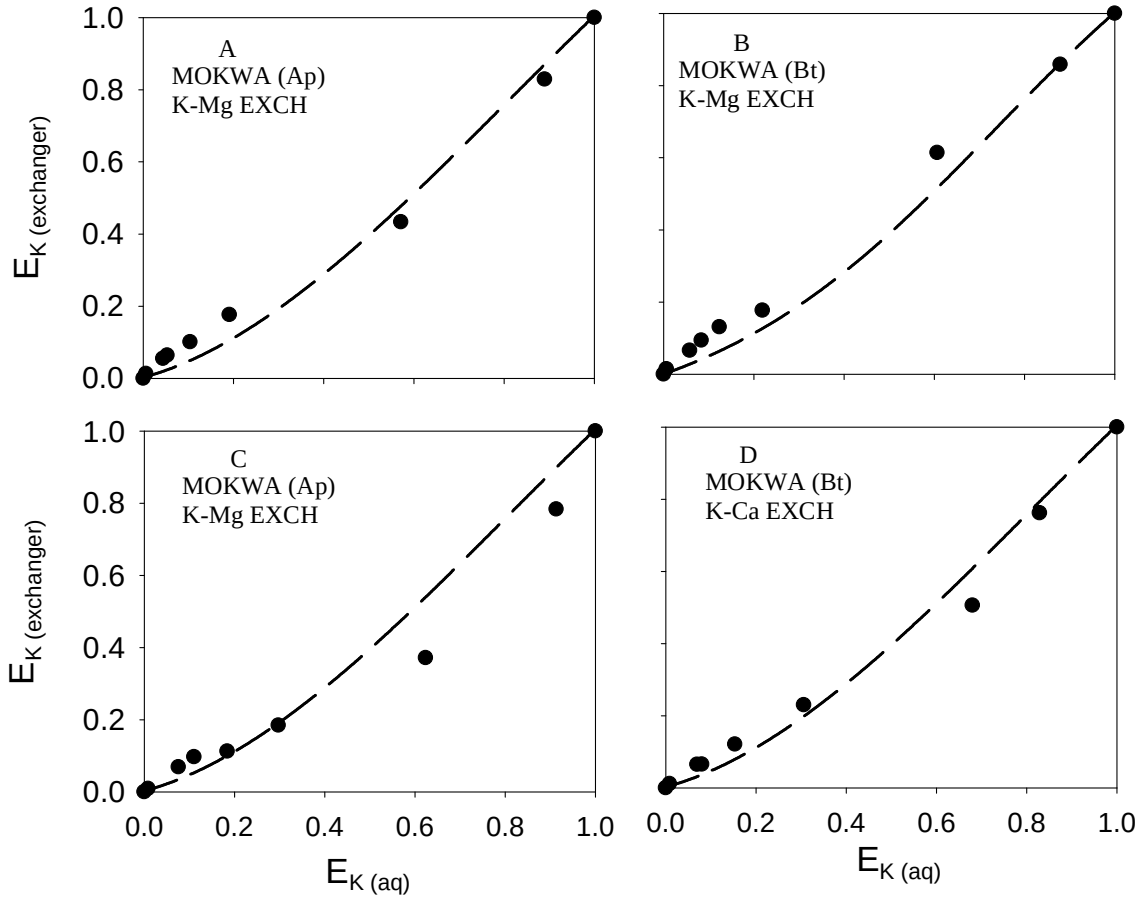


Figure 4. The K adsorption isotherms of Ap and Bt horizons of the Mokwa soil. The dashed line is the thermodynamic non-preference line

The experimental points falling above the TNI line indicated a preference for K in the Zaria soil, and in Mokwa soil up to $E_{K(aq.)} < 0.4$, but above $E_{K(aq.)} > 0.4$, a preference for Ca and Mg was exhibited by the Mokwa soil.

The marked selectivity for K over Ca and Mg by the soils used in this study is in agreement with observations in several 2:1 and 1:1 clays as well as in kaolinitic soils (Jensen and Babcock, 1973; Udo, 1978; Thellier and Sposito, 1989 and Feigenbaum et al., 1991). Except for the work of Udo (1978), studies of heterovalent cation exchange reactions are rare in soils of the tropics dominated by variable charge colloids. The selectivity of K over Ca and Mg clearly exhibited by these soils is inconsistent with valence consideration as a basis for selectivity of cations by soil

exchanger phase. Galindo and Bingham (1977) clearly showed a preferential adsorption of divalent to monovalent cations in variable charge soils from Chile in contrast to the K preference by these soils.

It is generally believed that kaolinitic soils have a low K preference as compared to Ca^{2+}. Goulding and Talibudeen (1980), however, reported that the kaolinites they studied exhibited an unusually high K selectivity because of the presence of illite as impurities in the kaolinitic clays. Unfortunately, the mineralogy of the soils used in this study was not examined, but Ojanuga (1979) had studied the clay mineralogy of representative soils from the southern and northern Guinea savanna of Nigeria, the same ecological region as the soils used in this study. He reported that kaolinite was the dominant clay mineral in the soils with micaceous minerals present in trace amounts. Agbenin (unpublished) found that the clay mineralogy of a typical savanna soil from Zaria (*Typic Haplustalf*) determined by x-ray diffraction was dominated by kaolinite and 1.0 nm minerals thought to be mica when the clays were saturated with K. But on heating, the kaolinitic clays collapsed, whereas the 1.0 nm mineral became clearly evident. Thus, the presence of mica in the clay suite could partly account for high K selectivity exhibited by the soils, especially for the soil from Zaria. Examination of Ca-K exchange in five aluminosilicate minerals by Goulding and Talibudeen (1980) established the following order of K preference: mica > vermiculite = illite > kaolinite > montmorillonite. Based on cation isotherm, the soil from Mokwa showed a change of selectivity from K to Ca and Mg at $E_K > 0.4$ in both the Ap and Bt horizons (Fig. 4). This is probably indicative of a change from external to internal exchange sites. Internal exchange sites tend to show preference for divalent to monovalent cations (Karmakar et al., 1991).

4.4 Thermodynamic Exchange Constant (K_{ex}) and the Change in Free Energy (ΔG_{ex}) of Exchange

Goulding (1983), in a review, pointed out that it is not proper to use exchange isotherm to assign selectivity of cations because it varies with ionic strength, but did not indicate at what ionic strength selectivity coefficients are invalid. According to Goulding (1983), overall selectivity is best expressed by the thermodynamic exchange constant (K_{ex}) or free energy of exchange (ΔG_{ex}), and that changes in selectivity are best expressed as a graph of ln K_{GT} versus K saturation (E_K). In this study, plots of ln K_V as a function of E_K to assess K, Mg and Ca selectivity were made. In the Zaria soil, ln K_V decreased sharply with increasing E_K but remained nearly constant at E_K > 0.1 (Fig. 5) whereas in the Mokwa soil, ln K_V decreased gradually with increasing E_K up to E_K = 0.1, but thereafter it also remained nearly constant at E_K > 0.1. Since ln K_V was generally greater than zero with increasing K saturation in both soils, it is an indication of K

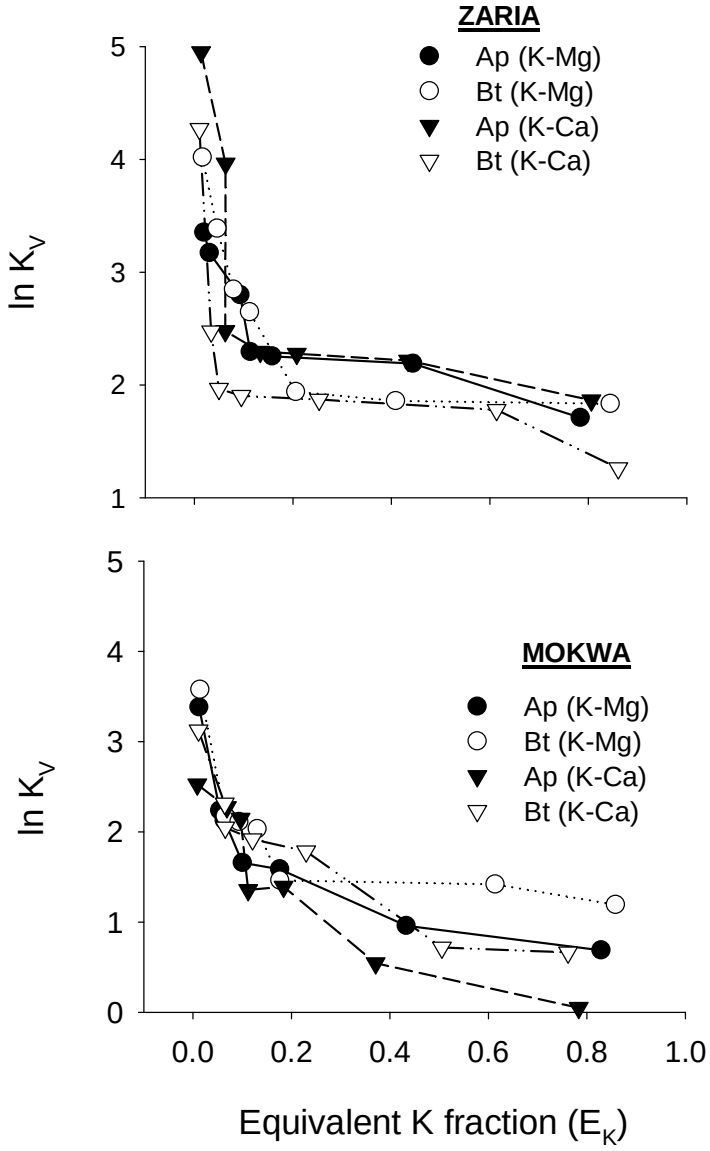


Figure 5. A plot of ln K_v with equivalent fractions of adsorbed K (E_K) in the two soils used for the study.

preference or selectivity over Ca and Mg. The decreasing K_V as the E_K increased has been attributed to the heterogeneity of surface exchange sites (Ogwada and Sparks, 1986), and might probably reflect decreasing specificity of the surface sites for K^+. The extremely high selectivity at $E_K < 0.1$ can be attributed to high energy of surface sites probably located in the silicon tetrahedral sheet caused by the isomorphic substitution of Al^{3+} for Si^{4+}, to which K^+ is adsorbed, as it is the right ionic size to fit snugly into the vacant site.

The rational activity coefficients of adsorbed K (f_K), Ca (f_{Ca}) and Mg (f_{Mg}) in relation to variations in K saturation and K_V are given for MgX_2-KX in Table 7, and for CaX_2 -KX in Table 8. As the activity coefficients of adsorbed ions, they reflect the fugacity of adsorbed ions. The fugacity expresses the degree of freedom an adsorbed ion has to leave the adsorbed state as compared to a standard state of maximum freedom of unity (Goulding, 1983; Sparks, 2003; Essington, 2004). Plots of f_K, f_{Ca} and f_{Mg} as a function of E_K to show the changes in freedom of the adsorbed ion in the exchanger phase were made (figs. 6 & 7). As K saturation (f_K) increased, whereas f_{Ca} and f_{Mg} decreased with increasing E_K. The increasing f_K with increasing E_K throughout is inconsistent with the observation of Talibudeen (1972) and Deist and Talibudeen (1967a) who reported minimum, maxima and inflection of f_K with increasing K saturation, though a weak inflection point seemed to have occurred at E_K approximately 0.5. Also in agreement with the results of Deist and Talibudeen (1967b), f_{Ca} decreased smoothly with increasing K saturation as also reported by Goulding (1983). The increasing f_K and decreasing f_{Ca} with E_K is just an evidence of non-ideality because of the heterogeneous surface sites and the heterovalent cations,

Table 7. The Vanselow selectivity coefficient (K_V), rational activity coefficients and the thermodynamic equilibrium exchange constant as a function of the equivalent fraction of Mg^{2+} (E_{Mg}) on the exchange complex for $KX\text{-}MgX_2$ exchange on a surface (0-15 cm) and sub-surface layer (15-30 cm) of *Typic Haplustalf* from Zaria and a *Ustult* from Mokwa

	E_K	K_V	$ln\ K_V$	f_{Mg}	f_K	K_{ex}
			ZARIA			
0-15 cm	0.093	16.39	2.797	0.994	0.740	9.058
	0.113	9.90	2.293	0.991	0.751	5.614
	0.158	9.52	2.254	0.982	0.772	5.772
	0.444	8.93	2.189	0.866	0.893	8.211
	0.784	5.52	1.709	0.638	0.983	8.345
15-30 cm	0.016	55.56				
	0.080	17.24	2.847	0.995	0.721	9.026
	0.112	14.08	2.645	0.991	0.737	7.677
	0.206	6.94	1.938	0.969	0.784	4.407
	0.409	6.41	1.858	0.885	0.874	5.536
	0.845	6.25	1.833	0.594	0.991	10.32
			MOKWA			
0-15 cm	**0.055**	**9.35**	**2.235**	**0.997**	**0.660**	**4.088**
	0.064	8.40	2.128	0.996	0.665	3.728
	0.101	5.24	1.656	0.991	0.686	2.494
	0.176	4.88	1.585	0.972	0.729	2.668
	0.433	2.61	0.959	0.840	0.861	2.308
	0.829	**1.99**	**0.688**	**0.528**	**0.986**	**3.671**
15-30 cm	**0.066**	**8.77**	**2.171**	**0.997**	**0.788**	**5.477**
	0.094	8.26	2.111	0.995	0.799	5.322
	0.131	7.63	2.032	0.991	0.814	5.081
	0.177	4.31	1.461	0.983	0.831	3.029
	0.614	4.13	1.418	0.814	0.960	4.686
	0.858	3.29	1.191	0.668	0.995	4.802

E_K = equivalent fraction of adsorbed K^+

f_{Mg} = rational activity coefficient for MgX_2

f_K = rational activity coefficient for KX

K_{ex} = thermodynamic exchange constant

Table 8. The Vanselow selectivity coefficient (K_V), rational activity coefficients and the thermodynamic equilibrium exchange constant as a function of the equivalent fraction of Ca^{2+} (E_{Ca}) on the exchange complex for KX-CaX_2 binary exchange on a surface (0-15 cm) and sub-surface (15-30 cm) of *Typic Haplustalf* from Zaria and a *Ustult* from Mokwa

	E_K	K_V	$ln\ K_V$	f_{Ca}	f_K	K_{ex}
			ZARIA			
0-15 cm	0.065	11.91	2.477	0.995	0.714	6.063
	0.134	9.90	2.293	0.986	0.750	5.651
	0.208	9.71	2.273	0.967	0.786	6.221
	0.434	9.17	2.216	0.865	0.884	8.227
	0.806	6.45	1.864	0.608	0.985	10.34
15-30 cm	**0.034**		**11.91**	**2.477**	**0.999**	**0.800**
7.603						
	0.050	7.14	1.966	0.999	0.806	4.645
	0.095	6.71	1.904	0.996	0.822	4.562
	0.253	6.49	1.870	0.970	0.875	5.143
	0.614	5.92	1.778	0.835	0.965	6.607
	0.861	3.53	1.261	0.702	0.995	4.987
	MOKWA					
0-15 cm	**0.069**	**9.71**	**2.273**	**0.993**	**0.538**	**2.816**
	0.097	8.55	2.146	0.986	0.556	2.695
	0.112	3.88	1.356	0.982	0.569	1.279
	0.184	4.02	1.391	0.952	0.621	1.629
	0.371	1.74	0.554	0.821	0.763	1.203
	0.783	**1.05**	**0.049**	**0.415**	**0.967**	
2.363						
15-30 cm	**0.065**	**10.10**	**2.313**	**0.995**	**0.592**	
3.546						
	0.089	7.75	2.048	0.994	0.593	2.738
	0.121	6.80	1.917	0.982	0.630	2.739
	0.230	5.95	1.783	0.938	0.701	3.118
	0.506	2.05	0.718	0.736	0.864	2.074
	0.762	1.94	0.663	0.499	0.967	3.630

E_K = equivalent fraction of adsorbed K^+

f_{Ca} = rational activity coefficient for CaX_2

f_K = rational activity coefficient for *KX*
K_{ex} = thermodynamic exchange constant

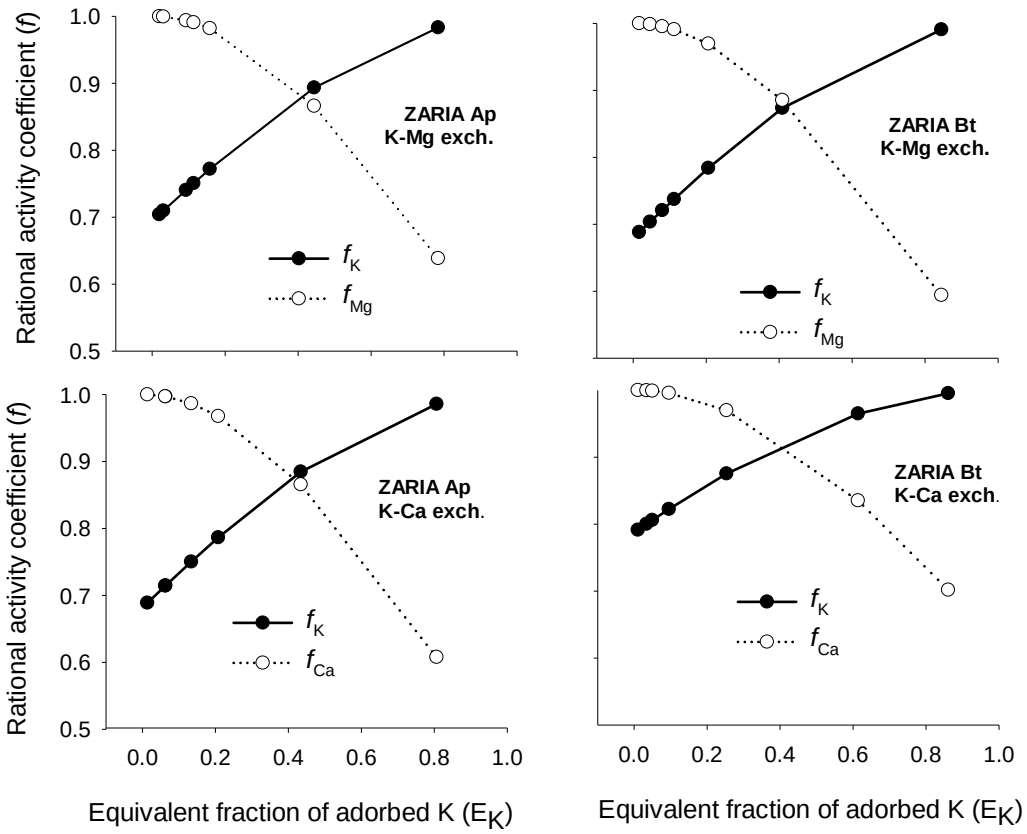


Figure 6. The relationships of rational activity coefficients (f) with K saturation or the equivalent K fractions (E_K) in the exchanger surface of the Zaria soil.

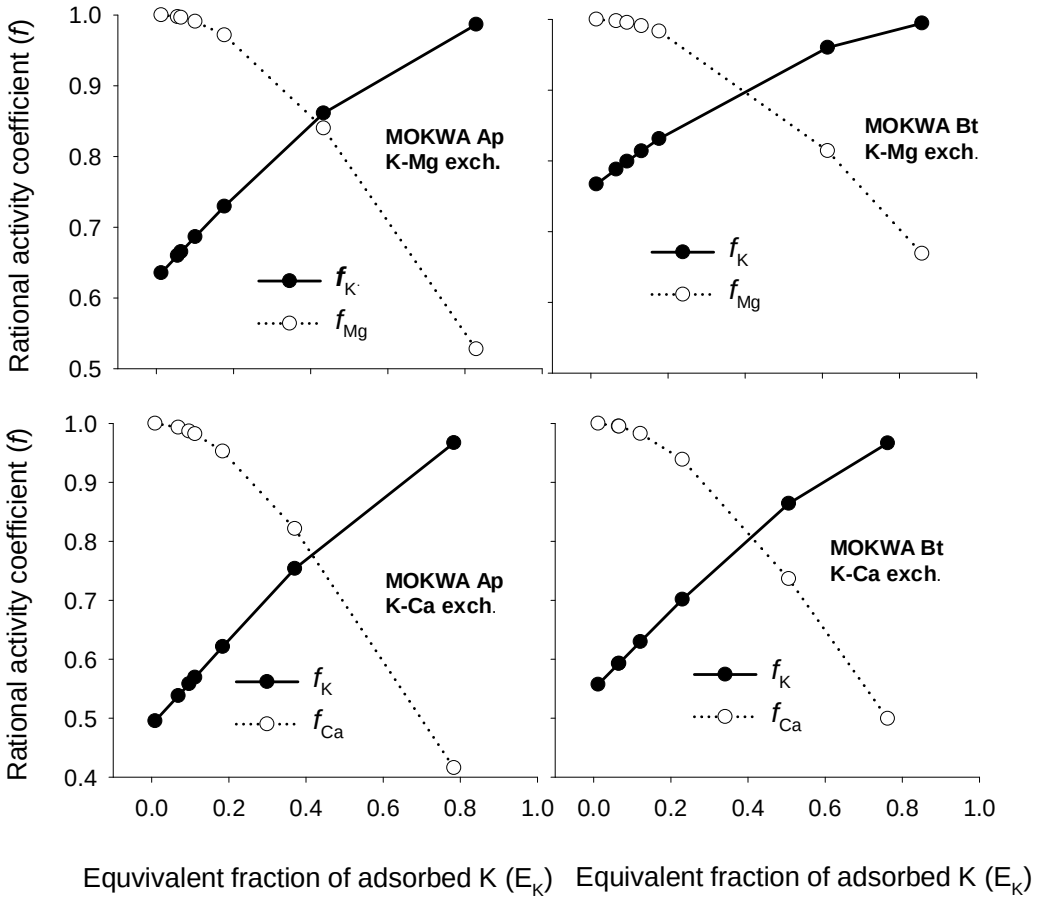


Figure 7. The relationships of rational activity coefficients (f) with K saturation or the equivalent K fractions (E_K) in the exchanger surface of the Mokwa soil

and f_{Ca} are to correct the departure of the mole fraction terms from ideality (Goulding, 1983; Sparks, 2003; Sposito, 2004).

The cations adsorbed to the soil exchanger phase are distributed between the Stern Layer and the Diffuse Double Layer (DDL). Calcium as a divalent ion is readily sorbed into the Stern Layer as well as the DDL. It has been reported that cations sorbed to the Stern Layer do not move as freely (less fugacity or lower activity coefficient) as cations in the DDL (Barshad, 1950; Dennis and Ellis, 1963; Deist and Talibudden, 1967b). It is possible, as hypothesized by Deist and Talibudeen (1967b) that as K replaces Ca in the DDL, the smaller activity coefficients of ions in the Stern Layer contribute to the eventual decrease in f_{Ca} (Deist and Talibudeen, 1967b). Whereas, the increasing f_K with increasing K saturation might suggest that K was largely adsorbed in DDL. Furthermore, on the basis of hydrated radii, Ca and Mg have higher hydrated radii (Ca = 4.12 A^o; Mg = 4.28 A^o) than K (3.13 A^o), hence the fugacity of adsorbed Ca and Mg (freedom of movement) in the DDL will be quite smaller than K, consistent with the decreasing f_{Ca} and f_{Mg} with increasing K saturation of the exchanger phase. Thus, the preferential adsorption of K to Ca and Mg is both consistent with the hydrated radii and the ionic sizes of Ca (1.06 A^o) and Mg (0.78 A^o) as compared to the ionic size K (1.33 A^o).

The relatively high hydration shell of Ca and Mg as compared to K limits the rate of diffusion of Ca and Mg from the soil solution to the surface exchange sites as compared to K. Agbenin and van Raij (1999) reported that film diffusion is the rate-limiting step in the adsorption and desorption of these cations from the surface exchange sites. Although cation exchange theory predicts selectivity on the basis of valence and ionic size considerations. It seems that crystalline and hydrated radii had overridden valence consideration in the selectivity of K, Ca and Mg by the soil exchanger phase in this study.

The thermodynamic exchange constant K_{ex} calculated by means of Eq. [33] and [34] showed some variability with exchanger phase composition especially at $E_K < 0.1$ (Tables 7 and 8), whereas at $E_K > 0.1$, K_{ex} was nearly constant with exchanger phase composition as expected. At $E_K < 0.1$, K_{ex} was unusually high for Ca-K exchange in the Zaria soil but quickly decreased to almost constant values $E_K > 0.1$ (Table 8). As already alluded to in Section 4.3, traces of mica in the clay suite of the Zaria soil would have been responsible for the extremely high K selectivity at low K saturation. It is also possible at $E_K < 0.1$, K was probably sorbed to balance charge deficit in the tetrahedral structure of kaolinite, arising from isomorphic substitution of Al for Si, as K^+ is the right ionic size to fit squarely into the vacant site.

Apart from calculating K_{ex} by means of Eq. [33] and [34] determining the rational activity coefficients to correct for mole fractions, as the mole fractions cannot truly reflect the activity of adsorbed ion (Gaines and Thomas, 1953), K_{ex} can also be determined by integrating the relationship between ln K_V and E_K (Gaines and Thomas, 1953; Goulding, 1983; Sposito, 1989; Sparks, 2003; Essington, 2004) as follows:

$$\ln K_{ex} = \int_0^1 \ln K_V \, dE_K$$

For the Mg-K exchange, K_{ex} for the Ap and Bt horizon was reasonably close for the Zaria soil. In the Ap horizon, K_{ex} = 7.98 and 7.81 in the Bt (Table 9). In the Mokwa K_{ex} was not as close as in the Zaria soil. The K_{ex} was 3.12 in Ap and 1.95 in Bt, suggesting greater selectivity of K over Mg by Bt than Ap horizon of the soil. However, the soils' selectivity for K over Mg was greater in Zaria than Mokwa, supported by the larger K_{ex} in Zaria than Mokwa. Nonetheless, in both soils K_{ex} was several orders of magnitude greater than unity, clearly demonstrating K selectivity over Mg by the soils from the two locations.

In Ca-K system, K_{ex} for the Ap horizon of Zaria soil was 9.49 as compared to 4.60 for Mokwa. But K_{ex} sharply declined in the Zaria soil to 5.86 in the Bt horizon, whereas in the Mokwa soil, as compared to the Ap horizon K_{ex} decreased from 4.60 in Ap to 3.21 in Bt (Table 9). Consistent with observations in the Mg-K

system, the soils' selectivity for K over Ca was greater in Zaria than Mokwa, supported by the larger K_{ex} in Zaria than Mokwa. As pointed out by Goulding (1983) in his review, K_{ex} combined with values of ΔG_{ex} offer the best measure of cationic selectivity by soil colloids. The ΔG_{ex} for Mg-K system ranged from –3.81 kJ mol^{-1} in the Mokwa soil to –11.85 kJ mol^{-1} in the Zaria soil. For the Ca-K, it varied from –8.72 kJ mol^{-1} in the Ap horizon of the Mokwa soil to -12.84 kJ mol^{-1} for the Zaria soil (Table 9). The generally negative values of ΔG_{ex} are consistent with K selectivity over Mg in the Mg-K system and over Ca in the Ca-K system.

Very little is reported for ΔG_{ex} of Mg-K exchange in soils and clays. Jensen and Babcock (1973) reported –4.06 kJ mol^{-1} for Mg-K exchange in a loam soil. From the perspective of using ΔG_{ex} to assess selectivity, this is almost two times lower than –6.50 KJ mol^{-1} for Ap and –8.72 KJ mol^{-1} for the Bt layer of the Mokwa soil, and about three times lower than the –11.85 kJ mol^{-1} for Ap and – 11.73 kJ mol^{-1} for Bt layer of the Zaria soil.

Table 9. The thermodynamic equilibrium constants and Gibbs Free Energy (ΔG_{ex}) of Mg-K and Ca-K exchange for two savanna soils from Zaria and Mokwa, northern Nigeria

		MgX_2-KX			CaX_2 - KX		
Soil depth (cm)		*ln* K_{ex}	K_{ex}	ΔG_{ex}	ln K_{ex}	K_{ex}	ΔG_{ex}
Zaria	(0-15)	2.076	7.977	-11.85	2.250	9.487	-12.84
	(15-30)	2.055	7.810	-11.73	1.768	5.860	-10.09
Mokwa	(0-15)	1.137	3.117	-6.490	1.527	4.604	-8.716
	(15-30)	0.667	1.949	-3.807	1.167	3.211	-6.658

Several investigators have reported on ΔG_{ex} for Ca-K exchange in a wide range of soils across the world. Deist and Talibudeen (1967a, b) reported a range of -4 to -14.3 kJ mol^{-1} in 10 British soils, whereas Goulding and Talibudeen found between +1.10 to –4.70 kJ mol^{-1}. Ogwada and Sparks (1984) found a restricted range of ΔG_{ex} values of just -

4.61 to – 4.74 kJ mol^{-1}. The range of ΔG_{ex} for Ca-K exchange in the Ap and Bt layers of the soils used in this study, ranging from –3.81 to 12.84 kJ mol^{-1} is somewhat close to the range of –4 to 14 kJ mol^{-1} reported by Deist and Talibudeen (1967b) for a number of British soils. Udo (1978) reported that ΔG_{ex} for K-Ca exchange in soils from Western Nigeria was –6.90 kJ mol^{-1} which is just similar to –6.66 kJ mol^{-1} observed for Bt layer in the Mokwa soil.

Generally, therefore, the strong negative values of ΔG_{ex} for Ca-K and Mg-K exchange seemed to lend additional credence to the notion that K was strongly preferred to Ca and Mg by the soils. Based on the magnitude of ΔG_{ex} values, it can be concluded that the ease of replaceability of Mg and Ca by K in the Zaria soil was greater than Mokwa soil evidenced by the higher negative ΔG_{ex} values in Zaria than Mokwa soil. That is to say that the binding strength of K (Agbenin and van Raij, 1999) in the Zaria soil was greater than the Mokwa soil. Since information on the fertilization history of soil from the two locations is not available, if the Mokwa soil has had a long history of K fertilization, residual K^+ in the soil will decrease its K binding strength. Goulding and Talibudeen (1980) reported that residual K^+ from long-term application of K fertilizers decreased K^+ selectivity by decreasing K binding strength in British soils. Similar effect was reported for long-term application of manure (Goulding, 1983).

As also previously alluded to, mineralogical studies of soils from Zaria have shown the presence of mica in the clay suite (Ojanuga, 1979; Agbenin, unpublished), whereas evidence of mica in soil from the Mokwa area has not been demonstrated. Because mica exhibits extremely high K selectivity (Goulding, 1983), the stronger selectivity of K in Zaria than Mokwa soil can, thus, also be explained by presence of mica in the clay suite.

4.5 Implications for K-fixation and Plant Nutrition

Potassium selectivity and fixation has been identified as an essential aspect of K nutrition and availability in soil (Bolt et al., 1963; Mengel and Kirby, 1980). It is believed that weathered soils dominated by kaolinitic clays and other variable charge colloids have low preference for K (Mengel and Kirby, 1980) as compared to Ca and Mg (Chan et al., 1979). However, this traditional view of K selectivity in weathered soils has rarely been supported by experimental evidence as can be seen from the results of Ca-K and Mg-K exchange data from the two savanna soils studied. Similar conclusions have been derived by Udo (1978) from soils of Western Nigeria.

Potassium in soil can be sorbed to three different sites in soils namely planar, edge and inter-lattice position in aluminosilicate clays (Schouwenburg and Schuffelen, 1963). The K selectivity of these sites differs in the order: inter-lattice >> edge > planar; the inter-lattice site having the strongest affinity or selectivity for K^+ (Mengel and Kirby, 1980) as indexed by Gapon selectivity coefficient (K_G) (Bolt et al., 1963) or by potassium activity ratio ($AR_{,k}$) (Agbenin, 2003). The three different sites can be inferred from the changes in K_G as a function of K saturation of exchange sites or E_K (Goulding and Talibudeen, 1980). The resulting curve is arbitrarily divided into three parts, representing the three different exchange sites for K^+ in soil (Schouwenburg and Schuffelen, 1963; Bolt et al., 1963). The edge and planar sites are rapidly exchangeable with relatively low K_G, whereas the inter-lattice sites are not readily exchangeable and have very high specificity for K^+ ions, thus giving rise to high K_G values (White and Zelazny, 1986).

Plots of K_G as a function E_K for the Zaria soils showed a very steep decline in K_G with increasing E_K up to 0.1. But at $E_K > 0.1$, K_G increased very slightly with increasing E_K, and cannot be precisely divided into three distinct segments representing the inter-lattice, edge and planar sites as suggested by

Schouwenburg and Schuffelen (1963). However, what is clear is the very sharp decline in K_G as E_K increased from 0 to 0.1, representing changes in sites responsible for K adsorption, from an initially very high K selective site to a site that is less selective. The initially very high K selective site can be attributed to inter-lattice position, whereas the less selective sites are the planar and edge sites, but the specific points in the curve (Fig. 8) at which the edge or planar sites can be differentiated are difficult to determine. In the Mokwa soils, K_G initially declined gradually up to E_K = 0.1 in contrast to the steep decline in the Zaria soil (Fig. 8), suggesting that there were no inter-lattice or wedge sites for K^+ adsorption in the Mokwa soils. Potassium was probably adsorbed to the edge and planar sites in soils from Mokwa.

Wedge or inter-lattice sites are only present in soils with 2:1 phyllosilicates such as mica, vermiculite and montmorillonite. The absence of wedge or inter-lattice sites in the Mokwa soil as deduced from the relationship between K_G and E_K (Fig. 8) as compared to the Zaria soil is suggestive of the absence of 2:1 phyllosilicate minerals, whereas the presence of inter-lattice or wedge sites in the Zaria soil further supports the presence of 2:1 phyllosilicate minerals (Mengel and Kirby, 1980), especially mica in the Zaria soil, as observed in two separate mineralogical studies (Ojanuga, 1979; Agbenin unpublished).

To satisfy crop nutrition in savanna soils, exchangeable K must exceed between 0.7 and 2.0 $mmol_c\ kg^{-l}$, or must be more than 2 % of the sum of exchangeable bases (Boyer, 1972). The savanna soils studied in this report did not have appreciable ability to fix K as can be deduced from the narrow range of E_K in which K_G declined steeply in the Zaria soil. Thus, the quantity of K adsorbed to the inter-lattice position is actually less than 10 % of adsorbed K by the Zaria soil. In the Mokwa, the relationship between E_K and K_G did not show evidence of

K^+ adsorption to inter-lattice position, suggesting that nearly all the adsorbed K^+ was exchangeable. The wedge or inter-lattice sites are responsible for fixation or irreversibility of K sorbed (Mengel and Kirby, 1980; White and Zelazny, 1986).

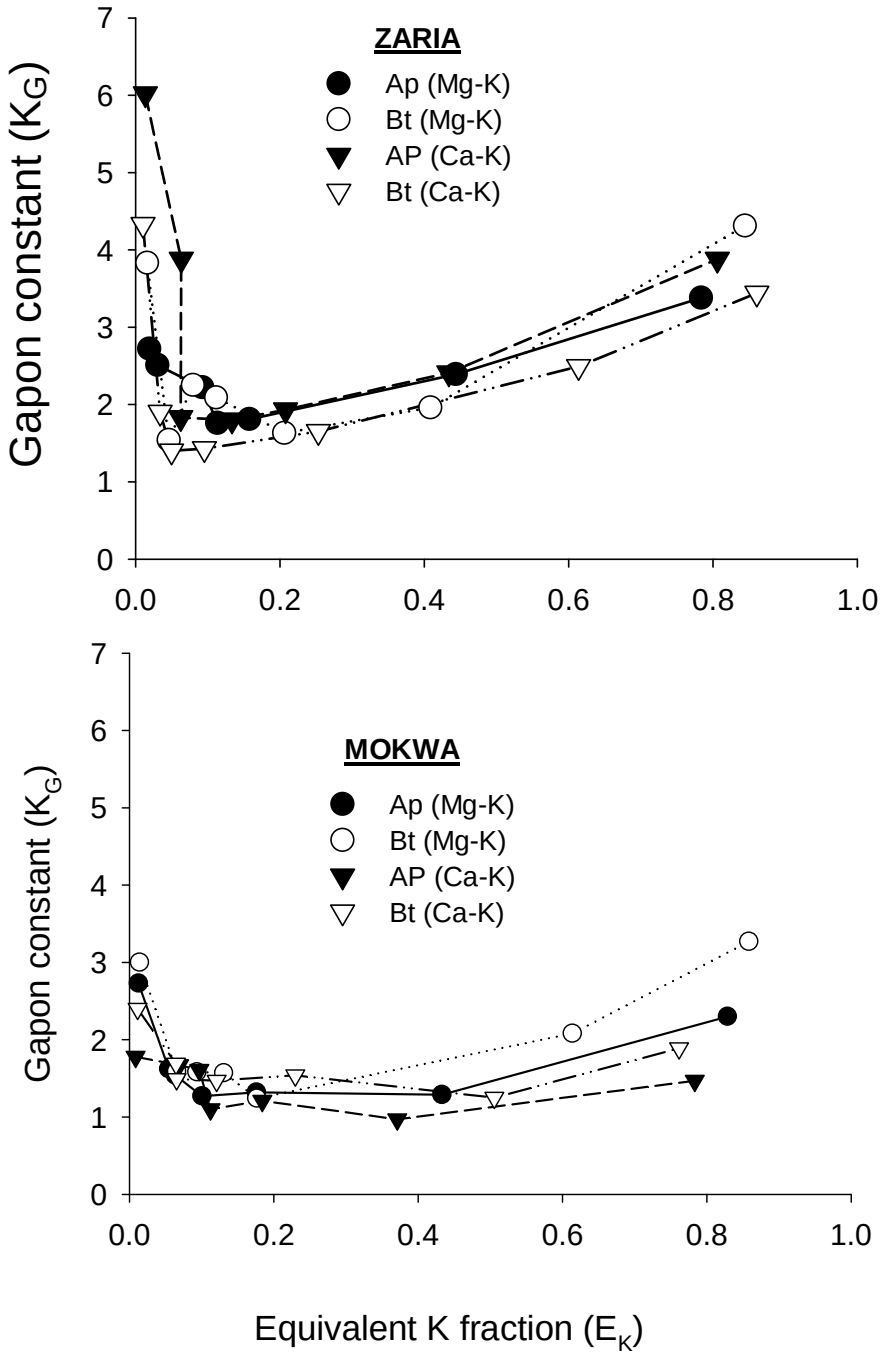


Figure 8. Plots of K_G for Mg-K and Ca-K exchange as a function of equivalent fraction of adsorbed K (E_K) in the Zaria and Mokwa soils.

The high K selectivity over Ca and Mg in the soils has serious implication for Ca and Mg availability and crop nutrition in the savanna. Although Ca deficiency has not been conclusively demonstrated in savanna soils, Lombin (1979) had alluded to the prospects of Mg deficiency in the savanna. Long-term cultivation complemented with regular K fertilization, as is currently the practice in the savanna is likely to engender Mg deficiency in the soil because of preferential retention of K. The displacement of Mg^{2+} by K^{+} from the exchange sites in the soil colloids predisposes Mg to leaching beyond the root zone, thereby inducing Mg deficiency on the long run. The picture for Ca is, however, not as bleak as that of Mg because of the widespread application of single superphosphate fertilizer with considerable concentration of Ca. This appears to have masked Ca deficiency in most savanna soils under long-term cultivation complemented with K fertilization (Agbenin, 2003). Some localized Ca deficiency problem evidenced in blind nuts in groundnut (*Arachis hypogea*) has been identified in the savanna (Jones and Wild, 1975). The spatial extent of Ca deficiency in the savanna, 30 years after the first report of Ca deficiency, has not been established. This problem is likely to assume some significance in the future as cultivation becomes intense with regular K fertilization. Consequently, Jones and Wild (1975) have cautioned that in soils with low cation exchange capacity, to which we add, and high selectivity for K over Ca and Mg, a carefully calculated addition of Ca and Mg may be required regularly or once per rotation for sensitive crops. Thus, current fertilization practices involving only K must be re-examined in the light of Ca-K and Mg-K exchange equilibria in these savanna soils.

CHAPTER FIVE
SUMMARY AND CONCLUSIONS

Actually K deficiency has not been widely established in the savanna, but many of the soils are assumed to be potentially deficient of K (Jones and Wild, 1975). Therefore, routine K fertilization is practiced in the region. Ion exchange equilibria affect availability of cationic nutrients in soils. The basic cations of interest in plant nutrition are K, Mg and Ca. The exchange characteristics of these cations are important in designing appropriate soil management practices to avoid cationic imbalances in soil solution and plant nutrition. This study examines Ca-K and Mg-K exchange equilibria with a view to establishing their preferential retention in savanna soils. To date, no studies of cation exchange equilibria have been undertaken for savanna soils dominated by low-activity clays. Two representative savanna soils, with slightly differing weathering intensity and dominated by variable charge colloids, were sampled from Mokwa and Zaria for this study. The soil from Zaria can be classified in the US Taxonomy as *Typic Haplustalf* (Valette and Ibanga, 1984), whereas the soil from Mokwa can be tentatively classified as *Typic Haplustult*, but the actual classification of this soil is uncertain.

The total metal charge was generally lower than the CEC of the soil, due probably to pH-dependent charges, since the CEC was determined by the neutral ammonium acetate method. Several selectivity coefficients were determined for Ca-K and Mg-K exchange equilibria in the soil from the reactions:

$$CaX_2 + 2K^+ = 2KX + Ca^{2+}$$

$$MgX_2 + 2K^+ = 2KX + Mg^{2+}$$

The various selectivity coefficients determined were Kerr selectivity coefficient (K_K), Vanselow selectivity coefficient (K_V), Gapon selectivity coefficient (K_G), Gaines and

Thomas selectivity coefficient (K_{GT}) and the Davies selectivity coefficient (K_D).

For the soils studied, each of the selectivity coefficient varied with exchanger phase composition, thus suggesting the heterogeneity of the surface sites available for cation adsorption. Variations in selectivity coefficient as a function of the exchanger phase composition were greater for K_K and K_V than the other selectivity coefficients. At $N_K > 0.1$, the K_G and K_{GT} were nearly constant as N_K increased, suggesting that K_G and K_{GT} fairly well modeled Ca-K and Mg-K exchange equilibria in the soils. The fact that all selectivity coefficients were far greater than unity as N_K increased, suggested preferential retention of K^+ by the soil.

Cation exchange isotherms determined by the plot of equivalent fraction of adsorbed K ($E_{K(ex)}$), Ca ($E_{Ca(ex)}$) and Mg ($E_{Mg(ex)}$) against the soil solution equivalent fraction of K ($E_{K(aq)}$), Ca ($E_{Ca(aq)}$) and Mg ($E_{Mg(aq)}$) respectively, further supported the selectivity of K^+ over Ca^{2+} and Mg^{2+} by the soil. The experimental data points were above the thermodynamic non-preference isotherm (TNI) line when $E_{K(ex)}$ was plotted as a function of $E_{K(aq)}$. In the same vein, all the experimental data points were far below the TNI line when either $E_{Ca(ex)}$ or $E_{Mg(ex)}$ was plotted against $E_{Ca(aq)}$ or $E_{Mg(aq)}$ in soil solution, clearly suggesting non-preference for Ca^{2+} and Mg^{2+} by the soil.

Cation exchange isotherm is not an unambiguous index of cation selectivity in soil because it is greatly influenced by ionic strength. The thermodynamic exchange constant (K_{ex}) and the change in standard free energy (ΔG_{ex}) of the exchange reaction are considered the best indices of cation selectivity. The K_{ex} ranged from 3.21 to 9.49 for Ca-K and from 1.95 to 7.98 for Mg-K exchange in the soil. These K_{ex} values were suggestive of more stable KX than CaX_2 and MgX_2, consistent with the negative ΔG_{ex} values for the exchange reactions. However, based on the K_{ex} and ΔG_{ex}, it can be concluded that the Zaria soil exhibited

stronger K selectivity than the Mokwa soil in agreement with the values of K_K, K_V, K_G, K_{GT} and K_D. The stronger selectivity of K by the Zaria than the Mokwa soil might be reflective of qualitative and quantitative differences in mineralogical composition. It can be surmised that the presence of mica in the clay suite of the Zaria soil was probably responsible for its stronger K selectivity than the Mokwa soil. Mica has extremely strong affinity for K^+ in soil. To our knowledge, there has been no report of mica in soils from Mokwa, but if present, the quantity is likely to be far less than the Zaria soil.

The results of this study did not substantiate two main aspects of the Guoy-Chapman model of cation exchange theory in soils. Implicit in the diifuse double layer (DDL) theory of Guoy-Chapman is the notion that kaolinitic soils, such as these, have low preference for monovalent cations as compared to divalent cations. The results of this study did not support the DDL prediction. Secondly, DDL theory predicts preferential retention of Ca^{2+} and Mg^{2+} to K^+ based on valence consideration. However, the selectivity of K^+ over Ca^{2+} and Mg^{2+} by these soils is, thus, inconsistent with valency as a basis for cation selectivity by soil colloids. In this study, a basis for the selectivity of K^+ seems to be crystalline ionic size and hydrated radii. The ionic size of K^+ is greater than Ca^{2+} or Mg^{2+}. Consequently the hydrated radii of Ca^{2+} and Mg^{2+} are greater than K^+. According to cation exchange theory, ions can approach the charged surface as much as their effective radii would allow. Thus, ions with larger crystalline sizes and smaller hydrated radii can approach the surface exchange sites more closely than ions with smaller crystalline size and larger hydrated radii. Furthermore, hydrated sizes affect ionic mobility or diffusion across the film layer of water held firmly around colloidal particles to reach the exchange sites on the adsorbing soil surfaces (Agbenin and van Raij, 1999).

We, thus, speculate that ionic sizes and hydrated radii provided a more rational basis for K^+ selectivity over Ca^{2+} and Mg^{2+} by the soil than valence consideration.

In conclusion, the two factors that seemed to have favoured the preferential K^+ retention over Ca^{2+} and Mg^{2+} by the soils were the nature and characteristics of the clay suite and the crystalline ionic size / hydrated radii. The implication of the results of this study is that under long-term cultivation complemented with regular K fertilization, as is currently the practice in the savanna, Mg and Ca deficiencies are likely to show up. It is possible that most crops are already suffering incipient Mg deficiency because of the displacement of Mg^{2+} by K^+ from cation exchange sites, thus predisposing Mg^{2+} to leaching beyond the root zone. However, Ca deficiency in savanna soil appears to have been masked by widespread application of single superphosphate fertilizer that contains high concentration of Ca. Were single superphosphate fertilizer to be discontinued as phosphate source in the savanna, Ca deficiency is likely to pose nutritional problem in soils under long-term cultivation and fertilization with K. Because of the high K^+ selectivity over Ca^{2+} and Mg^{2+} exhibited by these soils, a carefully calculated addition of Ca and Mg may be required regularly or once per rotation for sensitive crops. Hence current fertilization practices involving only K in the savanna must be re-examined in the light of the results of Ca-K and Mg-K exchange equilibria study in soils from the region.

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