

Potassium Sorption Characteristics in Relation to K Forms in Two Contrasting Mineralogical Compositions in Southeastern Nigeria

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Abstract

The study on potassium sorption characteristics in relation to K forms was determined in two pedons of contrasting mineralogical compositions, namely: Amakama soil dominated by Kaolinite, small quantities of goethite, gibbsite and haematite and Ibeku soil dominated by Kaolinite, detectable quantities of montmorillonite, small quantities of goethite, gibbsite and plagioclase feldspar. A free survey technique guided by the geologic map of the study area was used for the study. Profile pits were sampled and described according to the procedure of the USDA Natural Resource Conservation Service (NRCS) guidelines for profile description. Potassium sorption isotherms were constructed using known standards. Adsorption data were fitted into Langmuir and Freundlich equations. Result showed that Freundlich equation explained K sorption behavior better than Langmuir equation. On the average, the amount of K sorbed was more in Ibeku soil (81.3 to 196.3 mgKkg⁻¹) than Amakama soil (62.9 to 200.0 mg K Kg⁻¹). While the extent (K) and energy (1/n) at which K was sorbed was more in soil dominated with Kaolinite, gibbsite, haematite (Amakama Soil) (K =1.06mg Kg⁻¹; 1/n = 1.27) than Ibeku soil (K=0.95 mg kg⁻¹; 1/n = 1.01). Mean exchangeable K, Non-exchangeable K, and total K were higher in soil dominated by kaolinite, detectable quantities of montmorillonite, small quantities of goethite, gibbsite and plagioclase feldspar (Ibeku soil) (Exchangeable K =0.20; Non-exchangeable K = 0.58; and Total K =19.01 cmolkg⁻¹) than Amakama soil dominated by kaolinite, small quantities of goethite, gibbsite and haematite (exchangeable k = 0.02, Non-exchangeable K=0.06, Total K= 3.63 cmolkg⁻¹). The nitric acid- extractable K (HNO₃-extractable K) was greater in soil dominated by Kaolinitic montmorillonite gibbsite, and plagioclase feldspar (Ibeku soil) (HNO₃-extractable K= 0.78 cmolkg⁻¹) than Amakama soil with kaolinite, gibbsite, geothite, haematite as clay mineralogy (=0.08 cmolkg⁻¹) thus, the capacity to supply K under continuous cropping, was greater in Ibeku soil than Amakama soil. Exchangeable K related positively with HNO₃-extractable K while the energy of adsorption (1/n) related negatively with non-exchangeable K (r=-0.55*; P <0.05) and Total K (r = -0.56*; P<0.05) in the two soils studied. Exchangeable and HNO₃-extractable K gave a better indication for k potential and soil quality management.

Keywords: Mineralogical composition, Potassium forms, Sorption Characteristics, Soil properties.

1. Introduction

Potassium is an essential and major nutrient for crop production (Zhang, Wang, Feng, Qian & Pandschoenau, 2011). It occurs in soil in the frame work of feldspars and in the interlayer spaces of phyllosilicates. It is adsorbed on clay surfaces and organic matter and small amount exists in soil solution (Johnston & Goulding, 1990).

Soil potassium exists in four forms in order of their availability to plants and microbes as solution (water soluble) > exchangeable > Non-exchangeable and mineral K (Sparks, 1987; Sparks, 2000). Readily available potassium is a dissolved form of K (water-soluble) that is held on the surface of clay particles (exchangeable K) (Raheb & Heidari, 2011). Soil solution k is subject to leaching and directly taken up by plants and microbes. Exchangeable K is the K that is held by the negative charges of organic matter and clay minerals. It is made available to plants in exchange form with other cations (Sparks, 1987). Non-exchangeable K contains 90-98 % of total soil K (Sparks, 1987).

The non-exchangeable K can be found in soils of K-rich 2:1 clay minerals such as illites and vermiculite (Moritsuka *et al.*, 2004; Britzke *et al.*, 2012). Soils with high content of 2:1 clay minerals contain large amount of non-exchangeable K than those with Kaolinite and other siliceous minerals (Ghosh and Singh, 2001). Bhonsle *et al.* (1992) in their study on K form relationship and release characteristics with clay mineralogy stated that the quantity of exchangeable K in (NH₄OAc-K) to nitric acid extractable K (HN03-K) (K – supplying power) was higher in Smectite followed by kaolinite and mixed and lowest in illite clay mineral.

The non-exchangeable K can be released into the exchangeable form when the quantity of K in the exchangeable and soil solution K form has been reduced through crop removal, leaching and high microbial activity (Sparks, 2000). Also non exchangeable K plays part in plant nutrition when exchangeable K is low (Schneider, 1997a) Plants take up both exchangeable and non-exchangeable forms of potassium. The status of soil K can be accessed from exchangeable K. Mineral k, including fixed k and native k in k – bearing mineral (biotite, muscovite and feldspars) make up the major proportion of total soil k (>90%) and is released slowly to plants through weathering (Martin & Sparks, 1985; Sharpley, 1989). However, the availability depends on the level of k in other forms, and the degree of weathering of the feldspars and micas constituting the mineral k fraction (Sparks, 1987). Martin & Sparks (1985) reported that k minerals that is most effective for plant growth is greater in Illite followed by muscovite, orthoclase and lowest in plagioclase. These clay minerals produced generally have higher k content (Yong, 2010).

Potassium release from clay minerals is influenced by particle size distribution and chemical composition (Huang, 2005). Sorption of cations from solution, by clay minerals, by soils and sediments containing these minerals is a simple ion exchange process. Some of these cations are sorbed more than other cations. These cations are held more tightly by other cations which prevents them from being replaced (sawhney, 1972).

Potassium in soils are sorbed to soil particles . The sorbed K can be desorbed into soil solution, taken up by plants or moved down to lower soil horizons. Sorption of K depends on the equilibrium that exist between different phases of soil K. These processes may be affected by factors such as type of clay minerals, ionic strength of the soil solution, charge density, degree of interlayering concentration (Sparks, & Huang, 1985) soil

temperature, soil pH, moisture and applied fertilizer K (Zhang *et al.*, 2011; Raheb, & Heidari, 2012). Therefore, the knowledge of clay mineralogy is important in understanding the nutrient status of soils and its supplying power to crops. Soil mineral composition can influence K dynamics (surapanemi *et al.*, 2002). The relationship that exist between mineralogical composition and the k forms can be used in predication of K for optimum plant uptake and for evaluating soil fertility (Sharpley ,1989)

The sorption of potassium in soils can be described by two empirical models namely langmuir and freundlich isotherms. Although these equations were originally derived on the basis of kinetic theory to describe the adsorption of gases, on solids, it has also frequently been applied to the adsorption of ions from solutions (Sposito, 1989). These models have been used in mathematical description of K sorption in soils and laboratory sorption data where specific models are lacking (Lotti *et al.*, 2009). The freundlich equation has been useful for modeling sorption of K especially solids with heterogenous surfaces (Dufey & Delvaux, 1989). This has frequently proved superior to the langmuir equation (Sposito, 1980; Arias *et al.*, 2005). These models are regarded simply as curve – fitting parameters (Sposito, 1982). Some parameters of these models, such as maximum sorption quality and the distribution coefficient are widely acceptable in characterizing K sorption capacity of soils (Holm *et al.*, 2003; Shahem, 2009).

The soils of Amakama and Ibeku are of the agricultural soils of Southeastern Nigeria that have been developed on bedrock or sediment (Jungerius & levelt, 1964; Igwe *et al.*, 1999). These soils differ widely in soil pH, sesquioxides content and other physical, chemical and mineralogical properties which are known to significantly affect sorption processes. The reserve for fixed k that has been built up little by little has been influenced by soil parent materials, degree of weathering, intensive cultivation and nutrient balance (Bertsch & Thomas, 1985; Simonsson *et al.*, 2007). This has resulted to the increase in K deficiency. Relationship between K sorption and potassium forms can be used in evaluating K fertility and plant uptake. This information is necessary because it can provide insight into the equilibrium and release of exchangeable and non-exchangeable k and to make K fertilizer recommendable to plants (Spanks *et al.*, 1980a, Bhonsle *et al.*, 1992). This study therefore was conducted to investigate K sorption characteristics in relation to k forms in two contracting mineralogical composition in southeastern Nigeria.

2. Materials and Methods

2.1. Study Area

The study area comprising of Amakama and Ajata Ibeku in Umuahia, Abia State is located between latitudes 05° 26' 40" N and 05° 32' 51" N and longitudes 07° 28' 49" E and 07° 33' 34" E. The major geological formations include Coastal Plain Sand (Benin formation) for Amakama and Clay shale (Bendi-Ameki formation) for Ajata-Ibeku (Orajaka, 1975). Amakama has mixed mineralogy dominated by kaolinite, small quantities of goethite, gibbsite and haematite, while Ajata – Ibeku, the mineralogy in dominated by kaolinite, detectable quantities of montmorillonite, and small quantities of goethite and gibbsite and plagioclase feldspar (Chikezie, Eswaran, Asawalam, Ano 2010). The presence of montmorillonite and plagioclase feldspars shows that the soil contains some weatherable minerals. Amakama in dominated by plains and lowlands (Ofomata, 1975) while in Ajata – Ibeku, the landscape has deeply incised valleys as a result of the influence of erosion on the

parent material which is Sandstone and Shale that makes up Bende-Ameke (Chikezie *et al.*, 2010). The rainfall in the area is very intensive with an annual range of 1750 – 3000 mm. The distribution is bimodal with peaks in July and September with a brief dry spell in August known as August break. The temperature is high and ranges between 27 – 35°C. The high rainfall and temperatures prevalent in this area intensive weathering and leaching. The area is dominated by rainforest vegetation whose density has been altered by anthropogenic activities. Farming is the major socio-economic activity of the area. The presence of poor drainage conditions in soil of Ibeku has resulted to the alteration of this mineral and accounted for the presence of some of the 2:1 clay minerals in the soils of the study site.

2.2. Field studies

A free survey technique guided by the geologic map of the study area was used in situating the profile pits in the field. Two profile pits each were cited in Amakama and Ibeku. The profile pits were cited according to selected parent materials. The profile pits were sampled and described according to the procedures of the USDA Natural Resource conservation service (NRCS) guidelines for profile description (Soil Survey Staff, 2002). The soil sample collected were air –dried and sieved using 2 mm sieve in preparation for laboratory analyses.

Particle size distribution was determined by hydrometer method (Gee & Or, 2002). Soil pH was determined in water using 1:2.5 soil – liquid ratio (Thomas, 1996). Exchangeable cations (Ca, Mg, K and Na) were determined by 1N Ammonium acetate extraction procedure (Thomas, 1982). Calcium and Magnesium were determined by ethylenediaminetetracetic acid while sodium and potassium was determined using flame photometer (Jackson, 1962). Exchangeable acidity was determined in 1N KCl (Mclean, 1982). Organic Carbon was determined by wet oxidation method (Nelson & Sommers, 1996). Effective cation exchange capacity was determined by summation of exchangeable base plus exchangeable acidity expressed in cmolkg^{-1} .

Total K was determined by Nitric acid (HNO_3) and perchloric acid (HClO_4) digestion method (Jackson, 1964). Water soluble K was measured in a saturated extract following shaking of a 2.5 g soil sample end – over –end with 50 ml distilled water for 1hr. Exchangeable K was determined by extraction with 1N ammonium acetate (1N NH_4OAc) buffered at pH 7. Nitric acid-extractable K termed the K – supplying power was extracted by boiling the soil sample with 1.0 M HNO_3 for 1hr (Haylock, 1956). Non-exchangeable k was determined by the method of Graley *et al.*, (1960). Mineral K was calculated as the difference between total K and 10 M HCl extractable K which was determined according to the procedure of Finck (1962). Potassium in the extract was determined by the use of flame photometer.

2.3. Potassium Sorption Studies

For the potassium sorption isotherm, different concentrations:0, 10, 20, 30, 40ppm were prepared and used for the study. For the 0 ppm, 0.01M CaCl_2 was prepared in 3 litres of distilled water. The procedure was repeated for 10, 20, 30, 40 ppm with different quantities of added KCl. Ten (10ml) of 0.01 M CaCl_2 containing KCl at different concentrations (ranging from 10 to 40 mgKL^{-1}) was added to 0.5 g of calcium saturated soils. The samples were shaken on a reciprocal Shaker for 7hours. At the end of the equilibration time, the soil samples were centrifuged for 2 mins until the separation of the liquid and solid phases occurred. 5ml of the supernatant was pipetted into 25ml volumetric flask and was made up to the mark with distilled water. Potassium in the supernatant solution was

measured by flame photometer. The amount of potassium sorbed by soil was calculated by subtracting the equilibrium K concentration from the amount of potassium initially added. The values obtained were fitted into Langmuir and Freundlich equation. The adsorption models employed are given below:

Langmuir equation

$$X/M = \frac{Kbc}{1 + Kc} \quad 1$$

where X/M = amount of adsorption per unit mass of adsorbent

b = adsorption maximum

c = equilibrium concentration of adsorbate in solution

k = a constant relating bonding energy of the adsorbent for the adsorbate

The Freundlich sorption isotherm was also used to describe the relationship between the concentration of an adsorbate and the amount of its adsorption by an adsorbent.

The formular for this model is:

$$x/m = Kc^{1/n} \quad 2$$

where x/m = amount of adsorbate per unit of adsorbent

C = equilibrium concentration

K and n = empirical constants characteristics of the system investigated

2.4. Statistical Analyses

Soil properties and various K forms were subjected to simple means, standard deviation and correlation coefficient using PROC Mix – model of SAS (2003). The coefficient of variation was ranked according to the procedure of Wilding *et al*, 1994. Thereafter values of sorption characteristics were correlated with selected soil properties and k – forms to ascertain degree of relationship.

3. Results and Discussion

The results of the physicochemical properties of the soils are shown in Table 1, which indicated that soils dominated with Kaolinite, small quantities of goethite, gibbsite, and haematite (Amakama) had higher values of Sand (669.0 g kg^{-1}) than soils dominated with kaolinite, detectable quantities of montmorillonite, small quantities of goethite, gibbsite and presence of plagioclase feldspar (Ibeku soil) (150.13 g kg^{-1}). The dominance of sand in soil with kaolinite clay minerals (Amakama) could be attributed to parent materials (Coastal Plain Sand) and land use. Higher values of silt and clay were found in soil dominated with kaolinite montmorillonite and plagioclase feldspars (Ibeku soil) (Silt = 153.4 g kg^{-1} ; clay = 696.5 g kg^{-1}) compared to the soil dominated with Kaolinite, small quantities of goethite, gibbsite and haematite (Amakama soil) (Silt = 44.0 g kg^{-1} ; Clay = 287.0 g kg^{-1}) probably due to parent

material component and poor internal drainage conditions of the area which may have led to the transportation of dislodge lighter soil particles (Silt and Clay) in Ibeku soil. The textural class for soils dominated with kaolinite, small quantities of goethite, gibbsite and haematite (Amakama soil) was sandy clay loam while in Ibeku soil, it ranged from silty clay loam to clay probably due to the influence of the underlying geology through weathering. The clayey nature of soil with kaolinite, montmorillonite and plagioclase feldspar (Ibeku soil) suggests the capacity of this soil to hold more water and nutrients than Amakama soil with sandy clay loam texture (Chikezie *et al.*, 2010). Soils are generally acidic with pH value from 4.6 in soil dominated with kaolinite, montmorillonite, plagioclase feldspar (Ibeku soil) to 4.7 in soil dominated with Kaolinite clay mineral, goethite, gibbsite (Amakama soil). Exchangeable bases (Ca, Mg, K, Na) were higher in soils with montmorillonite, plagioclase feldspar (Ibeku soil) compared to soil with mixture of kaolinite clay mineral, goethite, gibbsite (Amakama soil). Exchangeable Ca and Na were detected in trace amount in soil of Amakama while in Ibeku soil the value of exchangeable Ca was higher (8.8 cmol kg^{-1}) and exchangeable Na was only present in two depths (128-164 and 164 -190 cm) respectively. Also, exchangeable Mg was higher in Ibeku soil ($\text{Mg} = 0.5 \text{ cmol kg}^{-1}$) while in Amakama soil, exchangeable Mg was only present on the soil surface (0-13 cm depth; $\text{Mg} = 0.01 \text{ cmol kg}^{-1}$; Table 1) while in the subsurface, it was not detected. The higher exchangeable Ca and Mg in Ibeku soil could be attributed to the type of clay minerals present and parent material composition of this soil which may have been eroded in earlier cycles of weathering (Ojanuga *et al.*, 1981) and run off (Ogbodo, 2012). However, the exchangeable Na that was only detectable in trace amount and the absent of exchangeable Mg in some of the horizons in Amakama soil may be due to the intensive weathering and rapid leaching due to high rainfall and temperature prevalent in the area (Chikezie *et al.*, 2010). This accounted for the low amount of Ca, and Mg in the area. Exchangeable k was low and similar in the two soils studied ($\text{K} = 0.02 \text{ cmol kg}^{-1}$; Table 1) possibly due to the erosion and rapid leaching. Higher losses of K have been reported in soils (Ambeager, 2006) while IFPRI (1999) reported losses of K in wetland soils.

Furthermore, exchangeable acidity was higher in soil dominated with kaolinite, montmorillonite, plagioclase feldspar (Ibeku soil) ($\text{EA} = 25.6 \text{ cmol kg}^{-1}$) compared to soil with kaolinite, goethite, gibbsite (Amakama soil) ($\text{EA} = 6.8 \text{ cmol kg}^{-1}$). Effective cation exchange capacity (ECEC) was higher in Ibeku soil ($\text{ECEC} = 35.18 \text{ cmol kg}^{-1}$) than Amakama soil ($\text{ECEC} = 6.90 \text{ cmol kg}^{-1}$). The difference in ECEC was due to variation in the vegetation, plant residue and organic matter (OC) level of the area. Consequently, organic matter (OC) plays important role in nutrient supply, detoxification of harmful soil constituent, moisture, nutrients retention as well as structure formation (Woomer & Muchenna, 1993), hence the higher the soil organic matter (OC), the higher the soil CEC and buffer capacity. Similarly, organic C was higher in soil of Ibeku (1.05 g kg^{-1}) than Amakama soil (0.80 g kg^{-1}). The low OC in Amakama soil may be related to high temperature and rainfall which favours the rapid decomposition and mineralization of organic matter (OC) in the area.

Table 1 Some Physical and Chemical characteristics of the soils

Location	Depth (cm)	Sand gkg ⁻¹	Silt	Clay	Texture P ^H	Soil Carbon	Organic gkg ⁻¹	Ca cmol/kg	Mg	K	Na Acidity	Exch CEC cmol/kg	Effective cmol/kg
Amakama	0 – 13	758.0	36.0	206.0	SCL	4.5	2.07	0.3	0.1	0.04	TR	11.1	11.6
	13 – 27	727.0	31.0	242.0	SCL	4.6	1.43	0.1	-	0.03	TR	9.8	9.9
	27 – 63	681.0	37.0	282.0	SCL	4.6	0.57	TR	-	0.02	TR	6.6	6.6
	63 – 99	639.0	48.0	313.0	SCL	4.7	0.43	TR	-	0.01	TR	6.5	6.5
	99– 127	650.0	37.0	313.0	ScI	4.7	0.37	TR	-	0.01	TR	5.1	5.2
	127– 159	585.0	87.0	328.0	CL	4.8	0.25	-	-	0.02	TR	4.7	4.7
	159– 210	643.0	32.0	325.0	SCL	4.9	0.23	TR	-	0.01	TR	3.9	3.9
	Mean	669.0	44.0	287.0		4.7	0.80	0.06	0.01	0.02	TR	6.8	6.9
	SD	58.3	19.7	46.0		0.13	0.71	0.04	0.04	0.01	TR	2.69	2.83
	CV	8.7	44.9	16.3		2.9	92.6	98.4	94.6	97.7		39.4	40.9
Ibeku	0– 9	341.0	267.0	392.0	SiCL	5.0	3.39	7.3	1.6	0.24	-	24.4	33.6
	9– 28	317.0	228.0	455.0	SiC	4.8	2.26	4.2	0.5	0.23	-	25.5	29.4
	28–60	103.3	148.0	749.0	C	4.8	0.98	3.2	0.2	0.22	-	22.8	26.5
	60–80	62.0	121.0	817.0	C	4.7	0.57	4.1	0.3	0.21	-	24.6	29.4
	80–101	84.0	111.0	805.0	C	4.7	0.41	4.4	0.2	0.18	-	25.7	30.7
	101–128	127.0	92.0	781.0	C	4.5	0.29	8.8	0.2	0.18	-	29.2	38.7
	128–164	81.0	87.0	832.0	C	3.8	0.25	16.2	0.4	0.16	0.1	29.4	46.7
	164–190	86.0	173.0	741.0	C	4.2	0.27	22.2	0.6	0.16	0.1	22.9	46.4
	Mean	150.1	153.4	696.5		4.6	1.05	8.80	0.50	0.20	0.03	25.60	25.60
	SD	112.3	65.4	172.2		0.4	1.16	6.87	0.47	0.03	0.05	2.53	2.53
CV	75.0	42.6	24.7			90.2	78.1	93.8	16.0	85.2	9.9	9.9	

SCL - Sandy Clay Loam, CL – Clay Loam, SiCL - Silty Clay Loam, SiC - Silty Clay, C – Clay. TR - Detected in Trace Amounts, ND – Not Detected

3.1. Forms of K

As shown in Table 2, water soluble K ranged from 0.022-0.027 cmol kg^{-1} with a mean value of 0.02 cmol kg^{-1} in soil dominated with kaolinite, goethite, gibbsite, haemathite (Amakama soil), while in soil with kaolinite, montmorillonite, plagioclase feldspars (Ibeku soil), water soluble K ranged from 0.015-0.031 cmol kg^{-1} with a mean value of 0.02 cmol kg^{-1} , implying that the quantity of potassium in the soil solution between the two soils studied was low and similar (water soluble k = 0.02 cmol kg^{-1} ; Table 2). Haby *et al.* (1990) reported that the quantity of K in the soil solution varies from 2 to 5 mg K L^{-1} for normal agricultural soils of humid regions. Therefore, the low Levels of solution K in the soils studied could be due to the influence of the equilibrium and Kinetic reactions that occur between the forms of soil K, the soil moisture content, and the concentrations of bivalent cations in solution and on the exchanger phase (Sparks, & Huang, 1985; Sparks, 2000). However, in exchangeable K, soils dominated with kaolinite, montmorillonite, plagioclase feldspare (Ibeku soil) had higher exchangeable K (0.20 cmol kg^{-1}) compared to soils dominated with kaolinite, gibbsite, goethite, haematite (Amakama soil) (0.02 cmol kg^{-1}) possibly due to higher organic carbon in the study site and differences in the clay mineralogy of this soil. This is true because the clay mineralogy of this soil is dominated by expanding phyllosilicate where the negative charge is mainly on the internal surfaces of the 2:1 clay mineral. This has resulted in greater amount of soil K forms and K saturation than Kaolinite (Sharpley, 1989). In other words, the quantity of potassium availability in this soil will be higher and can be exchanged with other cations and also readily available to plants than Amakama soil (Kaolinite clay mineral with small quantities of Geothite, gibbsite). The high organic carbon in Ibeku soil reflects the higher exchangeable K in this soil. Similar relationship has been reported by Fagbami *et al.*, 1985; Ano, 1991). Also, Tisdale and Nelson (1974) reported that organic matter (OC) possesses a greater capacity to retain K ions and other cations. However, exchangeable K has a significant positive relationship with ECEC ($r = 0.89$; $P < 0.05$) and a significant negative relationship with clay ($r = -0.92$; $P < 0.05$) in Amakama soil. Similar result was reported with Choudhary and Prasad, (1997). Also, exchangeable K had significant positive relationship with pH ($r = 0.87$; $P < 0.05$). This is in agreement with the finding of Ano (1991) who reported that a decrease in exchangeable K would lead to decrease in potassium saturation, resulting to lowering of Soil pH. Exchangeable K related positively with water - soluble K in both soils. The relationship between exchangeable K and water soluble increased from soil with Kaolinite mixed with goethite and gibbsite (Amakama soil) ($r = 0.78$) to soil with kaolinite, montmorillonite, and plagioclase feldspar (Ibeku soil) ($r = 0.94$; $P < 0.05$) (Table 3). In other words, at a given soil exchangeable K content, a greater amount was water soluble in clay mineral with Kaolinite, montmorillonite, gibbsite, goethite and plagioclase feldspars (Ibeku soil) than mixed kaolinite, gibbsite, and goethite (Amakama soil). Exchangeable K related positively with HNO_3 - extractable K ($r = 0.80$; $P < 0.05$).

Table 2: Mean, range and standard deviation of K forms for each soil group

K forms cmolkg ⁻¹	Mixed clay mineralogy dominated by Kaolinite, goethite, gibbsite, haematite (Amakama Soil)			Mixed clay mineralogy with kaolinite, detectable quantities of montmorillonite, goethite, gibbsite and plagioclase feldspar (Ibeku Soil)		
	Mean	Range,	STD	Mean,	Range,STD	
Water soluble K	0.02	0.022-0.027	0.002	0.02	0.015-0.031	0.001
Exchangeable K	0.02	0.01-0.04	0.012	0.20	0.16-0.24	3.190
Non-exchangeable K	0.06	0.02-0.09	0.029	0.58	0.46-0.65	0.088
HNO ₃ -extractable K (K supplying power)	0.08	0.04-0.13	0.039	0.78	0.68-0.89	0.069
Total K	3.63	2.69-4.62	0.863	19.01	10.28-23.21	4.774

K – forms = potassium forms, STD = Standard Deviation, K = Potassium, HNO₃ –extractable k =Nitric acid extractable k

Furthermore, Non-exchangeable K was higher in soil dominated with Kaolinite, montmorillonite, gibbsite, goethite and plagioclase feldspars (Ibeku soil) ($0.58 \text{ cmol kg}^{-1}$) compared to soil with kaolinite, gibbsite and goethite as the clay mineral (Amakama soil) ($0.06 \text{ cmol kg}^{-1}$) (Table 2) possibly due to the differences in the clay mineralogy and clay mineralogical compositions (Moritsuka *et al.*, 2004). Soils that have higher content of 2:1 clay minerals have large amount of non-exchangeable K than those with Kaolinite and other siliceous minerals (Ghosh & Singh, 2001; Britzke, *et al.*, 2012). Additionally, potassium become fixed when the binding forces between K and the clay surfaces are greater than the hydration forces between individual K^+ ions resulting in a partial collapse of the crystal structures and K^+ ions making K release a slow, diffusion, controlled process (Sparks, 1987). This indicates that the quantity of K that was fixed was more in soil with kaolinite montmorillonite, gibbsite, plagioclase feldspars (Ibeku soil) compared to soils with kaolinite, small quantities of gibbsite and goethite (Amakama soil). Therefore plants to take up non-exchangeable K, appears to be related to the plant species, root mass, root length and root Morphology (Mengel, 1985; Mengel & uhlenbecker 1993). However, the Amakama soil correlated significantly and positively with organic C and ECEC ($r = 0.80, 0.81; P < 0.05$) and negatively with clay ($r = - 0.88; P < 0.05$, Table 3). The positive relationship between non-exchangeable K and ECEC ($r = 0.81$) indicated that some of the non-exchangeable K may be present in the lattice of clay minerals which could not be exchanged but could be extracted with HNO_3 , by partial dissolution of clay minerals. Contrastingly, Ibeku soil had positive correlation with clay ($r = 0.73; P < 0.05$) and a negative correlation with organic C ($r = - 0.73; P < 0.05$) (Table 3).

Also, one molar nitric acid extractable K (HNO_3 – extractable K) known as the K – supplying power measures the readily available K and the ability of a soil to supply K under continuous intensive cropping (Sharpley, 1989). It was highest in soil with Kaolinite, montmorillonite, gibbsite, plagioclase (Ibeku soil) ($\text{KSP} = 0.78 \text{ cmol kg}^{-1}$) compared to soil with kaolinite, small quantities of gibbsite, goethite and haematite as the clay mineral (Amakama soil) ($\text{KSP} = 0.08 \text{ cmol kg}^{-1}$) (Table 2). The higher value of HNO_3 -extractable K (K – supplying power) in soil of Ibeku was a function of clay content which varied between each soil group. Besides the clay content, K – bearing minerals and clay mineralogy plays an important role in determining the extractable K status in this soil (Raheb & Heidary, 2011). The proportion of HNO_3 – extractable K (K – supplying power) increased from soil dominated by kaolinite, small quantities of gibbsite, goethite, and haematite (Amakama soil) to kaolinite with detectable quantities of montmorillonite, gibbsite, goethite and plagioclase feldspars) (Ibeku soil), with clay content when the 2:1 type clay (Ibeku soil) become more dominant than 1:1 type clay (Amakama soil), the supply of K to plant increases (Sharpley, 1989). Also, soils with high 2:1 clay minerals contain larger amounts of HNO_3 - extractable K than kaolinite and other siliceous minerals (Martina & Sparks, 1985; Sharpley, 1989; Ghosh & Singh, 2001).

Unamba- Oparah (1985) reported that potassium supplying power (HNO_3 – extractable K) value that is less than $0.31 \text{ cmol kg}^{-1}$ by IM HNO_3 – extractable method are K deficient (Unamba – Oparah, 1985). In other words, Amakama soil may be considered K deficient. Soils whose potassium supplying power between 0.31 and $0.49 \text{ cmol kg}^{-1}$ can respond to K fertilization. Additionally, if such soil is coarse textured and the rate at which K is removed is high, the K response to fertilization will be high. However, soils with potassium supplying power greater than $0.49 \text{ cmol kg}^{-1}$ will not response to K fertilization (Unamba – Oparah, 1985). Based on the information above, Ibeku soil with mineralogical composition of

kaolinite, montmorillonite, small quantities of goethite, gibbsite and plagioclase feldspars is said to be sufficient with K while Amakama soil with low buffering power ($KSP = 0.08$) would require indicated frequent fertilization. $HN03$ – extractable K had positive correlation with total K in both Amakama ($r = 0.98$; $P < 0.05$) and Ibeku soil ($r = 0.78$) (Table 3).

Furthermore, total K in the two soil studied varied more in Ibeku soil (Kaolinite, montmorillonite, gibbsite, goethite, plagioclase feldspar) ($19.01 \text{ cmol kg}^{-1}$) than Amakama soil with kaolinite as the dominant clay mineral ($3.63 \text{ cmol kg}^{-1}$) (Table 2). When compared with total k elsewhere, it was observed that the total K in Ibeku soil was higher than the value $14.6 \text{ cmol kg}^{-1}$ which was for soils of Sudan Savanna Zone of Nigeria (Iwuafor *et al.*, 1980). It was lower than the values obtained from British soil ($35.90 \text{ cmol kg}^{-1}$) and inceptisols of India ($84.61 \text{ cmol kg}^{-1}$) (Gajbhiye, 1985). Thus, Amakama soil had total K ($3.63 \text{ cmol kg}^{-1}$) lower than the values obtained in the Nigerian and British soils mentioned above.

Table 3: Correlation Coefficient (r) for Linear Relationships between the various K forms and Soil Properties for each Soil group

Properties	Water Soluble K	Exchangeable k	Non-exchangeable K cmolkg ⁻¹	HN ₃ -extractable K	Total K
Mixed clay mineralogy dominated by Kaolinite goethite, gibbsite, haematite (Amakama Soil)					
pH	-0.98*	-0.75 ^{ns}	-0.73 ^{ns}	-0.78*	0.02 ^{ns}
Organic C	0.84*	0.93*	0.80*	0.89*	-0.38 ^{ns}
Clay	-0.89*	-0.92*	-0.88*	-0.94*	0.34 ^{ns}
ECEC	0.93*	0.89*	0.81*	0.88*	-0.22 ^{ns}
Water-soluble k	-	0.78*	0.75 ^{ns}	0.80*	-0.03 ^{ns}
Exchangeable K		-	0.74 ^{ns}	0.80*	-0.03 ^{ns}
Non-exchangeable K			-	0.98*	0.32 ^{ns}
HN ₃ -Extractable K				-	0.32 ^{ns}
Total K					-
Kaolinitic upper horizon, with detectable quantities of montmorillonite, goethite, gibbsite, plagioclase feldspar (Ibeku Soil)					
pH	0.88*	0.87*	-0.50 ^{ns}	-0.25 ^{ns}	-0.63 ^{ns}
Organic C	0.84*	0.84*	-0.73*	-0.55 ^{ns}	-0.79*
Clay	-0.81*	-0.74*	0.73*	0.60 ^{ns}	0.79*
ECEC	-0.70 ^{ns}	-0.78*	0.41 ^{ns}	0.17 ^{ns}	0.60 ^{ns}
Water-soluble K	-	0.94*	0.67 ^{ns}	-0.43 ^{ns}	-0.84*
Exchangeable K		-	-0.71*	-0.45 ^{ns}	-0.84*
Non-exchangeable K			-	-0.95*	0.89*
HN ₃ extractable K				-	0.73*
Total k					-

K = Potassium, ECEC = Effective cation exchange capacity, organic C = Organic Carbon, HN₃- K = Nitric acid extractable K, * = Significant, ns = not significant at 5% level of probability

Additionally, total K in soil usually reflects the nature and degree of weathering of the parent materials. Soils containing K – bearing minerals like K feldspars and Micas and subjected to mild weathering conditions would have higher K content while soils formed on unconsolidated sandy deposits and subjected to high rainfall regime would contain low levels of total K (Udo & Ogunwale, 1978). Also, the ability of a soil to supply potassium to a crop depends on both the total K content of the soil, and the different forms of K as influenced by the physicochemical properties of the soils (Chandra & Singh, 1985). Soils derived from Shale and basement complex rocks contain K feldspar and micaceous minerals (Unamba – Oparah, 1985), while soils derived from Sandstone, Coastal Plain Sand and alluvium are intensively weathered and contain kaolinite soil mineral (Udo, 1982). The dominance of Coastal Plain Sand as the parent material and kaolinite in soil of Amakama (Chikezie *et al.*, 2010) agrees with the findings of Jungerius and Levelt (1964) and Igwe *et al.*, (1999) on the soils of eastern Nigeria that the mineralogy of the soils of this area has been inherited from the bedrock or sediment. The presence of Kaolinite clay mineral suggests that the soil of this area is at an advanced stage of weathering. In other words, the low content of total K implies that Amakama soil is strongly weathered (Chikezie *et al.*, 2010) and most of the potassium released during the process of weathering has been lost through leaching because of the coarse nature of the soil and heavy rainfall prevalent in the area. However, when related to soil properties, no significant relationship existed with total K in soil of Amakama dominated by Kaolinite clay, small quantities of gibbsite, goethite, haematite with Coastal Plain Sand as the parent material. While in Ibeku soil dominated by Kaolinite, montmorillonite, gibbsite, goethite and plagioclase feldspar, Total K related significantly and positively with clay ($r=0.79$; $P < 0.05$, Table 3). The significant positive correlation between total K and clay is an indication of potassium fixation in clay lattice which reveals its association with higher K content (Tomar *et al.*, 1997). Therefore the proportion of exchangeable K, non-exchangeable, HNO_3 -extractable K and total K in Ibeku soil with kaolinite, montmorillonite, gibbsite, plagioclase feldspars as the clay mineral was greater than the proportion of these forms in Kaolinite, small quantities of goethite, gibbsite, haematite (Amakama soil).

Table 4 shows the mineralogical composition of these soils. The result shows that Amakama soil has mixed mineralogy dominated by kaolinite, small quantities of goethite, gibbsite and haematite. While Ibeku soil contain Kaolinite at the upper 100 cm and detectable quantities of montmorillonite, and small quantities of goethite and gibbsite and presence of plagioclase feldspar at 164-190 cm (Chikezie *et al.*, 2010). Differences in clay mineralogy sites were most probably related to land management, parent materials (Bende Ameki clay Shale group for Ibeku soil) and Coastal Plain Sand for Amakama) and soil drainage conditions.

Table: 4: Mineralogy of Clay particle (< 0.002mm) for the studied soils

Horizon	Depth cm	Xraypeak size.....	TGA%	Interpretation
Mixed clay mineralogy dominated by kaolinite (Kaolinite, goethite, gibbsite, haematite (Amakama Soil))				
Ap1	0-13	KK4	GI I HE I GE I	KK69 GI 2 GE 18 CMI X
Bo1	27-63	kK4	HE I GE I GI I	KK60 GE 15 G1 2 CMI X
Bo2	63-99	KK4	GE1 GI I HE I	KK62 GE 13 G1 2 CMI X
B04	127-159	KK4	HE I GE I GI I	KK62 G12 CMI X
Kaolinite upper horizon, with detectable quantities of montmorillonite goethite, gibbsite, plagioclase feldspar (Ibeku soil)				
Ap1	0-9	KK5	MT 2 Q21 GE1	KK44 GE 22 G12 KAOL
Bt	28-60	KK5	MT 2 GE1	KK55 KAOL
2Btg	60-80	KK5	MT 2 GE1	KK55 GE 50 GI I KAOL
2 Bssg2	101-128	KK5	MT 3 GE1	KK51 CMIX
2 Bgss 154-190	KK5	MT 4	GE1 QZ1	KK39 G I I CMIX

GI = Gibbsite, HE = Hematite, KK= Kaolinite, VR = Vermiculite, GE = Geothite
 Peak size: 5 = very large, 4 = Large, 3=Medium, 2 = small, 1 = very small 6 = No peak
 Source: Chikezie et al., 2010

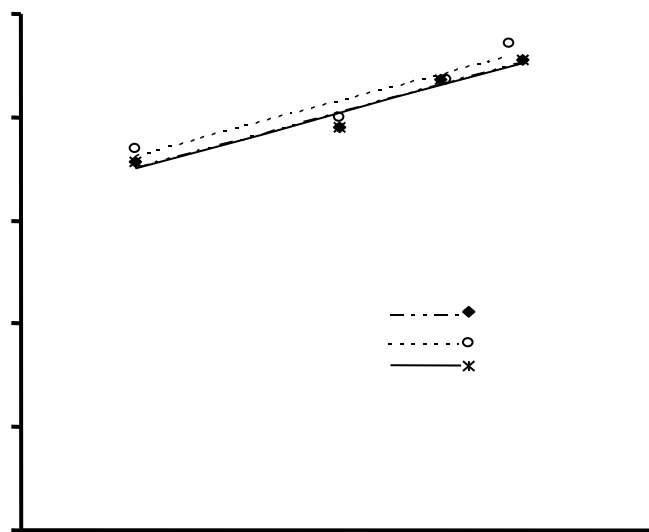
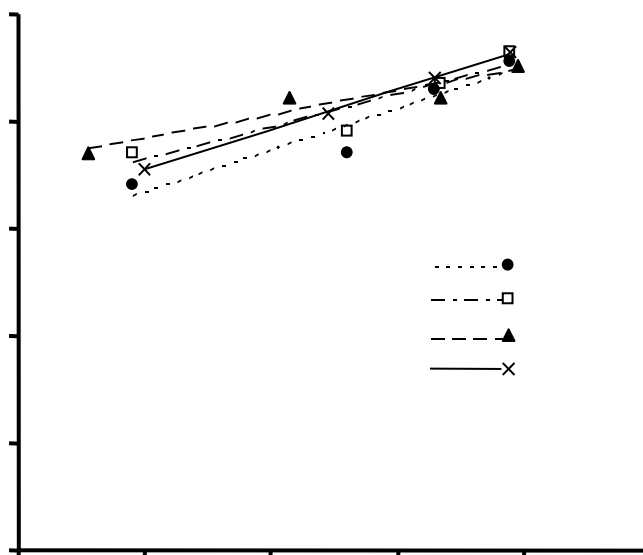
3.2. Potassium Sorption Isotherm

The sorption isotherms were obtained by plotting the amounts of K sorbed in mgkg^{-1} of soil against equilibrium solution concentration in MgKL^{-1} in 1 M CaCl_2 . The shape of these isotherms showed a progressive increase of K sorbed per unit amount of soil for each increment in concentration of K in solution for the two soils studied (Figs 1 and 2). Potassium sorption for soil dominated by kaolinite, montmorillonite, gibbsite, goethite and plagioclase feldspar (Ibeku soil) increased from 81.3, to 296.3 mgkg^{-1} (Table 5) at concentration 10, 20, 30 and 40 (MgKL^{-1}) respectively, whereas in soil dominated with kaolinite, small quantities of gibbsite and goethite (Amakama soil), K sorbed ranged from 62.9-200.0 mgkg^{-1} for the same respective concentrations (Table 5). In other words, K – sorbed was more in soils dominated with kaolinite, montmorillonite, gibbsite, goethite and plagioclase feldspar (Ibeku soil) compared to soils dominated with kaolinite, small quantities of gibbsite and goethite (Amakama soil) possibly due to differences in clay mineralogy composition which is related to land management, difference parent materials and soil-drainage condition (Raheb & Heidari, 2011). Also, the high values of sorbed K in Ibeku soil were associated with soils that contain high amount of fine fractions (silt and clay). Additionally, increase in ionic strength, ion binding affinities, its charge density, degree of interlayering, low hydration energy increases sorbed K in soil dominated by kaolinite, montmorillonite, gibbsite, goethite and plagioclase feldspar (Ibeku soil) (Sawhney, 1971). Saniya & De Datta (1991) reported that increased ionic strength lowers the activity coefficient and raises the concentration of reaction product in soil as per solubility product principle. Furthermore, soil organic carbon (organic matter) plays a major role in the sorption of organic compounds in soil dominated by kaolinite, montmorillonite, gibbsite, plagioclase (Ibeku soil). This result is agreement with the report of Gaultier *et al.*, (2008); Sameni *et al.*, (2011). They attributed increased K sorption by AL-organic matter complex with pH. The condensation to Organic matter resulted in increased accessibility of K to adsorption site on the hydroxyl Al.

The sorption data were tested for their conformation to the Langmuir and Freundlich equation. Langmuir equation did not conform well. The inability of the Langmuir equation to describe the data may be related to the fact that there were several discrete types of K sorption site, each with a different selectivity for K in these soils (Dufey & Delvaux, 1989). However, all log transformed data in the two soils studied confirmed well to Freundlich adsorption isotherms (Figs. 1a,b and 2a,b) by giving a straight line graph. The result is in line with Singh *et al.* (1987); Hannan *et al.* (2007) who also reported a straight line graph with Freundlich equation.

Table 5: Potassium in the Equilibrating Solution in the Solid phase and K in the Aqueous phase and Potassium Sorption Parameters for each Soil group in the Studied Sites

Horizon	Depths cm	Potassium in solution at equilibrium				Potassium Adsorbed (X/M) at equilibrium				k	1/n
		10	20	30	40	10	20	30	40		
Mixed clay mineralogy dominated by Kaolinite (Kaolinite, goethite, gibbsite, haematite (Amakama Soil))											
AP1	0-13	7.5	16.5	23.0	30.5	50.0	70.0	140.0	190.0	0.80	1.03
AP2	13-27	7.5	16.5	23.5	30.5	70.0	90.0	150.0	210.0	1.13	1.31
B01	27-63	6.5	13.5	23.5	31.5	70.0	130.0	130.0	180.0	1.44	1.86
B02	63-99	8.0	15.5	23.0	30.5	60.0	110.0	160.0	210.0	0.94	1.19
B03	99-127	7.5	16.0	23.0	31.0	60.0	90.0	150.0	190.0	1.01	1.22
B04	127-159	7.5	16.0	23.5	29.5	70.0	100.0	150.0	230.0	1.09	1.19
B05	159-210	7.5	16.0	23.0	31.0	60.0	90.0	150.0	190.0	1.01	1.27
Mean		7.4	15.7	23.2	30.6	62.9	91.1	147.1	200.0	1.06	1.30
Kaolinitic upper horizon, with detectable quantities of montmorillonite, goethite, gibbsite, plagioclase feldspar (Ibeku soil)											
A _p 1	0-9	6.5	13.0	20.0	27.0	100.0	170.0	230.0	290.0	1.40	1.36
A _p 2	9-28	7.5	15.0	21.5	28.0	70.0	120.0	200.0	260.0	0.96	1.00
Bt	28-60	6.0	14.5	20.5	26.5	110.0	140.0	220.0	300.0	1.46	1.47
2Btg	60-80	8.0	14.0	22.0	25.5	70.0	150.0	190.0	320.0	0.79	0.84
2Bssg1	80-101	8.0	15.5	21.0	26.5	80.0	130.0	220.0	310.0	0.86	0.89
2Bssg2	101-128	8.5	14.5	21.0	27.0	80.0	160.0	230.0	310.0	0.82	0.85
2Bssg3	128-164	9.0	16.5	22.0	27.5	60.0	110.0	200.0	290.0	0.43	0.72
2Bgss	164-190	9.0	15.5	22.5	28.5	80.0	150.0	210.0	290.0	0.86	0.91
Mean		7.8	14.8	21.3	23.6	81.3	141.3	212.5	296.3	0.95	1.01



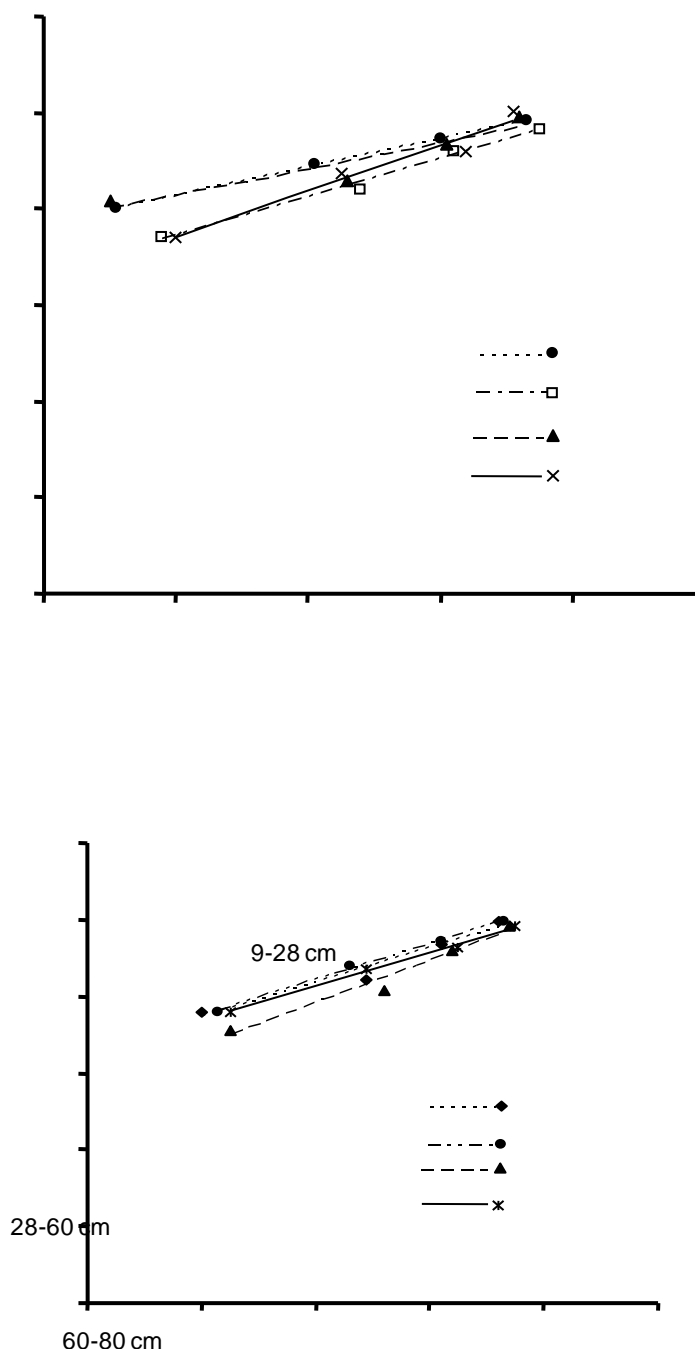


Fig. 1a: Freundlich plot of potassium adsorption at 0-13, 13-27, 27-63 and 63-99 cm soil at Amakama, Abia State.

The Freundlich sorption coefficient (k) and the Freundlich Sorption exponent ($1/n$) represents the intercept and slope of the sorption isotherm and measures the extent of sorption and energy of adsorption respectively. However, the extent (K) and the energy ($1/n$) at which potassium was sorbed was higher in soil with kaolinite clay mineral, small quantities of goethite, gibbsite and haematite (Amakama soil) ($K = 1.06 \text{ mg kg}^{-1}$; $1/n = 1.27$) than soils dominated with kaolinite, montmorillonite, haematite, plagioclase feldspars (Ibeku soil) ($K = 0.95 \text{ mg kg}^{-1}$; $1/n = 1.01$) (Table 5). This could be attributed to the differences in clay minerals, its amount, different parent material and soil drainage condition. Amakama soil

whose mineralogy is dominated by kaolinite have lower degree of crystalline which has been one of the factors affecting kaolinite mineral in strongly weathered soils of the tropics (Singh & Gilkes, 1992). The crystallinity of kaolinite in this soil has been related to chemical and morphological properties of this clay mineral and pedo- environmental factors of the soil. The presence of the structural Fe in kaolinite reduces crystallinity of this mineral and increases the surface area thereby increasing the sorption capacity of K in this soil (Singh & Gilkes, 1992).

Also, the higher intensity of adsorption (energy of adsorption, $1/n$) in Amakama soil could be related to external surface sites and higher degree of sand content. Sparks & Jardine (1984) reported that kaolinite minerals have few sites for adsorption of ions and K ions sorbed in these soils are held by stronger energy. However, the low extent and energy of sorption in Ibeku soil ($K = 0.95$; $1/n = 1.01$, Table 5) may be due to the poor drainage condition of the area, besides the clay mineralogy of this soil. The poor internal drainage condition in the area retards the alteration of this mineral and accounts for the presence of some 2:1 clay minerals in this soil (Chikezie *et al.*, 2010). The presence of montmorillonite (2:1 clay mineral) and plagioclase feldspar in Ibeku soil suggests that the soil contains some weatherable minerals. The presence of large sites and large surface areas in this mineral allows water penetration between unit cells causing the expansion of this mineral and movement of K^+ ion in and out of such place (Shaviv *et al.*, 1985).

Relating exchangeable K, Non-exchangeable K, Nitric acid-extractable K (HNO_3 -extractable K known as K supplying power, and total K with the extent of adsorption (K) and energy of adsorption ($1/n$), for the two soils studied, non-exchangeable K, HNO_3 – extractable K and total K had no relationship with the extent of adsorption (K). However, energy of adsorption (intensity; $1/n$), related negatively with non-exchangeable ($r = - 0.55$; $- 0.60$, $P < 0.05$), HNO_3 – extractable K ($r = - 0.50$; -0.58 , $P < 0.05$) and total K ($r = - 0.56$; -0.65 , $P < 0.05$) (Table 6), suggesting that clay content, k – bearing mineral, clay mineralogy, HNO_3 extractable K plays more important role in determining the soil's extractable K status in these soils (Raheb & Heidari, 2011).

Table 6: Correlation Coefficient between Freundlich Constant (K) (mgKg⁻¹), 1/n) and some Soil properties for each Soil group

Soil Properties

**Mixed clay mineralogy dominated
by kaolinite (kaolinite, goethite, gibbsite, haematite (Amakama Soil)**

	K	1/n
pH	0.01 ^{ns}	-0.16 ^{ns}
Organic carbon	0.36 ^{ns}	-0.21 ^{ns}
Clay	0.21 ^{ns}	0.04 ^{ns}
ECEC	-0.28 ^{ns}	-0.14 ^{ns}
Exchangeable K	0.45 ^{ns}	0.31 ^{ns}
Non-exchangeable K	-0.36 ^{ns}	-0.55*
HNO ₃ -extractable K	-0.29 ^{ns}	-0.50*
Total K	-0.39 ^{ns}	-0.56*

**Kaolinitic upper horizon with detectable quantities of montmorillonite, goethite,
gibbsite, plagioclase feldspars (Ibeku Soil)**

pH	0.79*	0.67 ^{ns}
Organic C	0.64 ^{ns}	0.62 ^{ns}
Clay	-0.56 ^{ns}	-0.53 ^{ns}
ECEC	-0.60 ^{ns}	-0.54 ^{ns}
Exchangeable K	0.35 ^{ns}	0.32 ^{ns}
Non-exchangeable k	-0.22 ^{ns}	-0.60*
HNO ₃ -extractable K	0.30 ^{ns}	-0.58*
Total K	0.40 ^{ns}	-0.65*

* = Significant at 5%, ns = not significant at 5% level of probability

4. Conclusion

From the study it was found that soils were acidic. Soil with detectable quantities of montmorillonite, goethite, gibbsite and plagioclase feldspar (Ibeku soil) had high amount of exchangeable K, non exchangeable K, total k and high amount of sorbed K. On the other hand, soil with dominated by kaolinite, small quantities of goethite, gibbsite and haematite (Amakama soil) had low amount of exchangeable K, non – exchangeable K, Total K, and low amount of sorbed K. The soil with mixed mineralogy detectable quantities of montmorillonite, gibbsite, plagioclase feldspar had a better indication of supply power with higher HNO_3 -extractable K than the kaolinite dominated mineral (Amakama soil). The extent and the energy at which K was adsorbed was more in soil dominated by kaolinite (Amakama soil) than soil with mixed mineralogy with detectable quantities of montmorillonite, goethite, gibbsite and plagioclase feldspar (Ibeku soil). Therefore the soil with kaolinite dominated mineral, small quantities of goethite, gibbsite and haematite (Amakama soil) would be exhausted with K and the need K fertilization more than the soil with montmorillonite, gibbsite, plagioclase feldspar (Ibeku soil). The need for K fertilization will be required and in frequent doses in soil dominated with kaolinite, gibbsite, goethite and haemathite (Amakama soil) than soil dominated with kaolinite, montmorillonite, gibbsite, plagioclase feldspar (Ibeku soil).

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