International Journal of Agriculture and Forestry 2013, 3(7): 294-302
DOI: 10.5923/j.ijaf.20130307.06

Determination of Potassium Levels in Intensive Subsistence Agricultural Soils in Nyamira County, Kenya

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Abstract Assessment of potassium levels in agricultural soils of Nyamira County, Kenya was necessitated by the observed progressive drops in maize acreage yields over the years despite use of phosphorus and nitrogenous fertilizers. In the study, concentration levels of potassium and other soil fertility indices such as, organic carbon, cation exchange capacity, exchangeable cations, soil pH, available nitrogen, total and available phosphorus were determined. Five composite soil samples were collected at depths of between 0-30 cm from five farms that have consistently been under intensive cultivation. Fractionation of potassium was achieved by sequential extraction of soil sampleswith distilled water, ammonium acetate and nitric acid in that order. Concentration levels of potassium in the extracts were determined using a flame photometer. Potassium concentration levels obtained from the water soluble soil extracts were used to calculate thermodynamic parameters such as free energy of replacement, potassium activity ratio and ionic strength of the soil solution. The relationship between the adsorbed and equilibrium potassium concentration, quantity/intensity was determined by plotting Freundlich adsorption isotherms. The isotherm was used to determine the buffering capacity ofpotassium and the concentration levels of potassium adsorbed on un-specific sites in the soil. The suitability of the adsorption equation was determined by applying the least square regression analysis. From the study available potassium in the soils ranged from 57 to 70 mg/kg and had amean value of $60 \pm 5.54.2$ mg/kg (ammonium acetate method). The water soluble potassium ranged from 1.8 to 2.2 mg/kg with a mean of 2.02 ± 0.16 mg/kg. Nitric acid extracted potassium had a mean of $149.\pm 2.306$ mg/kg. The mean free energy of replacement, ΔF, was found to be -3572 ± 44.98 cal/mol indicating that the soils have low supplying power of potassium. The potassium buffering capacity of the soils was found to have a mean of 1.189 ± 0.06 mg/kg. The amount of potassium adsorbed on un-specific sites of the soilshad a mean value of 6.993 ± 2.378 L/kg. These findingsreveal the extent of potassium depletionin the soils of this region and will form a baseline for working acreage potassium doses required for remediation.

Keywords Potassium Buffering Capacity, Adsorption, Freundlich Isotherm, Thermodynamics Parameters, Free Energy of Replacement, Soil Fertility Indices

1. Introduction

A major contributing factor to low agricultural yields in developing countries is low soil fertility[1]. This has mainly led to the decline in crop productivity in Kenya[2]. Soil fertility has been declining because of continuous use of the agricultural land without adequate replenishment of utilized nutrients[3] leading to reduction of nutrient stocks in the soil[4]. For instance, it has been reported that an annual depletion of -112 kg N ha^{-1}, -31 kg P ha^{-1} and -70 kg K ha^{-1} occurs in Kisii and Western Kenya[5]. This has been attributed to poor agricultural practices that include: removal of crop residue for livestock, overgrazing, burning of stock to ease land preparation, limited usage of inorganic fertilizers, lack of knowledge on types of fertilizer and insufficient information on fertilizer usage[6,7].

Potassium is a primary plant and animal nutrient that plays a major role in ensuring maximum growth and economic yields from agricultural farms. Management of potassium and other essential nutrients is key to achieving a balanced fertility program[8]. Potassium plays key roles in several physiological processes such as regulating the uptake of nitrates from soil, balancing phosphorus uptake, strengthening stalks of plants hence helping in resisting fungal and bacterial attacks as well as lodging. Further it promotes the formation of good quality seeds, influences the rate of transpiration, synthesis of carbohydrates, proteins and translocation of the synthesized food. In fact, more than 50 enzymes responsible for energy transfer and formation of sugars, starch and proteins are affected by presence of potassium in plants[9]. However, excess K levels can be harmful to crops by suppressing the uptake of boron and magnesium by plant roots and damages seeds during germination[10].

The forms and concentration levels of potassium vary

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Published online at http://journal.sapub.org/ijaf

from place to place depending on the degree of mineral weathering and type of parent rock. For example, micaceous clay minerals such as illites and vermiculites can fix potassium to a greater extent than clays with low charge density such askaolinite. The four forms of potassium insoil include solution, exchangeable, fixed (non-exchangeable) and mineral potassiumin theirorder of availability to plants and microbes respectfully[11]. The equilibrium reactions between the four forms determine whether the applied potassium fertilizer is absorbed by plants, leached to lower layers or converted to forms unavailable to plants[12]. The equilibrium constant is important in predicting the levels available and remediation dose requirements.

Many researchers have used variety of techniques, equations and mechanistic models in evaluating potassium requirement and availability to crops[13]. The traditional methods used include extraction with 1N ammonium acetate to determine the concentration levels in forms that are available for plant uptake and extraction with nitric acid to evaluate the total concentration levels in the soil. More recently, new techniques that use adsorption isotherms and thermodynamic parameters such as ionic activity, activity coefficient,ionic strength and free energy of replacement todetermine potassium levels and its availability for plant uptake have been reported[14].

In Nyamira County, Kenyaan intensive subsistence farming system that ensures maximum utilization of all cultivable land is practiced. In fact, double or even triple planting is done within a single year. Despite this, there is limited information on the available and total concentration levels of potassium in these soils. Further, the farmers have limited themselves to sole use of P and N-fertilizers with the assumption that potassium is a non-limited nutrient in the soils. Therefore this study aims to determine the available and total concentration levels of potassium using thermodynamic measurement as well as ammonium acetate method.

2. Materials and Methods

Experimental site

The experiments were carried out in Gachuba location of Nyamira County, Kenya. The soils found in the region are mainly classified as nitosol sand are well drained[15]. The area receives a mean annual rainfall of between 1700-1800 mm. Due to its high population density all the land in the region is under cultivation with only very small portion left for pasture. The main crops grown in the area include maize, beans, bananas, sugarcane, coffee, cassava, finger-millets, kales and cabbage.

Sampling

Five farms that have consistently been under cultivation were identified. From each farm acomposite sample was obtained from the farm's soil within a depth between 0-30 cm. due to uniform soil characteristics in the area, grid sampling was employed whereby15 to 20 cores (a core is an individual boring or coring spot in a field) were collected from each farm at random with the help of a soil auger. The cores were mixed thoroughly in a clean plastic pail to make composite soil samples. The bulk composite samples were air dried, ground, passed through a 2 mm sieve, packed in clean polythene bags and kept to cool.

Laboratory analysis

The physical-chemical parameters of the soil were determined using standard procedures described below. All chemical analysis was done in triplicate. Soil pH and electrical conductivity (*EC*) of soil pastes (soil to water weight ratio of 1:2.5) were determined using electrical pH and conductivity meters respectively. Total organic carbon was determined using the standard Walkey Black rapid titration method[16]. The concentration levels of phosphorus content were determined using the Olsen method[17] and calorimetric measurement[18]. Nitrogen concentration levels were determined by the Kjeldal method[19]. The concentration levels of potassium in the various forms were obtained by extracting with water, ammonium acetate and nitric acid as described in literature[20] and measurements in extracts done using a flame photometer, 410 Corning model.

Adsorption studies

2.50 grams of the soil samples were put in 25mL solutions of 0.01M $CaCl_2$ that contained potassium concentrations of 0, 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 mgL^{-1} and shaken for 24 hours at 25±1°C to achieve equilibration. The contents were filtered using Whatman filter papers No. 42. The concentration levels of potassium in the filtrate were measured using a flame photometer.

Calculations of thermodynamic data

Adsorption isotherms were constructed as per the method described by Rowell[21]. The amount of K adsorbed was obtained by subtracting the amount found in filtrate from the initial amount that was in solutions as shown in equation 1.

$$\Delta K = (CK_i - CK_f) * (V / M) \quad \Longrightarrow \text{Eq (1)}$$

ΔK is the change of amount K in solution (represent amount adsorbed)

A positive ΔK values indicate adsorption whereas negative values indicate desorption of potassium by the solid phase of soil.

CK_i and CK_f are the initial K concentration added and final equilibrium concentrations of K in solution respectively. V and M are the solution volume and mass of the soil used. The amount of K desorbed in the extract containing zero KCl treatment was added to the amount of K adsorbed in the extracts containing various initial K concentrations. The K adsorption data were fitted into the Freundlich linearised adsorption equation 2 given[22].

$$log\left(\frac{X}{m}\right) = loga + blogC \quad \Longrightarrow \text{Eq (2)}$$

Where $\left(\frac{X}{m}\right)$ is the mass of adsorbed Kper unit mass of soil ($mgkg^{-1}$), C is the equilibrium K concentrations of solutions (mgL^{-1}), *a* and *b* are constants obtained from the intercept and slope respectively.

The ionic strength in the soil was calculated by a formula proposed by Griffin and Jurinak[23] in 1993 as shown in equation 3.

$$\text{Ionic strength}\mu = 0.0129 \times EC \qquad \Longmapsto \text{Eq (3)}$$

Where EC is the electrical conductivities of soil pastes in mmhos/cm

Activities of calcium, potassium and magnesium ions, (a_i), in the water extracts were tabulated as the product of their activity coefficients, (fi), and their concentrations, (ci), as shown in equation 4.

$$a_i = f_i \times c_i \qquad \Longmapsto \text{Eq (4)}$$

The fi of the ions were determined using the extended Debye-Huckel equation 5

$$log f_i = -AZ_i^2 \frac{\sqrt{\mu}}{1+Bd_i\sqrt{\mu}} \qquad \Longmapsto \text{Eq (5)}$$

Where Z_i = valence of ion, $A = 0.508$ for water at 298 Kelvin, $B = 0.328 \times 10^8$ for water at 298 Kelvin, d_i = effective size of hydrated ions and μ = Ionic strength of cation

The activity ratio of potassium ions were tabulated using equation 6

$$\text{Activity ratio} = \frac{a_K}{\sqrt{a_{Ca} + a_{Mg}}} \qquad \Longmapsto \text{Eq (6)}$$

The free energy of replacement was calculated by woodruff 1955 proposed formula shown in equation 6.

$$-\Delta F = 2.303RTlog \frac{a_K}{\sqrt{a_{Ca} + a_{Mg}}} \qquad \Longmapsto \text{Eq (7)}$$

Where R = Gas constant $= 1.987\ Cal/K.mol$, T = Absolute temperature at 25°C = 298 K and a = activity of the metal ions.

3. Results and Discussion

Basic soil characteristics

The percentage of the total organic content was found to range between 1.10-2.07 % and a mean value of 1.82± 0.41 % . This falls within the moderate range that is considered to range from 1.5 to 3.0%. The concentration levels of available phosphorus were found to range from 9.62 mg/kg to 9.77 mg/kg with a mean value of 9.71±0.056 mg/kg.These levels were below the critical level of 10 mg/kg[24]. The low levels of available phosphorus obtained are illustrative of phosphorus insufficiency that is endemic in many of the farms in the region. Phosphorus deficiency in many soils in Kenya is largely due to low occurrence of phosphorus containing minerals and inadequate phosphorus fixation[25]. Concentration levels of total nitrogen content obtained in the study ranged from 0.173-0.196 % and had a mean of 0.179±0.017 %. This is below the critical levels[8]. Low crop yields due to the low availability soil phosphorus and nitrogen nutrients are expected from these findings in consistence with the FAO, 2004 report[26]. The concentration levels of available potassium obtained from ammonium acetate extracts ranged from 57-70 mg/kg with a mean of 60.2±5.541 mg/kg. The cation exchange capacity of the soil ranged from 17.25-28.05 Cmol/kg with a mean of 21.25 ±4.124 Cmol/kg. These medium values of cation exchange capacity indicate that the soils can moderately hold nutrients. The soil pH ranged from 4.81-5.61 with a mean of 5.19±0.28 indicating that the soils were strongly acidic. The electrical conductivity which is an indirect measure of total amounts of soluble salts in soil was found to range from 0.20-0.31mmhos/cm with mean of 0.25±0.05 mmhos/cm an indication these soils are non-saline.

Table 1. Summary of some physical and chemical properties of soil samplesstudied

Parameter	Units	Mean valuesn = 15	Critical values
EC	mmhos/cm	0.25±0.05	-
pH	-	5.19±0.28	-
Organic carbon	%	1.82±0.041	3
Total P (Olsen)	mg/Kg	31.31±0.107.	-
Available P (Olsen)	mg/Kg	9.71±0.056	10
Total N	%	0.179±0.017	0.25
CEC	Cmol/Kg	21.25±4.124	-
Nitrates	Ppm	2.66±0.659	10
Exchangeable cations	Cmol/Kg	-	-
Calcium ions	□	3.23±0.60	2.0
Magnesium ions	□	1.78±0.16	1.0
Potassium ions	mg/Kg	60.2±5.541	160
Textural class		Loam	

Potassium fromwater extracts

The concentration levels of water soluble potassium in the soils ranged from 1.8-2.2mg/kg and had a mean of 2.02±0.164 mg/kg. This amount of potassium represents the amount present in solution form. The amounts obtained are very low when compared with the critical value of 19.5 mg/kg proposed by International Potash Institute[27]. This indicates that a very small portion of available potassium is in solution form to support plant growth. This water soluble potassium was only about 3.36 percent of available potassium (potassium extracted by ammonium acetate). The low percentage is an indication that the equilibrium does not favor water soluble form.

Available potassium

The concentration levels of potassium obtained from ammonium acetate extracts ranged from57 to 70 mg/kg and had a mean of60.2±5.541 mg/kg. Potassium levels from ammonium acetate extracts are considered as estimates of the amounts in the soil that are available for plant uptake. The values obtained are below the critical value of 160 mg/kg[28]. This shows that the available potassium in these soils is insufficient. These low values might be as result of long-term continuous cropping without replenishing with potassium fertilizers. Itmay also imply that the soils positive response to potassium fertilization is highly probable.

Potassium saturation percentage

In soils,cations are held on the clay and organic matter and can be replaced by other cations thus, they are exchangeable. The total number of cations that soil can hold is related to its total negative charge and constitutes the soil's cation exchange capacity (CEC). The Percent Nutrient Saturation refers to a measure or estimate of the percent of the soil CEC that is occupied by a particular nutrient (nutrient saturation). The percentage portion of soil cation exchange capacity (CEC)that was occupied by potassium was found to range from0.6399-0.8621and had a mean of 0.7383±0.087.The values show that onlya very small proportion of the CEC is occupied by potassium ions. This is far below the critical value of 2.3[15].

Table 2. Speciation of potassium forms in the studied soil

Forms of potassium	Unit	Range	Value n = 15
Water soluble-K	mg/kg	1.8-2.2	2.02±0.164
Ammonium acetate-K	□	57-70	60.2±5.541
Nitric acid-K	□	147-152	149.6±2.302
K-saturation percentage	□	0.64-0.86	0.738±0.087
H_2O soluble-K:NH_4OAC-K			0.034±0.0022
NH_4OAC-K:ACID-K			0.402±0.034
Basal saturation percentage			0.2523±0.049

Potassium extracted by nitric acid

The concentration levels of potassium found in nitric acid extracts ranged from 147-152 mg/kg and had a mean of 149.6±2.302 mg/kg. This narrow range suggests that the soils may have similar mineralogy and parent rock. Potassium in this form is considered to represent the soil supplying power for potassium for long term cropping[29]. The values obtained are low compared with the critical value 400 mg/kg [15]. This shows that the soils have poor supplying power of potassium for future cropping and plant growth.

Potassium buffering capacity (KBC) and related quantity/intensity factors

The soils' capacity to resist change in the concentration of potassium in soil solution is called potassium buffering capacity (KBC). It is also defined as the capacity of soil to maintain a given potassium level in soil solution. High values of buffering capacity are indicative of adequate potassium availability for long periods while low value simply that there is need for frequent fertilization[30]. Potassium buffering capacity (KBC) is obtained from the slope of the sorption isotherms[31].

A plot of log of adsorbed potassium against log equilibrium potassium concentration (EKC) gave linear graphs shown on figures 1-5. The goodness of the fit was ascertained by looking at the values of r^2 which ranged between 0.927-0.985 and gave a mean value of 0.957±0.021. This indicated high conformity of the adsorption data to Freundlich model, thus the Freundlich isotherm gave a better fit to the adsorption data of the soils. Freundlich isotherms assume unlimited sorption sites of heterogeneous medium and hence are expected to give better correlations for the mixed mineralogy contained in soils. This is in agreement with cited literature. Chaudhry et al 2003 and Hussain et al 2006 reported that data obtained from Freundlich equations was independent of time and temperature and the values depend on the concentration of potassium in soil solution [32,33].

Table 3. amount of adsorbed potassium and the equilibrium potassium concentration (EKC) at various initial concentration doses

Initial k conc c_i	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	EKC c_f mg/l	Adsorbed (ci-cf) v/m Mg/kg	EKC $c_f$mg/l	Adsorbed (ci-cf) * v/m Mg/kg	EKC $c_f$mg/l	Adsorbed (ci-cf) v/m Mg/kg	EKC $c_f$mg/l	Adsorbed (ci-f) v/m Mg/kg	EKC $c_f$mg/l	Adsorbed (ci-cf) v/m Mg/kg
0	2	-20	1	-10	2	-20	2	-20	3	-30
25	13	120	15	100	15	100	12	130	14	110
50	22	280	17	330	21	290	18	330	23	270
75	35	400	33	420	31	440	36	390	30	450
100	46	540	49	510	48	520	43	570	49	510
125	57	680	56	690	50	750	54	710	58	670
150	64	860	60	900	58	920	62	880	61	890
175	70	1050	69	1060	72	1030	73	1020	71	1040
200	79	1210	88	1120	79	1210	75	1250	79	1210
225	85	1400	89	1360	84	1410	80	1450	86	1390
250	94	1560	92	1580	93	1570	90	1600	94	1560

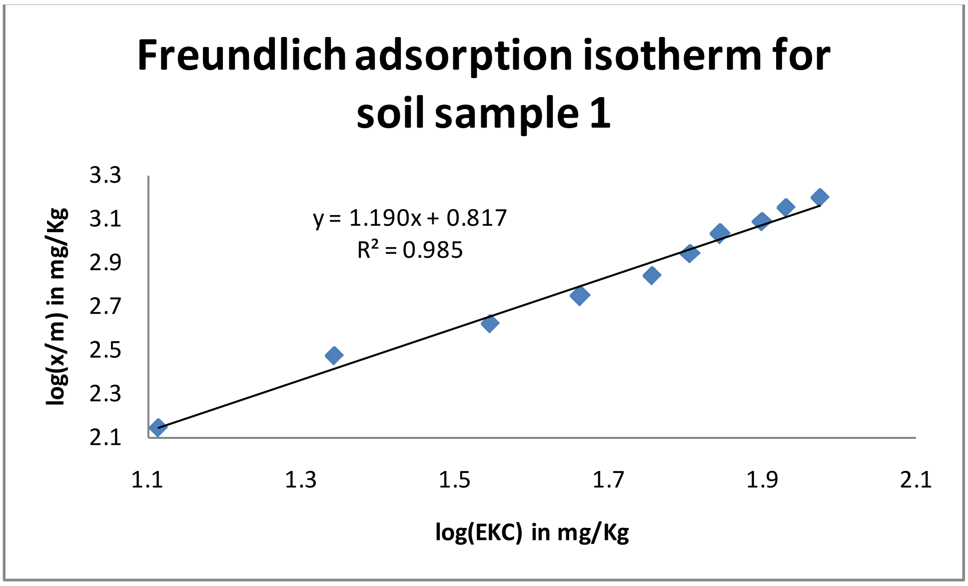

Figure 1. Freundlich adsorption isotherms for the studied soil sample 1

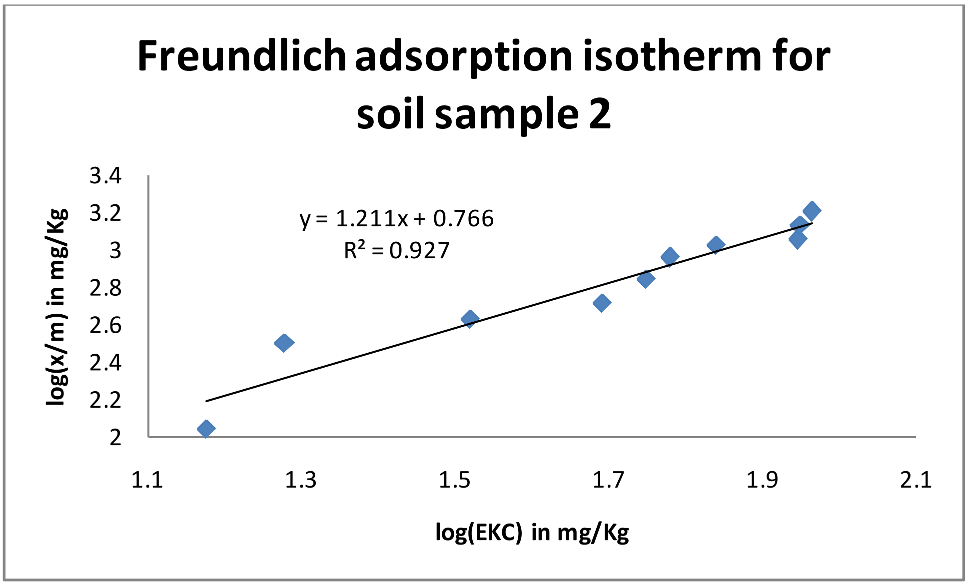

Figure 2. Freundlich adsorption isotherms for the studied soil sample 2

Table 4. Potassium adsorption parameters of the Freundlich model

Soil samples	Amount adsorbed (a) in mg/kg	Buffering capacity (b) in kg/mg	Correlation coefficient (r^2)
1	6.561	1.190	0.985
2	5.834	1.211	0.927
3	4.977	1.270	0.959
4	11.091	1.079	0.947
5	6.501	1.195	0.968
Mean	6.993	1.189	0.957
SD	2.378	0.069	0.021

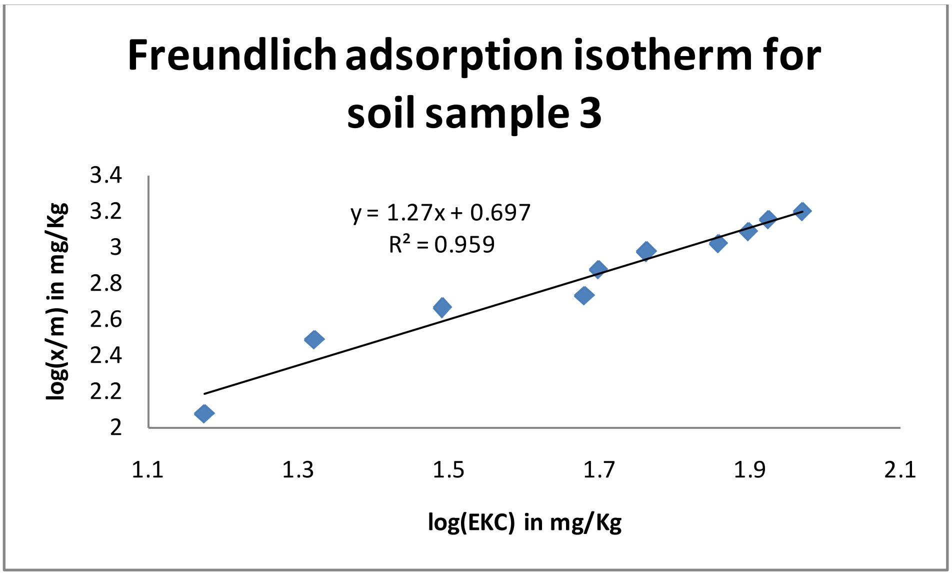

Figure 3. Freundlich adsorption isotherms for the studied soil sample 3

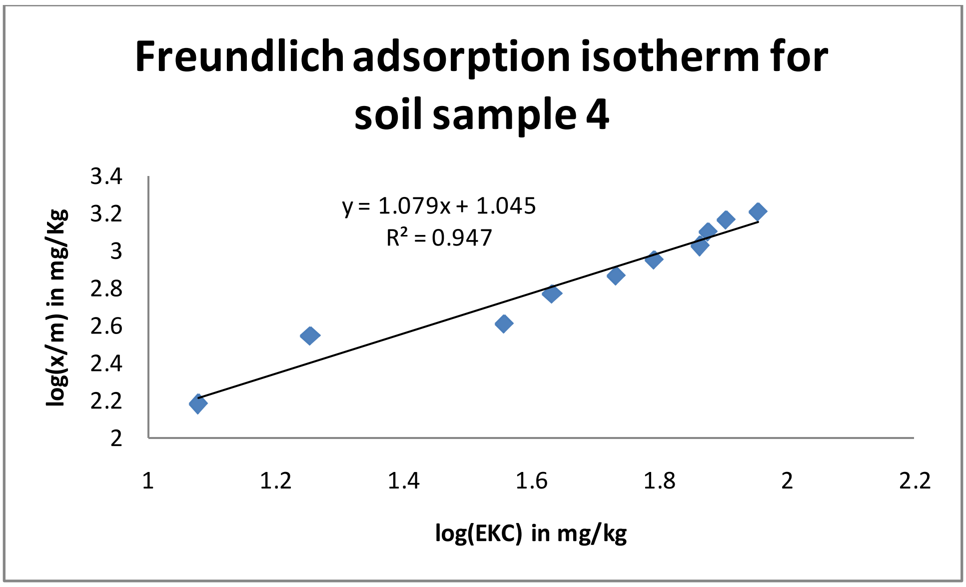

Figure 4. Freundlich adsorption isotherms for the studied soil sample 4

Table 5. Freundlich equation Forms for the studied soils

Soil sample	Model form	Linear form
1	$x/m = 6.561C^{1.190}$	$Y = 1.190X + 0.817$
2	$x/m = 5.834C^{1.211}$	$Y = 1.211X + 0.766$
3	$x/m = 4.977C^{1.270}$	$Y = 1.270X + 0.697$
4	$x/m = 11.091C^{1.079}$	$Y = 1.079X + 1.045$
5	$x/m = 6.501C^{1.195}$	$Y = 1.195X + 0.813$

From the potassium sorption isotherms, the buffering capacities (b values in equation 2) were found to range from 1.079-1.270 kg/mg and gave a mean of 1.189±0.069kg/mg. The adsorption capacities (*a* values in equation 2)of the soils ranged from 4.977-11.091 mg/kg with a mean of 6.993±2.378 mg/kg. The (*a*) value represents the amount of potassium held on un-specific sites and ready to be released for uptake by plants during a cropping season. Based on the data, the values of potassium adsorbed (*a*) was low compared to available soil potassium. This suggests that part of exchangeable potassium is held on exchange sites by high bonding energy.

Thermodynamics determinants of Potassium in the studied soil

The thermodynamic determinants used to evaluate the levels potassium in soils included free energy of replacement, activity ratio and ionic activity. They give an indication on the rate at which potassium adsorbed on the solid phasecan replenish the soil solution potassium[34]. This method can be used to determine fertilizer dosage required to obtain optimum concentration levels in soil solution.

Table 6. Thermodynamic properties of the studied soils

Soil Sample	Electrical conductivity EC	Ionic strength µ(mol/L)	Kactivity coefficient γ_k	K activity in mol/ L	Activity ratio
1	0.28	0.00361	0.9361	0.0000528	0.00261
2	0.20	0.00258	0.9452	0.0000436	0.00217
3	0.24	0.00310	0.9404	0.0000506	0.00250
4	0.22	0.00284	0.9427	0.0000459	0.00227
5	0.31	0.00400	0.9331	0.0000502	0.00248
Mean	0.25	0.00323	0.9395	0.0000486	0.00241
SD	0.04	0.00058	0.0049	0.00000375	0.00018

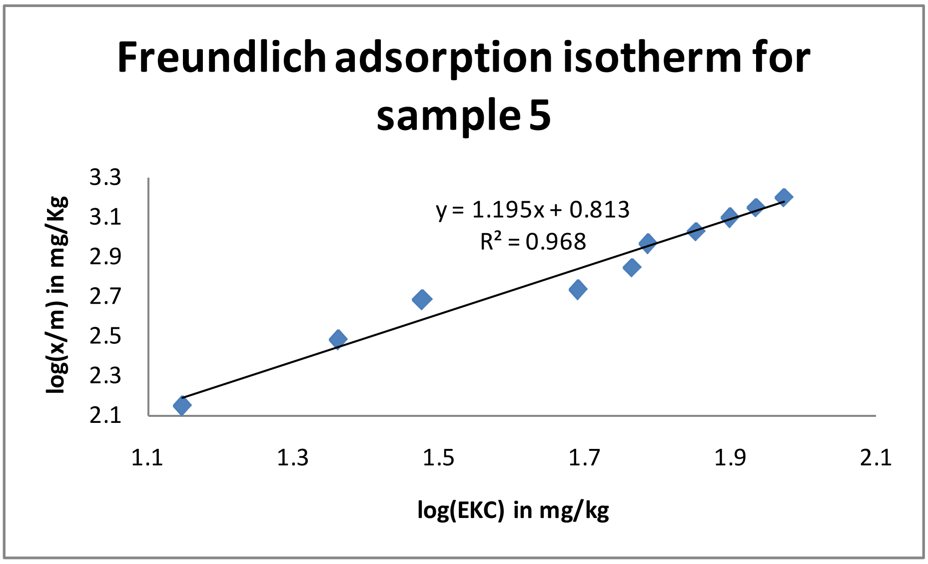

Figure 5. Freundlich adsorption isotherms for the studied soil sample 5

The ionic strength (µ): The values of the ionic strengths of potassium in the soils were tabulated using equation 3. They were found to range from 0.00258-0.00400 and gave a mean value of 0.00323±0.00 mol/L as shown in table 6. This ionic strength is an indication that the potassium for maximum crop yields[14]. in the studied soils existed in active form in the soil solution.

The activity ratio: The activity ratio of the soils was tabulated using equation 6. Theywere found to range from 0.00217 to 0.00261 and had a mean value of 0.00241±0.00. The values of activity ratios normally reflect the chemical potential of the soil. High activity ratio value simply more potassium available for plant absorption.

The free energy of replacement (Δ*F*): The free energy of replacement was tabulated using equation 7. These values are used to classify the supplying power of potassium in soils shown in Table 7[35].

According to the table, soils with lower than (Δ*F*) – 3500 cal.mol^{-1} have poor supplying power of potassium and those with -3500 to - 2000 cal.mol^{-1} have medium supplying power of potassium. Finally, soils with less than - 2000 cal.mol^{-1} are poor in supplying power of potassium. The values obtained from our study ranged from -3632 to -3523 cal.mol^{-1} and averaged to the value -3572±44.98 cal.mol^{-1} as shown in table 8. This implies that the soils had poor supplying power of potassium.

Table 7. woodruff free energy classification

Δ*F*(cal.mol^{-1})	Interpretation
Less than -3500	Low supplying power of potassium
-3500 to-2000	Medium/marginal supplying power of potassium
Greater than -2000	High supplying power of potassium

4. Conclusions

From the result, it's clear that the soils are not only poorly supplied with the various forms of potassium but also with the other basic major nutrients such as nitrogen and phosphorus. Therefore the farmers' assumptions that potassium is a non-limited nutrient are inaccurate. Thisimplies that addition of considerable amounts of potassium to the soils is required to improve on yields.

Table 8. Summary of free energy of replacement of studied soil samples

Samples	1	2	3	4	5	mean	SD
Δ*F*(Cal.mol^{-1}	-3523	-3632	-3548	-3606	-3553	-3572	44.98

5. Recommedations

With the low fertility status of the soils, fertilization is necessary; specifically with potassium, nitrogen and phosphorus fertilizer to boost crop yield. Using this data, optimum potassium acreage dosage for the soils is in progress.

ACKNOWLEDGEMENTS

The authors give special thanks to Chemistry Department of Kenyatta University and Food Science Department of Jomo Kenyatta University for proving the required apparatus, equipment and technical assistance.

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