

Sorption and Availability of Potassium in Selected Soils from Western Kenya

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Abstract

Sorption is one of the most important processes in the soil which affects the fate, mobility and availability of nutrients. This process also takes into account intensity, quantity and capacity factors which are important for predicting the amount of nutrients required for maximum plant growth. A field study on sorption and availability of potassium (K) in soils sampled from maize and sugar cane growing sites of Sioya, Tabuti and Watoya in Bungoma County was conducted. The purpose of the study was to determine the effect of pH, organic matter and K^+ ion levels on adsorption capacity of the soils. Sampled soils from each site at 0-20 cm depths were air dried, ground and sieved through 2 mm sieve. Jenway pH meter measured soil pH; organic matter was determined by standard method while K^+ ions were determined using flame photometer. Adsorption isotherms were evaluated by equilibrating soils with different K^+ ionic levels in deionized water. The results show that the mean pH levels in the three areas were 6.25, 5.90 and 5.91 while organic matter was 5.1597, 5.4553 and 15.0367, respectively. Although the amount of K^+ adsorbed was similar in the three sites and was found to increase with organic matter and pH, there was a significant difference ($p \leq 0.05$) with these two parameters. The results fitted to both the Langmuir and Freundlich isotherms showing these two models successfully describe the K^+ adsorption process with R^2 values > 0.95 . However, the data fitted better to the Langmuir isotherm, implying sorption process is a surface, homogeneous and monolayer in these soils. Organic matter and liming should be applied to the soils in the study areas in order to increase K^+ adsorption.

Key Words: Sorption, Mobility, Adsorption, Capacity, Organic Matter, Langmuir, Freundlich, Isotherm

INTRODUCTION

Potassium fertilizers have been found to increase yields of food crops in soils. It has been established that increased use of N and P fertilizers accelerates the uptake and deficiency of nutrients like K taken up by plants in large quantities (Jones, 2012). Deficiencies may, therefore, emerge in areas where nutrient gains from weathering of parent materials and mineralization of organic matter is less than losses through crop uptake, leaching, soil erosion and surface runoff. Soil nutrient depletion and declining crop yields are common in sub-Saharan Africa (Smaling *et al.*, 1997).

Despite the importance of K in osmotic regulation, assimilation and translocation of manufactured food to plant's storage organ, its concentration and availability in most soils is unknown (Simonis & Helentsadilas, 2005). It is therefore necessary to establish the availability of K in the soils so as to determine whether or not K fertilization is required. Furthermore, uptake of N-fertilizers and synthesis of protein is aided by K because it is used for adenosine triphosphate (ATP) synthesis (Smaling *et al.*, 1997). K fixation in soils is the transformation of available K forms into unavailable ones. It has a direct effect on K availability and on the degree of fertilizer K uptake by plants. Consequently, the study of K fixation problems in soils is of particular agronomic and practical interest (Simonis & Helentsadilas, 2005). It permits a better understanding of the soil behaviour to the application of fertilizer and it generally contributes to the more effective evaluation of crop needs for K. Hence it is imperative to know the fixation characteristics of soils with a view to making rational recommendations about K-fertilizers. Soils differ in tendencies to fix applied K in forms unavailable to plants and each soil has its fixing capacity for K which must be satisfied before a change in soil solution occurs.

The application of fertilizers and organic manures that contain K results in accumulation of the K reserves, hence an increase in K levels in soils (Stewart *et al.*, 2005). Types of clay minerals present and clay content determines the release, absorption, fixation and leaching behaviour of K in soil. The first fast release of K is primarily from the fine and coarse clay fractions, with a slower rate of release mainly from the coarse clay and fine silt fractions. This is because, release rates of K increase as particle size decreases (Cox & Joern, 1997).

According to William (2008), K uptake in plants is biphasic, involving two processes, low-affinity K^+ uptake and high-affinity K^+ uptake. The low-affinity K^+ uptake can be thought of as a passive influx of K^+ down an electrochemical gradient using specific inward rectifying K channels. The high-affinity K^+ uptake involves an energy-dependent (ATP) inward K^+ pump against an electrochemical gradient usually in combination with an outflow of either H^+ or Na^+ .

The organic content is the ratio, expressed as a percentage, of the mass of organic matter in a given mass of soil to the mass of the dry soil solids. Soil organic constituents may strongly affect the kinetics of soil chemical processes, including K exchange reactions (Wang & Huang, 2001).

The effect of pH on the K adsorption using Langmuir and Freundlich isotherms shows that the amount of adsorbed K increases as pH and initial concentration increase (Mitsios *et al.*, 2008). An adsorption isotherm is a mathematical model that describes the distribution of the adsorbate between liquid and solid phases, based on a set of thermodynamic assumptions related to the heterogeneity/homogeneity of the solid surface, the type of coverage, and the likelihood of interaction between the adsorbate species. The equation parameters of these equilibrium models provide insight into both the sorption mechanism and the surface properties and affinity of the sorbent. Among the widely used adsorption isotherms, only a few have been used to describe adsorption on mesoporous materials (Jovan *et al.*, 2006).

Sorption isotherms describe the relation between the amount of substance that is absorbed by the solid phase of the soil and its equilibrium amount of soil solution and are conducted to determine whether plant nutrients react, fix or make complex with soil. Sorption is the most important chemical process in the soil, which affects the fate and mobility of nutrients in the soil. K^+ exchange isotherm of soil can be established to show sorption of K (Kolahchi & Jalali, 2007) and the amount of K adsorbed is determined by;

$$CK = \frac{C(K_i - K_f)}{\frac{V}{W}} \quad (1)$$

Where ΔK is the change of K^+ in soil solution. Positive K values shows adsorption by the soil solid phase whereas negative values indicate desorption by the soil. CK_i is the initial K^+ concentration added, CK_f is the final equilibrium concentrations of K^+ in solution volume and W is soil mass.

The Freundlich isotherm describes non-ideal sorption on heterogeneous surfaces as well as multilayer sorption (Kolahchi & Jalali, 2007). The empirically derived Freundlich isotherm is defined as shown below;

$$q_e = K_f C_e^{1/n} \quad (2)$$

Where; q_e : amount adsorbed per unit weight of adsorbent at equilibrium (mg/g), (mol/g)

C_e : equilibrium concentration of adsorbate in solution after adsorption (mg/g), (mol/L)

K_f : empirical Freundlich constant or capacity factor (mg/g), (mol/g)

$1/n$: Freundlich exponent

The Freundlich exponent $1/n$ is descriptive of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent. When $1/n = 1$, the isotherm is linear and the system has a constant free energy at all adsorbate concentrations. When $1/n < 1$, the isotherm is concave and adsorbates are bound with weaker and weaker free energies, and when $1/n > 1$, the isotherm is convex and more adsorbate presence in the adsorbent enhancing the free energies for further adsorption (Schwarzenbach, 2003).

The good fit of Freundlich isotherm to an adsorption system implies there is almost no limit to the amount of substance adsorbed and there is a multilayer adsorption. The applicability of the Freundlich equation to a given system is tested by plotting $\log q_e$ against $\log C_e$ from the logarithmic form of Equation 3

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

Such a plot should yield a straight line with intercept equal to $\log K_f$ and slope equal to $1/n$.

Freundlich isotherm, however, is often criticized for lacking a fundamental thermodynamic basis since it does not reduce to Henry's law at low concentrations (Schwarzenbach, 2003).

According to Pal *et al.* (1999) the Freundlich equation for the study of K isotherm in different soils is expressed as shown below;

$$\log \frac{x}{m} = aC^b \quad (4)$$

By rearranging, the equation leads to;

$$\log (x/m) = \log a + b \log C; \quad (5)$$

Where x/m is the mass of K^+ adsorbed per unit mass of soil (mg kg^{-1}), C is the equilibrium solution of K^+ concentration (mg L^{-1}), a and b are constants whose values are obtained from the intercept and slope, respectively.

An alternative equation is the Langmuir; the basis of a definite case and nature of the adsorption process is from solution. The Langmuir adsorption isotherm was developed by assuming that; a fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy, adsorption is reversible, monolayer adsorption occurs and that there are no lateral interactions among the adsorbates (Pal *et al.*, 1999).

It is one of the most widely used adsorption isotherms since it produces appreciable agreement with a wide variety of experimental data. The Langmuir adsorption isotherm is defined as:

$$q_e = \frac{K_L C_e q_o}{1 + K_L C_e} \quad (6)$$

Where; q_e : amount adsorbed per unit weight of adsorbent at equilibrium (mg/g), (mol/g)

C_e : equilibrium concentration of adsorbate in solution after adsorption (mg/g), (mol/L)

q_o : empirical Langmuir constant which represents maximum adsorption capacity (mg/g), (mol/g)

K_L : empirical Langmuir constant (L/mg), (L/mol).

The q_0 represents the total number of surface sites per unit weight of adsorbent. Ideally, q_0 would be equal for all adsorbates. However, q_0 varies between different compounds because of differences in adsorbate sizes. Therefore, it describes the maximum achievable surface concentration of a given compound. The constant K_L , the Langmuir constant, is defined as the equilibrium constant of the adsorption reaction. The K_L implies a constant adsorbate affinity for all surface sites (Schwarzenbach, 2003).

Rearranging the above equation (6) gives,

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0} \quad (7)$$

and plotting of C_e / q_e against C_e gives a straight line with slope $1/q_0$ and intercept $1/q_0 K_L$.

At low sorbate concentrations the Langmuir isotherm effectively reduces to a linear isotherm and thus follows Henry's law. Alternatively, at high sorbate concentrations, it predicts a constant – monolayer – sorption capacity.

The equation is also expressed as;

$$\frac{C}{\frac{x}{m}} = \frac{1}{kb - \frac{C}{b}} \quad (8)$$

This is according to Pal *et al.* (1999) and can be used to study sorption of K in different soils.

Where C is equilibrium solution K concentration (mg L^{-1}), x/m is the mass of K adsorbed per unit mass of soil (mg kg^{-1}), k is the constant related to bonding energy of K to the soil and b is the maximum k adsorption capacity of the soil.

K^+ availability index rating is based on the amount of extractable K^+ and is used to determine crops to be grown. It also shows the type and cost of fertilizer to be used. In order to supply the needs of a crop the soil has to contain more extractable K than the amount taken up since not all exchangeable K^+ is accessible to the roots.

According to Teo *et al.* (1994), soil solution concentration, soil buffer power and the effective diffusion coefficient determines the availability of K. The growth of roots also plays a major role in availability of K as well as soil bulk density (Dolan *et al.*, 1992; Seiffert *et al.*, 1995). The exchangeable K is approximately sufficient for near-maximum yields, when the K content in the soil solution is 5% of the exchangeable K, and approximately 5% of the K requirement of a crop is in solution at one time. In soils with small amounts of micaceous minerals, less preferential bonding to the clay would allow a larger percentage of the K to be in the solution phase. Most clay soil contain significantly large amount of K^+ released yearly from non exchangeable form, minimum application of fertilizer is therefore required in such soils which are ideal for sugarcane growing.

Sustainable maize production requires K. However, farmers seldom use K for maize nutrition due to high cost of K fertilizer, which results in big yield gaps. Hence, the exploration of alternate sources of K nutrition of maize is highly crucial for sustainable maize production. Organic K fertilizer, developed from fruits and vegetable wastes, in enhancing the growth and biomass production of maize has been recommended (Seema *et al.*, 2012). K application does not affect maize growth in soil high in clay content, however, K^+ uptake increases with an increase in K^+ level in soils low in clay contents (Abdul *et al.*, 2005).

Sugarcane requires a soil that provides nutrients, water and anchorage to the roots. The optimum soil pH is about 6.5 but sugarcane can tolerate considerable degree of soil acidity and alkalinity.

In Kenya, there are 3 sugar belts namely the Nyando, the Western sugar belt and the South Nyanza sugar zone (Kenya Sugar Board, 2003). The sugar industry in Kenya has struggled for many years for various reasons (Njue, 1993); the most common is poor farm management which has led to a serious increase in poverty.

MATERIALS AND METHODS

The areas under study were Sioya, Tabuti and Watoya in Bungoma County that practice sugar cane and maize farming with application of fertilisers to improve crop production. A field study was conducted in these areas to assess the sorption isotherm based soil solution. Random soil samples from each area were collected at 0-20 cm depth and mixed to obtain respective composite samples which were put in well labeled polythene papers indicating time of sampling, name of the farm and the region. The samples were then air dried, ground, passed through a 2 mm sieve and analyzed for pH, organic matter and adsorption isotherms in the laboratory.

A paste of 10 g of soil was prepared by adding distilled water to the soil in a beaker, then stirred with a glass rod and left to stand for ten minutes.

Jenway 350 pH meter was used to determine the pH of saturated soil paste with a glass rod. Buffer solutions of pH 7.0 and 9.2 were used as standards. The glass rod of the pH meter was cleaned with distilled water before immersing in the next sample.

Soil organic matter was measured with ASTM D 2974 – Standard Test Method for organic matter as peat and organic soils. An empty, clean, dry crucible was weighed. An amount of 2 g of dry soil was added and placed in a muffle furnace and the temperature gradually increased to 440°C. It was then left in the furnace for 24 hours then later removed and allowed to cool to room temperature. The mass of the crucible containing the burned soil was recorded. The difference in mass was used to calculate the % organic matter using the formula below:

Percentage organic matter content,

$$\% MO = \frac{M_O}{M_D} \times 100$$

Where OM is organic matter, M_O is mass of organic matter and M_D is mass of the dry soil.

A 0.9500 g of KCl, analar grade from sigma Aldrich, was weighed and diluted with 500 ml demonized water in a 500 ml volumetric flask. This solution was approximately 500 ppm. Standard solutions of K that contained 0-15 ppm were prepared using serial dilutions. The standards were then taken to a flame photometer where the intensity of K was measured. The values were used to construct a curve that produced a straight line and the equation was used to calculate the concentration of K^+ from soils which were subjected to adsorption studies. The flame photometer used was; Sherwood Flame photometer, 410 from Shimadzu with an optical filter of potassium at 768 nm.

For the construction of K adsorption isotherm, 2.5 g of soil samples were equilibrated with different K^+ concentration levels (0, 25, 50, 100, 150, 200 and 250 mg L^{-1}) in 25 ml solution de- ionized water at $25 \pm 1^\circ C$. Samples were put into 50 ml tubes followed by shaking for 24 hours after which time it was assumed that equilibrium had occurred. The samples were then centrifuged for thirty minutes and the supernatant collected for the analysis of K with an aim of constructing K adsorption isotherms. Sample determination was done in triplicate. The amount of K adsorbed was determined by the equation 1. The K adsorption data were fitted into the following adsorption equations 5 and 8 to evaluate the constants.

Data were subjected to analysis of variance (ANOVA). Factorial two design was used with site and concentration. Means were separated using least significance differences (LSD).

RESULTS AND DISCUSSIONS

Table 1 shows soil pH in the study areas ranged from 5.90 - 6.25 while organic matter was relatively high, ranging from 5.1597% - 15.0367%, which reflects high levels of applied organic matter, most likely coupled with low rates of mineralization.

Table 1. pH and organic matter of soils selected in the three different sampling regions

Sampling Region	pH	% Organic matter
Sioya	6.25	5.1597
Tabuti	5.90	5.4553
Watoya	5.91	15.0367

Soil pH in these study areas were acidic with Sioya recording a higher value which could possibly be due to the repeated use of fertilisers to increase crop production (Jensen,

2010). The —ideall soil pH is close to neutral, and neutral soils are considered to fall within a range from a slightly acidic pH of 6.5 to slightly alkaline pH of 7.5. It has been determined that most plant nutrients are optimally available to plants within this 6.5 to 7.5 pH range, plus this range of pH is generally very compatible to plant root growth. Such acidic soils should therefore have the pH raised from around 5.9 up to 6.5 or approaching neutrality.

Tables 2 - 4 show adsorbed K levels in the different sampling places

Table 2. Concentration of adsorbed K in soil from Sioya

Spiked Conc.(ppm)	Adsorbed conc. (ppm) 1 st trial	Adsorbed conc. (ppm) 2 nd trial	Adsorbed conc. (ppm) 3 rd trial
0	0	0	0
25	24.40417	23.8083	24.1063
50	48.51043	47.3188	47.81529
100	95.53128	94.9345	94.73684
150	144.8361	144.9355	144.5382
200	194.3396	193.7438	192.3535
250	237.1897	237.3883	237.0904

Table 3. Concentration of adsorbed K in soil from Tabuti

Spiked Conc. (ppm)	Adsorbed conc.(ppm) 1 st trial	Adsorbed conc. (ppm) 2 nd trial	Adsorbed conc. (ppm) 3 rd trial
0	0	0	0
25			
	24.40417	24.70209	24.40417
50	49.10626	48.60973	48.60973
100	97.02085	96.82224	96.42502
150	144.3396	144.6375	144.6375
200	192.4528	192.8500	192.2542
250	236.7925	236.2959	236.9911

Table 4. Concentration of adsorbed K in soil from Watoya

Spiked Conc. (ppm)	Adsorbed conc. (ppm) 1 st trial	Adsorbed conc. (ppm) 2 nd trial	Adsorbed Conc. (ppm) 3 rd trial
0	0	0	0
25	24.20556	24.40417	24.40417
50	48.51043	48.90765	49.00695
100	97.21946	97.81529	98.11321
150	145.9285	146.425	145.6306
200	195.3327	194.6375	195.0348
250	238.0834	238.7786	238.0834

Similar results were obtained and the amount of K^+ adsorbed increased with the spiked concentration. However, percentage organic matter for both Sioya and Tabuti was similar but Watoya had almost three times more organic matter. This could be possibly due to higher sugar cane farming in Watoya that leaves a lot of sugar cane remains on farms as organic matter since the primary source of organic matter contained in soil is vegetal (Brady & Weil, 1999; Périé & Ouimet, 2008).

Fitting the data into K sorption isotherms, the respective Langmuir and Freundlich adsorption isotherms for the three different sites in the study area were obtained. Figures 1-3 show the Langmuir adsorption model plots.

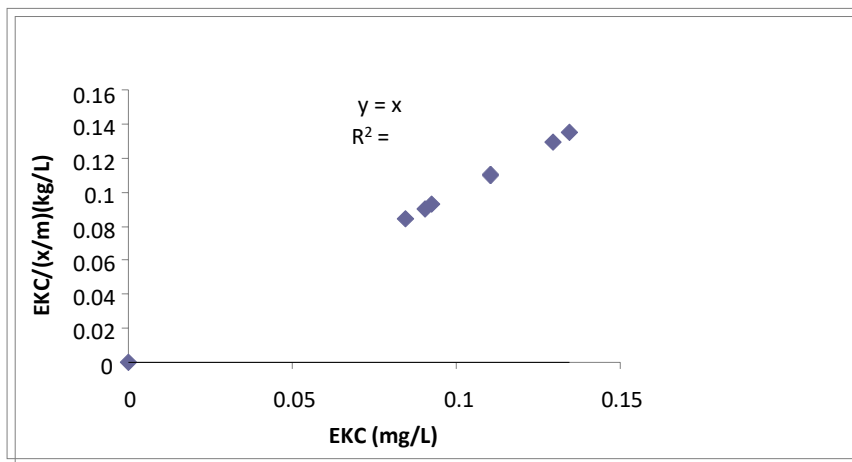


Figure 1. Langmuir adsorption isotherm of soil from Sioya

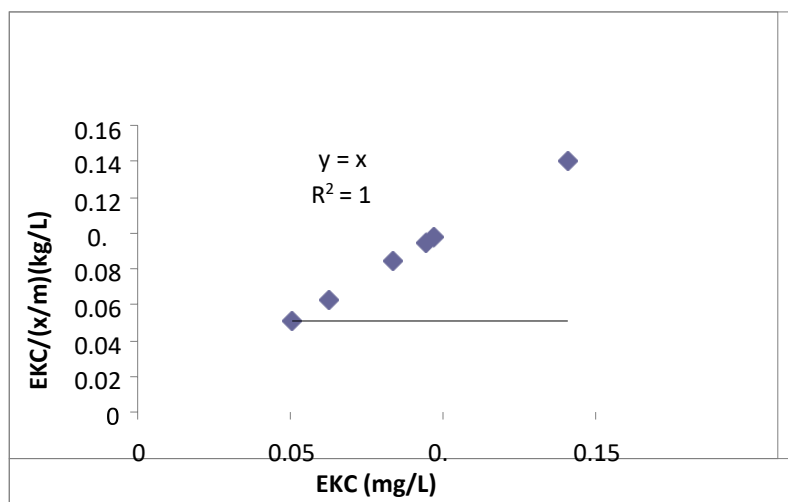


Figure 2. Langmuir adsorption isotherm of soil from Tabuti

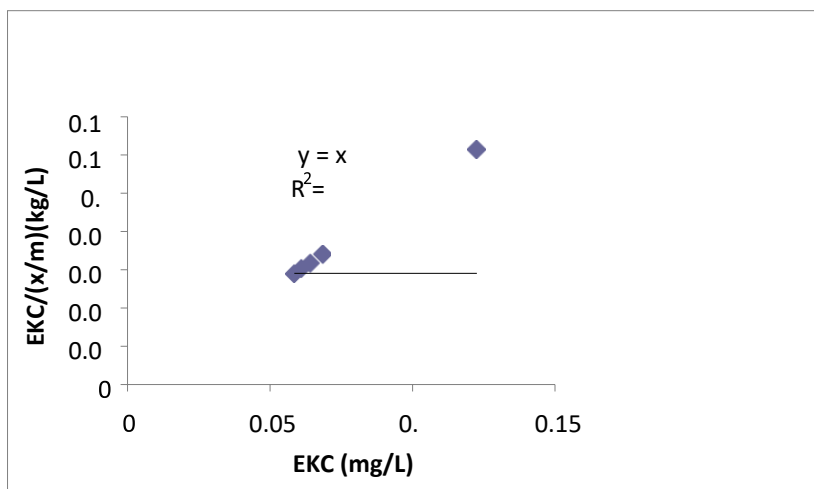


Figure 3. Langmuir adsorption isotherm of soil from Watoya

The Figures 4-6 show log of K equilibrium concentration plotted against log of adsorbed K.

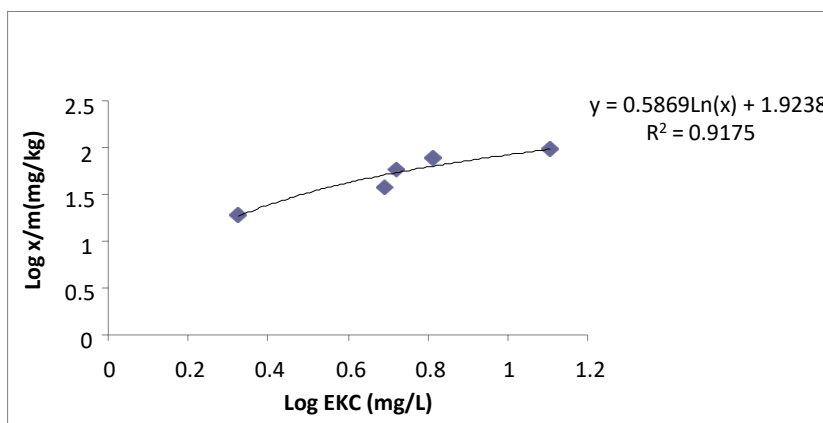


Figure 4. Freundlich adsorption isotherm of soil from Sioya

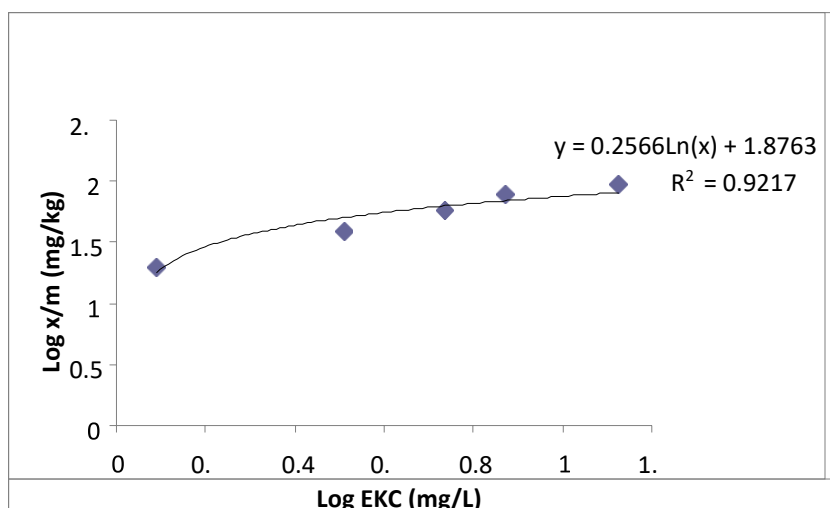


Figure 5: Freundlich adsorption isotherm of soil from Tabuti

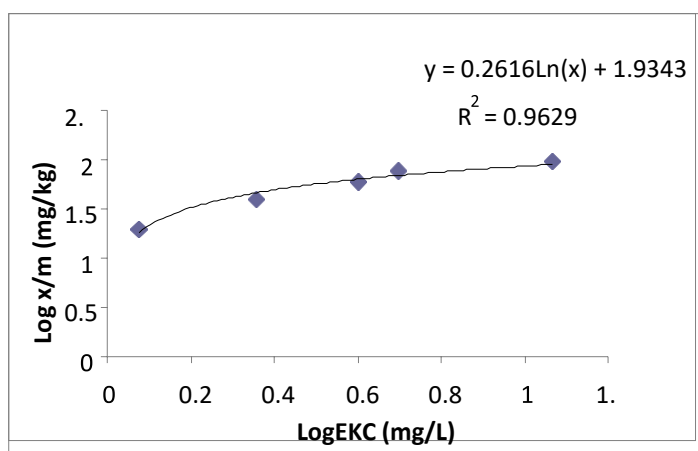


Figure 6: Freundlich adsorption isotherm of soil from Watoya

The initial critical level of soil K determines the fate of added K as fertilizer. Further the concentration of K in soil solution depends upon the rate of K removal by plants and the rapidity at which it can be desorbed from the adsorbed phase. Thus by use of adsorption isotherm technique, K concentration provides a better index of K availability. In the Freundlich isotherm, log of K equilibrium concentration was plotted against log of adsorbed K and a linear relationship was obtained for different samples from the three areas (Figures 1-6). This could be due to the Freundlich model assuming unlimited sorption sites of heterogeneous medium (Schwarzenbach, 2003).

In the Langmuir isotherm, a highly linear relationship was obtained and fitted well to K sorption data with R^2 value of 1 (comparing both plots for each area, for instance, Figures 1 and 4). The Langmuir model assumes homogeneity of sorption sites with complete monolayer adsorption of solutes and this is in agreement with results obtained by (Dufey & Delvaux, 1989; Pal *et al.*, 1999).

CONCLUSIONS

The following can be concluded from this study:

1. Soil pH in all the sites studied was slightly acidic, but a bit favourable for maize and sugarcane growth.
2. Langmuir model was best fitted to K sorption data of soil as was evident from R^2 values for Langmuir being 1 from all the three sites while Freundlich was 0.9, hence monolayer mechanism was more prevalent for K adsorption.
3. Soil organic matter was high in all the sites with Watoya being the highest implying organic matter is left on fields to decay rather than burn it.

RECOMMENDATIONS

To avoid making soils acidic, future liming and use of neutral fertilizers should be encouraged.

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BIO-DATA

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