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Full Length Research Paper

Potassium Release Kinetics as Influenced by Time and Parent Materials in Parts of Akwa Ibom State, Nigeria

Umoh, F. O.*, Uduak, I. G and Ekanem, C. E.

Department of Soil Science, Akwa Ibom State University, Mkpat Enin, Nigeria.
*Corresponding Author E-mail: florenceumoh@aksu.edu.ng Tel: 08080692159

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ABSTRACT: The goal of the study was to evaluate potassium (K) release in soils derived from three parent materials (shale, sandstone, and alluvium soils), and to identify the best-fitting equations to describe K release to 0.01M $CaCl_2$ extraction over the course of 1–128 hours at various concentrations of added K ranging from (0, 50, 100, 150, 200mgL^{-1}K). Two gram (2g) soil suspended in 20 ml of 0.01M $CaCl_2$ was shaken at 25^{0}C on a reciprocating shaker and subsequently centrifuged. The K concentration in the supernatant was determined. Potassium release with time was modeled using zero and first order equations. The results revealed a sharp increase in K release from 0mgL^{-1} to 50mgL^{-1} in the soils. The highest concentration was found in alluvial soil, while the lowest concentration was found in shale soil. In zero order equations, the trends were Alluvium 146.3 > sand stone 108 > shale 72.27 mgkg-1 and in first order equations, Alluvium 5.308 > sand stone 4.983 > shale 4.557mgkg-1. The concentration of K released in the soil increased as time passed in the soils. The results also revealed that the zero order equation adequately described the K release reactions, with the highest mean R^2 values of 0.997.

Keywords: Potassium, parent material, kinetics released, first order equation, zero order equation, texture

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INTRODUCTION

Potassium (K) is a macronutrient element in soil that serves many purposes for plants. It is essential for regulating stomatal function, controlling water relations, influencing the water balance of the plant system, and ensuring agronomic productivity and sustainability (Srinivasarao *et al*., 1994) As a result, severe K depletion in soils caused by long-term continuous cropping without supplemental K results in minimal exchangeable K. The crop(s)' K requirement is met by the reserve K fraction (Srinivasarao *et al*., 1994; Taiwo *et al*., 2018). Negative K balance occurs in soil under intensive cropping due to low external input and large crop removal, resulting in depletion of non-exchangeable or reserve K. (Taiwo *et al*., 2018). Most soils have potassium (K) fixation, emphasizing the importance of the nutrient addition as a fertilizer nutrient and its availability to plants. Many soil factors influence soil K release, including texture, organic matter content, pH, and the amount and type of clay. (Umoh *et al*., 2018) and Umoh *et al*. (2017) found that aluminum (A1) in soil interlayers of 2:1 and mixed layered silicates has a strong affinity for K. Umoh *et al*. (2014) found a high affinity for P sorption in these soils, attributing it to the presence of Fe and Al oxide. This will invariably alter K exchange reactions and crop availability in highly weathered tropic soils. However, specific K adsorption sites in soils have resulted in the nutrient being strongly adsorbed on A1, Ca, or Mg in tropical soils (Taiwo *et al*. 2018). As a result of this, nutrient cycling and the residual effect of K fertilization on soils improve nutrient stability. The majority of soils in Nigeria's sub-humid zone have a high ability to fix applied K (Tening *et al*.,1995); however, Taiwo *et al*. (2018) reported that K release in soils could be attributed to soil and clay type. It has been proven that an exchange between the K and hydrated cations causes K release from micaceous clays like muscovite and biotite. It might also be due to mineral dissolution, which happens before weathering products are formed.

The stability of these soil minerals in soil environments is the basis for their significance in K chemistry (Spark, 2000). The level of K content determines whether there are significant amounts of K in the interlayer lattice. However, a number of studies, including Agyenim-Boateng *et al*. (2006) and Srinivasarao *et al*. (1999), claimed that the addition of organic manures could promote biological activity.

This is especially important in Nigeria, where soils are generally deficient in K and large amounts of animal manure produced are regarded as waste products from the livestock industry. For optimal crop nutrition, the replenishment of a K-depleted soil solution is primarily influenced by the release of K from clay minerals and organic matter. As a result, for maximum crop growth, soil solution and exchangeable K must be continuously replenished with K through the release of non-exchangeable K or the addition of K fertilizers.

Kinetic equations are intended to provide an index of reaction equilibrium with time and to reveal the mechanism involved in the reaction. How soil K is released into solution and the rate at which the element is released are critical to plant nutrient availability and crop production. To describe the kinetics of K release in soils, numerous equations have been developed. Srinivasarao *et al*. (2006), Samadi *et al*. (2010), and Hosseinpur *et al*. (2012) used parabolic diffusion, power functions, and simplified Elovich equations to successfully describe K release from ten calcareous soils.

Hosseinpur and Safari (2007) investigated the relationship between kinetic equation rate constants and garlic indices. They discovered that the Elovich and Zero-order equations' release rate constants were significantly correlated with garlic indices. The release characteristics based on extraction methods are used to estimate soil K availability.

Furthermore, more information on the K release characteristics of alluvium, shale, and sand stone soils is required. As a result, the study's goal is to use different equations to assess K release from soils with varying K status as influenced by time.

MATERIALS AND METHODS

Study area

The study was conducted in selected locations representing different parent materials in Akwa Ibom State which lies between latitude 4^{o} 32 and 5^{o} 33N′ and longitudes 7^{o}25′ and 8^{o}25E′. The state is bounded with Abia State in the North, Cross River State in the Southeast and the Atlantic Ocean in the South. It has a land-mass of 8412 km ^{2} and a shore line of 129 km^{2} long encompassing Akwa Ibom River Basin, the eastern part of lower Cross River Basin and half of the Imo River estuary (Table 1 and Figure 1).

Field sampling and samples preparation

The surface bulk soil samples were collected from three locations on the study area based on their parent materials, 0 – 20cm depth with soil augers shown in (Table 1). These samples were air dried, crushed and passed through a 2mm mesh sieve preparatory to routine analysis and incubation studies then use for physicochemical analysis and potassium release study.

Physicochemical analysis

Particle size distribution was determined by the Bouyoucos hydrometer method using sodium hexametaphosphate as dispersing agent. (Klute, 1986). The soil pH was measured in water at the soil to water ratio of 1:2.5 using a glass electrode pH meter. (Udo *et al.,* 2009). Electrical Conductivity was measured in the extract from 1:2.5 soils: Water suspension using a conductivity bridge as described by Udo *et al.,* (2009). Soil organic carbon was determined by wet oxidation method as described by Spark (2000). The value was multiply with factors of 1.72 to obtained organic matter. Total nitrogen was determined by micro Kjedahi method as described by Udo *et al.,* (2009). Available P in the soil was determined by Murphy and Rilay method as described by Udoh *et al.,* (2009) after extraction by Bray P-^{1} extractant. The exchangeable cation in the soil was extracted using in NH_4 OAC K and Na in the extracts was measured using flame photometry while Mg and Ca were determined by atomic absorption spectrophotometry. Effective Cation Exchangeable Capacity (ECEC) was obtained by the summation of the exchangeable cation and exchangeable acidity as described by Udo *et al.,* (2009). Base Saturation (%) was calculated by the sum of exchange cation x 100/ECEC.

Potassium kinetic release studied

Two (2) grams of <2mm sieved soils were weighed into

Table 1: Information on locations of the selected soils.

Soil	Location	Vegetable Cover	Land Use Type	Parent Material	Coordinate
1.	Mbiabong Ikot Udo	Tropical Rain Forest	Cassavas, Maize,	Shale	$5^0$24'N 7^o 44' E
2.	Nto Ndang	Tropical Rain Forest	Cassavas, Yam	Sandstone	$5^0$24'N $7^0$58'E
3.	Uta Ewa	Mangrove	Timber, Oil Palm	Alluvium	$4^0$59 'N $7^0$57'E

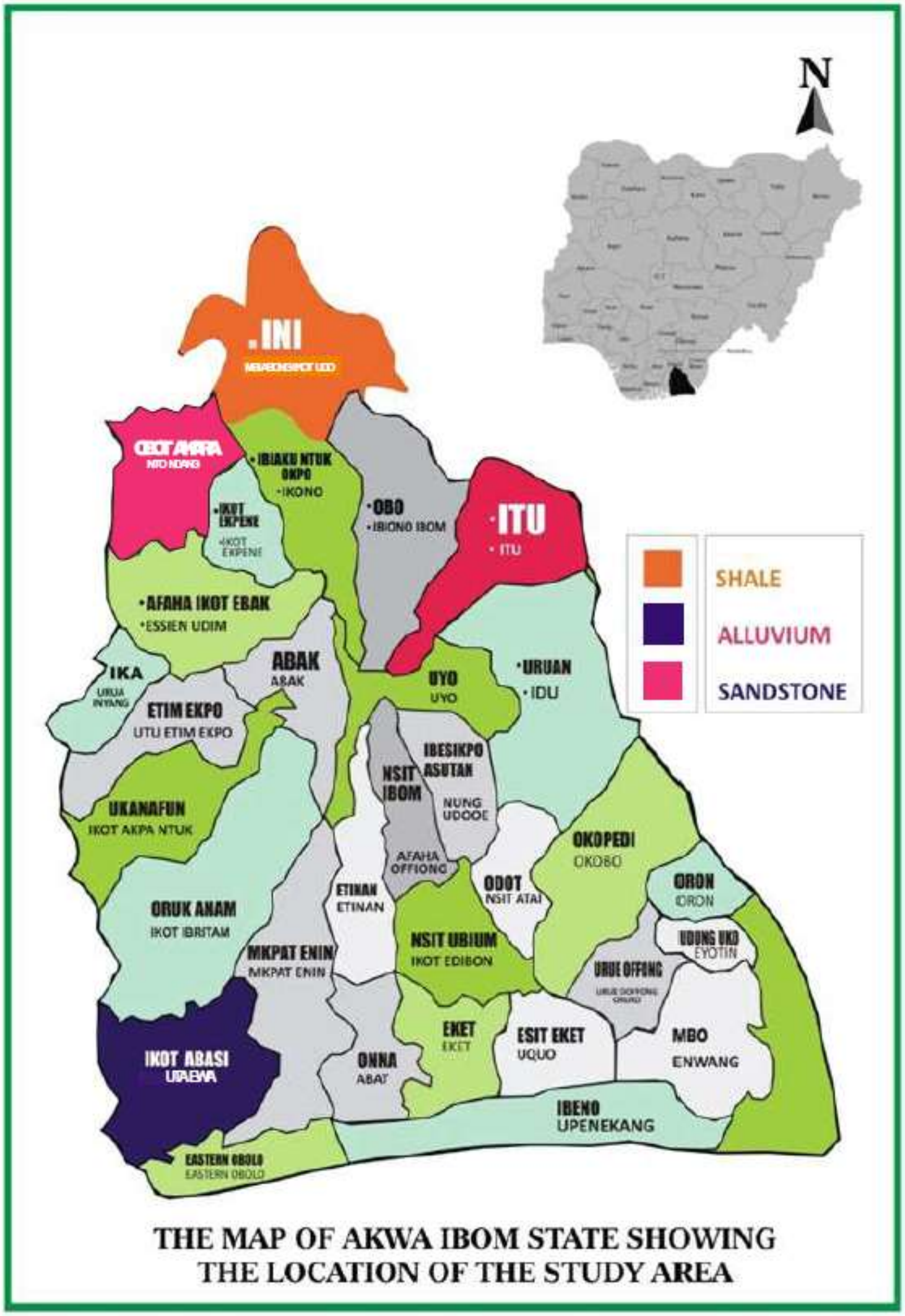

Figure 1: A map of the study area showing soil sampling locations

Table 2: Kinetic equations used in the study.

Kinetic Equation	Expression Form
Zero order reaction	$Ko – K_t = a – Kt$
First – order reaction	$In (Ko - K_t) = a –K_l$

Ko – Amount of K (mg/kg) released at equilibrium, Kt – Amount of K (mg/kg) released at time t (h). a and b, are – Intercept, k,b – Indices of K release rates. Source: Hosseinpur *et al. (*2012).

separate 50ml centrifuge tubes containing 10 ml of 0.05m $CaCl_2$ and stock K solution of $1000Kml^{-1}$ Kcl prepared were added at varying concentration of 0, 50, 100, 150 and 200mg/litres; and allowed to equilibrate by shaking daily for 30 minutes at different time intervals of 1, 2, 4, 8, 16, 32, 64 and 128 h. At the end of the equilibrium periods, the Supernatants were separated by centrifugation and extraction was repeated by adding another 10ml $CaCl_2$. The potassium extracted was measured using flame photometry and potassium released with time was fitted to the two equations in (Table 2).

Experimental design

The soil sample from the three (3) parent material was treated with five different rates of K solution using (KCl) as follows: 0, 50, 100, 150, 200mg/L. This was extracted for varying periods of 1, 2, 4, 8, 16, 32, 64 and 128 hours, making up of 120 samples replicated 3 times and total of 360 samples were generated. The treatment combination was factorial experiments fitted into a randomized complete block design (RCBD), with 3 parent materials, 5 rates of K, 8 times of extraction and 3 replications.

Statistical analysis

The linear forms of the kinetic equations (Table 2) were fitted to the experimental data; least square regression analysis was used to ascertain the equation that best described K released in these soils. The goodness of fit was determined by the coefficient of determination (R^2)

RESULTS AND DISCUSSION

Physical and chemical properties of the studied soil

The physical and chemical properties of the soils are presented in (Table 3). The sandstone derived soil had the highest sand content (74.2%) while shale derived soil had the least sand content (56.4%). The sandstone had the highest silt (12.4%) and least clay content (13.4%). While shale had least silt content (10.2%) and highest clay content (33.4%). The variation in percentage sand, silt and clay fractions reflects the differences in the parent materials. The texture of a soil will affect the water, nutrient retention and nutrient release in soils (Umoh *et al.* 2018). The soil pH in water ranged from 5.0 to 5.4 with a mean of 5.2 respectively. The ranged is considered moderately acidic which is satisfactory for crop production (Okalebo *et al*., 2002). The electrical conductivity (EC) is low, ranged from 0.02 to 0.08 ds m^1, indicating that the soil is salt free. Organic matter contents of the soils were below the critical level of (20g kg^{-1}) proposed by Aduayi *et al*. (2002) for soils of Eastern Nigeria. The Total Nitrogen was low due to poor drainage system. Available phosphorous were below the critical level except sandy soil with value 22.0 which fall within the medium range of 20-30mgkg for soils of eastern Nigeria (Aduayi *et al*. 2002). The order of abundance of exchangeable cation were Ca > Mg>K>Na and were adequate in the soil (Okalebo *et al*., 2002). Effective cation exchange capacity (ECEC) was below the critical level of $12cmolKg^{-1}$. The soil recorded high base saturation. The value rages from 65.2 (Alluvium) 79.8 (Sandstone) 86.6 (Shale).

Potassium release kinetics of the soils

The Potassium K release from soils of three parent materials obtained from the relationship between K extracted from the soils by 0.0lm $CaCl_2$ at varying concentration of K added and at different extraction time (h) is presented in figures 2. The letters A to E denote the amount of K added to the soil, as a=0, b=50, c=100, d=150 and e=$200mgl^{-1}K$. The figures are plots of the concentration of K release and extraction time (h) ranging from 1 to 128 hours. From (Figure 2a) where no K was added, shown a wide variation in the cumulative K released between soils. The highest concentration of K release was observed in alluvium while shale soils was lowest, the trend were Alluvium > sand stone > shale parent materials. The concentration of K release in the soil increased with increasing rates of K added within the time of extraction. The differences in K release among the soil could be attributed to native K level in the parent materials in which the soil was formed and could also attributed to the amount of clay and silt present in the soil as shown in (Table 3). Umoh *et al*., (2018) reported that soil texture has a great effect on released of potassium

Table 3: Physicochemical properties of the Soils.

Soil Properties	Unit	Sand Stone	Alluvium	Shale
Sand	%	74.2	64.8	56.4
Silt	%	12.4	13.0	10.2
Clay	%	13.4	22.2	33.4
Texture	--	SL	SCL	SC
pH (H_2O)	--	5.0	5.4	5.2
pH (Kcl)	--	4.8	4.9	5.0
EC	ds m^{-1}	0.07	0.08	0.02
OM	g/kg	4.8	4.2	3.4
Total N	g/kg	0.2	0.3	0.4
AV.P	(mg/kg)	22.0	10.5	8.7
Ex. Ca	Cmolkg$^-$	6.0	3.8	4.7
Mg^1	Cmolkg$^-$	2.6	1.5	3.0
Na	Cmolkg$^-$	0.05	0.08	0.08
K	Cmolkg$^-$	0.1	0.2	0.3
EA	Cmolkg$^-$	2.1	3.0	1.25
ECEC	Cmolkg$^-$	11.07	8.6	9.3
Basic Saturation	%	79.8	65.2	86.6

OM – Organic Matter, Av.P - Available Phosphorus, EA - Exchangeable acidity, ECEC – Effective Cation Exchange Capacity, SL – Sandy Loam, SCL - Sandy Clay.

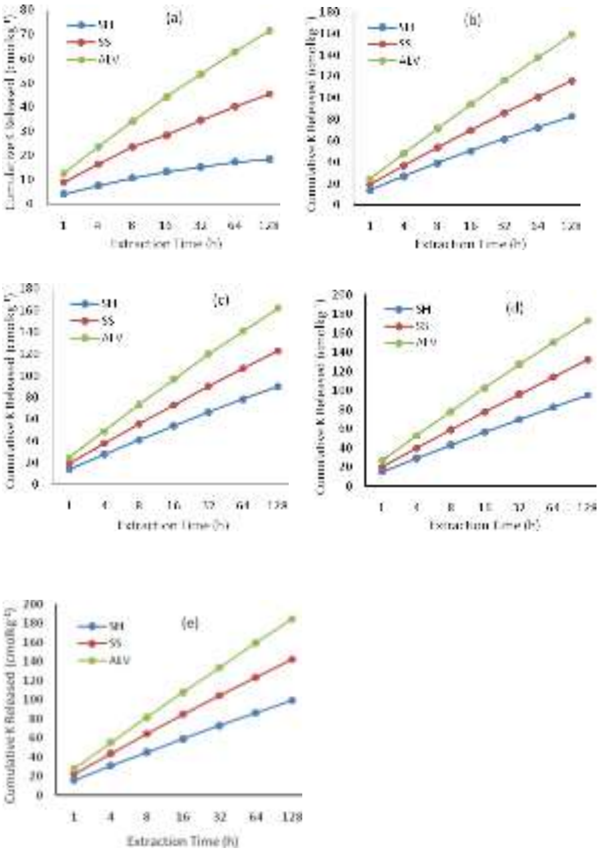

Figure 2: K release from soils of three parent materials at varying concentration of K, (a) 0 (b) 50 (c) 100 (d) 150 and (e) 200mgL^{-1} extracted by 0.01m Cacl$_2$ in Alluvium (AV), Sandstone (SS), and (SH) as influenced by time and parent material.

Table 4: Slope, intercept and Coefficient of determination for Zero order reaction of K release from soils of three parent materials.

	0mgl^{-1}	**50 mgl^{-1}**	**100 mgl^{-1}**	**150 mgl^{-1}**	**200 mgl^{-1}**	**Mean**
			(Shale)			
	0	50	100	150	200	Mean
a	-2.3925	-11.42	-12.658	-13.356	-13.949	10.755
k	15.645	78.781	87.56	92.586	06.777	72.270
R^2	0.975^{**}	0.998^{**}	0.999^{**}	0.999^{**}	0.999^{**}	0.994^{**}
			(Sand Stone)			
a	-6.0245	-16.161	-17.209	-18.618	-19.995	15.602
k	41.297	111.71	119.29	129.54	138.67	108.102
R^2	0.996^{**}	0.999^{**}	0.999^{**}	0.999^{**}	0.999^{**}	0.998^{**}
			(Alluvium)			
a	-9.7991	-22.435	-22.919	-24.353	-26.022	-22.106
k	67.514	155.78	158.32	168.59	181.27	146.295
R^2	0.999^{**}	0.999^{**}	0.999^{**}	0.999^{**}	0.999^{**}	0.999^{**}

All coefficients of determination (R^2) are significant at the 0.05 level. ($^{**}R^2$ is highly significant ($P<0.01$) a – intercept of equations, k or b – release rate constant of the equations

and sand soils exhibited high K released in the soil than high clay content. The pattern of successive extraction of K from soils at differences concentration of K added is presented in Figure 1 (b-e). The concentration of K released after extraction time (h) differ greatly among soils. The released within one hour was significantly lower than the concentration observed at 128 hours. This is an indication that a considerable portion of non-exchangeable K was remaining in the soil, also showed that unreleased non-exchangeable K will be released with time. This agreed with work of Dhaliwal *et al.* (2006) who observe increased in K release with increasing time but differs from the report of Dalta (1993) who observed equilibrium in the 8 hours of extraction after 128 hours. The amount of K release in the studied soil increase with increasing rates of K added. The amount releases at 0mg/L of K, where no K was added was significantly lower than one where K where added as shown in (Figure 2a -e). The result showed that the release was rapid from 0 to 50mgL^{-1}K added, these was observed across the figures and from 50mgL^{-1}K to 200mgL^{-1}K did not record such sharp increase in K releases. These indicate that proportions of the solution K were adsorbed on the external surfaces of clay that cause the slow release of K. Among the parent materials, alluvium soil releases the highest amount of K while shale soil releases the lowest concentration across the varying concentration of K added. The trends were alluvium >sandstone >shale. The difference could be attributed to nature of parent materials in which the soil is form as well as the amount of clay and silt content (Table 3). The differences in the amount of K release from the soils could be attributed to the nature of K- bearing minerals which may include crystal structure, chemical composition, degrees of depletion layer charge alteration and soil environment. The highest concentration of K release in Alluvium could be that the soil is not well developed (young soil) with low clay content, low charge density that easy the release while shale is well developed with layer silicate which could trapped the element. The lower K release in shale soil could be attributed to the higher clay content as shown in table 1, the result indicated that more K was highly retained in shale soils. This agreed with finding of Mahdi and Ranga, (2011) who reported that the soil properties (silt, clay and sand fractions) affect the release of K in soils. The release of non-exchangeable K was an exchange reaction when this slow exchange occurs; the K first enters the unexpanded interlayer without its hydration Hosseinpur *et al.,* (2012), reported that the interlayer will expand upon hydration of these ions K allowing fixed or trapped (K) to hydrate and slowly diffuse to exchange sites on outer part of the clay particle. The release in sandstone could be attributed to the sandy nature of that parent material (Table 1). This showed that light textured soils are more prone to high nutrient released.

Potassium k release by kinetic equations

The two mathematical equations were used in assessing the release of K from the soils as presented in (Table 2). Potassium release with time (t) =K_1 and K_0, a and b are constants, which was calculated from the slope and the intercept with y-axis of the plot Vs x axis and, time respectively. Results of the statistical analysis obtained from the graphs which were fitted between the equations and experimental data reflected by the coefficients of determination (R^2). The zero order reaction result is presented in (Table 4). Amount of K release in shale soil ranged from 15.645 to 96.777 mg kg^{-1} (mean 72.270 mg kg^{-1}), sandstone (ss) ranged from 41.297 to 138.67 mgkg^{-1} (mean of 108.102 mg kg^{-1}) and Alluvium ranged from

Table 5: Slope, intercept and coefficient of determination for first order reaction of K release from soil of three parent materials.

	0mgl^{-1}	**50 mgl^{-1}**	**100 mgl^{-1}**	**150 mgl^{-1}**	**200 mgl^{-1}**	**Mean**
			(Shale)			
k	-0.4725	-0.3626	-0.3603	-0.3579	-0.3551	-0.382
a	3.3327	4.7494	4.8529	4.9053	4.9053	4.557
R^2	0.943^{xx}	0.945^{**}	0.941^{**}	0.939^{**}	0.941^{**}	0.942
			(Sand Stone)			
k	-0.3746	-0.3615	-0.3569	-0.3506	-0.3558	-0.360
a	4.1261	5.0989	5.1563	5.2269	5.3043	4.983
R^2	0.940^{xx}	0.941^{**}	0.941^{**}	0.941^{**}	0.941^{**}	0.941
			(Alluvium)			
k	-0.3658	-0.3542	-0.3622	-0.3593	-0.3501	-0.358
a	4.6019	5.4183	5.4482	5.5072	5.5632	5.308
R^2	0.944^{**}	0.940^{**}	0.943^{**}	0.940^{**}	0.938^{**}	0.941

$^{**}R_2$ is highly significant (P<0.01). a – intercept of equations, k or b – release rate constant of the equations

67.514 to 181.27 mg kg^{-1} (mean of 146.30 mg kg^{-1}). The mean R^2 value range from 0.999 in (Alluvium)> 0.998 (sandstone)>0.994 (shale) soil and there was a significant difference (P<0.01) between soils in K released concentration. This difference was highest for Alluvium soil and lowest for shale soil. This result is strongly affirmed with the highest R^2 0.999 recorded in Alluvium soil. The differences among soils in K release could be attributed to the soil properties (Table 1) and fertility statues of the soils. First order reaction of K release in soils is presented in (Table 5). Amount of K release in shale soil ranged from 3.3327 to 4.9435mg kg^{-1} (mean 4.557 mg kg^{-1}), sandstone ranged from 4.1261 to 5.3043mg kg^{-1} (mean 4.983 mg kg^{-1}), and Alluvium soil ranged from 4.6019 to 5.5632 mg kg^{-1} (mean 5.5631 mg kg^{-1}). The mean R^2 values ranged from 0.941 to 0.942 (mean 0.947) and was not significantly difference (P<0.01) within the soils indicating that released of K was not affected by time respective of the parent material.

Generally, among the three parent material studied, highest amount of K release was observed in Alluvium soils while lowest recorded in shale soils. The highest release of K in Alluvium could be attributed to negative K level in the parent material, and amount of clay present and the lowest release observed in Shale soil could be attributed to the soil properties, such as amount of clay. The difference in the amount of K release from the studies soils ranged from Alluvium > Sandstone >Shale, the differences could be attributed to the nature of K-bearing minerals, which may include crystal structure, chemical composition and soil environment (Taiwo *et al*., 2018), The mathematical equations that best described the release of K at all concentration using R^2 is the zero order equation with highest R^2 value of 0.999.

Conclusion and Recommendation

The result indicated that sandstone had the highest sand content while shale had the lowest sand content, the trends were; Sandstone 74.2% > Alluvium 65.8%>Shale 56.4%. The trend for silt were Alluvium 13.0% > Sandstone 12.4% > Shale 11.2 %, while clay content ranged from Shale 33.4%> Alluvium 22.2 >Sandstone13%. The pH value range from 5.0 to 5.4 and is moderately acidic. Organic matter was low in the soils. The result shows that the soil was low in nutrient. Alluvium soil recorded the highest cumulative K released while Shale had the lowest release. The result also reveals that the amount of K release increased with increasing time of extraction. 128 hours being the highest; and amount of K release increase with increasing amount added. Omgl^{-1}being the lowest and 200 mg^{1} being the highest concentrations. From the two equation used, zero order equation best described the K released power with the highest R^2 values of 0.999, compared to the first order equation with the lowest R^2 values 0.994. The zero order equation is recommended to be used in describing the K Release Kinetics in the studied soils.

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