



Research article

Potassium adsorption capacity and desorption kinetics in soils of Qenberenaweti sub-watershed, central highlands of Ethiopia

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ABSTRACT

Determining the supply and uptake of K nutrient and the dynamic equilibrium (adsorption-desorption) reactions among the K forms in the soils are not commonly addressed in the highlands of Ethiopia. A study was therefore initiated to determine the adsorption capacity of the exchangeable K and the release kinetics of the non-exchangeable K in the soils of the Qenberenaweti Sub-watershed. Twelve disturbed surface (0–20 cm) soil sub-samples were collected from every farmland which was representative of each pre-identified soil type (Vertic Cambisols, Pellic Vertisols, Pisoplinthic Luvisols, Relictistagnic Cambisols, Pisoplinthic Cambisols, and Plinthofractic Cambisols). A composite sample was made in duplicate for the determination of K adsorption capacity and desorption kinetics per soil type. The mean maximum (69.47 ± 4.31 %) and minimum (56.16 ± 6.04 %) K adsorption rates were obtained from the Plinthofractic Cambisols and Vertic Cambisols, respectively. Among the tested isotherm models, the goodness of the Freundlich was better fit the data of all experimental soils; hence, a modified equation of this model ($q_e = aCe^{b/a}$) could be used to describe the theoretical doses of K fertilizers required to develop K levels in soil solutions. The highest constant K releases from the Plinthofractic Cambisols (47 mg kg^{-1}), Pisiopllintic Cambisols (46 mg kg^{-1}), and Pisoplinthic Luvisols (44 mg kg^{-1}) were attained at the 9th extraction. In comparison, it was noticed at the 7th and 11th extractions of the Relictistagnic Cambisols (45 mg kg^{-1}) and both Pellic Vertisols (48 mg kg^{-1}) and Vertic Cambisols (42 mg kg^{-1}), respectively. The equation of power function was the best to successfully describe the released K^+ from all the experimental soils. Eventually, determining the adsorption capacity and release kinetics of K at a site-specific level helps to know the relative potential of the soils to supply K and also plan for an effective K fertilization strategy.

1. Introduction

Potassium is an essential macro-nutrient in plant, animal, and human nutrition [1,2]. It is among the exhaustively extracted elements under intensive cropping systems [3,4]. The availability of native and applied K nutrients to plants depends on their buffering and adsorption capacities in the soils [5]. Continual refill of the K-depleted soil solution and exchangeable sites via the release of the non-exchangeable K^+ reserves notably contributes to the optimal K^+ nutrition of crops [6,7]. Without optimum soil K supply, 70–90 % of plants' K demand comes from the non-exchangeable pool [8].

The supply of K is a complex phenomenon involving many biogeochemical properties and processes in the soil [9,10] that

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determine the equilibrium kinetic reactions between the K forms [11]. Different studies revealed factors such as the degree of weathering [12,13], nature of parent materials [12,14], and soil taxonomy [15,16] had great effects on K release and fixation. For example, the action of rainfall and temperature causes excessive leaching of K in highly weathered tropical soils [17]. According to Refs. [18,19], Vertisols and Vertic subgroups released more K than Alfisols, Inceptisols, Entisols, and Aridisols. Toposequence also determines the K distribution due to the influence of slope on erosion, transportation, and deposition of soil materials [20].

Under the K depletion condition, the ability of clay minerals to release K normally follows the sequence of tri-octahedral micas > di-octahedral micas > K feldspars [21,22]. For instance, illite and vermiculite rich soils have high electro-negativity and K^+ specificity with much slower rate of K^+ adsorption than smectite and kaolinite types [22–24]. Similarly, montmorillonite and kaolinite clay minerals easily release all of their fixed K compared to illite and vermiculite [25,26]. Stoichiometric dissolution can be an important means for K release from tri-octahedral micas at low pH; but selective loss of interlayer K (part of the vermiculitization process) accounts for most K release from micas and illites [25,27]. This process may consistently modify the K exchange reactions and availability to crops in highly weathered soils of the tropics [28,29]. Instead, the di-octahedral vermiculite is a principal K-fixing clay mineral in acid soils owing to the marked K^+ affinity from Al^{3+} in the interlayer of 2:1 clays and mixed-layered silicates [30,31].

The K adsorption-desorption process depends on the level of soil solution K^+ , the type of clay minerals, and soil moisture [17,32]. However, the fixation of K is faster than the release [13,17] due to the strong binding by the inorganic (clay) and organic (organic matter) colloids [33,34]. Based on the rate and speed of K removal, the initial adsorption equilibrium in the soil solution phase serves as the K release index [35,36]. The appropriate K nutrient management practice for increasing crop production should consider the adsorption-desorption mechanism [2,37]. Hence, the concept of quantity-intensity has received attention to make better K fertilizer recommendation because of its key information on K availability [38,39].

In addition to factors determining the supply and uptake of K nutrient, its fixation capacity and release kinetics in the soils are not frequently addressed in Ethiopia and yet not done particularly in the study area. Since it determines the effectiveness of fertilization strategies [40] by predicting the possible fates of the applied K nutrient [41], assessment of K dynamics in soils under a given watershed is crucial [42,43]. Therefore, this research was conducted to determine the adsorption capacity of the exchangeable K and the desorption kinetics of the non-exchangeable K in the soils of the Qenberenaweti sub-watershed.

2. Material and methods

2.1. Description of the study area

The study was conducted in Qenberenaweti sub-watershed, which is located between $09^{\circ} 35' 03''$ to $09^{\circ} 33' 50''$ N latitude (Top-Bottom) and $39^{\circ} 32' 50''$ to $39^{\circ} 33' 54''$ E longitude (Left-Right). It is found at about 120 km from Addis Ababa on the way to Debre Berhan and 18 km from Chacha town. The site has a total area coverage of 317 ha and is situated on a plateau of the central Ethiopian highland system with elevation ranging between 2808 and 2960 m above sea level.

The mean annual temperature of the study area is $14.3^{\circ}C$ with a monthly mean value ranging between $15.6^{\circ}C$ in May and $13^{\circ}C$ in October and November. The rainfall distribution is bimodal having short and long rainy seasons from March to April and June to September, respectively with a mean annual precipitation of 928.5 mm. The study area falls under the Tepid to Cool Sub-Moist Mid-Highland agro-ecological zone [44] with major soil groups of Cambisols, Leptosols, and Vertisols [45].

2.2. Soil sampling and laboratory analysis

Twelve disturbed surface (0–20 cm) soil sub-samples were collected in zig-zag mode from farmland representing each of the three typical soil mapping units under pre-identified soil types (Relictistagnic Cambisols, Plinthofractic Cambisols, Pisoplinthic Cambisols, Vertic Cambisols, Pellic Vertisols, and Pisoplinthic Luvisols). The samples were thoroughly mixed and prepared in duplicate for the analysis of their K adsorption capacity and desorption kinetics per soil type. The K adsorption capacity was determined as per the method used by Ref. [41]. Composites of 2.50 g air-dried soil samples were equilibrated in 100 ml plastic bottles with 25 ml of 0.01 M $CaCl_2$ solution containing 0, 25, 50, 75, 100, 125, 150, 175, 200, 225, and 250 mg $K L^{-1}$. The suspensions were shaken for 24 h at room temperature ($25 \pm 1^{\circ}C$) and filtered through Whatman filter paper No. 42. Then, the K contents in the filtrate were measured using a flame photometer. The amount of K adsorbed was calculated with equation (1) outlined by Ref. [46].

$$qe = (C_i - C_e) * \frac{V}{M} \quad (1)$$

Where: qe ($mg\ kg^{-1}$) is the amount of K absorbed; C_i and C_e ($mg\ L^{-1}$) are the initial and

equilibrium solution concentrations, respectively; V (ml) is the volume of the solution and M (kg) is the mass of the soil.

The K adsorption rate (ΔK) was obtained using equation (2) below [47].

$$\Delta K (\%) = \left(\frac{qe * 100}{C_i} \right) \quad (2)$$

Adsorption isotherms were created through a combination of experimental data collection (adsorbent-adsorbate preparation, equilibrium reaches with time, and analytical separation and measurement) and mathematical modeling (data analysis, isotherm plotting, and fitting) [46]. The quantitative K adsorption data were fitted into the linearized form of equations on the most common

adsorption isotherm models such as Langmuir, Freundlich, and Temkin.

The Langmuir model, which generates theoretical monolayer reactions in the soils, was used to fit the data into the equations as given by Ref. [48] with equation (3).

$$\frac{Ce}{(qe)} = \frac{1}{kb} + \left(\frac{Ce}{b}\right) \quad (3)$$

Where: C_e is the equilibrium K concentrations of solutions (mg L^{-1}), q_e is the mass of.

Adsorbed K per unit mass of soil (mg kg^{-1}), k is a constant related to the bonding energy of K to the soil, and b is the maximum K adsorption capacity of the soil.

The Freundlich model, which considers an empirical adsorption phenomenon in the soils, was checked if fitted the data into equation (4) as formulated by Ref. [48]:

$$\log qe = \log a + b \log Ce \quad (4)$$

Where: q_e is the mass of adsorbed K per unit mass of soil (mg kg^{-1}), C_e is the equilibrium K concentrations of solutions (mg L^{-1}), a , and b are constants obtained from the intercept and slope, respectively.

The Temkin model, which accounts for uneven distribution of adsorption adsorbed molecules on the surface, was used to fit the adsorption data into the theoretical equation (5) [48]:

$$qe = a + b \ln Ce \quad (5)$$

Where: q_e is the mass of adsorbed K per unit mass of soil (mg kg^{-1}), C_e is the equilibrium K concentrations of solutions (mg L^{-1}), a , and b are constants obtained from the intercept and slope, respectively.

Finally, the release kinetics of non-exchangeable K^+ was carried out as per the method used by Ref. [49]. A weight of 2.50 g composite sample from each soil type was transferred into a 100 ml plastic bottle. The samples were repeatedly extracted with 25 ml 0.01 M CaCl_2 at room temperature ($25 \pm 1^\circ\text{C}$) for 2, 4, 6, 12, 24, 48, 72, 96, 120, 144, 168, 192, 216, 240, 264, and 288 h (until a nearly constant release rate was attained). The suspensions were shaken for 30 min, allowed to equilibrate for a moment, and shaken for another 30 min before being centrifuged at 1000 revolutions per minute for 10 min. Then, the suspension was filtered through Whatman filter paper No. 42 to measure the released amounts of non-exchangeable K^+ using a flame photometer. The release kinetics of non-exchangeable K^+ was studied by plotting the amount of desorption (mg kg^{-1}) on Y-axis against time (h) on X-axis [50], and fitted using equations (6)–(11) of the following six mathematical models [51].

$$\text{Zero order reaction } (q = a - bt) \quad (6)$$

$$\text{First order reaction } (\ln q = a - bt) \quad (7)$$

$$\text{Second order reaction } (1/q = 1/a + bt) \quad (8)$$

$$\text{Parabolic diffusion } (q = a + bt^{0.5}) \quad (9)$$

$$\text{Power function } (\ln q = \ln a + b \ln t) \quad (10)$$

$$\text{Elovich } (q = a + b \ln t) \quad (11)$$

Where: q = amount of K (mg kg^{-1}) released at some time, t = time (h), a = initial K desorbed (mg kg^{-1}) and intercept, b = rate constant (mg kg^{-1}) of the tested equations and slope which indicates the desorption rate of non-exchangeable K.

2.3. Statistical analysis

The goodness of diverse K adsorption and desorption models to fit both measured and predicted amounts of K was analyzed by looking for the highest coefficient of determination (R^2) and the lowest standard error of estimate (SE) values. The SE was calculated using equation (12).

$$\left[\frac{(q - q')^2}{n-2} \right]^{0.5} \quad (12)$$

Where: q and q' represents the measured and predicted K^+ released at time t (h),
Respectively, and n is the number of data points evaluated.

3. Results and discussion

3.1. Dynamics of exchangeable potassium adsorption capacity in the experimental soils

The equilibrium K concentrations in the solution (C_e) and the amounts of K adsorbed on the colloidal surfaces (q_e) were inconsistently increased with increasing added K (C_i) throughout the experimental soils. Generally, all the soils showed clear variation in their K adsorption characteristics with oppositely acting C_e and q_e values. As shown in Table 1, the highest C_e and q_e , or the lowest q_e and C_e , values were recorded from the Plinthofractic Cambisols and Vertic Cambisols, respectively. Hence, these soils had the mean maximum (69.47 ± 4.31 %) and minimum (56.16 ± 6.04 %) K adsorption rates (ΔK) that ranged from 62.6 to 78.1 % and 49.16–68.7 %, respectively (Table 1).

Except for the rise between concentration gradients of 25 and 50 mg L⁻¹, all the soils showed a declining mode of ΔK as the C_i was increased to 250 mg L⁻¹ (Fig. 1). This result might be due to the quantity-intensity relationship of the soils which causes a decrease in the K adsorption rate following the saturation of exchange sites by an increasing addition of initial K concentrations in the soil solution. Such trends of the curve were supported by Ref. [40] who found a non-linear mass action exchange at sites on external surfaces.

The variabilities of C_e , q_e , and ΔK could be related to the differences in clay types and amounts, OM and other cations (Ca and Mg) contents, and soil pH and CEC levels [34,40], reported that soils with high clay and CEC values fixed more K compared to soils with low clay and CEC. The release of anions (COOH⁻ and OH⁻) into the rhizosphere up on OM oxidation may enrich the net negative surface charge of the soils [52,53] which consequently enhances the adsorption of K⁺ ions [54,55]. The increase in pH can cause high amounts of K adsorption due to the formation of new sites together with a decrease in competition between H⁺ and K⁺ for the same sites [56, 57]. Depending on the amount and type of clay minerals, about 57 % of the applied K can be adsorbed by clay colloids [35,36]. In agreement with the results of the present work [58], confirmed that soils with high adsorption capacity had low exchangeable K at any initial added K, whereby more of the applied K was adsorbed by the soils as compared to those with low adsorption capacity.

The adsorption data of the experimental soils were fitted to the linearized equation form of the Langmuir adsorption isotherm which allows the calculation of soil nutrient adsorption maxima and the binding energy for nutrient sorption. However, the data poorly conformed to fit, as plots of C_e/q_e vs C_e produced were relatively not straight lines with less coefficient of determination (R^2) values ranging from 0.7864 to 0.9208 (Table 2). This might be due to the presence of a wider range of nutrient concentrations and Langmuir's assumption of an ideal monolayer reaction in the soils. The Langmuir equation correlates the amount of nutrient adsorbed with the equilibrium aqueous nutrient concentrations at low range [59]. That means, it does not yield a straight line when q_e is plotted against C_e over a wide range of nutrient concentrations [60,61]. Besides, the model hypothetically assumes homogeneous surface sites with complete adsorption of solutes on the monolayer adsorbent [48,62]. Thus, it does not adequately describe nutrient sorption on exchanging surfaces as heterogeneous as the soil colloids [63,64].

The Temkin adsorption equations were obtained after plotting the adsorbed potassium (q_e) against the natural logarithm of the equilibrium solution concentration (Ln C_e). The R^2 values ranged from 0.9096 to 0.9721 for the Pisolplinthic Luvisols and Pisiopllintic Cambisols (Table 2). Thus, the Temkin had a slightly higher R^2 than the Freundlich in the Pisiopllintic Cambisols; but the much lower buffering capacity (slope = 0.0019 L kg⁻¹) made it inferior in fitting the K adsorption data. Equations of the three models followed different assumptions for nutrient sorption affinity which either decreases linearly (Temkin), decreases logarithmically (Freundlich), or remains constant (Langmuir) with an increase in surface saturation [65–67]. Moreover, there is a closer association between the slope (b) of both Temkin and Freundlich equations, and the constant of maximum absorption (b) plus binding energy (k) of the Langmuir equation [68,69].

Though the slopes of the Temkin equation (b) were higher than the adsorption maximum (b) of the Langmuir, both had lower values than the Freundlich constant (b) for all soils of the study area (Table 2). The goodness of the Freundlich model to fit the adsorption data was the best with R^2 values ranging from 0.9694 (Relictistagnic Cambisols) to 0.9757 (Pisolplinthic Luvisols). Besides,

Table 1
Mean amount of adsorbed potassium in the soils of Qenberenaweti sub-watershed.

Ci (mg L ⁻¹)	Soil types											
	Plinthofractic Cambisols		Pisiopllintic Cambisols		Relictistagnic Cambisols		Pisiopllintic Luvisols		Vertic Cambisols		Pellic Vertisols	
	Ce (mg L ⁻¹)	qe (mg kg ⁻¹)	Ce (mg L ⁻¹)	qe (mg kg ⁻¹)	Ce (mg L ⁻¹)	qe (mg kg ⁻¹)	Ce (mg L ⁻¹)	qe (mg kg ⁻¹)	Ce (mg L ⁻¹)	qe (mg kg ⁻¹)	Ce (mg L ⁻¹)	qe (mg kg ⁻¹)
0	4.35	-43.50	5.25	-52.50	4.55	-45.5	4.70	-47.0	5.60	-56.0	6.30	-63.0
25	9.70	153.0	7.80	172.0	8.98	160.25	8.40	166.0	7.25	177.50	7.55	174.50
50	15.65	343.50	12.55	374.50	14.53	354.75	13.68	363.25	10.95	390.50	11.60	384.0
75	30.68	443.25	21.85	531.50	28.90	461.0	27.45	475.50	20.13	548.75	20.93	540.75
100	41.38	586.25	31.53	684.75	39.60	604.0	38.48	615.25	28.68	713.25	30.53	694.75
125	53.98	710.25	41.38	836.25	52.60	724.0	51.90	731.0	38.18	868.25	40.23	847.75
150	68.20	818.0	51.18	988.25	63.95	860.50	62.35	876.50	45.85	1041.50	49.68	1003.25
175	82.83	921.75	63.45	1115.50	81.30	937.0	74.10	1009.0	57.60	1174.0	61.68	1133.25
200	98.05	1019.50	75.15	1248.50	95.95	1040.50	84.75	1152.50	66.90	1331.0	70.05	1299.50
225	112.88	1121.25	90.10	1349.0	110.23	1147.75	95.65	1293.50	76.53	1484.75	81.63	1433.75
250	127.10	1229.0	102.10	1479.0	122.58	1274.25	109.28	1407.25	93.50	1565.0	96.38	1536.25

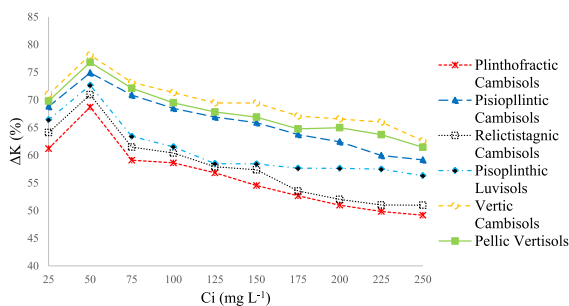


Fig. 1. Potassium adsorption rate and initial solution saturation of experimental soils.

Table 2
Regression equations and R² values for the eight soil samples.

Soil types	Model form	Linear Equation	R ²
Plinthofractic Cambisols	Langmuir	$y = 0.0004x + 0.0523$	0.9122
	Temkin	$y = 0.0024x + 2.1409$	0.9565
Pisiopllintic Cambisols	Freundlich	$y = 0.7380x + 1.5527$	0.9697
	Langmuir	$y = 0.0003x + 0.0355$	0.9162
	Temkin	$y = 0.0019x + 1.9290$	0.9721
Relictistagnic Cambisols	Freundlich	$y = 0.7746x + 1.6495$	0.9717
	Langmuir	$y = 0.0004x + 0.0467$	0.9208
	Temkin	$y = 0.0024x + 2.0537$	0.9534
Pisiopllintic Luvisols	Freundlich	$y = 0.7158x + 1.6178$	0.9694
	Langmuir	$y = 0.0003x + 0.0464$	0.7864
	Temkin	$y = 0.0020x + 2.1687$	0.9096
Vertic Cambisols	Freundlich	$y = 0.7639x + 1.5843$	0.9757
	Langmuir	$y = 0.0003x + 0.0319$	0.8485
	Temkin	$y = 0.0018x + 1.8906$	0.9603
Pellic Vertisols	Freundlich	$y = 0.7964x + 1.6729$	0.9699
	Langmuir	$y = 0.0003x + 0.0343$	0.8602
	Temkin	$y = 0.0018x + 1.9379$	0.9568
	Freundlich	$y = 0.7894x + 1.6543$	0.9718

Freundlich’s plot of $\log(q_e)$ against $\log(C_e)$ gave linear graphs that better described the K fixation characteristics of the soils at medium and high equilibrium concentrations (Fig. 2). Since the Freundlich isotherm assumes an infinite number of fixation sites in a heterogeneous medium with diverse physicochemical properties, it is the best-fitted model to have inclusive data in soils with multi-layered sorption surfaces and mixed mineralogy [70–72]. Independent of the time and temperature, the adsorption data obtained from the Freundlich equations were affected by the concentration of K in the soil solution [73,74]. Concurrent to this work [40,41,74], observed that the Temkin had a good fit than the Langmuir; but its superiority was lesser as compared to the Freundlich isotherm model.

The Freundlich isotherm corresponds to a model with more realistic assumption in which the affinity term decreases exponentially as the number of adsorptions rises [61,75]. Over a limited range of concentration, the simple equation form of the Freundlich ($q_e = aC_e^b$) often describes adsorption well [61,76]. Where ‘a’ is the amount of K adsorbed (mg kg^{-1}) as the concentration C_e is 1 mg L^{-1} and ‘b’ is the buffer power (L kg^{-1}) found by the slope of the sorption curve at a point where $q_e/C_e = 1 \text{ L kg}^{-1}$.

Since the point at which the value of $q_e = C_e$ occurs varies between different soils, the modified equation of the Freundlich model ($q_e = aC_e^{b/a}$) was used to describe the soils in this study. For instance, the theoretical doses of K fertilizers required to develop K levels in soil solutions under field conditions were computed from this modified equation of the Freundlich model (Table 3). The main advantage of this equation is that the ‘a’ and ‘b’ are found at the same point on the curve where $C_e = 1 \text{ mg L}^{-1}$ and this point is the same for all the soils [77]. Parameters ‘a’ and ‘b’ of the Freundlich equation were estimated by regression of the natural logarithmic form of the data gained from adsorption isotherms [78]. However, the parameters have been considered meaningless because the values of sorption capacity ‘a’ and buffering energy ‘b’ were practically zero at equilibrium concentrations for all soils.

The exponent ‘b/a’ values for the Relictistagnic and Vertic Cambisols were 0.7158 and 0.7964 L kg^{-1} , respectively (Table 3). All the values were less than one, implying that they are related to the properties of the adsorbent (soil colloids). According to Refs. [70,79], the values range between 0 and 1 whereby the soil surfaces become more heterogeneous as the value approaches zero, and a value below one indicates the chemisorption process.

Potassium buffering capacity is the soil’s ability to withstand sudden changes in K levels of the soil solution at which a high value indicates that adequate K is available for a long time, whereas a low value suggests frequent fertilization is required [80,81]. Therefore, the exponent values represented the amount of K held on unspecific sites and ready to be released for plant uptake during a cropping season. The values of K adsorbed ‘a’ ranged from 4.7242 to 5.3276 mg kg^{-1} in the study soils (Table 3); but they were lower than the

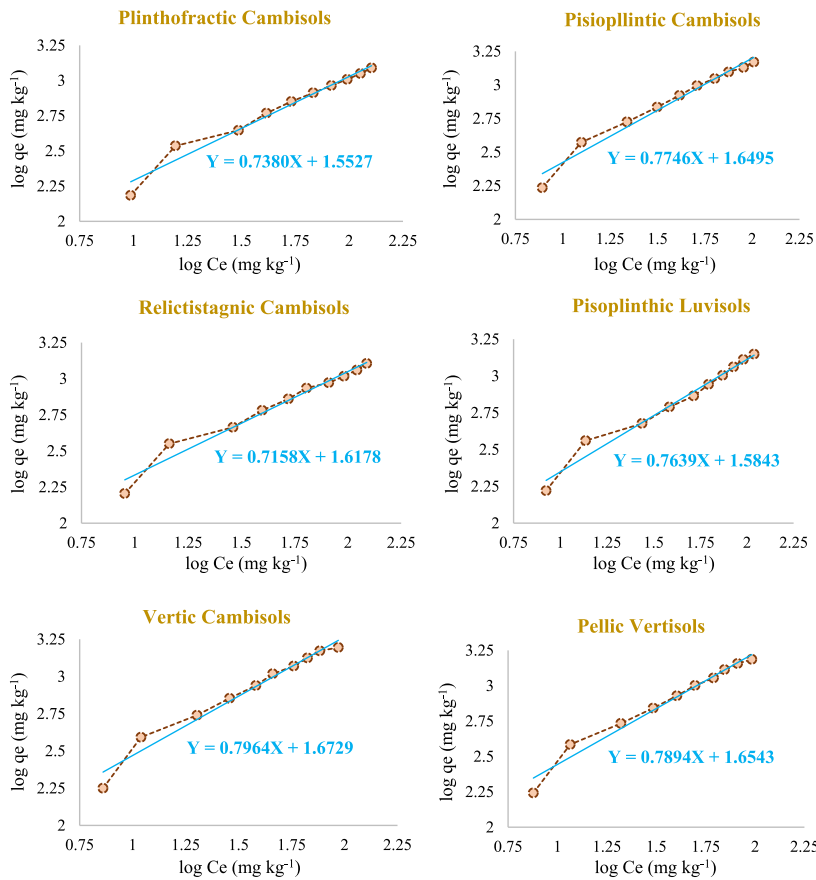


Fig. 2. Potassium adsorption data of the experimental soils fitted to the Freundlich model.

Table 3
Potassium adsorption characteristics of experimental soils in the Freundlich model.

Soil types	Model form	Linear form	a (mg kg ⁻¹)	b (L kg ⁻¹)
Plinthofractic Cambisols	$q_e = 4.7242C_e^{0.7380}$	$y = 0.7380x + 1.5527$	4.7242	3.4865
Pisiopllintic Cambisols	$q_e = 5.2043C_e^{0.7746}$	$y = 0.7746x + 1.6495$	5.2043	4.0313
Relictistagnic Cambisols	$q_e = 5.0420C_e^{0.7158}$	$y = 0.7158x + 1.6178$	5.0420	3.6091
Pisioplinthic Luvisols	$q_e = 4.8759C_e^{0.7639}$	$y = 0.7639x + 1.5843$	4.8759	3.7247
Vertic Cambisols	$q_e = 5.3276C_e^{0.7964}$	$y = 0.7964x + 1.6729$	5.3276	4.2429
Pellic Vertisols	$q_e = 5.2294C_e^{0.7894}$	$y = 0.7894x + 1.6543$	5.2294	4.1281

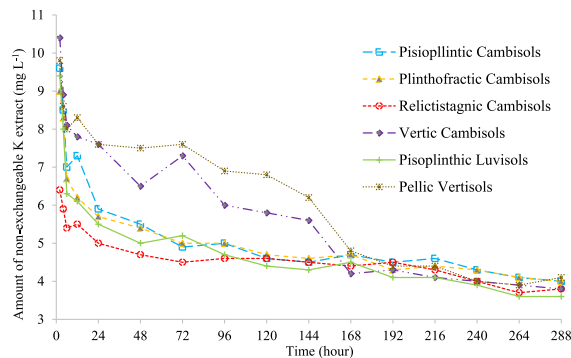


Fig. 3. Release kinetics of non-exchangeable K in the experimental soils.

amount of available K. This suggests that part of exchangeable K is held on exchange sites by high bonding energy [41,82]. It was also considered as a capacity factor implying that soil with a higher 'a' value has greater adsorbing capacity than that having a lower value [61,83]. Additionally [84], reported the value of sorption capacity 'a' as a practically useful parameter to brief adsorption properties over a wide range of equilibrium concentrations.

3.2. Equilibrium desorption kinetics of non-exchangeable potassium in the study soils

In general, the release kinetics of non-exchangeable K were characterized by rapid desorption for the first 12 h; then, declined for the next 72–168 h and remained nearly constant in subsequent extractions until the end of 288 h (Fig. 3). The released amount of non-exchangeable K was the highest at the initial extraction from the Vertic Cambisols consequently followed by the Pellic Vertisols, Pisolplinthic Cambisols, Pisolplinthic Luvisols, Plinthofractic Cambisols and Relictistagnic Cambisols (Fig. 3; Table 4).

The highest constant K releases from the Plinthofractic Cambisols (47 mg kg⁻¹), Pisiopllintic Cambisols (46 mg kg⁻¹), and Pisolplinthic Luvisols (44 mg kg⁻¹) were attained at the 9th extraction (120 h) while the highest releases were found from Relictistagnic Cambisols (45 mg kg⁻¹) and both Pellic Vertisols (48 mg kg⁻¹) plus Vertic Cambisols (42 mg kg⁻¹) at the 7th (72 h) and 11th (168 h) extractions (Table 4).

Higher values of K release in the initial period could be attributed to the isomorphic substitution of K⁺ by Ca²⁺ at surface exchange sites of different clay minerals such as smectite, vermiculite, mica, and illite [85,86]. However, further exchange of K⁺ by Ca²⁺ would be slower, as the size of hydrated Ca²⁺ (4.3 Å) is larger than hydrated K⁺ (3.3 Å) [87,88]. This can also be attributed to non-exchangeable K⁺ in the soils being more tightly retained due to the prevalence of micaceous minerals [13,89]. [2,13,90] reported the decline of interlayer K of micas and other clay minerals with the constant release of K from sources with no exchangeable K.

The three phases of K⁺ release characteristics shown in Fig. 3 are a diffusion-controlled process [91,92]. The first curvilinear part indicated rapid K⁺ release from the surface sites; whereas the second and third linear parts represented K⁺ release from the edge and internal sites of clay minerals, respectively [93,94]. The observed patterns of initial rapid release followed by a slower release in time were also reported in other studies [16,95].

The variation in the rates of K desorption in different soils indicates that the cations retained on the surface sites influenced the rate of K desorption [96,97]. According to Refs. [98,99], the highest K release rate of some soils is most likely due to the transfer of non-exchangeable K to the extractant solution. Soils with delayed constant K release are thought to have large K reserves and a greater long-term K supply [100,101]. The releasing power denotes the total availability of nutrients in the soil does not correspond to the actual available K in the soil indicating the K releasing power of the soil [102,103]. As a result, it could be concluded that the experimental soils except Relictistagnic Cambisols were capable of providing a high amount of K during intensive cropping [99,104]. revealed that the virtue of soils to release K is more determined by the amount of smectite clays than the other 2:1 minerals. According to Ref. [105], Vertisols and other soils with vertic nature had higher K release rates as compared to the other soils due to the dominance of expansible clay minerals.

A plot of cumulative K release vs time displayed discontinuities in slope at time intervals of 2–6, 6–24, and 24–288 h, whereby the highest (1029 mg kg⁻¹) and the lowest (758 mg kg⁻¹) values were recorded from the Pellic Vertisols and Relictistagnic Cambisols, respectively (Fig. 4). Such segments on the curves are typically associated with the rate of K release process that varies with the soil types and is controlled by various mechanisms [96].

The initial rapid K release is thought to be caused by mass action exchange from the planar surface of the clay [25,106]. Also, it is mostly attributed to the release of water-soluble and exchangeable K [106]. The second short-term transitional stage of K release represents the rate at which K is desorbed from the edge exchangeable sites and helps refill the liable soil K [106,107]. The third long-term segment in the cumulative K release represents the rate at which the interlayer K is slowly exchanged by calcium [82,106].

Table 4
Amount of desorbed potassium (mg kg⁻¹) in soils of Qenberenaweti sub-watershed.

Time (hour)	Soil types					
	Plinthofractic Cambisols	Pisiopllintic Cambisols	Relictistagnic Cambisols	Pisolplinthic Luvisols	Vertic Cambisols	Pellic Vertisols
2	90.0	96.0	64.0	94.0	104.0	98.0
4	83.0	85.0	59.0	80.0	89.0	86.0
6	67.0	70.0	54.0	63.0	81.0	80.0
12	62.0	73.0	55.0	61.0	78.0	83.0
24	57.0	59.0	50.0	55.0	76.0	76.0
48	54.0	55.0	47.0	50.0	65.0	75.0
72	50.0	49.0	45.0	52.0	73.0	76.0
96	50.0	50.0	46.0	47.0	60.0	69.0
120	47.0	46.0	46.0	44.0	58.0	68.0
144	46.0	45.0	45.0	43.0	56.0	62.0
168	47.0	47.0	44.0	45.0	42.0	48.0
192	43.0	45.0	45.0	41.0	43.0	44.0
216	44.0	46.0	43.0	41.0	41.0	44.0
240	43.0	43.0	40.0	39.0	40.0	40.0
264	41.0	41.0	37.0	36.0	39.0	39.0
288	40.0	40.0	38.0	36.0	38.0	41.0

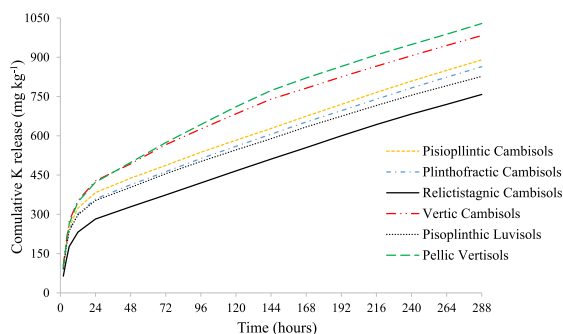


Fig. 4. Cumulative desorption amount of non-exchangeable K in the experimental soils.

The variation in cumulative K desorption of the study soils indicates that the cations fixed on the surface of clay micelle may influence the rate of desorption in the calcium-potassium system [106]. Soil development and the type of soil minerals had a greater impact on K release [16]. [18] found a higher cumulative release of non-exchangeable K from Vertisols and Vertic sub-groups than in Alfisols, Inceptisols, Entisols, and Aridisols.

Among the tested models, the zero-order and parabolic diffusion equations fit the data from the Relictistagnic Cambisols relatively better than the second-order, and Elovich models did for the Pisioplinthic Luvisols and Vertic Cambisols, respectively (Table 5). However, none of them were adequate for describing the cumulative K-release data. The power function and first-order models were the best in successfully describing the K^+ release from all experimental soils, based on a higher coefficient of determination (R^2) and lower standard error of the estimate (SE) values. Since the power function had acceptable values of R^2 and SE than the first order, it was considered as the most suitable model to describe the rating process [106]. chose the first-order equation as the most suitable model to determine the release rate coefficient of K. According to Refs. [108,109], the power function model is used to represent the slow diffusion of K^+ from the interlayer sites of mica. Similar findings [16,110,111] were reported on the efficacious presentation of non-exchangeable K^+ release with a power function equation.

The constants 'a' and 'b' of each model represent the intercept and the slope of the linear curves obtained by plotting the released K against time. The constant 'a' represents the initial amount of K released [97,111] which shows the amount of equilibrium K initially available for plant uptake [111,112]. The constant 'b' reflects the release rate of the non-exchangeable K [97,111]. Thus, the 'b' value is known to correlate well with K^+ for plant uptake [113]. Negative values of 'b' were obtained in all the soils for first-order, zero-order, and second-order mathematical model equations. Negative 'b' values implied for insufficient K release from non-exchangeable K to meet the K need of the crop [106]. The variation in the equation constants was also observed which could be due to the soil type, clay mineralogy, pH, $CaCO_3$, adsorption-desorption balance, soil depth, and mathematical models tested [114].

The initial amount of K released ranged from 4.4895 to 4.7114 $mg\ kg^{-1}$ with releasing rates ranging from 0.3675 to 0.4228 $mg\ kg^{-1}\ min^{-1}$ (Table 5). The values of K release among the studied soils indicated their relative potential to supply plant-available K [109]. For all soils, the slope derived from the power function was less than one, indicating that the K-release rate decreased over time [110,111]. The variabilities in K release among the soils could be ascribed to the differences in types of clay minerals, contents of clay and silt, and climate conditions [115]. Besides [116], revealed that soil available K is primarily regulated by the rate of K released into forms suitable to be taken up by plants. Vertisols showed higher K release than the other soil orders mainly due to higher mica and/or smectite clay contents with a relatively lower abundance of illite clay. According to Ref. [117], Vertisols, smectitic Alfisols, and Inceptisols could have superior K-release due to larger wedge zones and expandability of smectites, whereas K in illitic soils is tightly held and exchange of K is slower.

4. Conclusion

The results of this study revealed that the nature and distribution of the different soil types of the Qenberenaweti sub-watershed had a great effect on the K release and fixation. Generally, the equilibrium K concentrations of the soil solution (C_e) and amounts of K adsorbed on the colloidal surfaces (q_e) were inconsistently increased with the rising of the initially added K (C_i) throughout the experimental soils. The goodness of the Freundlich isotherm model to fit the data was better for describing the K adsorption characteristics of all experimental soils than that of the Langmuir and Temkin models. Thus, the modified equation of the Freundlich model ($q_e = aC_e^{b/a}$) was used to describe the theoretical doses of K fertilizers required to develop K levels in soil solutions. The release kinetics of non-exchangeable K was characterized by rapid desorption that lasted for the first 12 h; then, declined during the next 72–168 h, and remained nearly constant in the subsequent extractions to the end of 288 h. Among the tested models, the power function was the best to successfully describe the cumulative K^+ release data of all experimental soils. Overall, assessing the adsorption capacity of the exchangeable K and the release kinetics of the non-exchangeable K at a site-specific level helps know the relative potential of the soils to supply plant-available K and plan for an effective K fertilization strategy.

Table 5
Kinetics of non-exchangeable K release in soils of Qenberenaweti sub-watershed.

Kinetic models	Values	Soil types					
		Plinthofractic Cambisols	Pisopliintic Cambisols	Relictistagnic Cambisols	Pisopliintic Luvisols	Vertic Cambisols	Pellic Vertisols
Zero-order	R ²	0.9408	0.9340	0.9568	0.9370	0.9180	0.9241
	SE	60.2459	64.9822	47.1342	59.0843	82.4905	85.3990
	a	621.48	631.14	578.45	584.89	688.52	740.48
	b	-2.320	-2.3630	-2.1436	-2.2021	-2.6663	-2.8796
First-order	R ²	0.9372	0.9361	0.9343	0.9404	0.9566	0.9625
	SE	0.2206	0.2239	0.2244	0.2198	0.1982	0.1861
	a	6.6067	6.6227	6.5395	6.5516	6.7202	6.7974
	b	-0.0089	-0.0089	-0.0088	-0.0091	-0.0097	-0.0098
Second-order	R ²	0.4204	0.4193	0.4147	0.4368	0.4134	0.4086
	SE	0.0020	0.00187	0.00291	0.00188	0.00177	0.00191
	a	0.0048	0.0045	0.0065	0.0047	0.0041	0.0043
	b	-0.00002	-0.00002	-0.00002	-0.00002	-0.00001	-0.00002
Parabolic diffusion	R ²	0.9847	0.9825	0.9874	0.9852	0.9859	0.9894
	SE	30.602	33.478	25.411	28.661	34.216	31.926
	a	99.619	112.01	50.237	105.59	124.04	105.27
	b	43.803	44.725	40.187	41.669	50.992	54.985
Power function	R ²	0.9604	0.9590	0.9675	0.9637	0.9651	0.9690
	SE	0.1296	0.1299	0.1306	0.1203	0.1236	0.1231
	a	4.5749	4.6439	4.1895	4.6009	4.7114	4.6340
	b	0.3790	0.3730	0.4228	0.3675	0.3856	0.4086
Elovich	R ²	0.9309	0.9363	0.9140	0.9358	0.9564	0.9527
	SE	65.0494	63.8816	66.5226	59.6561	60.0990	67.4197
	a	-53.761	-46.922	-84.960	-41.601	-63.161	-93.881
	b	141.74	145.30	128.67	135.15	167.15	179.56

Data availability statement

There is no data deposited into a publicly available repository, hence it will be made available on request.

Declaration statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Haymanot Awgchew: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sheleme Beyene:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Conceptualization. **Alemayehu Kifilu:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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