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Potassium Mobility Potential of Forest Soil In Kurdistan Region, Iraq, As Estimated By Quantity- Intensity (Q/I) Relationships

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Abstract

This study aimed to assess potassium(K) 's potential mobility for some soils located in the Kurdistan Region of Iraq. Five soil samples were collected from a depth of (0-30) cm. For each sample, 5g of soil was equilibrated with 50 ml of 0.01 M $CaCl_2$, amended with different K concentrations, and incubated for 24 h at 298 Kelvin. The supernatant was filtered, and K, Ca, and Mg were determined. Potassium exchange equilibrium was calculated from quantity-intensity (Q/I) isotherms. Mean AReK values for all studied soils ranged between $2.4x10^{-3}$ to $3.6x10^{-3}$(mol L^{-1})$^{1/2}$, which reveals that K was preferentially held at inner potions. The amount of labile K(KL) ranged from 0.479 to 1.191cmolc kg-1 in studied soils. The highest value of KL was in Kanypanka while the lowest value was in Goizha. The potential buffering capacity (PBCK) was between 619.56 and 857.37 cmolc kg^{-1}(mol L^{-1}) $^{-1/2}$. All studied soils were characterized by low percent K saturation and a high ability to replenish K concentration in the soil solution. Gapon selectivity coefficient was relatively high and ranged from 5.64 to 7.88 L mol^{-1}. Higher values of KL indicate a greater K release into the soil solution. Such a high affinity of K for the solid soil phase was attributed to both the elevated organic matter content in these soils and their strong buffering capacities.

Keywords: *Forest soils, Gapon selectivity coefficient, labile K, Potential buffering capacity, Potassium quantity-intensity isotherms.*
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I. INTRODUCTION

Potassium (K) is an essential nutrient that affects most biochemical and physiological processes that influence plant growth and metabolism. It also contributes to the survival of plants exposed to various biotic and abiotic stresses [1].

The availability of K in soil solution depends on the status between its forms in the soil. Pal, et al. [2] argue that more than 50% of the K applied to soils can be adsorbed onto colloidal surfaces depending on the amount and type of clay minerals. Similarly, Ogwada and Sparks [3] and Metha and Singh [4] showed that K adsorption rate on mineralogy with illite and vermiculite adsorbing are much slower than montmorillonite and kaolinite.

Knowledge about the equilibrium between the quantity and intensity phases of K in the soil and the difference in K adsorption among soils is necessary to make precise K fertilizer recommendations [3, 5]. That due to the different adsorption behavior of K in soils affects the pathways of added K fertilizer and influences crop response.

A typical Q/I curve is shown in Fig. 1. Various interpretations of parameters AR^Ke, ΔK_0, PBC^K, and K_X have been made, which can be derived from a Q/I plot [6]. The slope of $\Delta Q/\Delta I$ measures the amount of labile K that can be removed before ARe^K falls by more than a given amount that is a gradient of the linear part of the graph has generally been representing Potential BufferingCapacity (PBC^K) of the soil [7].

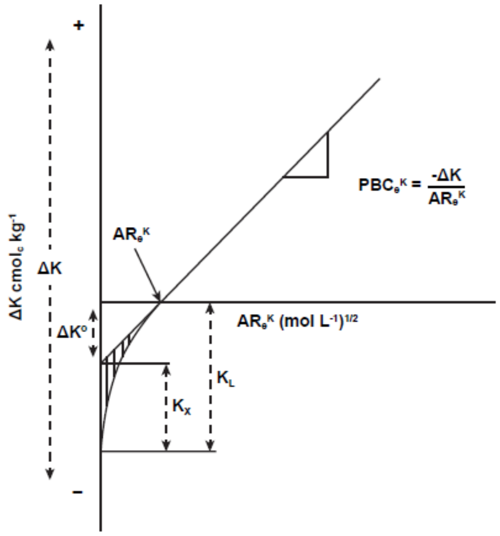

Fig. 1. Typical quantity-intensity (Q/I) plot for labile soil K estimation

The intercept of the curve with the activity ratio axis (ΔK =0) gives the value of AR_e^K in the soils. This expresses the availability or intensity of labile K in the soil. Schouwenburg

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and Van Schuffelen [8] theorized that if the AR_e^K value is less than 0.001 $(\text{mol L}^{-1})^{1/2}$, the adsorbed K will be at edge positions, and if it is more than 0.01 $(\text{mol L}^{-1})^{1/2}$, the adsorbed K would be at planar positions, however, if the ARe^K values ranged between 0.001 to 0.01 $(\text{mol L}^{-1})^{1/2}$ K is preferentially held at inner potions.

The lower bent portion of the curve (Fig. 1) is an indicator of the exchange reactions of labile K retained at the position that demonstrates a higher affinity to K(i.e., ends of clay grains and wedge positions of weathered micas). Low values of AReK characterize this portion because fixed K is releasing from the soil particle. The upper linear portion of the curve represents non-specific (planar surface) positions of K.

ΔK° is the measure of K adsorption on p-positions (non-specific positions on outer crystal surfaces) which plant accessible. Kx refers to the capability of the specific positions (potassium adsorption on e-positions; i.e., specific exchange positions taking place on the edges, bends, and projections of crystal surfaces) that are characterized by lower plant availability [9]. The value of ΔK at AReK = 0 refers to labile potassium (KL) in the adsorption curve. It indicates the overall amount of labile K in a given soil (ΔK°+Kx). Such an indicator reveals the readily available amount of K, which can exchange during a period of equilibrium between the colloids and the soil solution.

The slope of ΔQ/ΔI (i.e., PBCK) is an index for the soil capacity to retain the high intensity of K in the soil solution. The PBCK deals with sorption-desorption mechanisms taking place in the soil. According to Zharikova (2004) can be PBCK grouped into five categories; very low (<20), low (20-50), medium (50-100), elevated (100-200), and high (>200 cmolc kg^{-1}[mol L-1]$^{-1/2}$). Soils with the greatest PBCK values have the lowest K saturation rates, indicating a greater possibility of replenishing K intensity in the soil solution. The aims of this paper are; (i) evaluate K status in the forest soils from the Kurdistan Region of Iraq, (ii) study adsorption of K by using thermodynamic approaches, and (iii) evaluate K- supplying power for the forest soils using Q/I parameters.

II. MATERILAS AND METHODS

A. Sudy Site

The study area is located in northeastern Iraq. Five forest areas were chosen, including Bakhy Bakhteyare (35° 34′ 8″ N 45° 22′ 8″ E), Bakrajo (35° 34′ 36″ N45° 21′ 29″ E), Kanypanka (35° 22′ 56″ N 45° 42′ 58″ E), Khalakan (35° 59′ 18″ N 44° 52′ 34″ E), and Goizha (35° 34′ 4″ N 45° 28′ 39″ E). Soil samples were taken at a depth of 0 to 30 cm. The samples were air-dried ground passed through a 2mm sieve stored in plastic sample bags prior to laboratory analysis.

B. Laboratory Analysis

1) Physico-chemical analysis

The physicochemical analysis used in this study is shown in Table I. Soil texture was determined by the standard pipette method [10]. The ICARDA [11] method used to determine total calcium carbonate and active calcium carbonate was determined [12]. Soil organic matter was determined by the Walkley and Black method. Both the pH and electrical conductivity were determined in the soil saturation extract [13]. Soluble cations and anions were quantified in the soil extract solution; calcium and magnesium were determined titrimetically method using 0.01 Nethylenediaminetetra-acetic acid disodium salt (EDTA-Na2) as described in [13]. Potassium and sodium were measured by flame emission photometry following [14]. Carbonate and bicarbonate were determined by a titrimetric method using 0.01 N H2SO4 and phenolphthalein and methyl orange as indicators [15]. Chloride was determined by titration with AgNO3 and K2CrO4 as an indicator [13].

2) Thermodynamic approaches

Ionic strength was calculated following (Griffin &Jurinak, 1973) as:

$$I = 0.0129\ EC_e \qquad (1)$$

Where I is the ionic strength (mol L^{-1}), and EC_e represents electrical conductivity in dS m^{-1} at 25°C.

The empirical Davies equation was used for calculating activity coefficients [16]

$$\log \gamma_i = -0.512\ Zi^2\ [\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I] \qquad (2)$$

Where γ_i is the mean activity coefficient of the electrolyte, Z_i is the species valence of the ion, and I is ionic strength in mol L^{-1}.

The activity ratio of potassium (AR^K) was determined according to the ratio law [17].

$$AR^K = \frac{a_K}{\sqrt{a_{Ca} + a_{Mg}}} \qquad (3)$$

Where a represents the activity of ions in mol L^{-1}.

The free energy of K replenishment at equilibrium (ΔG_e^K), was determined using the following equation, as suggested by Kotur & Rao (1988):

$$\Delta G_e^K = -RTlnAR^K \qquad (4)$$

Where ΔG_e^K is the free energy of replenishment at equilibrium (kJ mol^{-1}), AR^K is the K equilibrium activity ratio $(\text{mol L}^{-1})^{1/2}$, and R and T are the gas constant and absolute temperature, respectively.

Gapon selectivity coefficient (k_G) was used to understand K replacement capability in the soil. Here, k_G, as described by Beckett, et al. [18] and [19], was calculated as follows:

$$k_G = PBC^K/CEC \qquad (5)$$

where k_G is units $(\text{L mol}^{-1})^{1/2}$, PBC^K is in units of cmol$_c$ kg^{-1}(mol L^{-1})$^{-1/2}$, and CEC is the cation exchange capacity (cmol$_c$ kg^{-1}).

3) 2.2.3. Quantity/Intensity relationship

Q/I relationship of K for soil samples under study was assessed using the procedure described by *Beckett* (1964b). Five grams of each soil sample in duplicate were placed in 100 ml plastic bottles and equilibrated with 50 ml of 0.01 *M* $CaCl_2$ at different concentrations of K, 0, 5, 10,25,50, 100, 200, and 300 mg L^{-1}, as KCl was added to the soils. The bottles were stoppered, shaken in a rotative shaker for three hours, and incubated for 24 h at 298 Kelvin to reach an equilibrium state. The supernatants were centrifuged and passed through filter paper Whatman No. 42, and the extract was kept to determine exchangeable calcium, magnesium, and potassium [13] and measure electrical conductivity.

The quantity of K acquired or wasted (ΔK) by the soil was measured through the difference between the quantity of K added and the quantity recovered in the final solution.

The *Q/I* parameters were obtained by plotting ΔK ($cmol_c\ kg^{-1}$) against the activity ratio of potassium (AR_e^K) (mol $L^{-1})^{1/2}$. The variance between the lower and upper portions reveals the quantity of K held at particular sites (K_x) when the activity ratio is zero. Moreover, extending the lower curved portion of the ΔK axis gives the overall quantity of K in the labile pool (K_L). The x-axis intercept is considered the equilibrium activity ratio (AR_e^K) in the soil when ΔK is zero. It gauges the availability or intensity of labile K in the soil.

The y-axis intercepts for the lower portion of the curve represents the amount of K held in the soil at each site ($-\Delta K$). Another *Q/I* parameter is the potential buffering capacity of K at equilibrium (PBC_e^K), which is calculating as follows:

$$PBC_e^K = \frac{-\Delta K^o}{AR_e^K} \qquad (6)$$

Where PBC^K is the potential buffering capacity, $-\Delta K^o$ is the labile K (quantity of K desorbed or a portion of labile K situated on planar surfaces), and AR_e^K is the equilibrium activity ratio for K.

III. RESULTS AND DISCUSSION

A. Soil Propoerties

Selected properties of the studied soils are presented in Table I. The soil of all studied areas found as slightly alkaline with the pH ranged from 7.62 to 8.03. ECe values ranged from 0.22 to 1.37dS m-1 or non-saline soils because the ECe values were found < 2.5 dS m-1, organic matter content ranged from 16.21 to 27.94 g kg-1. The total calcium carbonate equivalent and active calcium carbonate content were ranged from 42.80 to 272.60 and 15.00 to 135.00 g kg-1 respectively; the studied soils are calcareous. Cation exchange capacity (CEC) ranged from 37.50 to 46.68 cmolc kg-1, Table II.

TABLE I. PHYSICAL AND CHEMICAL PROPERTIES OF STUDIED SOIL SAMPLES

Properties		**Locations**				
Particle Size		**Bakhybakhtyare**	**Bakrajo**	**Kanypanka**	**Khalakan**	**Goizha**
Distribution (PSD)	Sand	76.40	126.60	80.20	260.60	54.30
	Silt	333.20	407.90	422.20	304.10	507.10
g kg^{-1}	Clay	590.40	465.50	497.60	435.30	438.60
Texture Class		C	Si C	Si C	C	Si C
pH		7.72	7.88	8.01	7.62	8.03
$EC_{e,}$ dS m^{-1}at 25ºC		0.26	0.56	0.88	1.37	0.22
	Ca^{2+}	5.20	3.96	6.28	11.17	2.65
	Mg^{2+}	3.00	1.86	3.04	7.76	1.75
	K^+	0.35	0.40	0.70	0.13	0.63
Soluble ions	Na^+	0.15	0.90	0.16	0.28	0.11
mmol L^{-1}	HCO_3^-	3.60	3.15	3.90	12.00	2.60
	CO_3^{2-}	Nil	Nil	Nil	Nil	Nil
	Cl^-	1.20	0.70	0.50	2.65	1.10
	SO_4^{2-}	4.50	2.60	5.30	6.90	1.70
O M, g kg^{-1}		23.98	21.73	27.94	19.32	16.21
$CaCO_3$ equivalent	Total	222.25	272.6	207.10	251.20	42.80
g kg^{-1}	Active	135.00	130.00	80.00	60.00	15.00

TABLE II. QUANTITY/INTENSITY PARAMETER FOR STUDIED SOILS

Locations	L_K $cmol_c$ kg^{-1}	PBC^K	CEC $cmol_c$ kg^{-1}	k_G
Bakhybakhtyare	1.002	635.47	46.68	19.45
Bakrajo	1.063	774.93	39.30	16.85
Kanypanka	1.191	682.38	41.22	15.16
Khalakan	0.804	619.56	37.50	18.66
Goizha	0.479	857.37	37.70	22.78

TABLE III. Energies of exchange, -ΔGeK (kJ mol-1), for different amount of added potassium and corresponding equilibrium activity RATIOS, AR_E^K

Soil series	Bakhybakhtyare		Bakrajo		Kanypanka		Khalakan		Goizha	
Added K mg L^{-1}	AR_e^K $(mol\ L^{-1})^{1/2}$	$-\Delta G_e^K$ kJ mol^{-1}	AR_e^K $(mol\ L^{-1})^{1/2}$	$-\Delta G_e^K$ kJ mol^{-1}	AR_e^K $(mol\ L^{-1})^{1/2}$	$-\Delta G_e^K$, kJ mol^{-1}	AR_e^K $(mol\ L^{-1})^{1/2}$	$-\Delta G_e^K$ kJ mol^{-1}	AR_e^K $(mol\ L^{-1})^{1/2}$	$-\Delta G_e^K$ kJ mol^{-1}
0	0.0007	-18.00	0.0007	-18.00	0.0008	-17.67	0.0004	-19.38	0.0001	-22.82
5	0.0011	-16.88	0.0008	-17.67	0.0011	-16.88	0.0008	-17.67	0.0004	-19.38
10	0.0015	-16.11	0.0012	-16.66	0.0015	-16.11	0.0011	-16.88	0.0004	-19.38
25	0.0019	-15.52	0.0019	-15.52	0.0020	-15.40	0.0019	-15.52	0.0012	-16.66
50	0.0027	-14.65	0.0027	-14.65	0.0032	-14.23	0.0026	-14.75	0.0019	-15.52
100	0.0043	-13.50	0.0041	-13.62	0.0045	-13.39	0.0044	-13.44	0.0033	-14.16
200	0.0069	-12.33	0.0068	-12.37	0.0068	-12.37	0.0071	-12.26	0.0055	-12.89
300	0.0096	-11.51	0.0071	-12.26	0.0090	-11.67	0.0088	-11.73	0.0063	-12.55
Mean	0.0036	-14.82	0.0032	-15.09	0.0036	-14.72	0.0034	-15.20	0.0024	-16.67

B. *Equilibrium activity ratio of K(AReK)*

AR_e^K means value for all studied soils ranged between 0.0024 to 0.0036 $(mol\ L^{-1})^{1/2}$ as shown inTable 3. The results of this study support the idea that AR_e^K serves as an indicator for the condition of the instantly available K, and therefore regulates the exchange of K ions from the exchange complex to the solution phase [20]. This result reveals that K was preferentially held at inner potions, according to Schouwenburg and Van Schuffelen [8] theory. These results disagree with the finding by Mam-Rasul [21], who studied K adsorption for some calcareous soils in the Kurdistan Region of Iraq and found that the K adsorbed was held at planar positions because the values of AR_e^K in that study ranged from 0.011 to 0.073 $(mol\ L^{-1})^{1/2}$ with the mean of 0.035 $(mol\ L^{-1})^{1/2}$ or more than(0.01) $(mol\ L^{-1})^{1/2}$.

C. *Labile K (L_K)*

Labile K indicates the quantity of K capable of ion-exchange equilibrium conditions between soil solids and solution [7].

The data presented in Table II and Fig. 2 shows the total amount of K in the labile pool ranged between 0.479 and 1.191 $cmol_c$ kg^{-1} in studied soils; this variation may be due to the amount of $CaCO_3$ equivalent in the soils. The higher levels of labile K (1.191$cmol_c$ kg^{-1}) present in the soil at the Kanypanka location indicate that higher amounts of loosely bonded K^+ ions exist in exchangeable positions. Similar results were found by [22, 23] as they reported that higher values of labile K indicated a large K release into soil solution resulting from a large pool of soil K.The lower value of labile K (0.479 $cmol_c$ kg^{-1}) in the soil of Goizha location. This may be due to the high amount of 2:1 expanding clay minerals in surface soils at the Goizha location, which causes retention of K [24]. A higher value of labile K is an indicator of a large K release into the soil solution [6].

D. *Potential buffering capacity (PBC^K)*

The potential buffering capacity (PBC^K) is a measure of the amount of labile K that can be removed before AR_e^K falls by more than given an amount; here, it is the slope of the linear portion of the Q/Icurve (ΔQ/ΔI) [19, 25].

The data shown in Table II indicate that the value of PBC^K for the studied soils ranged from 619.56 to 857.37 $cmol_c$ $kg^{-1}(mol\ L^{-1})^{-1/2}$. The values of PBC^K for all studied soils were more than 200$cmol_c$ $kg^{-1}(mol\ L^{-1})^{-1/2}$, which indicates a high K buffering capacity for the studied soils, according to Zharikova [26] categories. These results disagree with Mam-Rasul [21] results, who found medium K buffering in calcareous soils of the Kurdistan Region of Iraq because the values of PBC^K

in that study ranged between 52.31and 92.42cmol$_c$ kg^{-1} (mol L^{-1})$^{-1/2}$.

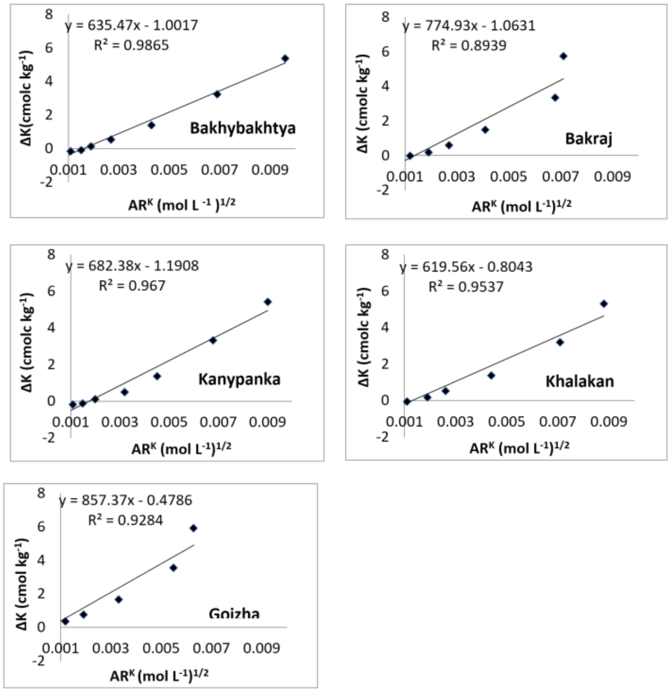

Fig. 2. Quantity/Intensity plots for studied locations

E. Gapon selectivity coefficient (kG)

The soils' relative affinity was also estimated using the Gapon selectivity coefficient for potassium, which reflects the relative affinity developed by the soil for K with the existence of Ca for both the solid phase and solution phase of the soil during equilibrium condition [23]. The kG values fluctuated within the range of 15.16 to 22.78 (L mol-1)1/2, suggesting that the relative affinity for K was quite similar and high (Table II). This means that all studied soils have exhibited quite similar performance for K. Such a high affinity of K to the solid soil phase was attributed to the high content of organic matter and the strong buffering capacities. These results align with Sharma, et al. [27] finding that soils with high values of kG indicate a high affinity for K.

F. Free energy of potassium replenishment at equilibrium (ΔGeK)

Table III includes the results of -ΔGeK for the studied soils; the highest value of -ΔGeK was -14.72 and the lowest value was -16.67 kJ mol-1. That means the K supply for all soils relatively high (i.e., ΔGeK less than -0.6 kJ mol-1), according to the standard for -ΔGeK suggested by Woodruff [28]. These results are identical with Abaslou and Abtahi [29] findings who found similar results in their study on some soils of Iran.

IV. CONCLUSIONS AND RECOMMENDATIONS

The present study describes the K mobility in five forest soil samples in the Kurdistan Region of Iraq. Potassium Q/I relation is utilized for forecasting K$^+$ availability for plants. Q/I approach offers valuable information to better understand K availability in calcareous soils and might be exploited in K fertilizer recommendations.

The Kurdistan Region soil is calcareous, and smectite is the predominant soil mineral, which has a high capacity for K fixation. In this study, AR$_e^K$ values indicate that K was preferentially held at inner positions, levels of labile K were generally high, and K buffering capacity was very high. The high affinity of K to the solid soil phase was attributed to both the high organic matter content and the strong buffering capacities of all the studied soils. Soils that have the greatest buffering capacity showed lesser K saturation rates, which consequently indicate the higher ability to replenish K concentrations in the soil solution. To sum up, thermodynamic approaches better estimation of plant available K.

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