

## Potassium Exchange Isotherms as a Plant Availability Index in Selected Calcareous Soils of Western Azarbaijan Province, Iran

Abbas SAMADI

Soil Science Department, Urmia University, P.O. Box 165, Urmia, 57134, I.R. IRAN

Received: 08.02.2005

**Abstract:** Potassium (K) exchange isotherms (quantity-intensity technique, Q/I) and K values derived from the Q-I relationship provide information about soil K availability. This investigation was conducted to study the relationships among K Q/I parameters, available K extracted by 1 N  $\text{NH}_4\text{AOC}$  (exchangeable K plus solution K), potassium saturation percentage (K-index, %), and the properties of 6 different calcareous agricultural soils. In addition, the relationship of tomato plant yield response to the K requirement test based on K exchange isotherms was investigated. The Q/I parameters included readily exchangeable K ( $\Delta K^0$ ), specific K sites ( $K_x$ ), linear potential buffering capacity ( $\text{PBC}^K$ ), and energy of exchange of K ( $E_K$ ). The results of X-ray diffraction analysis of the oriented clay fractions indicated that some mixed clay mineral, some chlorite/illite clay minerals, along with palygorskite and kaolinite were present in the soils. The soil solution K activity ratio at equilibrium ( $\text{AR}^0$ ) ranged from 0.0014 to 0.028 ( $\text{moles l}^{-1}$ )<sup>0.5</sup>. The readily exchangeable K ( $\Delta K^0$ ) was between 0.044 and 2.5 ( $\text{cmol}_e \text{ kg}^{-1}$  soil), which represented an average of 51% of the exchangeable K ( $K_{ex}$ ). There was a significantly positive relationship between  $\Delta K^0$  and  $\text{NH}_4\text{AOC}$ -extractable K ( $r = 98$ ,  $P < 0.001$ ). The soils showed high capacities to maintain the potential of K against depletion, as they represented very high linear potential buffering capacities ( $\text{PBC}^K$ ) [44-177  $\text{cmol kg}^{-1}/(\text{mol l}^{-1})^{0.5}$ ]. The  $E_K$  values for the check treatments ranged from -2736 to -4117  $\text{calories M}^{-1}$ , and, for the treatments in which 120  $\text{mg K l}^{-1}$  was added, varied between -2193 and -2657  $\text{calories M}^{-1}$ . The percentage of K saturation (K-index, %) ranged from 3.8% to 10.2%. Analysis of variance of the dry matter (DM), K concentrations, and K uptake of tomato plants indicated that there were no significant differences ( $P < 0.05$ ) among the adjusted levels of K as determined by the exchange-isotherm curve.

**Key Words:** Readily exchangeable K, specific K sites, buffering capacity, energy of exchange, K-index, availability

### Introduction

Potassium is one of the most important plant nutrients in soils, and has thus been studied extensively (Potash and Phosphate Institute, 1980). However, in spite of much study and diligent efforts, the fundamental chemical and physical phenomena that govern its fate, movement, and availability to plants in different soils have yet to be fully characterized (Bertsch and Thomas, 1985).

Exchangeable K is widely used as a testing method to characterize the soil K status and to predict crop K requirements. In recent years, there have been various attempts to find a suitable method for determining the availability of soil K in order to evaluate the amount of K fertilizers needed by a particular crop. For a greater understanding of the fertility status of agricultural soils, the quantity-intensity (Q/I) relationship has been used to

measure the availability of potassium in soils (Akinrinde, 1999; Wang and Scott, 2001).

A typical Q/I curve is shown in Figure 1. This relationship implies that the ability of a soil system to maintain a certain concentration of a cation in solution is determined by the total amount of the cation present in readily available forms (exchangeable and soluble) and the intensity by which it is released into the soil solution (LeRoux and Sumner, 1968).

Various interpretations of the parameters  $\text{AR}_e^K$ ,  $\Delta K^0$ ,  $\text{PBC}^K$ ,  $K_x$ , and  $E_K$  have been made, which can be derived from a Q/I plot. The linear portion of the curve has been ascribed to nonspecific sites for K (Beckett, 1964), while the curved portion has been attributed to specific sites with high K affinity (LeRoux and Sumner, 1968). The nonspecific sites have been attributed to planar surfaces

\* Correspondence to: a.samadi@mail.urmia.ac.ir

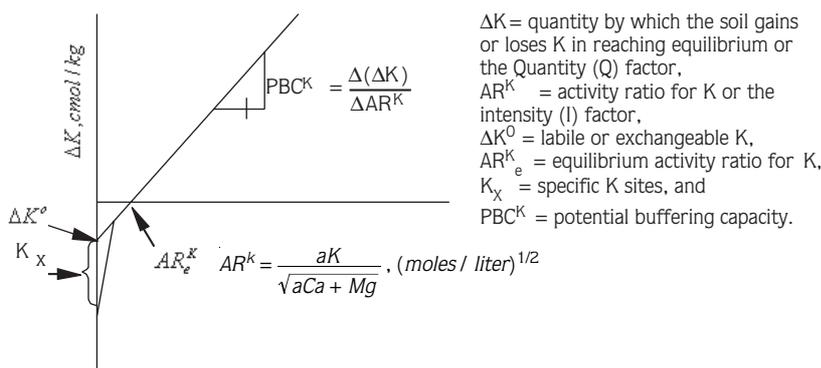


Figure 1. A typical Quantity / Intensity (Q/I) plot.

(Lee, 1973), whereas the specific sites have been ascribed to edges of clay crystals and to wedge sites of weathered mica (Rich, 1964). The  $AR_e^k$  value is a measure of availability or intensity of labile K in soil. Beckett (1964), and LeRoux and Sumner (1968) found that K fertilization increased  $AR_e^k$  values. LeRoux (1966) noted that  $\Delta K^0$  was a better estimate of soil labile K than normal exchangeable K. He found that higher values of labile K ( $\Delta K^0$ ) indicated a greater K release into soil solution, resulting in a larger pool of labile K. The labile K pool increased with K fertilization (LeRoux and Sumner, 1968). The  $PBC^k$  value is a measure of the ability of the soil to maintain the intensity of K in soil solution and is proportional to CEC (Lee, 1973). LeRoux (1966) noted that a high soil  $PBC^k$  value is indicative of good K availability, whereas a low- $PBC^k$  soil would suggest a need for frequent fertilization. The quantity of  $E_k = RT \ln \alpha_k / (\alpha_{Ca} + \alpha_{Mg})^{1/2}$  may be presented as a measure of the free energy of exchange of K in the soil by Ca, and hence, as a measure of the availability of K (Woodruff, 1955). The energy of exchange ( $E_k$ ) for sorption equilibrium solution K level required for maximum growth of tomatoes was  $-2485 \text{ calories M}^{-1}$  (Singh and Jones, 1975).

While numerous studies have been conducted on the quantity of  $NH_4AOC$ -extractable K in calcareous soils of Western Azarbaijan Province (Malakoti and Gheibi, 2000), Iran, little is known of the Q/I relationships of these soils and soil properties. The objectives of this study were: 1) to determine K-exchangeable sorption characteristics of selected soils; 2) to relate Q/I parameters to soil properties; 3) to determine the free energies of exchange ( $E_k$ ) for the sorption process; 4) to evaluate the relationship of yield response of tomato plants with the K requirement test based on K exchange

isotherms, the conventional soil K test ( $NH_4AOC$ -extractable K).

## Materials and Methods

### Soils

Six soil samples belonging to four 4 agriculturally important soil series were taken from agricultural regions in the south of Urmia, Western Azarbaijan Province. The soil series from Rashakan, Kokia, Dash Agher, and Balanej are Typic Calcixerepts. They are very deep, clayey, and calcareous, with angular blocky structures and weak drainage. All soil series studied were classified as Inceptisols according to USDA (United States Department of Agriculture) Soil Taxonomy (Soil Survey, 1999).

The soil samples were air dried and ground to pass through a 2-mm sieve prior to analysis. Some characteristics of these soils are provided in Table 1. Measurement of pH was determined using 1:5 soil to 0.01 M  $CaCl_2$  suspension with a glass electrode, and particle size was determined by the hydrometer method (Bouyoucos, 1951). The total  $CaCO_3$  in soil expressed as the calcium carbonate equivalent (CCE) was determined by a rapid titration method (Rayment and Higginson, 1992). Organic matter was determined by dichromate oxidation (Walkley, 1947). Exchangeable K ( $E_{ex}$ ) and CCE were measured by the method of 1 M  $NH_4OAc$  buffered at pH 7 (Thomas, 1982). K saturation (K-index, %) can be estimated from the following equation (Mutscher, 1995):

$$\text{K-index (\%)} = \frac{K_{ads}(\text{cmol}_c\text{kg}^{-1})}{\text{CEC}(\text{cmol}_c\text{kg}^{-1})}$$

Table 1. Some physical and chemical characteristics, and clay mineralogy of the studied soils.

Soil no.	Soil series	Soil classification <sup>†</sup>	Depth	pH (0.01M CaCl <sub>2</sub> )	O.C.*	CCE*	Clay	Soil* texture	CEC*	EC*
			cm			g kg <sup>-1</sup>			cmol <sub>c</sub> kg <sup>-1</sup> soil	S m <sup>-1</sup>
1	Rashakan	Typic Calcixerepts	0-30	7.6	13	145	250	SCL	11	1.17
2	Rashakan	Typic Calcixerepts	0-30	7.5	6.2	175	490	CL	28	0.71
3	Kokia	Typic Calcixerepts	0-30	7.6	18	215	430	CL	20	1.34
4	Dash Agher	Typic Calcixerepts	0-30	7.6	9.6	210	450	CL	26	0.70
5	Dash Agher	Typic Calcixerepts	0-30	7.6	7.6	240	450	SiCL	18	1.12
6	Baranduz	Fluventic Haploxerepts	0-30	7.7	11	215	350	CL	15	1.02

<sup>†</sup> Based on U.S.D.A. Soil Taxonomy (1975), moisture regime of soils is xeric;

\*: CCE = Total calcium carbonate equivalent; O.C. = Organic carbon; SCL = Sand clay loam, CL = Clay loam SiCL = Silt clay loam

### Mineralogy analyses

Mineralogy analyses, consisting of X-ray diffraction, were performed on the <2 mm clay fraction. Prior to soil mineral fractionation, sub samples were treated with 30% H<sub>2</sub>O<sub>2</sub> to remove organic matter (Kunze, 1965) and with Na-dithionite-citrate-bicarbonate to remove Fe oxides (Mehra and Jackson, 1960). Sand was separated from silt and clay by wet sieving, and clay was separated from silt by centrifugation and decantation. X-ray diffractograms were obtained with a Shimadzu XRD-6000 diffractometer employing a Cu<sub>Kα</sub> radiation source from oriented clay. The semi-quantitative mineralogical composition of the clay fraction treated by Mg-saturation, Mg-plus ethyleneglycol-saturation, K-saturation, and K-saturation and heat was determined by X-ray diffraction analysis.

### Potassium exchange isotherms [Quantity-Intensity relations (Q/I)]

The Q/I curves were determined as follows: 2.5 g duplicate samples of the soil were equilibrated in 50 ml centrifuge tubes containing 25 ml of solution containing from 0 to 120 mg l<sup>-1</sup> K in 0.01 M CaCl<sub>2</sub> solution. Suspensions were shaken for 24 h at 298 K, centrifuged, and then the supernatants were analyzed for K with flame emission photometry. Concentrations of Ca and Mg in the solution were measured by titration using EDTA. Activity ratios were calculated with the Davis equations (Davis, 1962). The amount of K gained or lost (ΔK) by the soil was calculated from the difference between the amounts of K added and recovered in the final solution.

From a plot of ΔK versus the activity ration [ $AR^K = a_K/a_{(Ca+Mg)}^{0.5}$ ], the Q/I parameters were obtained. The intercept of the Q/I curve on the AR<sup>K</sup> axis gave the equilibrium AR for K, AR<sup>0</sup>, which denotes the soil solution K activity relative to the Ca+Mg at equilibrium. The linear part of the curve was extrapolated to intercept the ΔK axis; this represents the amount of readily exchangeable K held in the soil (ΔK<sup>0</sup>). Energies of exchange were calculated using the following equation:

$$E_K = RT \ln a_K / (a_{Ca} + a_{Mg})^{0.5}$$

where  $E_K$  refers to energy of exchange, and  $a_K$ ,  $a_{Ca}$ , and  $a_{Mg}$  are the activity of K, Ca, and Mg, respectively. Finally, the potential buffering capacity (PBC<sup>K</sup>) was determined from the slope of the linear portion of the curve.

### Glasshouse study

The glasshouse study was conducted on tomato plants to evaluate the indices of K availability, including the conventional soil test for K (NH<sub>4</sub>AOC-extractible K), K concentrations in equilibrium solution (EKC), energy of exchange of K ( $E_K$ ), and K saturation percentage (K-index, %). Five levels of K were established in the soils. The amounts of K required to bring the soils to levels of 0.5, 0.75, 1, and 1.25 mmol K l<sup>-1</sup> were determined from the exchange isotherm curves obtained after 24 h of equilibration. There were also check treatments for which no K was added. Potassium added as a solution of KCl was mixed with the soil after which soil water was adjusted to field capacity and equilibrated for 1 week. During equilibration, samples were thoroughly mixed to

ensure uniform contact with the soil. Basal plant nutrients ( $\text{NH}_4\text{NO}_3$ ,  $100 \text{ mg kg}^{-1}$ ;  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $15 \text{ mg kg}^{-1}$ ;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $8 \text{ mg kg}^{-1}$ ;  $\text{H}_3\text{BO}_3$ ,  $8 \text{ mg kg}^{-1}$ ; Fe-chelate,  $8 \text{ mg kg}^{-1}$ ) were applied in solution. The amounts of P were estimated from a previous phosphate sorption-isotherm study (Samadi, 2003) and added in solution. After the addition of K addition, the supplemental nutrients were mixed thoroughly with the soil by shaking in a plastic bottle for 1 min. Five kilograms of each treated soil was placed on 200 g of washed sand in plastic pots. The experiment was laid out in a completely randomized design and replicated 3 times. Tomato (*Lycopersicon esculentum* var. 'Spectrum 882') seedlings were planted until the formation of the first cluster of tomato fruits and leaf sample collection for K concentration measurement was performed at this stage of growth. The whole plants were clipped and dried at  $75^\circ\text{C}$  for dry matter yield, K concentration, and K uptake measurement.

### Statistical analysis

Variance of plant dry matter yield and plant P content was analyzed using the GenStat program (Lane et al., 1987), assuming a randomized complete-block design. Correlation/regression analysis of data was carried out using the StatView program (Abacus Concepts, 1996).

## Results and Discussion

### Properties of soils

Selected properties of the soils studied and the mineral contents in the clay fractions are presented in Table 1. The predominant minerals in the clay fractions were chlorite and illite, and together, both minerals accounted for more than 77% of the clay fraction, and chlorite was the most abundant.

Figure 2 presents a diffractogram of one of the soil series (Rashakan soil series, no. 1). This trace shows a definite (001) chlorite peak at a d spacing of approximately 14.1, a (002) peak at 7.1, a (003) peak at 4.74, and a (004) peak at 3.54. Illite can also be seen in this trace with an (001) peak around a d spacing of 10, a (002) peak at 4.9, and a (003) peak at 3.32, as well as some quartz at a d spacing of 4.25.

### Available, exchangeable and solution K

Values of available K ( $K_{av}$ ), soil solution K ( $K_{so}$ ) and exchangeable K ( $K_{ex}$ ) varied greatly between the studied soils (Table 2). The  $K_{av}$  values varied from 207 to 538  $\text{mg kg}^{-1}$ , indicating that the soils were medium to high in K availability, except soil no. 5 (Dash Agher soil series), which had an excessive value ( $1217 \text{ mg kg}^{-1}$ ) that may have been due to over-fertilization with K fertilizer.

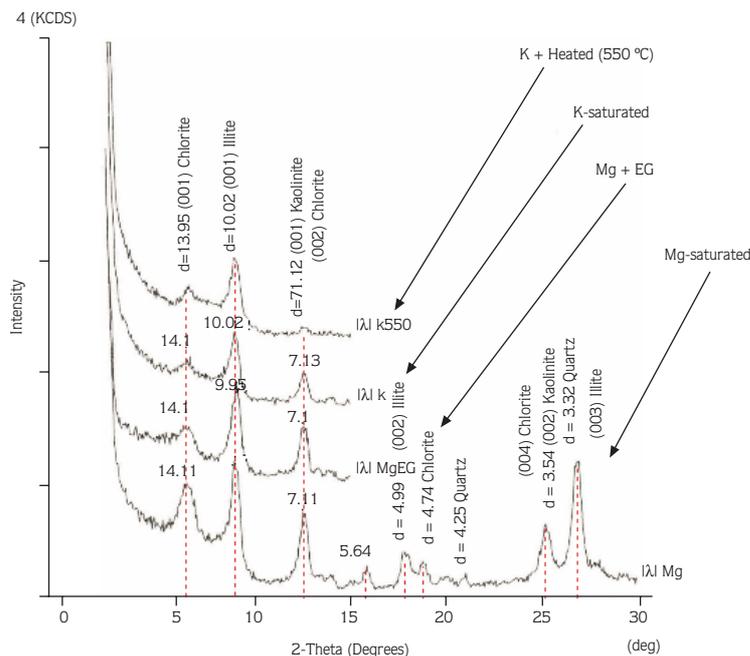


Figure 2. X-ray diffractogram of soil no. 1 (Rashakan soil series).

Exchangeable K ( $K_{ex}$ ) contents in the soils ranged from 160 to 441 mg kg<sup>-1</sup>. These values were high compared with those normally recommended for soils with different textures. For example, Meyer and Wood (1985) suggested a critical  $K_{ex}$  level of 120 mg kg<sup>-1</sup> for light and medium textured soils and 240 mg kg<sup>-1</sup> for heavy textured soils. Concentrations of K in soil solution ranged from 2.4 to 9.5 mg l<sup>-1</sup>, with a mean value of 5.7 mg l<sup>-1</sup>. In consideration of the high levels of  $K_{ex}$  found in this study and the fact that  $K_{so}$  is in equilibrium with  $K_{ex}$ , the low concentrations of  $K_{so}$  were surprising. This was presumably due to high affinity of reactive surfaces of 2:1 clays, in particular, micaceous clays (K-bearing minerals) for adsorbed K as compared to smectitic clays (Gawander et al., 2002).

#### Potassium saturation percentage (K-index)

The soils contained a significant percentage of K saturation (K-index, %). The K-index varied from 3.7% to 10.2% (Table 2). In some countries, the K-index (%) is used for assessment of soil K-status (Mutscher, 1995).

#### Potassium exchange isotherms (Q/I relations)

Q/I relationships for the soils studied are illustrated in Figure 3. The Q/I plots showed the common shapes described in the literature (Wang and Scott, 2001; Gawander et al., 2002). All soil series studied, except soil no. 1, were linear over the range of the activity ratios found in these soils, without the curvature of the lower part, which has been observed by Beckett (1964) and Alafifi (1996). The values for the Q/I plot components ( $AR^0$ ,  $\Delta K^0$ ,  $K_x$ , and  $PBC^K$ ) are shown in Table 2.

The values of the equilibrium activity ratio ( $AR^0$ ) ranged between 0.0014 and 0.028 (moles l<sup>-1</sup>)<sup>0.5</sup>. In all the soil series studied, except soil no. 5, the  $AR^0$  values were lower than those reported by Sparks and Liebhardt (1981). Since illitic clays were the dominant clay minerals in the soil studied (Figure 2), the lower amount of  $AR^0$  could be attributable to a greater number of specific K sites, which could fix K. The high value in soil no. 5, which was due to K fertilization history, suggests that the adsorbed K was primarily held at planer positions since the  $AR^0$  values were >0.01 (Sparks and Liebhardt, 1981). The  $AR^0$  values have significant relationships with labile K ( $\Delta K^0$ ) and NH<sub>4</sub>AOC-extractable K (Table 3). There was no relationship between  $AR^0$  and the ability of any of the studied soils to supply K over an extended period of time ( $PBC^K$ ). This result is in agreement with that obtained by Alafifi (1996) for the calcareous soils of the United Arab Emirates.

The labile K ( $\Delta K^0$ ) values were 0.044-2.5 cmol kg<sup>-1</sup> soil (Table 2), and the highest values were associated with the soil series having the greatest amount of CEC, except the Dash Agher soil series (soil no. 5), which had been fertilized with K. The  $\Delta K^0$  value of soil no. 5 was more negative indicating that a greater amount of K released into soil solution, resulting in a large pool of labile K (LeRoux and Sumner, 1968) as compared to the other soils studied, whose values of labile K were less negative, demonstrating that these soils had a strong ability to adsorb K (Sparks and Liebhardt, 1981). LeRoux and Sumner (1968) observed that  $\Delta K^0$  is a better estimate of soil labile K than exchangeable K. The  $\Delta K^0$  values made up

Table 2. Values of available K ( $K_{ex} + K_{so}$ ), solution K ( $K_{so}$ ), exchangeable K ( $K_{ex}$ ), percentage of K saturation (K-index, %) and Q/I parameters.

Soil No.	Soil series	$K_{ex} + K_{so}$ ( $K_{av}$ )	cmol <sub>c</sub> kg <sup>-1</sup>			$K_x$	$K_{so}$	$AR^0$ (moles l <sup>-1</sup> ) <sup>0.5</sup>	$PBC^K$ cmol <sub>c</sub> kg <sup>-1</sup> / (mol l <sup>-1</sup> ) <sup>0.5</sup>	K-index %
			$K_{ex}$	$\Delta K^0$						
1	Rashakan	0.53	0.41	0.044	0.48	4.7	0.0089	44	3.8	
2	Rashakan	1.13	1.04	0.25	0.88	3.6	0.0014	177	4.3	
3	Kokia	1.38	1.13	0.62	0.76	9.6	0.0065	95	4.1	
4	Dash Agher	1.04	0.98	0.25	0.79	2.4	0.0019	128	3.7	
5	Dash Agher	3.12	1.84	2.5	0.62	49.8	0.028	75	10.2	
6	Baranduz	0.79	0.58	0.31	0.48	8.3	0.0050	62	4.0	

$AR^0$ : equilibrium activity ratio;  $\Delta K^0$ : labile or easily exchangeable K;  $K_x$ : K held on specific or slow release sites;  $PBC^K$ : potential buffering capacity

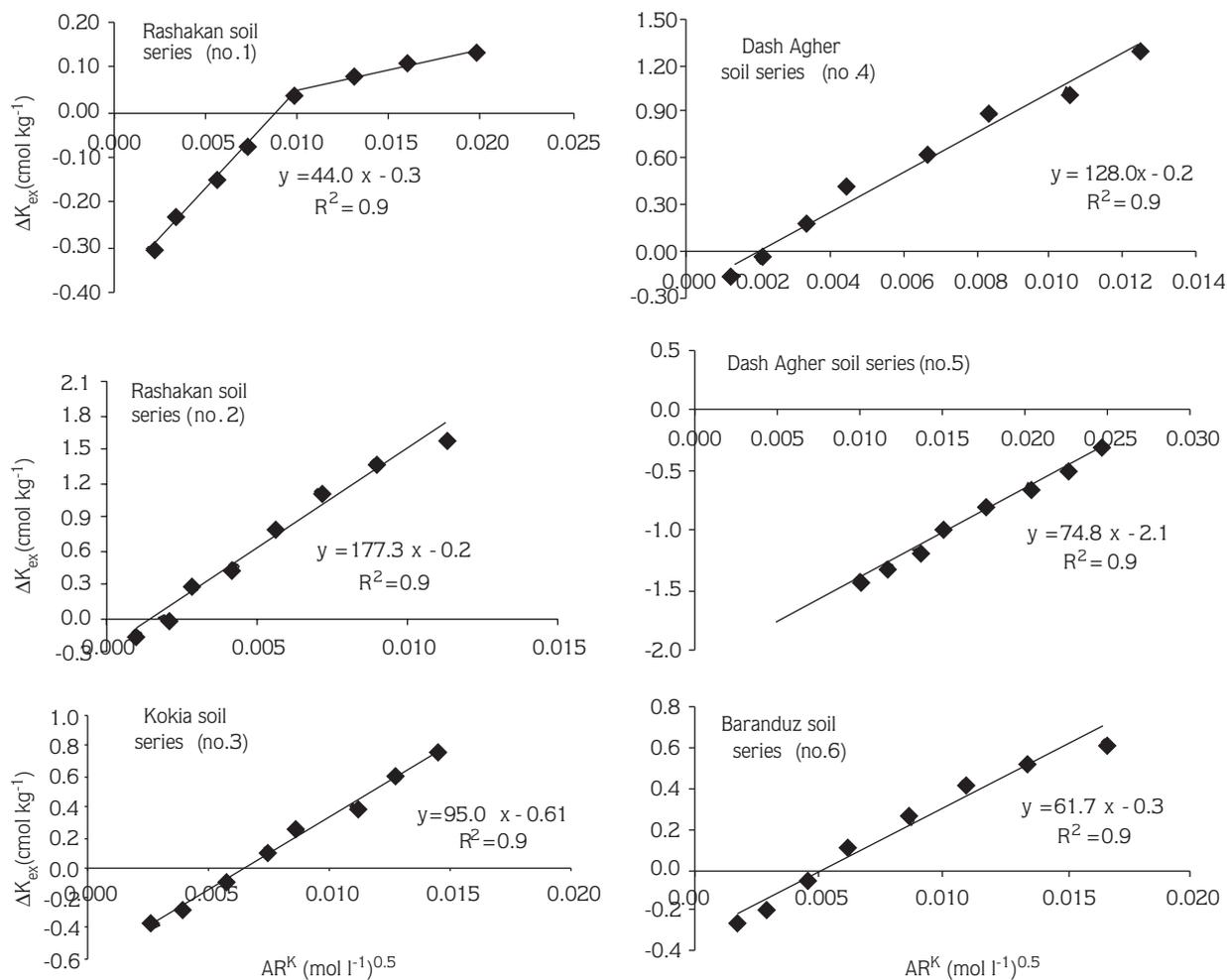


Figure 3. Quantity/Intensity (Q/I) plots for the soil series studied.  $AR^K$ , potassium activity ratio.

Table 3. Correlation coefficients (r) for linear relationships among Q/I parameters and between Q/I parameters and K availability (K-index and  $NH_4AOC$ -extractable K ( $K_{av}$ )).

	$AR^0$	$K_x$	$PBC^K$	$K_{av}$	K-index	$E_K$	$K_G$
$K_x$	-0.36 <sup>ns</sup>						
$PBC^K$	-0.46 <sup>ns</sup>	0.94**					
$K_{av}$	0.86**	0.11 <sup>ns</sup>	-0.012 <sup>ns</sup>				
K-index	0.95**	-0.11 <sup>ns</sup>	-0.18 <sup>ns</sup>	0.96**			
$E_K$	0.97***	-0.34 <sup>ns</sup>	-0.51 <sup>ns</sup>	0.85*	0.89*		
$K_G$	-0.40 <sup>ns</sup>	0.61 <sup>ns</sup>	0.84*	-0.13 <sup>ns</sup>	-0.15 <sup>ns</sup>	-0.56 <sup>ns</sup>	
$\Delta K^0$	0.93**	-0.067 <sup>ns</sup>	-0.18 <sup>ns</sup>	0.98***	0.98***	0.92**	-0.25 <sup>ns</sup>

between 8.4% and 80% of  $\text{NH}_4\text{AOC}$ -extractable K (Table 2). There was a significantly positive relationship ( $P < 0.001$ ) between  $\Delta K^0$  and  $\text{NH}_4\text{AOC}$ -extractable K (Table 3). The values of  $\text{NH}_4\text{AOC}$ -extractable K were considerably higher than  $\Delta K^0$  values (Table 2), suggesting that there were more specific sites for K in the soil studied (Sparks and Liebhardt, 1981). This was likely since the clay contents of the soils were relatively high and the clay mineralogy of all soils studied was dominated by micaceous clays (Figure 2); thus the number of specific sites as measured by  $K_x$  was appreciable. Richard and Bates (1988) stated that in clay minerals having the specific K site, ammonium could displace  $\text{K}^+$  from these specific sites, resulting in a higher prevalence of exchangeable K with  $\text{NH}_4\text{AOC}$ . It seems that in the soil series we studied,  $\text{NH}_4\text{AOC}$  would tend to over-predict exchangeable K, which agrees with similar observations by Hosseinpour and Kalbasi (2000).

The  $K_x$  values ranged between 0.48 and -0.88  $\text{cmol kg}^{-1}$ , comprising of 20% to 92% of  $\text{NH}_4\text{AOC}$ -extractable K, the average being 64%. The high amount of  $K_x$  (78% of exchangeable K) in the Rashakan soil series (soil no. 2) resulted in reducing  $\text{AR}^0$  in this soil.  $K_x$  values depend on the type of clay minerals present in a soil sample (Hosseinpour and Kalbasi, 2000). In soils having clay minerals with more specific K sites, the amount of  $K_x$  is high, indicating that the significant amount of K was adsorbed on the high energy specific site. The lack of a relationship between  $K_x$  and  $\text{NH}_4\text{AOC}$ -extractable K values (Table 3) showed that the specific K site ( $K_x$ ) was related to the clay minerals type rather than the 1 M  $\text{NH}_4\text{AOC}$ -extractable K.

The slope of the linear part of the Q/I plot ( $\text{PBC}^K$ ), being a measure of soil ability to supply K activity (intensity factor) in soil solution, varied between 44 and 177 [ $\text{cmolc kg}^{-1} / (\text{mol l}^{-1})^{0.5}$ ] (Table 2). The  $\text{PBC}^K$  values were indicative of the relatively high CEC of these soils that were high in clay content (Table 1). The high values for  $\text{PBC}^K$  indicated that these soils had a very high capacity to protect the soil solution K concentration from depletion. The highest value for  $\text{PBC}^K$  was associated with soil no. 2, which had the greatest amount of clay content, and the lowest  $\text{PBC}^K$  value was related to soil no. 1, which had the least amount of clay content and CEC. The lack of a significant relationship between  $\text{PBC}^K$  and both clay content and CEC may be attributed to the relatively high variation in the physicochemical properties of the soils studied, which resulted in inconsistent  $K_G$  values being

estimated from the equation  $\text{PBC}^K = \text{CEC} \times K_G$  (Evangelou and Karathanasis, 1986). Hosseinpour and Kalbasi (2000) reported a poor relationship between  $\text{PBC}^K$  and CEC ( $R^2 = 0.43$ ,  $P < 0.01$ ), while Jimenez and Parra (1991) found a strong relationship between these properties ( $R^2 = 0.94$ ,  $P < 0.001$ ) for the calcareous soils of Spain. Al-Kanani et al., (1989) and Rasnake and Thomas (1976) did not observe any relationships between  $\text{PBC}^K$  and CEC for calcareous soils and alluvial soils in Kentucky, respectively.

### Energy of Exchange

The energy of exchange of K ( $E_K$ ) for divalent cations was calculated from  $E_K = -RT \ln \text{AR}_e^K$ . The values of equilibrium activity ratios ( $\text{AR}_e^K$ ) and  $E_K$  for the unfertilized and fertilized Dash Agher soil series (soil no. 4 and soil no. 5) are presented in Table 4. The results show that energies of sorption were more negative at lower concentrations of added K. The same trends were observed for all soils studied (data not shown). Singh and Jones (1975) reported that energies of exchange for the replacement of Ca with K ranging from -3500 to -4000 calories  $\text{M}^{-1}$  were associated with K deficiency in plants. A range of -2500 to -3000 calories  $\text{M}^{-1}$  indicated suitable balances between Ca and K. Energies of exchange less than -2000 were related to excessive amounts of K in relation to the amounts of Ca that were present. The  $E_K$  values for the check treatments ranged from -2736 to -4117 calories  $\text{M}^{-1}$ , and for the treatment in which 120  $\text{mg K l}^{-1}$  was added,  $E_K$  varied from -2193 to -2657 calories  $\text{M}^{-1}$  (data not shown).

Table 4. Energies of exchange,  $E_K$  (calories/M), for different amounts of added potassium and corresponding equilibrium activity ratios,  $\text{AR}_e^K$ .

Soil series	Dash Agher (no. 4)		Dash Agher (no. 5)	
	$\text{AR}_e^K$	$E_K$	$\text{AR}_e^K$	$E_K$
Added K ( $\text{mg l}^{-1}$ )				
0	0.0013	-3930	0.0099	-2736
10	0.0020	-3673	0.0117	-2637
25	0.0033	-3384	0.0135	-2553
40	0.0044	-3214	0.0148	-2496
60	0.0066	-2974	0.0175	-2397
80	0.0084	-2834	0.0202	-2312
100	0.0105	-2701	0.0224	-2250
120	0.0125	-2598	0.0247	-2193

Table 5. The dry matter (g), K concentration (%) and K uptake (mg kg<sup>-1</sup>) of tomato plant grown on the selected soil series in relation to adjusted levels of K in solution. Values are means + SD of the various K treatments.

Soil No.	Soil series	Adjusted K levels, mg/L														
		No K applied			20			30			40			50		
		DM	K conc.	K uptake	DM	K conc.	K uptake	DM	K conc.	K uptake	DM	K conc.	K uptake	DM	K conc.	K uptake
1	Rashakan	12 ± 2.7	3.4 ± 0.06	0.41 ± 0.08	9.8 ± 3.4	3.1 ± 0.040	0.31 ± 0.11	9.7 ± 0.98	3.1 ± 0.10	0.31 ± 0.04	8.5 ± 2.0	3.4 ± 0.40	0.29 ± 0.08	10.0 ± 3.0	3.1 ± 0.24	0.32 ± 0.10
2	Rashakan	10.8 ± 0.25	3.2 ± 0.11	0.34 ± 0.005	9.0 ± 1.6	3.4 ± 0.22	0.30 ± 0.04	9.5 ± 2.1	2.9 ± 0.18	0.28 ± 0.07	12.2 ± 2.3	3.2 ± 0.0	0.39 ± 0.07	13.0 ± 1.8	3.0 ± 0.25	0.39 ± 0.8
3	Kokla	9.1 ± 1.2	2.8 ± 0.14	0.26 ± 0.02	9.9 ± 3.6	2.7 ± 0.46	0.31 ± 0.13	9.5 ± 0.13	2.9 ± 0.51	0.27 ± 0.03	8.6 ± 3.8	2.4 ± 0.15	0.21 ± 0.10	9.0 ± 0.3	2.8 ± 0.15	0.25 ± 0.01
4	Dash Agher	11.6 ± 2.0	4.1 ± 0.10	0.48 ± 0.06	8.1 ± 1.1	2.5 ± 0.48	0.21 ± 0.06	7.1 ± 0.81	3.0 ± 0.39	0.21 ± 0.01	9.4 ± 1.7	3.0 ± 0.28	0.28 ± 0.04	8.8 ± 2.0	2.6 ± 0.48	0.23 ± 0.08
5	Dash Agher	9.4 ± 1.9	3.0 ± 0.29	0.29 ± 0.11	14.3 ± 3.0	3.8 ± 0.10	0.55 ± 0.10	8.7 ± 1.6	4.0 ± 0.32	0.34 ± 0.06	13.7 ± 4.1	4.0 ± 0.16	0.55 ± 0.17	10.6 ± 1.7	4.2 ± 0.55	0.45 ± 0.11
6	Baranduz	12.0 ± 2.2	3.4 ± 0.48	0.41 ± 0.06	9.9 ± 1.2	3.2 ± 0.10	0.32 ± 0.03	9.7 ± 0.87	3.5 ± 0.54	0.37 ± 0.02	8.4 ± 1.3	3.5 ± 0.10	0.29 ± 0.05	9.3 ± 1.7	3.0 ± 0.11	0.28 ± 0.06

DM, dry matter; K conc., K concentration

### Greenhouse study

The mean values of dry matter yield (DM), K concentration, and K uptake of tomatoes in relation to adjusted levels of K in soil solution for some selected soil series studied are presented in Table 5. Analysis of variance of DM, K concentrations, and K uptake of tomato plants indicated that there were no significant differences ( $P < 0.05$ ) among the adjusted levels of K as measured with sorption-isotherm curves in all soil series studied (Table 5).

Currently, the accepted critical level of  $\text{NH}_4\text{AOC-K}$  for tomatoes in calcareous soils of Western Azarbaijan Province is  $300 \text{ mg K kg}^{-1}$  soil (Malakouti, 2000). It is, therefore, expected that soil K test results lower than  $300 \text{ mg K kg}^{-1}$  or the application of K fertilizer to soils with  $\text{NH}_4\text{AOC-K}$  levels lower than this level should result in increased tomato yield. The results showed that tomatoes grown in soil no. 1 did not respond to the

applied K. It is speculated that the lack of response to high rates of K might have been due to normal uptake of solution K maintained by the replenishment of K from exchangeable and non-exchangeable pools. This experiment illustrates that the soils in which plants were not responsive to applied K in the glasshouse study supported sufficient amounts of K in tomato plants.

### Acknowledgments

This research was supported by Urmia University, Urmia, Iran. The author expresses his gratitude to the staff of the Vice Chancellor Research Office for their cooperation and assistance. The assistance of the staff and technicians of the Soil Science Department, Mr. B. Dovlati, Mr. M. Barin, and Mr. Y. Hasirchi in the collection of and analyses of soil samples is gratefully acknowledged.

### References

- Akinrinde, E.A. 1999. Quantity-intensity parameters of potassium in relation to uptake by Guinea corn in representative soils of the ecological zones of Nigeria. *Comm. Soil Sci. Plant Anal.* 30: 2695-2710.
- Al-Kanani, T., A.J., Hussien and N.N., Barthakut. 1989. Potassium exchange equilibria in calcareous soils. *Soil Sci.* 148: 286-292.
- Alafifi, M.A. 1996. Potassium potential and potential buffering capacity of Torripsammments in the United Arab Emirates. *Commun. Soil Sci. Plant Anal.* 27: 27-36.
- Beckett, P.H.T. 1964. Studies on soil potassium: II. The immediate Q/I relations of labile potassium in the soil. *J. Soil. Sci.* 15: 9-23.
- Bertsch, P.M. and G.W. Thomas. 1985. Potassium Status of Temperate Region Soils. In *Potassium in Agriculture*; Munson, R.D. Ed.; American Society of Agronomy: Madison, WI, 131-162.
- Bouyoucos, G.J. 1951. Recalibration of hydrometer method of making mechanical analysis of soil. *Agron. J.* 43: 434-435.
- Davis, C.W. 1962. *Ion Association*. Butterworths, London, England.
- Evangelouand, V.P. and A.D. Karathanasis. 1986. Evaluation of potassium quantity-intensity relationships by a computer model employing the Gapon equation. *Soil Sci. Soc. Am. J.* 50: 58-62.
- Gawander, J.S., P., Gangaiya and R.J., Morrison. 2002. Potassium studies on some sugarcane growing soils in Fiji. *S. Pac. J. Nat. Sci.* 20: 15-21
- Hosseinpour A.R. and M. Kalbasi. 2000. Potassium quantity-intensity ratio and the correlation of its parameters with soil properties in some Iranian soils. *Journal of Science and Technology of Agricultural and Natural Resources.* 4: 43-55.
- Jimenez, C. and M.A. Parra. 1991. Potassium quantity-intensity relationships in calcareous Vertisols and Inceptisols of southern Spain. *Soil Sci. Soc. Am. J.* 55: 985-989.
- Kunze, G.W. 1965. Pretreatment for mineralogical analysis. (Ed. C. A. Black) *Methods of soil Analysis. Agronomy. American Society of Agronomy, Madison, Wisconsin. USA.* Pp. 210-221.
- Lee, R. 1973. The K/Ca Q/I relation and preferential adsorption sites for potassium. *New Zealand Soil Bureau Scientific Report II.*
- LeRoux, J. 1966. Studies on ionic equilibria in Natal soils. Ph.D. diss. Univ. Of Natal., Republic of South Africa.
- LeRoux, J. and M. E. Sumner. 1968. Labile potassium in soils: I. Factors affecting the quantity-intensity (Q/I) parameters. *Soil Sci.* 106:35-41.
- Malakouti, M.J. and M.N. Gheibi. 2000. Determination of nutrients critical levels in soil, plant and fruit. Agricultural training publication, TAT organization, Agricultural Ministry, Karj, Iran.
- Mehra, O.P. and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* 7, 317-327.
- Meyer, J.H. and R.A. Wood. 1985. Potassium nutrition of sugarcane in South African sugar industry. In: *Proc. of the Potassium Symposium, Pretoria 1985.* p 205-213.
- Mutscher H. 1995. Measurement and assessment of soil potassium. IPI Research Topics No. 4 (revised version), International Potash Institute Basel, Switzerland, 102 pp.
- Potash and Phosphate Institute. 1980. Potassium for Agriculture - A Situation Analysis. Potash and Phosphate Institute, Atlanta. 216 p.

- Rasnake, M. and W. Thomas. 1976. Potassium status of some alluvial soils in Kentucky. *Soil Sci. Soc. Am. Proc.* 40: 883-887.
- Rayment, G.E. and F.R. Higginson. 1992. Oxalate-extractable Fe and Al. In " Australian Laboratory Handbook of Soil and Water Chemical Methods". Inkata Press, Melbourne.
- Rich, C.I. 1964. Effect of cation size and pH on potassium exchange in Nason soil. *Soil Sci.* 98: 100-106.
- Richards, J. and T.E. Bates. 1988. Studies on the potassium supplying capacities of southern Ontario soils. II. Nitric acid extraction of non-exchangeable K and its availability to crops. *Can. J. Soil Sci.* 69: 199-208.
- Samadi, A. 2003. Predicting phosphate fertilizer requirement using sorption isotherms in selected calcareous soils of Western Azarbaijan Province, Iran. *Commun. Soil Sci. Plant Anal.* 34: 2885-2899.
- Singh, B.B. and J.P. Jones. 1975. Use of sorption-isotherms for evaluating potassium requirement of plants. *Soil Sci. Soc. Am. Proc.* 39: 881-896.
- Soil Survey 1999. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*. USDA-NRCS, Agriculture Handbook No. 436. U.S. Government Printing Office. p. 870.
- Sparks, D.L. and W.C. Liebhardt. 1981. Effect of long-term lime and potassium application on quantity-intensity relationships in sandy soil. *Soil Sci. Soc. Am. J.* 45: 786-790.
- Thomas, G.W. 1982. Exchangeable cations. In: A.L. Page et al. (ed.) *Methods of Soil Analysis: Part 2. Chemical and microbiological properties*. ASA Monograph. 9: 159-165.
- Walkely, A. 1947. A critical examination of a rapid method for determining soil organic carbon in soils. Effect of variations in digestion conditions and inorganic soil constituents. *Soil Sci.* 63: 251-263.
- Wang, J.J. and A.D. Scott. 2001. Effect of experimental relevance on potassium Q/I relationships and its implications for surface and subsurface soils. *Commun. Soil. Sci. Plant Anal.* 32: 2561-2575.
- Woodruff, C.M. 1955. The energies of replacement of calcium by potassium in soils. *Soil Sci. Soc. Am. Proc.* 19: 36-40.