

## USE OF THERMODYNAMIC PARAMETERS OF Q–I ISOTHERMS TO EVALUATE OF K–AVAILABILITY IN SOME EGYPTIAN SOILS

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### ABSTRACT:

Quantity–intensity (Q/I) isotherms were applied to evaluate the availability of  $K^+$  in four different Egyptian soils. Wheat plant was used as an indicator to achieve this goal. After wheat sowing, soils were fertilized by  $K_2SO_4$  at different rates of 0, 50, 100 and 150% of wheat's fertilizer recommendation.

The obtained results showed that increasing added  $K^+$  concentrations led to increase the activity ratio of  $K^+$  ( $AR_K^0$ ) and corresponding changes in labile  $K^+$  (K) at equilibrium. The equilibrium activity ratio of  $K^+$  ( $AR_K^0$ ) varied between  $2.88 - 15.01 \times 10^{-3} (\text{mol L}^{-1})^{0.5}$  in initial stage and  $1.39 - 17.31 \times 10^{-3} (\text{mol L}^{-1})^{0.5}$  in the last stage. The labile  $K^+$  ( $K_L$ ) fraction ranged from 0.047 – 0.456 and 0.02 – 0.45  $\text{cmol kg}^{-1}$  before sowing and at harvesting time of wheat plant, respectively. The potential buffering capacities of  $K^+$  ( $PBC_K$ ) fluctuated from 16.3 – 30.4 and 11.9 – 29.9  $\text{cmol kg}^{-1} (\text{mol L}^{-1})^{-0.5}$  before sowing and at harvesting stage of wheat plant. The free energy of  $K^+$  exchange ( $-\Delta G$ ) ranged from  $-3.37$  to  $-2.42$  ( $\text{kcal. mol}^{-1}$ ) prior to cultivation to reach  $-3.79$  to  $-2.34$  ( $\text{kcal. mol}^{-1}$ ) at the end of cultivation period. In general, Silt, pH, EC, OM, Soluble K,  $NH_4OAcK$  and  $HNO_3K$  exhibited substantial correlations with  $K_L$ ,  $PBC_K$ ,  $AR_K^0$ ,  $K_G$  and  $\Delta G$ , whereas pH had inverse correlation with mentioned parameters, except  $K_G$ . Furthermore, a substantial correlation was observed between thermodynamic characteristics of K extracted by  $H_2O$ , 1 M  $NH_4OAc$  and 1M  $HNO_3$ .

**Conclusively:** from these results it could be concluded that, significant correlation of the tested thermodynamic parameters with physicochemical soil characteristics. Thus, the study contributed significantly to practical  $K^+$  management by providing important information on  $K^+$  dynamics in typical Egyptian soils.

**Keywords:** Q/I relations; –Thermodynamic parameters of K; forms of K; Activity ratio of K; Gibb's Free Energy.

## INTRODUCTION

For all plants, potassium (K) is one of the most essential macronutrients. Except for nitrogen, it is taken up by plants in amounts that may surpass those of the other elements. According to the necessary nutrient requirements for most plants, it is a vital component for all plants. (Manahan, 2017). It also has a significant impact on agricultural output, both in terms of quantity and quality.

The study of K-behavior in soils is important because of its importance for plants especially the development of farming towards intensive agriculture. As a result, it is now important to reevaluate K supply capacity on a thermodynamic basis to identify K availability by evaluating soil K using intensity/quantitative (Q/I) characteristics. In an attempt to describe the mechanisms of K release and fixation from the soil solid phase to the soil solution phase, the Quantity-Intensity relationship (Q/I) was first introduced by (Woodruff, 1955b) and further developed by (Beckett, 1964a,b) as a specialized version of sorption curves experimentation for describing K potential buffering characteristics. Although the universality of scope in forecasting available K has sometimes been questioned, quantity intensity experiments remain one of the primary tools in understanding K dynamics in soils over seven decades since these original efforts. This explains why a lot of newly published research on K dynamics still looks at the availability of K via the perspective of the Q/I relationship (Islam *et al.*, 2017; Panda & Patra, 2018; Das *et al.*, 2019; Jiang *et al.*, 2019; Suttanukool *et al.*, 2019; Zhu *et al.*, 2020). Parameters included from Q/I isotherms include equilibrium activity ratio ( $AR_K$ ) which is a measure of K soil solution intensity (Intensity Factor), a quantity (Quantity Factor) parameter ( $\Delta K_0$ ) which is assumed to represent soil labile K ( $K_L$ ), and the potential buffering capacity ( $PBC_K$ ), which is an indicator of soil's buffering ability to resist soil solution K changes. Furthermore, Gibb's free energy of exchange ( $\Delta G$ ) is the amount of energy released when one equivalent of K in the standard state is replaced by equivalents of Ca and/or Mg in the soil solid phase. According to Evangelou *et al.* (1994) in their thorough review on the Q/I connections ( $K_G$ ), several recent research has utilized thermodynamic criteria to assess the availability of K in soil, but conventional techniques of assessing the quantity of K suitable for extraction after employing 1 M  $NH_4OAc$  have limited its application. In many situations, a quantitative criterion like this did not provide the desired result (Cooke, 1979). As a result, scientists began using thermodynamic criteria, which are thought to be a more accurate means of determining how much soil can supply. Furthermore, Wang *et al.* (2004), Pasricha & Bansal (2002), Surapaneni *et al.* (2002), Samadi (2006), Zarrabi & Jalali (2008), Al obidi *et al.* (2011) shown that K dynamics between the solid and liquid phases of soils are

influenced by the ion-exchange theory for the ions  $K^+$ ,  $Ca^{2+}+Mg^{2+}$ . We can compute several thermodynamic parameters (*i.e.*,  $-\Delta G$ ,  $PBC_K$ ,  $K_L$ ,  $AR_K$ ) that may be utilized to determine the K fertilizer demands of soils utilizing ionic exchange. As the effectiveness ratios represent it in the releasable storage (Beckett, 1964b; Sparks, 2000), specialized and nonspecialized sites (Sparks, 2000; Wang et al., 2004) that play an important role in providing K to the liquid soil phase (Subba & Srivastava, 2001). Either Khamis (2000) or Al obidi et al. (2011) demonstrated that thermodynamic characteristics may be utilized to assess K levels in soil solids and solutions. Cation exchange capacity (CEC) alone may not be able to show the true condition of soils when K fixation and liberation are dominant in terms of biological features (Beckett et al., 1966a). One of the fundamental approaches used to study K's PBC was outlined in the papers of the K International Institute (Krauss, 2002). Clay soils contained more K than sand soils, according to Krauss (2002), while Wang et al. (2004) noted that  $AR_K$  represents the concentration of K in soils characterized by their liquid-solid phase equilibrium.

As a result, the goal of the study was to investigate the availability of K using various thermodynamic characteristics, as well as its relationship to soil characteristics of several typical Egyptian soils and their influence on wheat yields produced in such soils.

## MATERIALS & METHODS

### *1. The experiment location and treatments:*

Four different types of typical Egyptian soils were used in a pot experiment at the Ismailia Research Station Farm (Location: 30°39'32.2"N 32°14'54.9"E). Soil samples were taken from several sites (Locations: 30°29'04.9"N 32°04'37.0"E; 30°32'33.6"N 32°12'09.4"E; 30°34'36.6"N 32°08'29.9"E; 30°21'14.3"N 30°00'46.8"E). The studied soils differed in texture, physicochemical properties, and K thermodynamic parameters, as shown in Table 1. Figure 1 presents the initial plot of the quantity-intensity relationship in tested soils. Soil samples were placed in plastic pots (5 kilograms each) and fertilized with the recommended nitrogen (Urea 46 % N) and phosphorus (P) (Calcium monophosphate 15 %  $P_2O_5$ ). On December 4, 2018, wheat seeds (*Triticum aestivum* Var. Misr 1) were sowed. During the 2018/2019 winter season, the soils were watered once a week. According to the Egyptian Ministry of Agriculture and Land Reclamation, soils were fertilized with  $K_2SO_4$  (46 %  $K_2O$ ) at rates of 0, 50, 100, 150 % of recommended rate and

**Table (1):** Initial characteristics and thermodynamic parameters of the tested soils.

Property	Soil 1	Soil 2	Soil 3	Soil 4
<b>Particles size distribution (g hg<sup>-1</sup>)</b>				
Sand	80.5	37.5	12.5	44.5
Silt	18.0	51.0	48.0	48.0
Clay	1.5	11.5	39.5	7.5
<b>Texture<sup>1</sup></b>	Sandy	Silty loam	Silty clay loam	Loamy
pH <sup>2</sup>	8.22	7.89	7.87	8.21
EC <sup>3</sup> (dS m <sup>-1</sup> )	2.87	3.88	3.08	3.82
CaCO <sub>3</sub> (g Kg <sup>-1</sup> )	12.60	25.21	21.03	184.84
Organic matter (g Kg <sup>-1</sup> )	1.61	1.93	12.01	2.41
CEC (cmol Kg <sup>-1</sup> )	10.12	16.86	24.16	13.25
<b>Extractable K (cmol Kg<sup>-1</sup>) by:</b>				
H <sub>2</sub> O-K	0.022	0.037	0.045	0.031
NH <sub>4</sub> OAc-K	0.197	0.732	0.756	0.412
HNO <sub>3</sub> -K	0.292	1.456	2.897	0.578
<b>Some thermodynamic parameters</b>				
K <sub>L</sub> (cmol kg <sup>-1</sup> )	0.047	0.259	0.456	0.187
PBC <sub>K</sub> (cmol kg <sup>-1</sup> )/(mol L <sup>-1</sup> ) <sup>0.5</sup>	16.30	25.2	30.4	18.2
AR <sub>K</sub> <sup>0</sup> (mol L <sup>-1</sup> ) <sup>0.5</sup> × 10 <sup>-3</sup>	2.883	10.258	15.007	10.247
Relative affinity for K (L mol) <sup>0.5</sup>	1.611	1.495	1.258	1.374
-ΔG (kcal. mol <sup>-1</sup> )	-3.37	-2.64	-2.42	-2.64

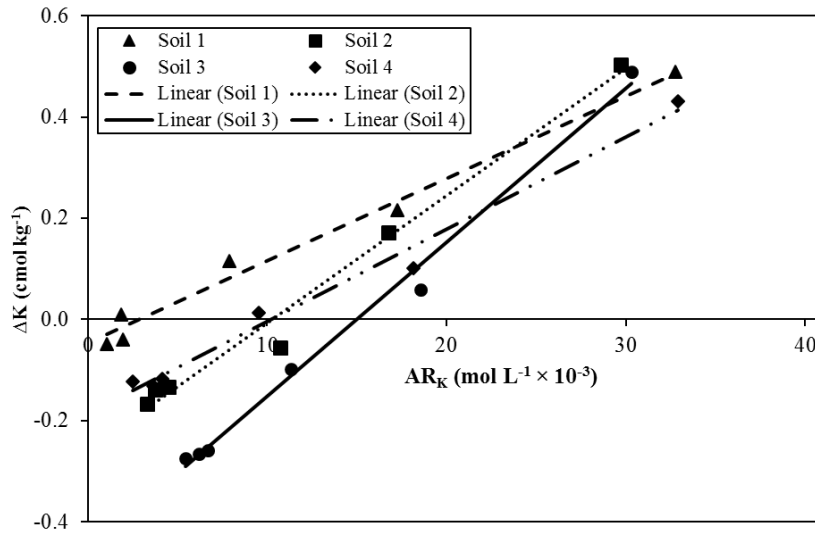
1, soil texture was measured by the USDA textural triangle; 2, pH was measured a 1:2.5 suspension; 3, EC was measured in soil paste extract.

in two doses (early and middle of the season). Wheat plants were harvested, separated, dried, and weighed during the harvest stage.

## 2. Methodology:

### 2.1. Laboratory analyses:

Particle size distribution was assessed using a soil hydrometer method, pH was measured using a pH meter, organic matter was quantified using a wet oxidation technique (H<sub>2</sub>CrO<sub>7</sub>), and CaCO<sub>3</sub> was determined using a back-titration method. The titration technique with EDTANa<sub>2</sub> was used to determine Ca<sup>2+</sup>+Mg<sup>2+</sup>. The electrical conductivity of the soil paste extract was also measured using an EC meter. Potassium (K) was measured using a flame photometer, and extractable K was extracted using 1M NH<sub>4</sub>OAc and 1 M HNO<sub>3</sub> according to the description of Estefan *et al.* (2013).



**Fig. (1):** Initial Quantity-Intensity plot of the tested soil.

According to Beckett's procedure, the exchange equilibrium state of K was investigated between the liquid and solid phases of soil (1964b). Five grams of oven-dried soil was mixed with 50 ml of 0.01 M CaCl<sub>2</sub> solution with 0.0, 0.1, 0.2, 1.0, 2.0 and 4.0 mM KCl solution. The samples were agitated for 3 hours, then equilibrated for 24 hours before being extracted the next day.

**2.2 Calculation methods:**

The parameters were calculated based on the below equations:

**a- Ionic strength (I)** was calculated According to (Griffin & Jurinak, 1973):

$$I = 0.0129EC(dS/m) \quad [Eq. 1]$$

Where: *I*; is ionic strength, *EC* is electrical conductivity.

**b- Activity coefficient of K (Log γ<sub>i</sub>)** was calculated according to Extended Debye-Huckel equation as:

$$\log \gamma_i = -AZ_i^2 \frac{\sqrt{I}}{(1+Bd_i\sqrt{I})} \quad [Eq. 2]$$

Log γ<sub>i</sub> is the activity coefficient of K, A = 0.509, Z<sub>i</sub> is a charge of the ion, I is ionic strength, B is 0.33, and d<sub>i</sub> is ion diameter

**c- Activity of K<sup>+</sup> (a<sub>i</sub>):**

$$a_i = \gamma_i m_i \quad [Eq. 3]$$

Where: *a<sub>i</sub>* is K – activity, γ<sub>i</sub> is coefficient of K– activity, and *m<sub>i</sub>* is a concentration of K (M)

**d- Activity ratio of K<sup>+</sup> (AR<sub>K</sub>):**

$$AR_K = \frac{a_K}{\sqrt{(aCa+aMg)}} \quad [Eq. 4]$$

Where:  $aK$  is K-activity,  $aCa$  is Ca- activity, and  $aMg$  is Mg- activity.

**e- Gibb's Free energy ( $\Delta G$ )** was calculated According to (Woodruff, 1955b)  
 $\Delta G \text{ (cal mol}^{-1}\text{)} = RT \ln AR_K^0$  [Eq. 5]

Where: R is the universal gas constant, T is the absolute temperature.

**f- Gabon selectivity coefficient ( $K_G$  or relative affinity)** was calculated According to (Sparks, 1998)

$$K_G = \frac{PBC_K}{CEC} \quad [\text{Eq. 6}]$$

$$PBC_K = \frac{\Delta K}{AR_K} \quad [\text{Eq. 7}]$$

### 3. Statistical analysis

All data were statistically analyzed according to the variance analysis technique for the randomized completely plot design, correlation, and regression coefficients using the SPSS V. 26 software package. The significant differences between the mean values of treatments were achieved by the LSD method.

## RESULT & DISCUSSION

### 1. Impact of some soil properties on thermodynamic parameters of K:

Tables 1 and 2 show some of the physicochemical and thermodynamic parameters of the investigated soils before planting (Table 1) and after harvest (Table 2). Most physicochemical parameters, such as pH, EC, CEC,  $\text{CaCO}_3$ , organic matter, and soil texture, differed in the investigated soil. In general, soil 3 had the highest clay content, organic matter and CEC.  $\text{CaCO}_3$  differed among the tested soils, which gave the highest value in soil 4 (a calcareous soil) and the lowest in soil 1 (a non-calcareous one).

The concentration of extracted K differed according to the used extraction method (water, 1 M  $\text{NH}_4\text{OAc}$  and 1M  $\text{HNO}_3$ ). In the initial stage of the season, soils 1, 2, 3, and 4 recorded 0.022, 0.037, 0.045, 0.031  $\text{cmole kg}^{-1}$  for  $\text{H}_2\text{O}$  extraction, 0.197, 0.732, 0.756, 0.412  $\text{cmole kg}^{-1}$  for 1 M  $\text{NH}_4\text{OAc}$  extraction, and 0.292, 1.456, 2.897, 0.578  $\text{cmole kg}^{-1}$  for 1M  $\text{HNO}_3$  extraction (Table 1), respectively. Clay loam soil (soil 3) had the highest value, whereas sandy soil had the lowest concentrations (soil 1). Furthermore,  $K_L$  values in the studied soils were lower during harvest than at beginning of the experiment. Soil 3 had a higher potential buffering capacity of K ( $PBC_K$ ) values than soil 1. For soil 3 and the other three soils, the highest  $AR_K^0$  value was 0.015 ( $\text{mol L}^{-1}$ )<sup>0.5</sup> and the lowest was 0.0028 ( $\text{mol L}^{-1}$ )<sup>0.5</sup>, respectively. In the case of relative affinity or  $K_G$  and  $\Delta G$ , the scenario was reversed, soil 1 recorded the

**Table (2): Some physicochemical characteristics and thermodynamic parameters of the studied soils at harvest stage.**

Soil Code	Soil1					Soil2					Soil3					Soil4				
	0%K	50%K	100%K	150%K	0%K	50%K	100%K	150%K	0%K	50%K	100%K	150%K	0%K	50%K	100%K	150%K	0%K	50%K	100%K	150%K
$K_d$ (cmol kg <sup>-1</sup> )	0.03	0.02	0.05	0.09	0.24	0.21	0.28	0.35	0.32	0.28	0.31	0.45	0.14	0.09	0.14	0.25				
PBC <sub>x</sub> (cmol kg <sup>-1</sup> )(mol L <sup>-1</sup> ) <sup>0.5</sup>	11.9	13.6	18.7	13.9	26.2	29.9	29.4	26.9	21.4	25.5	26.5	27.3	14.8	15.1	20.1	14.4				
AR <sub>x</sub> <sup>0</sup> (mol L <sup>-1</sup> ) <sup>0.5</sup> × 10 <sup>-3</sup>	2.49	1.39	2.48	6.38	9.06	6.91	9.33	13.12	15.01	11.10	11.58	16.49	9.43	5.72	7.17	17.31				
Relative affinity for K (L mol) <sup>0.5</sup>	1.66	1.88	2.60	1.85	1.56	1.76	1.73	1.58	0.89	1.06	1.09	1.11	1.11	1.13	1.49	1.07				
-ΔG (kcal. mol <sup>-1</sup> )	-3.45	-3.79	-3.46	-2.91	-2.71	-2.87	-2.68	-2.50	-2.42	-2.59	-2.57	-2.36	-2.69	-2.98	-2.84	-2.34				
Silt (g Kg <sup>-1</sup> )	175	177	177	165	515	514	514	515	460	466	460	480	465	465	472	480				
Clay (g Kg <sup>-1</sup> )	140	135	142	155	110	113	110	115	405	401	406	385	78	78	78	78				
pH*	8.22	8.22	8.21	8.22	7.89	7.88	7.89	7.89	7.87	7.87	7.87	7.87	8.21	8.22	8.21	8.21				
EC** (dS m <sup>-1</sup> )	2.87	2.88	2.88	2.87	3.88	3.86	3.74	3.88	6.08	6.06	6.03	6.08	4.92	4.63	4.62	4.92				
CaCO <sub>3</sub> (g Kg <sup>-1</sup> )	12.60	12.30	12.40	12.60	25.21	26.13	26.22	25.21	21.03	21.31	21.34	21.03	184.84	19.21	19.22	184.84				
CEC (cmol kg <sup>-1</sup> )	7.17	7.22	7.18	7.51	16.76	17.02	17.02	17.00	24.09	24.01	24.21	24.70	13.29	13.32	13.45	13.40				
OM (g Kg <sup>-1</sup> )	1.61	1.47	1.41	1.61	1.93	1.82	1.91	1.93	12.01	12.21	12.21	12.01	2.41	2.33	2.14	2.41				
Soluble-K (cmol kg <sup>-1</sup> )	0.01	0.01	0.01	0.01	0.02	0.03	0.02	0.02	0.03	0.03	0.03	0.05	0.02	0.02	0.01	0.02				
NH <sub>4</sub> OAc (cmol kg <sup>-1</sup> )	0.16	0.16	0.18	0.20	0.64	0.67	0.73	0.77	0.86	0.88	0.88	1.16	0.37	0.37	0.46	0.54				
HNO <sub>3</sub> (cmol kg <sup>-1</sup> )	0.29	0.37	0.36	0.40	1.44	1.51	1.87	2.09	2.79	2.83	2.87	2.58	0.50	0.51	0.86	1.08				

\*pH was measured a 1:2.5 suspension, \*\*EC was measured in soil paste extract.

highest, while soil 3 gave the lowest is 1.61 and 1.26 (L mol)<sup>0.5</sup>, respectively, and concerning  $-\Delta G$ , the registered values being negatively associated with above-named parameters and so, the greatest and lowest value of -2.42 and -3.37 kcal mol<sup>-1</sup> realized in soil 1 and soil 3, respectively in the first stage.

The labile  $K_L$  values in the investigated soils changed during harvest, as shown in Table 2 and Fig. 2. For 0, 50, 100 and 150 % K levels, the studied soil recorded values of 0.03, 0.02, 0.05, 0.09 cmol kg<sup>-1</sup> for soil 1, 0.24, 0.21, 0.28, 0.35 cmol kg<sup>-1</sup> for soil 2, 0.32, 0.28, 0.31, and 0.45 cmol kg<sup>-1</sup> for soil 3, and 0.14, 0.09, 0.14, 0.25 cmol kg<sup>-1</sup> for soil 4. In sandy soil, the lower  $K_L$  value was 0.02 cmol kg<sup>-1</sup> of 50% K level in soil 1, while the higher value was 0.45 cmol kg<sup>-1</sup> by using a 150% K rate in soil 3. The high clay, silt, surface area, CEC values, and a number of loosely bound  $K^+$  ions present at the exchangeable site may be linked to the increased  $K_L$  values (Simard *et al.*, 1992; Khamis, 2000; Krauss, 2000; Samadi, 2006; Al-Salam & AL-Kaysi, 2013; Hamed & Amin, 2017). Furthermore, high labile K levels resulted in an increase in K availability due to increased K release into the soil solution. In addition, K fertilizer may increase the labile K in the soil (Yawson *et al.*, 2011) since K fertilizers are fully soluble in soils. Furthermore, the lowest  $K_L$  values soil 1-4 varied from 0.03 to 0.09 cmol kg<sup>-1</sup>. This could be due to the highest sand content in the soil. Because of their lower CEC or clay content compared to soil 3, therefore most of the K supplied by mineral fertilizer or released from organic amendments in calcareous or sandy soils (soil 1, 4) is subjected to leaching (Hamed & Amin, 2017). In regard to soil 1, 2, 3 and 4, values of  $PBC_K$  were 11.9, 13.6, 18.7, 13.90, 26.2 cmol kg<sup>-1</sup>/(mol L<sup>-1</sup>)<sup>0.5</sup>, 26.2, 29.9, 29.4, 26.9 cmol kg<sup>-1</sup>/(mol L<sup>-1</sup>)<sup>0.5</sup>, 21.4, 25.5, 26.5, 27.3 cmol kg<sup>-1</sup>/(mol L<sup>-1</sup>)<sup>0.5</sup> and 14.8, 15.1, 20.1, 14.4 cmol kg<sup>-1</sup>/(mol L<sup>-1</sup>)<sup>0.5</sup> for 0, 50, 100, 150% K, respectively.

Furthermore,  $PBC_K$  levels varied substantially from 11.9 to 29.9 cmol kg<sup>-1</sup>/(mol L<sup>-1</sup>)<sup>0.5</sup>. In addition, the Equilibrium activity ratio of K ( $AR_K^0$ ) is calculated to determine the intensity of a labile K ( $K_L$ ) in the soil (Intensity factor) and represent the K that is accessible to crop roots immediately (Yawson *et al.*, 2011).

Furthermore, potassium fertilization enhanced the activity ratio of  $K^+$  ( $AR_K^0$ ) in equilibrium solutions in the investigated soil. At equilibrium, the concentration of  $AR_K^0$  varied from 1.39 to 17.31 (mol L<sup>-1</sup>)<sup>0.5</sup> × 10<sup>-3</sup>. In addition, the  $K^+$  activity ratio ( $AR_K^0$ ) provides a good estimation of  $K^+$  availability in soil. These variations in  $K^+$  activity ratio ( $AR_K^0$ ) in soils might be related to the changes in  $K^+$  concentrations in equilibrating solutions, equilibration duration, Ca<sup>2+</sup> and/or Mg<sup>2+</sup> contents, and most likely variances in the mineralogical composition of the soils (Yawson *et al.*, 2011). The  $AR_K^0$  is a measure of how much  $K^+$  is available to plants. Increased  $AR_K^0$  levels are



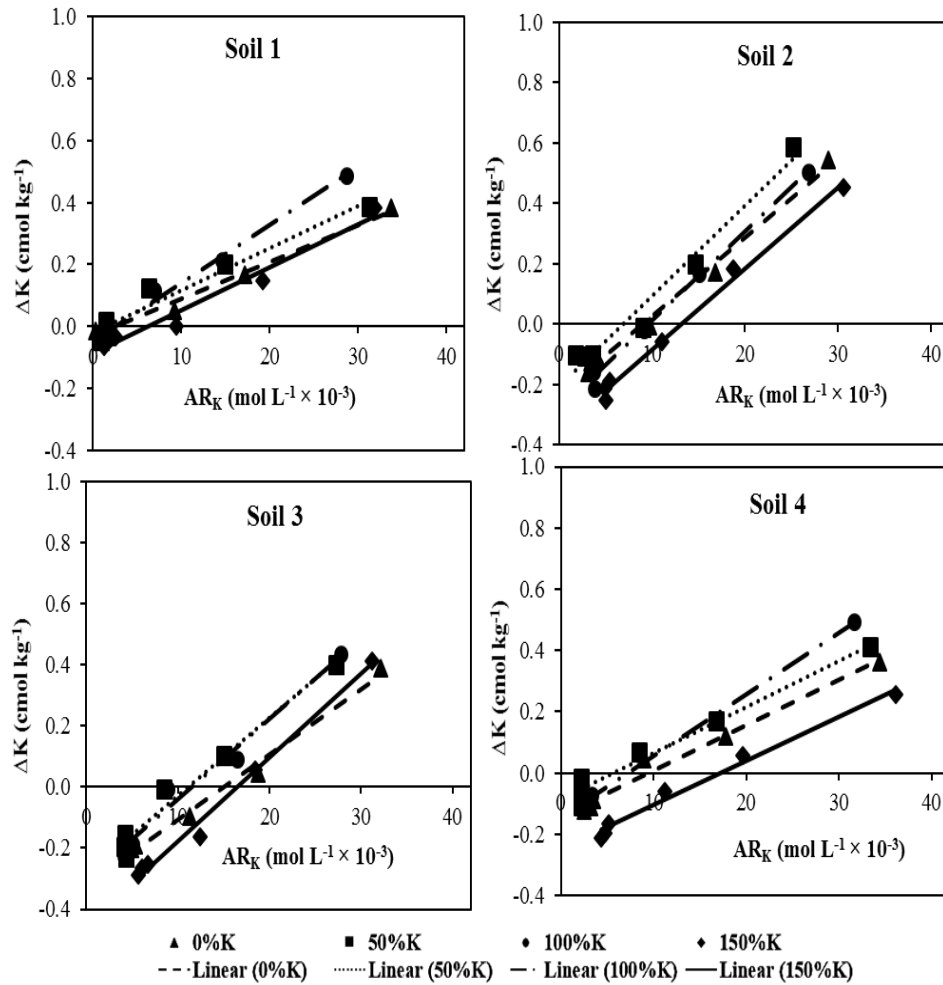


Fig. (2): Quantity–Intensity plots of the studied soil at harvest.

linked to higher  $K^+$  ionic strength in solution and therefore higher  $K^+$  availability to plants in comparison to  $Ca^{2+}$  and  $Mg^{2+}$  cations (Beckett, 1964 a& b). In general, soils with high contents of exchangeable and non-exchangeable  $K^+$  had higher  $AR_K^0$  values, while soils with lower contents of exchangeable and non-exchangeable  $K^+$  had lower  $AR_K^0$  values (Jagadeesh *et al.*, 2005; Panda & Patra, 2018).

The lower levels of  $AR_K^0$  in some soils may be attributed to the presence of a higher number of particular  $K^+$  sites that can fix  $K^+$  (Abaslou & Abtahi, 2008; Panda & Patra, 2018). The highest values in soils 2 and 3 indicate that adsorbed  $K^+$  was largely retained at planar positions, implying a higher  $K^+$  supply intensity and hence more  $K^+$  being absorbed by plants more quickly. In

contrast, because soils 1 and 4 have the highest sand concentration, there is a risk of  $K^+$  leachability (Panda & Patra, 2018). Furthermore, soil 1 with low levels of labile and nonlabile  $K^+$  which exhibited low  $AR_K^0$  may respond to  $K^+$  fertilization. In this case, regular application of  $K^+$  fertilizer at multiple dosages to  $K^+$  deficient soils may be recommended. Additionally, relative affinity values ( $K_G$ ) of the exchange complex ranged between 0.89 to 2.60 (L mol)<sup>0.5</sup>. The average  $K_G$  values for soil 1, 2, 3 and 4 were 2.00, 1.66, 1.04 and 1.20 (L mol)<sup>0.5</sup>, respectively. Gibb's free energy ( $-\Delta G$ ) in soil samples differed substantially. Sandy soils had a lower  $-\Delta G$  value, but clay soils had a much higher  $-\Delta G$  value (Yawson *et al.*, 2011). Gibb's free energy values varied between  $-3.79$  to  $-2.34$  (kcal. mol<sup>-1</sup>), with average values of 3.40, 2.69, 2.49, and 2.71 (kcal. mol<sup>-1</sup>) for the tested soil 1, 2, 3, and 4, respectively. The greatest  $\Delta G$  change of  $K^+$  exchange in investigated soils was shown to be associated with decreased extractable  $K^+$ . Increases in these chemical and soil  $K^+$  parameters resulted in increases in  $-\Delta G$  values in soils, as seen by the strong connection of  $\Delta G$  with soil pH, CEC, organic matter,  $K_L$ , and  $K^+$  reserves. The strong correlation between  $-\Delta G$  and pH indicates that when pH increases, less energy is required to remove one mol of  $K^+$  from the solution. Furthermore, this might imply that lower  $K^+$  content at equilibrium is more easily displaced than greater content, but releasing  $K^+$  from  $K^+$  reserves with the lowest  $PBC_K$  values requires high energy (Yawson *et al.*, 2011).

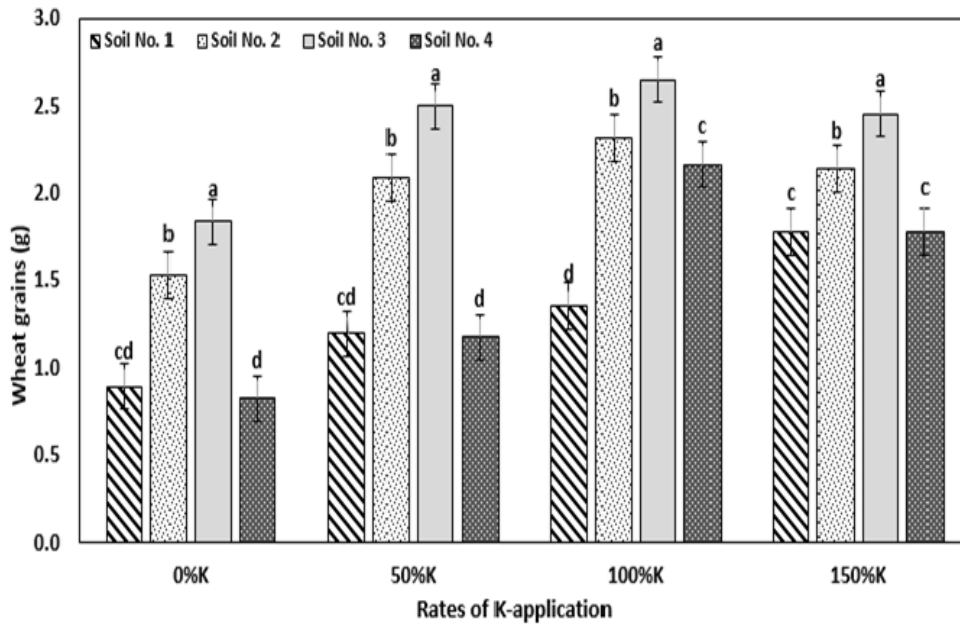
Table (3) shows the correlation coefficient and describes the link between various soil characteristics and K's thermodynamic parameters. Labile potassium ( $K_L$ ) was shown to be strongly associated with all other thermodynamic parameters, as well as soil characteristics examined. Except for clay content, EC, CEC and OM.  $PBC_K$  values varied in soil samples and were strongly correlated with several characteristics of studied soils. Except for CEC, the levels of activity ratios at equilibrium ( $AR_K^0$ ) were highly correlated with all of the characteristics of tested soils. Furthermore, all examined characteristics of tested soils including pH were adversely correlated with relative affinity or  $K_G$  values. Also, there is a strong correlation between  $-\Delta G$  and the examined soil characteristics; however, the correlation coefficient was not significant with clay content or CEC.

## **2. Wheat yield vs thermodynamic parameters:**

Figure (3) illustrates the yield of wheat grown on studied soils. The yield obtained from potassium fertilization treatments using of 0, 50, 100, 150% varied recording average value of 0.90, 1.20, 1.36, 1.78 g pot<sup>-1</sup>, 1.53, 2.09, 2.32, 2.14 g pot<sup>-1</sup>, 1.84, 2.50, 2.65, 2.46 g pot<sup>-1</sup>, 0.83, 1.18, 2.17, 1.78 g pot<sup>-1</sup> for soil 1, 2, 3, 4, respectively. When K levels raised from 0 to 150 %, wheat grains increased considerably. With compared to the control treatments, these

**Table (3):** Correlation coefficient between some thermodynamic parameters of K and some physicochemical characteristics with and without K-fertilization.

Parameter	Silt	Clay	pH	EC	CEC	CaCO <sub>3</sub>	OM	Soluble-K	NH <sub>4</sub> OAc-K	HNO <sub>3</sub> -K
K <sub>f</sub>	0.736**	0.572*	-0.836**	0.714**	0.039	0.891**	0.657**	0.834**	0.968**	0.896**
PBC <sub>K</sub>	0.662**	0.370	-0.913**	0.367	-0.316	0.730**	0.391	0.624**	0.803**	0.765**
AR <sub>K</sub> <sup>0</sup>	0.694**	0.448*	-0.550*	0.760**	0.393	0.752**	0.579**	0.703**	0.804**	0.722**
K <sub>g</sub>	-0.618**	-0.456*	0.305	-0.858**	-0.369	-0.684**	-0.629**	-0.591**	-0.585**	-0.543*
-ΔG	0.800**	0.373	-0.590**	0.751**	0.346	0.774**	0.518*	0.665**	0.802**	0.710**



**Fig. (3):** Effect of interaction means between soil type and rates of K-application of wheat yield (g).

increases were 97.8, 39.87, 33.70, and 114.45 % and 150%. In soil 2, on the other hand, wheat yield increased by 39.78 %.

In comparison to the other tested soils, soil 3 had the best treatment for wheat production, at  $2.65\text{g pot}^{-1}$ . This could be attributed to the high clay and silt content. Soil 1 and 4 have lower fertility than soils with high clay and silt content (Soil 2, 3). These findings are in line with those of Akhtar & Khalid (2015), El-Defan *et al.* (2016), and Kubar *et al.* (2019), who found that applying K increases wheat yield and quality. Furthermore, the reduction of available K form led to decrease wheat yield and quality. This drop-in wheat production was more pronounced in the lowest  $K_L$  of soil 1 and soil 4 than in the higher  $K_L$  of soil 2, soil 3, and it was reflected in wheat yield.

## CONCLUSION

The studied soil samples differed in their physical-chemical properties, *i.e.*, soil texture, EC, pH, OM,  $\text{CaCO}_3$ , CEC, water extracted-K, 1 M  $\text{NH}_4\text{OAc}$  extracted-K, and 1 M  $\text{HNO}_3$  extracted-K. In this study, certain soils exhibited a high K-intensity but a low  $\text{PBC}_K$  content. In terms of relative affinity  $K_G$  and Gibbs free energy  $\Delta G$ , the situation was different. In general, the amounts of  $\text{AR}_K^0$ ,  $-\text{K}^0$ , and  $\text{PBC}_K$  increased when the silt, clay content, CEC and organic matter of the soil samples tested increased. These findings were evident in the

variance in wheat yield. It is suggested that organic amendments be applied to these soils, particularly the sandy ones, to enhance potassium status and the K/Q/I relationship.

#### ACKNOWLEDGEMENT

Special thanks go to the Water and Soil Science staff and staff of Ismailia Research Center for their valuable help during this study.

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## استخدام المعايير الثيرموديناميكية لنموذج السعة – الشدة لتقييم جاهزية البوتاسيوم في بعض الأراضي المصرية

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### الملخص:

طبق نموذج السعة-الشدة (Q/I) لتقييم صلاحية البوتاسيوم في أربعة أنواع مختلفة من الأراضي المصرية الشائعة وعلاقتها ببعض خواص الأراضي المدروسة. استخدم نبات القمح كمؤشر لهذه المعايير الثيرموديناميكية. بعد زراعة القمح، سُمدت التربة بواسطة بكتريبات البوتاسيوم بنسب 0، 50، 100، 150٪ وفقاً للإحتياجات الموصى بها لنباتات القمح.



أزدادت نسبة فاعلية البوتاسيوم ( $AR_K^0$ ) والتغيرات المقابلة في البوتاسيوم المتحرك ( $\pm \Delta K$ ) عند الإتران مع زيادة تركيزات البوتاسيوم في الأراضي. تراوحت نسبة فاعلية البوتاسيوم عند الإتران ( $AR_K^0$ ) بين  $15.01 - 2.88 \times 10^{-3}$  (مول لتر<sup>-1</sup>)<sup>0.5</sup> في بداية الموسم وفي أواخر الموسم كانت  $17.31 - 1.39 \times 10^{-3}$  (مول لتر<sup>-1</sup>)<sup>0.5</sup>. تراوحت قيم البوتاسيوم المتحرك ( $K_L$ ) من  $0.047 - 0.456$  و  $0.02 - 0.45$  سنتيمول كجم<sup>-1</sup> قبل الزراعة وبعد الحصاد. تذبذبت القدرة التنظيمية للبوتاسيوم ( $PBC_K$ ) من  $16.3 - 30.4$  ، و  $11.9 - 29.9$  سنتيمول كجم (مول لتر<sup>-1</sup>)<sup>0.5</sup> قبل الزراعة وبعد حصاد محصول القمح. تراوحت الطاقة الحرة للتبادل ( $-\Delta G$ ) من  $-3.37$  إلى  $-2.42$  (كيلو سعر مول<sup>-1</sup>) في بداية الموسم ومن  $-3.79$  إلى  $-2.34$  (كيلو سعر مول<sup>-1</sup>) بعد الحصاد. بشكل عام، كان لكل من  $K_L$  و  $PBC_K$  و  $AR_K^0$  و  $K_G$  و  $\Delta G$  ارتباطات معنوية مع السلت والأس الهيدروجيني والتوصيل الكهربائي و المادة العضوية و البوتاسيوم المستخلص بالماء و بخلات الأمونيوم 1 مولر و بحامض النيتريك 1 مولر. بينما كانت هناك علاقات عكسية بين الأس الهيدروجيني وهذه المعايير في الترب المدروسة ما عدا  $K_G$ . أيضاً، وجدت زيادة معنوية بين المعايير الترموديناميكية للبوتاسيوم مع البوتاسيوم المستخلص بالماء و بخلات الأمونيوم 1 مولر أو بحامض النيتريك 1 مولر.

**التوصية :** نستنتج أن هناك علاقة ارتباط معنوية بين هذه المعايير الترموديناميكية مع معظم خصائص التربة. وبالتالي، فقد قدمت الدراسة معلومات مفيدة لفهم ديناميكيات البوتاسيوم في التربة المصرية الشائعة وتقديم مساهمة كبيرة في إدارة البوتاسيوم في تلك الأراضي.

**الكلمات الدالة:** منحنى السعة/الشدة؛ المعايير الترموديناميكية؛ صور البوتاسيوم؛ نسبة فعالية البوتاسيوم؛ الطاقة الحرة.

