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A Study of the Quantity and Intensity Relationship of Potassium in Some Soils of Thi- Qar Province, Southern Iraq

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Abstract

The study aims to use thermodynamic criteria derived from intensity and quantity relationships to estimate the supply capacity of potassium for selected soils from agricultural and non-agricultural sites northern of Dhi-Qar Governorate/ southern Iraq. Results of thermodynamic criteria in this study showed that all studied soils were low in the K-availability , the value of the activity of potassium (ARK0) ranged widely from (6.14 - 10.83)$\times 10^{-4}$ in agricultural soils to 3.35 - 6.57$\times 10^{-4}$ (mol. L^{-1})$^{0.5}$ in non-agriculture soils , labile KL (ΔK_0) (6.64 -7.17) and (7.02 - 8.25) cmol .kg^{-1},and the potential buffering capacity (PBC^K) 64.51 – 113.10$\times 10^{-2}$ cmol. kg^{-1} (mol. L^{-1}) $^{0.5}$, and 110 - 245 cmol. kg^{-1} (mol. L^{-1}) $^{0.5}$, and the Gapon Selectivity Coefficient (KG) 0.028 - 0.048 ,and 0.041 – 0.100 (mol. L^{-1}) $^{0.5}$, and the Free Energy (-ΔG) range between -4044 to - 4380 ,and -4340 to -4739 Cal.$mole^{-1}$for agriculture and non-agriculture respectively. The study provided more accurate information about the dynamics potassium of soil that plays an important role in describing the behavior of potassium in the saline soils of southern Iraq.

Keywords: Potential Buffering Capacity, Free Energies, Gapon Selectivity Coefficient, Equilibrium Activity Ratio.

دراسة علاقة الكم والشدة للبوتاسيوم في بعض ترب محافظة ذي قار، جنوب العراق

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الخلاصة

تهدف الدراسة الى استخدام المعايير الثرموديناميكية المستنبطة من علاقات الشدة والكمية لتقدير القدرة الامدادية لعنصر البوتاسيوم لترب مختارة من مواقع زراعية وغير زراعية شمال محافظة ذي قاؤ/ جنوب العراق. اوضحت الدراسة انخفاض جاهزية البوتاسيوم في جميع ترب الدراسة ,حيث تراوحت نسبة فعالية البوتاسيوم $AR^K{}_0$ (6.14 – 10.83 × 10^{-4}) مول لتر$^{-1}$ في الترب الزراعية و(3.35 – 6.57 × 10^{-4}) مول لتر$^{-1}$ في الترب غير الزراعية والبوتاسيوم المتحرك (ΔK_0) تراوحت قيمته بين (6.64 – 7.17) و (7.02 – 8.25) سنتي مول كغم$^{-1}$ في الترب الزراعية وغير الزراعية على التوالي .ومقدار السعة التنظيمية لجهد البوتاسيوم PBC^K تتراوح (64.51 – 113.10 × 10^{-2}) ومن (110 – 245)سنتي مول كغم$^{-1}$ / (مول لتر$^{-1}$)$^{2/1}$ في الترب الزراعية وغير الزراعية على التوالي، أما قيمة معامل كابون فقد تراوحت بين (0.028 – 0.048) و (0.041 – 0.100) مول لتر$^{-1}$ ، وتراوحت قيمة الطاقة الحرة ($-\Delta G$) (-4044 الى - 4380) ومن (-4340 الى - 4739) سعرة مول$^{-1}$ للترب الزراعية وغير الزراعية بالتعاقب . قدمت الدراسة معلومات دقيقة عن ديناميكية البوتاسيوم والتي لعبت دورا مهما في وصف سلوك البوتاسيوم في الترب الملحية في جنوب العراق.

1. Introduction

The status of the potassium (K) in Iraqi soil has been studied by many researchers [1], [2], [3] using thermodynamic methods showed that the rate of release of K from Iraqi soils is very low and this may explain the response of most Iraqi soils to the application of K fertilizers in spite of their high content of K, availability of K to plant depends on its intensity, capacity, and renewal rate in soils. Intensity is the K concentration in soil solution, capacity is the total amount of K in soil solids available to go into the solution, and the renewal rate is a kinetic factor describing the K transfer rate from capacity to intensity potassium exchange-equilibrium parameters were the outcome from the quantity- intensity (Q/I) isotherms. K equilibrium activity ratio equilibrium, potential buffering capacity for K (PBC^K) The quantity-intensity (Q/I) concept has been narrowly promulgated in the scientific literature to investigate the K of borne soils. In this approach immediate availability of K is related to intensity factor; reserve less of non-exchangeable K to the quantity factor and replenishment capacity to the buffering capacity [4], [5]. Several attempts have been made to describe the relationship between capacity Q and intensity I of soil -K or soil K buffering phenomena [6]. It was referred that higher values of labile K indicated a greater K release into soil solution resulting from a larger pool of soil K. A higher potential buffering capacity for potassium (PBC^K) value is indicative of a good K availability while a low PBC^K soil would suggest a need for fertilization. Some agricultural practices such as K fertilization and liming were found to induce changes in the magnitude of the K activity ratio at equilibrium ($AR^K{}_0$), labile K_{Lab} and PBC^K values [4], [7] [8]. If, however, a Q/I is to be of any value in indicating the amount of soil K available for uptake during the growing season, its form must be unaffected by the amount of K fixation or release that is likely to occur during one growing season. [9], [10] have reported that K uptake by growing plant generally affect the pool of readily available K forms and moreover these changes, if considerable, might be expected to alter the form of the Q/I of a soil. Since plant growth is not directly limited by the amounts of exchangeable soil K, therefore it should be necessary to elucidate this phenomenon on the basis of equilibrium studies in order to test the immediate power of soils to supply K to plants. This approach needs the use of equilibrium (Q/I) concept which should be a good tool, whose application may provide sufficient data about K dynamics soils under plant cropping.

Such comprehensive studies are intended to outline some specific information, which should clearly determine the capacity of soils for K supply and replenishment [11]. The descriptions of K-parameter provide a wide basis for comparing soils and study the effect of fire on potassium status. The aims of this study were: Evaluate of potassium fertility status in soil southern of Iraq by using thermodynamic approaches

2. Materials and Methods

Soil samples were taken from twelve sites of agricultural and non-agricultural Locations northern of Dhi-Qar Governorate/ southern Iraq, which are classified as Aridisols according to the index [12]. The soil samples were air dried and ground to pass through a 2 mm sieve prior to analysis. Some chemical and physical properties of the soil were estimated according to the methods were done as described by [13] (Table 1).

2.1 Potassium adsorption (quantity-intensity) (Q/I) study

It was performed according to the procedure described by [4] and applied by [5], (2.00 gm) duplicate samples of the soils were equilibrated in 100 ml polypropylene tubes containing 40 ml of solution containing from (0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, and 2.0 mmol K^+L^{-1} as KCl in 0.01M $CaCl_2$. suspensions were shaken for one hour at 298K° (Isotherm reaction) and let to equilibrate for 48 hours and then centrifuged. The supernatant were analyzed for K, Ca, Mg, and EC, and the K were determine by flame photometer while Ca, Mg were determined by titration with EDTA disodium salt solution. The EC were measured in each solution by EC meter.

The change in amount of K in solution gained or lost by the soil (±ΔK) was calculated from the difference in K+ concentration between the initial and final solutions after equilibration with soil. This amount expressed in ($cmol_c kg^{-1}$).was calculated according the following equation [14]:

$$(\pm\Delta K) = (Ci - Cf) \times V/m \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where:
V=Volume of solution cm^3 or m^{-3}, m=mass of dry soil Kg
Ci and Cf = concentration of potassium before and after equilibrium $mg.L^{-1}$

The K intensity factor in liquid phase of soil expressed as activity ratio AR^K, it was computed from the measured concentration of Ca, Mg and K in the supernatant solution after equilibration. The activity ratio of potassium (AR^K) was calculated according to Ratio law as:

$$AR^K = \frac{a_K}{\sqrt{a_{Ca} + a_{Mg}}} \quad \ldots\ldots\ldots(2)$$

a_i = ionic activity species (Ca, Mg and K). The ionic activity was calculated according to the Lewis equation as described by [14].

$$a_i = C_i + \gamma i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where: a_i = ionic activity. C_i = the species concentration of ions in mol. L^{-1}.
The ionic activity coefficients were calculated by the empirical Davies equation given by [14] as:

$$\text{Log } fi = -0.509\, Zi^2 \,[\sqrt{I}/1 + \sqrt{I} - 0.3\, I\,] \ldots(4)$$

Where: fi= the mean activity coefficient of the electrolyte. Z_i= the species valence of ion. I = ionic strength in mol $.L^{-1}$.

$$I = 0.013 * EC \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where:
I = Ionic strength in $mol.L^{-1}$ and EC = dSm^{-1}

From a plot of (±ΔK) versus the activity ratio the Q/I parameters were obtained. The intercept of the Q/I curve on the AR^K_{equ} axis, where K=0, gave the soil K activity ratio at equilibrium

(AR^K_0), which denotes the soil solution K activity relative to the Ca + Mg at equilibrium. The equilibrium potential buffering capacity for potassium (PBC^K) was calculated as the slop of the linear section of the Q/I curve. The labile potassium (ΔK_0) was obtained from the intercept of the extrapolated linear part of the Q/I isotherm on the quantity axis. The free energy of the K replenishment ($-\Delta G^K_{equ}$) was computed from the following equation [16]:

$$-\Delta G^K_{equ} = 2.303RT\log AR^K_0 \text{ ………..(6)}$$

Where:
R and T are gas constant and absolute temperature, respectively.

The Gapon selectivity coefficient (K_G) should provide good comprehensive and indicative information of K replenishment capacity of the soils. The K_G calculated as follows:

$$K_G= PBC^K/CEC \text{ ……….….(7)}$$

Where:
K_G = Gapon constant, PBC^K= Potassium Potential buffering capacity
CEC= Cation exchange Capacity

3. Results and Discussion

Tables 1, 2 shows that the studied soils are distinguished by texture classes are predominantly with sandy clay loam – clay (SCL - C). Particle size distribution of samples ranged from (263 - 517), (130 - 417) , (191- 451) gm kg^{-1} .for clay ,silt and sand fractions respectively . Soil pH in saturated paste extract ranged from 7.11 - 7. 80 These values indicate that all soil samples are alkaline reaction. Also, the results in Tables (1, 2) show that all soil samples are saline with EC_e ranged from 2.60 - 62.50 dS m^{-1}. The results showed that there are different content of organic matter were low 6.11 to 21.8gm kg^{-1}. The total $CaCO_3$ equivalent range from 400 - 750 gm kg^{-1} these results indicate that all soil samples are calcareous [15].

3.1 Isotherm adsorption (Quantity-Intensity (Q/I) relationships)

The Q/I plots showed a linear relationship at high activity ratios, and the shape of the Q/I plots is similar for all studied soils, as confirmed by [16]. Fig. 1 and Fig. 2 as were described previously [17]. Several authors confirm this observation.

Table 1- Selected physical and chemical properties in the agricultural soils

Soil No.	Location	EC	pH	CEC	gm . Kg^{-1}					Texture
		$dS.m^{-1}$		$cmol.Kg^{-1}$	O.M	$CaCO_3$	Sand	Silt	Clay	
1	Al-Shatra	6.50	7.22	24.4	8.08	470	378	130	492	C
2	Al-Naser	41.50	7.23	26.0	6.19	460	191	292	517	C
3	Al-Dawaea	62.50	7.11	25.0	6.11	750	451	175	374	SC
4	Al-Alrifaee	18.25	7.18	26.5	8.08	450	443	267	290	SCL
5	Al-AlQalaa	58.75	7.53	24.7	11.50	520	241	405	354	CL
6	Al-Alfajer	22.18	7.60	20.0	16.56	490	318	382	300	CL

Table 2- Selected physical and chemical properties in the non-agricultural

Soil No.	Location	$dS.m^{-1}$	pH	$Cmol.Kg^{-1}$	gm . Kg^{-1}					Texture
		EC		CEC	O.M	$CaCO_3$	Sand	Silt	Clay	
1	Al-Shatra	5.40	7.20	23.3	9.77	490	253	355	392	CL
2	Al-Naser	22.01	7.13	23.1	8.25	650	191	330	479	C
3	Al-Dawaea	7.30	7.3	23.1	8.57	400	250	393	357	CL
4	Al-Alrifaee	19.30	7.21	24.0	19.25	540	379	358	263	L
5	Al-AlQalaa	38.80	7.80	20.1	15.60	550	379	321	300	CL
6	Al-Alfajer	2.60	7.40	20.0	21.80	490	313	417	270	CL

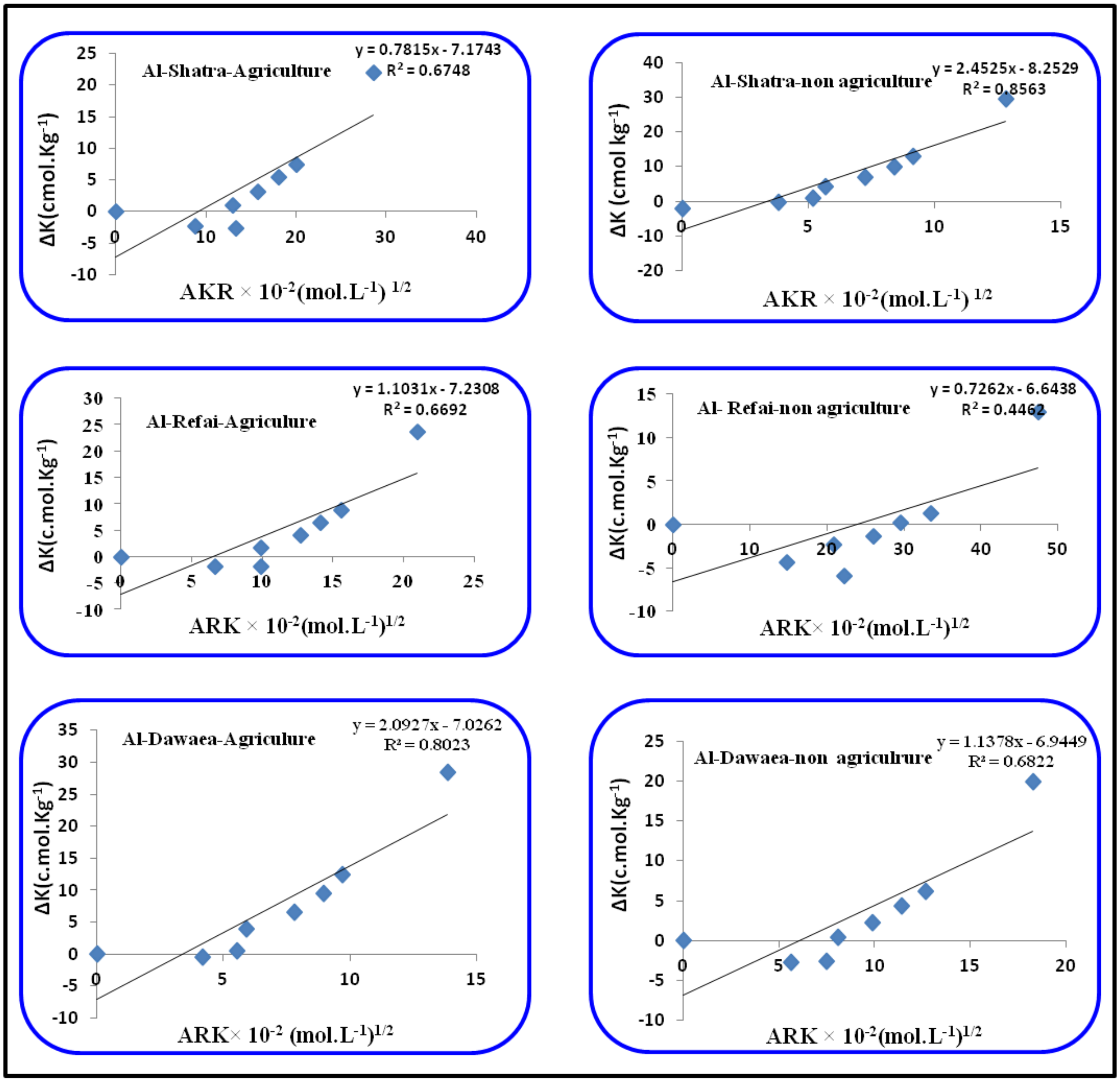

Figure -1 (Q/I) relationships for agriculture and non-agriculture soils of Al- Shatra , Al-Refai and Al- Dawaea

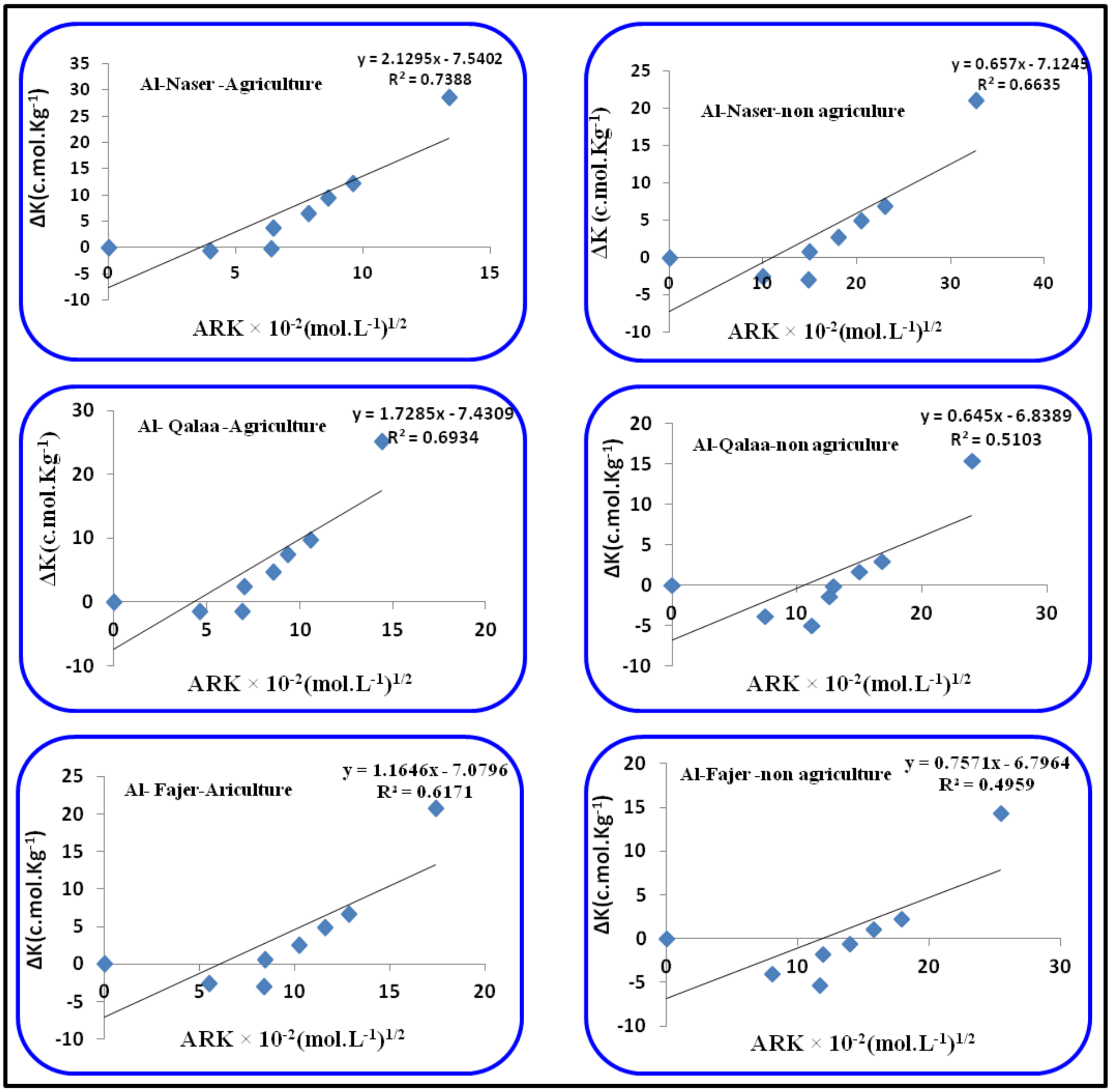

Figure 2- (Q/I) relationships for agriculture and non-agriculture soils of Al- Naser , Al-Qalaa and Al- Fajer

3.2 Equilibrium activity ratio $AR^K{}_o$

The $AR^K{}_o$ value is a measure of the availability or intensity of labile K in soil [7]. The equilibrium concentration ratio of K ($AR^K{}_o$) increased with increasing K concentration, and the mount of $AR^K{}_o$ in (Tables 3, 4) ranged widely from (6.14-10.83)$\times 10^{-4}$ in agriculture soils to (3.35 - 6.08)$\times 10^{-4}$ (mol. L^{-1})$^{0.5}$ in non-agriculture soils. The results of the present study are agreed with [18] in some Iraqi soils. The variation of $AR^K{}_o$ may be caused by cropping with or without K-fertilization, leaching [7].

Table 3- (Q/I) parameters for agriculture soils

Soil No	KL cmol.kg^{-1}	$AR^K{}_0\times 10^{-4}$ (mole L^{-1})$^{0.5}$	$PBC^k\times 10^{-2}$ cmol kg^{-1} /(mol. L^{-1})$^{0.5}$	-ΔG Cal mole^{-1}	K_G (mol. L^{-1})$^{0.5}$
1	7.17	9.17	78.15	4143	0.033
2	7.12	10.83	65.70	4044	0.028
3	6.94	6.14	113.10	4380	0.048
4	6.64	9.14	72.62	4145	0.030
5	6.83	10.58	64.51	4058	0.032
6	6.80	8.98	75.71	4155	0.037

Table 4- (Q/I) parameters for non-agriculture soils

Soil No.	KL cmol.kg^{-1}	$AR^K{}_0\times 10^{-4}$ (mole.L^{-1})$^{0.5}$	$PBC^k\times 10^{-2}$ cmol.kg^{-1} /(mol .L^{-1})$^{0.5}$	-ΔG Cal.mole^{-1}	K_G (mol. L^{-1})$^{0.5}$
1	8.25	3.36	245	4738	0.100
2	7.54	3.55	212	4705	0.081
3	7.02	3.35	209	4739	0.083
4	7.23	6.57	110	4340	0.041
5	7.43	4.49	172	4566	0.069
6	7.08	6.08	116	4386	0.058

Soils non-agriculture showed a higher value of $AR^K{}_o$. The results of the present study further support the idea that the ARK e indicates the status of the immediately available K and therefore regulates the exchange of K ions from the exchange complex to solution phase [17], also results suggests that the adsorbed was primary held at planar positions [19] theorized when $AR^K{}_o < 0.01$ (mol L^{-1})$^{0.5}$, it suggests the predominance of K adsorbed to edge of the layer (e- position) , whereas $AR^K{}_o > 0.01$ (mol L^{-1})$^{0.5}$, indicates a predominance of K adsorbed to planar surface (P- position) it is interesting that in no field was $AR^K{}_o$.

3.3 Potential buffering capacity (PBC^K)

The potential buffering capacity of potassium (PBC^K) is a measure of the ability of the soil to maintain the potassium potential in the soil against the processes of potassium depletion. It was calculated from the regression of the relationship (Q / I). According to [20], high PBC_K values are a measure of constant availability of K in the soil solution over a long period, whereas low PBCK would suggest the need for frequent K supply throughout fertilization practices .The PBC^K values as shown in (Tables 3 and

4) refer that all studied soil poorly K-buffered. This can be attributed to their high content in $CaCO_3$ equivalent. These values of K-parameter ranged between 64.51- 113.10 × 10^{-2} cmol. kg^{-1} /(mol. L^{-1})$^{0.5}$ in the agriculture soils and 116 -245 × 10^{-2} cmol. kg^{-1} /(mol. L^{-1})$^{0.5}$ in non- agriculture soils, The results of the study Soil showed a decrease in the values of the potential buffering capacity of potassium(PBC^K) for the study soils Compared to the of PBC^K (Table 5). The differences in the PBCK values in soils could be attributed to the differences In the number of qualitative Locations for potassium in the soil and its ability to hold potassium in addition in past cropping and management practices [16], [21].

Table 5- Soil classification according to the values potential buffering capacity of potassium (PBC^K)

PBC_K [cmol.kg^{-1}]/(M L^{-1})0. 5]	PBC_K Classes
less than20)	Very low
20-50	Very low
50- 100)	moderately
100-200	high
more than 200	very high

3.4 Free energies (-ΔG)

Tables (3 and 4) shows the free energy values of the studied soils and it shows that all free energy values are negative this indicates a spontaneous reaction It ranged between (-4044 to -4380) Cal.$mole^{-1}$ for agricultural soils and (- 4340 to 4739) Cal.$mole^{-1}$ for non-agricultural soils. According to the classification proposed by [22], it is noted that the soils of the agricultural and non-agricultural study suffer from a deficiency in the supply of potassium, so all the soils of the study need potassium fertilization .The free energy values of the soil samples of the studied locations were close to the values obtained [23] when studying some Iraqi soils. The use of the concept of free energy, according to the opinion of many researchers, and the classification [22] in assessing the readiness of potassium in the soil reflects the state of potassium in the dissolved and exchanged in soil [24] and the free energy criterion is considered necessary to determine the readiness of potassium in the soil.

3.5 Gapon selectivity coefficient (K_G)

The Gapon selectivity coefficient It can be taken as a criterion or measure of soil preference for a particular ion over another ion, and that the relatively low values of the K_G that there is little selectivity for the soil exchange complex for K adsorption compared to the competing ions (Ca + Mg) [21], most of the K_G values fluctuated within the range 0.028 to 0.048 and 0.041 to 1.00 (mole L^{-1})$^{0.5}$, for agriculture and non - agriculture respectively suggesting that the relative affinity for K was quite similar (Tables 3 and 4) these values are low . This may be due to the binding of potassium to the surface locations of clay minerals in the soil planar surface (P- position), and these sites are characterized by a relatively weak binding force compared to other binding sites for potassium. Gapon selectivity coefficients, reported by [23] varied between 2.3 and 5.3 (mole L^{-1})$^{1/2}$, [18] reported also in some northern Iraqi soils in values varied between (0.09 and 0.82 mole L^{-1}) $^{1/2}$ within a mean 0.42 (mole L^{-1}) $^{1/2}$. The Gapon selectivity coefficients reported by [25] varied between 2.3 and 5.3 (mole L^{-1}) $^{1/2}$. The changes in K_G values are basically attributable to the levels of exchangeable Ca and Mg [26]. Soil selective behavior for K in comparison with dominant Ca and Mg may also be attributed to preferential attraction of K ions over Ca and Mg [27] at some planar sites of soil colloids.

4. Conclusions

All the studied soils were characterized by good potassium reserves, but low release. This may be attributed to their high calcium carbonate content, which reduces the release of potassium from the soil, as well as the dominance of some clay minerals that are characterized by their ability to fix potassium, which reduces the availability of potassium to the plant. Therefore, these soils require special management to prevent soils degradation, improve its fertility, and increase the availability of nutrients in it, including potassium.

Conflicts of Interest:
The authors declare no conflict of interest.

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