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Research Article

Quantity-intensity ratio of potassium in gypsiferous soils in Iraq[1]

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ABSTRACT

In gypsiferous soils, potassium (K) undergoes leaching, precipitation and other reactions that reduce its availability. This study aimed to evaluate the physicochemical behavior of K in gypsiferous soils of the Salahaddin province (Iraq), in twelve locations chosen according to the variation in their soil physical and chemical properties. The K adsorption phenomenon was described by using thermodynamic parameters according to the quantity-intensity ratio (Q/I), with the following results: equilibrium activity ratio of 16 to 48 x 10^{-5} (mol L^{-1})$^{1/2}$, total labile K of 19 to 80 x 10^{-3} $cmol_c$ kg^{-1}, potential buffering capacity of 22 to 42 $cmol_c$ kg^{-1} (mol L^{-1})$^{-1/2}$, free energy of exchange of -1.237 to -1.086 kJ mol^{-1} and Gapon selectivity coefficient of 3.86 to 5.45 (L mol^{-1})$^{1/2}$. All the investigated soils are characterized by good potassium reserves, but low in release.

KEYWORDS: Exchangeable-K, buffering capacity, labile potassium, Gapon selectivity.

RESUMO

Relação quantidade-intensidade de potássio em solos gipsíferos no Iraque

Em solos gipsíferos, o potássio (K) sofre lixiviação, precipitação e outras reações que reduzem sua disponibilidade. Objetivou-se avaliar o comportamento físico-químico do K em solos gipsíferos da província de Salahaddin (Iraque), em doze locais escolhidos de acordo com a variação das propriedades físicas e químicas do solo. O fenômeno de adsorção de K foi descrito utilizando-se parâmetros termodinâmicos de acordo com a relação quantidade-intensidade (Q/I), com os seguintes resultados: razão de atividade de equilíbrio de 16 a 48 x 10^{-5} (mol L^{-1})$^{1/2}$, K lábil total de 19 a 80 x 10^{-3} $cmol_c$ kg^{-1}, capacidade de tamponamento potencial de 22 a 42 $cmol_c$ kg^{-1} (mol L^{-1})$^{-1/2}$, energia livre de troca de -1,237 a -1,086 kJ mol^{-1} e coeficiente de seletividade de Gapon de 3,86 a 5,45 (L mol^{-1})$^{1/2}$. Todos os solos investigados caracterizaram-se por boas reservas de potássio, mas com baixa liberação.

PALAVRAS-CHAVE: Potássio trocável, capacidade de tamponamento, potássio lábil, seletividade de Gapon.

INTRODUCTION

Gypsum is considered a rock-forming mineral that also occurs in soils. In arid and semi-arid environments, gypsum can be a significant soil component (Kamal & Rashid 2020). However, its composition is sometimes overlooked or misexpressed, even though its chemical formula ($CaSO_4.2H_2O$) is quite simple (Herrero et al. 2009).

The total estimated area of gypsiferous soils in the world is 100 million hectares, with 5.42 million hectares being prevalent in Iraq (the study area), where it constitutes about 12 % of the total area and 38 % of the total arable land (AL-Kayssi & Mustafa 2016). Gypsum soils cover large tracts of land in the center and north of the Iraq sedimentary plain. Most of these lands suffer from multiple problems affecting their agricultural productivity (Ismaeal 2022). These problems are related to the physical, chemical and biological properties of these soils, so researchers are seeking ways to increase the agricultural area by reclaiming these lands which suffer from many problems.

Gypsum soils are highly deficient in nutrient availability, especially potassium (K), due to the competition for exchange sites by calcium, sedimentation and conversion of nutrients from the available situation to the unavailable one (Elrashidi et al. 2010). So, gypsum soils suffer from the lack of K necessary for plant growth.

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The thermodynamic approach most often used in understanding, characterizing and evaluating the K^+ supplying capacity of the soil is the quantity-intensity (Q/I) isotherm of K^+ (Beckett 1964). Among the several laboratory methods used to assess the K supplying power of soils to plants, a fundamental approach based mainly on the labile pool of K is strongly advocated (Beckett 1964). This approach uses the relationship between the quantity (Q), which indicates the K reserves of non-exchangeable and total elemental K, and the intensity factor (I), which indicates the immediately available K, to describe the buffering capacity (BC), which is a measure of the resistance to a change in the K-potential in soils.

Soil labile K may be more reliably estimated by Q/I than by the measurement of exchangeable K with 1 M NH_4OAc (Page et al. 1982). Higher values of labile K indicate a greater K release into the soil solution, resulting in increased K availability. K fertilization will also increase the labile K and Q/I measures the ability of the soil to maintain the intensity of its K solution, being proportional to the cation exchange capacity (CEC). A high value represents a good K-supplying power (BC), while a low value suggests a need for K fertilization. There are two aspects of K buffering capacity: buffering of the potential by the exchangeable pool and buffering of the exchangeable pool by non-exchangeable reserves (Al-Hamandi et al. 2019). The availability of K to plants depends on its intensity, capacity and renewal rate in soils. Intensity is the K concentration in the soil solution. Capacity is the total amount of K in soil solids available to go into the solution (Lin 2010) and renewal rate is a kinetic factor describing the K transfer rate from capacity to intensity of K exchange-equilibrium parameters that outcome from quantity-intensity (Q/I) isotherms (Bar-Yosef et al. 2015), i.e., K equilibrium activity ratio, potential buffering capacity for K (PBC_K), labile K (ExK^o), free energy of K replenishment ($-\Delta G^K$) and Gapon selectivity coefficient (k_G) (Wang et al. 2004). It was found that soils do not generally differ in their exchangeable potassium, but do for %K saturation as an estimate of K liability (Bilias & Barbayiannis 2019).

In recent years, however, there have been various attempts to find a suitable method for determining the availability of K in soils, 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 proposed and expanded by Shil et al. (2021) has been used to measure the availability of K in soils (Panda & Patra 2018).

The K status in Iraq soils has been studied by some researchers (Ahmed & Sheikh-Abdullah 2020, AL-Hamandi 2020). The use of thermodynamic methods showed that the release rate of K from Iraq soils is very low, and this may explain the response of most of them to K-fertilizers application, in spite of their high K contents. The Q/I soil relation describes the relation between K availability or intensity (I) in the soil to the amount (Q) present in the soil, that is, changes of K sorbed to changes of K in solution concentration (Auge et al. 2018).

The K content in soil depends mainly on the type and degree of soil weathering and the forms in which it exists in the soil, hence the K availability in the soil solution (intensity) and the inherent capacity of the soil to buffer this concentration against changes are among the important parameters that determine the effective availability of K to plants (Bilias & Barbayiannis 2018). In some cases, even though the soil contains a considerable amount of total K, its availability to plants is negligible. This is because the availability of K to plants depends not only on its availability, but also on its viz. dynamics, intensity, capacity and renewal rate in soils. Finally, knowing the equilibrium constants is vital for predicting the status and supplying K for the plant (Khan et al. 2015). The misunderstanding of these dynamics leads to the mismanagement of soil fertility.

These methods have been proved reliable for many soil types, but less reliable for soils that contain significant amounts of clay minerals that fix K, like illite or vermiculite, or for soils under intensive cropping (Khan et al. 2014). Thus, the prediction of K availability using methods that extract only soluble K and exchangeable K, as in the studied soils, has been quite frequently proved inadequate, even though the contribution of non-exchangeable K can be significant (up to 80-100 % of total K availability) (Islam et al. 2017). Evangelou et al. (1994) considered that the buffering capacity of a soil to resist changes in K concentration in the soil solution is related to the cation exchange capacity (CEC) and Gapon selectivity coefficient. However, from a typical Q/I isotherm curve, no clear conclusions can be deduced concerning the specific K pool (exchangeable or non-exchangeable K), because that is involved in the form of an isotherm curve. Since the projection of the curvilinear part that represents specific sites of K adsorption gives only an estimation of non-exchangeable K, it cannot be always predicted with adequate accuracy.

Thus, this study aimed to determine the Q/I parameters of some gypsiferous soils of Iraq and relate them to the K availability in these soils.

MATERIAL AND METHODS

Twelve representative surface soil samples were collected from locations surrounding the Salahaddin province, in Iraq (34º36’N, 43º41’E and altitude of 250 m above the mean sea level) (Figure 1), depending on their gypsum content (Table 1), for the years 2018-2019. The climate of the study area is semi-arid and sub-tropical, with average annual rainfall of 150 mm, which occurs from October to April (rainy season), with uneven distribution. The average annual temperature, relative humidity, wind speed, sunshine duration per day and potential evapotranspiration are, respectively, 17.4 ºC, 52.9 %, 2.8 m s^{-1}, 11.2 h and 1,986 mm.

The samples were labeled as soil 1 to soil 12, dried, crushed and passed through a 2-mm mesh sieve, and then the chemical and physical analyses were conducted. The soils are classified as fine, mixed, active, hyperthermic, calcareous, Typic Torrifluvents (Ditzler et al. 2017). The soil chemical and physical characteristics were determined based on methods proposed by Page et al. (1982); organic matter by dichromate oxidation; cation exchange capacity (CEC) by dissolving soil with neutral 1N NH_4OAc; electrical conductivity (E_C) and soil pH using 1:2.5 soil to water suspension; water-

Figure 1. Soil sampling locations in Salahaddin, Iraq.

Table 1. Coordinates of the soil sampling locations in the study areas using GPS.

Sample number	Soil location	Latitude (N)	Longitude (E)
1	Shirqat 1	35º32’25.84”	43º13’50.38”
2	Shirqat 2	35º32’23.27”	43º15’07.41”
3	Makhool	35º08’20.13”	43º27’44.04”
4	Makhool 2	34º57’23.43”	43º26’02.88”
5	Baje 1	34º55’46.52”	43º31’22.54”
6	Baje 2	34º50’19.44”	43º32’51.23”
7	Tikrit 1	43º43’49.66”	34º46’28.55”
8	Tikrit 2	43º39’17.16”	34º43’29.39”
9	Dour 1	43º51’30.46”	34º31’07.55”
10	Dour 2	43º49’19.91”	34º29’17.65”
11	Tuz 1	44º24’59.48”	34º40’51.09”
12	Tuz 2	44º28’21.34”	34º53’20.66”

soluble, exchangeable and total K extracts by flame photometer; and mineralogy analyses and X-ray diffraction were performed on the < 2 µm clay fraction. The sub-samples were treated with distilled water to remove the soluble salts, then with NaOAc at pH = 5.0 to remove the $CaCO_3$, and treated with sodium hypochlorite (NaOCl 14 %). The organic matter and Na-dithionite-citrate-bicarbonate and Fe oxides were removed, and clay was separated by decantation. X-ray diffract grams were obtained with a Philips X-ray diffract meter with Ni-filtered Cukα radiation generated at 40 kv and 2θ mA. The semi-quantitative mineralogical composition of the clay fraction was treated by Mg-saturation, Mg-plus ethylene glycol-saturation and K-saturation, and K was determined by X-ray diffraction analyses. A paired t-test was used to compare at the probability levels of 0.01 and 0.05 (Johnson & Bhattacharyya 2019).

The K^+ quantity-intensity was determined according to Beckett (1964), by adding 50 mL of 0.01M $CaCl_2$ solutions containing 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 5, 7 and 10 mmol L^{-1} of KCl concentrations to 2.5 g of soil sample. The soil suspensions were shaken vigorously for 2 h and left overnight (24 h) for equilibration and then centrifuged. The suspensions of the soil samples were filtered and the supernatants analyzed for K^+ by a flame photometer and for Ca^{++} and Mg^{++} by titration with Senate (Carter & Gregorich 2007). The K^+ intensity (I) or the activity ratio of K^+ (AR^K) relative to Ca^{++} Mg^{++} species of each equilibrium solution was calculated. The change in the amount of K in solution gained or lost by the soil (±ΔK) was calculated according to the following equation: $\pm\Delta K = (Ci - Cf) \times V/W$, where: V is the volume of solution (cm^3); W the weight of dry soil (kg); Ci the concentration of added K; and Cf the K concentration after equilibrium (mg L^{-1}).

The K intensity factor in the liquid phase for soil is expressed as activity ratio (AR^K), and was computed from the measured concentration of Ca, Mg and K in the supernatant solution after equilibrium. The K activity ratio was calculated according to Beckett (1964), as: $AR^K = a_K/\sqrt{}a_{Ca} + a_{Mg}$, where: a is the ionic activity of the species (Ca, Mg and K). The ionic activity (a_i) was calculated according to the Lewis equation: $a_i = C_i \times y_i$, where: C_i is the concentration of ions in the species (mol L^{-1}); and y_i the ionic activity coefficients calculated by the empirical Davies equation (Sposito 2008), as: $\text{Log } y_i = -0.509\, Z_i^2\, [\sqrt{I}/1 + \sqrt{I} - 0.3I]$, where: y_i is the mean activity coefficient of the electrolyte; Z_i the ion species valence; I the ionic strength (mol L^{-1}); and $I = 0.013 * EC$, where: I is the ionic strength (mol L^{-1}) and EC = dSm^{-1}.

From a plot of ±ΔK *versus* 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 K (PBC_{K0}) was calculated as the slope of the linear section of the Q/I curve. The labile K (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, as reported by Beckett (1964): $-\Delta G^K_{equ} = 2.303RTlog\, AR^K_0$, where R and T are the gas constant and absolute temperature, respectively. The Gapon constant was calculated according to Evangelou & Karanthansis (1986), as: $k_G = PBC_K/CEC$, where: k_G is the Gapon constant, PBC_K the K potential buffering capacity and CEC the cation exchange capacity.

RESULTS AND DISCUSSION

Table 2 shows that the studied soils are distinguished by gypsum soil rates ranging between 20 and 220 g kg^{-1}. The highest lime value (350 g kg^{-1}) was observed in soil 4 (sample 4) and the lowest one (200 g kg^{-1}) in soil 7 (sample 7). The E_C ranged from 1.5 to 3.74 dS m^{-1} and the pH was neutral (7.0-7.7). The results of X-ray diffraction for clay samples showed the clay minerals order as smectite, chlorite, palygorskite, kaolinite and illite.

The Q/I plots for every layer showed a linear relationship at high activity ratios and curvilinear at low-intensity levels. The data show that the shape of the Q/I plots is similar for all layers, as confirmed by Ahmed & Sheikh-Abdullah (2020). The slopes of the plots not only depended on CEC, but also on k_G at low K surface coverage (where the slopes equated to PBC_K). The existence of curvature in the lower portion of the Q/I plots was the major difference among these gypsiferous soils. It is not clear why this curvature exists, but there are two possibilities: i) since the K^+ exchange coefficient was found to be independent of calcite solubility, it is probable that the interactions between K^+ and soil minerals may have contributed to

Table 2. Physical and chemical characteristics of selected gypsiferous soils.

Sample number	Location	PSD (g kg^{-1})				pH	E_C (S m^{-1} at 25 ºC)	CEC ($cmol_c$ kg^{-1})	OM	$CaSO_4$	$CaCO_3$
		Sand	Silt	Clay	Texture				g kg^{-1}		
1	Shirqat	540	230	230	SCL	7.50	1.50	10.0	12.0	20	300
2	Shirqat	505	285	210	L	7.40	2.30	11.0	14.0	35	330
3	Makhool	498	314	188	L	7.25	2.70	9.2	10.0	50	240
4	Makhool	484	348	168	L	7.50	2.00	8.9	10.0	62	270
5	Baje	500	349	151	L	7.50	2.80	8.3	8.0	83	350
6	Baje	600	256	144	SL	7.00	2.50	8.7	9.5	103	300
7	Tikrit	510	355	135	L	7.70	3.00	7.4	8.0	121	200
8	Tikrit	533	342	125	SL	7.30	2.20	6.6	6.5	150	240
9	Dour	526	359	115	SL	7.60	2.70	6.6	6.0	172	300
10	Dour	582	308	110	SL	7.40	2.90	5.5	4.0	196	325
11	Tuz	600	305	95	SL	7.10	3.74	7.0	7.5	205	296
12	Tuz	630	280	90	SL	7.50	3.52	4.8	3.3	220	210

SCL: sandy clay loam; L: loam; SL: sandy loam; PSD: particle size distribution; E_C: electrical conductivity; CEC: cation exchange capacity; OM: organic matter.

the relatively high values of the exchange coefficient; ii) a masking effect produced by a relatively high concentration of exchangeable K^+.These are possible factors responsible for the discrepancy between our results and those by the aforementioned authors.

Clay minerals differ in their ability to fix K, since illite and vermiculite constituted between 5 and 20 % of the silica clay content, respectively, and because of the difference in the crystalline structure, location and quantity of negative charges within the crystals. Illite has the ability to fix K from the soil solution and return it. Thus, the distance between the illite mineral plates remains constant. The size of silica tops in silica sheets is similar to two adjacent layers of mica, but this K is slowly released to the soil solution of these calcareous soils when the level of exchangeable K reduces in the solid phase. The K^+ minerals interactions may indeed be contributing factors for these linear graphs. These plots also show the relation between the quantity factor, as a function of the intensity factor (KAR) (chemical potential) for labile K, and the chemical potential of Ca^{2+} and Mg^{2+} ions that move to the soil solution (Shil et al. 2021) (Figure 2). The plots refer clearly to the variation of values of slops and intercept these variations due to the variation in the soils chemical, physical and mineralogical properties (Zhu et al. 2020). The upper parts of these plots are linear and also allow determining the AR^K_o and soil buffering for K saturation (Figure 3). Also, linear parts of the plots refer to the exchangeable K that will be released from readily available sites of multiple adsorption layers with low adsorption, while the curve part of these plots will be from sites that hold extremely (specific sites) (Al-Hamandi et al. 2019).

The AR^K_e amount ranged widely [16 to 48 x 10^{-5} (mol $L^{-1})^{1/2}$, with a mean of 27 x 10^{-5} (mol $L^{-1})^{1/2}$]. These results are in line with Al-Hamandi et al. (2019). In some Iraq soils, the AR^K_e variation may be caused by cropping with or without K-fertilization and leaching process (Wang et al. 2004). The present study further supports that AR^K_e indicates the status of the immediately available K and, therefore, regulates the exchange of K ions from the exchange complex to the solution phase. Results in all soil samples also suggest that the adsorption was primarily held at planar positions. Jalali (2007) suggests the predominance of K adsorbed to edge sites, whereas $AR^K_e > 0.01$ (mol $L^{-1})^{1/2}$ indicates a predominance of K adsorbed to planar, but there was no field with $AR^K_e < 0.001$ (mol $L^{-1})^{1/2}$, what is an indication of K adsorbed to the interlattice position. Furthermore, the variation in K adsorption sites in the soils seems to clarify why exchangeable K was a poor predictor of K intensity. This represents the amount of K which is capable of ion exchange during the period of equilibrium between soil solids and soil solution (Sharma et al. 2012).

The labile K (L_K) comprises two distinct components, namely the non-specifically held or immediate source of available K (ΔK_0) and difficultly available K (K_x) (Bilias & Barbayiannis 2018). The lowest value of L_K was 19 x 10^{-3} $cmol_c$ kg^{-1} in soil 12, while the higher value was 80 x 10^{-3} $cmol_c$ kg^{-1} in soil 2 (Table 3). This variation may be due to the presence of $CaCO_3$ and $CaSO_4$, clearly indicating that under

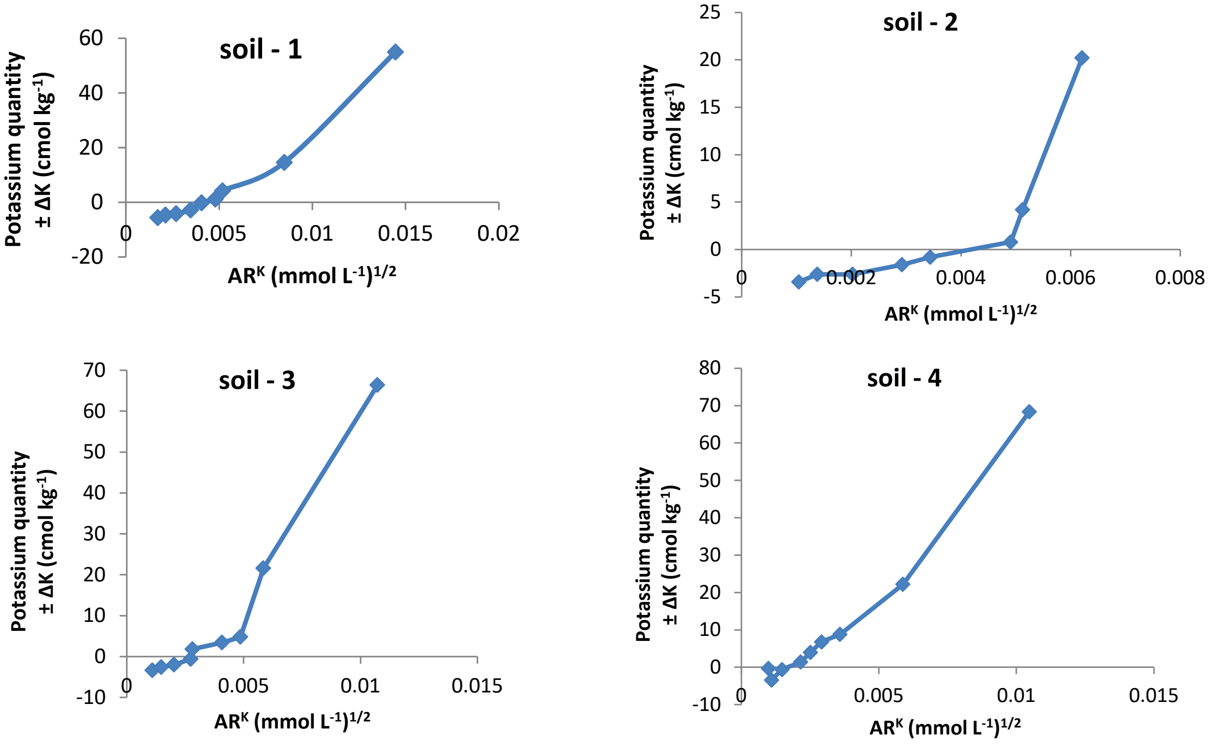
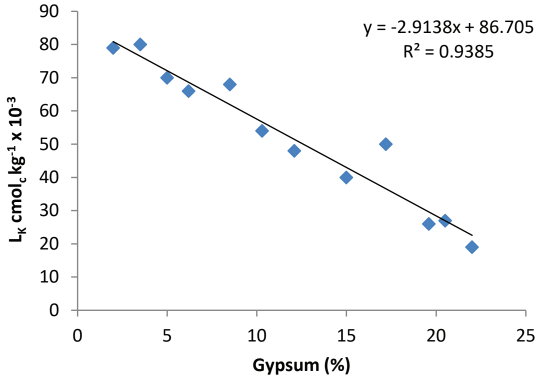


Figure 2. Quantity-intensity curves of potassium for the soils 1, 2, 3 and 4 (see table 2). AR^K: potassium activity ratio.

intensive cropping the cultivated soil has a higher potential to replenish the K concentration in the soil solution for a longer period. The labile K values seem to be more affected by the particle size distribution of the soils. Potassium has a high tendency to adsorb in the solid phase, and therefore needs more energy to be released into the liquid soil phase. In addition, increasing the adsorption to maximize the adsorbed K layers contributes to reduce the binding energy, which makes the K easy to release. On this basis,



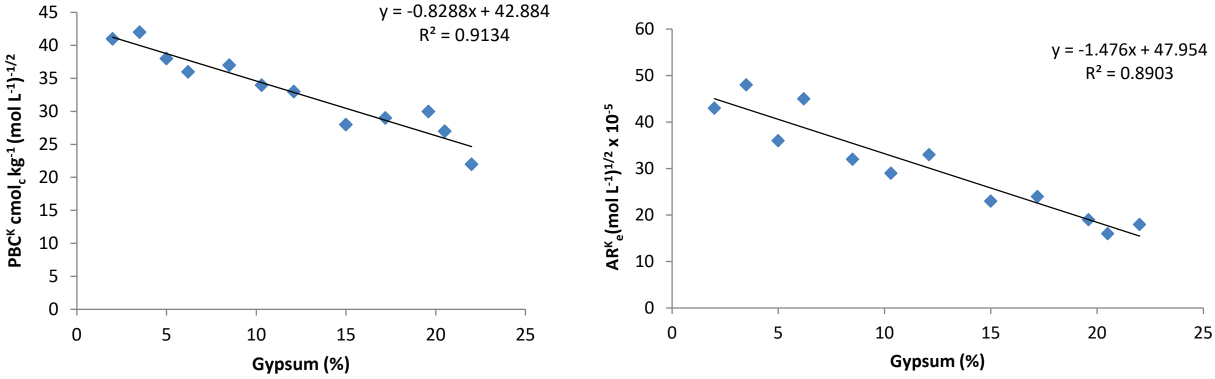


Figure 3. Effect of soil gypsum content on the potassium activity ratio (AR^K_e), labile potassium (L_K) and potential buffering capacity (PBC_K).

Table 3. Thermodynamic parameters of potassium in the soil samples.

Sample number	AR^K_e (mol $L^{-1})^{1/2}$ x 10^{-5}	L_K $cmol_c$ kg^{-1} x 10^{-3}	PBC_K $cmol_c$ kg^{-1} (mol $L^{-1})^{-1/2}$	-ΔG kJ mol^{-1}	k_G (L $mol^{-1})^{1/2}$
1	43	79	41	-1.097	4.10
2	48	80	42	-1.082	3.82
3	36	70	38	-1.123	4.13
4	45	66	36	-1.091	4.04
5	32	68	37	-1.139	4.46
6	29	54	34	-1.153	3.91
7	33	48	33	-1.135	4.46
8	23	40	28	-1.186	4.24
9	24	50	29	-1.180	4.39
10	19	26	30	-1.213	5.45
11	16	27	27	-1.237	3.86
12	18	19	22	-1.221	4.58

AR^K_e: equilibrium activity ratio; L_K: labile K pool; PBC_K: potential buffering capacity; -ΔG: free energies of exchange; k_G: Gapon selectivity coefficient.

the K-bonding strength in the fine soil texture is higher than in the coarse soil texture. The labile K in Iraq soils represents 70-80 % of the exchangeable potassium. Therefore, clay minerals contribute to increasing the number of specific and non-specific sites responsible for K adsorption and retention. This is reflected in the amount of K adsorbed in the soil. The fine soil texture, which has a high adsorption capacity, needs more K supplying to the plant growth, while coarse soils need less K to reach the highest soluble concentration in the soil solution, although they do not have sufficient reserves to supply the plant with the required amount during the growth period. The $-\Delta K^o$ value represents the proportion of labile K which is located on the planar surface (Panda & Patra 2018, Bilias & Barbayiannis 2019). According to Al-Hamandi et al. (2019), it makes up a constant percentage (70-80 %) of exchangeable K, and thus will seem $-\Delta K^o$ and K on the higher energy sites of clay fraction particles. This means that the number of high energy sites is a function of the amount of exchangeable K, rather than a soil property. The $-\Delta K/K_{ex}$ percentage ranges between 0.09 and 6.13. This, however, disagrees with findings by Ahmed & Sheikh-Abdullah (2020), and may be attributed to a high level of $CaSO_4$ equivalent contents prevailing in these soils.

The potential buffering capacity (PBC_K) equal to the amount of labile K can be removed before the AR^K_e is reduced by more than a given amount. The straight line section of the Q/I plot represents the linear buffering capacity (PBC_K) of the soils, which is a measure of the ability of the soil to maintain the intensity of K in the soil solution (Zhu et al. 2020). The differences in the PBC_K values in soils could be attributed to the differences in past cropping and management practices (Ahmed & Sheikh-Abdullah 2020), or the PBC_K values are indicative of soil capacity for maintaining a given K activity (concentration) at equilibrium conditions, in case of K uptake by plants or leaching (Auge et al. 2018). The PBC_K values of the studied soils help to explain the limiting validity of the equilibrated ratio values in describing the potassium status of many of the studied soils. The PBC_K values (Table 4) show that all the studied soils are poorly K-buffered. This can be attributed to their high contents in $CaCO_3$ and $CaSO_4$ equivalent, since the value of this K parameter ranged between 22 $cmol_c$ kg^{-1} (mol $L^{-1})^{-1/2}$ in soil 12 and 42 $cmol_c$ kg^{-1}(mol $L^{-1})^{-1/2}$ in soil 2. Soils with the highest PBC_K value were characterized by the lowest percentage of K saturation, being an indicative of the higher potential to replenish the K concentration in the soil solution (Yuan et al. 2021).

The free energy of exchange ($-\Delta G$), represented by the term $RT\ ln\ AR^K_e$, is related to one chemical equivalent of K in the standard state replacing one chemical equivalent of calcium on clay, followed by the liberation of certain calories or joules of energy (Al-Hamandi et al. 2019). The amount of $-\Delta G$ varied among the soil locations and the energies of exchange (Table 4), with values between -1.237 and -1.082. Samadi (2006) observed that soils with higher exchangeable K (%K saturation) are generally characterized by low $-\Delta G^K_e$ values. The K fertility evaluation according to the free-energy indicates a critical fertility situation between the efficiency and the decrease. The amendment of this shortage through

Table 4. Potassium forms and clay minerals in the studied soils.

Sample number	K-forms (cmol$_c$ kg^{-1})				Mineral contents (%)				
	Soluble	Exchangeable	Non-exchangeable	Total	Smectite	Illite	Kaolinite	Palygoriskite	Chlorid
1	0.014	0.11	0.31	22.3	++++	+++	+++	++	+
2	0.014	0.11	0.21	21.5	+++	+++	+++	++	++
3	0.013	0.10	0.20	20.8	+++	+++	+++	+++	+
4	0.012	0.09	0.19	20.1	+++	++++	++	+	+
5	0.011	0.10	0.20	19.7	+++	+++	++	+	++
6	0.012	0.08	0.18	19.3	+++	++	++	++	++
7	0.011	0.07	0.17	18.6	+++	+++	+++	++	++
8	0.011	0.06	0.16	18.2	+++	++	+++	++	++
9	0.010	0.07	0.17	17.7	++++	+++	++	+++	+
10	0.008	0.04	0.14	17.4	++++	++++	+++	++	+
11	0.006	0.04	0.14	16.8	+++	++	+	+	++
12	0.004	0.03	0.13	16.5	+++	++	+	+	+

++++: dominant (50-90 %); +++: major (20-50 %); ++: minor (5-20 %); +: trace (< 5 %).

fertilization will make the K to be adsorbed on the planner surfaces, and thus it will be difficult to release it to the soil solution during the short growth period (Islam et al. 2017).

The Gapon selectivity coefficient for K expresses the relative affinity that soils may develop toward K in the presence of Ca and Mg, both in the soil solid phase and soil solution under equilibrium conditions. Most of the k_G values fluctuated within the range of 3.86 to 5.45 (L mole^{-1})$^{1/2}$, with mean of 4.65 (L mole^{-1})$^{1/2}$, suggesting that the relative affinity for K was quite similar (Table 4). The Gapon selectivity coefficients reported by Samadi (2006) varied between 2.3 and 5.3 (L mole^{-1})$^{1/2}$. The changes in k_G values are basically attributable to the levels of exchangeable Ca and Mg (Panda & Patra 2018). The soil selective behavior for K, in comparison with dominant Ca and Mg, may also be attributed to the preferential attraction of K ions over Ca and Mg at some planar sites of soil colloids (AL-Hamandi 2020).

Table 5 shows the correlation coefficients between Q/I parameters and soil chemical properties. The potassium activity ratio (AR^K_e) showed the highest correlation with these soil properties at the 0.01 probability level. That reflects the potency of soil properties on the AR^K_e values in gypsiferous soils. The exchangeable free energy ($-\Delta G$) also has a high correlation with the studied soil properties at the 0.01 probability, because the $-\Delta G$ values are also directly correlated with AR^K_e values. For the labile potassium (L_K), the single parameters have no significant correlation with the soil properties, because L_K depends on clay content.

The potential buffering capacity (PBC_K) also has a high correlation with the soil properties, directly indicating the effect of the liquid phase of these soils on the supply of calcium and potassium. The Gapon coefficient (k_G) was not affected by these properties due to the low clay content and organic matter.

Table 5. Correlation coefficients between quantity-intensity ratio parameters and some soil properties.

Parameters	Soil properties				
	Ec	CEC	OM	CaSO$_4$	CaCO$_3$
AR^K_e	0.9873**	0.8359**	0.9986**	0.8923**	0.8511**
L_K	0.2930	0.1022	0.3325	0.1082	0.1004
PBC_K	0.6090*	0.8567**	0.4507	0.8086**	0.8526**
$-\Delta G$	0.9923**	0.8927**	0.9841**	0.9094**	0.8979**
k_G	0.3970	0.6767*	0.3330	0.6236*	0.6781*

AR^K_e: potassium activity ratio; L_K: labile potassium pool; PBC_K: potential buffering capacity; $-\Delta G$: free energies of exchange; k_G: Gapon selectivity coefficient; E_C: electrical conductivity; CEC: cation exchange capacity; OM: organic matter. * and **: significant at 0.01 and 0.05 of probability, respectively.

CONCLUSION

All the investigated soils are characterized by good potassium reserves, but low in release, according to the adsorption of the quantity-intensity ratio parameter to determine the soil potassium availability. Therefore, these soils require special management to prevent soil degradation and improve soil fertility and management.

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