

POTASSIUM STATUS IN SOME LEBANESE SOILS

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ABSTRACT

This study was conducted to evaluate K content and availability in Lebanese soils using the traditional methods of K measurement, K-thermodynamics and K-kinetics measurements. Nine surface soil samples (0-30 cm) were collected from major agricultural regions in Lebanon and were later exposed to the following laboratory measurements. Extraction of K with H₂O, 1N NH₄OAc and 1N HNO₃, and calculation of: K-fixation capacity, ionic strength, K-activity ratio, free energy of replacement (-ΔF), Q/I relationship. Five K-kinetic equations were compared by applying the least square regression analysis to determine the suitable ones for describing K release from soils. The results showed that the tested soil samples varied widely in K contents and K supplying power to plants. According to NH₄OAc and HNO₃ extraction methods, the K levels of samples 5 is high, 7 is medium, 9 is medium/low and the other 6 samples are low. The values of H₂O-K didn't follow the same order. The values of KSP were low in all samples except 5 & 6. The amounts of fixed K in the studied samples varied from 1.53 Cmol.Kg⁻¹ to 5.02 Cmol.Kg⁻¹. The activity ratio values ranged between 0.0008 and 0.018. The values of free energy of replacement (-ΔF) showed that soils 5 and 6 have medium K supplying power. The values of K-buffering capacity ranged between 22.0 Cmol.Kg⁻¹/mol/L and 297.8 Cmol.Kg⁻¹/mol/L. The values of labile K were lower than those of available K. This means that a part of exchangeable K exists on sites with high bonding energy. The release capacity ranged between 9.5% and 59.1%. From the five mathematical models which were tested, the first order equation was the most suitable and was selected to determine the release rate coefficient of K. The results show that K content in Lebanese soils differs widely and the results of soil testing should be compared to field responses.

Keywords: potassium release, availability, equilibrium reaction, K-thermodynamics, K-kinetics

INTRODUCTION

Potassium is an essential nutrient for agricultural crops because it plays an important role in several physiological processes in plant. There are about 50 enzymes, responsible for energy transfer and formation of sugars, starch and protein that are affected by potassium presence in plant (Krauss, 1997; Darst, 1992).

Potassium content in soils depends on the type of parent material and degree of soil and mineral weathering. Soil K exists in four forms that are in equilibrium, each differing in

its availability to crops. These forms, in increasing order are: mineral, non-exchangeable (fixed or difficultly available), exchangeable, and solution (Havlin *et al.*, 2004). The equilibrium reactions between K forms markedly affect whether applied potassium is taken by plant, leached into lower soil layers or converted into un-available forms (Sparks & Huang, 1985). Knowing the equilibrium constants is very important for predicting the status and supply of potassium for plant (Lindsay, 1979).

Different approaches or methods are used to evaluate the status and availability of potassium. Potassium extracted by 1 N ammonium acetate is considered as good indicator for potassium availability (Mishra & Singh, 1994), while other investigators (Memon *et al.*, 1988; Mangel & Kirkby, 1987; Al-Zubaidi & El-Semak, 1995) stressed on the contribution of acid extracted K on potassium nutrition and plant uptake.

Recently, new approaches for evaluating potassium status and its availability have been applied. Thermodynamic parameters including: ionic activity, activity coefficient, ionic strength, activity ratio, buffering capacity and free energy of replacement are considered by several researchers as accurate method for evaluating potassium status and its availability in soils. Several kinetic models and equations: zero order, first order, parabolic diffusion, Elovich and power function have been successfully used for mathematical description of potassium adsorption and release (Sparks, 1989; Al-Zubaidi & Al-Obudi, 2001).

Limited data research has been published on potassium status and supplying power in Lebanese soils (Sayegh *et al.*, 1990; Darwish *et al.*, 2003). The objective of this study was to evaluate the status of potassium in selected Lebanese soils using the traditional method of K analysis (NH_4OAc , -K), K-thermodynamics, and K-kinetic measurements.

MATERIALS AND METHODS

Nine surface soil samples (0-30 cm) were collected from major agricultural regions in Lebanon and where some field experiments are being conducted. Some physical and chemical properties of the soil samples (Table 1) were determined according to the methods described by Richards (1954).

Different potassium forms: water soluble ($\text{K} - \text{H}_2\text{O}$), potassium extracted by NH_4OAc ($\text{NH}_4\text{OAc-K}$) and potassium extracted by nitric acid (Acid-K) were determined by the methods described by Pratt (1965). The concentration of potassium in all extracts was measured by flame photometer.

Potassium fixation capacity

The soil K-fixation capacity was investigated using the method proposed by Jackson (1979). For replacement of exchangeable potassium, 0.5 M CaCl_2 solution was used instead of 1 N ammonium acetate, after treating the soil samples with KCl solutions to avoid the extraction of fixed potassium (Martin & Sparks, 1983). 0, 4, 8, 16, 32 and 64 mgs KCL were added to 5 gm of soil, in centrifuge tube, then 10 ml of distilled water was added. After shaking for 3 hours the suspension was left to stand for 72 hours for equilibrium. Fixed potassium (fixation capacity) was calculated by the following form:

$$\text{Soil K-fixation capacity} = (\text{added K} + \text{K in extract of zero KCL treatment} - \text{K in extract of each treatment}).$$

Thermodynamic measurements and calculations

Ionic strength (μ) mol/L in soil extracts was calculated by the formula proposed by Griffin & Jurinak (1973):

$$\mu = 0.0129 \text{ EC. (dS.m}^{-1}) \quad \text{EC} = \text{Electrical Conductivity}$$

Activities (a) of potassium, calcium and magnesium in water extracts were calculated as product of concentration of ions by their activity coefficient (f) values. Activity coefficient of ions was calculated using extended Debye-Hückel equation :

$$\text{Log}f_i = -AZ_i^2 \frac{\sqrt{\mu}}{1 + Bd_i\sqrt{\mu}}$$

Where:

Z_i : valency of ion

A: 0.508 for water at 25 °C

B: 0.328×10^8 for water at 25 °C

d: is the effective distance of closest approach measured in centimeter and corresponds roughly to the effective size of hydrated ions (d values for different ions are tabulated in Lindsay (1979).

The activity ratio of potassium (ARK) was calculated by the following form:

$$\text{ARK} = \frac{a_k}{\sqrt{a_{\text{Ca}} + a_{\text{Mg}}}}$$

Where (a) is the activity in mol/L.

The free energy of replacement ($-\Delta F$) of K – (Ca + Mg), was calculated by the formula proposed by Woodruff (1955):

$$-\Delta F = 2.303RT \log \frac{a_k}{\sqrt{a_{\text{Ca}} + a_{\text{Mg}}}}$$

Where R is gas constant and T is the absolute temperature.

Quantity / Intensity relationship

To determine the quantity- intensity relationships of potassium for the studied soil samples, the method proposed by Beckett (1964) was used. Duplicate soil samples of 2.5 gm each were treated with a series of KCl solutions containing potassium concentrations as follows: 0, 0.2, 0.4, 0.8, 2.0, 4.0, and 8.0 mmol/L with constant concentration (0.04M) of $\text{CaCl}_2 + \text{MgCl}_2$.

The suspensions of soil : solution (1:10) were shaken for 3 hours and left to stand for 24 hours for equilibrium, then the suspensions were centrifuged. Concentrations of K, Ca, Mg, and EC were measured in supernatants. The change in the amount of exchangeable potassium ($\Delta \text{exch.}$) which represents the quantity factor was calculated from the differences of concentrations of potassium in prepared solutions and equilibrated solutions. Activity ratio (ARK), which represents the intensity factor, was calculated. The relationships between the

quantity factor and intensity factor for the studied soil samples were drawn according to Beckett (1964). The values of potassium buffering capacity (BC_K) and labile potassium were calculated from the straight line equations of the quantity-intensity relationships (Beckett, 1964).

Kinetics Experiments

Duplicate soil samples of 1gm each were transferred into 50 ml centrifuge tubes containing 10ml of 0.5mM citric acid. The samples were then equilibrated on a shaker for periods: 1, 2, 4, 8, 16, 32, 64 and 128 hours. At the end of the equilibrium period, the supernatant was separated by centrifugation. A new portion of 10ml citric acid was then added and extraction was repeated (Simard *et al.*, 1992) and K concentration was measured. Potassium released with time was fitted using the following equations (Sparks, 1989):

$$\text{Zero order reaction : } (K_0 - K_t) = a - bt$$

$$\text{First order reaction : } \ln (K_0 - K_t) = a - bt$$

$$\text{Parabolic reaction : } K_t / K_0 = a + b \sqrt{t}$$

$$\text{Elovich equation : } K_t = a + \ln t$$

$$\text{Power function : } \ln K_t = a + b \ln t$$

Where K_t is the accumulative potassium released at time (t), K_0 is the maximum potassium released, (a) and (b) are constants and (t) is time in hour. These mathematical models were tested by least square regression analysis to determine which was the most appropriate for describing the potassium release from the soil. The standard errors of estimates were calculated as follows:

$$SE = \left[\frac{\sum (K_t - K_t^*)^2}{n - 2} \right]^{1/2}$$

Where K_t and K_t^* are the measured and calculated concentrations of potassium released at time (t) and (n) is the number of measurements. The rate constant of potassium release in citric acid was calculated from above equations.

RESULTS AND DISCUSSION

Description of soils

The result in Table 1 indicates that the studied soils are non saline, slightly alkaline and calcareous. The $CaCO_3$ ranged from 2.5% soil no. 1 to 29.7% soil no. 5. The organic matter was 5.1% in soil no.7 and ranged between 1.4-3.1% in the other samples. The exchangeable cations are described as follows: Ca is high, Mg is sufficient. In general the properties of all the soil samples are close except the CEC values which divide the 9 soil samples into three distinctive groups: CEC low (6.5 Cmol/Kg) sample No. 6; medium (21.7-31.0 Cmol/Kg) samples nos. 1,2,3,4,5 & 9 and CEC high (47.8-54.5 Cmol/Kg) samples nos. 7 & 8.

Water soluble potassium ($H_2O - K$)

Soluble K was extracted with distilled and dionized water at a ratio of 1:1 (soil: water). The concentration of soluble potassium ranged between 1.0 mg/Kg for sample no.1 to

11.2 mg/L in sample no. 6 (Table 2). These values are much lower than the critical value of 0.5 mM/L which was proposed by International Potash Institute (IPI, 2000). These low values do not retard the release of exchangeable K, but are not enough to support plant growth. Expressing the amount of H₂O – K in kg/hr, the values are much lower than the requirements of most crops as reported by Datta & Sastry (1988).

Water soluble K constitutes only (0.7 – 12.7%) of NH₄OAc - K (Table 2). This indicates that a very small part of available potassium is in soil solution. Also it is apparent from Figure 1 that the equilibrium is not in the favor of soluble potassium in the most studied soils. Comparing the values of H₂O – K with those obtained by Al Zubaidi (2003) for Iraqi soils (4 – 234 mg/L) it clearly shows that Lebanese soils contain much lower H₂O – K than Iraqi soils.

NH₄OAc extracted potassium (NH₄OAc – K)

The amounts of (NH₄OAc – K) which are an estimate to available potassium in soils are shown in Table 2. The amounts of NH₄OAc – K range between 42 – 575 mgkg⁻¹ which correspond to 168 – 2300 kgh⁻¹ with an average 151 mgkg⁻¹ = 604 kg.h⁻¹. These results agree with Darwish *et al.*, (2003) who reported that NH₄OAc – K values for some Lebanese soils, varying in clay mineralogy, range between 0.4 – 2.0 Cmol.kg⁻¹ (156 – 782 mg.kg⁻¹).

If the critical value is considered for available potassium = 160 mg.kg⁻¹ (Pagel, 1972; Al-Zubaidi & Pagel, 1979), then soils no. 1, 2, 3, 4, 6 and 9 are poor in available potassium and expected to positively respond to potassium fertilization, while soil samples nos. 5, 7, and 8 are characterized by medium-high level of potassium.

These values include the residual K originating from fertilization. According to this information about the history of fertilization of soil sample no. 5 from AREC, compound fertilizer 17-17-17 has been used repeatedly in fertilization of different crops at AREC and this may be a major reason for the very high values for K in AREC soil.

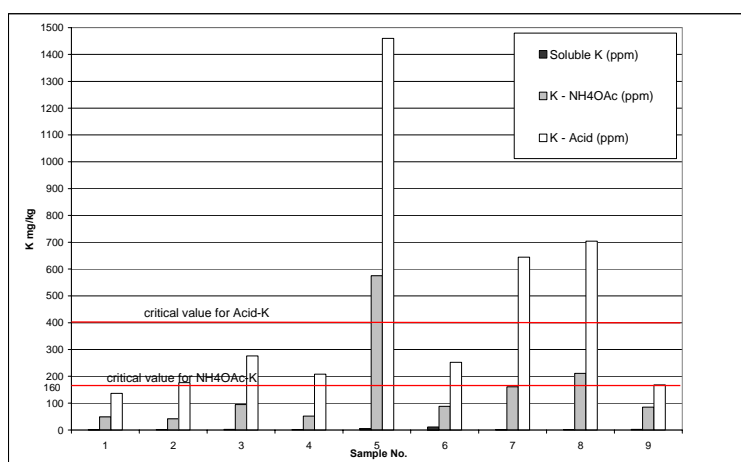


Figure 1. Distribution of different potassium forms in the studied soils.

TABLE 1
Locations and Properties of the Studied Soils

Sample No.	Location	Geographic Location	EC (dS/m)	pH	CEC (Cmol.kg ⁻¹)	CaCO ₃ (%)	OM (%)	Particle size analysis (g/kg)		Textural class			
								Ca	Mg	Sand	Silt	Sand	Clay
1	Al-Shaloutieh	Akkar/North	0.36	7.89	28.8	2.5	2.6	3560	793	416.4	134.4	449.2	Clay
2	Al-Mahfoudieh	Akkar/North	0.32	8.13	30.2	5.0	2.7	4740	796	296.4	194.4	509.2	Clay Sandy Loam
3	Afif Khoury Plot 32	Akkar/North	0.40	8.06	29.6	4.6	2.5	3980	795	336.4	114.4	549.2	Clay Sandy Loam
4	Afif Khoury Plot Ao1	Akkar/North	0.40	8.14	21.7	6.4	2.3	3580	726	236.4	134.4	629.2	Sandy Clay Loam
5	AREC	Bequa'a	0.28	7.67	31.0	29.7	2.6	5670	274	436.4	274.4	289.2	Clay
6	Hasbaya	West Bequa'a	0.23	7.28	6.5	13.1	1.4	2659	87	129.6	61.1	809.3	Sandy Loam
7	Al-Biri	West Bequa'a	0.39	7.64	54.5	9.4	5.1	11385	293	353.0	284.0	363.0	Clay Loam
8	Arab Salim	South/Eqlim Al-Tuffah	0.66	7.27	47.8	9.9	3.1	8951	524	455.0	294.0	251.0	Clay
9	406 Saydanaya	Hermel/North Bequa'a	0.62	7.46	27.8	7.2	2.5	3601	919	174.0	350.0	476.0	Loam

Table 2 also shows that $\text{NH}_4\text{OAc} - \text{K}$ consists 25 – 50% of $\text{HNO}_3 - \text{K}$ and the ratios of acid - K / $\text{NH}_4\text{OAc} - \text{K}$ range between 2.0 – 4.2, this indicates that $\text{NH}_4\text{OAc} - \text{K}$ constitutes a considerable part of supplying power of potassium in the studied soils. Comparing the $\text{NH}_4\text{OAc} - \text{K}$ values (42 – 575 mg.kg^{-1} ; average 150 mg.kg^{-1}) with the values of Iraqi soils (190 – 1177 mg.kg^{-1} ; average 422 mg.kg^{-1}) (Al-Zubaidi, 2003), indicates clearly that Lebanese soils contain much lower values of $\text{NH}_4\text{OAc} - \text{K}$ than the soils of Iraq.

TABLE 2
Forms of Potassium in the Studied Soils

Soil Sample	H ₂ O – K mgkg ⁻¹	NH ₄ OAc – K mgkg ⁻¹	Nitric acid – K mgkg ⁻¹	K – Saturation Percentage (KSP)	$\frac{\text{acid-K}}{\text{NH}_4\text{OAc-K}}$	$\frac{\text{NH}_4\text{OAc-K}}{\text{H}_2\text{O-K}}$	$\frac{\text{NH}_4\text{OAc-K}}{\text{acid-K}} \times 100$ (%)	$\frac{\text{H}_2\text{O-K}}{\text{NH}_4\text{OAc-K}} \times 100$ (%)
1	1	49	136	0.37	2.8	49.0	36.0	2.0
2	1.7	42	176	0.35	4.2	24.7	23.9	4.0
3	2.3	95	276	0.82	2.9	41.3	34.4	2.4
4	2	52	208	0.61	4.0	26.0	25.0	3.8
5	4.5	575	1460	7.75	2.5	127.8	39.4	0.8
6	11.2	88	252	3.46	2.9	7.9	34.9	12.7
7	1.1	161	644	0.20	4.0	146.4	25.0	0.7
8	1.9	211	704	1.13	3.3	111.1	30.0	0.9
9	2.4	85	168	0.78	2.0	35.4	50.6	2.8
Average	3.1	151	447	1.73	3.2	63.3	33.2	3.3

Nitric acid extracted potassium (Acid – K)

Acid extractable potassium represents the soil supplying power of potassium for long term of cropping (Jackson, 1958). The values of HNO₃ – K in the studied soil samples are shown in Table 2. The values show a wide variation, they range from 136 mg.kg⁻¹ in soil samples no.1 to 1460 mg.kg⁻¹ in soil samples no. 5. This is attributed to the different types and mineralogy of the studied soils. However, these values are typical for soils of arid and semi-arid regions (Pagel, 1972; Al-Zubaidi, 2003).

If the critical values of HNO₃ – K are considered to be 400 mg.kg⁻¹ as suggested by Pagel (1972), then soil samples nos. 1, 2, 3, 4, 6, and 9 are poor in supplying K, while soil samples No. 5, 7, and 8 can be characterized to have a high K supplying power.

The HNO₃ – K values of Lebanese soils are lower than the values of Iraqi soils (580 – 2200 mgkg⁻¹) as reported by Al-Zubaidi (2003)

Potassium saturation percentage (KSP)

The average value of potassium saturation percentage (KSP) of the studied soil samples is relatively low (1.73), while the values for all soils samples ranged from 0.26 for soil samples no. 7 to 7.75 for soil sample No. 5 (Table 2). Thus, all the analyzed samples, except soils nos. 5 and 6, have very low KSP values and much lower than the critical value (2.3) which was proposed by Pagel and Insa (1974). This indicates that potassium ions occupy a small portion of CEC in these soils. The KSP values of the studied Lebanese soils are lower than the Iraqi KSP values (2.02-9.91 with average of 4.51) as reported by Al-Zubaidi (2003).

Potassium fixation capacity

The data present in Figure 2 show that there are significant linear correlations between the amounts of fixed and applied potassium in all studied soils. However, the values of regression coefficient – potential for fixation of K, highest (0.320) in soil sample no. 7 and lowest (0.0697) in soil sample no. 6.

Values of fixed Potassium expressed as total amount and as a percentage of applied K for the studied soils are shown in Figure 3, the values of fixed potassium range from 1.53 Cmol. Kg⁻¹ in soil sample no. 6 to 5.02 Cmol. Kg⁻¹ in soil sample no. 7. Sayegh *et al.*, (1990) reported that the amount of native fixed potassium varies from 0.1-1.9 Cmol. Kg⁻¹ for different Lebanese soils, varying in kaolinite level. The highest percentage value (47.5%) was found in soil sample no. 7, and the lowest percentage value (17.4%) was found in soil sample no. 6. This could be attributed to the amount and type of clay minerals. Statistical analysis showed that there are significant correlations (P<0.05) among the amount of fixed potassium and CEC, clay % and (clay + silt) % in the studied soils. Similar relationships were reported in Iraqi soils (Edan *et al.*, 1987). Thus the obtained data indicate that, except for soil sample no. 6, which is sandy loam, the studied soil samples characterized by relatively high potential for potassium fixation (27.0 – 47.5%). These results should be taken into consideration when fertilization recommendations are made.

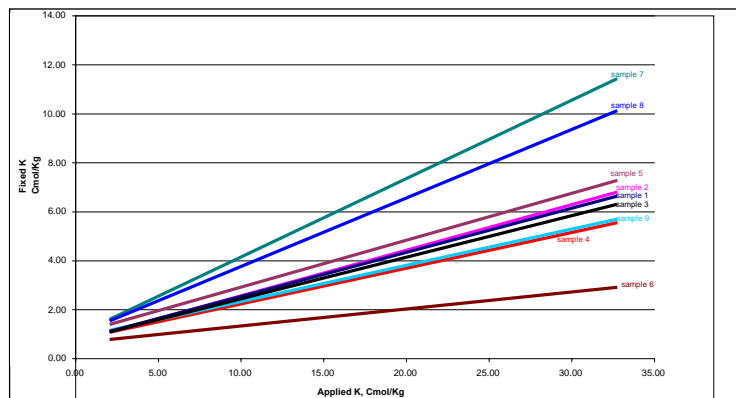


Figure 2. Amount of fixed potassium vs. applied potassium in the studied soils.

Equations:

sample 1:	$y = 0.1802x + 0.7431$	$R^2 = 0.9826$
sample 2:	$y = 0.1863x + 0.7084$	$R^2 = 0.9901$
sample 3:	$y = 0.1698x + 0.7534$	$R^2 = 0.984$
sample 4:	$y = 0.1459x + 0.7805$	$R^2 = 0.9795$
sample 5:	$y = 0.1918x + 1.0097$	$R^2 = 0.9799$
sample 6:	$y = 0.0697x + 0.6446$	$R^2 = 0.9193$
sample 7:	$y = 0.3203x + 0.9596$	$R^2 = 0.9945$
sample 8:	$y = 0.2798x + 0.9747$	$R^2 = 0.9908$
sample 9:	$y = 0.148x + 0.8592$	$R^2 = 0.973$

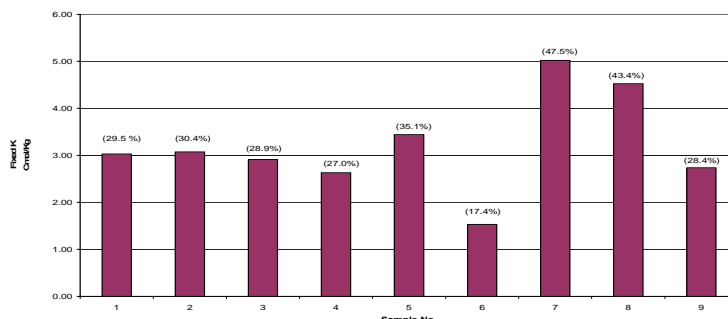


Figure 3. Amounts and percentages of fixed potassium in the studied soils.

Thermodynamics of potassium

To further evaluate the status of potassium in the studied soils, some thermodynamic parameters: ionic activity of potassium, activity ratio, free energy of replacement $[K - (Ca + Mg)]$ and Quantity/Intensity relationship (Q/I) were used. Thermodynamic parameters describe the rate at which potassium of solid phase replenish soil solution – K, (Rasnake & Thomas, 1976). Such approach has been successfully used to describe potassium replenishment in several soils (Cooke, 1979; Al-Zubaidi, 2003). The values of ionic strength, K-activity coefficient, K-activity, activity Ratio and free energy of replacement are shown in Table 3. The values of K-activity coefficient ranged between 0.90 and 0.93. These high values indicate that the majority of potassium ions exist in active form in soil solution because the ionic strength values are low in all samples.

TABLE 3

Thermodynamic Parameters of Potassium in the Studied Soils

Sample #	μ (mol/L) (ionic strength)	γ_K (activity coefficient)	K-Activity (mol/L)	Activity ratio	ΔF (Cal.mol ⁻¹)
1	0.00468	0.9276	0.0000237	0.001579	-3821
2	0.00416	0.9314	0.0000405	0.002138	-3642
3	0.03900	0.9241	0.0000544	0.002643	-3516
4	0.05200	0.9241	0.0000473	0.002491	-3551
5	0.00364	0.9354	0.0001077	0.005765	-3054
6	0.00299	0.9410	0.0002695	0.018103	-2376
7	0.00507	0.9250	0.0000260	0.000832	-4201
8	0.00858	0.9053	0.0000440	0.001270	-3950
9	0.00806	0.9078	0.0000557	0.002255	-3610

The activity ratio values, which reflect the chemical potential, ranged between 0.000832 in soil no. 7 to 0.018103 in soil no. 6; the higher the values of the activity ratio means that more potassium is available for plant uptake. The values of free energy of replacement ($-\Delta F$) varied from (- 4201 cal.mol⁻¹) in soil No. 7 to (-2376 cal.mol⁻¹) in soil no. 6. Woodruff (1955) classified the supplying power of soils according to the ($-\Delta F$) values as follows:

Soils with high supplying power of K have (ΔF) less than -2000 cal.mol⁻¹, and those of (ΔF) -2000 to - 3500 cal.mol⁻¹ have medium K supplying power, while soils that have (ΔF) values that are lower than - 3500 cal.mol⁻¹, are poor in supplying potassium.

The obtained data (Figure 4), shows that only two soils (no. 5 and no. 6) have medium in supplying power of K, while the rest of the samples are poor in K supplying power. It is important to point out here that soil no. 6 which its available potassium value is less than the critical level according to NH4OAc – K (Table 2), has a medium supplying K power according to ($-\Delta F$) value interpretation.

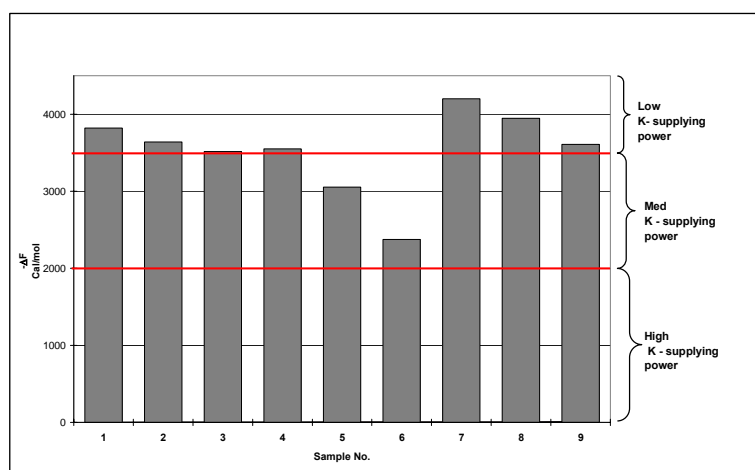


Figure 4. The distribution of the free energy ($-\Delta F$) according to Woodruff classification.

Quantity/Intensity concept

Mathews and Beckett (1962) presented a technique for describing the relationship between exchangeable – K and soil solution – K which they called the Q/I ratio. The quantity factor represents the change in exchangeable potassium (ΔK): $\pm \Delta K = [K]_{\text{original}} - [K]_{\text{equilibrium}}$. While the intensity factor is the activity ratio of potassium (ARK)

$$ARK = \frac{aK}{\sqrt{aCa + aMg}}$$

The obtained activity ratio values in the equilibrium solutions were plotted against the values of change in exchangeable K, a series of linear curves with high significant correlation coefficient values ($r = 0.98 - 0.99$) were obtained for the studied soils (Figure 5).

The high significant linear relationships confirm Gapon equation. The obtained linear curves differ in slopes and intercepts, this could be attributed to the variation of textural class and clay mineralogy types.

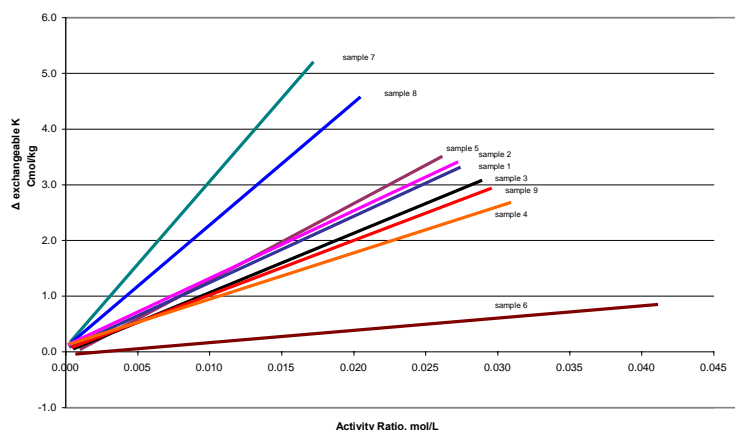


Figure 5. The Q/I relations of the studied soils.

Equations:	sample 1: $y=118.79x + 0.059$	$R^2 = 0.9938$
	sample 2: $y= 121.21x + 0.1114$	$R^2 = 0.9876$
	sample 3: $y= 106.66x -0.0029$	$R^2 = 0.9889$
	sample 4: $y= 83.199x+ 0.1141$	$R^2 = 0.9792$
	sample 5: $y= 137.78x - 0.0891$	$R^2 = 0.9817$
	sample 6: $y= 22x -0.0511$	$R^2 = 0.9619$
	sample 7: $y= 297.79x +0.0871$	$R^2 = 0.9869$
	sample 8: $y= 219.81x +0.0818$	$R^2 = 0.9776$
	sample 9: $y= 97.973x +0.044$	$R^2 = 0.9866$

It is very important to note that the vertical intercepts of all the curves except No. 6 are above (0-0) line, this indicates that the added potassium was fixed and no release will take place under the existing Ca and Mg concentrations.

Many workers have used the Q/I ratio curves to evaluate the ability of soils to maintain K level in soil solution (Beckett, 1964; Rasnake & Thomas, 1976; Al-Zubaidi, 2003). The values of the slope represent the K-buffering capacity and the values of the intercept, which represent the labile potassium in soil. The values of these two parameters were calculated from the obtained linear relationships (Table 4). This data show that the values of K-buffering capacity vary from 22.00 $\text{Cmol.kg}^{-1} \text{mol.L}^{-1}$ for soil no. 6 to 297.79 $\text{Cmol.kg}^{-1} \text{mol.L}^{-1}$ in soil no. 7, with an average value of 133.91 $\text{Cmol.kg}^{-1} \text{mol.L}^{-1}$. This variation could be attributed to the difference in the texture and mineralogy of the soils. Statistical analysis indicated that there is a high significant positive correlation ($r = 0.975$) at $P < 0.05$ between K-buffering capacity and CEC values of the studied soils.

The higher values of K-buffering capacity indicate that the soils have high maintenance power and resistance to change in potassium during the cropping season and *vice*

versa. Therefore, values of K-buffering capacity help us know how to manage potassium fertilization. For example, soil no. 7 has a greater potential to compensate the reduction in potassium level during a cropping season, than soil no. 6 ($297.79/22 = 13.5$ times). Also, this ratio tells us that soil no. 7 needs quantity of potassium fertilizer 13.5 times more than soil no. 6 to maintain its K-buffering capacity.

TABLE 4

Potassium Buffering Capacity and Labile Potassium in the Studied Soils

Sample	R	K-buffering capacity (Cmol/kg / mol/L)	Labile potassium (Cmol/kg)
1	0.9969	118.79	0.059
2	0.9938	121.21	0.111
3	0.9944	106.66	0.003
4	0.9895	83.20	0.114
5	0.9908	137.78	0.089
6	0.9808	22.00	0.051
7	0.9934	297.79	0.087
8	0.9887	219.81	0.082
9	0.9933	97.97	0.044
Average	0.9913	133.91	0.071

Also Table 4 shows the values of labile potassium of the studied soils, this parameter represents the amount of potassium that exists (adsorbed) on unspecific sites and ready to be released for uptake by plant during a cropping season. The obtained values of labile potassium are very low in the studied soils, the highest value ($0.114 \text{ Cmol.kg}^{-1}$) for soil no. 4, and the lowest value ($0.044 \text{ Cmol.kg}^{-1}$) for soil no. 9, (average = $0.071 \text{ Cmol.kg}^{-1}$).

When comparing the obtained values of labile potassium in Table 4 with those of available potassium ($\text{NH}_4\text{OAc} - \text{K}$) in Table 2, it is apparent that the values of labile K are lower than those of available K. This means that part of the exchangeable potassium in the analyzed soils is held on exchange sites with high bonding energy.

Kinetics of potassium release

The cumulative amount of released potassium versus time of extraction with 0.5 mM citric acid is shown in Figure 6. It seems that the amount of potassium released by successive extractions (8 times) increased with increasing time of extraction. The apparent equilibrium was obtained in 8th extraction after 128 hours. The patterns of the curves are related to the initial content of potassium. The curves indicate that there are two stages of release, the first stage, which is at the beginning of the extraction is characterized by extraction of soluble and weakly bonded potassium – mostly exchangeable – while the latter stage (after about 20 hours of extraction) is characterized by release of strongly bonded

potassium –mostly the non-exchangeable form. The variations in the total amount of released potassium from different soil samples (Figure 6) could be attributed to many factors such as particle size of K-bearing minerals and soil environment (Sparks & Huang, 1985). The nature of K-bearing minerals includes crystal structure, chemical composition, degree of depletion and layer charge alteration (Hosseinpour & Kalbasi, 2002).

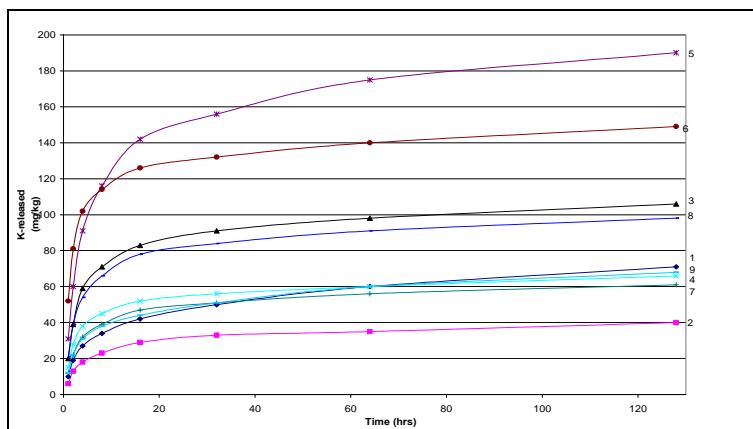


Figure 6. Cumulative released potassium vs. time.

Table 5 shows the values of percentages of citric acid – K (K-release capacity) of nitric acid – K (non-exchangeable potassium). The values ranged from 9.5% in soil sample no. 7 to 59.1% in soil sample no. 6, with an average value of 31.2%. These results indicate that after 128 hours of extraction with 0.5 mM citric acid, a considerable portion of total non-exchangeable potassium was still remaining in some soils. This means that the unreleased, non-exchangeable potassium will be released and utilized by plants for a long period of time.

TABLE 5

Ratios of Citric Acid – K: Nitric Acid – K

Soil sample No.	Nitric acid- K mg Kg ⁻¹	Citric acid- K mg Kg ⁻¹	$\frac{K - citric\ acid}{K - nitric\ acid} \times 100$
1	136	71	52.2
2	176	40	22.7
3	276	106	38.4
4	208	66	31.7
5	1460	190	13.0
6	252	149	59.1
7	644	61	9.5
8	704	98	13.9
9	168	68	40.5

Five mathematical models: zero order, first order, parabolic diffusion law, Elovich equation, and power function equations were tested by least square regression analysis for potassium release for the studied soils. Significant linear correlations were obtained as reported in Table 6.

Based on the highest value of correlation coefficient (R) and the lowest value of standard error (SE), the first order, parabolic diffusion law, Elovich equation, and power function equations satisfactorily describe the reaction rates of potassium release in the studied soils. However, the zero order equation could not describe the release of potassium as shown by higher SE and lower R values. Martin and Sparks (1983) reported that first order equation was the best to describe the reaction rate of potassium release from two coastal soils in USA. They mentioned also that parabolic law equation describes the data satisfactorily. The obtained results agree with the findings of many researchers. Havlin and Westfall (1985), Simard *et al.*, (1992), Al-Zubaidi and Al-Obudi (2001), Hosseinpour and Kalbasi (2002) also reported that the kinetic release of potassium from different soils was well described by first order, parabolic diffusion law, Elovich equation, and power function equations.

Potassium release rate coefficients were calculated for the studied soils using the first order equation (b values in Table 7), since it is one of the equations that best described the data, moreover it has a theoretical chemical foundation (Sparks, 1989). These values ranged from 0.0252 h^{-1} for soil No. 1 to 0.0347 h^{-1} for soil no. 8, with an average 0.031 h^{-1} . Comparing the obtained values with those obtained for the Iraqi soils (Al-Zubaidi & Al-Obudi, 2001), it seems that the studied Lebanese soils have higher values than those of Iraqi soils. This could be that soils of Lebanon are very young and the degree of weathering process is relatively higher than in Iraqi soils.

TABLE 6

Average Regression Equations, Correlation Coefficients (R) and Standard Error (SE) of the Estimates for the Kinetics to Describe Potassium Release to 0.5mM Citric Acid

Equation	R	SE	A	b
Zero order $K_0 - K_t = a - bt$	0.807	15.464	51.977	-0.8343
First order $\ln(K_0 - K_t) = a - bt$	0.942	0.279	3.866	-0.0313
Parabolic diffusion $K_t/K_0 = a + b\sqrt{t}$	0.910	0.113	0.274	0.0912
Elovich equation $K_t = a + Lnt$	0.986	4.078	25.972	14.8907
Power function $\ln Kt = a + bLnt$	0.932	0.196	3.156	0.3031

TABLE 7
Regression Equations for First Order Equation

Sample	First order $\text{Ln}(K_0 - K_t) = a - bt$			
	R	SE	A	b
1	0.976	0.142	3.923	-0.0252
2	0.922	0.303	3.191	-0.0287
3	0.935	0.328	4.051	-0.0344
4	0.917	0.331	3.504	-0.0303
5	0.958	0.260	4.763	-0.0346
6	0.915	0.363	4.077	-0.0329
7	0.944	0.291	3.540	-0.0332
8	0.939	0.320	3.952	-0.0347
9	0.972	0.172	3.789	-0.0281
Average	0.942	0.279	3.866	-0.0313

CONCLUSION

This study describes the K potential supplying power of nine soil samples collected from main agricultural regions in Lebanon using the traditional method of NH_4OAc extracted K, K-thermodynamics, and K-kinetics. An intensity parameter, which is the concentration or activity of K in soil solution; a quantity parameter which is the amount of K present in exchangeable or in available non-exchangeable forms was measured. Another approach which was followed to estimate K availability was based on determining the exchange energy of K (ΔF) with the prevalent divalent cations (Ca + Mg). The range of ΔF values is usually between -2000 to -4000 Cal/Mol, where the upper value (-2000) indicates a K-sufficiency and the lower (-4000) a deficiency.

The results of the various methods show that K availability in Lebanese soils differs widely and special attention should be paid for this fact by agronomists. Because of the limitations of each method of analysis for estimating the supplying power of available K to a crop during a growing season, it is necessary that the results of soil testing be compared to field responses.

Many farmers in Lebanon are under the impression that soils in Lebanon contain sufficient quantity of K, the results of this study show that this idea may be quite wrong. Since most of the farmers in Lebanon apply adequate rates of N & P, and as yields increase the demand for K increases. The results of this study show clearly that for the intensive agriculture in Lebanon which demands high yields, considerable quantities of K may be required.

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