Prediction of Potassium Desorption Kinetics in Various Soils of Egypt Using the Power Equation

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OIL samples (0-30cm) of five different soils were used to Dinvestigate the use of the power equation to predict K desorption kinetics. These samples were collected from El-Tahrir, Ganaklis, Bourg El-Arab, Maryout and El-Giza regions, representing different origins. Soils were initially treated with 0-250 mg K kg⁻¹ as KBr. The effects of initial Exchangeable K, contact time (5, 15, 30 & 60 min), dilution (10:1, 40:1, 100:1 & 300:1 water / soil ratio) on K desorption were investigated. Parameters of the power equation were calculated and compared for the different soils. This equation succeeded in describing the kinetics of K desorption in the studied soils. Further 22 surface soil samples, collected from various locations in West Delta and North Western Coast of Egypt, were used to establish correlation relationships between the equation parameters and some selected soil properties. CEC of the soils accounted for 93.6, 91.0 and 97.3% of the variability in the α , β and k parameters, respectively. Logarithmic regression between the CEC of the 27 soils and the calculated parameters were established. Thus prediction of K desorption kinetics using the CEC were possible ($R^2 = 0.89-0.96$).

Potassium is an essential element for plant growth and presents in the soil in water-soluble, exchangeable, and nonexchangeable forms. Movement of K between these pools occurs as K is added to soil as fertilizer, manure or residues, or removed by plant uptake or leaching. An understanding of the extent and rate of movement or desorption of soil K from exchangeable or nonexchangeable to solution pools is, thus, important for plant nutrition and modeling of its movement in soil (Schneider, 1997 and Trapp & Matthies, 1998).

Soil K desorption has been described by several equations. Simple first-order rate equations were used by Jardine & Sparks (1984); Munn et al. (1976); Ogwada & Sparks (1985); Dufey & Marot (1987); Sparks & Jardine (1981) and Sparks et al. (1980), to describe K desorption over short time periods (<1000h) from several soils, while Talibudeen et al. (1978) used three simultaneous rate terms. In contrast, Feigenbaum et al. (1981) described K desorption kinetics from three micas (biotite, muscovite and phlogopite) by a parabolic diffusion rate equation. The modified Elovich and power form equations were also used to describe K desorption from soils (Havlin et al., 1985 and Martin & Sparks, 1983) although their application has been limited to long time periods (>1000 h) and nonexchangeable K release.

Numerous investigators have shown that desorption of K is a diffusion controlled process (Feigenbaum & Shainberg, 1975; Quirk & Chute, 1968 and Sparks & Jardine, 1981). The power-form equation describing soil P desorption (Sharpley et al., 1981b) which assumes nonlinear ion diffusion (Sharpley & Ahuja, 1983) was proposed to describe short term (< 2h) soil K desorption. This equation has the form:

$$K_d = k K_0 t^{\alpha} W^{\beta}$$
 [1]

where K_d is the amount of K desorbed in time t, at a water/soil ratio W, with K_θ the initial exchangeable K present in the soil and k, α and β are constants for a given soil.

The kinetics of soil K desorption is related to clay mineralogy (Sparks, 1980). For example, soils dominated by kaolinitic clay minerals have been shown to exhibit a rapid rate of K desorption (Malcolm & Kennedy, 1969 and Selim et al., 1976). Consequently, the use of the power equation in predicting K desorption for a wide range of soils should take into account the relevance of the constants of this equation on the soil physical and chemical properties, such as clay content, cation exchange capacity, K saturation, exchangeable, nonexchangeable, and total K content.

The objectives of this study were to (i) investigate the use of the power form equation to describe the K desorption kinetics from five different Egyptian soils, and (ii) to establish regression relationships between the constants of the power equation and soil physical and chemical properties of 22 soils collected from different locations in West Delta and North Western Coast of Egypt.

Material and Methods

Soils

Surface samples (0-30 cm) of five different soils were used to investigate the goodness of the power-form equation (Eq. 1) to describe K desorption kinetics. These soil samples were collected from El-Tahrir, Ganaklis, Bourg El-Arab, Maryout and El-Giza regions which represent fluviatile, fluviomarine, marine deposits, lacustrine and Nile alluvial deposits, respectively. Soil analyses for some chemical and physical properties were carried out according to the methods outlined by Page et al. (1982) and are listed in Table 1. Cation exchange capacity of the soils was determined using the NaOAc method (Richards, 1954).

	Clau 7		OM	CaCO ₃	-u	CEC			K conten	ıt	
Soil		6	1	%		ole kg ⁻¹	1	Exch.	Nonexch. mg kg ⁻¹	Total	K Sat.
El-Tahrir Ganaklis Bourg El-Arab Maryout El-Giza	2.31 10.05 12.97 18.59 56.89	S SL SL SCL C	0.35 1.24 1.45 1.74 2.54	5.63 15.78 26.71 9.57 3.22	7.89 8.05 8.14 8.21 7.84	4.71 14.70 17.40 21.30 41.62	4 3 8	22 31 23 73 63	1255 1428 1373 4825 5870	1279 1463 1399 4906 5947	10.41 6.05 3.37 8.78 3.46

TABLE 1. Some physical and chemical properties of the studied soils.

Semi-quantitative and quantitative mineralogical analyses of the studied soils were carried out by Basta et al. (1982), Labib et al. (1982), Abdel-Hamid et al. (1988), Abd Ellatif (2000) and Abdou et al. (2000). The dominance of phyllosiliscate clay minerals in the clay fraction ($<2~\mu$) of these soils are presented in Table 2.

TABLE 2. Dominance of phyllosilicate minerals in the clay fraction (< 2 μ) of the studied soils.

Soil	Sequence of Dominance	Reference
El-Tahrir Ganaklis Bourg El-Arab Maryout El-Giza	Kaolinite > Mica > Illite > Vermiculite > Smectite. Smectite > Mica > Kaolinite > Attapulgite. Attapulgite > Smectite > Kaolinite > Illite. Smectite > Attapulgite > Kaolinite. Montmorillonite > Illite > Chlorite > Kaolinite.	Basta et al. (1982) Abd El-Latif (2000) Labib et al. (1982) Abdou et al. (2000) Abdel-Hamid et al. (1988)

Further twenty two disturbed surface soil samples were collected from the top $30\,\mathrm{cm}$ at different locations in West Delta and North Western Coast of Egypt. These samples represent soils of different origins. Soil samples were air dried, crushed and sieved to $< 2\,\mathrm{mm}$ and stored until analysis. Mean and range of these properties are listed in Table 3.

TABLE 3. Mean and range values of selected physical and chemical properties for the 22 collected surface soil samples.

Analysis	Mean	Range
Clay content, %	29.70	2.31 - 56.89
Organic Matter, %	1.43	0.11 - 2.53
EC, dS m ⁻¹	2.45	1.87 - 5.76
pH	7.91	7.74 - 8.49
CaCO ₃ , %	12.62	4.11 - 46.56
Cation Exchange Capacity, emol, kg-1	21.84	4.27 - 38.24
Water soluble K, mg kg-1	5.12	1.13 - 12.54
Exchangeable K, mg kg-1	112.31	2.94 - 305.21
Nonexchangeable K, mg kg-1	7.34	0.03 - 19.71
Total K, g kg.1	8.05	0.05 - 2.58
K Saturation, %	6.17	0.43 - 10.41

K desorption experiment

In this experiment, the kinetics of K desorption from the studied soils was evaluated. Study of the effects of initial exchangeable K, water/soil ratio and contact time on K desorption was investigated.

Soils were treated with K by incubation of 50 g soil with various amounts of K (0-250 mg K kg⁻¹ added as a solution of KBr) for 12 weeks at $30\pm2^{\circ}$. These applications are equivalent to 0-150 kg K ha. Soils were initially moistened with the KBr solution to their water holding capacity. During incubation soils were periodically rewetted with distilled water when dry.

Water soluble K (WSK) was measured in extract following shaking of 2.0 g soil with 20 nd water for 1.0 h. Exchangeable K (EK) was immediately extracted from the same soil with 20 nd 1.0M ammonium acetate (pH= 7.0) and shaking for 5 min. Total K (TK) was determined following digestion of 1.0 g soil with 48% HF and 6.0M HCl (Knudsen et al., 1982). Potassium saturation was calculated as the ratio of exchangeable K and sum of exchangeable cations, expressed as Percentage. Nonexchangeable K (NEK) was calculated as:

$$NEK = TK - (WSK + EK)$$
 [2]

Initial exchangeable K (K_0) was determined prior to desorption of each incubated soil following removal of water soluble K described earlier. The amount of K desorbed (K_d) by distilled water at water/soil ratios (W) of 10:1, 40:1, 100:1 and 300:1 after shaking the suspensions for different time periods (t) at $30\pm2^{\circ}$ for 5, 15, 30, to 60 min was determined.

Statistical Analysis

The constants of Equation 1 was calculated from the slope of the relationship between $\log K_d$ (amount of K desorbed) and $\log t$ (slope = α) and $\log W$ (slope = β). The constant k was calculated from the slope of the linear relationship between K_d and K_0 (slope = k t^{α} W^{β}). Analysis of variance for paired and unpaired data was performed using the SPSS Statistical Analysis Package (SPSS, 1999) to determine differences between population means. Stepwise regression analysis of the constants k, α and β versus some soil physical and chemical properties was also carried out.

Results and Discussion

The choice of these five soils to test Equation 1 was based on the wide variation in their physical and chemical properties (Table 1). From Table 2, the mineralogical composition of the clay fraction ($<2 \mu$) in El-Tahrir soil revealed that kaolinite 1:1-type clays were dominant, carrying a small negative charge (Basta et al., 1982). On the other hand, montmorillonite 2:1-type clays were dominant in El-Giza soil, carrying large negative charge (Abdel-Hamid et al., 1988). The clay mineralogy of the rest three soils was mixed (Labib et al., 1982; Abd El-Latif, 2000 and Abdou et al., 2000).

The logarithmic relationships between the amount of K desorbed and the contact time as well as the water:soil ratios were plotted for different K application rates. Examples of these plots are presented in Fig. 1 and 2. Desorption of K from the studied soils was found to be a rapid process. A linear logarithmic relationship was obtained between the K desorbed and both the contact time at any given water:soil ratio and the water:soil ratios at any given contact time for all K application rates. The rapid release of adsorbed K from soils is in agreement with the earlier results obtained by Sparks et al. (1980); Sparks & Rechcigl (1982); Sharpley (1987) and Schneider (1997). The results also revealed that K desorption is directly proportional to the contact time and water:soil ratio at constant water: soil ratio or contact-time, respectively. After 15 min contact time and for the 100:1 water: soil ratio, the amount of desorbed K was directly proportional to the initial K (K_0) in the soil when the contact time and water:soil ratio are constant (Fig. 3). Therefore, the effects of contact time, water: soil ratio and initial exchangeable K on K desorption can be accounted for by using the power equation on the form of Equation 1.

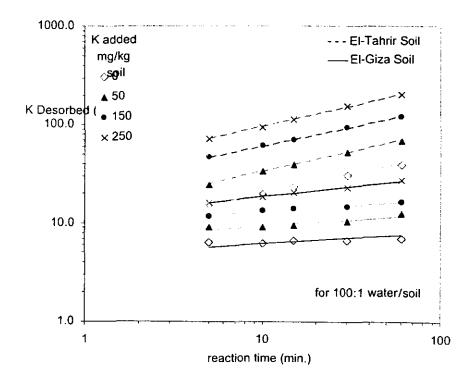


Fig. 1.Logarithmic relationship between K desorbed and the contact time for 100:1 water/soil ratio at different K application rates for El-Tahrir and El-Giza soils.

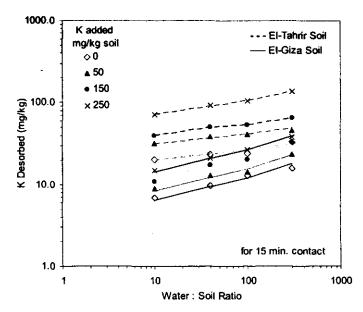


Fig. 2. Logarithmic relationship between desorbed K and the water/soil ratio after 15 min contact time at different K application rates for El-Tahrir and El-Giza soils.

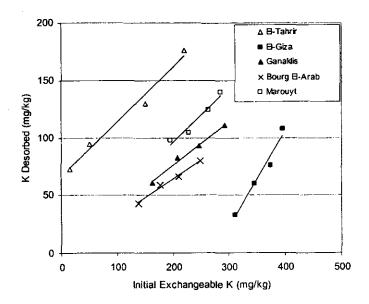


Fig.3. Linear relationships between the amount of desorbed K and initial exchangeable K at 100:1 water/soil ratio and after 15 min contact time for the five tested soils.

Egypt. J. Soil Sci. 44, No. 3 (2004)

Calculation of slope values of the logarithmic relationships between K desorbed and reaction time (α) and water/soil ratio (β) for each soil under different K application rates were carried out and are presented in Table 4. Statistical analysis of the obtained data revealed that variations in these two parameters for a given soil under the tested experimental conditions were not significant (at the 5.0% level). The same trend was obtained for the calculated values of the parameter (k) for all soils (Table 5).

TABLE 4. Values of constant (α) and (β) for the logarithmic regression of K desorbed vs. contact times or vs. water/soil ratio for different K application rates.

	K added	constant α at	constant B at
Soil	mg kg '	water/soil ratio	contact time (min)
	mg kg	10:1 300:1	5 60
	υ	0.0156a 0.0158a	0.0146f 0.0148f
El-Tahrir	50	0.0155a 0.01 56a	0.0145f 0.0146f
	150	0.0151a 0.0153a	0.0149f 0.0144f
	250	0.0159a 0.0152a	0.0151f 0.0141f
	U	0.0128b 0.0131b	0.0313g 0.0317g
Ganaklis	50	0.0133b 0.0134b	0.0319g 0.0322g
	150	0.0129b 0.0127b	0.0313g 0.0314g
	250		
	0	0.0096c 0.0094c	0.0301h 0.0305h
Bourg El-Arab	50	0.0098c 0 0092c	0.0309h 0.0311h
	150	0.0091c 0.0089c	0.0310h 0.0307h
	250	0.0093c 0.0095c	0.0308h 0.0312h
	O	0.0082d 0.0088cd	0.0314hi 0.0316hi
Maryout	50	0.0080d 0.0087cd	0.0313hi 0.0319i
	150	0.0081d 0.0078d	0.0323i 0.0318i
	250	0.0079d 0.0075d	0.0320i 0.0322i
		6.40-4	
	0	0.0059e 0.0063de	0.0411j 0.0415j
El-Giza	50	0.0054e 0.0062de	0.0415j . (0.0421j
	150	0.0056e 0.0053e	0.0424j 0.0422j
	250	0.0057e 0.0053e	0.0420j 0.0421j

Soil	Contact time	Water /soil ratio			
2011	min	10:1 100:1 300:1			
	5	0.0720a 0.0723a 0.0741a			
El-Tahrir	30	0.0701a 0.0711a 0.0740a			
or rainin	60	0.0720a 0.0731a 0.0737a			
<u> </u>	J				
	5	0.0407ь 0.0412ь 0.0409ь			
Ganaklis	30	0.0433b 0.0411b 0.0437b			
	60	0.0439b 0.0444b 0.0419b			
	5	0.0396bc 0.0395bc 0.0398bc			
Bourg El-Arab	30	0.0376c 0.0367c 0.0368c			
bodig El Titab	60	0.0370c 0.0369c 0.0361c			
]				
Maryout	5	0.0370cd 0.0362cd 0.0363cd			
	30	0.0357cd 0.0361cd 0.0365d			
	60	0.0347d 0.0346d 0.0348d			
		0.0010			
	5 (0.0235e 0.0242e 0.0239e			

TABLE 5. Calculated slope (constant k) of the relationship between K desorbed for several contact times and initial exchangeable K.

The parameter (α) in the power equation reflects the rate of K desorption from the soil. For El-Tahrir, this soil parameter was significantly greater than that for El-Giza soil. Sorption of K on El-Tahrir soil is expected to be on the external planar surfaces of low negatively charged kaolinite particles. Similar observations were found by Sparks & Jardine (1981) who explained the differences in the rate constants of K desorption on the basis of different clay mineralogy of the studied soil. However, the values of the parameter (β) for El-Tahrir soil were significantly lower than these of El-Giza soil, thus reflecting a higher buffering capacity of El-Giza soil than El-Tahrir soil. Due to the mixed mineralogical composition of Ganaklis, Bourg El-Arab and Maryout soils, the obtained values of α , β and k were intermediate between those for El-Tahrir and El-Giza soils.

0.0231c

0.0239e

0.0235e

0.0229e

0.0233e

0.0237e

30

60

El-Giza

As shown in Fig. 1 and 2, El-Tahrir soil released greater amount of K compared with El-Giza soil at the same K application rate. Because El-Tahrir soil contained more mica and vermiculite (Table 2), K could be desorbed from wedge zones by exchange with H₃O⁺ ions during desorption with water (Sharpley, 1987 & Sparks, 1986). Moreover, and while El-Giza soil contained more montmorillonite, collapse of interlayer spaces may occur if K is adsorbed and the soil is subjected to wetting and drying cycles and thus reduce the amount of exchangeable K. Consequently, the rate of K desorption is a function of clay type, while the amount of K desorbed is a function of both clay content and type.

The collected twenty two soil samples were used to examine the validity of the power equation in predicting the amount of desorbed K at different water/soil ratios, contact times and initial exchangeable K. Values of the α , β and k parameters were similarly obtained for each soil. Values of the α , β and k parameters ranged from 0.0053 to 0.0165, from 0.0141 to 0.0434 and from 0.0249 to 0.0761, respectively.

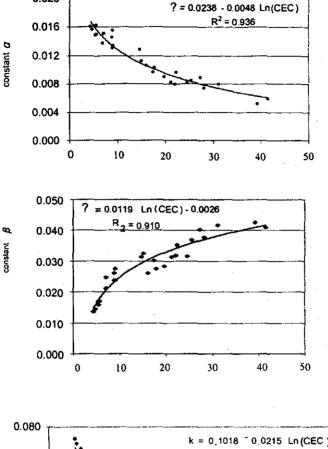
Regression relationships between values of these parameters and CEC, clay content, CaCO₃ content, organic matter content, exchangeable K, nonexchangeable K, K saturation and total K content of the soils were examined. It was found that these parameters were closely related to the natural logarithm of CEC of the tested soils (Fig. 4). CEC of the soils accounted for 93.6, 91.0 and 97.3% of the variability in the parameters α , β and k, respectively. Other soil properties accounted for less variability in these parameters (clay content 37-53%, CaCO₃ 10-18%, organic matter 21-32%, exchangeable K 15-20%, nonexchangeable K 18-23%, K saturation 21-26% and total K content 15-24%).

The β parameter represents a K buffering term as when β increases, dilution of the interacting soil and water has greater effect on K desorption (Sharpley, 1987 and Schneider, 1997). Consequently, β is expected to increase with increasing soil CEC. The k parameter, however, represents the desorbability or capacity term. This parameter expresses the proportion of exchangeable K that can be desorbed from the soil under given t and W conditions. Thus, k is inversely proportional to the soil CEC. An increase in k indicates that the proportion of K desorbed will increase. This is also consistent with the obtained results which are represented in Fig.4.

In general, the CEC value represents the soil mineralogy (Sparks, 1995; McBride, 1994 and Abdou et al., 2000). Soils of low CEC tend to be dominated by kaolinitic minerals (exhibiting mainly external planar sites for sorbed K), while soils with high CEC are dominated more 2:1 type minerals (with interlayer sorbed K). Consequently, desorbability of exchangeable K, desorption rate, and buffering capacity can be a function of clay mineralogy which was in this work indirectly related to CEC (Sharpley, 1987).

Calculated values of α , β and k parameters, using the obtained regression equations with CEC, were used to predict the amount of K desorbed from each soil. A correlation plot between the measured and predicted amount of desorbed K from each soil sample at different contact times, water/ soil ratios and initial exchangeable K were established. An example of these plots is presented in Fig. 5 for 10:1 water:soil ratio after 15 min contact time. High correlation coefficient values ($R^2=0.89\text{-}0.96$) were obtained.

0.020



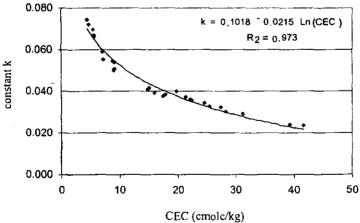


Fig. 4. Logarithmic regression between the cation exchange capacity of the soil samples and the calculated constants α , β and k.

Egypt. J. Soil Sci. 44, No. 3 (2004)

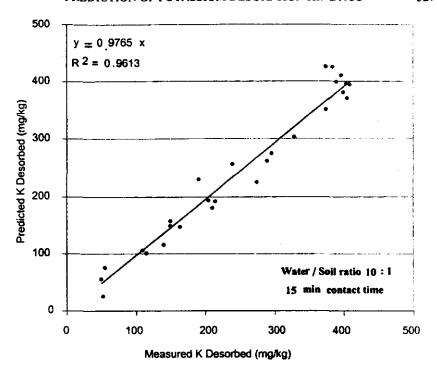


Fig. 5. Correlation relationship between the measured and predicted desorbed K at 10:1 water/soil ratio and after 15 min, contact time for the 27 soil samples.

Unlike earlier first-order rate, parabolic diffusion, power function, and Elovich equations describing desorption of soil K (Havlin et al., 1985; Martin & Sparks, 1983; Sparks et al., 1980 and Talibudeen et al., 1978), Equation 1 accounts for the effects of t, W, and K_0 on K desorption, and may thus have application to modeling of K movement within the soil and plant uptake. In fact, Equation 1 was previously used in predicting soluble P transport in runoff from agricultural land under simulated (Sharpley et al., 1981a) and natural rainfall (Sharpley et al., 1985). Application of Eq. 1 will be limited, however, unless the constants k, α and β can be estimated from readily available soil properties, rather than being measured. As CEC can also vary with method of determination, calibration of the relationships between the soil CEC and the kinetic constants of the power equation have to be carried out.

Conclusion

The rate and amount of K desorption from different soil materials were found to be dependent on their mineralogical composition, initial Exchangeable K, contact time and dilution effect. The CEC of the soil can be used to reflect the effect of the mineralogical assemblage of the soil. Hence, CEC of the tested soil was closely related to the parameters of the power equation. The power equation was successfully used to predict the kinetics of K desorption from 27 different surface soil samples of different origins. As CEC can vary with method of determination, calibration of the relationships between the soil CEC and the kinetic parameters of the power equation have to be carried out.

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التسنب ف بكيناتيكية إنطالق البوتاسيوم الأسواع مختلفة من الأراضي المصرية بإستخدام معادلة القسوة

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تهدف هذه الدراسة الى بحث إمكانية التبنؤ بمعدل إنطلاق البوتاسيوم من مجموعة من الأراضى المصرية المختلفة باستخدام معادلة القوة لإمكان إستخدام هذه المعادلة ضمن النماذج الرياضية التى تصف سلوك ومصير هذا العنصر في الأراضي المدروسة. كما تهدف الدراسة إلى إيجاد علاقة رياضية بين ثوابت معادلة القوة وبعض الخواص الطبيعية والكيماوية لعدد كبير من عينات الأراضي التي جمعت من منطقة غرب الدلتا والساحل الشمالي الغربي.

رقد تم جمع عينات سطحية (• - ٣٠ سم) من خمس مناطق مختلفة هي: جنوب التحرير - جناكليس - برج العرب - مريوط - الجيزة والتي تمثل أراضي ذات ظروف نشأة مختلفة. وتم تقدير بعض الخواص الطبيعية والكيماوية لها(نسبة الطين - نسبة المادة العضوية - كربونات الكالسيوم - السعة التبادلية الكاتيونية - البوتاسيوم الذائب والمتبادل والغير متائل - البوتاسيوم الكلي - نسبة التشيع بالبوتاسيوم).

تم معاملة هذه الأراضى بالبوتاسيوم بمعدلات نتراوح من صفر ٢٥٠٠ مليجرام بوتشيوم/ كجم أرض في صورة ملح بروميد البوتاسيوم KBr. ثم تعرضت هذه الأراضى المعاملة لعدة دورات من الإبتلال والتجفيف. وقد تم دراسة تأثير كل من معدل إضافة البوتاسيوم وزمن التفاعل (٥، ١٥، ٣٠، ١٠٠ دقيقة) ونسبة المتخفيف (نسبة الماء / الأرضى ١١٤، ١، ١، ١٠٤٠ ، ١، ١، ١٠٠٠) على معدل إنطلاق البوتاسيوم من تلك الأراضى. وبعد ذلك تم حساب ثوابت معادلة القوة ($K_d = k \ K_0 \ \ell^{\alpha} \ M^{\beta}$) لكل أرض ومقارنة قيمتها للأراضى المدروسة.