Potassium release kinetics and its correlation with pinto bean (*Phaseolus vulgaris*) plant indices

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ABSTRACT

The rate of potassium (K) release from soils is a dynamic process, and it is important to the evaluation of soil K availability to plant. The objectives of this study were to determine K release characteristics and the correlation of these parameters with bean plant indices in surface soils of 15 calcareous soils. The kinetics of K release was determined by successive extraction with 0.01 mol/L $CaCl_2$ in a period of 2–2017 h at 25 ± 1°C. The results showed that the cumulative K release ranged from 111 to 411 mg/kg. A plot of cumulative amount of K released showed a discontinuity in slope at 168 h. Thus, two equations were applied to segments of the total reaction time (2 to 168 and 168 to 2017 h). The amounts of K released during 2–168 and 168–2017 h ranged from 55 to 299 and 44 to 119 mg/kg, respectively. Release kinetics of K conformed fairly well to parabolic diffusion, simplified Elovich and power function models in two segments. Potassium released after 2–168 and 168–2017 h and K release rate constants were significantly correlated ($P < 0.05$) with bean plant indices, while correlation between K extracted by using 1 mol/L NH_4OAc (ammonium acetate) and plant indices was not significant. The results of this research showed that information obtained from K release studies in laboratory and kinetics equation parameters can help to estimate the K supplying power of soils.

Keywords: parabolic diffusion; calcareous soils; kinetics equations; successive extraction

Potassium (K) is a macronutrient in plants and animals. Under intensive cropping, in the absence of K fertilization, initially exchangeable K in soil contributes to plant K nutrition, but with further cropping, exchangeable K attains a certain minimal level; afterward, plant K removal from soil and contribution of nonexchangeable K to K uptake are almost synonymous and account for up to 90–95% of the total plant K uptake (Srinivasarao and Khera 1994). It was well established that a significant proportion of plant needs of K are met from nonexchangeable fraction of soil K (Srinivasarao et al. 1999). Because of the larger contribution of nonexchangeable K to plant K needs, lack of crop responses to applied K were reported even in soils with low exchangeable K (Mengel and Uhlenbecker 1993). For optimal nutrition of crop, the replenishment of a K-depleted soil solution is affected predominately by the release of K from clay minerals and organic matter. Therefore, for maximal crop growth, soil solution and exchangeable K need to be replenished continually with K through the release of nonexchangeable K or the addition of K fertilizers.

The questions of how soil K is released into solution and what rate the element is released, are of great importance to the plant nutrient availability and crop production (Havlin and Westfall 1985). Many different equations were used to describe K release kinetics (Srinivasarao et al. 2006, Hosseinpur and Safari Sinegani 2007, Lu et al. 2007, Samadi 2010, Hosseinpur and Motaghian 2012). Hosseinpur and Motaghian (2012) successfully described K release from 10 calcareous soils with parabolic diffusion, power function, and simplified Elovich equations. Hosseinpur and Safari Sinegani (2007) investigated that correlation of kinetic equation rate constants with garlic indices. They found that release-rate constants of the Elovich and zero-order equations were signifi-

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cantly correlated with garlic indices. Jalali (2006) reported that Elovich b values were correlated with K uptake by wheat ($r = 0.785^{**}$), while a values of the Elovich equation were less correlated with K uptake ($r = 0.690^{*}$) than b value.

The estimation of soil K availability are based on determination by extraction methods and do not consider K release characteristics. Moreover, more information is needed on the K release characteristics of calcareous soils. Therefore, the objectives of present study are (i) to evaluate the K release from soils varying in K status (ii) to examine the relationship of K release rate obtained in the kinetics studies with bean plant indices.

MATERIAL AND METHODS

Physicochemical properties of soils. Fifteen soil samples used in this study were collected from the surface (0–30 cm) soils of Chaharmahal-Va-Bakhtiari province, central Iran. The soil samples were air dried and ground to pass through a 2 mm sieve and determined some physic-chemical properties such as particle size distribution, electro conductivity (EC), pH, organic carbon (OC) (Nelson and Sommers 1996), calcium carbonate equivalent (CCE) (Loeppert and Suarez 1996) and cation exchange capacity (CEC) of the soils (Sumner and Miller 1996). Exchangeable and non-exchangeable K were determined by 1 mol/L NH_4OAc (Knudsen et al. 1982) and boiling 1 mol/L HNO_3, respectively. The predominant soils in the study area are Calcixerepts. The predominant clays in all soils were micas, smectites and chlorite, with lesser quantities of vermiculites and kaolinite.

Potassium release kinetics. Native solution K was removed from soils before initiating the kinetics studies. Two grams of soils, in duplicate, suspended in 20 mL of 0.01 mol/L $CaCl_2$ solution were equilibrated at 25 ± 1°C for 2 to 2017 h by shaking for 0.5 h before incubation and 0.5 h before the suspensions were centrifuged. The supernatant liquid was measured for K by flame photometer (Model Corning 410, UK). Potassium released with time was fitted by using different equations (Table 1).

Five models were tested by the least-square regression analysis to determine which equation described better the K release from the soils. Standard error of the estimate (SE) was calculated by:

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

where: K and K^* – the measured and calculated amounts of potassium in soil at time t, respectively, and n – the number of data points evaluated. Data of bean plant indices including K concentration, K uptake and relative yield are taken from Hosseinpur and Zarenia (2012). The correlation between K release characteristics and bean plant indices were studied by simple regression.

RESULTS AND DISCUSSION

Selected chemical and physical properties of the soils are given in Table 2. These results show that there was a wide variation in the selected chemical and physical properties of the soils. Clay and silt contents in all soils ranged from 21 to 53% and 20 to 52%, respectively. The CCE contents ranged from 6 to 40%. The CEC ranged from 15.5 to 24.3 $cmol_c$/kg. The exchangeable and non-exchangeable K ranged from 136–312 and 740–2250 mg/kg, respectively. These results showed that K fertility status of the studied soils were different.

The pattern of successive extraction of K from soils using 0.01 mol/L $CaCl_2$ is presented in Figure 1. The amounts of K released after 2017 h of extraction period ranged from 111 (soil 12) to 411

Table 1. Kinetic models used in this study

Kinetic equation	Expression form*	Reference(s)
Zero-order reaction	$(K_0 - K_t) = a - k_0 \times t$	Martin and Sparks (1983)
First-order reaction	$\ln (K_0 - K_t) = a - k_1 \times t$	Martin and Sparks (1983)
Parabolic diffusion	$K_t = a + R \times t^{0.5}$	Havlin et al. (1985)
Power function	$\ln K_t = \ln a + b \ln t$	Havlin et al. (1985)
Simplified Elovich	$K_t = a + (1/\beta) \ln t$	Havlin et al. (1985)

*K_0 – amount of K (mg/kg) can be released at equilibrium; K_t – amount of K (mg/kg) released at time t (h) and a – intercept; k_0, k_1, R, b and $1/\beta$ – index of K release rates

Table 2. Some chemical and physical properties of soils studied

Soil No.	Clay	Silt	CCE[a]	OC[b]	pH	EC (dS/m)	CEC[c] ($cmol_+/kg$)	NH_4OAc[d]	HNO_3[e]	K released 2–168 h	K released 168–2017 h
	(%)							(mg/kg)			
1	35	32	29	0.58	8.1	0.13	20.1	231	1.150	152	90
2	33	36	34	0.56	7.9	0.17	15.9	253	2.100	167	93
3	47	30	23	0.80	7.7	0.19	15.5	244	1.600	228	119
4	41	42	17	0.80	8.1	0.11	15.8	157	1.100	55	68
5	39	46	26	1.30	8.0	0.17	19.3	223	2.300	121	81
6	21	20	10	0.45	8.0	0.16	16.6	175	950	191	94
7	45	24	31	1.53	7.9	0.19	24.3	136	850	64	51
8	35	34	25	0.64	7.9	0.12	18.0	257	2.200	173	76
9	35	52	17	0.65	7.9	0.11	19.2	268	1.350	137	78
10	31	32	18	0.74	7.9	0.14	20.1	312	2.550	299	112
11	33	46	6	0.67	7.9	0.17	19.3	274	1.450	183	93
12	53	32	40	0.66	8.1	0.16	16.7	140	740	67	44
13	35	46	35	0.85	7.9	0.16	17.8	303	2.450	205	108
14	33	48	35	0.55	7.9	0.13	24.3	184	1.050	78	69
15	35	48	27	1.03	7.9	0.15	21.8	278	1.300	172	92

[a]CCE – $CaCO_3$ equivalent (percentage of calcium carbonate in the soil based on the equivalent of pure calcium carbonate as 100%); [b]OC – organic carbon; [c]CEC – cation exchange capacity; [d]1 mol/L NH_4OAc extractable K; [e]boiling 1 mol/L HNO_3 extractable K

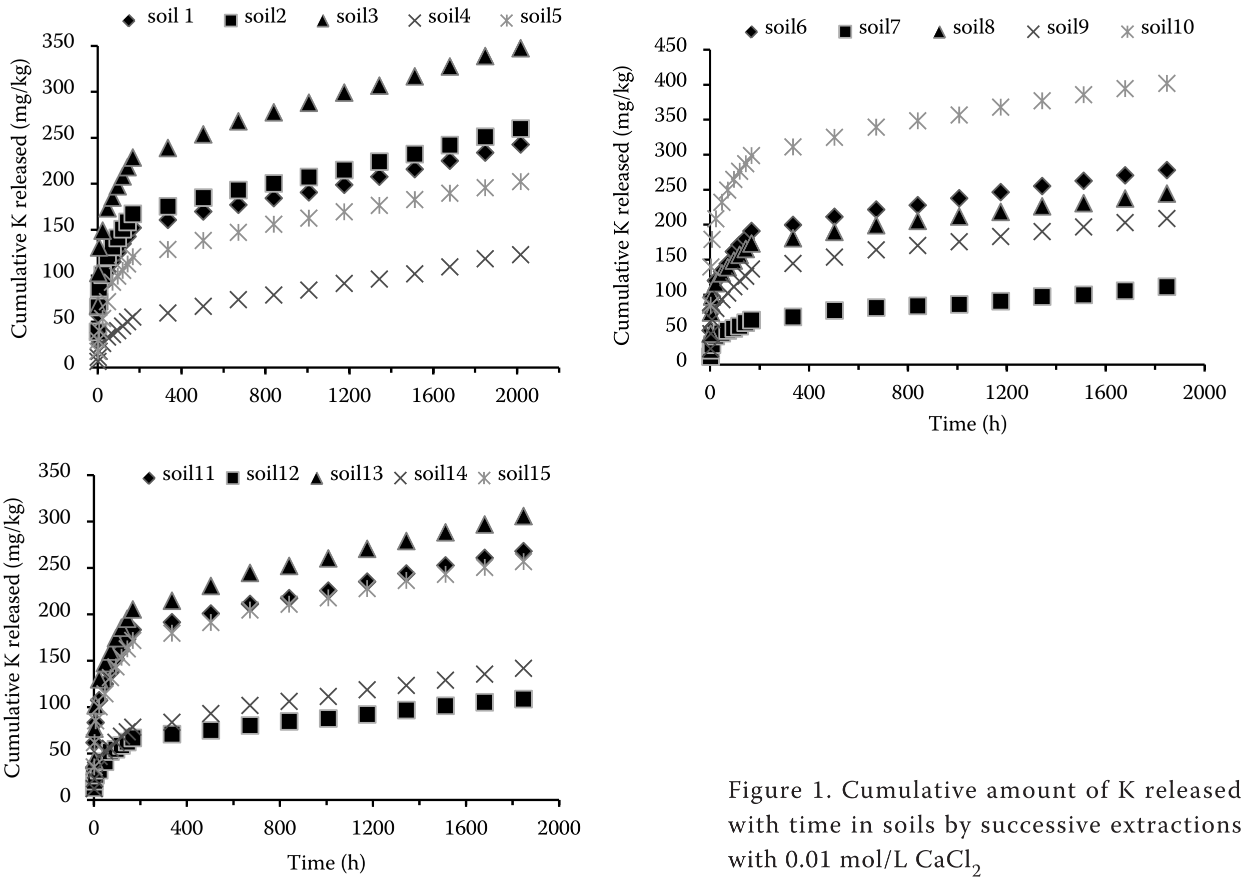

Figure 1. Cumulative amount of K released with time in soils by successive extractions with 0.01 mol/L $CaCl_2$

Table 3. Coefficient of determination (R^2) and standard error of the estimate (SE, mg/kg) of various kinetic models for two segments

		Zero-order		First-order		Parabolic diffusion		Simplified Elovich		Power function	
		range	mean	range	mean	range	mean	range	mean	range	mean
Segment 1	R^2	0.79–0.93	0.87	0.90–0.96	0.93	0.91–0.99	0.95	0.94–0.99	0.97	0.92–0.99	0.95
	SE	3.16–42.9	13.05	3.46–20.3	10.15	1.44–14.7	6.05	1.46–6.7	4.06	1.29–10.7	4.69
Segment 2	R^2	0.90–0.96	0.94	0.84–0.94	0.90	0.97–0.99	0.99	0.93–0.98	0.96	0.96–0.99	0.98
	SE	0.42–9.11	2.11	8.13–21.5	15.58	0.89–4.96	1.67	1.96–4.50	3.26	1.43–5.34	2.75

All coefficients of determination (R^2) are significant at the 0.01 level

(soil 10) mg/kg. There was a wide variation in the cumulative K released between soils. The differences in K release among the soils could be attributed to K fertility status, differences in amounts of clay and silt, and type of clay minerals.

A plot of cumulative amounts of K-release showed a discontinuity in slope at 168 h. So, two equations were applied to the segments of the cumulative K-release in the total reaction time (2–168 and 168–2017 h). This discontinuity represents different mechanisms controlling release process. It is possible that the K-release mechanism in the weathered periphery (2–168 h) is different from slow K-release in interior sites of the minerals structure (Hosseinpur and Safari Sinegani 2007). Bolt et al. (1963) attributed the fast initial release of K to release from edge interlayer sites and the subsequent slower release from interlayer sites.

The amounts of K released after 168 h ranged from 55 to 299 mg/kg. Also, the amounts of K released during 168–2017 h ranged from 44 to 119 mg/kg (Table 2). Different mathematical models (Table 1) were tested for their suitability to describe the release of K from different soils for two segments. Comparisons of R^2 and SE values (Table 3) indicated that the parabolic diffusion,

Table 4. Parameters a (mg/kg), R ($h^{-1/2}$), 1/β (mg/kg/h) and b (mg/kg/h) of models used to describe release kinetics of potassium for two segments

Soil No.	Parabolic diffusion				Simplified Elovich				Power function			
	segment 1		segment 2		segment 1		segment 2		segment 1		segment 2	
	a	R	a	R	a	1/β	a	1/β	a	b	a	b
1	38.4	8.9	102.0	2.9	18.41	24.1	−93.5	42.1	33.1	0.30	43.4	0.22
2	46.0	9.7	115.5	3.0	24.00	26.3	−85.6	43.3	39.8	0.28	50.7	0.21
3	79.1	12.0	164.0	3.9	51.05	32.8	−104.4	57.6	68.2	0.24	71.9	0.20
4	4.4	3.8	13.9	2.3	−3.31	10.1	−140.1	33.2	5.8	0.44	5.6	0.40
5	11.6	8.6	76.9	2.7	−5.77	22.9	−107.9	39.6	15.1	0.41	29.4	0.25
6	54.9	10.7	139.0	3.2	31.15	28.9	−75.3	46.0	48.5	0.27	62.6	0.20
7	14.2	3.9	38.5	1.6	4.99	10.7	−69.2	23.2	11.9	0.34	14.4	0.26
8	56.5	9.4	132.3	2.5	33.64	26.0	−40.6	37.1	46.9	0.26	63.3	0.18
9	28.7	8.4	95.3	2.6	9.40	23.0	−80.9	37.8	24.4	0.34	39.9	0.22
10	109.5	15.5	242.1	3.7	70.85	43.2	−8.7	53.7	90.7	0.24	126.6	0.15
11	39.6	11.4	129.6	3.1	14.39	30.8	−81.6	45.4	35.4	0.32	57.7	0.20
12	10.9	4.4	39.8	1.6	2.05	11.6	−65.4	22.6	11.5	0.34	15.1	0.26
13	53.2	12.3	148.7	3.6	24.58	33.6	−95.9	52.4	44.9	0.30	64.7	0.20
14	13.7	5.1	41.1	2.3	2.33	13.7	−113.2	33.1	12.3	0.37	14.2	0.30
15	41.1	10.4	121.0	3.1	18.30	27.9	−92.3	45.7	36.4	0.30	51.4	0.21

a – intercept of equations; R – release rate constant of parabolic diffusion equation; 1/β – release rate constant of simplified Elovich equation; b – release rate constant of power function equation

Table 5. Correlation coefficients between K release characteristics for two segments and K-NH_4OAc with plant indices

			Relative yield	Concentration	Uptake
Parabolic diffusion	segment 1	*a*	0.796^{**}	0.500^{ns}	0.735^{**}
		R	0.793^{**}	0.520^{*}	0.727^{**}
	segment 2	*a*	0.782^{**}	0.580^{*}	0.604^{*}
		R	0.817^{**}	0.410^{ns}	0.736^{**}
Simplified Elovich	segment 1	*a*	0.318^{ns}	0.551^{*}	-0.027^{ns}
		1/β	0.789^{**}	0.511^{*}	0.692^{**}
	segment 2	*a*	0.793^{**}	0.262^{ns}	0.602^{*}
		1/β	0.836^{**}	0.381^{ns}	0.717^{**}
Power function	segment 1	*a*	0.792^{**}	0.492^{ns}	0.711^{**}
		b	-0.717^{**}	-0.490^{ns}	-0.606^{*}
	segment 2	*a*	0.786^{**}	0.633^{*}	0.665^{**}
		b	-0.793^{**}	-0.613^{*}	-0.592^{*}
K released	(2–168 h)		0.814^{**}	0.571^{*}	0.57^{*}
	(168–2017 h)		0.811^{**}	0.420^{ns}	0.760^{**}
K-NH_4OAc			0.441^{ns}	0.411^{ns}	0.492^{ns}

$^{**}P < 0.01$; $^{*}P < 0.05$; ^{ns}not significant; *a* – intercept of equations; *R* – release rate constant of parabolic diffusion equation; 1/β – release rate constant of simplified Elovich equation; *b* – release rate constant of power function equation

power function, and simplified Elovich described the released K fairy well, as evidenced by the high coefficients of determination values and low standard error of the estimate.

There was a wide variation in the K-release characteristics between soils. Release rate constants (slope) and intercept of K for three models are given in Table 4. The release rate constants in parabolic diffusion, simplified Elovich and power function equations introduced an index of K release rates in the studied soils (Table 4).

In calcareous soils Ca^{2+} is the most common cation replacing interlayer K (Jalali 2006). Successive extraction of K with Ca^{2+} is one of the methods which is suitable to assess the kinetics of K release in calcareous soils (Jalali 2006, Hosseinpur and Safari Sinegani 2007). Successful description of K release in 0.01 mol/L $CaCl_2$ solution by simplified Elovich, parabolic diffusion and power function models was reported by Najafi Ghiri et al. (2011) and Hosseinpur and Motaghian (2012).

Probably the best supporting evidence for any equation used to describe the kinetics of K release is the comparison of the rate constants with plant indices on soils with a range of K supply. Correlation between K release characteristics and plant indices are shown in Table 5. Potassium release characteristics in two segments (except the *a* value in simplified Elovich equation in segment 1) were significantly correlated with the bean indices ($P < 0.05$). Instead correlation between K extracted by using 1 mol/L NH_4OAc and plant indices was not significant ($P > 0.05$).

In other studies significant correlations between constants of the kinetics equations with plant indices were reported (Jalali and Zarabi 2006, Hosseinpur and Safari Sinegani 2007). Hosseinpur and Safari Sinegani (2007) reported that a significant correlation was between zero-order rate constants of segment 1 (2–16 h) and K uptake ($r = 0.72^{*}$), K concentration ($r = 0.73^{*}$), relative yield ($r = 0.78^{*}$) and plant response ($r = 0.70^{*}$). Moreover, they observed a significant correlation between zero-order rate constants of segment 2 (168–2000 h) with K uptake ($r = 0.71^{*}$). Potassium uptake during plant growth is a dynamic process with periods of K depletion in the root zone and release of non-exchangeable K to exchange and solution phases by K bearing soil minerals.

The results of this study revealed that released K in the soils was rapid at first (2–168 h) and then became slower until equilibrium was attained. In two segments the parabolic diffusion, simplified

Elovich and power function equations could well describe K release data. Information obtained from mathematical models can help to explain the release mechanisms and estimate the K supplying power of soils. Significant correlation between plant indices and K release rate parameters were found, while correlation between K extracted by using 1 mol/L NH_4OAc and plant indices was not significant. These suggested that rate constants could be used to estimate the soil K supplying capacity and the crop response to K fertilizer.

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