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Research Paper

### Kinetics of Potassium Desorption from Some Calcareous Soil (Fars province, Southern Iran)

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**Abstract:** The release rate of nonexchangeable K (NEK) plays a significant role in supplying available K, particularly in soils containing K bearing minerals. Information about NEK release rate in soils of Iran is limited. The main objective of this research work was to investigate the kinetics of NEK release in fifteen surface soils (0-30 cm) of Fars Province by successive extraction with 0.01 M CaCl<sub>2</sub> over a period of 336 h. The results showed that the amount of NEK release after 336 h ranged from 286 mgKg<sup>-1</sup> in Alfisols to 104 mgKg<sup>-1</sup> in Aridisols. High clay content, nonexchangeable K and cation exchange capacity and also presence of potassium bearing minerals, in Alfisols, are the main reasons for the high nonexchangeable K release in these soils. In all soils, rate of potassium release was higher in the beginning and decreased, afterwards. The kinetics of cumulative NEK release were evaluated by using the Elovich, power function, first order, zero order and parabolic diffusion equations. By reason of the highest coefficient of determination (r<sup>2</sup>) and lowest standard error (SE), Elovich and power function could describe the NEK release kinetics equations fitted to the observed data satisfactorily; indicating that diffusion mainly controlled the K exchange. Rate constants were very different in soil samples. Which is mainly attributed to difference in particle size distribution, clay content and the type of clay minerals.

**Keywords:** Nonexchangeable K; Kinetics; K released

#### Introduction

soils have large contents of total K but relatively small amounts of available K and in arid and semiarid regions contain large quantities of exchangeable and nonexchangeable K(NEK), Potassium is found as a component of several minerals that release it to soluble and exchangeable forms by weathering at greatly different rates (Huang, 1977). Some of these minerals also have the capability of fixing added K back into their structures in non-exchangeable forms. Thus, the release of K by minerals to soluble and exchangeable forms and its adsorption from the soil solution by exchange sites are both forward and reverse reactions (McLean and Walson, 1985). These reactions are regulated by mechanisms that depend on their relative strengths for binding K (Ghosh and Singh, 2001). Non-exchangeable K (NEK) can be an important reservoir of K in soils. Several studies demonstrate that NEK from reserves makes an important contribution to plant K supply (Mengele and Ahlen Becker, 1993).

Huang (2005) concluded that K release from micas may be due to dissolution or transformation to 2:1 expandable layer silicates. Potassium release from soil is a dynamic process, and the investigation of K release kinetics is important to evaluate soil K availability for crops (Sparks and Huang, 1985). For optimal nutrition of crop, the replenishment of a K-depleted soil solution is affected predominately by the release of non-exchangeable K from clay minerals and organic matter. Therefore, high crop growth occur when soil solution and exchangeable K have been replenished continually with release of non-exchangeable K through the weathering of K reserves (Sparks and Huang, 1985; Sparks, 1987) or the addition of K fertilizers. The amount of non-exchangeable K in soils is greatly affected by the clay content and by the types of clay minerals that are present. Vermiculite, mica and illite are the clay minerals that have the greatest capacity to fix K. Fixation and release depends on K level in soil solution, type of clay minerals in soil, and wetting and drying process (Steffens and Sparks, 1997). Little information is available on the effect of organic acids on the kinetic of K release.

Sequential extraction of K with calcium (Ca) is a suitable method to evaluate the release kinetics of non-exchangeable K in calcareous soils, because of the high affinity of Ca to sorption sites (Jalali 2006). The objectives of this study were to investigate the kinetics of the release of nonexchangeable K (NEK) from calcareous soils by 0.01M CaCl<sub>2</sub> and to use various kinetic equations to describe this release from 15 soils of southern Iran. Kinetics of K from soils (Hagin and Feigenbaum 1962; Lopez-Pineiro and Garcia Navarro 1997; Bedrossian and Singh 2004; Jalali 2006; Najafi ghiri 2011). Various kinetic equations have been examined for describing K release and distinguish the prevailing mechanism of K release from minerals. These models include first-order (Srinivasarao et al. 1998), zero-order (Srinivasarao et al. 1998), parabolic diffusion (Sharma and Swami 2000), power function (Havlin et al. 1985), and the Elovich equation (Martin and Sparks 1983).

#### Materials and Methods

The fifteen soil samples used in this study were collected from the surface (0–30 cm) horizon of 5 soil orders in Fars province, southern Iran (Entisols, Inceptisols, Aridisols, Alfisols and Vertisols). Water soluble K was determined in the saturated extract. Exchangeable and nonexchangeable K was determined by 1.0 M NH<sub>4</sub>OAc (pH 7.0) and 1.0 M boiling HNO<sub>3</sub> respectively. Kinetics of K release was studied by successive extraction with 0.01 M CaCl<sub>2</sub>, before starting the kinetic studies; each of the soil samples was saturated with Ca<sup>+2</sup> to remove native exchangeable K. The samples were washed with distilled water until a negative test for Cl<sup>-</sup> was obtained with AgNO<sub>3</sub>. Afterward 1gr of each soil was placed in a centrifuge tube, and 10 mL of

the extractant solution was added to each tube in two replications. These tubes were shaken for 2, 6, 12, 24, 48, 72, 72,120,168,168 and 336 h at 25 °C. After each extraction period, the tubes were centrifuged and the concentration of K was determined in the clear solution by using a flame photometer (Corning 405), while the soil was mixed with a new portion of extractant, shaken, and centrifuged. This procedure was repeated 11 times. The experimental data were fitted to five kinetic models (power function, elovich, parabolic diffusion, zero order and first-order, the equations are as follows:

- Elovich equation:  $Y = a + b \ln t$
- parabolic diffusion law:  $Y = a + b t^{0.5}$
- power function:  $\ln Y = \ln a + b \ln t$
- zero order:  $(Y^0 - Y) = a - b t$
- first order:  $\ln (Y^0 - Y) = a - b t$

Where Y is the amount of released K at time t, t is the time of release, Y<sup>0</sup> is the maximum K released, and a and b are constants. The best mathematical models were determined by least-squares regression analysis. We obtained coefficients of determination (R<sup>2</sup>) by least-squares regression, and standard error of the estimate  $SE = [(Y - Y^*)^2 / (n - 2)]^{0.5}$ , where Y and Y\* represent the measured and calculated content of K released at time t, and n is data number

## Results

Selected chemical and physical properties, classification and potassium forms of the soils used in the study are given in Table1. There were large differences in the studied soils for soil calcium carbonate contents varied from 9.9 to 62.9%. The studied soils had different contents of sand, silt, and clay size fractions. Clay contents in all soils averaged 35 % and ranged from 8 to 48 percent. Sand contents ranged from 2 to 71% (average 36%), silt contents from 15 to 56 % ( average 36%), and the soils were low in EC and organic matter. The CEC ranged from 6 to 29cmolc kg-1. Exchangeable K ranged from 142 to 793mgkg<sup>-1</sup>. Soluble K ranged from 1 to 37 mg.kg<sup>-1</sup>, nonexchangeable K ranged from 247 to1446mg.kg<sup>-1</sup> structure(mineral) K ranged from 3792 to13110 mgkg<sup>-1</sup>, and total K ranged from 4352 to 15109mg kg-1.The dominate clays in all soils are illite, smectite, chlorite, palygorskite, interstratified minerals and quartz. Slighter amounts of kaolinite and vermiculite were also found in study area, the soils include aridic, xeric and ustic moisture regimes and mesic and hyperthermic temperature regimes (Banaei 1998), and have developed on alluvial fan, piedmont plains and low lands. All studied soils are calcareous, and belong to Entisols, Aridisols, Inceptisols, Alfisols and Vertisols.

**Table 1.** Some physic chemical properties and potassium status, of studied soils

Soil no.	Classification	Kt	Ksol	Kex			Kstr	CEC	EC	CCE	OC	Silt	Clay	Sand
				(Mg kg <sup>-1</sup> )										
1	Typic Ustorthents	6761	1.6	225	247	6288	25	0.8	47.1	1.4	43	38	19	
2	Aquic Haplustepts	6514	11.6	284	481	5737	19	2.2	55.2	2.8	56	42	2	
3	Calcic Haplustalfs	6150	5.3	255	452	5437	19	0.9	57.0	1.7	45	44	11	
4	Aquic Calcistepsts	6271	3.4	389	567	5311	19	1.4	59.4	0.7	45	40	15	
5	Aquic Calcistepsts	5563	0.9	226	566	4770	19	1.0	56.7	0.8	43	48	9	
6	Typic Torriorthents	4943	3.6	198	512	4230	8	0.7	62.9	0.3	21	16	63	
7	Typic Haplogypsis	7461	10.7	303	733	6414	11	6.1	50.8	0.3	26	22	52	
8	Typic Haplocambids	7012	4.6	327	680	6001	9	0.4	54.7	0.8	38	15	47	
9	Typic Calcigypsis	5221	1.7	175	536	4508	6	0.4	60.9	0.2	21	8	71	
10	Typic HaploCambids	5678	2.1	175	552	4950	11	0.8	58.2	0.7	17	17	65	
11	Typic Xerorthents	15109	3.7	564	1432	13110	29	0.3	9.9	0.4	15	28	57	
12	Typic Calcixerepts	12862	3.1	423	876	11560	21	0.5	31.2	0.6	22	19	59	
13	Calcic Haploxeralfs	15109	9.5	793	1446	12861	25	0.5	15.4	1.6	48	29	23	
14	Typic Calcixerepts	4352	3.5	142	415	3792	25	3.9	58.2	5.2	29	44	27	
15	Typic Haploxererts	9155	37.1	606	974	7538	21	3.6	39.6	3.9	54	26	20	

Kt, total K; Kex: exchangeable K, NEK non-exchangeable K; Ksol: soluble K, Kstr: structure or mineral K; CCE, CaCO<sub>3</sub> equivalent; CEC, cation exchange capacity; OM, organic matter

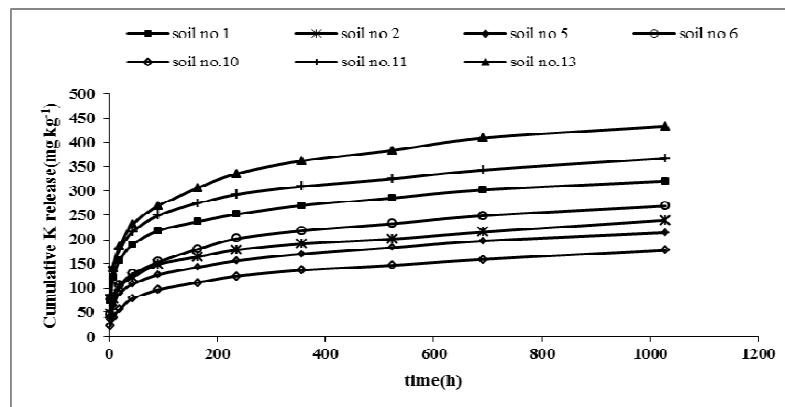
## Kinetics of Potassium Release

Cumulative NEK release in CaCl<sub>2</sub> 0.01M solution in some studied soils is shown in Table 2. The cumulative NEK released in 0.01 M CaCl<sub>2</sub> varied from 104 in Typic HaploCambids to 286 mg kg<sup>-1</sup> in Calcic Haploxeralfs. Cumulative NEK released from Alfisols and Aridisols were very high and low, respectively. Presence of K-bearing minerals (i.e., illite and chlorite), and high clay content of Alfisols were the main factors for releasing high NEK in these soils. The type of soil minerals has a significant effect on K release. Soil development had a significant effect on K release. Najafi-Ghiri et al. (2012) studied release of non-exchangeable K from calcareous soils of southern Iran. They indicated that cumulative K release was significantly higher in Vertisols and Vertic subgroups than in Mollisols and Entisols. Cumulative K release from study soils in CaCl<sub>2</sub> 0.01M were summed and plotted against cumulative times ranging from 2 to 1200h are shown in Figure1. Also Table 2 shows the cumulative amount of K release with 0.01M CaCl<sub>2</sub> during 1200 h that ranged from 104 to 286 mgkg-1 for study soils These

values almost close to compared with the findings of (Najafi ghiri 2011). cumulative K released by the extractant consisted of two parts in all soils. The nonexchangeable K release curves showed an initial rapid phase followed by a slow phase of K release from soils. Because all the exchangeable K had been removed in the pre-treatment, the first curvilinear part indicated rapid K release from the edge sites. This two-phase release is characteristic of a diffusion-controlled process (Martin and Sparks, 1983; Feigenbaum et al., 1981). The first curvilinear part indicated rapid K release from the surface sites. The second linear part represented K release from internal sites (Dhillon and Dhillon 1990 and jalali, 2008). The linear part was extrapolated to the ordinate to give the amount of surface (edge) exchangeable K (Talibudeen and Weir 1972). In this study the release was rapid from 2 to about 160 h and reached a slower phase after 160 h. The amount of K extracted during the first 2 h was highest, decreased during 2–160 h, and remained nearly constant after 160 h.

**Table 2.** Cumulative NEK released (mg Kg<sup>-1</sup>) from soil using a 0.01 M CaCl<sub>2</sub>

Soil no.	Classification	Non exchangeable K	Cumulative NEK release (mg kg <sup>-1</sup> )
1	Typic Ustorthents	247	135
2	Aquic Haplustepts	481	160
3	Calcic Haplustalfs	452	153
4	Aquic Calcustepts	567	221
5	Aquic Calcustepts	566	153
6	Typic Torriorthents	536	117
7	Typic Haplogypsis	733	170
8	Typic Haplocambids	680	148
9	Typic Calcigypsis	512	110
10	Typic HaploCambids	552	104
11	Typic Xerorthents	1432	212
12	Typic Calcixerepts	876	180
13	Calcic Haploxeralfs	1446	286
14	Typic Calcixerepts	415	113
15	Typic Haploxererts	974	253



**Figure 1.** Cumulative amount of nonexchangeable K release with time in some studied soil by 0.01 M CaCl<sub>2</sub>

The two phases of K release were also reported by others (Dhillon and Dhillon, 1990; Ghosh and Singh, 2001; Jalali, 2005). The amount of K extracted was greatest in the first extraction, declined during the next extractions, and then remained nearly constant in subsequent extractions. Several kinetic models were used to describe NEK release from the soils. The cumulative K was also well fitted to Elovich ( $r^2=0.975-0.998$ , mean=0.987), and power function equation ( $r^2=0.970-0.993$ , mean=0.981) as indicated by the highest coefficient of determination ( $r^2$ ) and the lowest values of standard error of estimate (SE). The K release rates (parameter b) represent the slope and can be used as an index of K release rates. The constant 'b' of the Elovich equation ranged from 22.33 to 52.28 mg kg<sup>-1</sup>.h<sup>-1</sup> (mean 32.99 mg kg<sup>-1</sup>.h<sup>-1</sup>) and for power function model ranged from 0.217 to 0.327 (mean: 0.256) mg kg<sup>-1</sup>.h<sup>-1</sup> for studied soils respectively (table 5). There was a significant and positive relationship between the constant 'b' of the Elovich equation and as well as cumulative K release, total K, exchangeable K, nonexchangeable K, and cation exchangeable capacity content are the most influential soil properties that predict the constant 'b' of the Elovich equation, and there was significant and positive relationship between the constant 'b' of the first order with cumulative K release, exchangeable K, soluble K and relationships between intercept value of power function equations were significantly correlated with cumulative K release, total K, nonexchangeable K, mineral K and cation exchangeable capacity, This is in agreement with finding of Bedrossian and Singh (2004), who indicated that the rate coefficient 'b' of the Elovich equation was correlated with water-soluble, exchangeable, and non-exchangeable forms of K. in other soil

properties such as CEC, generally showed good correlations with the coefficients of the elovich and power function for 0.01M CaCl<sub>2</sub> data. Successful description of K release in 0.01 CaCl<sub>2</sub> by the power function and first order equations was also reported by Cox et al. (1999) and by Dhillon and Dhillon (1990). Bedrossian and Singh (2004) reported that the order of application of various kinetics models to describe K release data in 0.01 M CaCl<sub>2</sub> was Elovich and power function equations fitted the data adequately. Jalali, (2006) and Najafi-Ghiri et al (2011) indicated that Elovich equation may describe K release from K-bearing minerals to CaCl<sub>2</sub> solution.

**Table 3.** Correlation coefficient (r) of the linear regression between Cumulative non exchangeable K and some soil properties

	release k	Kt	Ksol	Kex	Knon	Kstr	CEC	EC	CCE	OC	Silt	Clay
release k	1											
Kt	.588*	1										
Ksol	.266	.185	1									
Kex	.690**	.870**	.504	1								
Knon	.578*	.913**	.307	.894**	1							
Kstr	.571*	.998**	.146	.842**	.885**	1						
CEC	.690**	.551*	.131	.494	.388	.562*	1					
EC	-.164	-.221	.486	-.073	-.110	-.239	-.009	1				
CCE	-.687**	-.977**	-.203	-.844**	-.897**	-.975**	-.650**	.177	1			
OM	.286	-.150	.498	.042	-.118	-.163	.452	.451	.048	1		
Silt	.306	-.058	.492	.296	-.091	-.076	.303	.129	.054	.461	1	
Clay	.243	-.146	-.030	-.052	-.232	-.140	.640*	.163	.066	.481	.591*	1

Kt, total K; Kex: exchangeable K, NEK non-exchangeable K; Ksol: soluble K, Kstr: structure or mineral K; CCE, CaCO<sub>3</sub> equivalent; CEC, cation exchange capacity; OM, organic matter

Table 3 shows the correlation coefficients of the linear regression between Cumulative non exchangeable K and soil K forms and some soil properties such as CEC, calcium carbonate content, organic matter and etc. These were positive and significant correlations between different forms of K and other soil properties. Sinha and Biswas (2003) stated that water soluble, available and nonexchangeable potassium show positive and significant correlation with clay content and cation exchange capacity for soils of West Bengal, India. Generally, positive and significant correlations were found between cumulative K release and mineral K (n = 15, r = 0.571\*\*), exchangeable K (n = 15, r = 0.690\*\*), nonexchangeable K (n = 15, r = 0.578\*\*), and total K (n = 15, r = 0.588\*\*). and HNO<sub>3</sub>-extractable K. The percentage of non-exchangeable K that was released during 1200 h to 0.01 M CaCl<sub>2</sub> is shown in Table 3.

**Table 4.** Coefficient of determination (r<sup>2</sup>) and standard error of the estimate (SE) of various kinetic models used to describe release kinetics of non-exchangeable K from soils

Power function		Parabolic diffusion		Elovich		First order		Zero order		Soil no.
SE	r <sup>2</sup>	SE	r <sup>2</sup>	SE	r <sup>2</sup>	SE	r <sup>2</sup>	SE	r <sup>2</sup>	
0.082	0.970	28.136	0.883	4.125	0.998	0.433	0.933	45.821	0.691	1
0.070	0.980	18.280	0.918	6.970	0.988	0.510	0.892	32.330	0.743	2
0.077	0.972	19.454	0.879	2.455	0.998	0.353	0.946	31.558	0.683	3
0.071	0.977	18.782	0.903	5.269	0.992	0.483	0.900	31.648	0.725	4
0.086	0.978	16.111	0.927	7.185	0.986	0.423	0.925	29.481	0.757	5
0.073	0.984	20.025	0.931	10.464	0.981	0.435	0.928	37.866	0.755	6
0.040	0.993	11.850	0.937	6.730	0.980	0.340	0.948	22.840	0.764	7
0.065	0.986	18.435	0.916	6.875	0.988	0.330	0.956	33.160	0.729	8
0.080	0.982	14.934	0.920	5.932	0.987	0.382	0.936	26.930	0.740	9
0.085	0.985	13.008	0.941	8.494	0.975	0.450	0.910	25.453	0.774	10
0.077	0.972	32.198	0.881	4.206	0.988	0.483	0.915	52.327	0.685	11
0.060	0.988	12.780	0.937	7.170	0.980	0.434	0.915	24.499	0.768	12
0.076	0.980	36.229	0.910	11.052	0.992	0.464	0.930	63.668	0.721	13
0.066	0.986	20.078	0.936	10.721	0.982	0.520	0.897	38.193	0.768	14
0.074	0.983	24.693	0.930	11.565	0.985	0.497	0.911	46.111	0.756	15
0.040	0.970	11.850	0.879	2.455	0.975	0.330	0.892	22.840	0.683	min
0.086	0.993	36.229	0.941	11.565	0.998	0.520	0.956	63.668	0.774	max
0.072	0.981	20.333	0.917	7.281	0.987	0.436	0.923	36.126	0.737	average

**Table 5.** Parameters of models used to describe release kinetics of nonexchangeable K into 0.01 M CaCl<sub>2</sub> in studied soils

Power function		Parabolic diffusion		Elovich		First order		Zero order		
b (mg kg <sup>-1</sup> h <sup>-1</sup> )	a (mg kg <sup>-1</sup> )	b (mg kg <sup>-1</sup> h <sup>-1</sup> )	a (mg kg <sup>-1</sup> )	b (mg kg <sup>-1</sup> h <sup>-1</sup> )	a (mg kg <sup>-1</sup> h)	b*10 <sup>10</sup> (mg kg <sup>-1</sup> h <sup>-1</sup> )	A (mg kg <sup>-1</sup> )	b (mg kg <sup>-1</sup> h <sup>-1</sup> )	a (mg kg <sup>-1</sup> )	
0.222	74.040	7.243	119.830	39.318	41.088	0.045	5.332	0.195	156.310	1
0.249	44.800	5.708	73.977	30.255	15.255	0.041	5.167	0.156	131.440	2
0.217	52.657	4.914	84.258	26.743	30.528	0.042	4.889	0.132	105.160	3
0.221	53.925	5.353	85.281	28.670	28.859	0.041	5.082	0.146	122.100	4
0.270	35.237	5.374	60.392	28.307	5.986	0.042	5.092	0.148	122.210	5
0.274	43.306	6.902	73.392	36.191	4.188	0.0441	5.334	0.189	153.820	6
0.252	31.431	4.275	50.243	22.331	7.770	0.041	4.823	0.117	95.964	7
0.259	41.091	5.700	68.860	30.243	10.083	0.044	5.078	0.155	123.200	8
0.280	28.887	4.728	50.660	25.027	2.184	0.041	4.919	0.129	105.560	9
0.327	20.035	4.846	36.794	25.200	-10.834	0.041	4.999	0.134	112.140	10
0.218	87.086	8.181	139.450	44.487	50.156	0.045	5.462	0.219	176.680	11
0.269	29.660	4.599	49.363	24.034	3.628	0.040	4.935	0.127	106.000	12
0.255	80.616	10.740	136.180	52.289	24.043	0.048	5.708	0.291	231.830	13
0.265	47.981	7.169	79.673	37.512	8.155	0.043	5.426	0.198	165.270	14
0.268	55.902	8.425	94.368	44.284	9.402	0.045	5.572	0.231	189.710	15
0.217	20.035	4.275	36.794	22.331	-10.834	0.004	4.823	0.117	95.964	min
0.327	87.086	10.740	139.450	52.289	50.156	0.005	5.708	0.291	231.830	max
0.256	48.444	6.277	80.181	32.993	15.366	0.004	5.188	0.171	139.826	average

## Conclusion

The results of the present study was conducted to investigate the kinetics of non-exchangeable potassium (NEK) release from 15 soils of (Fars province) southern Iran with different properties. Surface soil samples (0-30 cm) of Entisols, Inceptisols, Aridisols, Alfisols and Vertisols were extracted with CaCl<sub>2</sub> 0.01 mol L<sup>-1</sup>, in sequential extractions ranging from 1 to 1200 h. The amount of NEK released after 1200 h ranged from 144 mg kg<sup>-1</sup> in Aridisols to 236 mg kg<sup>-1</sup> in Alfisols. Presence of K-bearing minerals (i.e., illite and chlorite), and high clay content of Alfisols were the main factors for releasing high NEK in these soils and Greater K release rate constants in Alfisols could be due to fine texture and larger wedge zones, and its swelling clay where the exchange is relatively easier. In all soils, rate of initial K release was high but decreased, afterwards. Five kinetic models (power function, elovich, parabolic diffusion, zero order and first-order) were used to describe non-exchangeable K (NEK) release. Kinetics of NEK release conformed well to the elovich ( $r^2=0.987$ ), and power function equation ( $r^2=0.981$ ) as indicated by the highest coefficient of determination ( $r^2$ ) and the lowest values of standard error of estimate (SE) and fitted the data adequately. Maximum Rate constants of the elovich were extracted from the Alfisols (52.28 mg kg<sup>-1</sup> h<sup>-1</sup>) and the smallest amounts was extracted from Aridisols (22.33 mg kg<sup>-1</sup> h<sup>-1</sup>). And highest and lowest intercept value of power function equations were extracted from the Typic HaploCambids(20.03mg kg<sup>-1</sup>) and Typic Xerorthents(87.08mg kg<sup>-1</sup>) respectively(table 5). Rate constants of the elovich was significantly correlated with cumulative K release, total K, exchangeable K, nonexchangeable, and cation exchanbale capacity( $r=0.96^{**},0.52^*,0.66^{**},0.57^*$ and  $0.61^*$ respectively) and intercept value of power function equations were significantly correlated with cumulative K release, total K, nonexchangeable K, mineral K and cation exchanbale capacity( $r=0.94^{**},0.57^*,0.62^{**},0.56^*$ and  $0.74^*$ respectively). And in conclusion Evidence achieved from mathematical models can help to explain the release mechanism and evaluation the potassium supplying power of soils.

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