

# Potassium Pools Distribution in Some Calcareous Soils as Affected by Climatic Conditions, Physiographic Units, and Some Physicochemical Properties in Fars Province, Southern Iran

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Received August 17, 2020; revised September 3, 2020; accepted October 24, 2020

**Abstract**—Experiments were conducted for thirty representative surface and subsurface soils collected from different physiographic units and moisture regimes in southern Iran to assess factors affecting K pools distribution and potassium release rate, using two organic and inorganic extractants and their association to mineralogy and some physical and chemical properties in calcareous soils. Mineralogical analysis indicated that illite, smectite, chlorite and palygorskite were the main clay minerals in the studied soils. The highest content of illite and smectite was observed in the piedmont plain (P.P) units, whereas that of smectite in Lowland (L.L) unit was higher than in soils of alluvial fans (A.F). It seems that the P.P unit which is in more stable landform position contains larger amounts of all K compounds due to higher clay and illite contents. The exchangeable, non-exchangeable (NEK), structural, and total potassium were found to be significantly and positively correlated to the clay content, cation exchange capacity, and the contents of illite, smectite, and vermiculite minerals, while a negative correlation as observed between the mentioned K forms and the calcium carbonate (CaCO<sub>3</sub>) content. The cumulative rate of K release to 0.01 M CaCl<sub>2</sub> and oxalic acid was examined for a period of 1200 h, ranging within 104–286 and 87–233 mg kg<sup>-1</sup> for the surface soil and 98–241 and 82–211 mg kg<sup>-1</sup> for the subsurface soil samples, respectively. The percentage of non-exchangeable K released varied greatly between the different units and moisture regimes. Higher values of NEK release were observed for P.P followed by A.F, and L.L units. Considering the obtained values of the highest amount of potassium compounds as well as the release values in the piedmont plain physiographic unit and the xeric moisture regime as well as the Alfisols, the results confirm that in addition to physicochemical and mineralogical properties, physiographic units and soil moisture regimes also play a key role in nature and in spatial distribution of different forms of potassium.

**Keywords:** potassium forms, calcareous soils, K release, clay minerals

**DOI:** 10.1134/S1064229321050021

## INTRODUCTION

Potassium (K) is an essential macronutrient for plants. Physicochemical properties of the soil and soil management are the most important factors affecting the composition of K forms in the soil. Regarding the significant role played by the K in the growth of crops and humans, deficiency of this element in agricultural farmlands has become a global problem. Nowadays, due to intensive farming and insufficient application of K-supplying fertilizers, many soils are being exposed to K deficiency [3]. Availability of K for plants is generally governed by different forms of K, e.g. water-soluble K, exchangeable K, fixed K and mineral K. Soluble and exchangeable K forms are known to be rapidly released into the soil, making them readily available for plants. A recent study showed that these

forms of K are considerably more abundant in the surface, rather than the subsurface, soil layer [14]. The distribution of K forms in the soil depends on particular properties of the soil such as the soil texture, content and type of clay minerals in the soil, content of organic matter (OM), land use, the soil moisture and temperature regimes, and the soil development [38]. Various factors can affect the composition and distribution of K forms in a soil sample, including the soil physical and chemical properties such as particle size distribution, the contents of carbonates and OM, cation exchange capacity (CEC) and electrical conductivity, the type and amount of K-bearing minerals of the soil such as mica and feldspar, the content of K-stabilizing minerals of the soil such as vermiculite, smectite and weathered mica, the soil moisture and temperature conditions, the soil evolution, land use, and

the soil physiographical status in the ground board, as studied by various researchers [17, 23, 30]. Non-exchangeable form of K has been less available as it occurs between the layers of mica; intensive crop production and insufficient application of K fertilizers has further reduced the availability of water-soluble and exchangeable K forms, thereby eliminating the non-exchangeable form of K from the layers of mica. Wang et al. [40] proposed a threshold for the K concentration in soil solution, above which the release of non-exchangeable K from clay minerals was inhibited. This threshold depended on the type of dominant clay mineral in the soil and the presence of calcium (Ca) and sodium (Na) ions. The presence of different cations in the soil solution affects the conversion of different forms of K into one another. With higher levels of hydration, energy and size than those of K, Ca ions cannot replace the interlayer K ions, as is evident in illite-bearing soils [37].

Clay minerals have a variety of sites for K storage, including surface, edges, and inner layers. The release of K from different sites is determined by the type of extractant. The K can be easily removed from the surface sites through an ion exchange mechanism, while the K ions on the edges and inner layers of the minerals require more energy to be released [7, 19]. In many cases, the soils in arid and semi-arid regions contain large amounts of non-exchangeable form of K as a result of their biotite and muscovite contents. The K ions trapped between the inner layers of clay minerals provide important source of K for plant growth in most soils. So far, various organic and mineral extractants have been used to investigate the mechanism and rate of K release from clay minerals in the soil. Due to its abundance in calcareous soils, the Ca ion has been the most common ion for exchanging the inter-layer K particles. Therefore, successive extraction of K with Ca has been an appropriate method for kinetic evaluation of non-exchangeable K release in these soils. The organic acid content of the soil contributes to weathering of the soil minerals by forming organic complexes [39]. Oxalic acid is an organic acid that largely contributes to the availability of nutrients in the soil. As the simplest dicarboxylic acid with two pKa values (*i.e.*, 1.23 and 4.19), it has been found in sediments, forests and agricultural soils, especially in the rhizosphere of plants [6]. There are several kinetic models to describe the K release process, including Elovich, parabolic diffusion, power function, and zero-order and first-order equations. In general, the use of different equations to examine the K release kinetics and determination of the best equation depend on the main mechanism affecting the K release, the chemical and mineralogical composition of the soil, the type of laboratory method used, and pretreatment of the soil before starting the experiment [36]. Today, optimal and accurate management of fields and fertilizer recommendations require a comprehensive set of information on the mineral composition of the soil,

various forms of K, and the relationship between the minerals and K stabilization and release. This sheds light on the need for comprehensive studies on the state of K forms in terms of their distribution in the soil, non-exchangeable K release, and the relationship among K forms, soil mineralogy, and soil properties across long-cultivated agricultural fields. Therefore, the present study aimed to investigate the composition and distribution of K forms, the kinetics of non-exchangeable K release using both organic and inorganic extractants, and their relationship with soil properties and clay mineralogy in highly cultivated calcareous soils in the southern of Iran.

## MATERIALS AND METHODS

### *Physicochemical Properties of Soils*

Based on previous soil survey maps, fifteen pedons with a wide range of different soil properties that were developed under different climatic conditions (aridic, xeric and ustic soil moisture regime) and physiographic positions (Alluvial fans (A.F), the Piedmont plains (P.P), and the Lowlands (L.L)), with calcareous parent materials were selected from northern and northwestern of Fars province, southern Iran (Fig. 1). To minimize the effect of potassium fertilizers, sampling was performed in autumn and before cultivation. Pits were dug, described and classified according to Keys to Soil Taxonomy [35]. All soil horizons were sampled (a total of 49 samples), air-dried and sieved (<2 mm) for laboratory analyses. Physical, chemical, and mineralogical properties of 30 surface and subsurface soils (15 pedon) of intensively cultivated regions in Fars Province used in the present study were determined. Soil particle-size distribution was determined using the hydrometer method [4]. Calcium carbonate equivalent (CCE) was measured by neutralization with HCl [15], and organic carbon (OC) was determined by wet oxidation method [24]. Soil pH was measured using the saturated paste extract, electrical conductivity (EC) was measured in soil saturation extract using conductometer, was determined using the saturated paste extract, cation exchangeable capacity (CEC) was analyzed by replacing exchangeable cations by NaOAc and exchanging Na<sup>+</sup> with NH<sub>4</sub>OAc [5], and gypsum was measured by precipitation with acetone [29].

### *Potassium Forms*

The content of potassium present in different forms was measured by methods outlined by Helmeke and Sparks [8]. Total K was determined following digestion (383°K) of 0.5 g soil sample with 10 mL of 48% HF and 1 mL of aqua regia.1 Solution K was measured in the saturated extract. Exchangeable K was determined by extraction of 5 g soil sample with 20 mL 1M ammonium acetate (pH 7) for 5 min.

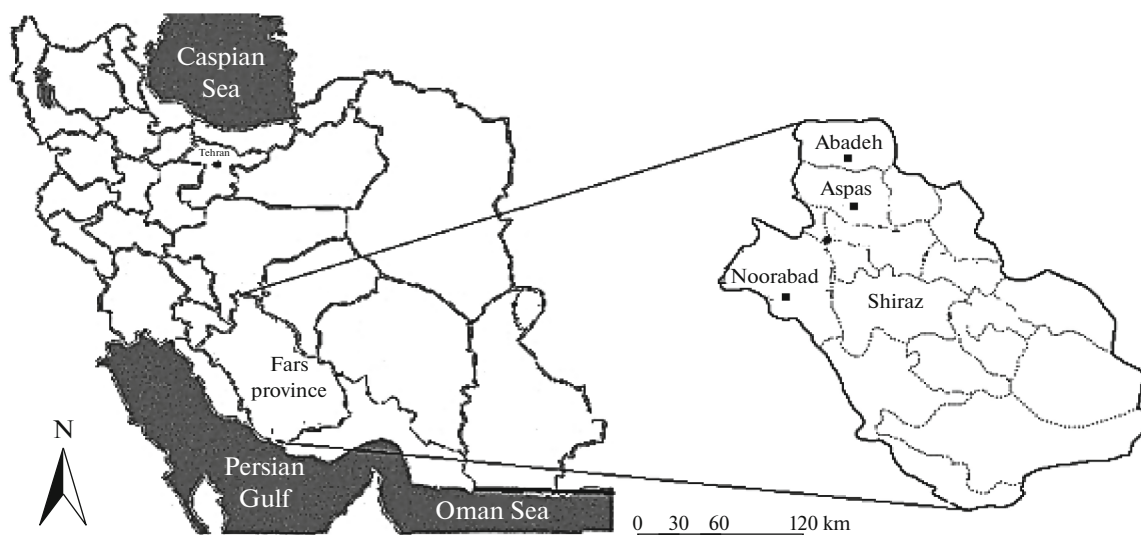


Fig. 1. Location of studied area in Fars Province, southern Iran.

$\text{HNO}_3$ -extractable K was measured by extraction of 2.5 g soil sample with 30 mL of boiling 1.0 M Nitric acid for 1 h. Non-exchangeable K was calculated as the difference between  $\text{HNO}_3$ -extractable K and  $\text{NH}_4\text{OAc}$ -extractable K. Potassium was measured in filtered extracts using flame photometer. Three replications were conducted for all the analyses and the results were presented as mean.

For assessing the cumulative non-exchangeable K release with time, we firstly removed the native K with saturation by equilibrating 10 g of soil with 1 M  $\text{CaCl}_2$  three times for 48 h. We then washed out the extra  $\text{Cl}^-$  by alcohol and deionized water. Samples were dried at  $65^\circ\text{C}$ . For each soil sample (30 in total), 2 g of Ca-saturated soil was placed in two centrifuge tubes (in duplicate) with different media including 10 mmol  $\text{CaCl}_2$  and 10 mmol oxalic acid solutions (20 mL in each tube) for 1200 h (2, 6, 12, 24, 48, 72, 72, 120, 168, 168, and 336 h) at  $25 \pm 1^\circ\text{C}$ . Subsequently, they were shaken for 1 h before the suspensions were centrifuged for 10 min. At each stage, the supernatant liquid was determined for K using the flame photometer (Elico Model CL-360, India) [16].

#### Mineralogical Analysis

Clay mineralogy was performed on the first and second horizon (total of 30 samples) of each pedon. Prior to mineralogical analysis, samples were repeatedly washed to remove gypsum and soluble salts. Carbonates were removed using 1N sodium acetate, buffered at pH 5; this reaction was performed in a water bath at  $80^\circ\text{C}$ . Organic matter was oxidized by treating the carbonate-free soils with 30%  $\text{H}_2\text{O}_2$ . Iron oxides were removed from the samples by the dithionite

citrate bicarbonate method [18]. The clay fraction was separated by centrifuge at 750 rpm for 5.4 min according to Kittrick and Hope [13] and Jackson [10]. After separation of clay fraction, samples were saturated with  $\text{Mg}^{2+}$  and  $\text{K}^+$ , using 1 N  $\text{MgCl}_2$  and 1 N  $\text{KCl}$ , respectively. The  $\text{Mg}^{2+}$  and  $\text{K}^+$  saturated samples were saturated by ethylene glycol and heated at  $550^\circ\text{C}$ , respectively. In addition, samples were treated with 1 N  $\text{HCl}$  to discriminate kaolinite and Fe chlorite. Relative peak positions identify clay minerals, and peak intensities are the basis for semiquantitative estimates of mineral percent. The semiquantitative percentage of the clay minerals were estimated from the relative first order XRD peak areas of ethylene glycol solvated samples according to Johns et al. [12].

## RESULTS AND DISCUSSION

### Soil Classification across the Study Area

Based on Soil Survey Staff [35] and considering the surface and subsurface horizons and the moisture and temperature conditions across the study area, the studied soils were classified under five orders, namely Entisols (soils no. 1, 6, and 11), Inceptisols (soils no 7, 9, 12, 14, and 15), Alfisols (soils no. 8, and 13), Aridisols (soils no. 2, 3, 4 and 5) and Vertisols (soils no. 10). The mentioned orders were belonged to three physiographical units, including the Alluvial fans (AF), the Piedmont plains (PP), and the Lowlands (LL) (Table 1). Given the climatic conditions across Fars Province, local precipitation level is less than enough to affect the leaching of the soluble salts, transportation of carbonates, sulfates and fine clays, accumulation of OM, and, in general, the soil evolution. Indeed, the local soil properties largely follow the composition of parent materials, with the high content of calcium car-

**Table1.** General characteristics and physico-chemical properties and Semi-quantitative analysis of clay minerals, <0.002 mm in studied area

Pedon	Physiographic Unit	Soil no.	Horizon	Classification, USDA	EC, dS/m	CEC, cmol, +/kg	Gypsum		pH	Clay %	Texture	Ill**	Chl	Sme	Pal	Kao	Ver	Mixed layer
							CEC, %	OC, %										
1	A.F*	1	Ap	TypicTorriorthents	0.69	7.7	1.3	62.9	0.3	8.1	16	SL	+++++	+	++	-	-	-
2	P.P	2	Ck1		1.47	8.8	1.0	60.7	0.2	8.2	30	CL	+++++	++	++	-	-	-
3	P.P	3	Ap	TypicHaplogypsis	6.12	11.3	3.1	50.8	0.3	8.0	22	SCL	+++++	++	-	-	-	-
4	P.P	4	Bw	TypicHaplogypsis	0.74	13.8	4.0	59.2	0.2	7.2	24	SCL	+++	++	++++	-	-	-
5	P.P	5	Ap	TypicHaplocambids	0.43	8.8	1.1	54.7	0.8	8.2	15	L	+++++	-	++	-	-	-
6	L.L	6	Bw		1.47	8.8	0.9	61.9	0.5	8.1	20	SCL	+++++	++	++	-	-	-
7	L.L	7	Ap	Typic Calcigypsis	0.43	6.5	1.7	60.9	0.2	8.1	8	SL	+++	-	++++	-	-	-
8	A.F	8	Bk	Typic Calcigypsis	0.30	7.7	3.2	66.4	0.1	8.4	8	SL	+++++	+	++++	-	-	-
9	L.L	9	A	TypicHaploCambids	0.75	11.3	1.2	58.2	0.7	8.1	18	SL	+++++	-	++	-	-	-
10	P.P	10	Bw		3.45	5.4	0.9	74.3	0.2	7.8	12	L	+++++	-	+++	-	-	-
11	P.P	11	A	Typic Xerorthents	0.26	20.5	0.9	9.9	0.4	8.0	28	SCL	+++	++	+++	-	-	-
12	P.P	12	C	Typic Xerorthents	0.28	20.5	1.1	31.2	0.8	7.8	42	C	+++++	+++	-	-	-	-
13	P.P	13	Ap	Typic Calcixerepts	0.48	20.5	0.9	31.2	0.6	7.9	19	SL	+++++	++	-	-	-	++
14	P.P	14	Bk	Typic Calcixerepts	0.25	19.2	1.0	39.6	0.4	7.8	42	C	+++	+++	-	-	-	-
15	P.P	15	A	Calcic Haploxeralfs	0.50	24.9	1.1	15.4	1.6	8.0	29	CL	+++++	+++	+++	-	-	+++
16	L.L	16	Btk1		0.38	24.9	1.1	22.3	0.9	7.8	45	C	+++	+++	-	-	-	+++
17	L.L	17	Ap	Typic Calcixerepts	3.91	24.9	1.3	58.2	5.2	7.4	44	C	++	+++	+++	-	-	+++
18	L.L	18	Bk	Typic Calcixerepts	0.63	16.4	1.1	62.6	0.5	7.6	62	C	++	+++	-	-	-	++
19	L.L	19	Ap	Typic Haploxererts	3.60	29.4	1.1	39.6	3.9	7.3	26	SL	++	+++	-	-	-	++
20	A.F	20	Bkss		5.43	24.9	1.2	43.6	2.6	7.6	41	C	+++	+++	-	-	-	-
21	P.P	21	Ap	Calci Ustorthents	0.77	14.9	0.5	47.1	1.4	7.9	38	SCL	+++	+++	-	-	-	+
22	P.P	22	Ck		0.32	13.4	1.0	49.5	0.7	8.0	40	C	++	+++	-	-	-	+
23	P.P	23	Ap	Aquic Haploustepts	2.17	19.2	0.6	55.2	2.8	7.4	42	SC	++	+++	++	-	-	++
24	P.P	24	Bkg1		0.34	17.8	0.6	57.4	0.8	7.2	48	SC	++	+++	+++	+	-	+++
25	P.P	25	Ap	Calcic Haploustafls	0.93	19.2	0.5	57.0	1.7	7.9	44	SC	+++++	+++	-	-	-	-
26	L.L	26	Btkg		1.01	17.8	0.6	55.0	0.4	8.2	54	C	+++++	+++	-	-	-	-
27	L.L	27	Ap	Aquic Calcistepts	1.40	19.2	1.1	59.4	0.7	7.0	40	SC	+++	+++	-	-	-	-
28	L.L	28	Bw		0.55	15.1	0.5	62.6	0.5	7.6	33	CL	+++	+++	-	-	-	-
29	L.L	29	Ap	Aquic Calcistepts	1.01	19.2	0.6	56.7	0.8	7.7	48	SC	++	+++	+++	-	-	-
30	L.L	30	Bkg		1.28	16.4	0.6	52.2	0.2	8.1	42	C	+	+++	+++	-	-	-

\* Alluvial fans, AF; Piedmont plains, P.P, Lowlands, L.L.

\*\* Sme, smectite; Ill, illite; Chl, chlorite; Ver, vermiculite; Kao, kaolinite; Pal, palygorskite; -, trace or not detected. +, content <15%; ++, content in the range of 15%–30%; +++, content in the range of 30%–50%; ++++, content >50%.

bonate inhibited the soils evolution. Among the soil-forming factors, the topography and climate have imposed the largest impacts on the soil particle size distribution, type and distribution of OM, type of diagnostic horizons, and degree of profile evolution. Table 1 presents physical and chemical properties of the studied soils. According to the table, the pH in the studied soils was in the neutral and weak alkaline range (7 to 8.4), with the highest pH values observed in the soils of the aridic moisture regime. The highest electrical conductivity (EC) values were observed in dry lands across the piedmont plains and lowland physiographic units. The studied soils were calcareous with  $\text{CaCO}_3$  contents in the range of 9.9 to 74.3% (mean 47.8% in surface soils and 52.6% in subsurface soils). The highest contents of  $\text{CaCO}_3$  were associated with the Aridisols developed under aridic moisture regime. The organic carbon content of the soil samples ranged from 0.1% to 5.2%. The highest OM content was measured in the surface horizons dominated by the xeric moisture regime, while the lowest OM content was found in the soils taken from arid regions. On average, the OM constituted 1.4 and 0.7% of the surface and subsurface soils, respectively. A study of the particle size distribution indicated a heavier soil texture as one moved from more arid parts of the study area to more humid parts. The clay content of the soil varied from 8 to 62% across the study area. On average, lower clay contents were observed in the Aridisols, while the samples taken from Inceptisols and Alfisols orders that were dominated by a xeric regime exhibited higher clay contents. Across the study area, the CEC changed from 5.2  $\text{cmol}(+) \text{kg}^{-1}$  in the soil of Aridisols order dominated by aridic regime to 29.4  $\text{cmol}(+) \text{kg}^{-1}$  for the soil of Vertisols order under xeric moisture regime.

#### *Clay Fraction Mineralogy*

X-ray diffraction analysis was performed to evaluate the clay fraction ( $<0.002 \text{ mm}$ ) in surface and subsurface soils, with the results presented in Table 1. The semi-quantitative analysis of clay fraction showed that the most important minerals in the clay fraction of the soils included illite, chlorite, smectite, and palygorskite, with trace amounts of vermiculite, kaolinite, quartz, and mixed minerals further detected. Illite was the most abundant mineral in all studied soil samples. Its wide availability and increasing content with depth in most profiles and the abundance in parent materials of the soil suggest that significant part the illite in the studied soils was of a hereditary origin and due to the presence of some of illite in the surface horizons; the process of illitization also seems probable. The highest amount of illite was observed in the P.P followed by A.F and L.L units. Smectite was the second dominant mineral in the clay fraction of the studied soil samples, constituting 10 to 45% (average: 24%) of the surface soils and 14 to 48% (average: 28%) of the subsurface soils. The smectite was seemingly come from different

sources depending on the weather conditions, the parent materials, and the physiography of the studied soil. Based on the results of the semi-quantitative analysis of the clay minerals, the amount of smectite was negligible in younger soil samples with no profile development. The presence of this mineral in the parent materials of the studied soils indicated that this mineral was inherited from the parent material. It was also observed that the content of this mineral increases with the soil development (Alfisol), demonstrating the pedogenesis of this mineral. Smectite content was highest in P. P followed by L.L, and A.F units. On the other hand, the content of this mineral was increased across the lands of inappropriate drainage conditions (lowlands in humid areas) or shallow groundwater levels. This might be attributed to the pedogenesis of this mineral from chlorite and mica, as confirmed by the reduction of these minerals across the studied area, or to neof ormation of soil solution, a proof of which is the contents of carbonated and Mg- and Ca-rich groundwater across these lands. Following the smectite, the chlorite and palygorskite minerals were the most abundant minerals in the clay fraction of surface and subsurface soils of the studied areas, comprising 21% and 11% of the clay fraction, respectively. On average, 13% and 16% of the surface and subsurface horizons were composed of palygorskite, respectively, with the highest levels observed in drier areas (mostly in pedons 1 to 5) and negligible levels in more humid areas. Only small amounts of vermiculite were found in the soil pedons 8, 9 and 10, with the other pedons exhibiting no amount of this mineral. Given the soil condition, the vermiculite is probably of an inheritance source. The illite and chlorite existed in all soil samples though at different contents. Some soil samples showed small amounts of kaolinite, with its average content being generally below 1%. The chlorite and kaolinite contents of the soils across the study area are of inherited origins, resembling the soils covering other southern parts of Iran. Azadi et al [2] reported the presence of chlorite, illite and kaolinite in the soils of arid areas and considered the hereditary origin as the main cause of their presence in the soil. Mixed minerals (i.e., illite-smectite and chlorite-smectite mixtures) constituted a small portion of the clay fraction (~1%). Najafi and Abtahi [22], Owliaie et al. [26], and Shakeri and Abtahi [32] reported similar results for calcareous soils in southern Iran. To sum up, based on their contents in the surface and subsurface horizons, the clay minerals were sorted in the following order illite > smectite > chlorite > palygorskite > vermiculite > kaolinite.

#### *Potassium Forms*

**Water-soluble and exchangeable K.** The water-soluble (or simply soluble) K is the form that can be absorbed by microorganisms and plants. Any form of K in the soil must be converted to a solution before it

**Table 2.** Amounts of different K forms and cumulative non-exchangeable K released in different media of extraction in representative Pedons

Pedon	Soluble K, mg/kg		Exchangeable K, mg/kg		Non-exchangeable K, mg/kg		Structural K, mg/kg		Cumulative non-exchangeable K			
	topsoil	subsoil	topsoil	subsoil	topsoil	subsoil	topsoil	subsoil	0.01 M CaCl <sub>2</sub>		0.01 M Oxalic acid	
									topsoil	subsoil	topsoil	subsoil
1	1.72	2.63	175.31	182.50	536.09	559.64	5221.46	5795.01	117	113	105	99
2	10.67	3.12	303.09	248.97	732.74	776.85	6414.02	6891.23	170	161	124	103
3	4.62	1.47	327.29	143.71	679.57	713.33	6000.86	4419.26	148	152	142	145
4	3.57	2.32	197.95	127.29	511.59	460.63	4230.35	4972.55	110	103	87	82
5	2.09	3.03	93.174	126.58	551.87	647.19	4949.54	4901.64	104	98	91	86
6	3.37	0.88	564.18	312.88	1431.53	894.99	13109.92	8446.65	212	198	185	179
7	3.06	1.72	423.08	312.04	876.02	732.74	11559.65	8581.35	180	171	160	155
8	9.45	2.90	792.61	502.85	1446.14	1131.52	12861.16	15836.65	286	241	233	211
9	3.52	1.30	141.66	128.31	415.28	219.42	3792.00	3692.99	113	102	95	88
10	37.11	4.10	605.98	172.92	973.72	489.31	7537.98	5012.10	253	192	209	186
11	1.60	0.49	224.94	144.69	246.81	505.75	6288.03	5802.03	135	134	131	127
12	11.61	0.52	284.24	144.66	480.94	445.06	5337.38	5862.72	160	153	143	133
13	5.28	0.84	255.45	121.07	452.38	380.11	5437.27	5648.37	153	144	137	129
14	3.41	2.65	389.36	198.87	566.87	403.75	5311.07	5189.75	221	217	190	177
15	0.87	0.82	225.99	125.97	566.08	493.61	4769.84	6646.65	153	145	123	117
Mean	6.80	1.92	333.62	199.55	697.84	590.26	6574.70	6513.26	168	155	144	135
Min	0.87	0.49	93.174	121.07	246.81	219.42	3792.00	3692.99	104	98	87	82
Max	37.11	4.1	792.61	502.85	1446.14	1131.52	13109.92	15836.65	286	241	233	211

can be taken up by a plant. This indicates the importance of soluble K in plant nutrition [9]. As can be seen in Table 2, amount of soluble K contents ranged within 0.87–37.11 mg kg<sup>-1</sup> and 0.49–4.1 mg kg<sup>-1</sup> in surface and subsurface horizons, respectively. The maximum value of soluble K was observed in the surface soil covering the lowlands dominated by the xeric moisture regime, and the minimum value was seen in the subsurface soil covering the piedmont alluvial plains dominated by ustic moisture regime (Higher values of water-soluble K were observed for L.L followed by P.P and A.F units). The higher levels of soluble K in the surface soils could be attributed to the transfer of soluble salts, including K, from the depth to the surface as a result of evaporation of the irrigation and precipitation moisture, greater weathering of K-bearing minerals on the surface, higher levels of OM on the surface, K uptake by the plant roots from depth and its release to the surface upon the plant depth, and application of chemical fertilizers to the soil surface [22]. In their study on the soils of southern Iran, Najafi Ghiri et al. [23] obtained high levels of soluble K in the soils of arid areas dominated by aridic moisture regime, hyperthermic temperature regime and lowland soils. Despite this, in the end, not significant difference was observed between different units and moisture regimes (Fig. 2). The soluble K form has found to be significantly

associated with OM content (0.522\*\*), exchangeable K form (0.503\*\*) and non-exchangeable K form (0.291\*\*), but with neither structural K form nor other physico-chemical properties of the soil. In general, a very small part of the total K of the studied soil samples (~0.1%) was composed of soluble K in both surface and subsurface horizons.

The exchangeable form of K can be easily used by the plant, exchanged with other cations, electrostatically bonded with OM and clay mineral surfaces. In the studied soil samples, the contents of exchangeable K ranged within 93.174–792.61 and 121.07–502.85 mg kg<sup>-1</sup> for surface and subsurface horizons, respectively, comprising a total of 4.2% and 2.7% of the total K content in the surface and subsurface soils, respectively (2.9% on average). The highest amount of exchangeable K was observed in surface horizons of profile 8 (Alfisol, 791.62 mg kg<sup>-1</sup>, on average). These surface horizons contained large amounts of OM and smectite. The lowest amount of exchangeable K was observed in profile 5 (Aridisols, lowlands). In their studies, Shakeri et al. [31] observed the lowest amount of exchangeable K in the soils that were dominantly composed of illite, chlorite, and palygorskite, which is consistent with the mineralogical results of the Aridisol soil in this study. Regarding the effect of physiographic units on the distribution of exchangeable potassium forms,

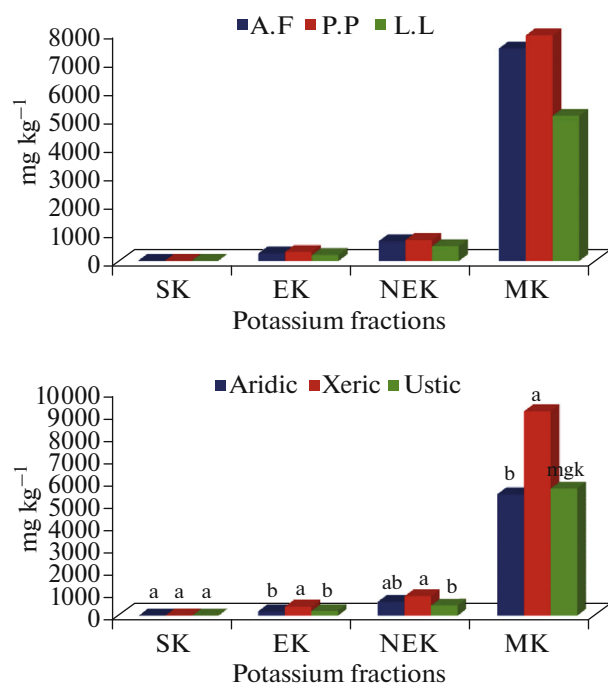


Fig. 2. Potassium fractions for various physiographic units and soil moisture regimes.

its higher values were observed in the P.P followed by A.F and L.L physiographic units (Fig. 2). The P.P unit in xeric moisture regime has more exchangeable potassium due to its high clay content and high levels of illite and smectite. Based on the findings, the CEC and the contents of  $\text{CaCO}_3$ , clay, illite, smectite, and vermiculite were significantly correlated to the content of the exchangeable K at 0.491\*, 0.729\*\*, 0.384\*, 0.449\*, 0.445\*\* and 0.534\*, respectively, in all pedons and horizons. No significant relationship was observed between the OM content and the content of exchangeable K in the studied soil samples. This highlighted the more important role of the clay fraction composition rather than the OM content in the retaining of this form of K in the studied soils. Sinha and Biswas [34] reported that soluble, exchangeable and non-exchangeable K forms have significant positive relationships with the clay content and CEC in the soils of western Bengal, India.

**Non-exchangeable and structural potassium.** Non-exchangeable K provides a major source of K for plants. The content of non-exchangeable K can be calculated by subtracting the exchangeable K content extracted by 1 M  $\text{NH}_4\text{OAc}$  solution from the experimentally extracted amount of K by nitric acid. Non-exchangeable K is somehow different from structural (mineral) K [36]. The content of non-exchangeable K changed within 246.81–1446.14 and 219.42–1131.52  $\text{mg kg}^{-1}$  in the surface and subsurface horizons, respectively, making up 8.9% and 8.3% of the

total K in the surface and subsurface soils, respectively. The highest levels of available (soluble and exchangeable forms) and non-exchangeable K forms were observed under the xeric moisture regime. The results showed that, like the exchangeable K, the content of this form of K was higher in the surface soils rather than the subsurface horizons. The highest amount of non-exchangeable K form (1446.14  $\text{mg kg}^{-1}$ ) was observed in the surface soil of the Alfisols order, and the lowest level was associated with the Inceptisols order. In their study on the soils covering Fars Province, Azadi et al. [1] stated that, except for the soluble K form, all K forms were maximal in more evolved soils of Alfisol with smectite and illite as dominant minerals. They further reported significant relationships among all forms of K, except the soluble K form, with illite as the predominant mineral. Raheb and Heidari [27] found that, due to the temperature and moisture conditions that favored the weathering of the primary minerals, the levels of exchangeable and non-exchangeable K forms in the surface soil were higher than those of the in-depth soil. Hosseinpour and Kavusi [9] suggested that the content of non-exchangeable K level was seemingly higher in heavy-texture soils (with higher clay contents) that were predominantly composed of smectite. Despite that P.P units had highest NEK, but no significant difference was observed between the physiographic units, while the xeric moisture regime contained the highest amount NEK between three moisture regimes (Fig. 2).

In all samples, the content of non-exchangeable K form exhibited significant correlations to CEC (0.354\*),  $\text{CaCO}_3$  (−0.788\*\*), clay content (0.474\*\*), smectite (0.481\*\*), illite (0.492\*\*) and vermiculite (0.534\*\*). The significant positive relationship between the clay content and the non-exchangeable K form in all soils shows the importance of the clay content in the content of this form of K [1, 31].

Structural K, which is found in the structure of K-bearing minerals such as mica and feldspar, is unavailable for the plant. However, by means of weathering, it can be converted to other forms of K that can be taken up by the plant in long run. On average, some 90% of total K in the studied soil samples from the surface and subsurface horizons was composed of structural K, indicating limited weathering of the soils of arid and semi-arid areas that led to higher content of hereditary illite and lower profile evolution. However, the contribution of the structural K form decreased in humid areas, indicating greater shares of exchangeable and non-exchangeable K forms due to further conversion of the illite to smectite and vermiculite. The surface and subsurface horizons contained exchangeable K form in the ranges of 30.35–13109.92 (mean: 6574.7) and 3692.99–15836.65  $\text{mg kg}^{-1}$ , respectively (Table 2), forming 86.8 to 88.9% of total K. As can be seen, the level of structural K in the surface horizons was less than that in subsurface ones. Environ-

**Table 3.** Pearson correlation coefficients between soil K forms, clay minerals and physical-chemical properties

Indicator	Ksol	Kexc	Knon	Kstr	CEC	CCE	OC	Clay	Ill	Sme	Ver
Ksol	1										
Kexc	0.503**	1									
Knon	0.291*	0.813**	1								
Kstr	0.127	0.758**	0.812**	1							
CEC	0.084	0.491**	0.354*	0.602**	1						
CCE	-0.164	-0.729**	-0.788**	-0.872**	-0.652**	1					
OC	0.522**	0.272	0.033	-0.004	0.552**	-0.142	1				
Clay	0.253	0.384*	0.474**	0.472**	0.437*	-0.455*	0.201	1			
Ill	0.200	0.449*	0.492**	0.664**	0.339	-0.548**	0.571**	0.531**	1		
Sme	0.057	0.445*	0.481**	0.612**	0.408*	-0.539**	0.343	0.677**	0.377*	1	
Ver	0.149	0.543**	0.534**	0.616**	0.312	-0.717**	0.268	0.468**	0.355*	0.753**	1
Sme + Ver	0.111	0.575**	0.612**	0.699**	0.454*	-0.655**	0.372*	0.578**	0.371*	0.840**	0.871**

Significance at  $P < 0.05$  level; \*\*, significance at  $P < 0.01$  level. Sol, soluble K; Exc, exchangeable K; Non-exc, non-exchangeable K; Str, structural K; CEC, cation exchangeable capacity; OC, organic carbon; CCE, calcium carbonate equivalent; Ill, illite; Sme, smectite; Ver, vermiculite.

mental conditions at surface (seasonal day-night temperature difference, higher moisture due to precipitation and irrigation, and microorganism activities) contribute to instability and weathering of minerals in the soil surface. As a result, more K ions are removed from primary and secondary minerals at surface. This has further led to the conversion of the structural K into exchangeable and non-exchangeable forms in surface horizons [31]. The highest level of structural K (15837 mg kg<sup>-1</sup>) was observed in pedon 8 (Alfisols, dominated by the xeric moisture regime). Like the NEK, this form of potassium, considering that it contained the highest amount in the P.P unit, but there was no significant difference between the studied units, but in examining the effect of moisture regime on Distribution of potassium fractions, xeric moisture regime also contained the highest amount (Fig. 2). As shown in Table 3, all around the study area, the structural K form content was significantly correlated to exchangeable K (0.758\*\*), non-exchangeable K (0.812\*\*), CEC (0.602\*\*), CaCO<sub>3</sub> (-0.872\*\*), clay content (0.472\*\*), illite (0.664\*), smectite 0.612\*\*), vermiculite (0.616\*\*), and total of smectite and vermiculite (0.699\*). These results suggest that the highly layered loads of smectite, vermiculite, and illite play important roles in the content of structural K in the studied soils. Sharma et al. [33] reported that all different forms of K are directly associated with the clay and silt contents and indirectly related to the sand content. The reason for the negative correlation of K forms to the contents of CaCO<sub>3</sub> and sand is the mass storage of K in the form of clay and the decrease in the K form content with increasing the sand content. In line with the results reported by Nabiollahi et al. [21], positive significant correlations were obtained between the contents of

different K forms in this study (Table 3), indicating some dynamic equilibrium among the forms [25].

*Kinetic Modeling of K Release  
(with CaCl<sub>2</sub> and Oxalic Acid as Extractants)*

The pattern of successive extraction of K from some representative soil samples using CaCl<sub>2</sub> and oxalic acid as extractants is plotted in Fig. 3. The release was initially rapid followed by a slower trend. The trend of the cumulative K release was non-linear and almost similar with the two extractants. The results showed that the maximum content of non-exchangeable K (1446.14 mg kg<sup>-1</sup> of soil) was found in the surface horizon of Alfisols (pedon 8) with a high clay content (29%) and relatively low calcium carbonate content (mean = 15.4%), whereas the minimum content of non-exchangeable K (82 mg kg<sup>-1</sup> of soil) was measured in the subsoil of Aridisols (pedon 4) with a low clay content (8%) and high calcium carbonate content (66.4%). With both extractants, the release rate of non-exchangeable K was higher in surface soil rather than the subsurface soil (Table 2). CaCl<sub>2</sub> and oxalic acid released more non-exchangeable K in the surface soil (24%) rather than the subsurface soil (21%) (Table 2). The trend of K release was characterized by an initial fast reaction (2–164 h), followed by a slow reaction (164–1200 h), showing different mechanisms controlling the K release process (Fig. 3). Using CaCl<sub>2</sub> and oxalic acid as extractant, one could release K at 104–286 mg kg<sup>-1</sup>(mean = 168 mg kg<sup>-1</sup>) and 87–233 mg kg<sup>-1</sup>(mean = 155 mg kg<sup>-1</sup>) from the surface soil samples and at 98–241 mg kg<sup>-1</sup> (mean = 155 mg kg<sup>-1</sup>) and 82–211 mg kg<sup>-1</sup> (mean = 135 mg kg<sup>-1</sup>) from the subsurface soil samples, respectively (Table 2). The results indicate that cumulative K release varied



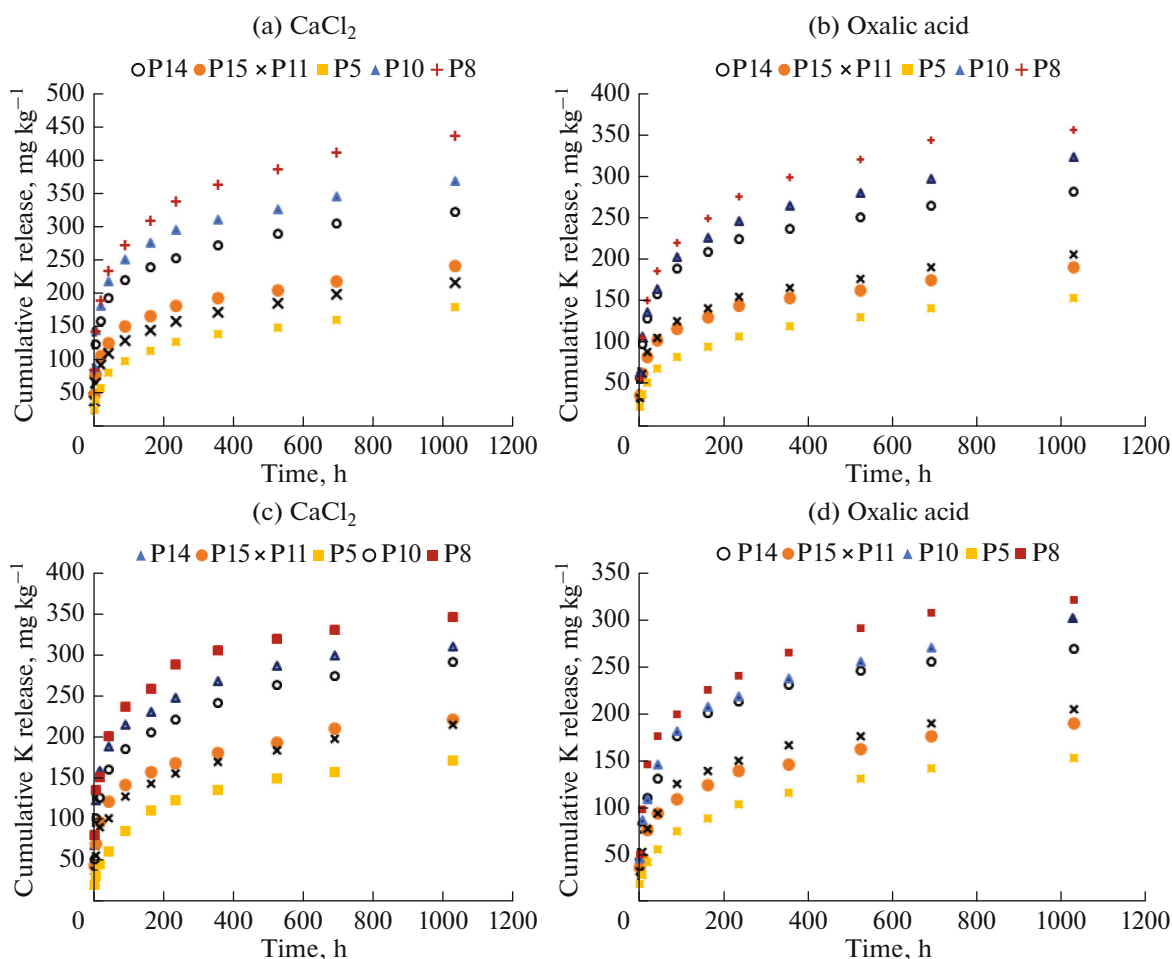


Fig. 3. The trend of cumulative K release by  $\text{CaCl}_2$  and oxalic acid for selected (a, b) topsoils and (c, d) subsoils.

greatly between the different physiographic unit and moisture regimes. The highest values of the percentage of nonexchangeable K released were attributed to P.P unit and xeric moisture regime (Fig. 4), In spite of containing a larger amount of illite, NEK and clay content (Table 1). Therefore, it can be stated that the process of NEK release with both extractants in addition to some important factor such as clay mineralogy (mica content), soil development and soil depth has been affected by moisture condition and physiographic position. Rezapour et al. [28], presented that Plateau and Piedmont plains which occurred on a more stable landform position had a higher content of all forms of K along with clay. Different mathematical models were tested to describe the kinetics of non-exchangeable K release with  $\text{CaCl}_2$  and oxalic acid as extractants over 1200 h. Statistical analysis was performed by fitting the experimental data to kinetic models and evaluating the coefficients of determination ( $R^2$ ) and standard error of estimation (SE) (Table 4, Fig. 3). Identified by the highest  $R^2$  values, the best fits for surface and subsurface soils were obtained by

applying the Elovich and power function equations, respectively.

Mousavi et al. [20] referred to the power function equation as the best equation for modeling the K release with  $\text{CaCl}_2$  and organic extractants such as oxalic and citric acids. Shakeri et al. [32] reported the power function, first-order and Elovich equations as the best ones for several selected soils in Kohgiluyeh and Boyer-Ahmad Province, Iran. Among other equations that were used to justify the K release (the power function, Elovich, and the first-order equations) with either extractant, the first-order equation returned the lowest initial rate of non-exchangeable K release (a), possibly because it provided fewer initially available K ions for the plant. At the other end of spectrum, the power function equation had the highest value of the initial release rate (a), indicating abundant available of K to the plant in the initial stage of release. Comparing the average K release rate (slope of equations) with both  $\text{CaCl}_2$  and  $\text{C}_2\text{H}_2\text{O}_4$  extractants, the Elovich and first-order equations set the scene for the highest and lowest K release rates, respectively. The Elovich and first-order equations were expected to

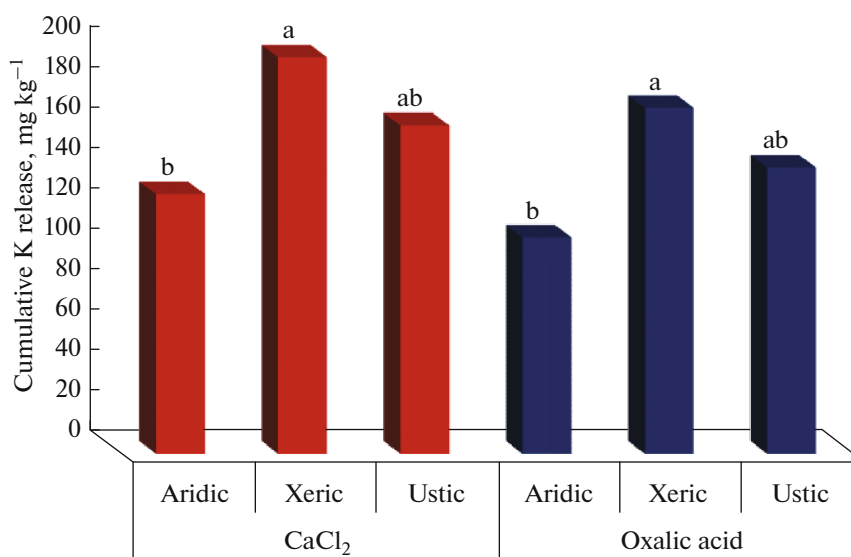


Fig. 4. Potassium released in various physiographic units and soil moisture regimes.

provide for the highest and lowest release rates (b), respectively, compared to other equations considered herein. The highest and lowest K release rates for the power function, Elovich, and the first-order equations were related to the Alfisol (soil profile 8) and the Aridisol (soil profile 5) orders, respectively. The correlation coefficients obtained with the selected equations, soil properties, and clay mineralogy with both CaCl<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> extractants are given in Table 5, respectively. When CaCl<sub>2</sub> was used as extractant, the release rates estimated by the power function equation were significantly correlated to a number of chemical and physico-chemical properties, including non-exchangeable K, clay content, CaCO<sub>3</sub> content, and the contents of illite and smectite content. When the Elovich equation was used instead of the power function, the release rate was significantly correlated to the

clay content, CEC, and the contents of illite and smectite (Table 5).

Due to the dilution effect, the release of the K from soils with CaCl<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> as extractants showed a significant negative correlation to the content of CaCO<sub>3</sub> at  $R = -0.472^{**}$  and  $R = -0.493^{**}$ , respectively, and significant positive correlations to non-exchangeable K, OM, CEC, and the contents of illite and smectite at (0.381\*, 0.366\*\*, 0.432\*, 0.557\*\*, 0.674\*\*) and (0.541\*\*, 0.272\*, 0.479\*, 0.566\*\*, 0.694\*\*), respectively. The results indicated that the clay composition, content, and particle size impose significant effects on the K release rate, so that the samples hosting the K release at the highest rates involved more amounts of smectite-bearing clay than the other samples. The smectite forms 2 : 1 clay with high CEC values and variable inter-layer spacing. Indeed, an isomorphic substitution induced a permanent negative charge on

Table 4. Coefficient of determination, R<sup>2</sup>, standard error of the estimates, SE, and a and b constants describing the kinetics of non-exchangeable K for soils

Indicator	Elovich				First order				Parabolic				powerfunction			
	A	b	R <sup>2</sup>	SE	a	b	R <sup>2</sup>	SE	a	b	R <sup>2</sup>	SE	a	b	R <sup>2</sup>	SE
CaCl <sub>2</sub> , 0.01 M																
Mean	15.54	33.57	0.98	7.49	5.21	0.004	0.92	0.44	81.38	6.39	0.92	20.56	49.26	0.26	0.98	0.07
Max	50.16	52.29	0.99	11.56	5.71	0.005	0.96	0.52	139.45	10.74	0.94	36.23	87.08	0.33	0.99	0.08
Min	-10.83	22.33	0.97	2.46	4.82	0.004	0.89	0.33	36.79	4.27	0.88	11.85	20.04	0.22	0.97	0.04
Oxalic acid, 0.01 M																
Mean	5.83	30.73	0.98	7.48	5.12	0.004	0.92	0.43	64.56	5.63	0.92	18.09	37.22	0.28	0.98	0.08
Max	23.55	50.33	0.99	10.86	5.66	0.005	0.96	0.54	101.22	9.48	0.95	30.54	60.41	0.32	0.99	0.11
Min	-8.39	20.35	0.97	3.86	4.72	0.004	0.87	0.31	32.98	3.88	0.88	10.12	19.07	0.23	0.91	0.06

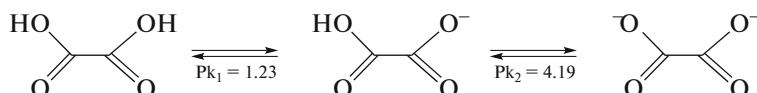
**Table 5.** Relationship between constant b values of kinetic models and cumulative K release, CaCl<sub>2</sub> and Oxalic acid, with clay mineralogy and some soil properties

Parameter,	Sme	Ver	Ill	Exc	Non-exc	Str	Clay	OC	CCE	CEC	bf	bp	be	Release
CaCl <sub>2</sub> , 0.01 M														
Sme	1													
Ver	0.753**	1												
Ill	0.777**	0.755**	1											
Exc	0.445*	0.543**	0.449*	1										
Non-exc	0.481**	0.534**	0.492**	0.853**	1									
Str	0.612**	0.616**	0.664**	0.722**	0.597**	1								
Clay	0.677**	0.468**	0.531**	0.384*	0.474**	0.472**	1							
OC	0.343	0.268	0.571**	0.138	0.010	0.299	0.201	1						
CCE	-0.539**	-0.717**	-0.548**	-0.692**	-0.637**	-0.723**	-0.0455*	-0.058	1					
CEC	0.408*	0.312	0.339	0.586**	0.534**	0.648**	0.437*	-0.098	-0.492**	1				
bf	0.139	-0.030	-0.026	0.088	0.172	-0.106	0.084	-0.067	-0.021	0.137	1			
bp	0.490**	0.474**	0.394*	0.846**	0.754**	0.753**	0.344	0.099	-0.642**	0.733**	0.183	1		
be	0.567**	0.384*	0.517**	0.499**	0.567**	0.502**	0.686**	0.252	-0.401*	0.309	0.251	0.557**	1	
Release	0.674**	0.428*	0.557**	0.326	0.381*	0.537**	0.612**	0.366*	-0.472**	0.432*	-0.161	0.460*	0.509**	1
Oxalic acid, 0.01 M														
Sme	1													
Ver	0.753**	1												
Ill	0.777**	0.755**	1											
Exc	0.445*	0.543**	0.449*	1										
Non-exc	0.481**	0.534**	0.492**	0.853**	1									
Str	0.612**	0.616**	0.664**	0.722**	0.597**	1								
Clay	0.677**	0.468**	0.531**	0.384*	0.474**	0.472**	1							
OC	0.343	0.268	0.571**	0.138	0.010	0.299	0.201	1						
CCE	-0.539**	-0.717**	-0.548**	-0.692**	-0.637**	-0.723**	-0.455*	-0.058	1					
CEC	0.408*	0.312	0.339	0.586**	0.534**	0.648**	0.437*	-0.098	-0.492**	1				
bf	0.139	-0.030	-0.026	0.088	0.172	-0.106	0.084	-0.067	-0.021	0.137	1			
bp	0.456*	0.461*	0.398*	0.789**	0.701**	0.670**	0.297	0.025	-0.575**	0.722**	0.339	1		
be	0.322	0.259	0.369*	0.239	0.331*	0.270	0.563**	0.179	-0.315*	0.306*	-0.169	0.244	1	
Release	0.694**	0.462*	0.566**	0.488**	0.541**	0.526**	0.615**	0.272*	-0.493**	0.479**	0.085	0.482**	0.509**	1

Significance at  $P < 0.05$  level: \*\*, significance at  $P < 0.01$  level; Exc, exchangeable K; Non-exc, non-exchangeable K; Str, structural K; CEC, cation exchangeable capacity; OC, organic carbon; CCE, calcium carbonate equivalent; Ill, illite; Sme, smectite; Ver, vermiculite; bf, first order; bp, power function; be, clovich equations

these clays, with the charge being neutralized by cations such as K. Due to their expandability and lower layer charge (especially in low-layer charge smectites), the smectite easily releases inter-layer K. Srinivasarao et al. [38] reported that the higher rate of non-exchangeable K release in soils dominated by smectite indicates the facilitation of the K release by the natural expansion of smectite on the edge of the mineral and wedged areas. The high correlation of OM content to the K release according to Elovich's equation could be linked to the mineral degradation and conversion (e.g., illite to smectite) under the effect of the OM. Comparing the non-exchangeable K release rate

between organic and inorganic extractants, the results showed lower non-exchangeable K release by  $C_2H_2O_4$  rather than  $CaCl_2$  in almost all samples. Shakeri and Abtahi [31] obtained similar results, and stated that the  $C_2H_2O_4$  occurs in the form of non-separated molecules at pH values below 3.5; accordingly, one of the hydrogens of the hydroxyl group is released at a pH between 3.5 and 4.5 and both hydrogens are released at pH values beyond 4.5, where negative free charges will become available for absorbing such cations as K, Ca and Na.



With  $C_2H_2O_4$  as extractant, the non-exchangeable K may be released through either mineral destruction or ion exchange [31]. The  $CaCO_3$  of the soil was high in the study area. Since the solubility constant of  $CaCO_3$  is higher than that of calcium oxalate, the soil contained large amounts of Ca for a given amount of hydroxyl ion. As a result, the hydrogen released from the  $C_2H_2O_4$ , which likely destroys the minerals in acidic soils, is used to neutralize the hydroxyl ions of the soil instead of attacking the minerals. The Ca in the soil solution forms calcium oxalate deposits with  $CaC_2O_4$  ions and prevents the reaction of K with oxalate. Since calcareous soils are rich in Ca ions and have a high buffering capacity, they cancel out the effect of the oxalic acid on minerals and release less K than both the acidic soils and soils with less  $CaCO_3$  contents. High buffering capacity of the soil contributes to lower K release in the soils of higher OM and  $CaCO_3$  contents, as compared to other soils [32, 41]. Comparing the two extractants (i.e.,  $CaCl_2$  and  $C_2H_2O_4$ ), Jalali and Zarabi [11] stated that  $C_2H_2O_4$  provides for higher K release rates, possibly due to the lower availability of  $CaCO_3$  in the studied soils (about 5–20%). Mousavi et al. [20] compared  $CaCl_2$  with organic extractants including  $C_2H_2O_4$  and citric acid ( $C_6H_8O_7$ ) on pure feldspar and muscovite minerals. They concluded that the organic acids tended to release the K at a 2.5–3 times faster rate than the  $CaCl_2$ . This may be attributed to the use of pure minerals instead of soil.  $C_2H_2O_4$  has been able to easily release K by destroying or replacing the minerals in absence of disturbing ions such as Calcium (Ca).

## CONCLUSIONS

Based on the results, the contents of all forms of K other than the soluble K form were found to be significantly correlated to the contents of illite, smectite,

CEC, clay content and inverse associations with the  $CaCO_3$  content. Also, the results showed that, in addition to mineralogical composition and soil physico-chemical properties such as the soil cation exchange capacity, calcium carbonate equivalent and particle size distribution, other factors such as moisture regime, soil order and physiographic units can affect the K distribution through the soil. Due to the similarity of the parent material in all three regions, two factors include: topography and climate, are effective in the amount of different forms of potassium. As shown in Table 2, the amount of different forms of potassium in the xeric moisture regime (pedons 6 to 10) is higher than in other regions. Therefore, climate is the most effective factor in determining potassium forms. However, in each region where the climate conditions are constant, different amounts of potassium are different in different physiographic units (geographical units). Therefore, with study the relationship between clay mineralogy and potassium forms in different soil moisture regimes and physiographic unit and the processes and mechanisms of potassium release we can apply controlled management and finally we expect to increase efficiency and productivity. on the other hand, Various factors affect the distribution of potassium (K) forms in calcareous soils. Knowledge of the presence and distribution of different forms of K in the soil can help optimize the application of the K fertilizers in terms of dosage and management procedure.

## CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

## FUNDING

This research did not receive any specific funding.

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