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Distribution of phosphorus and the effect of physicochemical properties and clay minerals on phosphorus release in some calcareous soils

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ABSTRACT- Phosphorus (P) is a nutrient essential for plant, which its availability in soils changes with aging process, leaching, precipitation processes, and the landform change. There is limited information available on kinetics release of P in calcareous soils. Therefore, the purpose of this study was to investigate distribution of P and the effect of physicochemical properties and clay minerals on its release in some dominant orders of the calcareous soils in Kohgiluyeh-and-Boyer-Ahmad province, using the 0.01 M calcium chloride ($CaCl_2$) extractant. The results showed that the P released rapidly from the soil and continued slowly. After 72 h, the amount of P released in the studied soils ranged between 3.2 and 25.4 mg kg^{-1}. Evaluation of the fitted different equations on P released in the studied soils revealed that the Simple Elovich and power function equations could well predict the P release process in the studied soils. The results of the correlation between soil properties and released P contents showed that P release coefficients (including the slope and intercept in the Simple Elovich equation) have a significant negative relationship with the amount of smectite and vermiculite minerals. Also, the release coefficient of the parabolic diffusion equation had a significant negative relationship with pH and the amount of illite and palygorskite minerals.

INTRODUCTION

Phosphorus (P) is one of the essential elements for the plant and consider as the most limiting element after nitrogen (N) in terms of crop production (Waldrip-Dail, et al. 2009). The supply rate of P to the plant is important from the plant nutrition viewpoint. P fertilizers could not be spread on the soil surface or fertigated to the root zone. If this is done, the given P will be fixed in the topsoil and will not reach the root zone. Due to the low solubility and movement of P in the soil, the P fertilizers should be applied to the soil before planting and placed directly in the root development area.

Due to the presence of various minerals and complex compounds in soil environment, investigating of the reaction rate and conducting the kinetic studies in soil are relatively more difficult than those in the systems containing a specific mineral. Therefore, little studies have been conducted on the soil environment. Understanding the kinetics of P release from soil can be important to reduce the P leaching into the runoff and groundwater (Sharpley, 1981). The low concentration of P in soils is due to the strong reactions with a number of organic and inorganic solid phases and the slow rate of many P release reactions. Therefore, in order to determine the available P changes in the soil, it is important to study the P sorption and release reactions over time. The balance between the P levels of soil in agriculture and its safe levels in the environment is essential. In this regard, the farmer's knowledge of the rate and capacity of the soil P release is important, as it represents the available P of the plant (Elkhatib and Hern, 1988).

In calcareous soils, awareness of soil properties and phosphorus fractions and their relationships are important for evaluation of phosphorous status in soil and understanding of soil chemistry that influences soil fertility (Azadi et al, 2016). The P release from the soil colloids is one of the processes that controls its sorption by roots and affecting the plant growth. Therefore, the kinetic study of P release from soil is a great tool to investigate the release process. Various extractants have been used to study the P release. The extraction of P in soils with bicarbonate was introduced in 1954 (Olsen *et al*., 1954). In later years, the extraction with resin was used by Amer et al. (1955), Cooke and Hislop (1963) and Agbenin et al. (2001). Several studies have been conducted using these methods over years. Furthermore, Freese et al. (1995) used the dialysis membrane tube impregnated in ferric oxide (Fe_2O_3) and hydrous ferric oxide (HFO) as a P sink with an unlimited sorption capacity. The $CaCl_2$ extractant was then used by researchers. The extraction method using the 0.01 molar (M) $CaCl_2$ has also been employed in calcareous soils by Jafari et al. (2008), Shariatmadari et al. (2006), Jalali and Peikam (2013) and Azadi and Baghernejad (2019). Younessi et al. (2010) introduced the parabolic and exponential function models as the appropriate ones using $CaCl_2$ extractant during 72 h. Jafari et al. (2008) and Shariatmadari et al. (2006) introduced the Elovich and simple Elovich models as the best equations for fitting the P release kinetic data. In a study on some calcareous soils, Azadi and Baghernejad (2019) reported that the P release kinetic data was better explained by the simple Elovich equation and the power function and first-order equations with the time-dependent P release data were fitted.

The climate and parent material variations, different heights and vegetation types in different regions of Kohgiluyeh-and-Boyer-Ahmad province have generated different soils with various properties. Except for limited and regional researches, no comprehensive researches have yet been conducted on the P release in this region (with calcareous soils). Therefore, this study aimed to investigate the application of kinetic equations to describe and predict the P release and the correlation of the coefficients in the release rates of these equations with a number of soil properties in some prominent soils of this province, using the 0.01 M $CaCl_2$ extractant.

MATERIALS AND METHODS

Study Area

The study region, with an area of 16264 km^2, is located in the southwest of Iran between 30° 9' to 31° 32' and 49° 57' to 50° 42' and is a mountainous and relatively high land, covered all in the north and east by the Zagros Mountains along with parallel ranges. The highest point of the province is Dena peak with the height of 4409 m and the lowest point is Lishter with the height of 500 m above sea level. The mountains' height, precipitation level and humidity significantly decrease considering the geographical conditions of the province along the main Zagros Mountains from northeast to southwest. This natural situation has created a dual climatic feature and divided the province into two cool and hot regions.

Soil Sampling and Analysis

At the first stage of study, the physiographic units were separated based on the information obtained from the aerial photographs and the topographic and geological maps. Then, several pedons were excavated in each unit. Totally, 54 control pedons were selected and different horizons of the pedons were sampled. Afterwards, 16 surface samples with a wide range of physical and chemical characteristics from different pedons were selected for experiments. To minimize the effect of phosphorus fertilizers, sampling was performed in autumn and before cultivation. In order to identify soil properties, the samples were passed through a 2 mm sieve after drying by the exposure to open air. A number of physical and chemical experiments were conducted. The experiments included the soil texture by the hydrometer method (Gee and Bauder, 1986), calcium carbonate equivalent (CCE) by back titration method (Loeppert and Suarez, 1996), cation exchange capacity (CEC) of the soil (Chapman, 1965), organic carbon by wet burning method with potassium dichromate ($K_2Cr_2O_7$) in the vicinity of concentrated sulfuric acid and the titration of residual potassium dichromate with ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2.6H_2O$) (Jackson, 1975). The amount of available P was extracted by Watanabe and Olsen (1965) method (extracted with sodium bicarbonate, pH=8.5)

Analysis of Clay Mineralogy

In order to prepare soil samples for the analyses of clay minerals, the cementation agents including carbonates, organic carbon and iron oxides were removed using 1 N HCl, 30% H_2O_2, and dithionite citrate bicarbonate mixed solution, respectively (Mehra and Jackson, 1960; Kittrick and Hope, 1963; Jackson, 1975). The samples containing gypsum were washed with distilled water. After separating the clay fraction, the samples were saturated with Mg^{2+} and K^+ using 1 N $MgCl_2$ and 1 N KCl, respectively. The Mg^{2+} and K^+-saturated samples were later saturated with ethylene glycol and heating at 550°C, respectively. In addition, the samples were treated with 1 N HCl to separate kaolinite and Fe chlorite. These five treatments (Mg^{2+}saturated, K^+ saturated, Mg-ethylene glycol (Mg-EG), K-550°C and HCL treatments) were X-rayed with a Philips D500 diffractometer using Ni-filtered Cuka radiation (40kV, 30mA). The relative frequency of clay minerals in the soil fractions was determined in a semi-quantitative manner using the ratio of X-ray peak areas (001) on the diffractograms of ethylene glycol solvate samples following the method of Johns et al. (1954).

Phosphorus Release Kinetics

To evaluate the P release rate, 2.5 grams of each soil sample was weighed and transferred into a 100 ml polyethylene container and treated with 100 μg of P per 1 g of soil in the form of KH_2PO_4 (potassium di-hydrogen phosphate). To do so, 5 ml of 50 mg l^{-1} P solution was added to each sample and samples were kept in the field capacity conditions for 35 days. The aforementioned experiment was conducted with two replications. After 35 days, 35 ml of 0.01 M $CaCl_2$ solution and a few drops of toluene were added to each sample to prevent the growth of microorganisms. Then, the samples were shaken during two different periods of 0.25 to 72 h (at the intervals of 0.25, 1, 2, 4, 8, 12, 24, 48, and 72 h) with an electric shaker. The suspension was then centrifuged at 2300×*g* for 15 min and the supernatant solution was extracted in each phase. Again, 35 ml of the fresh extractant solution was added to the sample and the soil was extracted 9 times during 72 h until the P concentration in the extract reached to a constant value. The concentration of P in the extracts was determined each time by Murphy and Riley (1962) method.

Then, in order to predict the P desorption rate, the simple Elovich, parabolic diffusion, power function, zero-order and first-order (Table 1) equations were used to fit the data. Afterwards, the statistical models were tested by the least-squares regression (LSR) analysis to determine the best equation describing the P release from the soil. According to *the coefficient* of *determination* (R^2) and standard error of estimate (SE), the equation or equations with the highest R^2 and the lowest SE were selected and the constants were calculated.

Table 1. Kinetic models used for describing phosphorus released in studied soils

Model	*Kinetic equation*	*Constants*
Zero order	$^{*}P_0 - Pt = a - k_o t$	a, ko
First order	$\ln (P_0 - Pt) = d - k_1 t$	d, k1
Simple Elovich	$Pt = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$	α, 1/β
Power function	$\ln Pt = \ln a + b \ln t$	a,b
Parabolic diffusion	$Pt/P_0 = c + rt^{1/2}$	c, r

The R^2 was calculated using the LSR measured in comparison to the estimated values. The SE was calculated according to the following formula (eq. 1):

$$SE = [\Sigma (P - P^*)^2/(n-2)]^{0.5} \qquad (1)$$

where P and P* represent the measured and predicted P values, respectively, and n represents the number of data evaluated.

Data Analysis

The relationships between P release and some physical, chemical and mineralogical properties of soils were analyzed using the Pearson correlation coefficient with the SPSS 24 statistical software after specifying the P release values of soils, fitting the equations and determining the coefficients in the studied soils. Excel 2016 software was used to draw the associated graphs.

RESULTS AND DISCUSSION

Properties and Clay Mineralogy of the Studied Soils

The results of this study showed that the tested soils had a wide range of physical and chemical properties (Table 2). The soil texture contents were different among the soil samples and the percentage of clay, silt, and sand were in the ranges of 16.7-46.7%, 19.6-45.3% and 15.3-56.9%, respectively. The soil texture varied from clay to sandy clay loam. The studied soils were calcareous with pH range of 7.4-8. The values of CEC, organic carbon, CCE and Olsen-extracted P were in the ranges of 9.1-39 cmol (+) kg^{-1}, 0.52-5.25%, 9.7-65.9% and 11.4-194.1 mg kg^{-1}, respectively (Table 2). The highest and lowest values of Olsen-extracted P were observed in soil No. 8 and 14, respectively. The results also showed that the studied pedons were classified into five orders including Entisols, Inceptisols, Mollisols, Alfisols, and Vertisols (Table 2). Also, the specified surface horizons of the soils in the study area included Mollic and Ochric. Entisols are the soils without a developed horizon and spread in alluvial plains and alluvial fans in all regions. Inceptisols are also located in the area next to Entisols. This soil is intermediate in terms of development and will be turned into other soils over time due to the climate conditions and parent materials. Mollisols exist in smaller parts of the region. The conditions for the formation of this soil are provided in the wider areas due to the good climate conditions, but the levels of these soils are reduced due to the inappropriate utilization and conversion of forest and pasture into agricultural lands. Alfisols are also found scattered in wet areas and less in semi-arid areas. The origin of these soils in high-calcareous semi-arid regions could be related to the past high-rainfall climate or the conversion of salty and sodium contained soils and clay transported by sodium through the soil dispersion (Abtahi, 1980). Vertisols are the soils with a high percentage of expandable clay and are rarely found in the wet parts of the Yasuj Plain (Dasht-e-Rum). The results of previous studies on the mineralogy of the soils in this study area (Shakeri and Abtahi, 2018, Shakeri and Saffari, 2019) indicated that the major clay minerals in the studied pedons were smectite, illite, chlorite, vermiculite, palygorskite, and kaolinite (Fig. 1). The dominant clay minerals in the areas with low rainfall (southern, central and western parts of the study area) are palygorskite, smectite, illite and chlorite; while smectite, illite and vermiculite minerals are the dominant ones in the areas with more rainfall (east and northeast parts of the study area). Illite and chlorite were observed in all surface and subsurface horizons of the studied pedons, however, the presence of these minerals are more expected in the young soils of sloping lands such as colluvial deposits, alluvial soils, and the areas with less rainfall (like south and west parts of the study area). According to the previous studies, it has been shown that illite and chlorite originated from parent materials (Shakeri and Abtahi, 2020., Azadi and Shakeri, 2020). Kaolinite could also form in the tropical conditions and originated from the studied soils inherited from parent materials. Smectite was identified as the main mineral of the clay part of the eastern, northern and some pedons of the western region of the province. Due to the fact that all soils had proper drainage, in addition to the presence of smectite in parent materials, the transformation of other minerals such as illite and palygorskite into this mineral might be the most important reason for their presence in the soils, especially in the wetter areas (east and north of the study area). In the present study, a very little amount of vermiculite was observed in the soils of study area. Palygorskite was identified as the dominant mineral in the regions with lower rainfall (south and west of the study area).

P Release using 0.01 M $CaCl_2$

The rate of the cumulative P release using 0.01 M $CaCl_2$ extractant after 72 h is shown in Table 2. The examination of the diagram in six selected samples, as presented in Fig. 2, indicated that the P release was a biphasic process. Also, the examination of P release diagram in all soil samples showed that the rate of P release from the soils was fast at early desorption phases and continued with a slower rate. Similar results of P biphasic desorption in different soils have been reported by many researchers (Nafiu, 2009; Jalali and Ahmadi Mohammad Zinli, 2011; Moazallahi and Baghernejad, 2018).

Table 2. Some of chemical and physical properties and Semi-quantitative analysis of clay minerals in the studied area

Sample No.	Clay (%)	pH	CCE (%)	OC (%)	Po[a)] Mg kg^{-1}	Prel[b)] Mg kg^{-1}	CEC (cmol kg	Sme[c)]	Ill[d)]	Chl[e)]	Ver[f)]	Kao[g)]	Pal[h)]	Taxonomy
1	36.7	7.9	44.1	1.16	12.4	12	15.6	+++	+++	++	+	++	++*	Typic Haplusto
2	37.4	7.8	45.4	1.08	144.4	23.8	21.7	+++	+++	++	+	+	++	Calcidic Argiustolls
3	27.4	7.9	55.2	0.96	24.5	25.4	11.1	+++	+++	+	+	+	++	Aridic Calciustepts
4	21.4	7.9	65.2	1.34	72.1	24.6	14.0	++	++	++	+	++	+	Typic Ustifluve
5	16.7	8.0	53.3	0.52	19.6	21.8	9.1	++	+++	++	–	–	+++	Gypsic Haplustepts
6	32.7	7.8	62.3	0.96	34.4	21.6	17.0	+++	+	++	+	+	+	Typic Xerofluvents
7	37.4	7.6	41.8	1.50	44.1	21.1	17.7	+++	++	++	+	+	++	Calcic Haploxeralfs
8	37.3	7.4	37.3	5.25	194.1	20.7	39.0	+++	++	++	+	++	–	Typic Haploxerolls
9	45.4	7.8	9.7	1.14	21.6	8.3	30.1	+++	++	+	++	+	–	Chromic Calcixererts
10	42.7	7.8	20.2	1.26	44.1	7.9	26.7	++++	+	+	+	++	+	Aquic Haploxerepts
11	38.7	7.7	52.0	1.64	90.0	3.2	24.4	++++	+	+	++	++	–	Calcic Haploxeralfs
12	34.7	7.7	48.1	3.11	109.9	8.4	25.9	+++	++	++	++	–	++	Typic Haploxerolls
13	23.4	8.0	65.9	0.65	24.2	14.4	9.9	+++	++	++	++	–	+	Typic Xerorthe
14	46.7	8.0	20.2	0.88	11.9	7.4	30.1	++++	+++	–	++	++	–	Mollic Haploxeralfs
15	25.4	7.8	47.8	1.16	16.5	10.5	25.1	+++	++	–	++	+	++	Calcic Haploxeralfs
16	34.7	7.9	22.6	1.37	167.2	20.7	21.3	+++	+	+++	–	++	+	Typic Xerorthe
Mean	33.7	7.8	43.2	1.5	64.4	15.7	21.2							

* a) P_O (P- Olson), b) P_{rel} (release) , c) Sme: smectite, d) Ill: illite, e) chl: chlorite, f) Ver: vermiculite, g) Kao: kaolinite, h) Pal: palygorskite, CCE: calcium carbonate equivalent, OC, organic carbon, CEC, cation exchangeable capacity, -: trace or not detected, + : <15%, ++:15-30%, +++: 30-50%, ++++ : >50%

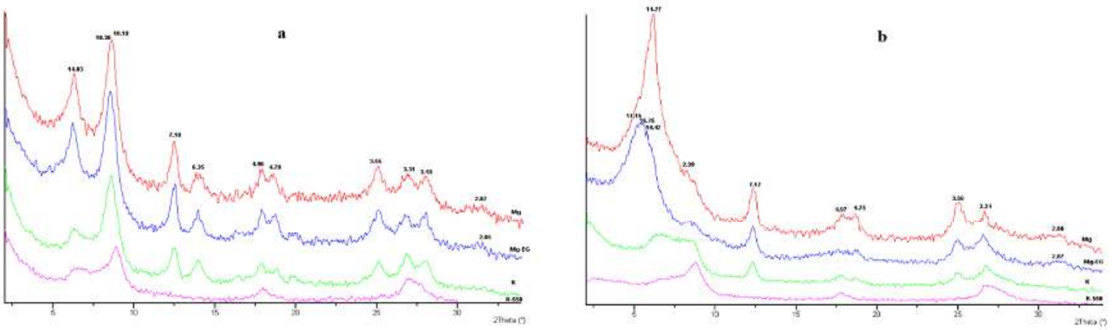


Fig. 1 XRD (X-ray diffraction) patterns of clay in (a) the areas with low rainfall and (b) the areas with more rainfall.

In a previous research (Saha *et al.*, 2004) has been suggested that the heterogeneous sorption sites with different sorption intensities is the main reason for the biphasic pattern of the P desorption. It has been reported that the rapid release of P in the early phases could be attributed to the rapid dissolution of the amorphous phosphates with a low bond energy (Jalali and Ahmadi Mohammad Zinli, 2011). On the other hand, the slow P desorption in the secondary phase of the P release can be attributed to the dissolution of crystalline phosphate compounds (including octacalcium phosphate (OCP) and calcium hydroxyapatite). Therefore, it can be stated that the primary and secondary phases of the P desorption in the current study were associated with labile P and low–mobility P, respectively. In most soil samples, the highest P release occurred within the first 10 h of desorption process, and then, a slight decreasing desorption process was observed. Elrashidi et al. (1975) suggested that there are two forms of P in calcareous soils; one is released rapidly and the other is released slowly and gradually. These two forms are released simultaneously during the first 6 to 12 h of desorption process, but, afterwards, only the second form of releasing continues for 72 h until the balance is achieved. Sharpley et al. (1981) reported that the P desorption during the short periods is a process with a low activation energy. Also, these researchers suggested that the diffusion of the P released from the water films surrounding the soil particles outward is the determining phase of the P release during short periods due to the low activation energy over these periods.

The P that retained at low activation sites is released during the early phases of releasing, whereas the P that retained at high activation sites is desorbed during the late phases (Moazallahi *et al.*, 2018). The average P release in the studied soils was 15.7 mg kg^{-1}. The highest amount of P release (25.4 mg kg^{-1}) was observed in sample no, 3, that was the surface horizon of Inceptisols (Table 2). This soil had a clay loam texture and less contents of CEC, clay and organic carbon, relatively higher CCE and sand compared to the other soils studied in this research. On the other hand, the lowest amount of P release (3.2 mg kg^{-1}) was observed in sample no, 11, which was the surface horizon of an Alfisol with silty clay loam texture and relatively high contents of organic carbon, CEC, and clay. The data of preliminary phases of the P release were fitted to the Simple Elovich, first-order, parabolic diffusion and power function equations. The results are presented in Table 3. According to the results, the Elovich and power function equations, which had the highest R^2 with the mean of 0.97 and 0.98, respectively, were selected as the best equations describing the relationship between P release and time in the studied soils (Table 3). Finally, considering the two parameters of SE and R^2, the Simple Elovich, power function, first-order and parabolic diffusion model were the best equations, respectively, describing the P release in the studied soils. The Simple Elovich equation has also been reported as a good equation describing the P release rate by some researchers (Azadi and Baghernejad, 2019; Shariatmadari et al., 2006). The Simple Elovich equation describes the P desorption data based on a number of reaction mechanisms including the diffusion. In other words, one of the theories introduced in the Simple Elovich model is the diffusion mechanism (Sparks, 1999). In the study of Wahaba et al. (2002), the Simple Elovich equation was introduced as the best equation for the P sorption and desorption processes. It was found that the P sorption capacity in Montmorillonite mineral was higher than that in Kaolinite and illite (Wahaba et al., 2002).

The slope and intercept values of the statistical models used to investigate the kinetics of P release are shown in Table 4. The 1/β, b and r constants, which are the indicators of the P release rate in the Simple Elovich, power function and parabolic diffusion equations, respectively, are important constants. These equations show a greater correlation with the P release kinetics. In this regard, the relationship between the P release and the coefficients of the Simple Elovich and power function equations is presented in Fig. 3.

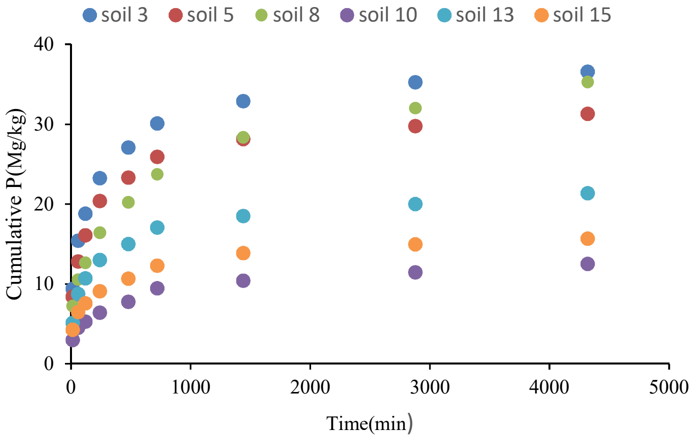


Fig.2. Cumulative amount of P released from some representative soils through successive extractions with 0.01 M CaCl$_2$

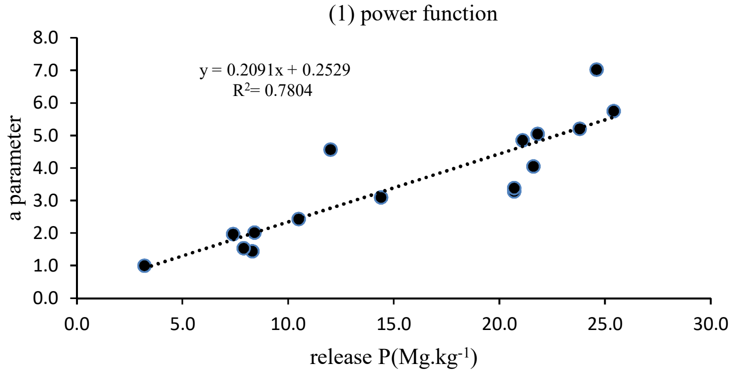
Table 3. Coefficient of determination (R^2) and standard error of the estimate (SE) of various kinetic models for total P release in studied soils

Soil no.	first order SE	zero order R^2	power function SE	parabolic R^2	Simple Elovich equation SE	first order SE	zero order R^2	power function SE	parabolic R^2	Simple Elovich equation SE
1	1.18	0.8493	1.79	0.7359	0.02	0.9953	1.04	0.9099	0.4	0.9871
2	0.3	0.9358	5.75	0.6494	0.09	0.9635	3.81	0.8463	1.04	0.9885
3	0.39	0.9066	6.18	0.6222	0.1	0.9533	4.19	0.8268	0.89	0.9921
4	0.32	0.9181	5.21	0.6289	0.08	0.9607	3.54	0.8282	0.71	0.9932
5	0.39	0.8933	5.3	0.6131	0.1	0.9532	3.63	0.8184	0.94	0.9877
6	0.38	0.9043	5.66	0.6305	0.12	0.9504	3.79	0.834	0.86	0.9915
7	0.37	0.8998	5.13	0.6259	0.1	0.9596	3.47	0.8291	0.95	0.9871
8	0.14	0.9859	4.81	0.7919	0.04	0.994	2.45	0.9459	1.96	0.9653
9	0.58	0.7472	2.31	0.6792	0.12	0.9542	1.5	0.8657	1.04	0.9355
10	0.33	0.8686	1.8	0.741	0.06	0.9871	1.05	0.9124	0.54	0.9766
11	0.83	0.4221	0.55	0.7657	0.08	0.9501	0.34	0.9133	0.31	0.925
12	0.28	0.8976	1.64	0.7633	0.06	0.9828	0.94	0.9221	0.47	0.9809
13	0.34	0.8929	3.42	0.6563	0.1	0.9561	2.25	0.8503	0.38	0.9957
14	0.39	0.8033	1.47	0.7297	0.06	0.9824	0.88	0.9028	0.41	0.9785
15	0.45	0.8226	2.35	0.6951	0.06	0.9816	1.45	0.8837	0.45	0.9887
16	0.21	0.9671	5.12	0.7319	0.08	0.9802	3.03	0.8463	1.18	0.9885
Min	0.14	0.4221	0.55	0.6131	0.02	0.9501	0.34	0.8184	0.31	0.925
Max	1.18	0.9859	6.18	0.7919	0.12	0.9953	4.19	0.9459	1.96	0.9957
Average	0.43	0.85715625	3.655625	0.69125	0.079375	0.969031	2.335	0.87095	0.783125	0.978733

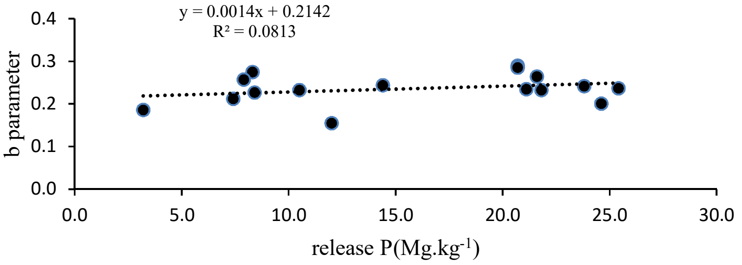
Table 4 . P release rate parameters derived from the kinetic equations fitted the P release data and the quantity of P released (mg kg^{-1} soil) after 0.25 or 72 h

Soil no.	First order		Power function		Simple Elovich		Parabolic	
	d^*	$K1^*$	a^*	b^*	α^*	$1/\beta^*$	c^*	r^*
1	2.4746	0.0017	4.5722	0.1551	4.4460	1.7391	0.4867	0.0088
2	2.8542	0.0007	5.2070	0.2413	1.7037	4.8597	0.3728	0.0111
3	2.8106	0.0008	5.7546	0.2369	2.0559	5.0413	0.3977	0.0109
4	2.6873	0.0007	7.0287	0.2008	3.5166	4.2806	0.4447	0.0099
5	2.6305	0.0007	5.0531	0.2323	1.8659	4.2616	0.4033	0.0108
6	2.741	0.0007	4.0552	0.2643	1.2622	4.6638	0.3586	0.0116
7	2.6363	0.0007	4.8550	0.2342	1.7086	4.1948	0.3934	0.0109
8	3.1533	0.0007	3.2871	0.2896	0.7334	5.2099	0.2423	0.0127
9	1.8825	0.0006	1.4477	0.2751	0.3429	1.9865	0.2911	0.0128
10	1.8959	0.0005	1.5373	0.2573	0.3990	1.7519	0.307	0.0118
11	0.6533	0.0004	1.0017	0.1857	0.4558	0.5545	0.3748	0.0122
12	1.8992	0.0005	2.0138	0.2271	0.6466	1.6846	0.3484	0.0109
13	2.3147	0.0006	3.0957	0.2435	1.0514	2.9257	0.3745	0.011
14	1.6311	0.0005	1.9739	0.2117	0.7234	1.4048	0.3816	0.0106
15	1.9933	0.0006	2.4351	0.2325	0.7847	2.1315	0.3683	0.0112
16	3.0166	0.0007	3.3872	0.2853	1.7037	4.8597	0.3896	0.0116
Average	2.3296	0.0007	3.5440	0.2357	1.4624	3.2218	0.3709	0.0112

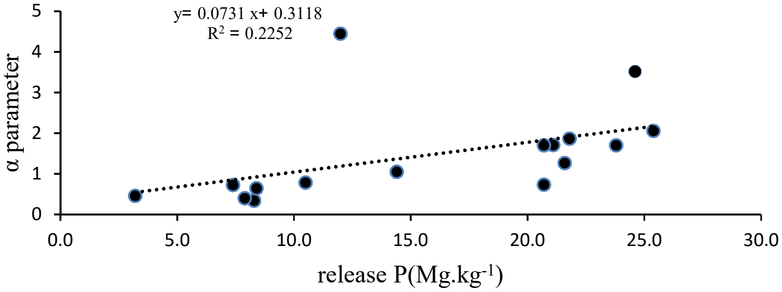
[*] Each constant is defined in Table 1.



(2) power function



(3) Elovich



(4) Elovich

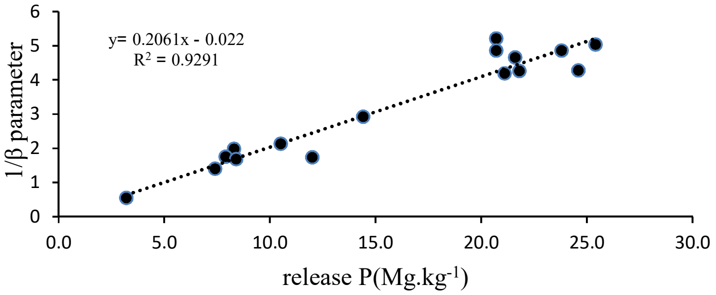


Fig. 3. The variation of "a" and "b" parameters of power function and Simple Elovich models with release P in the studied soils ("a" and "b" are defined in Table 1).

The mean of "1/β", "b " and "r"constant values in the Simple Elovich equation, power function equation and diffusion equation were 3.22, 0.23 and 0.01 mg kg^{-1}, respectively. The value of parameter *"a"* (intercept) that represents the preliminary rate of P release, can be considered as the initial P value available to the plant. The mean values of the intercept in the equations of Elovich, power function, and parabolic diffusion obtained 1.46, 3.54, and 0.37 mg kg-1, respectively.

Among the equations that justify the P release, the diffusion equation had the lowest initial P release rate (c) that was equal to 0.37. It can be justified to provide less available initial P for the plant compared to the other ones. Also, the power function had the highest initial P release rate (a = 3.54), which may indicate providing more available P for the plant in the initial release phases. Compared to the mean of the P release rate (slope of the equations), the Simple Elovich and diffusion equations had the highest and lowest values (3.22 and 0.01) of P release rates, respectively. It can be predicted that the Simple Elovich equation had the highest release rate of "1/β" and the diffusion equation had the lowest release rate of "b" among the equations that better justify the P release.

Correlation between Desorption, Physicochemical and Mineralogical Properties of Soil

According to the results obtained from the correlation of some physicochemical properties, significant positive correlation between the CEC with organic matter as well as clay content and the organic carbon with available P were observed. Azadi and Baghernejad (2016) reported that available P (P extracted by Olsen method) was significantly correlated with organic carbon. Also, among the soil properties, CCE had a significant negative correlation with clay and CEC, and negative correlations between pH with the organic carbon and CEC were also observed. Other correlations among the physico-chemical properties with each other were not statistically significant. The established positive correlation between organic carbon, available P and released P can decrease the P sorption in the soil due to the processes such as formation of organic carbon and P complexes (organic phosphates). Consequently, increasing in P mobility, organic anions that can be exchanged with P adsorbed onto the surfaces, and iron and aluminum oxides covering the humus. Moreover, it was reported that the organic carbons as a P source, by themselves, could increase the P release rate through the mineralization processes (Pierzynski et al., 2005). Phosphorus release that was observed in this study showed a significant negative relationship with both vermiculite and smectite, but a significant positive correlation with chlorite percentage (Table 5). The mineralogical results (Table 2) showed that the dominant minerals in the studied soils in arid and semi-arid regions included palygorskite, chlorite and illite, and in the more humid areas, they included smectite, illite and vermiculite. These are consistent with the results of Owliaie et al. (2006) and Shakeri and Abtahi (2018).

In order to investigate the influence of clay on the sorption of elements, both the type and amount of clay are usually considered. The study area had two different climates, with heavy rainfall in the northern and eastern parts of the province and low rainfall in the western and southern regions. In the areas with more rainfall, $CaCo_3$ is leached from the soil and consequently, the clay content will be higher. Also, in the areas with low rainfall, the amounts of chlorite and palygorskite are higher than those in the areas with high rainfall. On the other hand, the amount of palygorskite varies with the amount of smectite. Palygorskite contains a specific surface area (SSA) of about 180 m^2g^{-1} and CEC of about 12 Cmol(+) kg^{-1} [36], while smectite has a SSA of about 800 m^2g^{-1} and CEC of about 100 Cmol(+) kg^{-1}. In the areas with higher contents of $CaCo_3$, there is a less amount of clay. Also, the chlorite and palygorskite minerals with less SSA and CEC are the dominant ones. As a result of these conditions, the sorption of different forms of P in these soils is less than the soils with higher clay and dominant minerals of smectite and vermiculite, and the higher amount of P release is observed.

Clay minerals are considered as the important features of soil and have a significant role in the P desorption in the soil. However, P desorption process takes place at different rates, depending on the mineral type. Therefore, each mineral has a different effect on the P supply. The content of P stabilization in 1:1 clay is more than 2:1 clay, which is due to more hydroxyls (Sharpley, 1983). Significant correlations between the soil clay content and the sorption and desorption of P were reported by Rezaei and Gilkes (2005). In addition to the clay content, the effect of clay form should also be considered in the P sorption. The expandable and non-expandable clay minerals have different effects on the P desorption rate. The presence of expandable minerals affects the P desorption pattern over time and increases its release rate due to the changes in aggregate size and the decomposition as a result of soil humidity and lower surface functional groups. Due to the surface functional groups in non-expandable clay minerals such as kaolinite, they affect the P sorption, and the P release will be delayed. On the other hand, the sorption processes in kaolinite and smectite are faster than those in vermiculite and mica, because kaolinite and smectite have more sorption sites, and vermiculite and mica have multiple sites such as interlayer, edge and surface. Thus, not only expandability but also sorption sites affect the P release (Jafari et al., 2008). The coefficients of correlation between the constants of kinetic equations and some soil properties are shown in Table 6.

Table 5. Linear correlation (Pearson) coefficients between clay minerals and some physico- chemical properties with P_O(Olson) and P_{rel}(release)

	Sand	Clay	pH	CCE	OC	CEC	Sme.	Ver.	Chlo	Pal.	P_O
Clay	-0.856**										
pH	0.286	-0.345									
CCE	0.608*	-0.765**	0.115								
OC	0.03	0.22	-0.831**	-0.104							
CEC	-0.491	0.715**	-0.624**	-0.657**	0.661**						
Sme	-0.718**	0.772**	-0.193	-0.472	0.07	0.525*					
Ver	-0.271	0.319	-0.092	-0.028	0.059	0.356	0.48				
Chlo	.453	-.249	-. 090	.205	.185	-.310	-.455	-.646**			
Pal	0.31	-.602*	0.264	0.402	-0.309	-.631**	-.538*	-0.442	.224		
P_O	0.077	0.156	-0.569*	-0.107	0.697**	0.449	0.004	-0.28	.544*	-0.229	
P_{rel}	0.413	-0.46	-0.071	0.339	0.096	-0.355	-.616*	-0.712**	.577*	0.338	0.357

**: Correlation is significant at the 0.01 level,*: Correlation is significant at the 0.05 level.

Table 6. Correlation between P release parameters and selected properties of the studied soils

	First order		Power function		Parabolic		Simple Elovich	
	d	k1	a	b	C	r	α	1/β
sand	0.422	0.067	0.414	0.068	0.223	-0.249	0.296	0.380
silt	-0.257	-0.029	-0.108	-0.118	-0.145	0.200	-0.174	-0.129
clay	-0.360	-0.081	-0.586*	0.108	-0.405	0.346	-0.375	-0.407
pH	-0.063	0.147	0.192	-0.303	0.599*	-0.510*	0.317	-0.127
CCE	0.175	0.112	0.540*	-0.352	0.434	-0.387	0.370	0.277
OC	0.162	-0.086	-0.176	0.295	-0.581*	0.376	-0.231	0.139
CEC	-0.260	-0.320	-0.638**	0.344	-0.735**	0.588*	-0.578*	-0.279
Sme	-0.581*	-0.244	-0.734**	-0.004	-0.336	0.333	-0.537*	-0.556*
Ill	0.199	0.386	0.402	-0.370	0.355	-0.533*	0.382	0.086
Chol	0.616*	0.285	0.425	0.237	0.166	-0.105	0.391	0.567*
Verm	-0.700**	-0.330	-0.591*	-0.232	-0.235	0.157	-0.462	-0.696**
Kao	-0.088	0.186	-0.076	-0.146	0.025	0.017	0.193	-0.106
pal	0.413	0.338	0.527*	-0.219	0.490	-0.532*	0.425	0.279
Po	0.319	-0.175	0.005	0.409	-0.380	0.381	-0.133	0.398
Prel	0.917**	0.184	0.818**	0.389	0.099	-0.085	0.400	0.990**

Therefore, the correlation between the parameters derived from various equations fitted on the P desorption data and the physico-chemical properties shows that, except for the coefficient a of power function equation, there was no significant correlation between the other coefficients or components of equations related to the P release and the percentage of clay. This may be due to different types of minerals controlling the P solution in these soils. In a study, Dalal (1974) found that the physical and chemical properties affecting the P stabilization such as percentage of silt, clay and organic carbon had no significant correlation with the P release of the soils.

The coefficient of the release rate (0.01 M $CaCl_2$) in the Simple Elovich equation had a significant positive correlation with the amount of chlorite (0.567*) and a significant negative correlation with the amount of smectite (-0.556*) and vermiculite (-0.696**). Also, the release coefficient of the parabolic diffusion had a significant negative correlation with pH (-0.510*), illite (-0.533*) and palygorskite (-0.532 *) and a significant positive correlation with CEC (0.558 *). Martin et al. (2004) reported that some factors such as percentage of clay, organic carbon, pH, iron and aluminum oxides, calcium levels, ionic strength, soil minerals and parent materials, and soil texture affect the sorption and desorption of P. There was a significant positive correlation between the intercept of the power function equation and the equivalent $CaCo_3$ (CCE) and between the parabolic coefficient and the pH value. There was also a significant negative correlation between the intercept of the power function, parabolic and Simple Elovich equations and the CEC. In a study on the P release in some calcareous soils in the northwest of Iran, Biabanaki and Hosseinpur (2008) reported a significant correlation between the CCE and the intercept of the exponential function and parabolic equations. Sharpley (1983) reported a significant correlation between CCE content and release constants of the kinetic equations. He also stated that the content of CCE, organic carbon and clay of the soil was an indicator of the SSA reacting with P. In this research, no significant correlation was observed between the coefficients of the first-order equation and the soil chemical properties. García-Rodeja and Gil-Sotres (1997) reported that the slope of the first-order equation was not significantly correlated with any soil properties. A research conducted by Taghipour and Jalali (2013) showed that the P release rate in the soils had a significant positive correlation only with the soil clay content, and no correlation was observed with other soil properties. According to the studies of Shariatmadari et al. (2006), the release rate parameters of P had a significant positive correlation with the activated CCE, clay amount, dithionite citrate bicarbonate, and extractable aluminum of the soils, while the amount of CCE did not show a significant correlation with the P release.

CONCLUSIONS

The results of this study showed that in the P release process using $CaCl_2$ extractant based on two parameters including R^2 and SE, the Simple Elovich and power function and parabolic diffusion were the best equations describing the P release in the studied soils, respectively. According to the results of the correlation between some physicochemical properties, there was a significant positive correlation between CEC, organic carbon and percentage of clay, and between organic carbon and available P. The release rate coefficient (using 0.01 M $CaCl_2$) in the Simple Elovich equation had a significant positive correlation with chlorite and a significant negative correlation with smectite and vermiculite minerals. The release coefficient of the parabolic diffusion had a negative significant correlation with pH and illite and palygorskite minerals, and a significant positive correlation with CEC. Finally, the P release observed in this study showed a significant negative correlation with vermiculite and smectite, and a significant positive correlation with chlorite percentage. Therefore, since clay minerals are considered as important properties of soil which have a significant role in the soil P desorption, the influence of clay type, weathering phase and climate conditions of the area, in addition to clay amount, were considered to be important factors that affectd the P desorption.

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توزیع فسفر و اثر ویژگی‌های فیزیکوشیمیایی و کانی‌های رسی بر آزادسازی فسفر در تعدادی از خاک‌های آهکی

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کانی‌های رسی

خاک‌های آهکی

چکیده- فسفر به عنوان یک عنصر غذایی ضروری برای رشد گیاهان می باشد که دسترسی آن در خاک با گذشت زمان، آبشویی، ترسیب و تغییر زمین‌نما تغییر می‌کند. اطلاعات در مورد سینتیک آزاد سازی فسفر در خاک‌های آهکی محدود است. بنابراین هدف از این تحقیق، بررسی توزیع فسفر و تاثیر ویژگی‌های فیزیکوشیمیایی و کانی‌های رسی بر آزادسازی فسفر در تعدادی از رده‌های غالب خاک‌های آهکی استان کهگیلویه و بویراحمد، با عصاره‌گیر کلرید کلسیم ۰/۰۱ مولار بود. نتایج این پژوهش نشان داد، رها سازی فسفر از خاک در ابتدا سریع و سپس به آهستگی ادامه یافت. بعد از گذشت ۷۲ ساعت، مقدار فسفر آزاد شده در خاک‌ها در محدوده ۳/۲ تا ۲۵/۴ میلی‌گرم در کیلوگرم بود. بر اساس برازش معادلات مختلف بر داده های واجذبی فسفر، معادلات الوویچ و تابع توانی توانستند به خوبی فرایند رهاسازی فسفر را در خاک‌های مورد مطالعه پیش‌بینی کنند. نتایج مطالعات همبستگی خصوصیات خاک و اجزای رهاسازی فسفر در خاک‌ها نشان داد که برخی ضرایب آزاد شدن فسفر (از جمله شیب و عرض از مبدا معادله الوویچ) ارتباط منفی معنی‌داری با مقدار کانی اسمکتیت و ورمی‌کولیت دارند. همچنین، ضریب آزاد سازی معادله پخشیدگی پارابولیک رابطه معنی دار منفی با pH ، میزان ایلیت و کانی پالیگورسکیت نشان داد.