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# Desorption Kinetics and Chemical Forms of Phosphorus in Calcareous Soils along a Climotoposequence

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## ABSTRACT

Soil phosphorus (P) fertility can be significantly affected by the rate of P desorption and fractions in soil. The present study attempted to investigate the comprehensive relationships between different physic-chemical and mineralogical properties of different soils with desorption parameters and chemical forms of P in different soil orders of a climotoposequence. For this purpose, the collected soil samples were incubated with 50 µg P $g^{-1}$ soil (as $KH_2PO_4$) for 90 days. The kinetic data obtained from 0.05 M $NaHCO_3$ were used to simulate desorption equations. The results showed that P desorption in different soil samples was similar, and can be interpreted as an initial rapid release rate followed by a slower rate (biphasic pattern). Among equations fitted on desorption data, the simple Elovich, power function and two first-order reaction models had good prediction based on highest $R^2$ and lowest SE. In the case of studied soil samples, Ca-bound and residual P were found to be the most common chemical forms of P. Moreover, it was observed that the addition of P to soil samples increased the concentration of all fractions. Compared to unamended soil samples, there was an increase in relative percentage of exchangeable-P, Fe- and Al-bound fractions in amended samples. However, Ca-bound and residual P decreased in these samples. Additionally, the results indicate that apart from OM, CEC, silt, available-P and total-P were the significant properties which affected desorption of P; also, important minerals like kaolinite and illite played an important role in the behaviour of P in the studied samples.

**Keywords: Phosphorus, desorption kinetics, fractionation, clay minerals.**

## INTRODUCTION

Phosphorus (P) is one of the most essential nutrients for plant growth. Deficiency of this element, which is frequently related to formation of insoluble complexes such as calcium-phosphate, is commonly observed in calcareous soils. Several researchers have shown that the processes of adsorption as a monolayer on calcium carbonate and precipitation (octacalcium phosphate or dicalcium phosphate) are the main P control mechanisms in low and high concentrations in

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alkaline calcareous soils, respectively (Shariatmadari *et al.* 2006; Samadi 2010, Horta and Torrent 2007; Pierzynski and McDowell 2005). Obtaining information on dynamics and transformation of P in different soils should lead to better management of P fertilisers (Meason *et al*. 2009; Jalali and Ranjbar 2010). Soil buffering capacity (BC) is regarded as the most important factor in P uptake by plants. Phosphorus desorption in soils with low BC is more rapid than in soils with high BC. In most studies, changes in soil physical-chemical properties including clay minerals (metal oxides and phyllosilicate minerals), organic matter, and calcium content, have been identified as the most important factors affecting availability of P (Pierzynski and McDowell 2005). However, many of these studies did not deal with the important role of clay minerals on P behaviour in soils. Several studies have shown that metal oxides have a strong affinity for P, especially in acid soils (Fink *et al.* 2016; Bortoluzzi *et al*. 2015). However, a few studies have shown that phyllosilicate minerals play a more important role in P sorption of alkaline soils compared to metal oxides (Gérard 2016). Phyllosilicate minerals with higher anion exchange capacity (AEC) have a greater affinity for P which increases as pH decreases in pH-dependent clay minerals like1:1 type clays. Previous studies done in Iran have identified several clay minerals such as illite, chlorite, kaolinite, palygorskite, smectite, and vermiculite originating from various climatic conditions (Khormali and Abtahi 2003; Owliaie *et al*. 2006). Therefore, it appears that any study on behaviour changes of P in relation to these clay minerals can be useful for improving soil P management and crop production. Soil P exists in several forms including soil solution and in exchangeable form, Ca-bound and Fe–Al- bound phases such as solid phases and in residual form (Jalali and Ranjbar 2010). Investigation of chemical forms through sequential extraction methods can provide important information on labile and non-labile forms of P. Although, the use of sequential extraction techniques can be considered as a useful way for evaluating the state of P in soil, a lack of specific chemical extractants and some processes such as redistribution of ions can affect the accuracy of information obtained about chemical forms (Saffari *et al*. 2009). Using other methods such as kinetic modeling techniques can help researchers achieve an understanding of the behaviour of elements in soils. Nowadays, kinetic methods have been preferred over conventional sequential extraction methods for the evaluation of metal behaviour. Therefore, methods involving kinetic fractionation of metals in soils could be useful to understand the fate of metals (Santos *et al*. 2010). Several studies have been carried out on the correlation between P and clay minerals in acidic and non-calcareous soils, but no specific information has been reported in alkaline calcareous soils. In addition, evaluating the state of P through kinetic modeling can complete the information obtained from chemical forms. Therefore, the objectives of the present study were to determine (i) P desorption characteristics of selected soils; (ii) chemical fractionation of P; (iii) the relationships between the different P forms and P desorption properties; and (iv) the relationships between secondary clay minerals and P desorption kinetic parameters.

## MATERIALS AND METHODS

*Study Areas, Sampling Design and Laboratory Analysis*

The study was conducted across a toposequence transect near the city of Kerman Iran (Figure 1).

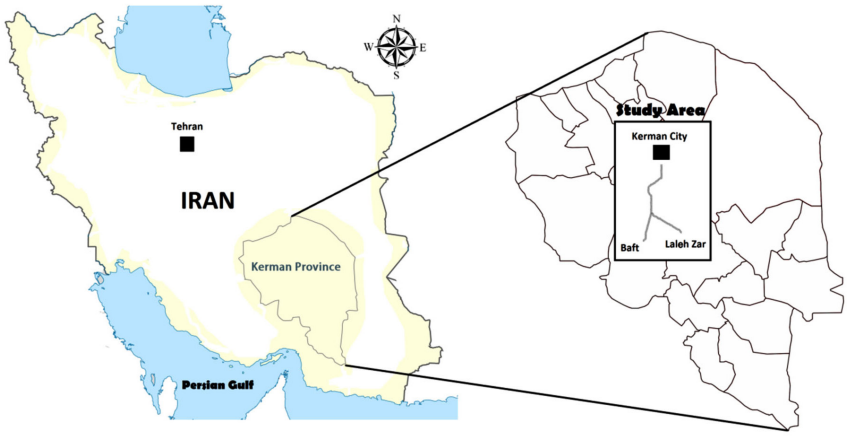


*Figure1: Location of the study area*

The studied climotoposequence covers an area of about 1200 km$^2$. The mean annual precipitation of the area varies from 116.1 to 238.70 mm year$^{-1}$ and the air temperature ranges between 15.7 °C in Kerman plain (30° 48' N, 57° 55' E, in the North of the transect, 1840 m above sea level) and 10.4$^o$ C in Lalehzar (29° 30' N, 56° 12' E, situated in the South of the transect, 3207 m above sea level), respectively (Meteorological Organization of Iran 2016). Soil moisture regime (MR) and temperature regime (TR) in the North of the transect are aridic and mesic, changing to xeric and mesic in the South of the transect (Banaei 1998). Different geomorphic surfaces such as the Kerman Plain, rock pediment, piedmont plain, and lowlands of Lalehzar Mountains were evaluated to determine their P status (Figure 2). Nine representative pedons on different geomorphic positions were selected. All soil horizons were sampled according to Soil Taxonomy (Soil Survey Staff 2014) and selected chemical and physical properties were determined using standard methods (Table 1). Soil texture was determined using hydrometer method (Bouyoucos 1962). pH was measured in saturated paste. Percentage of calcium carbonate equivalent (CCE) was determined by acid neutralisation (Loeppert and Suarez 1996). Organic matter (OM) content was determined using wet oxidation (Nelson and Sommers 1996).

Cation exchange capacity (CEC) was measured by replacing exchangeable cations with sodium acetate (Sumner and Miller 1996). Available P was determined using bicarbonate ($NaHCO_3$0.5 M, pH=8.5)-extractable P (Olsen and Sommers 1982). Total P was determined after digestion of soil samples in a nitric acid–percholoric acid mixture (Olsen and Sommers 1982). The amount of P in the

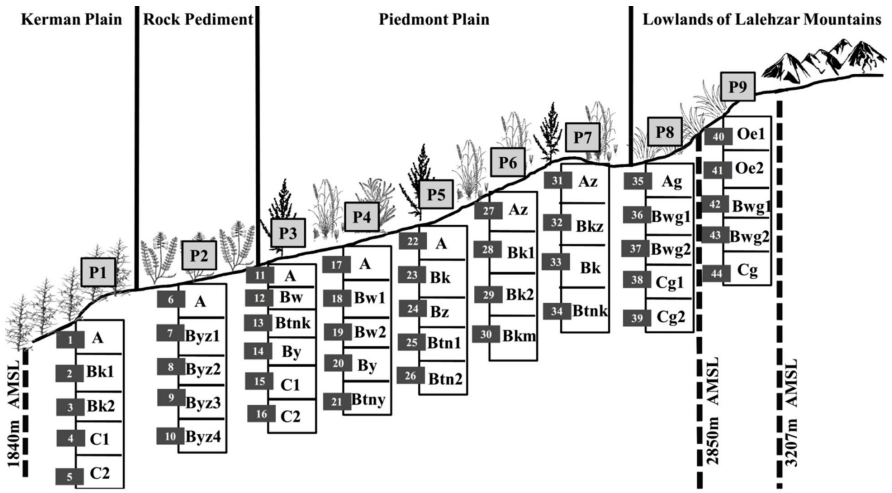


*Figure 2: Location of each pedon in the studied geomorphic surfaces of the area*

extractions was determined using colorimetric ascorbic acid method (Murphy and Riley 1962). In order to investigate the effectiveness of clay minerals on desorption and chemical forms of P, various minerals were identified in different horizons of some studied orders. To do this, a number of selected soil samples were washed to remove gypsum and soluble salts. Fe-oxides, carbonate, and organic matter were removed by citrate-bicarbonate-dithionite (CBD), sodium acetate (adjusted pH 5), and $H_2O_2$ (30%), respectively (Mehra and Jackson 1980). The clay fraction of the prepared samples was separated by centrifuge (Kittrick and Hope 1963). The centrifuged clay samples (Kittrick and Hope 1963) were treated with Mg (1N $MgCl_2$), Mg/ethylene glycol, K (1N KCl), and K/heated at 550ºC for 2 h. The clay minerals were analysed (Jackson and Barak 2005) using an X-ray diffractometer (Philips, PW 1130/00) and Ni-filtered CuKα radiation (40 kV, 30 mA). Semi-quantitative estimation of clay minerals was performed using the (001) peak intensities of the Mg-saturated and glycerol solvated samples (Johns *et al.* 1954). Before carrying out a test for desorption kinetics, all soil samples were treated with $KH_2PO_4$, because the amounts of the available P (P-Olsen) were relatively low in most of the studied soils. Thus, the soil samples were placed in a plastic container and P was added at a rate of 50 µg $Pg^{-1}$soil, as $KH_2PO_4$ ($3.674\times10^{-5}$ M in each soil). The soil samples were subsequently incubated for 90 days at 25 °C. Soil moisture was preserved at field capacity. After incubation, samples were air-dried and used for desorption kinetics and chemical fractionation of P. Desorption kinetics of P was studied by batch-type experiments (Jalali and Ahmadi Mohammad Zinli 2011). One gram of each soil sample, in triplicate, was placed in a polyethylene tube and extracted separately with 25 ml of 0.05 M $NaHCO_3$ at pH 8.5. Samples were shaken for 0.5 to 256 h (0.5, 1, 2, 4, 8, 16, 32, 64, 128, and 256 h) time periods at 25±2 °C. Finally, they were centrifuged immediately at 4000 rpm. The supernatants were filtered through filter paper and

P concentration was determined by ammonium molybdate–ascorbic acid method (Murphy and Riley 1962). Different kinetic equations were used to describe P desorption in the studied soils (Table 1).

TABLE 1
Equations fitted to describe P release kinetics

| Model | Equation | Parameters |
|---|---|---|
| Zero order | $q_t = q_0 - k_0 t$ | $K_0$, zero order rate constant (mg P $kg^{-1}$ $h^{-1}$) |
| First order | $ln\ q_t = ln\ q_0 - k_1 t$ | $k_1$, first-order rate constant ($h^{-1}$) |
| Second order | $1 / q_t = 1 / q_0 - k_2 t$ | $k_2$, second-order rate constant [(mg P $kg^{-1}$)$^{-1}$] |
| Third order | $t1/q_t^2 = 1/q_0^2 - k_3$ | k3, third-order rate constant[(mg P $kg^{-1}$)$^{-2}$ $h^{-2}$] |
| Simple Elovich | $q_t = 1 / \beta \ ln\ (\alpha_s \beta_s) + (1 / \beta_s)\ lnt$ | $\alpha_s$, initial desorption rate (mg P $kg^{-1}$ $h^{-1}$), $\beta_s$ desorption constant [(mg P $kg^{-1}$)$^{-1}$] |
| Parabolic diffusion | $q_t = q_0 - k_p t^{1/2}$ | kp, diffusion rate constant [(mg $P\ g^{-1}$)$^{-0.5}$] |
| Power function | $q_t = at^b$ | a, initial desorption rate constant (mg $P$ $kg^{-1}$ $h^{-1}$)$^b$<br>b, desorption rate coefficient [(mg $P$ $kg^{-1}$)$^{-1}$] |

$q_0$ and $q_t$ are the amount of P desorption (mg $kg^{-1}$) at time zero and t, respectively.

*Model Fitting to Kinetic Data*

A two first-order reaction model can divide elements into three fractions (Santos *et al.* 2010; Jalali and Sajadi Tabar 2013; Saffari *et al.* 2016), Q1, Q2 and Q3, where

$$q = Q_1(1 - e^{-k_1 t}) + Q_2(1 - e^{-k_2 t})$$

$$Q_3 = q_{\ total} - Q_2 - Q_1$$

$q$ (mg P $kg^{-1}$ $h^{-1}$): amount of element released at t time.
*Q1*(mg $kg^{-1}$): "labile" fraction, readily extractable, associated to the rate constant k1($min^{-1}$).
*Q2* (mg $kg^{-1}$): "moderately labile" fraction, less extractable, associated with the rate constant k2 ($min^{-1}$).
*Q3* (mg $kg^{-1}$): P fraction, which is not extractable
$q_{total}$(mg $kg^{-1}$): total concentration of P in soil

To detect the best-fitted model, a standard error of estimate was calculated for each equation and model. Relatively high values of coefficients of determination ($R^2$) and low values of standard errors of estimate (SE) were used as the criteria to obtain the best-fitted models. The standard error was calculated as follows:

$$\mathrm{SE} = \left[\frac{\sum(S - S')^2}{n - 2}\right]^{0.5}$$

where $S$ and $S'$ are the measured and calculated amounts of P desorption in soil at time $t$ respectively, and n is the number of measurements.

*Fractionation of P*

Chemical distribution of P in unamended and incubated soils (incubated with 50 $\mu g g^{-1}$ P) was determined using a modified version of the Hedley *et al.* (1982) procedure, as outlined by Zhang and MacKenzie (1997) (Table 2). The procedure was designed to separate P into four fractions (i) soluble and exchangeable P; (ii) Fe- and Al-bound P; (iii) Ca-bound ; and (iv) residual P. An outline of the method is presented in Table 3. The amount of P in each extracted sample was determined using colorimetric ascorbic acid method (Murphy and Riley 1962).

TABLE 2
Summary of the sequential extraction procedure used in this study

| g soil:mL solution | Extracting solution | Shaking time (h) | Chemical form of P | Symbol |
|---|---|---|---|---|
| 0.5:30 | 0.5 M $NaHCO_3$ (pH 8.5) | 16 | soluble and exchangeable | Exch-P |
| 0.5:30 | 0.1M NaOH | 16 | Fe- and Al-bound P | Fe-Al-P |
| 0.5:30 | 1M HCl | 16 | Ca-bound P | Ca-P |
| 0.5:30 | 5:2 mixture of concentrated $HNO_3$ and $HClO_4$ | 16 | Residual P | Res-P |

## RESULTS AND DISCUSSION

*Morphology of Studied Soils*

As can be seen in Figure 2, Kerman Plain, i.e. the first studied geomorphic surface, has the lowest elevation and precipitation compared to all the studied geomorphic surfaces. In the first Pedon (P1), located in Kerman Plain, two Bk horizons were observed and due to the arid MR in this landform, the Bt horizon has not been formed. This soil is classified as Typic Haplocalcids. In the second studied geomorphic surface (rock pediment), located on gypsiferous neogene formations (Geological Survey of Iran 1995), Gypsic Haplosalids was observed (P2). In this pedon, due to the existence of a high percentage of coarse gravel (10-80%), gypsum pendants were observed more frequently. The third studied geomorphic surface (Piedmont plain) was divided to two parts based on MR. In the first part, that is P3 - P5, the MR is aridic. On the other side, in the second part of this geomorphic surface, the MR is xeric (for P6 and P7). P3, P4, P5 were classified as Typic Natrigypsids, Typic Natrigypsids, and Calcic Haplosalids, respectively. More precipitation in P3 compared to positions in P1 and P2, and a high value of sodium adsorption ratio (SAR) led to formation of Btnk horizon. P4 had a polygon structure at the surface, which is due to this pedon in saline soil. On the other hand, a black surface originating from dissolved organic matter was observed in P5, probably stemming from a sodic soil. The existence of the salic horizon and petrocalcic horizon in P6 marked this soil as Petrocalcic

Calcixerepts. Towards the end part of the rock pediment geomorphic surface with a xeric moisture regime in P7 (Typic Natrixeralfs), the amount of clay increased with depth, forming the argillic horizon. In addition, the SAR value increased with depth causing the ormation of the $B_{tnk}$ horizon due to clay dispersion. P8 and P9 are located in the lowland geomorphic surface of Lalehzar Mountains. In P8, the Mollic epipedon with about 32.5 % organic matter and a xeric MR as well as a water saturated condition (for about 6 months during normal years), marked this soil as Typic Epiaquolls. In P9, the amount of organic matter was higher than in P8 (Table 3). This pedon is known as an organic soil because it has an intermediate decomposition of organic matter (Typic Haplohemists). Stream flow derived from melting snow and rainfall in the lowlands did not allow for decomposition of organic matter. Results from this geomorphic surface showed

TABLE 3
Selected chemical and physical properties of studied soils

| | Profile number | Taxonomy | Horizon | Depth (cm) | pH | OM | CCE | clay | sand | CEC | Olsen-p | Total P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | - | % | | | | Cmol (+) $kg^{-1}$ | mg $kg^{-1}$ | |
| **S1** | P1 | Aridisols | A | 0-30 | 8 | 0.55 | 19.4 | 20 | 74 | 10.3 | 8.6 | 582 |
| **S2** | P1 | Aridisols | Bk1 | 30-51 | 7.9 | 0.44 | 16.5 | 22 | 68 | 11.2 | 6.1 | 513 |
| **S3** | P1 | Aridisols | Bk2 | 51-85 | 8 | 0.34 | 16.3 | 14 | 80 | 7.1 | 5.2 | 478 |
| **S4** | P1 | Aridisols | C1 | 85-110 | 8.3 | 0.46 | 12.5 | 4 | 94 | 3.8 | 4.5 | 578 |
| **S5** | P1 | Aridisols | C2 | 110-140 | 8.2 | 0.36 | 14.3 | 4 | 90 | 2.9 | 2.4 | 422 |
| **S6** | P2 | Aridisols | A | 0-10 | 7.8 | 0.13 | 28.3 | 22 | 46 | 12.1 | 12.2 | 378 |
| **S7** | P2 | Aridisols | Byz1 | 10-50 | 7.6 | 0.46 | 25.1 | 6 | 82 | 4.2 | 9.6 | 320 |
| **S8** | P2 | Aridisols | Byz2 | 50-80 | 7.4 | 0.51 | 19.5 | 6 | 88 | 4.5 | 5.5 | 325 |
| **S9** | P2 | Aridisols | Byz3 | 80-110 | 7.6 | 0.51 | 22.1 | 6 | 88 | 4.3 | 4.2 | 280 |
| **S10** | P2 | Aridisols | Byz4 | 110-140 | 7.5 | 0.50 | 21.8 | 6 | 88 | 4.6 | 3.1 | 199 |
| **S11** | P3 | Aridisols | A | 0-20 | 8.2 | 0.51 | 18.9 | 7 | 83 | 4.6 | 18.6 | 586 |
| **S12** | P3 | Aridisols | Bw | 20-50 | 8 | 0.32 | 18.1 | 13 | 79 | 6.2 | 17.2 | 497 |
| **S13** | P3 | Aridisols | Btnk | 50-90 | 8.2 | 0.29 | 27.2 | 27 | 53 | 16.3 | 8.3 | 443 |
| **S14** | P3 | Aridisols | By | 90-140 | 8 | 0.24 | 22 | 22 | 58 | 11.5 | 2.2 | 478 |
| **S15** | P3 | Aridisols | C1 | 140-160 | 8 | 0.36 | 23.3 | 23 | 55 | 12.3 | 2.1 | 425 |
| **S16** | P3 | Aridisols | C2 | 160-200 | 8 | 0.11 | 22.9 | 15 | 73 | 7.5 | 1.4 | 357 |
| **S17** | P4 | Aridisols | A | 0-20 | 8.2 | 0.68 | 27.5 | 41 | 45 | 22.6 | 6.3 | 446 |
| **S18** | P4 | Aridisols | Bw1 | 20-40 | 8.5 | 0.41 | 24.1 | 39 | 51 | 20.5 | 6.1 | 389 |
| **S19** | P4 | Aridisols | Bw2 | 40-65 | 8.1 | 0.59 | 22.5 | 29 | 51 | 16.2 | 3.1 | 375 |
| **S20** | P4 | Aridisols | By | 65-95 | 8 | 0.41 | 22 | 31 | 43 | 17.3 | 2.4 | 347 |
| **S21** | P4 | Aridisols | Btny | 95-140 | 8.5 | 0.42 | 21.8 | 38 | 37 | 20.4 | 2.1 | 298 |
| **S22** | P5 | Aridisols | A | 0-5 | 7.4 | 0.8 | 25.2 | 29 | 16 | 19.1 | 3.5 | 378 |
| **S23** | P5 | Aridisols | Bk | 5-30 | 7.3 | 0.5 | 25.6 | 25 | 37 | 15.5 | 1.8 | 356 |
| **S24** | P5 | Aridisols | Bz | 30-60 | 7.5 | 0.6 | 19.3 | 25 | 75 | 14 | 1.8 | 311 |
| **S25** | P5 | Aridisols | Btn1 | 60-90 | 7.7 | 0.2 | 16 | 31 | 35 | 17.1 | 1.5 | 287 |
| **S26** | P5 | Aridisols | Btn2 | 90-120 | 7.6 | 0.45 | 15.1 | 47 | 35 | 25.3 | 1.6 | 248 |
| **S27** | P6 | Inceptisols | Az | 0-30 | 7.4 | 0.43 | 21.7 | 22 | 62 | 14.1 | 8.5 | 315 |
| **S28** | P6 | Inceptisols | Bk1 | 30-70 | 7.5 | 0.35 | 28.1 | 16 | 72 | 11.4 | 7.5 | 288 |
| **S29** | P6 | Inceptisols | Bk2 | 70-95 | 7.8 | 0.52 | 34.5 | 14 | 72 | 9.5 | 5.8 | 274 |
| **S30** | P6 | Inceptisols | Bkm | 95-132 | 7.7 | 0.42 | 47.7 | 16 | 56 | 10.2 | 2.1 | 266 |
| **S31** | P7 | Alfisols | Az | 0-5 | 7.4 | 0.85 | 12.5 | 19 | 75 | 11.3 | 14.1 | 413 |
| **S32** | P7 | Alfisols | Bkz | 5-30 | 7.4 | 0.38 | 17.3 | 21 | 75 | 14.2 | 14.5 | 389 |
| **S33** | P7 | Alfisols | Bk | 30-65 | 7.5 | 0.25 | 16.8 | 13 | 81 | 6.5 | 5.2 | 365 |
| **S34** | P7 | Alfisols | Btnk | 65-100 | 7.7 | 0.20 | 28.5 | 23 | 55 | 11.7 | 2.4 | 378 |
| **S35** | P8 | Mollisols | Ag | 0-30 | 6.1 | 32.5 | 10.5 | 44 | 34 | 82.36 | 22.3 | 873 |
| **S36** | P8 | Mollisols | Bwg1 | 30-60 | 6.4 | 11.4 | 9.8 | 32 | 46 | 43.5 | 20.5 | 834 |
| **S37** | P8 | Mollisols | Bwg2 | 60-90 | 7.5 | 6.1 | 9.1 | 16 | 66 | 23.5 | 21.1 | 854 |
| **S38** | P8 | Mollisols | Cg1 | 90-120 | 6.8 | 6.05 | 10.2 | 18 | 60 | 25.8 | 16.8 | 812 |
| **S39** | P8 | Mollisols | Cg2 | 120-150 | 7 | 7.5 | 8.5 | 22 | 56 | 15.7 | 15.5 | 789 |
| **S40** | P9 | Histosols | Oe1 | 0-30 | 7.5 | 46.3 | 15.1 | 14 | 36 | 120.1 | 122.4 | 1812 |
| **S41** | P9 | Histosols | Oe2 | 30-60 | 7.1 | 26.7 | 9 | 30 | 28 | 86.7 | 102.5 | 1687 |
| **S42** | P9 | Histosols | Bwg1 | 60-90 | 7.1 | 18.9 | 12.6 | 43 | 5 | 70.2 | 138.6 | 1477 |
| **S43** | P9 | Histosols | Bwg2 | 90-120 | 7.2 | 9.5 | 7.5 | 33 | 32 | 44.3 | 120.5 | 1419 |
| **S44** | P9 | Histosols | Cg | 120-150 | 7 | 10.3 | 9.1 | 26 | 28 | 39.1 | 134.3 | 1315 |

that parent materials, topography and climate changed following the movement up the transect. That is why soil properties as well as soil classifications also changed along with the transect.

*Physico-chemical Properties of the Studied Soils*

Selected chemical and physical properties of the studied soils are shown in Table 1. The soils were alkaline (except for Histosols soils). The pH value in these soils ranged from 6.1to 8.5. The OM and CCE values ranged from 0.11 and 46.3% to 7.5 and 47.7%, respectively. Higher OM values were observed in Mollisols (with an average of 12.71%) and Histosols (with an average of 22.43%). Such conditions do now allow for decomposition of organic matter. The highest and lowest average CCE values were found in Aridisols (P3) and Mollisols, respectively. The CEC varied from 2.9 to 120.1 cmol (+) $kg^{-1}$. The lowest and highest average of CEC values were found in Aridisols (P2) and Histosols, respectively. Olsen P in different soils types was significantly different. Available P (Olsen P) concentration varied from 1.4 to138.6 mg $kg^{-1}$ with an average of 20.81 mg $kg^{-1}$. The highest available P was observed in Histosols and Mollisols (at an average of 123.66 and 19.24 mg $kg^{-1}$, respectively) compared to Aridisols, Inceptisols, and Alfisols which had an average of 5.48, 5.97, 9.05 mg P $kg^{-1}$, respectively). However, total P concentration in all soil samples varied between 199 and 1812 mg $kg^{-1}$ with an average of 20.81 mg $kg^{-1}$, with only 20% of soil samples having P amounts higher than critical level (above 18 mg $kg^{-1}$). Generally, diversity of physic-chemical properties of the present soils would be useful for obtaining a better understanding of P status which should lead to better management of P and consequently improved soil responses to P fertilisers.

*Clay Mineralogy*

Clay minerals are considered an important part of the solid phase of soils as the structural composition and its qualitative and quantitative identification provide researchers with valuable information about the status of adsorption, fixation and release of cations and anions. In order to investigate the effectiveness of clay minerals on desorption and chemical forms of P, various minerals have been identified in different horizons of some studied orders and their quantity has been determined using PANalytical-X'Pert software. The quantitative results of various amounts of clay minerals in different horizons of different orders are found in Table 4. As can be seen, the relative abundance of smectite, illite and kaolinite clay minerals is similar in the majority of the studied soils.

Chlorite mineral was observed in all studied soils; however, its relative amount differed in different soils. The quantity of smectite-vermiculite interstratified minerals (interstratified in Table 4) as observed in some orders was very low (lower than 10%). The palygorskite mineral changes showed a decreasing process from the beginning (Aridisols order) to the end (Histosols order) of the studied area, with the palygorskite clay mineral not being found in both Mollisols and Histosols Orders. This may be due to the fact that any increase

TABLE 4
Semi-quantitative analysis of clay minerals in the clay fraction of some soils under study

| Soil number | Pedon | Horizon | Smectite | Illite | Chlorite | Interstratified | Kaolinite | Palygorskite |
|---|---|---|---|---|---|---|---|---|
| S2 | 1 | Bk1 | ++ | ++ | ++ | * | + | ++ |
| S6 | 2 | A | ++++ | ++ | + | * | - | - |
| S7 | 2 | Byz1 | +++++ | + | - | - | + | * |
| S11 | 3 | A | ++++ | ++ | - | * | + | + |
| S12 | 3 | Bw | ++++ | ++ | ++ | * | + | - |
| S13 | 3 | Btnk | +++ | +++ | - | * | + | + |
| S14 | 3 | By | ++++ | ++ | - | * | + | - |
| S17 | 4 | A | + | +++ | + | * | + | + |
| S18 | 4 | Bw1 | +++ | +++ | + | * | + | + |
| S22 | 5 | A | ++++ | ++ | - | * | + | + |
| S23 | 5 | Bk | +++++ | ++ | + | * | + | * |
| S24 | 5 | Bz | ++++ | +++ | + | - | + | * |
| S28 | 6 | Bk1 | +++ | +++ | ++ | * | + | - |
| S29 | 6 | Bk2 | ++++ | +++ | + | - | - | * |
| S30 | 6 | Bkm | +++++ | ++ | - | * | + | * |
| S32 | 7 | Bkz | ++++ | ++ | + | - | + | * |
| S35 | 8 | Ag | +++ | ++ | ++ | * | + | * |
| S36 | 8 | Bwg1 | ++++ | +++ | + | * | + | * |
| S40 | 9 | Oe1 | +++++ | + | + | * | + | * |
| S41 | 9 | Oe2 | +++++ | + | - | * | + | * |

*: not detected, -: < 10%, +: 10-20%, ++:20-30%, +++: 30-45%,++++ : 45-55%, +++++: >55%

in the humidity of the studied area from the beginning (Aridisols) to the end (Histosols), destroys palygorskite due to instability, resulting in the prevalence of smectite and vermiculite minerals (Moazallahi and Farpoor 2012). An increase in the smectite mineral in the Mollisol and Histosol Orders may be attributed to these changes.

*Kinetics of P Desorption*

The trends in cumulative desorption of P by 0.05 M sodium bicarbonate in different soil samples are shown in Figure 3. Based on the results obtained, biphasic patterns of P desorption are found at the beginning followed by slower desorption. Similar results have been found by others including Jalali and Zinli, (2011) and Nafiu (2009). Biphasic patterns of P desorption can be due to the adsorption of heterogeneous sites with different sorption affinities (Saha *et al.* 2004). Initial fast desorption of P could be related to rapid dissolution of amorphous phosphates with lower bonding energy (Jalali and Zinli 2011). On the other hand, P desorption in the slower second phase depends on the dissolution of the crystalline phosphate compounds such as octa-Ca-phosphate and Ca-hydroxyl-apatite.

Thus, it seems that the first and second stages of P desorption could be related to a labile P and also less mobile forms of P, respectively. In most of the soil samples, the first 8 h had the highest amount of P desorption, followed by a slight decrease in P desorption. Elrashidi *et al.* (1975) explained that in calcareous soils, there are two forms of P, one of which is rapidly released, while the other is slowly and gradually released. In the process of desorption, these two forms are abandoned simultaneously during the first 6 to 12 h, but after that, only the release of the second form lasts for up to 72 h until a balance is achieved. The gradual reduction in P desorption velocity with time may be due to reducing surface coverage and surface charge, thus reducing the potential energy of adsorbed phosphorous ions

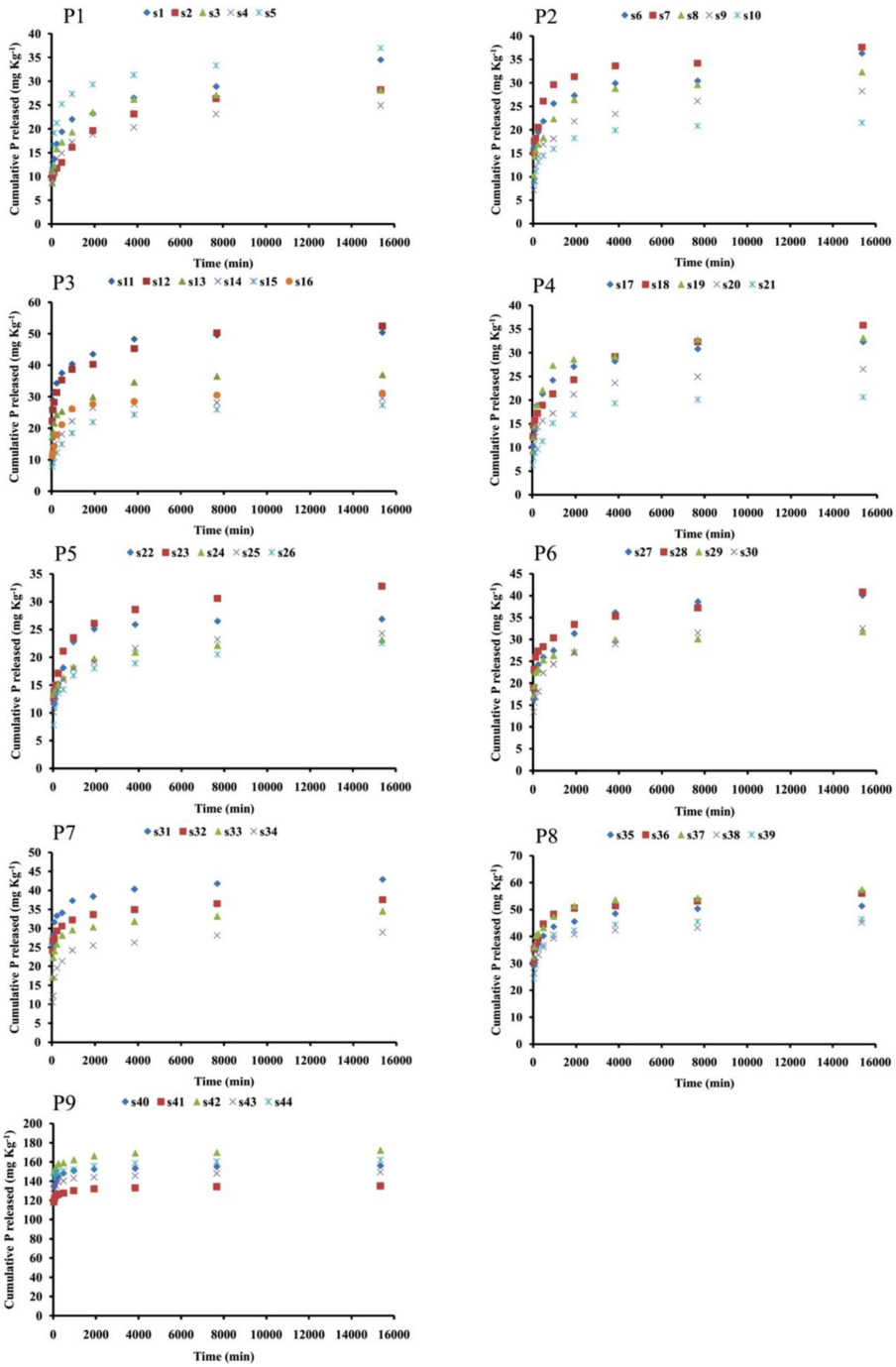


*Figure 3: Cumulative release of P with time in treated soils*

(Mikutta *et al.* 2006). The total average P released in the studied soils ranged from 25.94 to 154.94 mg $kg^{-1}$. The minimum (20.6 mg $kg^{-1}$) and maximum (172.1 mg $kg^{-1}$) amounts of P (average of profiles in each soil order) were in P5 (Calcic Haplosalids) and P9 (Typic Haplohemists), respectively (Figure 3). Phosphorus desorption in Histosols order was, on average, 6 times more than the cumulative P released in Aridisols, which could be due to a high amount of total P. Seven kinetic equations and one model were used for describing P desorption kinetics up to 256 h. Based on the results (Table 5), simple rate equations including zero order, first order, second order, and third order equations could not be used for the description of P desorption in the soil samples. Phosphorus desorption was certainly affected by many soil factors; needless to say desorption patterns of P could not be described through simple rate equations. An increase in the order of

TABLE 5
Parameter derived from seven equations for P desorption in studied soils

| Soil number | Zero order | | First order | | Second order | | Third order | | Parabolic diffusion | | Simple Elovich | | | | Two-constant rate | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | SE | $R^2$ | SE | $R^2$ | SE | $R^2$ | SE | $R^2$ | SE | αs (Ln) | βs | $R^2$ | SE | a | b | $R^2$ | SE |
| **S1** | 0.74 | 4.24 | 0.59 | 0.27 | 0.45 | 0.02 | 0.34 | 0.00 | 0.91 | 2.47 | 11.76 | 0.27 | 0.98 | 1.18 | 12.29 | 0.19 | 0.99 | 0.05 |
| **S2** | 0.76 | 3.63 | 0.67 | 0.25 | 0.57 | 0.02 | 0.49 | 0.00 | 0.94 | 1.83 | 9.13 | 0.31 | 0.93 | 1.95 | 9.91 | 0.19 | 0.97 | 0.08 |
| **S3** | 0.57 | 4.90 | 0.47 | 0.32 | 0.36 | 0.02 | 0.27 | 0.00 | 0.81 | 3.29 | 10.82 | 0.30 | 0.98 | 0.94 | 11.07 | 0.19 | 0.96 | 0.08 |
| **S4** | 0.67 | 3.39 | 0.55 | 0.26 | 0.42 | 0.02 | 0.32 | 0.00 | 0.88 | 2.09 | 9.78 | 0.38 | 1.00 | 0.42 | 10.07 | 0.17 | 0.98 | 0.05 |
| **S5** | 0.60 | 5.26 | 0.47 | 0.27 | 0.35 | 0.01 | 0.25 | 0.00 | 0.81 | 3.64 | 16.19 | 0.27 | 0.99 | 0.81 | 16.27 | 0.16 | 0.95 | 0.09 |
| **S6** | 0.74 | 3.71 | 0.64 | 0.18 | 0.55 | 0.01 | 0.47 | 0.00 | 0.91 | 2.17 | 16.43 | 0.31 | 0.97 | 1.35 | 16.88 | 0.13 | 0.98 | 0.04 |
| **S7** | 0.82 | 33.42 | 0.89 | 0.29 | 0.71 | 0.01 | 0.47 | 0.00 | 0.63 | 47.38 | -2.75 | 0.05 | 0.36 | 62.62 | 14.66 | 0.30 | 0.62 | 0.52 |
| **S8** | 0.62 | 4.88 | 0.51 | 0.28 | 0.39 | 0.02 | 0.28 | 0.00 | 0.84 | 3.16 | 12.92 | 0.28 | 0.98 | 1.12 | 13.25 | 0.17 | 0.96 | 0.08 |
| **S9** | 0.63 | 4.64 | 0.47 | 0.35 | 0.33 | 0.03 | 0.22 | 0.01 | 0.84 | 3.02 | 9.41 | 0.29 | 1.00 | 0.44 | 9.63 | 0.21 | 0.96 | 0.10 |
| **S10** | 0.56 | 3.38 | 0.47 | 0.26 | 0.38 | 0.02 | 0.30 | 0.00 | 0.80 | 2.31 | 9.71 | 0.44 | 0.99 | 0.52 | 9.84 | 0.16 | 0.97 | 0.07 |
| **S11** | 0.57 | 6.08 | 0.51 | 0.17 | 0.45 | 0.01 | 0.39 | 0.00 | 0.81 | 4.07 | 28.97 | 0.24 | 0.99 | 0.96 | 29.23 | 0.11 | 0.98 | 0.03 |
| **S12** | 0.67 | 6.27 | 0.57 | 0.20 | 0.47 | 0.01 | 0.38 | 0.00 | 0.88 | 3.85 | 25.15 | 0.20 | 0.99 | 0.90 | 25.63 | 0.14 | 0.99 | 0.03 |
| **S13** | 0.63 | 4.58 | 0.56 | 0.19 | 0.48 | 0.01 | 0.40 | 0.00 | 0.85 | 2.90 | 19.01 | 0.30 | 0.98 | 1.14 | 19.33 | 0.13 | 0.98 | 0.04 |
| **S14** | 0.54 | 4.94 | 0.45 | 0.28 | 0.36 | 0.02 | 0.27 | 0.00 | 0.77 | 3.46 | 13.03 | 0.31 | 0.97 | 1.25 | 13.18 | 0.17 | 0.95 | 0.09 |
| **S15** | 0.61 | 4.81 | 0.50 | 0.34 | 0.40 | 0.03 | 0.30 | 0.00 | 0.84 | 3.08 | 8.92 | 0.29 | 0.98 | 1.02 | 9.36 | 0.22 | 0.98 | 0.07 |
| **S16** | 0.49 | 5.85 | 0.41 | 0.32 | 0.34 | 0.02 | 0.27 | 0.00 | 0.73 | 4.27 | 13.30 | 0.28 | 0.96 | 1.57 | 13.37 | 0.18 | 0.94 | 0.10 |
| **S17** | 0.55 | 5.69 | 0.44 | 0.33 | 0.34 | 0.02 | 0.26 | 0.00 | 0.78 | 4.00 | 12.72 | 0.27 | 0.98 | 1.11 | 12.83 | 0.19 | 0.94 | 0.10 |
| **S18** | 0.78 | 4.02 | 0.67 | 0.22 | 0.54 | 0.01 | 0.43 | 0.00 | 0.95 | 1.94 | 13.11 | 0.27 | 0.96 | 1.72 | 13.85 | 0.17 | 0.99 | 0.03 |
| **S19** | 0.49 | 6.60 | 0.39 | 0.37 | 0.29 | 0.02 | 0.21 | 0.00 | 0.73 | 4.85 | 12.86 | 0.24 | 0.97 | 1.65 | 12.77 | 0.21 | 0.92 | 0.14 |
| **S20** | 0.65 | 3.88 | 0.55 | 0.26 | 0.45 | 0.02 | 0.35 | 0.00 | 0.87 | 2.39 | 10.48 | 0.34 | 0.98 | 0.82 | 10.86 | 0.17 | 0.99 | 0.04 |
| **S21** | 0.58 | 3.78 | 0.49 | 0.33 | 0.39 | 0.03 | 0.30 | 0.01 | 0.81 | 2.51 | 7.36 | 0.39 | 0.97 | 0.99 | 7.64 | 0.20 | 0.97 | 0.08 |
| **S22** | 0.48 | 4.75 | 0.43 | 0.27 | 0.38 | 0.02 | 0.34 | 0.00 | 0.73 | 3.45 | 12.86 | 0.35 | 0.94 | 1.55 | 13.02 | 0.15 | 0.94 | 0.09 |
| **S23** | 0.63 | 4.68 | 0.54 | 0.25 | 0.44 | 0.01 | 0.36 | 0.00 | 0.85 | 2.97 | 13.73 | 0.29 | 0.99 | 0.82 | 14.11 | 0.16 | 0.98 | 0.05 |
| **S24** | 0.67 | 2.21 | 0.62 | 0.13 | 0.56 | 0.01 | 0.51 | 0.00 | 0.88 | 1.31 | 13.54 | 0.58 | 0.98 | 0.58 | 13.72 | 0.10 | 0.98 | 0.03 |
| **S25** | 0.65 | 3.14 | 0.55 | 0.22 | 0.46 | 0.02 | 0.37 | 0.00 | 0.86 | 1.95 | 11.30 | 0.42 | 1.00 | 0.37 | 11.54 | 0.14 | 0.99 | 0.03 |
| **S26** | 0.63 | 2.98 | 0.50 | 0.24 | 0.37 | 0.02 | 0.26 | 0.00 | 0.83 | 2.01 | 10.20 | 0.46 | 0.99 | 0.53 | 10.28 | 0.15 | 0.95 | 0.08 |
| **S27** | 0.66 | 5.12 | 0.56 | 0.21 | 0.46 | 0.01 | 0.36 | 0.00 | 0.87 | 3.17 | 18.59 | 0.26 | 0.98 | 1.08 | 19.00 | 0.14 | 0.98 | 0.04 |
| **S28** | 0.67 | 4.12 | 0.56 | 0.16 | 0.46 | 0.01 | 0.36 | 0.00 | 0.86 | 2.70 | 22.35 | 0.31 | 0.98 | 0.90 | 22.52 | 0.11 | 0.96 | 0.05 |
| **S29** | 0.56 | 3.36 | 0.48 | 0.15 | 0.41 | 0.01 | 0.35 | 0.00 | 0.77 | 2.41 | 19.84 | 0.45 | 0.98 | 0.75 | 19.87 | 0.09 | 0.95 | 0.05 |
| **S30** | 0.61 | 4.54 | 0.52 | 0.23 | 0.44 | 0.01 | 0.36 | 0.00 | 0.84 | 2.95 | 15.16 | 0.31 | 0.99 | 0.74 | 15.45 | 0.15 | 0.98 | 0.05 |
| **S31** | 0.55 | 4.08 | 0.49 | 0.13 | 0.43 | 0.00 | 0.38 | 0.00 | 0.77 | 2.90 | 28.82 | 0.37 | 0.98 | 0.77 | 28.88 | 0.08 | 0.96 | 0.03 |
| **S32** | 0.60 | 2.97 | 0.55 | 0.10 | 0.50 | 0.00 | 0.45 | 0.00 | 0.82 | 2.00 | 26.17 | 0.47 | 0.99 | 0.37 | 26.25 | 0.07 | 0.98 | 0.02 |
| **S33** | 0.49 | 4.08 | 0.41 | 0.17 | 0.33 | 0.01 | 0.26 | 0.00 | 0.70 | 3.12 | 21.58 | 0.40 | 0.95 | 1.29 | 21.47 | 0.10 | 0.89 | 0.07 |
| **S34** | 0.46 | 5.02 | 0.37 | 0.30 | 0.28 | 0.02 | 0.21 | 0.00 | 0.69 | 3.82 | 14.07 | 0.33 | 0.95 | 1.47 | 13.86 | 0.16 | 0.89 | 0.12 |
| **S35** | 0.54 | 5.65 | 0.49 | 0.15 | 0.43 | 0.00 | 0.37 | 0.00 | 0.78 | 3.95 | 32.20 | 0.27 | 0.99 | 0.91 | 32.32 | 0.09 | 0.97 | 0.04 |
| **S36** | 0.52 | 6.41 | 0.46 | 0.16 | 0.40 | 0.00 | 0.34 | 0.00 | 0.74 | 4.68 | 34.56 | 0.24 | 0.97 | 1.57 | 34.61 | 0.10 | 0.95 | 0.05 |
| **S37** | 0.58 | 5.75 | 0.52 | 0.14 | 0.46 | 0.00 | 0.40 | 0.00 | 0.80 | 3.95 | 36.12 | 0.25 | 0.99 | 1.08 | 36.28 | 0.09 | 0.97 | 0.03 |
| **S38** | 0.54 | 4.45 | 0.49 | 0.13 | 0.43 | 0.00 | 0.38 | 0.00 | 0.77 | 3.17 | 29.80 | 0.34 | 0.98 | 0.93 | 29.86 | 0.08 | 0.96 | 0.04 |
| **S39** | 0.46 | 6.31 | 0.40 | 0.19 | 0.35 | 0.01 | 0.30 | 0.00 | 0.70 | 4.74 | 27.91 | 0.26 | 0.96 | 1.74 | 27.87 | 0.11 | 0.93 | 0.07 |
| **S40** | 0.43 | 6.26 | 0.42 | 0.04 | 0.40 | 0.00 | 0.39 | 0.00 | 0.66 | 4.85 | 138.56 | 0.28 | 0.94 | 1.99 | 138.54 | 0.02 | 0.93 | 0.01 |
| **S41** | 0.49 | 4.12 | 0.47 | 0.03 | 0.46 | 0.00 | 0.45 | 0.00 | 0.71 | 3.08 | 122.19 | 0.39 | 0.96 | 1.13 | 122.19 | 0.02 | 0.95 | 0.01 |
| **S42** | 0.58 | 5.47 | 0.57 | 0.03 | 0.55 | 0.00 | 0.54 | 0.00 | 0.81 | 3.67 | 152.16 | 0.26 | 0.99 | 0.87 | 152.23 | 0.02 | 0.99 | 0.01 |
| **S43** | 0.58 | 4.21 | 0.56 | 0.03 | 0.55 | 0.00 | 0.53 | 0.00 | 0.80 | 2.92 | 134.03 | 0.34 | 0.99 | 0.75 | 134.06 | 0.02 | 0.98 | 0.01 |
| **S44** | 0.68 | 3.59 | 0.66 | 0.02 | 0.65 | 0.00 | 0.63 | 0.00 | 0.87 | 2.26 | 146.34 | 0.36 | 0.96 | 1.29 | 146.40 | 0.02 | 0.96 | 0.01 |

reaction from zero to third order ended in a decrease in $R^2$ in the studied soils, as reported by Saffari *et al*. (2016) who relates this to desorption of Pb. $R^2$ and SE values shown in Table 5 indicate that simple Elovich and power function equations are the best-fitted equations for describing desorption of P. Elovich equation assumes that the active surfaces of the sorbent are heterogeneous, depending on which different activation energies for chemisorption are shown (Gupta and Babu 2006). Given the good fitting of desorption data with simple Elovich and power function equations, it can be concluded that the diffusion process is a limiting step in P desorption from soils.

Similar results were obtained by Garcia-Rodeja and Gil-sotres (1997) in P desorption in some acidic soils in Spain. The results obtained from previous experiments show that the rate of metal desorption increases as the value of 'αs' increases in simple Elovich equation (Chien and Clayton 1980). Among the studied soils, soil samples of Mollisols and Histosols were found to have the highest '*αs*' value from simple Elovich equation and "*a*" from power function equation. Kuo and Mikkelsen (1980) reported that an increase in the value of "*a*" increases the rate of metal desorption from soils. The model of two first-order reactions was used by several researches like Santos *et al.* (2010), Jalali and Tabar (2013) and Saffari *et al*.(2016) to predict metal behaviour. This model could be used as a kinetic method for metal speciation in soils and sediments (Saffari *et al*. 2015). The model of two first-order reactions exhibited biphasic reaction, i.e. rapid extraction followed by slow extraction of metal (Saffari *et al*. 2015). Hence, this model is expected to describe desorption of P adequately. This model approach indicates the quantity and the extraction rate of metal fractions (Santos *et al.* 2010). Table 6 shows the parameters of $Q_1$, $K_1$, $Q_2$, $K_2$, $R_2$, SE, and $Q_1/Q_2$. As the results indicated that $R^2$ was higher than 0.94 and the values of SE were lower than that of SE obtained from the Elovich equation, it was felt that this model could suitably describe kinetics of P desorption in soil samples. Moreover, the results showed that $K_1$ (coefficients of P for rapid desorption phase) were higher than $K_2$ (coefficients of P for slower desorption phase). The rate of $Q_1$ (quickly extracted) in Histosols and Mollisols was higher than in other soil orders, in fact this was the highest rate of P desorption. A high ratio of $Q_1/Q_2$ in Histosols, Alfisols, and Mollisols indicate that the labile metal fractions are higher than the less labile fractions.

*Fractionation of P in Unamended Soils*

Figure 4 shows the concentration of each chemical fraction of P in the native soils (unamended soils). Based on the results, in all soil samples P is strongly associated with Ca-P and Res-P fractions, which agrees with results obtained by many researchers including Kolahchi and Jalali (2012) and Castillo and Wright (2008). Jalali and Ranjbar (2010) reported that P in calcareous soils of western Iran was predominantly present in the Ca-P (65.9%) and Res-P (28.9%).

On the other hand, Exch-P, the most bioavailable form of P, has the lowest concentration among all P chemical forms. Distribution of chemical forms of

TABLE 6
Parameter values of two first-order P reaction model in examined soils

| Soil number | $Q_1$ | $K_1$ | $Q_2$ | $K_2$ | $R^2$ | SE | $Q_1/Q_2$ | Soil number | $Q_1$ | $K_1$ | $Q_2$ | $K_2$ | $R^2$ | SE | $Q_1/Q_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| S1 | 16.772 | 1.326 | 17.359 | 0.013 | 0.957 | 1.714 | 0.966 | S23 | 14.397 | 3.542 | 16.669 | 0.044 | 0.977 | 1.173 | 0.864 |
| S2 | 10.231 | 5.223 | 17.527 | 0.022 | 0.997 | 0.400 | 0.584 | S24 | 13.846 | 5.860 | 8.601 | 0.037 | 0.985 | 0.471 | 1.610 |
| S3 | 12.447 | 2.031 | 15.103 | 0.041 | 0.991 | 0.698 | 0.824 | S25 | 12.793 | 2.687 | 10.894 | 0.031 | 0.984 | 0.664 | 1.174 |
| S4 | 12.613 | 1.676 | 11.664 | 0.022 | 0.973 | 0.973 | 1.081 | S26 | 12.691 | 1.805 | 8.911 | 0.025 | 0.978 | 0.720 | 1.424 |
| S5 | 20.708 | 1.567 | 14.453 | 0.028 | 0.971 | 1.415 | 1.433 | S27 | 21.964 | 2.295 | 17.876 | 0.024 | 0.991 | 0.826 | 1.229 |
| S6 | 17.564 | 4.351 | 15.681 | 0.032 | 0.944 | 1.704 | 1.120 | S28 | 26.194 | 2.364 | 13.632 | 0.019 | 0.985 | 0.882 | 1.921 |
| S7 | 16.249 | 4.418 | 18.631 | 0.074 | 0.973 | 1.400 | 0.872 | S29 | 21.974 | 2.727 | 8.941 | 0.035 | 0.968 | 0.899 | 2.458 |
| S8 | 14.666 | 2.390 | 16.273 | 0.037 | 0.991 | 0.749 | 0.901 | S30 | 16.257 | 3.111 | 15.169 | 0.042 | 0.981 | 0.999 | 1.072 |
| S9 | 13.923 | 1.052 | 13.605 | 0.022 | 0.988 | 0.836 | 1.023 | S31 | 30.560 | 3.414 | 11.347 | 0.045 | 0.974 | 0.980 | 2.693 |
| S10 | 10.964 | 2.192 | 10.010 | 0.043 | 0.984 | 0.651 | 1.095 | S32 | 27.444 | 4.030 | 9.239 | 0.038 | 0.978 | 0.691 | 2.970 |
| S11 | 30.510 | 3.559 | 19.220 | 0.043 | 0.988 | 1.001 | 1.587 | S33 | 24.597 | 2.277 | 8.887 | 0.040 | 0.979 | 0.828 | 2.768 |
| S12 | 29.341 | 2.494 | 22.265 | 0.024 | 0.978 | 1.630 | 1.318 | S34 | 17.257 | 1.407 | 10.599 | 0.056 | 0.979 | 0.997 | 1.628 |
| S13 | 21.409 | 2.811 | 15.647 | 0.027 | 0.985 | 0.923 | 1.368 | S35 | 33.564 | 3.555 | 16.565 | 0.052 | 0.978 | 1.252 | 2.026 |
| S14 | 13.828 | 2.592 | 14.851 | 0.052 | 0.993 | 0.619 | 0.931 | S36 | 34.188 | 3.928 | 19.015 | 0.083 | 0.979 | 1.339 | 1.798 |
| S15 | 9.540 | 2.772 | 16.733 | 0.044 | 0.993 | 0.635 | 0.570 | S37 | 38.106 | 3.497 | 17.424 | 0.045 | 0.983 | 1.142 | 2.187 |
| S16 | 11.153 | 4.778 | 18.591 | 0.097 | 0.988 | 0.903 | 0.600 | S38 | 30.702 | 3.765 | 12.887 | 0.059 | 0.986 | 0.789 | 2.382 |
| S17 | 13.746 | 2.015 | 16.722 | 0.061 | 0.970 | 1.465 | 0.822 | S39 | 26.544 | 4.011 | 18.260 | 0.102 | 0.971 | 1.453 | 1.454 |
| S18 | 15.776 | 2.764 | 19.541 | 0.018 | 0.995 | 0.625 | 0.807 | S40 | 134.969 | 8.269 | 19.132 | 0.157 | 0.974 | 1.352 | 7.055 |
| S19 | 12.498 | 2.043 | 18.921 | 0.087 | 0.979 | 1.326 | 0.661 | S41 | 123.301 | 6.238 | 10.694 | 0.060 | 0.979 | 0.828 | 11.530 |
| S20 | 11.831 | 2.678 | 13.891 | 0.033 | 0.989 | 0.680 | 0.852 | S42 | 151.427 | 33.380 | 19.013 | 0.058 | 0.965 | 1.576 | 7.964 |
| S21 | 7.687 | 2.918 | 12.529 | 0.046 | 0.995 | 0.405 | 0.614 | S43 | 133.857 | 8.149 | 13.666 | 0.069 | 0.946 | 1.506 | 9.795 |
| S22 | 11.237 | 25.111 | 15.231 | 0.080 | 0.997 | 0.379 | 0.738 | S44 | 148.482 | 6.761 | 13.244 | 0.023 | 0.996 | 0.390 | 11.211 |

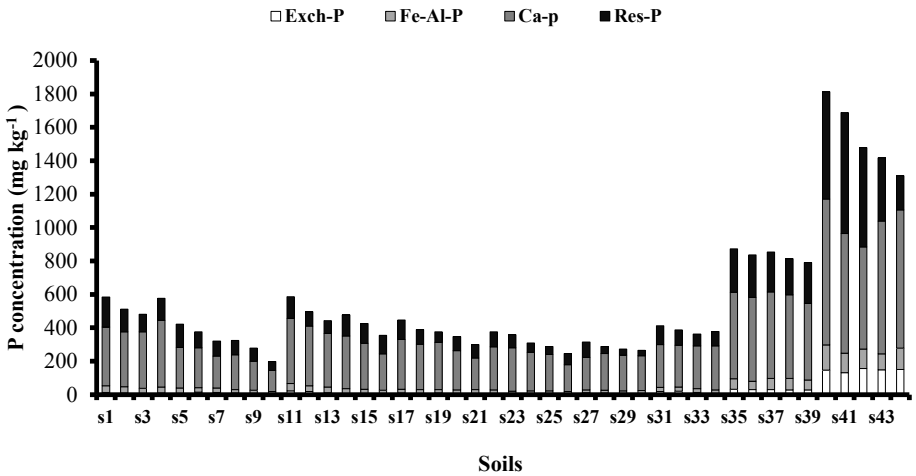


*Figure 4: Concentration of different P fractions in unamended soils*

P in unamended soils followed this order: Ca-P> Res-P>Fe-Al-P>Exch-P. The Ca-P form varied from 126.3 to 873 mg $kg^{-1}$ (41.2 to 78.7%). Jalali and Sajadi Tabar (2013) investigated soil P fractionation in calcareous soils and reported that Exch-P ranged between 0.9% and 1.3% of the total P. In alkaline soils (pH value above 7), P tends to precipitate as calcium phosphates or co-precipitate with carbonates (Jalali and Ranjbar 2010) as these are more stable than Exch-P and Fe-Al-P fractions (Diaz *et al*. 2006). A higher abundance of Ca-P (64.79%) compared with other chemical forms indicates that P is immobilised within the crystalline and secondary minerals; additionally, P is essentially non-labile in most of the studied soils. The main difference between soil orders in P distribution was observed in Ca-P form. The relative percentage of Ca-P in Inceptisols, Aridisols, Alfisols, Histosols and Mollisols constituted 73.6%, 66.8%, 66.6%, 50% and 60% respectively. Histosols and Mollisols had the lowest Ca-P concentrations because they had the least CCE among all soil orders. Furthermore, Jalali and Tabar (2013) believe that soil irrigation by groundwater containing large quantities of soluble salts such as $Ca^{2+}$ and $Na^{+}$, encourage P retention in the Ca-P fraction. Whereas the studied Histosols and Mollisols were not under cultivation and the main source of their moisture was melting snow and rainfall, thus it seems that a high quality of water in this region caused the Ca-P fraction in these Orders to be lower than in others. The concentration of Res-P, Fe-Al-P and Exch-P ranged between 32.3, 12, 2.1 and724.5 mg $kg^{-1}$ (12.2 to 42.9%) 152.1 mg $kg^{-1}$ (4.2 to 9.8 and to 156.9 mg $kg^{-1}$ (0.5 to 11.4%), respectively. Res-P is known for its stable and recalcitrant chemical forms. Compared to Ca-P, Histosols and Mollisols had the highest Res-P in all soil orders. Jalali and Tabar (2013) observed that land uses with minimal management and no fertilisation such as pasture, had more P in residual fraction. The P bound to amorphous oxyhydroxide surfaces and crystalline Fe and Al oxides, for all soil samples had the second lowest P content of all chemical forms. The concentration of Fe-Al-P form was higher for

Histosols (7.95%) and Mollisols (7.4%) as compared to other soil types. Wright (2009) studied chemical forms of P in Histosols of Florida. He reported that the average Fe-Al-P in turf grass and sugarcane were 2.9 and 11.4% of the total P, respectively. Jalali and Sajadi Tabar (2013) investigated chemical fractionation of P in calcareous soils and showed that the average Fe-Al-P fraction was 4.9 to 7% of the total P for different land uses. As explained above, Exch-P has the lowest concentration fraction among all P chemical forms. The Exch-P was higher for Histosols and Mollisols (averaged 146.5 and 29.26 mg P $kg^{-1}$, respectively) than Aridisols (7.67 mg P $kg^{-1}$), Inceptisols (8 mg P $kg^{-1}$), and Alfisols (15.3 mg P $kg^{-1}$). The Exch-P with an average of 3.25% of total P was the least abundant P fraction in the studied soils.

*Fractionation of P in Amended Soils*

Addition of P to the soils (50 µg $g^{-1}$) increased the concentration of all fractions. However, the relative percentage of Exch-P and Fe-Al-P fraction in amended soils increased but Ca-P and Res-P decreased as compared to unamended soils (Figure 5). Since Exch-P and Fe-Al-P forms represent the least recalcitrant pools, P in these forms likely represents recent inputs from fertilisers (Wright 2009). Exch-P concentration in amended soils was about double in comparison to the unamended soil samples. The Exch-P concentration ranged between 16.2 and 24.5 mg $kg^{-1}$ (with an average of 20.6 mg $kg^{-1}$). These results are in agreement with many previous observations (Jalali and Sajadi Tabar 2013; Andrade 2007) that the addition of P increases Exch-P in soil. The highest increases of Exch-P and Fe-Al-P fractions were observed in Mollisols. For all amended soil samples, Ca-P was the dominant P form, but with a decreased percentage. The highest and lowest amounts of the applied P to exchangeable fraction were obtained in Mollisols and

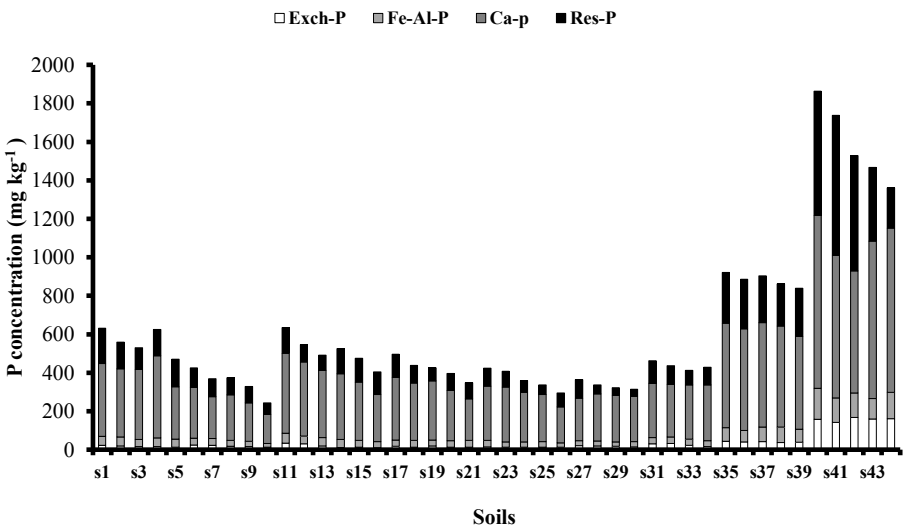


*Figure 5: Concentration of different P fractions in amended soils*

Aridisol soils, respectively. On the other hand, the highest and lowest amounts of changing P added to Ca-P were observed in Aridisols and Mollisols soils, respectively. Exch-P is considered an available form of P for plants; therefore, it has higher absorbency and leaching compared to other forms. Considering the fact that less than 20% of P fertiliser consumed is transferred to Exch-P fraction, we can say that more than 80% of the applied fertiliser temporarily changed to a non-available form in the studied soils due to the calcareous character and high pH. A high amount of such P is defined as labile and can be released at various stages and introduced as a supplier of the plant's initial need.

Song *et al.* (2011) investigated chemical forms of P in Mollisols and showed that application of P increased relative percentage of Ca-P and Al-P, but decreased relative percentage of occluded P. They concluded that the applied P had been transformed to these sparingly soluble forms for a short time. A sharp decrease in Ca-P and Res-P fractions were observed in Inceptisols and Mollisols, respectively. Correlation between Desorption and Chemical Forms Indices, Physic-Chemical and Mineralogical Properties of the Soils

A simple correlation coefficient between some physical and chemical properties of the studied soils, available-P, total-P and desorbed-P at the beginning, middle and the end of P released times is shown in Table 7.

TABLE 7
Simple correlation coefficient (r) between available P, total P, released P at different times and soil properties in studied soils

| | pH | OM | CCE | Clay | CEC | EC | Sand | Silt | Olsen-P | Total-P |
|---|---|---|---|---|---|---|---|---|---|---|
| Olsen-P | -0.321 | 0.862** | -0.520* | -0.052 | 0.877** | -0.258 | -0.375 | 0.518* | | |
| Total-P | -0.408 | 0.908** | -0.665** | 0.114 | 0.930** | -0.366 | -0.467* | 0.521* | 0.964** | |
| T0.5 | -0.335 | 0.855** | -0.509* | -0.060 | 0.871** | -0.245 | -0.375 | 0.524* | 0.996** | 0.956** |
| T1 | -0.337 | 0.852** | -0.519* | -0.063 | 0.869** | -0.246 | -0.367 | 0.515* | 0.995** | 0.957** |
| T32 | -0.339 | 0.865** | -0.524* | -0.061 | 0.879** | -0.274 | -0.382 | 0.533* | 0.995** | 0.965** |
| T128 | -0.304 | 0.861** | -0.530* | -0.063 | 0.874** | -0.300 | -0.365 | 0.513* | 0.994** | 0.965** |

As can be seen from the results, there is a significant positive correlation between OM, CEC, silt, available-P, total-P, and the P parameters. On the other hand, among the soil properties, only CCE showed a significant negative relation with the P parameters. Other correlations observed were not statistically significant. A positive correlation between OM and available-P and P released might be due to four processes: (i) the formation of organic matter complexes with P, which results in the formation of organic phosphates and an increase in P mobility; (ii) organic anions, which can be exchanged with surface-adsorbed-P;(iii) Fe-Al oxides coatings on humus formations reduce the soil P sorption; and ( iv) as a source of P, organic matter can also increase the amount of released P through the mineralisation processes. Correlation between parameters extracted from fitted equations and P desorbed data (Table 8) shows that OM, CEC, silt,

available-P, total-P and desorbed-P at the beginning, middle and the end of P released times had a significant positive correlation with "*as*" value from the Elovich equation, "$\alpha$" from the power function equation, and $Q_1$, $K_2$,and $Q_1/Q_2$ parameters and a significant negative correlation with "b" parameter from the power function equation. Also, CCE, unlike other mentioned properties, had a significant positive correlation with "*b*" parameter from the power function equation, and a significant negative correlation with "a" from the power function equation and $Q_1/Q_2$.

TABLE 8
Simple correlation coefficient (r) between parameters of two first-order reactions, simple Elovich, power function and soil properties, available P, total P, released P at different times, in studied soils.

| | pH | OM | CCE | Clay | CEC | EC | Sand | Silt | Olsen-P | Total-P | T1 | T32 | T128 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| bs | -0.109 | -0.049 | -0.013 | 0.168 | -0.007 | 0.189 | -0.024 | -0.086 | -0.006 | -0.041 | 0.031 | -0.033 | -0.055 |
| as | -0.135 | 0.717** | -0.216 | -0.205 | 0.706** | -0.164 | -0.236 | 0.445* | 0.743** | 0.671** | 0.721** | .735** | 0.733** |
| b | 0.352 | -0.588** | 0.473* | -0.107 | -0.605** | 0.263 | 0.257 | -0.256 | -0.622** | -0.618** | -0.657** | -.630** | -0.625** |
| a | -0.336 | 0.858** | -0.516* | -0.054 | 0.874** | -0.258 | -0.376 | 0.521* | 0.995** | 0.959** | 1.000** | .997** | 0.994** |
| $Q_1$ | -0.323 | 0.851** | -0.519* | -0.061 | 0.866** | -0.259 | -0.357 | 0.501* | 0.994** | 0.955** | 0.999** | .995** | 0.994** |
| $K_1$ | -0.176 | 0.115 | 0.081 | 0.078 | 0.145 | -0.025 | -0.524* | 0.620** | 0.121 | 0.117 | 0.112 | 0.112 | 0.089 |
| $Q_2$ | 0.254 | 0.094 | -0.105 | -0.043 | 0.076 | -0.434 | -0.048 | 0.092 | 0.041 | 0.110 | -0.009 | 0.056 | 0.094 |
| $K_2$ | -0.461* | 0.708** | -0.297 | -0.059 | 0.715** | -0.059 | -0.448* | 0.616** | 0.679** | 0.679** | 0.666** | .698** | 0.673** |
| $Q_1/Q_2$ | -0.348 | 0.710** | -0.488* | 0.007 | 0.741** | -0.149 | -0.331 | 0.421 | 0.902** | 0.861** | 0.924** | .900** | 0.892** |

Other relationships obtained were not statistically significant. Jalali and Ranjbar (2010) reported a significant positive relationship between a parameter from power function equation and preliminary available-P of the soil. The correlation between chemical forms of P (the results obtained before and after adding P fertiliser were the same), available-P and extracted parameters from two first-order reaction models (Table 9) shows that all forms of P indicate a significant positive relationship with three $Q_1$, $K_2$ and $Q_1/Q_2$ parameters as well as available-P. It appears that the existence of a significant relationship between all forms of P and available-P indicates a lack of specific extraction from relative forms, because it is predicted that only Exch-P and Fe-Al-P may have a direct a significant relationship with available-P

On the other hand, unlike chemical forms of P, $Q_1$ as an indicator of available-P had a significant positive relationship with Olsen-P, and $Q_2$ as P with low availability did not have a significant relationship with Olsen-P. Therefore, it can be stated that the study of desorption kinetics of P may have more predictive ability for P availability compared to the sequential extraction technique. However, there is a need to investigate the relationship between plant reaction and extracted parameters from two first-order reaction models fitted on P desorption data in future studies. The study of simple correlations between clay minerals of studied soil and parameters fitted on P desorption is shown in Table10.

Among the various minerals, significant correlations were observed only between two kaolinite and illite clays.. A significant negative correlation was found between kaolinite and "as" from simple Elovich equation as well as illite

TABLE 9
Simple correlation coefficient (r) between parameters of two first-order reaction models and chemical forms of P in studied soils

| | pH | $Q_1$ | $K_1$ | $Q_2$ | $K_2$ | Q1/Q2 | Exch-P | Fe-Al-P | Ca-P | Res-P |
|---|---|---|---|---|---|---|---|---|---|---|
| $Q_1$ | -0.323 | | | | | | | | | |
| $K_1$ | -0.176 | 0.089 | | | | | | | | |
| $Q_2$ | 0.254 | -0.012 | -0.058 | | | | | | | |
| $K_2$ | -0.461$^{*}$ | 0.643$^{**}$ | 0.406 | 0.196 | | | | | | |
| Q1/Q2 | -0.348 | 0.928$^{**}$ | 0.072 | -0.285 | 0.433 | | | | | |
| Exch-P | -0.355 | 0.994$^{**}$ | 0.121 | 0.015 | 0.673$^{**}$ | 0.917$^{**}$ | | | | |
| Fe-Al-P | -0.363 | 0.954$^{**}$ | 0.125 | 0.151 | 0.709$^{**}$ | 0.823$^{**}$ | 0.970$^{**}$ | | | |
| Ca-P | -0.389 | 0.909$^{**}$ | 0.088 | 0.208 | 0.681$^{**}$ | 0.772$^{**}$ | 0.923$^{**}$ | 0.973$^{**}$ | | |
| Res-P | -0.430 | 0.952$^{**}$ | 0.135 | 0.027 | 0.647$^{**}$ | 0.907$^{**}$ | 0.969$^{**}$ | 0.961$^{**}$ | 0.941$^{**}$ | |
| Olsen-P | -0.321 | 0.994$^{**}$ | 0.121 | 0.041 | 0.679$^{**}$ | 0.902$^{**}$ | 0.998$^{**}$ | 0.970$^{**}$ | 0.920$^{**}$ | 0.959$^{**}$ |

TABLE 10
Simple correlation coefficient (r) between parameters of two first-order reaction models, simple Elovich, power function and clay minerals in studied soils

| | **bs** | **as** | **b** | **a** | **$Q_1$** | **$K_1$** | **$Q_2$** | **$K_2$** | **Q1/Q2** |
|---|---|---|---|---|---|---|---|---|---|
| **Kaolinite** | 0.103 | -0.487$^{*}$ | 0.119 | -0.325 | -0.322 | -0.134 | 0.137 | 0.333 | 0.182 |
| **Illite** | 0.385 | -0.500$^{*}$ | -0.003 | -0.560$^{*}$ | -0.553$^{*}$ | -0.179 | -0.319 | -0.529$^{*}$ | -0.441 |
| **Chlorite** | 0.023 | 0.035 | -0.064 | -0.018 | -0.011 | -0.148 | 0.125 | -0.054 | -0.054 |
| **Smectite** | -0.022 | 0.235 | -0.221 | 0.394 | 0.393 | 0.092 | -0.084 | 0.314 | 0.389 |
| **Interstratified** | 0.406 | -0.112 | 0.013 | -0.162 | -0.158 | -0.089 | -0.189 | -0.087 | -0.018 |
| **Palygorskite** | -0.163 | -0.196 | 0.372 | -0.356 | -0.358 | 0.063 | 0.336 | -0.355 | -0.388 |

and "as" from simple Elovich equation, and a" from power function equation, $Q_1$ and $Q_1/Q_2$. Moreover, the study of correlation between clay minerals and chemical forms of P (the results obtained before and after adding P fertiliser were the same) showing that kaolinite and illite have a significant negative relationship with Exch-P (Table 11).

Also, illite showed a significant positive relationship with Exch-P. Studies carried out by Penn *et al.* (2005) showed that sorption and desorption of P have a good correlation with Al-contained minerals such as hydroxy-interlayer vermiculite (HIV)minerals and amorphous Al, while maintenance of P has a negative relationship with kaolinite content, with this relationship being confirmed by isotherms performed on pure clay minerals. The present study shows that apart from clay content, the effect of clay type should be considered (non-significant negative correlation with desorption parameters) in P desorption. Expandable and non-expandable clay minerals have different effects on P desorption rate. In correlation to clay minerals, smectite mineral showed a non-significant positive relationship with "as" from simple Elovich equation and "a" from power function equation. Because of changes in the size of aggregates and their fraction due to wetting of the soil and lower surface functional groups, the existence of expandable minerals affects the P dispersion pattern with time and increases P release rate (Sparks 1998). With regard to the effect of clay minerals on P kinetic in the

TABLE 11
Simple correlation coefficient (r) between P chemical forms and clay minerals in studied soils

| | Exch-P | Fe-Al-P | Ca-P | Res-P |
|---|---|---|---|---|
| Kaolinite | -0.483* | -0.369 | -0.373 | -0.320 |
| Illite | -0.585** | -0.389 | -0.307 | 0.546* |
| Chlorite | 0.001 | 0.026 | 0.119 | 0.027 |
| Smectite | 0.368 | 0.307 | 0.232 | 0.308 |
| Interstratified | -0.170 | -0.284 | -0.353 | -0.258 |
| Palygorskite | -0.328 | -0.233 | -0.214 | -0.274 |

Cairo region of Egypt, Wahba *et al.* (2002) showed that rate equations as well as the P released for montmorillonite mineral was more than that from kaolinite. Due to the presence of surface functional groups, non-expandable clay minerals such as kaolinite are more effective in P sorption, and their P release is delayed. This is confirmed by the results obtained from the present research. On the other hand, the sorption processes occur faster in some minerals such as kaolinite and smectite compared to vermiculite and mica. This results from the fact that kaolinite and smectite have more adsorbent surfaces, but vermiculite and mica have multi-locations such as inter-layer, edge, and plate layer surfaces. Therefore, not only expandability, but also sorbent locations affect the P release, indicating that the more the locations, the more the P sorbed. This has the consequent effect of increasing the saved available P in soil and decreasing desorption. In the present study, as the height from sea level increased, there was a higher release of expandable minerals such as OM and montmorillonite.. As a result, there was an increase in "as" from Elovich equation, "a" from power function equation, and $Q_1$ from two first-order reaction models, indicating a higher release of expandable minerals such as montmorillonite.

## CONCLUSION

The present study attempted to investigate the comprehensive relationships between different physic-chemical and mineralogical properties of various soils with desorption behaviours and chemical forms of P in different soil orders of a climotoposequence. The results obtained show that P desorption (with biphasic pattern) had a significantly increasing trend from the beginning (Aridisols order) till towards the end (Histosols order) of the studied area. This may be attributed to a high content of total P at the first glance. However, the increasing trend of OM content as well as expandable montmorillonite clay may be another reason for the released P in the soils at the end of the studied transect. Among the equations fitted on desorption data, simple Elovich, power function and two first-order reaction models could have good prediction based on the highest $R^2$ and the lowest SE. The study of chemical forms of P in the studied area showed that Ca-P and Res-P are the most common forms of important P in the studied soils. The relative percentage of Ca-P from the beginning till towards the end of the studied area showed a

decreasing trend due to calcium carbonate of soil as well as the high quality of the area water. Addition of P to the studied soils increased the content of all chemical forms of P. However, the relative percentage of Ca-P, Res-P decreased, and Exch-P and Fe-Al-P increased. The highest and the lowest amount of the P added to the studied soils in Exch-form were observed in Mollisols and Aridisols orders, respectively. These changes are predictable according to physic-chemical mineralogical properties of the soils. Moreover, the obtained results show that, in addition to OM, CEC, silt, available-P and total P as the significant properties affecting the desorption of P, two important kaolinite and illite minerals also play an important role in the status of P behaviour in the studied soils. Generally speaking, according to topographic-climatic properties, it appears that adding P fertilisers to soil in order to access more P at the beginning of the experiment (the transformation of added P to non-adsorbable and mobile forms) must be done with greater caution (fertilisation at several times during cultivation) compared to the end of the experiment. Also, the study on the effects of clay minerals on P release has been done qualitatively and in the presence of other soil components in this study. Therefore, it is recommended that the process of P behaviours in the absence of clay minerals, especially palygorskite mineral (although it did not show significant effects on phosphorus behaviour in this study), be specifically studied in arid and semi-arid regions.

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