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Simultaneous Dynamics and Kinetics of Soil Phosphorus Under Different Fertilizer Systems During Two-Growth Seasons of Maize

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ABSTRACT

This study investigated phosphorus (P) dynamics and kinetics in calcareous soil under inorganic, organic, and integrated (inorganic+organic) fertilizer systems during two growing seasons of maize in two soil depths (0–0.15 and 0.15–0.30 m). A field experiment was conducted with 150, 300, and 400 kg ha\(^{-1}\) triple superphosphate (TSP), 7.5 and 15.0 ton ha\(^{-1}\) (on dry matter basis) farmyard manure (FYM), and integrated systems. In order to analyze Olsen P, soil samples were collected in 30-day-intervals after planting. The results showed that at the end of the two growing seasons of maize, the lowest magnitudes of Olsen P\(_{0.0–0.15\text{ m}}\) were 6.0, 6.8, 7.4, and 7.6 mg kg\(^{-1}\) for the control, 7.5 FYM, 15 FYM, and 150 TSP, respectively. The highest magnitudes of Olsen P\(_{0.0–0.15\text{ m}}\) were 12.4, 11.5, 11.4, and 11.1 mg kg\(^{-1}\) for 300 TSP +15 FYM, 400 TSP +7.5 FYM, 400 TSP +15 FYM, and 300 TSP +7.5 FYM, respectively. The same trends were observed for Olsen P\(_{0.15–0.30\text{ m}}\). Heterogeneous diffusion model demonstrated that Elovich equation could best describe the experimental data (mean; \(R^2 = 0.98\), SE = 0.29). The highest P supply rates (PSR) were 4.73, 3.91, and 3.86 mg kg\(^{-1}\) day\(^{-1}\) (days after application) for 400 TSP, 400 TSP +15 FYM, and 300 TSP, respectively. The models of P supply capacity of soil could estimate P supply of soil under different fertilizer systems (\(R^2 = 0.84–0.95\)). The present study improved the understanding of the capacity and rate of P supply by considering P uptake by grain maize. Fertilizer recommendations depend on the accessibility of fertilizer types suggested to help choose the best fertilizer systems.

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KEYWORDS

Fertilizer systems; heterogeneous diffusion model; P supply capacity of soil; P supply rate; P uptake; maize

Introduction

Sustainable crop production needs fertilizer applications. Chemical fertilizers provide essential nutrients such as phosphorus (P), nitrogen (N), and potassium (K). Under P deficiency of soils, increasing crop yields with the use of other nutrients is not appropriate unless P restrictions have been overcome (Nziguheba, Merckx, and Palm 2002). However, limiting nonrenewable resource of P (i.e., phosphate rock), increasing P demand, decreasing the quality of the remaining phosphate rock, and increasing production costs are the most important challenges in modern agriculture (Cordell, Drangert, and White 2009). Besides food security, pollution problems as a result of overusage of P fertilizers should also be considered as an unexpected environmental issue.

The mechanisms of P retention and its bioavailability in calcareous soils have been largely reported. In general, P retention investigates the processes that reduce P solubility after P fertilizers have been added to the soils. The main mechanisms of P retention in calcareous soils are (i) surface adsorption on clay minerals, organic matter (OM), ferrous (Fe) and aluminum (Al) oxides and hydroxides (amorphous and crystalline), and calcium carbonate (CaCO\(_3\)) surfaces and (ii)
precipitation of calcium (Ca) as Ca-phosphates, which may be subsequently released (Arai, Livi, and Sparks 2005; Delgado and Torrent 2000; Penn and Warren 2009; Samadi 2006). Standard methods of P sorption magnitudes measure only fast reversible adsorbed P onto surface sites, more labile, and bioavailable P forms. More recalcitrant forms of adsorbed P (i.e., deposited P iron or aluminum oxide minerals or precipitated calcium phosphate) are not captured by routine analyses (McGechnan 2002). Jalali and Sajadi Tabar (2011) reported that P is associated with labile and Ca-bound P as the less (<2%) and most abundant P fractions (61–78% of the total P) in calcareous soils. Isotherm experiments are one approach to predict the potential P supply of soils (Abdala et al. 2015; Penn and Warren 2009).

As shown in previous studies, sorption isotherms cannot capture annual soil P surpluses, which did not remain in the fast P-binding pools (Riskin et al. 2013). Besides, the needed isotherm parameters to predict the soil P supply potential may change in time by several factors such as sorption capacity, Fe and Al oxides, total desorbable P content, reversibly adsorbed P, and P intensity (Van Rotterdam et al. 2012). Therefore, the short-term study of P reactions in soils at the laboratory scale may not provide a complete picture of the long-term fate of P applied to soils; therefore, long-term experiments should also be considered. Van Rotterdam et al. (2012) reported that the changes that occur in extractable P and unextractable but active soil P after the addition of P fertilizers should be calculated annually using a dynamic model. This model requires the updated levels of these soil P fractions for each year from the annual balance of P. They suggested that the needed time step for calculations should not be less than one year. Shorter time steps had little effect on the simulated values of extractable P.

It is important to determine the extractable P magnitude, but the rate of transformation of soluble to less soluble P forms should also be considered. This phenomenon controls P bioavailability in soils (Samadi 2006). The availability of added P has been investigated with kinetics study for 1 to 160 days incubation experiment by (Samadi 2006). In this study and the study by Samadi and Gilkes (1999), P was measured using the Olsen method. However, there is little information about P kinetic release from inorganic and organic inputs (Fekri, Gorgin, and Sadegh 2011; Hosseinpur and Pashamokhtari 2013; Liang et al. 2014; Toor and Bahl 1999).

Calcareous soils, which are dominant in the Middle East, have high pH (7.6–8.3) and low (< 1%) organic matter (OM) content (Malakouti 2008). Therefore, the availability of native soil P to plants is expected to be restricted by high pH, low OM content, precipitation as Ca-P compounds, and adsorption of P on CaCO₃ surfaces. To avoid P deficiencies, various P systems including inorganic fertilizers, organic inputs, or their combinations can be applied (Nziguheba, Merckx, and Palm 2002). Manure has an increasing role as a P fertilizer for crops and may help to alleviate environmental problems (Li et al. 2011).

Kermanshah province is ranked third in maize production in Iran. Based on our knowledge, there is no information about the simultaneous P dynamics and kinetics in calcareous soils during plant growing seasons of maize (Zea mays L.). This study has been conducted to improve the understanding of P chemistry in calcareous soils under inorganic, organic, and integrated (organic + inorganic) fertilizer systems in calcareous soils of Kermanshah city, during two growing seasons of maize. The study will improve the understanding of soil P dynamics and kinetics to predict the fate of added P from inorganic, organic, and integrated sources.

Materials and methods

Study site

This study was carried out in an experimental field at the Research Farm, Mahidasht Plain, Kermanshah, Iran (34° 8’ N, 46° 26’ E, 1365 m above sea level). The mean annual rainfall is 397 mm and the mean annual temperature is 12°C. The monthly precipitation, air temperature and evaporation of the experimental area are shown in Table 1. The field experiment was conducted on a
fine-clayey, mixed, thermic calcixerepts soil (Soil Survey Staff 2014) in 2010 and 2011. The soil of the research farm is calcareous with more than 38% calcium carbonate equivalent (CCE) in the surface layer. The texture of the soil was a silty clay loam. The average of the bulk density of 0.30 m depth soil is approximately 1.30 Mg m$^{-3}$. Soil pH was moderately alkaline. Major mineral measured nutrients showed that the soil does not have sufficient nitrogen (N), P, and OM content (Soltanpour, Malakouti, and Ronaghi 1995). Also, the studied soil has no previous history of manure application. Soil samples (0–0.15 and 0.15–0.30 m depth) were obtained and analyzed for some characteristics before beginning the experiments (Table 2). Soil texture (hydrometer method), pH (saturated paste method), electrical conductivity (EC), organic carbon (OC; the Walkley-Black method), extractable P (Olsen’s method), available potassium (K, NH$_4$OAc extraction method), and available micronutrients contents (DTPA extraction method) were determined (Sparks et al. 1996). Farmyard manures’ (FYM’s) samples were air-dried and ground to 1 mm for the analysis. For FYM, the pH, EC, OC, total N, available P (Olsen’s method), and available K (NH$_4$OAc method) and micronutrients were measured.

**Field management of the experiment**

The experiment was conducted using a randomized complete block design (RCBD) with three replications on 5 × 4 m$^2$ plots in each field with 2 m distance between plots and replications. The P fertilizer treatments included in this study were control soils without P fertilizer: 150, 300 and 400 kg ha$^{-1}$ triple superphosphate (TSP); 7.5 and 15.0 ton ha$^{-1}$ FYM on a soil dry weight basis and FYM + triple superphosphate (150 TSP + 7.5 FYM, 300 TSP+7.5 FYM, 400 TSP+15 FYM), which were applied in 2011 and 2012. The FYM contained macro- and micro-nutrients as follows: 1.23% N, 0.89% P, 2.72% K, 1625 mg kg$^{-1}$ iron (Fe), 50 mg kg$^{-1}$ copper (Cu), 10 mg kg$^{-1}$ manganese (Mn), and 71.5 mg kg$^{-1}$ Zn. FYM was added to the soil and immediately after the application and before planting P fertilizer was added. The mineral N was applied as urea (CO(NH$_2$)$_2$; 46% N) and divided in all plots during the vegetative stage for all treatments. Potassium fertilizer was not applied because the studied soil contains an initial K level of 278 mg kg$^{-1}$ (Table 2). Since the concentrations of micronutrients, with exception of Cu, were below the determined critical levels, micronutrient fertilizers were applied in all plots based on fertilizer recommendations. The maize (Single Cross 704) seeds were sown on May 15, 2011 and May 16, 2012.

### Table 1. Average monthly air temperature, total monthly rainfall, and total monthly pan evaporation for 2011 and 2012 growing seasons Mahidasht Plain.

<table>
<thead>
<tr>
<th>Month</th>
<th>Air temperature °C</th>
<th>Rainfall mm</th>
<th>Pan evaporation mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>May (15–31 May)</td>
<td>16</td>
<td>16.9</td>
<td>28.1</td>
</tr>
<tr>
<td>June</td>
<td>24.5</td>
<td>24.9</td>
<td>0</td>
</tr>
<tr>
<td>July</td>
<td>28.8</td>
<td>28.1</td>
<td>0</td>
</tr>
<tr>
<td>August</td>
<td>29.8</td>
<td>29.8</td>
<td>0</td>
</tr>
<tr>
<td>September</td>
<td>25</td>
<td>25.9</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 2. The physico-chemical characteristics of soil from field study site at Mahidasht Plain before maize planting.

<table>
<thead>
<tr>
<th>Year</th>
<th>Depth m</th>
<th>Clay %</th>
<th>Silt %</th>
<th>Sand %</th>
<th>OC</th>
<th>CCE*</th>
<th>pH</th>
<th>Bulk density Mg m$^{-3}$</th>
<th>EC dS m$^{-1}$</th>
<th>P mg kg$^{-1}$</th>
<th>K mg kg$^{-1}$</th>
<th>Fe mg kg$^{-1}$</th>
<th>Mn mg kg$^{-1}$</th>
<th>Zn mg kg$^{-1}$</th>
<th>Cu mg kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>0–0.15</td>
<td>41.0</td>
<td>42.0</td>
<td>17.0</td>
<td>0.8</td>
<td>38.2</td>
<td>7.8</td>
<td>1.3</td>
<td>0.8</td>
<td>7.3</td>
<td>290.0</td>
<td>5.5</td>
<td>6.5</td>
<td>0.8</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>0.15–0.30</td>
<td>0.8</td>
<td>39.2</td>
<td>7.8</td>
<td>1.3</td>
<td>0.9</td>
<td>7.5</td>
<td>290.0</td>
<td>5.8</td>
<td>6.5</td>
<td>0.8</td>
<td>1.6</td>
<td>0.8</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>0–0.15</td>
<td>41.0</td>
<td>42.0</td>
<td>17.0</td>
<td>0.8</td>
<td>38.0</td>
<td>7.9</td>
<td>1.3</td>
<td>0.8</td>
<td>7.1</td>
<td>270.0</td>
<td>6.0</td>
<td>6.5</td>
<td>0.8</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>0.15–0.30</td>
<td>0.88</td>
<td>39.2</td>
<td>7.9</td>
<td>1.3</td>
<td>0.8</td>
<td>7.8</td>
<td>270.0</td>
<td>5.9</td>
<td>5.5</td>
<td>0.8</td>
<td>1.6</td>
<td>0.8</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

*Calcium carbonate equivalent (CCE).
Irrigations were applied according to the need of the crop. Weed and pathogen controls were also performed during the growing seasons. The grain maize samples were collected in September 30 from 10 m$^2$ area in the center of each plot to determine grain weights and grain P content. Soil samples were collected from two soil depths, 0–0.15 and 0.15–0.30 m before the experiment and again at the harvest time (150 days after planting). The Olsen P of each soil depth was determined and referred to hereafter as Olsen P$_{0–0.15}$ m and Olsen P$_{0.15–0.30}$ m, respectively.

**Soil P extraction method**

Since integrated treatments (inorganic+organic) include both inorganic and organic P forms, to evaluate the extractable P as an indicator of bioavailable P, a variety of extraction methods were explored. Delgado and Torrent (2000) reported that the amount of P released to 0.002 M CaCl$_2$ was greater than bioavailable P. Kleinman et al. (2001) showed that the oxalate method was not a reliable method to evaluate the amount of P potentially released to water, especially whenever different soils were compared. The supposed suitability of Olsen P method (Olsen 1954) (0.5 M NaHCO$_3$), for a wide range of soils, has been reported in comparison with Bray-1 and Mehlich-3 (Kleinman et al. 2001). They investigated the correlation between P measured by Olsen, Bray-1, and Mehlich-3 methods. Relationships were found between Olsen- and Bray-1 P (r = 0.77–0.94) or Olsen and Mehlich-3 P (r = 0.84–0.94). Bicarbonate (NaHCO$_3$) can also extract readily exchangeable soil organic P and probably represents an active pool of organic P in soil (Bowman and Cole 1978). Magid, Tiessen, and Condron (1996) found that NaHCO$_3$-extractable organic P represented a labile pool of organic P in temperate soils. Much NaHCO$_3$-extractable organic P can be hydrolyzed by common soil phosphatase enzymes and have been considered to be potentially bioavailable (Turner, Cade-Menun, and Westermann 2003). NaHCO$_3$ and sodium hydroxide (NaOH) extraction methods have been suggested to be the most useful in the examination of net long-term changes in organic P forms which took place in response to alterations in land use and/or soil management (Condron et al. 1996; Rubaek and Sibbesen 1995). Some studies reported that the bioavailable P was highly correlated with Olsen P (Delgado and Torrent 2000; Poulton, Johnston, and White 2013; Yu et al. 2006). Based on earlier reviewed results and calcareous nature of the studied soil, Olsen extraction method was chosen to estimate bioavailable P for soil treated with inorganic and/or organic fertilizers.

**Soil P changes through time**

To estimate P dynamics, soil sampling was performed in 30 days interval after maize planting from soil depth 0–0.30 m in 2011 and 2012. In total, 432 soil samples were collected from all treatments. Also at the end of each growing season, Olsen P$_{0–0.15}$ m Olsen P$_{0.15–0.30}$ m under different fertilizer systems were measured.

Many soil chemical processes are dependent on time (Sparks 2003). The changes of P amounts through time, needed to be described by an equation. To understand the dynamics of Olsen P$_{0–0.30}$ m under different fertilizer management and predict the fate of P applied with time, it is important to study the kinetic reaction first. Therefore, kinetic equations and models including zero-order, first-order, Elovich, power function equations, and parabolic diffusion model were examined.

Zero – order equation : $q = a + bt$  
First – order equation : $ln(q - q_i) = a - bt$  
Elovich equation : $q = a + blnt$  
Power function equation : $lnq = lna + blnt$  
Parabolic Diffusion model : $q = a + bt^{1/2}$
Here $q$ is the Olsen $P_{0.30\text{ m}}$ at 150 days after planting; $q_1$ is the quantity of Olsen $P_{0.30\text{ m}}$ at time $t$, $t = \text{time (day)}$, $q_0$ is the maximum measured Olsen $P_{0.30\text{ m}}$, and $a$ and $b$ are constants.

To choose the best model predicted the relationship between experimental and predicted data, the coefficient of determination ($R^2$) and standard errors of estimate (SE) are compared (Table 3).

The standard error of estimate (SE) was calculated by the equation below:

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

$q$ and $q^*$ are measured Olsen $P_{0.30\text{ m}}$ and calculated Olsen $P_{0.30\text{ m}}$, respectively, with the unit of mg kg$^{-1}$ and $n$ is the number of data points evaluated.

### Soil $p$ dynamics

The P inputs in this study were calculated as the following. For the inorganic system, the P amount of TSP was calculated by multiplying coefficient 0.44 by the added amounts of $P_2O_5$ of TSP (containing 46% $P_2O_5$). For the organic system, bioavailable P was calculated by multiplying coefficient 0.89% (i.e., the percentage of Olsen P content of FYM) by the added FYM amounts. For the integrated system, the sum of these two calculations was considered. To input these data to $P$ dynamics calculations, the P added in kg ha$^{-1}$ was converted to mg kg$^{-1}$ by calculating the weight of 1 ha from soil bulk density data and considering soil depth as 0-0.30 m, which equals 3,900,000 kg. Native P amounts of two soil depths from control treatment were added to apply P to each fertilizer treatment.

The removals in this study include precipitation or adsorption of P fertilizers by soil components and P uptake by grain maize. Here, P leaching was considered negligible because there is no rainfall during the growing period and irrigations were applied according to the need of the crop. The reasons for this idea are the adsorption of phosphate on calcite (Kaloi et al. 2011), $Fe^{3+}$ and $Al^{3+}$ oxides and hydroxides (amorphous and crystalline) (Penn and Warren 2009), clay minerals and OM (Araki, Livi, and Sparks 2005) or precipitation $Ca^{2+}$-phosphates compounds in the presence of $Ca^{2+}$ and alkaline condition of soil (Devau et al. 2011). The stated conditions caused P to be strongly adsorbed by the soil and prevent P leaching. Besides, P uptake by plant prevents P movement toward

### Table 3. Coefficients of determination ($R^2$) and standard errors of the estimate (SE) for Olsen $P_{0.30\text{ m}}$ changes using several kinetic models.

<table>
<thead>
<tr>
<th>Fertilizer systems</th>
<th>Model$^1$</th>
<th>Zero-order $R^2$</th>
<th>SE$^6$</th>
<th>First-order $R^2$</th>
<th>SE</th>
<th>Elovich $R^2$</th>
<th>SE</th>
<th>Power function $R^2$</th>
<th>SE</th>
<th>Parabolic diffusion $R^2$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic</td>
<td>0</td>
<td>0.95 0.03</td>
<td>0.86 0.09</td>
<td>0.86 0.07</td>
<td>0.85 0.00</td>
<td>0.92 0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>150TSP</td>
<td>0.87 0.86</td>
<td>1.00 0.01</td>
<td>0.98 2.70</td>
<td>0.99 0.00</td>
<td>0.94 0.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300TSP</td>
<td>0.91 0.45</td>
<td>0.76 0.15</td>
<td>1.00 0.04</td>
<td>1.00 0.00</td>
<td>0.96 0.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400TSP</td>
<td>0.90 0.89</td>
<td>0.92 0.05</td>
<td>0.99 0.12</td>
<td>1.00 0.00</td>
<td>0.96 0.41</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic</td>
<td>7.5FYM</td>
<td>0.97 0.06</td>
<td>0.99 0.01</td>
<td>1.00 0.05</td>
<td>0.99 0.00</td>
<td>0.99 0.01</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>15FYM</td>
<td>0.98 0.05</td>
<td>0.97 0.01</td>
<td>0.99 0.02</td>
<td>0.98 0.00</td>
<td>1.00 0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Integrated</td>
<td>150TSP+7.5FYM</td>
<td>0.91 0.38</td>
<td>0.98 0.01</td>
<td>0.98 0.07</td>
<td>0.99 0.00</td>
<td>0.96 0.18</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>300TSP+7.5FYM</td>
<td>0.95 0.22</td>
<td>0.97 0.03</td>
<td>1.00 0.03</td>
<td>0.99 0.00</td>
<td>0.99 0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400TSP+7.5FYM</td>
<td>0.97 0.23</td>
<td>1.00 0.00</td>
<td>1.00 0.05</td>
<td>0.98 0.00</td>
<td>0.99 0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>150TSP+15 FYM</td>
<td>0.91 0.34</td>
<td>0.98 0.02</td>
<td>0.99 0.05</td>
<td>0.99 0.00</td>
<td>0.96 0.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300TSP+15 FYM</td>
<td>1.00 0.02</td>
<td>0.98 0.02</td>
<td>0.97 0.11</td>
<td>0.96 0.00</td>
<td>1.00 0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400TSP+15 FYM</td>
<td>0.96 0.30</td>
<td>0.99 0.01</td>
<td>0.99 0.12</td>
<td>0.98 0.00</td>
<td>0.99 4.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$Zero-order equation: $q = a + bt$, first-order equation: $ln(q/q_0) = a + bt$, Elovich equation: $ln(q/q_0) = a + btln(t)$, power function equation: $ln(q/q_0) = a + bt$, parabolic diffusion model: $q = a + bt + c$, $t$ = time (day), $q_0$ is the maximum measured Olsen $P_{0.30\text{ m}}$ at 150 days after panting; $q$ is the quantity of Olsen $P_{0.30\text{ m}}$ at time $t$, $t = \text{time (day)}$, $q_0$ is the maximum measured Olsen $P_{0.30\text{ m}}$, and $a$ and $b$ are constants.

$^6$SE is standard error of estimate, which was calculated by the difference between measured Olsen $P_{0.30\text{ m}}$ or $q$, and calculated Olsen $P_{0.30\text{ m}}$ or $q^*$, with the unit of mg kg$^{-1}$ and $n$ is the number of data points evaluated. The equation used for the calculation of SE is $SE = \sqrt{\frac{\sum(q - q^*)^2}{n-2}}$.

Values are the mean of 36 data (i.e., 6 times, 3 replications of 2 years).
the lower depth to be leached. Olsen $P_{0-0.30}$ amounts at the end of growing season (after plant harvest) were considered as bioavailable $P_{150\text{ days}}$, which is not adsorbed or precipitated by soil. P supply capacity of soil has been estimated by subtracting bioavailable $P_{150\text{ days}}$ from P inputs.

Phosphorus uptake by grain was calculated in kg ha$^{-1}$, and then converted to mg kg$^{-1}$ by dividing by weight of 1 ha. Since in the study area, maize stover is not returned to the soil and burned by local farmers, then P uptake by maize stover was not calculated here. Moreover, Roberts and Rhee (1993) reported that the estimation of total nutrient removal by cropping is feasible using dry matter basis nutrient concentrations in grain.

**P content of grain maize**

The P content of grain maize was determined by the molybdovanadate procedure (Thomas, Sheard, and Moyer 1967). Phosphorus uptake by grain maize was calculated by multiplying P content and grain maize yield.

**Statistical analysis**

All data were presented as the average of six data including three replications during two growing seasons collected from each fertilizer systems. The data were subjected to analysis of variance (ANOVA) using SPSS v.16 (SPSS, Inc., Chicago, I.L.) and the differences between treatments’ means were compared using Tukey’s test at $P < 0.05$.

**Results**

**Mathematical models of olsen p changes during growing season**

Under all treatments, there was a wide variation in Olsen $P_{0-0.30}$ magnitudes by the time between different fertilizer treatments (Figure 1). The highest amounts of Olsen $P_{0-0.30}$ were observed in 30 days after maize planting. Olsen $P_{0-0.30}$ reduces with time exponentially under each fertilizer management when compared with the control (7.9 mg kg$^{-1}$). Olsen $P_{0-0.30}$ of the control treatment remained almost unchanged (Figure 2). In 150 days after maize planting, the lowest amounts of Olsen $P_{0-0.30}$ were 8.3, 8.5, and 8.8 for 150 TSP+7.5 FYM, 150 TSP+15 FYM, and 150 TSP, respectively. Whereas, the highest amounts were 12.8 mg kg$^{-1}$ for 400 TSP+15 FYM, 11.1 mg kg$^{-1}$ for 400 TSP+15 FYM, 400 TSP and 300 TSP, 10.9 and 10.4 mg kg$^{-1}$ for 400 TSP+7.5 FYM and 15 FYM, respectively.

**Soil p dynamics**

Input amounts of the added P under different fertilizer systems were 16.9 to 45.1 mg P kg$^{-1}$ in TSP system, 17.1 to 34.2 mg P kg$^{-1}$ in FYM system, and 34.0 to 79.4 mg P kg$^{-1}$ in integrated systems (Table 5). Summation of these amounts to native Olsen $P_{0-0.15}$ and Olsen $P_{0.15-0.30}$ (Table 2) resulted in 15.1 (control) to 94.4 mg P kg$^{-1}$ as P inputs under different fertilizer systems (Table 5).

Phosphorus uptake by grain maize was higher in the integrated system as compared with inorganic and organic systems (Table 5). The ANOVA showed that there were significant differences in P uptake by grain maize between different fertilizer systems ($P < 0.05$). The lowest amounts of P uptake were related to 7.5 FYM and 150 TSP (0.85 mg kg$^{-1}$), respectively. The highest amounts of P uptake (1.35 mg kg$^{-1}$) were observed for 300 TSP+15 FYM followed by 1.32 mg kg$^{-1}$ for 400 TSP+15 FYM, and 1.30 mg kg$^{-1}$ for 300 TSP+7.5 FYM.

The lowest magnitudes of Olsen $P_{0-0.15}$ were 6.0, 6.8, 7.4, and 7.6 mg kg$^{-1}$ for the control, 7.5 FYM, 15 FYM, and 150 TSP, respectively. However, the highest magnitudes of Olsen $P_{0-0.15}$ were
12.4, 11.5, 11.4, and 11.1 mg kg$^{-1}$ for 300 TSP+15 FYM, 400 TSP+7.5 FYM, 400 TSP+15 FYM, and 300 TSP+7.5 FYM, respectively. Generally, the same trends were observed for Olsen P$_{0.15-0.30}$ for inorganic and organic fertilizer systems (Table 5). However, the lowest (5.2 mg kg$^{-1}$) and highest magnitude of Olsen P$_{0.15-0.30}$ (11.5 mg kg$^{-1}$) were observed for 150 TSP and 400 TSP+15 FYM, respectively (Figure 1). The lowest magnitudes of Olsen P$_{0-0.15}$ and Olsen P$_{0.15-0.30}$ changed in the following order: organic < inorganic < integrated. However, the highest magnitudes of Olsen P$_{0-0.15}$ and Olsen P$_{0.15-0.30}$ changed in the following order: integrated > inorganic > organic.
Generally, the integrated system could increase Olsen $P_{0-0.30}$ bioavailability rather than the other systems. The ANOVA showed that under integrated systems, Olsen $P_{0-0.15}$ and Olsen $P_{0.15-0.30}$ magnitudes were more when compared with separate application of inorganic or organic fertilizers ($P < 0.05$). Halajnia et al. (2009) reported that the combined application of cattle manure and fertilizer P increased P recovery as Olsen P when compared with the separate application of fertilizer P.

Differences of bioavailable $P_{150}$ days from P inputs amounts resulted in 4.0 to 71.5 mg kg$^{-1}$ which is considered as P supply capacity of the soil. The lowest magnitudes of P supply capacity of the soil were 18.2 and 19.2 mg kg$^{-1}$ attributed to 7.5 FYM and 150 TSP, respectively. However, the highest magnitudes of P supply capacity of the soil were 71.5 and 61.4 mg kg$^{-1}$ attributed to 400 TSP+15 FYM and 300 TSP+15 FYM, respectively.

**Discussion**

**Mathematical models of Olsen $P_{0-0.30}$ changes during growing season**

Almost all kinetic models could describe the data very well as shown in Table 3. One of the reasons why a particular kinetic model appears to be applicable is answered by Sparks (2003). Sparks (2003) explained that it may be related to the conducted time range of the study, when the model is most appropriate. Another reason is that diffusion models describe a number of soil chemical processes in most cases. It can be explained by the fact that mass transfer and chemical kinetic phenomena occur simultaneously and this makes it difficult to separate them (Sparks 2003). Aharoni and Ungarish (1976) by writing power function, Elovich, and first-order equations as the explicit function, introduced the reciprocal of the rate $Z$, which is $(dq/dt)^{-1}$. Aharoni and Sparks (1991) expressed heterogeneous diffusion mathematically as follows.

$$d(q/q_\infty)/d \ln t = 1/\rho$$ (7)
In this equation and present study, \( t = \text{time} \); \( \rho = \ln(t_m/\tau) \); \( \tau_i = \text{smallest } \tau \) and \( \tau_m = \text{largest } \tau \); \( \tau = r^2/D \), where \( r \) is the maximum length of the diffusion path, \( D \) is the diffusion coefficient; \( q_\infty \) is the quantity of Olsen \( P_{0.30} \) in 150 days after planting; and \( q \) is Olsen \( P_{0.30} \) at a certain \( t \). A plot of \( Z \) vs. \( t \) could be convex, linear, or concave when the power function, the Elovich or the first-order equations are appropriate, respectively (Sparks 2003). Table 4 shows that the relationship between \( q/q_\infty \) and \( \ln t \) is linear (\( R^2 = 0.86–1.00 \)) for the two growing seasons for all fertilizer systems and suggested that Elovich equation is appropriate to describe the experimental data best. Some researchers reported that Elovich equation could describe P release kinetics under manure, compost or inorganic P fertilizers under laboratory experiments (Fekri, Gorgin, and Sadegh 2011; Hosseinpur and Pashamokhtari 2013; Liang et al. 2014; Toor and Bahl 1999).

### The soil P supply rate

The absolute values of \( b \) coefficient of Elovich equation (Table 4) were chosen to compare the rate of soil PSR. The PSR increased by adding P in inorganic, organic or integrated systems when compared with the control. There were significant differences of absolute values of \( b \) coefficient of Elovich equation between treatments of inorganic and integrated and fertilizer systems (Table 4). There were no significant differences of the PSR between 150 TSP+7.5 FYM, 150 TSP+15 FYM, 150 TSP, and 300 TSP+7.5 FYM. The lowest PSR were 1.05, 1.07, and 1.10 mg kg\(^{-1}\) day\(^{-1}\) for the control, 15 FYM, and 7.5 FYM, respectively. However, the highest PSR were 4.73, 3.91, and 3.86 mg kg\(^{-1}\) day\(^{-1}\) for 400 TSP, 400 TSP+15 FYM, and 300 TSP, respectively.

### Effect of fertilizer management on Olsen P

The integrated system resulted in significantly greater increases in Olsen P when compared with the values of separate application of TSP and FYM during the growing seasons (Figure 1). Generally, Olsen \( P_{0.30} \) of the control remained quietly unchanged during both growing seasons. By increasing Olsen \( P_{0.30} \) Olsen \( P_{0.15-0.30} \) was also increased in the treated soils when compared with the control. Waldrip et al. (2015) showed that the continued application of poultry litter, other livestock manure, or inorganic fertilizer could increase the concentrations of organic and inorganic P due to lack of available sorption sites in the soil. Manure is a source of sub surface P and an effective mobilizing agent by blocking P sorption sites (by organic acids) and complexation of exchangeable Al and Fe in the soil. In the presence of metal cations, strong complexes between inorganic P and

### Table 4. Heterogeneous diffusion equations fitted on the Olsen \( P_{0.30} \) data and Elovich equation coefficients.

<table>
<thead>
<tr>
<th>Fertilizer systems</th>
<th>Treatments</th>
<th>Heterogeneous diffusion equations*</th>
<th>( R^2 )</th>
<th>Elovich ( b ) coefficient</th>
<th>Elovich ( a ) coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic</td>
<td>0</td>
<td>( y = -0.74x + 10.61 )</td>
<td>0.86</td>
<td>(-1.05(0.2)aA)</td>
<td>(10.64(0.6)aA)</td>
</tr>
<tr>
<td></td>
<td>150 TSP</td>
<td>( y = -2.90x + 23.14 )</td>
<td>0.98</td>
<td>(-3.10(0.2)bBC)</td>
<td>(22.77(0.8)bB)</td>
</tr>
<tr>
<td></td>
<td>300 TSP</td>
<td>( y = -3.09x + 26.45 )</td>
<td>1.00</td>
<td>(-3.86(0.2)bCD)</td>
<td>(27.77(0.9)bCD)</td>
</tr>
<tr>
<td></td>
<td>400 TSP</td>
<td>( y = -4.05x + 31.30 )</td>
<td>0.99</td>
<td>(-4.73(0.4)cD)</td>
<td>(32.64(1.3)dD)</td>
</tr>
<tr>
<td>Organic</td>
<td>7.5 FYM</td>
<td>( y = -2.54x + 22.56 )</td>
<td>1.00</td>
<td>(-1.10(0.2)aA)</td>
<td>(11.92(0.6)aA)</td>
</tr>
<tr>
<td></td>
<td>15 FYM</td>
<td>( y = -2.45x + 22.94 )</td>
<td>0.99</td>
<td>(-1.07(0.3)aA)</td>
<td>(13.65(0.7)bA)</td>
</tr>
<tr>
<td>Integrated</td>
<td>150TSP+7.5FYM</td>
<td>( y = -2.67x + 22.33 )</td>
<td>0.99</td>
<td>(-2.67(0.2)bBC)</td>
<td>(22.34(0.6)bB)</td>
</tr>
<tr>
<td></td>
<td>300TSP+7.5FYM</td>
<td>( y = -3.22x + 27.43 )</td>
<td>1.00</td>
<td>(-3.22(0.5)bBC)</td>
<td>(27.43(1.6)bcdBCD)</td>
</tr>
<tr>
<td></td>
<td>400TSP+7.5FYM</td>
<td>( y = -3.51x + 29.64 )</td>
<td>1.00</td>
<td>(-3.48(0.4)bBC)</td>
<td>(29.54(1.5)bcdCD)</td>
</tr>
<tr>
<td></td>
<td>150 TSP+15FYM</td>
<td>( y = -2.91x + 24.30 )</td>
<td>0.99</td>
<td>(-2.97(0.5)bBC)</td>
<td>(24.51(1.5)bcdBC)</td>
</tr>
<tr>
<td></td>
<td>300 TSP+15FYM</td>
<td>( y = -2.21x + 24.17 )</td>
<td>0.97</td>
<td>(-2.21(0.4)abAB)</td>
<td>(24.18(1.1)bBC)</td>
</tr>
<tr>
<td></td>
<td>400 TSP+15FYM</td>
<td>( y = -3.91x + 31.64 )</td>
<td>0.86</td>
<td>(-3.91(0.4)cCD)</td>
<td>(31.66(1.9)dD)</td>
</tr>
</tbody>
</table>

*In heterogeneous diffusion equations: \( y = q/q_\infty \) and \( x = \ln t \). Different small letters indicate statistically significant differences among treatments within each fertilizer system (Tukey's test \( P < 0.05 \)). Different capital letters indicate statistically significant differences among treatments between different fertilizer systems (Tukey's test \( P < 0.05 \)).
Table 5. The changes of Olsen P$_{0-0.30m}$ and Olsen P$_{0.15-0.30m}$, bioavailable P$_{150day}$ and P supply capacity of soil during two growing seasons under different fertilizer systems.

<table>
<thead>
<tr>
<th>Fertilizer systems</th>
<th>Treatments</th>
<th>Added total P by fertilizers kg ha$^{-1}$</th>
<th>P inputs mg kg$^{-1}$</th>
<th>P uptake by grain maize mg kg$^{-1}$</th>
<th>Bioavailable P$<em>{150d}$ Olsen P$</em>{0.0-0.15m}$</th>
<th>Olsen P$_{0.15-0.30m}$</th>
<th>Olsen P$_{0.0-0.30m}$</th>
<th>P supply capacity mg kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic</td>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>15.1</td>
<td>6.8±(0.0)aA</td>
<td>6.0±(0.5)aA</td>
<td>11.1</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>15OTSP</td>
<td>30.4</td>
<td>16.9</td>
<td>32.0</td>
<td>8.5±(0.0) abAB</td>
<td>7.6±(0.5)abAB</td>
<td>12.8</td>
<td>19.2</td>
</tr>
<tr>
<td></td>
<td>300TSP</td>
<td>60.7</td>
<td>33.8</td>
<td>48.9</td>
<td>9.2±(0.1) abABC</td>
<td>9.1±(0.3)abABC</td>
<td>16.5</td>
<td>32.4</td>
</tr>
<tr>
<td></td>
<td>400TSP</td>
<td>81.0</td>
<td>45.1</td>
<td>60.2</td>
<td>10.3±(1.1) bBC</td>
<td>9.7±(0.7)ABC</td>
<td>17.3</td>
<td>42.9</td>
</tr>
<tr>
<td>Organic</td>
<td>7.5FYM</td>
<td>66.8</td>
<td>17.1</td>
<td>32.2</td>
<td>8.5±(0.1)bAB</td>
<td>6.8±(0.5)aA</td>
<td>18.8</td>
<td>35.6</td>
</tr>
<tr>
<td></td>
<td>15FYM</td>
<td>133.5</td>
<td>34.2</td>
<td>49.3</td>
<td>9.9±(0.1)bBC</td>
<td>7.4±(0.4)aAB</td>
<td>13.7</td>
<td>35.6</td>
</tr>
<tr>
<td>Integrated</td>
<td>15OTSP+7.5FYM</td>
<td>132.8</td>
<td>34.0</td>
<td>49.1</td>
<td>9.3±(0.0)bABC</td>
<td>9.0±(0.7)abABC</td>
<td>16.2</td>
<td>32.9</td>
</tr>
<tr>
<td></td>
<td>300TSP+7.5FYM</td>
<td>198.8</td>
<td>51.0</td>
<td>66.0</td>
<td>13.0±(0.1)dD</td>
<td>11.1±(1.1)bBC</td>
<td>19.0</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>400TSP+7.5FYM</td>
<td>242.8</td>
<td>62.2</td>
<td>77.3</td>
<td>11.7±(0.1)cDCD</td>
<td>11.5±(1.0)bC</td>
<td>21.0</td>
<td>56.3</td>
</tr>
<tr>
<td></td>
<td>15OTSP+15FYM</td>
<td>199.5</td>
<td>51.2</td>
<td>66.2</td>
<td>10.4±(0.1)bcBC</td>
<td>9.8±(1.1)a bABC</td>
<td>17.4</td>
<td>48.8</td>
</tr>
<tr>
<td></td>
<td>300TSP+15FYM</td>
<td>265.5</td>
<td>68.1</td>
<td>83.1</td>
<td>13.5±(0.0)dD</td>
<td>12.4±(1.3)bC</td>
<td>21.7</td>
<td>61.4</td>
</tr>
<tr>
<td></td>
<td>400TSP+15FYM</td>
<td>309.5</td>
<td>79.4</td>
<td>94.4</td>
<td>13.2±(0.0)dD</td>
<td>11.4±(0.7)cB</td>
<td>11.1</td>
<td>71.5</td>
</tr>
</tbody>
</table>

The values presented in the columns are mean value ± standard error. Different small letters indicate statistically significant differences among treatments within each fertilizer system (Tukey's test $P < 0.05$). Different capital letters indicate statistically significant differences among treatments between different fertilizer systems (Tukey's test $P < 0.05$). Added total $P$ in kg ha$^{-1}$ was calculated for TSP by multiplying coefficient 0.44 by P$_{2O_5}$ amounts of TSP (containing %46 P$_{2O_5}$); for organic system by multiplying coefficient %0.89 by added FYM amounts and for integrated system the sum of these two calculations was considered. Added total $P$ in mg kg$^{-1}$ was calculated by dividing added total $P$ in kg ha$^{-1}$ by the weight of 1 hectare from soil bulk density (1300 kg m$^{-3}$) and soil depth 0–0.30 m which equals 3,900,000 kg. $P$ inputs were calculated by summation of added total $P$ amounts and native Olsen P$_{0-0.15m}$ and Olsen P$_{0.15-0.30m}$. $P$ supply capacity was calculated by summation of Olsen P$_{0-0.30m}$ and bioavailable P$_{150day}$. Different small letters indicate statistically significant differences among treatments within each fertilizer system (Tukey's test $P < 0.05$). Different capital letters indicate statistically significant differences among treatments between different fertilizer systems (Tukey's test $P < 0.05$).
humates were formed. Therefore, the addition of humic materials to manure increases recovery of Olsen P (Von Wandruszka 2006).

The ANOVA showed the significant differences between magnitudes of Olsen P for both soil depths (P < 0.001). For the inorganic system, there were also significant differences of Olsen P_{0.0-0.30 m} and Olsen P_{0.15-0.30 m} between treatments (P < 0.001) with the exception 300 and 400 TSP (P > 0.05). For the organic system, there were also significant differences of Olsen P between treatments (P < 0.001); therefore, no significant differences were found in Olsen P_{0.15 m} and Olsen P_{0.15-0.30 m} (P > 0.05) between 7.5 and 15 FYM. For the integrated system, there were no significant differences of Olsen P_{0.015 m} and P_{0.15-0.30 m} between 150 TSP+15 FYM, 300 + 7.5 FYM, 400 + 7.5 FYM, and 300 + 15 FYM treatments.

Also, the overall comparisons of Olsen P_{0.0-0.15 m} and Olsen P_{0.15-0.30 m} between inorganic, organic, and integrated systems have been performed. Based on the added P which is measured as Olsen P_{0.15 m} (Table 5), treatments can be categorized into five categories: (i) control, 7.5 FYM; (ii) 150 TSP, 15 FYM; (iii) 150 TSP+7.5 FYM, 300 TSP, 400 TSP, 150 TSP+15 FYM; (vi) 300 TSP+7.5 FYM; and (v) 400 TSP+15 FYM, 400 TSP+7.5 FYM, and 300 TSP+15 FYM. For Olsen P_{0.15-0.30 m}, there were three categories: (i) control, all organic treatment and 150 TSP, (ii) 150 TSP+7.5 FYM, 300 TSP, 150 TSP+15 FYM, 400 TSP, 300 TSP+7.5 FYM, 300 TSP+15 FYM, and 400 TSP+7.5 FYM; and (iii) 400 TSP+15 FYM. These results showed that the distributions of added P fertilizers between two depths are not the same. Generally, integrated systems provided more bioavailable P in two depths in comparison with inorganic and organic systems separately.

**Relationship between estimated p supply capacity of soil and p uptake by grain maize**

Figure 3 shows the relationship between the estimated P supply capacity of soil and P uptake by grain maize. There were relationships \( R^2 = 0.84 \text{–} 0.95 \) between estimated P supply capacity in mg kg\(^{-1}\) (x) and P uptake by grain maize in mg kg\(^{-1}\) (y). The relationships were found for inorganic, organic, and integrated systems as follows:

![Figure 3](image-url)
Inorganic system:

\[ y = 0.12x + 6.5 \quad R^2 = 0.94 \]  

(8)

Organic system:

\[ y = 0.12x + 6.8 \quad R^2 = 0.86 \]  

(9)

Integrated system:

\[ \begin{align*}
TSP + 7.5FYM : y &= 0.07x + 6.3 \quad R^2 = 0.95 \quad (10) \\
TSP + 15FYM : y &= 0.08x + 6.0 \quad R^2 = 0.84 \quad (11)
\end{align*} \]

Since P supply capacity of soil was calculated according to bioavailable P under 150 day, the present models provided simple equations to evaluate P uptake by grain maize by calculating P supply capacity of soil under inorganic, organic, or integrated systems. Since P uptake by grain maize is taken into account, these results improved our understanding about P supply capacity of soil during maize growing seasons.

**Fertilizer recommendations**

Given the fact that P is a scarce resource and if it can be deduced, therefore, optimal application rates were recommended as represented data in Table 5. According to similar P uptake amounts, there were three categories as follows: (i) 7.5 FYM, 150 TSP, 300 TSP, 150 + 7.5 FYM; (ii) 15 FYM, 400 TSP, 150 TSP+15 FYM, and (iii) 300 TSP+7.5 FYM, 300 TSP+15 FYM, 400 TSP+15 FYM. Therefore, three recommendations were suggested as follows: (i) 150 TSP or 7.5 FYM or 150 + 15 FYM; (ii) 400 TSP or 15 FYM or 150 TSP+15 FYM and (iii) 300 TSP+7.5 FYM; depending on one to select inorganic, organic, or integrated systems.

**Conclusion**

This study represents a first look at the fate of inorganic, organic, and integrated P fertilizer systems in calcareous soil in relation to soil depths and different times after planting during two maize growing seasons. These results are probably representative of almost all P reactions in soils, which happened during the maize growing; they are not unimportant. The kinetic studies showed a heterogeneous diffusion reaction. Due to the linear relationships between the inverse of the rate of reactions, it was suggested that Elovich equation best described the reaction rates of Olsen P amounts. The PSR increased by adding P. The highest values for PSR were observed for 400 TSP and 400 TSP+15 FYM, respectively. The models of P uptake by grain maize vs. P supply capacity of soil under inorganic, organic, or integrated systems during maize growing season have been achieved. The integrated system could increase Olsen P of two soil depths rather than the other systems. Additionally, the most P uptakes were observed under integrated systems. Fertilizer recommendations depending on the accessibility of fertilizer types were suggested to help small farmers of Mahidasht Plain and similar regions of Kermanshah province to select the best fertilizer systems.

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References


