Phosphorous desorption kinetics under saturated and field capacity condition in a calcareous soil

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**ABSTRACT**

An experiment was conducted to investigate the effects of soil water regimes on soil phosphorous desorption kinetics. Phosphorous was added (100 mg P kg⁻¹ soil, as KH₂PO₄) to polyethylene pots containing 100 kg soil and incubated for two months at 25°C under two different moisture condition (water saturated and field capacity). After 2 months soil phosphorous was extracted using 0.01 M CaCl₂ at 10 different shaking times (15, 30, 60, 120, 240, 480, 960, 1920, 3840 and 7680 min). The results showed that as time passed, the extractability of added P rapidly decreased during the initial times of incubation followed by a slight decrease in P release. Air drying of samples before extraction resulted in increase of P release and change of desorption kinetics of added P and led us to recommend that time dependent studies of soils should be conducted in initial soil moisture.

**INTRODUCTION**

Desorption behavior is an important processes controlling nutrient mobility and bioavailability in the environment [9]. Phosphorous (P) release rate and capacity from soils would insight invaluable information on the P fate and transport as a plant nutrient and potential risk of surface and ground waters contamination [1, 8]. Thus, in order to improve nutrient management, risk assessments, and predictions about the mobility of contaminants, it is critical that time-dependent P desorption behavior be understood, as well as the mechanisms of desorption reactions under various soil conditions [17]. Although soil P dynamics mostly controlled by the soil pH and carbonates in calcareous soils [5], soil moisture regime is known to affect P transformation through reduction/oxidation processes [13,16]. Anaerobic soil conditions increase soluble P and Fe in soils via dissolution of Ca-P due to increased CO₂ concentration as well as reduction in Fe-P minerals [18]. Ma et al. (2010) reported that the Olsen-P of soil decreased after each field saturation process and increased after each draining process [7]. Thus, in time dependent investigations it is critical to consider the initial sample condition in each time series as well as initial soil moisture, but due to the implications during the moist soil analysis the samples may be air dried before extraction. The authors believed that this pretreatment can affect P behavior so the aim of this study were to investigate 1) P desorption behaviors in two different soil moisture regimes (field capacity and water saturated); and 2) the air drying pretreatment effect of soil samples before extraction on kinetics models of P desorption in a calcareous soil.

**MATERIALS AND METHODS**

**Soil sample preparation and analysis:**
A bulk soil sample from calcareous soils in an arid region of Khuzestan Province, Southwestern Iran was collected and transported to laboratory. The climate is varied from semi-arid to arid with a mean annual precipitation and class A pan evaporation of 240 and 3000 mm, respectively [2]. The soil was air dried, ground, passed through a 2-mm sieve and some analysis were made by standard methods including: particle size distribution (hydrometer method) [4]; Soil Organic Matter (SOM) content (Walkley-Black procedure; [11]); Soil pH (glass electrode in saturation extracts); and electrical conductivity by a conductivity meter. Calcium carbonate equivalent (CCE) was determined by neutralization with hydrochloric acid [6], NaHCO₃-P was extracted using Olsen et al., (1954) procedure and determined by Murphy and Riley (1962).
Desorption experiment:

In desorption experiment phosphorous was added (100 mg P kg\(^{-1}\) soil, as KH\(_2\)PO\(_4\)) to polyethylene pots containing 100 g soil and incubated for two months at 25\(^\circ\)C in two subset including two different moisture conditions (water saturated and field capacity). After 2 months soil phosphorous was extracted using 0.01 M CaCl\(_2\) at 10 different shaking time (15, 30, 60, 120, 240, 480, 960, 1920, 3840 and 7680 min) and determined using spectrophotometer [11]. Before extracting the soil P each soil samples for each time was divided to two subset one extracted in initial soil moisture and other was dried in oven at 60\(^\circ\)C then after extracted for bicarbonate extractable P.

The suitability of eight kinetics models (Table 1) for describing the data trend was tested using least-square regression analysis. High values of the coefficient of determination (R\(^2\)) and low standard error of estimate were used as indices for comparing the validation and suitability of models. The standard error of the estimate was obtained as follows:

\[
SE = \sqrt{\frac{\sum (q - q')^2}{(N-2)}}
\]

where \(q\) and \(q'\) are the measured and calculated amounts of Cd in soil at time \(t\), respectively and \(N\) is the number of measurements.

RESULTS AND DISCUSSION

The studied soil was highly calcareous with 47% calcium carbonate equivalent. A sandy loam soil with the clay, silt, and sand percentage of 10, 22 and 68, respectively. The pH was 7.1 and electrical conductivity was measured 1.16 dS m\(^{-1}\). Bicarbonate extractable P was low (5.4 mg kg\(^{-1}\)) in the studied soil.

Several parameters including pH, clay type and content, carbonates, organic matter, redox condition, aging time, and complexing agents influenced the release of sorbed P from soil particles [15]. The release of P, by means of 0.01 M CaCl\(_2\) extraction is presented Fig. 2. It is clear that the amount of released P was increased with increasing time and equilibrium is reached in almost 16 h, followed by a slight decrease in desorption. The experimental data showed that air drying of the soil samples before extraction resulted in increased desorbed P in field saturation and field capacity water regimes in almost all extraction times (Table 2).

Fig. 1: Phosphorus desorption by 0.01 M CaCl\(_2\) for soils incubated under field capacity and field saturation and pretreated air drying and moist before extraction
The results revealed that the amounts of desorbed P were significantly greater in the samples which were air dried before extraction comparing to those extracted in initial soil moisture in two water regime of field capacity and field saturation (Table 2). Generally, the amounts of released P were higher in soils incubated under field saturation compared to those for field capacity. In the first extraction time (15 min) the amount of released P in field saturated soil was 0.683 mg kg$^{-1}$ which increased by air drying the sample before extraction to 1.224 mg kg$^{-1}$. As well as in field capacity condition released P was 0.646 mg kg$^{-1}$ when samples were in field capacity at time of extraction which increased to 1.650 mg kg$^{-1}$ when air dried and extracted for P. It is revealed that there is a direct correlation between P solubility in soil and soil redox conditions. The availability and solubility of P can be affected in cyclically waterlogged and drained environments [3, 14].

Table 2: The CaCl$_2$-extractable P in two moisture regimes pretreated before extraction (moist and air dried) at different extraction times.

<table>
<thead>
<tr>
<th>Moisture regime</th>
<th>Time (min)</th>
<th>15</th>
<th>30</th>
<th>120</th>
<th>480</th>
<th>960</th>
<th>1920</th>
<th>3640</th>
<th>7680</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field Saturation</td>
<td>moist</td>
<td>0.683</td>
<td>0.591</td>
<td>0.906</td>
<td>0.887</td>
<td>0.969</td>
<td>1.023</td>
<td>0.962</td>
<td>1.105</td>
</tr>
<tr>
<td>Air dried</td>
<td>1.224</td>
<td>1.612</td>
<td>1.675</td>
<td>1.671</td>
<td>1.982</td>
<td>2.140</td>
<td>2.216</td>
<td>2.099</td>
<td></td>
</tr>
<tr>
<td>Field Capacity</td>
<td>moist</td>
<td>0.646</td>
<td>0.518</td>
<td>0.720</td>
<td>0.752</td>
<td>0.944</td>
<td>0.679</td>
<td>0.825</td>
<td>0.816</td>
</tr>
<tr>
<td>Air dried</td>
<td>1.650</td>
<td>1.522</td>
<td>1.725</td>
<td>1.594</td>
<td>1.851</td>
<td>1.977</td>
<td>1.860</td>
<td>1.526</td>
<td></td>
</tr>
</tbody>
</table>

The values of the rate parameters for the six equation used for describing P release from three soils under different treatments are shown in Table 4. From the two constant rate equations, the rate equation (b) for P release was used to compare the relative rate of P releasing from solid phase to the bulk solution under two moisture regimes. The b values averaged 0.082 for field saturated soils, which decreased to 0.042 in soils incubated under field capacity.

Table 3: Coefficients of determination ($R^2$) for the fitted functions of pretreated soils under two moisture regimes.

<table>
<thead>
<tr>
<th>Moisture regime</th>
<th>Equations</th>
<th>Zero</th>
<th>First</th>
<th>Second</th>
<th>Third</th>
<th>Parabolic</th>
<th>Exponential</th>
<th>Elovich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field Saturation</td>
<td>moist</td>
<td>0.48*</td>
<td>0.41</td>
<td>0.36</td>
<td>0.30</td>
<td>0.66</td>
<td>0.81</td>
<td>0.84</td>
</tr>
<tr>
<td>Air dried</td>
<td>0.44</td>
<td>0.41</td>
<td>0.36</td>
<td>0.32</td>
<td>0.68</td>
<td>0.85</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>Field Capacity</td>
<td>moist</td>
<td>0.17</td>
<td>0.18</td>
<td>0.19</td>
<td>0.19</td>
<td>0.29</td>
<td>0.49</td>
<td>0.47</td>
</tr>
<tr>
<td>Air dried</td>
<td>0.25</td>
<td>0.26</td>
<td>0.26</td>
<td>0.27</td>
<td>0.25</td>
<td>0.57</td>
<td>0.57</td>
<td></td>
</tr>
</tbody>
</table>

The correlation coefficients obtained from the application of several kinetics models to describe P release pattern for four different moisture conditions. The zero-, first-, second-, third-, and parabolic equations poorly described the extraction kinetics based on $R^2$. However, the two constant rate (Exponential), and simple Elovich equations were the suitable models in describing the extraction kinetics of P from treated soils. Moreover Exponential and simple Elovich equations fitted better in soils treated under field saturation (Table 3). Anaerobic soil conditions increase oxalate-soluble P and Fe in soils [18]. Ma et al. (2010) reported that the Olsen-P of soil decreased after each inundating process and increased after each draining process [10].

Table 4: Major parameters of the kinetics equations of P desorption from soils incubated under field saturation and field capacity

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>First</th>
<th>Second</th>
<th>Third</th>
<th>Parabolic</th>
<th>Exponential</th>
<th>Elovich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Field Saturation</td>
<td>0.79</td>
<td>10$^3$</td>
<td>5.1×</td>
<td>0.78</td>
<td>10$^3$</td>
<td>-6.0×</td>
</tr>
<tr>
<td>Air dried</td>
<td>1.64</td>
<td>10$^3$</td>
<td>4.8×</td>
<td>1.62</td>
<td>1.7×10$^3$</td>
<td>1.59</td>
</tr>
<tr>
<td>Field Capacity</td>
<td>0.68</td>
<td>10$^3$</td>
<td>0.3×</td>
<td>0.67</td>
<td>0.0001</td>
<td>-3</td>
</tr>
<tr>
<td>Air dried</td>
<td>0.68</td>
<td>10$^3$</td>
<td>0.1×</td>
<td>0.68</td>
<td>10$^3$</td>
<td>-9.8×</td>
</tr>
</tbody>
</table>

Conclusions:

Our results implied that under the anaerobic condition of field saturation, phosphorus release increased in terms of amounts and rate compared to field capacity conditions. Previous findings related the elevated soluble P in saturation condition to releasing P from Ca-P and Fe-P minerals. We also implied that pretreatment of moist soil samples (air drying) before extraction resulted in change in amounts and rates of P release and would complicate the comparison of inter laboratory data. The authors believed that a universally accepted procedures
in terms of reagents, extractions conditions such as temperature, reagent concentration, solid to solution ratio, treatment time, pH control, and shaking time are required for desorption studies that data to be comparable inter laboratory.

REFERENCES


