Elucidation of phosphorous sorption by calcareous soils using principal component analysis

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Elucidation of phosphorous sorption by calcareous soils using principal component analysis

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This study was conducted to understand the mechanisms governing P-sorption and desorption by calcareous soils (up to 48% CaCO₃). Batch experiments with KCl as background were carried out by adding varying amount of P up to 100 mgP.L⁻¹. The desorption percentage (%DES) results show that little P was released from the adsorbed phase. Principal component analysis was applied to evaluate the combined influence of soil components on P sorption. The complex P sorption process can be related to specific soil components by the following equation: P-sorption = -2.20(CaCO₃%) - 0.04(Fe-oxide) + 0.04(pHe) + 11.02(sand%) + 3.35(silt) - 10.73(clay) - 1.24(EC) - 1.93(P-Olsen)(R² = 0.9941, SSE = 380). Sand% and clay% are the most significant variables for modelling P sorption data. The derived equation could be applied to predict P sorption in other soils that have similar compositions to those investigated herein. The degree of P saturation (DPS) threshold level for all soils was less than 3% except in the soil with the lowest iron oxide. All of the studied soils have exceeded the environmentally unacceptable P concentration except the soil with the lowest iron oxide content.

Keywords: calcareous soils; phosphorus; principal component analysis; sorption/desorption isotherms

1. Introduction

Phosphorus (P) is the most common limiting nutrient. Therefore, P fertiliser is used intensively to increase crop production. However, long-term application of P fertilisers can cause the accumulation of P in topsoil, increasing potential P losses to surface-water and ground-water. Indeed, many agricultural soils are already classified as over-fertilised with respect to P.[1] The transport of P to surface waters, which occurs via discharge of domestic sewage and industrial effluents in addition to agricultural runoff,[2,3] causes eutrophication, which has been a worldwide environmental concern.[e.g. 4] The accumulation of bioavailable P in surface waters leads to algae proliferation, an increase in oxygen demand, and deterioration of water quality.

Phosphorus leaching to groundwater has previously been assumed to be negligible in most soils, and the effect of P accumulation in groundwater has seldom been studied, even though there are combinations of soil properties, agricultural management practices and climatic conditions...
that may result in significant P accumulation in subsoil and leaching to groundwater.\[5\] The P concentration in groundwater depends on the soil’s ability to retain P.\[6\] Therefore, determining the rate of P-release from soils is necessary in order to minimise the impact of P on surface and groundwater quality. Moreover, the P sorption isotherm provides a more accurate prediction of P fertiliser requirements for dry-land wheat than the Olsen soil P test.\[7\] The P-Olsen is used to evaluate P availability in both acid and calcareous soils by extracting P with buffered alkaline solution (ammonium bicarbonate).

There are several processes governing the sorption and desorption of phosphorus in soils. Adsorption by carbonate minerals is known to be the most dominant,\[8\] and some studies have shown that availability of P fertiliser in calcareous soils negatively correlates with CaCO\(_3\) content of the soil,\[e.g. 9\] The P sorption to carbonates is expected to be influential at low pH (<8),\[10\] whereas precipitation of P with Ca is expected at higher pH.\[11\] Many studies have sought to characterise the reaction mechanisms leading to P retention in calcareous soils.\[12,13\] These studies concluded that adsorption and precipitation are major P retention processes decreasing the availability of applied P.

Recently, P sorption in calcareous soils has been described as rapid adsorption of P onto particle surfaces followed by slow conversion into poorly available forms such as mineral Ca-P.\[14\] Interestingly, some studies have shown that rapid P sorption is related to Fe oxides and not to the total or active CaCO\(_3\) content in soil,\[e.g. 15–17\], whereas another study found that CaCO\(_3\) is the primary geochemical factor controlling P fixation and retention within arid soils.\[18\] Carbonate often plays a secondary role in P sorption owing to the strong impact of Fe and Al oxyhydroxides,\[e.g. 19\] which have a larger specific surface area and sorbing capacity than carbonates (\(\approx 100–400 \text{ m}^2 \text{ g}^{-1}\) and \(2.5 \mu \text{mol} \text{ m}^{-2}\), versus \(3.0 \text{ m}^2 \text{ g}^{-1}\) and \(0.13 \mu \text{mol} \text{ m}^{-2}\), respectively).\[20\]

Soil sorption and retention processes are often investigated with respect to experimental factors such as soil mass, solution pH, shaking time, ionic strength, temperature, and solute concentration.\[21–23\] Soil properties such as cation exchange capacity (CEC), pH of zero point of charge (pHzpc), organic matter (OM), and electrical conductivity (EC) are also considered. The main reason for studying such a large number of factors is to identify the optimal conditions for sorption of a particular solute such as P. Most soil sorption studies employ univariate analysis to investigate the influence of a single factor while maintaining other factors at appropriate fixed levels. However, the individual and combined influence of all factors on solute sorption by complex soil substrates could be studied using principal component analysis or multi-linear regression, and this may facilitate simultaneous optimisation of all factors for a given soil sorption process.\[24\] Multivariate analysis may also reveal the nature of the relationships (i.e., linear or non-linear) between experimental variables and solute sorption by soil. Application of multivariate analysis in optimising chemical reactions, chemical analysis, clustering of objects, and designing experimental procedures is outlined in the literature.\[24,25\] However, application of multivariate analysis is limited in soil sorption studies, and is not reported for P sorption in calcareous soils.

Previous work on the same soils indicated that P sorption by CaCO\(_3\)-rich soils at high P levels (100–500 mg L\(^{-1}\)) was positively correlated with Fe-oxide and CEC, whereas carbonate content, soil pH, EC, and OM content have no significant effect.\[26\] However, little is known about P sorption and release mechanisms in calcareous soils at high (>30%) CaCO\(_3\) level, despite the common occurrence of such soils and heavy application of P fertilisers. Therefore, the objectives of this study are (i) to examine factors that control P sorption in calcareous soils under arid and semi-arid conditions at P levels less than 100 mg kg\(^{-1}\); (ii) to reveal the relationships between soil physical–chemical characteristics and P sorption affinity for representative surface calcareous soils; (iii) to apply principal component analysis (PCA) to evaluate the combined influence of soils components on P sorption; and (iv) to evaluate the possibility of P leaching from these soils.
2. Materials and methods

2.1. Soil sampling and soil chemical properties

Five representative calcareous topsoil samples (0–20 cm) were collected from different urban areas in Al-Hashemiya, eastern Jordan. The study area lies in the middle of Zarqa city (0.8 million inhabitants) within Amman-Zarqa basin between altitudes 32.09–32.15 and 36.11–36.19 longitudes. The climate of the basin is semiarid with mean annual rainfall of 270 mm, where rainfall happens in winter, whereas summer is extensively dry and hot. Soils in the study area are formed on limestone and dolomitic limestone parent material. Two main soil subgroups are found in the study area, *Xerochreptic Calciorhids* and *Xerochreptic Camborthids* (Hunting Technical Services and Soil Survey and Land Research Centre, 1994). The soil samples were collected randomly to include soils with high CaCO3, where 4 sub-samples were collected at each site to obtain a representative average sample. The sampling procedure was intended to obtain a representative average sample made of 4 sub-samples collected at each site.

Soil samples were air dried and ground to pass through a 2-mm sieve in preparation for sorption experiments. Selected soil properties were determined in triplicate according to standard methods.[27] Particle size distribution (percentage sand, silt, and clay) was determined by the pipette method after pre-treatment to remove soluble salt, organic matter, and carbonates. Soil pH was determined using saturated paste. Electrical conductivity in the saturation extract (ECe) was measured by a meter–ohm conductivity meter. The cation exchange capacity (CEC) was determined by extraction with 1 M NH4OAc (pH 7.0). Organic carbon content (OC) was determined by the dichromate oxidation method. The organic matter was then calculated by multiplying the OC by a factor of 1.9. The total carbonate (CaCO3) was determined using a pressure calcimeter. Amorphous Fe oxides were extracted with ammonium oxalate buffered at pH 3. The P-Olsen was determined using a soil to solution ratio of 1:20 with 30 min of shaking. Phosphorus in the extractant was determined by using the ammonium molybdate–ascorbic acid method as described by Murphy and Riley.[28] All chemicals were of analytical grade. All glassware containers were previously soaked in 10% (v/v) nitric acid for at least 24 h, then rinsed with double deionised water.

2.2. Phosphate sorption

Concentration variation procedure was performed to determine PO4 sorption affinity toward different calcareous soils. In 50-mL centrifuge tubes, 30 mL of 50 mM KCl containing 0, 10, 30, 50, 70, 90, or 100 mg P L\(^{-1}\) was combined with 3.00 g soil. The tubes were shaken 24 h at room temperature and centrifuged at 1800 rpm for 15 min to separate soils particles. The supernatant was filtered using 0.45 μm membrane. Phosphorus in the final supernatant was determined spectrophotometrically using ammonium molybdate–ascorbic acid method.[28] Briefly, an acidified solution of ammonium molybdate containing ascorbic acid reacts rapidly with phosphate ion to produce a blue-purple compound. Absorbance at 880 nm is then measured after 10 min.

The soil pH was determined in the soil suspension after 24 h reaction time.

The net amount of P sorbed by soils (\(q_n\)) and total amount of P sorbed (\(q_t\)) were calculated as described in the following Equations (1 and 2):

\[
q_n = \frac{(C_i - C_f) \times V}{W_s}
\]

\[
q_t = \frac{(C_i - (C_f - C_o)) \times V}{W_s}
\]
where \( C_i \) is the initial concentration of P added (mg P L\(^{-1}\)), \( C_f \) is the concentration of P in solution after equilibration (mg P L\(^{-1}\)), \( C_0 \) is the measured concentration of P in the equilibrium solution at \( C_i = 0 \) (i.e. the amount originally available in the soil); \( V \) is the volume (in L) of P solution added, and \( W_s \) is the mass of dry soil (kg). The \( C_e \) is \( (C_f - C_0) \). The \( q_n \) and \( q_t \) are converted to the standard soil sorption unit of centimoles of charge per kilogram of soil (cmolc kg\(^{-1}\)) to describe the amount of P uptake by soil.

2.3. Phosphate desorption

After completion of the sorption study, 0.050 M KCl solution was added to each tube that contained soil with sorbed P to reach the total solution volume of 15 mL. The desorption was performed by shaking the suspension for 24 h. The same procedures (centrifugation and filtration) used for P sorption, were also used for measuring P desorption. The leached P in solution was measured using ammonium molybdate–ascorbic acid method as described above. The amount of P desorbed was calculated as follows:

\[
P\text{-desorbed} = C_{fd} \times \frac{V}{W_s}
\]

where \( C_{fd} \) is the amount of P released in the solution after 24 h, \( V \) is the volume of the solution and \( W_s \) is the oven dry soil (kg).

The percent P desorption (\%DES) at 100 mg P L\(^{-1}\) was calculated as:

\[
\text{DES}\% = \frac{P\text{-desorbed (cmol kg}^{-1}\text{)}}{P\text{-sorbed (cmol kg}^{-1}\text{)}} \times 100
\]

2.4. Principal component analysis

The individual and combined influence of the studied factors on P sorption was studied using principal component analysis (PCA), a popular tool of multivariate analysis. By conducting five sorption experiments, the effect of CaCO\(_3\)%, Fe-oxide%, sand%, silt%, clay%, OM, P-Olsen, pH, EC, and CEC on P sorption by five soils is studied (See Table 4 for the levels of each variable/factor in soils). Initially, sorption data were collected in a matrix of 5 \times 10 dimension (5 experiments and 10 soils properties) and subjected to PCA for assessing the significance of the studied variables and relation between them on P sorption. Analysis was carried out by decomposing A matrix into its loading (variables) and score (soils/experiments) vectors using the popular singular value decomposition technique.[25,26] PCA is a powerful statistical method that is often used for factor analysis, clustering of objects and also for modelling purposes.[25] PCA was carried out using Matlab\textsuperscript{®} program. The raw sorption data were normalised to 100% before PCA analysis. More details on estimation of U, V, and d will be given in the following section.

3. Results and discussion

3.1. Chemical and physical properties of the soil samples

Averages of chemical and physical properties of the studied soils are given in Table 1. Electrical conductivity ranged from 3.3 to 40.2 mS. cm\(^{-1}\). All samples were calcareous soils (CaCO\(_3\) > 25%) with low OM (<2.5%), low clay content (<16%), and high pH, CaCO\(_3\), and salinity (Table 1). All the soils had high Olsen-P (P > 5 mg kg\(^{-1}\) soil). The soil texture was sandy loam for soil 1, 2, 4, and 5, and loamy sand for soil 3.
Table 1. Statistical averages and relative standard deviation (RSD) in parenthesis of the main physicochemical parameters of the soil samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>CaCO₃ %</th>
<th>Fe-oxide mg kg⁻¹</th>
<th>pH %</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>Soil texture</th>
<th>ECₑ mScm⁻¹</th>
<th>%OM</th>
<th>CEC cmol_c kg⁻¹</th>
<th>P-Olsen mg kg</th>
<th>Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.9</td>
<td>643</td>
<td>7.7</td>
<td>65</td>
<td>19</td>
<td>16</td>
<td>Sandy loam</td>
<td>40.2</td>
<td>1.5</td>
<td>3.9</td>
<td>20</td>
<td>Illite, quartz, calcite</td>
</tr>
<tr>
<td></td>
<td>(7.3)</td>
<td>(6.5)</td>
<td>(0.5)</td>
<td>(2.5)</td>
<td>(2.7)</td>
<td>(2.9)</td>
<td></td>
<td>(0.3)</td>
<td>(8)</td>
<td>(4.2)</td>
<td>(0.56)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>47.1</td>
<td>1503</td>
<td>7.8</td>
<td>69</td>
<td>21</td>
<td>9</td>
<td>Sandy loam</td>
<td>14.5</td>
<td>2.2</td>
<td>9.0</td>
<td>67</td>
<td>Calcite, corundum, graphite</td>
</tr>
<tr>
<td></td>
<td>(1.7)</td>
<td>(7.8)</td>
<td>(0.48)</td>
<td>(3.1)</td>
<td>(2.9)</td>
<td>(3.0)</td>
<td></td>
<td>(0.38)</td>
<td>(7.8)</td>
<td>(1.1)</td>
<td>(0.54)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>38.7</td>
<td>499</td>
<td>7.4</td>
<td>73</td>
<td>25</td>
<td>2</td>
<td>Loamy sand</td>
<td>25.6</td>
<td>1.1</td>
<td>4.8</td>
<td>12</td>
<td>Calcite, quartz</td>
</tr>
<tr>
<td></td>
<td>(0.78)</td>
<td>(4.3)</td>
<td>(0.36)</td>
<td>(3.8)</td>
<td>(3.4)</td>
<td>(3.0)</td>
<td></td>
<td>(0.40)</td>
<td>(8.9)</td>
<td>(0.46)</td>
<td>(0.75)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>36.5</td>
<td>494</td>
<td>7.8</td>
<td>59</td>
<td>27</td>
<td>15</td>
<td>Sandy loam</td>
<td>5.1</td>
<td>1.5</td>
<td>10.6</td>
<td>16</td>
<td>Calcite, corundum, quartz</td>
</tr>
<tr>
<td></td>
<td>(0.8)</td>
<td>(4.0)</td>
<td>(0.5)</td>
<td>(1.9)</td>
<td>(2.0)</td>
<td>(2.8)</td>
<td></td>
<td>(0.49)</td>
<td>(7.9)</td>
<td>(3.5)</td>
<td>(0.52)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>34.1</td>
<td>722</td>
<td>8.1</td>
<td>61</td>
<td>27</td>
<td>12</td>
<td>Sandy loam</td>
<td>3.3</td>
<td>1.7</td>
<td>10.5</td>
<td>28</td>
<td>Calcite, corundum, quartz</td>
</tr>
<tr>
<td></td>
<td>(2.9)</td>
<td>(7.0)</td>
<td>(0.43)</td>
<td>(3.9)</td>
<td>(4.0)</td>
<td>(3.7)</td>
<td></td>
<td>(0.39)</td>
<td>(9.8)</td>
<td>(1.3)</td>
<td>(0.52)</td>
<td></td>
</tr>
</tbody>
</table>
3.2. **Phosphorus sorption**

In this study the term sorption refers to removal of P from solution by either adsorption or precipitation. The sorption isotherms of phosphate onto the five soils are shown in Figure 1. There was a surprising amount of variability in P sorption affinity among the different soils. The sorption isotherm of soil 3, which had the lowest OM%, clay content, and pH, shows a trend similar to the H-type isotherms.[29] This isotherm indicates a high affinity for P and is characterised by a steep slope at the beginning. The solution pH of this soil increased from 6.7 to 7.4, suggesting that the P sorption onto this soil is an inner-sphere process involving ligand exchange with OH.[30]

For other soils (1, 2, 4, and 5), the isotherms generally indicated a two-step sorption process: at low equilibrium concentrations there is an initial steep increase in sorption followed by a moderate increase approaching steady state sorption at high equilibrium concentrations (Figure 1). This isotherm shape suggests an initial surface adsorption/complexation, followed by surface precipitation of adsorbed phosphate.[31,32] Most of the soil samples did not reach their maximum P-sorption capacity.

The results show that as the P concentration in solution increased above $10^{-4}$ M, the slope of the sorption isotherm changed abruptly in all soils (Figure 1). This may result from P precipitation on the carbonate surface. Freeman and Rowell [32] reported that P precipitates on carbonate at a P concentration of $10^{-4}$ M. Two phase sorption isotherms in calcareous substrates have also been reported by others.[32,33] The stepwise sorption isotherms result from sorption reactions at low P concentrations and precipitation of Ca-P minerals at higher initial P concentrations with the adsorbed P acting as nuclei for crystal growth.[32,33]

The Langmuir and Freundlich isotherm equations are widely used to describe the sorption processes. The linear form of these isotherm equations can be written as follows:

$$ \frac{1}{q_t} = \left( \frac{1}{q_{\text{max}}K} \right) \frac{1}{C_f} + \frac{1}{q_{\text{max}}} $$

$$ \ln q_t = \ln K_d + \frac{1}{n} \ln C_f $$

where $q_t$ is total sorbed P (cmolc Kg$^{-1}$); $C_f$ is the P concentration in the equilibrium solution, $q_{\text{max}}$ is the maximum sorbed P (cmolc Kg$^{-1}$), and $K$, $K_d$, and $n$ are constant parameters of the two models. The P-sorption for all soils (Table 2) fit both the Langmuir and Freundlich isotherms well ($R^2 = 0.92$–0.96 and 0.90–0.98, respectively). Therefore, all parameters of both models were calculated and summarised in Table 2.
Table 2. Estimated Langmuir and Freundlich parameters ($q_{\text{max}}$, $K$, $K_d$ and $n$) of phosphorous all topsoil samples.

<table>
<thead>
<tr>
<th>Soil NO</th>
<th>Linearised Langmuir equation</th>
<th>$R^2$</th>
<th>$q_{\text{max}} \mu g \text{ g}^{-1}$</th>
<th>$K$</th>
<th>Linearised Freundlich equation</th>
<th>$R^2$</th>
<th>$K_d$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$y = 0.14x + 0.81$</td>
<td>0.92</td>
<td>380.89</td>
<td>5.80</td>
<td>$y = 0.5x + 0.14$</td>
<td>0.94</td>
<td>1.15</td>
<td>1.96</td>
</tr>
<tr>
<td>2</td>
<td>$y = 0.14x + 0.75$</td>
<td>0.94</td>
<td>415.87</td>
<td>5.23</td>
<td>$y = 0.53x + 0.22$</td>
<td>0.96</td>
<td>1.25</td>
<td>1.88</td>
</tr>
<tr>
<td>3</td>
<td>$y = 0.03x + 0.44$</td>
<td>0.95</td>
<td>703.95</td>
<td>17.39</td>
<td>$y = 0.65x + 1.76$</td>
<td>0.90</td>
<td>5.82</td>
<td>1.54</td>
</tr>
<tr>
<td>4</td>
<td>$y = 0.05x + 0.70$</td>
<td>0.94</td>
<td>444.39</td>
<td>13.43</td>
<td>$y = 0.45x + 0.49$</td>
<td>0.95</td>
<td>1.63</td>
<td>2.24</td>
</tr>
<tr>
<td>5</td>
<td>$y = 0.09x + 0.70$</td>
<td>0.96</td>
<td>446.70</td>
<td>7.46</td>
<td>$y = 0.50x + 0.38$</td>
<td>0.98</td>
<td>1.45</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Figure 2. Phosphorus sorption isotherms for all top soils as a function of added P.

Low-OM% soil 3 had the highest P-sorption capacity ($K_d$), whereas high-CaCO$_3$ soil 1 had the lowest $K_d$. This suggests that low-OM% soils have high P affinity, while high-CaCO$_3$ soils have low P affinity at low P concentrations. Phosphorus sorption capacity of soil is considered important as it affects the partitioning of P between the solid phase and soil solution and releasing of P from soil.[34] Subsurface P movement is impacted by high concentrations of P in surface soils. The highest maximum P-sorption was for soil 3, which has lowest OM, pH, and clay, whereas the lowest was for soil 1 with the highest CaCO$_3$%, highest clay content, highest EC, and lowest CEC (Table 2).

Figure 2 shows that the amount of P-uptake for all soils increased with increasing initial P-concentrations. The dominant mineral of the soil samples in this study is calcite. The P-sorption on calcite is thought to be controlled by precipitation of Ca phosphate,[35] although a recent work indicated different mechanisms may control P sorption.[36] The high concentrations of phosphate in this study are likely to induce precipitation of calcium phosphates. However, it is possible that newly introduced P competed with the native adsorbed P at low phosphate concentrations, which would also explain the increase in P-uptake with increasing P concentration.

Zeta-potential measurements of calcite in water show that the point of zero charge of the mineral occurs at about pH 8.2.[37] It is clearly illustrated that orthophosphate species are chemically adsorbed onto calcite for pH values greater than 8.2. In this study, for pH between 7.4 and 8.1, the adsorption seems to be due both to electrostatic and chemical interactions. Therefore, the speciation of aqueous orthophosphate as well as hydrolysis at the calcite surface should be considered to explain the mechanism of adsorption. HPO$_4^{2-}$ species prevail for pH between 7 and 10.[38] Considering hydrolysis reactions of calcite, it follows that cationic species, such as Ca$^{2+}$, CaHCO$_3^-$ and CaOH$^-$, prevail for pH less than 8, rendering the mineral surface positively charged.[39]
3.3. *Phosphorus desorption from soils*

In Figure 1 the x-intercept is termed as the equilibrium P concentration ($EPC_0$). At this point, there is no net adsorption or desorption from the solid phase at this solution concentration. The $EPC_0$ is also the solution concentration at which soils display their maximum buffering capacity for solution P. These values were estimated and summarised in Table 3. The highest equilibrium P concentrations ($EPC_0$) occur in soil 1 and 2, suggesting that these soils tend to act as sources of P at very low solution P concentrations, whereas the lowest $EPC_0$ of soil 3 suggests that this soil may act as a sink of P.

Desorption of initially bound phosphate from soil components is important for plant availability of P and for predictions of P leaching. The desorbed concentration of P in the five soil samples ranged from 0.36 mg L$^{-1}$ to 12.0 mg L$^{-1}$ after the 24 h desorption experiment. The desorption percentage (%DES) results are shown in Table 3. Figure 3 shows that only a little P was released from the adsorbed phase, suggesting that P was strongly adsorbed. The high desorption of P in soils 2 and 5 may have resulted from the high amounts of Fe-oxide and OM%. Therefore, in these two soils Fe-oxide played a major role in releasing more P into the liquid phase. Soil 3 showed the smallest amount of P-release owing to the high affinity of this soil for P (Figure 1).

All soils demonstrated sorption–desorption hysteresis, with the most pronounced irreversibility in soil 3, which had the lowest pH, clay%, OM%, and P-Olsen. In this soil more than 98% of the added P remained in the adsorbed phase (Table 3). The irreversibility of sorption–desorption reactions has been generally attributed to a shift in the form of P held at the surface from a loosely bound to a tightly bound species. In this study the shift occurred when the added P started to precipitate. Therefore, the mechanisms proposed here include precipitation of discrete phosphate

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>P-equilibrium (in 0.05 M KCl) (C) mg L$^{-1}$</th>
<th>P-equilibrium at zero sorption (EPC$_0$) mg L$^{-1}$</th>
<th>P-Olsen $\mu$g g$^{-1}$</th>
<th>Degree of P saturation (DPS)</th>
<th>Percent P desorption (% DES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.048</td>
<td>23.40</td>
<td>20</td>
<td>5.3</td>
<td>6.3</td>
</tr>
<tr>
<td>2</td>
<td>0.024</td>
<td>23.22</td>
<td>12</td>
<td>2.9</td>
<td>10.8</td>
</tr>
<tr>
<td>3</td>
<td>0.019</td>
<td>4.329</td>
<td>67</td>
<td>9.5</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>0.000</td>
<td>17.59</td>
<td>28</td>
<td>6.3</td>
<td>8.9</td>
</tr>
<tr>
<td>5</td>
<td>0.096</td>
<td>19.91</td>
<td>16</td>
<td>3.6</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Figure 3. Phosphorus desorption isotherms for all top soils
minerals. These mechanisms were observed previously,[40] along with diffusive penetration of surface-sorbed P into soil components.[41]

The small amount of P released from all soils in this study is most likely attributable to the conversion of poorly crystalline indigenous Ca phosphates into hydroxyapatite, desorption of adsorbed P from the clay mineral and carbonate surfaces, and dissolution of hydroxyapatite. In calcareous soils, the carbonate Ca is a very strong complexing agent for P, as P is mainly precipitated as Ca phosphates or co-precipitates with carbonates.[42] In this study the Minteq results indicated that phosphate removed from the solution primarily precipitated as Ca-bound P. Previous studies have suggested that these Ca-P fractions are stable and are barely desorbed once formed.[43–45]

The potential P release was assessed by two parameters; the equilibrium P concentration in solution after the soil was shaken in 0.050 M KCl containing 0 P for 24 h (C), and EPC₀ (Table 3). The results show that the P-equilibrium is mostly higher than the critical environmental concentration thresholds (0.010–0.076 mg L⁻¹). In other words, net P release from soils 1, 2, 3 and 5 occurred even when the solution contained as much as 0.019 to 0.096 mg P L⁻¹. The value of EPC₀ had the same trend as C, but a greater magnitude, ranging from 4.3 to 23.4 mg L⁻¹ for all soils. This means that net P release from these treated soils occurred even when the solution contained as much as 4.3 to 23.4 mg P L⁻¹.

The degree of P saturation (DPS) has been used as an environmental index of soil P available to be released through runoff and leaching to surface and subsurface waters. This concept has been applied successfully to different soils.[13,46] Phosphorus saturation is defined as:

\[
DPS\% = \frac{P\text{-Olsen} (\mu g \, g^{-1})}{q_{\text{max}} (\mu g \, g^{-1})} \times 100 \tag{7}
\]

Therefore, in this study to estimate the potential of P concentration in runoff from soils, the degree of saturation was used. The P-Olsen method is used to determine extractable P concentrations in calcareous soils. In this study, qmax was calculated from the Langmuir model. Previous studies have shown that once DPS reaches a threshold level, the concentration of P in leachate or runoff increases rapidly, and can exceed environmentally unacceptable P concentrations for flowing waters (0.010–0.076 mg L⁻¹). There are different threshold DPS in the literature; for example it is 56% for typical soils in the Mid-Atlantic region of the USA,[47] 25% for Netherlands soils,[48] and 20% for Florida sandy soils.[49] In our study the DPS threshold level for all soils ranges from 3.6 to 9.5%. All of these soils have exceeded the environmentally unacceptable P concentration except soil 4, which had the lowest Fe oxide content.

3.4. PCA analysis of P sorption data

PCA was applied to P sorption data given in Table 4 to evaluate the influence and the combined influence of soil properties on P sorption. Before analysis, the data matrix A was normalised to 100% as mentioned earlier. PCA was carried out on a data matrix of dimension 5 × 10, where 5 is the number of experiments or soils and 10 is the number of variables of soils. After decomposing adsorption matrix, the obtained eigen-values (which account for principal components PC) were 3,721,932, 6611, 900, 197, and 4. The earlier values indicated that P sorption data is satisfactorily presented using only one principal component PC which captured >99% of variances in the original data. Accordingly, the first two loading vectors and score vectors were generated for diagnostic purposes. The plots of score and loading vectors for the first and second principal components (PC1 and PC2) are shown in Figure 4.

Figure 4(A) shows the loadings plot (loadings account for soils variables) and this plot indicated that Fe-oxide% has a high positive score on PC1 and a slight negative score on PC2. Moreover,
Table 4. Correlation matrix of P sorption data ($P = 0.01, 99.99\%$ confidence limit).

<table>
<thead>
<tr>
<th>Variable</th>
<th>P mg kg$^{-1}$</th>
<th>CaCO$_3$</th>
<th>Fe-oxide</th>
<th>pH</th>
<th>sand</th>
<th>silt</th>
<th>clay</th>
<th>EC</th>
<th>OM</th>
<th>CEC</th>
<th>P-Olsen</th>
</tr>
</thead>
<tbody>
<tr>
<td>P mg kg$^{-1}$</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>1.000</td>
<td>0.549</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-oxide</td>
<td>1.000</td>
<td>0.2541</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>pH</td>
<td>1.000</td>
<td>-0.751</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sand</td>
<td>1.000</td>
<td>-0.403</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>silt</td>
<td>1.000</td>
<td>-0.161</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>clay</td>
<td>1.000</td>
<td>-0.049</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>1.000</td>
<td>-0.338</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OM</td>
<td>1.000</td>
<td>0.509</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEC</td>
<td>1.000</td>
<td>0.325</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-Olsen</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Figure 4. PC loadings (A) and scores (B) plots obtained from P sorption data.

sand$\%$ has a high positive score on PC2 and a small positive score on PC2. The earlier results indicated that both Fe-oxide and sand$\%$ have a strong influence on P sorption. Sand$\%$ and P sorption appeared in the same direction indicating an intense influence of sand$\%$ on P sorption, while Fe-oxide and P-Olsen appeared away from P sorption indicating their negative influence.
on the process. Interestingly, Figure 4(A) shows that CEC, EC, OM, and the remaining variables are close to each other indicating their comparable influence on P sorption. The main conclusion that can be deduced from the PCA analysis is that P sorption is significantly increased at higher sand% levels, and changing other variables has no influence on the process. One of the interesting features of PCA is its ability to cluster objects/experiments of similar behaviours or structures; moreover, PCA can easily detect outliers.[25] Figure 4(B) indicated that soils 1, 3, 4, and 5 form a cluster, while soil 2 significantly deviates from that cluster. In fact, the main reason behind this deviation is the high contents of Fe-oxide and P-Olsen in soil 2.

The correlation between variables and their influence on P sorption are apparent in the correlation matrix presented in Table 4, with correlation values >0.8 in bold. Silt% is negatively correlated with CaCO3% with a correlation value of −0.979. This is also true for P-Olsen and Fe-oxide% with a correlation value of 0.995. The only variable that has a strong correlation with P sorption is clay% (−0.882). This indicates that the P release rate is high in soils with high clay content, most likely attributable to the correlation between clay content and the P diffusion coefficient.[50]

The significant principal component factors were plotted for diagnostic purposes. PCA was used to find the coefficients in the following general equation that represent P sorption by the soils:

\[
P_{\text{sorption}} = b_1(CaCO_3\%) + b_2(Fe\text{-oxide}) + b_3(pHe) + b_4(sand\%) + b_5(silt) + b_6(clay) + b_7(EC) + b_8(OM) + b_9(CEC) + b_{10}(P\text{-Olsen})
\]

(8)

The correlation between P sorption and soil properties was modelled assuming linear, non-linear (quadratic), or interaction relationships. The earlier equation shows that linear coefficients \((b_1–b_{10})\) are the most effective. For principle component regression (PCR), the calibration vectors are calculated as follows: \(k = (U^T U)^{-1} U^T A\), and the coefficients of factors affecting P sorption are calculated as follows: \(d = V_k\), where score matrix \(U\) and loading matrix \(V\) were estimated using the PCR algorithm with the optimum number of factors.[26] The components of vector \(d\) are the \(b_1–b_{12}\) coefficients. PCA was also used to predict P sorption values from the experimental data. Based on PCA, the following equation was obtained:

\[
P_{\text{sorption}} = -2.20(CaCO_3\%) - 0.04(Fe\text{-oxide}) + 0.04(pHe) + 11.02(sand\%) + 3.35(silt) - 10.73(clay) - 1.24(EC) - 0.22(OM) - 0.81(CEC) - 1.93(P\text{-Olsen})
\]

\(R^2 = 0.9941, \ \text{SSE} = 380\)  

(9)

The larger the coefficient, the greater its significance. From the earlier equation, both clay% and sand% were the most significant variables affecting P sorption with coefficients +11.02 and −10.73, respectively. Silt% and CaCO3 would play some role in P sorption under the studied experimental conditions. One of the experimental variables that should be studied is solution pH, and this variable was not considered to avoid soil leaching at highly acidic or basic media (is this true). The extremely low weight for pHe factor (0.04 only) is attributed to the fact that the tested soils had comparable pH values. Assessment of modelling power of PCA for P sorption data was carried out by calculating the sum of squares errors (SSE), and lower values of SSE indicate better fit to the model.[51] SSE is estimated from the formula:

\[
\sum_{i=1}^{n} (q_{i,\text{calc}} - q_{i,\text{pred}})^2
\]

(10)

where \(q_{i,\text{calc}}, q_{i,\text{pred}}\), and \(n\) represent the calculated \(q\) values, predicted \(q\) values and the number of experiments; respectively. SSE values were estimated including linear, non-linear, and interactions,
Table 5. Significance t-test for experimental variables on P sorption by the soils\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Coefficient\textsuperscript{b}</th>
<th>(V)</th>
<th>(t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO(_3)</td>
<td>2.20</td>
<td>39.5</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe-oxide</td>
<td>0.04</td>
<td>176,328.7</td>
<td>0.00</td>
</tr>
<tr>
<td>pH(_e)</td>
<td>0.04</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>sand</td>
<td>11.02</td>
<td>32.8</td>
<td>0.22</td>
</tr>
<tr>
<td>silt</td>
<td>3.35</td>
<td>13.2</td>
<td>0.11</td>
</tr>
<tr>
<td>clay</td>
<td>10.73</td>
<td>31.7</td>
<td>0.22</td>
</tr>
<tr>
<td>EC</td>
<td>1.24</td>
<td>236.3</td>
<td>0.01</td>
</tr>
<tr>
<td>OM</td>
<td>0.22</td>
<td>0.16</td>
<td>0.06</td>
</tr>
<tr>
<td>CEC</td>
<td>0.81</td>
<td>10.19</td>
<td>0.03</td>
</tr>
<tr>
<td>P-Olsen</td>
<td>1.93</td>
<td>495.8</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\textsuperscript{a}SSE = 380, \(s = 76\) and \(N = 5\).

\textsuperscript{b}Coefficients were taken from PCA equation shown above.

and the final values were 380, 382, and 356, respectively. Interestingly, linear terms of the variables were effective for modelling P sorption data, and this is consistent with the high prediction power of the developed equation \(R^2 = 0.9941\) and lower SSE as well. Student’s \(t\)-test was used as a statistical indicator to assess the significance of each variable on P sorption as depicted in the earlier equation. The significance \(t\)-test was carried out as follows [26]: a) the square covariance matrix was calculated for both systems, and the variances \((\nu – \text{the diagonal values of the covariance matrix})\) were obtained, b) SSE, which was calculated as indicated earlier, c) determination of mean error sum of squares \((s)\) by dividing SSE by number of degrees of freedom which is taken as number of experiments (five experiments) in this case, and d) estimation of \(t\)-value, \(t = b/(s\nu)^{1/2}\) – the higher this ratio, the more significant the factor at the desired confidence level. The obtained \(\nu\) and \(t\) values were summarised in Table 5.

The tabulated \(t\) value at 4 degrees of freedom is 2.78 at 95% confidence level. The calculated \(t\) values were less than \(t_{\text{table}}\) and this reflected that all studied variables have a significant effect on P sorption, however, with different magnitudes. As indicated from PCA, both clay and sand contents are the most significant factors (as they have the highest coefficients) on P sorption. It is highly possible to apply the derived equation for predicting P sorption on soils having comparable compositions to those provided in this work and this will be investigated in our future work.

### 4. Conclusions

Phosphorus sorption onto calcareous soils mainly occurred within 24 h, then reached dynamic equilibrium. The maximum phosphorus sorption capacity of the soils estimated from the Langmuir model ranged from 380.89 µg/g to 703.95 µg/g. The desorption percentage (%DES) results show that little P was released from the adsorbed phase; however, soils with high amounts of Fe-oxide and OM% released more P compared with other soils. There was a significant negative correlation between P sorption and clay content, whereas calcium carbonate and iron oxide have no correlation with P sorption. The results indicated that the DPS threshold level for all soils ranges from 3.6 to 9.5. All of these soils have exceeded the environmentally unacceptable P concentration except the soil with the lowest iron oxide content. PCA was found useful for modelling P sorption data and for assessing the studied variables on sorption processes. A practical equation was derived with aid of PCA and this equation was predicted P sorption by the soils with \(R^2 = 0.9941\) and SSE = 380). Diagnosis of P sorption data by PCA revealed that sand% is the most significant factor. Significant
\[t\]-test also revealed that the studied factors are significant for modelling adsorption data. The derived equation could be applied for other soils to evaluate P sorption behaviour.

Acknowledgements

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References