FACTORS AFFECTING PHOSPHATE SORPTION AND PHOSPHATE RETENTION IN A DESERT ECOSYSTEM

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In a study of soils from a chronosequence in southern New Mexico, where CaCO₃ accumulation is primarily derived from aeolian input, P adsorption was greatest in the most highly calcic horizons and least in horizons of clay and oxyhydroxide accumulation. Similarly, adsorption capacity was most highly correlated with CaCO₃ content. Iron and Al oxyhydroxide contents increased with increasing soil age, and absolute levels were as high as in calcareous soils developed in more humid conditions. Calcium carbonate appears to be the primary geochemical agent capable of the fixation and retention of P within the soil profile in this ecosystem.

Sorption and desorption reactions between phosphate and soils have long been studied by soil scientists, but have only recently been examined by ecosystem ecologists to explain phosphorus movement and phosphorus retention within ecosystems. In both temperate and tropical forest ecosystems, phosphate is very tightly conserved within soil compartments (Laverdiere 1982; Wood et al. 1984), and loss of phosphorus in stream water is generally very low (Goldich 1938; Hendricks and Whittig 1968; Wood et al. 1984).

Phosphorus is geochemically fixed in soils through interactions with calcium-, aluminum-, and iron-phosphate minerals (Lindsay and Moreno 1960; Marion and Babcock 1977). Iron and Al sesquioxides can cause high levels of P fixation in highly weathered or acidic soils. In Spodosols of the Hubbard Brook Experimental Forest, Wood et al. (1984) demonstrated that phosphorus adsorption capacities were highly correlated with concentrations of HCl-extractable Fe and Al. Richardson (1985) demonstrated that P sorption and retention capacity were best predicted by concentrations of amorphous Al in many wetland ecosystems.

Adsorption of P onto CaCO₃, and the coprecipitation of Ca-P minerals occur in both alkaline aquatic and terrestrial systems (Cole and Olsen 1959; Holford and Mattingly 1975a; Avmimelech 1983). Similarly, Tiessen et al. (1984) and Lajtha and Schlesinger (1988) suggest that Ca-bound forms of P constitute the dominant pool of mineral soil P in arid and semiarid soils of the southwestern United States. However, several P adsorption studies in calcareous soils derived from limestone have found stronger relationships between P adsorption capacity and hydrolysis oxides of Fe and Al than with CaCO₃ content (Holford and Mattingly 1975b; Ryan et al. 1985). Perhaps part of this discrepancy may be explained by differences between calcareous soils derived from limestone parent materials and arid soils in which the presence of high levels of CaCO₃ is due to pedogenic accumulations of aeolian-derived salts. Arid-land soils are relatively less weathered and thus pedogenically younger than soils developed in more humid climates, and thus one might expect lower accumulations of oxidized Fe and Al compounds (Olsen and Watanabe 1967). In addition, the nature and form of Fe and Al oxyhydroxides could be qualitatively different in arid soils and soils of humid regions. Initially weathered Fe oxyhydroxides occur as paracrystalline, high-surface-area particles known as ferrihydrite (Schwertmann and Fischer 1973). Over time, ferrhydrite recrystallizes to more stable and more highly crystalline forms, such as goethite and hematite. The timing of these transformations depends, however, on ambient climatic conditions.4 These different crystalline forms of oxidized Fe and Al could vary in their ability to fix soil P (Ryan et al. 1985).

The purpose of this study was to identify the primary geochemical agent capable of retaining

P within an arid ecosystem in southern New Mexico. To accomplish this objective, the amounts and relative proportions of paracrystalline and total secondary Fe and Al oxhydroxides were measured along a chronosequence of soils derived from quartz monzonite, and the relative importances of these oxhydroxides and pedogenic CaCO₃ in P adsorption and P accumulation within the soil profile were assessed.

METHODS

Study site

Soils for this study were collected along a piedmont slope of Mt. Summerford in the Jornada del Muerto Basin, 40 km NNE of Las Cruces, New Mexico, an area near the northern limits of the Chihuahuan Desert. The permanent transects of the Desert Long Term Ecological Research site (LTER) of New Mexico State University are also situated along this bajada. Several geomorphic surfaces of distinct ages have been identified along this slope (Table 1; Fig. 1; Gile et al. 1981) and form a four-stage soil chronosequence. The youngest soils are of Holocene age and form the Organ geomorphic complex. Organ II soils show little visible evidence of pedogenic alteration, high percentages of coarse gravel, and relatively high levels of organic matter. Organ I soils show distinct but relatively weakly developed horizons and contain less organic matter in upper horizons, possibly due to the erosional nature of soils in this landscape position. The oldest soils along this slope form the Jornada II geomorphic surface. These soils show distinct horizons of clay accumulation (argillic, or Bt horizons) overlying zones of CaCO₃ accumulation (caliche, or Bk horizons), characteristic of Pleistocene-age soils. Isaack’s Ranch soils are presumed to have been deposited near the end of the last glacial pluvial cycle and form a discontinuous surface that locally buries Jornada II soils. Horizons of clay and carbonate accumulation are not as well developed in these soils as in older Pleistocene soils, but are better developed than in Holocene soils.

Field sampling and soil analysis

Five soil pits were dug in each of the four geomorphic surfaces along the chronosequence to a minimum depth of 1 m or until a caliche horizon was encountered. Soil samples were collected by genetic horizon in the Organ I, Isaack’s Ranch, and Jornada II pits, and by depth interval in Organ II soils. All soils were sieved to pass a 2-mm-mesh screen, to screen out the relatively large chunks of unweathered parent rock material that are found in these soils. Carbonate determinations were made by weighing the water displaced by evolved CO₂ after soils were treated with 6 M HCl (Horton and Newsom 1953). The percentage of organic carbon was determined by a modified Walkley-Black technique after acid pretreatment to remove carbonates (Allison 1960) by the Agronomy Analytical Laboratory of Cornell University. Bicarbonate-extractable P was determined according to methods of Olsen et al. (1960). Total soil P analyses were performed using a lithium borate fusion in graphite crucibles (Thompson and Walsh 1983), followed by colorimetric determination using an automated molybdate-ascorbic acid procedure on a Technicon AutoAnalyzer (Lennox 1979).

Extractable Fe and Al

Soils were powdered in a Spex 8000 mixer-mill to pass a 100-mesh screen prior to Fe and Al extraction. An oxalate extraction solution

<table>
<thead>
<tr>
<th>Soil</th>
<th>Estimated age, yr BP*</th>
<th>Organic carbon, %</th>
<th>Bicarbonate-extractable P, µg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Late Organ</td>
<td>1100–2200</td>
<td>0.41 (.07)</td>
<td>10.5 (4.3)</td>
</tr>
<tr>
<td>(Organ II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Early Organ</td>
<td>2200–7000</td>
<td>0.21 (.08)</td>
<td>7.0 (2.6)</td>
</tr>
<tr>
<td>(Organ I)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isaack’s Ranch</td>
<td>8000–15 000</td>
<td>0.31 (.11)</td>
<td>8.1 (3.1)</td>
</tr>
<tr>
<td>Jornada II</td>
<td>25 000–75 000</td>
<td>0.33 (.12)</td>
<td>6.8 (2.2)</td>
</tr>
</tbody>
</table>

* Gile et al. (1981).
Fig. 1. Soil geomorphic surfaces along the piedmont of Mt. Summerford in southern New Mexico. JI = Jornada II; JI = Jornada I; Jornada = undifferentiated Jornada deposition. Isaac’s Ranch surface forms a discontinuous surface that locally buries the Jornada II surface and thus is not mapped separately.

Described by McKeague and Day (1966; 0.2 M ammonium oxalate buffered to pH 3 with 0.2 M oxalic acid) was used to estimate the paracrystalline ferrhydrite content of soils (\(\text{Fe}_o\)). The total secondary, or total “free,” Fe and Al content of soils was estimated as dithionite-extractable Fe and Al (\(\text{Fe}_d\) and \(\text{Al}_d\); Holmgren 1967). Magnetite was removed using a hand magnet prior to both extractions to avoid Fe dissolution from magnetite during the oxalate extraction (McFadden and Hendricks 1986). Fe and Al in both extracts were analyzed on a Perkin-Elmer 6000 inductively coupled plasma emission spectrometer (ICP). The ratio of \(\text{Fe}_o\) to \(\text{Fe}_d\) was calculated as an index of the degree of crystallinity of secondary oxyhydroxides.

**Phosphorus adsorption capacity**

Phosphate solutions, ranging in concentration from 0 to 30 \(\mu\)g P/ml as \(\text{KH}_2\text{PO}_4\) in 0.02 M CaCl\(_2\), were added to 3 g of sieved, unground soil in 50-ml polypropylene centrifuge tubes with 1 drop of chloroform to give a soil:solution ratio of 1:10. Soil solutions were shaken for 96 h at 27°C and centrifuged at 5000 rpm for 10 min; P in the supernatant was determined using the molybdate-ascorbic acid procedure on a Technicon AutoAnalyzer (Lennox 1979). The adsorption capacity of soils (\(X_m\)) for each solution concentration (\(m\)) was calculated as the difference between the initial and the equilibrium solution P content and expressed as \(\mu\)g P/g soil. The phosphorus adsorption index (\(\text{PAl}_m\)) of Bache and Williams (1971) was calculated as \(X_m/\log (C_m)\), where \(C_m\) = equilibrium solution P concentration in \(\mu\)g/L at an initial solution concentration of \(m\). This index has been found to be highly correlated with the sorption maximum determined from Langmuir isotherm calculations (Bache and Williams 1971; C. J. Richardson unpublished data), with the advantage of needing fewer P solution points per soil to calculate the index. In addition, there are no inherent assumptions that the energy of adsorption does not vary with the surface coverage as in the Langmuir equation, an assumption that has been often questioned in empirical studies (Gunary 1970). As Bache and Williams (1971) also demonstrated a high correlation between absolute sorption capacity (\(X_{10}\)) at high initial solution additions (thus making it possible to ignore \(E\), the initial amount of sorbed P in the soil) and the Langmuir adsorption maximum, \(X_{10}\) and \(X_{50}\) were similarly used as relative sorption indexes.

**Statistical analyses**

As the number of soils within each soil age category was unequal, the GLM procedure of SAS (SAS Institute 1982) was used in lieu of the ANOVA procedure to analyze profile accumulation data. When the GLM procedure indicated statistical significance, Tukey’s HSD range test was used to separate differences among geomorphic surfaces. The GLM procedure was used to perform all regressions with adsorption data.

**Results**

The percentage of \(\text{CaCO}_3\) was very low and did not vary with depth in the youngest Holocene soil (Table 2). In the three older soils,
TABLE 2

Extractable Fe and Al oxyhydroxides and % CaCO₃ in soil horizons from soils of the four geomorphic units*  

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Fe₀, mg/g</th>
<th>Feₐ, mg/g</th>
<th>Alₐ, mg/g</th>
<th>Feₐ/Fe₀</th>
<th>CaCO₃, %</th>
<th>Total P, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organ II</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>6.25</td>
<td>25.14</td>
<td>2.83</td>
<td>0.25</td>
<td>0.17</td>
<td>1.225</td>
</tr>
<tr>
<td>8-20 cm</td>
<td>4.33</td>
<td>23.13</td>
<td>2.80</td>
<td>0.19</td>
<td>0.20</td>
<td>1.145</td>
</tr>
<tr>
<td>20-30</td>
<td>6.95</td>
<td>23.09</td>
<td>3.07</td>
<td>0.31</td>
<td>0.20</td>
<td>1.107</td>
</tr>
<tr>
<td>30-45</td>
<td>5.04</td>
<td>25.08</td>
<td>3.55</td>
<td>0.20</td>
<td>0.35</td>
<td>1.119</td>
</tr>
<tr>
<td>45-60</td>
<td>7.14</td>
<td>24.84</td>
<td>3.12</td>
<td>0.28</td>
<td>0.25</td>
<td>1.157</td>
</tr>
<tr>
<td>60-100</td>
<td>5.53</td>
<td>21.36</td>
<td>2.49</td>
<td>0.26</td>
<td>0.25</td>
<td>1.236</td>
</tr>
<tr>
<td>Mean</td>
<td>5.82A</td>
<td>23.50AB</td>
<td>2.91AB</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organ I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>8.98</td>
<td>21.71</td>
<td>2.94</td>
<td>0.43</td>
<td>0.62</td>
<td>0.752</td>
</tr>
<tr>
<td>B1t</td>
<td>6.39</td>
<td>24.71</td>
<td>2.93</td>
<td>0.25</td>
<td>0.46</td>
<td>0.631</td>
</tr>
<tr>
<td>B2k</td>
<td>4.68</td>
<td>21.01</td>
<td>2.47</td>
<td>0.22</td>
<td>6.42</td>
<td>0.732</td>
</tr>
<tr>
<td>B3k</td>
<td>4.88</td>
<td>22.85</td>
<td>2.58</td>
<td>0.22</td>
<td>11.08</td>
<td>0.709</td>
</tr>
<tr>
<td>Mean</td>
<td>6.22AB</td>
<td>22.42A</td>
<td>2.72A</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Issaack’s Ranch</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>4.87</td>
<td>25.74</td>
<td>2.89</td>
<td>0.10</td>
<td>0.16</td>
<td>0.726</td>
</tr>
<tr>
<td>B1t</td>
<td>10.88</td>
<td>32.67</td>
<td>4.30</td>
<td>0.31</td>
<td>0.18</td>
<td>0.572</td>
</tr>
<tr>
<td>B2k</td>
<td>4.33</td>
<td>25.40</td>
<td>2.94</td>
<td>0.17</td>
<td>3.01</td>
<td>0.700</td>
</tr>
<tr>
<td>B3k</td>
<td>7.79</td>
<td>24.90</td>
<td>2.55</td>
<td>0.21</td>
<td>2.05</td>
<td>0.771</td>
</tr>
<tr>
<td>Mean</td>
<td>7.51AB</td>
<td>28.20B</td>
<td>3.39B</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jornada II</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>10.57</td>
<td>27.85</td>
<td>3.68</td>
<td>0.37</td>
<td>0.23</td>
<td>0.711</td>
</tr>
<tr>
<td>B1t</td>
<td>12.01</td>
<td>39.61</td>
<td>4.56</td>
<td>0.30</td>
<td>0.23</td>
<td>0.478</td>
</tr>
<tr>
<td>B2k</td>
<td>8.20</td>
<td>40.00</td>
<td>3.87</td>
<td>0.21</td>
<td>2.35</td>
<td>0.562</td>
</tr>
<tr>
<td>B3k</td>
<td>6.95</td>
<td>32.91</td>
<td>3.99</td>
<td>0.22</td>
<td>3.26</td>
<td>0.729</td>
</tr>
<tr>
<td>B4k</td>
<td>6.41</td>
<td>14.35</td>
<td>1.49</td>
<td>0.44</td>
<td>21.36</td>
<td>0.862</td>
</tr>
<tr>
<td>Mean</td>
<td>9.51B</td>
<td>35.61C</td>
<td>4.04C</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>0.02</td>
<td>0.0001</td>
<td>0.0001</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Different letters within columns of oxyhydroxide data denote significantly different means by Tukey’s HSD at alpha = 0.05; p values under each column are from analysis of variance comparisons of means of geomorphic units excluding B4k horizons. Values are means of n = 5 (SE).
however, the percentage of CaCO₃ increased with depth up to a maximum of >20% in the Pleistocene caliche (B4k) horizon. Organic C was very low in all soils, never exceeding 0.5% in surface horizons (Table 1). Bicarbonate-extractable P ranged from 10.5 μg/g in the youngest soils to a mean of 7.3 μg/g for the three older soils.

Concentrations of oxalate-extractable iron (Feₐ) and dithionite-extractable iron (Feₐ₆) and aluminum (Alₐ) increased with increasing soil age along the chronosequence (Table 2). This was true both when individual horizons and profile means were compared. Values for free Fe and Al from caliche horizons were very low, presumably due to precipitation at high pH levels near the surfaces of these horizons, and were excluded from this analysis to prevent a strong horizon bias in comparisons across soil ages. The Feₐ/Feₐ₆ ratio did not show a clear pattern with soil age and varied around a mean value of 0.27. In the three soils with well-defined argillic (Bt) horizons, concentrations of Feₐ, Feₐ₆, and Alₐ all showed midprofile maximum values, with this pattern becoming more pronounced with increasing soil age. Concentrations in Organ II profiles did not show such a clear redistribution pattern. Concentrations of Feₐ and Alₐ were significantly correlated in all soils (p < 0.0001, r = 0.53). Feₐ and Alₐ were even more highly correlated (p < 0.0001, r = 0.88).

Concentrations of total P in surface soils decreased significantly with soil age (Table 2). In the three older soils there was a midprofile decrease in total P relative to surface horizons, followed by an increase in concentration with increasing depth. There were no significant correlations between total P accumulation and Feₐ, Feₐ₆, or Alₐ, either alone or in multiple combinations.

None of the soils released P into solution when equilibrated with distilled water. All soils, with the exception of four from the Organ II surface, sorbed all P from the 1-μg P/ml solution. Therefore P sorption measured at 10 and at 30 μg P/ml (X₁₀ and X₃₀) and the PAI at each of these solution supply rates were used as indexes of the sorption capacities of the soils (Table 3). None of these indexes showed a linear or a logarithmic relationship to Feₐ, Feₐ₆, or Alₐ.

### Table 3

<table>
<thead>
<tr>
<th>Horizon</th>
<th>X₁₀, μg/g</th>
<th>X₃₀, μg/g</th>
<th>PAI₁₀</th>
<th>PAI₃₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organ II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>23.9 (1.8)</td>
<td>34.1 (3.8)</td>
<td>2.7 (0.2)</td>
<td>3.4 (0.04)</td>
</tr>
<tr>
<td>8-20 cm</td>
<td>27.9 (2.0)</td>
<td>45.6 (2.3)</td>
<td>3.1 (0.2)</td>
<td>4.5 (0.2)</td>
</tr>
<tr>
<td>20-30</td>
<td>33.0 (3.1)</td>
<td>65.3 (3.2)</td>
<td>3.7 (0.7)</td>
<td>6.5 (0.3)</td>
</tr>
<tr>
<td>30-45</td>
<td>26.5 (2.7)</td>
<td>51.4 (3.3)</td>
<td>2.9 (0.3)</td>
<td>5.1 (0.03)</td>
</tr>
<tr>
<td>45-60</td>
<td>27.6 (0.08)</td>
<td>45.6 (1.6)</td>
<td>3.1 (0.1)</td>
<td>4.5 (0.2)</td>
</tr>
<tr>
<td>60-100</td>
<td>33.9 (2.4)</td>
<td>53.9 (7.8)</td>
<td>3.8 (0.3)</td>
<td>5.3 (0.8)</td>
</tr>
<tr>
<td>B1t</td>
<td>45.3 (1.3)</td>
<td>73.5 (6.2)</td>
<td>5.2 (0.2)</td>
<td>7.4 (0.6)</td>
</tr>
<tr>
<td>B2k</td>
<td>49.9 (2.0)</td>
<td>93.2 (9.3)</td>
<td>5.8 (0.3)</td>
<td>9.5 (1.0)</td>
</tr>
<tr>
<td>B3k</td>
<td>78.2 (1.2)</td>
<td>161.9 (4.9)</td>
<td>10.0 (0.01)</td>
<td>17.2 (0.6)</td>
</tr>
<tr>
<td>B3k</td>
<td>76.6 (4.5)</td>
<td>113.1 (3.9)</td>
<td>9.6 (0.7)</td>
<td>11.8 (4.1)</td>
</tr>
<tr>
<td>Isaack's Ranch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>45.2 (0.7)</td>
<td>70.5 (9.3)</td>
<td>5.2 (0.1)</td>
<td>7.1 (1.0)</td>
</tr>
<tr>
<td>B1t</td>
<td>46.6 (0.03)</td>
<td>93.2 (4.1)</td>
<td>5.4 (0.01)</td>
<td>9.4 (0.4)</td>
</tr>
<tr>
<td>B2k</td>
<td>60.6 (4.9)</td>
<td>135.6 (5.7)</td>
<td>7.3 (0.7)</td>
<td>14.1 (0.6)</td>
</tr>
<tr>
<td>B3k</td>
<td>52.0 (0.4)</td>
<td>106.8 (4.3)</td>
<td>6.1 (0.2)</td>
<td>10.9 (1.2)</td>
</tr>
<tr>
<td>Jornada II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>49.8 (1.8)</td>
<td>101.9 (14.9)</td>
<td>5.8 (0.2)</td>
<td>10.4 (1.6)</td>
</tr>
<tr>
<td>B1t</td>
<td>57.4 (3.3)</td>
<td>104.9 (2.7)</td>
<td>6.8 (0.4)</td>
<td>10.7 (0.3)</td>
</tr>
<tr>
<td>B2k</td>
<td>63.4 (6.3)</td>
<td>119.6 (13.7)</td>
<td>7.7 (0.9)</td>
<td>12.4 (1.5)</td>
</tr>
<tr>
<td>B3k</td>
<td>69.9 (1.5)</td>
<td>141.1 (6.7)</td>
<td>8.7 (0.5)</td>
<td>14.8 (0.8)</td>
</tr>
<tr>
<td>B4k</td>
<td>89.6 (1.7)</td>
<td>222.8 (4.8)</td>
<td>12.6 (0.5)</td>
<td>25.8 (0.9)</td>
</tr>
</tbody>
</table>

*Values are means of n = 5 (SE).
either alone or in multiple correlations. All indexes were significantly correlated with the CaCO$_3$ content of the soils at $p < 0.0001$ (Figs 2, 3). PAI$_{10}$ and PAI$_{50}$ demonstrated the highest linear correlations with percentage of CaCO$_3$

$$\text{PAI}_{10} = 0.392 \times \text{CaCO}_3 + 5.232 \quad (r = 0.84)$$

$$\text{PAI}_{50} = 0.839 \times \text{CaCO}_3 + 8.189 \quad (r = 0.85)$$

Absolute adsorption capacities ($X_{10}$ and $X_{50}$) were also significantly correlated with CaCO$_3$ content, but had better fits to log(CaCO$_3$)

$$X_{10} = 19.583 \times \log(\text{CaCO}_3) + 56.270$$

$$\quad (r = 0.79)$$

$$X_{50} = 53.462 \times \log(\text{CaCO}_3) + 112.339$$

$$\quad (r = 0.80)$$

Adding Fe$_{\text{total}}$, Fe$_{\text{ed}}$, or Al$_{\text{ed}}$ in multiple regressions did not improve these fits. In all cases, correlations were significantly stronger when only those soils that had significantly measurable amounts of CaCO$_3$ ($\geq 1\%$ CaCO$_3$) were included, and all indexes were most highly correlated with log(CaCO$_3$)

$$X_{10} = 32.220 \times \log(\text{CaCO}_3) + 49.842$$

$$\quad (r = 0.91)$$

$$X_{50} = 110.322 \times \log(\text{CaCO}_3) + 73.550$$

$$\quad (r = 0.88)$$

$$\text{PAI}_{10} = 6.119 \times \log(\text{CaCO}_3) + 4.979$$

$$\quad (r = 0.95)$$

$$\text{PAI}_{50} = 14.349 \times \log(\text{CaCO}_3) + 6.241$$

$$\quad (r = 0.89)$$

Even when those soils without a significantly measurable level of carbonate ($<1\%$ CaCO$_3$) were analyzed separately, none of the sorption indexes were correlated with Fe$_{\text{total}}$, Fe$_{\text{ed}}$, Al$_{\text{ed}}$, or percentage of organic C, either alone or in multiple correlations.

**DISCUSSION**

The ratio of Fe$_{\text{total}}$:Fe$_{\text{ed}}$ can be used as a measure of the increasing crystallinity of oxyhydroxides during pedogenic development (Alexander 1974; Evans and Cameron 1979; McFadden). In a series of soil chronosequences from xeric to arid climates in southern California, McFadden found that the Fe$_{\text{total}}$:Fe$_{\text{ed}}$ ratio reached a maximum in Holocene to late Pleistocene soils and then decreased in Pleistocene-Pliocene soils as the easily weathered mafic minerals were depleted and paracrystalline ferrihydrite was transformed into hematite. In soils of this study, however, both Fe$_{\text{total}}$ and Fe$_{\text{ed}}$ continued to increase with increasing soil age through recent Pleistocene soils, and thus there was not a significant shift in the crystallinity of Fe oxyhydroxides—and thus the sorption reactivity—with time.

It was initially suggested that semiarid to arid soils might differ from calcareous soils developed in more humid climates by being pedogenically younger than mesic soils of a similar chronological age and thus might have a lower
oxyhydroxide content. Although clay mineral authigenesis appears to be relatively limited in arid soils, these soils are subject to and affected by aeolian processes to a larger degree than mesic soils and thus are more likely to contain significant amounts of externally derived oxyhydroxides. The range and mean of Fe$_8$ values in soils of this study were similar, although at the lower end of the range reported in surface soils derived from limestone in Britain (Holford and Mattingly 1975b); both Fe$_6$ and Fe$_8$ were well within the range measured in calcareous soils from Lebanon (Ryan et al. 1985), suggesting that differences in sorption characteristics among these studies are unlikely to be due to large differences in total oxyhydroxide content.

The strong correlation between P adsorption and soil CaCO$_3$ content found in this study is consistent with soil P fractionation patterns observed previously in these soils (Lajtha and Schlesinger 1988), namely, that over 50% of the total P content of these soils is in a Ca-P bound form. However, results from this study differ sharply from those of Ryan et al. (1985) and Holford and Mattingly (1975b). Perhaps this difference can be ascribed to the fact that these earlier studies were of surface soils derived from limestone parent material, whereas the source of CaCO$_3$ in the soils of the present study is aeolian. In their soils derived from Jurassic limestone, Holford and Mattingly (1975c) demonstrated that the specific surface areas of the carbonate component were an inverse function of the percentages of CaCO$_3$ that they contained; the more weathered the soil, the lower the percentage of CaCO$_3$, the smaller the particle size, and thus the larger the specific surface area. As sorption should be more directly related to the surfaced area of the reactive fraction of soils than to the total content, it is not surprising that authors have not found a relationship between CaCO$_3$ content and P sorption, even in calcareous soils. In soils where CaCO$_3$ is from aeolian dust, one would not expect such an inverse relationship between CaCO$_3$ surface area and content. Indeed, it is quite likely for all soils in an arid environment to undergo periodic cyclic dissolution and reprecipitation to form small, high-surface-area CaCO$_3$ grains that would be highly reactive, independent of pedogenic age.

The relationship between P sorption and percentage of CaCO$_3$ appears to have broad ecosystem implications for the retention of P, both within the soil profile and within the landscape. Total P decreased with increasing soil age over the chronosequence, presumably due to weathering and leaching losses. However, in the three oldest soil geomorphic surfaces with well-defined profile development, total P increased in the lowest, calcic soil horizons relative to mid-profile horizons, suggesting a secondary precipitation of Ca-P minerals or strong sorption reactions of P with CaCO$_3$. Such reactions could potentially reduce leaching losses of P from the ecosystem. In contrast, total P was lowest in those horizons with the highest levels of Fe and Al oxyhydroxides, suggesting that oxyhydroxides are not significant geochemical agents capable of P retention within this system.

Soils of humid or tropical forests, rich in free Fe and Al oxyhydroxides and sesquioxides, tend to have high P-fixing capacities that render P very immobile. Soil horizons in forested Spodosols with high concentrations of free Al and Fe
have been shown to represent zones of strong
geochmical fixation that effectively control
losses of P to stream water (Wood et al. 1984).
In this chronosequence of Aridisols from southern
New Mexico, pedogenic CaCO₃ was found
to have a higher capacity for P adsorption than
Fe or Al oxyhydroxides, and thus CaCO₃ appears
to be the primary geochemical agent capable of
fixation and retention of P in this ecosystem.

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