Temperature-Dependency of Phosphorus Sorption by Goethites and Tropical Soils Amended with Woodchip Biochar

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Core Ideas
• Freundlich and Langmuir isotherms described P sorption by oxides and soils, respectively.
• Biochar increased the extent and relative strength of P sorption by goethite at 15°C.
• Biochar reduced P sorption but increased P binding strength for sandy loam at 35°C.

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ABSTRACT
Phosphorus is a key nutrient in agriculture but also a common contaminant. Bioavailability and transport of P are controlled by, among other things, the presence of Fe and Al oxides in tropical soils. Biochar has been suggested for improving the bioavailability and reducing the off-site transport of P. The objective of this study was, therefore, to evaluate the effect of biochar on P sorption by goethite, aluminum-substituted goethite (Al-goethite), and two tropical soils amended with 0, 20, and 40 g biochar kg⁻¹ at 15, 25, and 35°C. Sorption by goethite and Al-goethite was adequately described by the Freundlich isotherm although the Langmuir isotherm was a better fit for the two soils tested. At 15°C, biochar application increased P sorption by goethite from 9.5 to 11 g kg⁻¹ (mg L⁻¹)⁻¹ as indicated by the increase in the Freundlich constant, Kf, and the increase in relative sorption strength represented by a reduction in the Freundlich exponent (1/n) from 1.2 to 0.8. At 35°C, biochar addition significantly reduced the Langmuir sorption maximum (Smax) from 17.3 to 15.8 g kg⁻¹ (mg L⁻¹)⁻¹ for the sandy loam soil, indicating a reduction in P sorption capacity in the presence of biochar. Biochar addition also significantly increased the Langmuir constant, (KL) for the sandy loam from 0.04 to 1.7 L mg⁻¹ at 35°C, indicating greater P binding strength in the presence of biochar. The sorption data from this study provide insights into the effect of temperature on P sorption by Fe oxides and tropical soils in the presence of biochar.

Abbreviations: o-FeOOH, goethite; AICC, Akaike Information Criterion (corrected); Al-goethite, aluminum-substituted goethite; ANOVA, analysis of variance; EDS, energy dispersive spectroscopy; Kf, Freundlich constant; KL, Langmuir constant; Smax, Langmuir sorption maximum; XRD, X-ray diffraction.

osphorus is an essential macronutrient, and its deficiency can reduce plant growth and yield potential. Phosphorus is a limiting nutrient in most soils and is becoming increasingly scarce and expensive (Cordell et al., 2009). Management of P to improve its availability for plant uptake while minimizing adverse environmental impacts via offsite transport to surface water bodies is critical (Cordell et al., 2011). Phosphorus sorption is a major process governing P availability for plant uptake and in most weathered soils around the world is attributed to oxides of Fe and Al (Pierzynski and McDowell, 2005). Goethite is a common Fe oxide in most soils, but Al can substitute for up to one-third of its Fe content (Carlson, 1995). This is because Al is ubiquitous and abundant in soils and rocks, from which it is mobilized, together with Fe, during weathering (Cornell and Schwertmann, 2003).

The high content of iron oxides in highly weathered soils, particularly those in tropical areas, can have an adverse effect on P availability in agricultural soils because of the high sorption capacity of the soils. For example, P sorption capacities of up to 1197 mg P kg⁻¹ soil were reported for highly weathered soils in South Africa (Bainbridge et al., 1995; Henry and Smith, 2002; Gichangi et al., 2008). In a study on P adsorption by clays from Brazilian Oxisols, Fontes and Weed (1996) reported adsorption maxima ranging from 70 to 160 mmol P kg⁻¹ day and demonstrated that P adsorption was primarily related to goethite, gibbsite, and other oxides of Fe and Al.

The use of biochar to improve productivity in agricultural soils dates back approximately 2500 yr to the time of Native American settlements in the Amazon region, Brazil (Atkinson
Biochar is variably charged, with a high surface area and high porosity. When incorporated into soil, biochar has been shown to reduce soil bulk density; increase soil pH (Atkinson et al., 2010), increase cation exchange capacity (Kookana et al., 2011; Liang et al., 2006), increase anion exchange capacity (Lawrenzenko and Laird, 2015), and enhance the availability of macronutrients such as N and P (Atkinson et al., 2010; Kookana et al., 2011). There is a growing interest in the use of biochar as a soil amendment for improved agricultural productivity and also as a means of abating climate change by sequestering carbon (Laird et al., 2010; Sohi et al., 2010).

Phosphorus has a high affinity for oxides of Fe and Al and for biochar. Dissolved organic compounds can enhance or hinder P sorption, thus altering P phytoavailability in soils dominated by Fe and Al oxides (Borggaard et al., 2005; Guppy et al., 2005). Biochar application has also been shown to alter P availability in soils amended with biochar (Chintala et al., 2014a; Jiang et al., 2015; Novak et al., 2009; Parvage et al., 2013; Xu et al., 2014). It is known that P sorption is endothermic and an increase in temperature may enhance P sorption in soils (Barrow, 1979; Chien et al., 1982; Gardener and Jones, 1973; Sah and Mikkelsen, 1986; Singh and Jones, 1977) and the strength of P binding (Sah and Mikkelsen, 1986; Sparks, 1989; Weber et al., 1991). However, there is a dearth of information on the effect of temperature on P sorption by biochar-amended soils or oxides. Therefore, the objective of this study was to determine the temperature-dependency of biochar effects on P sorption by goethite and Al-goethite and by two tropical soils that are known to contain these minerals.

**MATERIALS AND METHODS**

**Oxides and Soils**

Goethite (α-FeOOH) was synthesized by mixing KOH and Fe(NO₃)₃·9H₂O according to the method developed by Cornell and Schwertmann (2003). Similarly, Al-substituted goethite was synthesized by mixing 1 M Fe(NO₃)₃·4H₂O, AlCl₃·6H₂O, and KOH. Specific procedures employed have previously been described by Pereira et al. (2018).

Synthesized goethite minerals were characterized using X-ray diffraction (XRD) analysis, and Al substitution in the goethite was measured with scanning electron microscopy with X-ray microanalysis coupled with energy dispersive spectroscopy (EDS). Based on the analysis described by Pereira et al. (2018), it was concluded that the synthesized materials were indeed goethite and Al-goethite.

Biochar (Diacarbon Energy, Burnaby, BC, Canada) was produced from the pyrolysis of wood chips at 500°C. Selected chemical properties of the biochar are presented in Table 1.

Two soils (0- to 15-cm layer) from locations in South Africa were tested: a red sandy loam (Oxic Haplustalf) from Mafeking (25°48’ S, 25°38’ E) and a dark, olive gray clay (Typic Hapluderts) from Rustenburg (25°40’51.4” S, 27°13’58.4” E). The sandy loam contained 55.6% sand, 32.6% silt, and 11.8% clay whereas the clay contained 44% sand, 7% silt, and 49% clay. Other properties of the two soils are presented in Table 1. These soils typically contain high levels of Fe and Al oxides (e.g., Bernini et al., 2013; Tsai et al., 2007) and are widespread in South Africa and other tropical and subtropical regions of the world.

**Experimental Design**

Two sorption experiments, one with the two oxides and another with the two soils described above, were laid out as a completely randomized design with a 2 × 3 × 3 factorial treatment structure. The factors were oxide (goethite and Al-goethite [aluminum-substituted goethite]) or soil type (red sandy loam and dark, olive gray clay), biochar rate (0, 2, and 4 g of biochar kg⁻¹ soil), and temperature (15, 25, and 35°C). The range of temperatures is typical of the regions from which the soils were collected. All treatments were replicated three times.

**Batch Equilibration Study**

Triplicate 0.1-g subsamples of each oxide (goethite and Al-goethite) (Ruan and Gilkes, 1996; Sibanda and Young, 1986) and 1-g subsamples of each soil (Graetz and Nair, 2009) amended with the above biochar rates were added into 125-mL Erlenmeyer flasks containing 0, 5, 10, 50, 100, 200, and 300 mg P L⁻¹ in a 100-mL solution of KH₂PO₄ in 0.01 M KCl. The tubes were shaken for 24 h at 200 rpm in a C24KC refrigerated incubator shaker at reaction temperatures of 15, 25, and 35°C. Following equilibration, each suspension was allowed to settle for 1 h and then filtered through a Whatman no. 42 filter paper. The supernatant was filtered through

<table>
<thead>
<tr>
<th>pH</th>
<th>CEC cmol dm⁻³</th>
<th>TOC g kg⁻¹</th>
<th>Total N</th>
<th>Total P mg kg⁻¹</th>
<th>Ca mg kg⁻¹</th>
<th>Mg mg kg⁻¹</th>
<th>K mg kg⁻¹</th>
<th>Na mg kg⁻¹</th>
<th>S mg kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6</td>
<td>1.8</td>
<td>427</td>
<td>0.27</td>
<td>61</td>
<td>200</td>
<td>20</td>
<td>96</td>
<td>81</td>
<td>28</td>
</tr>
<tr>
<td>4.07</td>
<td>1.8</td>
<td>1.45</td>
<td>0.95</td>
<td>13</td>
<td>185</td>
<td>58</td>
<td>143</td>
<td>3</td>
<td>0.72</td>
</tr>
<tr>
<td>6.34</td>
<td>45</td>
<td>9.94</td>
<td>1.55</td>
<td>21</td>
<td>3830</td>
<td>3050</td>
<td>128</td>
<td>30</td>
<td>2.80</td>
</tr>
</tbody>
</table>

† Methods of biochar analysis: pH, 1:10 biochar/water suspension; total C and total N, Nitrogen and Carbon Analyzer (FlashEA 1112; Thermo Scientific Waltham, MA, USA); total organic carbon (TOC), by difference between total C and calcium carbonate equivalent C; total P, Ca, Mg, K, Na, and S, ICP–MS following H₂O₂ + HNO₃ digestion.

‡ Methods of soil analysis: pH, saturated paste; NH₄⁺–N, 1:5 soil/0.1 M K₂SO₄; Bray 1 P, 1:7.5 soil/Bray 1 solution; exchangeable cations: Ca, Mg, K, Na, 1:10 soil/1 M NH₄CH₃CO₂ at pH 7; and Zn, 1:4 soil/0.1 M HCl.

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parameters

\[ S = K_f C^{1/n} \]

where \( S \) is the total amount of P sorbed per unit of sorbent (g kg\(^{-1}\)), \( C \) is the final P concentration in the solution (mg L\(^{-1}\)) at equilibrium, \( K_f \) is the total amount of P sorbed per unit of sorbent (g kg\(^{-1}\)), and \( 1/n \) are empirical constants.

For the two soils, the Langmuir isotherm (Eq. [2]) provided a better fit to the sorption data, also based on the AICC (Littell et al., 2006):

\[ S = \frac{K_f S_{max} C}{1 + K_f C} \]

where \( S \) is the total amount of P sorbed per unit of sorbent (g kg\(^{-1}\)), \( S_{max} \) is the Langmuir sorption maximum (g kg\(^{-1}\) [mg L\(^{-1}\)]\(^{-1}\)), and \( C \) is the final P concentration (mg L\(^{-1}\)) in the equilibrium solution.

Langmuir and Freundlich sorption isotherm parameters were estimated separately for each replicate using PROC NLIN in SAS 9.4 (SAS Institute, 2013). Values estimated by the NLIN procedure for \( S_{max} \) and \( K_f \) were normally distributed, based on the Shapiro-Wilk test, while those for \( K_f \) and \( 1/n \) followed a \( \beta \) distribution. Values for \( S_{max} \) and \( K_f \) were subjected to analysis of variance (ANOVA) using PROC GLIMMIX in SAS, with soil, biochar rate, and temperature as fixed effects. Values for \( K_f \) and \( 1/n \) were similarly analyzed with oxide, biochar rate, and temperature as fixed effects. The Tukey multiple comparison procedure was used for pairwise comparison of treatment means if a significant effect was indicated by the omnibus \( F \)-tests. Treatment differences were considered significant at \( \alpha = 0.05 \).

### RESULTS AND DISCUSSION

#### Freundlich Sorption Parameters for Oxides

The Freundlich \( K_f \) ranged from 8.99 to 11.9 g kg\(^{-1}\)/(mg L\(^{-1}\))\(^{1/n}\) for goethite and from 9.97 to 12.1 g kg\(^{-1}\)/(mg L\(^{-1}\))\(^{1/n}\) for Al-goethite, whereas \( 1/n \) ranged from 0.68 to 0.78 for goethite and from 0.67 to 0.74 for Al-goethite. At 15°C, \( K_f \) for goethite was greater when biochar was added compared with the no-biochar control (Table 2, Fig. 1). Since \( K_f \) is related to sorption capacity (Summers et al., 2010), the higher \( K_f \) values with biochar addition indicate that goethite retains more P in the presence of biochar at a reaction temperature of 15°C. Increased P retention with biochar addition has previously been reported for soils (Novak et al., 2009; Xu et al., 2014), but the underlying mechanisms remain poorly understood and are a subject of ongoing research. However, at the higher temperatures tested (25 and 35°C), \( K_f \) did not vary significantly among biochar rates.

For Al-goethite, \( K_f \) was significantly greater at the biochar rate of 20 g kg\(^{-1}\) oxide than at the 0 and 40 g kg\(^{-1}\) rates at 35°C (Fig. 1), but there was no significant difference between the 0 and 40 g kg\(^{-1}\) rates. Also, \( K_f \) was not significantly affected by biochar rate at 15 and 25°C.

### Statistical analysis

Sorption data for goethite and Al-goethite were fitted using PROC NLIN in SAS 9.4 (SAS Institute, 2013). The Freundlich isotherm (Eq. [1]) provided a better fit to the sorption data, based on the corrected Akaike Information Criterion (AICC) (Littell et al., 2006):
At 15°C, 1/n for goethite varied significantly with biochar rate and increased in the order 20 g kg⁻¹ < 40 g kg⁻¹ < no biochar treatment (Fig. 2). Since 1/n is inversely related to relative sorption strength (Summers et al., 2010), the lower 1/n for goethite in biochar treatments compared with the no-biochar treatment indicates that biochar addition increased P sorption strength at the 15°C reaction temperature. In contrast, 1/n for goethite was not significantly affected by biochar rate at 25 and 35°C.

For Al-goethite at 15°C, 1/n did not differ significantly between the zero and the 20 g kg⁻¹ biochar rates, but was significantly lower for the two rates than the 40 g kg⁻¹ rate (Fig. 2). At 35°C, 1/n for Al-goethite was significantly smaller at 20 g biochar kg⁻¹ than at the 40 g kg⁻¹ rate, but there was no significant difference between the 0 and 20 g kg⁻¹ rates and between the 0 and 40 g kg⁻¹ rates.

**Langmuir Sorption Parameters for Soils**

Maximum sorption capacity (S_max) ranged from 15.8 to 17.4 g kg⁻¹ (mg L⁻¹)⁻¹ for the sandy loam and 15.6 to 16.4 g kg⁻¹ (mg L⁻¹)⁻¹ for the clay. The corresponding K_L were 0.49 to 0.85 L mg⁻¹ for the sandy loam and 0.14 to 0.17 L mg⁻¹ for the clay.

At 35°C, biochar addition significantly reduced S_max for the sandy loam relative to the no-biochar treatment, indicating a reduction in P sorption capacity in the presence of biochar (Table 3, Fig. 3). However, there was no significant difference in S_max between 20 and 40 g kg⁻¹ biochar rates for the sandy loam at 35°C. Biochar rate also had no significant effect on S_max at 15 and 25°C. Consistent with our results at 35°C, Chintala et al. (2014b) reported a reduction in P sorption for an acidic clay loam with the incorporation of 40 g kg⁻¹ biochar. Biochar application can increase soil pH in acid soils, thereby altering P sorption on minerals of metals such as Fe³⁺, Al³⁺, and Ca²⁺ and thus may reduce P sorption and increase plant availability of P in soil (Chintala et al., 2014a; Yuan et al., 2011).

For the clay soil, at 15 and 25°C, the 0 and 40 g biochar kg⁻¹ soil rates produced significantly greater S_max, hence greater sorption capacity, compared with the 20 g kg⁻¹ rate (Fig. 3). However, S_max did not differ significantly between the 0 and 40 g kg⁻¹ rates.

Biochar addition significantly increased K_L relative to the no-biochar treatment for the sandy loam at 35°C, indicating greater P binding strength in the presence of biochar, but there was no significant difference in K_L between the 20 and the 40 g kg⁻¹ biochar rates (Fig. 4). Further, K_L did not vary among biochar rates at 15 and 25°C.

**Table 3. Effect of biochar, soil, and temperature on the Langmuir parameters S_max and K_L.†**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>S_max (g kg⁻¹ (mg L⁻¹)⁻¹)</th>
<th>K_L (L mg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biochar, g kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>16.3(0.03)‡</td>
<td>0.34(0.005)</td>
</tr>
<tr>
<td>20</td>
<td>16.0(0.03)</td>
<td>0.42(0.006)</td>
</tr>
<tr>
<td>40</td>
<td>16.1(0.03)</td>
<td>0.42(0.006)</td>
</tr>
<tr>
<td>Soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandy loam</td>
<td>16.3(0.03)</td>
<td>0.68(0.004)</td>
</tr>
<tr>
<td>Clay</td>
<td>16.1(0.03)</td>
<td>0.17(0.003)</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>16.1(0.03)</td>
<td>0.38(0.006)</td>
</tr>
<tr>
<td>25</td>
<td>16.1(0.03)</td>
<td>0.38(0.006)</td>
</tr>
<tr>
<td>35</td>
<td>16.3(0.03)</td>
<td>0.43(0.006)</td>
</tr>
</tbody>
</table>

*P*-value

| Biochar | <0.001 |
| Soil | <0.001 |
| Temperature | <0.002 |
| Biochar × Soil | <0.001 |
| Biochar × Temperature | <0.001 |
| Soil × Temperature | <0.001 |
| Biochar × Soil × Temperature | <0.001 |

† Mean separation letters are not applied because the interactions are significant. Significant interactions are plotted in Fig. 3 and 4.

‡ SEM, standard error of the mean.
CONCLUSIONS

Biochar application to goethite increased P sorption ($K_L$) and relative sorption strength $(1/n)$ at 15°C. At 35°C, biochar addition significantly reduced $K_{max}$ for the sandy loam relative to the no-biochar treatment, indicating a reduction in P sorption capacity in the presence of biochar, but significantly increased $K_L$ relative to the no-biochar treatment, indicating greater P binding strength in the presence of biochar. The sorption data from this study provide insights into the effect of temperature on P sorption by Fe oxides and tropical soils in the presence of biochar, which may have important implications on the improvement of soil productivity in the tropics. Studies with a range of soils and various biochars are needed before field level P and biochar management strategies can be implemented. Additionally, studies using isotopes ($^{32}$P) will help understand the mechanisms of P sorption by Fe oxides and soils in the presence of biochar.

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REFERENCES


