Phosphate Adsorption by Ferrihydrite-Amended Soils

F. E. Rhoton* and J. M. Bigham

ABSTRACT

New technology and approaches for reducing P in runoff from high-sediment yield areas are essential due to implementation of increasingly rigorous water quality standards. The objectives of this research were to characterize ferrihydrite (Fe$_5$H$_{10}$O$_8$·4H$_2$O) in terms of its ability to adsorb P from soil solutions and relate its P adsorptive capacity to several soil properties that influence P mobility. A naturally occurring ferrihydrite, collected as an Fe oxide sludge by-product from a water treatment facility, was equilibrated with soil samples at equivalent rates of 0, 0.34, 3.36, 16.80, and 33.60 Mg ha$^{-1}$ for a 60-d period. Individual 2-g subsamples of each soil were then equilibrated with 0, 5, 10, 20, and 40 mg kg$^{-1}$ P in 20 mL of 0.01 M CaCl$_2$ on a reciprocating shaker for 24 h. After 24 h, P in solution was measured by colorimetric methods, and designated as final P concentrations. The data indicated that the unamended soils with a pH of <6.0 adsorbed, in some cases, 50 times more P than soils with a pH of >7.0. The final P concentrations, averaged for all initial P concentrations and ferrihydrite rates, ranged from 0.09 to 4.63 mg kg$^{-1}$, and were most highly correlated with pH ($r = 0.844$; $P < 0.01$), oxalate-extractable Fe ($r = -0.699$; $P < 0.10$), and dithionite-extractable Fe ($r = -0.639$; $P < 0.10$) contents of the unamended soils. In terms of individual soils, correlation coefficients ($r$) for final P concentrations versus ferrihydrite amendment rates indicated a statistically significant ($P < 0.001$) negative relationship at all initial P concentrations for most A horizons. The $r$ values for the high Fe oxide content B horizon soils did not show a statistically significant response to ferrihydrite amendments. The results indicate that P adsorption, in soils amended with ferrihydrite, will be greatest under acid pH conditions below the ferrihydrite zero point of charge (pH 5.77), and low incipient Fe oxide contents.

The eutrophication of waters by phosphorus has been documented by numerous researchers for decades. This nutrient is the primary reason for algal-related problems in freshwater lakes, streams, reservoirs, and headwaters of estuarine systems (Correll, 1998). Phosphorus contributions from agricultural sources to these waters represent a major problem (Parry, 1998). Thus, considerable effort is directed toward onsite management of source areas to lower the amount of P available for transport. These efforts include reducing the P content of feed, placing P fertilizers and manures in the subsurface, and treating manures with amendments such as alum to reduce P solubility (Daniel et al., 1998).

The reduction of P losses from agricultural fields is increasingly critical as water quality standards become more rigid. Compliance with such increasing standards in the southern United States will be especially difficult due to a larger percentage of conventional till practices than other regions, highly erodible, low organic matter soils, and high rainfall amounts that occur primarily as intense thunderstorms. In addition to elevated levels of native soil P in some extensive areas, and the surface application of P fertilizers in expanding no-till farming practices, this region has an ever-increasing feedlot and poultry industry that produces enormous quantities of manure that is applied to farmlands. This combination of factors represents a potential problem relative to the contamination of surface and subsurface water supplies through overapplication of P by either fertilizers or manures (Hansen et al., 2002; Sims et al., 1998). In terms of P leaching losses, Sims et al. (1998) report that the soil conditions most conducive to significant P leaching include those with high sand contents, high organic matter contents, reducing conditions, and preferential flow paths. The leaching of P in high organic matter soils is due to both low Fe and Al contents, and the blockage of their associated exchange sites by organic matter.

The use of Fe oxides to adsorb P on-site and reduce its concentrations in runoff and leachates is a proven approach to potentially lowering P loadings of water bodies (Moore and Miller, 1994; Elliott et al., 2002; Gallimore et al., 1999). Numerous laboratory studies have been directed at the sorption of phosphate on Fe oxides (Parfitt, 1978; Harrison and Berkheiser, 1982; Ainsworth et al., 1985; Barrón et al., 1988). Some studies have attempted to quantify differences in phosphate adsorption associated with variations in mineral properties such as surface area, morphology, and chemical composition (Barrón et al., 1988; Torrent et al., 1990). Further, preliminary studies by Pratt et al. (1969) and Bigham et al. (1978) support the idea that differences in P adsorption between otherwise similar soil materials can be directly related to the types of Fe oxide present.

Ferrihydrite is perhaps the most effective of these minerals in terms of P adsorption in soils due to its small particle size, high surface area, and gel-like form. In nature, ferrihydrite is formed by the rapid oxidation of Fe(II) in Fe-rich waters (Rhoton et al., 2002), which produces a hematite-like structure (Eggleton and Fitzpatrick, 1988). Ferrihydrite is considered a transient phase in the Fe oxide crystallization sequence unless its surfaces are contaminated by compounds such as phosphate, organic acids, and Si (Schwertmann and Fechter, 1982; Childs, 1992), a normal occurrence under natural conditions. Specifically, ferrihydrite formed in nature can be considered very stable relative to synthetically derived specimens commonly used in the laboratory. Although considerable research has been conducted on phosphate adsorption by Fe oxides, the use of ferri-
hydrite specifically in such studies is limited. Instead, reference is made to oxalate-extractable Fe gel and amorphous Fe, which undoubtedly includes a ferrihydrite component. McLaughlin et al. (1981) described the P sorptive capacity of a laboratory-prepared Fe gel as being 10 times greater than its crystalline analog of hematite, goethite, and akaganeite, and that precipitation of Fe gel onto kaolinite surfaces increased P adsorption by 10-fold. Other researchers (Wauchop and McDowell, 1984) reported a strong relationship between oxalate-extractable Fe and absorbed P for lake and stream sediments. Borggaard et al. (1990) indicate that poorly crystalline Fe and Al oxides, extractable by oxalate, accounted for 96% of the variation in P adsorption maximum. In fact, in cases where poor correlations were found between the oxalate-extractable soil component and P adsorptive capacity, they occurred where this amorphous fraction existed in low concentrations (Karim and Adams, 1984).

The lack of more definitive, larger-scale studies involving ferrihydrite adsorption of P, particularly under field conditions, has been due to the absence of an abundant supply of relatively pure material. The use of synthetically prepared material outside the laboratory is cost prohibitive. Recently, large supplies of ferrihydrite have been identified as a by-product of water treatment plants in the lower Mississippi River valley where aquifers contain high concentrations of dissolved Fe. Previous research (Rhoton et al., 2003) has shown this material to be a very pure source of ferrihydrite that is an effective stabilizer of soil aggregates with a high potential for adsorbing P. Thus, this research was conducted to characterize this naturally occurring ferrihydrite in terms of its capacity to adsorb P from soil solutions.

MATERIALS AND METHODS

This P adsorption study was conducted with the same soil samples used in a previous study to evaluate the effect of ferrihydrite on soil erodibility (Rhoton et al., 2003). The soil samples were collected in Major Land Resource Areas (MLRA) 77 (Southern High Plains) near Lubbock, TX, and 134 (Southern Mississippi Valley Silty Uplands) near Senatobia, MS (USDA Soil Conservation Service, 1981). The MLRA 77 soils were Amarillo fine sandy loam (fine loamy, mixed, superactive, thermic Aridic Paleustolls), Gomez loamy fine sand (coarse loamy, mixed, active, thermic Aridic Calciusteps), and Olton clay loam (fine, mixed, superactive, thermic Aridic Paleustolls). The soils obtained from MLRA 134 were Grenada silt loam (fine, mixed, active, thermic Oxyaquic Fraglossudalfs) and Routon silt loam (fine, mixed, active, thermic Typic Epiaqualfs).

Basic characterization data were collected for samples that had been air-dried, crushed, and sieved to <2 mm. Particle size distribution was determined by the pipette method of Day (1965) following overnight dispersion in Na-hexametaphosphate. The water dispersible clay content (WDC) was determined by similar methods using only distilled water as a dispersant. Extractable cations were determined by the 1 M ammonium acetate method of Thomas (1982). Phosphorus contents of the unamended soils were measured after extraction with double acid (Olsen and Sommers, 1982). Soil pH was measured in a 1:1 soil to distilled water suspension (McLean, 1982). Total C was measured by combusting soil samples in a CN-2000 carbon analyzer (LECO, St. Joseph, MI). The inorganic (carbonate) fraction of the total C was quantified by treating a separate 1-g sample with 5 N HCl in a sealed decomposition vessel (200 mL) fitted with a rubber septum. Carbon dioxide pressure generated by the acid decomposition of the sample was measured with a Tensimeter (Soil Measurement Systems, Tucson, AZ) probe inserted through the septum. Pressure readings were converted to C contents using a standard curve, which were then subtracted from total C to obtain organic C. The dithionite (d)- and oxalate (o)-extractable Fe contents were determined according to the procedures of Mehra and Jackson (1960) and Schwertmann (1964), respectively. All extracts were analyzed with a Model 2380 atomic absorption spectrophotometer (PerkinElmer, Wellesley, MA), with the exception of extractable P. A Model CR-200 chroma meter (Konica Minolta, Tokyo, Japan) was used for quantitative soil color determinations.

Ferrihydrite was collected as a sludge by-product from a Memphis, TN, water treatment plant where it had been filtered from drinking water supplies. In the laboratory, the ferrihydrite suspension was concentrated to approximately 100 g L⁻¹ by sedimentation and decantation procedures. Ferrihydrite specimens were characterized identically to the soil samples using the same procedures. Total elemental analysis was determined by inductively coupled plasma optical emission spectroscopy following ferrihydrite dissolution in aqua regia. Acid insoluble residues were dried and weighed. The zero point of charge (ZPC) was measured with a Zeta-Meter instrument (Zeta-Meter, Stanton, VA). Ferrihydrite mineralogy was characterized by powder X-ray diffraction (XRD) analysis using a Model APD 3520 X-ray diffraction unit (Philips, Eindhoven, the Netherlands) using CuKα radiation (35 kV, 20 mA). Specific surface area measurements followed the Brunauer–Emmett–Teller (BET) triple point method using a Flowsorb II 2300 surface area analyzer (Micromeritics, Norcross, GA), with N₂ as the adsorbate. Magnetic susceptibility was measured with a Model MS-2 magnetic susceptibility meter (Bartington Instruments, Oxford, UK).

The soil samples used for the P adsorption study were subsamples of larger samples used in Rhoton et al. (2003) to evaluate the effect of ferrihydrite on erodibility. Those samples were sieved to <8 mm and amended with ferrihydrite at rates equivalent to 0, 0.34, 3.34, 16.80, and 33.60 Mg ha⁻¹, or 0.15, 1.5, 7.5, and 15 g ferrihydrite kg⁻¹ soil. The ferrihydrite amendment was applied as a slurry using a paint sprayer while the soil was rotated in a rotary mixer (56.4 L). This mixture was subjected to two wetting–drying cycles over a 60-d period that involved wetting to saturation point and drying down to <10% water content. Subsamples were then obtained from these soil–ferrihydrite mixtures, crushed, sieved to <2 mm, and used for P adsorption evaluation. Phosphorous adsorption capacity of the ferrihydrite-amended soils was determined according to the procedure of Kuo (1988) except for the pH adjustment to 6.0 during equilibration. Instead, these soil–ferrihydrite mixtures were equilibrated at their normal pH by treating a separate 1-g sample with either 0, 10, 20, or 40 mg kg⁻¹ P in 20 mL of 0.01 M CaCl₂ on a reciprocating shaker for 24 h. At the end of this time period, final P concentrations in solution were measured colorimetrically by the ascorbic acid–molybdate blue method (Olsen and Sommers, 1982) at a wavelength of 882 nm with a Spectronic 1001 split beam spectrophotometer (Bausch & Lomb, Rochester, NY).

RESULTS AND DISCUSSION

The physical characteristics of the untreated soils used in this study (Table 1) indicate a considerable difference
Table 1. Selected physical properties of the untreated soils.

<table>
<thead>
<tr>
<th>Soil, horizon</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>Munsell color</th>
<th>Water dispersible</th>
<th>Magnetic susceptibility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10^-8 m^3 kg^-1</td>
</tr>
<tr>
<td>Amarillo A</td>
<td>68.8</td>
<td>13.6</td>
<td>17.6</td>
<td>5.7YR</td>
<td>4.0</td>
<td>4.0 44.9</td>
</tr>
<tr>
<td>Gomez A</td>
<td>85.9</td>
<td>4.2</td>
<td>9.9</td>
<td>7.1YR</td>
<td>5.4</td>
<td>2.9 10.8</td>
</tr>
<tr>
<td>Olton A</td>
<td>52.2</td>
<td>24.4</td>
<td>23.4</td>
<td>6.5YR</td>
<td>3.4</td>
<td>3.0 59.3</td>
</tr>
<tr>
<td>Grenada A</td>
<td>2.8</td>
<td>78.9</td>
<td>18.3</td>
<td>9.7YR</td>
<td>4.8</td>
<td>3.6 49.0</td>
</tr>
<tr>
<td>Grenada B</td>
<td>1.1</td>
<td>71.3</td>
<td>27.6</td>
<td>9.3YR</td>
<td>5.2</td>
<td>4.6 42.6</td>
</tr>
<tr>
<td>Routon A</td>
<td>1.2</td>
<td>87.3</td>
<td>11.5</td>
<td>9.6YR</td>
<td>5.6</td>
<td>2.6 9.5</td>
</tr>
<tr>
<td>Routon B</td>
<td>1.2</td>
<td>67.8</td>
<td>31.9</td>
<td>0.1Y</td>
<td>6.5</td>
<td>1.9 9.0</td>
</tr>
</tbody>
</table>

† Size < 2 μm. ‡ Size < 0.2 μm.

Table 2. Selected chemical properties of the untreated soils.

<table>
<thead>
<tr>
<th>Soil, horizon</th>
<th>pH</th>
<th>Organic Carbon</th>
<th>Extractable†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td></td>
<td>gkg</td>
<td>cmol kg^-1</td>
<td>gkg</td>
</tr>
<tr>
<td>Amarillo A</td>
<td>6.6</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Gomez A</td>
<td>7.6</td>
<td>10.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Olton A</td>
<td>7.5</td>
<td>5.5</td>
<td>4.3</td>
</tr>
<tr>
<td>Grenada A</td>
<td>5.2</td>
<td>27.1</td>
<td>27.1</td>
</tr>
<tr>
<td>Grenada B</td>
<td>5.2</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Routon A</td>
<td>5.1</td>
<td>20.4</td>
<td>20.4</td>
</tr>
<tr>
<td>Routon B</td>
<td>5.1</td>
<td>2.7</td>
<td>2.7</td>
</tr>
</tbody>
</table>

† Ammonium acetate–extractable Ca, Mg, K, and Na; double acid–extractable P. ‡ Cation exchange capacity. § Acid insoluble residue.

between individual soils resulting from differences in parent materials and climatic conditions. Specifically, the soils collected in Texas (Amarillo, Gomez, Olton) have higher sand and lower silt contents relative to the soils collected in Mississippi (Grenada, Routon). On the average, fewer differences were observed in the clay contents of the A horizon soils, but the Texas soils exhibited decidedly redder hues. Magnetic susceptibility, which ranged from 10.8 to 59.3 10^-8 m^3 kg^-1, was similar among the soils. The chemistry of these two groups of soils is more dissimilar than the physical properties (Table 2). Generally, the Texas soils have a higher pH, but lower extractable cations and extractable Fe contents. The physical and chemical properties of the ferrihydrite used to amend the soils are shown in Table 3. Most notable of these properties is a surface area of 250 m^2 g^-1, a zero point of charge of 5.77, and 436 g kg^-1 oxalate-extractable Fe, which indicates that the ferrihydrite specimen is essentially 100% soluble in acid ammonium oxalate. The X-ray diffraction pattern (Fig. 1) indicates that the specimen is primarily two-line ferrihydrite, with broad bands at 0.15 and 0.25 nm (Rhoton et al., 2003).

The P adsorption data are shown (Fig. 2 and 3) for the various soils as final P concentrations in solution at the end of the 24-h equilibration period as a function of ferrihydrite amendment rates and initial P concentrations in the equilibrating solutions. For the Texas soils (Fig. 2), the P distribution curves are generally similar with respect to decreases in P concentrations with each successive addition of ferrihydrite; however, the Gomez soil generally adsorbed more P than did the Amarillo or Olton soils. These two soils adsorbed comparable amounts of P at all initial concentrations and ferrihydrite amendment rates. Few changes were observed in the final P concentrations for these three soils until the ferrihydrite rates exceeded 3.36 Mg ha^-1. In fact, in some cases, the addition of ferrihydrite created an increase in the final P concentration in solution. At the 16.8 Mg ha^-1 rate, the final P concentrations were reduced by approximately 50% of that associated with the 0 ferrihydrite rates for the Texas soils. The higher P adsorptive capacity of the Gomez relative to the Amarillo and Olton soils can probably be attributed to the relative high concentrations of Ca (Table 2) occurring as calcium carbonate, which enhanced P adsorption of the Gomez soil, primarily as dicalcium phosphate (Samadi and Gilkes, 1999). The decrease in P adsorptive capacity of these three soils once ferrihydrite was added at the lower rates is unexplained. A possible mechanism is that the

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addition of ferrihydrite at rates of 0.34 Mg ha\(^{-1}\) reduced
the anion exchange capacity of the unamended soil by
blocking exchange sites on sesquioxides and organic
matter. As the ferrihydrite rates are progressively in-
creased the anion exchange capacity of the system is
gradually increased to the extent that it exceeds that of
the amended soils leading to an enhancement of the P
adsorptive capacity, and the gradually decreasing final
P concentration in solution.

The P adsorptive capacity of the two unamended Mis-
sissippi soils (Fig. 3) was substantially greater than the
capacity of the Texas soils as indicated by the much
lower final P concentrations at the 0 ferrihydrite amend-
ment rate. For the 40 mg kg\(^{-1}\) initial P concentration,
approximately 81\% was adsorbed by the Grenada A
horizon, and 99\% by the B horizon. The addition of
33.60 Mg ha\(^{-1}\) ferrihydrite reduced the final P concen-
tration to 0.2 mg kg\(^{-1}\) for the B horizon material. At the
same initial P concentration, the unamended Routon A
horizon soil adsorbed 67\% and the B horizon adsorbed
89\%. The greater adsorptive capacity of these two soils,
relative to the Texas soils, is attributed to the much
higher ammonium oxalate–extractable iron (Fe\(_a\)) and
citrate–bicarbonate–dithionite-extractable iron (Fe\(_d\))
concentrations, higher clay contents, and lower pH (Ta-
bles 1 and 2). At soil pH values of <5.77 (zero point
of charge of the ferrihydrite) the ferrihydrite develops
a net positive charge, which should increase the P ad-
sorptive capacity of a soil. The A horizons of these soils
also exhibited an increase in final P concentrations after
ferrihydrite was added at the 0.34 Mg ha\(^{-1}\) rate, and
also at the 3.36 Mg ha\(^{-1}\) rate for Routon B. Thus, this
anomaly appears to be consistent among soils.

The correlation coefficients calculated for ferrihydrite
amendment rates versus final P concentrations (Table 4)
indicate that a statistically significant (\(P \leq 0.001\)) nega-
tive relationship was obtained for all rates applied to
the Texas soils. Conversely, the addition of ferrihydrite
to the Grenada A horizon soil did not result in a signifi-
cant negative relationship until the initial P concentra-
tion exceeded 10 mg kg\(^{-1}\). No significant relationships
were found for the B horizon soil at either initial P
concentration, which is attributed to the high incipient
Fe oxide levels, which effectively adsorbed most of
the initial P, including the 40 mg kg\(^{-1}\) concentration. The
Routon A horizon soil behaved similarly to the Texas
soils in terms of significant negative relationships be-
between final P concentrations and ferrihydrite amendment rates at all initial P concentrations. However, the decrease in final P concentrations, as a function of ferrihydrite rates, was not significant at initial P concentrations below 20 mg kg\(^{-1}\).

The final P concentrations of the ferrihydrite-amended soils are also shown as an average of all amendment rates and initial P concentrations (Table 5). Based on these overall data, which ranged from 0.09 to 4.63 mg kg\(^{-1}\), the Grenada A and B and Routon B horizon soils were statistically similar with respect to P concentration.

**Table 4. Correlation coefficients (r) determined for final P concentrations in solution versus ferrihydrite amendment as a function of initial P concentration.**

<table>
<thead>
<tr>
<th>Soil, horizon</th>
<th>Initial P concentration (mg kg(^{-1}))</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amarillo</td>
<td>-0.777</td>
<td>-0.971***</td>
<td>-0.970***</td>
<td>-0.980***</td>
<td>-0.960***</td>
<td></td>
</tr>
<tr>
<td>Gomez</td>
<td>0.840*</td>
<td>-0.967***</td>
<td>-0.953***</td>
<td>-0.979***</td>
<td>-0.968***</td>
<td></td>
</tr>
<tr>
<td>Olton</td>
<td>-0.812*</td>
<td>-0.958***</td>
<td>-0.970***</td>
<td>-0.974***</td>
<td>-0.949***</td>
<td></td>
</tr>
<tr>
<td>Grenada A</td>
<td>-0.387</td>
<td>0.389</td>
<td>-0.900***</td>
<td>-0.975***</td>
<td>-0.952***</td>
<td></td>
</tr>
<tr>
<td>Grenada B</td>
<td>-0.378</td>
<td>0.412</td>
<td>0.672</td>
<td>-0.400</td>
<td>-0.803</td>
<td></td>
</tr>
<tr>
<td>Routon A</td>
<td>0.147</td>
<td>0.948***</td>
<td>-0.941***</td>
<td>-0.977***</td>
<td>-0.992***</td>
<td></td>
</tr>
<tr>
<td>Routon B</td>
<td>0.827*</td>
<td>-0.914</td>
<td>-0.794</td>
<td>-0.943***</td>
<td>-0.958***</td>
<td></td>
</tr>
</tbody>
</table>

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.

All these were statistically greater (\(P \leq 0.05\)) than the Amarillo, Gomez, and Olton soils. These average final P concentrations were correlated with soil property data (Table 6) for the seven soils to help explain the contribution of soil properties on an individual basis. These correlation coefficients (\(r\)) indicated that final P concentrations in solution were most highly correlated with soil pH, which had an \(r\) value of 0.844 (\(P \leq 0.01\)). Both \(\text{Fe}_0\) (-0.699) and \(\text{Fe}_d\) (-0.639) were significantly correlated with final P at the 10% level of significance. The only other property correlated above the 20% level of significance was \(\text{NH}_4\) acetate-extractable Ca (-0.564) by virtue of the formation of dicalcium phosphate or

**Table 5. Final P concentrations in solution averaged over all amendment rates for individual soils.**

<table>
<thead>
<tr>
<th>Soil, horizon</th>
<th>P concentration (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amarillo A</td>
<td>4.63a†</td>
</tr>
<tr>
<td>Gomez A</td>
<td>3.72ab</td>
</tr>
<tr>
<td>Olton A</td>
<td>4.62a</td>
</tr>
<tr>
<td>Grenada A</td>
<td>1.34cd</td>
</tr>
<tr>
<td>Grenada B</td>
<td>0.69d</td>
</tr>
<tr>
<td>Routon A</td>
<td>2.43bc</td>
</tr>
<tr>
<td>Routon B</td>
<td>0.67d</td>
</tr>
</tbody>
</table>

† Means followed by the same letter are not significantly different at the 0.05 probability level.
Table 6. Correlation coefficients determined for final P concentrations in solution as a function of soil properties (Fe$_{0}$, ammonium oxalate–extractable iron; Fe$_{6}$, citrate–bicarbonate–dithionite–extractable iron).

<table>
<thead>
<tr>
<th>Soil property</th>
<th>Correlation coefficient ($r$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{0}$</td>
<td>-0.699†</td>
</tr>
<tr>
<td>Fe$_{6}$</td>
<td>-0.639†</td>
</tr>
<tr>
<td>Organic matter</td>
<td>-0.168</td>
</tr>
<tr>
<td>pH</td>
<td>0.844**</td>
</tr>
<tr>
<td>Ca</td>
<td>0.564†</td>
</tr>
<tr>
<td>Fine clay</td>
<td>-0.147</td>
</tr>
<tr>
<td>Total clay</td>
<td>-0.519</td>
</tr>
</tbody>
</table>

** Significant at the 0.01 probability level.
† Significant at the 0.10 probability level.
‡ Significant at the 0.20 probability level.

by chemisorption of P on calcite (Samadi and Gilkes, 1999). These results indicate that pH through its control of the variable charge has the greatest influence on P adsorption by these ferrihydrite-amended soils.

CONCLUSIONS

Based on the results of this research, ferrihydrite can be used as an amendment for adsorbing P from soil solutions, but the level of effectiveness will be determined by soil pH. Due to the pH dependent charge nature of the ferrihydrite, P adsorption will be greatest for soils with an acid pH. Specifically, the naturally occurring ferrihydrite used in this study develops a net positive charge below pH 5.77, which increases the P adsorption capacity of the material. Above pH 5.77, the ferrihydrite develops a net negative charge that reduces its adsorptive capacity. This partially explains the greater P adsorption of the two strongly acid soils from Mississippi versus the calcareous soils from Texas.

The relatively high P adsorption rate of the Gomez soil compared with the other high-pH Texas soils is attributed to an abundance of free CaCO$_3$, that enhances P adsorption in the form of Ca phosphates. The greater P adsorptive capacity of the Grenada B horizon is attributed to a relatively high natural concentration of Fe oxides, which produced P adsorption capacities approximately 10 times that of the low-pH Routon B horizon soil, which has initial Fe oxide contents six times lower than Grenada B.

In terms of most effective amendment rates, the more significant relationships between ferrihydrite added and P adsorption capacity occurred between 3.36 and 16.80 Mg ha$^{-1}$ for all the soils with the exception of the Grenada and Routon B horizon soils. No significant relationships were identified between P adsorption capacity and ferrihydrite addition to the Grenada B, nor to the Routon B soil, below 16.80 Mg ha$^{-1}$.

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