Characterizing Sorption and Modeling Phosphorus Movement on Candler and Immokalee Fine Sand

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Abstract
Laboratory and computer experiments were conducted to 1) determine the effect of supporting electrolyte on mass distribution coefficient (Kₐ) for predicting P movement at 30- and 60-cm soil depths using HYDRUS-1D and 2) compare the temporal P concentrations as a function of soil type. The results on Candler fine sand at Lake Alfred showed that P contents for the Kₐ estimated with 0.01 M KCl and 0.005 M CaCl₂ were 10 to 15% higher than those predicted with a Kₐ value measured with fertilizer mixture. The predictions on Immokalee fine sand showed that P contents for the Kₐ estimated with fertilizer mixture and 0.005 M CaCl₂ were 12 to 20% higher than those predicted with a Kₐ value measured with 0.01 M KCl. The outputs with Kₐ measured with 0.005 M CaCl₂ appear to be close to those predicted with a Kₐ measured with fertilizer mixture on Immokalee fine sand. However, the analysis of the Kₐ values across all electrolytes on the two soils studied revealed that 0.01 M KCl is the electrolyte that yields Kₐ values fairly close to fertilizer mixture on Candler fine sand and would be appropriate to use for the coated sand while 0.005 M CaCl₂ was comparable with fertilizer mixture on Immokalee fine sand and would be an appropriate electrolyte to use for such uncoated sands. The results of study will help in improving estimation of Kₐ's and description of P transport in citrus production systems of Florida sandy soils. This would provide necessary information for sustainable environmental management and reduce problems of eutrophication and prevent groundwater contamination.

Keywords
Phosphorus adsorption, Simulation modeling, Entisol, Spodosol

Introduction
Adsorption is the mechanism that soil cations and anions (including various phosphorus (P) compounds) are retained by soil particles. The adsorption process tends to restrict compound’s mobility and bioavailability [1]. Thus, the procedure for determining the P sorption isotherms could then provide information on their mobility in the soil. The supporting electrolyte concentration is chosen to mimic that of soil solution. Most commonly 0.01 M CaCl₂ [2,3], 0.01 N CaCl₂ [4], 0.005 M CaCl₂ [1], 0.1 to 3 mM KCl [5], 0.05 M KCl [6,7], and 0.01 M KCl [8,9] have been used as electrolytes in studies on P and K sorption. Nair, et al. (1984) [10] reported that P adsorption was generally lower with K⁺ as the supporting electrolyte cation compared with Ca²⁺. These studies and others have not explained the rationale behind use of a particular electrolyte other than equilibrating the solutions in deionized or tap water.

The chemical characteristics of soils dominating the Flatwoods and Ridge regions of Florida are well described in [11] and some were also determined in this study. The soil at the Flatwoods consists of nearly level and poorly drained on the Flatwoods classified as Immokalee fine sand...
sand (sandy, siliceous, hyperthemic Arenic Hapludolls) with the spodic horizon lying within 1 m from the soil surface. The soil at the Ridge, classified as Candler fine sand (hyperthermic, coated Typic Quartzipsamments) is a well-drained sandy soil with no continuous layer limiting vertical water movement [11]. The Immokalee and Candler fine sand are moderately acidic (pH ranging from 4.9 to 5.6) with > 94% sand textural composition, have low organic matter content (ranging from 0.41 to 0.61% on Immokalee fine sand and from 1.6 to 1.96% on Candler fine sand) and low cation exchange capacity (CEC) (ranging from 2 to 6 cmol (+) kg⁻¹), have inorganic N in the range of 8.2 and 11.2 mg kg⁻¹, moderate to very high P concentrations from potassium dihydrogen phosphate (KH₂PO₄) for P in 0.005 M CaCl₂, were 10, 25, 50 mg PL⁻¹. To determine P sorption isotherms, soil samples were obtained from 5 random positions per site at two depths giving a total of 10 samples. Each sample was weighed in triplicates plus a blank control. A 10 g air-dried, subsample of soil < 2 mm particle size was placed in a centrifuge tube and equilibrated with 20 ml (soil solution ratio 1:2) of 3 initial concentrations of P solutions. The centrifuge tubes were shaken for 24 h, centrifuged for 20 min, and filtered through a filter paper (Whatman, #42). All these procedures were done at room temperature ~25 ± 1 °C as recommended by [14] but the filtrate was later stored at < 4 °C until analyzed for P.

### Phosphorus sorption isotherm determination

The solutions from the adsorption study were analyzed for P using ICP-AES and calibration standards of 10, 30 and 50 mg PL⁻¹ preparation in fertilizer mixture (with additions of 0.027 mM NH₄NO₃ and 0.013 mM KCl), 0.01 M KCl and 0.005 M CaCl₂. The amount of chemical sorbed to the soil was calculated from the difference between the initial and equilibrium solution concentration:

\[
S_e = \frac{V}{m} (C_O - C_e)
\]

Where \(S_e\) is the adsorbed concentration (mg kg⁻¹); \(V\) is the volume of initial solution (L); \(m\) is the soil mass (kg); \(C_O\) is the initial concentration of the standard solution (mg L⁻¹), and \(C_e\) is the soil solution concentration at equilibrium (mg L⁻¹).

### Materials and Methods

#### Laboratory adsorption study

The baseline soil chemical and physical properties for soils used in the study are described in (Table 1 and Table 2). Sorption isotherms on the disturbed soil samples (0-15 cm, 15-30 cm) were determined using the batch equilibration procedure [14]. The initial solution concentrations from potassium dihydrogen phosphate (KH₂PO₄) for P in 0.005 M CaCl₂ were 10, 25, 50 mg PL⁻¹. To determine P sorption isotherms, soil samples were obtained from 5 random positions per site at two depths giving a total of 10 samples. Each sample was weighed in triplicates plus a blank control. A 10 g air-dried, subsample of soil < 2 mm particle size was placed in a centrifuge tube and equilibrated with 20 ml (soil solution ratio 1:2) of 3 initial concentrations of P solutions. The centrifuge tubes were shaken for 24 h, centrifuged for 20 min, and filtered through a filter paper (Whatman, #42). All these procedures were done at room temperature ~25 ± 1 °C as recommended by [14] but the filtrate was later stored at < 4 °C until analyzed for P.
Sorption isotherms for P were calculated using the Freundlich equation:

$$S_e = K_f C_e^N$$  \hspace{1cm} (2)$$

Where $K_f$ is the Freundlich sorption coefficient (mg$^{1-N}$ kg$^{-1}$ L$^N$) and N is an empirical constant related to adsorption phenomena [15]. The linearized form of the Freundlich equation was used to calculate $K_f$ and N:

$$\ln S_e = \ln K_f + N \ln C_e$$  \hspace{1cm} (3)$$

Where $S$ is the adsorbed equilibrium concentration (mg kg$^{-1}$); $C_e$ is the equilibrium concentration (mg L$^{-1}$) and $C_{\text{max}}$ is the estimated maximum concentration (mg L$^{-1}$) and $K_f$ and N are calculated from the intercept and slope of Equation 3. To find average linearized $K_f$, the integrals form of the equation was used:

$$K_D = \frac{\int_{c_{\text{min}}}^{c_{\text{max}}} NK_f C_e^{N-1} dc}{\int_{c_{\text{min}}}^{c_{\text{max}}} dc} = K_f C_{\text{max}}^{N-1}$$  \hspace{1cm} (4)$$

Concepts and governing equations for the simulations

The governing flow equations for water flow and nutrient transport are given by the [16] and convection-dispersion equations (CDE) [17-19]:

$$\frac{\partial \theta}{\partial t} + \frac{\partial}{\partial x_i} \left( K \left( K_y \frac{\partial h}{\partial x_j} + K_z \frac{\partial h}{\partial z} \right) \right) - s(h) = 0$$  \hspace{1cm} (5)$$

Where $\theta$ is the volumetric water content [L$^3$L$^{-3}$], $h$ is the pressure head [L], $x_i$ (I = 1, 2) are the spatial coordinates [L], t is time [T], $K_y$ and $K_z$ are components of a dimensionless anisotropy tensor $K^*$ (which reduces to the unit matrix when the medium is isotropic), K is the unsaturated hydraulic conductivity function (LT$^{-1}$), and s is a sink/source term [L$^3$L$^{-3}$T$^{-1}$], accounting for root water uptake (transpiration). The sink/source represents the volume of water removed per unit time from a unit volume of soil due to plant water uptake. Thus, s is defined as:

$$s(h) = \alpha b L T_p \frac{T_p}{w}$$  \hspace{1cm} (8)$$

Where the water stress response function $\alpha(h)$ is a prescribed dimensionless function of the soil water pressure head, b is the normalized water uptake distribution, L is the width of the soil surface associated with the transpiration process and $T_p$ is the potential transpiration rate (LT$^{-1}$) and $w$ is the water stress index.

The nonlinear, predictive equations for the unsaturated hydraulic function in terms of soil water retention parameters are given by [23] as:

$$\theta(h) = \frac{\theta_r + \theta_s - \theta_r}{\left( 1 + \alpha h \right)^m} h < 0$$  \hspace{1cm} (9)$$

$$\theta(h) = \theta_s h \geq 0$$  \hspace{1cm} (10)$$

$$K(h) = K_s S_e \left[ 1 - \left( S_e^{1/m} \right)^m \right]^2$$  \hspace{1cm} (11)$$

Where

$$m = 1 - \frac{1}{n}, \hspace{1cm} n > 1$$  \hspace{1cm} (12)$$

Where $\theta_r$, $\theta_s$, $K_s$, and $l$ are residual water content (L$^3$L$^{-3}$), saturated water content (L$^3$L$^{-3}$), saturated hydraulic conductivity (LT$^{-1}$), and pore connectivity parameter (estimated to be an average of 0.5 for many soils respectively). Parameters $\alpha$ (L$^{-1}$) and $n$ are empirical coefficients affecting the shape of the hydraulic functions [23]. We estimated the hydraulic functions $\alpha$ and $n$ after fitting the water content and matric potential data using the liquid phase [L$^3$T$^{-1}$]. The term $r_s$ represents the root nutrient uptake (ML$^{2}$T$^{-1}$) which is the sum of actual active and passive nutrient uptake. The solid phase concentration, $c_s$, accounts for nutrient either sorbed in the solid phase or precipitated in various minerals. This is usually quantified by the adsorption isotherm relating $c_1$ and $c_2$ described by the linear equation of the form:

$$c_1 = K_d c_2$$  \hspace{1cm} (7)$$

Where $K_d$ is the mass distribution coefficient for species $1$. A tracer (e.g. bromide) are assumed to have a $K_d = 0$ cm$^{-1}$ g$^{-1}$. The first order decay constant ranges from 0.36-0.56 d$^{-1}$ [20]. For P, $K_d$ is reportedly in the range of 19 to 185 cm$^3$ g$^{-1}$ [21,22]. Bulk density for the soil is in the range 1.59-1.72 g cm$^{-3}$ (Immokalee) and 1.55-1.93 g cm$^{-3}$ (Lake Alfred) (T.A. Obreza, unpublished).

The sink term, s, for the Richards equation represents the volume of water removed per unit time from a unit volume of soil due to plant water uptake. Thus, s is defined as:

$$s(h) = \alpha b L T_p \frac{T_p}{w}$$  \hspace{1cm} (8)$$


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van Genuchten model in Community Analyses System (CAS) 2007 [24] developed for determination of soil hydraulic functions (Table 3).

**Cumulative flux and concentration**

The P concentration and flux were predicted at 30 cm soil depth. Assuming isotropy and a homogeneous profile, the concentration and fluxes at 60 cm soil depth were also predicted.

**Results and Discussion**

**Characterizing the P isotherms**

The results of P adsorption were described by a Freundlich model with linearized $K_d$ ranging from 0.50 ± 0.19 to 0.75 ± 0.13 $\text{kg L}^{-1}$ for Immokalee fine sand and from

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth (cm)</th>
<th>Supporting electrolyte</th>
<th>$K_d$ ($\text{L kg}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immokalee</td>
<td>0-15</td>
<td>0.01 M KCl</td>
<td>0.53 ± 0.11</td>
</tr>
<tr>
<td>Immokalee</td>
<td>15-30</td>
<td>0.01 M KCl</td>
<td>0.50 ± 0.19</td>
</tr>
<tr>
<td>Candler</td>
<td>0-15</td>
<td>0.01 M KCl</td>
<td>2.87 ± 0.43</td>
</tr>
<tr>
<td>Candler</td>
<td>15-30</td>
<td>0.01 M KCl</td>
<td>3.79 ± 0.87</td>
</tr>
<tr>
<td>Immokalee</td>
<td>0-15</td>
<td>0.005 M CaCl$_2$</td>
<td>0.75 ± 0.13</td>
</tr>
<tr>
<td>Immokalee</td>
<td>15-30</td>
<td>0.005 M CaCl$_2$</td>
<td>0.74 ± 0.32</td>
</tr>
<tr>
<td>Candler</td>
<td>0-15</td>
<td>0.005 M CaCl$_2$</td>
<td>3.46 ± 0.65</td>
</tr>
<tr>
<td>Candler</td>
<td>15-30</td>
<td>0.005 M CaCl$_2$</td>
<td>4.43 ± 0.50</td>
</tr>
<tr>
<td>Immokalee</td>
<td>0-15</td>
<td>Fertilizer mixture</td>
<td>0.45 ± 0.10</td>
</tr>
<tr>
<td>Immokalee</td>
<td>15-30</td>
<td>Fertilizer mixture</td>
<td>0.43 ± 0.20</td>
</tr>
<tr>
<td>Candler</td>
<td>0-15</td>
<td>Fertilizer mixture</td>
<td>1.73 ± 0.15</td>
</tr>
<tr>
<td>Candler</td>
<td>15-30</td>
<td>Fertilizer mixture</td>
<td>2.05 ± 0.89</td>
</tr>
</tbody>
</table>

Statistics

- Soil type ($S$): ***
- Electrolyte ($E$): ***
- Depth ($D$): ***
- $S \times D$: ***
- $S \times E$: ***
- $E \times D$: ***
- $E \times S \times D$: ***

$K_d$: Linearized $K_d$ using Equation 12 presented as mean ± one standard deviation of 3 replications and a $C_{\text{max}}$ of 15 mg L$^{-1}$; ***: ‘Significant at 0.001 probability level’.

**Table 3**: Soil water retention parameters of Immokalee and Candler fine sand estimated using CAS software developed by Bloom (2009) [24].

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth (cm)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$n$</th>
<th>$m$</th>
<th>¶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immokalee</td>
<td>0-15</td>
<td>0.03</td>
<td>1.87</td>
<td>0.47</td>
<td>0.5</td>
</tr>
<tr>
<td>Immokalee</td>
<td>15-30</td>
<td>0.04</td>
<td>1.29</td>
<td>0.23</td>
<td>0.5</td>
</tr>
<tr>
<td>Immokalee</td>
<td>30-45</td>
<td>0.03</td>
<td>2.06</td>
<td>0.52</td>
<td>0.5</td>
</tr>
<tr>
<td>Immokalee</td>
<td>45-60</td>
<td>0.03</td>
<td>1.71</td>
<td>0.42</td>
<td>0.5</td>
</tr>
<tr>
<td>Candler</td>
<td>0-15</td>
<td>0.03</td>
<td>2.22</td>
<td>0.55</td>
<td>0.5</td>
</tr>
<tr>
<td>Candler</td>
<td>15-30</td>
<td>0.04</td>
<td>1.70</td>
<td>0.41</td>
<td>0.5</td>
</tr>
<tr>
<td>Candler</td>
<td>30-45</td>
<td>0.02</td>
<td>2.50</td>
<td>0.60</td>
<td>0.5</td>
</tr>
<tr>
<td>Candler</td>
<td>45-60</td>
<td>0.02</td>
<td>1.82</td>
<td>0.45</td>
<td>0.5</td>
</tr>
</tbody>
</table>

¶Pore connectivity parameter (estimated to be an average of 0.5 for many soils [18].

**Table 4**: Sorption coefficients for P on Immokalee and Candler fine sand using three electrolytes.

Figure 1: Selected Freundlich isotherms for P for immokalee and candler sand using 0.005 M CaCl$_2$.
soil pH Ca-P minerals would precipitate while at lower pH (< 4.5), Al-P and Fe-P compounds dictate P adsorption. Barrow, et al. (1980) [25] also showed that at equal ionic strength below pH = 6, there was more phosphate adsorption from CaCl₂ than from NaCl on goethite. This phenomenon, according to Barrow and colleagues [25], is caused because high concentration of positive charges near the negatively charged soil surface may be induced by replacing a monovalent cation with a divalent one and also if the added divalent cation has a specific affinity for the adsorption surface. Addition of cations from the supporting electrolyte, unlike using the fertilizer, induced a greater positive charge for phosphate (and orthophosphate anion) adsorption. The higher KDs for Candler fine sand might be due to high organic matter and some Fe/Al coatings that might bind P. The high Kf value in the top 0-15 cm than the 15-30 cm layer is ascribed to higher organic carbon and organic matter in the former layer resulting in increased P adsorption. Our results are comparable to those reported on Margate sand and Immokalee fine sand by Muwamba, et al. (2016) [26].

Phosphorus movement with microsprinkler irrigation as function of time

Phosphorus movement was predicted using three different KDs estimated with fertilizer mixture, 0.01 M KCl and 0.005 M CaCl₂ for of 21 days, assuming no rainfall events (Figure 3). The assumption is that a KD value ob-
tained using fertilizer mixture typifies that of field conditions with regard to chemical processes. The results on Candler fine sand at Lake Alfred showed that that P contents for the $K_d$ estimated with 0.01 M KCl and 0.005 M CaCl$_2$ were 10 to 15% higher than those predicted with a $K_d$ value measured with fertilizer mixture. The predictions on Immokalee fine sand showed that that P contents for the $K_d$ estimated with fertilizer mixture and 0.005 M CaCl$_2$ were 12 to 20% higher than those predicted with a $K_d$ value measured with 0.01 M KCl. The outputs with $K_d$ measured with 0.005 M CaCl$_2$ appear to be close to those predicted with a $K_d$ measured with fertilizer mixture on Immokalee fine sand. Thus, the analysis of the $K_d$ values across all electrolytes on the two soils studied revealed that 0.01 M KCl is the electrolyte that yields $K_d$ values (0.42 to 0.69 L kg$^{-1}$ on Immokalee fine sand and 0.42 to 1.06 L kg$^{-1}$ on Candler fine sand) fairly close to fertilizer mixture on coated sands while 0.005 M CaCl$_2$ tends to give $K_d$ values (2.44 to 4.66 L kg$^{-1}$ on Immokalee fine sand and 2.81 to 4.93 L kg$^{-1}$ on Candler fine sand) two to threefold in magnitude to those determined with fertilizer mixture on sands with Fe coatings. This suggests that 0.005 M CaCl$_2$ would tend to overestimate P sorption and retardation during unsaturated or saturated flow on coated sand while estimating the adsorption process satisfactorily on uncoated sands than 0.01 M KCl. It appears the addition of a supporting electrolyte with a divalent or monovalent cation, unlike fertilizer mixture, increases the surface charge for adsorption of orthophosphate anions on sands with coatings. The use of 0.01 M KCl appears not to be influenced by presence of sand coatings compared with CaCl$_2$ and, thus, would present an appropriate supporting electrolyte for Candler fine sand while CaCl$_2$ would be appropriate for the Immokalee fine sand.

**Conclusion**

The results show that P adsorption in the top 0-15 cm was greater for Candler than Immokalee sand using the fertilizer mixture, 0.005 M CaCl$_2$ and 0.01 M KCl. The
mass distribution coefficients (K_D) for P estimated using 0.01 M KCl were similar to values determined using fertilizer mixture for Candler fine sand. The K_D values determined using 0.005 M CaCl₂ as the supporting electrolyte were two- to threefold greater than the K_D of the fertilizer mixture on Candler fine sand suggesting that divalent Ca might result in overestimation of P sorption on Candler sandy soils. On Immokalee fine sand, fertilizer mixture and 0.005 M CaCl₂ were comparable and resulted in greater P adsorption than 0.01 M KCl. Thus, it would be appropriate to use 0.01 M KCl as supporting electrolyte for Florida’s Candler fine sand and 0.005 M CaCl₂ on Immokalee fine sand.

References