Chapter

Sorption of Phosphorus from Fertilizer Mixture

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Abstract

Studying phosphorus (P) sorption behavior is among the prerequisites for P management in the crop fields. The work presented in this chapter described P sorption data when fertilizer mixture (NH_4NO_3, KH_2PO_4, and KCl) was used to characterize sorption on soil. In addition to using fertilizer mixture, sorption experiments were also conducted using KH_2PO_4 prepared in 0.01 M KCl, 0.005 M $CaCl_2$, and deionized water. The 24-h batch sorption experiments were conducted using a sandy soil to solution ratio of 1:2, and the equilibrium solution and sorbed data were described using Freundlich isotherm. Sorption kinetics experiments were conducted using times, 4, 8, 12, and 24 h. The Freundlich isotherm constant and sorbed P kinetics data for 0.005 M $CaCl_2$ were significantly greater ($p < 0.05$) than for 0.01 M KCl and/or fertilizer mixture. The Freundlich isotherm constant and sorbed P kinetics data for deionized water were significantly lower ($p < 0.05$) than for 0.01 M KCl and/or fertilizer mixture. There was no significant difference in Freundlich isotherm constant and sorbed P kinetics data for 0.01 M KCl and fertilizer mixture. The sorption data showed the importance of using the fertilizer mix applied to the field when conducting sorption experiments.

Keywords: fertilizer mixture, isotherm, sorption coefficient, sorption kinetics

1. Introduction

Phosphorus (P) is applied with different nutrients to crop fields. Examples of field crops that need fertilizer mixture are shown in **Table 1**. Varying nutrients combinations can significantly affect the interactions of P with soil due to varying ionic strength and pH [1–7]. For example ionic strength was positively correlated to P sorption [2]. The specific affinity and the valence of the cation on the soil exchange site were also associated to P sorption capacity [7]. Supporting electrolytes are used for conducting P sorption experiments assuming representation of the true chemistry of the field solutions without necessarily considering the varying fertilizer mix applied to the soil. **Table 2** shows examples of supporting electrolytes that were used to characterize P sorption in the past studies. In this chapter, it was hypothesized that P sorption isotherm constants and kinetics data for fertilizer mix were significantly different from supporting electrolytes commonly used for conducting P sorption.

Sorption isotherms are used to describe relationships between sorbed and solution P in a given sorption experiment at constant temperature and act as indicators

Field crop	Fertilizer mixture distribution
Sugarcane	200 kg N, 50 kg P_2O_5, and 200 kg K_2O per acre
Canola spring type	160 lb N, 30 lb P_2O_5, and 40 lb K_2O per acre
Canola winter type	175 lb N, 30 lb P_2O_5, and 40 lb K_2O per acre
Corn (for grain) dryland	120 lb N, 20 lb P_2O_5, and 20 lb K_2O per acre
Corn (for grain) irrigated	180 lb N, 70 lb P_2O_5, and 70 lb K_2O per acre
Cotton (1500 lb yield goal)	105 lb N, 140 lb P_2O_5, and 80 lb K_2O per acre
Grain sorghum	80 lb N, 80 lb P_2O_5, and 80 lb K_2O per acre
Peanuts	0 lb N, 80 lb P_2O_5, and 80 lb K_2O per acre
Small grain-barley	100 lb N, 80 lb P_2O_5, and 80 lb K_2O per acre
Small grain-oats	105 lb N, 80 lb P_2O_5, and 80 lb K_2O per acre
Small grain-cover crop	60 lb N, 80 lb P_2O_5, and 80 lb K_2O per acre
Small grain-wheat	120 lb N, 80 lb P_2O_5, and 80 lb K_2O per acre
Small grain silage	160 lb N, 100 lb P_2O_5, and 160 lb K_2O per acre
Sorghum silage	150 lb N, 80 lb P_2O_5, and 160 lb K_2O per acre
Soybeans	0 lb N, 70 lb P_2O_5, and 100 lb K_2O per acre
Sunflower	80 lb N, 80 lb P_2O_5, and 80 lb K_2O per acre
Sweet sorghum	80 lb N, 80 lb P_2O_5, and 80 lb K_2O per acre
Tobacco	50 lb N, 100 lb P_2O_5, and 180 lb K_2O per acre
Kenaf	175 lb N, 100 lb P_2O_5, and 100 lb K_2O per acre
Truffles	50 lb N, 80 lb P_2O_5, and 80 lb K_2O per acre

Table 1.
Field crop and fertilizer mixture distributions.

of field P retention potential [24–27]. Sorption coefficient is among the coefficients described in the isotherms that is used to model P movement in the field [28]. Phosphorus sorption capacity has also been used as an important management tool in many crop fields [29]. Therefore, there is a need to identify the appropriate chemistry of the field solutions before conducting P sorption experiments and modeling P movement in the crop fields. Sorption kinetics data trends were reported to provide clues on the mechanisms of sorption reactions [30]; appropriate solution chemistry should also be carefully chosen for the sorption kinetics experiments. It was also hypothesized that the isotherms that describe sorption data from fertilizer mixture are different from isotherms that describe data from typical laboratory supporting electrolytes.

The importance of laboratory P sorption and kinetics data in modeling and understanding of the P dynamics in crop fields has been documented [31, 32]. The P sorption characteristics help to properly calibrate theoretical models that aim at mimicking field processes [31, 32]. Accurate laboratory sorption data collected using true field solution chemistry will therefore improve models as predictive tools for P movement. The objective of the study was to determine the differences in P sorption behavior for P in fertilizer mixture (N, P, and K) prepared in deionized water and in P fertilizer (KH_2PO_4) prepared in 0.01 MKCl, 0.005 M $CaCl_2$, and deionized water.

Electrolyte	Isotherm	Soil	Reference
0.1 M $CaCl_2$	ND	- Typic Argiudolls - Typic Hapludolls - Entic Haplustolls - Abruptic Argiudolls - Petrocalcic Paleudolls	[8]
0.01 M $CaCl_2$	- Langmuir - Freundlich - Temkin	- Vertisol - Rhizospheric soil - Haploboroll - Hapludoll - Eutrochrept - Haplaquept - Brunic Arenosols (dystric) - Haplic Regosol (dystric) - Sandy mixed Humic Dystrochrept - Very fine, mixed, semiactive, Oxyaquic Haplocryoll - Fine, illitic, frigid Typic Haplquept - Coarse-loamy, mixed, mesic Oxyaquic, Eutrochrept	[1, 9–14]
0.001 M $CaCl_2$	- Freundlich	- Haplustalf - Orthent - Tropaquept	[15]
0.01 M KCl	-Langmuir -Linear	- Sandy, siliceous, hyperthermic Aeric Alaquods - Alaquods and Alorthods - Loamy, siliceous, subactive, thermic Arenic Paleudults - Fine-loamy, siliceous, subactive, thermic Aquic Paleudults - Fine, mixed, semiactive, thermic Typic Umbraquults - Fine-loamy, mixed, semiactive, acid, thermic Histic Humaquepts	[16–19]
0.02 M KCl	- Langmuir	- Loamy, siliceous, hyperthermic Arenic Glossaqualf	[20]
0.05 M KCl	- Langmuir - Freundlich - Linear	- Quartzipsamments - Paleudults - Loamy-skeletal, carbonatic hyperthermic Lithic Udorthents - Loamy, carbonatic, hyperthermic, shallow Typic Fluvaquents - Loamy, skeletal, carbonatic, hyper thermic, Lithic Udorthents	[4, 21, 22]
0.1 M $NaNO_3$	- Langmuir	- Sandy, siliceous, hyperthermic Ultic Alaquod	[23]
0.1 M NaCl	ND	- Aquic or Oxyaquic Haplocryods	[3]
Deionized water	ND	- Aquic or Oxyaquic Haplocryods	[3]

ND, not determined.

Table 2.
Supporting electrolytes, soils, and sorption isotherms for the literature studies.

2. Sorption experiments and trends in sorption data

2.1 Determination of soil properties

The soil samples used for sorption experiments were air dried, passed through 2-mm sieve and first analyzed for pH, total carbon, oxalate extractable iron, oxalate extractable aluminum, and exchangeable calcium. Particle size distribution of the soil samples was also determined. A soil to water solution ratio of 1:2 was prepared, and the soil pH was measured using a standardized pH meter (model: AR15; manufacturer: Fisher Scientific) [33]. The combustion method with the element analyzer (Carbo-Erba NA 2500 instrument (Model: NA 2500; manufacturer: CE instruments, Italy) was used to measure total carbon. The inductively coupled plasma (ICP) (model: Optima 700 DV; manufacturer: Perkin Elmer) was used to analyze for oxalate iron and aluminum after extraction with oxalate solution [34]. Exchangeable calcium was also analyzed using ICP after extraction with 0.2 M NH_4Cl [35]. Particle size distribution was determined by hydrometer method [35] .

2.2 Determination of sorption isotherms

An example of P sorption experiment that involved using KH_2PO_4 fertilizer prepared in 0.01 M KCl, 0.005 M $CaCl_2$, and deionized water and fertilizer mixture (NH_4NO_3, KH_2PO_4, and KCl) prepared in deionized water was used for this study. The fertilizer rates, 50 kg P_2O_5 ha^{-1}, 200 kg N ha^{-1}, and 200 kg K_2O ha^{-1}, applied to sugarcane fields were used to prepare the fertilizer mixture. Potassium chloride and calcium chloride were used because they are commonly used to conduct P sorption experiments with the assumption that the solutions' ionic strength and pH are close to those of the crop fields. The concentration, 0.005 M for $CaCl_2$ and 0.01 M for KCl were used to attain the equivalences of Ca^{2+} and K^+. Deionized water was used because irrigation water is used to provide the necessary plant moisture.

The two sandy soils, Margate (sandy, siliceous, hyperthermic Mollic Psammaquents) and Immokalee (sandy, siliceous, hyperthermic Arenic Alaquods) used for the experiment contribute the most to the greatest percentage of soils used for sugarcane production in Southwestern Florida. Five soil samples of each of the soil horizons, A and Bh for Immokalee soil and A and Bw for Margate soil, were used to represent the varying soil properties (e.g., total carbon, iron, and aluminum). The soil samples were sampled from two sugarcane fields each of 12 ha located in Hendry County, southwestern Florida (26.75° N, 80.93° W).

The initial P concentrations (C0) used for the experiment ranged from 8 to 60 mg L^{-1}. The soil to solution ratio of 1:2 (10 g of soil and 20 mL of solution) was used and equilibrium solution concentration was analyzed after 24 h of shaking. Blanks where soil was shaken with only 0.01 M KCl, 0.005 M $CaCl_2$, and deionized water were also included in the experiment, and the blank equilibrium concentrations were subtracted from the treatment sample equilibrium concentrations. The experiments were conducted at room temperature (25°C). Before analyzing the solution concentrations, soil solutions were centrifuged at 5000 rpm for about 20 min and filtered using 42 Whatman filter. The spectrophotometer (HACH DR/4000U) was used to analyze solution P at a detection wavelength of 880 nm.

Sorbed P (S) was equal to V/M (C0 − Ce) where V, M, C0, and Ce are volume of solution, mass of soil, initial solution P concentration, and equilibrium P concentration, respectively. Sorption data for all the supporting electrolytes were fitted to Freundlich isotherm [sorbed (S) versus equilibrium solution (C) concentration]. The Freundlich sorption isotherm is represented by Eq. (1).

$$S = K_f C^N \quad (1)$$

where S is the amount of P sorbed (mg kg^{-1}), C is the solution P concentration (mg L^{-1}), K_f is the Freundlich sorption coefficient (L^N, kg^{-1} mg^{1-N}), and N is an empirical constant. The coefficients for fertilizer mixture were compared to coefficients for 0.01 M KCl, 0.005 M $CaCl_2$, and deionized water. The paired t-test was used to identify significant differences in Freundlich sorption coefficients.

2.3 Sorption kinetics experiments

The sorption of P has been assumed as a kinetic process [15, 28]. Three initial concentrations (C0), 19, 29, and 38 mg L^{-1} were used for conducting sorption kinetics experiment. The A horizon of Immokalee soil was used for sorption kinetics experiment, and the soil to solution ratio of 1:2 (10 g of soil and 20 mL of solution) was used. Solution concentrations were analyzed after 4, 8, 12, and 24 h. The paired t-test was used to identify significant differences in relative concentrations (C/C0) and sorbed concentrations between fertilizer mixture and supporting electrolytes. R-software was used for statistical analyses. Graphs of relative concentrations (C/C0) and sorbed concentrations (S) versus time were plotted to show the data trends over a 24 h period.

2.4 Selected soil properties

The average percent sand, pH (1:2 soil:water volume), total carbon, oxalate iron, oxalate aluminum, and exchangeable Ca for A horizon of Immokalee soil were 97.0%, 6.8, 15.2 g kg^{-1}, 234.0 mg kg^{-1}, 280.4 mg kg^{-1}, and 3.6 cmolc kg^{-1}, respectively. The average percent sand, pH (1:2 soil:water volume), total carbon, oxalate iron, oxalate aluminum, and exchangeable Ca for A horizon of Margate soil were 97.5.0%, 8.3, 11.2 g kg^{-1}, 661.1 mg kg^{-1}, 307.3 mg kg^{-1}, and 6.6 cmolc kg^{-1}, respectively. The average percent sand, pH (1:2 soil:water volume), total carbon, oxalate iron, oxalate aluminum, and exchangeable Ca for Bh were 87.5%, 6.8, 39.7 g kg^{-1}, 114.4 mg kg^{-1}, 305.0 mg kg^{-1}, and 5.4 cmolc kg^{-1}, respectively. The average percent sand, pH (1:2 soil:water volume), total carbon, oxalate iron, oxalate aluminum, and exchangeable Ca for Bw were 97.2%, 8.4, 3.9 g kg^{-1}, 149.0 mg kg^{-1}, 89.0 mg kg^{-1}, and 2.0 cmolc kg^{-1}, respectively.

2.5 Changes of sorption isotherm coefficients with supporting electrolytes

Although all sorption data fitted Freundlich isotherms with R^2 values greater than 0.9, the Freundlich coefficients varied with the type of supporting electrolytes (**Table 3**). For both 0.01 M KCl and fertilizer mixture, the Freundlich isotherm constant was significantly lower ($p < 0.05$) than for 0.005 M $CaCl_2$ and significantly greater ($p < 0.05$) than for deionized water (**Table 4**). Although the same equivalence was used for K^+ and Ca^{2+}, sorption was greater for 0.005 M $CaCl_2$ than

Soil	Horizon	0.01 M KCl	0.005 M $CaCl_2$	Deionized water	Fertilizer mixture
Immokalee soil	A	$S = 4.8\ C^{0.5}$	$S = 13.5\ C^{0.4}$	$S = 2.7C^{0.8}$	$S = 4.6C^{0.5}$
Margate soil	A	$S = 7.2\ C^{0.6}$	$S = 24.6\ C^{0.3}$	$S = 5.4C^{0.5}$	$S = 7.3\ C^{0.6}$
Immokalee soil	Bh	$S = 19.1C^{0.6}$	$S = 79.0C^{0.2}$	$S = 13.1C^{0.8}$	$S = 21.1C^{0.6}$
Margate soil	Bw	$S = 10.3C^{0.3}$	$S = 28.0\ C^{0.2}$	$S = 6.7C^{0.4}$	$S = 9.5C^{0.3}$

Table 3.
Average sorption isotherms of five replicates showing variabilities in Freundlich sorption coefficients.

Comparisons	A-Immokalee	A-Margate	Bh	Bw
Fertilizer mixture versus deionized water	S	S	S	S
Fertilizer mixture versus 0.005 M $CaCl_2$	S	S	S	S
Fertilizer mixture versus 0.01 M KCl	NS	NS	NS	NS

NS, no significant difference (α = 0.05); S, significantly greater or lower (α = 0.05).

Table 4.
Comparisons of Freundlich sorption coefficients and sorbed phosphorus concentrations.

for 0.01 M KCl and fertilizer mixture likely due to the influence of charge (+2) on Ca^{2+} that reduce the electrostatic repulsion effect between phosphate and the soil surface. A similar trend ($Ca^{+2} > K^{+}$) for P sorption was identified in other sorption studies [36]. Phosphorus sorption was also reported to increase with increase in background electrolyte concentration [37]. The sorption characteristics of P (KH_2PO_4) prepared in deionized water was lower than for 0.01 M KCl and fertilizer mixture probably due to significantly lower K^{+} concentration that contributes less to ionic strength than in the latter two. The greater Freundlich coefficients for Bh were greater than A horizon because of the greater total carbon, oxalate iron, and oxalate aluminum that enhance greater P sorption. Soils with greater free aluminum and iron were associated with greater P sorption by different researchers [38–40].

2.6 Trends in sorption kinetics data for different supporting electrolytes

Figure 1 shows the sorbed P concentrations as a function of initial concentrations for a 24 h time step with no significant difference in sorbed concentrations for 0.01 M KCl and fertilizer mixture. **Figure 2** shows the trends in relative solution concentrations (C/C0) and sorbed concentrations (P). While the relative solution concentrations decreased over time, sorbed concentrations increased over time. For both 0.01 M KCl and fertilizer mixture, sorbed P kinetics data were significantly lower ($p < 0.05$) than for 0.005 M $CaCl_2$, and significantly greater ($p < 0.05$) than for deionized water (**Table 4**). Sorption was fast for the first hours due to the presence of high P affinity sorption sites on the exchange sites and gradual for the following hours (**Figure 2**). A fast P sorption first phase followed by a steady phase was also documented in other studies [2, 15, 41].

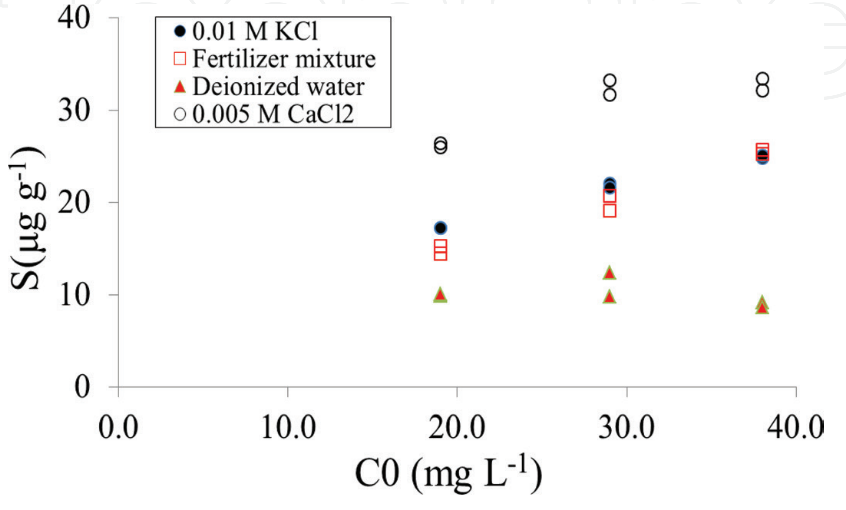

Figure 1.
Sorbed P (S) concentration as a function of initial concentrations (Co) for A horizon of Immokalee soil.

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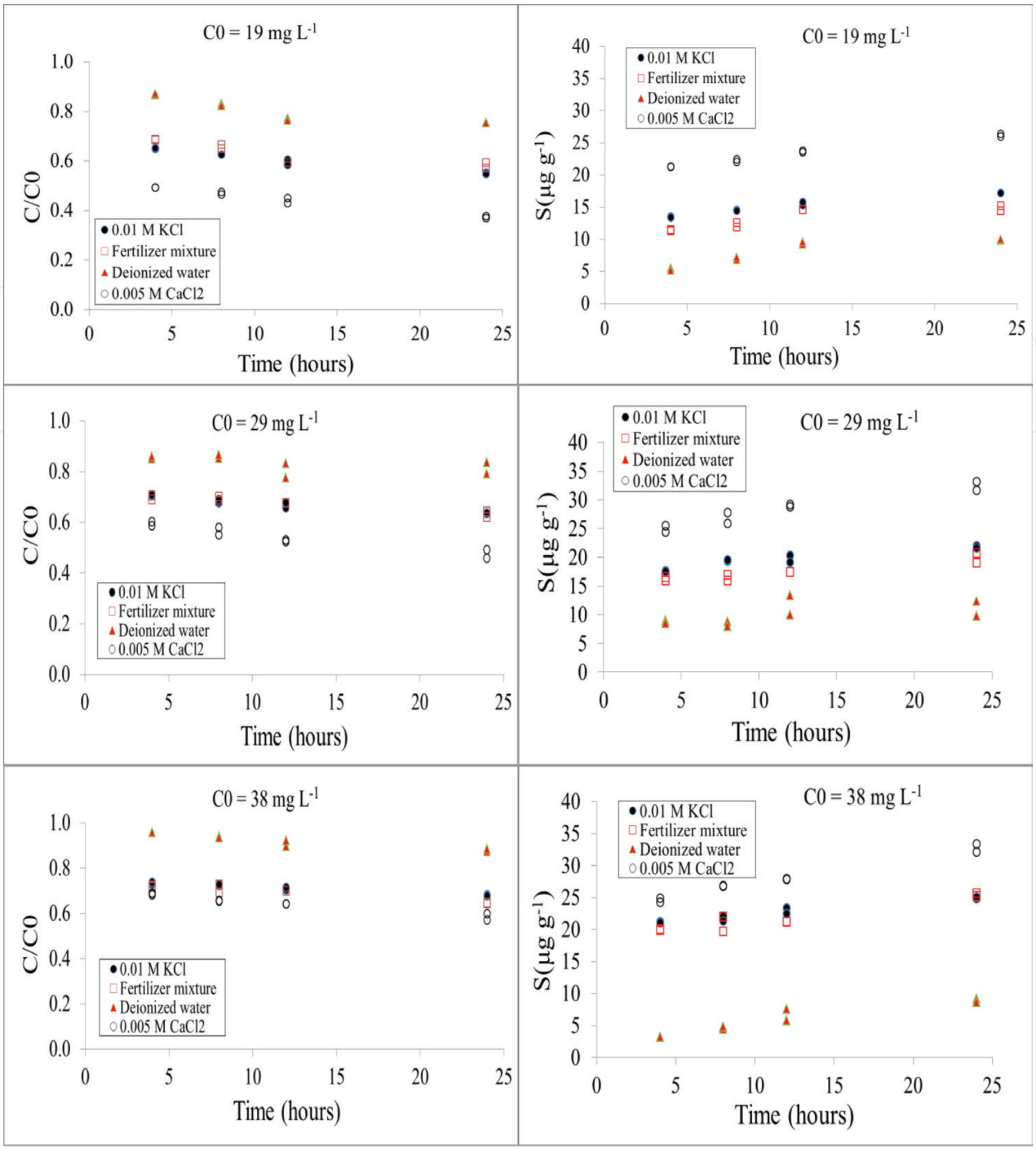

Figure 2.
Relative solution (C/Co) and sorbed (S) concentration as a function of time for A horizon of Immokalee soil.

3. Summary/conclusions

The results presented in this chapter suggest that if another nutrient is applied with P in the field, the P sorption behavior should be studied with the applied fertilizer mix, and P prepared in recommended supporting electrolyte as well. The sorption characterization with the two scenarios will help in identifying the appropriate sorption characteristics (sorption isotherm coefficients and kinetics constants) used for predicting P movement and P management options.

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