Chemical Distribution of Phosphorus in Soils used during the Development of Sorption Isotherms

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This study was developed to provide initial information on the chemical distribution of P into the different soil P pools after a soil sample underwent P sorption using 17 soil samples from the United States (13) and Brazil (4). During the sorption phase, soil samples were equilibrated with solutions containing increasing P concentrations (0–75 mg P L^{-1}) following standard procedures. Following the sorption phase, the soil samples were allowed to air dry for 72 h and underwent a chemical fractionation (in water, anionic resin, 0.5M $NaHCO_3$, 0.1M NaOH, and 1.0M HCl). A wide range of sorption strength ranging from 0.043 to 0.289 L kg^{-1} and a maximum sorption ranging from 189 to 789 mg kg^{-1} were observed. More than 59% of the sorbed P was found in the water + resin fraction, which is considered the most labile pools where the binding energy is assumed to be low. In contrast, less than 25% of the sorbed P was found in the nonlabile pools where the binding energy is assumed to be the greatest. Although less than 25% of the sorbed P was found in the non-labile pools, the NaOH+HCl fraction contributed 2 to 61% of the overall sorption strength estimated for the soils studied. The results of this study suggest that sorption strength calculated from sorption studies are heavily skewed toward the nonlabile fraction, which was found to constitute a very small portion of the binding sites occupied during sorption studies.

Abbreviations: b, the sorption maximum; ICP–OES, inductively coupled plasma optical emission spectroscopy; b_f, sorption maximum determined using the sequential fractionation data; b_i, sorption maximum estimated using the method of Nair et al. (1984); k, a coefficient unique to each soil that has been used as a measure of the sorption strength between soil particles and P; k_f, the sorption strength parameter determined using the sequential fractionation data; k_i, the sorption strength parameter estimated using the method of Nair et al. (1984); OM, organic matter; P_i, inorganic P; P_o, organic P; W_{kft}, cumulative weighted sorption strength.

Core Ideas

- **Soil P adsorption studies provide misleading information regarding how P binds to soil.**
- **Phosphorus adsorption studies might not correctly estimate the true potential for a soil to hold P.**
- **Adsorption strength calculated using adsorption studies are skewed towards the nonlabile pool, which does not represent where the majority of P binds during such studies.**

When P is added to soils in the form of fertilizer, a series of reactions takes place, ranging from diffusion of P from the fertilizer granules into the soil solution, sorption of P into soil particles, and, with time, P precipitation (Hedley and McLaughlin, 2005). In the soil, inorganic P (P_i) will adsorb or precipitate by chemically binding with Al, Fe, or Ca (Lombi et al., 2006; Khatiwada et al., 2012; Eriksson et al., 2015). The solubility of phosphorus in soil is controlled by several factors, including how much P is originally adsorbed in the soil, how much P is precipitated in the soil, the soil pH, clay mineralogy, organic matter content, what types of minerals were formed during P precipitation, and the concentration of Ca, Al, Fe, and other cations in solution (Delgado and Torrent 2000; Violante and Pigna, 2002; Shigaki and Sharpley 2011; Weng et al., 2012; Eriksson et al., 2015; Gérard, 2016). McLaughlin et al. (2011) has shown that the amount of Ca, Al, and Fe, in the soil solution controls P solubility and mobility from the inside of the fertilizer granule to the surrounding soil particles. In alkaline soils, P will primarily bind to Ca; in weathered acidic soils, P will pri-

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marily bind to Al and Fe hydroxides (Delgado and Torrent 2000; Chien et al., 2014; Eriksson et al., 2015). Therefore, the amount of P in the soil solution that is free to move with water through the soil profile (leaching) or horizontally (runoff) or to be taken up by plant roots will depend on the sorption capacity of a given soil and probablythe Ca concentration (in alkaline soils) (Olsen and Watanabe, 1957; Bache and Williams 1971; Sharpley 1995; Kamprath 1999; Leytem and Westermann 2003; Laboski and Lamb 2004; Gama-Rodrigues et al., 2014).

To study the sorption capacity of soils, many researchers have used sorption studies, where a given amount of soil is mixed with solutions made up with various P concentrations (Nair et al., 1984). The amount of P adsorbed onto the soil is estimated as the difference between the initial and final solution P concentrations (Olsen and Watanabe 1957; Nair et al., 1984). Therefore, one can describe P adsorption in soils as:

$$Q = f(c)\,, \qquad [1]$$

where Q is the amount of P adsorbed as a function of the P equilibrium concentration in the solution (c) (Havlin et al., 2005). Two primary equations have been used to described the adsorption behavior of soils: the Freunddlich and the Langmuir equations (Olsen and Watanabe 1957; Bache and Williams 1971; Leytem and Westermann 2003; Laboski and Lamb 2004; Guardini et al., 2012; Oliveira et al., 2014). The Freundlich equation has limitations and is preferred when the solution P concentrations used in the study are low (e.g., from 0 to 20 mg L^{-1}), whereas the Langmuir equation is used at a wider range of P concentrations in solution (e.g., from 0 to 80 mg L^{-1}) (Havlin et al., 2005). The Freundlich equation in its simplest form can be described as:

$$Q = kc^{b}\,, \qquad [2]$$

where Q and c are the same as previously described and k and b are coefficients that are unique to each soil (Sparks 2003; Havlin et al., 2005). The parameter k has been used as a measure of the sorption strength between soil particles and P (Sparks 2003). The Langmuir equation is used more often than the Freundlich and is described as:

$$Q = \frac{bkc}{1+kc}\,, \qquad [3]$$

where Q, c, and k are the same as previously described and b is the sorption maximum or the maximum amount of P that can adsorb to a given soil in units of mg P kg^{-1} soil (Olsen and Watanabe 1957; Sparks 2003; Havlin et al., 2005). Although Eq. [2] and [3] have been widely used to describe adsorption behavior, they provide no information regarding the actual adsorption mechanisms involved in the reactions. As mentioned earlier, Ca, Al, and Fe hydroxides and clay particles are active participants in P sorption reactions in soils; however, the Freundlich or Langmuir equations are incapable of indicating or even suggesting which process is at work.

In 1982, Hedley et al. (1982) developed a sequential extraction procedure as a tool to investigate changes in individual soil P pools as affected by various management strategies. The extractable fractions have been functionally defined as follows: soluble (labile) P_i is extracted in the resin; P_i and organic P (P_o) are extracted in 0.5 M $NaHCO_3$; P_i and P_o associated with Al and Fe are extracted with 0.1 M NaOH; P_i occluded in the interiors of amorphous Al or Fe hydrous oxides is extracted in 0.1 M NaOH with sonication; P_i associated with Ca and primary minerals and P_o are extracted with 1.0 M HCl; and the most stable P_o and any remaining occluded P_i are estimated after H_2SO_4 + H_2O_2 digestion of the residue (Hedley et al., 1982; Cross and Schlesinger 1995). Soils that have been amended with ordinary fertilizers or organic nutrient sources such as animal manure usually show differing increases in the P content of the different P pools (Hedley et al., 1982; Buehler et al., 2002, Waldrip et al., 2015). However, the partitioning of P into any pool is an intrinsic property and is specific for each soil. For example, alkaline soils with a high amount of Ca will have higher accumulation of P in the HCl-extractable pool than in other pools (Bair et al., 2014); highly weathered soils will accumulate most of the added P in the NaOH-extractable fraction (Negassa and Leinweber 2009). Although several researchers have constructed sorption isotherms using the method of Nair et al. (1984) or a modification of it, there is no clear indication of the partitioning of P into the various soil P pools after the sorption reactions are completed. Most often, the soil samples are discarded after the sorption study is concluded.

This study was designed to provide an initial analysis of where P is binding in soils during the construction of sorption isotherms. This study combined two widely used methods for characterizing P in soils: (i) the sorption isotherm as described by Nair et al. (1984) with the parameters being estimated using the Langmuir equation (Eq. [3]) and (ii) the chemical sequential fractionation method modified from the original method proposed by Hedley et al. (1982). The hypothesis of this study was that the distribution of P pools in soil, according to the chemical fractionation, would relate to the parameters developed with the Langmuir isotherm. In other words, we expected that soils with high sorption strength (k) and high maximum sorption (b) would have a high concentration of P extracted in the nonlabile pools (NaOH and HCl fractions). This study used soil samples with contrasting chemical and physical properties that were collected from two states in Brazil (Parana, one sample; Sao Paulo, three samples) and two states in the United States (Iowa, one sample; Minnesota, 12 samples). The use of soils encompassing a wide range of origins, textures, and chemical compositions should allow for broader inferences regarding the P sorption behavior of the soils studied.

MATERIAL AND METHODS

Soil Collection and Characterization

Soil samples were collected from Minnesota [Clarion loam (fine-loamy, mixed, superactive, mesic Typic Hapludolls), Cordova clay loam (fine-loamy, mixed, superactive, mesic Typic Argiaquolls), Fargo silty clay (fine, smectitic, frigid Typic

Epiaquerts), Gunclub silty clay loam (fine-silty, mixed, superactive, frigid Aeric Calciaquolls), Hubbard loamy sand (sandy, mixed, frigid Entic Hapludolls), Nicollet clay loam (fine-loamy, mixed, superactive, mesic Aquic Hapludolls), Normania loam (fine-loamy, mixed, superactive, mesic Aquic Hapludolls), Storden loam (fine-loamy, mixed, superactive, mesic Typic Eutrudepts), Ves loam (fine-loamy, mixed, superactive, mesic Calcic Hapludolls), Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed, superactive, mesic Typic Hapludolls), Wheatville fine sandy loam (coarse-silty over clayey, mixed over smectitic, superactive, frigid Aeric Calciaquolls), and Zimmerman sand (mixed, frigid Lamellic Udipsamments)], Iowa (Estherville clay loam; sandy, mixed, mesic Typic Hapludolls), and from Brazil including one soil sample from Parana (Maringa clay, hereafter Brazil-C) and three soil samples from Sao Paulo: a sandy clay loam (Ultisol, no known series, hereafter Brazil-A), a silty clay loam (Inceptsol, no known series, hereafter Brazil-D), and a clay (Oxisol, no known series, hereafter Brazil-E). Most of the soils were from cropped fields under conventional agricultural practices but had differing histories of cropping system, management, and fertilizer use. All soil samples were collected from 0 to 15 cm to represent the depth most affected by tillage operations and fertilizer application.

After collection, soils were air-dried, sieved (2 mm), and stored at room temperature (22°C) until analysis. Soil pH was measured in water (1:1 ratio w/w). Organic matter (OM) content was measured by loss on ignition at 360°C and particle size analyses were performed using the hydrometer method of Bouyoucos (1962). Soil test P was extracted with the Bray–1 and Olsen reagents (Brown, 1998) and determined by the molybdate blue method of Murphy and Riley (1962) using a Biotek Epoch microplate spectrophotometer (Biotek, Winooski, VT). In addition, P, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+} were extracted using the Mehlich–3 procedure (Brown, 1998) and determined by inductively coupled plasma optical emission spectroscopy (ICP–OES) (PerkinElmer, Optima 8x00, Norwalk, CT). A summary of the properties measured in the soil samples used in this study is presented in Table 1.

Sorption Isotherm and Sequential Fractionation

Phosphorus sorption isotherms were constructed to determine the maximum sorption (*b*) and sorption strength (*k*) coefficients according to Nair et al. (1984). Briefly, 1 g of dry soil was equilibrated with 25 mL of KH_2PO_4 solution with increasing P concentrations containing 0.0, 2.5, 5.0, 10.0, 25.0, 50.0, and 75.0 mg P L^{-1} in a 0.01 M $CaCl_2$ background solution. Each of these concentrations was replicated four times for each soil. In many cases, including the original work of Nair et al. (1984), concentrations lower than 2.5 mg P L^{-1} have been used. However, our intent was to develop isotherm models that showed a clear picture of the sorption process, which required having many P concentrations. Including very low P concentrations would add a significant number of samples to further be used in the fractionation portion without changing the shape of the isotherm. Therefore, we opted to omit very low P concentrations. The soil suspension was shaken for 16 h at 22°C then centrifuged for 10 min at 3400 × *g* and the supernatant was transferred to a clean centrifuge tube. Immediately, the soil residue was washed with 5 mL of ultrapure water and the tubes were centrifuged for 10 min at 3400 × *g* and the wash-water was discarded. The washing

Table 1. Summary of selected soil properties of soils used in the development of isotherm sorption isotherms.

Soil series	Olsen†	Bray-1	Ca	Mg	Fe	Al	Sand	Clay	OM	pH	k_i	k_f	b_i	b_f
			mg kg^{-1}					%			L kg^{-1}		mg kg^{-1}	
Brazil-A	2	8	451	137	43	702	78.2	20.1	2.8	5.3	0.273	0.320	346	322
Brazil-C	12	21	488	177	37	1121	25.0	60.0	4.7	5.5	0.197	0.286	726	606
Brazil-D	11	13	1781	338	293	583	12.5	30.0	3.7	5.7	0.236	0.322	503	407
Brazil-E	26	16	1794	348	105	525	10.0	60.0	6.8	5.0	0.289	0.466	789	604*
Clarion	44	75	2770	593	201	586	36.2	38.4	4.4	6.2	0.112	0.095	326	358
Cordova	35	46	4899	566	82	11	17.4	29.6	8.9	7.5	0.075	0.080	451	411
Estherville	33	24	2165	458	143	695	60.1	22.7	3.9	7.0	0.117	0.146	296	249*
Fargo	42	87	3606	1410	47	17	5.2	6.7	6.8	7.7	0.043	0.054	489	483
Gunclub	20	20	2829	1215	27	0	34.1	8.7	5.4	8.2	0.078	0.077	406	391
Hubbard	20	82	580	95	95	716	82.5	11.8	1.3	6.6	0.139	0.105	253	250
Nicollet	17	9	2757	647	120	347	36.1	35.1	4.4	6.7	0.136	0.090*	377	406
Normania	23	44	2414	608	231	703	37.0	30.9	4.4	8.2	0.098	0.099	468	444
Storden	25	42	1995	349	162	656	43.3	30.9	4.8	5.5	0.090	0.085	320	330
Ves	9	13	1995	459	168	704	44.2	35.8	3.9	5.4	0.150	0.103*	398	421
Waukegan	25	40	2109	616	108	290	16.1	31.5	4.9	7.2	0.103	0.110	371	336
Wheatville	22	24	3062	925	20	0	19.3	11.5	4.7	8.3	0.068	0.100	473	395*
Zimmerman	15	38	1561	60	211	368	81.0	14.3	1.9	8.0	0.119	0.089	189	147*

* Significance difference ($P < 0.05$) between the parameters estimated on the basis of the sorption isotherm and estimated on the basis of sequential extraction.

† Olsen, extractable P in 0.5 M $NaHCO_3$; Bray-1, HCl + NH_4F-extractable P; Ca, Mehlich-3-extractable Ca; Mg, Mehlich-3-extractable Mg; Fe, Mehlich-3-extractable Fe; Al, Mehlich-3-extractable Al; k_i, sorption strength based on the sorption isotherm; k_f, sorption strength based on sequential P extraction in water, $NaHCO_3$, NaOH, and HCl; b_i, sorption maximum based on the sorption isotherm; b_f, sorption maximum based on sequential P extraction in water, $NaHCO_3$, NaOH, and HCl; OM, organic matter.

was done to avoid the transfer of P that was not sorbed onto the soil particles in the sequential fractionation procedure (described below). After washing, the soil samples were allowed to air-dry at room temperature (22°C) for 72 h. Phosphorus concentration in the supernatant of the solutions with initial concentrations equal to or lower than 10 mg P L^{-1} was determined by the molybdate blue method of Murphy and Riley (1962), whereas P concentrations of the solutions with an initial concentration greater than 10 mg P L^{-1} were determined by ICP–OES. Analysis of solutions with high P concentration has shown lower variability when the solution is analyzed directly via ICP–OES than when it is diluted for color development (do Nascimento et al., 2015). The P concentration in the final solution was the measured value for c in Eq. [3]. The value for Q was estimated by the difference between the initial solution's P concentration and the final solution P concentration (c). The sorption parameters b_i and k_i (the subscript $_i$ identifies the parameters estimated using the method of Nair et al. (1984) and Eq. [3]) are reported in Table 1.

For the sequential fractionation, the original procedure of Hedley et al. (1982) was used with several modifications: the soil mass was increased from 0.5 to 1.0 g (to allow for 100% of the soil used in the sorption phase also be used in the fractionation phase) and the extraction solution volume was decreased from 25 to 20 mL, the first extraction was in ultrapure deionized water (18.2 MΩ cm^{-1}), the 0.1 M NaOH extraction following the ultrasonication step was omitted, and the fraction residue left after the HCl extraction was not analyzed. The modifications of the original method were primarily because sonication was not possible in our laboratory and because the sorption experiment required higher volumes of soil than what was needed for the Hedley et al. (1982) fractionation method. Briefly, soil samples (1.0 g dry weight, four replications per sample) were sequentially extracted with ultrapure deionized water (20 mL) for 16 h at 22°C on an orbital shaker (Eberbach E6003, Eberbach, Ann Arbor, MI) at 250 rpm. Extracts were then centrifuged at 3400× g for 15 min at 4°C and the supernatants were carefully decanted into clean 50-mL tubes. Soil residues retained in the tubes were then sequentially extracted with 20 mL each of ultrapure water and one strip of an anionic resin (2 cm^2 surface area per side), 0.5 M $NaHCO_3$ (pH 8.5), 0.1 M NaOH, and 1.0 M HCl for 16 h, with extraction conditions and supernatant collection as previously described. Phosphorus extracted in the resin fraction was recovered by allowing P desorption from the resin into 10 mL of a 0.5 M HCl solution by shaking the resin–HCl solution at 250 rpm for 2 h. Inorganic P in all extracting solutions was determined using the method of Murphy and Riley (1962), with the exception of the NaOH extract, which was determined according to the method of He and Honeycutt (2005).

After the sequential fractionation was completed, the total P_i extracted was calculated by summing up the P from each individual fraction and Eq. [3] was used to estimate the fractioned k_f and b_f parameters (the subscript $_f$ identifies the parameters determined using the sequential fractionation data). The P_i extracted from all fractions during the chemical fractionation for the 0 mg P L^{-1} concentration was removed from the other concentrations, as it represented the indigenous amount of P_i extractable from the soils. In addition, the k_{fx} and b_{fx} parameters for each individual fraction (x: water, resin, $NaHCO_3$, NaOH, and HCl fractions) were calculated to provide an estimation of the contribution from each fraction to the overall k_f and b_f parameters. Weighted values for k_{fx} were calculated to allow for the estimation of the correct percentage that each fraction contributed to the total k_f Weighted values for k_{fx} were calculated as:

$$Wk_{fx} = k_{fx}\frac{\sum_{r=1}^{6}\left(\frac{Pxr}{Ptr}\right)}{6}, \qquad [4]$$

where Wk_{fx} is the weighted sorption strength for the fraction x (water, resin, $NaHCO_3$, NaOH, or HCl), P_{xr} is the P concentration for the x fraction at the r concentration (r is the P concentration from 2.5 to 75.0 mg L^{-1}), P_{tr} is the total P concentration calculated by summing up the P_i extracted in all fractions for the concentration r, and 6 is the number of P concentrations used in the study (0 is omitted). The Wk_{fx} was calculated for each soil using all four replications. The cumulative W_{kf} (Wk_{ft}) was calculated by summing all five Wk_{fx} values; likewise, the cumulative b_{fx} (b_{ft}) was calculated by summing up the b_{fx} values estimated for each fraction.

Statistical Analysis and Data Modeling

Nonlinear regression was used to estimate the parameters b and k from Eq. [3]. All nonlinear regression fitting was performed using R, an open-source statistical software package (R Development Core Team, 2007). Pairwise t-tests were used to compare the sorption parameters k_i, k_f, b_i, and b_f. Correlation analysis carried out in the R package was used to correlate the parameters k_i, k_f, b_i, and b_f with the selected soil properties measured. Stepwise regression, forward and backward, was used to correlate the sorption parameters with the soil properties as well as with the P forms determined during the fractionation study (P-water, P-resin, P-$NaHCO_3$, P-NaOH, and P-HCl). The stepwise regression was done using the regsubsets algorithm from the library leaps in R. The Akaike information criterion value was used as the model selection criterion to determine which model was the best after the stepwise regression was performed.

RESULTS AND DISCUSSION

Selected Soil Properties

The soils selected for this study showed a wide range in their measured chemical and physical properties (Table 1). The physicochemical properties reported in Table 1 were selected because these are the properties most often reported as affecting the sorption properties of soils (Hinsinger 2001; Laboski and Lamb 2004; Allen and Mallarino 2006; Devau et al., 2011; McLaughlin et al., 2011; Eriksson et al., 2015). For example, soil pH and clay content are reported to have a strong relationship with the P sorption capacity of soils, as they are related to the

Table 2. Summary of the correlation analysis with the respective correlation *P*-values.

	Olsen †	Bray-1	Ca	Mg	Fe	Al	Sand	Clay	OM	pH	k_i	k_f	b_i	b_f
Olsen	1	0.69‡	0.66	0.50	-0.03	-0.39	-0.38	-0.08	0.54	0.34	-0.57	-0.39	-0.02	0.05
Bray-1	0.002§	1	0.23	0.23	0.01	-0.16	0.03	-0.34	0.04	0.30	-0.53	-0.49	-0.28	-0.19
Ca	0.004	0.365	1	0.70	-0.07	-0.77	-0.55	-0.22	0.75	0.54	-0.65	-0.51	0.01	0.12
Mg	0.039	0.376	0.002	1	-0.36	-0.73	-0.57	-0.41	0.54	0.56	-0.62	-0.45	0.12	0.27
Fe	0.925	0.977	0.781	0.154	1	0.33	0.10	0.17	-0.31	-0.14	0.13	0.02	-0.25	-0.27
Al	0.119	0.531	0.001	0.001	0.201	1	0.38	0.56	-0.50	-0.67	0.56	0.44	0.12	0.09
Sand	0.133	0.921	0.022	0.016	0.694	0.132	1	-0.34	-0.78	-0.04	0.12	-0.14	-0.70	-0.74
Clay	0.750	0.188	0.389	0.107	0.512	0.019	0.187	1	0.25	-0.65	0.55	0.59	0.65	0.63
OM	0.026	0.867	0.001	0.024	0.226	0.043	0.001	0.325	1	0.11	-0.23	0.01	0.55	0.61
pH	0.185	0.237	0.025	0.019	0.587	0.003	0.866	0.005	0.665	1	-0.76	-0.67	-0.32	-0.31
k_i	0.017	0.029	0.005	0.008	0.627	0.020	0.658	0.023	0.371	0.001	1	0.93	0.42	0.29
k_f	0.125	0.045	0.038	0.070	0.945	0.080	0.594	0.013	0.972	0.003	0.001	1	0.65	0.47
b_i	0.934	0.272	0.974	0.647	0.340	0.653	0.002	0.004	0.021	0.216	0.090	0.005	1	0.95
b_f	0.860	0.464	0.654	0.297	0.296	0.726	0.001	0.007	0.009	0.226	0.267	0.059	0.001	1

†Olsen, extractable P in 0.5 M $NaHCO_3$; Bray-1, HCl + NH_4F-extractable P; Ca, Mehlich-3-extractable Ca; Mg, Mehlich-3-extractable Mg; Fe, Mehlich-3-extractable Fe; Al, Mehlich-3-extractable Al; k_i, sorption strength based on the sorption isotherm; k_f, sorption strength based on sequential P extraction in water, $NaHCO_3$, NaOH, and HCl; b_i, sorption maximum based on the sorption isotherm; b_f, sorption maximum based on P sequential extraction in water, $NaHCO_3$, NaOH, and HCl; OM, organic matter.

‡ Values to the right above the diagonal are the correlation (*r*) values.

§Values to the left below the diagonal are the *P*-values for the *r*-values.

amount of Al, Fe, and Ca present in the soil solution (Violante and Pigna, 2002; Devau et al., 2011; Bair et al., 2014; Eriksson et al., 2015; Gérard, 2016). However, the effects of pH on P sorption are much more complex because during exchange reactions, OH^- groups are replaced with phosphate ions, causing a pH change in the vicinity of the reaction. Furthermore, the amount of phosphate that can sorb on the same mineral will change as the pH of the material changes (Gérard, 2016). It has been reported that changes in the pH of clay minerals have a larger impact on phosphate sorption than pH changes of Fe or Al oxides (Gérard, 2016). The wide range in the properties measured suggests that the results of this study would be applicable to agricultural soils that fall within the range of soil properties used here.

The sorption parameters k_i and b_i estimated in this study were well within the values reported in the literature for soils with similar properties (Laboski and Lamb 2004; Wang and Li 2010; Oliveira et al., 2014; Bortoluzzi et al., 2015) (Table 1). Several soil properties were significantly correlated with the k_i and b_i parameters (Table 2). The highest correlations ($r > 0.60$ or $r < -0.60$) were observed for Ca ($r = -0.65$), Mg ($r = -0.62$), and pH ($r = -0.76$) for the k_i parameter and sand ($r = -0.70$) and clay ($r = 0.65$) for the b_i parameter (Table 2). Similarly, there were several correlations between soil properties and the k_f and b_f parameters. For k_f, the highest correlation ($r > 0.60$) was found to be with soil pH ($r = -0.67$) but for the b_f parameter, the highest correlations were found for sand ($r = -0.74$), clay ($r = 0.63$), and OM ($r = 0.61$) content (Table 2). Violante and Pigna (2002) studied the competitive sorption of arsenate and phosphate in several sorbents. The authors reported a decrease in the amount of P sorbed as the solution pH increased from 4 to 8. Gérard (2016) performed a thorough review of the literature on phosphate binding and also reported that the amount of P sorbed onto different minerals decreased as the pH increased. Gérard (2016) hypothesized that the changes in pH can lead to a shift from monolayer sorption to multilayer sorption prior to phosphate precipitation. Calcium, Al, Fe, and silicate or oxyhydroxide clays are well known for their capacity to sorb P ions from a solution; however, there is a range in the affinity and strength of the bond, depending on where the P is binding (Castro and Torrent 1998; Weng et al., 2012). For example, Ca-bound P, as well as Fe- and Al-bound P can form insoluble precipitates, whereas P bound to clay surfaces is readily exchangeable (Freeman and Rowell 1981; Torrent et al., 1992; de Mesquita Filho and Torrent 1993). The type of clay can also have a dramatic effect on the rate, strength, and total amount of P sorbed; for example, kaolinite can sorb 53.5 times more phosphate than montmorillonite and illite (Shang et al., 2013; Gérard, 2016). Shang et al. (2013) investigated P sorption properties in goethite, kaolinite, gibbsite, and montmorillonite and reported that goethite sorbed as much as nine times more P than gibbsite and montmorillonite. Abdala et al. (2015) reported that increased Fe and Al oxyhydroxides and hydroxides in soils caused by long-term manure application increased the ability of the soil to sorb P. Other authors have reported that phosphate can also penetrate the inter-lamellar or the amorphous regions of clay minerals (Muljadi et al., 1966a, 1966b). Although correlations between the sorption parameters and soils properties were observed in this study, some have reported no correlations at all in their studies (Castro and Torrent 1998; Marshall and Laboski 2006).

The parameters k_i and k_f, as well as b_i and b_f were highly correlated with each other (Table 2). The high correlation among the sorption parameters reflects the fact that in the majority of the soils, there were no significant differences between k_i and k_f or b_i and b_f, which suggests that all P sorbed during the sorption isotherm study could be recovered in the chemical fractionation (Table 1). Only two soils showed a significant difference between the k_i and k_f parameters, (Nicollet and Ves), whereas there were four soils that showed a significant difference between the b_i and b_f parameters: Brazil-E, Estherville, Wheatville, and Zimmerman (Table 1). In all cases when significant differences were observed among the sorption parameters, the parameters estimated on the basis of the sequential fractionation were lower than those calculated directly from the equilibrium solution. Overall, the majority of the sorbed P (>59%) was recovered in the water and resin fractions (Table 3), suggesting that P is weakly bound to the soils during the development of sorption isotherms. Penn and Heeren (2009) reported that, on average, about 50% of the P sorbed during a study of P sorption on kaolinite was recovered after 10 sequential water extractions. Therefore, it is possible that the significant differences observed between the sorption parameters (k_i and k_f and b_i and b_f) could be caused by small amounts of loosely bound P being removed during the rinsing of the soils prior to the beginning of the sequential fractionation. As mentioned earlier, after the sorption study was completed, the soil samples were rinsed with ultrapure water to ensure that all of the equilibrium solution was removed prior to allowing the soil samples to air dry. The rinsing water was not analyzed for P content because this was a quick procedure of just a few seconds and we did not expect large amounts of P to be removed from the soil samples. Although no other study has sequentially extracted P from soils used in sorption studies, research on the sequential fractionation of animal manure has shown that a significant amount of P can be lost during the washing of the residue between extractants (Turner and Leytem 2004; He et al., 2009; Pagliari and Laboski 2012).

Chemical Sequential Fractionation

Results from the sequential fractionation showed that water-soluble P ranged from 34 to 46% of the total sorbed P in soils from the United States and from 10 to 18% of the total sorbed P in soils from Brazil (Table 3). In contrast, the percentage of sorbed P that was resin-extractable was greatest in soils from Brazil and lowest in soils from the United States (Table 3). This difference is most likely to be a result of differences in clay mineralogy among the origins of the soils. The Brazilian soils used in this study are mostly comprised of 1:1 clay minerals such as kaolinite and Fe oxyhydroxide minerals such as goethite, whereas soils from the United States (such as the ones used here) are mostly comprised of 2:1 clays such as those present in the smectite and vermiculite groups. As reported by Shang et al. (2013) 1:1 clay minerals can adsorb a significant greater amount of P than 2:1 clay minerals. Together, the water- and resin-extractable P accounted for 67% on average of the total P extracted in the sequential fractionation (Table 3). The amount of P recovered in the $NaHCO_3$, NaOH, and HCl fractions showed no distinct separation between the soil origin as those observed for the water and resin fractions. Overall, on average, $NaHCO_3$ extracted 14% of total P, NaOH extracted 12% of total P, and HCl extracted 7% of total P (Table 3). Hedley et al. (1982) used the results from the sequential fractionation to separate the data into two functional groups: a labile pool and a nonlabile pool. If the same approach is used in the current study, then, on average, 81% of the P sorbed during the sorption study was sorbed into the

Table 3. Sorption strength calculated on the basis of P recovered in each fraction, the percentage of P recovered in each fraction, weighted sorption strength based on sequential P extraction in water (Wk_f, according to Eq. [4]), and measured sorption strength based on sequential P extraction in water (k_f).

	Water		Resin		$NaHCO_3$		NaOH		HCl				
Soil series	k_{fw}	%†	k_{fr}	%	k_{fb}	%	k_{fn}	%	k_{fh}	%	Wk_{ft}	k_f	LSD‡
Brazil-A	0.218	18	0.329	48	0.234	13	0.421	20	0.579	1	0.318	0.320	0.25
Brazil-C	0.101	15	0.285	54	0.157	12	0.472	18	0.327	1	0.276	0.286	0.25
Brazil-D	0.058	10	0.284	48	0.225	15	0.462	19	0.719	7	0.318	0.322	0.43
Brazil-E	0.079	12	0.464	48	0.156	17	1.570	12	1.887	12	0.661	0.466	0.35
Clarion	0.063	43	0.120	26	0.091	13	0.109	12	0.154	7	0.093	0.095	0.04
Cordova	0.055	46	0.055	23	0.138	13	0.108	9	0.123	9	0.077	0.080	0.06
Estherville	0.131	43	0.138	25	0.457	10	0.011	15	0.426	6	0.167	0.146	0.16
Fargo	0.024	45	0.042	24	0.082	9	0.092	9	0.130	13	0.054	0.054	0.05
Gunclub	0.050	41	0.157	28	0.042	11	–§	6	–§	14	0.069	0.077	0.04
Hubbard	0.091	43	0.182	24	0.172	15	0.001	13	0.047	5	0.112	0.105	0.07
Nicollet	0.067	39	0.136	33	0.194	13	0.069	10	0.012	4	0.105	0.090	0.04
Normania	0.052	35	0.093	31	0.123	14	0.223	13	0.333	6	0.115	0.099	0.07
Storden	0.060	40	0.083	28	0.094	14	0.606	13	0.064	5	0.145	0.085	0.19
Ves	0.048	34	0.128	30	0.140	15	0.314	17	0.089	5	0.133	0.103	0.05
Waukegan	0.066	42	0.154	30	0.216	12	0.279	11	0.139	6	0.137	0.110	0.07
Wheatville	0.075	39	0.037	24	0.217	18	–§	3	–§	16	0.077	0.100	0.04
Zimmerman	0.053	46	0.105	28	0.143	7	0.002	2	0.280	4	0.075	0.089	0.04

† Percent is calculated as:

$$\frac{\sum_{r=1}^{6}\left(\frac{P_{xr}}{P_{tr}}\right)100}{6}$$

, where *P* is the amount of P sorbed, *x* is the specific fraction, and *r* is the P concentration.

‡ LSD between Wk_{ft} and k_f.

§ Not determined because no relationship was observed (flat response).

Table 4. Maximum P desorption within each fraction (b_{fx}) and percentage recovered in the water + resin (Wa+Res, the most soluble fractions), water + resin + $NaHCO_3$ (W+R+B, total labile fraction), and NaOH + HCl (Na+HCl, nonlabile fraction) fractions.

Soil series	Water (b_{fw})	Resin (b_{fr})	$NaHCO_3$ (b_{fb})	NaOH (b_{fn})	HCl (b_{fh})	b_{ft}	b_f	LSD†	Wa+Res	W+R+B	Na+HCl
	mg P kg^{-1}								%		
Brazil-A	79	153	44	47	4	326	322	52	71	84	16
Brazil-C	156	324	83	73	4	640	606	119	75	88	12
Brazil-D	91	222	69	48	10	441	407	103	71	87	13
Brazil-E	163	269	139	79	19	668	604	80	65	85	15
Clarion	173	88	44	41	22	368	358	38	71	83	17
Cordova	220	113	43	21	33	429	411	67	77	87	13
Estherville	111	63	21	47	13	254	249	38	68	76	24
Fargo	199	130	36	17	49	431	483	116	76	85	15
Gunclub	201	85	56	30	40	412	391	95	69	83	17
Hubbard	110	53	34	42	17	256	250	40	64	77	23
Nicollet	180	117	42	46	48	433	406	86	69	78	22
Normania	196	143	60	46	20	465	444	46	73	86	14
Storden	150	94	45	28	19	336	330	41	73	86	14
Ves	190	119	55	52	23	440	421	34	70	83	17
Waukegan	172	90	33	27	20	342	336	39	77	86	14
Wheatville	167	133	58	19	51	427	395	81	70	84	16
Zimmerman	79	37	8	6	3	134	147	17	87	93	7

† LSD between cumulative b_{fx} (b_{ft}) and sorption maximum based on sequential P extraction (b_f).

labile pool (water + resin + $NaHCO_3$). These results contradict our hypothesis that soils with high k values would have a greater amount of NaOH- and HCl-extractable P after the sorption study was completed. The results of this study further challenge the real meaning of the parameters determined by sorption studies. It appears that the k value is more closely related to water- and resin-extractable P, which have been considered to be weakly bound P, than to the more stable P forms extractable in NaOH and HCl.

The data collected from the sequential fractionation were used to separate the sorption parameters k_f and b_f into the five different fractions measured (Table 3 and Table 4, and Fig. 1 and Fig. 2). Table 3 and Table 4 show the partition of k_{fx} and b_{fx} in each fraction and their respective percentages as a function of total P sorbed. The LSD values presented in Table 3 show that there were few differences between the k_f values and the Wk_{ft} values. Therefore, partitioning the k_f values into the five different fractions could be a useful tool for better understanding the significance of the soil k_f values. Figure 1 and Fig. 2 show the additive effect and the contribution of each fraction to the total amount of P sorbed for two soils (Clarion and Brazil-A). Although the shape of the isotherm and the maximum sorption value are different among all 17 soils used, it is easy to infer from Fig. 1 and Fig. 2 that during a sorption study, most P is sorbed to the labile pool. The data presented in Fig. 1 and Fig. 2 very clearly show the difference in the amount of P recovered in the water and resin extraction in relation to the total P recovered, emphasizing the role that clay mineralogy plays in sorption studies.

Stepwise regression analysis was used to find the soil properties that were more likely to influence each of the k values estimated in this study (Table 5). The use of stepwise regression could help us to develop models that would estimate the k and b values directly from the soil properties as opposed to having to perform sorption studies in any given soil to obtain those parameters. The results of the stepwise regression showed that good fits were observed for k_{fr} and k_{fn}; moderate fits were observed for k_i, k_f, and k_{fw}; and very poor fits were observed for k_{fb} and k_{fh} (Table 5). There were no consistent trends for the two parameters k_{fh} and k_{fb}, which had the poorest fits (Table 5). In general, the soil properties of extractable Ca and Al, soil OM, pH, and initial P status were found to

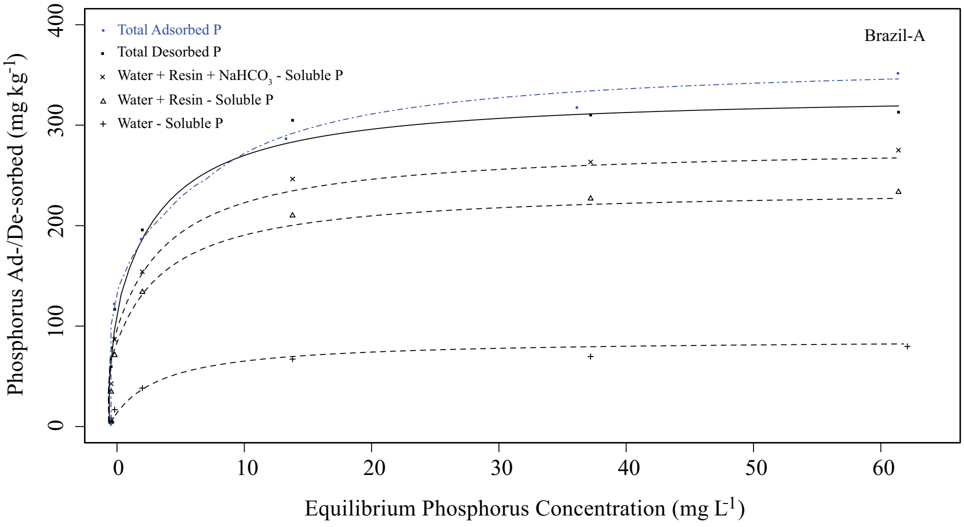

Fig. 1. Cumulative contribution of P soluble in water, water + resin, water + resin + $NaHCO_3$, and total sequentially extracted P on the total sorbed P for the Brazil-A soil.

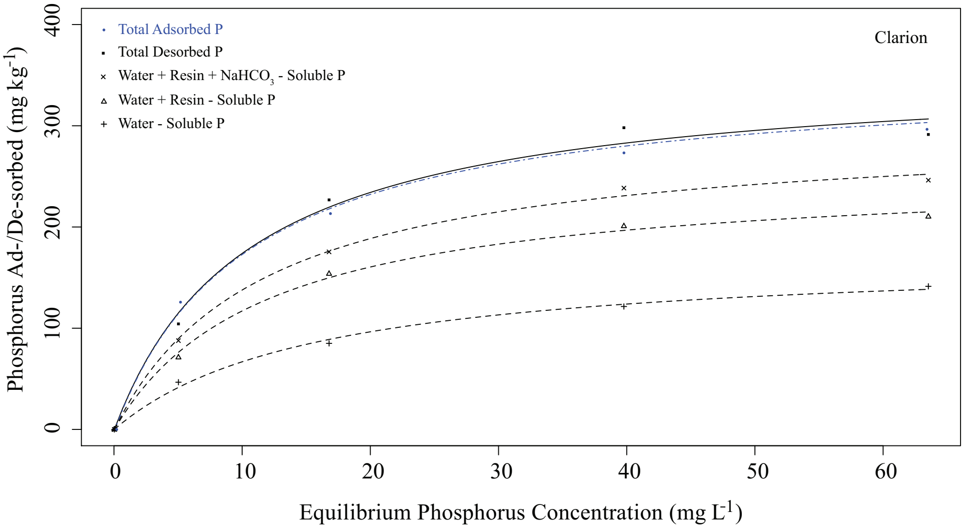

Fig. 2. Cumulative contribution of P soluble in water, water + resin, water + resin + $NaHCO_3$, and total sequentially extracted P on the total sorbed P for the Clarion soil.

be the major contributors to a soil *k* value. Other researchers have also reported that P sorption in soils is dependent on pH, Ca, the initial P status of the soils, and OM (Weng et al., 2012; Perassi and Borgnino 2014). However, Kang et al. (2009) and Weng et al. (2012) reported that dissolved OM in soil can reduce the sorption potential of a soil because of its interaction with Al and Fe, which would otherwise sorb P from solution and organic compounds can out-compete phosphate groups for biding sites. In our study, soil OM also had a negative impact on the k_i and k_f parameters (Table 1 and Table 2). The Cordova, Fargo, and Gunclub soils had high levels of soil OM and the lowest k_i and k_f parameters. The fact that the initial P status (Olsen or Bray−1 extractable P) of the soils correlates with multiple k_f values suggests that either the soil test P or the modified Hedley fractionation procedure lacks specificity regarding which forms of P are extracted.

Table 5. Summary of stepwise regression used to correlate the sorption parameters sorption strength parameter (*k*) estimated using the method of Nair et al. (1984) (k_i), sorption strength parameter determined using the sequential fractionation data (k_f), *k* from the water fraction (k_{fw}), *k* from the resin fraction (k_{fr}), *k* from the $NaHCO_3$ fraction (k_{fb}), *k* from the NaOH fraction (k_{fn}), k from the HCl fraction (k_{fh}), estimated sorption (b_i), sorption maximum (*b*)determined from the sequential fractionation data (b_f), *b* from the water fraction (b_{fw}), *b* from the resin fraction (b_{fr}), *b* from the $NaHCO_3$ fraction (b_{fb}), *b* from the NaOH (b_{fn}), and *b* from the HCl fraction (b_{fh}) with soil properties.

Sorption parameter	Soil properties indicated by the stepwise regression	R^2
k_i	pH, Olsen, Mg, b_i	0.71
k_f	OM†, Bray-1, Ca, Al, Fe	0.65
k_{fw}	Sand, OM, Olsen, Bray-1, Fe	0.66
k_{fr}	Sand, pH, OM, Ca, Al, Fe, b_{fr},	0.85
k_{fb}	Bray-1	0.12
k_{fn}	pH, OM, Bray-1, Ca, Al, Fe	0.87
k_{fh}	Clay, Ca, Al	0.27
b_i	Sand, pH, OM, Al, Fe, k_i	0.88
b_f	Sand, Al, Fe	0.78
b_{fw}	Clay, Sand, Ca, Mg	0.73
b_{fr}	Sand, pH, Olsen, Bray-1, Ca, Al, Fe, k_{fr}	0.91
b_{fb}	Sand, OM, Ca	0.55
b_{fn}	Clay, Ca, Mg	0.70

† OM, organic matter

The contribution of each k_{fx} value ($\%k_{fx}$) to the total Wk_{ft} can be calculated by multiplying k_{fx} by the percentage in the respective *x* fraction and then dividing it by Wk_{ft}. The $\%k_{fw}$ (the water fraction) contributed 1 to 37% of Wk_{ft}, $\%k_{fr}$ (resin) contributed 7 to 58% of Wk_{ft}, $\%k_{fb}$ (the $NaHCO_3$ fraction) contributed 4 to 32% of Wk_{ft}, $\%k_{fn}$ (the NaOH fraction) contributed 0 to 56% of Wk_{ft}, and $\%k_{fh}$ (the HCl fraction) contributed 0 to 37% of k_{ft} (data calculated directly from Table 3). Separating the data into the labile and non-labile pools shows that the labile pool contributed from 39 to 98% to the Wk_{ft}; while the remaining 2 to 61% was the non-labile contribution. Penn et al. (2014) reported that during P titration studies used to develop sorption isotherms, it was observed that at low P concentrations, P tended to sorb to soil through ligand exchange sites; whereas at higher P concentrations, P was likely to precipitate with Al and Fe. In a separate study, Perassi and Borgnino (2014) investigated P sorption onto $CaCO_3$ montmorillonite and P was found to precipitate with Ca under high solution P concentrations, whereas at low concentrations, P seems to sorb to carbonates surfaces (Olsen and Watanabe 1957; Castro and Torrent 1998). Olsen and Watanabe (1957) suggested that during a P sorption study, there is an initial chemisorption of P onto Al, Fe, and Ca sorbed onto the edges of clay minerals; with time, or after drying, some of the P could start to precipitate and become unexchangeable. Tunesi et al. (1999), who studied P behavior in calcareous soils, reported that sorption predominated at low concentrations (below ~0.5 mM); above this level, precipitation became predominant. Our results corroborate the results of Penn et al. (2014), Perassi and Borgnino (2014), and Olsen and Watanabe (1957) as a small portion of the P was indeed found in the NaOH fraction, which has been reported to be mostly Al- and Fe-precipitated P, and in the HCl fraction, which has been reported to be mostly Ca-precipitated P (Hedley et al., 1982). However, in our study, the percentage of P recovered in the NaOH and HCl fraction with respect to the total P sorbed for any given concentration was constant (data not reported). This suggests that either P precipitation was taking place at all times during our experiment regardless of the solution P concentration or that the same percentage of P from any concentration would precipitate as a result of drying prior to sequential fractionation. The fact that our results suggest that P precipitation was probably taking place at all times contradicts the results of other researchers, who reported that P precipitation during adsorption studies are related to the solution P concentration (Arai and Sparks, 2007, Gérard, 2016). As indicated earlier, solution P concentrations lower than 2.5 mg P L^{-1} were omitted to better address the objective of this study. However, one might argue that using lower concentrations (<2.5 mg P L^{-1}) could help elucidate the questions of when or at which concentration P precipitation starts to develop or stops. Therefore, future work should investigate the P sorption behavior in lower P concentrations that were omitted in this research. In addition, the use of modern techniques such as X-ray adsorption near-edge spectroscopy could help in the differentiation of precipitation and sorption in the different P pools.

In the present study, the parameter b_f was also partitioned into five subparameters (b_{fx}) for each respective sequentially extracted fraction (Table 4). Table 4 presents the values for b for each individual fraction (b_{fx}), the contribution of each b_{fx} within b_{ft} and also within b_f. In general, b_{fw} and b_{fh} tended to be higher in soils from the United States, whereas b_{fr}, b_{fb}, and b_{fn} tended to be higher in the soils from Brazil. However, these differences disappear when labile P (water + resin + $NaHCO_3$) and nonlabile P (NaOH + HCl) are considered (Table 4). On average, water and resin extracted similar amounts of P from the soils studied, which was about three, five, and six times higher than the P extracted in the $NaHCO_3$, NaOH, and HCl fractions, respectively (Table 4). The most soluble fractions, water- and resin-soluble P, contributed 72% on average to the total b_{ft}. Adding the $NaHCO_3$ fraction to the water- and resin-soluble P, or the total labile pool, increased the average to 84%, whereas the nonlabile pool accounted for an average of 16% of b_{ft} in the soils studied. As observed for Wk_{ft}, b_{ft} mostly comprised relatively soluble soil-bound P. Stepwise regression was also used to try to explain the variability in b_i, b_f, b_{fw}, b_{fr}, b_{fb}, b_{fn}, and b_{fh} using the measured soil properties (Table 5). Regression models with good fit were also observed for the b parameters (Table 5). The soil properties that had the greatest influence on the b parameters were soil texture, pH, Ca, Al, and Fe. Soil OM was not a significant factor for the b parameter, which contradicts the results of Kang et al. (2009) and Weng et al. (2012), who reported that high OM levels would minimize a soil's ability to adsorb P from a solution.

CONCLUSION

Sorption studies have been done to provide an understanding of the binding energy and amount of P that a soil can hold. However, until this study was performed, there were no data showing the distribution of P within the different pools after sorption studies were completed. The results of this study are noteworthy, as they show a consistent distribution of P into the different pools, labile and nonlabile, regardless of the measured sorption strength values. The major difference among the soils used was observed for the labile pool, as the Brazilian soils were found to have greater concentrations of resin-extractable and lower concentrations of water-extractable P than the US soils. In general, the majority of the P (>59%) was found in the water and resin fractions, which are considered the most labile pools where the binding energy is assumed to be low. In contrast, less than 25% of the sorbed P was found in the nonlabile pools, where the P binding energy is assumed to be the greatest. Although less than 25% of the sorbed P was found in the non-labile pools, the NaOH and HCl fractions contributed from 2 to 61% to the overall sorption strength estimated for the soils studied. The results of this study suggest that sorption strength calculated on the basis of sorption studies are heavily skewed toward the nonlabile fraction, which was found to constitute a very small portion of the binding sites occupied during sorption studies. In conclusion, neither isotherm studies nor the chemical fractionation used here can provide specific information about the chemical form of P and how it is bound to soil particles. Techniques such as X-ray adsorption near-edge spectroscopy and nuclear magnetic resonance are likely to be needed to determine the chemical structure of P after sorption studies have been performed.

REFERENCES

Abdala, D.B., I.R. da Silva, L. Vergütz, and D.L. Sparks. 2015. Long-term manure application effects on phosphorus speciation, kinetics and distribution in highly weathered agricultural soils. Chemosphere 119:504–514. doi:10.1016/j.chemosphere.2014.07.029

Allen, B.L., and A.P. Mallarino. 2006. Relationships between extractable soil phosphorus and phosphorus saturation after long-term fertilizer or manure application. Soil Sci. Soc. Am. J. 70:454–463. doi:10.2136/sssaj2005.0031

Arai, Y., and D. Sparks. 2007. Phosphate reaction dynamics in soils and soil components: A multiscale approach. Adv. Agron. 94:135–179. doi:10.1016/S0065-2113(06)94003-6

Bache, B.W., and E.G. Williams. 1971. A phosphate sorption index for soils. J. Soil Sci. 22:289–301. doi:10.1111/j.1365-2389.1971.tb01617.x

Bair, K.E., J.R. Davenport, and S.D. Burton. 2014. Speciation of phosphorus in anthropogenically acidified soils. Soil Sci. Soc. Am. J. 78:1474–1480. doi:10.2136/sssaj2013.12.0540

Bortoluzzi, E.C., C.A.S. Pérez, J.D. Ardisson, T. Tiecher, and L. Caner. 2015. Occurrence of iron and aluminum sesquioxides and their implications for the P sorption in subtropical soils. Appl. Clay Sci. 104:196–204. doi:10.1016/j.clay.2014.11.032

Bouyoucos, G.J. 1962. Hydrometer method improved for making particle size analyses of soils. Agron. J. 54:464–465. doi:10.2134/agronj1962.00021962005400050028x

Brown, J.R. 1998. Recommended chemical soil test procedures for the North Central Region. Missouri Agricultural Experiment Station, University of Missouri–Columbia. http://msue.anr.msu.edu/uploads/234/68557/Rec_Chem_Soil_Test_Proce55c.pdf (accessed 14 Dec. 2016).

Buehler, S., A. Oberson, I.M. Rao, D.K. Friesen, and E. Frossard. 2002. Sequential phosphorus extraction of a P-labeled Oxisol under contrasting agricultural systems. Soil Sci. Soc. Am. J. 66:868–877. doi:10.2136/sssaj2002.8680

Castro, B., and J. Torrent. 1998. Phosphate sorption by calcareous Vertisols and Inceptisols as evaluated from extended P-sorption curves. Eur. J. Soil Sci. 49:661–667. doi:10.1046/j.1365-2389.1998.4940661.x

Chien, S.H., D. Edmeades, R. McBride, and K.L. Sahrawat. 2014. Review of maleic–itaconic acid copolymer purported as urease inhibitor and phosphorus enhancer in soils. Agron. J. 106:423–430. doi:10.2134/agronj2013.0214

Cross, A.F., and W.H. Schlesinger. 1995. A literature review and evaluation of the Hedley fractionation: Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. Geoderma 64:197–214. doi:10.1016/0016-7061(94)00023-4

de Mesquita Filho, M.V., and J. Torrent. 1993. Phosphate sorption as related to mineralogy of a hydrosequence of soils from the Cerrado region (Brazil). Geoderma 58:107–123. doi:10.1016/0016-7061(93)90088-3

do Nascimento, Carlos A.C., P.H. Pagliari, D. Schmitt, Z. He, and H. Waldrip. 2015. Phosphorus concentrations in sequentially fractionated soil samples as affected by digestion methods. Sci. Rep. 5:17967. doi:10.1038/srep17967

Delgado, A., and J. Torrent. 2000. Phosphorus forms and desorption patterns in heavily fertilized calcareous and limed acid soils. Soil Sci. Soc. Am. J.

64:2031–2037. doi:10.2136/sssaj2000.6462031x

Devau, N., P. Hinsinger, E. Le Cadre, B. Colomb, and F. Gérard. 2011. Fertilization and pH effects on processes and mechanisms controlling dissolved inorganic phosphorus in soils. Geochim. Cosmochim. Acta 75:2980–2996. doi:10.1016/j.gca.2011.02.034

Eriksson, A.K., J.P. Gustafsson, and D. Hesterberg. 2015. Phosphorus speciation of clay fractions from long-term fertility experiments in Sweden. Geoderma 241-242:68–74. doi:10.1016/j.geoderma.2014.10.023

Freeman, J.S., and D.L. Rowell. 1981. The adsorption and precipitation of phosphate onto calcite. J. Soil Sci. 32:75–84. doi:10.1111/j.1365-2389.1981.tb01687.x

Gama-Rodrigues, A.C., M.V.S. Sales, P.S.D. Silva, N.B. Comerford, W.P. Cropper, and E.F. Gama-Rodrigues. 2014. An exploratory analysis of phosphorus transformations in tropical soils using structural equation modeling. Biogeochemistry 118:453–469. doi:10.1007/s10533-013-9946-x

Gérard, F. 2016. Clay minerals, iron/aluminum oxides, and their contribution to phosphate sorption in soils. A myth revisited. Geoderma 262:213–226. doi:10.1016/j.geoderma.2015.08.036

Guardini, R., J.J. Comin, D.R. Dos Santos, L.C. Gatiboni, T. Tiecher, D. Schmitt, et al. 2012. Phosphorus accumulation and pollution potential in a hapludult fertilized with pig manure. Rev. Bras. Cienc. Solo 36:1333–1342. doi:10.1590/S0100-06832012000400027

Havlin, J.L., S.L. Tisdale, J.D. Beaton, and W.L. Nelson. 2005. Soil fertility and fertilizers: An introduction to nutrient management. 7.ed. Pearson Education, Upper Saddle River, NJ.

He, Z., and C.W. Honeycutt. 2005. A modified molybdenum blue method for orthophosphate determination suitable for investigating enzymatic hydrolysis of organic phosphates. Commun. Soil Sci. Plant Anal. 36:1373–1383. doi:10.1081/CSS-200056954

He, Z., H. Waldrip, C.W. Honeycutt, M.S. Erich, and Z. Senwo. 2009. Enzymatic quantification of phytate in animal manure. Commun. Soil Sci. Plant Anal. 40:566–575. doi:10.1080/00103620802647116

Hedley, M., and M. McLaughlin. 2005. Reactions of phosphate fertilizers and by-products in soils. In: J.T. Sims and A,N. Sharpley, editors, Phosphorus: Agriculture and the environment. ASA, CSSA, and SSSA, Madison, WI. p. 181–252.

Hedley, M.J., R.E. White, and P.H. Nye. 1982. Plant-induced changes in the rhizosphere of rape (*Brassica napus* var. Emerald) seedlings. III. Changes in *L* value, soil phosphate fractions and phosphatase activity. New Phytol. 91:45–56. doi:10.1111/j.1469-8137.1982.tb03291.x

Hinsinger, P. 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: A review. Plant Soil 237:173–195. doi:10.1023/A:1013351617532

Kamprath, E.J. 1999. Changes in phosphate availability of ultisols with long-term cropping. Commun. Soil Sci. Plant Anal. 30:909–919. doi:10.1080/00103629909370256

Kang, J., D. Hesterberg, and D.L. Osmond. 2009. Soil organic matter effects on phosphorus sorption: A path analysis. Soil Sci. Soc. Am. J. 73:360–366. doi:10.2136/sssaj2008.0113

Khatiwada, R., G.M. Hettiarachchi, D.B. Mengel, and M. Fei. 2012. Speciation of phosphorus in a fertilized, reduced-till soil system: In-field treatment incubation study. Soil Sci. Soc. Am. J. 76:2006–2018. doi:10.2136/sssaj2011.0299

Laboski, C.A.M., and J.A. Lamb. 2004. Impact of manure application on soil phosphorus sorption characteristics and subsequent water quality implications. Soil Sci. 169:440–448. doi:10.1097/01.ss.0000131229.58849.0f

Leytem, A.B., and D.T. Westermann. 2003. Phosphate sorption by Pacific Northwest calcareous soils. Soil Sci. 168:368–375. doi:10.1097/01.ss.0000070911.55992.0e

Lombi, E., K. Scheckel, R. Armstrong, S. Forrester, J. Cutler, and D. Paterson. 2006. Speciation and distribution of phosphorus in a fertilized soil. Soil Sci. Soc. Am. J. 70:2038–2048. doi:10.2136/sssaj2006.0051

Marshall, S.K., and C.A.M. Laboski. 2006. Sorption of inorganic and total phosphorus from dairy and swine slurries to soil. J. Environ. Qual. 35:1836–1843. doi:10.2134/jeq2005.0281

McLaughlin, M.J., T.M. McBeath, R. Smernik, S.P. Stacey, B. Ajiboye, and C. Guppy. 2011. The chemical nature of P accumulation in agricultural soils—implications for fertiliser management and design: An Australian perspective. Plant Soil 349:69–87. doi:10.1007/s11104-011-0907-7

Muljadi, D., A. Posner, and J. Quirk. 1966a. The mechanism of phosphate adsorption by kaolinite, gibbsite, and pseudoboehmite. Part I: The isotherms and the effects of pH on adsorption. J. Soil Sci. 17:212–228. doi:10.1111/j.1365-2389.1966.tb01467.x

Muljadi, D., A. Posner, and J. Quirk. 1966b. The mechanism of phosphate adsorption by kaolinite, gibbsite, and pseudoboehmite. Part II: The location of the adsorption sites. J. Soil Sci. 17:212–228. doi:10.1111/j.1365-2389.1966.tb01467.x

Murphy, J., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27:31–36. doi:10.1016/S0003-2670(00)88444-5

Nair, P.S., T.J. Logan, A.N. Sharpley, L.E. Sommers, M.A. Tabatabai, and T.L. Yuan. 1984. Interlaboratory comparison of a standardized phosphorus adsorption procedure. J. Environ. Qual. 13:591–595. doi:10.2134/jeq1984.00472425001300040016x

Negassa, W., and P. Leinweber. 2009. How does the Hedley sequential phosphorus fractionation reflect impacts of land use and management on soil phosphorus: A review. J. Plant Nutr. Soil Sci. 172:305–325. doi:10.1002/jpln.200800223

Oliveira, C.M.B., L.C. Gatiboni, D.J. Miquelluti, T.J. Smyth, and J.A. Almeida. 2014. Capacidade máxima de adsorção de fósforo e constante de energia de ligação em latossolo bruno em razão de diferentes ajustes do modelo de langmuir. Rev. Bras. Cienc. Solo 38:1805–1815. doi:10.1590/S0100-06832014000600015

Olsen, S.R., and F.S. Watanabe. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Sci. Soc. Am. J. 21:144–149. doi:10.2136/sssaj1957.03615995002100020004x

Pagliari, P.H., and C.A.M. Laboski. 2012. Investigation of the inorganic and organic phosphorus forms in animal manure. J. Environ. Qual. 41:901–910. doi:10.2134/jeq2011.0451

Penn, C., D. Heeren, G. Fox, and A. Kumar. 2014. Application of isothermal calorimetry to phosphorus sorption onto soils in a flow-through system. Soil Sci. Soc. Am. J. 78:147–156. doi:10.2136/sssaj2013.06.0239

Penn, C., and D. Heeren. 2009. Investigating phosphorus sorption onto kaolinite using isothermal titration calorimetry. Soil Sci. Soc. Am. J. 73:560–567. doi:10.2136/sssaj2008.0198

Perassi, I., and L. Borgnino. 2014. Adsorption and surface precipitation of phosphate onto $CaCO_3$–montmorillonite: Effect of pH, ionic strength and competition with humic acid. Geoderma 232–234:600–608. doi:10.1016/j.geoderma.2014.06.017

R Development Core Team. 2007. R: A language and environment for statistical computing. R Foundation for Statistical Computing. http://www.R-project.org (accessed 13 Dec. 2016).

Shang, C., L. Zelazny, D. Berry, and R. Maguire. 2013. Orthophosphate and phytate extraction from soil components by common soil phosphorus tests. Geoderma 209:22–30. doi:10.1016/j.geoderma.2013.05.027

Sharpley, A.N. 1995. Dependence of runoff phosphorus on extractable soil phosphorus. J. Environ. Qual. 24:920–926. doi:10.2134/jeq1995.00472425002400050020x

Shigaki, F., and A.N. Sharpley. 2011. Phosphorus source and soil properties effects on phosphorus availability. Soil Sci. 176:502–507. doi:10.1097/SS.0b013e318225b457

Sparks, D.L. 2003. Environmental soil chemistry. Academic Press, San Diego, CA,

Torrent, J., U. Schwertmann, and V. Barron. 1992. Fast and slow phosphate sorption by goethite-rich natural materials. Clays Clay Miner. 40:14–21. doi:10.1346/CCMN.1992.0400103

Tunesi, S., V. Poggi, and C. Gessa. 1999. Phosphate adsorption and precipitation in calcareous soils: The role of calcium ions in solution and carbonate minerals. Nutr. Cycl. Agroecosyst. 53:219–227. doi:10.1023/A:1009709005147

Turner, B.L., and A.B. Leytem. 2004. Phosphorus compounds in sequential extracts of animal manures: Chemical speciation and a novel fractionation procedure. Environ. Sci. Technol. 38:6101–6108. doi:10.1021/es0493042

Violante, A., and M. Pigna. 2002. Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil Sci. Soc. Am. J. 66:1788–1796. doi:10.2136/sssaj2002.1788

Waldrip, H.M., P.H. Pagliari, Z. He, R.D. Harmel, N.A. Cole, and M. Zhang. 2015. Legacy phosphorus in calcareous soils: Effects of long-term poultry litter application. Soil Sci. Soc. Am. J. 79:1601–1614. doi:10.2136/sssaj2015.03.0090

Wang, Q., and Y. Li. 2010. Phosphorus adsorption and desorption behavior on sediments of different origins. J. Soils Sediments 10:1159–1173. doi:10.1007/s11368-010-0211-9

Weng, L., W.H. Van Riemsdijk, and T. Hiemstra. 2012. Factors controlling phosphate interaction with iron oxides. J. Environ. Qual. 41:628–635. doi:10.2134/jeq2011.0250