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Application of Isothermal Calorimetry to Phosphorus Sorption onto Soils in a Flow-Through System

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The degree, mechanisms, and kinetics of phosphorus (P) sorption onto soils can have a significant influence on leaching losses of P from soil. The objectives of this study were to measure the impact of retention time (RT) on P sorption in a flow-through system intended to simulate downward movement of a P solution through two different riparian soils, and determine if isothermal titration calorimetry (ITC) can provide useful information reflective of flow-through results. Topsoil from two riparian/alluvial sites (Barren Fork and Clear Creek) was sampled and characterized for P concentrations and parameters related to P sorption. Flow-through P sorption experiments were conducted to examine the effect of RT and inflow P concentration on P sorption; this was compared to results of ITC experiments where the heat of reaction was measured with the addition of P to soils. Results of ITC experiments were reflective of both soil characterization and flow-through sorption in that the Barren Fork soil sorbed less P, but at a faster rate, compared to Clear Creek. Based on thermograms, the dominant P sorption reaction was ligand exchange onto Al/Fe oxides/hydroxides, with a lesser degree of precipitation. Phosphorus removal for both soils was limited by physical nonequilibrium instead of chemical nonequilibrium (sorption kinetics). The calorimetry approach presented can help provide soil-specific information on the risk of P inputs to leaching (degree of P sorption) under different conditions (flow rate or RT), and potential for desorption (P sorption mechanisms).

Abbreviations: DPS, Degree of phosphorus saturation; ITC, Isothermal titration calorimetry; M3, Mehlich-3; WSP, Water soluble phosphorus.

Phosphorus transport from soils to surface waters is an important contributor to eutrophication (Ryther and Dunstan, 1971). Phosphorus losses from soils occur in both the particulate and dissolved forms. Particulate P consists of sediment that has P sorbed on it, and is typically transported in runoff. Dissolved P is simply P that is already in solution, free from the solid phase. Most best management practices (BMPs) focus on reducing particulate P that is transported in runoff through erosion control and capturing sediment before runoff exits a field or enters a water body (Fox and Penn, 2013; Rao et al., 2009). Such practices include no-till management, grassed waterways, vegetated buffer strips (VBS), and contour farming. Among floodplains, use of VBS along the riparian areas of the surface water is common (Fox and Penn, 2013; Fox et al., 2010; Muñoz-Carpena et al., 2010; Sabbagh et al., 2009; Osborne and Kovacic, 1993). However, while effective at reducing particulate P, VBS and other traditional BMPs are less effective at reducing dissolved P transport among soils recently amended with P and soils that have become excessive with regard to soil P concentrations (Fox and Penn, 2013; Owens and Shipitalo, 2006). In addition, most BMPs have little impact on reducing P leaching under such scenarios.

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In general, P will leach mostly in the dissolved form, except in cases of excessive preferential flow (Djodjic and Bergstrom, 2004; Simard, 2000). As dissolved P leaches downward from the high P topsoil or applied P amendment, the lower soil horizons can sorb P through several reactions depending on soil properties. Factors that control the quantity of P leaching are mostly related to soil chemical properties which dictate the capacity and kinetics of the soil to sorb P (Maguire and Sims, 2002), and physical properties that impact the rate of water movement through the soil profile (Fuchs et al., 2009) which can also impact the rate of P sorption. The kinetics of P sorption is critical to the P leaching process since the soil will have limited contact time (i.e., retention time) with the moving P-rich solution. Simply put, if the contact time required for adequate P sorption is greater than the contact time of the moving P solution, then limited P sorption will occur resulting in greater transport of P to the subsurface.

Movement of P downward is especially important in the riparian floodplains of northeastern Oklahoma and northwestern Arkansas since these alluvial soils possess a relatively shallow topsoil with underlying gravelly silt loam to gravelly loam. Not only do these gravelly subsoils have an extremely high hydraulic conductivity (Sauer and Logsdon, 2002; Sauer et al., 2005) that range from 0.2 to 844 m d⁻¹ (Fuchs et al., 2009), but they have also been shown to be directly hydrologically connected to adjacent streams via the gravel subsurface behaving as a stage-dependent storage zone (Heeren et al., 2011, 2010; Fuchs et al., 2009). Therefore, sorption of a leaching P solution by the thin topsoil is especially critical to preventing transport of dissolved P to surface waters.

Phosphorus transport requires both a P source and physical connectivity (Nelson and Shober, 2012). It is clear that as soils increase in P concentration, particularly as they become more saturated with P, the risk for P leaching increases if the hydraulic conditions are appropriate. Such information is easily obtained through soil testing. However, there are factors that influence the “gap” between P source and the physical transport of P, including P sorption mechanisms and kinetics of sorption. In regard to mechanisms, not only is the degree of P sorption important to potential P leaching, but the mechanism in which P is sorbed will dictate how strongly the P is held and under what conditions. For example, P bound with Ca typically becomes more soluble as the pH decreases. Kinetics can also influence P transport in the context of a moving solution (i.e., leaching) because of the time required for a sorption reaction to occur. Fuchs et al. (2009) found that a decreased contact time (increased flow rate) of a P solution through the fine fraction of a riparian subsoil resulted in a decrease in P sorption and therefore increase in P leaching.

This study proposes a new and simple tool to aid in studying P leaching; isothermal titration calorimetry (ITC) measures the heat of reaction while solutions or soil suspensions are titrated with chemicals (such as P). The quantity and patterns of heat measured can provide information on the degree of reaction, type of reaction, and kinetics (Harvey and Rhue, 2008; Rhue et al., 2002; and Kabengi et al., 2006a). For example, Penn and

Warren (2009) were able to distinguish between P sorbed by ligand exchange vs. surface precipitation in titration of kaolinite with a P solution. Calorimetry also provided useful information on kinetics in regard to ammonium exchange with potassium in zeolite materials (Penn et al., 2010). The objectives of this study were to measure the impact of contact (retention) time on P sorption in a flow-through system intended to simulate downward movement of a P solution through two different riparian soils, and determine whether ITC can provide useful information reflective of flow-through results.

MATERIALS AND METHODS

Soils

Two floodplain soils from within the Illinois River watershed were sampled for use in this study. The Barren Fork Creek site (latitude: 35.90°, longitude: -94.85°) is a fourth order stream with a historical median discharge of 3.6 m³ s⁻¹. The study area at the Barren Fork Creek was located on the outside of a meander bend which was being actively eroded by the stream. The soils were classified as Razort gravelly loam underlain with alluvial gravel deposits. Thickness of the loam ranged from 0.3 to 2.0 m, with dry bulk densities ranging from 1.3 to 1.7 g cm⁻³. The Clear Creek alluvial floodplain site flows into the Illinois River (latitude: 36.13°, longitude: -94.24°). Soils were loamy and silty, deep, moderately well drained to well drained. Thickness of the top loam layer ranged from 0.3 to 2.0 m, with dry bulk densities ranging from 1.5 to 1.7 g cm⁻³. The land use in the study area was pasture and consisted of Razort (Fine-loamy, mixed, active, mesic Mollic Hapludalfs) gravelly loam soils. Both soils were sampled at a depth of 0 to 10 cm. Soils were air-dried and sieved to 2 mm for extraction and use in ITC experiments.

Soil Characterization

All analyses were conducted in duplicate. Soil characterization consisted of (i) pH and electrical conductivity (EC; 1:1 soil/solution ratio); (ii) organic matter by combustion; (iii) sand, silt, and clay by the hydrometer method (Day, 1965); (iv) water soluble (WS) P, Al, Fe, and Ca (1:10 soil/deionized water, 1-h reaction time, filtration with 0.45-μm Millipore membrane [Kuo, 1996]); (v) specific surface area by gas adsorption (N₂: 16-h outgassing at 160°C) with a BET isotherm as determined by an Autosorb-1C (Quantachrome, Boynton Beach, FL); (vi) oxalate extractable P, Al, and Fe (P_{ox}, Al_{ox}, Fe_{ox}; 1:40 soil: 0.2M acid ammonium oxalate (pH 3), 2-h reaction time in the dark; McKeague and Day, 1966); and (vi) Mehlich-3 (Mehlich, 1984) P, Al, and Fe (M3-P, M3-Al, and M3-Fe: 1:10 soil:0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.015 M NH₄F + 0.13 M HNO₃ + 0.001 M EDTA, 5 min reaction time, filtration with Whatman #42 paper [Kuo, 1996]); Extracted P, Ca, Al, and Fe were analyzed by ICP-AES. The ratio of Mehlich 3 and ammonium oxalate extractable P to (Al + Fe) (all values in mmol kg⁻¹) was expressed as:

$$\left[\frac{P}{(Al + Fe)} \right] 100 \quad [1]$$

and will be referred to as M3 degree of P saturation (DPS_{M3}) and ammonium oxalate degree of P saturation (DPS_{ox}). Note that this is exactly the same as the traditional soil degree of phosphorus saturation (DPS) calculations (Pautler and Sims, 2000) except without the empirical constant α which is used to relate soil P sorption capacity to Al_{ox} and Fe_{ox} and the denominator acts to express the effective total soil P sorption maximum. The α value was unknown, so no α value was used. Beauchemin and Simard (1999) noted that various studies have applied an α value of 0.5 to all soils, regardless of soil properties. The authors claimed that the α value is empirical and needs to be determined for each soil type and experimental conditions. In addition, Beck et al. (2004) recommended that the α value be omitted from the DPS calculation.

Flow-Through Phosphorus Sorption Experiments

To test the effect of retention time (RT) and P concentration on P sorption in a flow-through setting, flow-through cells (high density polyethylene) were constructed as described in Stoner et al. (2012). A diagram of the setup is found in Fuchs et al. (2009) and Penn and McGrath (2011). Depending on the P concentration and RT utilized, some soils were mixed with acid washed, lab-grade sand (pure Si sand, 14808–60–7; Acros organics, Morris Plains, NJ) to achieve a total pore volume of 1.26 cm^3 (5 g of sand + soil; 50% porosity). Soils were then placed in a flow-through cell. The proportion of soil to sand varied depending on how P sorptive the material was. Less soil mass was used for more sorptive soils tested under low P inflow concentrations. The mass of soil material used in a flow through cell varied from 1 to 5 g. A suitable amount that would not result in 100 or 0% P removal for the duration of the entire experiment was typically determined by trial and error. The purpose of this was to allow a more complete picture of P breakthrough (i.e., P sorption curve). A $0.45\text{-}\mu\text{m}$ filter was placed beneath the materials and the bottom of the cell was connected to a single channel peristaltic pump (VWR variable rate “low flow” and “ultra low flow”, 61161–354 and 54856–070) using plastic tubing. The desired RT ($\text{RT} [\text{min}] = \text{pore volume} [\text{mL}] / \text{flow rate} [\text{mL min}^{-1}]$) was achieved by varying the pump flow rate which pulled solution through the cell. Flow rates required to achieve the desired RTs of 3 and 10 min were 0.75 and 0.22 mL min^{-1} , respectively. Essentially, the RT is the amount of time required for the solution to pass through the cell. A constant head Mariotte bottle apparatus was used to maintain a constant volume of P solution on the soils. Materials were subjected to flow for 5 h in which the “outflow” from the cells was sampled at 0, 30, 60, 90, 120, 150, 180, 210, 240, 270, and 300 min. Solutions were analyzed for P by the Murphy-Riley molybdate blue method (Murphy and Riley, 1962). Discrete P sorption onto materials was calculated at each sampling time as a percentage decrease in outflow relative to inflow P concentration (i.e., source bottle). Results are presented as cumulative P sorption as a function of cumulative P addition (both in units of mg P kg^{-1} soil). Initial flow-through experiments were performed with KCl which im-

mediately flowed through the thin layer of soil with no retardation based on measured specific conductance.

Two different P concentrations were tested: 1 and 10 mg L^{-1} using solutions made from potassium phosphate. These P concentrations correspond with the range measured in studies of runoff from high P soils ($>300 \text{ mg kg}^{-1}$ Mehlich 3-P) or soils to which manure or chemical fertilizer P have been recently applied to the surface (Vadas et al., 2007; Edwards and Daniel, 1993). The matrix of the solution consisted of 5.6, 132, 110, 10, and 17 mg L^{-1} of Mg, Ca, S, Na, and K, respectively, using chloride and sulfate salts, followed by adjustment to pH 7. Note that ionic strength only slightly varied due to differences in P concentrations only. This matrix was chosen as it was found to be representative of agricultural runoff measured in a previous study. All flow-through RT and P concentration combinations were duplicated for each material.

Isothermal Titration Calorimetry Experiments

All ITC experiments were conducted on a CSC 4200 Isothermal Titration Calorimeter (CSC Inc., Lindon, UT) at 25°C . The ITC had a sensitivity of 0.418 mJ detectable heat effect and a “noise level” of $\pm 0.0418 \text{ mJ s}^{-1}$ (deconvoluted signal). For all soil ITC experiments, 100 mg of soil sample were placed in a 1.3-mL reaction vessel and suspended in 0.75 mL of deionized (DI) water. Soil titrations were replicated three times. For each experiment, a blank was determined by titration of a 0.01-M NaH_2PO_4 solution into deionized (DI) water under the same conditions employed for the actual experiment. Data produced from the blank titrations were subtracted from the sample titrations.

Two different types of titrations were conducted; 25 consecutive $10\text{-}\mu\text{L}$ titrations (300 s intervals) of P solution into the suspended soil sample, and a “single shot” titration consisting of all $250 \mu\text{L}$ of P solution. For both experiments, a 0.01 M NaH_2PO_4 solution was used as the titrant and soil suspensions were stirred in the reaction vessel throughout the duration of the experiment. With regard to the single shot test, after titration, change in heat was monitored for 5 h.

Statistical Analysis

All values were averaged over replication. The log of the relationship between cumulative P added to soil and cumulative P sorption was tested among each set of conditions (i.e., inflow P concentration and RT) to determine whether the relationships (slope and intercept) were significantly different from each other at $P = 0.05$. The null hypothesis was that one equation could be used to describe cumulative P sorption vs. cumulative P addition for both soils. This was tested by using a series of “contrast” statements in SAS (SAS Institute, 2003) to determine whether the slope and intercept were significantly different based on soil sample.

RESULTS AND DISCUSSION

Soil Properties

General soil properties important to P retention are shown in Table 1. Soil from the Barren Fork site was more acidic, and

as a result, contained more water soluble Al and Fe than the Clear Creek soil. The Barren Fork soil also contained more water soluble Ca. This is expected since Al, Fe, and Ca containing minerals tend to be more soluble in water as pH decreases below 7. However, ammonium oxalate extractable Al and Fe (Al_{ox} and Fe_{ox}) were greater in the Clear Creek soil. Soil Al and Fe that is extractable with ammonium oxalate is considered to represent amorphous Al and Fe minerals, which typically sorb and retain the majority of soil P among near neutral and acid soils (Schoumans, 2000; Sakadevan and Bavor, 1998; McKeague and Day, 1966). The greater value for DPS_{ox} for the Barren fork soils suggests that the main P sorption sites (Al_{ox} and Fe_{ox}) are more saturated with P than Clear Creek soils (Penn et al., 2006). Generally, as DPS_{ox} increases for soils, their capacity to further sorb additional P decreases, and the potential to release P to solution increases (Pautler and Sims, 2000). Evidence for this is clearly seen by the fact that the Barren Fork soils possessed greater water soluble P concentrations (Table 1). However, the water soluble P concentrations are below the threshold for increased P leaching (8.6 mg kg^{-1}) as proposed by Maguire and Sims (2002).

Although the soils contained appreciable amounts of Ca as indicated by the Mehlich-3 (M3) extraction, it was not very soluble based on the water extraction (Table 1). Only about 3 and 7% of Mehlich-3 extractable Ca was soluble in water for the Clear

Creek and Barren Fork samples, respectively. Mehlich-3 extractable Fe and Al was reflective of ammonium oxalate Al and Fe, except that ammonium oxalate extracted more than Mehlich-3 solution. Sims et al. (2002) suggested values of 10 to 15% DPS_{M3} as a threshold to identify soils with increased risk as P sources for nonpoint P transport. In addition, Maguire and Sims (2002) found that there was a "break-point" value of 20% for the relationship between DPS_{M3} and dissolved P in leachate. Above this 20% level, the concentration of dissolved P in leached increased rapidly with increases in DPS_{M3} . Soil organic matter (OM) was similar between soils (Table 1). Although OM is not related to P sorption in non-sandy soils with appreciable Al and Fe (Leinweber et al., 1997; Lookman et al., 1996; Mozaffari and Sims, 1994; Syers et al., 1971; Zhang et al., 2005), OM can indirectly impact P sorption through interaction with Fe and Al oxides and hydroxides. This interaction between OM and Al+Fe has been shown to increase the amorphous nature of Al and Fe oxides and hydroxides, thereby increasing surface area, and potential P sorption (Loveland et al., 1983; Mozaffari and Sims, 1996; Niskanen, 1990; Saunders, 1965). However, such interactions and the resulting amorphous nature of Fe and Al are accounted for through extraction with ammonium oxalate. This is why most studies conducted on P sorption indicate a strong correlation between P sorption and Al_{ox} , Fe_{ox} , and DPS_{ox} (Zhang et al., 2005; Sims et al., 2002; Khiari et al., 2000; Maguire and Sims, 2002).

Table 1. Characterization of the soils collected from two different riparian sites that were used in the flow-through sorption and calorimetry studies. All values in mg kg^{-1} unless shown otherwise.

Site	Clear Creek	Barren Fork
pH	6.3	5.8
EC, $\mu\text{S cm}^{-1}$	68	132
Organic matter, %	1.73	1.58
Surface area, $\text{m}^2 \text{ g}^{-1}$	10.14	9.04
Sand, %	16.3	41.3
Silt, %	61.3	37.5
Clay, %	22.5	21.3
WS Ca†	55	115
WS Fe	127	209
WS Al	238	370
WS P	2.6	7.1
Al_{ox} ‡	904	707
Fe_{ox}	2033	1955
P_{ox}	92	170
DPS_{ox} , %§	4.25	8.96
M3-Ca¶	1804	1698
M3-Fe	161	163
M3-Al	824	688
M3-P	2.5	49
DPS_{M3} , %‡	0.46	3.1

† Water soluble.

‡ Ammonium oxalate extractable.

§ Degree of phosphorus saturation. $P_{ox}/(Al_{ox}+Fe_{ox})$; calculated on a molar basis.

¶ Mehlich-3 extractable.

Degree of phosphorus saturation. $M3-P/(M3-Al+M3-Fe)$; calculated on a molar basis.

Phosphorus Sorption under Flow-Through Conditions

Under flow-through conditions of constant addition of 1 mg P L^{-1} inflow solution, the longer RT, or slower flow rate, appeared to reduce P sorption for the Barren Fork soil (Fig. 1a). However, this decrease in P removal with increase of RT from 3 to 10 min was not statistically significant with regard to the slope and intercept for the relationship shown in Fig. 1. Table 2 provides the slope and intercept values for the relationship between log cumulative P added and cumulative P sorbed, including statistical differences. Note that the relationship between cumulative P added and cumulative P sorbed was nearly exactly the same for the 3 and 10 min RT for the Clear Creek soil (Fig. 1b and Table 2). Similar results were obtained when an inflow P concentration of 10 mg P L^{-1} was used (Fig. 2a and 2b), except that the slope and intercept were statistically different between the 3 and 10 min RT for the Barren Fork soil (Table 2). After application of the P sorption data set to equations developed by Stoner et al. (2012) for estimating maximum P sorption under flow-through conditions, it was apparent that the Clear Creek soil was able to sorb more P under certain flow-through conditions compared with the Barren Fork soil.

Under inflow conditions of 10 mg P L^{-1} , maximum P sorption by the Clear Creek soil was 214 and 284 mg kg^{-1} (not significantly different) at a RT of 3 and 10 min, respectively, while Barren Fork could only remove a maximum of 165 and 127 mg kg^{-1} (significantly different) at a RT of 3 and 10 min, respectively. However, under inflow conditions of 1 mg P L^{-1} , the soils would remove similar maximum amounts of P; 103 and 101 mg kg^{-1} at

a RT of 3 and 10 min, respectively for Clear Creek compared with 100 and 88 mg kg⁻¹ at a RT of 3 and 10, respectively for Barren Fork. Note that there was no significant difference in P removal at a 1 mg P L⁻¹ inflow concentration between a 3 min and 10 min RT. The higher amount of P sorption for the Clear Creek soil is not a surprise since it possessed a lower DPS_{ox} and DPS_{M3}, meaning that it contained a greater number of “unused” P sorption sites than the Barren Fork soil. Hooda (2000) noted that the amount of P leached was dominantly a function of the soil P saturation.

The increase in P sorption for the Barren Fork soil at the lower RT compared with the higher RT (i.e., lower flow rate) may seem counter intuitive at first. However, it does suggest that P sorption kinetics were relatively fast for this soil. While increased RT can increase P sorption in some cases, this is less likely for a scenario with fast kinetics since little time would be required for sorption to take place. The overall P removal process consists of both physical and chemical processes. As P is sorbed by the soil through precipitation, anion exchange, or ligand exchange reactions, the reactants (solution P and available sorption surfaces or ions) are “used up” (decrease) and the products (sorbed P and any resulting ions) increase. The combination of the reduction of reactants and increase in products decreases the chemical potential for further sorption reactions to occur. Simply put, a faster flow rate (lower RT) removes solution reaction products and replenishes the depleted solution reactants (i.e., inflow P) more efficiently than a slow flow rate (higher RT), thereby resulting in a greater chemical potential for further P sorption at any given point (Penn and McGrath, 2011). A similar observation was made by Stoner et al. (2012) in examination of P removal by industrial by-products under flow-through conditions.

One hypothesis to explain this phenomenon would be that at an increased flow rate, the flow in the pore space would be more turbulent, which would reduce the thickness of the low velocity boundary layer of fluid near the mineral surface. More turbulent mixing would increase the transport within the pore, that is, from the bulk flow, through a smaller boundary layer via diffusion, and to the surface where sorption can occur. However, Reynolds numbers calculated from specific discharge during the flow through experiments and a characteristic grain size (d₅₀) (following Chin et al. [2009], and Bear, [1972]) ranged from 2 × 10⁻⁵ to 2 × 10⁻⁴. These are well below the critical Reynolds number (typically ranging from 1 to 10 for flow in porous media) where flow changes from Darcian/linear flow to transitional flow, and a Reynolds number of 100 where flow has become fully

Fig. 1. Cumulative P sorption onto soils in a flow-through setting with an inflow P concentration of 1 mg L⁻¹ using two different retention times (RT). Soils tested were sampled from the (a) Barren Fork and (b) Clear Creek sites.

turbulent. Peclet numbers (Pe) were 60 and 170 for the Barren Fork and Clear Creek sites, respectively, with Pe > 10 indicating that dispersion was negligible compared with advective transport. Although flow conditions in the flow cells were laminar according to this analysis, it should be remembered that this is not flow through a straight conduit but through a pore space with tortuosity, dead-end pores, and a wide range of pore sizes. These flow cell data for the Barren Fork soil indicate that, even under laminar flow, higher flow rates result in faster transport of reactants from the bulk flow to the mineral surface, and/or faster transport of reaction products away from the mineral surface

Table 2. Slope and intercept values for the relationship between log of cumulative phosphorus (P) added (mg kg⁻¹) and cumulative P sorbed (mg kg⁻¹) during the flow-through sorption experiments conducted at two different retention times (RT: 3 and 10 min) and inflow P concentrations (1 and 10 mg L⁻¹).

Soil	RT = 3 min		RT = 10 min	
	1 mg P L ⁻¹ inflow			
	Slope	Intercept	Slope	Intercept
Barren Fork	56.4	-52.7	46.9	-45.7
Clear Creek	55.9	-53.6	44.9	-39.4
	10 mg P L ⁻¹ inflow			
Barren Fork	130.7*	-177.9*	63.6	-73.5
Clear Creek	149.5	-214.5	144.1	-202.2

* indicates significant difference at P = 0.05 between RT 3 and 10 within soil type and inflow P concentration.

Fig. 2. Cumulative P sorption onto soils in a flow-through setting with an inflow P concentration of 10 mg L⁻¹ using two different retention times (RT). Soils tested were sampled from (a) the Barren Fork and (b) Clear Creek sites.

Fig. 3. Thermogram (a) for the titration of the Barren Fork soil with 0.01 mol L⁻¹ NaH₂PO₄ using an isothermal titration calorimeter; and (b) the heat curve produced by integration of the thermogram.

into the bulk flow. Either way, a higher flow rate prevented the sorption reaction from coming to a relatively “pre-mature chemical equilibrium,” that is, chemical equilibrium has been reached, but only because of limitations of the physical process. Increasing the flow rate reduces the physical limitation which allows the rate of P sorption to increase. Analogous to this is the observation that volatilization of a gas (a chemical process) can be prevented by imposing increased pressure (a physical process) on a system.

In other words, for the Barren Fork site it appears that P removal was limited by physical nonequilibrium at the pore scale. It should be noted that this process (transport from bulk flow to the mineral surface as a function of flow rate) is different than mechanical dispersion, which by definition occurs at a large enough scale to integrate the effects of many pores (Fetter, 1999).

Calorimetry as an Indicator of Phosphorus Sorption

Phosphorus can sorb to soils by several mechanisms: anion exchange, ligand exchange (adsorption), and precipitation. Soils with elevated pH (>8) and high soluble Ca concentrations are able to precipitate P as Ca phosphate minerals. However, this precipitation reaction occurs much more slowly at low pH levels compared with high pH. For soils at or below a pH of 7, P sorption dominantly occurs via ligand exchange mechanisms on the surface of amorphous Al and Fe oxide and hydroxide minerals (Violante, 2013). If there is Al and Fe in the soil solution, added P can also precipitate as Al and Fe phosphates. Under certain conditions, continued P loading to the surface of a Fe or Al oxy/hydroxide mineral can result in P removal by precipitation of Al or Fe phosphate at the surface of the Al or Fe source mineral (Kim and Kirkpatrick, 2004; Ler and Stanforth, 2003). Isothermal titration calorimetry data can be used to somewhat distinguish between these mechanisms. For example, exothermic (producing heat) reactions regarding P sorption in neutral and acid soils indicate ligand exchange mechanisms onto Al and Fe minerals and kaolinite (Appel et al., 2013; Penn and Zhang, 2010; Rhue et al., 2002; Harvey and Rhue, 2008). On the other hand, endothermic (absorbing heat) reactions indicate precipitation of Al and Fe phosphates (Penn and Warren, 2009; Rhue et al., 2002).

Figures 3 and 4 show that the heat of reaction decreases with each successive titration of P solution; this is expected since the P sorption sites are becoming saturated with each P addition. Examination of the 25 titrations of a P solution to the soils, and considering the near-neutral to acid pH of the soils, it appears that P sorption onto the Barren Fork (Fig. 3a) and Clear Creek (Fig. 4a) soils occurred by both ligand exchange

and Al/Fe phosphate precipitation. Note that there are 25 sets of peaks; one set for each P titration. In fact, Fig. 3a and 4a show that for each P addition, both an exothermic and endothermic reaction occurred. It is common for soils with pH 7 or less to display an initial exotherm immediately after titration of P, followed by a smaller endothermic peak (Penn and Zhang, 2010). However, notice that integration of each of the 25 titration peaks reveals that the net heat release for each additional titration becomes less exothermic and more endothermic (Fig. 3b and 4b). This indicates two processes. First, ligand exchange sites (i.e., terminal hydroxyls on the edges of Al/Fe oxyhydroxides) are becoming filled up or “saturated” with P, which decreases the chemical potential for further ligand exchange reactions; this decreases the exotherms. Second, the source Al and Fe minerals are able to slightly dissolve and produce Al and Fe for precipitation with P on the surface of the minerals; this increases the endotherms. Further evidence for precipitation of P was established by conducting a geochemical speciation of the solution using the MINTEQ2 program (Allison et al., 1991). A “sweep” was conducted to simulate the addition of P into the soil solution as performed in the calorimetry experiment; the model predicted precipitation of variscite (Al phosphate mineral). Due to the relatively high concentrations of water soluble Al and Fe measured in these soils (Table 1), it was not unexpected that added P would partially precipitate with such metals in solution. The use of calorimetry to detect simultaneous ligand exchange and precipitation reactions and general changes in mechanisms is also found in previous studies (Penn and Warren, 2009; Kabengi et al., 2006a; Partyka et al., 1989; Machesky et al., 1989; Imai et al., 1981).

A multiple linear regression equation was developed by Penn and Zhang (2010) to relate soil Al_{ox} and the heat of the first titration to P sorption in a batch isotherm which added 500 mg P kg^{-1} soil. Application of the heat of the first titration (Fig. 3 and 4) and Al_{ox} (Table 1) into this equation yielded a prediction of P sorption of 167 and 177 mg P kg^{-1} for the Barren Fork and Clear Creek soils, respectively. Note that these predicted P sorption values are similar to cumulative P sorption values under flow-through conditions at P loading values approaching 500 mg kg^{-1} (Fig. 2).

Examination of the single P titration to the soils provided valuable information regarding the degree of, and kinetics of P sorption. Figure 5 indicates that the degree of P sorption for the Clear Creek soil was greater than the Barren Fork soil as evidenced by the area under the peak. Several studies have related total heat release to the degree of P sorption (Harvey and Rhue, 2008; Miltenburg and Golterman, 1997; Imai et al., 1981). The greater heat release from P titration of Clear Creek compared with Barren Fork soil is supported by the larger amount of P sorption measured in the flow-through experiments (Fig. 1 and

Fig. 4. Thermogram (a) for the titration of the Clear Creek soil with $0.01 \text{ mol L}^{-1} \text{NaH}_2\text{PO}_4$ using an isothermal titration calorimeter; and (b) the heat curve produced by integration of the thermogram.

2). Note that overall P sorption was net exothermic even though both exothermic and endothermic reactions were occurring, suggesting that ligand exchange was the most dominant P removal mechanism as supported by Fig. 3 and 4. Observation of the single titration peaks also showed that P removal reactions by the Barren Fork soil were faster than Clear Creek (Fig. 5).

For example, the heat production rate after P addition to the Barren Fork soil returned to equilibrium in approximately 4 min (Fig. 5a). However, the broad peak for the Clear Creek soil suggests that P sorption was not completed until at least 50 min, although much of the reaction occurred within 10 min (Fig. 5b). While P sorption reactions (chemical process) indeed require time to occur, transport kinetics for sorbate from liquid to solid (soil) must also be considered. For example, Aharoni and Sparks (1991) describe sorbate transport processes in a solid–liquid system with several scenarios: transport of sorbate in the soil solution, transport across a liquid film at the solid–liquid interface, transport in a liquid-filled micropore, and diffusion of a sorbate at the soil surface or into a micropore. The “slow burn” (Rhue et al., 2002) displayed by the Clear Creek soil has been observed in other studies (Kabengi et al., 2006b; Harvey and Rhue, 2008). Since both soils were dominated by ligand exchange chemical mechanisms which are extremely fast (Sposito, 1994), a possible

Fig. 5. Thermogram for a single titration of 250 mL of 0.01 mol L⁻¹ NaH₂PO₄ into 0.1 g of soil sampled from the (a) Barren Fork and (b) Clear Creek sites. Peaks above zero indicate exothermic reactions. Titration made at 100 s. The inset shows the first 1000 s after titration for greater detail.

explanation for the long “slow burn” for P sorption in the Clear Creek soil is that after the initial P sorption reactions occurred on the surfaces of minerals, further P sorption occurred only after the slow physical transport and diffusion of P into micropores (micropore scale physical nonequilibrium). This suggests that for Clear Creek, the overall P removal process was appreciably limited by the kinetics of a physical process (transport of sorbate from liquid to solid) rather than a chemical process. It is typical for removal of a sorbate by soil to be limited by physical processes due to the presence of a porous solid phase (Sparks, 1989). Essentially, P sorption reactions were able to occur much faster than the physical processes which deliver phosphate to the soil surface. A possible explanation for why this “slow burn” was observed in the Clear Creek sample and not the Barren Fork might be that either the Barren Fork soils did not possess the same type of inner-porosity, or such zones were already occupied with P due to the higher initial soil P concentrations (Table 1). Since the soils consisted of the same soil type, had similar surface area (Table 2), and because Barren Fork had twice the P saturation as Clear Creek, the explanation is likely the latter. A similar “slow

burn” diffusion preceded by a fast reaction was observed by Penn et al. (2010).

The difference between P sorption kinetics becomes more apparent when comparing the distribution of the area under the peaks of Fig. 5. For Barren Fork, nearly 100% of the reaction occurred within 3 min. Contrast this to the Clear Creek sample in which only 50% of the 10 min reaction was completed within 3 min. In addition, about 31% of the total reaction occurred after 10 min, which suggests that additional retention time beyond 10 min for the Clear Creek soil will improve P sorption. This supports the results of the flow-through P sorption experiments that suggested that the Barren Fork soil sorbed P faster than the Clear Creek soil.

SUMMARY

Isothermal titration calorimetry provided non-detailed background information with regard to the degree of, mechanisms, and kinetics of P sorption onto soils when evaluated based on characterization data and flow-through P sorption experiments. Both single titrations and 25 consecutive titration calorimetry experiments predicted the greater P sorption capacity of the Clear Creek compared with Barren Fork soil. In fact, P sorption under flow-through conditions was well predicted using an equation previously developed by Penn and Zhang (2010), which utilized heat values from calorimetry and soil Al_{ox} concentrations.

Calorimetry data also provided information on P sorption mechanisms. Both soils in this study displayed thermal patterns typical of P sorption by ligand exchange mechanisms onto Al and Fe oxides and hydroxides, followed by a lesser degree of Al and Fe phosphate precipitation. Knowledge of these mechanisms is important since the manner in which P is held can have an impact on the resistance to P desorption. The impact of chemical conditions on P desorption will also vary depending on the mechanism in which P is held. For example, P bound onto Fe and Al is typically more stable than P bound onto Ca (McDowell et al., 2002; Penn et al., 2011), and sorption of P by Ca phosphate precipitation is usually more sensitive to RT than sorption by ligand exchange reactions (Sposito, 1994).

Perhaps most important, calorimetry proved to be a useful tool in regard to providing an initial assessment of kinetics and therefore the impact of RT on P removal. In contrast to a batch isotherm, the rate of P sorption in a flow through system depends on transport of products and reactants as well as the kinetics of sorption.

This study demonstrated that soils which appear similar based on routine characterization can differ greatly in regard to P sorption behavior under flow-through conditions. Isothermal titration calorimetry was a quick and inexpensive method to initially assess P sorption behavior among different soil samples. The calorimetry approach presented in this study can help to provide soil-specific information on the risk of P inputs to leaching (i.e., degree of P sorption) under different conditions (i.e., flow rate or RT), and potential for desorption (P sorption mechanisms).

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