INORGANIC AND ORGANIC PHOSPHORUS INTERACTIONS WITH HYDROXY-INTERLAYERED SOIL MINERALS

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ABSTRACT OF THESIS

INORGANIC AND ORGANIC PHOSPHORUS INTERACTIONS WITH HYDROXY-INTERLAYERED SOIL MINERALS

Phosphorus (P), a necessary plant and animal nutrient, can also lead to eutrophication of fresh waters when in excess. Appropriate P management is necessary to prevent fresh water pollution. Mineralogy of soil clays has been shown to affect P adsorption, desorption, and movement through soils. Specifically, hydroxy-interlayered minerals have been shown to adsorb and retain inorganic P in soil systems. This study was designed to determine the sorption and desorption characteristics of inorganic, organic, and mixed forms of P interacting with soil hydroxy-interlayered vermiculites (HIV) and smectites (HIS), and compare the findings to sorption and desorption processes of natural aluminum (Al) and Iron (Fe) hydroxide minerals. Results indicate natural Al and Fe hydroxide minerals sorbed and retained P more strongly than hydroxy-interlayered minerals in our samples and inositol hexakisphosphate was more highly sorbed and retained than inorganic P.

KEYWORDS: Phosphorus, Inositol Hexakisphosphate, Hydroxy-interlayered Vermiculite, Hydroxy-interlayered Smectite, Eutrophication

Paul D. Shumaker II

______________ 6/9/2008
INORGANIC AND ORGANIC PHOSPHORUS INTERACTIONS WITH HYDROXY-INALAYERED SOIL MINERALS

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THESIS

Paul Daniel Shumaker II

The Graduate School
University of Kentucky
2008
INORGANIC AND ORGANIC PHOSPHORUS INTERACTIONS WITH HYDROXY-
INTERLAYERED SOIL MINERALS

THESIS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the College of Agriculture at the University of Kentucky

By
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Lexington, Kentucky
2008
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Dedication

This work is dedicated to my family, friends (Christopher Scott Kauffman (1981-2002)), loved ones, and The Phat Mavericks who inspire me to be myself.
Acknowledgments

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CHAPTER 1: INORGANIC AND ORGANIC PHOSPHATE INTERACTIONS WITH HYDROXY-INTERLAYERED SOIL MINERALS

1.1. General Introduction

In 2005 the top agricultural commodities in Kentucky were horses, broilers, and cattle (USDA factsheet, 2007). These animals produce considerable wastes, which are traditionally disposed of by application to surrounding lands for use as an organic fertilizer based on plant N requirements (Sharpley et al., 1994). This practice often leads to over application of phosphorus (P), a buildup of P in the soil, and transport of P to surface and ground water bodies (Sharpley et al., 1996; Jongbloed and Lenis, 1998). Phosphorus is often the limiting nutrient for eutrophication in these water bodies, and can be detrimental to water quality (Sharpley et al., 1994; Haygarth and Jarvis, 1999). Because of the link between manure application and water quality, it is important to develop strategies to accurately apply manure for plant needs without compromising environmental quality (Carpenter et al., 1998).

Many physical, chemical, and biological processes involving P may follow land application of manure (Figure 1-1). Most P transport to water sources occurs through surface runoff as dissolved P (DP) or erosion as particulate P (PP) (Sims and Pierzynski, 2005) while some sub-surface flow and leaching occurs (Gaynor and Findlay, 1995; Haygarth and Sharpley, 2000; Sharpley et al., 2000). Dissolved P is that which passes through a <0.45µm filter, while PP is sorbed to inorganic or organic particles larger than 0.45µm (McDowell et al., 2001). Dissolved P is vital to plant nutrition but also likely to cause eutrophication because it is immediately available to plants and algae. Transport of
DP from soils to water bodies can be minimized through appropriate P applications and runoff control (Sharpley et al., 1994). Particulate P is not directly available to plants or algae, and its loss can be minimized through erosion control practices (Sharpley et al., 1994). Dissolved P and PP are interchangeable through adsorption and desorption processes. Adsorption and desorption processes involving soil particles and P are important to understanding pathways of P transport into surface and ground water bodies (Frossard et al., 2000).

Knowing the effects of soil properties such as clay, organic matter (OM), amorphous aluminum (Al) and iron (Fe) oxide content, soil nutrient levels, and mineralogy on P cycling can lead to accurate fertilizer and manure applications. Clay content and amorphous or crystalline Al and Fe oxide content generally have a positive relationship to P adsorption, while OM content generally has a negative relationship with P adsorption because OM and P compete for reactive sites (Parfitt, 1977; McCallister and Logan, 1978; Bhatti et al., 1998; Barreal et al., 2001). Clay particles have the most extensive surface area of mineral soil materials, resulting in more reactive sites for anion/cation sorption than larger inorganic soil particles (Borggaard, 1983).

Much of the phosphate adsorption capacity of acid soils is attributed to crystalline or amorphous Al and Fe oxide/hydroxides (Hansen et al., 1999; Barreal et al., 2001; Bigham et al., 2002; Huang et al., 2002; Sims and Pierzynski, 2005). Three ligand exchange complexes between these oxides/hydroxides and P have been proposed: monodentate, bidentate, and binuclear (Figure1-2) (Goldberg and Sposito, 1985; Pierzynski et al., 2000; Sims and Pierzynski, 2005). These are inner sphere complexes, which are not readily reversible, however monodentate complexes are considered more
reversible than the other mechanisms (Sims and Pierzynski, 2005). The capacity of these metal oxides/hydroxides to bind P is pH dependent; as pH increases, P sorption capacity decreases (Figure 1-2).

Soils often contain metal hydroxides as components of clay mineral structures (e.g. kaolinite, vermiculite, smectite, gibbsite, chlorite) and as free minerals. Chlorite, hydroxy-interlayered vermiculite (HIV), and hydroxy-interlayered smectite (HIS) are minerals with the interlayer space completely or partially filled with metal hydroxides. Chlorite is structured similar to mica, with a complete metal hydroxide sheet in the interlayer space, while HIV and HIS are structured similar to vermiculite and smectite, respectively with an incomplete metal hydroxide sheet occupying the interlayer (Figure 1-3) (Barnhisel and Bertsch, 1989; Schulze, 1989; Schulze, 2002). The interlayer metal hydroxides satisfy the cation exchange capacity (CEC), increase the anion exchange capacity (AEC), and increase the external surface area of these soil clay minerals leading to more P sorption and retention (Rich, 1968; Barnhisel and Bertsch, 1989; Inoue and Satoh, 1992; Inoue and Satoh, 1993). Hydroxy-interlayered minerals (HIV and HIS) are ubiquitous in the southeastern United States (Rich, 1968; Karathanasis et al., 1983; Karathanasis, 1985).

Laboratory synthesized HIV and HIS can increase P sorption and retention because of P sorption on Al hydroxides in the interlayer (Saha and Inoue, 1997; Saha et al., 1998). Penn et al. (2005) observed a stronger correlation between percent hydroxy-interlayered vermiculite and P sorbed than between clay content and P sorbed. In Kentucky, HIV is more prevalent than free Fe and Al hydroxides, so it has strong implications for the P binding capacity of many Kentucky soils. If HIV and HIS bind P,
soils containing appreciable amounts of these minerals pose less risk for waste applications and P transport to water bodies, and may need higher P inputs to satisfy plant needs.

Previous research has focused on sorption of inorganic P by free Al- and Fe-hydroxide minerals, while little work has included organic P or desorption experiments (Penn et al., 2005). Generally, research done with HI-minerals has involved lab synthesized HIV and HIS (Saha and Inoue, 1997; Saha et al., 1998). Our work used naturally occurring HIV, HIS, Al hydroxide (gibbsite), and Fe hydroxide (goethite) minerals interacting with inorganic (KH₂PO₄), organic (C₆H₁₅O₂₄P₆KMg i.e. magnesium inositol hexakisphosphate), and mixed pools of P before and after amorphous Al and Fe removal. Currently, adsorption and desorption processes involving these minerals and organic P or the two P forms in competition are not well understood so it will be interesting to determine whether the same management can be used for inorganic, organic, and competing P forms.

1.2. Research Objectives

1. Determine sorption and desorption characteristics of organic, inorganic, and mixed phosphates interacting with soil hydroxy-interlayered vermiculite and smectite minerals before and after amorphous Al and Fe removal.

2. Compare findings with sorption and desorption processes involving Al and Fe hydroxide minerals (gibbsite and goethite) before and after amorphous Al and Fe removal.
3. Evaluate reaction time effects on P sorption and desorption involving soil hydroxy-interlayered vermiculite and smectite minerals before and after amorphous Al and Fe removal.

1.3. Hypotheses

- Free Al- and Fe-hydroxide minerals will show the highest P-sorption capacity and the strongest P-retention potential.
- Hydroxy-interlayered vermiculite and smectite soil minerals will show a positive correlation with P sorption and retention resulting from interactions between P and the interlayer Al- and Fe-hydroxide components.
- Hydroxy-interlayered vermiculite will show a stronger P-sorption and retention affinity than HIS because of stronger bonding characteristics.
- Longer reaction time will result in higher P adsorption and lower P desorption because sorption will become stronger and more permanent over time.
- The interaction of organic and mixed (organic + inorganic) P forms with HI-minerals will not follow the same trends as inorganic P:
  - Inositol hexakisphosphate (IHP) will exceed $P_i$ in adsorption and result in less desorption because of stronger bonding characteristics.
  - Mixing IHP and $P_i$ will reduce $P_i$ adsorption because of preferential adsorption of IHP to reactive sites.
1.4. Tables and Figures

Figure 1-1: The soil P cycle (Pierzynski et al. 2000)

Figure 1-2: Phosphorus adsorption mechanisms by metal hydroxides (a) and metal hydroxide pH dependent charge (b) (Fixen and Grove, 1990). *M = Al, Fe
Figure 1-3: Structure of chlorite and HIV/HIS (Schulze, 1989)
1.5. Bibliography


CHAPTER 2: INORGANIC PHOSPHORUS INTERACTIONS WITH HYDROXY-INTERLAYERED SOIL MINERALS

2.1 Introduction

Inorganic phosphorus ($P_I$), while directly available to plants when in solution, represents 50-75% of the $P$ in mineral soils and 60-90% of $P$ in manure (Sharpley and Moyer, 2000; Sims and Pierzynski, 2005). Understanding its role in sorption/desorption processes is vital to proper $P$ management. Dissolved $P_I$ is in the form of orthophosphates, $PO_4^{3-}$, $HPO_4^{2-}$, or $H_2PO_4^-$, depending on pH of the soil solution (Figure 2-1) (Sims and Pierzynski, 2005). Because $P_I$ represents a large portion of plant available $P$ and total $P$ in soils and manures and can cause eutrophication research involving $P_I$ is necessary for environmental protection and plant nutrition.

Considerable literature has focused on $P_I$ interactions with Al and Fe hydroxide minerals such as gibbsite and goethite (Cabrera et al., 1977; Goldberg and Sposito, 1985; Saha and Inoue, 1997; Saha et al., 1998; Penn et al., 2005). Aluminum and iron hydroxides are thought to bind $P$ through fast and slow phase reactions (Chen et al., 1973). The fast phase involves ligand exchange reactions (e.g. monodentate, bidentate), while the slower phase involves stronger, less reversible, ligand exchange (e.g. binuclear) and precipitation reactions (Chen et al., 1973; Goldberg and Sposito, 1985).

Hydroxy-interlayered vermiculite (HIV) and smectite (HIS) have also been shown to retain $P_I$, most likely through interactions between $P_I$ and interlayer metal hydroxides (Saha and Inoue, 1997; Saha et al., 1998). Recent research noted a significant correlation between oxalate extractable Al and HIV content and $P_I$ sorbed to soils and clays (Penn et al., 2005). Phosphorus desorption also has implications for $P_I$ movement within soil.
Quantifying P desorption is necessary to understanding soil P release into the soil solution and appropriate fertilizer or manure P application rates (Frossard et al., 2000). Phosphorus retention by these minerals could prevent P transport and leaching within soil pedons.

Once P is sorbed to a soil particle, the strength of retention depends on the sorption mechanism. According to Goldberg and Sposito (1985), the most easily desorbed P would be involved in a monodentate ligand exchange while bidentate and binuclear bonds would more strongly retain P. Desorption results in P leaving the particulate P pool and entering the dissolved P pool, making it plant and algae available, and at the same time more easily transported from soils into surface and ground water sources (McDowell et al., 2001). Because of the importance of P desorption in the process of P transport to water sources, we quantified P desorption from hydroxy-interlayered soil minerals, attempting to better understand the dynamics of P transport within soils.

Inorganic P sorption and desorption experiments were used to determine the capacity of clay samples to bind and retain P in the presence and absence of amorphous Fe and Al. This allowed separation of the portion of the P sorption and desorption contributed by HIV/HIS compared to amorphous Al and Fe. These experiments set a baseline to compare further experiments involving interactions between organic and mixed pools of P with these minerals.
2.2 Objectives

1. Determine sorption and desorption characteristics of P\textsubscript{i} interacting with soil hydroxy-interlayered vermiculites and smectites before and after amorphous Al and Fe removal.

2. Compare findings with sorption and desorption processes involving Al and Fe hydroxide minerals (gibbsite and goethite) and P\textsubscript{i} before and after amorphous Al and Fe removal.

3. Evaluate reaction time effects on P\textsubscript{i} sorption and desorption by hydroxy-interlayered minerals before and after amorphous Al and Fe removal.

2.3 Materials and Methods

Six soil clays containing ≥30% hydroxy-interlayered vermiculite (HIV) from the University of Kentucky’s archived soils (A.D. Karathanasis, personal communication), two soil clays containing ≥49% hydroxy-interlayered smectite (HIS) from the University of Kentucky’s archived soils (A.D. Karathanasis, personal communication), and one of each aluminum hydroxide (gibbsite) and iron hydroxide (goethite) geologic reference minerals (Ward’s Natural Science Establishment, Inc., Rochester, NY) were used in the experiments (Table 2-1; Table 2-2).

Clay fractions were separated from whole soils using de-ionized water to prevent chemical and mineralogical alterations (Seta and Karathanasis, 1996). Fifteen gram samples were placed in 250 ml centrifuge tubes, which were filled with de-ionized water to 9 cm above the settled soil, shaken at low speed for 30 min, sonicated in an ultra-sonic bath for 3 min, and centrifuged for 3.5 min at 750 rpm. The supernatant was decanted into 1 L beakers. Following the first centrifugation the process was repeated, reducing
shaking time to 3 min and sonication time to 30 seconds between centrifugations. This procedure was repeated until sufficient clay to complete treatments was collected.

Water was evaporated from clay solutions at 60°C to reach a minimum concentration of 2.5 g clay L⁻¹. To validate the concentration, 40 mL sub-samples were placed in Teflon beakers that were previously dried at 100°C to determine tare weights. The sub-samples were dried at 100°C overnight, stored in a desiccator for 30 min to cool, and weighed. Concentrations in g L⁻¹ were then determined. Geologic reference minerals were ground and passed through a 100 µm sieve before treatments.

2.3.1 Mineralogical Quantifications

The mineralogical composition of the samples was quantified by x-ray diffraction (XRD) and thermogravimetric analysis (TGA) (Karathanasis and Hajek, 1982; Karathanasis and Harris, 1994). Clays underwent no physico-chemical pretreatments to prevent chemical or mineralogical changes. X-ray diffraction analysis was performed with a Phillips PW 1840 diffractometer/PW 1729 x-ray generator equipped with a cobalt X-ray tube (40kV, 30 mA). Thermogravimetric analysis was conducted with a 951 DuPont TG module at a heating rate of 20°C / minute under N₂ atmosphere.

Hydroxy-interlayered mineral interpretations were based on criteria as follows. Hydroxy-interlayered vermiculite has a 1.4 nm peak on x-ray diffractograms when saturated with Mg (Figure 2-2; Figure 2-4). Upon heating, the 1.4 nm peak moves towards 1.0 nm, less movement towards 1.0 nm and more area under the peak indicates more extensive/crystalline Al/Fe interlayering (Figure 2-2; Figure 2-4), HIS also has a 1.4 nm peak on x-ray diffractograms when saturated with Mg but reacts differently to
treatments. Its peak approaches 1.8 nm upon glycerol saturation and reacts similar to HIV with K saturation and heating (Figure 2-3; Figure 2-5).

2.3.2 Phosphorus Adsorption and Desorption Experiments

Single point adsorption isotherms were obtained using a modified method of Penn et al. (2005). The pH of samples was 3.0-3.5. Thirty four ml of 0.01 M CaCl₂ and 4 ml of 500 mg L⁻¹ KH₂(PO₄) were added to 250 ml centrifuge tubes containing 0.2 g of clay or geologic reference mineral suspended in 79.75 ml of de-ionized water to provide a P load of 10 mg P g⁻¹ clay. Samples were duplicated and shaken at low speed on a reciprocating shaker at 25°C. Separate samples were shaken for 1, 3, and 7 days. Following shaking, samples were centrifuged at 2000 rpm for 10 min, filtered through 0.45µm filters, and analyzed for Pₗ by the malachite green method (Van Veldenhoven and Mannaerts, 1987; D’Angelo et al., 2001). Phosphorus sorbed was calculated as the amount of P added minus P left after shaking and expressed in terms of mg P sorbed g⁻¹ clay.

Following completion of the adsorption experiments, desorption experiments were conducted on the same samples using the method of Penn et al. (2005). Forty ml of 0.01 M CaCl₂ was added to the samples, shaken at low speed for 1 hour, and filtered through 0.45µm filters four consecutive times. Samples were then analyzed using the malachite green method (Van Veldenhoven and Mannaerts, 1987; D’Angelo et al., 2001). Percent of P retained was calculated using the total P desorbed over four desorptions

\[
\frac{\text{Adsorbed P after four desorptions}}{\text{P adsorbed from single point isotherm}} \times 100 \quad \text{[Eqn. 1]}
\]
2.3.3 Ammonium Oxalate Extraction

Untreated samples of the separated clay fractions and geologic reference minerals suspended in 79.75 ml of de-ionized water were placed in 250 ml centrifuge tubes. The samples were centrifuged until the solution was clear and the supernatant was decanted. Eight ml of acidified (pH 3) 0.2 M ammonium oxalate were added (40:1 ratio of oxalate to clay), and the samples were shaken at low speed in the dark for two hr (McKeague and Day, 1965). Centrifugation at 3000 rpm for 20 min and analysis for Fe\textsubscript{ox}, Al\textsubscript{ox}, and P\textsubscript{ox} using inductively coupled plasma (ICP) spectrometry followed (Penn et al., 2005).

Mineralogical quantification and adsorption/desorption experiments were completed with oxalate extracted samples in the same manner as previously described.

2.3.4 Statistical Analysis

Data from the adsorption and desorption experiments were analyzed for significant differences at the 95% confidence level using the t-test and least squared differences (LSD) procedures of the Statistical Analysis System, Version 9.1 (SAS Institute, 2002-2003). Correlations were based on the correlation procedure of SAS.

2.4 Results and Discussion

2.4.1 Mineralogical Quantification

X-ray diffractograms and TGA output for the samples are presented in Figures 2-2 through 2-9. Hydroxy-interlayered vermiculite rich clays contained 30-77% HIV, 15-35% kaolinite, and smaller quantities of other minerals such as mica, feldspars, goethite, quartz, interstratified minerals, and smectite (Table 2-1; Table 2-2). The HIV clays varied in quantity as well as the degree/quality of hydroxyinterlayering. For example, the Shelocta clay contained 46% HIV while other clays (Nicholson, Lonewood, Allegheny)
contained higher quantities, however the 1.4 nm peak for the Shelocta clay did not shrink as close to 1.0 nm and has a larger area underneath the HIV peak than the other clays after heating to 300°C indicating a better degree/quality of hydroxy-interlayering compared to clays with higher quantities of HIV (Figure 2-2; Figure 2-4). It is important to recognize that the samples with a better degree/quality of interlaying rather than samples with higher quantities of hydroxy-interlayered minerals may result in higher P sorption and retention. Hydroxy-interlayered smectite rich clays contained 49-69% HIS, 11-30% kaolinite, 7-40% vermiculite, and were almost completely comprised of these minerals (Table 2-1; Table 2-2). The HIS clays also varied in the quantity as well as the degree/quality of hydroxyinterlayering. This may, again, result in behavior in which samples with less HIS but a higher degree/quality of hydroxyinterlayering may have higher P sorption and retention than samples with more HIS but lower degree/quality of hydroxyinterlayering. The gibbsite and goethite were determined to be 90% pure (Figure 2-7; Figure 2-9).

2.4.2 Phosphorus Adsorption and Desorption Experiments

Before Oxalate Extraction

Reaction Time Effects

Reaction time seemed to have no significant effect on P sorption. Individual clays indicated no significant difference in the amount of P sorbed with increased shaking times with the exception of the Shelocta clay and gibbsite (Figure 2-10). The somewhat larger deviations observed for these samples are most likely within the range of experimental error. The lack of a distinct reaction time effect on P sorption was reiterated by adsorption data averaged within mineralogical classes (HIV = 2.27 mg P g⁻¹)
clay, HIS = 3.37 mg P g⁻¹ clay, gibbsite = 0.64 mg P g⁻¹ clay, goethite = 1.39 mg P g⁻¹ clay) (Figure 2-11).

In contrast, numerous significant differences were found between shaking times for Pᵢ desorption, not necessarily following a consistent trend. In some cases a longer shaking time resulted in lower Pᵢ desorption (Shelocta one/seven day = 0.68/0.49 mg P g⁻¹ clay) while in other cases it resulted in higher Pᵢ desorption (Lonewood one/seven day = 0.43/0.49 mg P g⁻¹ clay) (Figure 2-10). A contributing factor may be the initial P concentration of the sample following the P adsorption experiments, particularly because a significant positive correlation was observed between Pᵢ sorbed and Pᵢ desorbed (Table 2-3). To explore this issue, desorption data were expressed as a proportion of the Pᵢ adsorbed (Figure 2-12; Figure 2-13). This resulted in fewer significant differences in Pᵢ desorption between reaction times (Figure 2-12; Figure 2-13). The only significant difference in Pᵢ desorption involved goethite and the Shelocta clay (Figure 2-12; Figure 2-13). Inorganic P desorption from goethite was proportionally higher from samples reacted for seven days (14%) than samples reacted for one (10%) or three days (12%). In contrast, Pᵢ desorption from the Shelocta clay was proportionally higher from one (22%) and three day (19%) samples than from seven day samples (14%) (Figure 2-12; Figure 2-13). The goethite interaction was somewhat unexpected considering that a stronger sorption mechanism could take effect over time, resulting in less Pᵢ desorption.

Mineralogy Effects

The mineralogical class had a significant affect on Pᵢ sorption and desorption in many cases (Figure 2-14; Figure 2-15; Figure 2-16; Figure 2-17). Inorganic P sorption and desorption increased in the order of gibbsite < goethite < HIV < HIS (Figure 2-14).
Hydroxy-interlayered vermiculite was expected to adsorb more $P_i$ than HIS because of stronger bonding characteristics (Barnhisel and Bertsch, 1989) but data showed the opposite to be true ($HIV = 2.27 \, \text{mg P g}^{-1} \, \text{clay}; \, \text{HIS} = 3.27 \, \text{mg P g}^{-1} \, \text{clay}$) (Figure 2-14; Figure 2-15). This apparent anomaly may have resulted from interferences by free Al/Fe hydroxides or the degree and quality of hydroxy-interlayer materials. In general, HIS clays had a higher concentration of $Alox$ than HIV clays ($\text{HIS} = 120 \, \text{ppm}; \, \text{HIV} = 72 \, \text{ppm}$) (Table 2-4) and a significant positive correlation was observed between $Alox$ and $P$ sorption (Table 2-3). This is consistent with previous research (Penn et al., 2005) and likely the reason for higher $P_i$ adsorption by these clays.

Surprisingly HIV content had no significant correlation with $P_i$ adsorption, while HIS content had a significant negative correlation with $P_i$ adsorption (Table 2-3). These findings contradict previous research (Penn et al., 2005) and somewhat disprove our hypothesis that HIV/HIS-minerals contribute significantly to $P_i$ sorption. Free Al hydroxides may have out-competed hydroxy-interlayered minerals for $P_i$ sorption, resulting in less interaction between $P_i$ and hydroxy-interlayered minerals. Another explanation may be the differences in the degree/quality of hydroxy-interlayering of the HIV and HIS samples that compensated for the quantitative range of the minerals studied.

Although significant positive correlations existed between $P_i$ desorbed and HIS/HIV/kaolinite/$Alox$ content, desorption data also indicated a significant positive correlation between $P_i$ sorbed and $P_i$ desorbed (Figure 2-14; Figure 2-15; Table 2-3). To clarify this effect further desorption data were expressed as a proportion of the $P_i$ adsorbed during adsorption experiments (Figure 2-16; Figure 2-17). Desorption as a proportion of $P$ adsorbed in most treatments increased in the order goethite < gibbsite <
HIS < HIV (Figure 2-16; Figure 2-17). Although geologic reference minerals adsorbed overall less Pᵢ than soil clays, they retained a higher proportion in most cases (Pᵢ retained: HIV = 77%; HIS = 80%; gibbsite = 83%; goethite = 88%).

**Ammonium Oxalate Extraction Effects**

Adsorption data indicated that ammonium oxalate extractions significantly reduced Pᵢ adsorption by HIS clays (before/after oxalate treatment = 3.27/1.52 mg P g⁻¹ clay) and Allen and Bedford clays (Figure 2-18 (a); Figure 2-19 (a)). Higher Al₉x concentrations in the HIS clays compared to other samples (Table 2-4) may explain this change (HIS = 120 ppm; HIV = 72 ppm; gibbsite = 55 ppm; goethite = 6 ppm). The ammonium oxalate treatment removed free Al hydroxides, which were likely responsible for much of the Pᵢ adsorption. This led to a reduction in Pᵢ adsorption by the samples (Allen before/after oxalate treatment = 2.09/1.3 mg P g⁻¹ clay; Bedford before/after oxalate treatment = 2.47/0.98 mg P g⁻¹ clay) (Figure 2-18 (a); Figure 2-19 (a)).

Desorption data also indicated that ammonium oxalate extractions significantly reduced Pᵢ desorption by hydroxy-interlayered clays (HIV before/after oxalate treatment = 0.52/0.32 mg P g⁻¹ clay; HIS before/after oxalate treatment = 0.66/0.31 mg P g⁻¹ clay) (Figure 2-18 (b)). When desorption was expressed as a proportion of adsorption oxalate extraction significantly reduced Pᵢ desorption from HIV and gibbsite, but not from HIS samples (HIV before/after oxalate treatment = 23/15%; HIS before/after oxalate treatment = 20/20%; gibbsite before/after oxalate treatment = 17/4%; goethite before/after oxalate treatment = 12/9%). This suggests that much of the Pᵢ released during desorption experiments came from free Al/Fe hydroxides and not from hydroxy-
interlayered minerals. Further evidence for this is the significant positive correlation
between Al\textsubscript{ox} content and P\textsubscript{i} desorption (Table 2-3).

**After Oxalate Extraction**

**Reaction Time Effects**

Adsorption data indicated that longer reaction times caused significantly higher P\textsubscript{i}
sorption than shorter reaction times (e.g. Nicholson one/seven day = 0.85/6.49 mg P g\textsuperscript{-1}
clay) (Figure 2-20; Figure 2-21). In cases where no significant difference existed, there
was still a positive trend between reaction time and P\textsubscript{i} sorption (e.g. HIV one/three/seven
day = 1.51/2.03/2.87 mg P g\textsuperscript{-1} clay) (Figure 2-20 (b,c,j); Figure 2-21 (a,d)). This may
have resulted from stronger sorption or precipitation mechanisms taking place as part of
the slow phase of P adsorption (Chen et al., 1973) or P\textsubscript{i} gaining access to more interaction
sites with time.

Desorption data showed a strong correlation with P\textsubscript{i} adsorbed (Table 2-3), so these
data are most relevant when expressed as a proportion of the P\textsubscript{i} adsorbed (Figure 2-22;
Figure 2-23). In general, longer reaction times did not significantly affect the proportion
of P\textsubscript{i} desorbed (e.g. Shelocta one/seven day = 13/15%) (Figure 2-22; Figure 2-23),
suggesting that over the longer reaction time sorption mechanisms remain the same.

**Mineralogy Effects**

The mineralogical class had a greater effect on P\textsubscript{i} desorption than on P\textsubscript{i} adsorption
(Figure 2-24; Figure 2-25; Figure 2-26; Figure 2-27). The only significant difference in
P\textsubscript{i} adsorption comparisons among samples was with gibbsite, which sorbed significantly
less P\textsubscript{i} than any other sample in the one day reaction time (HIV one day = 1.51 mg P g\textsuperscript{-1}
clay; HIS one day = 1.48 mg P g\textsuperscript{-1} clay; gibbsite one day = 0.37 mg P g\textsuperscript{-1} clay; goethite
one day = 0.81 mg P g$^{-1}$ clay) (Figure 2-24). This is most likely due to the purely crystalline nature of this sample. When adsorption was expressed on an individual clay basis, most differences were sporadic but a few stuck out for their consistency (Figure 2-25). For example, the Shelocta clay seemed to consistently adsorb more P$_i$ than most other HIV samples (Shelocta = 3.41 mg P g$^{-1}$ clay; Nicholson = 2.77 mg P g$^{-1}$ clay; Allegheny = 2.16 mg P g$^{-1}$ clay; Lonewood = 2.18 mg P g$^{-1}$ clay; Allen = 1.3 mg P g$^{-1}$ clay; Bedford = 0.98 mg P g$^{-1}$ clay). Adsorption by some samples increased drastically when reaction time was increased (e.g. Nicholson one/seven day = 0.85/6.49 mg P g$^{-1}$ clay; gibbsite one/seven day = 0.37/4.22 mg P g$^{-1}$ clay) (Figure 2-25). Adsorption was most likely dominated by stronger sorption (e.g. binuclear) or precipitation reactions with longer reaction times (Chen et al., 1973; Goldberg and Sposito, 1985) and in turn resulted in higher sorption than samples reacted for less time.

Following oxalate extraction, no significant correlation was observed between HIV and P$_i$ adsorption, but a strong correlation between HIS and adsorption existed. This again brings the issue of degree/quality of the hydroxy-interlayer material that may compensate for the overall quantity of the mineral to some extent. Adsorption data indicated a strong positive correlation (0.99**) between HIS content and P$_i$ adsorption following oxalate extraction as expected (Table 2-3), most likely as a result of interactions between hydroxy-interlayer materials and P$_i$ because amorphous Al/Fe were no longer present. Significant correlations also existed between Fe$_{ox}$/Al$_{ox}$/P$_{ox}$ content and P$_i$ adsorbed (Table 2-3). This indicates that as more of these amorphous materials were removed during oxalate extraction more P$_i$ was subsequently adsorbed by the samples. This could be expected for P$_{ox}$, because when it was removed it vacated interaction sites
leaving crystalline reactive sites available for adsorption. However, greater amorphous Al/Fe removal was expected to lower the adsorption capacity of samples because fewer interaction sites were available. It may be the case that removal of these materials allowed more interaction between hydroxy-interlayer materials and $P_i$.

Significant positive correlations existed between HIV/HIS/kaolinite/$A_{ox}$ content and $P_i$ desorption (Table 2-3). However, because a strong correlation was observed between $P_i$ desorption and adsorption, desorption data were expressed as a proportion of $P_i$ adsorbed (Figure 2-26; Figure 2-27). As was seen earlier a higher proportion of adsorbed $P_i$ was desorbed from hydroxy-interlayered mineral rich clays than from gibbsite and goethite (HIV = 15%; HIS = 18%; gibbsite = 5%; goethite = 8%)(Figure 2-26; Figure 2-27). This again suggests that Al and Fe hydroxide geologic reference minerals had a stronger $P_i$ sorption mechanism than hydroxy-interlayered minerals.

2.5 Conclusions

Reaction times seemed to have little effect on $P_i$ adsorption or desorption before ammonium oxalate extraction. Inorganic $P$ adsorption seemed to be dominated by free metal hydroxides suggesting they were more accessible for $P$ adsorption than crystalline or interlayer materials. This resulted in less interaction between $P_i$ and hydroxy-interlayered minerals. Because free metal hydroxides accounted for a large portion of $P$ sorption proportionally the same amount of $P_i$ desorbed from the samples.

Mineralogy significantly affected $P_i$ adsorption before ammonium oxalate extraction. Contrary to our hypothesis, HIS samples adsorbed more $P_i$ than HIV samples. This was most likely the result of combined interactions of $P_i$ with hydroxy-interlayered minerals and free Al/Fe hydroxides. Mineralogy also significantly affected $P_i$ desorption.
before oxalate extraction. Reference minerals retained proportionally more $P_i$ than hydroxy-interlayered materials, suggesting that their higher degree of crystallinity caused the $P_i$ sorption interactions to be less reversible. The lack of positive correlation between HIV or HIS and $P_i$ adsorption was most likely the result of amorphous Al/Fe hydroxide interferences or differences in the quality/degree of the interlayer Al/Fe materials.

Longer reaction times often resulted in higher $P_i$ adsorption by samples following ammonium oxalate extraction. It is likely that following the removal of free Al/Fe hydroxides, $P_i$ adsorption was dominated by crystalline minerals or interlayer metal hydroxides which required longer reaction time for access than free metal hydroxides. Significantly more $P_i$ was desorbed from hydroxy-interlayered minerals than geologic reference minerals. This resulted from weaker sorption mechanisms (e.g. monodentate) from the less crystalline interlayered materials than by crystalline gibbsite and goethite (e.g. binuclear) (Goldberg and Sposito, 1985).

Following ammonium oxalate extractions, the mineralogical class had a lesser effect on $P_i$ adsorption than before oxalate treatment. This may have resulted from the presence of similar P sorbing materials in all samples and no interference from amorphous Al/Fe hydroxides. Desorption expressed as a proportion of $P$ adsorbed showed that geologic reference minerals retained a significantly higher proportion of $P_i$ than hydroxy-interlayered materials, resulting from stronger sorbing mechanisms by the more crystalline Al/Fe hydroxides.

The strong positive correlation between HIS content and $P_i$ adsorption after oxalate extraction is apparently the result of the free Al/Fe hydroxide removal, which no longer interfered with sorption of $P_i$ by HIS. On the other hand, the lack of significant
correlation between HIV content and $P_i$ adsorbed is most likely the result of differences in the degree/quality of interlayer Al/Fe materials among samples.

### 2.6 Tables and Figures

Figure 2-1: Phosphate forms in solution as a function of pH (Pierzynski et al., 2000)
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Figure 2-3: X-ray diffractograms of HIS soil clays treated with Mg (a), Mg and glycerol (b), and K and heated to 300°C (c).
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Figure 2-8: Thermogravimetric analysis output for HIV clays after ammonium oxalate extraction.
Figure 2-9: Thermogravimetric analysis output for HIS clays and reference minerals after ammonium oxalate extraction.
<table>
<thead>
<tr>
<th>Soil</th>
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<th>HIS</th>
<th>Smectite</th>
<th>Vermiculite</th>
<th>Mica/Smectite/Vermiculite</th>
<th>Kaolinite</th>
<th>Quartz</th>
<th>Goethite</th>
<th>Gibbsite</th>
<th>Feldspars</th>
<th>Mica</th>
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<td>-</td>
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<td>-</td>
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<td>4</td>
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<td>3</td>
<td>-</td>
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<td>2</td>
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<td>-</td>
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<td>16</td>
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<td>-</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>26</td>
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<td>Arundel</td>
<td>Fine, smectitic, thermic Typic Hapludult</td>
<td>Arundel</td>
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<td>49</td>
<td>-</td>
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<td>-</td>
<td>11</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Conecuh</td>
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<td>-</td>
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Table 2-2: Mineralogy of samples after ammonium oxalate extraction

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<td>-</td>
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<td>5</td>
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<td>9</td>
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<td>-</td>
<td>-</td>
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Table 2-3: Pearson correlation coefficients between mg P sorbed g\(^{-1}\) clay from a single point isotherm, mg P desorbed g\(^{-1}\) clay and clay mineral quantity. *, **, indicates significance at 0.05 and 0.01 probability levels respectively.

<table>
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<tr>
<th>Parameter</th>
<th>Before Oxalate Extraction</th>
<th>After Oxalate Extraction</th>
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<tr>
<td></td>
<td>P adsorbed</td>
<td>P desorbed</td>
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<tr>
<td>HIV</td>
<td>-0.26</td>
<td>0.55**</td>
</tr>
<tr>
<td>HIS</td>
<td>-0.70**</td>
<td>0.93**</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-0.28</td>
<td>0.39*</td>
</tr>
<tr>
<td>Fe(_{ox})</td>
<td>0.07</td>
<td>0.12</td>
</tr>
<tr>
<td>Al(_{ox})</td>
<td>0.70**</td>
<td>0.43**</td>
</tr>
<tr>
<td>P(_{ox})</td>
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<td>0.05</td>
</tr>
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<td>P(_{adsorbed})</td>
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</tr>
<tr>
<td>Reaction Time</td>
<td>0.04</td>
<td>0.23</td>
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</table>

*% of P Desorbed = the proportion of phosphorus desorbed:P adsorbed
Table 2-4: Oxalate extractable Al, Fe, and P concentrations of clay samples.

<table>
<thead>
<tr>
<th>Soil Clay/Reference Mineral</th>
<th>Al&lt;sub&gt;ox&lt;/sub&gt;</th>
<th>SD</th>
<th>Fe&lt;sub&gt;ox&lt;/sub&gt;</th>
<th>SD</th>
<th>P&lt;sub&gt;ox&lt;/sub&gt;</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allen</td>
<td>54</td>
<td>3</td>
<td>33</td>
<td>21</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Allegheny</td>
<td>58</td>
<td>4</td>
<td>35</td>
<td>4</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
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<td>Nicholson</td>
<td>78</td>
<td>2</td>
<td>301</td>
<td>15</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Lonewood</td>
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<td>5</td>
<td>30</td>
<td>4</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Bedford</td>
<td>43</td>
<td>4</td>
<td>17</td>
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<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
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<td>&lt; 1</td>
</tr>
<tr>
<td>HIV</td>
<td>72</td>
<td>34</td>
<td>86</td>
<td>109</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Arundel</td>
<td>124</td>
<td>10</td>
<td>58</td>
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<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Concecuh</td>
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<td>47</td>
<td>86</td>
<td>26</td>
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<tr>
<td>HIS</td>
<td>120</td>
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<td>72</td>
<td>20</td>
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<td>&lt; 1</td>
</tr>
<tr>
<td>Gibbsite</td>
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<td>24</td>
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<td>1</td>
</tr>
<tr>
<td>Goethite</td>
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<td>&lt; 1</td>
<td>33</td>
<td>3</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
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</table>
Figure 2-10: Comparison of P₃ adsorption and desorption data for individual clays and reference minerals across shaking times for Nicholson (a), Lonewood (b), Allegheny (c), Allen (d), Bedford (e), Shelocta (f), Conecuh (g), Arundel (h), gibbsite (i), and goethite (j) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-11: Comparison of P<sub>i</sub> adsorption and desorption data for HIV clays (a), HIS clays (b), gibbsite (c), and goethite (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-12: Inorganic P desorption data expressed as a percentage of $P_i$ adsorbed for individual clays and reference minerals across shaking times for Nicholson (a), Lonewood (b), Allegheny (c), Allen (d), Bedford (e), Shelocta (f), Conecuh (g), Arundel (h), gibbsite (i), and goethite (j) before oxalate extraction.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-13: Inorganic P desorption data expressed as a percentage of P\textsubscript{i} adsorbed for HIV clays (a), HIS clays (b), gibbsite (c), and goethite (d) before oxalate extraction.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-14: Inorganic P adsorption and desorption by clays averaged within mineralogical class reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-15: Inorganic P adsorption and desorption by individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-16: Inorganic P desorption by clays before oxalate extractions expressed as a percentage of P_i adsorbed during adsorption experiments averaged within mineralogical class reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d).

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.*
Figure 2-17: Inorganic P desorption by individual clays before oxalate extractions expressed as a percentage of Pi adsorbed during adsorption experiments reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d).

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-18: Inorganic adsorption (a), desorption (b), and desorption expressed as a percentage of P$_i$ adsorbed during adsorption experiments (c) before and after oxalate extractions.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-19: Comparison of P₃ adsorption (a), desorption (b), and desorption expressed as a percentage of P₃ adsorbed before and after oxalate for individual clays averaged across times.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-20: Comparison of P₃ adsorption and desorption data for individual clays and reference minerals across shaking times for Nicholson (a), Lonewood (b), Allegheny (c), Allen (d), Bedford (e), Shelocta (f), Conecuh (g), Arundel (h), gibbsite (i), and goethite (j) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-21: Comparison of P$_i$ adsorption and desorption data for HIV clays (a), HIS clays (b), gibbsite (c), and goethite (d) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-22: Inorganic P desorption data expressed as a percentage of P<sub>i</sub> adsorbed for individual clays and reference minerals across shaking times for Nicholson (a), Lonewood (b), Allegheny (c), Allen (d), Bedford (e), Shelocta (f), Conecuh (g), Arundel (h), gibbsite (i), and goethite (j) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-23: Inorganic P desorption data expressed as a percentage of P$_i$ adsorbed for HIV clays (a), HIS clays (b), gibbsite (c), and goethite (d) after oxalate extraction.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-24: Inorganic P adsorption and desorption by clays averaged within mineralogical class reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-25: Inorganic P adsorption and desorption by individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-26: Inorganic P desorption by clays after oxalate extractions expressed as a percentage of P$_i$ adsorbed during adsorption experiments averaged within mineralogical class reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d).

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 2-27: Inorganic P desorption by individual clays after oxalate extractions expressed as a percentage of Pi adsorbed during adsorption experiments reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d).

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.*
2.7 Bibliography


CHAPTER 3: ORGANIC PHOSPHORUS INTERACTIONS WITH HYDROXY-INTERLAYERED SOIL MINERALS

3.1 Introduction

Organic P (P_o) accounts for 30-65% of total P in mineral soils, 60-90% of P in organic soils (Turner et al., 2002; Sims and Pierzynski, 2005), 10-40% of P in manures (Sharpley and Moyer, 2000), and up to 50% of P transported in runoff (Pierzynski et al., 2000). Relative to P_i bioavailability, retention, and transport of P_o are not well understood (Turner et al., 2002; Condron et al., 2005).

Dissolved P_i is directly available to plants while some questions remain about the plant availability of P_o. However, most literature agrees that at least some P_o compounds are available for plant uptake (Whiting and Heck, 1926; Allison et al., 1941; Bertramson and Stephenson, 1942; Spencer and Willhite, 1944; Dalal, 1977; Foda and Andersen, 1978). Because cyanobacteria that directly contribute to eutrophication have been shown to utilize P_o compounds, P_o transport into surface and ground waters directly affects water quality (Whitton et al., 1991). Organic P compounds also release plant available P_i through mineralization (Dalal, 1977; Harrison, 1987). Many P_o compounds are rapidly mineralized in most soil environments, resulting in low concentrations in soils while some resist mineralization and have higher concentrations in soils, particularly inositol phosphates (Turner et al., 2002).

Inositol phosphates represent much of the P_o in manures and soils (Peperzak et al., 1958; Anderson and Alaridge, 1962; Anderson et al., 1974; Dalal, 1977; Celi et al., 1999). They are composed of a six carbon ring with one to six phosphate groups attached. The most common inositol phosphate in soils is inositol hexakisphosphate.
(IHP), having six phosphate groups (Fig. 3-1) (McKercher and Anderson; 1968; Greaves and Webley, 1969; Turner et al., 2002; Condron et al., 2005). Soil particles bind inositol phosphates through interactions between the phosphate groups and edge hydroxyls (Celi et al., 1999). Increased numbers of phosphate groups associated with the inositol structure increase the chances of adsorption by soil particles (i.e. IHP is more likely to be sorbed than inositol monophosphate) (Goring and Bartholomew, 1950; Shang et al., 1990). In theory, between two and four of the six phosphate groups in the IHP structure participate in adsorption reactions, while more cannot participate because of structural hindrances (Celi et al., 1999). This would be a less reversible sorption mechanism and lead to less P desorption than when only one phosphate group is involved in the ligand exchange. When adsorbed to soil particles $P_o$ is not as susceptible to mineralization as when in solution. Because they have such strong adsorption mechanisms and less susceptibility to mineralization, inositol phosphates generally account for much of the $P_o$ in soils (Harrison, 1987; Shang et al., 1990; Turner et al., 2002).

Literature suggests that inositol phosphates can remove $P_i$ from sorption sites and prevent further $P_i$ sorption (Anderson et al. 1974). This interaction would result in more plant available $P_i$ in solution that could be more easily transported from soils to water sources and become an immediately-available $P$ source to algae.

Significant work has focused on sorption of IHP and other $P_o$ molecules by some soils, clays, clay minerals, and sesquioxides (Goring and Bartholomew, 1950; Anderson and Arlidge, 1962; Anderson et al., 1974; Shang et al., 1990; Shang et al., 1992; Celi et al., 1999) however no research has addressed the interaction of hydroxy-interlayered minerals with inositol phosphates. This portion of the project tested the ability of soil...
hydroxy-interlayered vermiculites (HIV) and smectites (HIS) to bind and retain IHP before and after removal of amorphous Al/Fe components. Further, the study compared IHP interactions with hydroxy-interlayered clays to IHP interactions with Al and Fe geologic reference minerals (gibbsite and goethite).

3.2 Objectives

1. Determine sorption and desorption characteristics of inositol hexakisphosphate (IHP) interacting with soil hydroxy-interlayered vermiculites and smectites in the presence and absence of amorphous Fe and Al.
2. Compare findings with sorption/desorption processes involving IHP and Al and Fe hydroxide minerals before and after amorphous Fe and Al removal.
3. Evaluate the effects of reaction time on adsorption and desorption of IHP involving the same clays before and after amorphous Fe and Al removal.

3.3 Materials and Methods

Clay fractions and geologic reference minerals were prepared with the same samples as for P$_i$ treatments using identical analytical methods so for further exploration of these methods refer to section 2.3.

3.3.1 Mineralogical Quantifications

The mineralogical composition of the samples was quantified by x-ray diffraction (XRD) and thermogravimetric analysis (TGA) (Karathanasis and Hajek, 1982; Karathanasis and Harris, 1994). Clays underwent no physico-chemical pretreatments to prevent chemical or mineralogical changes. X-ray diffraction analysis was performed with a Phillips PW 1840 diffractometer/PW 1729 x-ray generator equipped with a cobalt
X-ray tube (40kV, 30 mA). Thermogravimetric analysis was conducted with a 951 DuPont TG module at a heating rate of 20°C / minute under N₂ atmosphere.

3.3.2 Phosphorus Adsorption and Desorption Experiments

Single point adsorption isotherms were obtained using a modified method of Penn et al. (2005). Thirty four ml of 0.01 M CalCl₂ and 4 ml of 500 mg L⁻¹ IHP were added to 250 ml centrifuge tubes containing 0.2 g of clay or geologic reference mineral suspended in 79.75 ml of de-ionized water to provide a P load of 10 mg P g⁻¹ clay. Samples were duplicated and shaken at low speed on a reciprocating shaker. Separate samples were shaken for 1, 3, and 7 days. Following shaking, samples were centrifuged at 2000 rpm for 10 min and filtered through 0.45µm filters. For total P analysis samples underwent a kjeldahl digestion, converting Po to orthophosphate (Appendix A; personal communication J. Crutchfield. University of Kentucky). Samples were analyzed by the malachite green method for Pi (Van Veldenhoven and Mannaerts, 1987; D’Angelo et al., 2001). Phosphorus sorbed was calculated as the amount of P added minus P left after shaking and expressed in terms of mg P sorbed g⁻¹ clay.

Following the completion of adsorption experiments, desorption experiments were conducted on the same samples using the method of Penn et al. (2005). Forty ml of 0.01 M CaCl₂ were added to the samples which were shaken at low speed for 1 hour, filtered through 0.45µm filters, and digested, four consecutive times. Samples were then analyzed using the malachite green method (Van Veldenhoven and Mannaerts, 1987; D’Angelo et al., 2001). Percent of P retained was calculated as total P desorbed over four desorptions (Equation 1).
3.3.3 Ammonium Oxalate Extraction

Untreated samples of the separated clay fractions and geologic reference minerals suspended in 79.75 ml of de-ionized water were placed in 250 ml centrifuge tubes. The samples were centrifuged until the solution was clear and the supernatant was decanted. Eight ml of acidified (pH 3) 0.2 M ammonium oxalate were added (40:1 ratio of oxalate to clay), and the samples were shaken at low speed in the dark for two hr (Mckeague and Day, 1965). Centrifugation at 3000 rpm for 20 min and analysis for Fe$_{ox}$, Al$_{ox}$, and P$_{ox}$ using inductively coupled plasma (ICP) spectrometry followed (Penn et al., 2005).

Mineralogical quantification and adsorption/desorption experiments were completed with oxalate extracted samples in the same manner as previously described.

3.3.4 Statistical Analysis

Data from the adsorption and desorption experiments were analyzed for significant differences at the 95% confidence level using the t-test and least squared differences (LSD) procedures of the Statistical Analysis System, Version 9.1 (SAS Institute, 2002-2003). Correlations were based on the correlation procedure of SAS.

3.4 Results and Discussion

3.4.1 Phosphorus Adsorption and Desorption Experiments

Before Oxalate Extraction

Reaction Time Effects
Reaction time significantly affected IHP adsorption by hydroxy-interlayered clays but not geologic reference minerals (Figure 3-2; Figure 3-3). Adsorption significantly increased with increased reaction time by all individual hydroxy-interlayered clays (Figure 3-2), but HIV was the only mineralogical class that had significantly higher adsorption with longer reaction time (HIV one/three/seven day = 6.25/7.83/8.69 mg P g\(^{-1}\) clay) (Figure 3-3). Although P adsorption by HIS minerals did not significantly increase with time, this mineralogical class adsorbed nearly all the IHP added (10 mg P g\(^{-1}\) clay) with all reaction times (HIS one/three/seven day = 9.78/9.81/9.92 mg P g\(^{-1}\) clay) (Figure 3-3). Inositol hexakisphosphate adsorption by HIS clays took effect immediately, while IHP adsorption by HIV required longer reaction time to take effect possibly because of precipitation of Al inositol phosphates in HIS samples (Jackman and Black, 1951; Anderson et al., 1974).

Reaction time significantly reduced IHP desorption by many samples, but the quantities desorbed were nearly negligible (HIV = 0.02-0.07 mg P g\(^{-1}\) clay; HIS = 0.02 mg P g\(^{-1}\) clay; gibbsite = 0.01-0.02 mg P g\(^{-1}\); goethite = 0.02 mg P g\(^{-1}\)) (Figure 3-2; Figure 3-3) indicating sorption was dominated by strong sorption (e.g. binuclear) or precipitation reactions. Some small differences resulted when desorption data were expressed as a proportion of P adsorbed (Figure 3-4; Figure 3-5) but because P adsorbed and desorbed were not correlated (Table 3-1) data were not as relevant as P\(_i\) data when expressed this was. The Bedford one day sample proportionally desorbed much more P than all other clays (typically < 1%) but still accounted for only 7% of the P adsorbed. Because this sample adsorbed quite a bit less (Bedford one day = 3.92 mg P g\(^{-1}\) clay; HIV one day average = 6.25 mg P g\(^{-1}\) clay) and desorbed more (Bedford one day = 0.27 mg P g\(^{-1}\) clay;
HIV one day average = 0.07 mg P g\textsuperscript{-1} clay) IHP than other clays, a comparably weaker yet still fairly strong sorption mechanism during short reaction times is very likely. In contrast, Bedford samples reacting for longer times showed higher sorption (Bedford three/seven day = 7.47/8.12 mg P g\textsuperscript{-1} clay) and lower desorption (Bedford three/seven day = 0.07/0.05 mg P g\textsuperscript{-1} clay) of IHP, indicating IHP accessed more interactive sites over time (Figure 3-2).

Overall, reaction time was significantly correlated with IHP adsorption but not with IHP desorption (Table 3-1). The most interesting result was the high proportion of IHP sorbed by all samples (excluding the Bedford one day sample) (59-100%), especially the HIS clays (96-100%) (Figure 3-2; Figure 3-3).

Mineralogy Effects

Adsorption increased in the order of HIV (7.59 mg P g\textsuperscript{-1} clay) < goethite (9.01 mg P g\textsuperscript{-1}) = gibbsite (9.24 mg P g\textsuperscript{-1}) = HIS (9.84 mg P g\textsuperscript{-1} clay) when averaged across reaction times and with most individual reaction times (Figure 3-6). This was surprising because HIV clays were expected to adsorb more P than HIS clays. The HIV clays contained lower quantities of Al\textsubscript{ox} than HIS clays (HIV = 71.75 ppm; HIS = 119.72 ppm) which could explain this discrepancy. Oxalate extractable Al was positively correlated with IHP adsorption, suggesting that free Al hydroxides contributed to IHP sorption in our treatments, and led to higher P sorption by samples with higher Al\textsubscript{ox} content. Data showed that all HIV clays except the Shelocta series adsorbed less IHP than any HIS clay or geologic reference mineral (Figure 3.7). The Shelocta series most likely adsorbed more P than other HIV samples because it contained more Al\textsubscript{ox} (Shelocta = 137.82 ppm; HIV average = 71.75 ppm) (Table 2-4).
Although HIS content was negatively correlated with IHP adsorption (Table 3-1), all HIS samples adsorbed most of the IHP added (9.78-9.92 mg P g\(^{-1}\) clay) with little variation in the data, hinting that amorphous Al dominated adsorption by HIS samples and masked P interaction processes between hydroxy-interlayer material and IHP.

Desorption data indicated that nearly all the IHP adsorbed was retained by all samples. When averaged within mineralogical classes, all classes desorbed statistically the same amount of IHP (HIV = 0.04 mg P g\(^{-1}\) clay; HIS = 0.02 mg P g\(^{-1}\) clay; gibbsite = 0.02 mg P g\(^{-1}\) clay; goethite = 0.02 mg P g\(^{-1}\) clay) with similar proportions of P adsorbed (HIV = 0.8%; HIS = 0.2%; gibbsite = 0.2%; goethite = 0.2%) (Figure 3-6; Figure 3-8). Differences in IHP desorption when analyzed on an individual clay basis existed, however such small quantities (0.01-0.27 mg P g\(^{-1}\) clay) of P desorbed that they were considered negligible compared to adsorption (Figure 3-7; Figure 3-9). As mentioned earlier, the Bedford one day sample had quite a higher quantity (0.27 mg P g\(^{-1}\) clay) and proportion (7%) of P desorbed in these treatments compared to other samples (0.01-0.05 mg P g\(^{-1}\) clay; 0.1-0.9%) so it was considered to have a weaker and more reversible mechanism for P sorption than other samples.

Although, several significant correlations existed between desorption data and clay/reference mineral parameters (Table 3-1), the small quantities and proportions of P desorbed made further interpretations meaningless.

The most important finding of this phase of the experiment was the large proportion of IHP adsorbed (Figure 3-2; Figure 3-3; Figure 3-6; Figure 3-7). A possible explanation is that IHP contains six phosphate groups and only one needs to participate in a ligand exchange (e.g. monodentate, bidentate, binuclear) to remove six phosphate
groups from solution because although all phosphate groups associated with the inositol structure are not involved in the ligand exchange they are removed from solution as part of the IHP structure. As a result even adsorption of a small quantity of individual IHP molecules removed significant quantities of P from solution.

**Oxalate Extraction Effects**

Oxalate extraction significantly reduced IHP adsorption by most of the samples (Figure 3-10 (a); Figure 3-11 (a)). When averaged within mineralogical classes oxalate extraction significantly decreased P adsorption by every class (HIV before/after = 7.59/6.13 mg P g⁻¹ clay; HIS before/after = 9.84/3.65 mg P g⁻¹ clay; gibbsite before/after = 9.24/4.45 mg P g⁻¹; goethite before/after = 9.01/5.02 mg P g⁻¹) (Figure 3-10 (a)). This suggests that free Al/Fe hydroxides increased IHP adsorption but significantly interfered with interactions between IHP and hydroxy-interlayered/geologic reference minerals. This is supported by the results showing less reduction in P sorption by HIV (19%) which had a lower quantity of Al₂O₃ than HIS (62%) (HIV = 71.57 ppm; HIS = 119.72 ppm)(Figure 3-10 (a); Table 2-4). Because oxalate extraction affected P adsorption so strongly, data from treatments following oxalate extraction better pinpointed interactions between hydroxy-interlayered/crystalline minerals and IHP.

Desorption significantly decreased following oxalate extraction, however, once again because of the extremely small quantities desorbed interpretations involving oxalate treatment effects on IHP desorption may be less important than with P₀ (before oxalate extraction = 0.02-0.27 mg P g⁻¹ clay; after oxalate extraction = 0.01-0.04 mg P g⁻¹ clay) (Figure 3-10 (b); Figure 3-11 (b)). When expressed as a proportion of P adsorbed, data indicated no significant change in P desorption after oxalate extraction (before oxalate
extraction (excluding Bedford one day) = 0.1-0.9%; after oxalate extraction = 0.01-0.16%) (Figure 3-10 (c); Figure 3-11(c)) implying reactive sites responsible for IHP adsorption bound IHP as tightly with oxalate treatment as without.

Overall, oxalate extraction significantly reduced the nearly irreversible adsorption before and after oxalate extraction by all clays/reference minerals, indicating that amorphous Al/Fe and \( P_{\text{ox}} \) interfered and therefore underlining the importance of oxalate extraction in elucidating hydroxy-interlayered mineral interactions with IHP.

**After Oxalate Extraction**

**Reaction Time Effects**

Reaction time was positively correlated with P adsorption (Table 3-1) resulting in significantly more P adsorption with longer reaction times for most samples (Figure 3-12; Figure 3-13). This was evident for many of the HIV and geologic reference minerals (e.g. Lonewood one/three/seven day = 4.52/7.02/9.97 mg P g\(^{-1}\) clay) (Figure 3-12) but not as clear for HIS clays (e.g. Arundel one/three/seven day = 3.27/3.31/4.02 mg P g\(^{-1}\) clay). However, when averaged within mineralogical classes samples adsorbed significantly more IHP with one day reaction time than seven day reaction (HIV one/seven day = 4.00/7.95 mg P g\(^{-1}\) clay; HIS one/seven day = 3.56/4.17 mg P g\(^{-1}\) clay; gibbsite one/seven day = 3.28/6.34 mg P g\(^{-1}\); goethite one/seven day = 3.87/6.68 mg P g\(^{-1}\)) (Figure 3.13). These data suggest that hydroxy-interlayered minerals required longer reaction time than amorphous Al/Fe for IHP to access interactive sites.
Desorption of P was not significantly correlated with reaction time (Table 3-1). Such small quantities were desorbed from samples (0.01-0.04 mg P g\textsuperscript{-1} clay) that it was most likely the result of excess P, that was not involved in a ligand exchange, in the samples and was considered negligible compared to adsorption (Figure 3-12; Figure 3-13). This was also the case for desorption expressed as a proportion of P adsorbed (0.1-1.6%) (Figure 3-14; Figure 3-15).

The overall trend was that longer reaction time significantly increased IHP adsorption by most samples, with the sorption mechanisms being nearly irreversible with any reaction time.

Mineralogy Effects

HIV clays adsorbed significantly more IHP than HIS clays given long enough reaction time (HIV three/seven day = 6.43/7.95 mg P g\textsuperscript{-1} clay; HIS three/seven day = 3.21/4.17 mg P g\textsuperscript{-1} clay) (Figure 3-16; 3-17). These data agreed with our hypothesis that HIV clays would adsorb more P than HIS due to stronger bonding characteristics. However, the sorption mechanisms responsible for IHP adsorption by HIV clays required longer reaction time to take full effect while HIS clay mechanisms seemed to be effective almost immediately.

No significant correlation existed between HIV content and IHP adsorption (Table 3-1), which again brings the issue of degree/quality of interlayer materials as discussed in chapter 2. Kaolinite and IHP adsorption were negatively correlated (Table 3-1) agreeing with previous findings (Penn et al., 2005), while P\textsubscript{ox} and IHP were
positively correlated because more interaction sites became available for adsorption when P was removed.

Because such small quantities (0.01-0.04 mg P g\(^{-1}\) clay) and proportions (0.1-1.6\%) of IHP desorbed from samples, adsorption mechanisms were considered fairly irreversible (Figure 3-16; Figure 3-17; Figure 3-18; Figure 3-19). Therefore, inositol phosphates are highly bound by mineral soil components and are not easily transported in solution but through erosion can enter surface and ground water bodies.

3.5 Conclusions

Increased reaction time resulted in increased IHP adsorption by HIV samples before ammonium oxalate extraction. The HIS and geologic reference samples sorbed and retained almost all the added IHP regardless of reaction time. The adsorption by HIS samples was most likely resulted from Alox interactions with IHP because these parameters were positively correlated and IHP adsorption was reduced following oxalate extraction.

Hydroxy-interlayered vermiculite clays adsorbed less IHP than other samples before oxalate extraction, most likely because they had less Al\(_{ox}\) than other samples. Reaction time affected HIV clays more than other samples suggesting that less accessible hydroxy-interlayer materials rather amorphous Al/Fe was responsible for adsorption by these clays. The lack of correlation between HIV content and adsorption and the negative correlation between HIS content and adsorption were most likely due to differences in the degree/quality of hydroxy-interlayer Al/Fe materials amongst samples.

Ammonium oxalate extraction resulted in a significant reduction in IHP adsorption by most samples. This was most drastic for HIS clays (which had the highest Al\(_{ox}\) content)
and geologic reference minerals. Oxalate extraction also removed P from exchange sites resulting in higher P sorption by samples with higher $P_{ox}$. This was evident because $P_{ox}$ and IHP adsorption following oxalate extraction were positively correlated.

Following oxalate extraction, reaction time still strongly affected adsorption by HIV clays and geologic reference minerals, while this was not as evident with HIS clays. Reaction time and IHP adsorption following oxalate extraction were positively correlated, suggesting that hydroxy-interlayered minerals continuously adsorbed IHP over longer reaction times.

Hydroxy-interlayered vermiculite clays varied in P adsorption not only because of differences in quantity but also degree/quality of hydroxy-interlayer materials and in the absence of amorphous Al/Fe components HIV clays had higher IHP adsorption and retention capabilities than HIS clays. Desorption by all samples accounted for such small quantities and proportions of P adsorbed that it was considered negligible in comparison.

The overall conclusion from this portion of the project is that samples adsorbed and retained most of the IHP added in many of the treatments. This suggests high loads of this P molecule could be added to soils containing high quantities of hydroxy-interlayered minerals or amorphous Al hydroxides without threat of transport away from soils and into surface or ground waters. However, erosion control practices would be necessary to ensure the P is not transported into water sources as particulate P.
3.6 Tables and Figures

Table 3-1: Pearson correlation coefficients between mg P sorbed g\(^{-1}\) clay from a single point isotherm, mg P desorbed g\(^{-1}\) clay and clay mineral quantity. *, **, indicates significance at 0.05 and 0.01 probability levels respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before Oxalate Extraction</th>
<th>After Oxalate Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P adsorbed</td>
<td>P desorbed</td>
</tr>
<tr>
<td>HIV</td>
<td>0.13</td>
<td>-0.20</td>
</tr>
<tr>
<td>HIS</td>
<td>-0.84**</td>
<td>0.75**</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-0.11</td>
<td>-0.09</td>
</tr>
<tr>
<td>Fe(_{ox})</td>
<td>0.04</td>
<td>-0.14</td>
</tr>
<tr>
<td>Al(_{ox})</td>
<td>0.42**</td>
<td>-0.17</td>
</tr>
<tr>
<td>P(_{ox})</td>
<td>-0.05</td>
<td>-0.15</td>
</tr>
<tr>
<td>P(_{adsorbed})</td>
<td>-</td>
<td>-0.60**</td>
</tr>
<tr>
<td>Reaction Time</td>
<td>0.34**</td>
<td>-0.25</td>
</tr>
</tbody>
</table>

*% P Desorbed = the proportion of phosphorus adsorbed during adsorption experiments that desorbed during desorption experiments
Figure 3-1: Structure of inositol hexakisphosphate (Condron et al., 2005)
Figure 3-2: Comparison of Pₐ adsorption and desorption data for individual clays and reference minerals across shaking times for Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Bedford (e), Shelocta (f), Conecuh (g), Arundel (h), gibbsite (i), and goethite (j) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-3: Comparison of \( P_o \) adsorption and desorption across shaking times for HIV clays (a), HIS clays (b), gibbsite (c), and goethite (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-4: Organic P desorption data expressed as a percentage of $P_0$ adsorbed for individual clays and reference minerals across shaking times for Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Bedford (e), Shelocta (f), Conecuh (g), Arundel (h), gibbsite (i), and goethite (j) before oxalate extraction.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-5: Organic P desorption data expressed as a percentage of P₀ adsorbed for HIV clays (a), HIS clays (b), gibbsite (c), and goethite (d) before oxalate extraction.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-6: Organic P adsorption and desorption by clays averaged within mineralogical class reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-7: Organic P adsorption and desorption by individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-8: Organic P desorption expressed as a percentage of $P_0$ adsorbed during adsorption experiments by clays averaged within mineralogical class reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extractions.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-9: Organic P desorption by individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction expressed as a percentage of $P_o$ adsorbed during adsorption experiments.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-10: Organic adsorption (a), desorption (b), and desorption expressed as a percentage of $P_0$ adsorbed during adsorption experiments (c) before and after oxalate extractions.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-11: Comparison of P\textsubscript{i} adsorption (a), desorption (b), and desorption expressed as a percentage of P\textsubscript{i} adsorbed before and after oxalate for individual clays averaged across times.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-12: Comparison of P₄ adsorption and desorption data for individual clays and reference minerals across shaking times for Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Bedford (e), Shelocta (f), Conecuh (g), Arundel (h), gibbsite (i), and goethite (j) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-13: Comparison of $P_0$ adsorption and desorption data for HIV clays (a), HIS clays (b), gibbsite (c), and goethite (d) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-14: Organic P desorption data expressed as a percentage of $P_0$ adsorbed for individual clays and reference minerals across shaking times for Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Bedford (e), Shelocta (f), Conecuh (g), Arundel (h), gibbsite (i), and goethite (j) after oxalate extraction.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-15: Organic P desorption data expressed as a percentage of $P_o$ adsorbed for HIV clays (a), HIS clays (b), gibbsite (c), and goethite (d) after oxalate extraction.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-16: Organic P adsorption and desorption by clays averaged within mineralogical class reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-17: Organic P adsorption and desorption by individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-18: Organic P desorption by clays averaged within mineralogical class reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extractions expressed as a percentage of P\textsubscript{o} adsorbed during adsorption experiments.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 3-19: Organic P desorption by individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction expressed as a percentage of P₀ adsorbed during adsorption experiments.

*Similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
3.7 Bibliography


Spencer, V. E., and F.M. Willhite. 1944. Phosphate studies. II. Chemical availability of phosphorus in various organic and inorganic carriers, as indicated by the Neubauer test. Soil Sci. 58:151-161.


CHAPTER 4: MIXED PHOSPHORUS INTERACTIONS WITH HYDROXY-INTERLAYERED SOIL MINERALS

4.1 Introduction

Soil clays can adsorb inorganic P (P\textsubscript{i}) and inositol hexakisphosphate (IHP) through interactions with free Al/Fe hydroxides, edge hydroxyls of mineral structures, and possibly hydroxy-interlayered materials (Goldberg and Sposito, 1985; Shang et al., 1990; Celi et al., 1999; Penn et al., 2005) and given enough reaction through precipitation reactions (Chen et al., 1973; Celi et al., 1999).

Aluminum (Al) and iron (Fe) hydroxides form inner-sphere ligand exchange complexes with P\textsubscript{i} (Goldberg and Sposito, 1985). These can be of mono/bi-dentate or binuclear bond type and are generally not readily reversible. The bond strength usually increases in the order: monodentate < bidentate < binuclear < precipitation (Goldberg and Sposito, 1985).

Clays can form similar complexes with IHP, however the process involves between two and four phosphate groups and interactive sites, rather than one, and results in stronger less reversible complexes than P\textsubscript{i} (Celi et al., 1999). Not only is IHP theorized to form a stronger less reversible complex that P\textsubscript{i}, but interactive sites have been shown to preferentially adsorb IHP over P\textsubscript{i} (Anderson et al., 1974; Harrison, 1987). Inositol hexakisphosphate and P\textsubscript{i} sorption by soils, clays, and sesquioxides have been studied extensively, but little work has included desorption studies, tested competition between the two P forms when introduced simultaneously, or involved hydroxy-interlayered vermiculite (HIV)/smectite (HIS) minerals (Anderson and Arlidge, 1962; Anderson et al., 1974; Shang et al., 1990; Celi et al., 1999). Competition between P forms for interactive
sites, strength of P retention, hydroxy-interlayered mineral content, and degree/quality of hydroxy-interlayer Al/Fe materials are expected to have impacts on P availability to plants and mobility in soils.

Previous portions of this project evaluated the ability of hydroxy-interlayered soil minerals and geologic reference minerals to adsorb and retain P, and IHP individually. This portion deals with competition between the two P forms interacting with hydroxy-interlayered minerals and geologic reference minerals when they are introduced simultaneously.

4.2 Objectives

1. Determine sorption and desorption characteristics of mixed phosphate forms (inorganic and organic) interacting with soil hydroxy-interlayered vermiculites and smectites before and after amorphous Fe and Al removal.

2. Compare findings with sorption and desorption processes involving Al and Fe hydroxide minerals and mixed P forms before and after amorphous Fe and Al removal.

3. Evaluate the effects of reaction time on adsorption and desorption of mixed P involving the same clays before and after amorphous Fe and Al removal.

4.3 Materials and Methods

Four soil clays containing ≥30% HIV from the University of Kentucky’s archived soils (Dr. A.D. Karathanasis), two soil clays containing ≥49% HIS from the University of Kentucky’s archived soils (Dr. A.D. Karathanasis), and one of each aluminum hydroxide
(gibbsite) and iron hydroxide (goethite) geologic reference minerals (Ward’s Natural Science Establishment, Inc., Rochester, NY) were used in the experiments.

Sample preparation was exactly the same as with previous treatments (Refer to section 1.3).

4.3.1 Mineralogical Quantifications

The mineralogical composition of the samples was quantified by x-ray diffraction (XRD) and thermogravimetric analysis (TGA) (Karathanasis and Hajek, 1982; Karathanasis and Harris, 1994). Clays underwent no physico-chemical pretreatments to prevent chemical or mineralogical changes. X-ray diffraction analysis was performed with a Phillips PW 1840 diffractometer/PW 1729 x-ray generator equipped with a cobalt X-ray tube (40kV, 30 mA). Thermogravimetric analysis was conducted with a 951 DuPont TG module at a heating rate of 20°C / minute under N2 atmosphere.

4.3.2 Phosphorus Adsorption and Desorption Experiments

Single point adsorption isotherms were obtained using a modified method of Penn et al. (2005). Thirty four ml of 0.01 M CalCl2, 2 ml of 500 mg L⁻¹ KH₂(PO₄), and 2 ml of 500 mg L⁻¹ IHP were added to 250 ml centrifuge tubes containing 0.2 g of clay or geologic reference mineral suspended in 79.75 ml of de-ionized water to provide a P load of 10 mg P g⁻¹ of clay. Samples were duplicated and shaken at low speed on a reciprocating shaker. Separate samples were shaken for 1, 3, and 7 days. Following shaking, samples were centrifuged at 2000 rpm for 10 min, filtered through 0.45μm filters, and analyzed for Pᵢ by the malachite green method (Van Veldenhoven and Mannaerts, 1987; D’Angelo et al., 2001). Inorganic P sorbed was calculated as the amount of Pᵢ added minus Pᵢ left after shaking and expressed in terms of mg P sorbed g⁻¹.
clay. Solutions were analyzed for total P by the malachite green method following a kjeldahl digestion (Attachment 1) (Van Veldenhoven and Mannaerts, 1987; D’Angelo et al., 2001). Organic P content was considered total P minus P\textsubscript{i} in solution. Organic P sorbed was calculated as the difference between P\textsubscript{o} in left in solution following adsorption experiments and the amount of P\textsubscript{o} added.

Following completion of adsorption experiments, desorption experiments were conducted on the same samples using the method of Penn et al. (2005). Forty ml of 0.01 M CaCl\textsubscript{2} was added to the samples and shaken at low speed for 1 hour and filtered through 0.45\textmu m filters, four consecutive times. Samples were then analyzed for P\textsubscript{i} using the malachite green method (D’Angelo et al., 2001; Van Veldenhoven and Mannaerts, 1987). Percent of P\textsubscript{i} retained was calculated using the total P\textsubscript{i} desorbed over four desorptions as previously described by Equation 1. Total P concentration was determined using the malachite green method following a kjeldahl digestion (Attachment 1) and percent of P\textsubscript{o} retained was calculated using the total P\textsubscript{o} desorbed over four desorptions (Equation 2) (Penn, et al. 2005).

\[
\text{Adsorbed } P_o \text{ after four desorptions} \times 100 \hspace{4cm} \text{[Eqn. 2]}
\]

\[
P_o \text{ adsorbed from single point isotherm}
\]

4.3.3 Ammonium Oxalate Extraction

Untreated samples of the separated clay fractions and geologic reference minerals suspended in 79.75 ml of de-ionized water were placed in 250 ml centrifuge tubes. The samples were centrifuged until the solution was clear and the supernatant was decanted. Eight ml of acidified (pH 3) 0.2 M ammonium oxalate were added (40:1 ratio of oxalate to clay), and the samples were shaken at low speed in the dark for two hr (Mckeague and
Day, 1965). Centrifugation at 3000 rpm for 20 min and analysis for Fe$_{ox}$, Al$_{ox}$, and P$_{ox}$ using inductively coupled plasma (ICP) spectrometry followed (Penn et al., 2005).

Mineralogical quantification and adsorption/desorption experiments were completed with oxalate extracted samples in the same manner as previously described.

3.3.4 Statistical Analysis

Data from the adsorption and desorption experiments were analyzed for significant differences at the 95% confidence level using the t-test and least squared differences (LSD) procedures of the Statistical Analysis System, Version 9.1 (SAS Institute, 2002-2003). Correlations were based on the correlation procedure of SAS.

4.4 Results and Discussion

4.4.1 Mineralogical Quantification

Hydroxy-interlayered vermiculite rich clays contained 30-77% HIV, 15-35% kaolinite, and smaller quantities of other minerals such as mica, feldspars, goethite, quartz, interstratified minerals, and smectite while HIS rich clays contained 49-69% HIS, 11-30% kaolinite, 7-40% vermiculite, and were almost completely comprised of these minerals (Table 4-1; Table 4-2).

4.4.2 Phosphorus Adsorption and Desorption Experiments

Before Oxalate Extraction

Reaction Time Effects

Contrary to our hypothesis, reaction time did not necessarily increase adsorption and decrease desorption of P$_i$ and IHP. In some cases nearly all the IHP was adsorbed
even with shorter reaction times so trends could have been more evident with a higher P load.

In general, increased reaction time significantly increased P\textsubscript{i} adsorption by HIV clays and had no significant affect on P\textsubscript{i} adsorption by other samples (Figure 4-1; Figure 4-2). The significantly positive correlation between reaction time and P\textsubscript{i} adsorption resulted from the significant increase in P\textsubscript{i} adsorption by HIV clays (Table 4-3). This suggests that longer reaction time allowed P\textsubscript{i} to access more interactive sites on the HIV clays but not HIS or geologic reference samples.

Increased reaction time did not increase IHP adsorption by any of the samples (Figure 4-1; Figure 4-2). However, because the hydroxy-interlayered clays adsorbed nearly all the IHP added with every reaction time (HIV one/three/seven day = 4.94/4.84/5.00 mg P g\textsuperscript{-1} clay; HIS one/three/seven day = 5.00/5.00/5.00 mg P g\textsuperscript{-1} clay) it was unclear whether reaction time would have any effect with higher P loads. Geologic reference minerals adsorbed less IHP with increased reaction time (gibbsite one/seven day = 2.80/3.07 mg P g\textsuperscript{-1} clay; goethite one/seven day = 2.30/3.06 mg P g\textsuperscript{-1} clay) with no significant change in IHP adsorption with longer reaction (Figure 4-1; Figure 4-2), hinting that IHP adsorption occurred strongly and quickly but did not continue past the initial phase. No significant correlation existed between reaction time and total P adsorption (Table 4-5).

Increased reaction time resulted in changes P\textsubscript{i} desorption patterns (Figure 4-3; Figure 4-4) but because of the significant positive correlation between P\textsubscript{i} adsorption and desorption (0.90**) (Table 4-3) further interpretations were based on desorption expressed as a proportion of P\textsubscript{i} adsorbed. When expressed in this manner there was no
change in $P_i$ desorption with increased reaction time for any sample (Figure 4-5; 4-6) and no significant correlation between reaction time and $P_i$ desorption (Table 4-3). However, because a significant positive correlation existed between the proportion of $P_i$ desorbed and the quantity of $P_i$ adsorbed (0.53**) (Table 4-3) $P_i$ desorption appeared to be more a function of the amount of $P_i$ adsorbed rather than reaction time.

Inositol hexakisphosphate adsorption was not significantly correlated with IHP desorption (Table 4-4), so interpretations were made from quantitative desorption data. Longer reaction time resulted in less IHP desorption by all samples (HIV one/seven day = 0.04/0.002 mg P g$^{-1}$ clay; HIS one/seven day = 0.03/0.001 mg P g$^{-1}$ clay; gibbsite one/seven day = 0.04/0.004 mg P g$^{-1}$ clay; goethite one/seven day = 0.04/0.02 mg P g$^{-1}$ clay) (Figure 4-3; Figure 4-4). Desorption expressed as a proportion of IHP adsorbed also showed a significant negative correlation with reaction time (Table 4-4) and in many cases proportionally more P was desorbed from samples reacted for less time (HIV one/seven day = 1/0%; HIS one/seven day = 1/0%; gibbsite one/seven day = 1/0%; goethite one/seven day = 2/0%) (Figure 4-5; Figure 4-6). Apparently, sorption mechanisms became stronger and less reversible over time and resulted in lower IHP desorption. Although, desorption trends suggest that stronger sorption mechanisms took place over longer reaction time, very small quantities and proportions of IHP were desorbed (0.04-<0.001 mg P g$^{-1}$ clay; 0-2%).

Mineralogy Effects

The most important mineralogical aspect, in terms of P sorption, was $A_{lox}$ content. This clay/geologic reference mineral parameter was significantly positively correlated to $P_i$, IHP, and total P adsorption while other mineralogical parameters that were expected
to be responsible for part of the P sorption capacity of samples (e.g. HIV, HIS, Fe$_{ox}$) were less consistently correlated.

Inorganic P adsorption increased in the following order: gibbsite (average = 0.61 mg P g$^{-1}$ clay) < goethite (average = 0.74 mg P g$^{-1}$ clay) < HIV (average = 0.87 mg P g$^{-1}$ clay) < HIS (average = 1.39 mg P g$^{-1}$ clay) (Figure 4-7; Figure 4-8). Most likely, HIS clays had higher P$_i$ adsorption because of higher oxalate extractable Al (Alox) content (Table 4-6), which was significantly positively correlated with P$_i$ adsorption in mixed P treatments (Table 4-3). Other significant correlations with P$_i$ adsorption were negative and included kaolinite and HIS content (Table 4-3). The negative correlation between P$_i$ adsorption and kaolinite was expected because of previous findings (Penn et al., 2005) but HIV and HIS content were expected to be positively correlated with P adsorption because of interactions between P and hydroxy-interlayer Al/Fe. Several possible explanations for this anomaly include: the degree/quality of interlayering, which could have compensated for the quantitative range of the HIV and HIS samples, and free Al/Fe hydroxides interferences with hydroxy-interlayered clay interactions with P$_i$.

Inositol hexakisphosphate adsorption was highest and accounted for nearly all the IHP added for hydroxy-interlayered minerals, while lower quantities of IHP were adsorbed by geologic reference minerals (HIV average = 4.77 mg P g$^{-1}$ clay; HIS average = 5.00 mg P g$^{-1}$ clay; gibbsite average = 2.82 mg P g$^{-1}$ clay; goethite average = 2.85 mg P g$^{-1}$ clay) (Figure 4-7; Figure 4-8). This contradicts part of our hypothesis, expecting geologic reference minerals to adsorb more P than hydroxy-interlayered minerals. Several possible explanations include: hydroxy-interlayered clay samples may have had higher surface area than geologic reference samples and higher quantities of amorphous
Al/Fe materials in hydroxy-interlayered clays led to higher P adsorption. Inositol hexakisphosphate adsorption was significantly positively correlated with HIV and Al\textsubscript{ox} content while no significant correlation existed with HIS content. These positive correlations most likely arose from interactions between free and interlayered Al/Fe hydroxide interactions with IHP. Positive trends between HIS content and IHP adsorption may have been masked by the degree/quality of interlayering, Al\textsubscript{ox} content of samples, or the fact that nearly all IHP added was sorbed by the HIS samples (≈5 mg P g\textsuperscript{-1} clay). Overall, soil hydroxy-interlayered clays showed stronger bonding characteristics with IHP than geologic Al/Fe hydroxide minerals, in spite of some interference from amorphous Al/Fe hydroxides.

Inorganic P desorption increased in the same sequence as P\textsubscript{i} adsorption: gibbsite (0.03 mg P g\textsuperscript{-1} clay) < goethite (0.05 mg P g\textsuperscript{-1} clay) < HIV (0.13 mg P g\textsuperscript{-1} clay) < HIS (0.25 mg P g\textsuperscript{-1} clay) (Figure 4-9; Figure 4-10). There was a strong positive correlation between P\textsubscript{i} adsorbed and desorbed (0.90**) even when desorption data were expressed as a proportion of P\textsubscript{i} adsorbed (0.53**), suggesting that the underlying reason for increased P\textsubscript{i} desorption was the higher quantities of P\textsubscript{i} present at the beginning of desorption experiments (Table 4-3).

All mineralogical classes desorbed small quantities and proportions of IHP (HIV = <0.001-0.04 mg P g\textsuperscript{-1} clay / 0-1%; HIS = <0.001-0.29 mg P g\textsuperscript{-1} clay / 0-1%; gibbsite = 0.004-0.04 mg P g\textsuperscript{-1} clay / 0-1%; goethite = 0.01-0.04 mg P g\textsuperscript{-1} clay / 0-2%) (Figure 4-9; Figure 4-10; Figure 4-11; Figure 4-12) suggesting the presence of strong sorption/precipitation mechanisms.
Although both forms of P were more highly sorbed by hydroxy-interlayered clays than by geologic reference minerals, desorption did not follow the same trend. Hydroxy-interlayered clays had higher Pᵢ desorption and lower IHP desorption than geologic reference minerals. Overall, hydroxy-interlayered clays seemed to have higher P sorption capacities than geologic reference minerals, with the sorption mechanism being much stronger for IHP than Pᵢ.

**Phosphorus Competition**

All samples adsorbed significantly more IHP than Pᵢ (Figure 4-7; Figure 4-8) agreeing with previous research (Anderson et al., 1974; Celi et al., 1999). This likely resulted from stronger sorption mechanisms between IHP and soil clays involving more than one type of phosphate group or interactive site or the formation of Al and Fe phases that were highly insoluble in acid media (Jackman and Black, 1951; Anderson, 1963; Anderson et al., 1974; Celi et al., 1999).

All hydroxy-interlayered clays desorbed significantly less IHP than Pᵢ again because of the stronger sorption or precipitation mechanisms noted earlier (HIV IHP/Pᵢ desorption = <0.001-0.04 / 0.10-0.16 mg P g⁻¹ clay; HIS IHP/Pᵢ desorption = <0.001-0.03 / 0.19-0.30 mg P g⁻¹ clay) (Figure 4-9; Figure 4-10; Figure 4-11; Figure 4-12). Geologic reference samples generally had less IHP desorption than Pᵢ, but with one day reaction time IHP desorption often equaled or exceeded Pᵢ desorption (gibbsite one day Pᵢ/IHP desorption = 0.02/0.04 mg P g⁻¹ clay; goethite one day Pᵢ/IHP desorption = 0.04/0.04 mg P g⁻¹ clay) (Figure 4-9 (a)). Increasing the reaction time resulted in nearly irreversible adsorption or precipitation of IHP, while Pᵢ adsorption was much more reversible (proportion of IHP/Pᵢ desorbed from HIV clays = 0/15%; proportion of IHP/Pᵢ desorbed...
from HIS clays = 0/18%; proportion of IHP/Pi desorbed from gibbsite = 1/5%; proportion of IHP/Pi desorbed from goethite = 1/6%) (Figure 4-11; Figure 4-12).

**Oxalate Extraction Effects**

Surprisingly, P\textsubscript{i} adsorption increased following oxalate extraction for HIV clays and geologic reference minerals while it remained statistically the same for HIS clays (HIV before/after oxalate extraction = 0.87/1.69 mg P g\textsuperscript{-1} clay; HIS before/after oxalate treatment = 1.39/1.16 mg P g\textsuperscript{-1} clay; gibbsite before/after oxalate treatment = 0.61/0.89 mg P g\textsuperscript{-1}; goethite before/after oxalate extraction = 0.73/1.09 mg P g\textsuperscript{-1}) (Figure 4-13; Figure 4-14). Oxalate extraction reduced IHP adsorption by hydroxy-interlayered clays but not geologic reference minerals (HIV before/after oxalate extraction = 4.93/3.71 mg P g\textsuperscript{-1} clay; HIS before/after oxalate extraction = 5.00/2.71 mg P g\textsuperscript{-1} clay; gibbsite before/after oxalate extraction = 2.82/3.44 mg P g\textsuperscript{-1}; goethite before/after oxalate extraction = 2.85/3.45 mg P g\textsuperscript{-1}) (Figure 4-13; Figure 4-14). Because P\textsubscript{i} adsorption increased and IHP adsorption decreased following oxalate extraction for hydroxy-interlayered clays (Figure 4-13; Figure 4-14) it seems that P\textsubscript{i} was adsorbed by crystalline or interlayered material while IHP was preferably adsorbed to amorphous Al/Fe materials. Apparently, oxalate extraction resulted in easier access to interactive sites for P\textsubscript{i} and removal of a significant portion of interactive sites for IHP. The lack of change in either P\textsubscript{i} or IHP adsorption following oxalate extraction by geologic reference samples (Figure 4-13; Figure 4-14) can be attributed to their high degree of crystallinity, which inhibited oxalate extraction effects on reactive sites.
Total P adsorption was significantly reduced for HIS clays following oxalate extraction (HIS total P adsorption before/after oxalate extraction = 6.58/3.87 mg P g⁻¹ clay). This reduction might be associated with the higher quantities of Alox removed during oxalate extraction from these clays compared to other samples (Table 4-6). This clay parameter (Alox) was highly correlated with P adsorption (Table 4-3; Table 4-4; Table 4-5), and most likely interfered with P interactions in HIS clays more than in other samples.

Oxalate extraction significantly reduced Pᵢ desorption from hydroxy-interlayered clays and goethite while it had no significant effect on Pᵢ desorption from gibbsite (HIV before/after oxalate extraction = 0.13/0.09 mg P g⁻¹ clay; HIS before/after oxalate extraction = 0.25/0.03; gibbsite before/after oxalate extraction = 0.03/0.02 mg P g⁻¹; goethite before/after oxalate extraction = 0.05/0.02 mg P g⁻¹) (Figure 4-15). No significant decrease in Pᵢ desorption occurred for any individual HIV clay following oxalate extraction with the exception of the Allegheny clay (Nicholson before/after oxalate extraction = 0.13/0.12 mg P g⁻¹ clay; Allegheny before/after oxalate extraction = 0.13/0.03 mg P g⁻¹ clay; Lonewood before/after oxalate extraction = 0.11/0.13 mg P g⁻¹ clay; Allen before/after oxalate extraction = 0.13/0.07 mg P g⁻¹ clay) (Figure 4-16), which strongly influenced the overall average reduction in Pᵢ desorption from HIV clays following oxalate extraction and made this average misleading (HIV before/after oxalate extraction = 0.13/0.09 mg P g⁻¹ clay) (Figure 4-15; Figure 4-16). This most likely resulted from dominance of similar sorption mechanisms (e.g. monodentate, bidentate, binuclear) by HIV samples before and after oxalate treatment (Goldberg and Sposito, 1985). Significantly less Pᵢ was desorbed from all HIS samples following oxalate extraction.
extraction (Conceuh before/after oxalate extraction = 0.21/0.03 mg P g\(^{-1}\) clay; Arundel before/after oxalate extraction = 0.29/0.03 mg P g\(^{-1}\) clay) (Figure 4-16). Amorphous Al/Fe dominated P\(_i\) adsorption by HIS clays and had more reversible sorption mechanisms than crystalline material. Evidence of this is the stronger effect that oxalate extraction had on P\(_i\) adsorption and desorption interactions involving HIS samples, which had higher Alox contents than HIV and geologic reference samples (HIS = 120 ppm; HIV = 62 ppm; gibbsite = 55 ppm; goethite = 6ppm) (Table 4-6).

Because there was a highly significant positive correlation between P\(_i\) adsorbed and desorbed (0.72**) (Table 4-3) desorption was expressed as a proportion of P\(_i\) adsorbed. Proportionally less of the P\(_i\) adsorbed was desorbed from all samples following oxalate extraction (HIV before/after oxalate extraction = 15/5%; HIS before/after oxalate extraction = 18/3%; gibbsite before/after oxalate extraction = 5/2%; goethite before/after oxalate extraction = 6/2%) (Figure 4-17; Figure 4-18). This supports the conclusion that crystalline/hydroxy-interlayered materials had stronger P\(_i\) sorption mechanisms than amorphous Al/Fe hydroxides.

Desorption of IHP was not significantly effected by oxalate extraction in most cases accounted for very small quantities/proportions of IHP before and after oxalate extraction (IHP quantities desorbed before/after oxalate extraction = 0.01-0.02/0.01-0.01 mg P g\(^{-1}\) clay; proportions of IHP desorbed before/after oxalate extraction = 0-1%/0-1%) (Figure 4-14; Figure 4-15; Figure 4-16; Figure 4-16).

Because P\(_i\) accounted for such a high proportion of total P desorbed, total P desorption trends were similar to P\(_i\) desorption trends and interpretations were not as meaningful as when P\(_i\) and IHP desorption data were analyzed individually (HIV P\(_i\)/total
P desorbed = 0.13/0.14 mg P g⁻¹ clay; HIS Pᵢ/total P desorbed = 0.25/0.26 mg P g⁻¹ clay; gibbsite Pᵢ/total P desorbed = 0.03/0.05 mg P g⁻¹; goethite Pᵢ/total P desorbed = 0.05/0.07 mg P g⁻¹) (Figure 4-15; Figure 4-16; Figure 4-17; Figure 4-18).

**After Oxalate Extraction**

**Reaction Time Effects**

Although reaction time rarely had a significant effect on Pᵢ adsorption for any individual clay (Figure 4-19), there was a significant positive correlation between reaction time and Pᵢ adsorption for all samples (Table 4-3), and particularly for HIV clays (HIV one/seven day Pᵢ adsorption = 0.80/2.66 mg P g⁻¹ clay) (Figure 4-20). This suggests that Pᵢ gained access to more interactive sites over longer reaction time and led to increased adsorption.

The effect of reaction time on IHP adsorption was similar to the Pᵢ adsorption. Although many individual samples were not significantly affected, the average IHP adsorption by mineralogical classes significantly increased with longer reaction times (HIV one/seven day = 2.93/4.54 mg P g⁻¹ clay; HIS one/seven day = 2.05/3.63 mg P g⁻¹ clay; gibbsite one/seven day = 1.87/5.00 mg P g⁻¹; goethite one/seven day = 2.27/4.80 mg P g⁻¹) (Figure 4-19; Figure 4-20). Even in cases where there was no significant effect, IHP adsorption still increased with longer reaction times (Nicholson one/seven day = 2.93/5.00 mg P g⁻¹ clay; Allegheny one/seven day = 2.93/3.60 mg P g⁻¹ clay; Lonewood one/seven day = 2.56/5.00 mg P g⁻¹ clay; Allen one/seven day = 2.81/4.56 mg P g⁻¹ clay; Conecuh one/seven day = 1.93/3.26 mg P g⁻¹ clay; Arundel one/seven day = 2.17/4.00 mg P g⁻¹ clay) (Figure 4-19). This suggests that IHP gained access to more interactive
sites with longer reaction times or Al and Fe precipitates (e.g. aluminum inositol phosphate) formed over longer reaction time (Anderson et al., 1974).

Desorption was generally not significantly affected by reaction time for either P$_i$ or IHP (Figure 4-21; Figure 4-22; Figure 4-23; Figure 4-24). Inorganic P desorption was highly correlated to P adsorbed (0.72**) (Table 4-3) and was mainly a function of P concentration at the beginning of desorption experiments rather than reaction time, suggesting that P$_i$ did not become involved in stronger sorption mechanisms over time. Quantities and proportions of IHP desorbed were very small in all cases (0.002-0.04 mg P g$^{-1}$ clay; 0-1%) indicating nearly irreversible binding mechanisms.

**Mineralogy Effects**

The only significant correlations for IHP and P$_i$ adsorption following oxalate extraction were between reaction time and adsorption (Table 4-3; Table 4-4). There were no significant differences in IHP or P$_i$ adsorption between individual clays or mineralogical classes (Figure 4-25; Figure 4-26). This suggests that all samples had similar P sorption mechanisms and the differences observed between samples before oxalate extraction were most likely caused by interferences from amorphous Al/Fe hydroxides.

Several significant correlations existed between sample parameters and P desorption (Table 4-3; Table 4-4; Table 4-5), but the amount of P adsorbed had the most significant effect. Again very small quantities and proportions of IHP desorbed (0.01-0.04 mg P g$^{-1}$ clay; 0-1%) (Figure 4-27; Figure 4-28; Figure 4-29; Figure 4-30). Although desorption was higher for P$_i$ than IHP (P$_i$ desorption = 0.01-0.23 mg P g$^{-1}$
clay), most P$_i$ adsorbed was retained (90-100%), suggesting dominance of irreversible adsorption mechanisms for all samples.

**Phosphorus Competition**

Similar P adsorption trends resulted from samples following oxalate extraction as samples with no oxalate extraction (Figure 4-7; Figure 4-8; Figure 4-25; Figure 4-26). Inositol hexakisphosphate dominated total P sorption and accounted for significantly higher quantities of P adsorbed than P$_i$ by every treatment (P$_i$ adsorbed = 0.50-3.80 mg P g$^{-1}$ clay; IHP adsorbed = 1.89-5.00 mg P g$^{-1}$ clay) (Figure 4-25; Figure 4-26). It seems that hydroxy-interlayered Al/Fe materials and geologic reference minerals preferentially adsorbed IHP over P$_i$ with stronger sorption mechanisms as discussed for samples before oxalate extraction.

Desorption trends were also similar to samples before oxalate extraction. In general, very low quantities of both forms of P were desorbed (P$_i$ desorbed = 0.02-0.23 mg P g$^{-1}$ clay; IHP desorbed = 0.002-0.04 mg P g$^{-1}$ clay), with adsorption being fairly irreversible for both (IHP more so than P$_i$) (Figure 4-27; Figure 4-28; Figure 4-29; Figure 4-30).

**4.5 Conclusions**

Increased reaction time generally increased P$_i$ adsorption before and after oxalate extraction (most drastically for HIV samples), apparently because P$_i$ gained access to more interactive sites over time. The effect of increased reaction time on IHP adsorption before oxalate extraction was unclear because nearly all IHP added was sorbed by hydroxy-interlayered clays most likely because of interferences from amorphous Al hydroxides. Following oxalate extraction, increased reaction time was significantly
correlated with IHP adsorption suggesting that the more crystalline and interlayered Al/Fe materials required longer reaction time for IHP to access interactive sites than amorphous Al. Oxalate extraction resulted in significant changes in IHP adsorption suggesting that amorphous Al/Fe might have been responsible for much of the P sorption by samples before oxalate extraction.

Before oxalate extraction data showed that hydroxy-interlayered minerals adsorbed more \( P_i \) and IHP than geologic reference minerals but after oxalate extraction this trend was not as evident. This may be the consequence of higher concentrations of \( Al_{ox} \) in hydroxy-interlayered clays which out-competed the geologic reference materials for P sorption before oxalate treatment. When amorphous materials were removed hydroxy-interlayered minerals and geologic reference minerals had similar P sorption mechanisms and capacities.

Inorganic P desorption seemed to be a function of the amount of \( P_i \) adsorbed during adsorption experiments before and after oxalate extraction, suggesting that all samples had similar \( P_i \) sorption mechanisms that did not become stronger with longer reaction time. Most IHP adsorbed during adsorption experiments was retained by samples before and after oxalate extraction, suggesting that IHP interactions involved stronger sorption mechanisms than \( P_i \) and with possible precipitation of Al/Fe inositol phosphates that were insoluble in acid media (Jackman and Black, 1951; Anderson et al., 1974)

Oxalate extraction decreased P adsorption by HIS samples the most because they contained the highest \( Al_{ox} \) content which accounted for some P sorption. However, they were still able to adsorb nearly the same amount of P before and after oxalate extraction sufficient reaction time. This suggests that amorphous Al/Fe more quickly sorbed P than
hydroxy-interlayered materials, but given enough time hydroxy-interlayered Al/Fe could adsorb and retain P just as strongly as amorphous Al/Fe.

Total P adsorption was highest with IHP before and after oxalate extraction while total P desorption was dominated by P\textsubscript{i}. Apparently, IHP was involved in stronger, less reversible, sorption mechanisms and out-competed P\textsubscript{i} for amorphous and hydroxy-interlayered Al/Fe hydroxide reactive sites when the two P forms were introduced simultaneously.
### 4.6 Tables and Figures

Table 4-1: Mineralogy of samples without ammonium oxalate extraction

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Table 4-2: Mineralogy of samples after ammonium oxalate extraction

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<td>Arundel (Fine, smectitic, thermic Typic Hapludult)</td>
<td>-</td>
<td>69</td>
<td>-</td>
<td>12</td>
<td>-</td>
<td>18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Conecuh (Fine, smectitic, thermic Vertic Hapludult)</td>
<td>-</td>
<td>63</td>
<td>-</td>
<td>7</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4-3: Pearson correlation coefficients between mg P$_i$ sorbed g$^{-1}$ clay from a single point isotherm, mg P$_i$ desorbed g$^{-1}$ clay, proportion of P$_i$ adsorbed desorbed and clay mineral quantity. *, **, indicates significance at 0.05 and 0.01 probability levels respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before Oxalate Extraction</th>
<th>After Oxalate Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P adsorbed</td>
<td>P desorbed</td>
</tr>
<tr>
<td>HIV</td>
<td>-0.01</td>
<td>-0.10</td>
</tr>
<tr>
<td>HIS</td>
<td>-0.75**</td>
<td>-0.96**</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-0.36*</td>
<td>-0.39*</td>
</tr>
<tr>
<td>Fe$_{ox}$</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>Al$_{ox}$</td>
<td>0.71**</td>
<td>0.80**</td>
</tr>
<tr>
<td>P$_{ox}$</td>
<td>-0.09</td>
<td>-0.16</td>
</tr>
<tr>
<td>P$_{adsorbed}$</td>
<td>-</td>
<td>0.90**</td>
</tr>
<tr>
<td>Reaction Time</td>
<td>0.32*</td>
<td>0.17</td>
</tr>
</tbody>
</table>

*% P Desorbed = the proportion of phosphorus adsorbed during adsorption experiments that desorbed during desorption experiments
Table 4-4: Pearson correlation coefficients between mg P\textsubscript{o} sorbed g\textsuperscript{-1} clay from a single point isotherm, mg P\textsubscript{o} desorbed g\textsuperscript{-1} clay, proportion of P\textsubscript{o} adsorbed desorbed and clay mineral quantity. *, **, indicates significance at 0.05 and 0.01 probability levels respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before Oxalate Extraction</th>
<th>After Oxalate Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P adsorbed</td>
<td>P desorbed</td>
</tr>
<tr>
<td>HIV</td>
<td>0.44*</td>
<td>0.02</td>
</tr>
<tr>
<td>HIS</td>
<td>-0.20</td>
<td>0.05</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-0.23</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe\textsubscript{ox}</td>
<td>0.28</td>
<td>-0.04</td>
</tr>
<tr>
<td>Al\textsubscript{ox}</td>
<td>0.64**</td>
<td>-0.19</td>
</tr>
<tr>
<td>P\textsubscript{ox}</td>
<td>0.16</td>
<td>0.00</td>
</tr>
<tr>
<td>P\textsubscript{adsorbed}</td>
<td>-</td>
<td>0.25</td>
</tr>
<tr>
<td>Reaction Time</td>
<td>0.10</td>
<td>-0.73**</td>
</tr>
</tbody>
</table>

*% P Desorbed = the proportion of phosphorus adsorbed during adsorption experiments that desorbed during desorption experiments
Table 4-5: Pearson correlation coefficients between mg total P sorbed g⁻¹ clay from a single point isotherm, mg total P desorbed g⁻¹ clay, proportion of total P adsorbed desorbed and clay mineral quantity. *, **, indicates significance at 0.05 and 0.01 probability levels respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before Oxalate Extraction</th>
<th>After Oxalate Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P adsorbed</td>
<td>P desorbed</td>
</tr>
<tr>
<td>HIV</td>
<td>0.40*</td>
<td>-0.14</td>
</tr>
<tr>
<td>HIS</td>
<td>-0.76**</td>
<td>-0.93**</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-0.39*</td>
<td>-0.40*</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;ox&lt;/sub&gt;</td>
<td>0.26</td>
<td>0.02</td>
</tr>
<tr>
<td>Al&lt;sub&gt;ox&lt;/sub&gt;</td>
<td>0.72**</td>
<td>0.80**</td>
</tr>
<tr>
<td>P&lt;sub&gt;ox&lt;/sub&gt;</td>
<td>0.11</td>
<td>-0.17</td>
</tr>
<tr>
<td>P&lt;sub&gt;adsorbed&lt;/sub&gt;</td>
<td>-</td>
<td>0.83**</td>
</tr>
<tr>
<td>Reaction Time</td>
<td>0.17</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*% P Desorbed = the proportion of phosphorus adsorbed during adsorption experiments that desorbed during desorption experiments
Table 4-6: Oxalate extractable Al, Fe, and P concentrations of samples.

<table>
<thead>
<tr>
<th>Soil Clay/Reference Mineral</th>
<th>( \text{Al}_{\text{ox}} )</th>
<th>SD</th>
<th>( \text{Fe}_{\text{ox}} )</th>
<th>SD</th>
<th>( \text{P}_{\text{ox}} )</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allen</td>
<td>54</td>
<td>3</td>
<td>33</td>
<td>21</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Allegheny</td>
<td>58</td>
<td>4</td>
<td>35</td>
<td>4</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Nicholson</td>
<td>78</td>
<td>2</td>
<td>301</td>
<td>15</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Lonewood</td>
<td>59</td>
<td>5</td>
<td>30</td>
<td>4</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>HIV</td>
<td>62</td>
<td>4</td>
<td>100</td>
<td>3</td>
<td>3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Arundel</td>
<td>124</td>
<td>10</td>
<td>58</td>
<td>6</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Conceuh</td>
<td>115</td>
<td>47</td>
<td>86</td>
<td>26</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>HIS</td>
<td>120</td>
<td>7</td>
<td>72</td>
<td>20</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>55</td>
<td>2</td>
<td>37</td>
<td>24</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Goethite</td>
<td>6</td>
<td>&lt; 1</td>
<td>33</td>
<td>3</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>
Figure 4-1: Comparison of reaction times for P$_i$ and P$_o$ adsorption data from mixed P treatments for individual clays and reference minerals: Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Conecuh (e), Arundel (f), gibbsite (g), and goethite (h) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-2: Comparison of reaction times for Pi and Po adsorption data from mixed P treatments for mineralogical classes: HIV (a), HIS (b), gibbsite (c), and goethite (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-3: Comparison between reaction times for Pi and Po desorption data from mixed P treatments by individual clays and reference minerals: Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Conecuh (e), Arundel (f), gibbsite (g), and goethite (h) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-4: Comparison between reaction times for Pi and Po desorption data from mixed P treatments for mineralogical classes: HIV (a), HIS (b), gibbsite (c), and goethite (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-5: Comparison between reaction times for Pi and Po desorption data expressed as a proportion of adsorption from mixed P treatments by individual clays and reference minerals: Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Conecuh (e), Arundel (f), gibbsite (g), and goethite (h) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-6: Comparison between reaction times for Pi (capital letters) and Po desorption data expressed as a proportion of adsorption (lower case letters) from mixed P treatments for mineralogical classes: HIV (a), HIS (b), gibbsite (c), and goethite (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-7: Comparison between $P_i$ and $P_o$ adsorption within mineralogical class (numbers) and $P_i$ (capital letters) and $P_o$ (lower-case letters) adsorption between mineralogical classes reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-8: Comparison between Pᵢ and Pₒ adsorption by individual clays (numbers) and Pᵢ (capital letters) and Pₒ (lower-case letters) adsorption between individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-9: Comparison between Pi and Po desorption within mineralogical class (numbers) and Pi (capital letters) and Po (lower-case letters) desorption between mineralogical classes reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-10: Comparison between Pᵢ and Pₒ desorption by individual clays (numbers) and Pᵢ (capital letters) and Pₒ (lower-case letters) desorption between individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-11: Comparison between Pi and Po desorption expressed as a proportion of adsorption within mineralogical class (numbers) and Pi (capital letters) and Po (lower-case letters) desorption expressed as a proportion of adsorption between mineralogical classes reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-12: Comparison between Pi and IHP desorption expressed as a proportion of adsorption by individual clays (numbers) and Pi (capital letters) and Po (lower-case letters) desorption expressed as a proportion of adsorption between individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) before oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-13: Comparison of P (a), IHP (b), and total P (c) adsorption before and after oxalate extraction for mineralogical classes.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-14: Comparison of Pi (a), IHP (b), and total P (c) adsorption before and after oxalate extraction for individual clays and reference minerals.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-15: Comparison of Pi (a), IHP (b), and total P (c) desorption before and after oxalate extraction for mineralogical classes.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-16: Comparison of Pi (a), IHP (b), and total P (c) desorption before and after oxalate extraction for individual clays and reference minerals.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-17: Comparison of Pi (a), IHP (b), and total P (c) desorption expressed as a proportion of adsorption before and after oxalate extraction for mineralogical classes.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-18: Comparison of desorption expressed as a proportion of adsorption of Pi (a), Po (b), and total P (c) before and after oxalate extraction for individual clays and reference minerals.

* Comparisons between untreated and oxalate extracted treatments only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-19: Comparison of reaction times for Pi and Po adsorption data from mixed P treatments for individual clays and reference minerals: Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Conecuh (e), Arundel (f), gibbsite (g), and goethite (h) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-20: Comparison of reaction times for Pi and Po adsorption data from mixed P treatments for mineralogical classes: HIV (a), HIS (b), gibbsite (c), and goethite (d) after oxalate extraction.

*Within case (capital/lowe case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-21: Comparison between reaction times for $P_i$ and $P_o$ desorption data from mixed P treatments by individual clays and reference minerals: Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Conecuh (e), Arundel (f), gibbsite (g), and goethite (h) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-22: Comparison between reaction times for Pᵢ and Pₒ desorption data from mixed P treatments for mineralogical classes: HIV (a), HIS (b), gibbsite (c), and goethite (d) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-23: Comparison between reaction times for Pi and Po desorption data expressed as a proportion of adsorption from mixed P treatments by individual clays and reference minerals: Nicholson (a), Allegheny (b), Lonewood (c), Allen (d), Conecuh (e), Arundel (f), gibbsite (g), and goethite (h) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 4-24: Comparison between reaction times for Pi (capital letters) and Po desorption data expressed as a proportion of adsorption (lower case letters) from mixed P treatments for mineralogical classes: HIV (a), HIS (b), gibbsite (c), and goethite (d) after oxalate extraction.

*Within case (capital/lower case) similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.*
Figure 4-25: Comparison between Pi and Po adsorption within mineralogical class (numbers) and Pi (capital letters) and Po (lower-case letters) adsorption between mineralogical classes reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*all comparisons at the 95% confidence level
Figure 4-26: Comparison between Pi and Po adsorption by individual clays (numbers) and Pi (capital letters) and Po (lower-case letters) adsorption between individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*all comparisons at the 95% confidence level
Figure 4-27: Comparison between Pi and Po desorption within mineralogical class (numbers) and Pi (capital letters) and Po (lower-case letters) desorption between mineralogical classes reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*all comparisons at the 95% confidence level
Figure 4-28: Comparison between P_i and P_o desorption by individual clays (numbers) and P_i (capital letters) and P_o (lower-case letters) desorption between individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*all comparisons at the 95% confidence level
Figure 4-29: Comparison between $P_i$ and $P_o$ desorption expressed as a proportion of adsorption within mineralogical class (numbers) and $P_i$ (capital letters) and $P_o$ (lower-case letters) desorption expressed as a proportion of adsorption between mineralogical classes reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*all comparisons at the 95% confidence level
Figure 4-30: Comparison between Pi and Po desorption expressed as a proportion of adsorption by individual clays (numbers) and Pi (capital letters) and Po (lower-case letters) desorption expressed as a proportion of adsorption between individual clays reacted for 1 day (a), 3 days (b), 7 days (c), and averaged across reaction times (d) after oxalate extraction.

*all comparisons at the 95% confidence level
4.7 Bibliography


CHAPTER 5: COMPARISONS BETWEEN INORGANIC, ORGANIC, AND MIXED PHOSPHORUS INTERACTIONS WITH HYDROXY-INTERLAYERED SOIL MINERALS

5.1 Introduction

In natural soil environments mineral soil components are rarely in contact with merely one form of phosphorus (P) and the chemistry of the soil solution is constantly dynamic. Some forms of P can be dissolving, becoming part of the soil solution, while others are simultaneously precipitating into the solid phase with other chemicals (Ca often in alkaline soils and Al and Fe in acid soils) (Anderson et al., 1974; Shaprley and Sisak, 1997). Because of the dynamics of P chemistry in natural soil environments and the role of P in eutrophication it is important to understand soil interactions with different phosphorus forms both individually and when in competition with each other, pinpointing the effect one form may have on the other when interacting with soil minerals.

Significant literature exists involving inorganic (Pi) and organic P (Po) (especially inositol hexakisphosphate) interacting with soil minerals, but rarely has research involved the two forms introduced simultaneously, included desorption experiments, or involved hydroxy-interlayered soil minerals (Anderson et al., 1974; Celi et al., 1999; Penn et al. 2005)

5.2 Objectives

1. Compare sorption and desorption characteristics of Pi, Po, and mixed P interacting with soil hydroxy-interlayered vermiculite and smectite soil minerals before and after amorphous Al and Fe removal.
2. Compare findings with sorption and desorption processes involving Al and Fe hydroxide minerals (gibbsite and goethite) and P\textsubscript{i}, P\textsubscript{o}, and mixed P before and after amorphous Al and Fe removal.

5.3 Materials and Methods

Materials and quantitative methods were as previously described (Chapter 2, Chapter 3, and Chapter 4). Data from all treatments were compared in the current chapter.

5.4 Results and Discussion

5.4.1 Phosphorus Adsorption and Desorption Experiments

Before Oxalate Extraction

Inorganic P Treatment vs. Organic P Treatment

Consistently, IHP treatment resulted in higher sorption and lower desorption than P\textsubscript{i} treatment (Figure 5-1). Sorption accounted for 5-47% of the P\textsubscript{i} and 61-100% of the IHP added and desorption accounted for 9-40% of the P\textsubscript{i} and 0-1% of the IHP sorbed. Penn et al. (2005) observed higher proportions of P\textsubscript{i} added adsorbed to HIV clays, but this may have resulted from higher P loads in our study compared to theirs. Literature suggests precipitation with Fe and Al may be responsible for the high sorption and low desorption of IHP (Anderson, 1963; Anderson et al., 1974; Reddy et al., 1980).

Effect of Mixed P Treatment on P\textsubscript{i} Interactions with Hydroxy-interlayered Minerals

Surprisingly, in most treatments P\textsubscript{i} adsorption was not significantly depressed when IHP and P\textsubscript{i} were simultaneously interacting with hydroxy-interlayered or geologic reference minerals (P\textsubscript{i} treatment adsorption = 5-47%; mixed P treatment = 11-40%) as
literature suggests (Anderson et al., 1974) (Figure 5-2). Quantitative adsorption data from the two treatments were not comparable because of the difference in the P<sub>i</sub> load (P<sub>i</sub> treatment = 10 mg P<sub>i</sub> g<sup>-1</sup> clay; Mixed P treatment = 5 mg P<sub>i</sub> g<sup>-1</sup> clay) so data were displayed as the proportion of P<sub>i</sub> added adsorbed (Figure 5-2 (b)). Because nearly all the IHP added in mixed P treatments was adsorbed by hydroxy-interlayered clays (71-100%) the adsorptive capacity was not fulfilled and it is impossible to know if higher IHP loads would have depressed P<sub>i</sub> adsorption (Figure 5-3).

Desorption of P<sub>i</sub> was depressed by mixed P treatments, especially for geologic reference minerals (Figure 5-2). However, proportions P<sub>i</sub> desorbed are within the quantitative range of desorption data from Penn et al. (2005) and the decrease in P<sub>i</sub> desorption may be a function of the lower quantities of P<sub>i</sub> present at the beginning of desorption experiments with mixed treatments compared to P<sub>i</sub> treatments (Figure 5-2).

Effect of Mixed P Treatment on P<sub>i</sub> Interactions with Hydroxy-interlayered Minerals

As expected IHP adsorption was not significantly depressed by P<sub>i</sub> additions for hydroxy-interlayered minerals but surprisingly it was for geologic reference minerals (IHP adsorption from organic/mixed treatments: HIV = 38-100% / 71-100%; HIS = 96-100% / 99-100%; gibbsite = 82-97% / 50-62%; goethite = 79-93% / 45-66%) (Figure 5-3), suggesting P<sub>i</sub> inhibited IHP adsorption by geologic reference minerals contrary to the literature (Anderson et al., 1974).

Desorption of IHP was very low with both organic and mixed P treatments (organic = 0-7%; mixed = 0-2%) so strong sorption or precipitation mechanisms
(Anderson et al., 1974; Goring and Sposito, 1985) are expected to dominate IHP adsorption in both cases (Figure 5-3).

**After Oxalate Extraction**

**Inorganic P Treatment vs. Organic P Treatment**

As expected adsorption and desorption trends for oxalate extracted samples were consistent with samples before oxalate extraction, IHP treatment resulted in higher sorption and lower desorption than P$_i$ treatment (Figure 5-4). Sorption accounted for 3-64% of the P$_i$ and 21-100% of the IHP added and desorption accounted for 2-30% of the P$_i$ and 0-1% of the IHP sorbed. Again this is most likely the result of weaker sorption mechanisms for P$_i$ (e.g. monodentate) than IHP (e.g. binuclear, precipitation) (Anderson, 1963; Anderson et al., 1974; Reddy et al., 1980).

**Effect of Mixed P Treatment on P$_i$ Interactions with Hydroxy-interlayered Minerals**

Anderson et al. (1974) suggests that the presence of IHP depresses P$_i$ adsorption in soils by blocking interactive sites however our data disagree (Figure 5-5). If any significant change in P$_i$ adsorption occurred between inorganic and mixed P treatments it was an increase in the proportion of P$_i$ added that adsorbed with mixed treatments (Figure 5-5). This could have resulted from lower quantities of P$_i$ added in mixed P treatments than in P$_i$ treatments (mixed = 5 mg P$_i$ g$^{-1}$ clay; inorganic = 10 mg P$_i$ g$^{-1}$ clay) or an abundance of interactive sites in our samples which allowed equivalent P$_i$ adsorption when interacting with samples alone and in the presence of IHP.

Desorption of P$_i$ was depressed by mixed P treatments (Figure 5-5). The decrease in P$_i$ desorption may have been a function of lower quantities of P$_i$ that were present at
the beginning of desorption experiments of mixed treatments compared to Pᵢ treatments (Figure 5-5).

Effect of Mixed P Treatment on Pᵢ Interactions with Hydroxy-interlayered Minerals

Presence of Pᵢ did not significantly decrease the proportion IHP adsorbed by hydroxy-interlayered or geologic reference minerals following oxalate extraction (HIV organic/mixed = 61/74%; HIS organic/mixed = 37/54%; gibbsite = 45/69%; goethite = 50/69%) (Figure 5-6). Lower IHP quantities added in mixed compared to organic treatments (mixed = 5 mg IHP g⁻¹ clay; organic = 10 mg IHP g⁻¹ clay) could have masked the effect of the presence of Pᵢ, similar to Pᵢ interactions.

Once again, because IHP desorption accounted for such small proportions of the IHP adsorbed (typically < 1%) in all cases, very strong sorption mechanisms most likely dominated (e.g. binuclear, precipitation) (Anderson et al., 1974; Goring and Sposito, 1985).

5.5 Conclusions

Overall, IHP was preferentially adsorbed over Pᵢ by hydroxy-interlayered clays and geologic reference minerals in mixed treatments and significantly more of the P added was sorbed with IHP treatment compared to Pᵢ treatment. Mechanisms of adsorption for IHP seem to be stronger compared to Pᵢ because such little IHP desorbed. This most likely resulted from precipitation of Al/Fe inositol phosphates (Anderson et al., 1974) while Pᵢ was most likely involved in ligand exchange reactions (e.g. monodentate, bidentate) that were more reversible than the precipitation reactions (Goldberg and Sposito, 1985).
5.6 Tables and Figures

Figure 5-1: No oxalate extraction Pi vs. Po treatments: adsorption (a), percent of P added adsorbed (b), desorption (c), and desorption expressed as a percentage of P adsorbed (d).

* Comparisons between inorganic and organic P only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 5-2: No oxalate extraction Pi vs. Pi from mixed P treatments: adsorption (a), percent of P added adsorbed (b), desorption (c), and desorption expressed as a percentage of P adsorbed (d).

* Comparisons between inorganic and organic P only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 5-3: No oxalate extraction Po vs. Po from mixed treatments: adsorption (a), percent of P added adsorbed (b), desorption (c), and desorption expressed as a percentage of P adsorbed (d).

* Comparisons between inorganic and organic P only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 5-4: After oxalate extraction Pi vs. Po treatments: adsorption (a), percent of P added adsorbed (b), desorption (c), and desorption expressed as a percentage of P adsorbed (d).

* Comparisons between inorganic and organic P only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 5-5: After oxalate extraction $P_i$ vs. $P_i$ from mixed P treatments: adsorption (a), percent of P added adsorbed (b), desorption (c), and desorption expressed as a percentage of P adsorbed (d).

* Comparisons between inorganic and organic P only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
Figure 5-6: After oxalate extraction Po vs. Po from mixed treatments: adsorption (a), percent of P added adsorbed (b), desorption (c), and desorption expressed as a percentage of P adsorbed (d).

* Comparisons between inorganic and organic P only, similar letters represent no significant difference and different letters represent a significant difference at the 95% confidence level.
5.7 Bibliography


CHAPTER 6: GENERAL CONCLUSIONS

6.1 Project Summary

This project was split into inorganic, organic, and mixed (organic + inorganic) phosphorus (P) interactions with hydroxy-interlayered soil minerals with the goal of understanding the effect of hydroxy-interlayered Al/Fe materials on P adsorption and desorption processes in soils. Experiments were designed to test the effects of reaction time, mineralogy, oxalate treatment, and mixing P forms on P sorption by, and desorption from samples.

In most cases increased reaction time increased P sorption but this effect was generally better displayed following removal of amorphous materials. Desorption trends with reaction time were fairly random. In the case of inorganic P, significant desorption occurred but no significant correlation in either direction was observed between inorganic P desorption and reaction time. With inositol hexakisphosphate (IHP) nearly all the adsorbed IHP was retained by samples and the sorption mechanisms with IHP were dominated by mechanisms that were irreversible by our treatments.

Generally, phosphorus adsorption and desorption were not significantly positively correlated with hydroxy-interlayered mineral content of clays while in most cases a significant positive correlation was observed between oxalate extractable aluminum (Al\textsubscript{ox}) before oxalate treatment. The degree/quality of interlayer material may have compensated for the quantitative range of hydroxy-interlayered minerals, but degree/quality of interlayering is much more difficult to measure than quantifying the mineralogy. Our results support that not only is Al\textsubscript{ox} an easier soil parameter to measure
it also seems to be a better indicator of the P sorption capacity of soils than hydroxy-interlayered mineral content.

Oxalate treatment decreased the P sorption capacity of most samples because many reactive sites were removed. Treatments following oxalate treatment better pinpointed the interaction between hydroxy-interlayered minerals and P because amorphous materials could no longer interfere.

Inorganic P and IHP reacted similarly when mixed as when they were introduced together.

### 6.2 Overall Conclusions

Oxalate extractable aluminum seems to be the best parameter for understanding the P adsorption/desorption by soil clays. This parameter was in most cases more highly correlated with P sorption than hydroxy-interlayered mineral content. Hydroxy-interlayers participate in P sorption however amorphous aluminum out-competes the interlayered Al/Fe and is a better clue to the P binding capacity of a soil/clay. Also, this parameter is easier to quantify than hydroxy-interlayered minerals. On a large scale Al\textsubscript{ox} is suggested as the easiest and most reliable soil parameter to measure to estimate the P binding capacity of soils.

Of the two P forms added IHP was more highly sorbed so soils can bind and retain higher loads of IHP than inorganic P and higher loads of IHP could be applied to soils than P\textsubscript{i} without degradation of environmental quality.
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