PHOSPHORUS IN ALUM AMENDED POULTRY LITTER SYSTEMS: DISTRIBUTION, SPECIATION, AND INTERACTIONS WITH ALUMINUM OXIDES

by

Kristin Estelle Staats

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Approved: ____
Donald L. Sparks, Ph.D.
Professor in charge of thesis on behalf of the Advisory Committee

Approved: ____
Donald L. Sparks, Ph.D.
Chair of the Department of Plant and Soil Sciences

Approved: ____
Robin Morgan, Ph.D.
Dean of the College of Agriculture and Natural Resources

Approved: ____
Conrado M. Gempesaw II, Ph.D.
Vice Provost for Academic and International Programs

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And Mike, do you remember this quote by our good friend Wendell Berry?: "…[W]hen you leave familiar ground and step off alone to a new place, there will be, along with feelings of curiosity and excitement, a little nagging of dread. It is the ancient fear of the unknown…. What you are doing is exploring. You are understanding the first experience, not of the place, but of yourself in that place. It is the experience of our essential loneliness, for nobody can discover the world for anybody else. It is only after we have discovered it for ourselves that it becomes common ground, and a common bond, and we cease to be alone" (1991). So it is my time to explore myself in a new place, and have new experiences. I prefer to think of it as temporary, "essential aloneness," because with the love and friendship that we share, I could never be lonely. Thank you for giving me the courage to find and be myself.

To Buster

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ABSTRACT

Phosphorus (P) enrichment of aquatic environments has altered their ecological functioning and diminished their commercial, recreational, and aesthetic values. As the limiting nutrient factor for algal growth in natural waters, P must be controlled in order to mitigate and/or prevent these negative impacts. Therefore, recent investigations have focused on understanding the role of agronomic point-source nutrient pollution, such as confined animal feeding operations (CAFOs) (i.e. poultry production facilities), in the decreased water quality in the Mid-Atlantic Region (PA, MD, DE, VA, WV, and Washington D.C.) of the United States. Because of intensive poultry production on the Delmarva (Delaware, Maryland and Virginia) Peninsula, manure management policies have recently been implemented, of which the benefits remain to be quantified. These laws require comprehensive nutrient budgets for farms which land apply animal waste. As best management practices (BMPs) are becoming incorporated into environmental legislation, an understanding of their chemical basis, on a molecular-scale, will ensure their potential to preserve and improve environmental quality.

Initially, a fundamental understanding of the components in PL which react with P is needed. Therefore, the first objective of this study is to differentiate the forms of phosphate in PL, based on the order of their removal during a routine sequential extraction. Fast and inexpensive, this fractionation procedure may prove useful for manure analyses required in nutrient management plans. However, a chemical understanding of the extraction process will determine its accuracy for

assessing the chemical composition of animal wastes. Chapter 2 provides a critical evaluation of an extraction method commonly used to determine P speciation in animal wastes. By implementing a P-specific analytical tool, x-ray absorption near edge structure spectroscopy (XANES), new interpretations of this traditional soil science technique is possible. This will allow for more accurate risk assessment when evaluating the nutrient content of PL which is to be land applied.

The second objective is to understand the adsorption of phosphate onto aluminum surfaces, similar to those found in alum amended poultry litter. These reactions are extremely complex due to the presence of organic compounds in the waste in addition to varying pH conditions as the birds develop. Overall, the aim is to provide a molecular-scale understanding of P retention at the aluminum oxide-water interface, because of the importance of this reaction in the alum amendment BMP. In Chapter 3, Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy is used to investigate the sorption of phosphate and an organic acid (oxalate) onto a model surface, amorphous aluminum oxide. In conjunction with batch aqueous sorption experiments, this technique shows how these two anions, present simultaneously and in large quantities in PL, react with a mineral surface in the presence of each other. The results and interpretation from this study can then be extrapolated to the more complex PL system, to improve and optimize the alum amendment practices. By integrating novel spectroscopic techniques with traditional soil science methods, more in-depth solutions to nutrient management concerns can be developed and current management practices can be fully understood so that improvements, if needed, are possible.

Chapter 1.0

LITERATURE REVIEW

1.1 Phosphorus and Eutrophication

As a plant macronutrient, P is often applied to agronomic crops in order to obtain profitable grain yields. Where animal production is practiced and small grains, used for feed, are grown on neighboring fields, the animal waste is land-applied as an inexpensive source of P and other macronutrients (nitrogen (N) and potassium (K), e.g.) (Robinson and Sharpley, 1995). In addition, the cost of transporting the manure off-site is eliminated. With the exception of the past several decades, nitrogen was considered the limiting nutrient for agronomic crop growth and development; therefore, applications were based on their N value, without regard for other nutrients in the manure. Because of high application rates needed to meet crop N needs, which alternatively add excessive P beyond plant requirements, agronomic soils became saturated with respect to phosphorus (Sims and Wolf, 1994).

When a soil's P sorption maximum is reached, and additional P is continually added, the probability of P losses from that soil is increased (Pote et al., 2003; Vadas and Sims, 1999). Phosphorus is thought to be transported via runoff or erosion, bound to the particles. However, in soils with a shallow water table and lacking components which would retain P, leaching and subsurface flow are also active transport pathways (Sims et al., 1998). In addition to these physical means, reducing conditions can solubilize metal species and release phosphorus that would be bound in oxidizing environments (Vadas and Sims, 1998). In low-lying portions of crop fields, extensive networks of tile and other drainage systems are designed to lower the water table so that the soil can support traffic of large farm equipment and maintain proper drainage for optimum plant root growth and minimal disease. These ditches, which ultimately may lead to surface water bodies, are the destination of leached phosphorus from the fields and can undergo oxidation/reduction cycles due to repeated wetting and drying (Sallade and Sims, 1997a; Sallade and Sims, 1997b). All of these conditions, both physical and chemical, contribute to the increasing levels of nutrients in adjacent waters.

Eutrophication and nutrient enrichment of bays in the Mid-Atlantic region have been the catalyst for investigations on the roles that different elements play in this process. When concentrations of nutrients increase in an aquatic system, phytoplankton, algae and submerged plants flourish. Large algal blooms can shade sunlight and inhibit the growth of beneficial organisms, in addition to reducing dissolved oxygen levels (Sims and Wolf, 1994) upon their death and decomposition. In addition, high nutrient levels can promote the growth of toxin-producing organisms, such as *Pfiesteria*. Overall, the value of the ecosystem, recreationally, commercially, and aesthetically, is compromised (Sharpley et al., 1994). While much attention had previously been paid to nitrogen (because of its role in groundwater pollution) and carbon (C), Schindler (1977) determined that P supply, not N or C, was the limiting factor in phytoplankton productivity in freshwater systems. This created a paradigm shift where P-based soil and manure tests were encouraged and policies dealing with P management requirements were drafted.

1.2 Nutrient Management Legislation

Confined Animal Feeding Operations (CAFOs), such as large poultry production facilities, have contributed greatly to the environmental degradation caused by excessive P concentrations in surface water, especially in the Mid-Atlantic region. Due to the increasing intensity of animal production, federal, state, and local governments are taking actions to control nutrient pollution from these recently declared “point sources”.

The United States Environmental Protection Agency (USEPA) and United States Department of Agriculture-Natural Resources Conservation Service (USDA-NRCS) devised policies which shift the focus in nutrient management from nitrogen to phosphorus (Sharpley et al., 2003). In May 2002, NRCS made their 590 standard effective, which requires documentation of manure management practices of CAFOs. Later that same year, the USEPA signed into effect the final rule of the National Pollutant Discharge Elimination System (NPDES) Permit Regulation and Effluent Limitation Guidelines and Standards for CAFOs. These laws require CAFOs to obtain permits, based on land use practices, annual manure production, and operation size, which will dictate waste management procedures. Confined Animal Feeding Operations with greater than 8 animal units (approximately 1600 broilers, assuming finishing weight of ~ 5 pounds(Delmarva poultry industry, 2000) or plans to apply nutrients to an area greater than 10 acres must “develop and implement a nutrient management plan (NMP)” as part of the permitting procedure (USEPA, 2003).

Individual states are implementing this federal policy through water quality-based laws of their own. The Delaware Nutrient Management Commission (DNMC) was established, under Delaware Title 3: Chapter 22, Subchapter II, as part of the Delaware Nutrient Management Law of 1999. This organization oversees and enforces nutrient management legislation in the state, as well as promoting and developing sound nutrient management practices. Overall, the goal of the commission and NMPs is to retain the economic profitability of agriculture while efficiently using waste materials and preserving environmental quality. These comprehensive documents include soil analyses, documentation of land use, yield expectations, data from manure/waste (destined for land application) testing, etc. Research on the use of waste amendments, as well as composting and storage protocols, may become incorporated into policy, as best management practices, to be included in a farmer's NMP. Alternatives to land application, to fields which may already possess elevated P levels, are also proposed. This would include transportation of litter to regions with P deficient soils or where it is used for livestock feed (DDA, 2004). According to the Delaware Handbook for Nutrient Management Certification, by January of 2003, the DNMC began the review of NMPs, of which all will be implemented by 2007.

Maryland's Water Quality Improvement Act of 1998, initiated because of a correlation found, by a gubernatorial commission, between *Pfiesteria*-induced fish deaths and high nutrient concentrations, mandates that CAFOs devise and abide by comprehensive NMPs by 2005 (Simpson, 1998).

To make these deadlines realistic, federal and local assistance is available to farmers. With the help of certified conservation personnel, poultry producers are to build a site/operation specific plan of best management practices for their operation. In addition to planning and advisement from the conservation district, the financial obligation, to implement the best management practices set forth in their NMP, can be partially alleviated through cost-share programs.

1.3 Environmental Sources and Cycles of Phosphorus

1.3.1 Natural Sources

1.3.1.1 Organic Phosphorus

Phosphorus is a plant macronutrient that occurs in the soil in both organic and inorganic forms. In soil organic matter, such as humus and biological residues, P is the second most abundant nutrient. Like organic C, organic P is often found more abundantly in no-till or undisturbed surface horizons of the soil (Vaithiyanathan and Correll, 1992). Unlike nitrogen and sulfur, phosphorus undergoes no electron reduction before being incorporated into organic compounds; therefore, it remains in the P (V) oxidation state (Condron et al.).

The three major types of natural organic phosphate compounds, orthophosphate esters, phosphonates, and anhydrides, are all classified by the type of P bond present in the molecule (Condron et al.). Inositol phosphates, a type of orthophosphate monoester, make up the bulk of organic P (up to 50% in some soils) (Dalal, 1977). These phosphate compounds, occurring in a variety of isomeric forms, are very stable and are thought to be microbially synthesized (Stevenson and Cole, 1999). Of notable importance is the hexaphosphate ester, phytic acid, which occurs in small grain crops used as feed for livestock. The predominance of these compounds in the organic P fraction of soil is likely, because inositol phosphates can form recalcitrant complexes with Fe, Ca, and Al.

Other phosphate monoesters (sugar phosphates and phosphoproteins) and diesters (phospholipids, nucleic acids, etc.), are less resistant to microbial degradation and therefore make up a smaller proportions of soil organic P. For instance, nucleic acids (i.e., RNA and DNA) and phospholipids (containing phosphate which is covalently bonded to C), combined, make up less than 5-7% of soil organic P (Stevenson, 1982). The ratio of phospholipids found in plant matter to that found in the soil is high, indicating their rapid cycling between these two pools. Current extraction methods make quantification of this fraction of soil organic P difficult; however, it is known that these compounds are continuously being added to the soil and readily assimilated by microbes (Dalal, 1977). Included in soil organic P, but occurring in even smaller quantities, are the metabolic byproducts (i.e., ATP and ADP) known as orthophosphate anhydrides. These energy-rich polyphosphates, inherently unstable in natural systems, often break down into their orthophosphate ester components (Condron et al.). Although these and previously mentioned compounds have been identified as constituents of soil organic P, there is still little information available to identify and quantify the nearly 50% of organic P which is still unknown (Schnitzer and Khan, 1978). It has been assumed in the past that organic P is relatively insignificant in plant nutrition when compared to inorganic soil P, partially because of the limited information available on this aspect of soil nutrient cycling. However, if these organic P pools have rapid mineralization and cycling rates, their bioavailability is likely of great importance (Schnitzer and Khan, 1978).

1.3.1.2 Inorganic Phosphorus

Naturally occurring, inorganic phosphorus originates from apatite-(rock phosphate) rich parent material. Apatites, a group of primary minerals, are insoluble tricalcium phosphates often found in associations with chlorine, fluorine, hydroxyl, or carbonate ions. The breakdown products of apatites release P into the soils and environment where they reenter into the phosphorus cycle (Stevenson and Cole, 1999).

Orthophosphate ions (dissociated ions of phosphoric acid) are the most reactive form of phosphate in soils. The degree of protonation of the oxyanion, determining its reactivity with cations, depends on the proton concentration (pH) in the system: H_3PO_4 ($pK_a = 2.1$), $H_2PO_4^-$ ($pK_a = 7.2$), HPO_4^{2-} ($pK_a = 12.3$). A pC (log of concentration) vs. pH diagram (Figure 1.1) displays relative abundance of the forms of orthophosphate with respect to hydrogen ion (H^+) concentration:

Because most soils being used for agronomic purposes are adjusted to a pH range from 5 to 8, the orthosphosphate ions that predominate in solution are $H_2PO_4^-$ and HPO_4^{2-}. These ions are available for immediate biological uptake, and therefore play a major role in crop nutrition and microbial activity. Soil solution concentrations of these ions are dictated by the type of soil material, sources of P (types and abundance) to the system, and biological activity. Doubly and singly protonated orthophosphate may undergo sorption and precipitation reactions, which will determine, for nutrient management purposes, their availability and extractability.

In addition to orthophosphate anions, secondary minerals form when P reacts with cations (Al, Fe, Ca) in the soil. Vivianite and strengite (iron-phosphates) and wavellite and variscite (aluminum-phosphates) are examples of secondary P minerals commonly found in environmental systems. While most soil P, especially in sandy soils, is found to be associated with Al, the Ca-P phases, such as monetite, dicalcium phosphate dihydrate, and hydroxylapatites should also be considered when predicting inorganic P speciation and reactivity (Lookman et al., 1996; McDowell et al., 2002).

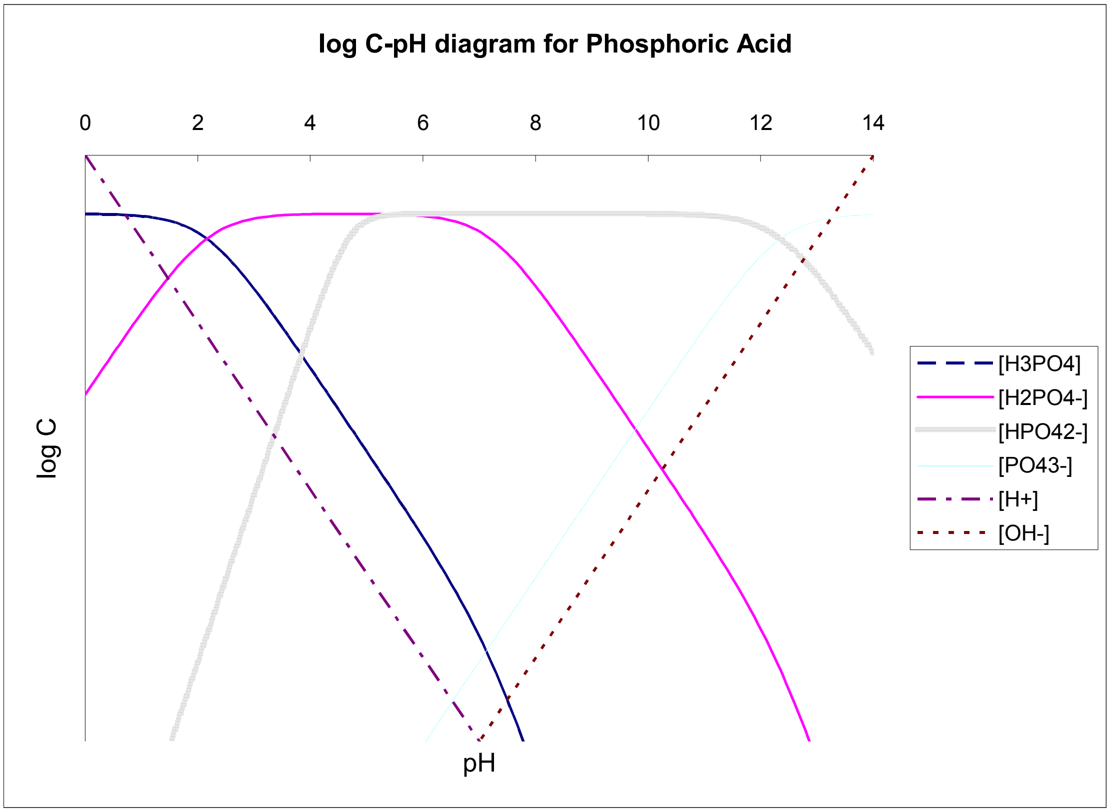


Figure 1.1 **Phosphoric Acid Speciation Diagram**

1.3.2 Anthropogenic Additions

While P is abundant in some soils, due to mineralogy and soil chemistry, deficiencies occur in highly leached, weathered soils or those which lack P-rich parent material. If a low P soils is to be used for agriculture, additions of phosphate fertilizer are necessary for crop health and productivity. Manufactured P fertilizer can be applied to meet the P needs of the plants when inexpensive sources of P, such as animal manures and crop residues, are unavailable or in low supply. These fertilizers are manufactured by acidifying apatite to create different weight percents of P in the end product (Stevenson and Cole, 1999). In addition to fertilizers, synthetic herbicides, fungicides, insecticides and plant hormones, often used in commercial agriculture, have a major P component.

1.3.3 Phosphorus Cycles in the Soil and Atmosphere

The soil phosphorus cycle is a combination of chemical and physical reactions that involve all aspects of the soil environment, including plants, microbes, and soil constituents (Figure 2).

During pedogenesis, mineral P weathers, slowly releasing phosphate ions to the soil solution. Other direct inputs, such as crop fertilizers, plant and animal residues, municipal wastewater treatment effluent, and runoff from industrial sources, also contribute to soil P concentrations. Soil solution P (mainly orthophosphate ions and dissolved organic P) may be removed by physical processes, such as leaching and erosion, plant uptake, reactions with other ions (predominantly calcium (Ca), iron (Fe), and aluminum (Al)), and/or precipitated as secondary minerals. In addition, orthophosphate ions may also be sorbed, desorbed, or fixed by clay minerals and metal oxide coatings on soil constituents. All of these chemical and physical processes are linked and complicated by biological activity.

There is a constant conversion from organic to inorganic P through mineralization and immobilization reactions. Immobilization refers to the transformation of inorganic phosphorus to organic forms, such as microbial cellular material. Mineralization occurs when organic biomass decomposes, releasing inorganic phosphorus. Because these reactions are mediated by the microbial populations, mineralization and immobilization rates depend on physical and chemical factors that regulate and limit cellular growth and activity. These include temperature, soil moisture content, nutrient availability, pH, relative proportions and quality of carbon (C), nitrogen (N), sulfur (S) and P, and energy sources for the organisms. For instance, as the C: organic P ratio increases above 300, so does immobilization of inorganic P (Hedley et al., 1982). Mineralization also depends on cellular production of phosphatase enzymes, which provide the final hydrolysis of organic P compounds (Stevenson and Cole, 1999).

Additions of organic P, like manures, crop residues or other carbon-based soil amendments, may initially cause an increase in P fixation as the microbes assimilate the material; however, after this initial period of immobilization, inorganic P pools increase as the mineralization of biomass occurs (Sharpley and Smith, 1989). However, this trend is not always consistent when comparing soils of different climates (due to differences in P content and the rates at which soil organic and inorganic P supply P to the soil solution) so generalizations across soil types cannot be made (Reddy et al., 1996).

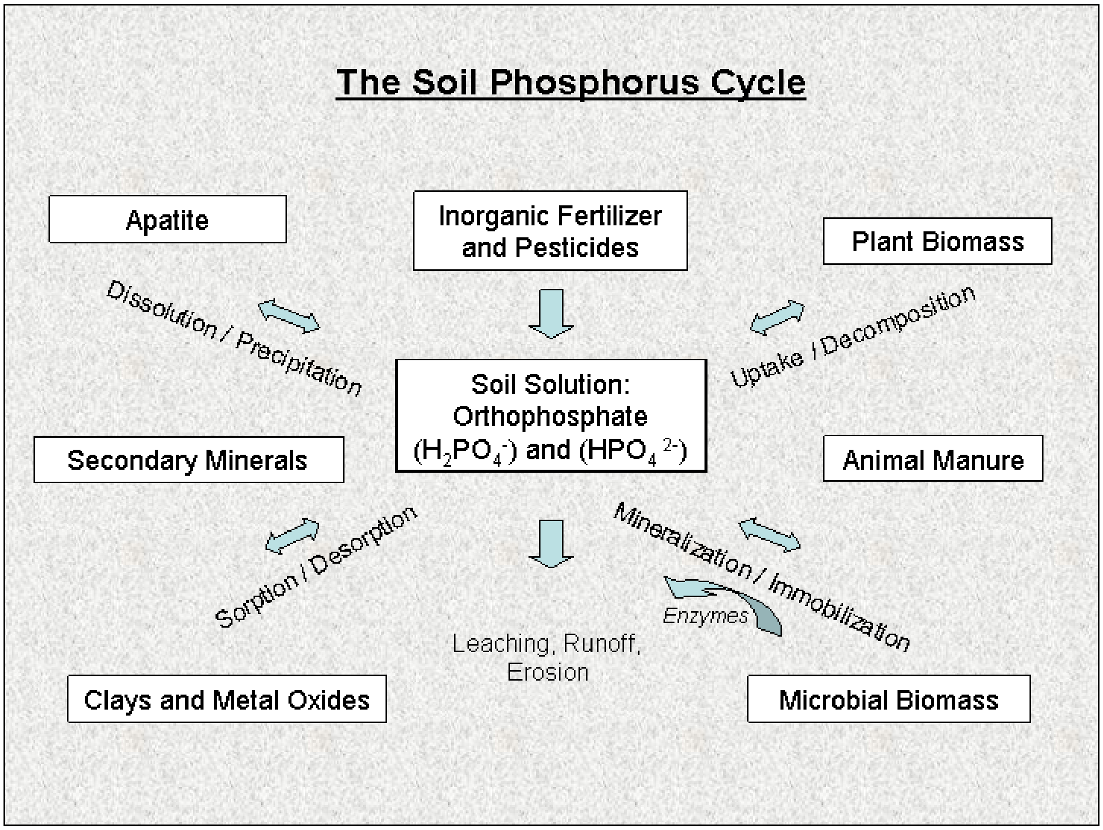


Figure 1.2 The Soil Phosphorus Cycle

1.4 Phosphorus Interactions with Environmental Media

Reactions with soils and soil components determine the fate and mobility of the phosphate oxyanion in environmental systems.

1.4.1 Phosphorus Adsorption and Desorption

Adsorption refers to the "accumulation of a substance or material at an interface between the solid surface and bathing solution" (Sparks, 2003). The solid surface (sorbent) can be defined as well characterized, ideal oxides and clays or as heterogeneous mixtures of the environmental components which make up a soil.

Direct and indirect, in-situ and ex-situ techniques are used to observe and investigate the local bonding environment of phosphate with these surfaces.

1.4.1.1 Phosphorus Adsorption on Clays and Metal Oxides

In order to understand the mechanisms by which phosphate reacts in complex systems such as manure material and soils, it is vital to recognize how the anion reacts with the individual components of these media. Over the past forty years, published literature concerning the properties of adsorption and desorption of phosphate on well-characterized surfaces has surged, with focuses on kinetic and equilibrium based theory. Mathematic functions, kinetic models and equilibrium based isotherms, which manipulate sorption data, are used to extrapolate bonding information and reaction rates.

Early equilibrium based studies, such as the work of Muljadi, et al. (1966a; 1966b), defined three distinct regions of phosphate adsorption (I, II, III), based on the ease with which sorption to Al-bearing surfaces was reversed. Region I, that with the highest binding energy, represents chemisorption of P (only reversible with increased pH) at surface/edge hydroxyl or water sites (ligand exchange), while region III is more physically sorbed P, which has penetrated into more amorphous regions of the clay, but is the most reversible. The equilibrium dependent regions (I, II, and III) are analogous to “compartments” A, B, and C defined by the kinetic approach of Barrow and Shaw (1974), representing short-term and long-term supply of phosphorus to the soil solution (region III being equivalent to compartment B) (Ryden and Syers, 1977a). An early study states that phosphate migrates from sites suitable for physical adsorption under high concentrations and to areas of higher binding strength with washing (Kafkafi et al., 1967). Others suggest that at low concentrations phosphate undergoes ligand exchange (Parfitt, 1978); where, at high concentrations, it seems that some destruction of the sorbent can occur; creating new sorption sites (Rajan and Perrott, 1975).

Equilibrium based isotherms rely on bond strengths, charge properties, and concentration-distribution relationships. The Langmuir equation [1.1] has been widely used to describe the sorption of phosphate in many of the aforementioned studies (Cabrera et al., 1977; Rajan and Perrott, 1975; Ryden and Syers, 1977a; Ryden et al., 1977b; Ryden et al., 1977c).

$$(c/x) = (c/xm) + (1/Kxm) \qquad [1.1]$$

where c is the solution concentration, x is the amount of adsorbed ion, xm is the sorption maximum, and K is the adsorption energy constant (Parfitt, 1978). Using this equilibrium based model, Cabrera et al. (1977) concluded that Al oxides are more reactive with phosphate than iron oxides. However, even with alterations to account for two energy regimes for sorption sites, this model was derived for gas sorption onto a uniform, unchanging surface (Parfitt, 1978); therefore, is not particularly well suited for more complex surfaces and ions. Madrid and Posner (1979) determined that slow, reversible adsorption of phosphate with increased time followed the Stern model, where the surface potential and charge of the diffuse and Stern layers are related to the number of available sorption sites (Sparks, 2003).

Attempts to find an equation that accurately describes the P sorption isotherm, for metal oxides, and accounts for variables within the system (pH, [P]) led to use of the Constant Capacitance surface complexation model [1.2]:

$$\sigma = (CSa/F)\,\psi \qquad [1.2]$$

where σ is the net surface charge, C is the capacitance density, S is the specific surface area, a is solution density of the solid, F is the Faraday constant, and ψ is surface potential.

Because this equation assumes ligand exchange and the alterations to the surface with increased sorption, it is more suited for phosphate isotherms. Through the addition of surface protonation constants and phosphate sorption density parameters, this model accurately predicts phosphate adsorption maxima in response to changes in pH. Application of this equation suggests that phosphate reacts similarly with both Al and iron oxides, as well as indicating that phosphate surface speciation cannot be predicted through aqueous speciation (Goldberg and Sposito, 1984a; Goldberg and Sposito, 1984b).

Still, when considering phosphate sorption, some maintain that this reaction is kinetically driven (Ryden and Syers, 1977a; Ryden and Syers, 1977b). Kinetic models describe sorption reactions in terms of time-dependency. Atkinson et al. (1972) used the Elovich equation [1.3] to model isotopic exchange data, and propose a bidentate, binuclear bridging complex, making iron oxide surface sites inert:

$$q = (1/\beta) \ln \alpha\beta + (1/\beta) \ln t \qquad [1.3]$$

where q is the amount sorbed at time t, α and β are constants during the sorption/desorption experiment.

In addition, Parabolic Diffusion [1.4] (Evans and Jurinak, 1976) and first- and second-order kinetics have all been applied to phosphate adsorption data; supporting the argument that the reaction is time dependent.

$$q_t/q_\infty = R_D t^{1/2} + \text{constant} \qquad [1.4]$$

where q_t is the amount of sorbate per unit mass of sorbent at time t, q_∞ is the quantity of sorbate at equilibrium, and R_D is the overall diffusion coefficient. However, many kinetic models, because of adjustable parameters within the equations, may fit the same set of data (Ogwada and Sparks, 1986). So, while modeling and batch sorption experiments are useful data and surface complexation theory can be used to deduce bonding structures, it is impossible to gain mechanistic information through the use of indirect, macroscopic observations.

With the advent of spectroscopic techniques, more definite understanding of P complexation was gained. Russell et al. (1974), using infrared (IR) absorption, directly show that hydroxyl (OH-) groups are lost from the goethite surface when P is adsorbed. This confirms that ligand exchange is the mechanism by which phosphate attaches to iron oxides, forming an inner-sphere complex, much like arsenate (Goldberg and Johnston, 2001). With this understanding of the binding mechanism, further studies, using IR techniques, defined the surface complex by which phosphate was held: a bidentate, binuclear bridging complex with Fe(III) on crystalline and amorphous iron oxide surfaces (Parfitt and Russell, 1977; Parfitt et al., 1975; Tejedor-Tejedor and Anderson, 1990) and on the edge sites of Al oxides (Parfitt et al., 1977). Furthermore, bidentate complexes, of phosphate on iron-bearing surfaces, are directly dependent upon loading levels and pH, where at higher loading and lower pH they are not present (Arai and Sparks, 2001; Parfitt and Russell, 1977), possibly because monodentate complexes form (Persson et al., 1996) so that more metal sites are available.

1.4.1.2 Phosphorus Adsorption on Soils

With the knowledge gained from working with ideal, well defined surfaces, we can begin to investigate the mechanisms of phosphate fixation by complex, heterogeneous systems, like soils.

Depending on the pH and composition of any given soil, phosphorus sorption and release will be controlled by any combination of factors. A survey of soil properties, such as reactive oxides, relative phosphorus fractions, elemental composition and texture, indicate that exchangeable and amorphous Fe, and to a greater extent, Al (Ballard and Pritchett, 1974) contribute most to P retention (Ballard and Fiskell, 1974; Maguire et al., 2001a). At pH near 5, amorphous Al phosphates control the solution equilibrium because they are most stable (Lookman et al., 1997), but above pH 5.5 calcium phosphates predominate (White and Taylor, 1977a). In addition to calcium phases, discreet Al- and Si-bearing precipitates have been found in soils (Pierzynski et al., 1990a; Pierzynski et al., 1990b). Whether this is the result of P saturation of the soil solution adjacent to fertilizer particles, or long-term weathering of Al surfaces in the presence of phosphate, these precipitate phases would be expected to be more stable than sorbed phases (Kyle et al., 1975).

Many of the P sorption properties of soils are similar to those of iron and Al oxides. For instance, it is apparent that there are several forms of phosphorus in the soil: solution phases, adsorbed phases, and those which have penetrated into the soil's structures (Barrow, 1983a). Of the adsorbed phase, there is the physically, loosely bound, P and chemisorbed P. Under high initial concentrations, phosphate binds weakly (physically) to the surface, and with increasing time migrates to a chemically bound form which is more recalcitrant to desorption; therefore, there is a strong relationship between the incubation time and the strength with which phosphate is held in the soil (Barrow and Shaw, 1975; Ryden et al., 1977a; Ryden et al., 1977b; Ryden et al., 1977c; White and Taylor, 1977b). With time, as P sorption sites become occupied, the buffering ability of the soil is decreased, leading to decreased P adsorption (Barrow, 1974).

The transformation from physically to chemically adsorbed phosphate leads to a hysteresis between adsorption and desorption isotherms (Barrow, 1983b; Barrow, 1985; Parfitt et al., 1975; Zhou et al., 1997), making kinetic modeling of the uptake and release of P in soils a complex task. Chien and Clayton (1980) describe the contradictory results that may be obtained through the use of the parabolic diffusion equation[1.4] and first- and second-order kinetic equations, suggesting that the Elovich equation [1.3] is more suitable and reliable for comparatively describing the forward and reverse reactions, over the entire reaction time, in soils.

1.4.1.3 Phosphate Desorption

If adsorption is the accumulation of a material at a surface, then desorption is the release of the sorbate (sorbed material) to the sorptive solution. Although understanding the retention of phosphorus by soils is important to understand its reactivity, applying this knowledge to the release, or desorption, is relevant to environmental concerns.

With the knowledge from P sorption on soils and soil components, and the importance of metals (Al, Fe, and Ca) in sorption reactions, predicting P loss based on soil properties should be possible. Iron-impregnated filter paper (van der Zee et al., 1987), anion exchange resins (Amer et al., 1955), iron oxide filled dialysis membranes (Freese et al., 1995; Lookman et al., 1995), batch replenishments (Kafkafi et al., 1967), isotopic exchange (Atkinson et al., 1972; Kyle et al., 1975), and stirred-flow techniques (Carski and Sparks, 1985) have all been used to study P exchange and release from soils. In all of these studies, Al and Fe oxides (both crystalline and amorphous) (Dalal, 1974; Maguire et al., 2001a; Maguire et al., 2001b), clay content and in more alkaline soils, complexes with Ca (McDowell et al., 2002; Sharpley, 1983), have all been considered as factors in P release predictions. Depending on the soil, the relative proportions of these components change, therefore affecting the release behavior. Regardless of soil composition, desorption follows the same biphasic pattern as adsorption, with a fast release in the initial time periods, followed by a slower release (Barrow, 1979; Barrow and Shaw, 1975; Breeuwsma and Lyklema, 1973; McDowell et al., 2001). Also, like sorption, there are incongruencies between sorption and subsequent desorption curves which are not entirely understood.

To assist in explaining the incongruence in kinetic observations, other studies suggested that, with time, phosphorus migrated from areas of low binding strength (physical adsorption) to areas of high binding strength (chemically adsorbed) within the sorbent, leading to the hysteresis (Ryden and Syers, 1977a; Ryden et al., 1977c). From another perspective, these reactions may be limited by processes outside of kinetics. If, for instance, equilibrium is not reached within the system during the initial sorption reaction, then desorption is reduced. This would suggest that some high energy sites were available for further P additions. However, if equilibrium is reached, and all of the high energy sites react with phosphate, then any P added to the system is easily removable (White and Taylor, 1977b). In iso-pH conditions, as in agricultural settings where lime is added to maintain a consistent availability of micronutrients, only physically adsorbed phosphate is desorbable. If the pH becomes alkaline, the OH- ions can out-compete the chemisorbed phosphate and remove it from the sorbent (Ryden and Syers, 1977b).

So, P speciation, concentration, frequency of addition, soil properties and components, and incubation times all play a part in the way phosphate adsorbs in a soil as well as the rate and ease with which it desorbs.

1.4.1.4. Phosphorus Adsorption in the Presence of Organics

Inorganic anions such as selenate, arsenate, silicate and molybdate have structures similar to phosphate, providing the ability for them to compete for adsorption sites (Ryden et al., 1987). Organic ions with similar atomic radii and charge properties may also inhibit the uptake of phosphorus, in addition to metals and metalloids (Grafe et al., 2001; Yamaguchi et al., 2001). Of particular importance in our study is the presence of organic (carbon-based) compounds found in animal waste and how they influence phosphate retention onto Al hydroxides. The importance of Al and organic acids in relationship to PL and the larger scope of this project will be discussed in chapter 3.0.

Soil organic matter carries a net negative charge, making it very reactive with metal cations like Al. In addition to an electrostatic attraction, the tortuous nature of long carbon chains, which compose soil organic matter, can bind metals so strongly that they can be used to mitigate the negative plant response to high monomeric Al concentrations in soil solutions (Hue et al., 1986). Functional groups, such as carboxyls (-COOH), react with monomeric Al, short-order polymeric Al , and Al surface sites on clays (Parfitt et al., 1999). Consequently, up to 95% of metals in the soil solution can be associated with organic matter (van Hees and Lundstrom, 2000).

Because such a large proportion of non-structural metals are in organic associations, phosphate sorption and precipitation reactions in soils are affected by the presence and reactivity of naturally occurring, C-bearing compounds. Using soil-extracted organic material, Yuan (1980), suggests that there may be some sites in soils that have an affinity for both organic matter and phosphate, which may increase the release of phosphate in the presence of dissolved organic species (Sibanda and Young, 1986). Phosphate is also observed to be more labile when organic residues from crops, root exudates, or dissolved carbon are added to or present in soil systems (Anderegg and Naylor, 1988; Evans, 1985; Fox and Comerford, 1992; Fox et al., 1990b). Compounds found in feed grain (Evans, 1985) and those excreted by plant roots (Shen et al., 2002) increase available P in solution, impacting the availability of macronutrients to the crops (Anderegg and Naylor, 1988). In soils, these increases in extractable P are explained by three mechanisms: an exchange between the inorganic P and the organic ions (Fox et al., 1990a); chelation (by the organics) of metals which would normally retain P (Ohno and Erich, 1997); or hydrolysis of P-containing organic materials (Lopez-Hernandez et al., 1979). If the metals are chelated by the organic matter and phosphate reacts with the bound metal, Zhou et al. (1997) showed that the organo-metallic complexes, while being able to initially sorb more phosphorus than horizons without the organic components, release sorbed P more easily than if it where directly sorbed to the metal oxide alone.

Individual organic acids, as well as the more complex HA and FA found in the soil, have been investigated, under varying conditions, as competitors with phosphate on metal-bearing surfaces (De Cristofaro et al., 2000; Kafkafi et al., 1988; Violante and Huang, 1989; Violante and Gianfreda, 1993). All of these studies demonstrate that P sorption is compromised across a range of pH values. Protonation of phosphate and organic acids is controlled by pH, influencing the potential for interaction. At low pH the undissociated organic anions are responsible for most of the competition with phosphate; however, at higher pH values (above neutral) release of phosphate is caused by the competition from hydroxyl groups. Specifically, oxalate (pK of 1.2 and 4.2) and tartrate are more aggressive competitors at low pH (De Cristofaro et al., 2000; Violante and Gianfreda, 1993), while citrate (pK at 3.13, 4.76, and 6.40) causes a greater release in sorbed P at higher pH(Kafkafi et al., 1988).

Several explanations are available for the way in which organics interfere with phosphate reactions. First of all, some organic ions are bound to the surface by the same mechanism (ligand exchange) and create the same surface complexation structure (binuclear complex) when binding to metal oxides (Parfitt and Russell, 1977); therefore, active sorption sites are limited. In precipitation reactions, HA, FA, tannic and citric acids are proven to block crystal growth sites of Ca-P minerals and inhibit precipitation (Grossl and Inskeep, 1992; Inskeep and Silvertooth, 1988). Violante and Huang (1989) show that, not only do organic ligands (citric, tartaric, and tannic acid) sorb to the surface of aluminum precipitates, they are also incorporated into the structure of the products, when present during the precipitation reaction, and can reduce P sorption capacity. In addition, humic materials can interrupt and slow the formation of crystalline precipitates by hindering Al-Si interactions (Huang, 1991).

1.5 Poultry Litter: Phosphorus and Chemical Amendments

Depending on the animal rearing conditions on a given farm (i.e. bedding material, number of birds, frequency of cleanings, etc), PL can range widely in physical and chemical properties. Overall, up to 60% of PL is accounted for in total carbon, with nitrogen, phosphorus and sulfur and aluminum making up much smaller portions. Water-soluble P concentrations, thought to be the most weakly bound, can be as high as 34,000 mg kg^{-1} (Sims and Luka-McCafferty, 2002). Because of such high concentrations of weakly-bound nutrients, manure management strategies are being developed to reduce environmental impacts from concentrated land application.

Composting, active drying, and pelletizing reduce moisture content and increase the efficiency of transporting PL to areas where soils are P deficient (Sharpley et al., 1994; Sims and Wolf, 1994). Dietary supplements, such as phytic acid and vitamin-D metabolite, have been used to increase P assimilation by broiler chickens (Maguire et al., 2003). (Maguire et al., 2003), decreasing the need for dietary inorganic P additives. However, in many cases, inorganic P is still added to feed and the concentrations of P in the waste material are still large enough to cause nutrient enrichment in adjacent waters.

Unlike dietary supplements to increase P-use efficiency during broiler development, amendment of waste materials aims to change the chemical properties of litter, so that continued land application will not cause water and soil quality degradation. Chemical precipitants have been used extensively in the wastewater treatment process for removal of P (Ippolito et al., 1999; Ulmgren, 1975). When alum (aluminum sulfate, $Al_2(SO_4)_3$) is added as the precipitant, the resulting sludge (alum hydrosolid) has been used as a soil amendment to reduce available P (Cox et al., 1997; Haustein et al., 2000; Ippolito et al., 1999; Kyle and Mcclintock, 1995; Peters and Basta, 1996). Soils, converted from agricultural fields to wetlands, also respond well to treatments such as alum for decreasing soluble P concentrations (Ann et al., 2000a;

Ann et al., 2000b). However, the application of chemical precipitants to reduce soluble P concentrations in animal manures was first studied by Moore and Miller (1994). In addition to decreasing ammonia volatilization from PL, which benefits the birds and poultry workers, alum proved to be the most effective in reducing water soluble P, in comparison to Ca and Fe compounds (Moore et al., 1996). Because of the decrease in dissolved P, concentrations in runoff from pastures which received broadcast applications of alum amended, verses unamended litter, were greatly reduced (Moore et al., 1999; Moore et al., 2000; Moore et al., 1998; Shreve et al., 1995). Decreases in dissolved P and increases in nitrogen value (by decreases gaseous losses) (Kithome et al., 1999) make the litter a more valuable and environmentally sound nutrient source.

However, the long-term potential for alum amendments to decrease the environmental impacts associated with PL application is uncertain. For example, little is known about how phosphate is retained in these heterogeneous, alum amended PL systems. Peak et al. (2002) used in-situ molecular-scale techniques to suggest that amorphous aluminum phases are adsorbing the aqueous phosphate. Hunger et al. (2004), using NMR techniques to show the presence of aluminum bound P in alum amended litters, but also stressed the importance of Ca-bound and organic P in the waste. With limited research focusing on direct speciation of P in these organic amendments, the questions of stability, kinetics, and bonding mechanisms remain elusive.

Chapter 2.0

XANES SPECTROSCOPY STUDY OF PHOSPHORUS FORMS REMOVED FROM ALUM-AMENDED POULTRY LITTER DURING SEQUENTIAL EXTRACTIONS

2.1 Introduction

Sequential extractions are often used to describe the relative distribution of an element between different species, or pools, in a soil or heterogeneous system. It is useful to know how nutrients are bound in a soil and with what other substances or surfaces they are interacting, so that interpretations can be made as to their reactivity, mobility, or likelihood to cause risk. In soils, metals, organic matter and plant nutrients exist in a variety of forms. These forms include being sorbed to soil components, incorporated into the structure of clays and metal oxides, immobilized in organic phases, or as aqueous ions in the soil solution. Fractionation procedures are based on the assumption that these forms are differentially extractable, with reactivity of one form being clearly distinguishable from another. In agronomic-based studies, the sequential extraction of phosphorus (P) from soils and organic amendments has become commonplace when describing their nutrient status. Fractionation of soil inorganic P is often conducted with the method of Chang and Jackson (1957). The methods of McAuliffe and Peech (Barnett, 1994a; Barnett, 1994b; 1949) and Hedley et al. (1982) have also been modified to draw conclusions about relative abundance and forms of soil organic and inorganic P (He et al., 2003; Levy and Schlesinger, 1999). The Hedley procedure uses sequential extractions with water (H_2O), sodium bicarbonate ($NaHCO_3$), sodium hydroxide (NaOH) and hydrochloric acid (HCl), presumably removing bioavailable P, labile inorganic and organic P as well as "microbial P", aluminum- and iron-chemisorbed P, and mineral-occluded P, respectively (Hedley et al., 1982).

The link between P influxes to surface waters and their subsequent decline in overall health has shifted the focus of environmental legislation, from nitrogen (N), to P based management. Of utmost concern is the excessive, long-term use of high-P animal manures, like that of poultry, as fertilizers for grain crops. Farming communities on the Delmarva Peninsula, where broiler production dominates the economy, must find environmentally responsible means of dealing with the 50 000 Mg of manure that is generated annually (Mozaffari and Sims, 1996). Recent federal nutrient management laws impose strict regulations on manure management practices, requiring nutrient budgets and implementation of best management practices (BMPs) for confined animal feeding operations (CAFOs) (i.e. poultry production facilities). In addition to dietary supplements (Maguire et al., 2003), composting, and pelletizing, the use of chemical amendments, primarily aluminum sulfate (alum, $Al_2(SO_4)_3$), can alter the litter chemistry to decrease the soluble reactive P which is released from the litter (Moore et al., 1999; Moore et al., 2000). Short-term studies have shown that alum amendments reduce soluble P exports from farms; however, little is known about how this chemical treatment changes P speciation and distribution to produce the desirable end-product.

In order to understand why these BMPs, such as alum, are effective, there must be a way of characterizing manures and litters after they have been subjected to these treatments. Because sequential extractions have been so widely used in soil science, these techniques are being used to understand the chemical variability of animal waste (Dou et al., 2000; Eneji et al., 2001; Eneji et al., 2003; He and Honeycutt, 2001; Hunger et al., 2004; Sharpley and Moyer, 2000). While being cost and time efficient, fractionation procedures are thought to provide indirect information about chemical speciation. However, these methods were designed for soils, of mostly mineral composition, with much lower concentrations of nutrients than animal wastes; and, the extrapolations of solution parameters to speciation and sorption mechanisms are based on macroscopic observations with no direct, fundamental chemical data to support them. Because of the need to address the release of P from these systems, to ensure that CAFOs are complying with nutrient management regulations, we must determine precisely what information these extractions provide. A fundamental chemical understanding of these techniques would provide the power to quickly and inexpensively analyze manure and calculate the risk associated with land application.

One study (Hunger et al., 2005)used spectroscopic techniques to understand the forms of phosphorus that were removed from the solid phase of alum-amended poultry litter (PL) throughout the Hedley fractionation procedure. After extraction, solid state ^{31}Phosphorus-Nuclear Magnetic Resonance (NMR) was used to determine what phases of P remained in the sample residue. While the combination of these two techniques confirmed the extraction of aluminum (Al) and calcium (Ca) bound P in the NaOH and HCl fractions, the authors note that there is not enough information to definitively determine how these extractants react with the different species of P in the PL. Moreover, solid state P-NMR is not a sensitive enough technique for these heterogeneous materials. Turner and Leytem (2004) used solution

^{31}P NMR to investigate the P speciation within the supernatant after each extraction step in a modified Hedley procedure. They found that phosphate monoesters, phospholipids, nucleic acids, and inositol phosphates were important P species in a variety of animal wastes. Until that study, there had been little focus on organic P, as none of the soil-based interpretations account for the variability in organic P compounds removed by the Hedley method. However, solution state NMR requires significant sample treatment to acquire quality data. Also, understanding P species remaining on the solid after the extraction products are removed is important to provide a mass balance of P in the system.

X-ray absorption near edge structure (XANES) spectroscopy, offers a means of analyzing solids without extensive alteration to the samples. Therefore, we can investigate the properties of the residue, with respect to P speciation, without significant sample treatment. This is the first study which attempts to use a sophisticated data analysis approach to perform solid state P speciation in alum amended PL. Principle component analysis (PCA), in combination with linear combination fitting procedures, allow for the spectra from PL samples to be described in terms of the P-containing components on the surface.

2.2 Materials and Methods

2.2.1 Sample Characterization

All PL samples were obtained from Dr. J.T. Sims (University of Delaware) from a previously conducted study (Sims and Luka-McCafferty, 2002). In the time between this study and the time of sample collection, these litters were stored in a cold room, at 4°C, to minimize any biological or chemical changes. Without drying or grinding, the PL samples were first passed through an 841μm sieve (number #20 mesh screen). This size fraction, while particularly useful for XANES spectroscopy, has also been studied, separate from the coarser material (lower in nutrients) that could be recycled as bedding or fuel, as the nutrient-dense fine fraction most useful as a crop fertilizer (Ndegwa et al., 1991). A new poultry litter palletizing plant, in Seaford, Delaware, creates a pressed pellet form of PL which can easily be stored and shipped for later land applications. This operation accepts only clean PL material, which has been separated from the cake (moist, dense top layer of PL material, containing large particles of bedding, feathers, dead birds, etc) (B. Malone, personal communication, July 19, 2005). Therefore, the particle size considered suitable for palletizing and land application is the finer portion. Moisture content was estimated by drying several grams of the sieved material at 65°C until constant weight was achieved, usually for 48 h. Total Al, Fe, Ca, and P were determined by digesting 0.5 g of the moist, sieved PL with 10 ml of 1:1 concentrated HNO_3:H_2O overnight, followed by the addition of 3 ml of 30% H_2O_2 for 1 h. The mixture was then heated to105°C for 2 h on a DigiPREP MS digestion block (SCS Science, Quebec, Canada). Fully digested samples were then diluted to a final volume of 50 ml and vacuum filtered through 0.45 μm Millipore filter paper, before analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES). For determination of water soluble (WS) constituents, a 1:10 H_2O: solid mixture was shaken for 1 h on an end-over-end shaker, centrifuged for 15 min, and vacuum filtered. Supernatants were then analyzed for P, Al, Fe, and Ca using ICP-AES. All results are presented on a dry weight basis.

2.2.2 Sequential Extraction of Phosphorus

The method of Dou et al. (Dou et al., 2000) was used for P fractionation. This method is a modification of the original Hedley method (Hedley et al., 1982). All extractions were done in triplicate. The method is briefly described as follows: A 0.3 g sample of PL, in its *in situ* moisture content, was placed in a 50 ml polyethylene centrifuge tube, suspended in 30 ml of H_2O (1:100 solid: solution ratio), shaken for 1 h on an end-over-end shaker, then centrifuged for 15 min. Dou et al. (Dou et al., 2000) shows that P release was not significantly affected by using the shorter shaking time; therefore, we used this method in our study. Supernatants were then removed using a glass Pasteur pipette, taking care not to remove any solid from the bottom of the centrifuge tube. This solution was then vacuum filtered and analyzed for the aforementioned elements by ICP-AES and by a modified version of the colorimetric phosphomolybdate method (He et al., 1998; Murphy and Riley, 1962). These steps were then repeated using 0.5 M $NaHCO_3$, 0.1 M NaOH, and 1 M HCl, respectively. Statistical analysis of the sequential extraction data was completed using SIS version 8.2 (SAS Institute, 1999). The PROC GLM procedure was used, with Tukey's test being used to evaluate the difference between the means. A probability (P) less than 0.05 was considered significant.

2.2.3 Spectoscopic Analysis

After each step in the sequential extraction procedure, one of the replicates was sacrificed for XANES analysis. Sufficient replicates were completed so that at the end of the extraction profile triplicates remained for statistical analysis. The samples were shock-frozen with liquid nitrogen and freeze dried for 24 hours. The material was then ground with a mortar and pestle (to achieve uniform thickness and eliminate diffraction peaks in the XANES spectra) immediately prior to mounting on adhesive tape attached to the sample holder. All XANES spectroscopy was conducted at beam line X-19A at the National Synchrotron Light Source on the premises of Brookhaven National Laboratory, Upton, NY. The beam was calibrated with NaH_2PO_4 powder standard, and the maximum of the first derivative of the standard spectra was assigned an energy value of 2158.5 eV (Peak et al., 2002). This value will be referred to as the white line energy and relative shifts will be expressed as distance from this value. A minimum of three to five reproducible scans were collected for each sample or standard.

Spectra were collected, as described above, of numerous other organic and inorganic P-containing standards. These references include the following: Ca- and Al-phosphate minerals and salts; nucleic acids (deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)); polyphosphates (adenosine 5’ triphosphate (ATP) and adenosine 5’ diphosphate (ADP)); phosphonates ((2-amino ethyl) phosphonic acid (AEP) and phosphosphocreatine); phospholipids (L-α phosphatidyl choline); sodium phytate; other monoesters (2’ deoxyguanosine 5’ monophosphate (DGMP)); and inorganic polyphosphates (calcium pyrophosphate).

Self absorption is a concern when collecting XANES spectra of reference materials. To avoid problems associated with self absorption, the reference materials were finely ground with a mortar and pestle and spread as a thin film onto the sample holder. This method for analyzing high P samples eliminated self absorption features in our experimental spectra (W.A. Caliebe, personal communication, June 10, 2004). An attempt was made to also analyze these samples after dilution in boron nitride powder; however, this method negatively impacted the quality of the XANES spectra and was therefore no longer used. Mathematical corrections of self absorption effects are also problematic because artificial shifts in the spectra are possible.

2.2.4 Data analysis

Using WINXAS version 2.3, reproducible scans for each sample were averaged, followed by a linear background correction from 2120 to 2140 eV (-30 to -18.5 eV relative energy). The remainder of each spectrum was normalized so that all baselines are standardized.

Principle Component Analysis (PCA) software, developed at beam line 10.3.2 of LBNL, was used for further data analysis. This software is available at http://xraysweb.lbl.gov/uxas/Index.htm. First, PCA was used to determine the smallest number of abstract mathematical functions, principle components (PCs), required to sufficiently describe a composite data set of all experimental spectra. During this procedure, the number of PCs is increased until a local minimum in the change in Sum Square $_{\text{total}}$ occurs, indicating that further addition of PC is not statistically improving the quality of the fit. These separate mathematical functions are represented graphically and used, in combination, for the Target Transformation. PCA was performed on the data as two sets: spectra from alum amended litters and those from control litters.

In Target Transformation, the spectra from reference compounds are individually compared to the collection of mathematical principle components. The software “transforms” the experimental reference spectra to fit a combination of the chosen number of PCs selected during PCA. The degree to which the reference must be changed to fit the PCs is measured in a SPOIL value. A high SPOIL value indicates a poor fit, giving a first suggestion that this standard is not well represented in our collection of sample spectra (represented by the PCs). The reference spectra are then split into groupings based on their SPOIL values and given a rating of excellent (0-1.5), good (1.5-3), fair (3-4.5), or poor (>4.5).

The last step in data analysis is Linear Combination Fitting. In this step, individual sample XANES spectra (extracted PLs) are fit to the groupings of reference spectra, mentioned above, in order to determine what reference functions best compose the unknown sample.

2.3 Results and Discussion

2.3.1 Characterization and Sequential Extractions

Total P, Al, Fe and Ca, WS-P and -Al, and the Al:P ratio for all PLs are listed in Table 2.1 Data from the sequential extractions are shown in Figure 2.1. The extractions were efficient for removing a large percentage of the total P from the samples (PL 129, 97.8% removed; PL 181, 91.4% removed; PL 182, 88.7% removed; PL 519, 108.4% removed; and PL 525, 86.3% removed).

There is a distinct difference in P solubility between alum amended and control litters (Fig. 2.1.A). First, the H_2O-extractable fraction is significantly lower for all of the alum amended litters, when compared to the controls, supporting the use of alum to reduce P losses from PL (Moore and Miller, 1994; Moore et al., 1999). According to traditional interpretations of these extractions, NaOH removes P bound to Al (Hedley et al., 1982), and since alum addition is thought to created additional Al-surfaces for P to bind (Peak et al., 2002), it is not surprising that the NaOH-extractable P increases in the alum amended PLs. The percentages of P removed by

$NaHCO_3$ and HCl did not follow a trend that would suggest that alum treatment affected these fractions.

Molybdate (Mo) reactive phosphorus (as a percentage of the amount of P removed in the extraction) is expressed in Figure 2.2. Although some acid hydrolysis of organic and condensed P compounds can occur during the color formation, mostly inorganic P is thought to be molybdate reactive (Turner et al., 2002); therefore, upon comparison to the total P data (ICP-P) in Figure 2.1, a relative distribution of P between inorganic and organic phases within an extract can be estimated. In all samples the majority of H_2O and $NaHCO_3$ extractable P was molybdate reactive (inorganic) and less than 10% of the HCl was inorganic. Since the HCl fraction is the largest P fraction for all of the litters (Figure 2.1), this suggests that most of the P in these PL samples is organic. Interestingly, the alum amended and control PLs differ greatly in the amount of NaOH P which is Mo reactive. In the control samples (# 519 and 525), the NaOH extractable P is almost entirely inorganic, while the opposite is true of the alum amended samples.

Aluminum data, from the same set of extractions, is presented in Figure 2.1.B. Changes in the extractability of Al, between alum amended and control PL, are easily distinguishable. Most importantly, for plant health and soil quality concerns, the H_2O-extractable Al (Figure 2.1 B) is not statistically different between the two treatments. For the control litters, a majority of the Al (93% for PL 519 and 66% for PL 525) is recalcitrant to removal by all but the strongest extractant (1 M HCl); whereas, in the alum amended PL, the majority of Al was removable with the alkaline extraction step (0.1 M NaOH). This may be because the Al in the control samples originates from structural network of minerals from soil mixed into the PL from the floor of the house. This structural Al would be more recalcitrant than an amorphous $Al(OH)_3$, thought to be the dominant Al phase in the amended PL, to the high pH conditions of the NaOH extractant.

For Ca, the only fraction that was clearly different due to alum treatment was H_2O-extractable fraction. The pH of the alum amended litter is slightly lower than that of the control, which may provide for a higher percentage of dissolved Ca in the PL. In all of the litters the Ca-HCl fraction was the largest, indicating that most of the Ca in these systems is either in a form which is stable and non-reactive, except in highly acidic conditions. Phytic acid is present in corn grain fed to the birds. Turner et al. (2003) showed that this stable orthosphosphate monoester, does not degrade in the presence of NaOH; therefore, it is possible that the large portion of Ca-HCl originates from calcium phytate as well as calcium carbonate and calcium phosphate added as dietary supplements (McGrath et al., Unpublished data).

2.3.2 Principle Component Analysis and Linear Combination Fitting

Applying a finger-printing data anlaysis technique to XANES spectra from this study would be extremely difficult and possibly inaccurate, because of how similar they are. Figure 2.3.A shows the spectra from alum amended samples #129. With close inspection of the white line region (0 eV Relative Energy) and the oxygen oscillation (15-20 eV), subtle differences in shape and position of these curves are visible. A more quantitative alternative, to visual inspection and comparison, is desirable for differentiating the P species represented in these XANES data. Principle Component Analysis and LCF provide a means for distinguishing the more subtle differences in the spectra, reflected in Figures 2.3.B and 2.3.C.

When divided into alum and control samples, 6 and 3 PCs, respectively, were required to describe the variability within the two data sets. These values also reflect the number of PCs which yielded the most “excellent” and “good” SPOIL values during the target transformation. Results from the target transformation are presented in Table 2.2. These data show that the reference materials used in our fitting procedures fit the alum amended and control samples quite differently. This shift in P speciation between these two types of PLs will become more apparent upon review of the Linear Combination Fits (LCF).

Spectra of reference materials that were dominant in the linear combination fitting are presented in Figure 2.4. In Figure 2.5, a complete representation of the LCF for each of our sample spectra is shown. In 2.5 B, C, and E, the H_2O extraction is not present in the bar graphs because we were unable to acquire enough scans of these samples to average for data analysis. Each graph is divided into sets of bars, each set representing the components required to make up the LCF for one spectra. For instance, in Figure 2.5.A., the first set of four bars show the relative amount of four references selected to achieve a LCF for the “129 As Is” spectra (collected from the alum amended litter #129, before any extractions were conducted). By examining which references make up each spectra and how the amounts of those references change across the extraction series, we can begin to determine how the sequential procedure affects the PL sample.

Before examining the progression of the extractions for each litter, there are several points about the overall LCFs that require discussion. First, for samples with low P concentrations, XANES data become very noisy and therefore, difficult to fit using this method of data analysis. For each of the PL samples, the spectra after the

HCl step were noisy and the components, and the contribution from these components, required to fit the spectra are not consistent with the others in the extraction series. Secondly, in addition, it is well noted that phytic acid is a major contributor to the organic P content of PL (Toor et al., 2005; Turner and Leytem, 2004; Turner et al., 2003); however, this component is not well represented in our fits, despite a "Good" spoil value in the target transformation. To address this issue, the phytic acid reference standard was subjected to LCF as if it were a sample of unknown composition. The fits showed that sodium phytate could be accurately depicted with a mixture of orthophosphate diesters and Ca-P (to a smaller extent), or a mixture of our phospholipids standards and a small amount of Ca-P. Therefore, because nucleic acids, ortho-P diesters, are noted as being unstable in solution (Turner et al., 2003), it is likely that the nucleic acid component in these fits is predominantly a misrepresentation of the phytic acid reference.

In the first three graphs (Figures 2.5A-C), the compositions of the alum amended samples are displayed. The fits for the "As Is" spectra show a combination of everything from aqueous PO_4, to monoesters, phosphonates, and inorganic P metal-P associations. Composition changes sharply between these samples and the next two extractions, H_2O and $NaHCO_3$, which are often grouped to describe the weakly-bound P pool. In these data, contributions from aqueous phosphate, phosphonate, and a signal from monoesters are easily removed from the samples. It appears as though aqueous and other inorganic, loosely bound P components (Ca-P) were removed in the water extraction.

Between the bicarbonate extraction and each of the NaOH and HCl fractions, there are more distinct changes in spectral composition. First of all, the contribution from the Al-P component slowly decreases across the entire extraction procedure, with a large decrease between the $NaHCO_3$ and the NaOH steps. Unlike previous interpretations of sequential extractions, these results suggest that the Al-P component is not removed entirely in the NaOH step, but decreases across a continuum with the increasing strength of the extractants.

Next, for all three alum amended PLs, the polyphospates (ADP and ATP) persist throughout the entire profile. As noted by Tuner et al. (2003), these organic phosphates are not degraded by the NaOH extractant, which may explain their persistence. However, Turner later showed that organic polyphosphates should be removed by NaOH (Turner, 2004). Our extractions were only conducted for 1 h, which may results in incomplete removal of organic polyphosphates in PL. A contribution from “nucleic acids” is removed after the HCl extraction, but that component is present in all of the previous fits. Assuming that a large proportion of the nucleic acid signal, in conjunction with some Ca-P, is due to the presence of phytic acid, inositol phosphates are not likely broken down and removed with less stringent extractants.

The LCFs for the control samples are shown in Figures 2.5 D and 2.5 E. Data are missing from PL #525 due to incomplete spectra collection while at the beam line, resulting in an insufficient number of scans to calculate and average. These samples have a much stronger Ca-P contribution throughout all of the fractions, which is not surprising, considering the Ca additions to PL and the relatively low concentration of other P-complexing elements (i.e., Al and Fe). In both samples, #519 and #525, the Ca-P contribution decreases across the extraction procedure, much like Al-P in the alum amended samples. The “As Is” samples can be described with a mixed fit of Ca-P and aqueous phosphate, which reinforces Toor et al. (Toor et al., 2005). With the removal of the weakly bound species, other components, such as monesters, phospholipids, and nucleic acids are calculated in the linear combination fits. In these PLs, polyphosphates appear to be decreasing, instead of remaining constant, with increasing extraction. The lack of phytic acid as a contributor to the fits is problematic here as well. However, if we again consider the nucleic acids or phospholipids, in conjunction with a small portion of the Ca-P signal, to be indicative of the phytic acid signature, then we can see that the combination of these two components decreases across the extraction profile as well.

After the NaOH extraction, in all five litters, there is a strong presence of ortho-P monoesters which is inconsistent with the previous extraction steps within the sequence. Linear combination fitting gives a composition based on the dominant species contributing the XANES spectra. Therefore, components that are present are not always calculated in a fit, because there are dominant signals from other references that mask the weaker, less significant components. This makes it difficult to make direct correlations between the “As Is” spectra and each step in the fractionation series.

2.4 Conclusions

This chapter aimed to determine how alum changes the P distribution and speciation within the PL system, resulting in a decrease in P solubility. According to LCF results, aqueous phosphate, phosphonates, ortho-P monoesters, and easily soluble or loosely-bound inorganic Ca-P and Al-P components are easily extracted with H_2O and $NaHCO_3$. Hunger et al. (2005) stated that only HCl could remove calcium phosphate phases. This may be true for discreet calcium phosphate mineral phases, but for more soluble fractions, such as dicalcium phosphate, weaker extractants may remove them from the PL (Toor et al., 2005). An important finding was that some standards, such as phytic acid, could be fit with combinations of other reference materials. Our data suggest that no one extraction removes an entire species of P in one step; rather, these components are removed across a continuum of increasingly astringent extractants. When using macroscopic extraction techniques, such as sequential extractions, care must be taken when trying to make assumptions about chemical speciation. This is especially true for heterogeneous materials which contain inorganic nutrients and biologically important organic compounds. In addition, to these results, we see that phosphate bound to aluminum oxide is present in the alum amended PL samples. This, along with the known complexity of heterogeneous waste materials, provides the basis for the work conducted in Chapter 3.0.

2.5 Tables

Table 2.1 Elemental Analysis for the <841µm fraction of all PL samples.

			Total [a]					Water Soluble[b]	
PL Sample	pH	Treatment	P	Al	Fe	Ca	Al:P	P	Al
			mg kg^{-1}					mg kg^{-1}	
525	7.90	Control	17802	976	406	29000	0.055	866	10.3
519	7.95	Control	20734	680	398	29225	0.033	1192	6.53
182	7.03	Alum	22943	27577	841	28196	1.20	521	22.3
181	7.15	Alum	24601	27629	871	31231	1.12	485	23.7
129	6.94	Alum	18235	12789	437	27154	0.70	331	22.9

[a] Concentrations are calculated on a dry weight basis and are the mean of duplicate experiments. [b] Concentrations are calculated on a dry weight basis and are mean of triplicate experiments.

Table 2.2 Target Transformation results for alum amended and control PL samples.

	Alum Amended PL	Control PL
SPOIL	Reference	
Good (1.5-3.0)	Sodium Phytate	Sodium Phytate (Inositol)
	Aluminum Phosphate $AlPO_4$	Wavellite (Al-P mineral)
	Tribasic Calcium Phosphate $Ca_3(PO_4)_2$	Calcium Fluorophosphate (Apatite)
		ADP (Polyphosphate)
Fair (3.0-4.5)	P sorbed on $Al(OH)_3$	NaPO4
	Wavelite	DNA (Ortho-P diester)
	DNA	Phosphocreatine
	DGMP (Ortho-P monoester)	AEP (Phosphonate)
	Calcium Fluorophosphate (Apatite)	Brushite (Ca-P Mineral)
	Phosphocreatine	
Poor (4.5-10)	RNA (Ortho-P diester)	RNA
	AEP	Phosphatidyl Choline (Phospholipid)
	ADP	Tribasic Calcium Phosphate $Ca_3(PO_4)_2$
	NaPO4	DGMP
	Phosphatidyl Choline	
	Barrandite	
	Brushite	

2.6 Figures

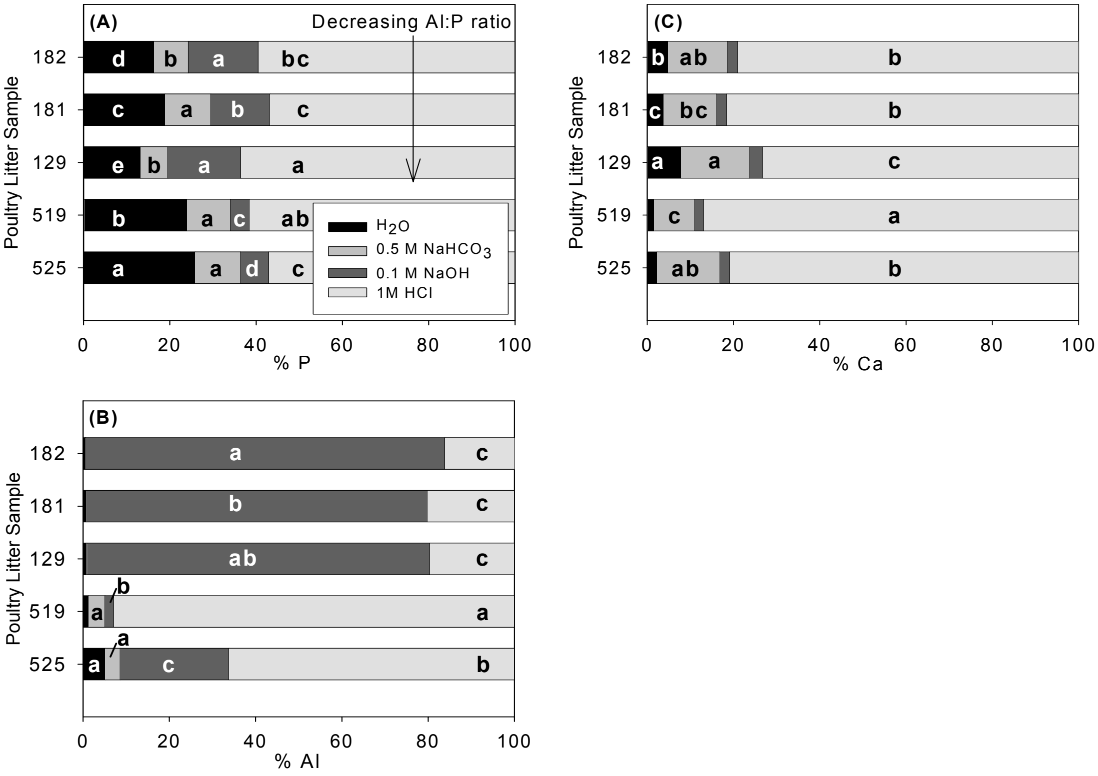


Figure 2.1 **Percent of P(A), Al(B), and Ca(C) extracted in 1:100 suspension of PL and extractant (1 h shaking). Letters within the same extraction indicate statistical difference in the means between PL samples (P<0.05).**

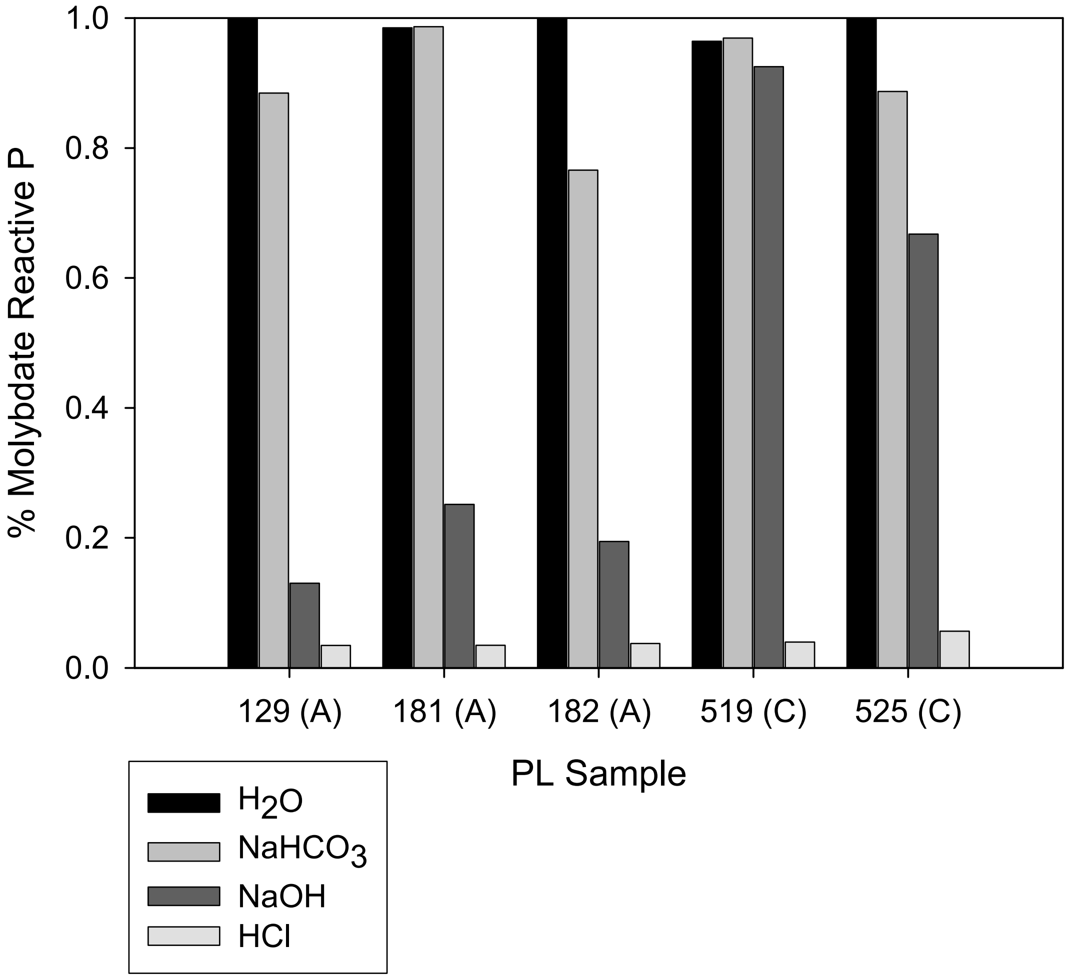


Figure 2.2 **Molybdate reactive phosphorus in extracts from alum amended and control PL samples after each step in sequential fractionation procedure.**

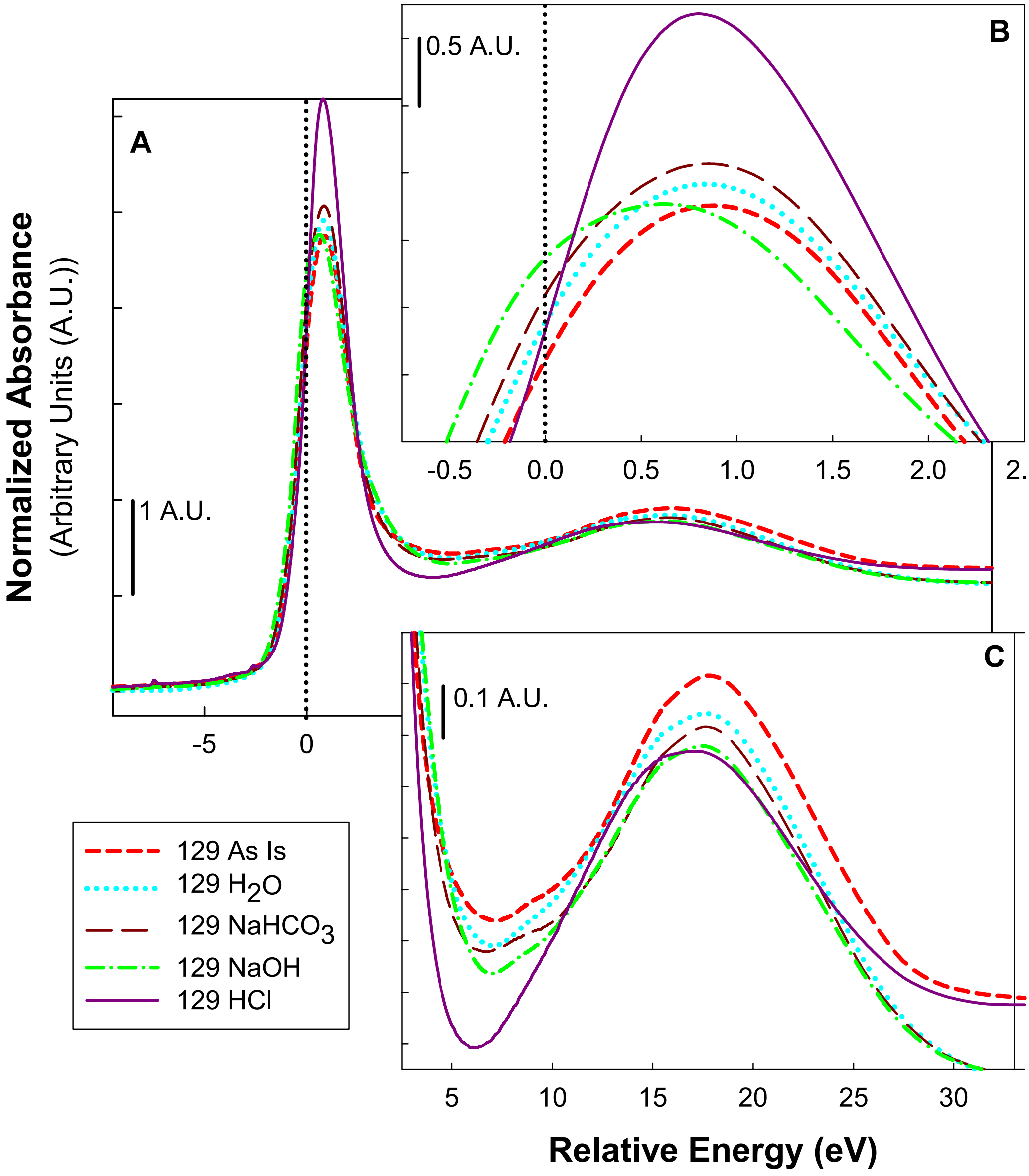


Figure 2.3 **XANES data collected from PL #129: (A) Entire sequential extraction sequence as a function of relative energy (eV); (B) Magnification of the white line region (0 eV) of the XANES spectra presented in (A); (C) Magnification of the oxygen oscillation (17 eV) from the XANES spectra in (A).**

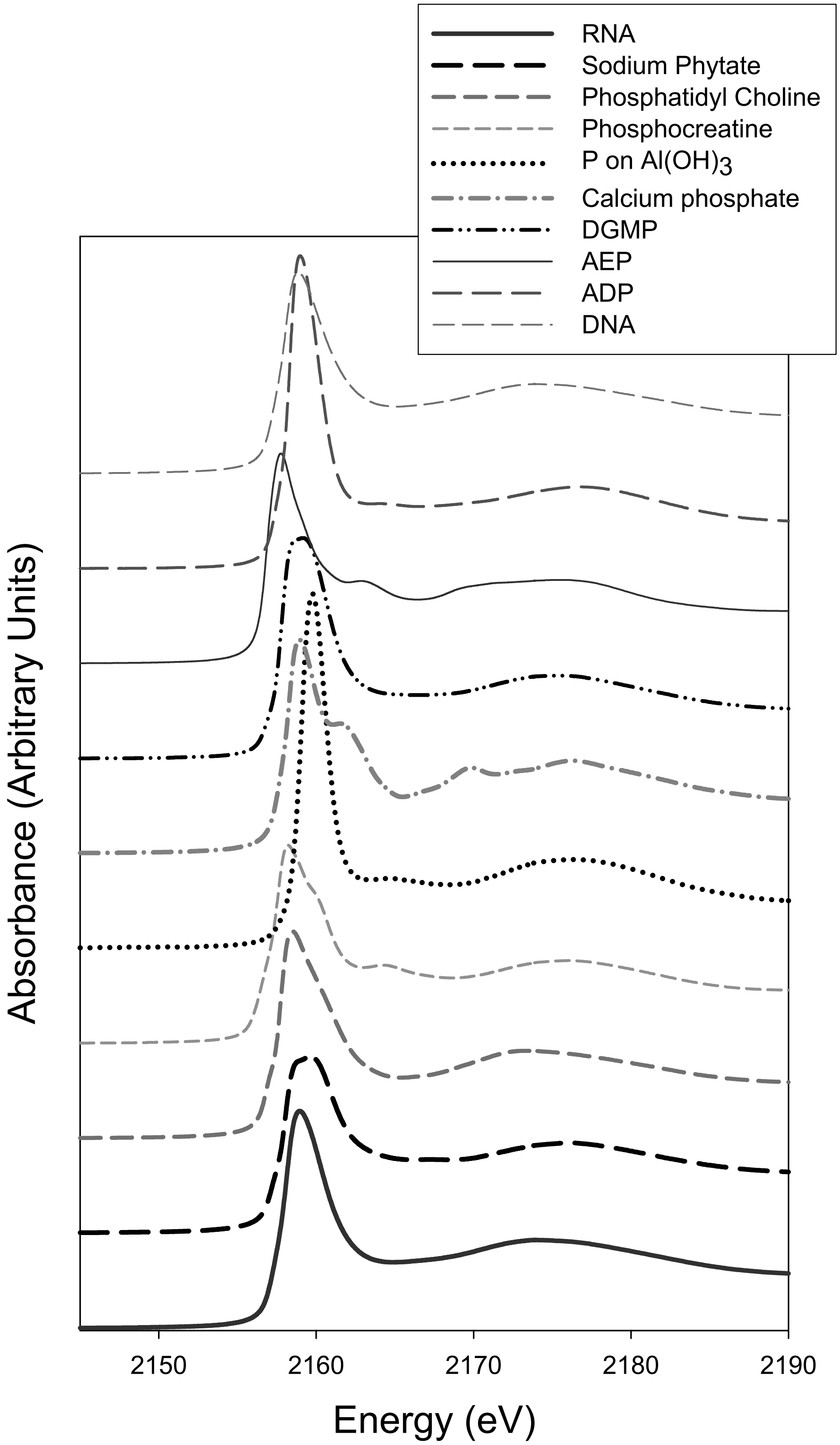

RNA
Sodium Phytate
Phosphatidyl Choline
Phosphocreatine
P on Al(OH)3
Calcium phosphate
DGMP
AEP
ADP
DNA
Absorbance (Arbitrary Units)
2150
2160
2170
2180
2190
Energy (eV)

Figure 2.4 XANES spectra of reference materials used in Linear Combination Fitting procedures.

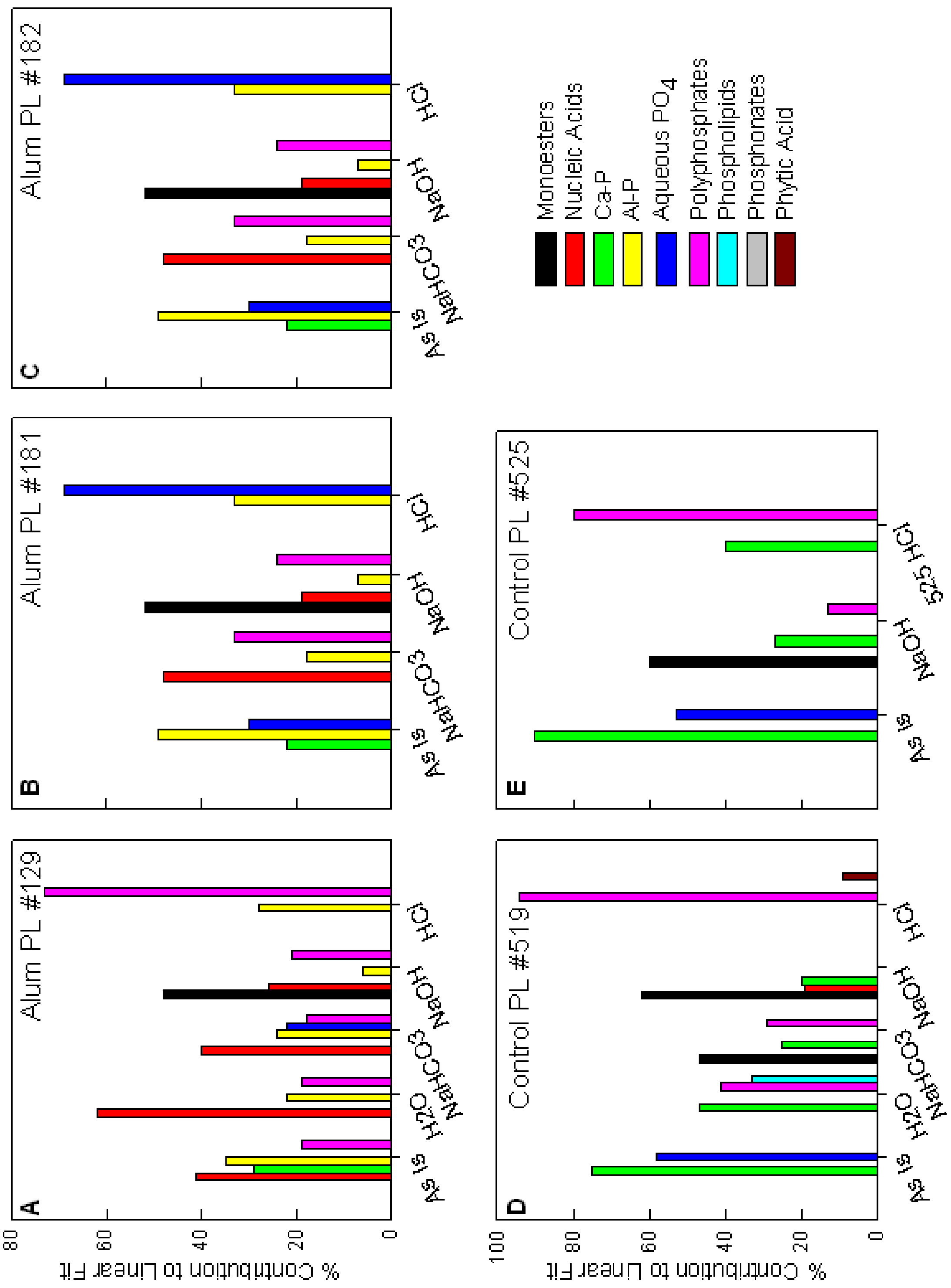

A
Alum PL #129
B
Alum PL #181
C
Alum PL #182
D
Control PL #519
E
Control PL #525
% Contribution to Linear Fit
0
20
40
60
80
100
As is
H2O
NaHCO3
NaOH
HCl
525 HCl
Monoesters
Nucleic Acids
Ca-P
Al-P
Aqueous PO4
Polyphosphates
Phospholipids
Phosphonates
Phytic Acid

Figure 2.5 Linear Combination Fitting results for alum amended and control PL samples.

Chapter 3.0

PHOSPHATE AND OXALATE SORPTION ONTO AMORPHOUS ALUMINUM OXIDE

3.1 Introduction

Metal oxides are often used as a proxy for understanding the most basic reactions between anions, metals, colloids, etc. and environmental media such as soils, sediments and other heterogeneous mixtures. Iron and aluminum oxides, which form naturally as weathering products of primary minerals, are important in soils because coatings of these materials on mineral grains provide a reactive surface for sorption/desorption and oxidation/reduction processes as well as dictating the physicochemical properties (cation exchange capacity, surface charge, pH).

In addition to naturally occurring metal oxides, some form as a result of engineered management practice. For instance, aluminum salts are particularly useful in wastewater treatment, and the spent residuals are non-crystalline oxyhydroxides which have a high capacity to sorb and irreversibly retain anions (Butkus et al., 1998). Borrowing from the wastewater industry, animal production facilities, which produce large amounts of nutrient-rich waste, have employed aluminum salts water treatment residuals (WTRs) (Haustein et al., 2000; Ippolito et al., 1999) as a means of controlling P solubility in agronomic systems. The use of alum ($Al_2(SO_4)_3$) has been shown to dramatically decrease soluble phosphorus release from poultry litter (PL), which is often destined for land application, as a crop fertilizer (Moore and Miller, 1994; Moore et al., 1999; Sims et al., 2000). This salt dissolves in the moist PL and an amorphous aluminum hydroxide precipitates, providing a reactive surface with a high affinity for phosphate (Peak et al., 2002). This Al phase, as opposed to a well-ordered crystalline oxide, probably forms due to the presence of organic acids in the poultry waste, soil, and bedding material in the litter. Organic acids are known to poison the crystallization process and inhibit the formation of well-ordered precipitates (De Cristofaro et al., 2000; Violante and Huang, 1984).

After the addition of alum to the poultry waste and excess bedding material in the poultry house, the pH of the litter is approximately 5.5. Due to ammonia addition with the waste from the subsequent flock, the pH is 8.0 by the end of a broiler grow out period (approximately 6 weeks) (Moore et al., 1999). These two values straddle pK_2 of phosphoric acid, affecting phosphate's protonation and reactivity. In addition, the many metal oxides have points of zero charge near the end value of this pH range. Therefore, the surface charge of the amorphous aluminum hydroxide (am-$Al(OH)_3$) and the charge on phosphate will be impacted by this chemical change in the litter and may effect the sorption reactions between the two.

However, phosphate is not the only ion present, in the animal waste, which readily sorbs to high surface area metal oxides. In addition to other inorganic molecules, simple organic acids and biological macromolecules can have similar charge properties to phosphate, and react strongly with a positively charged mineral surface. Of particular interest are the carboxylic acids, because of their ubiquity in soils and natural organic matter (Stevenson, 1982). Understanding the competition or interactions of these ions with phosphate, in various chemical conditions, will provide a detailed understanding of the management practices so that they can be improved.

While many studies have investigated the competitive sorption of oxalate and phosphate onto aluminum oxides, the approaches most often employed are macroscopic batch studies or equilibrium isotherms (Kafkafi et al., 1988; Violante and Huang, 1984; Violante and Huang, 1989; Violante and Gianfreda, 1993; Violante et al., 1991; Yuan, 1980). Spectroscopy techniques allow for more direct investigation of the sorbate-sorbent interaction. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy is useful when looking at polarizable molecules both in solution and at the solid-liquid interface (Hind et al., 2001; Lefevre, 2004). In conjunction with group theory, molecular symmetry arguments and, more recently, molecular orbital/ density functional theory calculations, the geometry of how these sorbates attach to a mineral surface can be deduced. The use of ATR-FTIR has been used extensively to study phosphate interactions on iron oxides (Arai and Sparks, 2001; Parfitt and Atkinson, 1976; Parfitt and Russell, 1977; Parfitt et al., 1975; Persson et al., 1996; Russell et al., 1974; Tejedor-Tejedor and Anderson, 1990) and oxalate on aluminum oxides (Axe and Persson, 2001; Clausen et al., 2003; Dobson and McQuillan, 1999; Hug and Sulzberger, 1994; Johnson et al., 2004; Rosenqvist et al., 2003; Yoon et al., 2004). However, there are no competitive studies which look at both anions as competing sorbates on aluminum oxides.

With respect to water quality, the retention of P in chemically amended PL is the concern which drives research on these materials. By using a simple two-ligand system on a well-defined surface, we can begin to fundamentally understand how phosphate binds to the am-$Al(OH)_3$ surface in the presence of other anions. With an understanding of the reactions occurring at this surface, we can better understand the retention capability imparted by introducing alum to the PL system. Hopefully, these data can be extrapolated to the types of reactions occurring in alum amended PL to help in optimization of management practices so that eutrophication and other environmental degradation can be limited.

3.2 Materials and Methods

3.2.1 Aluminum Oxide Synthesis and Characterization

Amorphous aluminum oxide [pseudo-boehmite; (am-$Al(OH)_3$)] was synthesized, at room temperature (approximately 25°C) according to the method of Su and Suarez (1995). Pseudo-boehmite was used as the sorbent in this work because it is thought to form in alum amended PL (Peak et al., 2002). This oxide then provides a surface to which phosphate irreversibly sorbs, decreasing dissolved reactive P in the waste. Briefly, 200 mL of a 1.5 M $AlCl_3$ solution, in a 1 L polycarbonate vessel, was vigorously stirred with a magnetic stir bar and plate while being slowly titrated with 400 ml of 2 M NaOH (added via a 50ml polycarbonate syringe). The suspension was divided into four parts, in 250 mL centrifuge bottles, and washed three times (resuspension and 10 min centrifugation at 10,000 rpms) with deionized water. After the final washing, the material was then placed in a temperature controlled chamber (25°C) and allowed to dry for 48 h. This did not sufficiently remove the entrained water from the material, so each of the smaller vessels was covered with a KimWipe and placed in a vacuum dessicator for 2 d.

To confirm the amorphous nature of the material, X-ray diffraction was performed at the Institute for Energy Conversion at the University of Delaware, by Brian McCandless. Relative abundance of aluminum coordination was determined by

Nuclear Magnetic Resonance (NMR) spectroscopy, by Dr. Brian Phillips in the Department of Geosciences at Stony Brook University, Stony Brook, NY. Because the Brunauer-Emmett-Teller (BET) isotherm is not appropriate for amorphous materials, the ethylene glycol monoethyl ether (EGME) method (Heilman et al., 1965) was used to estimate specific surface area of the synthesized pseudo-boehmite.

The pH of the isoelectric point (pH_{iep}) for the material was measured with the help of Marc Michel and Dr. Martin Schoonen in the Department of Geosciences at Stony Brook University, Stony Brook, NY. A 0.2 g L^{-1} suspension of the am-$Al(OH)_3$ was made in 1mM KCl and sonicated for approximately 2 h. This suspension was then diluted to 0.04 mg L^{-1} and an aliquot was placed in a sample cuvet. The pH of the suspension was adjusted with 0.01 M NaOH directly in the cuvet and the zeta potential was determined on a Zeta Plus zeta potential analyzer (Brookhaven Instruments Corporation, Holtsville, NY). These measurements were conducted in equilibrium with atmospheric conditions.

To investigate the size and shape of the aluminum hydroxide particles, scanning electron microscope (SEM) images were collected on a Hitachi S-4700 FE-SEM Microscope at the Delaware Biotechnology Institute with the help of Debbie Powell.

3.2.2 Batch Phosphate and Oxalate Sorption Reactions

Before the batch sorption reactions were completed, an organic matter extract from alum amended PL was conducted to determine which organic acid would be a reasonable ion to compete with phosphate in the PL system. Five grams of alum amended PL were suspended in 100 ml of 0.25 M NaOH and shaken for 16h (Turner et al., 2003). The suspension was centrifuged and the supernatant was analyzed, on a Ge ATR crystal (method described in section 3.2.3)

To begin the sorption experiments, 0.75 g of am-$Al(OH)_3$ was suspended in 750 ml of 1 mM NaCl in a cylindrical Teflon ® reaction vessel. The suspension was placed in a sonic bath for 10-15 min, to allow for complete dispersion of mineral aggregates, and then gently stirred with a magnetic stir bar for 1 h. Then, the pH was automatically adjusted to pH 5.5 with 0.01 M NaOH in STAT mode on a 799 GPT Titrino (Metrohm Ion Analysis). After a 24 h hydration period, at room temperature (25°C), a sufficient volume of 500mM phosphate or oxalate stock solution (made from NaH_2PO_4 or $H_2C_2O_4$) was added to achieve 750 µM $[P]_{total}$ or $[C_2O_4^{2-}]_{total}$. Equimolar phosphate and oxalate concentrations were chosen so that competition was not artificially enhanced by a difference in concentration. Attempts were made to simulate the Al:P and C:P concentrations in alum amended PL. However, the percentage of Al in the amended PL which contributes to the formation of $Al(OH)_3$ precipitates is unknown. In addition, because the material is so heterogeneous, it would be difficult to model the solution chemistry with equilibrium based calculations. Therefore, oxalate and phosphate concentrations used in these experiments were based upon a survey of metal oxide/anion sorption literature. When the phosphate was added, a DOC program on the Titrino was simultaneously started. The DOC mode creates a linear pH increase over a designated “sweep time.” In these experiments, the sweep time was 6 d (518400 s), with the start pH as 5.5 and the endpoint set at 8.0. This represents a condensed timescale for a broiler grow-out period (approximately six weeks). The pH change is representative of that which occurs during this time frame in a poultry house where alum amendment has occurred

(Moore et al., 1999). Subsamples were collected from this reaction at specified times throughout the entire sweep time (five minutes before phosphate addition, at 2, 4 and 8 min, every 4 minutes from 12-60 minutes, every 20 minutes from 1-2 h , every 40 minutes from 2-4 h, every hour from 4-6 h, at 12h, and daily for the remainder of the reaction). Each sample was syringe-filtered through a 0.22 μm filter, at the time of collection, and refrigerated until analysis. All samples were analyzed for total P using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

3.2.3 ATR-FTIR Experiments and Data Analysis

All of the following experiments were conducted on a Thermo Electron Nexus 670 Spectrometer equipped with a MCT/A (Mercury-Cadmium-Telluride) detector and KBr beam splitter.

First, aqueous phase spectra of 60mM oxalate and phosphate solutions at pH 5.5 and 8.0 were collected. The spectra are representative of sixty-four averaged scans, collected at a resolution of 4 cm^{-1}.

For the static sorption experiments, 500 μL of 50 g L^{-1} pseudo-boehmite slurry was mixed with approximately 1 mL of 50% ethanol onto the ATR crystal and dried in an oven at 35°C. After the film was completely dried, 1 ml of 1mM NaCl, at the pH for the experiment, was pipetted onto the film. The crystal was covered and the film was allowed to hydrate for at least 16 h. This minimized spectral features due to the structural changes as the mineral film hydrates. A background spectrum of the film and bathing solution was collected before analytes were added to the system. The hydrated film was then repeatedly spiked with phosphate and/or oxalate to achieve the correct solution concentration in the ATR crystal trough.

For flow experiments, a film was dried, as previously described, onto a Germanium (Ge) ATR crystal placed into a flow cell trough. Equilibrating solution, 1 mM NaCl, at the pH of the experiment, was flowed through the cell with a peristaltic pump at a rate of approximately 0.5 mL min^{-1}. Spectra were collected every 5 min (128 average scans at 8 cm^{-1} resolution) to watch for changes in the mineral film. When the spectra were no longer changing with time (hydration was complete) the flow was stopped and a solution containing the anion(s) of choice was introduced to the hydrated surface. After the sorbates were introduced, spectra were collected, at 5 minute intervals. When no noticeable increase in absorbance for oxalate and/or phosphate was detected with time, the flow was stopped and the solution switched to the second, competing ion. In the case of coadsorption studies, both analytes were added simultaneously.

Experimental spectra represent a ratio of the raw data against a selected background file (the mineral surface hydrated in the electrolyte at the pH of the experiment). After collection, all spectra were baseline corrected with Omni 6.2 software (Thermo Electron Corporation). Static experimental spectra were fit in Origin 6.0 (Microcal, Inc., Northampton, MA) using the non linear curve fitting procedure with multiple Gaussian peaks. The peak centers calculated were later compared to theoretical calculations, conducted by Kristian Paul, which are intended to predict the experimental data. Gaussian03 program code was used to perform the molecular orbital/density functional theory (MO/DFT) geometry optimizations and frequency (peak position) calculations. GaussView software was used to analyze the normal modes from the frequency calculations. The restricted B3LYP exchange-correlation functional and the 6-31G (d) all-electron basis set were used in all DFT calculations.

3.3 Results and Discussion

3.3.1 Aluminum Oxide Characterization

The surface area of the pseudo boehmite, estimated by the EGME method, was approximately 84.2 $m^2 g^{-1}$. Figure 3.1 shows the x-ray diffractogram of the aluminum oxide synthesized in this study. The lack of distinct features in this diffraction pattern indicates that the oxide is x-ray amorphous (non-crystalline). A solid state NMR spectrum (Figure 3.2) displays the relative distribution of Al coordination states. From these data it is clear that the majority of the Al is coordinated to six oxygen (O) molecules, with lesser extents in 4 and 5 coordinations. There is also a feature at 62 ppm which is diagnostic of the Al_{13} ion. This consists of a central Al (coordination number (CN) of 4) with 12 6-coordinated Al surrounding it. Understanding these molecules and the distribution of CNs in a solid can help to determine how the oxide formed and give insight to its reactivity (Furrer et al., 2002). The isoelectric point (pH_{iep}) is estimated, from the zeta potential curve (Figure 3.3), as pH 7.4. This would indicate that the net charge on the surface below this pH is positive, while above this pH the net surface charge would be negative. This pH_{iep} is lower than the point of zero charge (PZC) sited in the synthesis method (PZC = 9.3) (Su and Suarez, 1995). This may be due to the conditions under which the synthesis was conducted (in equilibrium with atmospheric conditions), as adsorption of carbonates or other aqueous anions may effect the surface charge properties. Scanning electron microscope images of the synthesized amorphous aluminum hydroxide (am-Al(OH)$_3$) are shown in Figure 3.4. These images show that the aggregates of this material are irregular in shape, size (ranging from 30 to 100 μm), and texture.

3.3.2 Batch Phosphate and Oxalate Sorption Reactions

The organic matter extraction and subsequent ATR-FTIR analysis of the extract indicated that carboxylic (-COOH) functional groups were among the most prevalent (Figure 3.4). This is why oxalate was chosen as a competing ion, against phosphate, in the batch and FTIR sorption studies. There are other inorganic ions which are present at notable concentrations in this extract (i.e. sulfate as indicated by the band at 1102 cm^{-1}); however, the focus of this study, and Chapter 2.0 was to show the importance of organic compounds, because of the lack of information on these phases in animal manures. Chapter 2.0 focused on large organic P-containing compounds that are present in PL, but these compounds are investigated as sources of phosphate. Oxalate, however, has similar charge and size properties as orthophosphate and would likely compete for the same types of reaction sites in the PL system.

Rather than determining quantitative surface loading levels and/or rate reactions from these batch experiments, and the ATR-FTIR experiments (Section 3.3.3), the purpose of these studies was to develop a qualitative comparison of the sorption of phosphate and oxalate at various pHs for extrapolation to a much more complex system (PL). This approach strongly influenced the experimental design and conditions for achieving the results presented below. To be able to impact nutrient management practices, large differences in the sorption or release of a nutrient, like phosphate, must be shown. Therefore, we focused on major differences in our ATR-FTIR spectra, which can be clearly determined by visual evaluation.

The results of the batch pH stat sorption experiments are presented in Figures 3.5-3.7. Figure 3.6 expresses these results as %P sorbed verses time (min). The inset figure magnifies the initial time points so the difference between the "P sorption" and "Coadsorption" experiments is clear. In the "P sorption" experiment, most of the disappearance of P from solution occurs within the first four sample points. This quick sorption, followed by a slower sorption reaction, is very common with anionic sorbates and metal oxide sorbents (Sparks, 1986).

In the coadsorption study, the phosphate sorption is much slower due to the presence of oxalate. The "Coadsorption" curve does not approach the "P sorption" curve until approximately the 120 min sample point. According to previous literature (De Cristofaro et al., 2000; Violante and Huang, 1989; Violante et al., 1991), we can indirectly conclude that the oxalate is sorbing to the am-$Al(OH)_3$ surface and hindering the sorption of phosphate during the initial time points. The oxalate surface complex may physically block the sites which are responsible for the fast sorption of phosphate. While some reaction sites on the sorbent may not prefer one anion over another, there is evidence that some are specific to oxalate or phosphate (Yuan, 1980). In spite of this early out-competition, phosphate is able to reach the same level of adsorption as in the system without oxalate. Scanning electron microscope (SEM) images (Figure 3.4) of the aluminum oxide particles show that the shape and size of the aggregates is irregular. The large, complex $Al(OH)_3$ particles not only have the outer reactive surface area, but will also contain reaction sites within the aggregates which are not readily exposed to the sorptive solution. Therefore, diffusion processes may have a large role to play in the kinetics of the adsorption of oxalate and phosphate.

Because the sorption experiments were conducted over a linear pH increase (from pH 5.5 to pH 8.0), it is important to also express these sorption results in terms of this variable. Figures 3.6 and 3.7 are different representations of the same experimental data, since two variables (pH and time) are changing over the course of the experiment. A plot of P surface loading verses pH (Figure 3.7) shows that in the "P sorption" experiment, the P surface loading is consistently higher in the early pH (corresponding to early time points), than in the "Coadsorption" experiment. Once the maximum level of surface loading was achieved (approximately 11 μmol m^{-2}), there was no later release of P to solution. The expectation, before this experiment was completed, was that there would be some release of phosphate at pHs near and above the pH_{iep} because of the net negative charge on the am-$Al(OH)_3$ surface and competition from hydroxyl (OH^-) ions for surface sites. However, this did not occur, indicating that the phosphate sorption complex were recalcitrant to desorption (out-competition by OH^-) under these experimental conditions. It is commonly thought that phosphate adsorbs, as an inner sphere species, via a ligand exchange reaction. So, the phosphate most likely attaches under conditions that are electrostically favorable, but the increase in net negative charge on the surface does not affect its stability in this reaction. In fact, little sorption or desorption appeared to be occurring above pH 5.75 to 6.0; therefore, the ATR-FTIR experiments focus on the low pH regime of the batch studies. In terms of alum amendment and PL, these results are significant because they show that phosphate, once attached to the metal oxide surface, is stable against release to solution. Environmentally, this means that the nutrient would not be in a form available for use by aquatic flora and fauna.

To understand the effect that phosphate and oxalate sorption have on the am-Al(OH)$_3$ solid, Al solution concentrations, throughout all batch reactions, are presented in Figure 3.8. In the "Phosphate Sorption" experiment, there is negligible Al in solution throughout the entire reaction. However, in the "Coadsorption" study (oxalate introduced simultaneously with phosphate) $[Al]_{aq}$ is increased. This maybe due to oxalate promoted dissolution of the surface. The $[Al]_{aq}$ is highest in the coadsorption study. It is unclear why this occurs. Possible explanations include increased dissolution due to increased total ligand concentration in the reactor or faster oxalate adsorption in the presence of phosphate. Initially, in the oxalate sorption and coadsorption studies, the concentrations of Al are high, and they decrease with time over the first few sample points, before stabilizing. The dissolution of aluminum surfaces by ligands, such as oxalate, is also dependent on proton concentration (pH) (Amirbahman et al., 2000). This explains why, at higher pHs continued dissolution does not occur. The decrease of aluminum concentration could be explained two ways. The oxalate may complex the Al^{3+} in solution (Johnson et al., 2004) or the aqueous aluminum may polymerize as the pH increases (Amirbahman et al., 2000), both resulting in the decrease of $[Al]_{aq}$ with time. Mineral surface dissolution by oxalate ligands is dependent on a monodentate surface complex between the ion and the metal (Al) center. However, this batch sorption data and the data collected in the ATR-FTIR studies are not designed to conclude the geometry of oxalate sorption complexes.

In the “Coadsorption” study, the [Al] concentrations are much higher than in either of the other two experiments (“Phosphate Sorption” and “Oxalate Sorption”), and the concentration remains nearly the same with time. Because phosphate sorption is initially slow, oxalate is presumably sorbing quickly, as a monodentate species (Yoon et al., 2004), to the mineral surface. This promotes the dissolution of the oxide (Johnson et al., 2004). With time, the phosphate sorption increases and may stabilize the surface, making it resistant to further weathering.

There has been no evidence of Al toxicity in plants grown on soils that have received alum amended poultry litter. So, while the Al results are interesting in terms of ligand-metal complexation, they do not contribute to the nutrient management aspect of this study.

3.3.3 ATR-FTIR Experiments

3.3.3.1 Aqueous Standards

Aqueous phosphate standards, at pH 8.0 and 5.5 are shown in Figure 3.9. These pH values were chosen because they were the endpoints of the batch reactions described in Section 3.3.2. At pH 8.0, phosphate will be predominantly HPO_4^{2-} and displays two IR active bands at approximately 1075 and 990 cm^{-1}. At pH 5.5, the symmetry of the molecule ($H_2PO_4^-$) is decreased, and a third band, at 1170 cm^1 is shown, along with the shifting of the low wavenumber band (previously at 990 cm^{-1}) to 940 cm^{-1}. This is in agreement with previous ATR-FTIR phosphate literature (Arai and Sparks, 2001; Butkus et al., 1998).

Because the two pKs of oxalic acid are less than pH 5.5, both aqueous spectra are the same (Figure 3.10). This is because there is no difference in protonation, and therefore symmetry, of the molecule with an increase in pH. Oxalate is fully deprotonated ($C_2O_4^{2-}$) at both of these pHs. The bands present are located at 1570 and 1300 cm^{-1}, and can be attributed to ν(CO_2^-) absorptions (Dobson and McQuillan, 1999).

3.3.3.2 Static Sorption Experiments and Gaussian Fitting

Two static phosphate sorption studies, at pH 5.5 and pH 8.0 were completed to investigate the difference in ATR-FTIR spectra with respect to pH. Figures 3.11 and 3.12 show spectra for phosphate sorbed to am-Al(OH)$_3$ at pH 5.5 and 8.0, respectively. The broad feature, centered around 1100 cm^{-1} is the spectral signature of sorbed phosphate (Arai and Sparks, 2001). The distinct, narrow bands of the aqueous phase are no longer present. Results of the non-linear peak fitting estimate Gaussian peak centers at 1162, 1077, and 1008 cm^{-1} for pH 8.0 and 1143, 1089, and 1032 cm^{-1} for pH 5.5 (Table 3.1). Comparing the experimental data for P sorption at both pHs, it appears that both best represent a sorbed, deprotonated phosphate species. The change in pH did not change the peak center positions more than 24 cm^{-1}. While the peak positions are not exact, systematic shifts of +/- 20 cm^{-1} are within the error for the resolution attainable with this technique. In addition, our Gaussian peak fitting does not predict the nearly the number of peaks calculated for the protonated (biphosphate) species. However, with the amount of modeling and experimental data in this study, it is impossible to argue which of these configurations best describes the adsorption complex for phosphate on am Al(OH)$_3$. It would be necessary to conduct experiments at more pHs and model the FTIR spectra of phosphate sorbed in different geometric configurations to be sure that our data clearly support a single sorption mechanism.

Experimental spectra and Gaussian fitting for the static oxalate experiments are shown in Figures 3.13 and 3.14. Because the protonation state of oxalate is the same in both of these experiments, the experimental data and the peak fitting show peak centers at virtually identical positions (+/- 5 cm^{-1}) (Table 3.2). The band at ~1589 cm^{-1} in the experimental data from this work is likely due to aqueous oxalate. However, this is slightly shifted from the aqueous peak position (at 1570 cm^{-1}), therefore indicating that the symmetry of the molecule has somehow changed, and may possibly be interacting with the surface via some electrostatic, outer sphere complex. The high intensity, broader band at 1687cm^{-1} is representing both of the high wavenumber peaks in the other studies. Yoon et al. (2004) conclude that oxalate sorbs as a bidentate species; however, our data seem to be more inline with the model for oxalate in a mondentate end-on configuration (Table 3.2).

The purpose of these static experiments and Gaussian peak fitting was not to determine sorption mechanisms or configurations for these anions. By conducting these experiments on the am-$Al(OH)_3$ synthesized in this work, it was possible to compare this experimental data to previous studies to ensure that we were collecting quality spectra of sorbed oxalate and phosphate. In addition, these experiments are essential when investigating the flow cell experiments to know the spectral regions in which to look for changes.

3.3.3.3 Flow Cell Preadsorption Experiments

First of all, it is important to note that the oxalate and phosphate solutions used in the flow cell experiments were 50 μM. This concentration, in solution, was not detectable with this technique. Therefore, the spectra presented in conjunction with the following discussion are considered to be sorbed phases, or those closely associated with the am-Al$(OH)_3$ surface, and not aqueous.

The phosphate preadsorption experiment was conducted at pH 5.5. In Figure 3.15, spectra are shown at the end of the phosphate adsorption (before the flow of phosphate was stopped), just after the flow was switched to oxalate, and at the end of the oxalate adsorption. In the "PO_4 Preadsorption," the broad feature, from approximately 1200 cm^{-1} to 950 cm^{-1} is indicative of adsorbed phosphate. The sharp decrease in the spectra at 1040 cm^{-1} is not due to changes in phosphate geometry. A similar feature in this region has been described, in other FTIR work on aluminum oxides, as a structural OH bending mode (Dickie and McQuillan, 2004).

Upon the initial introduction of oxalate, there is not a change in the phosphate region, nor is there any oxalate signature. However, the "Oxalate (final)" spectra appear quite different from the previous two. In this spectrum, the phosphate signal is significantly decreased and oxalate features, at ~1700 cm^{-1} and 1300^{-1} are discernable. This suggests that there is some displacement of phosphate, by the oxalate, and this competing anion is then sorbing to the am-Al$(OH)_3$ surface.

The oxalate preadsorption experiment is represented in Figure 3.16. The second derivate of the "Oxalate Preadsorption" spectra is shown (Figure 3.16 B) to validate the oxalate features at ~1700, 1425, and 1300 cm^{-1}. The broad band, shown in both the spectra and the second derivative, around 1600 cm^{-1} is absorbance due to water. In most cases, using the background spectrum to ratio against the experimental spectrum eliminates the water absorption band; however, if for some reason the amount of solution changes within the cell, these bands may appear. This feature does not affect the diagnostic peaks for sorbed oxalate, (1425 and 1300 cm^{-1}), so the experiment was continued using these peaks to determine what changes occur with the introduction of phosphate. Other than the over-subtraction of water, the other features within the “PO_4 (initial)” and “PO_4 (final)” are not different than in the “Oxalate Preadsorption” spectra. This varies differently from the Phosphate Preadsorption study (Figure 3.15), in that oxalate is not displaced by the presence of the competitor, phosphate.

3.3.3.4 Flow Cell Coadsorption Experiments

In coadsorption studies, both analytes are in the flowing solution and introduced to the am-$Al(OH)_3$ simultaneously. These experiments were conducted at pH 5.5 and 8.0, as the end points of the macroscopic batch sorption experiments. From these spectra (Figure 3.17), features of both sorbed oxalate and phosphate are present under both pH conditions. With time, these features grow into the spectra at the same rate, and there is no decrease in intensity in any of the bands. The most noticeable comparison between the spectra collected at pH 8.0 and that collected at pH 5.5. The intensity of the features for both sorbates is much lower at the higher pH. The pH_{iep} of the solid is less than 8; therefore the am-$Al(OH_3)$ would have a net negative charge. Because both of the sorbing ions are negatively charged, the sorption reactions are not electrostatically favorable. So, when both oxalate and phosphate are present, there does not appear to be out competition or preference for either species. In addition, carbonate species would be present at high concentrations in solutions at pH 8.0. These aqueous species may adsorb to the surface and limit the number of surface sites available for phosphate and oxalate. However, in a PL system, carbonates and a variety of other inorganic and organic species would also be present;

therefore, eliminating them from our solutions would not create chemical conditions relevant to objectives of this study.

3.4 Conclusions

The competitive studies conducted here are designed to investigate how pH and anion competition may change the efficacy of alum amendment as a BMP. Based on a combination of both macroscopic batch techniques and ATR-FTIR spectroscopy, it seems that oxalate and phosphate affect the sorption of each other when presented as competing ions. In the batch systems, oxalate appears to slow the uptake of phosphorus by am-Al(OH)$_3$, but with time phosphate is able to reach the same surface loading as when the oxalate is not present. Because there is no release of phosphate to solution as the pH increases, there is no evidence from this portion of the study to change the alum amendment BMP to control pH conditions.

The ATR-FTIR studies show that when present simultaneously, both ions sorb to the material synthesized in this study, although both adsorb to a lesser extent at higher pHs. Because the solutions used in these studies where in equilibrium with atmospheric carbon dioxide, this decreased adsorption may be due to carbonate adsorption, which decreases the number of available surface sites for oxalate and/or phosphate. From our experimental and modeling data and that of previous studies, it appears as though phosphate sorbs as a deprotonated species and oxalate sorbs in a mononuclear configuration. This may contribute to the overall dissolution of the aluminum surface, to which phosphate adsorbs.

Preadsorption studies show that oxalate has the ability to displace phosphate from this mineral surface, while phosphate does not appear to be able to remove oxalate once it has sorbed. To extrapolate this small-scale, model system to the heterogeneous alum amended management practice, it seems as though some pH control of the PL, at the early time intervals, would enable the amorphous Al phases in the litter to sorb more phosphate. Because the litter remains in the poultry houses and these sorption complexes are allowed to age, it is likely that the phosphate in the PL will further stabilize with time and remain on the surface once land applied. Further batch studies and investigation of the PL system would be necessary to be certain of these effects.

3.5 Tables

Table 3.1 Summary of FTIR peak positions for phosphate sorption onto aluminum oxide from experimental and theoretical modeling done in this study.

Experimental Data		Molecular Orbital Modeling	
pH 5.5	pH 8.0	Bidentate Bridging Phosphate	Bidentate Bridging Biphosphate
		Peak Positions (cm^{-1})	
1143	1162	1165	1181
1089	1077	1123	1135
1031	1008	1014 & 1002	1097
		947 & 941	1052, 1046, & 1032
			1018
			849
			802

Table 3.2 Summary of FTIR peak positions for oxalate sorption onto aluminum oxides from this and previous work. Data from this work are the result of static experiments and peak positions were calculated by Gaussian peak fitting. The oxalate model (mononuclear) data are calculated frequencies for oxalate in a monodentate end-on configuration on a theoretical Al_xO_y cluster.

Experiment	Sorbate	Peak Positions (cm^{-1})				Reference
Oxalate pH 8.0	am-$Al(OH)_3$	1687	1589	1427	1302	This work
Oxalate pH 5.5	am-$Al(OH)_3$	1685	1584	1425	1298	This work
Oxalate $pK_1<pH<pK_2$	Al_2O_3	1720	1695	1424	1297	(Dobson and McQuillan, 1999)
Oxalate pH 8.5	γ-AlOOH	1722	1702	1413	1288	(Axe and Persson, 2001)
Oxalate pH 5.1	γ-AlOOH	1720	1700	1418	1286	(Johnson et al., 2004) #345}
Oxalate pH 5.1	Al_2O_3	1720	1699	1425	1294	(Yoon et al., 2004)
Oxalate model (mononuclear)	Al_xO_y cluster	1683	1616	1442	1263	(Yoon et al., 2004)

3.6 Figures

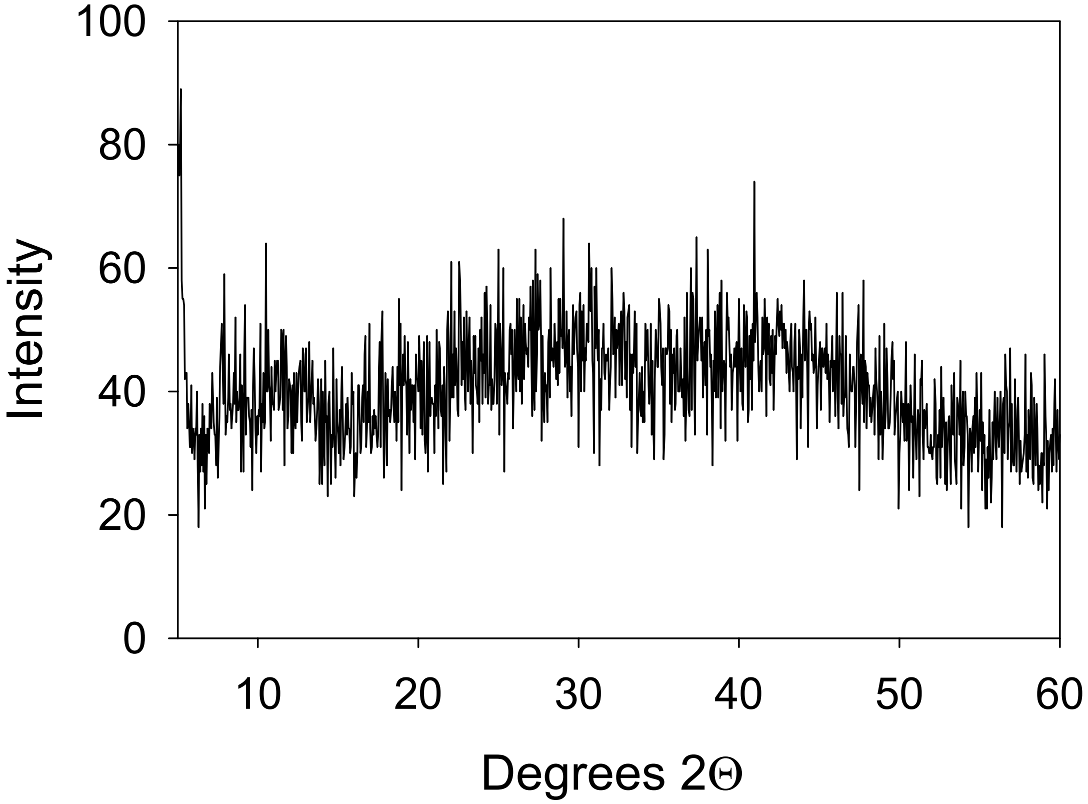


Figure 3.1 X-ray diffraction pattern for synthesized $Al(OH)_3$.

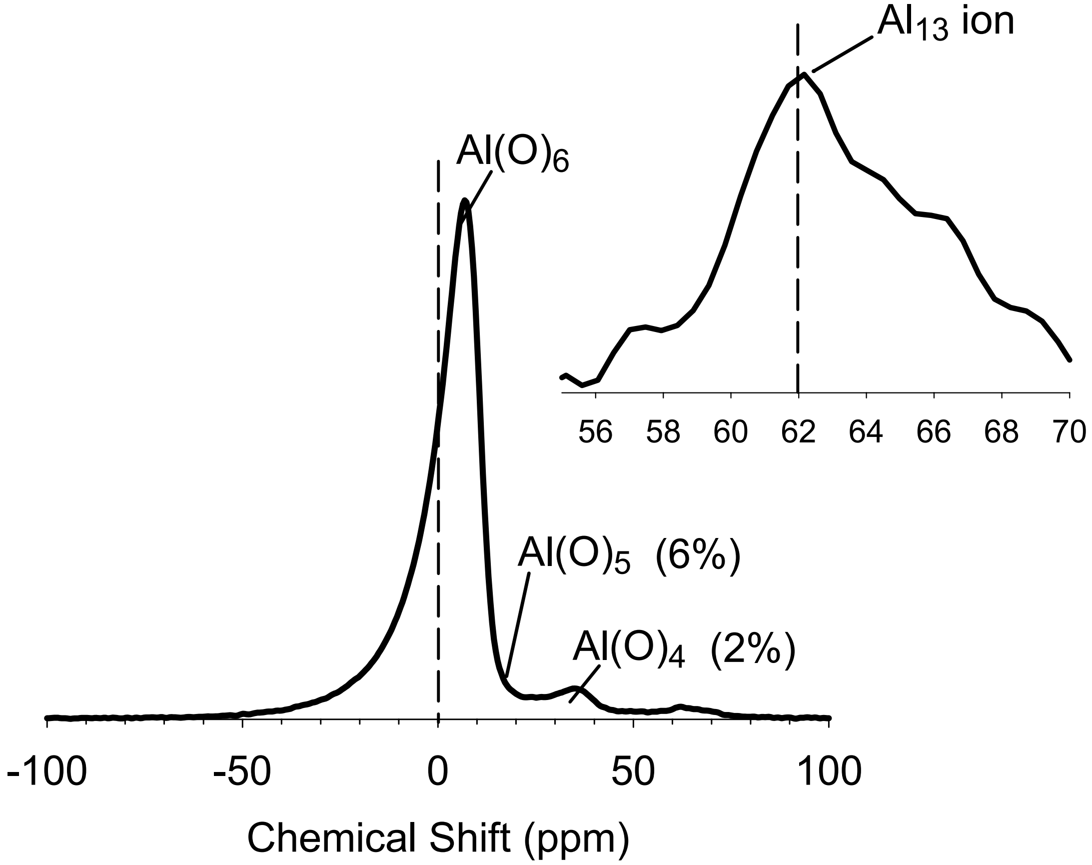


Figure 3.2 Solid State NMR spectra for synthesized $Al(OH)_3$.

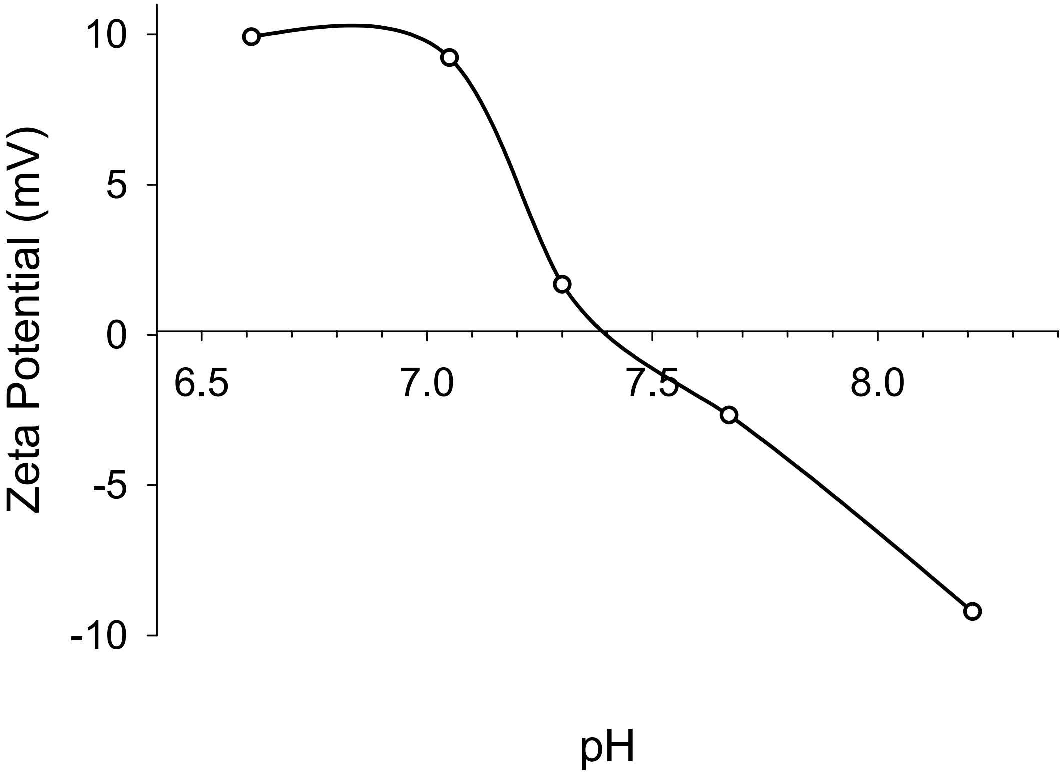


Figure 3.3 **Zeta Potential Curve for synthesized $Al(OH)_3$, displaying the pH of the isoelectric point (pH_{iep}) at approximately 7.4.**

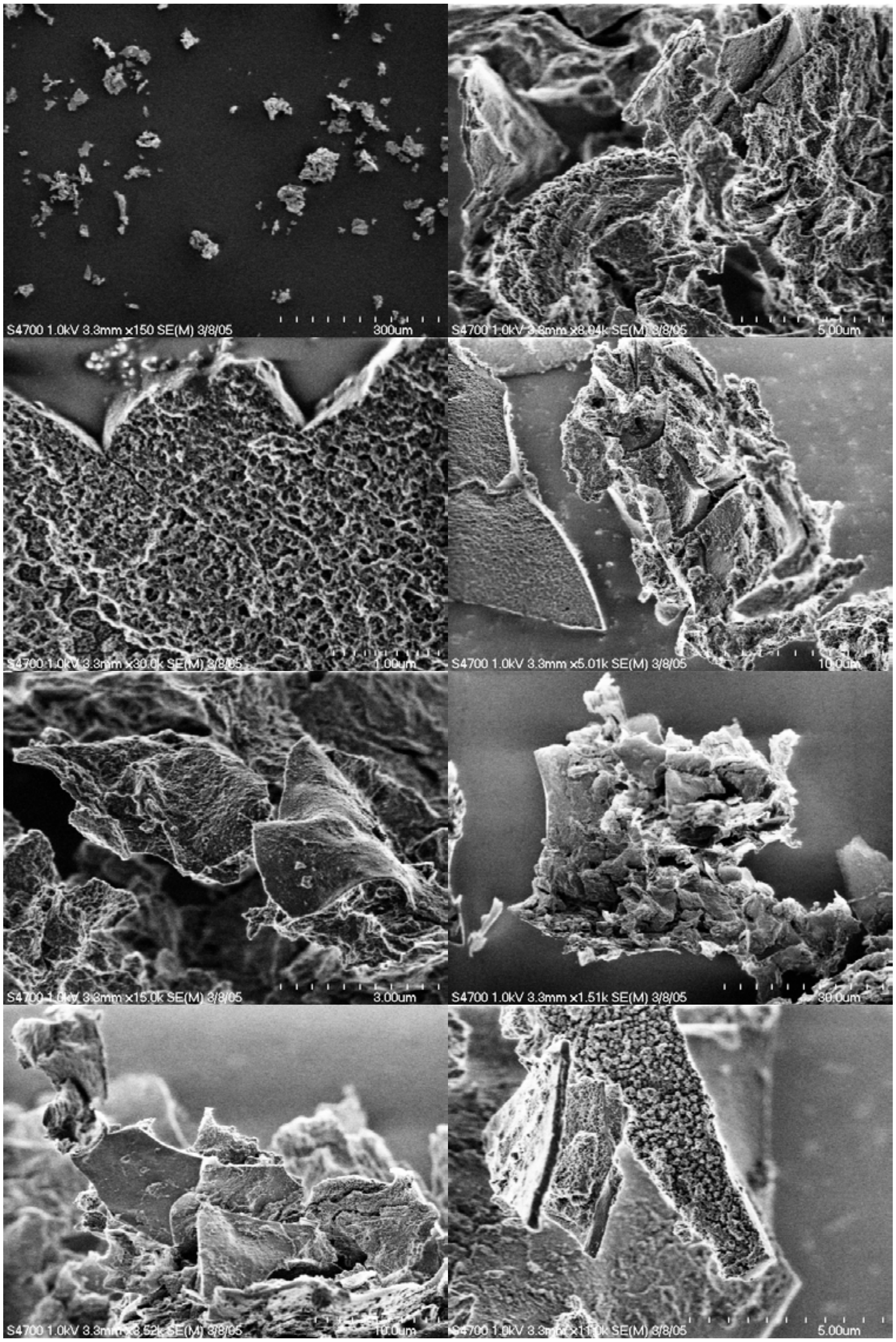

S4700 1.0kV 3.3mm x150 SE(M) 3/8/05 300um
S4700 1.0kV 3.3mm x8.04k SE(M) 3/8/05 5.00um
S4700 1.0kV 3.3mm x30.0k SE(M) 3/8/05 1.00um
S4700 1.0kV 3.3mm x5.01k SE(M) 3/8/05 10.0um
S4700 1.0kV 3.3mm x15.0k SE(M) 3/8/05 3.00um
S4700 1.0kV 3.3mm x1.51k SE(M) 3/8/05 30.0um
S4700 1.0kV 3.3mm x3.52k SE(M) 3/8/05 10.0um
S4700 1.0kV 3.3mm x11.0k SE(M) 3/8/05 5.00um

Figure 3.4 Scanning electron microscope images of synthesized amorphous aluminum hydroxide.

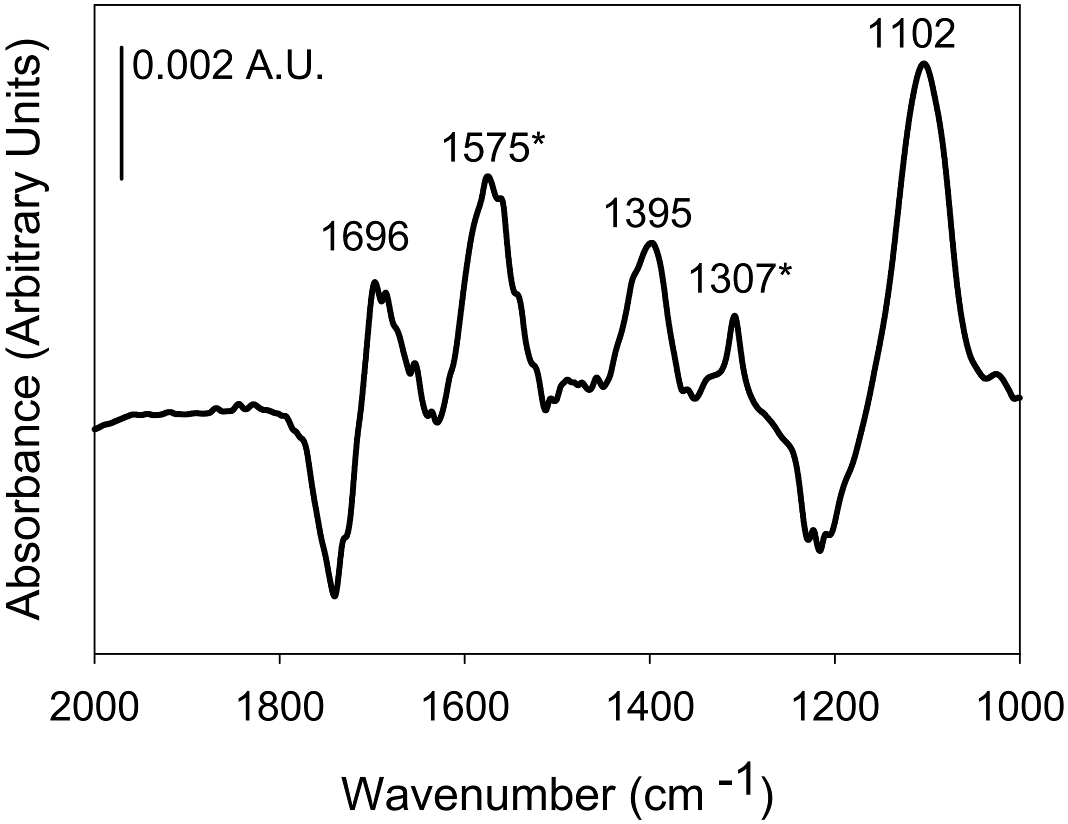


Figure 3.5 ATR-FTIR spectra collected from the organic matter extraction (0.25 M NaOH for 16h) of alum amended poultry litter (Ge ATR crystal). The bands centered at 1575 cm^{-1} and 1307 cm^{-1} are indicative of carboxylic functional groups present in the supernatant after the extraction.

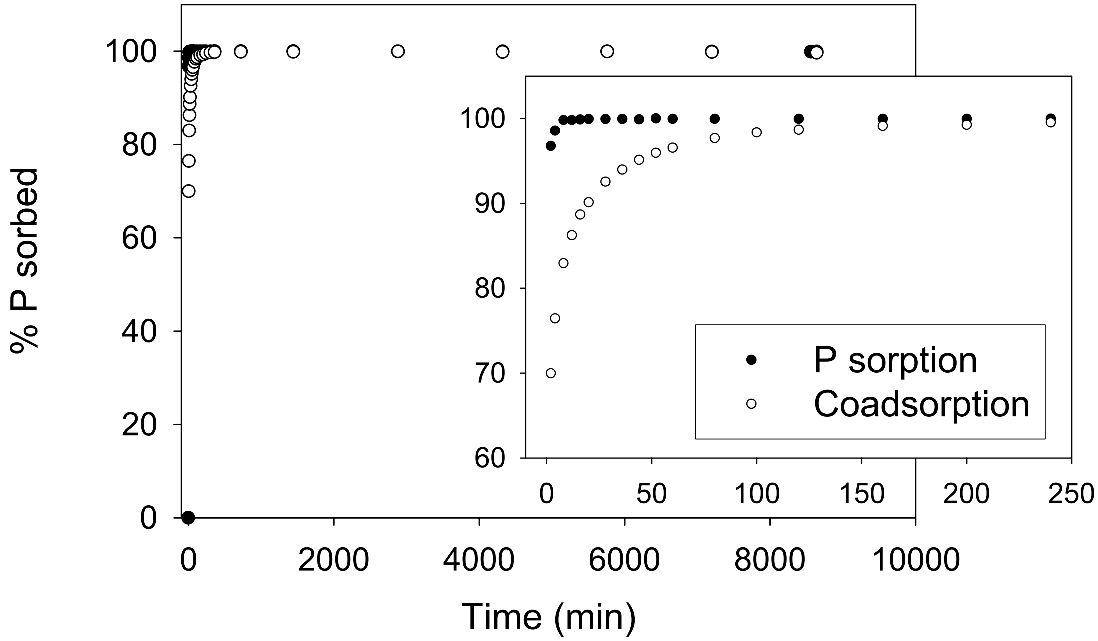


Figure 3.6 **Phosphate sorption with time, in the presence and absence of oxalate, onto amorphous $Al(OH)_3$. $[P]_{total}$ is 750 uM in both experiments and $[C_2O_4^{2-}]_{total}$ is 750 uM in the coadsorption experiment. Both experiments were completed at room temperature. Solution density of $Al(OH)_3$ is 1 g L^{-1}. These same data are expressed as a function of pH in Figure 3.7, because pH was also changing with time.**

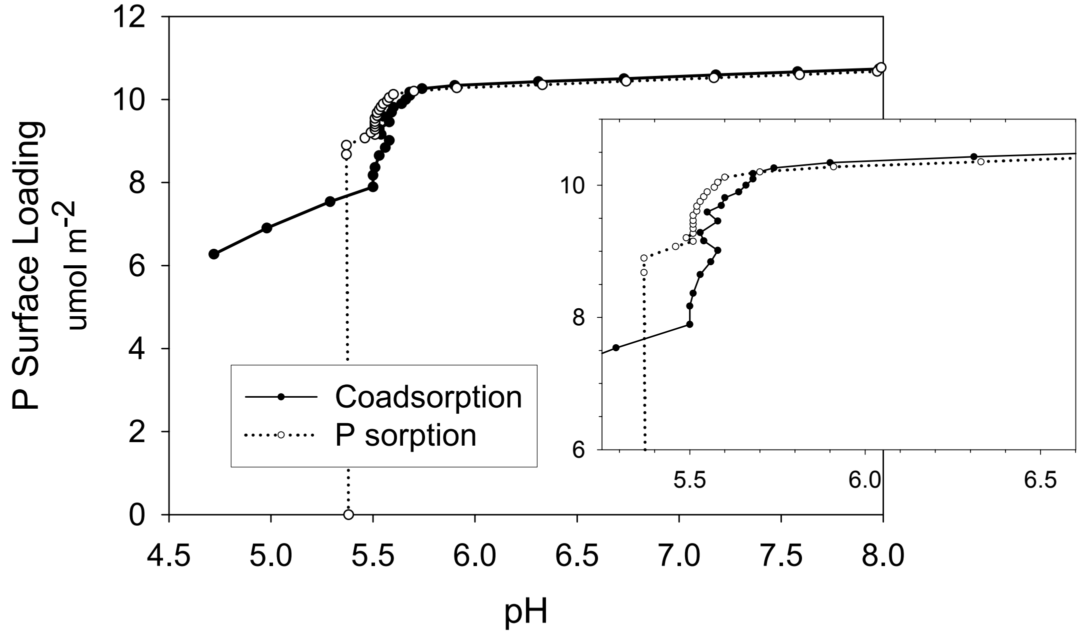


Figure 3.7 **Phosphate sorption, in the presence and absence of oxalate, onto amorphous $Al(OH)_3$ during a linear increase in pH over the time of the batch experiment. $[P]_{total}$ is 750 uM in both experiments and $[C_2O_4^{2-}]_{total}$ is 750 uM in the coadsorption experiment. Both experiments were completed at room temperature. Solution density of $Al(OH)_3$ is 1 g L^{-1}. These data are also expressed as a function of time in Figure 3.6, because the pH increase was conducted over a period of 6 d.**

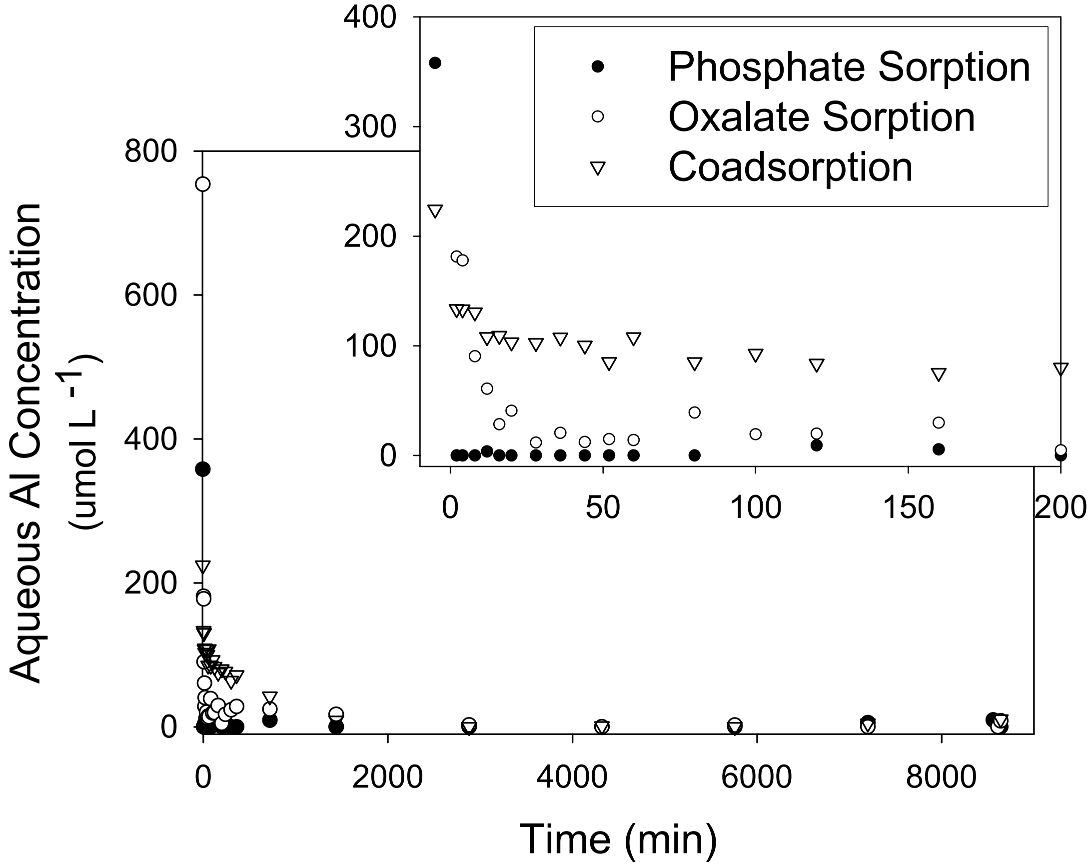


Figure 3.8 **Aluminum concentrations in solution as a function of time, for all sorption experiments. $[P]_{total}$ is 750 uM in “Phosphate Sorption” and “Coadsorption” experiment and $[C_2O_4^{2-}]_{total}$ is 750 uM in the “Coadsorption” experiment. Both experiments were completed at room temperature. Solution density of $Al(OH)_3$ is 1 g L^{-1}.**

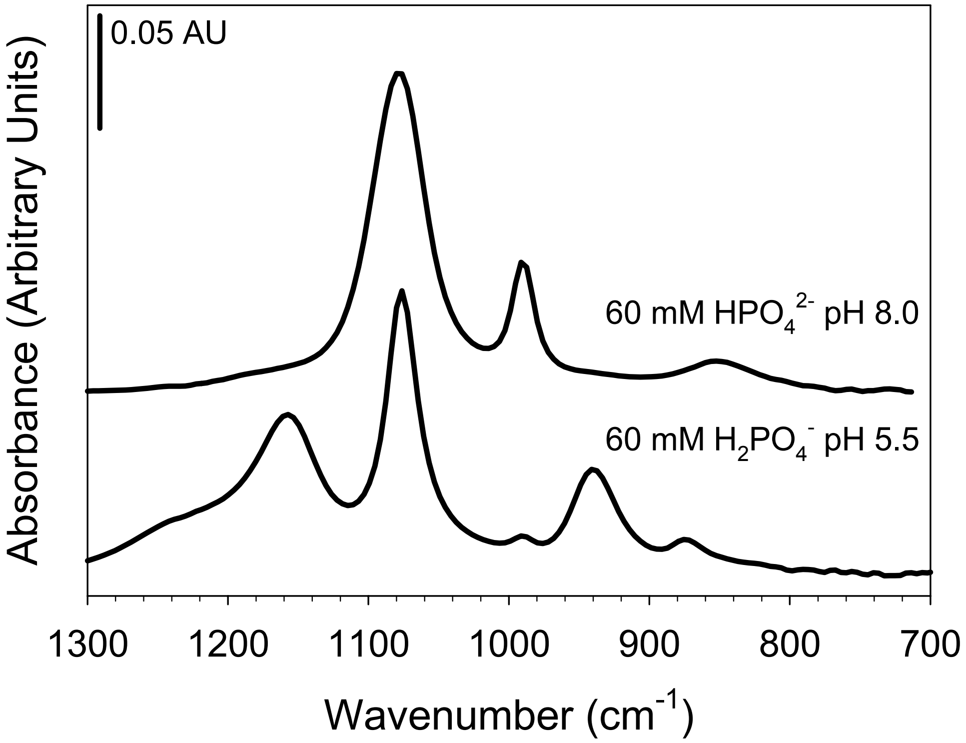


Figure 3.9 Aqueous phosphate standards. Spectra are averaged from 64 scans at 4 cm^{-1} resolution on a ZnSe ATR crystal.

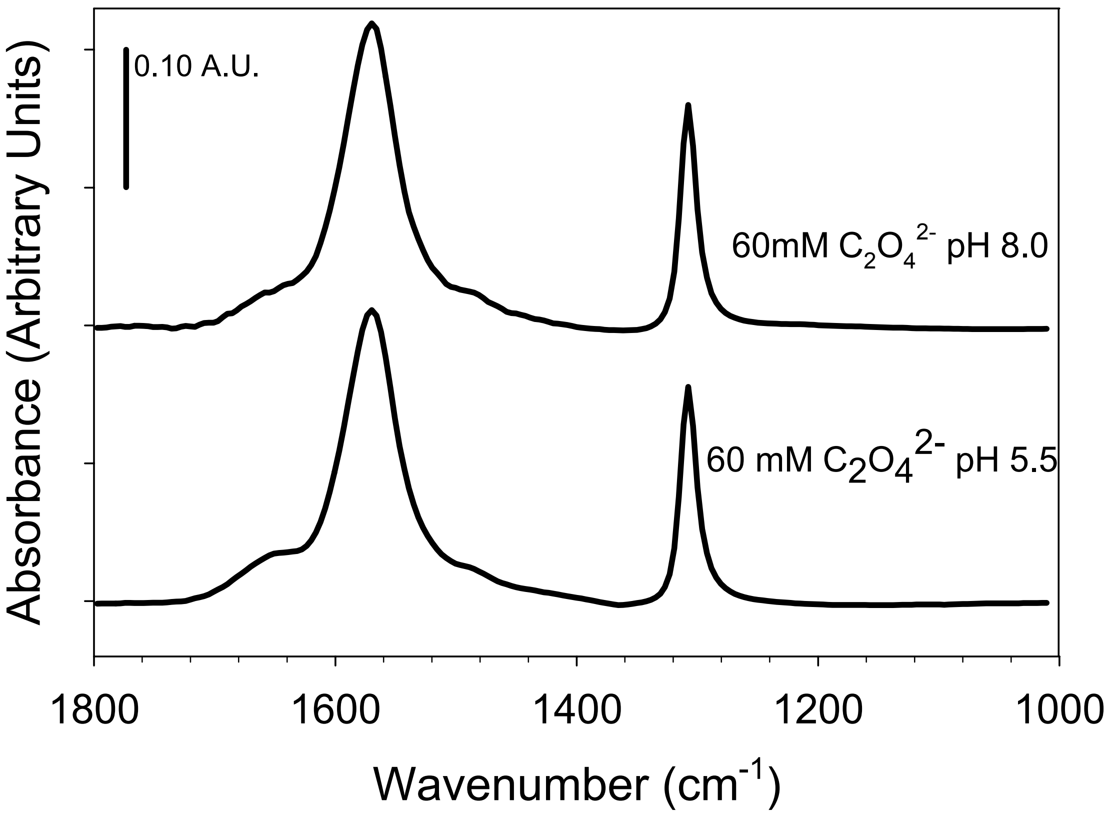


Figure 3.10 Aqueous oxalate standards. Spectra are averaged from 64 scans at 4 cm^{-1} resolution on a ZnSe ATR crystal.

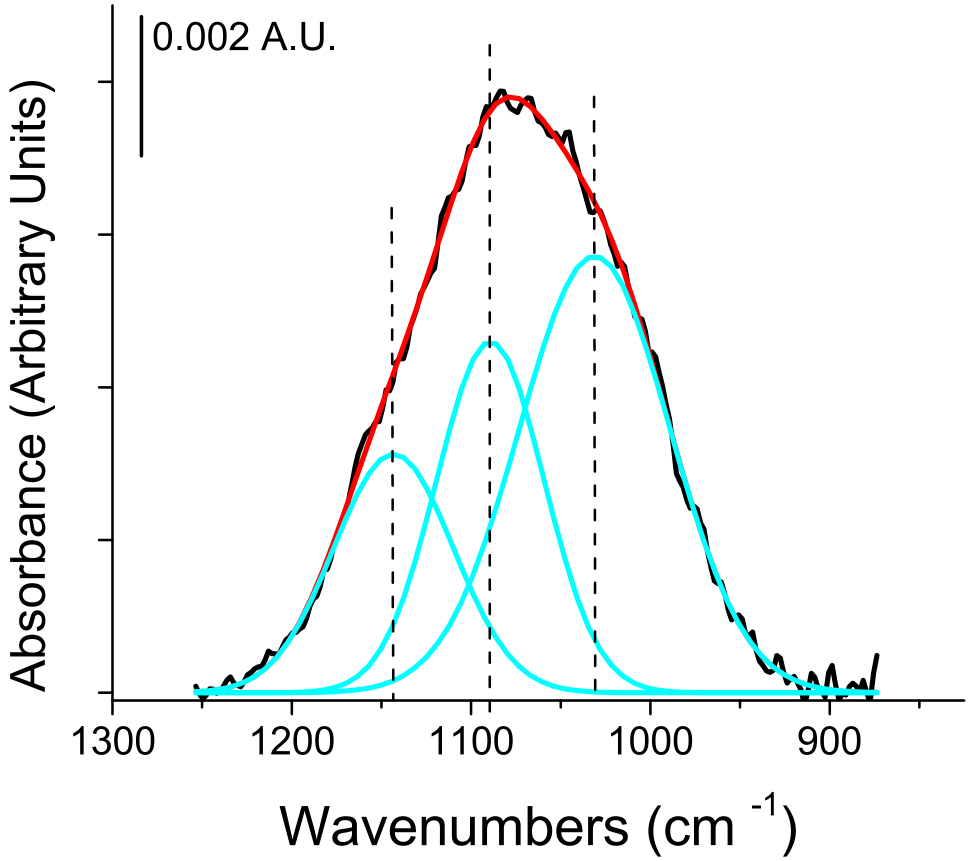


Figure 3.11 ATR-FTIR spectra of phosphate sorbed to am-Al(OH)$_3$ at pH 5.5 (static experiment on Ge ATR crystal). Experimental spectrum is an average of 128 scans at 8 cm^{-1} resolution. The experimental data, overall nonlinear curve fit, and multiple Gaussian peaks used in this fit are shown. Gaussians centers (shown with vertical dashed lines) are located at 1143, 1089, and 1031 cm^{-1}.

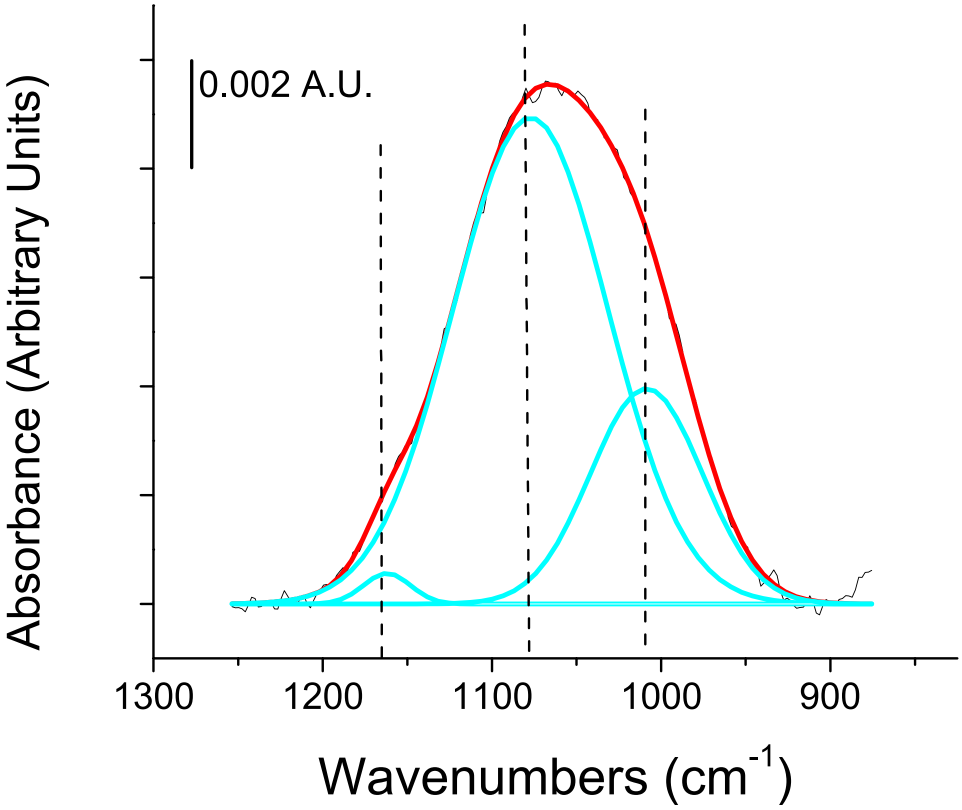


Figure 3.12 ATR-FTIR spectra of phosphate sorbed to am-Al(OH)$_3$ at pH 8.0 (static experiment on Ge ATR crystal). Experimental spectrum is an average of 128 scans at 8 cm^{-1} resolution. The experimental data, overall nonlinear curve fit, and multiple Gaussian peaks used in this fit are shown. Gaussians centers (shown with vertical dashed lines) are located at 1162, 1077, and 1008 cm^{-1}.

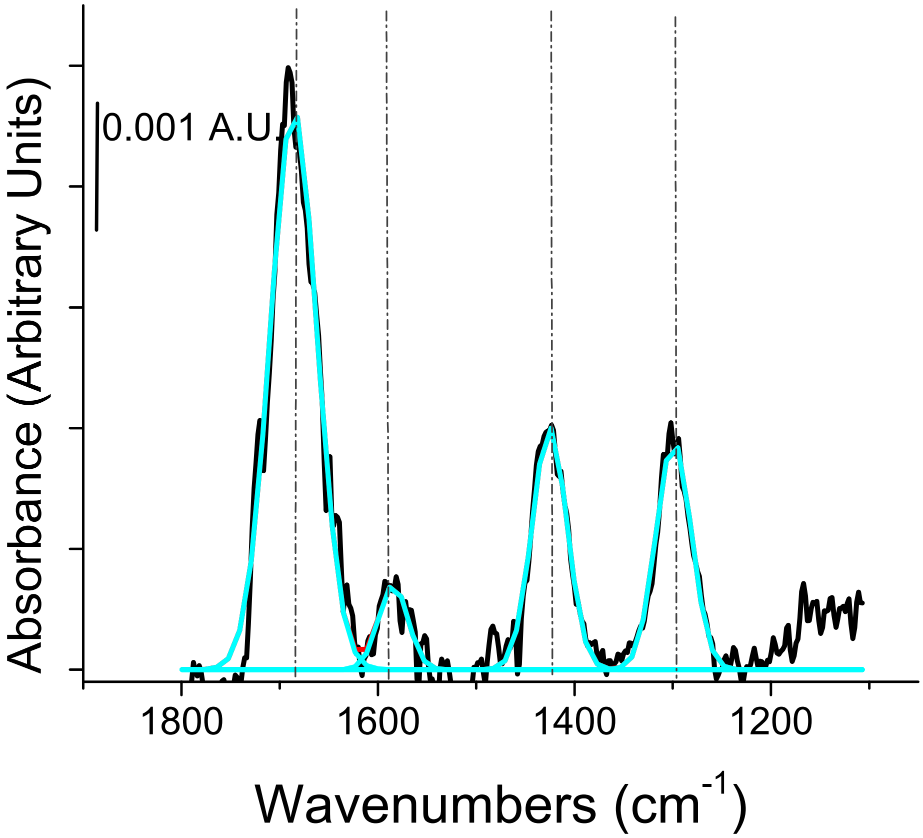


Figure 3.13 **ATR-FTIR spectra of oxalate sorbed to am-Al(OH)$_3$ at pH 5.5 (static experiment on Ge ATR crystal). Experimental spectrum is an average of 128 scans at 8 cm^{-1} resolution. The experimental data, overall nonlinear curve fit, and multiple Gaussian peaks used in this fit are shown. Gaussians centers (shown with vertical dashed lines) are located at 1685, 1584, 1425, and 1298 cm^{-1}.**

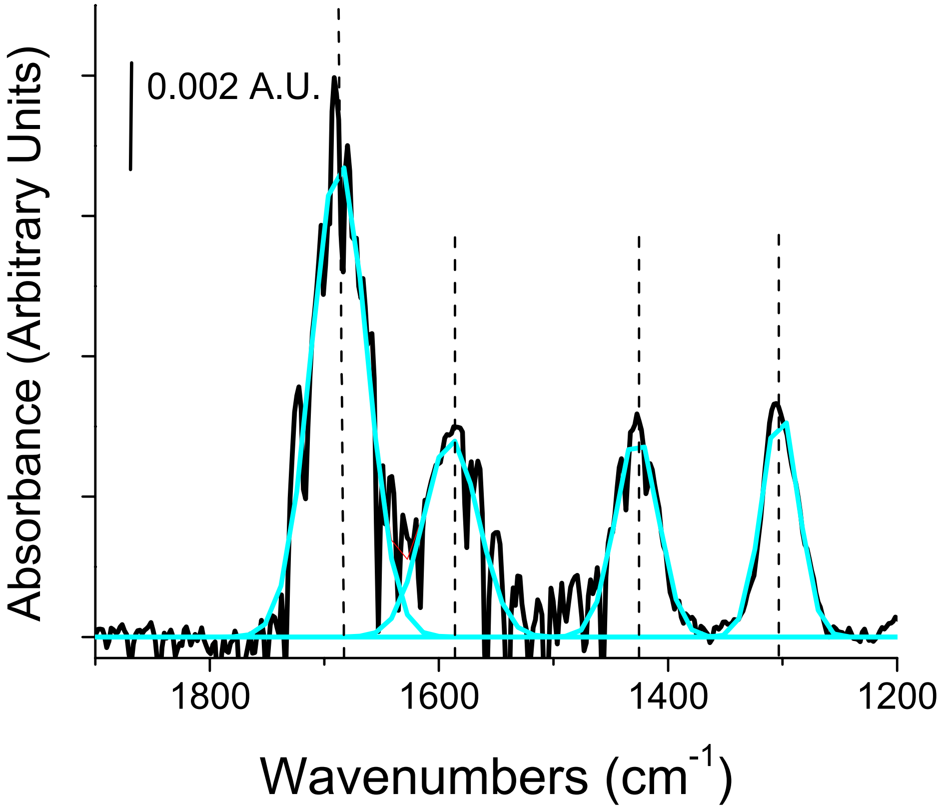


Figure 3.14 ATR-FTIR spectra of oxalate sorbed to am-Al(OH)$_3$ at pH 8.0 (static experiment on Ge ATR crystal). Experimental spectrum is an average of 128 scans at 8 cm^{-1} resolution. The experiment data, overall nonlinear curve fit, and multiple Gaussian peaks used in this fit are shown. Gaussians centers (shown with vertical dashed lines) are located at 1687, 1589, 1427, 1302 cm^{-1}.

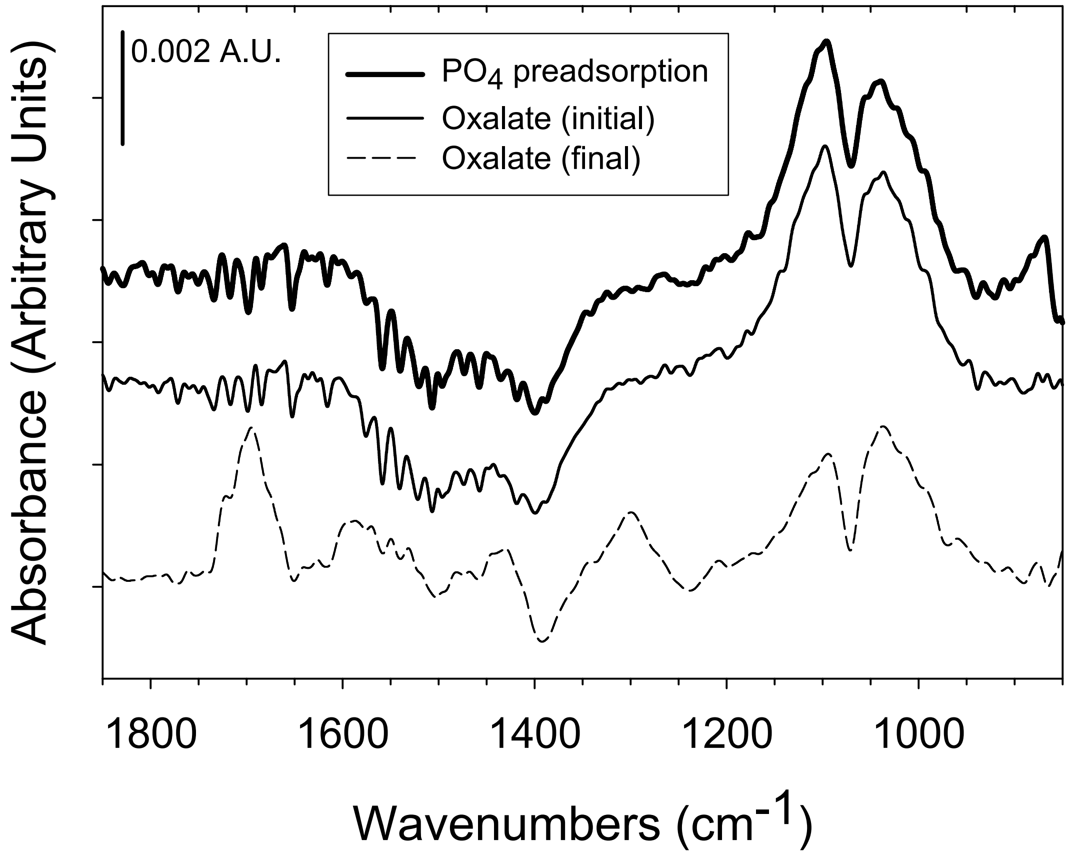
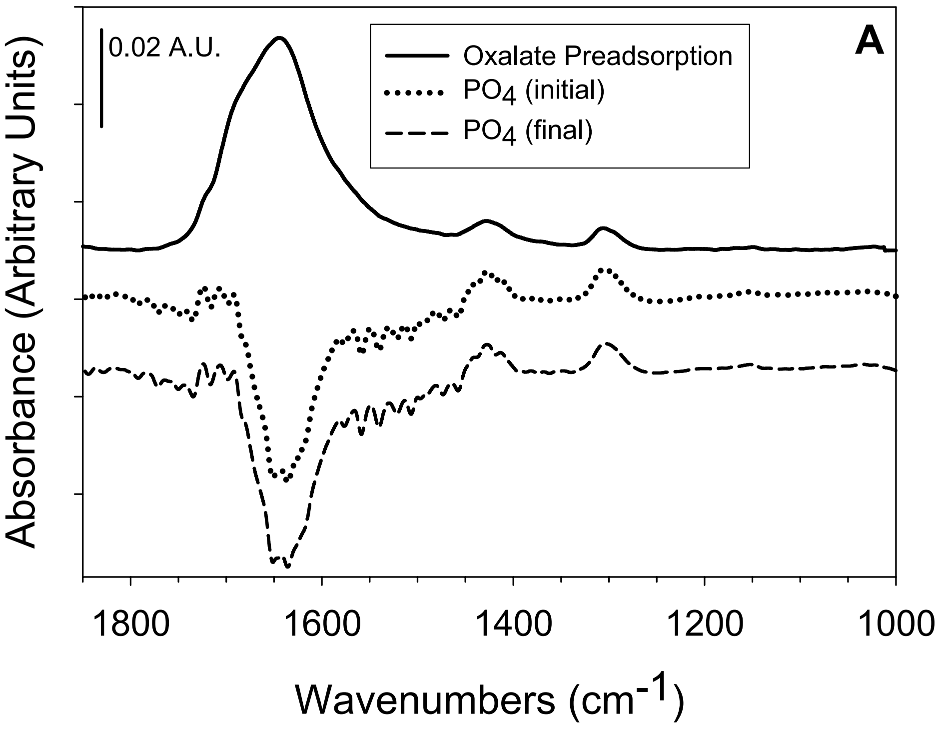


Figure 3.15 ATR-FTIR spectra of phosphate preadsorption study, conducted at pH 5.5 on Ge ATR flow cell (128 average scans at 8 cm^{-1} resolution). Oxalate and Phosphate concentrations in flowing solutions were 50 µM. Anion solutions were prepared in 1 mM NaCl.


0.02 A.U.
Oxalate Preadsorption
PO4 (initial)
PO4 (final)
A
Absorbance (Arbitrary Units)
1800
1600
1400
1200
1000
Wavenumbers (cm-1)

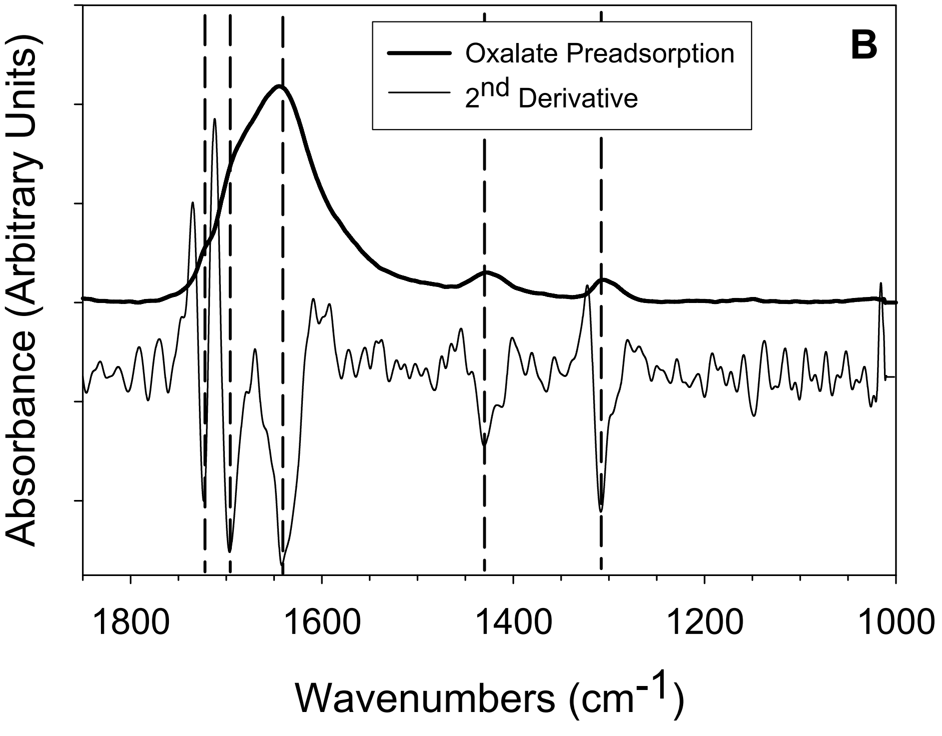

Oxalate Preadsorption
2nd Derivative
B
Absorbance (Arbitrary Units)
1800
1600
1400
1200
1000
Wavenumbers (cm-1)

Figure 3.16 **A) ATR-FTIR spectra of oxalate preadsorption study, conducted at pH 5.5 on Ge ATR flow cell (128 average scans at 8 cm^{-1} resolution). Oxalate and Phosphate concentrations in flowing solutions were 50 µM. Anion solutions were prepared in 1 mM NaCl. B) Oxalate preadsorption spectra with second derivative shown. Dashed vertical lines highlight features in second derivative which indicate real features in the experimental spectrum. Positions of these features are at 1720, 1698, 1427, and 1302 cm^{-1}.**

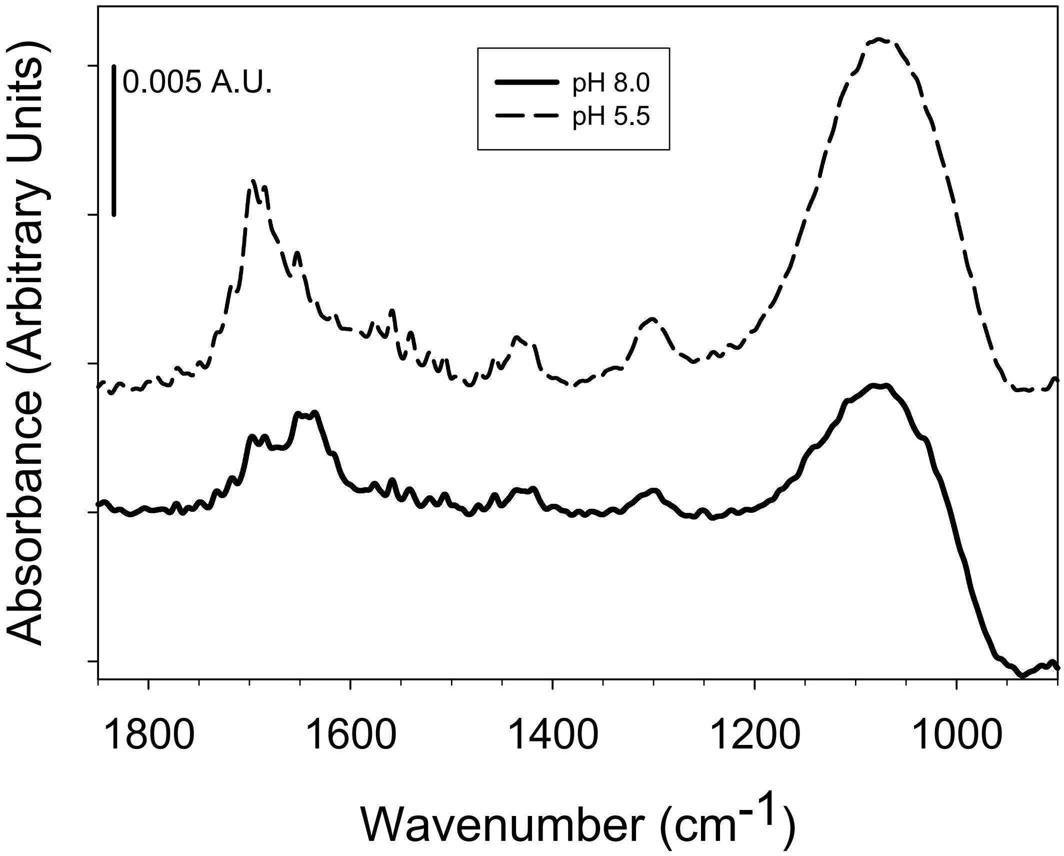


Figure 3.17 **ATR-FTIR spectra of phosphate and oxalate coadsorption study, conducted at pH 5.5 and pH 8.0 on Ge ATR flow cell (128 average scans at 8 cm-1 resolution). Oxalate and Phosphate concentrations in flowing solutions were 50 µM. Anion solutions were prepared in 1 mM NaCl.**

Chapter 4.0

FUTURE RESEARCH NEEDS

4.1 Summary and Future Research Needs

There are several questions which have arisen from the XANES data and LCF analyses. First, it would be extremely beneficial to quantitatively determine the species, or functional groups, which are present in the supernatant after each of the sequential extractions. Because some of this solution remains entrained in the solid when the samples are run as wet pastes, knowing the composition of this liquid could also improve data interpretation.

In addition, finding a means of collecting better spectra for the PL samples after the HCl extraction would make it possible to better define a relationship between this final step and the previous ones. Since the post-HCl samples have the lowest P concentrations, this may involve calibrating or normalizing the spectra so that some quantitative interpretations are possible. The references that we used in this study covered the classes of organic P compounds that are accepted as the dominant forms in soils and animal manures; however, using reference materials that are recalcitrant, organic P phases could help in the linear combination fits.

Analyzing the wet pastes, as opposed to freeze drying samples, is another option when developing extraction protocol. The effects of this treatment on the sample composition and XANES data quality are not well understood. Therefore, a study which compares the LCFs of freeze dried samples to those of fresh or moist samples would help to elucidate any changes that occur as a result.

To better understand how the complexity of PL affects P sorption on to aluminum hydroxide, Chapter 3.0 focused on an organic acid dicarboxylic acid (oxalate) as a competitor for sorption sites on amorphous aluminum oxide. Because there is a focus in recent literature to assign geometries or molecular configuration to sorption complexes, additional MO/DFT modeling would be useful in the arguments presented in this study. Understanding the way in which oxalate is bound to the synthetic am-$Al(OH)_3$ will confirm or negate whether ligand promoted dissolution is occurring during the batch experiments. Using microscopic techniques to investigate physical changes which occur to the metal oxide surface with the sorption of phosphate and/or oxalate may also provide information about these processes.

More controlled batch studies, which better simulate the chemical conditions of the PL (possibly higher ionic strengths, higher P concentrations, and the presence of more competing ligands) would help to create the link between this type of fundamental study and the management practice used in poultry production systems. It would also be beneficial to directly identify the Al phase present in PL (via quantitative microscopic techniques) as well as study the sorption in a wider range of pHs to optimizing P sorption by aluminum oxides and take the necessary steps to enhance the results of alum amendments.

Overall, the purpose of this thesis was to use advanced techniques to investigate traditional characterization methods, ensuring that past interpretations are accurate. Another aim was to study an ideal system with the hopes of better understanding a management practice that is impacting the health of aquatic and terrestrial ecosystems affected by nutrient influxes. Any future research which improves traditional methodology and interpretations to improve management practices will help our understanding of how to reduce negative impacts to the environment.

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