

Solid-State Speciation of Natural and Alum-Amended Poultry Litter Using XANES Spectroscopy

D. PEAK*

Department of Soil Science, University of Saskatchewan,
51 Campus Drive, Saskatoon SK S7N 5A8, Canada

J. T. SIMS AND D. L. SPARKS

Department of Plant and Soil Sciences, University of
Delaware, 149 Townsend Hall, Newark, Delaware 19717-1303

While alum amendments have shown to be effective in lowering water-soluble phosphate levels in poultry litter, the mechanism by which this occurs is not fully known. To determine the solid-state speciation of phosphate in litter samples, experiments were conducted with X-ray absorption near edge structure (XANES) spectroscopy. XANES analysis reveals that, in unamended samples, phosphate is present as weakly bound inorganic as well as some organic phosphate, with some dicalcium phosphate-type calcium phosphates also present. When alum is applied in the houses, XANES results suggest that it precipitates out as amorphous $\text{Al}(\text{OH})_3$ and then reacts with phosphate via an adsorption mechanism. No evidence was found of aluminum phosphate precipitation in any samples.

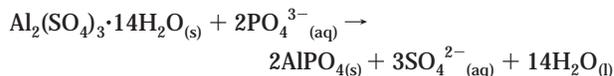
Introduction

Phosphate is one of the most studied of all oxyanions found in the soil environment. It is a plant macronutrient and initial soil chemical research was concerned with managing phosphate to improve agronomic yields. However, in the last three decades, phosphate research has shifted its emphasis from agricultural productivity to that of environmental protection. Repeated overapplication of organic fertilizers (both biosolids and manure) high in phosphate has led to extremely high levels of phosphate in soils of the mid-Atlantic region of the United States (1). Release of phosphate from soils amended with animal manures is quite variable and depends on the type of animal manure and soil properties. For example, poultry, cattle, and swine all have wastes that differ widely in total, inorganic, and organic phosphorus (2). Soil factors also influence phosphate mobility, as calcareous soils can stabilize mineral forms of phosphate in poultry manure, but in acidic soils, poultry manure can increase phosphate solubility by chelating aluminum and iron (3). Sharpley (4) suggested that understanding the factors that determine the dynamics of soil phosphorus is crucial to determining the risk to the environment in areas where excessive phosphorus levels are present. The bioavailability is affected by chemical reactions such as adsorption on aluminum and iron (hydr)oxides, precipitation as amorphous and crystalline aluminum, iron, and calcium phosphates, and interactions of organic matter with phosphate and with the above inorganic minerals.

In mid-Atlantic soils, a large amount of soil phosphate is commonly in an extremely soluble form and makes its way to waterways via erosion and surface flow (5, 6) and even leaching through the soil to the drainage and groundwaters in some cases (7). This is a serious environmental concern for several reasons. First, contamination of drinking water has occurred in some instances. An even more serious threat to the environment comes from eutrophication. Phosphorus is a limiting nutrient in many aquatic systems, and anthropogenic inputs of excessive phosphate can often lead to algal blooms and fish kills when the respiration depletes the available oxygen. Finally, there are emerging human health concerns, as phosphate levels have been linked to *Pfiesteria piscicida* growth (8). *Pfiesteria* is a toxic dinoflagellate that can cause neurophysiological effects such as memory loss in humans.

The major contributor to excessive phosphorus levels in Delaware soils and waters is poultry manure. Approximately 750 000 tons of poultry manure is produced per year, and this presents an incredible challenge to those trying to minimize the environmental effects of overapplication. Several possible solutions have been proposed, including the following: (i) genetic modification of feed grain to make phosphorus in corn more digestible to poultry by reducing levels of phytic acid and alleviating the need for large quantities of supplemental phosphate in feeds (9), (ii) dietary supplements of phytase to increase phosphate uptake from grain and minimize additional inorganic phosphate supplements in feed (10), and (iii) application of water treatment chemicals such as coagulants to immobilize phosphate in the poultry litter (11, 12). As an immediate solution, the use of coagulants has gained favor by researchers and farmers for its low cost, ease of use, and effectiveness at lowering levels of water-soluble P in poultry litter.

Coagulants containing aluminum appear to be the most useful for Delaware soils because ferric-based coagulants will tend to be reduced to iron(II) in anaerobic conditions, which will negatively influence phosphate sorption (13). In particular, there has been research (11, 12) on the use of alum (aluminum sulfate) to reduce water-soluble phosphate levels in poultry litter. Shreve and co-workers (12) determined that alum not only lowers water-soluble P concentrations in poultry litter but also continues to be effective at lowering P levels in runoff once the litter is applied to soils. It has been proposed (11) that the following chemical reaction occurs between alum and phosphate:



whereby alum reacts with aqueous phosphate in the litter to form an aluminum phosphate. However, it is important to consider that many environmental variables are affecting any chemical reactions that occur between phosphate and alum in the poultry litter. First, the animal waste (and therefore PO_4) is being produced continuously, while the alum is applied only at the beginning of each flock of birds. This means that an initial pH of 4–5 occurs due to acidification caused by alum solubilization. The pH then slowly increases to roughly pH 7 over the time the flock is in the house (11). Reactions may also be affected by the fact that mixing only occurs by the movement of birds in the houses, which is sporadic and imperfect. There are also fluctuations in water content and in temperature that could affect the pathway by which reactions proceed. Extrapolation

* Corresponding author. Phone: 306-966-6806. Fax: 306-966-6881. E-mail: derek.peak@usask.ca.

of aluminum/phosphate reaction mechanisms elucidated in controlled laboratory conditions to explain alum/litter reactions under such variable conditions is tenuous at best. Therefore, studies that monitor alum/litter reactions under conditions similar to the field are required to determine the mechanisms that are occurring and also whether reaction products change with residence time.

Understanding how alum reacts with litter to reduce levels of water-soluble P requires the use of molecular-scale spectroscopic techniques, as macroscopic techniques such as extractions cannot conclusively determine reaction mechanisms (14). For these molecular-scale techniques to be of predictive value, the studies should be conducted in conditions as close to the field environment as possible, with normal amounts of water present and at ambient pressures to avoid possible artifacts that can be caused by sample preparation. Researchers have successfully employed *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to determine the adsorption mechanisms of phosphate on goethite (15) and ferrihydrite (16). These studies provided detailed information about complexation mechanisms of phosphate on iron oxides, but conducting similar ATR-FTIR spectroscopic studies to determine phosphate bonding in poultry litter would be impractical due to overlapping infrared bands of different phosphate species as well as interferences from organic spectral features of the poultry litter. The complicated composition of the poultry litter and the high probability that any aluminum phosphates that form are amorphous make bulk X-ray diffraction also extremely difficult in this system. Several other techniques that are commonly used in studies of heavy metals (XPS, DRS) are also of less utility when lighter elements such as Al and P are being investigated. Fortunately, X-ray absorption spectroscopy (XAS) spectroscopy provides a molecular-scale method to probe the local chemical environment of P in the litter samples. Extended X-ray absorption fine structure (EXAFS) spectroscopic studies of the effects of phosphate on iron oxyhydroxide precipitation have shown that P K-edge EXAFS is possible (17), but the studies required considerable sample modification and were not composed of such a complex mixture of phosphate species as the litter samples in this study. Furthermore, iron is a much heavier backscatterer and makes the fitting of P EXAFS data much easier than dealing with aluminum, calcium, and carbon (the likely nearest neighbors to phosphate in poultry litter samples). On the other hand, X-ray absorption near edge structure (XANES) spectroscopy provides a method to probe the speciation of phosphate in poultry litter with minimal sample modification and much simpler data reduction. Unlike many other routine spectroscopic tools, XANES can be employed with heterogeneous samples (e.g., soils and poultry litter) and one can analyze samples *in situ* (normal amounts of water at room temperature and pressure). Useful and unique chemical information can be obtained from XANES such as oxidation state and approximate concentration (if calibrated). One of the most powerful aspects of EXAFS is the ability to utilize software code to fit theoretical scattering paths to experimental spectra and extract parameters such as nearest-neighbor identity, nearest coordination number, and bond distances (18). Unfortunately, XANES spectra are dominated by multiple scattering contributions, and *ab initio* fitting of XANES spectra for lighter elements such as phosphorus is not yet commonplace. Nonetheless, qualitative structural information about the average local chemical environment can also be elucidated via XANES spectroscopy by employing a fingerprinting technique, meaning that unknown samples are compared with a library of reference compounds to find similarities (19).

There are several examples in the literature (20–22) of the utility of XANES spectroscopy to the study of phosphates.

Franke and Hormes (20) studied the effects of many cations (mono-, di-, and tricationic) on P K-edge XANES spectra. They reported that chemical differences beyond the phosphate tetrahedron affected the spectra and that systematic shifts in the white line energy and intensity could be established. Continuum resonances in the P K-edge spectra were observed and attributed both to multiple scattering effects in the first coordination shell and to the interactions with atoms at higher coordination shells. More recently, Hesterberg and co-workers (21) used XANES spectroscopy to study adsorbed and mineral forms of phosphate. They found that it was possible to distinguish adsorbed from precipitated phosphate on iron and aluminum oxides based upon intensity and position of the white line energy as well as the absence or presence of preedge features in the P K-edge XANES region. Hesterberg also included P K-edge XANES spectra for a variety of calcium phosphate minerals and a soil sample from North Carolina. They observed that calcium phosphates (specifically dicalcium phosphate) were present in the soil sample. Okude and co-workers (22) also used P K-edge XANES to study 3d transition metal–phosphate samples and correlated the observed spectra with the electronic structure of the metal phosphates. It was determined that the intensity and position of a preedge peak and the position of the main peak could both be correlated with the number of 3d electrons in the transition metal. This was attributed to hybridization between 3p orbitals of phosphate with 3d and 4s orbitals of the transition metals.

The overall objective of this study is to perform direct speciation of poultry litter using XANES spectroscopy. Of particular interest are what mineral phases form in both unamended and alum-amended poultry litter and how the amount of alum added affects the speciation of phosphate.

Materials and Methods

Sample Collection and Preparation. Poultry litter samples were obtained from J.T.S. These samples were part of an extensive field study involving 200 poultry houses in southern Delaware that have similar history and operating practices. One hundred of these houses received alum application (in varying rates ranging from 0.6 and 1.1 aluminum/phosphate ratios in the final litter), and 100 houses received no alum addition. The chemical analysis of these samples had also been performed in Dr. Sims' laboratory prior to XANES analysis. The chemical analysis of these samples is summarized in Table 1. The EPA 3050 method was utilized for total elemental analysis of the litter samples, and water-soluble elements were extracted via shaking a 100 g/L slurry of poultry litter and deionized water for 1 h, filtering, and analyzing the filtrate with ICP-AES. All values are in milligrams per kilogram. Some generalizations about the effects of alum on poultry litter chemistry can be made from the chemical analysis. Total phosphorus concentrations in all samples are ~20 000 mg/kg of litter (2 wt %) regardless of whether alum is added or not. To understand how pH and alum/P ratio are affecting water-soluble P, the water-soluble P was divided by the total P to determine the percent of phosphate in the litter that is water soluble (labeled % soluble in Table 1). For the unamended samples, there is surprisingly no clear variation in the percentage of P that is water soluble with pH. However, a strong correlation between aluminum/phosphate ratios and water-soluble phosphate is observed. Water-soluble P levels in the litter decrease markedly upon alum addition when compared to the control houses. This occurs with an increase in levels of water-soluble Al. Interestingly, the observed concentrations of Al are above solubility limits, and so some colloidal aluminum (either hydroxide phases or aluminum–organic complexes) are likely passing through the filters used. With the exception of house 182, all of the alum-amended houses fall in the 1–3% water-

TABLE 1. Chemical Analysis of Poultry Litter Samples Used in XANES Spectroscopic Studies^a

house	total P (mg/kg)	water-sol P (mg/kg)	% soluble	Al/P ratio (wt %)	Al/P ratio (molar)	water-sol Al (mg/kg)	final pH
Control Houses							
536	20712	2679	12.9	0.04	0.05	3.8	7.91
504	20160	2225	11.0	0.04	0.05	4.8	7.81
509	19888	2222	11.2	0.04	0.05	4.4	7.74
519	21498	1557	7.2	0.04	0.05	5.4	7.95
507	21174	1910	9.0	0.05	0.05	2	7.42
592	21843	1672	7.7	0.05	0.06	5.4	7.38
541	19590	1308	6.7	0.05	0.06	6.1	8.23
Alum-Amended Houses							
131	21052	492	2.3	0.65	0.75	20.7	7.3
117	21867	732	3.3	0.66	0.76	23.3	7.36
181	20080	973	4.8	0.71	0.82	20.5	7.15
182	19410	1167	6.0	0.84	0.97	19.5	7.03
125	19696	332	1.7	0.90	1.04	18.9	7.23
184	19629	421	2.1	1.00	1.16	21.1	6.62
191	19132	542	2.8	1.13	1.31	18.8	6.89

^a Numbers are all expressed as mg/kg of litter.

TABLE 2. Chemical Analysis of Alum-Amended Poultry Litter Samples Reanalyzed to Compare the Reduction in Water Soluble Phosphate to the Amount of Alum Added^a

house	sol P decrease (mg/kg)	Al added (mg/kg)	Al/P ratio (wt %)	Al/P ratio (molar)
131	1447	13705	9.47	10.94
117	1207	14345	11.88	13.73
181	966	14176	14.68	16.96
182	772	16285	21.09	24.38
125	1607	17707	11.02	12.73
184	1518	19708	12.98	15.00
191	1397	21638	15.49	17.90

^a Numbers are all expressed as mg/kg of litter.

soluble P range, while the control houses range from 7 to 13% water-soluble P. Also bearing discussion is the fact that Al/P ratios, when presented as a molar ratio rather than by weight are all reasonably close to 1.0, which may indicate AlPO₄(s) precipitation in amended samples. However, there is a sizable fraction of the total P that is present as organic phosphate (10–40% depending upon sources and diet) that is not expected to react with aluminum. This makes using macroscopic information such as molar ratios unreliable. If one considers water-soluble phosphate levels from the unamended houses to be typical (1300–2700 mg/kg of litter), then a crude estimate of the phosphate associated with aluminum can be made by subtracting the water-soluble phosphate in the alum amended samples (300–1200 mg/kg of litter) from an average of the control houses (1940 mg/kg of litter on average). If this estimate for the amount of water-soluble phosphate removed from the litter by alum is compared to the aluminum added, then molar ratios of Al/P are much higher (10–20:1) and show a consistent trend. In houses where alum was most effective at lowering water-soluble phosphorus, the Al/P ratio is low. For houses where more water-soluble phosphate remained after alum addition, the Al/P ratio is larger. This is in contrast with the ratios obtained from total Al and P, which showed no consistent trend and reported molar ratios near 1. The results of this analysis are compiled in Table 2.

The difficulty in interpreting the macroscopic data highlights the need for direct speciation of the poultry litter. One other issue that needs to be discussed is the collection of additional chemical information, such as total and water-soluble calcium and sulfate for samples. Unfortunately, these numbers were not obtained for the samples used in this study,

although they would have been useful in interpretation of XANES results. In earlier studies, water-soluble sulfur and calcium were analyzed along with Al and P, and it was observed that in houses without alum that litter contained around 5000 mg/kg S and 275 mg/kg Ca while in houses that received 2.67 tons per house an average of 10 000 mg/kg S and 1400 mg/kg Ca was present.

Reference Preparation and Synthesis. Variscite, monetite, and wavelite reference minerals and XANES spectra were supplied by Dr. Y. A. Arai. Hydroxylapatite, ammonium sulfate, aluminum sulfate, and calcium sulfate were obtained from Fischer Scientific. These minerals were all ground with a mortar and pestle and analyzed as a dry powder. Aqueous references were prepared by dissolving reagent grade phytic acid (calcium salt), sodium phosphate, sodium sulfate, and calcium chloride in 18 MΩ deionized water. Synthetic minerals and adsorption samples were prepared and analyzed as wet pastes. Taranakite was synthesized according to the method of Liu et al. (23), and amorphous aluminum phosphate was synthesized by titrating a solution containing 0.1 M Al(Cl)₃ and 0.1 M NaH₂PO₄ to pH 4.5. For adsorption onto aluminum hydroxides, the reaction conditions were pH 5, 25 g/L sorbent, I = 0.1 M (NaNO₃), and 10 mM PO₄ added. Amorphous aluminum hydroxide was prepared by titrating a 0.1 M Al(Cl)₃ solution to pH 5 and then utilizing repeated centrifugation to wash the amorphous precipitate. Gibbsite was a high-crystallinity, low-surface area (18 m² g⁻¹) mineral obtained from Condea and used without further modification.

X-ray Absorption Near Edge Structure Spectroscopy. All XANES spectroscopic studies were conducted at beam line X19-A of the National Synchrotron Light Source at Brookhaven National Laboratory in Upton, NY. Samples were covered with a thin Mylar film and placed inside a helium-purged sample compartment. Samples of reference salts and crystalline minerals were analyzed as ground powders, and all synthetic minerals and adsorption samples were analyzed as moist pastes. The poultry litter samples chosen for XANES spectroscopy were analyzed “as is”, meaning that they were not air-dried and sieved prior to analysis. These samples contained between 20 and 35% moisture and were of widely heterogeneous composition. Since the samples were analyzed by mounting them on Scotch tape and then covering them with Mylar, some selection for the fine fraction of the litter sample was unavoidable due to the fact that larger particles such as wood chips did not adhere to the tape as well. Studies were conducted to assess the effects of analyzing different particle sizes and different subsamples on the XANES spectra.

A solid-state PIPS detector collected spectra in fluorescence mode. XANES spectra were collected from 10 eV below the P K-edge until 50 eV beyond the edge, which encompasses the near-edge region. Multiple scans of each sample were collected and averaged together to improve the signal-to-noise ratio. Limitations of the beam line prohibited going further below the P K-edge, making background subtraction sometimes a challenge for more dilute samples. For this reason, samples were not diluted in BN_3 , and instead, concentrations of standards occasionally were as high as 4 wt % P. Some self-absorption effects could be observed in the most concentrated samples, but since quantitative XANES analysis was not attempted then this was not a serious concern. Data reduction was done with WinXAS 2.1. The background was removed by fitting a first-order polynomial to the preedge region (2142–2148 eV), and the spectra were all normalized over the region from 2148–2200 eV. The beam line was calibrated using a sodium phosphate standard to an energy of 2185.5 eV for E_0 for all P samples. For S and Ca K-edge XANES studies, samples were collected from 100 eV below the edge to 50 eV above the edge to improve background subtraction.

Results and Discussion

To understand phosphate speciation in natural samples, it is necessary to determine how different chemical environments affect the XANES spectra of phosphate. This is particularly important in our studies since we are using a fingerprinting technique to compare poultry litter samples to references. The two cations that are most likely to interact with phosphate in the poultry litter are calcium and aluminum since their concentrations are much higher than any other ions in the litter. When the litter is in an unamended state, calcium is anticipated to be the dominant cation, while when alum is added to the poultry houses then both aluminum and calcium may potentially react with phosphate.

A portion of the total phosphorus in the poultry litter is present as organic phosphates. The exact amount is not known, but it can be assumed to be relatively constant in both alum-amended and nonamended samples. Figure 1 shows the XANES spectra of phytic acid (inositol phosphate) as an aqueous species (50 wt %) and as a calcium salt. Differences between the aqueous and solid forms of phytic acid may be exaggerated by effects of self-absorption in the spectrum of the salt. However, in both cases, the observed XANES spectra are devoid of features that readily distinguish them from aqueous phosphate. Therefore, quantitatively distinguishing between free inorganic P, very weakly bound phosphate (associated with organic matter), and organic P in the poultry litter samples is very difficult. However, there are some differences that are more qualitative in nature. Careful comparison reveals that organic phosphate spectra possess some broadening of the white line peak (2158.5 eV) as well as an increase in the postedge spectral height compared to aqueous phosphate. Neither of these differences is suitable for separating a mixture of organic and aqueous phosphates into individual components. However, it may be reasonable to assume that the primary source of organic phosphate in the litter is the animal waste itself and that formation of organic phosphate in the litter is relatively minor. This implies that the fraction of organic P is relatively constant in both control and amended samples while the fraction of weakly bound and aqueous phosphate is variable so that any changes in the importance of spectral features that can be attributed to either compound are due to differences in the amount of free or weakly bound phosphate in the litter.

For calcium phosphate references, samples were analyzed that encompass sorption onto calcium carbonates and also precipitation of both amorphous and crystalline calcium phosphates. The XANES spectra of these references can be

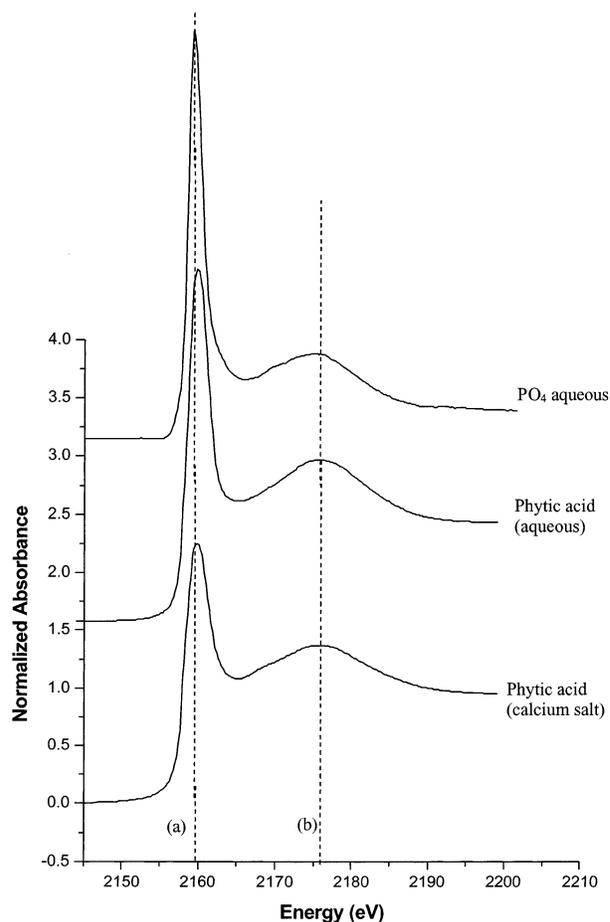


FIGURE 1. P K-edge XANES spectra of different organic phosphate reference materials. Phytic acid (inositol phosphate) was chosen as it is a major form of organic P in poultry feed, and aqueous phosphate was included for comparison. The dashed lines indicate different spectral features of importance and are labeled as follows: (a) absorption edge (white line energy) for P(V); (b) oxygen oscillation.

seen in Figure 2. Whether sorbed onto amorphous calcium carbonate or precipitated as calcium phosphate minerals, phosphate bound to calcium displays several features in the XANES region. The first and most important feature is the presence of a shoulder past the edge at 2160–2165 eV.

This feature is seen in all calcium phosphate references regardless of structure or crystallinity. As expected, peaks are sharper in crystalline hydroxylapatite than in the amorphous precipitate. There is a second peak that occurs at ~2170 eV in all references with a structure similar to hydroxylapatite ($\text{Ca}_2(\text{OH})\text{PO}_4$). This feature is present in the phosphate on CaCO_3 sample as well, suggesting that precipitation is likely occurring along with adsorption in that system. The position of these two spectral features is surprisingly similar to the spectra of $\text{Ca}_3(\text{PO}_4)_2$ reported by Franke and Hormes (20) and also very similar to the various calcium phosphate spectra reported by Hesterberg and co-workers (21). Finally, some calcium phosphate minerals have a CaHPO_4 structure, such as brushite (dicalcium phosphate dehydrate) and monetite (dicalcium phosphate). Dicalcium phosphates lack the peak at 2170 eV seen in apatite-type minerals. Interestingly, the spectrum of dicalcium phosphate in Figure 2 appears substantially different from the spectra of monetite and brushite reported elsewhere (21). In both cases, the shoulder past the white line characteristic of hydroxylapatite is missing, but our spectra contained a peak at 2164 eV that was not present in the spectra of ref 21. It is possible that our natural

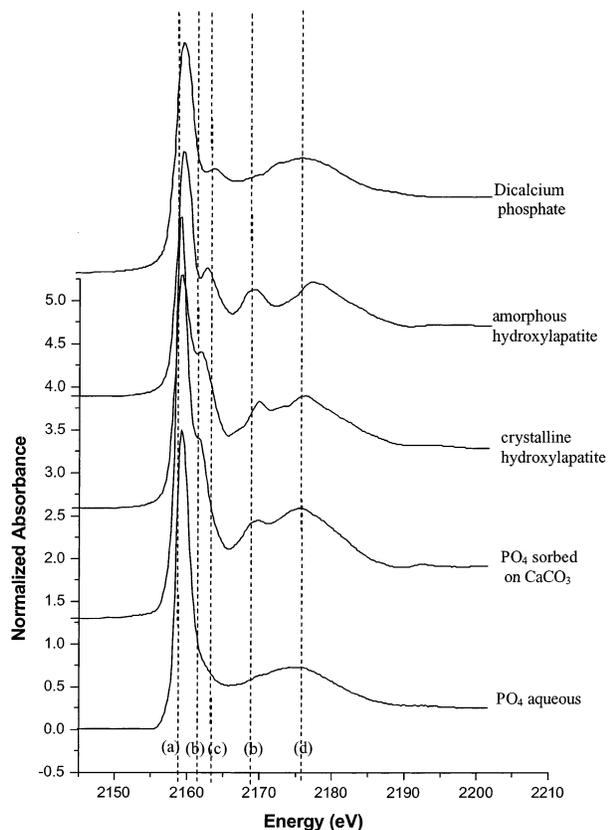


FIGURE 2. P K-edge XANES spectra of different calcium phosphate reference materials. Crystalline and amorphous mineral phases and sorption samples are included, with aqueous phosphate for comparison. The dashed lines indicate different spectral features of importance and are labeled as follows: (a) absorption edge (white line energy) for P(V); (b) unique spectral features of hydroxylapatite type calcium phosphates; (c) unique spectral feature of dicalcium phosphate type phases; (d) oxygen oscillation.

dicalcium phosphate (a natural sample of monetite) has a somewhat different structure from the dicalcium phosphates obtained from Aldrich or Sigma.

For aluminum phosphate references, samples were chosen that encompassed a range of aluminum–phosphate bonding environments: adsorption onto amorphous and crystalline aluminum oxides and precipitation of amorphous and crystalline aluminum phosphates.

The XANES spectra of these reference samples can be seen in Figure 3. The differences between spectra of phosphate adsorbed on aluminum oxides and $\text{PO}_4(\text{aq})$ are fairly subtle. Careful inspection of the spectra reveals a loss of the slight shoulder seen in $\text{PO}_4(\text{aq})$ past the edge jump (2160–2165 eV) and a shift in the position and shape of the oxygen oscillation at 2175 eV when phosphate is adsorbed on aluminum oxides. This means that it is possible to distinguish adsorbed phosphate from $\text{PO}_4(\text{aq})$. As the spectra of aluminum phosphate precipitates are examined, one notices an additional peak at 2165–2170 eV. This feature is broad in amorphous AlPO_4 and taranakite (AlNH_4PO_4) and becomes sharper and better defined in crystalline aluminum phosphates (wavelite and variscite). This spectral feature can also be observed in ref 20, although the crystallinity of the AlPO_4 that was examined was not discussed by the authors. Hesterberg and co-workers (21) included spectra of a variety of aluminum phosphates, but their spectra are only presented from -5 to $+10$ eV relative to the P(V) K-edge and it is very difficult to determine whether this feature is present in their data. From our spectra and ref 20, it seems clear that the presence of aluminum phosphates in a sample is ac-

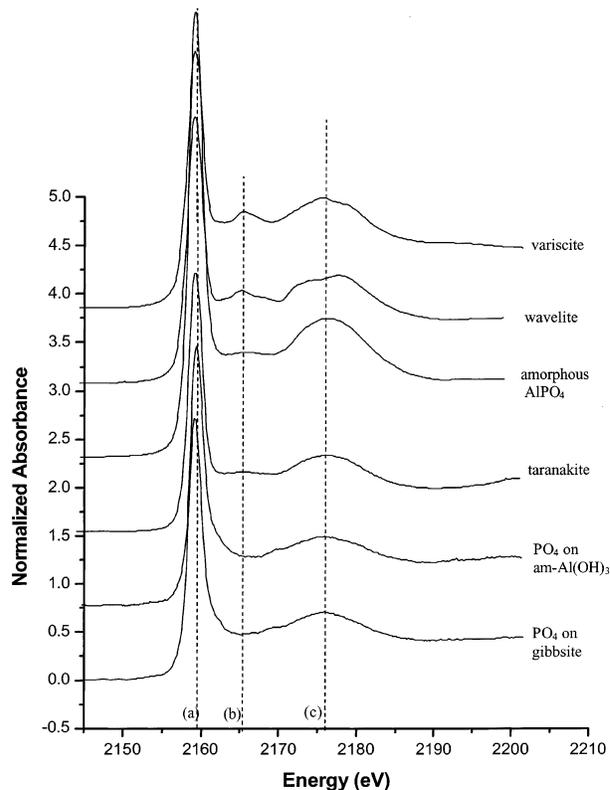


FIGURE 3. P K-edge XANES spectra of different aluminum–phosphate reference materials such as minerals and sorption samples. Amorphous and crystalline aluminum phosphates are shown along with phosphate adsorbed on both amorphous and crystalline aluminum oxides. Aqueous phosphate is also included for comparison. The dashed lines indicate different spectral features of importance, and are labeled as follows: (a) absorption edge (white line energy) for P(V); (b) unique spectral feature of aluminum phosphates; (c) oxygen oscillation.

companied by a small peak in the 2165–2170-eV region. This distinctive peak is therefore useful in determining whether aluminum phosphates are forming in amended litter samples.

Fortunately, the distinctive peaks for the aluminum and calcium phosphate minerals are located at different energies and so it is possible to distinguish calcium and aluminum phosphates in litter samples. It is also possible to distinguish between phosphate adsorbed on aluminum oxides and precipitated aluminum phosphate due to subtle differences in the XANES region.

XANES spectra of poultry litter samples from southern Delaware poultry houses are shown in Figures 4 and 5. Samples 504–592 are from houses where alum was not used (Figure 4), while samples 117–191 were obtained from houses where alum was applied at different aluminum/phosphorus ratios (Figure 5). All of the litter samples in Figures 4 and 5 were analyzed as is without drying to remove water present and without grinding to homogenize the sample. Unless otherwise noted, all samples analyzed were of a fine particle size ($20\ \mu\text{m}$ and less) as the majority of phosphate was in this fraction.

The spectra of several unamended samples are seen in Figure 4. The spectra at the top of the graph are references that could potentially match the samples. It is clear that all of the litter spectra are similar and that they all lack most of the features of phosphate found in aluminum phosphates (Figure 2) and apatite-type calcium phosphate minerals (Figure 1). The spectra most closely resemble aqueous phosphate and phytic acid, but the shoulder at 2160–2165 eV is much more pronounced than that of either reference

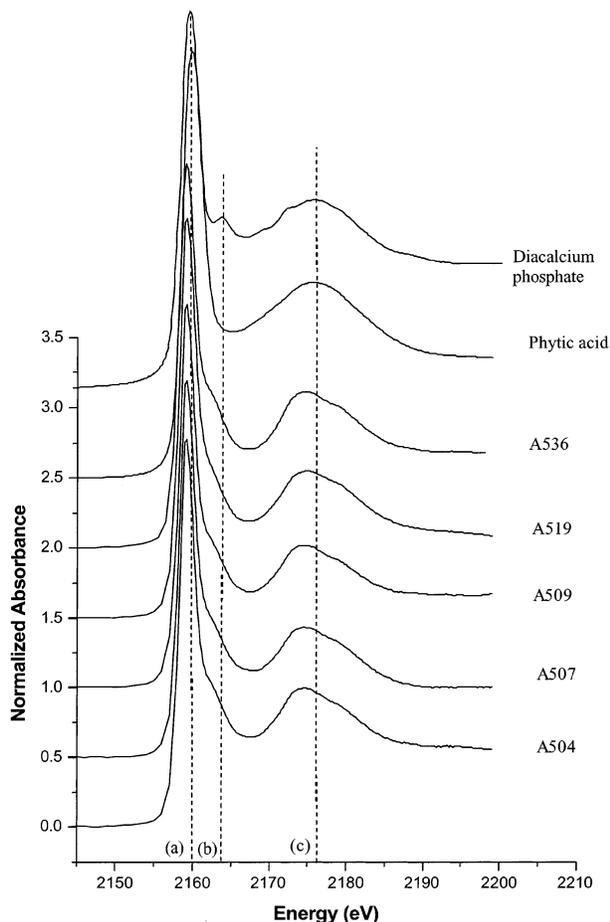


FIGURE 4. P K-edge XANES spectra of poultry litter samples from the control houses (no alum added). The spectra of aqueous phosphate, dicalcium phosphate, and amorphous hydroxyapatite are shown for reference. The litter samples are labeled according to the house from which they were taken, as in Table 1. The dashed lines indicate different spectral features of importance and are labeled as follows: (a) absorption edge (white line energy) for P(V); (b) unique spectral feature of dicalcium phosphate and also present in litter samples; (c) oxygen oscillation.

compound. The position of this shoulder is consistent with the presence of a small amount of dicalcium phosphate-type minerals in the samples. All of the samples appear essentially identical, suggesting that phosphate speciation is fairly consistent among all of the houses in the absence of alum. Since the poultry litter has a final pH of ~ 8 , it is not surprising that calcium phosphates are observed with XANES. However, the absence of more thermodynamically stable calcium phosphates such as hydroxylapatite in the unamended litter deserves further discussion. Brushite (dicalcium phosphate) and monetite (dicalcium phosphate dihydrate) have a similar structure and are common calcium phosphates in soils under supersaturated conditions (24). However, in the absence of organic matter, these more soluble dicalcium phosphate phases rapidly convert to hydroxylapatite, the stable end point of the calcium phosphate system in aqueous environments at neutral or slightly basic pH values (25, 26). In the presence of organic matter, however, the crystallization and transformations of calcium phosphates are far more complex. Inskeep and Silvertooth (27) and Grossl and Inskeep (24, 28) studied the effects that organic acids have on the precipitation rates of dicalcium phosphate dihydrate (brushite), octacalcium phosphate, and hydroxyapatite. Their studies employed a suite of organic acids with different sizes and functional groups, and the precipitation

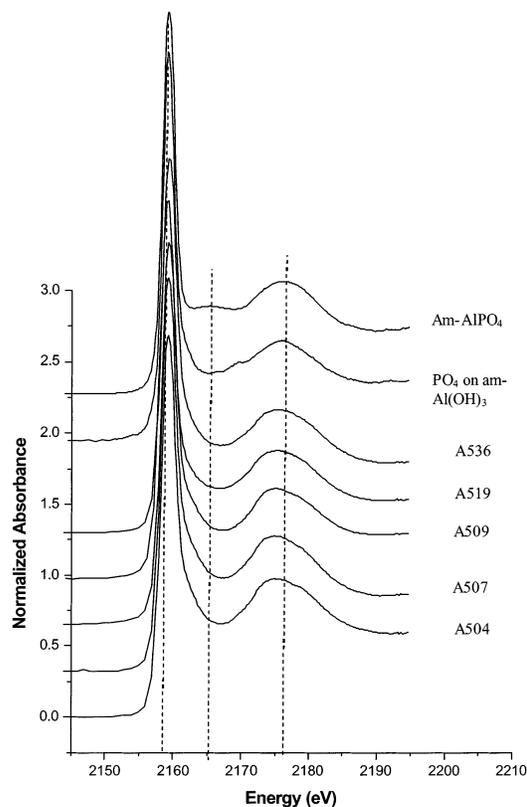


FIGURE 5. P K-edge XANES spectra of poultry litter samples from houses with alum added. The spectra of aqueous phosphate, phosphate adsorbed on amorphous aluminum hydroxide, and amorphous aluminum phosphate are shown for reference. The litter samples are labeled according to the house from which they were taken, as in Table 1. The dashed lines indicate different spectral features of importance, and are labeled as follows: (a) absorption edge (white line energy) for P(V); (b) unique spectral feature of aluminum phosphates (not observed in litter samples); (c) oxygen oscillation.

reaction was followed by adding seed crystals of the appropriate mineral to a slightly supersaturated solution. The principal findings of these studies were that large molecular weight organic acids decrease the rate of precipitation for all three calcium phosphates by sorbing onto the minerals and coating the crystal growth sites. However, the precipitation of dicalcium phosphate continues via overgrowth of dicalcium phosphate on the organic-coated seed crystal whereas octacalcium phosphate and apatite do not (24). Our XANES spectroscopic studies are consistent with the work of Grossl and Inskeep (24, 27, 28), since in poultry litter there is a huge quantity of organic matter that could coat any small calcium phosphate particles that form and inhibit crystal growth. In this chemical environment, brushite- or monetite-type calcium phosphates that are intimately associated with organic matter seem more favorable to form than other calcium phosphates that may be more thermodynamically stable in the absence of organic matter.

In the alum-amended samples (Figure 5) there are changes that can be observed as the Al/P ratio (the amount of alum added to the litter) is increased in the samples. At an Al/P ratio of 0.6, the spectra closely resemble those of unamended samples, suggesting that organic phosphate, weakly bound phosphate, and dicalcium phosphates are present. As aluminum content increases, however, the shoulder at 2160–2165 eV completely disappears, and the shape of the edge narrows while the oxygen oscillation at 2175 eV shifts slightly and becomes more rounded and symmetrical. These changes are consistent with the phosphate adsorbed on aluminum

oxide references. The two samples with highest Al/P ratios appear to contain only phosphate adsorbed onto aluminum oxides and possibly some organic phosphate (there are no clearly distinguishing features to separate these references other than a broadening of the white line peak in organic P). No aluminum phosphate precipitate phases were observed in any of the samples.

Similarly to the unamended samples, the speciation of phosphate in the alum-amended litter at first appears to be quite different from what one would predict from thermodynamic stability constants for aluminum phosphates. There are several reasons that aluminum phosphates might not occur in alum-amended litter, however. First, the litter's pH initially drops to pH ~5 upon alum addition and then gradually increases to pH ~7 when the flock is removed from the house. As the pH gradually increases above 5, aluminum phosphate stability decreases greatly. It is possible that aluminum phosphate precipitation occurs that is followed by dissolution as time (and pH) increases. Alternatively, the reactivity of aluminum and phosphate could be kinetically controlled rather than dictated by thermodynamics. If the precipitation rates of aluminum hydroxides are much faster than aluminum phosphate precipitation rates, then the sorption of phosphate on aluminum hydroxides could be expected to dominate the system. Furthermore, the presence of large quantities of organic matter may affect the precipitation rate of aluminum phosphates more than it does the precipitation of aluminum hydroxides.

One other issue regarding the alum-amended samples bears noting. The XANES data indicate that some dicalcium phosphate is present in the 0.75–0.85 molar Al/P ratio samples but not in the higher Al/P ratio samples. Another interesting observation is that the water-soluble phosphate amounts are not necessarily higher in these samples than in samples with higher total Al/P ratios where only phosphate sorbed on aluminum hydroxides is observed with XANES. This may possibly be explained by considering how phosphate enters the litter (from chicken feces) and hypothesizing about how it may interact chemically with alum in the litter. It is plausible that not all of the initial CaHPO_4 fed to the chickens as a dietary supplement dissolves, and so the chicken feces contains CaHPO_4 , Ca^{2+} , and HPO_4^{2-} . The CaHPO_4 is not completely water soluble at the neutral to slightly basic pH of the poultry litter. Alum addition results in precipitating out $\text{Al}(\text{OH})_3$, which adsorbs aqueous and weakly bound HPO_4^{2-} added to the litter by the feces. Aluminum hydroxide precipitation would be expected if the water-soluble P (~2000 mg/kg of litter) is the only pool readily available for reaction with Al. Alum addition will lower the litter pH, which decreases CaHPO_4 stability. When this occurs, further phosphate adsorption on aluminum hydroxides is expected. However, this relationship is complex, and so choosing the "optimum" Al/P ratio is not clear-cut. External factors such as feed formulation and chicken breed will affect the $\text{Ca}^{2+}/\text{HPO}_4^{2-}/\text{CaHPO}_4$ distribution in the feces, and water content of the litter may substantially affect alum performance. This hypothesis is consistent with the observation that CaHPO_4 spectral features can weakly be observed in the alum-amended houses with Al/P (total) ratios of ~0.6. Lower total additions of alum will not decrease the pH as much and so they may not completely dissolve the CaHPO_4 present in the feces. It also is a reasonable explanation for why some samples have higher Al/P ratios but not lower water-soluble P. No more CaHPO_4 is observed in the XANES for the high Al/P ratio samples and so presumably the conversion from calcium phosphates is complete. In some cases, however, the aluminum hydroxide/phosphate sorption complex may not be as effective a sink for the phosphate as was the original CaHPO_4 solid phase.

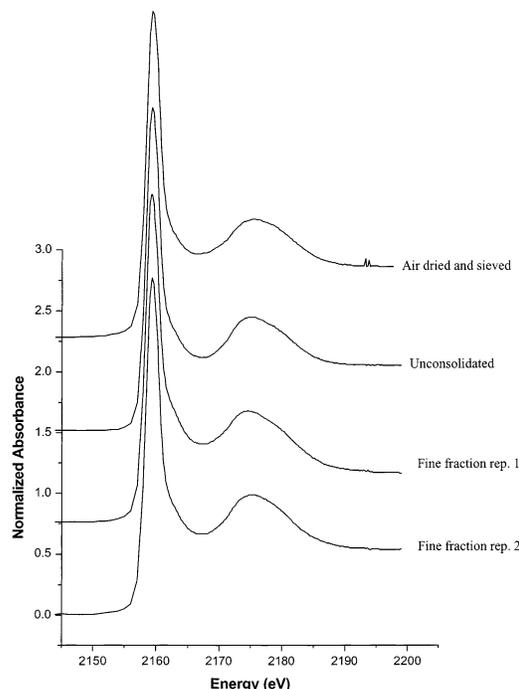


FIGURE 6. P K-edge XANES spectra of a sample from house 182 prepared in several different ways. The two fine fraction spectra result from spreading the as is sample on Scotch tape prior to sample collection to select for finer particles in the litter. The unconsolidated spectrum is the result of packing the entire litter sample into a holder. The dried and ground spectrum is the result of more intensive sample modification. All samples appear similar in local bonding environment of P.

Since XANES is an average local environment, and poultry litter is highly heterogeneous, experiments were also conducted to test the variability of the XANES spectra in the samples. Figure 6 shows a sample from house 182 prepared as a dried, ground, and sieved powder, as an unconsolidated as is sample packed into a sample holder, and as two separate samples prepared by selecting for the fine fraction by sieving the as is samples. The spectrum of the dried sample seems different and contains more free inorganic phosphate than the as is samples. The unconsolidated sample appears to have slightly more monetite-like calcium phosphate than the samples selected from the fine fraction. There is no difference in sample replicates taken from the fine fraction, and even the differences discussed above are very slight. In general, XANES spectroscopy seems able to capture spectra that are representative of the samples as a whole.

While the results from P XANES spectroscopy are consistent with dicalcium phosphate formation in the unamended samples and with phosphate adsorbed on aluminum hydroxides in the alum-amended samples, the differences in spectra are all relatively subtle. This makes conclusive phosphate speciation difficult. Furthermore, it is possible that other reference compounds not analyzed may have spectral features similar to the poultry litter samples. To verify that interpretation of P XANES spectra was correct and to obtain additional chemical information about litter samples, both Ca and S K-edge XANES studies were also conducted. Since dicalcium phosphate was observed at the P edge with XANES, one would expect that features consistent with dicalcium phosphate would also be present at the Ca edge. Results from studies at the Ca K-edge are presented in Figure 7. In the control houses, the observed Ca XANES spectrum is consistent with aqueous/weakly bound Ca^{2+} and some dicalcium phosphate. The contributions of dicalcium phosphate to the control sample can be seen by the peak at 4060

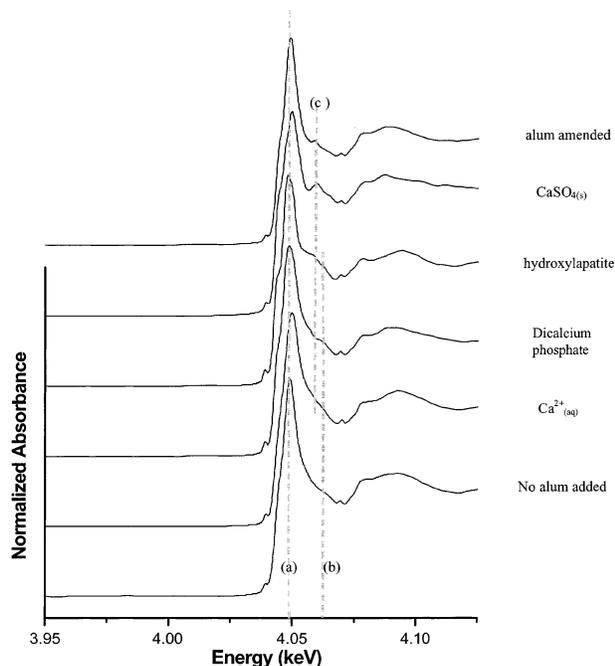


FIGURE 7. Ca K-edge XANES spectra of poultry litter samples with and without alum amendments compared to many calcium standards. It can clearly be seen that upon alum amendment the XANES spectra of the litter samples shifts from that of a mixture of weakly bound calcium and dicalcium phosphate to that of calcium sulfate. The dashed lines indicate different spectral features of importance and are labeled as follows: (a) absorption edge (white line energy) for Ca(II); (b) unique spectral feature of dicalcium phosphate; (c) unique spectral feature of calcium sulfate.

eV. This peak does not overlap with that of hydroxylapatite, and furthermore, the shape and position of the white line peak is not consistent with HAP. In the alum-amended sample, there are notable differences from the unamended spectra. The features attributed to dicalcium phosphate disappear, and new peaks appear in positions consistent with calcium sulfate. These results confirm the P XANES interpretation that in unamended soils dicalcium phosphate is present while in alum-amended soils it is not observed. The Ca XANES results also suggest that amendment of litter with alum results in an increase in the amount of CaSO_4 in the samples. This is reasonable, since alum addition would result in huge inputs of sulfate to the system.

To further investigate sulfate speciation in the litter, S K-edge XANES was also utilized. Figure 8 shows the S K-edge XANES spectra of an unamended and an alum-amended litter sample compared to aqueous sulfate and gypsum (CaSO_4). In both litter samples, S occurs primarily with an oxidation state of +6, with some reduced sulfur also present. The lower oxidation state sulfur is likely due to amino acids with cysteine linkages and methionine present in the organic matter of the litter. In the alum-amended sample, the amount of S(VI) increases substantially (which is expected with the huge input of sulfate from the alum). For both amended and control houses, the XANES spectra suggest that the dominant S(VI) species is CaSO_4 . A second sulfate species is present, but the features are not particularly well resolved from those of CaSO_4 . Formation of ammonium sulfate solid phases has been proposed as an explanation for this decrease in volatile ammonia, and the XANES spectra could possibly contain some ammonium sulfate.

When the P, Ca, and S XANES results are considered together, the overall speciation of mineral phases in poultry litter becomes much clearer. The overall reactions consistent with the XANES spectroscopy are summarized in Figure 9.

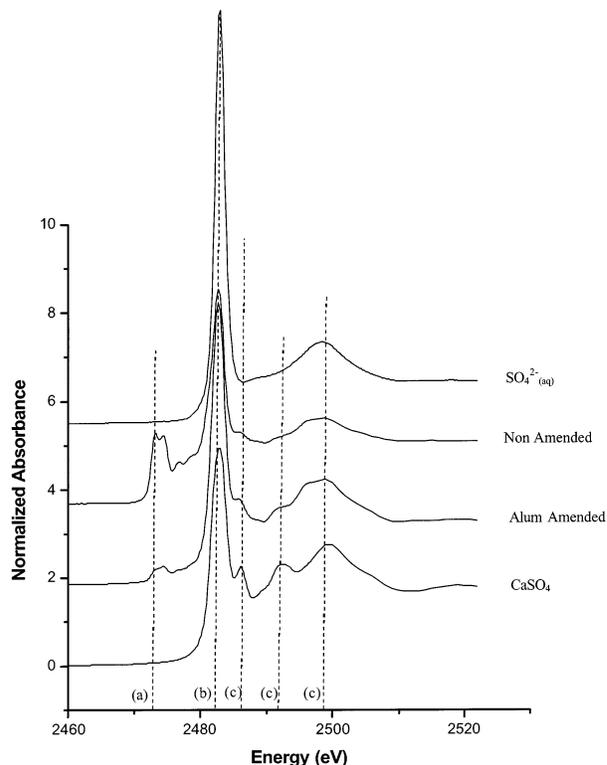
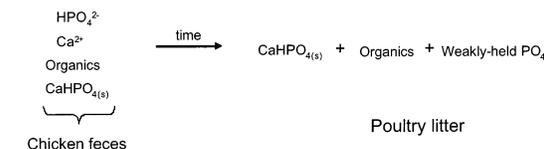


FIGURE 8. S K-edge XANES spectra of poultry litter samples with and without alum amendments compared to various sulfate references. The dashed lines indicate different spectral features of importance and are labeled as follows: (a) absorption edge (white line energy) for reduced S; (b) absorption edge (white line energy) for S(VI); (c) unique spectral features of calcium sulfate seen in samples and references.

a) Unamended Poultry Houses



b) Alum-amended Poultry Houses

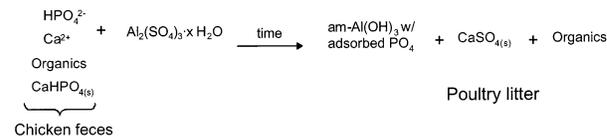


FIGURE 9. Summary of the reactions proposed to explain the P, Ca, and S XANES results. (a) contains reactions important in the control houses, while (b) shows how addition of alum affects speciation.

Initially, chickens are fed a diet of grain supplemented with calcium phosphate because the digestive tract of chickens is unable to extract sufficient phosphorus from phytic acid. Once the dietary calcium phosphate is inside the chicken's gastrointestinal tract, pH becomes acidic and some of the calcium phosphate dissociates to Ca^{2+} and aqueous phosphate. These ions may associate with organic materials or remain dissolved in solution. This organic matrix high in calcium and both inorganic and organic phosphate (primarily phytic acid) is then excreted as waste. The waste ages over time in the house as the chickens are raised, with continuous addition of fresh waste and mixing from movement of the birds. In the control houses, calcium and inorganic phosphate react to form dicalcium phosphates. Transformation to more

stable hydroxylapatite phases is retarded by the large amount of high molecular weight organic material in the litter. Aluminum sulfate (alum) addition produces an amorphous aluminum hydroxide and aqueous sulfate. Sulfate reacts with calcium to form calcium sulfate, and the inorganic phosphate then reacts with aluminum hydroxides via adsorption. No evidence of aluminum phosphate solid phases was seen with XANES spectroscopy.

The overall results of this XANES spectroscopic study demonstrate that phosphate chemistry in unamended poultry litter is dominated by calcium phosphate (most likely dicalcium phosphate) chemistry and by adsorption onto aluminum hydroxides in alum-amended litters. This means that the environmental fate of phosphate in alum-amended litter is determined primarily by the stability of phosphate adsorption complexes on aluminum hydroxides. Accordingly, there are many unanswered questions about phosphate chemistry in soils amended with poultry litter. Further research is needed to understand the long-term dynamics of phosphate desorption from alum-amended litter after it has been applied to soils. It is not known whether adsorbed phosphate will slowly convert to aluminum phosphate solid phases after incorporation in soils or whether the slow crystallization of amorphous aluminum hydroxides will result in a lowered surface area and phosphate release. Environmental effects such as mineralization of the litter and wetting/drying cycles of the sun may also affect phosphate stability but are not understood at this time. More controlled laboratory experiments where reaction variables such as pH, water content, Al/P ratio, and time are controlled should be conducted to provide insight into how management practices such as multiple small applications of alum and more rigorous pH controls may affect phosphate solubility. Fundamental studies on the comparative kinetics of aluminum phosphate and aluminum hydroxide precipitation in the presence of organic matter are also needed.

Acknowledgments

D.P. thanks the National Science Foundation for a graduate fellowship as well as research funding. The authors appreciate the help of Dr. W. Caliebe and Dr. L. Miller of the National Synchrotron Light Source at Brookhaven National Laboratory for beam line assistance and Dr. Y. A. Arai (U.S.G.S, Menlo Park) for providing several reference phosphate minerals and valuable conversations about phosphate chemistry in the soil environment. The authors also appreciate the insightful comments from S. Hunger (University of Delaware) regarding Al/PO₄/Ca speciation in similar systems with solid-state NMR.

Literature Cited

- (1) Sims, J. T. In *Uses of by-products and wastes in agriculture*; Rechl, J., Ed.; American Chemical Society: Washington DC, 1997; p 72.
- (2) Barnett, G. M. *Bioresource Technol.* **1994**, *49* (2), 139–147.
- (3) Toor, G. S.; Bahl, G. S. *Bioresource Technol.* **1999**, *69* (2), 117–121.
- (4) Sharpley, A. N. *Ecol. Eng.* **1995**, *5* (2–3), 261–279.
- (5) Sims, J. T.; Wolf D. C. *Adv. Agron.* **1994**, *52*, 1.
- (6) Sharpley, A. N.; Chapra, S. C.; Wedopohl, R.; Sims, J. T.; Daniel, T. C.; Reddy, K. R. *J. Environ. Qual.* **1994**, *23*, 437.
- (7) Sims, J. T.; Simard, R. R.; Joern, B. C. *J. Environ. Qual.* **1998**, *27* (2), 277.
- (8) Faith, S. A.; Miller, C. A. *Vet. Hum. Toxicol.* **2000**, *42* (1), 26–29.
- (9) Ertl, D. S.; Young, K. A.; Raboy, V. *J. Environ. Qual.* **1998**, *27* (2), 299.
- (10) Huff, W. E.; Moore, P. A.; Waldroup, P. W.; Waldroup, A. L.; Balog, J. M.; Huff, G. R.; Rath, N. C.; Daniel, T. C.; Raboy, V. *Poultry Sci.* **1998**, *77* (12), 1899.
- (11) Moore, P. A., Jr.; Miller, D. M. *J. Environ. Qual.* **1994**, *23*, 325.
- (12) Shreve, B. R.; Moore, P. A.; Daniel, T. C.; Edwards, D. R.; Miller, D. M. *J. Environ. Qual.* **1995**, *24*, 106.
- (13) Vadas, P. A.; Sims, J. T. *J. Environ. Qual.* **1999**, *28*, 1870.
- (14) Sparks, D. L. *Environmental Soil Chemistry*. Academic Press: San Diego, CA, 1995.
- (15) Tejedor-Tejedor, M. L.; Anderson, M. A. *Langmuir* **1990**, *6*, 602.
- (16) Arai, Y. A.; Sparks, D. L. *J. Colloid Interface Sci.* **2001**, *241*, 317.
- (17) Rose, J.; Flank, A. M.; Mason, A.; Bottero, J. Y.; Elmerich, P. *Langmuir* **1997**, *13*, 1827.
- (18) The FEF Project. Department of Physics, University of Washington, Seattle, WA, 1992–1999.
- (19) Fendorf, S. E.; Sparks, D. L. In *Methods of Soil Analysis: Part 3; Chemical Methods*; Sparks, D. L., Page, A. L., Helmke, P. A., Loeppert, R. H., Soltanpour, P. N., Tabatabai, M. A., Johnson, C. T., Sumner M. E., Eds.; Soil Science Society of America: Madison WI, 1996.
- (20) Franke, R.; Hormes, J. *Physica B* **1995**, *216* (1–2), 85–95.
- (21) Hesterberg, D.; Zhou, W.; Hutchison, K. J.; Beauchemin, S.; Sayers, D. E. *J. Synchrotron Radiat.* **1999**, *6*, 636–638.
- (22) Okude, N.; Nagoshi, M.; Noro, H.; Baba, Y.; Yamamoto, H.; Sasaki, T. A. *J. Electron Spectrosc.* **1999**, *101–103*, 607–610.
- (23) Liu, C.; Huang, P. M.; Zhou, J. M. *Soil Sci. Soc. Am. J.* **2002**, *66*, 109–116.
- (24) Grossl, P. R.; Inskeep, W. P. *Soil Sci. Soc. Am. J.* **1991**, *55*, 670.
- (25) Lindsey, W. L. *Chemical Equilibria in Soils*; John Wiley and Sons: New York, 1979.
- (26) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*; John Wiley and Sons: New York, 1996.
- (27) Inskeep, W. P.; Silvertooth, J. C. *Soil Sci. Soc. Am. J.* **1988**, *52*, 941.
- (28) Grossl, P. R.; Inskeep, W. P. *Geochim. Cosmochim. Acta* **1992**, *56*, 1955.

Received for review March 20, 2002. Revised manuscript received August 1, 2002. Accepted August 8, 2002.

ES025660D