Abstract No. peak599
Direct Speciation of Phosphate in Poultry Litter using XANES Spectroscopy
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Beamline(s) X19A

Introduction
Repeated over application of fertilizers high in phosphate (for example animal wastes and biosolids) has led to extremely high levels of phosphate in soils of the Mid-Atlantic region of the United States. One of the major contributors to excessive phosphorus levels in Delaware soils and waters is poultry manure. As an immediate solution, the use of aluminum-based wastewater treatment 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. However, verification of the mechanism that leads to a reduction in soluble P upon alum addition is unknown.

Materials and Methods
Poultry litter samples were obtained that had been air-dried and homogenized. All XANES spectroscopic studies were conducted at beamline X19-A of the National Synchrotron Light Source at Brookhaven National Laboratory in Upton NY. Samples (either ground powders or wet pastes) were covered with a thin mylar film and placed inside a helium-purged sample compartment. A solid state PIPS detector collected spectra in fluorescence mode. Reference spectra were collected of samples with a known structure and compared to the poultry litter samples. 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.

Results and Discussion
Phosphate speciation in unamended poultry litter is best described by a mixture of organic phosphate, aqueous phosphate and monetite-type calcium phosphate. When alum is added to the poultry litter, the dominant species becomes phosphate adsorbed onto aluminum oxides. This is contrary to fact that aluminum phosphate formation is predicted from stability constants. The presence of large amounts of organic acids and many other competing ions may influence the end point of aluminum phosphate reactions, or it is also possible that the rates of aluminum phosphate precipitation are simply much slower than those of aluminum hydroxide and so this apparently is a kinetically-driven system. Although phosphate adsorbed on aluminum oxides is more labile than aluminum phosphate precipitate phases, it is still preferable to the application of aqueous and calcium phosphates to soils. In southern Delaware, soil pH typically ranges from 4 to 5, and so phosphate adsorbed on aluminum oxides in poultry litter should remain adsorbed when incorporated into soil. On the other hand, calcium phosphates will be much more soluble at the lower pH of the soils. However, it is possible that the adsorbed phosphate will become a large source of phosphate in the soil solution if soluble levels of phosphate are decreased. Further research is needed to study the long term dynamics of phosphate desorption from alum-amended litter applied to soils. Another important research question is whether adsorbed phosphate will slowly convert to aluminum phosphate solid phases after incorporation in soils, or if the slow crystallization of amorphous aluminum hydroxides will result in a lowered surface area and phosphate release.