Legacy phosphorus desorption from U.S. Mid-Atlantic agricultural soils

Monica Elavarthi, Kathryn Szerlag and Donald Sparks

1. Abstract:

Phosphorus (P) is an essential nutrient for all life. Plants need P for photosynthesis, nitrogen fixation, and seed development. Due to its key role in plant nutrition, P is applied to fields in the form of chicken manure and fertilizers in U.S. Mid-Atlantic agricultural soils. The repetitive addition of P leads to a buildup of the nutrient, resulting in soils with high levels of legacy P. Through leaching, erosion, and runoff, excess P ends up in bodies of water, where it may contribute to eutrophication. Eutrophication is caused by the over enrichment of nutrients, promoting algae growth whose decomposition leads to toxic conditions for aquatic life. There are many different P species found within soil, each differing in solubility and bond strength. For this research, we collected agricultural soils with different physicochemical characteristics from the Mid-Atlantic region. We then completed desorption experiments using various extracting solutions to mimic the ionic strength of soil pore water (KCl), acid rain (HNO_3), and ligand exchange mechanisms (SiO_4^{2-}) to determine the rate at which P desorbs. By pairing the desorption curves with the other soil physicochemical characteristic data we collected (Mehlich-III extractable P, total P, and soil texture), we can begin to understand legacy P mobility in these soils. Desorption experiments show that KCl extracted the least amount of P in comparison to the other extraction solutions, for all soils. Additionally, we compared these bulk, wet chemical data with high resolution, micro X-ray fluorescence (μ-XRF) maps of the soil to determine P co-location with other elements of interest. We then used micro X-ray absorption near edge structure (μ-XANES) spectra of P hotspots to help determine the solid phase P speciation at the micron scale. Understanding the legacy P mobility and speciation in soils will help inform improved P management practices.

2. Introduction and Background:

P is essential for biological life forms due to its role in multiple reactions in organic chemicals. Plants in particular need the element in order to photosynthesize, fix nitrogen, and develop seeds. Due to its key role in plant health, P fertilizer is widely used in agriculture. The amount of P fertilizer added to the soil each year is important because if the soil P level is not at the optimum level it will limit the availability of P to crops (Gamble et al., 2017). P is sometimes used in moderation in order to ensure that the crops are able to produce an optimal yield. Approximately only one fifth of the P that is mined specifically for fertilizer ends up reaching the food consumed, the rest is either stored in the soil or escapes into local waterways (Jarvie et al., 2013). The buildup of these P stores in soil is referred to as legacy P and may release P long after the excess addition of P through fertilizer is reduced, which masks any progress made in P reduction efforts (Jarvie et al., 2013). Current models predict that soils with legacy P can release P for a few years to decades (Jarvie et al., 2013).

The excess/misused P fertilizer is it at risk of running off fields and into surface water bodies where it may be detrimental to aquatic life.The reason that eutrophication (or the over enrichment of nutrients) is so closely associated with P is that it is most often the limiting nutrient in freshwater systems, so the artificial introduction of P allows for expedited growth of algae blooms. The overgrowth of plant life in water bodies is not the explicit reason for the anoxic and hypoxic conditions related to P eutrophication, but is mostly due to the decomposition of the plants once they have died (Anderson et al., 2002). The excess algae once

it is dead undergoes decomposition, the organisms that facilitate this pull more oxygen from the water than can be replenished leaving that area in an anoxic state (Anderson et al., 2002). Even though an excess of P is detrimental to local aquatic ecosystems, it is absolutely essential to reach a certain level of this nutrient in agricultural lands to maintain an optimal level of crop production.

Different P compounds attach to soil molecules in different ways which leads to differences in the strength of the attachment. Certain compounds may be loosely bound through electrostatic interactions and are therefore more likely to become dissociated when incontact with rainwater. Other compounds may be attached to the soil particles via ligand exchange and are very resilient to desorption. These different P compounds may also have differences in rate of desorption. In this research, we determined the rate P desorbs from high legacy P agricultural soil and then paired this data with the solid P species found in the soil at the micron scale.

3. Methods and Experimental Design:

3.1 Soil Characterization
The soils that were chosen for this project are all from fields in the U.S. Mid-Atlantic area that we know to have phosphorus buildup over years of fertilizer and chicken manure application. The soil was prepared by being air dried and passed through a 2 mm sieve in order to exclude the analysis of any non soil materials (ex. twigs and rocks). It was then sent to the University of Delaware Soil Testing Lab where it was analyzed using various techniques. The first being the Mehlich-3 routine analysis to determine the agronomic availability of various elements over one growing season. Total concentration of the elements in the soil were then determined using microwave acid digestion. The last test that was performed at the soil testing lab was particle size analysis to determine the soil texture with respect to their separates (sand, silt and clay).

3.2 Desorption Experiments:
The desorption experiments were completed by shaking 200 mg of soil with 10 ml of various desorption agents, sampled at different time increments. The desorption agents consisted of 0.01 M KCl, 0.1 M HNO_3, 0.1 mM Na_2SiO_3 and were intended to mimic different environmental conditions that the soil could experience and the reactions that would result. The 0.01 M KCl is a dilute neutral salt solution and so was meant to simulate the soils' interaction with high ionic strength soil pore water. The 0.1 M HNO_3 (kept at pH 4) solution was used to mimic acid rain water since HNO_3 is responsible for approximately a quarter of the acidity of acid rain (Casidy et al., n.d). The 0.1 mM Na_2SiO_3 solution was used to possibly simulate the ligand exchange that may occur between the SiO_3^{2-} and PO_4^{3-} ligands in soil as this may allow for the desorption of more strongly held P compounds. The samples were shaken at 200 rpm and sampled at the time increments 0.5hr, 1hr, 2hr, 3hr, 6hr, 12hr, 24hr, 48hr, and 72hr. More samples were taken before the six hour mark to more accurately record the desorption rate at the time when a majority of the P the would desorb. Samples were taken as far out as 72 hours to make sure we were not stopping the experiments before the desorption plateaued.

3.3 Solid Phase Soil P Speciation:

Synchrotron technologies were utilized in order to conduct our speciation experiments. To prepare our samples, the soils were powder mounted onto tape in order to not disturb structures of soil so imaging is more accurate to its natural environment. These are important as they have not undergone any physical/chemical changes from their natural state, unlike our desorption experiments. Two beamlines were used in the direct analysis of the surface composition of our samples, Tender-Energy X-ray Spectroscopy (TES) and X-ray Fluorescence Microscopy (XFM). TES was used to locate and quantify lighter elements of significance to our project (Si, P, S, and Al). XFM was used to locate and quantify heavier elements of significance to our project (Fe, Ca, Mn and Mg).

4. Results:

4.1 Soil Characterization

The results of the soil characterization from the soil testing lab are given below in figure 1. The textural class of the soils signifies the relative proportions of the separates in each soil. Loam soils are generally composed of silt, sand and clay in fairly equal amounts. Silt loams are similar to loam soils but just have a higher proportion of silt which decreases the average particle size of the soil as silt is the smallest separate (Brady et al., 2010). Loamy sands are similar to loam soils but just have a higher proportion of sand which increases the particle size of the soil as sand is the largest separate (Brady et al., 2010).

Sample ID	Textural Class	M3-P (mg/kg)	P (mg/kg)	M3-Ca (mg/kg)	Ca (mg/kg)
CFT	Loam	256	482	807	984
MFT	Loam	331	551	698	885
EFT	Loam	303	726	1063	1298
CGAp	Silt Loam	198	937	773	1099
Manure Shed	Silt Loam	1121	2004	2061	3380
SLF2	Silt Loam	634	1109	1279	1691
Tingle 13-14	Loamy Sand	607	1023	646	944
Tingle 19-20	Loamy Sand	356	974	819	1264

Figure 1: Soil texture and composition of each soil sample with respect to their separates. The concentrations of the elements of interest in each soil following Mehlich III extraction and EPA3051 (specific acid digestion method).

4.2 Desorption Experiments

The first desorption agent used was KCl. Since each sample time was taken as a triplicate, the averages of the P concentration of each sample set is given in figure 2.
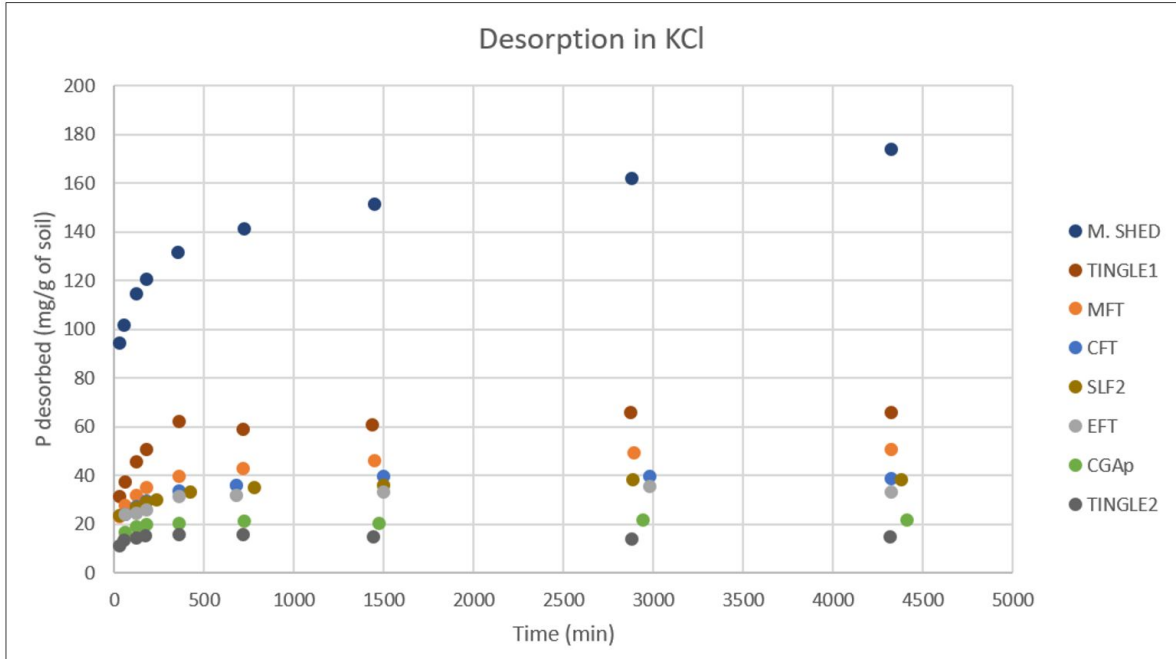
Figure 2: Average values of the concentration of P in all samples at each time interval that was collected.

Using the soil characterization data combined with the findings from the KCl desorption experiments we decided to further analyze the soils EFT (in figure 3), Tingle 13-14 (in figure 4), CGAp (in figure 5), and Manure Shed (in figure 6) with the other desorbing agents.
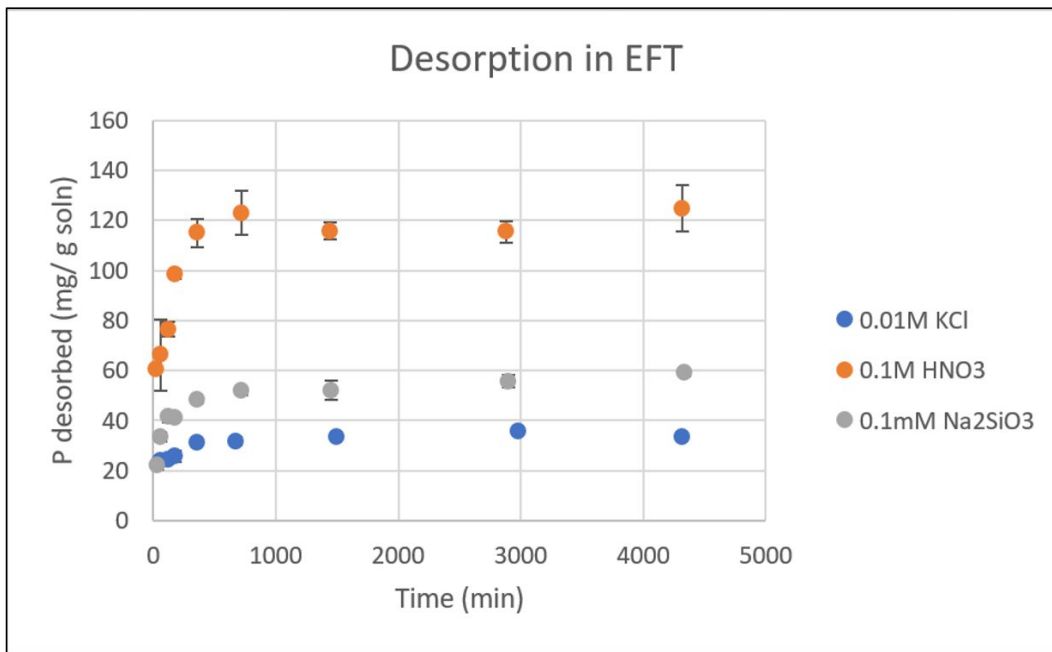

Figure 3: Average values of the concentration of P in all samples of EFT collected at each time interval and each desorption agent.
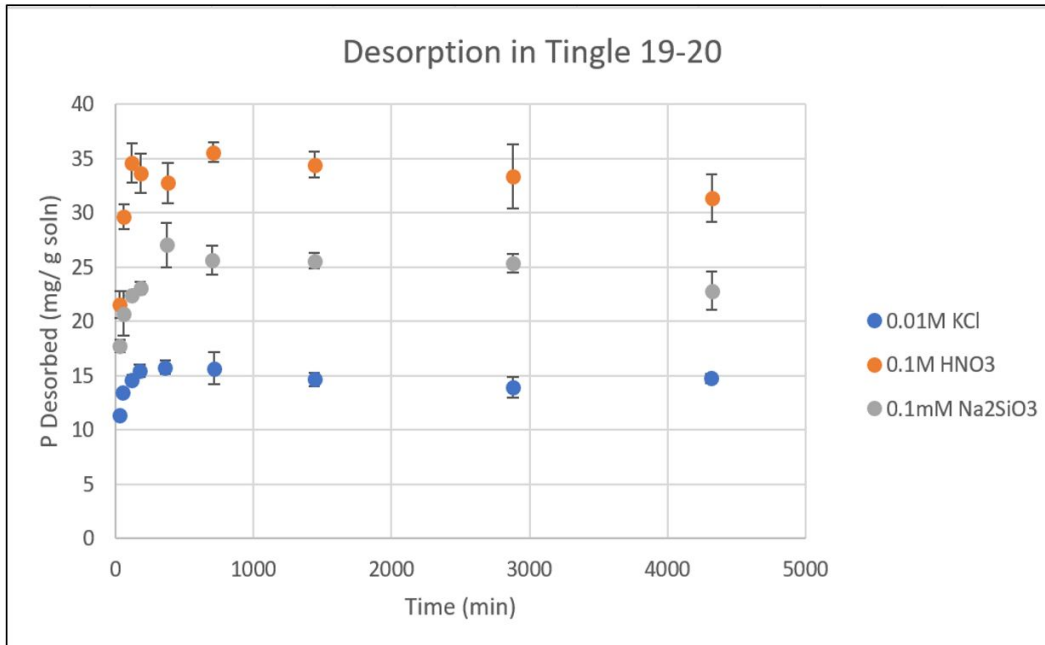
Figure 4: Average values of the concentration of P in all samples of Tingle 19-20 collected at each time interval and each desorption agent.
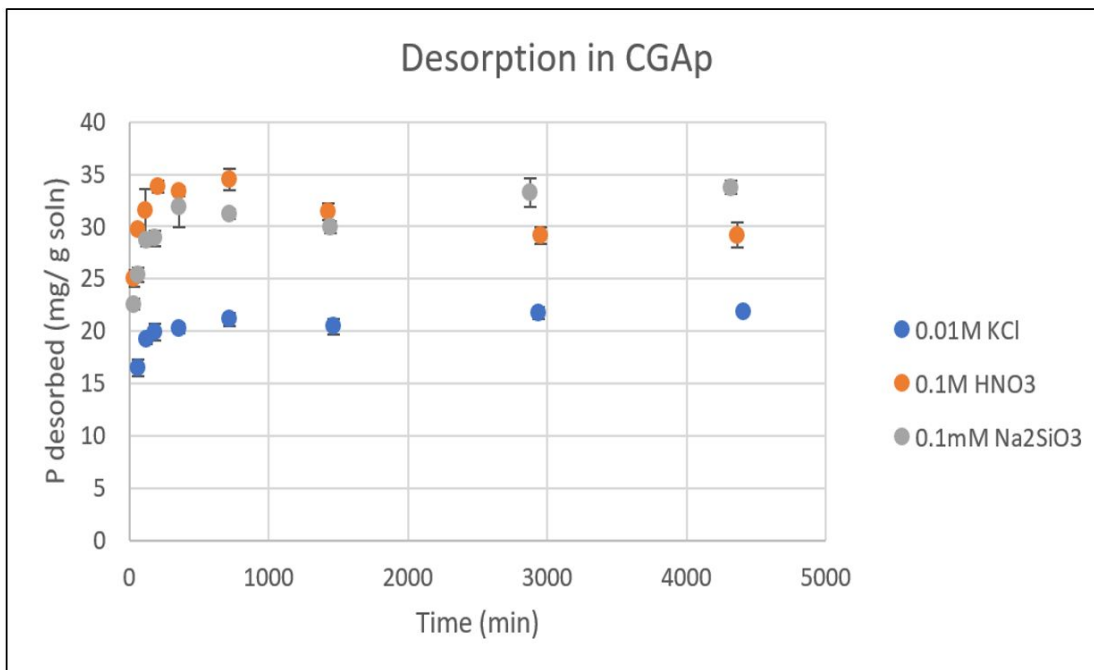

Figure 5: Average values of the concentration of P in all samples of CGAp collected at each time interval and each desorption agent.
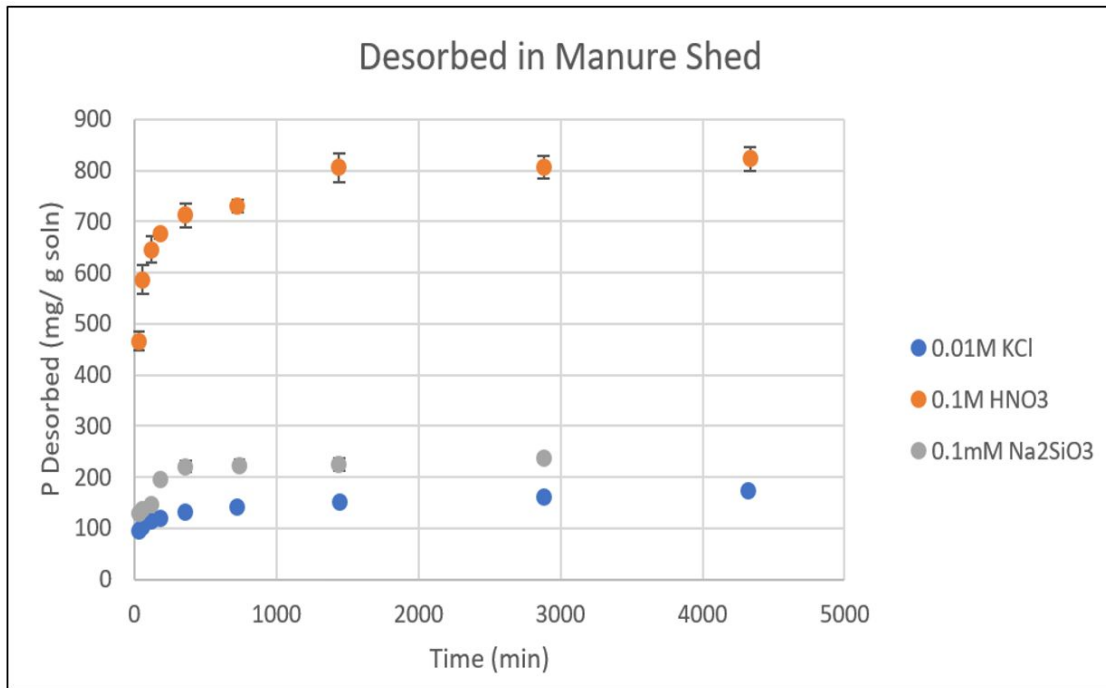
Figure 6: Average values of the concentration of P in all samples of Manure Shed collected at each time interval and each desorption agent.

4.3 Solid Phase Soil P Speciation

Figure 7 shows the Micro X-ray Fluorescence (µXRF) maps from both the TES and XFM beamlines ofthe EFT soil sample. EFT was chosen in particular due to its high concentration of both P and Ca. The two maps were then overlapped in order to determine if there were any instances of colocation of P with both the heavier elements and the lighter elements.
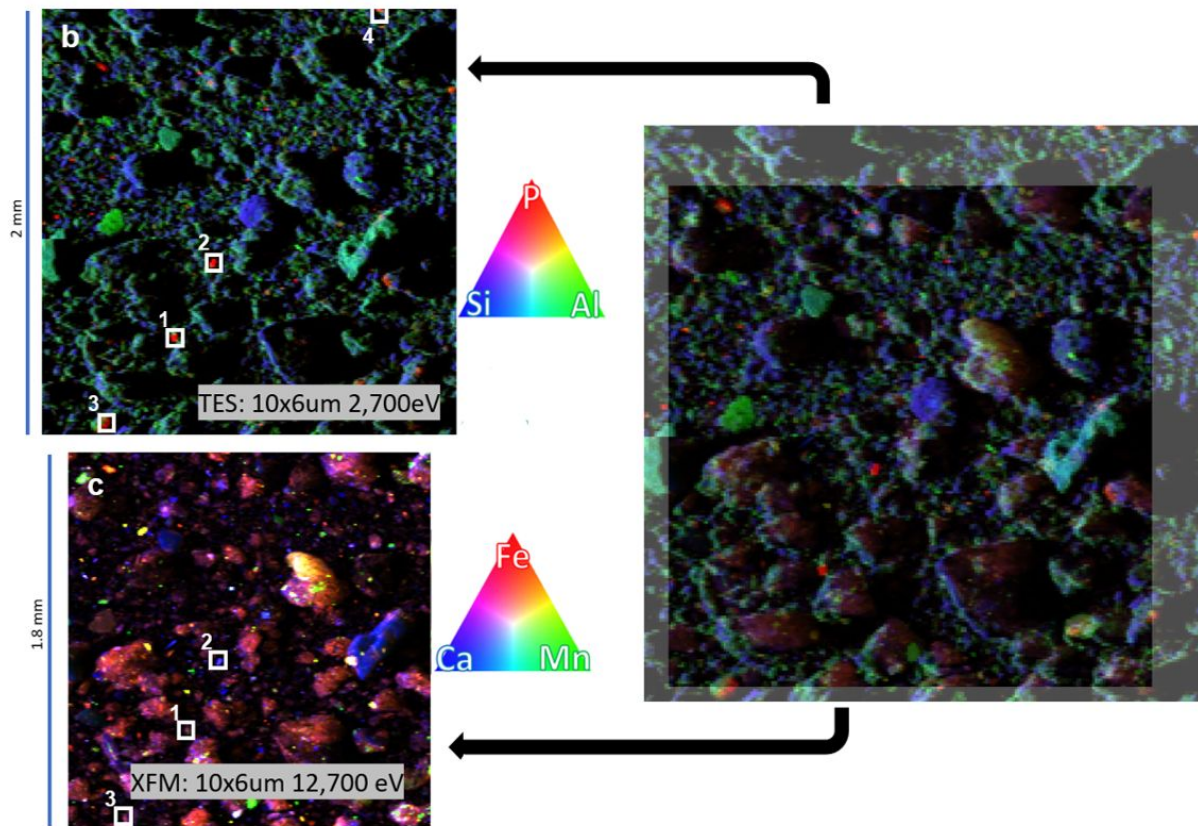
Figure 7: Overlay of XFM and TES µXRF maps of powder mounted EFT soil (<250 µm) in order to show P and other co-located elements.

Once the P hotspots were located on the TES µXRF map, µ-XANES spectra were taken of each P hotspot. This gives us a 'fingerprint' of the surface of the soil at that particular spot. This spectra can then be compared to spectra done of standards of pure samples (ex. Fluorapatite) in order to determine which P species are on the surface of the soil particles. The spectra are given in figure 8.
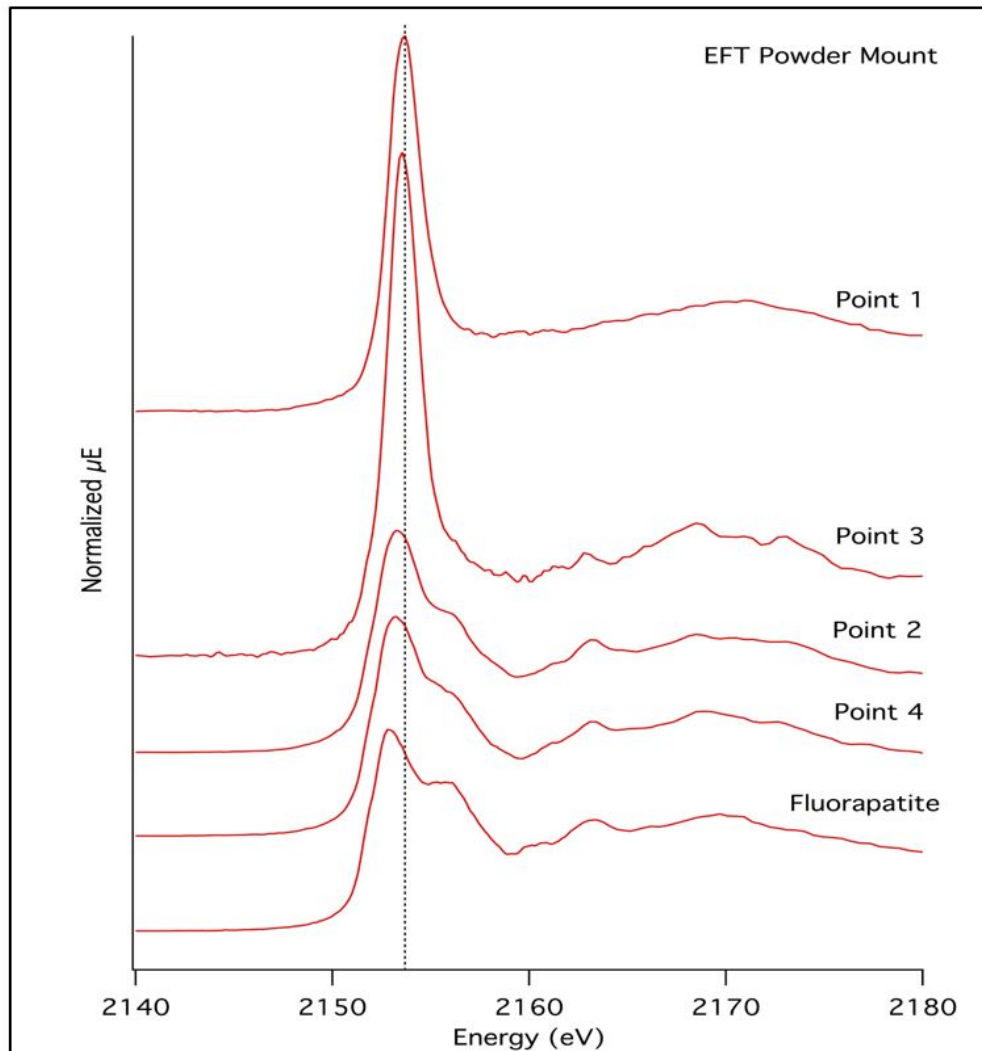
Figure 8: The TES μ-XANES spectra of each point of EFT presented together to help distinguish the P species present at that location.

5.Discussion:

From the textural class data, it seems as though the silt loam soils had the highest total P from the EPA 3051. The higher percentage of silt and clay and lower percentage of sand allows for a larger surface area and therefore increases the number of spots for P to bind to may be part of the reason for the high total P in these soils.

The manure shed soil results indicate a lot of loosely held P that is highly susceptible to transport off the field. We came to this assumption because manure shed had the highest P desorption in 0.01 M KCl at around 160 mg/kg, even though KCl was meant to act as a very light agent. Manureshed also desorbed approximately 56% of the total P was extracted with Mehlich III, which was also acting as a light wash. This shows that even in the presence of mostly non reactive solvents, this soil will give up a large amount of P. Manure shed is also a silt loam, which

supports our thinking that soils with higher fine particle composition provide more surface area and therefore active sites for P to bind on the surface.

The CGAp soil results indicate that it likely has the most tightly held soil P that is not very susceptible to transport off the field in the solution phase. We came to this conclusion because this soil had the lowest percent of Mehlich III extractable P removed at approximately 21%. CGAp also reached a low desorption equilibrium in 0.01 M KCl, at 22 mg/kg. Even though CGAp did not release a large amount of P with the Mehlich III extraction, it contained a large amount of P in total which could be because it is also a silt loam (more surface area).

Consistently KCl desorbed the least P from all soil samples. We used KCl to mimic the effect of pore water, which means pore water with K^+ and Cl^- ions alone may not be a major contributor to P leaving agricultural soil. Across all soils, the 0.1 mM Na_2SiO_3 desorbed more P than the 0.01 M KCl. This indicates that we may be extracting more tightly held P, perhaps through ligand exchange reactions. The desorption experiments completed using 0.1 M HNO_3 at pH 4 desorbed more P than both KCl and Na_2SiO_3, especially for soils with high Ca. Manure shed had the highest Ca and desorbed the most HNO_3 P by far. This may indicate preferential P desorption from the dissolution of calcium phosphate minerals (like fluorapatite). Comparison of the TES and XFM u-XRF maps show that the majority of P species probed in EFT are clearly associated with Ca. After comparing the spectra to that of fluorapatite, it seems as though our spectra matches fairly close. This indicates that the P is potentially in the form of fluorapatite.

6. References:

Anderson, D. M., Glibert, P. M., & Burkholder, J. M. (2002). Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences. *Estuaries, 25*(4), 704-726. doi:10.1007/bf02804901

Brady, N. C., & Weil, R. R. (2010). Chapter 4: Soil Architecture and Physical Properties. In *Elements of the nature and properties of soils*. Boston: Pearson.

Casiday, R., & Frey, R. (n.d.). Acid Rain. Retrieved from http://www.chemistry.wustl.edu/~edudev/LabTutorials/Water/FreshWater/acidrain.html

Gamble, A., & Sparks, D. L. (2017). *Speciation and reactivity of phosphorus and arsenic in Mid-Atlantic soils* (Doctoral dissertation, University of Delaware). University of Delaware.

Jarvie, H. P., Sharpley, A. N., Spears, B., Buda, A. R., May, L., & Kleinman, P. J. (2013). Water Quality Remediation Faces Unprecedented Challenges from "Legacy Phosphorus". *Environmental Science & Technology, 47*(16), 8997-8998. doi:10.1021/es403160a