Improving environmental health: Investigations into soil lead and phosphorus fate and transport

by

Joseph J. Weeks

B.S., Cornell University, 2012

## AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the requirements for the degree

# DOCTOR OF PHILOSOPHY

Department of Agronomy College of Agriculture

KANSAS STATE UNIVERSITY Manhattan, Kansas

### Abstract

Phosphorus (P) fertilizer use efficiency can be poor in calcareous and acid soils as a result of fixation reactions that occur between the orthophosphate anion and various forms of calcium (Ca), iron (Fe) or aluminum (Al). To overcome these reactions and prevent P deficiency, growers with access to fertilizers may apply more than the crop will remove. This may create a surplus of P in soil over time that is not highly labile but can still erode or leach into nearby waterbodies jeopardizing drinking water quality, recreational activities, and the of health aquatic wildlife. Where fertilizer access is limited by economic/political forces, ineffective P use manifests as low yields keeping destitute farmers stuck in a cycle of poverty. In both situations, simple, cheap techniques are required to get more "bang for the buck" out of P sources of fertility. One of the main objectives of this lab-based project was to investigate methods to improve plant recovery of applied P. Use of Petri dish incubations allowed for spatial inquiry of P fate and transport in mildly calcareous soils from Finney County, Kansas and an acidic Ultisol from São Paulo, Brazil. Treatments to prevent precipitation and inner-sphere complexation of P when applied as liquid fertilizers included co-application of commercially available humic substances, adjustment of application volume, and blending ortho- and polyphosphates. Anion exchange resin extractability as a percent of total P assessed potential plant availability, total elemental determination evaluated P diffusion, and synchrotron-based X-ray absorption nearedge structure (XANES) spectroscopy was implemented to probe reaction products and pathways along with a suite of other wet chemical analyses. Treatment efficacy was variable and soil specific. Blending ortho/polyphosphates and adjustment of application rate show promise for improving the plant recovery of P added to calcareous soils but not acid, while the impact of coapplication of humic substances remains inconclusive. What is certain is that the future of P

management will be to more specifically tailor P applications to soil conditions and crop requirements to minimize P loss and/or partitioning to unintended environmental pools and maximize plant uptake.

Another threat to human well-being related to the food system is soil contamination with trace elements such as lead (Pb). Urban gardening has been experiencing increasing popularity around the United States spurring a flush of research not only investigating the best growing techniques but also exploring areas of potential human health concern when these gardens are established on brownfields. Three pathways of exposure are typically cited for these soil Pb to enter the human body: ingestion of soil directly, consumption of produce containing or superficially contaminated with a hazardous substance and inhalation of soil dust. The contribution of the inhalation route has not been adequately investigated. An activity-based inhalation risk study was carried out in two urban soils located in Kansas City, MO by collecting dust while garden plots were rototilled. Although the study has been limited to one geographic area, very little dust was collected suggesting that inhalation is not a major exposure pathway for gardeners.

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Approved by:

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# Dedication

To my family and friends that have supported me in all my endeavors over the years.

Thank you.

# **Chapter 1 - Introduction**

Agronomy is a rather unique scientific field. Our future as a species relies upon the successful implementation of sound practices that guarantee food crops receive adequate nutrition to optimize yields to feed growing populations, yet those same practices are slowly depleting nonrenewable resources and poisoning our freshwater bodies at rates quick enough to measure but too slow for most individuals to concern themselves with (Cordell and White, 2015). Humans are not well equipped to handle large, ongoing problems that are the result of complex interactions of a multitude of factors and will typically never proactively revise their lifestyles until conditions degrade to the point in which no other option is available or alternatives are developed that simultaneously benefit the consumer while solving a greater problem. This situation is particularly salient in the case of phosphorus (P) fertilizers.

Worldwide billions of hectares of farmland possess yield-limiting concentrations of labile phosphorus (Dhillon et al., 2017). To remedy this situation, growers annually apply millions of tons of fertilizer to a wide array of agricultural systems. Unfortunately, in many soils, including those across the United States, a significant portion of the applied P is rapidly converted to forms that plants cannot readily use (i.e. fixing reactions) wasting grower capital and creating environmental hazards. Soils containing elevated levels of "plant unavailable" forms of P erode into lakes and streams nourishing cyanobacteria that produce the toxic blooms that endanger biodiversity, recreational opportunities and drinking water quality (Jarvie et al. 2017). To complicate matters further, some people believe that the world is running out of P. Global supply estimates of the resource claim 100-300 years of mineable rock phosphate remain given our current state of mining and refining technology. Thus, we need better ways to efficiently employ this vital resource (Cordell and White 2015).

Extensive research has been conducted to assess the fate and transport of various phosphorus fertilizers in diverse agricultural systems. Adequate plant nutrition is dependent upon the orthophosphate concentration in soil solution at a given time and the soil's ability to resupply the anion upon uptake (Syers et al. 2008). Both of these factors are reduced by fixation reactions. In weathered, acid soils, the process is driven largely by inner-sphere complexation on iron (Fe) and aluminum (Al) oxyhydroxides, while under alkaline, calcareous conditions, calcium mineral formation typically dominates. This means that one solution likely does not exist to solve all fertilizer related agronomic and environmental issues. Soil specific approaches that respect the nuanced interaction of P with soil components will be necessary to discover and then implement. A review of current literature in Chapter 2 reveals that many ideas are currently being explored with variable success.

A portion of the agronomic community makes the claim that co-application of organic chemical compounds have the ability to positively affect the way humans manage P in cropping systems, eliciting the mechanism by which the alleged products work has been a significantly different story. The dogma for decades was that humic substances, both found in soil and commercially sold (e.g. fulvic acid, humic acid, and humin), were highly complex molecules with a relatively consistent structure that just was yet to be determined. Now, more and more scientists agree that each subclass (i.e. fulvic acid) is likely to be highly heterogeneous based on the degree of decomposition and raw material from which the compound originates (Lehmann and Kleber, 2015). Growers and scientists are currently working to parse if the commercial versions of these products reliably confer benefit to cropping systems, and if so, what the mechanism of action may be (Lyons and Genc, 2016). One common hypothesis is that the high cation exchange capacity associated with many of these substances outcompetes P and blocks

fixation in soils (Lyons and Genc 2016). Degryse et al. (2013) concluded that this mechanism to prevent fixation was likely not viable however, though humic substances were not specifically vetted.

Use of humic substances is not the only approach available to improve the performance of P fertilizer application. Application of other types of carbon-based compounds and exploration the how the species of P applied interfaces with inherent soil constituents will be important as management of agricultural systems advances into the future as well. For example, studies have shown that condensed phosphates (e.g. pyrophosphate) can exhibit differential affinity for iron and aluminum oxyhydroxides compared to orthophosphate (McBeath et al. 2007). This may matter when deciding whether to apply monoammonium phosphate or ammonium polyphosphate to a specific field.

In addition to the need for high yielding, efficient field cropping systems, a rapidly growing percentage of the world population in moving into urban areas, and the availability of fresh, nutritious produce in low income areas has become cause for concern. (United Nations, 2018) "Food deserts," as they often have been called, are appearing in cities of not only the United States but around the world. These are places where grocery stores, if present, lack the means to obtain and/or sell quality fruits and vegetables in an economically efficient manner. Those with mobility limitations that are unable to travel out of these areas are left reliant upon fast food establishments and convenience stores to satisfy, at the very least, their daily caloric requirements (Hynes and Genevieve, 2004). One solution to this unfolding social injustice that has received widespread public and governmental support as well as a fair amount of success is the implementation of urban community gardening programs.

A major issue hindering the rapid implementation of urban gardens in many areas is anxiety over growing food in soil that may not be safe. University and government researchers are making information available to address these misgivings, but knowledge in reference to assessing the risks associated with urban gardening is still lacking in certain areas. In many communities, lead (Pb) contamination remains the primary concern. The heavy metal, an artifact of anthropogenic activity, has entered the soil primarily as a result of the prolonged use of leaded gasoline in the internal combustion engine and leaded paint applied inside and out of many buildings from approximately the 1920's until 1996 and 1978 in the United States, respectively (Binstock et al., 2008; Markey et al, 2008; McBride et al., 2011; Schwarz et al., 2012).

Three pathways of exposure are typically cited for soil Pb to enter the human body: ingestion of soil directly, consumption of produce containing or superficially contaminated with a hazardous substance and inhalation of soil dust. Of these three exposure pathways, inhalation exposure is yet to be thoroughly characterized.

In this dissertation, four studies were conducted to explore the fertilizer factors that dictate phosphorus fertilizer use efficiency in calcareous and acid soils and assess the risk that lead contaminated dust inhalation poses to urban gardeners.

#### **Objectives**

 The objective of the first study is to use two mildly calcareous soils to investigate the roles of liquid fertilizer formulation (e.g. P species, P concentration) and coapplication of sodium alginate on P lability and partitioning around the point of application in calcium-rich soils.

- 2.) The objective of the second study is to use two mildly calcareous soils to investigate the impact of co-application of commercial fulvic acids with liquid P fertilizers on P lability and partitioning around the point of application in calcium-rich soils.
- 3.) The objective of the third study is to use an Ultisol soil to investigate the roles of liquid P fertilizer formulation (e.g. P species) and co-application of commercial fulvic acids on P lability and partitioning around the point of application in an acidic soil.
- 4.) The objective of the fourth study were to conduct a site-specific investigation of how much dust a person could reasonably expect to inhale while rototilling a garden and evaluate the risk to human health that this dust may pose considering contamination with trace elements such as lead (Pb).

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# Chapter 2 - Triple Superphosphate was invented in the 1950s. What are we doing now? A review of the latest in phosphorus fertilizer technology.

#### Abstract

The invention of highly concentrated phosphorus (P) fertilizers, such as triple superphosphate, by the Tennessee Valley Authority (TVA) helped mark the beginning of a revolution in the way we manage food crop nutrition. Since then, scientists with the help of farmers have made great advancements in the understanding of P fate and transport across many environments but largely have failed to produce a new generation of products and/or application techniques that are widely accepted and vastly improve plant acquisition efficiency. Under certain conditions, important advancements have been made. For example, applying liquid formulations of phosphates in lieu of dry granules in some calcareous soils has dramatically reduced precipitation as sparingly soluble calcium phosphate minerals, but other attempts, such as the co-application of humic substances, sorption to layered double hydroxides, or use of nanoparticles, have not generated the kind of results necessary to continue economically increasing crop yields without further environmental cost. New sources of fertility will need to be affordable to produce/transport and furnish P to soil solution in a manner well synchronized with crop demand so as to minimize contact with the most reactive soil constituents. This paper will provide a review of recent literature on cutting edge phosphorus fertilizer technology. The goal is that this synthesis can then be used as a starting point from which a larger discussion on future efficient, responsible P supply research can be built.

#### Introduction

When alchemist Hennig Brand stumbled across phosphorus (P) in his attempts to create gold from urine around 1669, it's difficult to know if he realized the magnitude the discovery's affect would have on the world now 350 years later (Encyclopedia Britannica, 2014). From bombs to fertilizers, P has become a boon and burden to human existence. Essential to all life, application of the element to agricultural systems, much like nitrogen, has resulted in unprecedented increases in yield facilitating tremendous population growth and improved nutritional status of people globally. Unfortunately, over roughly the last century, lack of scientific and public understanding coupled with perverse economic incentives have created situations where this important agricultural tool has become a severe environmental pollutant. Eutrophication of waterbodies has created decreased water quality for both the aquatic life residing in these ecosystems and for humans using these sources for drinking water and recreation. Ongoing issues in the Lake Erie watershed are but one example (Jarvie et al., 2017). But agriculture is not solely to blame. Phosphorus, as well as nitrogen, enrichment is also the result of accidental and intentional septic system discharge in ill-suited soils and/or locations (Lapointe et al., 2015). In areas of the Earth where the high cost of fertilizer limits its use, precision techniques, like microdosing, are helping some smallholder growers maximize returns on their investments, but further innovation is required to ensure food security for these communities (Blessing et al., 2017).

Many of the P fertilizers used today were developed in the mid-1900s building on the development of single superphosphate by Gilbert and Lawes in the 1840s (Encyclopedia Britannica, 2018). Phosphate salt products, like triple superphosphate, possess the benefits of being both highly soluble and concentrated making for relatively economical application to soil.

While obviously advantageous in some respects, these properties do not always make for efficient nutrient use in terms of percentage taken up by the intended crop relative to loss to the surrounding environment. Maximum soil solution P coming from these fertilizers shortly after soil application as a result of their dissolution does not necessarily synchronize well with plant uptake. Thus, the degree to which the nutrient is ultimately used is highly dependent upon not only fertilizer characteristics but also inherent soil properties, climate/weather, and the cropping system (Syers et al., 2008, Vandamme et al., 2013).

Over the last couple of decades, scientists and engineers have been working to develop new products that reduce soil fixation reactions creating unfettered crop P supply maximizing yield. Essential to our progress as an agricultural community is the increased appreciation of just how complicated nourishing crops can be. What works well in one situation may be deleterious in another. A prime example is the decision to apply liquid or granular P. Liquid P formulations tend to significantly reduce fixation in calcareous soils and yield substantially better use efficiency, while the opposite result is often observed in iron and aluminum rich Ultisols, Oxisols and Andisols. (Hettiarachchi et al., 2006; Holloway et al., 2001; Lombi et al., 2004; Montalvo et al., 2014a, Pierzynski and Hettiarachchi, 2018). Ideal fertilization techniques may become more complicated in the future if one considers factors such as the proportion of Al in Fe/Al coprecipitates which has been shown to substantially impact P sorption behavior (Liu et al., 2011). As sensing and testing technology continues to improve, one can imagine a time in the future when we will be able to use our knowledge of site-specific nuance impacting P fate and transport to optimize practices. Whatever those future solutions may be, they are going to need to be practical to implement for average farmers. While it is true that "outside the box" ideas can be important components of progress in any scientific field, the constant market pressure for food

prices to be continually lowered means that growers will not adopt expensive solutions for which they cannot earn a financial return. Researchers need to keep this in mind if their work is to have real world impact.

This review is designed to discuss the most recent, relevant research related to innovation of commercial P fertilizers. The literature body is extensive, and to our knowledge, no current paper exists that aggregates recent approaches to fertilizer development of a more "mineral" nature; the scope of this discussion is limited to products that could be easily substituted into the current application practices of growers applying the traditional P salts. One hope the authors have is that the reader clearly sees that we as a scientific community need to be more deliberate and intelligent about the way we investigate fertilizer technology moving forward, so that results can be meaningfully integrated into production practices. Laboratory and greenhouse studies are just as important as field-scale trials, but if they are setup such that they cannot translate to any current or reasonably imagined future real-world applicability, then the utility of such work is called into question. The same applies to studies in the field. If adequate controls are not included and/or soils are not responsive to the amendment rates applied, then little useful information can be gleaned from the expense of many financial and labor resources. For a detailed discussion of methods to assess the efficiency of P fertilization practices, the authors direct readers to FAO Fertilizer and Plant Nutrition Bulletin 18 by Syers et al. (2008). This review will consider P availability for uptake in the growing season of application as the metric for assessing the products efficacy. The authors do fully acknowledge that a portion of that P is likely to remain labile for use by subsequent crops and may differ from product to product. The mechanisms of action being explored in this review are divided into four groups: slow-releasers, fixation blockers, biochemical response inducers, and alternative P species (Figure 2.1)


Figure 2.1 Outline of the various approaches being tested in search for a more efficient fertilizer.

## **Slow Releasers**

## Coatings

Coating granular fertilizers with polymers to slow the initial dissolution of the product is one of the oldest methods attempted to extend P release through a growing season and increase use efficiency (Nyborg et al., 1995). Many factors impact whether this approach is successful. Properties of the soil, coating, and fertilizer granule all contribute to determining the complex release pattern in a given system.

#### **Biodegradable Polymers**

Controlled release granules are typically traditional salt fertilizers, such as monoammonium phosphate (MAP) that are surrounded by a material that restricts water movement into the product and retards diffusion of P out to soil solution. Conceptually for a single controlled release coated granule, Shaviv et al. (2003a) describes a sigmoidal release curve with three distinct phases. The first is an initial lag period where water enters the granule and no nutrient exits. The duration of this phase is directly proportional to the product of the granule radius and thickness of the coating; the thicker the coating or larger the granule, the longer the period of time before P is released. Second, is a linear release phase where concentration of solution P inside the coated product is kept at equilibrium with the remaining solid material and the concentration gradient between inside granule and the surrounding environment is high, driving P across the coating barrier into the soil where it can be taken up by plants and microorganisms. Finally, when the interior granule is completely dissolved, the gradient approaches equilibrium with soil solution as P continues to leave the product, and release rate slows. This, of course, assumes that the coating is applied evenly around the granule and does not fail (e.g. crack) at any point in the process. Attention to coating thickness, it's

solute permeability, granule properties, such as density and solubility, and the variance of these properties across the entire applied population can allow for better control of timing and rate of P release when applying these products (Shaviv et al., 2003a, 2003b).

Experimentally, Fernandes da Cruz et al. (2017) demonstrated that coating thickness strongly regulates P diffusion. Castor Polyurethane applied at 3% or less produced release profiles very similar to no coating at all likely due to incomplete coverage of the granules. Coating of 4.5% - 7.5% showed moderate dissolution while 9.0% or greater drastically retarded P migration into an Oxisol soil. Consistent with the theoretical descriptions of Shaviv et al. (2003a), the 9.0% treatment showed the longest lag phase followed by steadily increasing P availability when the experiment ended after ~28 days. This result suggests that depending on crop demand, adjusting coating thickness could be an effective strategy to choreograph nutrient release with plant recovery of P over time (Nyborg et al., 1995). Similar results were also reported by Du et al. (2006) using a "polyurethane like" material. Increasing temperature appeared to reduce differences in release rates from coating of varying thickness. Interestingly, the lag time was slightly shortened when a thicker coating was applied to an NPK granule relative to a thinner coat. No explanation currently exists for this counterintuitive observation. For field practical purposes, the group suggested that perhaps blending granules with different coating thicknesses might help tune P release rates to correspond to crop need particularly when growing in cold spring soils (Du et al., 2006).

Over the years, many more products have been tested in this category for P and N than can be reasonably covered in this paper. Readers are referred to Majeed et al. (2015), for a more in-depth discussion.

### **Advanced Modifications**

Scientists are now not only focusing on coating materials themselves, but additional post coating modifications of the inner and outer structure are being explored to further tune granule performance. Xie et al. (2017) modified a cottonseed oil based polyurethane coating by roughening the surface with a SiO<sub>2</sub>-diatomite hydrosol followed by immersion in a perfluorodecyltrichlorosilane solution to attach fluoroalkylsilane groups making the original hydrophilic coating extremely hydrophobic. This conversion to hydrophobicity allowed for the creation of an air barrier between the granule and soil solution that only water vapor could cross slowing granule hydration and delaying nutrient release. The use of fluorine may be suspect however due to the element's pollution potential and the tendency for coating materials to resist degradation in soil for what can be long periods of time (Trenkel, 2010). Jin et al. (2013) took a different approach and embedded diammonium phosphate into a starch matrix and extruded a granular product. They further processed the granule by adding a starch/poly(acrylic acid-coacrylamide coating as a superabsorbent jacket. This processing appeared to slow N and P release but performance was measured based on the amount of nutrient remaining in the granule after specified durations of soil application, not how much of the nutrient was recoverable in the soil. Regrettably, soil property information is not provided, so true assessment of the efficacy of this product is difficult at this time.

Another concept being pursued for these materials is to make coatings that are responsive to environmental stimuli. Ma et al. (2013) explored the development of a thermosensitive coating composed of polydopamine-graft-Poly(N-isopropylacrylamide). Normally, as soil/solution temperatures increase, the amount of nutrient to cross the coating barrier increases as a result of accelerated chemical kinetics. The novel approach employed in this study creates a situation

where the opposite can be observed. The Poly (N-Isopropylacrylamide) strands attached to the outer surface of the coated granule possess a lower critical solution temperature (LCST) of approximately 32°C. At temperatures lower than the LCST, the strands extend radially into solution and allow nutrients in the granule to diffuse outward. At temperatures higher than the LCST, the strands collapse to the coating surface and restrict P release. While the utility of a such a system is not immediately obvious given that the temperature of many soils may never exceed 32°C in a growing season, the concept could be useful if the mechanism was engineered to be more responsive at lower temperatures. Consider that in the spring, the soil is generally cold, so granule dissolution would be slow, this type of coating would theoretically allow for faster supply but would restrict release during warmer parts of the growing season when granule dissolution might be more rapid than plant uptake. This type of system could limit P interaction with soil colloids and simultaneously provide adequate crop nutrition. Much more research will be necessary to establish the feasibility of these complex nutrient management approaches.

# Scaffolds

Another slow release approach is to load P onto solids that then allow the nutrient to be "cut loose" to soil solution by a combination of chemical mechanisms, such as ligand displacement and dissolution, dictated by the interactions between P, scaffold material, and environmental conditions.

### Nanoparticles

A particle commonly defines as being "nano-" when at least one-dimension measures less than 100nm in length (Powers et al., 2006). Interest in developing fertilizers using these very small products has seen a surge of interest over the last decade or so given the need for more efficient, slow releasing sources of nutrition and increased understanding how particle behavior

changes on the nanoscale relative to larger solids of the same composition. These particles tend dissolve much more quickly and can be more mobile in porous media, like soils, due to their small size and increased surface area (Montalvo et al., 2014). One issue is that they often readily aggregate when placed in aqueous solution meaning that they quickly lose advantageous "nano" properties (Liu and Lal, 2014).

Recent research strongly suggests that under situations in which the solution concentration of free orthophosphate is low, colloid associated P can become a significant contributor of nutrition to crops (Montalvo et al., 2015). The implications of this finding are yet to be fully explored but work by Santer et al. (2012) has demonstrated that P loaded nano-Al<sub>2</sub>O<sub>3</sub> possessed greater capacity to supply P to *Brassica napus* cv. Caracas compared to an unbuffered aqueous supply of orthophosphate in a hydroponic medium. Because P uptake is likely a diffusion limited process, nanoparticles that move into the diffusive layer around roots are capable of buffering P solution concentration. This has the effect of shortening the distance P is required to diffuse keeping P concentrations at transport sites of the root closer to bulk solution concentrations than would be capable without the additional benefit of colloidal transport. The efficacy of this sort of approach in soil is unknown but highlights an important mechanism by which nanoparticles may be able to better carry P in the future.

#### **Graphene Oxides**

Since first being discovered in 2004, graphene and its oxide form have become an important platform for innovation in a variety of sectors including the processed food industry, pharmaceuticals, and the military (Novoselov et al., 2012; Robinson et al., 2008; Yoo et al., 2014). The materials 2-D carbon structure creates an extremely high surface area with a theoretical maximum of  $2600m^2 g^{-1}$  that can be functionalized to suit myriad chemical

applications and likely be designed to be environmentally benign (Sanchez et al., 2012). Work is just beginning using this material as a scaffold to hold and slowly release P. Andelkovic et al. (2018) demonstrated in a small column study and through application to three soils of varying inherent characteristics that the product does slowly release P over time relative to more common salt fertilizers (e.g. MAP). The agronomic effectiveness of the product remains to be tested. The current iteration was capable of loading 48mg P per gram of graphene oxide making transportation and application economically challenging (MAP contains ~227g P g-1), but the authors are confident that further research will allow for the creation of products containing a greater concentration of the macronutrient. A small number of papers have been published citing the ability of graphene to reclaim P from enriched water, but their ability to then return the nutrient to crops in the form of a fertilizer remains to be tested (Luo et al., 2016; Tran et al., 2015).

#### Layered Double Hydroxides

Layered double hydroxides, sometimes dubbed "anionic clays," are often synthesized as magnesium and aluminum hydroxide sheets intercalated by anions, such as nitrate. Typically expressed by the generic formula  $[M^{2+}_{1-x} M^{3+}_x (OH)_2]^{x+}[A^{m-}_{x/m} \cdot nH_2O]^{x-}$  where  $M^{2+}$  and  $M^{3+}$  are di- and trivalent metallic cations ( $x = M^{3+}/(M^{2+}+M^{3+})$ ) and  $A^{m-}$  being the intercalated anion, the greater the proportion of aluminum included, the greater the anion exchange capacity of the material (Everaert et al., 2018). Used in a variety of applications, such as controlled release pharmaceuticals, recently, they have received attention both as a material capable of preferentially recovering P from wastewater, and as a slow release source of P fertility in agriculture (Koilraj et al., 2013; Nalawade et al., 2009).

In 2016, Everaert et al. found the optimal Mg:Al ratio to be 2:1 to increase both P loading and desorption (Everaert et al., 2018). Maximum sorption capacity by mass is currently similiar to the graphene oxides and seems to be around 4% (Benicio et al., 2016; Bernardo et al., 2018; Everaert et al., 2017). When blended in powder form with soil and compared against common fertilizers (e.g. MAP, TSP), the LDH treatments produced barley, maize, and wheat seedlings of greater or at least equal P uptake and biomass in tropical acid soils while the opposite seemed to be true in more neutral and calcium rich soils especially at higher P application rates (200mg P) kg<sup>-1</sup> soil). The improved performance under acid conditions may due to the increased pH observed as a result of LDH treatments as well as the fact that the slow release characteristics of the product prevent P interaction with highly reactive iron and aluminum oxyhydroxides (Bernardo et al., 2018; Benicio et al., 2016; Everaert et al., 2016). The pH increase in acidic media can be explained, in part, by the dissolution of the LDH scaffold as well as proton scavenging by released P in the dibasic form (Parello et al., 2010). Because assays that blend powdered fertilizers into soils do not accurately represent field situations where farmers typically add fertilizer as a liquid or dry granule, Everaert et al. in 2017 compared their performance as both powder and granules using a 100 day incubation study. When LDH were applied as a granule, 74-90% of the P remained within the product itself in three soils of varying characteristics. All soils showed a relatively small diffusion distance compared to granular MAP but the greatest movement was observed in the neutral soil followed by acid and then calcareous. Subsequent pot trials with wheat seedlings in both acid and an alkaline conditions, revealed that when applied as granules, MAP vastly outperformed the LDH treatments. Applying them as powders decreased differences but no powdered treatment performed as well as granular MAP (Everaert et al., 2017). The LDH product appears to definitely release P slowly but may, in fact,

be too slow to optimally supply the nutrient during crucial periods of plant development in some situations (Everaert et al., 2017).

One disadvantage of P loaded LDHs is that at maximum, only about half of the P is able to be desorbed from the scaffold on timescales relevant to crop growth leaving a large amount of P potentially unavailable in the soil. This coupled with the low total loading rate ( $\sim$ 4%), makes economical application of these products seemingly impractical at field scale (Benicio et al., 2016; Everaert et al., 2016). Mechanistic work on these products reveals that P becomes trapped on the interior of the interlayer gallery as the nutrient exchanges with anions closer to scaffold edges. Everaert et al. (2018) witnessed that isotopic exchangeability (proxy measure of lability) of P after LDH products were subject to desorption experimentation was indirectly correlated to the amount of P desorbed, and the amount of P desorbed was dependent on the concentration of sodium bicarbonate used as a competing anion. The higher the NaHCO<sub>3</sub><sup>-</sup> concentration, the more P was desorbed, and the less the remaining P was isotopically exchangeable. The authors state "the HCO<sub>3</sub><sup>-</sup> anions diffuse from the solution towards [LDH] surface sorption sites and into the interlayer galleries, thereby replacing the initially present PO<sub>4</sub> via anion exchange. The PO<sub>4</sub> at the crystal edges and at the periphery of the basal plane will be replaced first. However, further anion exchange between HCO<sub>3</sub><sup>-</sup> and intercalated PO<sub>4</sub> might be slow as a result of the counterdiffusion of PO<sub>4</sub> and HCO<sub>3</sub><sup>-</sup> anions. The PO<sub>4</sub> remaining in the center of the basal plane becomes more fixed as it needs to pass a layer of strongly bound intercalated HCO<sup>3-</sup> anions before desorption." This finding is unfortunate for the future of LDHs as it means a potentially significant proportion of the plant nutrient becomes locked into the product itself and provides little benefit to the intended crop. Perhaps under acid conditions, this is less of a problem as part of the LDH may dissolve releasing locked intercalated P (Everaert et al., 2016).

Interestingly LDH scaffolding may also have an adverse effect on the availability of other nutrients, such as sulfate, once the phosphate anion is released. This may be due to the affinity of the LDH for other anions necessary for plant production or due to the increases in soil pH often observed when these products are applied (Benicio et al., 2016; Everaert et al., 2016). Supplementation of sulfate allowed LDH-P to produce comparable biomass as potassium phosphate in a Calcic Cambisol when growth was otherwise hindered (Everaert et al., 2016). More work will be necessary to improve the performance of these products if they are to be successful on the market. Currently, commercial viability seems dubious given their low loading rate, poor solution supply profile, and potential for creating other nutrient deficiencies as they attempt to correct for solution P status.

### **Organic Matrices**

Supplying P in a network of carbon compounds may slow the anion's migration to soil solution by retarding diffusion rates through increased path tortuosity and/or requiring structural decomposition as a requisite to environmental exposure.

### **Superabsorbents**

A variety of superabsorbent compounds with water absorption capacities of many hundreds of times their own mass have been synthesized from synthetic and natural compounds. Some groups have attempted to suspend fertilizer nanoparticulates within the organic matrix, while others have actually reacted phosphoric acid with the absorbent compound itself. For example, Zhong et al. (2013) used a sulfonated corn starch based superabsorbent material to suspend rock phosphate passed through a 200 mesh screen. The material was dried but could absorb ~300x its own mass in water keeping moisture in the soil while slowly releasing P. Water soluble P was increased 6x as compared to normal rock phosphate but still only comprised 6% of

total P in the material. Zhan et al. (2004) on the other hand reacted phosphoric acid with polyvinyl alcohol to create a material with a maximum water absorption capacity of 480x its own mass that significantly slowed evaporation when applied to soil and exhibited slow release capabilities. Containing a total content of 13.6% P, when placed in a beaker of water, roughly one quarter of that total was released over the first twenty-four hours, while 79% had been discharged at the end of 28 days.

Unfortunately, the P supply efficacy of many of these materials have not really been tested in soil making evaluation of their current promise challenging. Additionally, the impact of some of these organic compounds on long- and short-term soil health remains to adequately assessed. Some suggest that soil physical properties, such as aggregation and water supply capacity, can be greatly enhanced, but the response of components, like the soil microbial community, require investigation (Wilske et al., 2014).

#### **Metal-Organic Frameworks**

Metal-organic frameworks are porous, crystalline precipitates of metal cations and organic, anionic "linkers." While more than 20,000 different forms have been discovered, many designed for industrial uses are composed of environmentally toxic transition metals and petroleum derived carbon-based anions. Some, though, have been developed in recent years that solely contain plant nutrients and/or carry useful agrochemical products that are easily decomposed by soil microbes (Yang et al., 2017; Xie et al., 2017). Because simple adjustments to synthesis techniques (e.g. reaction temperature, metal cation, organic anion) often allow for tuning the material's structure to control aspects like pore size and surface area, these materials have become increasingly attractive for researchers searching for new P fertilizers (Anstoetz et al., 2016).

Anstoetz et al. (2015) synthesized an oxalate-phosphate-amine metal-organic framework (OPA-MOF) (12.5% P) in an attempt to create a fertilizer that slowly released both N in the form of urea and OP as the oxalate scaffold of the material decomposes. Wheat (*Triticum aestivum* L.) pot trials in a Rhodic Ferralsol harvested at maturity and six weeks after sowing showed OPA-MOF addition increased yield and biomass as compared to control and nitrogen only treatments but less than P only and N+P amendment. These results suggest that in severely P deficient soils the OPA-MOF may be incapable of supplying P at a rate adequate for maximal plant growth. Testing in under different conditions is advised. For example, Fe<sup>3+</sup>, an important element of the OPA-MOF structure, would be released upon decomposition as well and may be useful in alkaline soils where Fe deficiency is often a problem. Further research on the impact of changing the molar ratio of urea as the structure-directing agent in the initial synthesis solution has produced results that are somewhat inconclusive to date. The urea content may alter the crystallite structure, final P and N content, and solubility of the resulting material. Refinement of this process could lead to a product that supplies both N and P at rates more optimal for crop production (Anstoetz et al., 2016, Usman et al., 2018).

As with other absorbent structures discussed in this paper, MOFs have been applied to P wastewater recovery efforts, too. Xie et al. (2017) investigated Fe-terephthalic acid and Fe- 2aminoterephthalic acid P sorption properties in eutrophic waters with reasonable success. The recovery products utility for future ag application remains to be seen as desorption from the Fe-P bond is slow. Perhaps potential exists for removing P from the loaded sorbent and repackaging the recovered product for field application.

### **Minerals of Limited Solubility**

Selective use of sparingly soluble phosphate minerals may provide a pool of OP that supplies nutrition later in the growing season or in subsequent cropping systems and/or recycle P in waste-streams that currently are being disposed of in a globally irresponsible manner.

### **Mineral Wastewater Recovery Products**

Management of human and animal waste on farms and in populous areas is a worldwide challenge. Historically, in addition to application to farmlands, significant portions of the nutrient rich material have been disposed of in landfills, incinerated, and discharged to the oceans (Paramashivam et al., 2017). These "solutions" represent large leaks in the global P budget. Increased use in agricultural systems is often hampered by the bulky nature of the manure making economical transport and field application untenable, N to P ratios ill-matched to crop demand, and increased real and perceived concern regarding soil/food contamination with toxic trace elements, pathogens and/or synthetic organic compounds (e.g. antibiotics and personal care products) (Paramashivam et al., 2017). As a result, a variety of approaches are being pursued to process the material into more concentrated, clean agricultural fertilizers. Szogi et al. (2015) nicely outlines many methods under development for animal manures, while Bunce et al. (2018) goes into detail surrounding human wastewater treatment plants and potential applications for small-scale domestic systems.

Of all the wastewater recovery processes being researched, struvite precipitation has received the majority of attention in regards to testing as a P fertilizer. With a chemical formula of MgNH<sub>4</sub>PO<sub>4</sub>•6H<sub>2</sub>O, the product possesses the ability to simultaneously supply three nutrients essential to plant growth. Synthesized via precipitation in wastewater or anion exchange sorbent eluant typically by either addition of high concentrations of MgCl<sub>2</sub> followed by

raising the pH with base (e.g. NaOH or KOH), or adding Mg in the form of MgO or Mg(OH)<sub>2</sub> and allowing the pH to increase naturally, the fertilizer has frequently been reported to perform as well as more conventional acidulated fertilizer products when ground and blended into soils (Ackerman et al., 2013; Antonini et al., 2012; Degryse et al., 2017; Le Corre et al., 2009; Sengupta and Pandit, 2011). Applied as granules, as dry fertilizers in agronomic situations commonly are, performance is often compromised however (Ackerman et al., 2013; Degryse et al., 2017, Everaert et al., 2017, Talboys et al., 2016).

With a solubility of 5% or less in distilled water but highly soluble in citric acid, the effectiveness of struvite granules appears to be greatly dependent upon soil conditions, cropping system, and the production method (Antonini et al., 2012; Degryse et al., 2017, Everaert et al., 2017; Talboys et al., 2016). For example, Everaert et al. (2017) observed that struvite granules in 100 day Petri dish incubation experiment showed less diffusion than MAP but greater lability in the soil < 8mm from the point of application. This is likely due to the fact that the granule did not completely dissolve in the acid, neutral, or calcareous soils tested. The grinding of the soil after incubation, use of a wide solution:soil ratio in extractions, and mixing of the excavated sample likely induced P dissolution beyond what would actually occur in an agricultural soil. Struvite diffusion distance from the point of application in each soil followed the pH order neutral > acid > calcareous, while lability favored the acid soil followed by the neutral and then calcareous. Struvite becomes more soluble as pH decreases, so this observation is not surprising (Lindsay, 1979).

According to Talboys et al. (2016), only roughly a third of struvite granules dissolved in a Eutric Cambisol (pH 6.0) in a 90 day spring wheat experiment and could be physically recovered while TSP granules could not. Further pot trials with buckwheat (*Fagopyrum* 

*esculentum*) exhibited P uptake comparable to diammonium phosphate (DAP), while spring wheat (*Triticum aestivum*) uptake was significantly diminished when struvite was the sole source of P. Lab dissolution experiments with a variety of naturally occurring low molecular weight organic acids (LMWOAs) revealed greater dissolution of struvite relative to pure water and infinite sink anion exchange resin results. Since buckwheat is known to exude LMOAS in greater quantities than spring wheat, the authors suggest that struvite might be a more appropriate fertilizer for some crops rather than others. Variable ability of different crop species to access sparingly soluble forms of P has been demonstrated elsewhere as well (Wang et al., 2011). This mechanism is further supported by μCT scan experiments by Ahmed et al. (2016) where struvite dissolution was not really observed until roots proliferated in close proximity to the granule. Solution P depletion creating a strong gradient promoting faster dissolution is also possible. It is likely that multiple factors are contributing to this observation.

As far as synthesis method is concerned. Those granules precipitated using MgCl<sub>2</sub> or exactly appropriate amounts of MgO perform better as those with excess MgO. The remaining base in the excess MgO treatments produce zones of increased pH that are counterproductive to struvite dissolution (Degryse et al., 2017). Regardless of conditions, most pot trials using granules fail to produce aboveground biomass equivalent to products like MAP. Under acidic conditions, Degryse et al. (2017) did find that grinding struvite produced comparable biomass to MAP suggesting that particle size be seriously considered when applying this product. Dissolution also appears to be accelerated by soils with high sorption capacity (Degryse et al., 2017; Everaert et al., 2017). As a way to integrate some of this waste stream recovery product into agricultural systems, Talboys et al. (2016) suggests that potentially blending the more traditional granular fertilizers with struvite may provide early and late season release. In their

study, early P uptake matched 100% DAP when 20:80 Struvite:DAP mixture was used. Important to note, DAP can inhibit struvite dissolution early on due to high solution P concentrations if the granules are collocated.

A smaller number of studies have looked at the agronomic effectiveness of calcium phosphate precipitates from wastes as well. Much like struvite, the water solubility of the products is low, but citrate solubility is very high (> 90%) suggesting that their utility will be best under more acid conditions and/or in concert with plant root LMWOA exudation (Szogi et al., 2010). Szogi et al. (2012) compared recovered Ca-P from swine and broiler manure to TSP and fresh broiler litter in vertical column studies filled with a sandy, coastal plains soil and found that when applied at a high rate  $(170 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1})$ , all were able to adequately supply cotton for the eight-week trial; P uptake and biomass exhibited no significant difference. Triple superphosphate did appear to leach further down the soil profile than the recovered products and all remained relatively labile according to Mehlich-3 extraction. Assessment of the true performance of the waste products is challenging however as the fertilizers were thoroughly mixed with top 15cm of soil and a very high rate of application was used. As has been noted before, unrealistic application methods obscure interpretation for real world use. Additionally, use of the acidic Mehlich-3 extraction (pH = 2.5) as an assessment of P plant availability may be suspect in experiments where short incubation periods are used. If the sparingly water-soluble recovery products did not completely dissolve in the sandy soil after the approximately two month experiment, the low pH extractant solution is likely to remove the remaining fertilizer and thus overpredict the amount of P that is truly available for plant uptake. The evidence is convincing though that these products can play a role in supplying P nutrition. Identifying the systems where they will be most effective will be key.

### Nano-Hydroxyapatite

Several studies have looked at the use of nano-hydroxyapatite (nHAP) as a way of turning a P source of little agronomic value to annual cropping systems into something cheap and effective for developing countries growing crops in highly weather soils (Montalvo et al. 2014b). The behavior of these particles upon addition to soil is complex. Wang et al. (2015) used columns of sand to highlight that pH, organic matter concentration/composition, and the presence of mineral colloids, such as goethite, can dramatically alter the ability of these particles to move in the profile and supply dissolved phosphate ions to plants. Application under basic conditions (pH = 10.5) prevented aggregation of particles enabling greater movement through pore channels, but HAP is highly insoluble under these conditions. The opposite was true at pH = 6.5. Particles agglomerated and did not transport well, but 10% of the material dissolved and thus would have been available for plant uptake. Montalvo et al. (2014b) explored nHAP movement relative to bulk HAP and triple superphosphate (TSP) in Andisols and Oxisols using both column experiments and a wheat pot study. A 0.1M trisodium citrate capping agent was used in an attempt to prevent nanoparticle aggregation; this was only marginally effective. The nHAP moved more readily than TSP in the Andisol column, however the opposite was observed in the Oxisol. Further investigation confirmed this was due to particulate, rather than soluble anion, translocation. Very few particles were found in the Oxisol leachate, and bulk HAP particles did not move in either column. The Andisol had a much higher OC concentration and lower bulk density that may have facilitated NP transport. Organic carbon compounds have been demonstrated to prevent NP clustering and promote blocking behavior in previous column studies (Wang et al., 2015). Wheat shoot biomass and P uptake at six weeks followed the general trend TSP  $\geq$  nHAP  $\geq$  bulk HAP. Liu and Lal (2014) demonstrated the capacity of nHAP applied

in a carboxymethyl cellulose solution to match the performance of dissolved Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> in a greenhouse pot study of soybean (*Glycine max*) utilizing a peat moss/ perlite growing medium. Phosphorus lost to leaching was not quantified unfortunately, so the final results are likely confounded if one P source preferentially leached from the porous material. A mildly and highly calcareous soil (7.1% and 34.7% respectively) soil were used to compare P supply capacities of phosphoric acid and nHAP to lettuce plants by Taskin et al. (2018). As was the case in the Lui and Lal (2014) study, biomass production seemed to increase in nHAP treatments but the results were not statistically significant. Potential appears to exist for application of nHAP to some soils, but further work is necessary to establish the fertilizer formulation, soil type, and growing conditions under which benefit can be reliably expected.

It should be noted that work is also going on to create urea-nHAP hybrids that show tremendous promise as a slower release source of N (Kottegoda et al., 2017). The symbiotic relationship of the co-application on the dynamics of the P component still needs to be quantified.

## **Blockers**

Much research has been dedicated to the idea that coaddition of large, carbon-based compounds possessing high negative charge with phosphate will block fixation reactions caused by antagonistic polyvalent cations (e.g.  $Ca^{2+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$ ) and ultimately lead to improved P lability. Evidence of the success of this approach is limited. Two of the major categories are described below.

#### AVAIL®

AVAIL® is a high negative charge density (1000 cmol<sub>c</sub> kg<sup>-</sup> at pH 6.2), maleic-itaconic, biodegradable polymer produced by Verdesian Life Sciences LLC (Doydora et al., 2017). When applied as a coating to fertilizer granules or mixed with liquid formulations, such as ammonium polyphosphate, the product is intended to complex antagonistic polyvalent cations in soil solution and/or compete for highly reactive, inner-sphere sorption sites on colloids to mitigate slowly reversible P fixation reactions (Doydora et al., 2017; Gordon, 2007). The validity of this product and mechanism of action is contested however as a result of claims made of experiments displaying a wide spectrum of methodological quality and results. A cohort of researchers argue that AVAIL demonstrates no reliable positive response, while several field-level studies suggest that under certain cropping systems, soil types, organic matter concentrations, moisture levels, and total P statuses increases in yield and P uptake are observable (Chien et al., 2014; Sanders et al., 2012). A meta-analysis of 503 published field studies by Hopkins et al. (2017) combed through as much available experimental data as was obtainable to show that under conditions of low soil test P, extreme pH (i.e. acid or alkaline conditions), and low fertilizer application rate, the average yield increase over a variety of crops was 4.6% compared to 2.1% when the entire dataset was applied. This paper highlights an important point that is not stated enough when evaluating these kinds of products: the conditions under which improved efficiency concepts are tested need to be such that an effect could reasonably be observed. Testing a product under high soil test phosphorus with a high fertilizer rate and concluding no treatment effect is in a way intellectually dishonest and counterproductive because there would be no reason for an effect to be observed (i.e. all of the P requirement would be satisfied with or without the fertilizer enhancement product). Whether or not a 4.6% increase in yield is economically viable for farmers is a concern specific to individual cropping systems (Hopkins et al., 2017). Opponents of the product state that an increase this low is well within the natural variance that could be observed of any set of studies and thus is insufficient to promote to farmers (Chien et al., 2014).

Laboratory scale and theoretical studies exploring the proposed mechanism of action for increased P use efficiency resulting in the observed increase in yield have not found conclusive evidence for the reduction in P fixation hypothesis (Chien and Rehm, 2016; Degryse et al. 2013; Doydora et al., 2017; Pierzynski and Hettiarachchi, 2018). Many reasons for this are possible. One is that the proposed mechanism is incorrect and the beneficial effect of Avail under certain conditions is due to an unknown mechanism. Experiments and stability constant calculations indicate that the concentration of antagonistic polyvalent cations in soils are too high and that their affinity for phosphate is too strong for a logistically feasible amount of maleic-itaconic polymer to be added and make a noticeable impact on P behavior (Chien and Rehm, 2016; Degryse et al., 2013; Doydora et al., 2017). The product is simply overwhelmed. Murphy and Sanders (2007) present very preliminary, basic evidence suggesting that under acid conditions, Avail may reduce aluminum toxicity. Another explanation could be that most of the lab-based studies do not include a live plant component. Degryse et al. (2013) did investigate Avail in a pot trial and found no benefit to adding the product but the wheat seedlings (Triticum aestivum L. 'Frame') were only grown to six weeks in 300g of soil. Pot trials have their limitations when it comes to field applicability and considering the plants were not grown to maturity, it is difficult to say why no effect was observed (Poorter et al., 2012). Perhaps the three soils tested were not responsive to the AVAIL mode of action, possibly there is a late season advantage, or a benefit that does not apply to wheat that is accounting for the successful field studies. More thoughtful, well designed experimentation will be necessary to establish the relevance of this product to improving P fertilization practices.

### **Humic Substances**

Some of the more controversial products sold to enhance fertilizer efficacy that frequently receive attention are the humic substances. Defined by the International Humic Substances Society (http://humic-substances.org/ - accessed 30 Jan. 2019) as "complex and heterogeneous mixtures of polydispersed materials formed in soils, sediments, and natural waters by biochemical and chemical reactions during the decay and transformation of plant and microbial remains." Growers and scientists are currently working to parse if the commercial versions of these products reliably confer benefit to cropping systems, and if so, what the mechanism of action may be (Lyons and Genc, 2016). One common hypothesis is that the high cation exchange capacity associated with many of these substances outcompetes P and blocks reactions with iron and aluminum in acid soils and calcium in calcareous soils (Lyons and Genc, 2016). Similar to Avail, Degryse et al. (2013) concluded that this mechanism to prevent fixation was likely not viable, though humic substances were not specifically vetted. Others have been unable to demonstrate the utility of this mechanism as well, but results in some published studies do suggest that humic substances or at least elevated levels of soil organic matter do seem to increase P extractability (Borggaard et al., 2005; Delgado et al., 2002; Guedes et al., 2016; Weeks and Hettiarachchi, 2018). Possible explanations for the discrepancies and constant debates are that the humic substances simply cannot economically be applied at the rates required to occupy the myriad sites available for reaction in soil, the organic matter content and inherent properties of the study soil are confounding the treatment effects, inconsistency in how P recovery is quantified, and/or that the range of products sold are not chemically similar enough to provide consistent results across studies. Humic and fulvic acid labels are operationally defined by their extraction procedures, so depending on the starting material and exact methods

employed, the final products could be quite dissimilar. Additionally, if cation sequestration is not the mechanism, others including stimulation of soil microbiota and plant hormonal interactions are postulated as well (Calvo et al., 2014).

### Inducers

Some researchers believe that one key to improved P cycling and efficiency in agricultural systems actually comes in the form of stimulating natural biogeochemical processes using compounds that do not contain P at all.

## "Oxide" Nanoparticles

A body of research is growing surrounding the soil application of nanoparticles that do not include P to induce greater recovery of P from plant unavailable pools. Anatase (TiO<sub>2</sub>), magnetite (Fe<sub>2</sub>O<sub>3</sub>), ZnO, and copper nanoparticles are among those most often investigated (Servin et al., 2015). The mechanisms of action are not abundantly clear and may vary by NP, crop, and soil type, but the evidence seems to be convincing that, at least in some cases, treatment effects are significant. Raliya et al. (2016) demonstrated in a greenhouse study of a sandy loam soil amended with manure that that foliar applications zinc oxide (ZnO) nanofertilizers synthesized by soil fungus Aspergillus fumigatus substantially increased above and belowground biomass production and yield of mung bean compared to both the no zinc added control and foliar application of bulk ZnO (size distribution was not reported) particles applied at the same concentration. Additionally, acid phosphatase, alkaline phosphatase, phytase, and dehydrogenase enzymatic activity in rhizosphere soil of ZnO NP treatments greatly increased along with the populations of fungi, bacteria, and actinomycetes. As a combined result of all these parameters, total P uptake was increased by ~11% as compared to control, while the bulk ZnO only increased P uptake by  $\sim 2\%$ . The authors attributed the results to nanoparticles

increased transport through the leaves, enhanced intracellular movement, greater ease of dissolution, and surface  $\zeta$  potential. Zahra et al. (2015) reported increased biomass production and P uptake in *Lactuca sativa* grown in a sandy loam amended with Fe<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub> nanoparticles. Further investigation of nano-TiO<sub>2</sub> by the same first author coupled with metabolomic analysis suggests that internal biochemical pathways are altered by the presence of these compounds. Whether this is in response to stress or a different mode of action is currently unclear (Zahra et al., 2017). Hanif et al. (2015) observed little change in Olsen extractable P but significant increased biomass production with application of TiO<sub>2</sub> and almost a full unit drop in soil pH after cultivation of Lactuca sativa in soil amended at 100 mg kg<sup>-1</sup>. The authors attributed the results to exudation of organic acids causing the acidification and subsequent P release.

Important to note that most of these studies are greenhouse pot studies that use relatively small volumes of soil. Raliya et al. (2016) doesn't report soil volume/mass and Zahra et al. (2015) grew one plant per pot but in only 300g of soil. As briefly mentioned previously, it is well known that small soil volumes in pots can create root bound effects limiting the field interpretation of greenhouse studies (Poorter et al., 2012). These investigations provide provocative results that should be explored but need to be critically evaluated further for useful applications to be developed.

### Alternative P

In nature, plants primarily utilize orthophosphate in the  $H_2PO_4^-$  and  $HPO_4^{-2}$  chemical forms. In recent years, systems utilizing more reduced forms of P (e.g. P(III) instead of P(V)) have been investigated.

### **Polyphosphates**

Ammonium polyphosphate is one of the most popular forms of liquid P fertilizer on the market today. Containing approximately one-quarter to one-half OP and the remainder polyphosphates (e.g. pyrophosphate, triphosphate) the fertilizer is typically chosen by farmers based on price per unit P and preferred application method, rather than the agronomic efficiency (IPNI). The condensed forms of P typically are oxidized to OP by enzymes released from soil microorganisms and plant roots. How quickly the conversion proceeds depends on environmental conditions such as temperature, P concentration, and pH (Dick and Tabatabai, 1986; McBeath et al., 2006; McBeath et al., 2009). One concern often raised is that because PP must go through the hydrolysis step for the nutrient to become plant available, early season growth may be compromised when this reaction is slow (McBeath et al. 2006). Whether or not the use of polyphosphates improves P acquisition efficiency is debated and certainly depends on soil conditions and cropping system. At least part of the confusion in both the scientific and grower community stems from the fact that liquid and granular P products can perform very differently in high P fixing soils (Lombi et al., 2004; Hettiarachchi et al., 2006; Montalvo et al., 2014; Pierzynski and Hettiarachchi, 2018). In lab-based incubation studies, Weeks and Hettiarachci (2017) demonstrated that the presence of polyphosphates in liquid formulations, even at concentrations as low as ~10% of total P, may dramatically reduce P precipitation as Ca-P relative to technical grade MAP in a calcareous soil. One hypothesis is that PP disrupt the crystal structure of Ca-P minerals rendering them more soluble (Fleisch et al., 1968). This advantage is not apparent, and PP application may even be detrimental in some iron and aluminum rich, acid soils where inner-sphere complexation is the dominant mechanism of fixation (Montalvo et al., 2014; Weeks and Hettiarachchi, 2018). Sorption experiments by

McBeath et al. (2007) show that PP and OP behavior can vary widely with soil characteristics beyond simply differences in pH as well. At this point, enough data does not exist to definitely determine exactly how the polyphosphates behave once applied to soil. Because polyphosphates are typically not used in granular form and orthophosphate based liquid fertilizers are less common, the liquid/granule and ortho-/polyphosphate impacts become confounded in studies that compare granular vs. liquid without adequate controls. Pot trials presented by Holloway et al. (2001) nicely illustrate that formulation by speciation interactions can be significant or not in soils of various characteristics. Polyphosphate species likely matters as well (Dick and Tabatabai, 1986; Torres-Dorante et al., 2006). Surely more lab and field work will be necessary to gain a nuanced understanding as to when the use of condensed P may be beneficial.

#### **Phosphorus Acid / Phosphite**

Application of phosphite (HPO<sub>3</sub><sup>2-</sup>) (Phi) salts as a source of P fertility in agricultural systems dates back to around the end of the Second World War and has produced highly variable results in traditional agriculture systems (Morton and Edwards, 2005; Thao and Yamakawa, 2009). Because Phi can be taken up by plants in roots and leaves but cannot replace orthophosphate in metabolic functions, the exact explanation for the inconsistent observations is complex (Ouimette and Coffey, 1990). When applied to crops on soil with sufficient OP availability, Phi may act as a fungicide that prevents negative effects of even minor infections by Oomycetes, like Pythophthora (Forster et al., 1998). Plants grown under low P status conditions where Phi has been applied, however, can do more poorly even when only a small fraction of total P is supplemented with Phi (Avila et al., 2012; Macintire et al., 1950). This is likely due to attenuation of the plant's phosphorus starvation response systems, such as release of enzymes to metabolize exogeneous nucleic acids and alterations of root morphology, that would normally attempt to compensate for low internal P status. As a result, P deficiency in crops is exacerbated as the plant's biochemical gene control systems "think" their P status is sufficient while not actually being able to use the P that is present (Ticconi et al., 2001). Once in the soil, Phi can remain several months before conversion to OP via bacterial oxidation rendering it's use as a fertilizer minimal in the growing season of application (Adams and Conrad, 1953).

Advancements in biotechnology may possess the ability to change the game in this arena, though. Considering Phi is a significant waste product of the chemical and automotive industry, being able to utilize the chemical as a plant nutrient would be a substantial step in the direction of closing the global P cycle and improving overall use efficiency (Kuroda and Hirota, 2015). Originally developed by Lopez-Arredondo and Herrera-Estrella (2012) in Arabidopsis, Manna et al. was able to successfully incorporate a codon optimized version of the PtxD gene from Pseudomonas stutzeri into rice (Oryza sativa) via an Agrobacterium tumefaciens mediated transformation in 2016. The gene codes for the production of the enzyme, Phi dehydrogenase, allowing the plant to catalyze the oxidation of Phi to OP internally, thus alleviating the deficiency issues observed in the original studies that investigated Phi as source of fertility. Further successful incorporation has been conducted in maize and cotton as well (Nahampun et al., 2016; Pandeya et al., 2018). Phosphite concentration in transgenic above-ground tissue was below detection limits but was present in wild type controls suggesting successful metabolism of Phi to OP in these trials and no risk to consumers (Lopez-Arredondo and Herrera-Estrella, 2012; Manna et al., 2016).

The benefits of using a Phi based P fertility system are not limited solely to diversification of P sources and fungal management. Weed growth also appears to be greatly suppressed, but not completely eliminated when Phi was applied relative to OP. Growth of

cotton, tobacco, and rice in competition experiments was significantly enhanced as a result of the reduced weed performance (Lopez-Arredondo and Herrera-Estrella, 2012; Manna et al. 2016; Pandeya et al., 2018). Both pre- and post-emergent control has been observed using Phi foliar application in greenhouse pot trials while simultaneously supplying adequate nutrition to the transgenic plants (Lopez-Arredondo and Herrera-Estrella, 2012; Manna et al. 2016). Because weeds cannot use the applied Phi, control is enhanced as crop canopy develops through increased shading further bolstering crop competitiveness (Pandeya et al., 2018). One concern of soil applying Phi is that repeated use could lead to a buildup of OP over time as soil microorganisms oxidize the reduced P species (Lopez-Arredondo and Herrera-Estrella, 2012; MacIntire et al., 1950). The impact of this on the efficacy of the transgenic approach is uncertain at this time and likely to be a function, at least in part, of inherent soil properties (MacIntire et al., 1950). There is a derth of investigations into Phi behavior in soils, but work completed by Rothaum and Ballie (1964) suggests that Phi binds less strongly to colloids than does OP. This may mean that less total P, relative to OP-based systems, will need to be added to achieve comparable or greater crop yields especially in soils with high fixation capacity (Lopez-Arredondo and Herrera-Estrella, 2012). Additionally, this would suggest that diffusion distance from the point of application might be greater under certain conditions possibly resulting in greater crop root interception and exploitation.

Additionally, surface water pollution may be mitigated by these systems as well. What Phi does runoff or leach may be more biologically relevant than OP. Because Phi is not metabolized by algae, algal bloom issues might be lessened in freshwater systems. Results suggest that the reduced compound is not toxic but appears to inhibit growth through competition with Pi much like the results of the reported terrestrial experiments (Loera-Quezada et al., 2015).

The rate of microbial oxidation from Phi to OP will likely dictate the efficacy with respect to this facet of the proposed system.

Field scale trials are mandatory to determine whether this fertility system is to be truly viable in the future (Lopez-Arredondo and Herrera-Estrella, 2012; Manna et al., 2016). There may be potential for creative applications of this technology to supplement current practices. For example, MacIntire et al. (1950) shows Phi is not useful or is detrimental to non-transgenic crops in first year but can provide similar performance to OP-based fertilizers in the second crop. Questions such as, could Phi be used in rotation systems like corn-soybean where P is only applied every other year to better supply second year crop, or be implemented in perennial stands, like alfalfa, to avoid competition in the year of establishment? remain to be answered.

## Conclusions

Phosphorus management in agricultural soils is never going to be simple, and one single solution whether outlined here or yet to be developed is not likely to solve the issue of providing all crops with optimal fertility without loss to the environment. The vast array of ideas being investigated is encouraging and opportunities for use of advancements in artificial intelligence and machine learning to elicit complex environmental biotic-abiotic interactions is exciting as well (Liakos et al., 2018 and Nelson et al., 2018).

One point that the authors wish to note is how diverse the disciplinary landscape is with respect to work on these materials. Many forms of chemists, engineers and agronomists are working in good faith to make progress in this arena but often the lack of interdisciplinary collaboration that would allow for greatly strengthened results with very little additional effort. While understanding that no study can be completely perfect, too frequently pieces are missing

that obscure interpretation of how the product will actually perform in real field situations. At the risk of sounding cliché, we strongly encourage more intentional formation of transdisciplinary research consortiums that use the collective knowledge of each group to make functional and useful products.

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# Chapter 3 - Exploring Phosphorus Fertilizer Lability in Mildly Calcareous Soils Through Simple Formulation Changes

# Abstract

Phosphorus fertilizer use efficiency is poor in many calcareous soils mainly as a result of precipitation reactions between the phosphate anion and calcium that limit the nutrient's availability to plants. In response to concern of crop P deficiency, growers tend to apply more than is necessary creating a surplus of P in soil that is not labile but can still erode or leach into nearby waterbodies compromising drinking water quality, recreational activities, and aquatic wildlife. This study investigated the effects of fertilizer type, application volume, and coapplication of a carbon-based gelling agent on phosphorus fixation reactions in a mildly calcareous soil from western Kansas. Technical grade monoammonium phosphate (MAP), technical grade diammonium phosphate (DAP), ammonium polyphosphate (APP), and an 80/20 MAP/APP mixture were applied at one P rate over two total solution volumes in addition to coapplication with alginate. Soils were incubated for four weeks in petri dishes and then sectioned in concentric rings from the point of application. Anion exchange resin extractability as a percent of total P assessed potential plant availability, total elemental determination evaluated P diffusion, and synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy was implemented to probe reaction products and pathways along with a suite of other wet chemical analyses. Blending small amounts of polyphosphates into orthophosphate fertilizers, co-application of gelling agents, and increasing application volumes by diluting with water all appear to significantly reduce fixation. Improved performance may be accomplished through a combination of at least two mechanisms: retarded ripening of calcium phosphate minerals to sparingly soluble forms and redirected partitioning to outer-sphere complexes on soil colloids.

Scaling these concepts to the field could result in significant fertilizer cost savings to farmers as well as prevent P loading of calcareous soils that eventually could threaten freshwater ecosystem health.

# Introduction

The development of cost effective, concentrated phosphorus fertilizers has been tremendously important in the fight to eradicate hunger and improve human nutritional health, but like many other technologies, has inadvertently compromised environmental quality in some areas, particularly freshwater systems. The ongoing algal blooms in Lake Erie are but one example of how costly, not just financially, non-point source nutrient pollution can be (Jarvie et al., 2017). One major barrier to ameliorating the P loss problem is poor alignment of incentive structures between the stakeholders that produce and eat food and the stakeholders of the adversely impacted waterbodies. Farmers do not wish to spend a lot of money on expensive specialty fertilizers that may perform more efficiently but do not provide a greater return on investment than less efficient fertilizers, nor do they want to apply less fertilizer than they think they need and risk reduced yields. Most consumers also do not desire to pay more than absolutely necessary for the food that they eat. Other than imposing governmental regulation on grower practices, which is not ever well received, innovation is necessary to make the less efficient fertilizers better or develop new ones that are so cost effective that adoption becomes not an environmentally conscious choice but a rational business decision.

The lability of P added to calcareous soil as fertilizers is thought to be primarily reduced through two mechanisms: precipitation with calcium (Ca) followed by ripening into mineral of low solubility and inner-sphere, "chemisorption" to Fe and Al oxyhydroxides (Ryan et al., 1985). The degree to which these "fixation" reactions decrease P plant availability is highly dependent upon environmental conditions (e.g. soil pH, mineralogy, rainfall, temperature) but broad improvements in P use efficiency need to come in one of two ways. Firstly and ideally, methods could be found to prevent fixation from taking place. Early progress on this front established the superiority of liquid P applications over granules alleviating P deficiency in wheat grown on highly calcareous, Australian soils (Holloway et al., 2001). More recently, blending orthophosphate with polyphosphates shows promise in keeping P solution activity higher when compared to applications entirely composed of one or the other in calcareous soils (Weeks and Hettiarachchi, 2016). The alternative to preventing fixation, is finding mechanisms by which fixed P can be rereleased to soil solution. Little progress has been made on this front but the use of beneficial microorganisms (e.g. mycorrhizae), including their exudates, may become more common as companies, such as Indigo Ag enter the marketplace.

Since the discovery of the superiority of liquid P to that of granules in calcareous soils, no study has seriously looked at how the concentration of P in that fertilizer impacts performance (Holloway et al., 2001). One reason may be that growers would resist applying greater solution volumes due to the fact that highly concentrated formulations save time by reducing the number of stops required to fertilize a given field. While this concern is valid, if the benefits of increased fertilizer use efficiency and thus lower total fertilizer costs are significant enough, then adoption of the practice is more likely. Applying more dilute solutions of P could prevent P fixation via precipitation by reducing the overall concentration of P at any given point in the soil. Additional solution volume should carry the P further from the point of application and allow for relatively homogenous distribution of the nutrient (Montalvo et al., 2014). Hettiarachchi et al. (2006) observed this advantage when comparing liquid MAP with granular MAP. Further diluting P may provide benefit beyond what was demonstrated in that study.

Another approach is to apply the P in an organic gel matrix that limits the degree to which the nutrient can physically interact with soil constituents. If P can move through soil pores but not diffuse quickly to colloid surfaces, this may delay the rate at which fixation reactions

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proceed forward. Alginate, the agent used in this study, is a natural polysaccharide produced by and extracted from brown algae (e.g. *Laminaria hyperborean*) that is commonly employed in the food industry as a thickening agent and has many applications within pharmaceutical industry such as medication encapsulation. The structure of compound is most basically described as unbranched, linear copolymers of  $\beta$ -D-mannuronic acid and  $\alpha$ -L-guluronic acid linked by 1-4 glycosidic bonds. Alginate possesses a high affinity for divalent cations meaning that an additional benefit may be conferred in that not only would the gel slow the chemical kinetics but the compound may sequester Ca<sup>2+</sup> into the gel matrix keeping P available to soil solution as well (Parreidt et al., 2018).

The objective of this study was to evaluate and investigate the performance of various liquid P fertilizers when applied to a calcareous soil at varying solution volumes and with and without a carbon-based gelling agent.

# **Materials and Methods:**

#### **Experimental Design**

The study consisted of three incubation experiments following the same preparation and treatment protocol. The first, hereon defined as the "Finney 1 - 125" experiment, was composed of twenty-four Petri dishes (88mm diameter and 12.9mm height) packed to a predetermined bulk density of 1.1g cm<sup>-3</sup> with a high pH, calcareous silt loam from Finney County, Kansas (see Table 3.1) prewetted to 18% of maximum water holding capacity by mass (MWHC). After packing, the soils were brought to 50% MWHC, the covers were placed on the dishes, the edges were

Soil	Texture (%) <sup>†</sup>		рН	CaCO <sub>3</sub>	CEC	Resin P	Total P	
	Sand	Silt	Clay	(1:10)	%	cmol kg⁻¹	mg kg⁻¹	mg kg⁻¹
Finney 1	22	56	22	8.7	7.7	18.4	47	744
Finney 2	24	51	25	8.6	10.6	29.1	56	727

Table 3.1 Select properties of calcareous soils collected from Finney County, Kansas.

<sup>†</sup> Texture = soil texture determined by pipette method,  $CaCO_3$  = calcium carbonate percent of total soil mass determined by manometer method; CEC = cation exchange capacity determined by ammonium acetate displacement; Resin P = Resin extractable phosphorus; Total P = Total extractable phosphorus

wrapped in Parafilm, dishes were inverted and allowed to equilibrate at room temperature (~24°C) for at least 24 hours. Treatments were then slowly administered to a small well formed in the soil surface using a syringe at the exact center of the dish. A treatment was defined as enough fertilizer to equal 9.2mg P dissolved in 125µL of E-pure water. The four treatments replicated six times (1 for synchrotron analysis, 5 for wet chemical analysis) consisted of a water only control, technical grade monoammonium phosphate (FisherBrand ACS Grade) (MAP), ammonium polyphosphate (11-37-0 Mosaic formulation) (APP), and an 80/20 blend of the previous two treatments respectively to account for the required amount of P (80/20). Nitrogen was not balanced as this may or may not take place in a field situation. Following treatment administration, Parafilm was again employed to seal dishes edges and mitigate moisture loss. The dishes were wrapped in aluminum foil to prevent light exposure, inverted and incubated for four weeks in the dark at 25°C. Following incubation, the dishes were excavated into four concentric circular sections with radii of 0-8mm, 8-15.5mm, 15.5-27mm and 27mm-dish edge

extending from the POA. The sections were then dried at 40°C, weighed and finely ground with a mortar and pestle. The second incubation from hereon labelled as the "Finney 1 - 625" experiment was comprised of nine dishes prepared and executed in the exact same manner as the first with the exception that a treatment was defined as enough fertilizer to equal 9.2mg P dissolved in 625µL of E-pure water and the treatments replicated three times each included technical grade monoammonium phosphate (FisherBrand ACS Grade) (MAP), technical grade diammonium phosphate (FisherBrand ACS Grade) (DAP), and ammonium polyphosphate (11-37-0 Mosaic formulation) (APP).

The third incubation experiment consisted of thirty-six dishes prepared in the same manner as the previous two, however a similar, but slightly more calcareous soil collected from the same location as the first was used instead, Finney 2. All treatments consisted of 9.2 mg P in 125 $\mu$ L treatment volume, and four fertilizer formulations were investigated: phosphoric acid (FisherBrand) (PA), technical grade monoammonium phosphate (MAP) (FisherBrand ACS Grade), (FisherBrand ACS Grade), ammonium polyphosphate (APP) (11-37-0 Mosaic formulation), and an 80/20 MAP/APP blend (80/20). Food-grade sodium alginate (Landor Trading Co., CAS Number 9005-38-3) was tested as well as a co-additive with the control, MAP, APP, and 80/20 treatments at a rate of 1.25mg per 125 $\mu$ L application. Alginate addition to the solution caused a viscous solution to form. Thus, to apply the treatment a small amount of soil (< 250mg) was required to be excavated from the dish center to accommodate treatment application. Preliminary work suggests that this modification did slightly increase P diffusion to the second section, so only the center (0-8mm) section will be discussed in this paper.

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#### Wet Chemical Analysis

Five replicates of the Finney 1 - 125, three for Finney 1 - 625, and four for Finney 2 - 625125 incubations were utilized for wet chemical analysis. Plant available P was assessed via the anion exchange resin (AER) technique validated by Myers et al. (2005), and total P was extracted with aqua regia followed by subsequent Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) (Varian 720-ES, Santa Clara, CA) analysis (Premarathna et al., 2010). Orthophosphate in resin P extractions was quantified colorimetrically soon after extraction using a Beckman-Coulter DU-800 spectrophotometer (Brea, CA). (Murphy and Riley, 1962). Because the molybdate reactive method is selective for the orthophosphate form and polyphosphates (PP) were included in treatments, AER extraction solutions were further digested after original colorimetric analysis to convert all P in solution to orthophosphate and determine if any condensed phosphates also remained labile (McBeath et al., 2006). A 2.5mL aliquot of AER extractant solution was heated with 400µL of concentrated sulfuric acid to 100°C for one hour. After heating, the solutions were brought to 25mL with E-Pure water and reanalyzed for molybdate reactive P (MRP). The difference between pre- and post-digest MRP in AER extraction solutions was termed "Other P" in acknowledgement of the fact that this process cannot distinguish whether all the P converted was originally PP as organic forms of P present in the soil could have been hydrolyzed as well. A combination electrode (Thermo Scientific Orion Star A111) was used to assess pH in a 1:10 soil:water suspension.

The percent of P added that was recovered in each section and the proportion of P that remains resin extractable were calculated according to the following equations.

Percent (%) P Added = 
$$\frac{(SPT \ x \ SMT) - (SPC \ x \ SMC)}{TPD} x \ 100$$

Where:

SPT = Total P concentration (mg kg<sup>-1</sup>) in the dish section

SMT = Section mass in kg of the treatment

SPC = Average P concentration of all control – water samples + 2 standard deviations

SMC = Section mass average of combined control – water within a section

TPD = Total P recovered in the entire dish

Resin Ext. P as % of Total 
$$= \frac{RPT}{SPT} \times 100$$

Where:

RPT = Resin extractable P concentration (mg kg<sup>-1</sup>) in the dish section

### **Sequential Extraction**

A sequential extraction originally conceived by Baifan and Yichu (1989) and further considered by Shariatmadari et al. (2007) was performed on the 0-8mm section of three replicates of each treatment. Briefly,  $0.500g \pm 0.005$  were weighed into 50mL centrifuge tubes. The soils were then sequentially exposed to a series of four 25mL solutions intended to target specific P species:

- 1.) pH 7.5 0.25M NaHCO<sub>3</sub> (dicalcium phosphate CaHPO<sub>4</sub> 2H<sub>2</sub>O)
   -Shake 1 hour
- 2.) pH 4.2 0.5M NH<sub>4</sub><sup>+</sup>-Acetate (octacalcium phosphate  $Ca_8H_2(PO_4)_6 \bullet 5H_2O$ )

- Shake with solution, wait 4 hours, shake 4 hours

3.) pH 8.2 0.5M NH<sub>4</sub>F (aluminum associated P - Al-P)

- Shake 1 hour

4.) 0.1M NaOH + 0.1M Na<sub>2</sub>CO<sub>3</sub> (iron associated P – Fe–P)

- Shake 2 hours, wait 16 hours, shake 2 hours

5.) "Remaining" (apatite-like Ca-P and P occluded inside Fe and Al oxyhydroxides)

- Summation of steps 1-4 subtracted from total P in section

All samples were centrifuged after extraction at 3200 RCF for 15 minutes and filtered through Whatman No 42 filter papers. Soils were washed twice with 25mL of a saturated sodium chloride solution between extractions, with exception of after the first in which 95% ethyl alcohol was used. All samples were analyzed via ICP-OES for P. Following the conclusion of the procedure the supernatants of steps one and two were digested by combining 2.5mL of solution with 500µL sulfuric acid and heating to 100°C for one hour. Samples pre- and postdigestion were analyzed using Murphy and Riley (1962) to again determine "Other P" in the section. Step one data was highly variable possibly due to polyphosphate hydrolysis postextraction, and therefore is not presented as the data was deemed unreliable.

#### **Synchrotron Investigation**

The synchrotron-based investigations were completed on one replicate for each soil treatment represented. Finney 1 - 125 sample spectra were collected at Beamline 6B1-1 - SXRMB of the Canadian Light Source (Saskatoon, SK), while Finney 1 – 625 and Finney 2 – 125 were collected at Sector 9-BM-B of Advanced Photon Source (Lemont, IL). For Finney 125 – 1, the 0-8mm sections were very finely ground and thinly spread onto carbon tape before being placed under vacuum for analysis. Three X-ray Absorption Near Edge Structure (XANES) scans were taken of each sample at the P K-edge (E0 = 2149eV). A double crystal, indium antimonide/silicon monochromator was utilized to scan an energy range extending from -33.5 to -9.5eV in 2eV steps, -9.5 to 31.5eV in 0.15eV steps and 31.5 to 91.5eV in 0.75eV steps. Each step was integrated over six seconds. In addition to XANES spectra X-ray Fluorescence (XRF) maps were collected for the MAP 125 treatment to probe colocalization of P with Fe, Al, and Ca.

For Finney 1 - 625 and Finney 2 - 125, collection parameters were the same however a double crystal, silicon/silicon monochromator and 4-element Vortex SDD detector were utilized to collect spectra and sample preparation was slightly different. Center section samples were finely ground and pelletized before being attached to carbon tape and placed into a helium filled chamber for analysis.

Background correction and linear combination fitting of the reported spectra using previously collected standards were completed in Athena (v.0.9.25 Ravel and Newville, 2005) according to the concepts set forth by Werner and Prietzel (2015). Two to three scans were merged to limit noise, pre-edge and normalization ranges were allowed to freely fluctuate to best accommodate each individual sample and all spectra were adjusted such that  $E_0$  (2149eV) corresponded to one half the height of the white line peak. Spectra were fit from -20 to 30eV

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relative to  $E_0$ . Fourteen reference spectra were used for linear combination fitting: orthophosphate sorbed to amorphous aluminum oxyhydroxide, orthophosphate sorbed to gibbsite, orthophosphate sorbed to goethite, orthophosphate sorbed to ferrihydrite, orthophosphate sorbed to calcium carbonate, inositol hexaphosphate bridged to montmorillonite by aluminum, orthophosphate bridged to montmorillonite by aluminum, monocalcium phosphate, brushite,  $\beta$ -tricalcium phosphate, octacalcium phosphate, hydroxyapatite, apatite, and calcium pyrophosphate.

#### **Statistics**

All data were analyzed in SAS (SAS 9.4, 2017) through the Proc MIXED procedure. The Tukey Pairwise Method was used for comparison of all treatments at a 0.05 level of significance

# **Results**

# pН

For all experiments, pH significantly decreased with P treatment relative to controls at the point of application (Tables 3.2 and 3.3). Ammonium polyphosphate addition resulted in the most dramatic reduction of close to a full unit drop in the 0-8mm section. Diammonium phosphate was the least acidifying agent, and alginate co-application in some instances caused a very slight pH drop. Phosphoric acid and MAP had a similar effect despite PA initially being a much more acidic product. The tendency of P fertilizers to acidify the POA of alkaline soils is the result of at least three factors working in concert. The first is that phosphate species in the case of PA, MAP and APP themselves are acidic therefore protons are released to solution upon application when the soil pH is greater than the fertilizer pH. Using MAP as an example, the pKa

	Dish Section (mm)					
Treatment †	0-8	8-15	15-27	27-edge		
Control – Water	8.6 a‡	8.8 a	8.7 a	8.5 ab		
<b>MAP 125</b>	8.0 c	8.6 b	8.5 ab	8.4 abc		
APP 125	7.7 e	8.4 bcd	8.4 b	8.4 c		
80/20 125	7.9 d	8.5 bcd	8.5 ab	8.4 bc		
<b>MAP 625</b>	7.9 cd	8.3 de	8.5 ab	8.5 a		
<b>DAP 625</b>	8.3 b	8.4 cd	8.4 b	8.4 abc		
APP 625	7.6 e	8.2 e	8.5 ab	8.5 ab		

Table 3.2 Soil pH after 28-day incubation of phosphorus fertilizers applied to Finney 1soil at four distances from the point of application.

 $\dagger$ MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 =

ammonium phosphate applied in 125 $\mu$ L solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125 $\mu$ L solution volume; MAP 625 = monoammonium phosphate applied in 625 $\mu$ L solution volume; DAP 625 = diammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution volume; APP 625 = ammonium phosphate applied in 625 $\mu$ L solution phosphate applied i

‡Means within a column (dish section) followed by the same letter are not significantly

different at P = 0.05 using Tukey's honest significance test.

	Dish Section (mm)				
Treatment †	0-8	8-15	15-27	27-edge	
Control – Water	8.6 a‡	8.6 a	8.6 a	8.6 a	
<b>Control - Alginate</b>	8.7 a	8.6 a	8.5 ab	8.6 a	
<b>Phosphoric Acid</b>	8.0 b	8.6 a	8.6 a	8.6 a	
MAP	7.9 bc	8.4 b	8.4 bc	8.5 b	
MAP + Alginate	7.8 de	8.3 bc	8.4 cd	8.4 b	
APP	7.6 f	8.3 c	8.4 cd	8.5 b	
APP + Alginate	7.5 f	8.1 d	8.3 d	8.4 b	
80/20	7.8 cd	8.3 bc	8.4 cd	8.5 b	
80/20 + Alginate	7.7 e	8.2 cd	8.4 cd	8.5 b	

Table 3.3 Soil pH after 28-day incubation of phosphorus fertilizers applied to Finney 2soil at four distances from the point of application.

 $\dagger$ MAP = monoammonium phosphate; APP = ammonium phosphate; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate

‡Means within a column (dish section) followed by the same letter are not significantly

different at P = 0.05 using Tukey's honest significance test.

of the transition between diprotonated and monoprotonated phosphate anion is 7.2, therefore when the diprotonated anion is added to the pH  $\sim$ 8.6 soil, H<sup>+</sup> is released, increasing the proton concentration, lowering the pH. Because the P in DAP is already monoprotonated, the pH is not lowered as much as the other treatments. Secondly, ammonium, the complementing cation in MAP, DAP, and APP, releases four protons per nitrogen atom when converted to nitrate during microbial nitrification. The additional nitrifying effect of MAP and the lack of ammonium in the PA treatment may be one reason why their overall treatment effect after four weeks was the same overall. Important to consider is that the conditions upon their addition was likely different. Because PA is highly acidic, the pH reduction was likely more dramatic and the rebound, quicker relative to the MAP application which would have had a less immediate acidifying effect and longer reactive period due to the bacterially mediated aspect of the nitrogen conversion. Finally, in the case of APP addition, the polyphosphates also undergo hydrolysis via exoenzymes like pyrophosphatase. The conversion to OP releases H<sup>+</sup> as a byproduct. All three mechanisms of acidification are working when APP is applied explaining why these treatments had the most significant pH effect.

#### **Diffusion of P Added**

For all experiments, the vast majority of P added to the calcium-rich soil remained within the first section (Figures 3.1 and 3.2). Restricted movement of the nutrient in calcareous soil is well documented and the result of strong precipitation and sorption reactions with calcium in soil solution, solid calcium carbonates, and other colloids (Hettiarachchi et al., 2006; Lombi et al., 2004; Pierzynski and Hettiarachchi, 2019). Additionally, the high clay content not only provides an abundance of reactive sites but increases channel tortuosity that slows radial migration via diffusion and/or mass flow. The same trends were observed by Pierzynski and Hettiarachchi (2019) in similar experiments also conducted on calcareous soils. Increasing the treatment volume significantly increased diffusion thereby enriching a large volume of soil. Similarly, polyphosphate containing (e.g. APP and 80/20) fertilizers permeated out to a greater volume of soil compared to orthophosphate-only formulations. Phosphoric acid-based applications proved most immobile. The lack of migration to the second section observed in the  $125\mu L$ orthophosphate-only treatments may be related to Ca-P precipitation interactions that are mitigated with the addition of extra treatment volume or incorporation of polyphosphates. Calcium phosphate mineral formation may be inhibited by polyphosphates through disruption of crystal structure organization by the larger condensed phosphate molecules (Amer and Mostafa, 1981). The lower P concentration in the initial solution of the 625µL treatments may keep the ion activity product low and the saturation index below zero, slowing development of the three dimensional Ca-P lattice. The increased application volume may move calcium ions released from calcium carbonate dissolution outward by mass flow keeping the polyvalent cation concentration in solution low as well.



Figure 3.1 Percentage of P added recovered in each section of the Finney 1 experiments. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; MAP 625 = monoammonium phosphate applied in 625µL solution volume; DAP 625 = diammonium phosphate applied in 625µL solution volume; APP 625 = ammonium phosphate applied in 625µL solution volume; APP 625 = ammonium



Figure 3.2 Percentage of P added recovered in each section of the Finney 1 experiments. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significance difference in section. Phosphoric Acid = phosphoric acid applied in 125µL solution volume; MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume.

#### **Resin Extractable P**

In terms of resin extractable orthophosphate, 80/20 (Figures 3.3 and 3.4), phosphoric acid (Figure 3.4), MAP 625 (Figure 3.3), MAP125 + Alginate, and 80/20 125 + Alginate (Figure 3.5) treatments all performed similarly with a large portion of the P added remaining labile. Phosphoric acid results were surprising given the limited mobility of the treatment, and the juxtaposition of MAP and DAP in the  $625\mu$ L incubation demonstrates just how important initial P fertilizer acidity and orthophosphate species appears to be. Final pH values all fall with a 0.4 unit range, yet resin extractability widely varied (Figure 3.3). The modification of the microenvironment surrounding the point of application by fertilizer acidity (e.g. dissolution of calcium carbonate) is definitely altering the reactive context. Calcium-phosphate precipitates formed while CaCO<sub>3</sub> is dissolving may result in varied Ca:P ratios and carbonate content. Both factors, as well as pH at the moment of precipitation, would impact the type of Ca-P that forms, mineral crystallinity, and thus stability determining solubility (Baig et al., 1999; Lei et al., 2017; Raynaud et al., 2002; Wang and Nancollas, 2008).

In the 125µL studies, treatments that included polyphosphates performed substantially better than MAP. Since precipitation as Ca-P minerals followed by ripening to sparingly soluble apatite-like minerals is a major mechanism of P fixation in calcium-rich soils, polyphosphates, as suggested above, may be acting as a crystallization inhibitor that disrupts crystal lattice formation keeping P in more soluble forms (Amer and Mostafa, 1981; Philen and Lehr, 1967). Important to note, is that once the "Other P" section is accounted for in APP treatments, their total P lability of that treatment is roughly equal to the other top performers (Figure 3.6). How quickly the conversion of PP to OP proceeds depends on environmental conditions such as temperature, soil type, P concentration, and pH (Dick and Tabatabai, 1986; McBeath et al., 2006; McBeath et al., 2009). One concern often raised is that because PP must go through this hydrolysis step for the nutrient to become useful to plants, early season growth may be compromised when this reaction is slow (McBeath et al., 2006). Whether or not the use of polyphosphates improves P acquisition efficiency is debated and certainly depends on the soil and cropping system. The increased lability of the 80/20 treatments (Figures 3.3 and 3.4), MAP and APP 625 (Figure 3.3), and the alginate (Figure 3.5) treatments, supports the notion that either P fixation occurs rapidly at the POA when fertilizer is applied due to high solution activity of Ca<sup>2+</sup> and P, and that if precipitation can be prevented at this crucial timepoint, t=0, then efficiency for the growing season may be improved, or that these mechanisms are not preventing Ca-P interaction but are slowing conversion of the associate to more stable, less soluble forms.

The increased diffusion afforded by the  $625\mu$ L treatment volume is also reflected in the resin extractability data where not only is the 8-15mm section more enriched with P, but that P appears to be more plant available as well. In the field this may have the overall effect of increased root interception.



Figure 3.3 Resin extractable orthophosphate expressed as a percentage of total P in each section of the Finney 1 experiments. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; MAP 625 = monoammonium phosphate applied in 625µL solution volume; DAP 625 = diammonium phosphate applied in 625µL solution volume; APP



Figure 3.4 Resin extractable orthophosphate expressed as a percentage of total P in each section of the Finney 2 experiment. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. Phosphoric Acid = phosphoric acid applied in 125µL solution volume; MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume



Figure 3.5 Resin extractable orthophosphate expressed as a percentage of total P in the 0-8mm section of the Finney 2 alginate experiment. Means within a soil section for each treatment containing the same letter are not significantly different at P =0.05 using Tukey's honest significance test. MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume



Figure 3.6 Resin extractable P expressed as a percent of P added to the 0-8mm section of Finney experiments. PO4 = orthophosphate; Other P = P recovered after digestion of extract solution. Phosphoric Acid = phosphoric acid applied in  $125\mu$ L solution volume; MAP 125 = monoammonium phosphate applied in  $125\mu$ L solution volume; APP 125 = ammonium phosphate applied in  $125\mu$ L solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in  $125\mu$ L solution volume; MAP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; DAP 625 = diammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume

#### **Sequential Extraction**

Sequential extraction results from the 0-8mm sections indicate that maximum resin extractability was achieved in at least a couple of ways. Figures 3.7 and 3.8 demonstrate that fertilizer type tremendously impacts the soil "pool" in which that P resides at least after the fourweek duration of these incubation experiments. While each subsequent extraction in this series in intended to target specific and more recalcitrant P species, it is important to note that these are operationally defined and that each bar may represent several P chemical forms of similar extractability. This makes interpretation challenging. For example, Finney 1 MAP 125 and APP 125 contained similar amounts P that was extractable in steps 1 and to a lesser extent step 2, but we know APP 125 contained much more resin extractable P. The authors believe that two simultaneous processes are occurring that may provide two separate approaches to improving P resin extractability and potentially use efficiency in this soil. The first mechanism is inhibition of forming stable, crystalline calcium phosphates of low solubility. When comparing the low performing MAP 125 and DAP 625 treatments (Figure 3.7) to those others that contained mostly or entirely orthophosphate (e.g. phosphoric acid, 80/20, MAP 625, MAP + alginate), one can observe that the absolute amount of P extracted in step 1 (amorphous calcium diphosphate) corresponds exceptionally well to the resin extractability (Figure 3.9). This suggests that preventing precipitation and/or retarding ripening of Ca-P to more stable forms, like octacalcium phosphate or apatite, is accomplished by reducing soil solution P concentrations upon application in the 625µL case, physically slowing Ca-P interaction with alginate gels, dissolving calcium carbonate thus eliminating sorption sites with phosphoric acid, or disrupting crystal structure with polyphosphates. All these means seem to reach the same end of slowing stable Ca-P formation or as the sequential extraction suggest, keeping the P in a dicalcium phosphate-like or

at least bicarbonate extractable state. Figure 3.10 demonstrates that APP treatments and to a lesser extent 80/20 harbor a significant amount of resin extractable P in the step 2 extractable "pool." Why is the entire APP step 2 resin extractable, but very little to none in the orthophosphate treatments? Perhaps, in the OP-only treatments the P extracted in step two is mostly Ca-P minerals, such as relatively insoluble octacalcium phosphate, whereas in APP treatments, the condensed phosphates are occupying two roles. The first is that the PP exists in another form that was not bicarbonate exchangeable in the first solution but was still resin extractable (e.g. outer-sphere complexation with iron/aluminum oxyhydroxides or phyllosilicates). The second is that the Ca-P in second section is actually on a solubility spectrum that PP is helping to keep on the more soluble side. This would explain why only a small portion, if any, step 2 extractable P in OP-only treatments is resin extractable, while that portion is slightly more soluble in 80/20 treatments, and most resin extractable in APP; the PP is keeping more stable Ca-P from forming.

Of further interest regarding APP, is that the "Other P" recovered from step 2 when considered as a percentage of the total P concentration was stable across APP treatments regardless of application volume even though the APP 625 samples contained significantly more total resin extractable "Other P" (Table 3.4). The apparent limit on the amount of polyphosphate capable of being relegated to step 2 supports the first assertion in the above paragraph that a sorbed, non-bicarbonate extractable P association exists in APP treatments. It is possible that there are a finite-number sorption sites for this type of reaction that once satisfied push PP to other pools. The reason more polyphosphate remains in the APP 625 samples relative to APP 125 is not abundantly clear. Many factors simultaneously effect the rate of P hydrolysis in calcareous soils (Dick and Tabatabai, 1987). One possibility is that the overall process proceeds

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as first-order reaction. If the concentration of the reactants is directly proportional to the rate at which it proceeds and the P in the  $625\mu$ L application is more diffuse, then conversion would be delayed (Stockbridge and Wolfenden, 2011).

The small addition of PP to the 80/20 treatments is not only evident in the altered step 1 and 2 partitioning but can also be observed in the enrichment of the step 4 extraction targeting Fe-P. When full strength APP is used, step 4 is increased slightly further but the P partitioned to step 3, Al-P, is dramatically increased as well suggesting that PP exhibits a preference for the step 4 extractable species, likely Fe oxyhydroxides, but once those sites are all occupied, then the aluminum interaction becomes important. The total resin extractability of P is greater than the total P extracted in steps 1 and 2 only for APP samples, so perhaps part of the remaining resin "other P" is coming from pools targeted in step 3 and/or 4.

Table 3.4 Proportion of "Other P" in anion exchange resin extraction and sequential
extraction step 2 relation to total P in the 0-8mm section of Finney soil experiments.

Treatment	<b>Resin Extractable Other</b> <b>P as Percent of Total P</b>	SE <sup>†</sup>	Step 2 Other P as a Percent of Total P	SE
	%		%	
1 - APP 125	18	0.5	12	0.1
1 - APP 625	36	0.9	13	0.3
2 - APP 125	20	2.7	14	1.1

† SE = standard error; 1 – APP 125 = ammonium polyphosphate applied to the Finney 1 soil in a 125 $\mu$ L application volume; 1 – APP 625 = ammonium polyphosphate applied to the Finney 1 soil in a 625 $\mu$ L application volume; 2 – APP 125 = ammonium polyphosphate applied to the

# Finney 2 soil in a $125\mu L$ application volume



Figure 3.7 Total P measured in each fraction of sequential extraction performed on 0-8mm section of Finney 1 experiments. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. Ca2-P = dicalcium phosphate; Ca8-P = octacalcium phosphate; Al-P = aluminum associated P; Fe-P = iron associated P; Remaining = summation of P in first four sections subtracted from total P in section. MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; MAP 625 = monoammonium phosphate applied in 625µL solution volume; DAP 625 = diammonium phosphate applied in 625µL solution volume; APP 625 = ammonium phosphate applied in 625µL solution volume



Figure 3.8 Total P measured in each fraction of sequential extraction performed on 0-8mm section of Finney 2 experiments. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. Ca2-P = dicalcium phosphate; Ca8-P = octacalcium phosphate; Al-P = aluminum associated P; Fe-P = iron associated P; Remaining = summation of P in first four sections subtracted from total P in section. Phosphoric Acid = phosphoric acid applied in 125µL solution volume; MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume


Figure 3.9 Comparison of the phosphorus concentration measured in the first step of the sequential extraction as a percent total in the 0-8mm section with the percentage of phosphorus that was resin extractable by P species. OP =orthophosphate-only treatments; APP = ammonium polyphosphate; ; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate



Figure 3.10 Distribution of resin extractable P within steps 1 and 2 of the sequential extraction of 0-8mm section for all Finney experiments. Phosphoric Acid = phosphoric acid applied in  $125\mu$ L solution volume; MAP 125 = monoammonium phosphate applied in  $125\mu$ L solution volume; APP 125 = ammonium phosphate applied in  $125\mu$ L solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in  $125\mu$ L solution volume; MAP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; DAP 625 = diammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = ammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; APP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; MAP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; MAP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; MAP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; MAP 625 = monoammonium phosphate applied in  $625\mu$ L solution volume; MAP  $625\mu$ L solution volum

#### **Synchrotron Analysis**

Synchrotron analysis of the center sections confirms that the majority of phosphorus in all treatments is found in association with calcium either as various Ca-P minerals or sorbed to calcium carbonate (Table 3.5). As expected from the resin extractable "Other P" results, highly soluble calcium pyrophosphate comprised a portion of the 1 - APP 625 and 2 – APP 125 treatments. Why Ca-PP was not found in 1 – APP 125 is not clear, but the slightly poorer LCF fit of spectra from this treatment suggests that perhaps a reference is missing from the procedure (Figure 3.11). Inclusion of PP sorbed species in the future could remedy this issue. To the author's knowledge, these reference spectra do not currently exist.

Incorporation of PP into OP fertilizer appears to decreased the percentage of P associated with calcium and/or increase the sorption of P to colloids (Table 3.5). As stated previously, PP may be preventing calcium phosphate precipitation allowing P to partition to other pools (Amer and Mostafa, 1981). If relegated to largely outer-sphere, reversible interactions, the altered fate helps explain the improved lability of the 125µL polyphosphate treatments compared to MAP 125. Combined with the sequential extraction data, we can be confident that PP shows a greater preference for iron and aluminum than purely orthophosphate-based fertilizers. What remains unclear though, is exactly how the polyphosphate species do partition to these other pools. The sequential extraction data suggest that PP prefers iron over aluminum in all experiments, but the XANES analysis indicates variable Al-P, Fe-P and Clay-Al-P associations. This discrepancy begs the questions, is the sequential extraction not actually pulling P solely from the targeted fractions? Or is the LCF analysis not as sensitive to distinguishing between sorbed forms of P as we would like?



Figure 3.11 Normalized Phosphorus K-edge XANES spectra of 0-8mm sections with results of linear combination (LC) fitting of all Finney experiments. Spectra are arranged in order of resin extractable OP with the greatest extractability placed at the top. Phosphoric Acid = phosphoric acid applied in 125µL solution volume; MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; MAP 625 = monoammonium phosphate applied in 625µL solution volume; DAP 625 = diammonium phosphate applied in 625µL solution volume; APP

Treatment†	Ca- PP‡	МСР	DCP	ОСР	Apatite	CaCO3- P	Clay- Al-P	Fe-P	Al-P	red. X <sup>2</sup>	% Resin OP
1 - 80/20 125	-	-	-	-	39	28	18	14	-	0.0066	66
1 - MAP 625	-	-	19	-	46	-	-	11	25	0.0050	65
2 - Phosphoric Acid	-	39	-	39	-	-	-	-	22	0.0046	60
2 - MAP 125 + Alginate	-	46	-	39	-	-	-	7	9	0.0045	58
1 - APP 125	-	-	-	-	14	42	15	30	-	0.0054	53
2 - APP 125	20	-	-	-	22	29	29	-	-	0.0009	43
1 - APP 625	20	-	-	-	-	40	6	-	34	0.0041	30
2 - MAP 125	-	-	-	23	45		-	17	16	0.0034	40
1 - MAP 125	-	-	-	12	32	50	-	6	-	0.0015	31
1 - DAP 625	-	-	-	-	50	37	-	6	7	0.0067	19

Table 3.5 Linear combination fitting results expressed as a percentage of Total P for all P K-edge spectra collected on the 0-8mm section of Finney experiments after 28-day incubation.

 $\dagger$ MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium

phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; MAP 625 = monoammonium phosphate applied in 625µL solution volume; DAP 625 = diammonium phosphate applied in 625µL solution volume; APP 625 = ammonium phosphate applied in 625µL solution volume

‡Ca-PP = calcium pyrophosphate minerals; MCP = Monocalcium phosphate; DCP = dicalcium phosphate;

 $OCP = octacalcium phosphate; CaCO_3-P = P$  sorbed to calcium carbonate; Ca-PP = calcium pyrophosphate;

Clay-Al-P = aluminum bridged phosphate sorbed to montmorillonite; Fe-P = iron sorbed P; Al-P = aluminum

sorbed P; % Resin OP = percentage of resin extractable orthophosphate relative to total P in the sample

Application of MAP 625, phosphoric acid, and MAP + Alginate seem to result in formation of Ca-P minerals of greater solubility than other orthophosphate-only treatments (Table 3.5) (Lindsay, 1979). This explains why these fertilizers exhibited higher resin and bicarbonate extractability values than the MAP 125 and DAP applications. Either something about MAP 625, phosphoric acid, and MAP + Alginate causes less stabile Ca-P minerals to form relative to MAP 125 and DAP, or that all treatments form these minerals initially and those with lower resin extractability progressed more rapidly to less soluble species. Further study will be required to elicit a more complete explanation.

## Conclusions

To the authors' knowledge, this is the most in-depth study to date exploring the reaction products of P fertilizers in a mildly calcareous soil. Significant differences were observed between types of fertilizers and application techniques. It appears that the same resin extractability is obtainable through preventing calcium phosphate precipitation, slowing Ca-P mineral ripening, and/or storing PP in other reversible "pools." What remains to be seen is whether the chemical differences observed in this study have any impact on actual plant uptake and P use efficiency. Additionally, these studies are one snapshot in time at four weeks after application. Whether P partitioning diverges further based on speciation or converges as the growing season progresses requires further investigations. If the trends observed here persist, one can imagine the need to revisit the use of soil testing solutions, such as Olsen. The sequential extraction steps 1 and 2 data would suggest that if APP is the typical source of fertility, then bicarbonate-based testing extractions could be severely underestimating the amount of P actually available to crops in soils rich in free calcium carbonates. Based on these results, farmers working calcareous soils may find blending polyphosphates into their orthophosphate fertilizers, increasing the amount of water P is applied in, co-application of alginate, or use of phosphoric acid to be effective methods to mitigate fixation and lower total P application requirements.

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# Chapter 4 - Can Humic Substances Alter Fertilizer-Phosphorus Reaction Pathways in Calcareous Soils?

# Abstract

Phosphorus fixation collectively refers to the precipitation and inner-sphere complexation processes that reduce the nutrient's availability to plants and soil biota. In calcareous soils, precipitation tends to dominate due to high concentrations of calcium, while chemisorption often prevails on iron and aluminum oxyhydroxides in acid soils. Finding economical and simple methods that grower's can implement to keep the nutrient in a plant available form will mitigate deficiency, increase yield, lower production costs, and reduce non-point source pollution of nearby surface waters. One proposed solution that often receives attention is to co-apply humic substances either coated on granules or blended into fluid fertilizers to complex antagonistic polyvalent cations that precipitate P and/or compete for high energy sorption sites on soil colloids. This study investigated the effects of fertilizer formulation and commercially available fulvic acid fertilizer enhancement products on phosphorus applied as liquid fertilizers to mildly calcareous soils from western Kansas. Monoammonium phosphate (MAP), diammonium phosphate (DAP), ammonium polyphosphate (APP), phosphoric acid (PA) and an 80/20 MAP/APP mixture (80/20) were applied at two concentrations with and without two commercial fulvic acid products. Soils were incubated for four weeks in Petri dishes and sectioned in concentric rings from the point of application. Anion exchange resin extractability as a percent of total P assessed potential plant availability, while a suite of other assessments, including synchrotron-based K-edge XANES analysis, were employed to investigate P fate and transport. Fulvic acid co-application did not consistently alter lability, but P formulation did. Blending polyphosphates into monoammonium phosphate, increasing application volume, and use of

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phosphoric acid all appear to improve P lability relative to monoammonium and diammonium phosphate. Synchrotron-based XANES analysis does suggest that although P resin extractability was not improved by FA addition, that nutrient's partitioning may have been altered. Further study will be necessary to determine if and how commercial humic substances should be utilized in future agricultural systems.

## Introduction

Significant adoption of phosphorus fertilization practices that increase crop use efficiency and mitigate freshwater pollution are not going to be implemented until at least one of three scenarios comes to fruition: A.) due to limited supply/quality, rock phosphate prices rise causing fertilizer prices to increase to the point that farmers cannot afford to allow any of the nutrient to be wasted, B.) freshwater bodies are polluted to an extent that the economic costs to non-farmers becomes so great that legislatures pass regulations that govern P application practices such as application rates based on total P instead of soil test P, or C.) new methods, such as novel fertilizers and/or fertilizer enhancement products (FEPs), are developed that are economical to purchase and produce such beneficial results that the market guides growers into more environmentally prudent practices that simultaneously widen profit margins. Of the three situations outlined above, scenario C is likely to provide the greatest aggregate benefit to all humans living within a given food production system thus our goal as scientists should be to create the solutions that lead to the market driven outcome.

One of the more controversial FEPs that frequently receives attention is the humic substances. For years, growers and scientists have been attempting to determine if these products are working in the field, and if they are, exactly how (Lyons and Genc, 2016). One possible explanation is that the high cation exchange capacity associated with many of these substances could be blocking P fixation reactions with iron and aluminum in acid soils or calcium in calcareous soils (Lyons and Genc, 2016). Degryse et al. (2013), however, concluded that this mechanism to inhibit fixation was likely not viable, though humic substances were not specifically vetted. Simple calculations demonstrate that the concentration of reactive entities (e.g. calcium cations) in soil solution vastly exceed the reactive sites on humic substances available for chelation. Others have also asserted that many soils contain organic carbon at concentrations far higher than what is added in fertilizer co-application, so perhaps these products are only beneficial in the most carbon deficient agricultural systems; the product effect is diluted beyond detection. If cation sequestration is not the mechanism, others including stimulation of soil microbiota and plant hormonal interactions are equally plausible (Calvo et al., 2014). Most lab-scale, mechanistic studies that have assessed these products have used granules coated with the material. We know that liquid and granular P react differently when applied to calcareous soil, so this study evaluated the impact of co-application of two commercially available fulvic acid (FA) products with common liquid phosphorus fertilizers on P lability in two similar mildly calcareous soils from western Kansas (Hettiarachchi et al., 2006; Holloway et al., 2001). The addition of a sequential extraction and synchrotron-based P K-edge XANES speciation make this study the most detailed investigation of FA on P fertilizer partitioning to date.

## **Materials and Methods**

#### **Experimental Design**

To assess P diffusion and lability, three Petri dish (88mm diameter and 12.9mm height) incubation studies were conducted. All soils (see Table 4.1) were prewetted to 18% maximum water holding capacity (MWHC) and packed in dishes to a bulk density of 1.1g cm<sup>-3</sup>. After packing, the soils were adjusted to 50% MWHC, covered, sealed with Parafilm, and allowed to equilibrate at room temperature (~24°C) for at least 24 hours. Treatments (target: 9.2mg P dissolved in 125µL or 625 µL of ultrapure water) were then slowly applied to the exact center of the dish using a 1mL syringe. Full experimental designs are outlined in Table 4.2. Briefly, a total

of five fertilizer formulations were investigated: phosphoric acid (FisherBrand ACS grade), technical grade monoammonium phosphate (MAP) (FisherBrand ACS Grade), technical grade diammonium phosphate (FisherBrand ACS Grade), ammonium polyphosphate (APP) (11-37-0 Mosaic formulation), and an 80/20 MAP/APP blend (80/20) with and without two commercial FA products: fulvic acid 1 (FA 1) and sub-fraction of fulvic acid (SF FA). One note is that the PA/ SF FA Blend is a product sold as a premixed formulation of PA and SF FA. Following treatment administration, dishes were covered, edges were again sealed with Parafilm and incubated for four weeks in the dark at 25°C. Following incubation, the dishes were excavated into four concentric, circular sections with radii of 0-8mm, 8-15.5mm, 15.5-27mm and 27mm-dish edge extending from the point of application (POA). The sections were then dried at 40°C, weighed, and finely ground.

	Tex	xture (%	6)†	рН	CaCO <sub>3</sub>	CEC	Resin P	Total P
	Sand	Silt	Clay	(1:10)	%	cmol kg⁻¹	mg kg⁻¹	mg kg⁻¹
Finney 1	22	56	22	8.7	7.7	18.4	47	744
Finney 2	24	51	25	8.6	10.6	29.1	56	727

Table 4.1 Select properties of calcareous soils collected from Finney County, KS.

<sup>†</sup> Texture = soil texture determined by pipette method,  $CaCO_3$  = calcium carbonate percent of total soil mass determined by manometer method; CEC = cation exchange capacity determined by ammonium acetate displacement; Resin P = Resin extractable phosphorus; Total P = Total extractable phosphorus

Experiment	Soil	Repetitions	Treatment Volume (µL)	Phosphorus Treatments	FA Treatment (Amount per Application)
1	Finney 1	6 1 – Synchrotron Analysis 5 – Chemical Analysis	125	MAP <sup>†</sup> APP 80/20	<b>FA 1</b> 1Χ (0.73μL)
2	Finney 1	3 (Only 1 included for Control – Water)	625	MAP DAP APP	<b>FA 1</b> 1Χ (0.73μL)
3	Finney 2	4	125	PA MAP APP 80/20	<b>SF FA</b> 1X (0.78µL) and 3X (2.34µL)

# Table 4.2 Experimental parameters for Experiments 1-3.

 $^{\dagger}MAP =$  monoammonium phosphate; DAP = diammonium phosphate; APP = ammonium phosphate; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate; PA = phosphoric acid; FA = fulvic acid; FA 1 = fulvic acid product number 1, SF FA = sub-fraction of fulvic acid product

#### Wet Chemical Analysis

Potentially plant available (labile) P in each soil section was assessed via the anion exchange resin (AER) technique with subsequent colorimetric analysis for molybdate reactive orthophosphate (MRP), and total P in each section was determined by aqua regia digestion followed by ICP-OES analysis (Murphy and Riley 1962, Myers et al., 2005 and Premarathna et al., 2010). Because the molybdate reactive method is selective for the orthophosphate form and polyphosphates (PP) were included in treatments, AER extraction solutions were further digested after original colorimetric analysis to convert all P in solution to orthophosphate and determine if any condensed phosphates had also been extracted. A 2.5mL aliquot of AER extractant solution was heated along with 400µL of concentrated sulfuric acid to 100°C for one hour. After heating, the solutions were brought to 25mL with E-Pure water and reanalyzed for MRP (modified version of McBeath, 2006). The difference between pre- and post-digest MRP in AER extraction solutions was termed "Other P" in acknowledgement of the fact that this process cannot distinguish whether all the P converted was originally PP as forms such as phytic acid present in the soil could have been hydrolyzed as well. An electrode was used to measure pH in a 1:10 soil:water suspension.

The percent of P added that was recovered in each section and the proportion of P that remains resin extractable were calculated according to the following equations.

Percent (%) P Added = 
$$\frac{(SPT \ x \ SMT) - (SPC \ x \ SMC)}{TPD} x \ 100$$

Where:

SPT = Total P concentration (mg kg<sup>-1</sup>) in the dish section

SMT = Section mass in kg of the treatment

SPC = Average P concentration of all control – water samples + 2 standard deviations

SMC = Section mass average of combined control – water within a section

TPD = Total P recovered in the entire dish

Resin Ext. P as % of Total 
$$=$$
  $\frac{RPT}{SPT}$  x 100

Where:

RPT = Resin extractable P concentration (mg kg<sup>-1</sup>) in the dish section

## **Sequential Extraction**

A sequential extraction originally conceived by Baifan and Yichu (1989) and further considered by Shariatmadari et al. (2007) was perform on three replicates of each treatment's center section (0-8mm). Briefly,  $0.500g \pm 0.005$  were weighed into 50mL centrifuge tubes. The soils were then exposed to a series of four 25mL solutions intended to target specific P species:

- 1.) pH 7.5 0.25M NaHCO3 (dicalcium phosphate CaHPO<sub>4</sub> 2H<sub>2</sub>O)
  -Shake 1 hour
- 2.) pH 4.2 0.5M NH<sub>4</sub><sup>+</sup>-Acetate (octacalcium phosphate  $Ca_8H_2(PO_4)_6 \bullet 5H_2O$ )

- Shake with solution, wait 4 hours, shake 4 hours

3.) pH 8.2 0.5M NH<sub>4</sub>F (aluminum associated P - Al-P)

- Shake 1 hour

4.) 0.1M NaOH + 0.1M Na<sub>2</sub>CO<sub>3</sub> (iron associated P – Fe–P)

- Shake 2 hours, wait 16 hours, shake 2 hours

5.) "Remaining" (apatite-like Ca-P and P occluded inside Fe and Al oxyhydroxides)

- Summation of steps 1-4 subtracted from total P in section

All samples were centrifuged after extraction at 3200 RCF for 15 minutes and filtered through Whatman No 42 filter papers. Soils were washed twice with 25mL of a saturated sodium chloride solution between extractions, with exception of after the first in which 95% ethyl alcohol was used. All samples were analyzed via ICP-OES. Following the conclusion of the procedure the supernatants of steps one and two were digested by combining 2.5mL of solution with 500µL sulfuric acid and heating to 100°C for one hour. Samples pre- and post-digestion were analyzed using Murphy and Riley (1962) to again determine "Other P" in the section. Step one data was highly variable likely due to polyphosphate hydrolysis post-extraction, and thus was discarded as the data was deemed unreliable.

#### **Fulvic Acid Characterization**

Potentiometric titration and NMR analysis were implemented to characterize the fulvic acid products. The titration was conducted at a concentration of  $2.15 \pm 0.15$ g L-1 in a background matrix of 0.1M sodium chloride to avoid significant ionic strength effects. Analysis was performed by first adjusting the solution to pH ~3 with 1M hydrochloric acid followed by titration with 0.2-0.4mL aliquots of 20mM sodium hydroxide. After each base addition, the solution was stirred and pH was recorded (Degryse et al. 2013). To obtain NMR spectra, a small aliquot of freeze-dried product was submerged in deuterated dimethyl sulfoxide (DMSO) and allowed to dissolve overnight. Only partial fractions of FA 1 and SF FA were soluble in the solvent. Thus, the spectra presented only represent the soluble portion. One dimensional <sup>1</sup>H spectra were collected over 1s at 499.82 MHz with a sweep width of 6008.88Hz.

#### **Synchrotron Investigation**

Synchrotron based investigations were completed for Experiment 1 at Beamline 6B1-1 -SXRMB of the Canadian Light Source (CLS) (Saskatoon, SK, CAN) and Experiments 2 and 3 at Sector 9-BM-B of Advanced Photon Source – Argonne National Lab (APS) (Lemont, IL, USA). After drying, at CLS the 0-8mm sections were finely ground and thinly spread onto carbon tape before being placed under vacuum for analysis. Three X-ray Absorption Near Edge Structure (XANES) scans were taken of each sample at the P K-edge (E0 = 2149eV). A double crystal, indium antimonide/silicon monochromator was utilized to scan an energy range extending from -33.5 to -9.5eV in 2eV steps, -9.5 to 31.5eV in 0.15eV steps and 31.5 to 91.5eV in 0.75eV steps. Each step was integrated over six seconds. For Experiments 2 and 3, collection parameters were the same however a double crystal, silicon/silicon monochromator and 4-element Vortex SDD detector were utilized to collect spectra and sample preparation was slightly different. Center section samples were finely ground and pelletized before being attached to carbon tape and placed into a helium filled chamber for analysis.

Background correction and linear combination fitting of the reported spectra using previously collected standards were completed in Athena (v.0.9.25 Ravel and Newville, 2005) according to the concepts set forth by Werner and Prietzel (2015). Two to three scans were merged to limit noise, pre-edge and normalization ranges were allowed to freely fluctuate to best accommodate each individual sample and all spectra were adjusted such that  $E_0$  (2149eV) corresponded to one half the height of the white line peak. For Fe, Fe foil was utilized to calibrate  $E_0$  to 7112eV to account for shifts caused by changes in valence. Phosphorus spectra were fit from -20 to 30eV, while iron was fit from -15 to 45eV relative to  $E_0$ . Fourteen reference spectra were used for linear combination fitting: orthophosphate sorbed to amorphous aluminum oxyhydroxide, orthophosphate sorbed to gibbsite, orthophosphate sorbed to goethite, orthophosphate bridged to montmorillonite by aluminum, orthophosphate bridged to montmorillonite by aluminum, monocalcium phosphate, brushite,  $\beta$ -tricalcium phosphate, octacalcium phosphate, hydroxyapatite, apatite, and calcium pyrophosphate.

# **Statistics**

All data were analyzed in SAS (SAS 9.4, 2017) through the Proc MIXED procedure. The Tukey Pairwise Method was used for comparison of all treatments at a 0.05 level of significance.

## Results

### **Humic Substance Characterization**

Potentiometric titration of the FA products (Figure 4.1) revealed buffering capacity between pH 3-4 and 7-10 with SF FA exhibiting the most suggesting a possible two-step polycarboxylic dissociation that would confer at least some cation chelation ability to the product under the conditions studied (Degryse et al., 2013). Buffering at the alkaline end could also be due to the presence of phenolic groups as well (Essington, 2004).

Qualitative analysis of the 1H NMR spectra suggest that the fulvic acid products are distinctively chemically different despite having been theoretically extracted according to similar processes. These data highlight one of the major limitations of the humic substance classification scheme. Namely, the same general chemical extraction procedure applied to different initial raw materials can result in vastly different final products that are sold under the same heading. This has caused great confusion in the field as distinguishing between what products may be working and those that don't and by what mechanism becomes greatly conflated. More characterization of the products is required to truly identify potential mechanisms of action. In these spectra, peaks at 8.92 (FA 1) and 7.61 (SF FA) may indicate the presence of phenolic groups as was suggested by the potentiometric titration. In contrast, carboxylic acid peaks in the 11-12ppm range were absent in the 1H NMR spectra.



Figure 4.1 Potentiometric titrations of fulvic acid products explored in Experiments 1-3. FA 1 = fulvic acid 1 product; SF FA = sub-fraction of fulvic acid product



Figure 4.2<sup>1</sup>H 500MHz NMR spectra of Fulvic Acid 1 (FA 1) product dissolved in deuterated dimethyl sulfoxide.



Figure 4.3 <sup>1</sup>H 500MHz NMR spectra of Sub Fraction of Fulvic Acid (SF FA) product dissolved in deuterated dimethyl sulfoxide.

pН

For all experiments, pH significantly decreased with P treatment relative to controls at the point of application and fulvic acid co-application had no statistically significant effect (Tables 4.3 - 4.5). Ammonium polyphosphate addition resulted in the most dramatic reduction of close to a full unit drop in the 0-8mm section. Diammonium phosphate was the least acidifying agent. Phosphoric acid and MAP had a similar effect despite PA initially being a much more acidic product. The tendency of P fertilizers to acidify the POA of alkaline soils is the result of at least three factors working in concert. The first is that phosphate species in the case of PA, MAP and APP themselves are acidic therefore protons are released to solution upon application when the soil pH is greater than the fertilizer pH. Using MAP as an example, the pKa of the transition between diprotonated and monoprotonated phosphate anion is 7.2, therefore when the diprotonated anion is added to the pH  $\sim$ 8.6 soil, H<sup>+</sup> is released, increasing the proton concentration, lowering the pH. Because the P in DAP is already monoprotonated, the pH is not lowered as much as the other treatments. Secondly, ammonium, the complementing cation in MAP, DAP, and APP, releases four protons per nitrogen atom when converted to nitrate during microbial nitrification. The additional nitrifying effect of MAP and the lack of ammonium in the PA treatment may be one reason why their overall treatment effect after four weeks was the same overall. Important to consider is that the conditions upon their addition was likely different. Because PA is highly acidic, the pH reduction was likely more dramatic and the rebound, quicker relative to the MAP application which would have had a less immediate acidifying effect and longer reactive period due to the bacterially mediated aspect of the nitrogen conversion. Finally, in the case of APP addition, the polyphosphates also undergo hydrolysis via extracellular enzymes like pyrophosphatase. The conversion to OP releases H<sup>+</sup> as a byproduct. All three

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	Dish Section (mm)					
Treatment †	0-8	8-15	15-27	27-edge		
Control – Water	8.62 a‡	8.75 a	8.67 a	8.49 a		
Control – FA 1	8.65 a	8.75 a	8.60 ab	8.49 a		
MAP 125	8.00 bc	8.57 ab	8.51 ab	8.44 ab		
MAP 125 + FA 1	8.02 b	8.58 ab	8.55 ab	8.39 ab		
APP 125	7.72 d	8.44 b	8.41 b	8.35 b		
APP 125 + FA 1	7.69 d	8.38 b	8.45 ab	8.34 b		
80/20 125	7.87 c	8.45 b	8.52 ab	8.42 ab		
80/20 125 + FA 1	7.88 c	8.49 b	8.50 ab	8.39 ab		

Table 4.3 Soil pH after 28-day incubation of phosphorus fertilizers applied to Finney 1soil in Experiment 1 at four distances from the point of application.

 $\dagger$ MAP = monoammonium phosphate; APP = ammonium phosphate; 80/20 = 80%

monoammonium phosphate / 20% ammonium polyphosphate; FA 1 = fulvic acid 1 co-

applicant

‡Means within a column (dish section) followed by the same letter are not significantly

different at P = 0.05 using Tukey's honest significance test.

Treatment †	Dish Section (mm)					
	0-8	8-15	15-27	27-edge		
Control – Water	8.76 a‡	8.82 a	8.78 a	8.74 a		
MAP 625	7.89 cd	8.32 b	8.48 b	8.54 b		
MAP 625 + FA 1	7.95 bc	8.38 b	8.46 b	8.46 bc		
DAP 625	8.26 b	8.39 b	8.37 b	8.43 bc		
DAP 625 + FA 1	8.23 b	8.38 b	8.43 b	8.37 c		
APP 625	7.63 de	8.18 b	8.49 b	8.50 b		
APP 625 + FA 1	7.57 e	8.27 b	8.45 b	8.46 bc		

Table 4.4 Soil pH after 28-day incubation of phosphorus fertilizers applied to Finney 1soil in Experiment 2 at four distances from the point of application.

†MAP = monoammonium phosphate; DAP = diammonium phosphate; APP = ammonium

phosphate; FA 1 = fulvic acid 1 co-applicant

‡Means within a column (dish section) followed by the same letter are not significantly

different at P = 0.05 using Tukey's honest significance test.

	Dish Section (mm)					
Treatment †	0-8	8-15	15-27	27-edge		
Control – Water	8.6 a‡	8.6 a	8.6 a	8.6 ab		
Control – 3X SF FA	8.6 a	8.6 a	8.5 a	8.6 a		
Phosphoric Acid 125	8.0 b	8.6 a	8.6 a	8.6 ab		
PA / SF FA Blend 125	8.0 b	8.6 a	8.5 ab	8.6 ab		
MAP 125	7.9 b	8.4 b	8.4 cd	8.5 abc		
MAP 125 + 1X SF FA	7.9 b	8.4 b	8.4 cd	8.4 c		
MAP 125 + 3X SF FA	8.0 b	8.4 b	8.4 bc	8.5 abc		
APP 125	7.6 d	8.3 c	8.4 d	8.5 bc		
APP 125 + 1X SF FA	7.6 d	8.3 c	8.4 cd	8.4 c		
APP 125 + 3X SF FA	7.6 d	8.3 c	8.4 d	8.4 c		
80/20 125	7.8 c	8.3 bc	8.4 cd	8.5 abc		
80/20 125 + 1X SF FA	7.8 c	8.3 bc	8.4 cd	8.5 abc		
80/20 125 + 3X SF FA	7.8 c	8.4 bc	8.4 cd	8.5 bc		

Table 4.5 Soil pH after 28-day incubation of phosphorus fertilizers applied to Finney 2soil in Experiment 3 at four distances from the point of application.

†MAP = monoammonium phosphate; DAP = diammonium phosphate; APP = ammonium

phosphate; SF FA = sub fraction of fulvic acid co-applicant

‡Means within a column (dish section) followed by the same letter are not significantly

different at P = 0.05 using Tukey's honest significance test.

mechanisms of acidification are working when APP is applied explaining why these treatments had the most significant pH effect.

## **Diffusion of P Added**

For all experiments, the vast majority of P added to these calcareous soils remained within the first section (Figures 4.4 - 4.6). Restricted movement of the nutrient in calcareous soil is well documented and the result of strong precipitation and sorption reactions with calcium in soil solution, solid calcium carbonates, and other colloidal fractions (Hettiarachchi et al., 2006; Lombi et al., 2004; Pierzynski and Hettiarachchi, 2019). Additionally, the high clay texture of the soils slow radial migration via diffusion and/or mass flow, while also providing a large amount of chemically reactive sorption sites close the point of fertilizer application. Similar results were observed by Pierzynski and Hettiarachchi (2019) in relatively similar experiments on three calcareous soils. Fulvic acid addition did not significantly enhance diffusion in any experiment, although there does seem to be a trends that suggests a positive correlation of P movement to the 8-15mm section with increased application rate of SF FA in MAP, APP, and 80/20 treatments of Experiment 3 (Figure 4.6) and a slightly negative correlation with addition of FA 1 (Figures 4.4 and 4.5). In regards to SF FA, if this product is preventing Ca-P mineral formation or sorption to soil colloids, increased diffusion down the concentration gradient would be observed resulting from higher solution P concentrations. If FA 1 happens to be encouraging dissolution of soil constituents through ligand promoted dissolution, this could actually restrict P movement by creating more possible sorption sites on colloids and/or higher concentrations of polyvalent cations in solution. Since the structures of the products used in this study are obviously different, and reactivities of the FAs are not fully understood, both beneficial and detrimental outcomes from their co-application are plausible.

In the case of Experiments 1 and 3 where a 125µL treatment volume was used, polyphosphate incorporation (e.g. APP and 80/20) was found to enrich a greater volume of soil as compared to orthophosphate-only formulations. Phosphoric acid-based applications proved very immobile.

Increasing the treatment volume significantly increased diffusion thereby enriching a large volume of soil (Figure 4.5). Similarly, polyphosphate containing (e.g. APP and 80/20) fertilizers permeated out to a greater volume of soil compared to orthophosphate-only formulations as well. Phosphoric acid-based applications proved most immobile (Figure 4.6). The lack of migration to the second section observed in the 125µL orthophosphate-only treatments may be related to Ca-P precipitation interactions that are mitigated with the addition of extra treatment volume or incorporation of polyphosphates. Calcium phosphate mineral formation may be inhibited by polyphosphate through disruption of crystal structure organization by the larger condensed phosphate molecules (Amer and Mostafa, 1981). The lower P concentration in the initial solution of the 625µL treatments may keep the ion activity product low and the saturation index below zero slowing development of the three-dimensional Ca-P lattice. Further discussion can be found in Chapter 3.



Figure 4.4 Percentage of P added recovered in each section of the Experiment 1 incubation of Finney 1 soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. MAP = monoammonium phosphate applied in 125µL solution volume; APP = ammonium phosphate applied in 125µL solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; FA 1 = fulvic acid 1 product co-applied at 0.73µL per dish



Figure 4.5 Percentage of P added recovered in each section of the Experiment 2 incubation of Finney 1 soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section.

MAP = monoammonium phosphate applied in  $625\mu$ L solution volume; DAP = diammonium phosphate applied in  $625\mu$ L solution volume; APP = ammonium phosphate applied in  $625\mu$ L solution volume; FA 1 = fulvic acid 1 product co-applied at 0.73 $\mu$ L per dish



Figure 4.6 Percentage of P added recovered in each section of the Experiment 3 incubation of Finney 2 soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significance difference in section. Phosphoric Acid = phosphoric acid applied in 125µL solution volume; PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate /20% ammonium polyphosphate applied in 125µL solution volume; 1X SF FA = Sub -fraction of fulvic acid co-applied at 0.78µL per dish; 3X SF FA = Sub -fraction of fulvic acid co-applied at 2.34µL per dish
#### **Resin Extractable P**

Co-application of FA did not significantly improve P lability as assessed by AER extractability after four weeks for any treatment, and no consistent trends were observed. Although the exact reason is currently uncertain, one proposed theory is that exchange sites on the organic acids were simply overwhelmed and that the diffusion trends are simply a product of coincidence and experimental error. Since the FAs are only applied at a rates of  $0.73 - 2.34\mu$ L per 9.2mg P treatment, it is possible that more fixing cations and P sorption sites reside in the impacted soil volume than the fulvate can guard P from (Degryse et al., 2013).

In terms of resin extractable orthophosphate, the 80/20, and phosphoric acid applications performed the best with a large portion of the P added remaining labile. Phosphoric acid results were surprising given the limited mobility of the treatment. In the 125µL studies treatments that included polyphosphates performed substantially better than MAP. Since precipitation as apatite-like minerals is a major mechanism of P fixation in calcium-rich soils, polyphosphates, as described above, may be acting as a crystallization inhibitor that disrupts crystal lattice formation keeping P in more soluble forms (Philen and Lehr, 1967). Important to note, is that once the "Other P" section is accounted for in APP treatments, the lability is equal to 80/20 (Figure 4.10). How quickly the conversion of PP to OP proceeds depends on environmental conditions such as temperature, P concentration, and pH (Dick and Tabatabai, 1986; McBeath et al., 2006; McBeath et al., 2009). One concern often raised is that because PP must go through the hydrolysis step for the nutrient to become plant available, early season growth may be compromised when this reaction is slow (McBeath et al., 2006). Whether or not the use of polyphosphates improves P acquisition efficiency is debated and certainly depends on soil conditions and cropping system. The increased lability of the 80/20 treatments, supports the notion that P fixation occurs

immediately at the POA when fertilizer is applied due to high solution activity of Ca<sup>2+</sup> and P. If precipitation can be prevented at this crucial timepoint, t=0, then efficiency for the growing season may be improved. Unfortunately, no further improvement appears possible using the cation complexing co-applicant approach.

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Figure 4.7 Resin extractable orthophosphate expressed as a percent of total P by section for the Experiment 1 incubation of Finney 1 soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. MAP = monoammonium phosphate applied in 125µL solution volume; APP = ammonium phosphate applied in 125µL solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution in 125µL solution volume; FA 1 = fulvic acid 1 product co-applied at 0.73µL per dish.



Figure 4.8 Resin extractable orthophosphate expressed as a percent of total P by section for the Experiment 2 incubation of Finney 1 soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. MAP = monoammonium phosphate applied in 625µL solution volume; DAP = diammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; FA 1 = fulvic acid 1 product coapplied at 0.73µL per dish



Figure 4.9 Resin extractable orthophosphate expressed as a percent of total P by section for the Experiment 2 incubation of Finney 1 soil. \*NS = no significance difference in section. No significant difference was observed between treatments for the 27 - edge section (not shown). Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. Phosphoric Acid = phosphoric acid applied in 125µL solution volume; PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution to 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; 1X SF FA = Sub -fraction of fulvic acid co-applied at 0.78µL per dish; 3X SF FA = Sub -fraction of fulvic acid co-applied at 2.34µL per dish



Figure 4.10 Resin extractable P expressed as a percent of P added to the 0-8mm section of Experiment 1. No FA effect was observed in Experiments 2 or 3 either (not shown). PO4 = orthophosphate; Other P = P recovered after digestion of extract solution. MAP = monoammonium phosphate applied in 125µL solution volume; APP = ammonium phosphate applied in 125µL solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution in 125µL solution volume; FA 1 = fulvic acid 1 product co-applied at 0.73µL per dish.

#### **Sequential Extraction**

Sequential extraction results from the 0-8mm section suggest that maximum resin extractability appears to be achievable in a variety of ways and the FA products did not impact P partitioning. Figures (4.11 - 4.13) demonstrate that fertilizer type tremendously impacts the soil "pool" in which that P resides at least after the four-week duration of these incubation experiments. While each subsequent extraction in this series in intended to target specific and more recalcitrant P species, it is important to note that these are operationally defined and that each bar may represent several P chemical forms. This makes interpretation challenging. For example, Finney 1 MAP 125 and APP 125 contained similar amounts P that was extractable in steps 1 and 2, but we know APP 125 contained much more resin extractable P. The authors believe that two simultaneous processes are occurring that may provide two mechanisms for improving P resin extractability and potentially use efficiency in this soil. The first mechanism is inhibition of forming stable, crystalline calcium phosphates of low solubility. When comparing the low performing MAP 125 and DAP treatments to those others that contain mostly or entirely all orthophosphate (e.g. phosphoric acid, 80/20, MAP 625), one can observe that the absolute amount of P extracted in step 1 – amorphous calcium diphosphate corresponds exceptionally well to the resin extractability (Figure 4.14). This suggests that by preventing precipitation or retarding crystallization of Ca-P to more stable forms like octacalcium phosphates is accomplished by bringing solution concentrations below the ion activity product in the  $625\mu$ L case, dissolving calcium carbonate with phosphoric acid or disrupting crystal structure with polyphosphates in 80/20 treatments. All these means reach the same end of slowing stable Ca-P formation. Figure 4.14 also demonstrates that APP treatments and to a lesser extent 80/20 harbor a significant amount of resin extractable P in the step 2 extractable "pool." Why is the entire APP step 2 resin extractable, but very little to none in the orthophosphate treatments? Because in the OP treatment step two is probably mostly Ca-P like octacalcium phosphate of limited solubility whereas in APP treatments, unhydrolyzed the PP is probably occupying two roles. The first is that the PP exists in another form that wasn't bicarbonate exchangeable in the first solution, but was still resin extractable, such as outer-sphere complexation with iron/aluminum oxyhydroxides or phyllosilicates. The second is that the Ca-P in second section is actually on a solubility spectrum that PP is helping to keep on the more soluble side but they are not soluble in pH 7.5 bicarbonate solution. This would explain why only a small portion, if any, OP treatment in step 2 extraction is resin extractable, while that portion is a little more in 80/20 treatments and most in APP; the PP is keeping more stable Ca-P from forming. The addition of acidic ammonium acetate may be strong enough to remove the more labile P associated with soil colloids but not inner-sphere complexed forms on iron and aluminum minerals. Interestingly, the small addition of PP to the 80/20 treatments is not only evident in the altered step 1 and 2 partitioning but can also be observed in the enrichment of the step 4 extraction targeting Fe-P. When full strength APP is used, step 4 is increased slightly further but the P partitioned to step 3, Al-P, is dramatically increased as well suggesting that PP exhibits a preference for the step 4 extractable species, likely Fe oxyhydroxides, but once those sites are all occupied, then the aluminum interaction becomes important. The total resin extractability of P is greater than the total P extracted in steps 1 and 2 only for APP samples, so perhaps part of the remaining resin P is coming from step 3 and/or 4.



Figure 4.11 Total P measured in each fraction of sequential extraction performed on 0-8mm section of Experiment 1 incubation of Finney 1 soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. Ca2-P = dicalcium phosphate; Ca8-P = octacalcium phosphate; Al-P = aluminum associated P; Fe-P = iron associated P; Remaining = summation of P in first four sections subtracted from total P in section. MAP = monoammonium phosphate applied in 125µL solution volume; APP = ammonium phosphate applied in 125µL solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; FA 1 = fulvic acid 1 product co-applied at 0.73µL per dish.



Figure 4.12 Total P measured in each fraction of sequential extraction performed on 0-8mm section of Experiment 1 incubation of Finney 1 soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. Ca2-P = dicalcium phosphate; Ca8-P = octacalcium phosphate; Al-P = aluminum associated P; Fe-P = iron associated P; Remaining = summation of P in first four sections subtracted from total P in section. MAP = monoammonium phosphate applied in 625µL solution volume; DAP = diammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; FA 1 = fulvic acid 1 product co-applied at 0.73µL per dish.



Figure 4.13 Total P measured in each fraction of sequential extraction performed on 0-8mm section of Experiment 1 incubation of Finney 1 soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. \*NS = no significant difference in section. Ca2-P = dicalcium phosphate; Ca8-P = octacalcium phosphate; Al-P = aluminum associated P; Fe-P = iron associated P; Remaining = summation of P in first four sections subtracted from total P in section. Phosphoric Acid = phosphoric acid applied in 125µL solution volume; PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; 1X SF FA = Sub -fraction of fulvic acid co-applied at 0.78µL per dish; 3X SF FA = Sub -fraction of fulvic acid coapplied at 2.34µL per dish



Figure 4.14 Distribution of resin extractable P within steps 1 and 2 of the sequential extraction of 0-8mm section for all experiments. Phosphoric Acid = phosphoric acid applied in 125µL solution volume; PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; MAP = monoammonium phosphate applied in 625µL solution volume; DAP = diammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; APP = ammonium phosphate applied in 625µL solution volume; SFFA = Sub -fraction of fulvic acid co-applied at 0.78µL per dish; 3X SF FA = Sub -fraction of fulvic acid co-applied at 2.34µL per dish; OP = orthophosphate; Other P = P recovered after digestion of extract solution

#### **Synchrotron Analysis**

Synchrotron analysis of the center section of all experiments and 8-15mm section of Experiment 1 suggest that FA treatments, in some cases, may have influenced P speciation. Visual inspection of spectra and LCF fitting reveals that the partitioning of P into various Ca-P associations and/or colloidal interactions may be occurring that are not captured by the wet chemical extractions (Figures 4.15 - 4.8 and Tables 4.6 - 4.7). This appears to be especially true when considering the orthophosphate dominant treatments in the 0-8mm section. Here is where the uncertainty of all the methods used in this study converge and leave a grey area in this field where further careful, detailed study is required. Because soils are such heterogeneous media in which biotic and abiotic processes are important and their interactions with elements, such as phosphorus, are numerous, it is conceivable that the same wet chemical extraction can be pulling P from different pools that are similarly susceptible to the same extraction method. In other words, the final P concentration measured could be the same but sourced differently. For example, the 2 - MAP 125 and 2 - MAP 125 + 3X SF FA treatments both contained statistically the same concentration of resin extractable phosphorus. However, linear combination fitting of the XANES spectra strongly suggest that more P was found in sorbed species rather than in Ca-P mineral forms, and that the proportion of P relegated to the sorbed pools differed when SF FA was present. These samples did seem to exhibit slightly greater diffusion from the POA further supporting the idea that FA addition did alter P partitioning. One plausible explanation posed initially in the diffusion section is that FA reduced Ca-P mineral formation. If a portion of the Ca-P formed in the MAP-only treatment was still soluble enough to be resin extractable, the FA effect would be missed but that does not mean the co-applicant is not doing anything. Important to note is that this incubation study is but one snapshot in time at four weeks post-fertilizer



Figure 4.15 Normalized phosphorus K-edge XANES spectra with linear

combination (LC) fitting results for the 0-8mm section of Experiment 1 using Finney 1 soil. MAP = monoammonium phosphate applied in 125 $\mu$ L solution volume; APP = ammonium phosphate applied in 125 $\mu$ L solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125 $\mu$ L

solution volume; FA 1 = fulvic acid 1 product co-applied at 0.73µL per dish.



Figure 4.16 Normalized phosphorus K-edge XANES spectra with linear combination (LC) fitting results for the 8-15mm section of Experiment 1 using Finney 1 soil. MAP = monoammonium phosphate applied in 125µL solution volume; APP = ammonium phosphate applied in 125µL solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; FA 1 = fulvic acid 1 product co-applied at 0.73µL per dish.



Figure 4.17 Normalized phosphorus K-edge XANES spectra with linear combination (LC) fitting results for the 0-8mm section of Experiment 2 using Finney 1 soil. MAP = monoammonium phosphate applied in 625 $\mu$ L solution volume; DAP = diammonium phosphate applied in 625 $\mu$ L solution volume; APP = ammonium phosphate applied in 625 $\mu$ L solution volume; FA 1 = fulvic acid 1 product coapplied at 0.73 $\mu$ L per dish.



Figure 4.18 Normalized phosphorus K-edge XANES spectra with linear combination (LC) fitting results for the 0-8mm section of Experiment 3 using Finney 2 soil. Phosphoric Acid = phosphoric acid applied in 125 $\mu$ L solution volume; PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP 125 = monoammonium phosphate applied in 125 $\mu$ L solution volume; APP 125 = ammonium phosphate applied in 125 $\mu$ L solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125 $\mu$ L solution volume; 1X SF FA = Sub -fraction of fulvic acid co-applied at 0.78 $\mu$ L per dish; 3X SF FA = Sub -fraction of fulvic acid co-applied at 2.34 $\mu$ L per dish

<b>Treatment</b> †	Ca- PP‡	МСР	DCP	OCP	BTP	Apatite	PO4- CaCO <sub>3</sub>	Clay- Al-P	Fe-P	Al-P	red. X <sup>2</sup>
1 – Control - Water	-	-	-	27	-	19	39	-	15	-	0.0055
1 - MAP 125	-	-	-	12	-	32	50	-	6	-	0.0015
1 - MAP 125 + FA 1	-	-	-	19	-	21	49	-	11	-	0.0019
1 - APP 125	-	-	-	-	-	14	42	15	30	-	0.0054
1 - 80/20 125	-	-	-	-	-	39	28	18	14	-	0.0066
1 - 80/20 125 + FA 1	-	-	-	-	33	-	40	17	11	-	0.0033
1 - DAP 625	-	-	-	-	-	51	37	-	6	7	0.0067
1 - DAP 625 + FA 1	-	-	-	-	-	51	25	-	8	16	0.0074
1 - MAP 625	-	-	19	-	-	46	-	-	11	25	0.0050
1- MAP 625 + FA 1	-	-	-	-	-	32	30	-	-	38	0.0112
1 - APP 625	20	-	-	-	-	-	40	6	-	34	0.0041
1- APP 625 + FA 1	15	-	-	-	-	-	42	10	-	32	0.0024
2 - Phosphoric Acid	-	39	-	39	-	-	-	-	-	22	0.0046
2 - PA / SF FA Blend	-	58	6	31	-	-	-	-	-	6	0.0051
2 - MAP 125	-	-	-	23	-	45	-	-	17	16	0.0034
2 - MAP 125 + 3X SF FA	-	-	-	-	-	44	37	-	7	13	0.0030
2 - APP 125	20	-	-	-	-	22	29	29	-	-	0.0009
2 - APP 125 + 3X SF FA	19	-	-	-	-	26	26	29	-	-	0.0010

 Table 4.6 Linear combination fitting results expressed as a percentage of Total P for all P K-edge spectra collected on the 0-8mm section of Finney experiments after 28-day incubation.

 $\dagger$ MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium

phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; MAP 625 = monoammonium phosphate applied in 625µL solution volume; DAP 625 = diammonium phosphate applied in 625µL solution volume; APP 625 = ammonium phosphate applied in 625µL solution volume; FA 1 = fulvic acid 1 co-applicant, SF FA = sub-fraction of fulvic acid co-applicant

 $Ca-PP = calcium pyrophosphate minerals; MCP = Monocalcium phosphate; DCP = dicalcium phosphate; OCP = octacalcium phosphate; BTP = <math>\beta$ -tricalcium phosphate; CaCO<sub>3</sub>-P = P sorbed to calcium carbonate; Clay-Al-P = aluminum bridged phosphate sorbed to montmorillonite; Fe-P = iron sorbed P; Al-P = aluminum sorbed P.

Treatment†	MCP‡	OCP	Apatite	CaCO <sub>3</sub> -P	Clay-Al-P	Fe-P	red. X <sup>2</sup>
1 - MAP 125	-	38	-	44	13	6	0.0028
1 - MAP 125 + FA 1	-	25	27	40	9	-	0.0030
1 - APP 125	15	38	-	37	11	-	0.0018
1 - APP 125 + FA 1	7	39	-	39	15	-	0.0012
1 - 80/20 125	12	50	-	22	17	-	0.0024
1 - 80/20 125 + FA 1	8	39	-	38	14	-	0.0016

 Table 4.7 Linear combination fitting results expressed as a percentage of Total P for P K-edge spectra collected on the 8-15mm section of Finney Experiment 1 after 28-day incubation.

<sup>†</sup>MAP 125 = monoammonium phosphate applied in 125µL solution volume; APP 125 = ammonium phosphate applied in 125µL solution volume; 80/20 125 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; FA 1 = fulvic acid 1 co-applicant ‡Ca-PP = calcium pyrophosphate minerals; MCP = Monocalcium phosphate; OCP = octacalcium phosphate; CaCO<sub>3</sub>-P = P sorbed to calcium carbonate; Clay-Al-P = aluminum bridged phosphate sorbed to montmorillonite; Fe-P = iron sorbed P

application. Had the experiment ended sooner or later, the results may have been different. At this point, we do not know if the altered P speciation, if it is in fact happening, would impact P lability to plants when considered over an entire growing season.

Subtle FA effects may also be observable in the speciation determined for the 8-15mm sections of Experiment 1. Very little MAP moved to this section in general but less moved with FA 1 possibly explaining why apatite appears in this treatment but not MAP-only. The control soil contained approximately 19% apatite, this may still represent a significant portion of the total P in this treatment since very little was added. Approximately 10% of the P added in the 80/20 and APP treatments was found in the second section. Here again we can see that more sorbed species were formed with FA 1 co-application compared to fertilizer-only. Also, the increased resin extractability of the APP and 80/20 treatments in this section seems to be related to the highly soluble monocalcium phosphate content. This agrees well with the Chapter 3 discussion of MAP 625 and phosphoric acid lability. No "Other P" was detected in the 8-15mm section of APP or 80/20 treatments (data not presented), so this mineral may be present because the Ca-P interaction formed later as the OP diffused and has yet to form more stable minerals.

Synchrotron analysis is not without its limitations that must be considered as well. Beamtime is limited, thus, only one sample is used from which the spectra are collected. This introduces the opportunity for soil heterogeneity to report differences in speciation that are by chance and not treatment effects. The samples are finely ground and the data are collected from an area approximately four square millimeters in size in an effort to minimize this chance, but the potential for false positives still exists. Additionally, many reference spectra for LCF analysis look similar and we assume that our library of reference spectra cover the range of species present but acknowledge that some may be missing. This could also result in erroneous interpretation of the data. The rather consistent FA effect of increased partitioning to sorbed species is extremely suggestive that these products are influencing P fate and transport.

## Conclusions

Fulvic acid addition to liquid P in this study did not significantly improve P lability but may have had a small influence on diffusion. Synchrotron-based analysis does hint that FA addition may be impacting P partitioning that is not discernable by the wet chemical methods to assess plant availability used in this study. Substantial differences were observed between types of fertilizers. Farmers working on calcareous soils may find blending polyphosphates into their orthophosphate fertilizers and increasing the amount of water P is applied in to be effective methods to mitigate fixation and lower total P application requirements. Further investigation will be required to determine if the fulvic acids effects can be replicated on other calcium-rich soils and what their mechanism(s) of action may be.

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# Chapter 5 - Liquid Phosphorus, Fulvic Acid, and a Highly Weathered Soil: The Effects of P Formulation and Co-Applicants Abstract

Fixation reactions with iron and aluminum oxyhydroxides can significantly reduce the use efficiency of phosphorus (P) fertilizers in tropical acid soils. Finding economical and simple methods that grower's can implement to keep the nutrient in a plant available form will mitigate deficiency, increase yield, lower production costs, and reduce non-point source pollution of nearby surface waters. Understanding how P fertilizer type contributes to / or prevents fixation is one step to improving P use efficiency. One proposed solution that often receives attention, albeit controversially, is to co-apply humic substances with fertilizers to complex solution cations that immobilize P and compete with P for sorption sites on soil colloids. This study investigated the effects of fertilizer type and commercially distributed co-applicants on phosphorus applied as liquid fertilizers to a Brazilian Ultisol. Monoammonium phosphate (MAP), diammonium phosphate (DAP), ammonium polyphosphate (APP), and an 80/20 MAP/APP mixture were applied with/without three commercial fulvic acid (FA) products. Soils were incubated for four weeks in Petri dishes and sectioned in concentric rings from the point of application. Anion exchange resin extractability as a percent of total P assessed potential plant availability, while synchrotron-based XANES analysis and suite of other wet chemical assessments were employed to investigate how P fate and transport were impacted. Orthophosphate based fertilizers remained more labile than polyphosphates, and co-applicant results varied but did not consistently alter lability. Although the wet chemical extractions did not reveal a consistent FA effect, XANES spectra of P and Fe suggest that the products may be influencing the P partitioning and iron mineralogy. Further study will be necessary to determine how and if humic substances can best

be utilized in future agricultural systems and whether the results of the fertilizer trials are reproducible across acid soils possessing a range of inherent characteristics.

## Introduction

The rate at which humans are progressing technologically suggests that some practices that we have commonly recognized as farming over the last several decades could look very different a decade or two in the future. The surge of interest and venture capital devoted to the development of lab grown meat, advances in RNAi based insecticides, and recent demonstration that manipulation of the photorespiratory system in the leaves of plants dramatically increases yield, if well adopted by regulating agencies and consumers, will change the way we think about tackling challenges, such as the United Nations Sustainable Development Goal of Zero Hunger (https://www.un.org/sustainable development/hunger/, Lopez-Calcagno et al., 2018; Mamta and Rajam, 2017; Tuomisto and Teixeira de Mattos, 2011). It remains to be seen how much arable land will be necessary to be under future cultivation to meet the nutritional requirements of the growing world population, but focus needs to be devoted towards the development of highly energy and nutrient efficient systems that do not diminish the surrounding environmental quality.

Adequate supply of phosphorus (P) to a crop is governed by the amount of the nutrient in soil solution and the rate in which P can be resupplied from the solid phase to solution upon depletion by plant roots (Syers et al., 2008). Resupply or buffering capacity is highly dependent upon the chemical form or "pool" to which the P is relegated and the inherent soil characteristics. For example, a P anion adsorbed to goethite via outer sphere complexation will release to solution much more easily than one occupying the crystal structure of strengite in an acidic, highly weathered Oxisol (Lindsay, 1979). The decisions about the way in which a farmer goes about fertilizing a field can have a significant impact on the chemistry of P after being added to the soil which directly impacts the future ability of that P to be supplied to the crops. Use of liquid phosphates in lieu of granular forms to mitigate fixation in highly calcareous soils is a

classic demonstration of the gravity these choices can have in how well the resource is utilized (Hettaiarachchi et al., 2006; Holloway et al., 2001).

Oxisols and Ultisols, which constitute more than 50% of global arable land, are highly likely to come under further cultivation in South America and Africa if the global food deficits emerge as predicted (Fink et al., 2016). Rich in iron and aluminum oxyhydroxides and 1:1 clay minerals with high P sorbing capacity, these are one set of soils in which substantial plant P acquisition efficiency progress needs to be made. Factors, such as amorphous iron and aluminum oxyhydroxide content, the degree to which aluminum is substituted into iron minerals, P fertilizer formulation, pH, and degree of sorption site saturation all play a role in the fate and transport of the element (Ainsworth et al., 1985; Hashimoto et al. 1969). Current literature suggests that P management in these soils is least efficient when cropping systems are first implemented and the total P status is low meaning many sites for strong chemisorption on sesquioxides and clay edges are vacant. Over decades, as fertilizer is annually applied, the most reactive sites eventually become saturated allowing for freshly applied P to only weakly sorb or remain in soil solution. At this point, P efficiency increases dramatically (McCollum, 1991). While a reaction site saturation approach does solve the low efficiency dilemma in the long run, the costs both financial and environmental are and can be significant (Roy et al., 2016). Fertilizer application strategies need to be developed that prevent this P "tax" imposed by strong inner sphere complexation and/or precipitation (collectively referred to as "fixation") to allow for efficient P application to low P status soil. This is particularly pressing for developing countries as they are often plagued with highly weathered soils and lack adequate access to fertilizers. Techniques, such as microdosing, are making progress on this front but substantial room for improvement still exists (Blessing et al., 2017).

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Some of the more controversial products sold to enhance fertilizer efficacy that frequently receive attention are the humic substances. Currently, growers and scientists are working to parse if these products reliably confer benefit, what the mechanism of action may be (Lyons and Genc, 2016). The hypothesis is that the high cation exchange capacity associated with many of these substances outcompetes P and blocks reactions with iron and aluminum in acid soils and calcium in calcareous soils (Lyons and Genc, 2016). Degryse et al. (2013) concluded, however, that this mechanism to prevent fixation was likely not a viable, though humic substances were not specifically vetted. Borggaard et al. (2005) was unable to demonstrate the utility of this mechanism as well, though studies have shown that increase soil organic matter does seem to increase P extractability (Guedes et al., 2016). Possible explanations for the discrepancies and constant debates are that the humic substances simply cannot economically be applied at the rates required to occupy the myriad sites available for reaction and/or that the range of products sold are not similar chemically enough to provide consistent results across studies. Humic and fulvic acid labels are operationally defined by their extraction procedures, so depending on the starting material and exact methods employed, the final products could be quite dissimilar. Additionally, if cation sequestration is not the mechanism, others including stimulation of soil microbiota and plant hormonal interactions are plausible as well (Calvo et al., 2014). To the authors' knowledge, the combination of various liquid phosphorus formulations with a range commercially available humic substances is yet to be explored at a mechanistic level in highly weathered, acid soils. This investigation evaluated the impact of co-application of three commercial fulvic acid (FA) products with liquid monoammonium phosphate, diammonium phosphate, and ammonium polyphosphate on P lability in an Ultisol from Piracicaba, Brazil.

## **Materials and Methods**

### **Experimental Design**

Eighty-four Petri dishes (88mm diameter and 12.9mm height) were packed to a bulk density of 1.1g cm<sup>-3</sup> with an acidic, sandy clay loam from Piracicaba, Brazil (see Table 5.1), prewetted to 18% maximum water holding capacity (MWHC). After packing, the soils were adjusted to 50% MWHC, the covers were replaced, the edges were wrapped in Parafilm, and the dishes were allowed to equilibrate at room temperature ( $\sim 24^{\circ}$ C) for at least 24 hours. Treatments were then slowly administered to the exact center of the dish using a 1mL syringe. The application target rate was defined as enough fertilizer to equal 9.2mg P dissolved in 125µL of ultrapure water. Treatments consisted of a water only control, technical grade monoammonium phosphate (MAP) (FisherBrand ACS Grade), technical grade diammonium phosphate (DAP) (FisherBrand ACS Grade) ammonium polyphosphate (APP) (11-37-0 Mosaic formulation), and an 80/20 blend of the MAP and APP (80/20), all with and without three commercial humic substances: two labeled solely as fulvic acids (FA 1 and FA 2) and one as a blend of fulvic acid sub-fractions (SF FA). Fulvic acid 1, FA 2, and SF FA were applied at 0.73µL, 1.43µL, and 0.78µL per 125µL treatment, respectively. Additionally, a standalone phosphoric acid / subfraction of fulvic acid blend (PA / SF FA) was included as well. Following treatment administration, Parafilm was again employed to seal edges and mitigate moisture loss. The dishes were wrapped in aluminum foil to prevent light exposure and incubated for twenty-eight days in the dark at 25°C. Following incubation, the dishes were excavated by hand into four concentric circular sections with radii of 0-8mm, 8-15mm, 15-27mm and 27mm-dish edge extending from the point of application (POA). The sections were then dried at  $40^{\circ}$ C, weighed and finely ground with a mortar and pestle.
Origin	Piracicaba, Brazil
Classification	Typic Haplustults
Texture	Sandy Clay Loam
Sand (%)	67
<b>Silt (%)</b>	8
<b>Clay</b> (%)	25
pH (1:10)	5.4
CEC (cmol kg <sup>-1</sup> ) <sup><math>\dagger</math></sup>	4.3
Resin P (mg kg <sup>-1</sup> )	6
Total P (mg kg <sup>-1</sup> )	206
Oxalate Extractable Fe (mg kg <sup>-1</sup> )	1565
Oxalate Extractable Al (mg kg <sup>-1</sup> )	666

Table 5.1 Select soil properties of an Ultisol collected in São Paulo, Brazil.

† Texture = soil texture determined by pipette method; CEC = cation exchange
capacity determined by ammonium acetate displacement; Resin P = Resin extractable
phosphorus; Total P = Total extractable phosphorus; Oxalate Extractable Fe and Al
determined by Loeppert and Inskeep (1996)

#### Wet Chemical Analysis

Plant available P was assessed using the anion exchange resin technique followed by colorimetric analysis for the molybdate reactive fraction ((Murphy and Riley, 1962; Myers et al. 2005). Total P was determined by aqua regia digestion analyzed by ICP-OES analysis (Premarathna et al., 2010). Oxalate extractable iron (Fe), aluminum (Al), and P were analyzed according to Loeppert and Inskeep (1996), and pH was assessed using an electrode in a 1:10 soil:water suspension. The percent of P added that was recovered in each section and the proportion of added P that remains resin extractable were calculated according to the following equations:

Percent (%) P Added = 
$$\frac{(SPT \ x \ SMT) - (SPC \ x \ SMC)}{TPD} x \ 100$$

Where:

SPT = Total P concentration (mg kg<sup>-1</sup>) in the dish section

SMT = Section mass in kg of the treatment

SPC = Average P concentration of all control – water samples + 2 standard deviations

SMC = Section mass average of combined control – water within a section

TPD = Total P recovered in the entire dish

Percent (%) Resin Extractable 
$$P = \frac{(RPT \times SMT) - (RPC \times SMC)}{(SPT \times SMT) - (SPC \times SMC)} \times 100$$

Where:

RPT = Resin extractable P concentration (mg kg<sup>-1</sup>) in the dish section

SMT = Section mass in kg of the treatment

RPC = Average resin extractable P concentration of all control – water samples

+ 2 standard deviations

SMC = Section mass average of combined control – water within a section

#### **Synchrotron Investigation**

The synchrotron-based investigation was completed using a composite sample of two replicates at Sector 9-BM of Advanced Photon Source (Lemont, IL). After drying, composites from the 0-8mm section were very finely ground and pelletized before being placed in a helium purged chamber for analysis. Composites consisted of equal amounts of two samples that were expected to be most representative of the wet chemical results. A double crystal, silicon/silicon monochromator and 4-element Vortex SDD detector were utilized to collect at least three scans of each sample at the P ( $E_0 = 2149eV$ ) and Fe ( $E_0 = 7112eV$ ) K-edges. A single scan for P was defined as 30eV in the pre-edge region with a 2eV step size, 35eV in the XANES region with 0.120eV step size and 111eV in the EXAFS region with a 0.050eV step. Each step was integrated over six seconds. For Fe, a scan was defined as 190eV in the pre-edge region with a 5eV step size, 45eV in the XANES region with 0.2eV step size and 345eV in the EXAFS region with a 0.05eV step. Each step was integrated over one second. Background correction and linear combination fitting of the reported spectra using previously collected standards were completed in Athena (v.0.9.25) according to the concepts set forth by Werner and Prietzel (2015) (Ravel

and Newville 2005). Two to three scans were merged to limit noise, pre-edge and normalization ranges were allowed to freely fluctuate to best accommodate each individual sample and all spectra were adjusted such that  $E_0$  (2149eV) corresponded to one half the height of the white line peak. For Fe, Fe foil was utilized to calibrate  $E_0$  to 7112eV to account for shifts caused by changes in valence. Phosphorus spectra were fit from -20 to 30eV, while iron was fit from -15 to 45eV relative to  $E_0$ . For P, nineteen reference spectra were used for linear combination fitting: anapaite, generic aluminum phosphate, generic iron (III) phosphate, apatite, brazilianite, bobierrite, heterosite, orthophosphate sorbed to amorphous aluminum oxyhydroxide, orthophosphate sorbed to gibbsite, orthophosphate sorbed to goethite, orthophosphate sorbed to ferrihydrite, inositol hexaphosphate bridged to montmorillonite by aluminum, orthophosphate bridged to montmorillonite by aluminum, phosphatidylcholine, phosphosiderite, phytic acid, strengite, variscite, vivianite. Twelve reference spectra were used for iron: generic Fe<sub>2</sub>O<sub>3</sub>, generic FeS<sub>2</sub>, generic amorphous aluminum substituted iron oxyhydroxide, ferrihydrite, goethite, greenrust, lepidocrocite, maghemite, magnetite, nontronite, siderite, vivianite.

## **Statistical Analysis**

All data were analyzed in SAS (SAS 9.4, 2017) through the Proc MIXED procedure. The Tukey-Kramer Pairwise Method was used for comparison of all treatments at a p = 0.05level of significance.

## **Results and Discussion**

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In general, treatment impact on soil acidity was attributed more to the P speciation in the fertilizer than co-application of fulvic substances. Most applications raised the pH at the POA (Table 5.2) as is common when employing these types of fertilizers to acid soil (Pierzynski and Hettiarachchi, 2018). The sole exception was the phosphoric acid/sub-fraction of fulvic acid blend that significantly reduced the pH in the center two sections. This is likely due to the very low first hydrogen dissociation constant of phosphoric acid (pka<sub>1</sub> = 2.15). Absent any neutralizing agents or strong buffering capacity in the sand rich soil, addition of a concentrated acid would result in substantial acidification. Increased pH, relative to the control, was most pronounced in the DAP treatments (Figure 1). The pKa of the transition between diprotonated and monoprotonated P anion is 7.2, therefore when the monoprotonated anion is added to the acid soil, H<sup>+</sup> is scavenged, reducing the proton concentration in soil solution, raising the pH. In addition, P chemisorption on oxyhydroxide surfaces releases hydroxyl groups to solution that complex with protons to form water, explaining why the diprotonated P anions (e.g. MAP) elevated the pH as well (Shang et al., 1992; Stoop, 1983).

Sample	Dish Section (mm)						
	0-8	8-15	15-27	27-edge			
Control - Water	5.4 def <sup>‡</sup>	5.4 ab	5.3 a	5.3 a			
Control - FA $1^{\dagger}$	5.3 ef	5.4 ab	5.3 a	5.3 a			
Control - FA 2	5.5 cdef	5.5 ab	5.4 a	5.3 a			
Control - SF FA	5.3 f	5.4 ab	5.3 a	5.3 a			
PA / SF FA Blend	4.6 g	5.0 b	5.2 a	5.3 a			
MAP	5.8 abcde	5.6 a	5.2 a	5.2 a			
MAP + FA 1	5.8 bcdef	5.6 ab	5.2 a	5.3 a			
<b>MAP + FA 2</b>	5.8 abcde	5.6 a	5.3 a	5.3 a			
MAP + SF FA	5.8 abcd	5.6 ab	5.2 a	5.3 a			
DAP	6.0 abc	5.7 a	5.4 a	5.4 a			
DAP + FA 1	6.3 a	5.9 a	5.7 a	5.5 a			
<b>DAP + FA 2</b>	6.2 ab	5.8 a	5.4 a	5.3 a			
DAP + SF FA	6.1 ab	5.5 ab	5.2 a	5.3 a			
APP	6.0 abc	5.7 a	5.3 a	5.3 a			
APP + FA 1	5.9 abc	5.5 ab	5.3 a	5.3 a			
<b>APP + FA 2</b>	6.2 ab	5.8 a	5.4 a	5.3 a			
APP + SF FA	6.0 abc	5.6 ab	5.3 a	5.3 a			
80/20	5.9 abcd	5.6 ab	5.2 a	5.2 a			
80/20 + FA 1	5.9 abc	5.7 ab	5.3 a	5.2 a			
80/20 + FA 2	5.9 abc	5.6 a	5.2 a	5.3 a			
80/20 + SF FA	5.8 abcd	5.5 ab	5.2 a	5.3 a			

Table 5.2 Soil pH after 28-day incubation of phosphorus fertilizers applied to aBrazilian Ultisol at four distances from the point of application.

†MAP = monoammonium phosphate; DAP = diammonium phosphate; APP =

ammonium phosphate; 80/20 = 80% monoammonium phosphate / 20% ammonium

polyphosphate; FA 1 = fulvic acid 1 co-applicant; FA 2 = fulvic acid 2 co-applicant;

SF FA = sub-fraction of fulvic acid co-applicant

‡Means within a column (dish section) followed by the same letter are not

significantly different at P = 0.05 using Tukey's honest significance test.

#### **Diffusion of P Added**

The soil possessed a sandy clay loam texture that allowed for substantial P movement away from the POA (Figure 5.1). The role of texture in P migration is highlighted when these results are compared to a similar study of an Ultisol by Pierzynski and Hettiarachchi (2018). The clay texture of the soil in that study kept the vast majority of P within the first two sections. Clay content increases pore channel tortuosity that may restrict transport by mass flow as well as increasing the concentration of chemically reactive sites available for P sorption.

Although not statistically significant, polyphosphate (PP) treatments appeared to remain closer to the POA than the orthophosphate (OP) treatments and DAP diffused the furthest. The phosphoric acid / sub-fraction of fulvic acid blend was the least mobile. The general consensus in literature, although conclusive data is somewhat lacking, is that under acid conditions orthophosphates sorb more strongly to iron and aluminum oxyhydroxides, while pyrophosphates, the dominant condensed P species in APP, possess a marginally greater affinity for kaolinite (Al-Kanani and MacKenzie, 1991; McBeath et al., 2007; Mnkeni and MacKenzie, 1985). One possible explanation for the slower diffusion of APP is that the pyrophosphate mobilized organic matter from the surface of oxyhydroxides at the POA and thus exposed more sorption sites than would have been available to the orthophosphates (Mnkeni and MacKenzie, 1985). Additionally, increased affinity for clay would mean that more sites were available for reaction as well (Al-Kanani and MacKenzie, 1991). Because APP is approximately half orthophosphate, this combination seems to create a worst of all worlds scenario for P binding in this kaolinite and Fe/Al oxyhydroxide-rich soil. Essentially the strongest fixing sites for both OP and PP could be occupied. In regards to the PA/SF FA blend, pH reduction at the POA may explain the treatments diminished capacity to diffuse. Phosphorus fixation on iron and aluminum



Figure 5.1 Percentage of P added recovered in each section of the incubation of a Brazilian soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP = monoammonium phosphate applied in 125µL solution volume; DAP = diammonium phosphate applied in 125µL solution volume APP = ammonium phosphate applied in 125µL solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; FA 1 = fulvic acid co-applicant 1 applied at 0.73µL per dish; FA 2 = fulvic acid coapplicant 2 applied at 1.43µL per dish; SF FA = Sub -fraction of fulvic acid coapplied at 0.78µL per dish

oxyhydroxides increases as pH decreases as a consequence of greater protonation of Type A surface functional groups facilitating ligand exchange with  $H_2PO_4^-$  (Essington, 2004).

#### **Resin Extractable P**

Phosphorus added as orthophosphate, MAP and DAP, demonstrated greater resin extractability as a percent of total P added than the APP and 80/20 treatments in the 0-8mm and 8-15mm sections (Figure 5.2). This is consistent with the findings of Hashimoto et al. (1969) and some others although there is not one hundred percent scientific consensus on whether OP or PP is retained more strongly in acid soils (Al-Kanani and MacKenzie, 1991; McBeath et al., 2007). This is certainly due to the multitude of factors that impact P behavior. Phosphorus concentration, Fe/Al mineralogy, pH, and organic matter type and content are just some of the governing variables. Coupled with its relative lack of mobility, the phosphoric acid / sub-fraction of fulvic acid blend was not desorbed as efficiently as MAP and DAP either. This is likely due to extremely acidic nature of the product and its pH lowering effect on the soil.

Co-application of FA did not reliably improve lability (Figure 5.2). Although the exact reason is currently uncertain, one proposed theory is that exchange sites on the organic acids were simply overwhelmed. Since the products are only applied at very small rates, it is likely that more fixing cations and P sorption sites reside in the impacted soil volume than the fulvate can guard P from (Degryse et al., 2013). Additionally, under acidic conditions negatively charged functional groups are protonated more often compared to neutral or alkaline soil resulting in an overall decreased cation sequestration capacity.



Figure 5.2 Resin extractable P expressed as a percentage of P added in each section of the incubation of a Brazilian soil. Means within a soil section for each treatment containing the same letter are not significantly different at P = 0.05using Tukey's honest significance test. No significance difference between treatments was observed for the 15-27mm and 27-edge (not shown) sections. PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP = monoammonium phosphate applied in 125µL solution volume; DAP = diammonium phosphate applied in 125µL solution volume, APP = ammonium phosphate applied in 125µL solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; FA 1 = fulvic acid co-applicant 1 applied at 0.73µL per dish; FA 2 = fulvic acid co-applicant 2 applied at 1.43µL per dish; SF FA = Sub -fraction of fulvic acid co-applied at 0.78µL per dish

#### **Oxalate Extraction**

Application of fertilizer to the soil slightly elevated the concentrations of amorphous iron and aluminum (Figure 5.3). The only treatment to substantially differ from the rest however was the phosphoric acid / sub-fraction of fulvic acid blend. The sudden application of a relatively strong acid to the soil caused more crystalline iron and aluminum minerals to dissolve and then reprecipitate in more amorphous forms. Not only would this result in more sites for P to sorb to but coupled with the reduced ambient solution pH would have allowed for more threedimensional metal – phosphate – metal ternary complexes (i.e. surface precipitation) to form that would sequester greater amounts phosphate than MAP or DAP mainly sorbing to the surface. Ler and Stanforth (2003) demonstrated the potential of this mechanism using goethite, but the authors see no reason why the same could not occur in the case of aluminum as well. At pH = 4.6, the concentration of aluminum in soil solution is probably orders of magnitude higher than iron as a result of greater inherent solubility of many Al minerals, so theoretically the effect should be greater (Lindsay, 1979). Additionally, the solution acidity at the time of application would have been even greater than reported in the pH section after four weeks, so the solution cation concentrations available for this sort of mechanism would have been quite high.

The orthophosphates, MAP and to a lesser extent DAP, increased the amorphous Al and Fe to a smaller degree although the measured Fe value was not statistically greater than the controls. That fact that MAP exhibited the greatest transformation of more crystalline Fe/Al to amorphous was no surprise as the acidic nature of this fertilizer (pH = ~4.5) means that upon addition to the pH = 5.4 soil, the acid would have dissolved some of the more soluble material before the buffering capacity and fixation reactions elevated the pH. This small effect would have also promoted some P entrapment within amorphous minerals as was likely the case with

PA / SF FA. This may explain why MAP was slightly less resin extractable than DAP. The small effect attributed to DAP may be the result of ligand promoted dissolution and/or redistribution of organic matter. The basic nature of the fertilizer (pH = ~8) could have dissolved mineral-organic assemblages that may have otherwise prohibited oxalate extraction under acidic conditions. Polyphosphate had a minimal effect. Interestingly, within the orthophosphates, the amount of both amorphous Fe and Al production followed the same order with respect to the humic substance co-additives: FA 1 > no additive > SF FA > FA 2 (Figure 5.3). This result, although not statistically significant, suggests that the humic substances are influencing iron and aluminum mineralogy and that product selection makes a difference as to what impact that co-additive has. Also worth noting, the absolute increase in the amount of oxalate extractable Fe and Al is almost all treatments are very similar despite there being almost twice as much amorphous iron to begin with. The only exceptions are the MAP and DAP treatments that contained FA 1. They appeared to have a greater impact on the Fe fraction.



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Figure 5.3 Oxalate extractable aluminum and iron in the 0-8mm section of an Ultisol amended with phosphorus fertilizers. Means for treatments containing the same letter are not significantly different at P = 0.05 using Tukey's honest significance test. PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP = monoammonium phosphate applied in 125µL solution volume; DAP = diammonium phosphate applied in 125µL solution volume; APP = ammonium phosphate applied in 125µL solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125µL solution volume; FA 1 = fulvic acid co-applicant 1 applied at 0.73µL per dish; FA 2 = fulvic acid co-applicant 2 applied at 1.43µL per dish; SF FA = Sub -fraction of fulvic acid co-applied at 0.78µL per dish

#### **Synchrotron Analysis**

Linear combination fitting of the P XANES spectra collected of the 0-8mm sections further confirms that the majority of the P in the soil was sorbed either to Fe/Al oxyhydroxides or bridged by aluminum to phyllosilicates (Figure 5.4 and Table 5.3). Often phyllosilicates are not discussed in the context of highly weathered soils, but this fraction may represent an association of P with reactive edges of kaolinite. Reference spectra for this form were not immediately available, so P bridged by Al to montmorillonite may be a close representation for LCF fitting. The control soil appears to contain mainly Fe-P minerals and Al sorbed species. This may be representative of what the P distribution looks like in this system when under lower total P status and Al or Fe P associations have been given time to age. The seeming P preference for aluminum, either in the form of an oxyhydroxide or sorbed to/component of a phyllosilicate clay can be found elsewhere in the literature, especially when the P solution concentration is high (Doyodora et al., 2016; Philen and Lehr, 1967). Because the Al solution concentration at any given acidic pH is maintained at concentrations orders of magnitude greater than that of Fe, at least two things may be happening (Lindsay, 1979). Although not measured, it is likely based on the beforementioned solubility and the ammonium oxalate data that the CEC would be occupied by more aqueous Al species than Fe at any given time thus explaining the significant portion of P attributed to the Al bridged clay. This fact, coupled with the small flush of Al and Fe released to solution as a result of the P addition, would provide opportunities for P to be occluded into Al / Fe sorption layers they are not quite organized to the point of being precipitates but are three dimensional aggregates of P anions and soluble cations (Ler and Stanforth, 2003). Again, this is almost certainly happening in the PA / SF FA treatment and may explain why MAP resin extractability is slightly lower than that of DAP. Secondly, the greater solubility of aluminum

compounds may mean that a fraction of the total aluminum pool goes through more dissolutionprecipitation cycles than Fe, this could result in not only greater surface distribution of secondary aluminum minerals on soil particles, like sand, but that those features are less crystalline and of greater surface area. A limitation of the ammonium oxalate extraction is that only content information is conveyed. The spatial distribution could look very different and would have profound impacts of P fate and transport. This, of course, assumes that frequent redox oscillations are not occurring that push this concept in favor of Fe (Ginn et al., 2017).

In general and as was observed in Chapters 3 and 4, it appears as though the polyphosphate treatments are more closely associated with the Al saturated clay, than oxyhydroxides (Table 5.3). Also, there seems to be a reliable Fe-P mineral component to PP treatment that manifests even in the 80/20 treatment where polyphosphates themselves compose less than < 10% of initial solution P. This may explain the poorer polyphosphate mobility relative to OP-only treatments. Higher P concentration in the center section over the 28-day period may have allowed for precipitation to occur. Philen and Lehr (1967) found that while orthophosphate precipitation occurs almost immediately upon addition, solid polyphosphate species can take weeks to begin forming. Diammonium phosphate showed the greatest sorption to Al oxyhydroxides, while MAP treatments exhibited the most variable partitioning. While, FA addition did not reliably manifest in the wet chemical results, the co-application of SF FA specially to MAP and DAP seems to have drastically altered P speciation. In both treatments, SF FA caused a shift to Fe-P mineral formation where none was detected in either the fertilizer-only or fertilizer + FA 1 samples. A substantial reduction in the Clay-Al-P fraction was simultaneously observed in these samples and was found in the APP + SF FA treatment as well.

Fertilizer formulation and FA influence were observed in the Fe XANES spectra as well (Table 5.4). For example, the complete disappearance of goethite and hematite in the PA / SF FA samples suggests that adding the strong acid dissolved the more stable iron minerals. Polyphosphate addition may have slowed hematite formation from less crystalline forms as well. Pyrophosphates are known to sequester solution Fe and Al. The absence of hematite in the control sample suggests that the mineral was formed as a result of P addition, not that the mineral was present before and then dissolved.

The consistency of certain features, especially within the orthophosphate treatments, such as the appearance of lepidocrocite only when FA 1 was added, lend credibility to the claim that these co-additions are having some effect. Although not statistically significant, the FA 1 treatments were observed to possess the greatest increase in amorphous Fe and Al content measured by ammonium oxalate extraction. The SF FA impact observed in the P XANES data may also be reflected in the Fe spectra. These samples appear to contain little to no hematite or ferrihydrite but unlike the other MAP and DAP treatments, the Fe appears in a more amorphous form with some limited Al substitution. These iron mineral transformations could be influencing P dynamics in this soil that may be agriculturally relevant although no mechanism for these transformation is currently obvious. Torrent et al. (1994) found that hematites exhibit more natural variability in P sorption capacity and slower uptake than goethite. The tendency for MAP and DAP to possess greater proportions of hematite relative to other treatments then may be one partial explanation as to why those fertilizers resulted in greater P diffusion.

The authors ask that the reader keep an open mind about what the observations of this investigation could mean for the future. As outlined in the introduction, in highly weather soils, the P tax is incurred when soils of low P status are fertilized (Roy et al., 2016). The most reactive

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sites have the greatest statistical probability of binding the added P, so depending on the agricultural system, decades of P application eventually saturate these sites significantly reducing fixation capacity keeping the P in plant acquirable forms (McCollum, 1991). To our knowledge, none of the long-term P application field studies have really investigated how iron and aluminum mineralogy change as this saturation takes place. Many studies over the years indicate that factors like type of mineral, crystallinity, pH, competing anions, etc. alter how P is distributed upon application. The data from this study suggest that the P form and FA chemical composition interact to specifically determine P partitioning and resulting Fe mineralogy. These results cannot be generalized, but we ask what the cumulative effect of say five or ten years of application in a controlled traffic system or repeated microdosing in the same location could be? Could we lower the "tax" if we get the combination right? With respect to humic substances, are we asking the wrong question? Of course the small amounts of FA being added commercially are not enough to out compete P for sorption sites. Maybe the overall change in the mineralogical system, especially over time, could make the difference.



Figure 5.4 Normalized phosphorus K-edge XANES spectra with linear combination (LC) fitting results for the 0-8mm section of the Brazilian soil. PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP = monoammonium phosphate applied in 125 $\mu$ L solution volume; DAP = diammonium phosphate applied in 125 $\mu$ L solution volume; APP = ammonium phosphate applied in 125 $\mu$ L solution volume; APP = ammonium phosphate applied in 125 $\mu$ L solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in 125 $\mu$ L solution volume; FA 1 = fulvic acid 1 co-applied at 0.73 $\mu$ L per dish; SF FA = Sub -fraction of fulvic acid co-applied at 0.78 $\mu$ L per dish

<b>Treatment</b> <sup>†</sup>	Fe-P <sup>‡</sup>	Al-P	Fe-P	Clay-Al-P	Red χ <sup>2</sup>
Control - Water	28	67	5	-	0.0162
PA / SF FA	-	41	28	31	0.0063
MAP	-	31	20	49	0.0087
<b>MAP + FA 1</b>	-	31	-	69	0.0089
MAP + SF FA	27	41	26	6	0.0055
DAP	-	47	21	32	0.0048
DAP + FA 1	-	44	30	26	0.0092
DAP + SF FA	20	57	23	-	0.0046
APP	23	-	10	67	0.0030
APP + FA 1	14	14	12	70	0.0023
APP + SF FA	20	25	15	40	0.0035
80/20	9	18	12	61	0.0044

Table 5.3 Linear combination fitting results expressed as a percentage of Total P for P Kedge spectra collected on the 0-8mm section of Ultisol experiments after 28-day incubation.

monoammonium phosphate applied in  $125\mu$ L solution volume; DAP = diammonium phosphate applied in  $125\mu$ L solution volume; APP = ammonium phosphate applied in  $125\mu$ L solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in  $125\mu$ L solution volume; FA 1 = fulvic acid co-applicant 1 applied at  $0.73\mu$ L per dish; FA 2 = fulvic acid co-applicant 2 applied at  $1.43\mu$ L per dish; SF FA = Sub -fraction of fulvic acid coapplied at  $0.78\mu$ L per dish

<sup>†</sup>PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP =

‡Fe-P = iron phosphate minerals; Ca-P = calcium phosphate minerals; Al-P = aluminum sorbed P;Fe-P = iron sorbed P; Clay-Al-P = aluminum bridged phosphate sorbed to montmorillonite

<b>Treatment</b> <sup>†</sup>	Hm‡	Goe	Sid	Fh	Viv	Mag	Non	Fe/Al Cop	Lep	Red χ <sup>2</sup>
<b>Control - Water</b>	-	22	5	-	-	-	35	39	-	0.0000372
PA / SF FA	-	-	-	33	4	-	20	44	-	0.0000493
MAP	40	11	2	47	-	-	-	-	-	0.0000141
MAP + FA 1	41	-	2	47	-	-	-	-	10	0.0000165
MAP + SF FA	-	20	6	-	-	-	38	36	-	0.0000424
DAP	40	37	2	-	-	21	-	-	-	0.0000210
DAP + FA 1	45	3	-	47	-	-	-	-	6	0.0000171
DAP + SF FA	8	31	-	-	-	21	-	40	-	0.0000338
APP	24	7	-	55	-	-	-	14	-	0.0000229
APP + FA 1	34	14	1	52	-	-	-	-	-	0.0000215
APP + SF FA	27	45	4	-	-	25	-	-	-	0.0000339
80/20	34	12	2	52	-	-	_	-	-	0.0000137

Table 5.4 Linear combination fitting results expressed as a percentage of Total Fe for Fe K-edge spectra collected on the 0-8mm section of Ultisol experiments after 28-day incubation.

<sup>†</sup>PA / SF FA Blend = blend of phosphoric acid and sub-fraction of fulvic acid; MAP =

monoammonium phosphate applied in  $125\mu$ L solution volume; DAP = diammonium phosphate applied in  $125\mu$ L solution volume; APP = ammonium phosphate applied in  $125\mu$ L solution volume; 80/20 = 80% monoammonium phosphate / 20% ammonium polyphosphate applied in  $125\mu$ L solution volume; FA 1 = fulvic acid co-applicant 1 applied at  $0.73\mu$ L per dish; FA 2 = fulvic acid co-applicant 2 applied at  $1.43\mu$ L per dish; SF FA = Sub -fraction of fulvic acid co-applied at  $0.78\mu$ L per dish ‡ Hm = hematite; Goe = goethite; Sid = siderite; Fh = ferrihydrite; Viv = vivianite; Mag = maghemite; Non = nontronite; Fe/Al Cop = Fe/Al coprecipitate; Lep = lepidocrocite

## Conclusions

The results of this study suggest that if liquid P fertilizers are being added to a highly weathered soils, that a MAP or DAP-based solution would likely be subject to less chemical fixation and may translate into greater P plant acquisition efficiency in the year of application. Not only did the treatments diffuse slightly farther, enriching a larger volume of soil, but what did move was as resin extractable or greater than the fertilizers containing polyphosphates.

The most surprising and definitely controversial findings of this investigation surround the co-application of fulvic acids with the liquid P fertilizers. Lab-based investigations aiming to find the mechanism of action for high cation exchange capacity fertilizer enhancement products have not been able to link significant differences in P lability to co-application (Borggaard et al.,2005; Degryse et al., 2013). This study largely agrees with those findings but is the first to employ synchrotron-based P and Fe K-edge XANES as part of the investigation. The consistent changes in P and Fe speciation indicate that a fulvic acid effect does appear to be present that is being missed by wet chemical methods of inquiry. The implications of these alterations for agriculture and the mechanisms by which fulvic acids are working, require further study to determine.

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# Chapter 6 - Urban Gardening on Brownfields Sites – A Breath of Fresh Air?

# Abstract

Urban gardening has been experiencing increasing popularity around the United States for a number of years now. Initially, many growers were unaware of the possibilities of soil contamination both with organic compounds and trace elements, but thankfully due to the diligent efforts of the scientific community, light has been shed on these seemingly "invisible" issues. Three pathways of exposure are typically cited for these pollutants to enter the human body: ingestion of soil directly, consumption of produce containing or superficially contaminated with a hazardous substance and inhalation of soil dust. The first two modes have received much attention, however the contribution of the inhalation route has not been adequately investigated due to the assumption that the pathway is the least significant. Two inhalation risk studies were carried out in urban gardens located in Kansas City, MO by collecting dust while 5m<sup>2</sup> plots were rototilled. Microclimatic variables were monitored and total inhalable dust mass was determined using a personal sampling train including a small pump and air filter. For the Study 1, soil lead (Pb) concentration was assessed via acid digestion with subsequent analysis using ICP-OES. Particle size distribution of collected particles was estimated through analysis of SEM images of filters. Little dust was collected at either site. Most particles captured, however, appeared to be less than 4µm in diameter suggesting that what was generated could enter deep into the human respiratory system. The amount of dust emitted appeared to be indirectly correlated with soil moisture in the 2-10cm and 10-20cm portion of the soil profile. Tilling reduced soil aggregate size and blended lead concentrations resulting in a more homogeneous distribution of the element. Dust inhalation while tilling is likely not a major lead exposure risk for gardeners, but

given the preponderance of very small particles in what was captured, care should be taken to prevent dust from entering the respiratory system as much as possible.

## Introduction

Over the last one and a half centuries, tremendous technological progress has been made to improve and extend human life on planet Earth. Horses have been replaced by the internal combustion engine, cellular phones are commonplace, and the internet is ever increasingly essential to our daily functioning lives. Sadly, with great advancement, comes great cost. Each passing day, the world becomes more polluted with harmful, naturally occurring and xenobiotic, compounds that inflict an often unnoticed cost on human health. Along with this advancement, a rapidly growing percentage of the world population is moving into urban areas, and the availability of fresh, nutritious produce in densely populated, low income areas has become cause for concern. (U.S. Census Bureau, 2012) "Food deserts," as they often have been called, are appearing in cities of not only the United States but around the world; places where grocery stores, if present, lack the means to obtain and/or sell quality fruits and vegetables in an economically efficient manner. Those unable to travel out of these areas are left reliant upon fast food establishments and convenience stores to satisfy, at the very least, their daily caloric requirements. One solution to this unfolding social injustice that has received widespread public and governmental support as well as a fair amount of success is the implementation of urban community gardening programs. Not only have these programs helped to alleviate malnourishment in economically unstable areas, but they have served to improve social relations creating networks that further foster improved community development (Hynes and Genevieve, 2004).

A major issue hindering the rapid implementation of urban gardens in many areas is the concern of growing food in soil that may not be safe. University and government research is making information available to address these misgiving. Knowledge in reference to assessing the risks associated with urban gardening is still lacking in certain areas however. In many communities, lead (Pb) contamination remains the primary culprit. The heavy metal, an artifact of anthropogenic activity, has entered the soil primarily as a result of the prolonged use of leaded gasoline in the internal combustion engine and leaded paint applied inside and out of many buildings from approximately the 1920's until 1996 and 1978 in the United States, respectively (Binstock et al., 2008; Markey et al., 2008; McBride et al., 2011; Schwarz et al., 2012). Human exposure has been linked to a variety of health maladies leading the Center for Disease Control (CDC) to recommend action at blood lead levels (BLL) exceeding 5 µg/dL (USCDC, 2019). Children are especially susceptible to the toxic effects of Pb resulting in developmental impairment due to their high frequency of hand to mouth activity and increased intestinal absorption capabilities. Adults are not immune though. Delta-aminolevulinic acid dehydratase (ALAD) inhibition has been documented at low concentration causing reduced heme production. Heme is a critical component of iron-containing proteins (e.g. hemoglobin) essential for human health (Hettiarachchi and Pierzynski, 2004). Direct ingestion and inhalation of Pb containing soil particles as well as consumption of plant material that has absorbed the contaminant are thought to be the three main pathways for the element to enter the bloodstream (Wortman and Lovell, 2014). Mielke et al. (1997) was able to demonstrate a direct correlation between high soil test levels and increased blood Pb concentrations in both children and adults. Understanding the mechanisms facilitating these pathways is essential to ensuring the implantation of safe urban gardening programs.

Of the three exposure pathways listed above, inhalation exposure is an area that is yet to be thoroughly characterized. Due to the extreme variability that exists both within and between garden sites, the applicability of the information once the data has been collected and analyzed

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remains to be seen. Although a plethora of instruments have been developed to measure concentrations and total mass transport of suspended, respirable dust, none possess the ability to measure concentrations in real time while still retaining large enough samples to allow for elemental and size distribution analysis. Kasumba et al. (2011) was successful in obtaining dust profiles resulting from disking operations of a cotton field in New Mexico, but elemental analysis of the dust itself was beyond the scope of the study. No research, to date, has been found in which the inhalation exposure of urban gardeners has been quantified on brownfield sites.

The goal of this investigation was to quantify the inhalation exposure risk to urban gardeners working on brownfield sites. The experiments were carried out in two urban soils on sites historically used for gardening located in Kansas City, MO by collecting dust while 5m<sup>2</sup> garden plots were rototilled. Microclimatic variables were monitored, and total inhalable dust mass was determined using a personal sampling train.

#### **Materials and Methods**

## **Experimental Design**

Two small dust collection studies modelled after United States Environmental Protection Agency's standard operating procedure for activity-based air sampling for asbestos were conducted to quantify the amount of dust that a gardener may be subjected to while rototilling a garden plot (USEPA, 2007). The first (Study 1), in 2014, was conducted at 39.082495° N, 94.551380° W on Montgall Avenue in the Washington Wheatley Community Garden. The soil was a loam (26% Sand, 48% Silt, 26% Clay). Four 5m<sup>2</sup> plots were established and rototilling was conducted on each alternating between an east-west and north-south orientation three separate times for 60 minutes during tillage event 1 and 45 minutes for events 2 and 3 over the

Date	Tillage Event	Temperature	$\mathbf{R}\mathbf{H}^{\dagger}$	Wind Speed	Solar Radiation
		٥C	%	$m s^{-1}$	W m <sup>-2</sup>
6/21/2014	1-A	30	59	0.6	803
6/22/2014	2-A	30	55	0.2	98
7/19/2014	1-B	26	54	0.6	111
7/22/2014	2-B	37	47	0.3	415
8/2/2014	3	30	45	0.5	298

Table 6.1 Study 1 collection dates and average weather parameters.

† RH = relative humidity

course of five collection days. Two plot blocks for the first two tillage events are referred to A and B. The rototiller was a Honda F-600 mid-tine tiller and was operated at full throttle. Two plots were tilled each of the first four days and all four plots were tilled for the third time on the final day. The first tillage event incorporated an established grass cover. Tillage dates and average weather parameters can be found in Table (6.1). The second collection study (Study 2) occurred in 2017 at a garden site on a loam soil (34% Sand, 44% Silt, 22% Clay) located along Vine St. in Kansas City, MO at 39.082738° N, 94.564027° W following the same protocols as the first. This time six 5m<sup>2</sup> plots were delineated and tilled three times each for 45 minutes in which the first incorporated a grass cover. The plots were divided into two blocks, A

Date	Tillage Event	Temperature	RH <sup>†</sup>	Wind Speed <sup>†</sup>	WS Max	Solar Radiation
		٥C	%	$m s^{-1}$	$m s^{-1}$	W m <sup>-2</sup>
9/15/2017	1-A	30	56	1.3	3.3	247
10/2/2017	1-B	29	50	1.7	4.1	312
11/3/2017	2-A	8	66	1.7	3.0	268
11/6/2017	2-B	6	61	1.4	3.1	260
12/1/2017	3-A	14	32	1.4	3.6	319
12/6/2017	3-B	8	41	N/A	N/A	238

Table 6.2 Study 2 collection dates and average weather parameters.

† RH = relative humidity; WS Max = maximum recorded wind speed
and B, therefore tillage occurred on three plots each sampling day. Tillage dates, duration, and average weather parameters can be found in Table (6.2).

# Weather Data

Weather at the sites was monitored using a small weather station equipped with a Campbell Scientific CR1000 datalogger located in the center of the research site (Figure 6.1). Temperature, relative humidity (RH), wind speed, and solar radiation were monitored using Campbell Scientific CS215, R.M. Young Wind Sentry (Study 1) /Wind Monitor (Study 2), and



Figure 6.1 Weather station operating at the Washington Wheatley site.



Figure 6.2 Rototiller operator equipped with personal sampling train.

Apogee SP110 pyranometer, respectively. Temperature was assessed at 1.5m above groundlevel, while the remaining parameters were collected at 2m.

# **Dust Sampling**

Dust sampling was completed during rototilling activity using a personal sampling train. A sampling train was defined as a Buck Libra Plus LP-5 sampling pump connected via clear PVC tubing to a 47mm polycarbonate filter holder (Gelman Sciences Inc. - Product 1119) modified such that the filter exposure area measured 35mm in diameter containing a 46.2mm Whatman polytetrafluoroethylene (PTFE) filter with polypropylene support ring and 2µm pore space. Pump flow rate was calibrated at the beginning of each day prior to collection using a Bios Defender 530, and air was sampled at a rate of approximately 4.8L min<sup>-1</sup> The filter holder was attached to the person performing the rototilling within 30cm of the nose and mouth high on the chest (See Figure 6.2). For reference, the researcher was 1.9m tall but was often bent over slightly in order to push the tiller unit. Control sample collections of 45 minutes were obtained on random sampling days prior to any tillage taking place to establish background dust concentrations. The sampling train was attached to the weather station at a height of 1.5m for this collection.

Filter mass was determined according to guidance provided by the United States Environmental Protection Agency's "Measurement Technology Laboratories PM2.5 Teflon Filters Quality Assurance Project Plan" (EPA project number PR-NC-09-10333) using a Sartorius XM1000P microbalance housed within a glovebox. The temperature was kept between 21-25°C and relative humidity was controlled by a saturated magnesium chloride solution such that the RH was between 35 and 40%. Individual filters were stored in Petri dishes (88mm diameter and 12.9mm height) and allowed to equilibrate to glovebox conditions before and after dust sampling for at least 24 hours prior to weighing. Filters were passed in front of a CEM Anti-Static Ionizer to neutralize any static charge that may have accumulated and disrupt accurate mass assessment over time. A successful weighing event was considered finalized when the filter mass could be recorded to the 1µg three consecutive times within a 5µg range. Blank mass is reported and was not subtracted from the final sample mass.

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#### **Soil Characterization**

Soil core samples were collected at depths of 0-2cm, 2-10cm, and 10-20cm at five locations within each plot for gravimetric water content evaluation and other wet chemical assessments. In Study 1, cores were stored separately, and in Study 2, cores were combined into composite samples. Gravimetric water content was determined according to Gardner (1986) for both studies. For Study 1, aggregate distribution was measured with a rotary sieve using four core locations from two time periods: initial sampling before tilling and samples collected immediately prior to the third tillage event. Total soil lead was also assessed for Study 1 using EPA method 3051a with Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis on single samples collected from the center of plots before each of the three tillage events.

#### **Particle Size Distribution**

Size distribution of particles entrapped by the PTFE filters was investigated using a FEI Nova Nano-SEM 430 scanning electron microscope (FE-SEM) (Hillsboro, Oregon) equipped with vCD and Oxford X-Max Large Area Analytical energy dispersive X-ray spectroscopy (EDS) silicon drift detectors. While under vacuum, using a spot size of 3.5 and accelerating voltage of 5kV, twenty-five images of approximately 150 x 140µm (2000x magnification) were captured in a 5x5 gridded pattern on the filter of the sample collected on plot 4 of the third round of tillage in study 1. Particles were identified and their diameter distribution were evaluated using the National Institutes of Health (NIH) program ImageJ. Energy dispersive X-ray spectroscopy was also implemented to look for elevated Pb concentrations in the captured particles.

#### **Statistical Analysis**

All statistics were determined in SAS (v. 9.4, 2017). Comparison of mean dust collection masses was conducted using Proc Mixed. The Tukey Pairwise Method was used for comparison of all treatments at an  $\alpha = 0.05$  level of significance.

## **Results and Discussion**

#### **Dust Capture**

Collection results suggest that under most of the rototilling conditions tested, very little dust was generated (Figures 6.1 and 6.2). In Study 1, only collections made during the third tillage event indicated that a large amount of particle matter was cast into the air, while the first event in Study 2 recorded the most dust efflux. Control collections made prior to rototilling suggest that the air was relatively clean when no gardening activity was taking place as their mass was not much higher than blanks (Table 6.3). Blank values are likely an indicator that the filter weighing procedure used was less than perfect rather than suggestive of mild contamination. Filters can accumulate small amounts of moisture that may not be fully corrected for during the twenty-four hour conditioning period. While less than optimal, the small increase in filter mass does not largely skew data interpretation; even in the most severe events, very little dust was generated. One major limitation of this study is that the temporal dust collection profile is not available. Because sampling was conducted over 45-60 minutes, we do not know if the rate of dust efflux was constant or if there were periods of time that were more potentially hazardous than others. In other words, during the sampling period, was the dust concentration generally consistent or were periods of low dust concentration punctuated by a few very dusty events.

Even though total dust collection was low, the lack of temporal resolution imposes some limitations on interpretation and refinement of best practices to protect gardeners.

Table 6.3 Control and blank filter masses for Washington Wheat	ey and	Vine St.			
dust collection studies.					

Site		Blank	Control
		μg	μg
Washington Wheatley	Mean	15	25
	SE †	5	10
	Range	-16-30	15-35
Vine St.	Mean	22	33
	SE	5	9
	Range	6-45	9-69

 $\dagger$  SE = standard error



Figure 6.3 Mass of dust collected on PTFE filters normalized to a 45-minute sampling period from Washington Wheatley tillage experiments. Box plots with the same letter indicate means that are not statistically different at P = 0.05 using Tukey's honest significance test. 1-A = first tilling, Block A; 1-B = first tilling, Block B; 2-A = second tilling, Block A; 2-B = second tilling, Block B; and 3 = third tilling, all blocks



Figure 6.4 Mass of dust collected on PTFE filters from Vine St. tillage experiments. Box plots with the same letter indicate means that are not statistically different at P = 0.05 using Tukey's honest significance test. 1-A = first tilling, Block A; 1-B = first tilling, Block B; 2-A = second tilling, Block A; 2-B = second tilling, Block B; and 3-A = third tilling, Block A; 3-B = third tilling, Block B

#### Soil Moisture

Interestingly, in this investigation the degree of tillage does not appear to be the primary driver of dust efflux, but rather that soil moisture plays the most determinant role in regulating emission. Figures 6.3 and 6.4 show that in both studies, regardless of how many times the soil was tilled, the driest conditions were what predicted the greatest dust capture. For both sites, the gravimetric water content of the 2-10cm layer had to reach less than 15% for significant dust capture to occur. The findings did not necessarily correlate with surface layer, this may be due to the fact that this fraction represents a small percentage of the total soil volume that is quickly incorporated with the rest upon disturbance. This is not the first study to document that dust efflux is dependent upon soil water. Munkhtsetseg et al. (2016) using a PI-SWERL device demonstrated a reliable decrease in threshold friction velocity as a bare sandy soil dried, while Li and Zhang (2014) observed the same while studying dust emission from the Horgin Sandy Land Area. The polar nature of water leading to its cohesive and adhesive properties helps to bind soil colloids to one another restricting their surface release. Fascinatingly, Li and Zhang (2014) observed more saltation of the  $\geq$  50µm fraction in wet soil than dry soil but less overall fine particle ( $0.1 \le d \le 20\mu m$ ) discharge. The sampling height on the operator of this study may have been too high to capture this process. One management practice that may prove protective of gardeners is to limit soil disturbance under extremely dry soil conditions.

Despite similar water content, fewer particles were captured in Study 2 Event 1-B compared to 1-A. This may be due to the fact the weather was slightly more windy during collection on 1-B (Table 6.2). While seemingly counterintuitive (i.e. more wind typically generates more dust), perhaps the air movement carried the particles off-site more quickly preventing their capture within the research plot using this experimental protocol. It is possible

our methods to assess gardener exposure do not completely reflect the absolute dust generation profile. For example, when rototilling with the wind direction, dust would be carried away from the operator and would not be sampled. The objective of this study was to assess exposure to the gardener so, this is not seen as an oversight, but is an aspect worth acknowledging when considering the dataset. Further study would be required to accurately assess what proportion of dust may be missed as a result of the subjective sampling position. It is conceivable that under windy, dusty conditions that only tilling in the direction of the wind may reduce operator exposure.

#### Aggregate Size

As expected, tilling does disrupt the aggregate size distribution of the soil (Figure 6.5) (Hou et al., 2013). Assessment of Study 1 aggregates shows that the 2-10cm and 10-20cm parts of the profile experienced a redistribution of particles from larger aggregate fraction (e.g. 6.35-14.05mm) to the smaller (e.g. < 2mm). This shift was not as evident in the 0-2cm layer, likely due to the originally more granular structure that already skewed towards the smaller side of the spectrum. This enrichment of the smaller size fraction could also help explain why the third tillage event of Study 1 generated the most dust. The combination of very dry, poorly aggregated soil would make for more ideal dust releasing conditions. Tatarko (2001) states in a review of soil processes related to dust emission that wind tunnels tests have shown that a soil with 1% of aggregates > 0.84mm is ten times more erodible than a soil with 53% of aggregates above the same threshold. By the third tillage of Study 1 the < 0.84mm fraction has been greatly enhanced.



Figure 6.5 Comparison of soil gravimetric water content with the amount of dust captured on PTFE filters while air sampling during rototilling activity in Study 1.



Figure 6.6 Comparison of soil gravimetric water content with the amount of dust captured on PTFE filters while air sampling during rototilling activity in Study 2.



Figure 6.7 Comparison of aggregate size distribution with the amount of dust captured on PTFE filters while air sampling during rototilling activity in Study 1.

### Soil Lead

Individual soil Pb measurements of Study 1 plots reveals relatively homogeneous, mild contamination throughout the 0-20cm profile with the exception of Plot 4 where a "hot spot" of 1977 mg kg was observed prior to tillage at the 2-10cm depth. Lead was not measured in Study 2 as the results were not deemed to be necessary to interpret the dust results. Dust generation is not likely contingent on lead concentration, so collection results really could be generalized to any concentrations of the contaminant for health assessments purposes. Table 6.4 nicely highlights the dilution effect that can occur when soil is disturbed (i.e. mixed by tilling). After two rounds of cultivation, the high concentration is then spread throughout the entire sampled depth. Blending cleaner soil with contaminated soil has been a suggested approach to mitigating the effects of Pb contamination exposure (Attanayake et al., 2014). The idea being that if a given

Plot	Sample Depth	Never Tilled	Tilled Once	<b>Tilled Twice</b>
	cm	mg kg <sup>-1</sup>	mg kg⁻¹	mg kg⁻¹
	0-2	237†	228	274
1	2-10	260	228	269
	10-20	141	216	194
	0-2	232	221	232
2	2-10	217	193	228
	10-20	222	222	220
	0-2	180	152	184
3	2-10	169	186	166
	10-20	182	157	448
	0-2	392	402	538
4	2-10	1977	412	548
	10-20	271	308	781

Table 6.4 Distribution of soil Pb by depth and tillage event in WashingtonWheatley plots as assessed according to EPA method 3051a

† all values are single measurements

amount of soil is going to enter the body, the lower the better. This data documents that phenomenon.

### **Particle Analysis**

Scanning electron microscopy interrogation of the filter from Plot 4 Study 1 Event 3 suggests that the vast majority of particles collected on the filters are less than  $4\mu$ m in diameter (Table 6.5). This is concerning as the smaller the particle, the further that particle can enter the respiratory system and cause damage human health. Additionally, the colloidal fraction is the most chemically reactive and tends to be enriched with Pb relative to the bulk concentration (Juhasz et al., 2011). A preponderance of these particles could lead to underestimation of contaminant exposure risk if bulk concentration analysis is used for assessment purposes. In this study, energy dispersive spectroscopy of individual particles revealed common soil elements such as silicon, calcium, and potassium but did not register Pb (Figure 6.8). The limit of detection for this method is approximately 1000 mg kg<sup>-1</sup>, so it may be that Pb was present but at undetectable concentrations.

Table 6.5 Size distribution of particles observed entrained in the PTFE filter usedto sample the dust generated from the third tilling of Plot 4 of the WashingtonWheatley study using FESEM.

Size Fraction	<b>Particle Count</b>	<b>Percent of Total Particle Count</b>
(um)	<b># of units</b>	%
< 4	99	73.9
4-10	33	24.6
10-100	2	1.5
<2.5	71	53.0
<10	132	98.5



Figure 6.8 FESEM EDS analysis of particles observed entrained in the PTFE filter used to sample the dust generated from the third tilling of Plot 4 of the Washington Wheatley study.

## **Risk Evaluation**

Although a couple of tillage events in this investigation did result in elevated amounts of dust capture, overall data suggests that dust inhalation is not a major soil Pb exposure pathway for urban gardeners even if contamination levels had been much higher. For example, the human adult body contains approximately 55dL of blood, so to raise blood Pb levels 1µg dL<sup>-1</sup>, 55µg of Pb would need to enter the body and be absorbed. The most dust generating event in this study captured 760µg of soil by sampling approximately 216L of air indicating a dust concentration of 3.5mg m<sup>-3</sup>. The highest soil Pb concentration measured was 1977mg kg<sup>-1</sup>, so under the absolute worst conditions measured, 27mg of soil at 100% bioavailability would need to be inhaled to raise blood Pb levels by 1µg. Under these conditions ~7.7m<sup>3</sup> would need to be inhaled. For

reference, the average person briskly walking for one hour only inhales  $\sim 1.5 \text{m}^{-3}$  per hour. Thus, this pathway appears to be minor. Also, important to note is that these  $5\text{m}^2$  were tilled for a much longer duration than a typical gardener would till them for, further exaggerating the potential risk presented here. This is not to say that dust is not important in other contexts. The half-life of lead in the blood is approximately 36 days, so prolonged exposure in a setting, such as a construction site on even mildly contaminated ground could prove to be quite hazardous over time (WHO, 1995). Also, as referenced in the results, the dust collection for these studies was a single point on a moving person performing the activity. Community members downwind could be accidently exposed more so than the individual gardener if they remain in the airflow carrying the particles offsite.

### Conclusions

The results of this investigation suggest that short-term dust exposure from rototilling on mildly contaminated brownfields sites is not a major Pb exposure pathway for urban gardeners. A couple of sampling events did record elevated air concentrations of dust relative to the others. This seems to be related to the gravimetric soil water content of the 2-10 and 10-20cm sections of the soil profile; the drier the soil, the more dust that is generated. The degree of tillage and subsequent reduction of aggregate size may play a role in encouraging particle emission, but the contribution seems to be less than the soil moisture. Particles that were collected tended to be less than  $4\mu$ m in diameter, and thus, could pose a risk to respiratory health. Out of an abundance of caution, gardeners tilling under dry conditions may choose to wear a dust mask to mitigate particle inhalation to the greatest extent possible.

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# **Chapter 7 - Summary and Conclusions**

As has been observed in many studies prior, calcium interactions largely governed phosphorus availability in the calcareous soils of this project and various sorption reactions with iron and aluminum drove P fate and transport in the Ultisol. This investigation found however that in the case of liquid P fertilizer that formulation (e.g. P species, P concentration) and coapplication of carbon-based compounds can alter P partitioning and/or lability around the point of application and may also be changing the surrounding mineralogy.

In the mildly calcareous soils, addition of condensed phosphates (e.g. pyrophosphate) as even a relative small proportion (~10%) of total P application had a significant impact on orthophosphate (OP) availability. The polyphosphates (PP) may be preventing Ca-P precipitation slowing the formation of sparingly soluble minerals, such as apatite, allowing for more adsorption, reversible processes to dominate. The greater affinity of the polyphosphates for iron and aluminum oxyhydroxides compared to OP was abundantly clear. The preference of PP for Fe or Al was not. Application of pure OP species in the form of phosphoric acid, monoammonium phosphate (MAP) in a dilute solution, and MAP with sodium alginate improved P resin extractability by keeping Ca-P interactions in highly soluble mineral forms. Further study will be required to fully understand whether all P applications first form these species and then ripen to less soluble forms or if these treatments induced more favorable Ca-P precipitates.

Co-application of fulvic acids with liquid P fertilizers to the calcium rich soils did not seem to improve P lability as assessed by anion exchange resin extractability but may have slightly impacted diffusibility positively with one product and negatively with another. Synchrotron-based XANES analysis is highly suggestive that the products are altering P

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chemistry in the soil however and that wet chemical analysis may be missing these impacts. Coapplication of fulvate seems to delay Ca-P mineral ripening to more stable forms and promote P sorption over Ca-P precipitation.

In the acid Ultisol from Brazil, the orthophosphates remained more labile than treatments that included PP. This observation is a logical manifestation of the strong affinity of PP for Fe and Al oxyhydroxides demonstrated in the calcareous soil experiments. Polyphosphate addition encouraged Fe-P mineral formation and showed a preference for aluminum associated with phyllosilicate clays, white DAP and MAP exhibited more even distribution amongst the Fe and Al-based colloids. Wet chemical analysis did not reveal any fulvic acid co-application effect, but again P and Fe XANES analysis of soil collected around the point of application shows consistent alterations in Fe mineralogy and P partitioning that suggests that the products do affect soil chemistry though the mechanism(s) of action are not clear at this time.

In general, the results of the phosphorus investigations are encouraging in that they suggest that a better understanding of how P species and co-applicants interact with soil colloids can result in vastly improved phosphorus fertilizer use efficiency in agricultural systems. Further study of these treatments on a range of soils with varying inherent characteristics is essential as will be the inclusion of actual crops. We know that plants can be incredibly plastic in adapting to the soil environment, so how much of an impact the observed chemistry differences translate to true plant nutrient uptake ability should be assessed.

The dust inhalation study conducted on brownfields in Kansas City provides preliminary evidence that inhalation is not a major pathway for lead to enter gardener's bloodstream. As one would expect, the amount of dust generated was strongly correlated with soil moisture; drier soil emitted more dust. The degree of tillage or soil disturbance seemed to play less of a role. While

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lead inhalation does not seem to be a major concern, the dust that was captured was largely less than  $4\mu m$  in diameter meaning that any that was inhaled could enter deeply into the respiratory system. Care should be taken by gardeners to protect themselves. Further study is required to more definitively quantify the on-site and off-site dust exposures. More dust monitoring devices should be deployed with greater temporal resolution to correlate spatial dust emission with weather parameters.