Blending MAP, APP Reduces Fluid Fertilizer Input Costs

While mitigating environmental impact in high pH soils.

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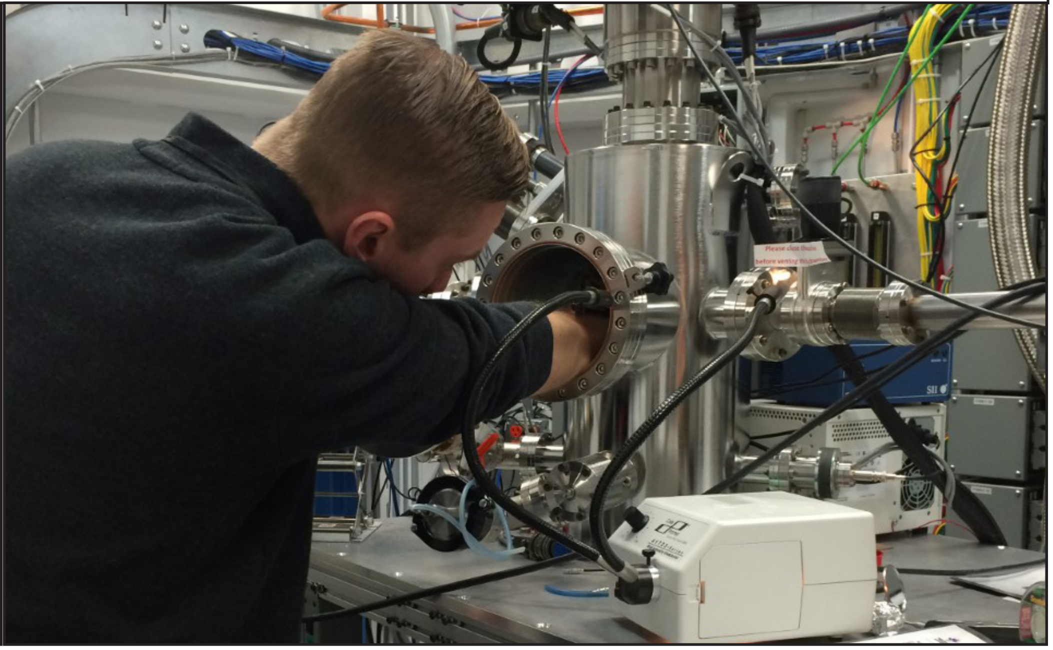
Summary: *Including small amounts of polyphosphates when applying fluid MAP to calcareous soils could potentially allow growers to apply less total phosphorus to agricultural systems without compromising plant performance. While more work is necessary, our group believes the blending approach possesses tremendous potential to reduce total P inputs to calcareous soils in the future, simultaneously saving grower capital, conserving a non-renewable resource, and protecting freshwater ecosystems.*



The challenge of efficiently managing phosphorus (P) in cropping systems on high pH, calcareous soils is one that many farmers are well acquainted with. Faced with high input costs, low commodity prices and stringent scrutiny from regulatory organizations, the Media and the general public, those who grow our food, find themselves in a frustrating situation. While the food culture in the United States continues to mature, one way progress can be made to benefit the collective as a whole is to find ways to produce low cost, environmentally friendly fertilizers that provide growers' crops with the nutrients they need, when they need them--no more, no less.

In the drier regions of the World, high pH calcareous soils are very common (FAO 2016). When P fertilizers, especially orthophosphate (OP) fertilizers, are applied to these soils much of the element that was intended for the plant quickly reacts with calcium (Ca) to form insoluble compounds that are not plant-available essentially wasting money and the non-renewable, vital resource. Unfortunately, the plant unavailable compounds, although not helping the farmer, can still erode into freshwater bodies and contribute to eutrophication along with its concomitant slew of human and environmental health consequences. Use of polyphosphates (PP), instead of OP, drastically improves fertilizer acquisition efficiency (FAE), but PP must undergo an enzyme mediated hydrolysis reaction before becoming useable by plants, causing growers to fear P deficiency in the early part of the growing season when soils are still cold (Holloway et al. 2001). Further investment into fertilizer research and development of new technologies is required to prevent or retard Ca-P "fixing" reactions to keep P plant-available in high pH calcium-rich soils.

Much work has already been done in this arena. As mentioned above, use of PP instead of OP in fertilizers can improve FAE. Additionally, fluid fertilizers prove superior to their granular counterparts in that they allow P to diffuse greater distances from the point of application. Greater diffusive distances give the fertilizer application a greater "footprint" and decrease the P concentration at any discrete point in the soil. High P concentrations promote the formation of plant-unavailable Ca-P compounds. Because fertilizer granules are very dry in comparison to the surrounding soil when they are applied, soil water, rich in Ca, rushes into the granule causing fixation to take place within the granule itself, severely arresting P diffusion (Lombi et al. 2004 and Pierzynski and Hettiarachchi 2016).

In response to the benefits and drawbacks of OP versus PP, some farmers blend fluid sources such that monoammonium phosphate (MAP), an OP source, accounts for 80% of the total P added and ammonium polyphosphate (APP) makes up the remaining 20%. The small addition of PP possibly allows for P to diffuse further into the profile, while the majority of OP mitigates the risk of early-season P deficiency. While this sounds like a reasonable approach, no controlled research of the actual chemical behavior of this mixture, compared to full applications of fluid MAP or APP, has been reported. To the surprise of the investigators, this initial study indicates potential for significant FAE increases when blending P sources compared to 100% OP applications, suggesting that this approach may actually be best.

Objective

The objective of this study was to investigate the chemical mechanisms responsible for the fixation of P in a mildly calcareous western Kansas soil when fluid formulations of MAP, APP, and an 80/20 mixture of MAP and APP, respectively, are applied. Both traditional wet chemical analysis and new-age synchrotron based assessment were employed in an effort to help the agricultural community better understand the fate and transport of P, allowing fertilizer application and formulation recommendations to be improved in the future.

Methodology

Design. Twenty-four Petri dishes (88 mm diameter and 12.9mm height) were packed to a bulk density of 1.1g cm-1 with a high pH, calcareous silt loam from Finney County, Kansas (see Table 1) pre-wetted to 18% maximum water-holding capacity (MWHC). After packing, the soils were brought to 50% MWHC, the covers were placed on the dishes, the edges were wrapped in Parafilm, dishes were inverted and allowed to equilibrate at room temperature (-24oC) for at least 24 hours. Treatments were then slowly administered using a syringe at the exact center of the dish. A treatment was defined as enough fertilizer to equal 9.2 mg P dissolved in 125µL of E-pure water. This is approximately the same amount of P found in a single fertilizer granule. The four treatments consisted of a water-only control, technical grade monoammonium phosphate (FisherBrand ACS Grade) ammonium polyphosphate (11-37-0 Mosaic formulation) and an 80/20 blend of the previous two treatments, respectively, to account for the required amount of P. 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 dish 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 25o C. Following incubation, the dishes were excavated into four concentric circular sections with radii of 0-8mm, 8-15.5 mm, 15.5-27mm and 27mm-dish edge extending from the point of application (POA). The sections were then dried at 40o C, weighed and finely ground with a mortar and pestle.

Chemical analysis. Five replicates were used for wet chemical analysis. Plant available P was assessed via the anion exchange resin technique with subsequent colorimetric analysis for the molybdate reactive fraction, and total P was determined via aqua regia digestion followed by ICP-OES analysis (Murphy and Riley 1962, Myers et al. 2005 and Premarathna et al. 2010). Orthophosphate in resin P extractions was quantified soon after extraction and again following digestion of the extraction in sulfuric acid to convert PP and other non-OP species to OP (McBeath 2006 and Murphy and Riley 1962). Oxalate extractable (amorphous) iron (Fe) and oxalate extractable P were analyzed according to Loeppert and Inskeep (1966), and pH was assessed using an electrode in a 1:10 soil:water suspension.

Synchrotron investigation. The synchrotron-based investigation was completed on the sixth replicate at Beamline 6B1-1-SXRMB of the Canadian Light Source (Saskatoon, SK). After drying, the 0-8mm and 8-15.5mm sections were very finely ground and thinly spread onto carbon tape before being placed under vacuum for analysis. Three scans were taken of each sample at the P K-edge (Eo = 2149eV). A double crystal indium antimonide/silicon monochromator was used 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. Background baseline manipulation 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 Manceau et al. (2012) and Werner and Prietzel (2015) (Ravel and Newville 2005).

Results

Affecting soil pH. As has been noted in prior P studies, the addition of APP causes pH to decrease in the fertilized zone of calcareous soils due to the hydrolysis of polyphosphates by phosphatase enzymes. Figure 1 shows that this effect is more or less localized to the area directly surrounding the POA. Phosphorus is considered to be most plant available near neutral pH, so one advantage of using APP is

Table 1. Inherent characteristics for a western Kansas, calcareous soil.

Texture	pH	Calcium Carbonate (%)	Cation Exchange Capacity (cmol kg^{-1})	Total P (mg kg^{-1})
Silt Loam	8.6	7.7	18.4	744

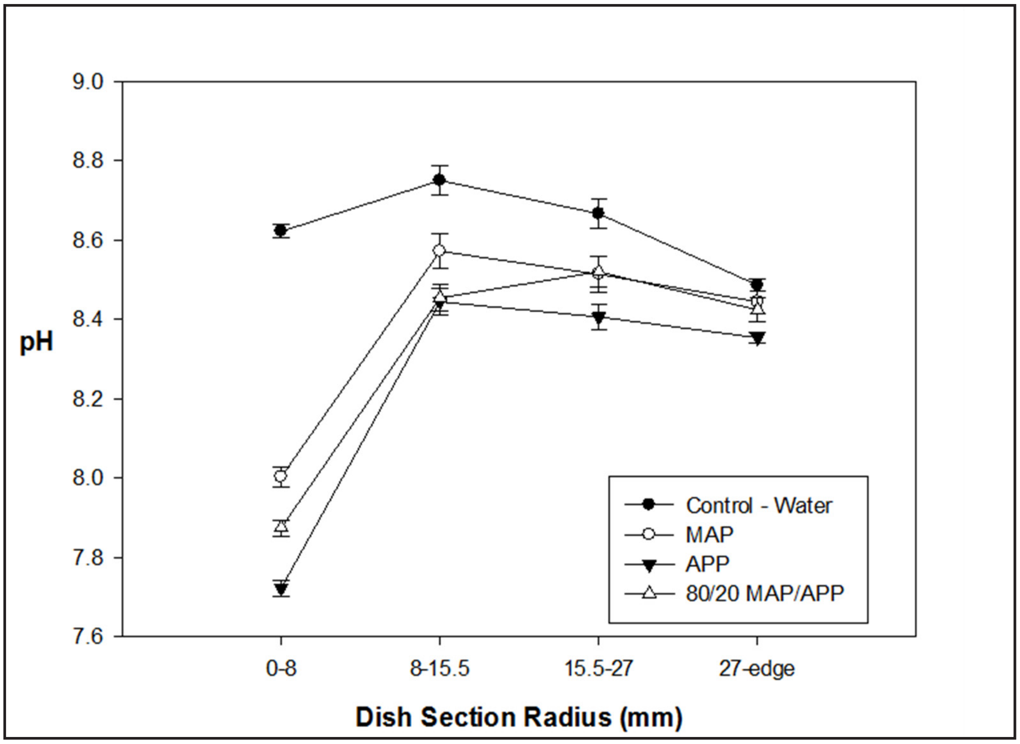


Figure 1. Soil pH as reported by dish section and treatment.

the acidulation effect that increases P availability.

Dealing with fixation. Resin extractable P results were somewhat surprising. Figure 2 reveals that the 80/20 blend of MAP and APP produced the greatest proportion of labile OP as compared to the total P present in the soil (native P + P fertilizer added) and MAP produced the least.

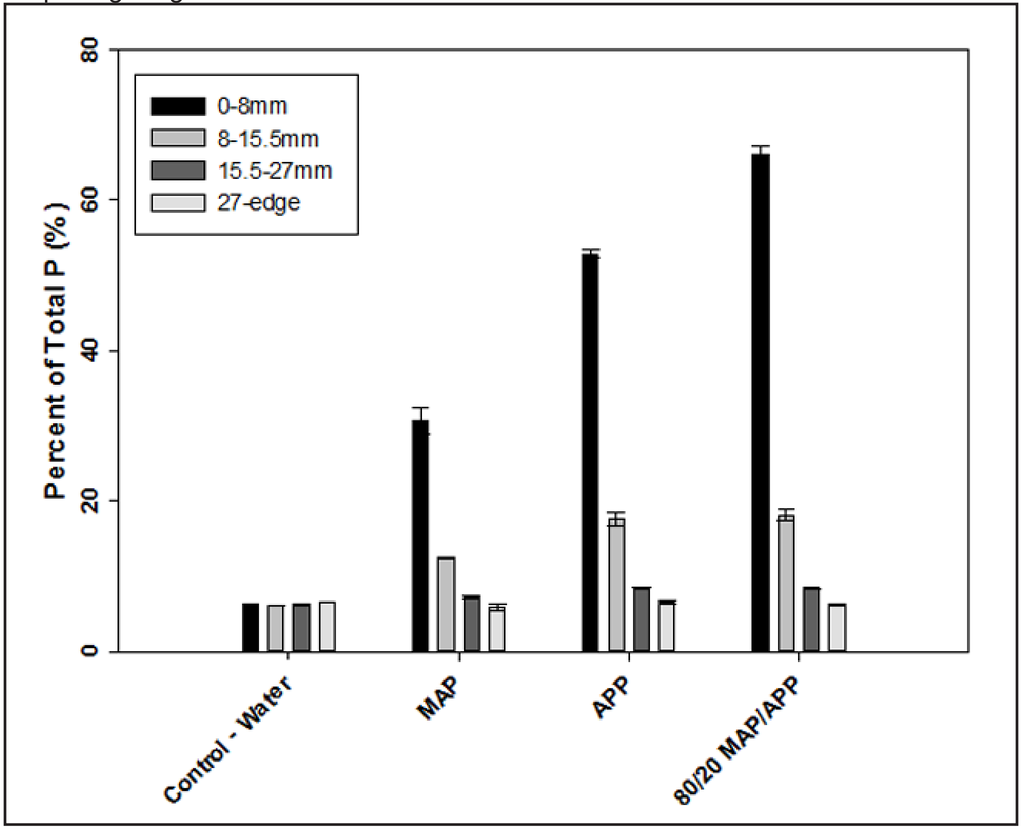


Figure 2. Resin extractable P as a percentage of total soil phosphorus.

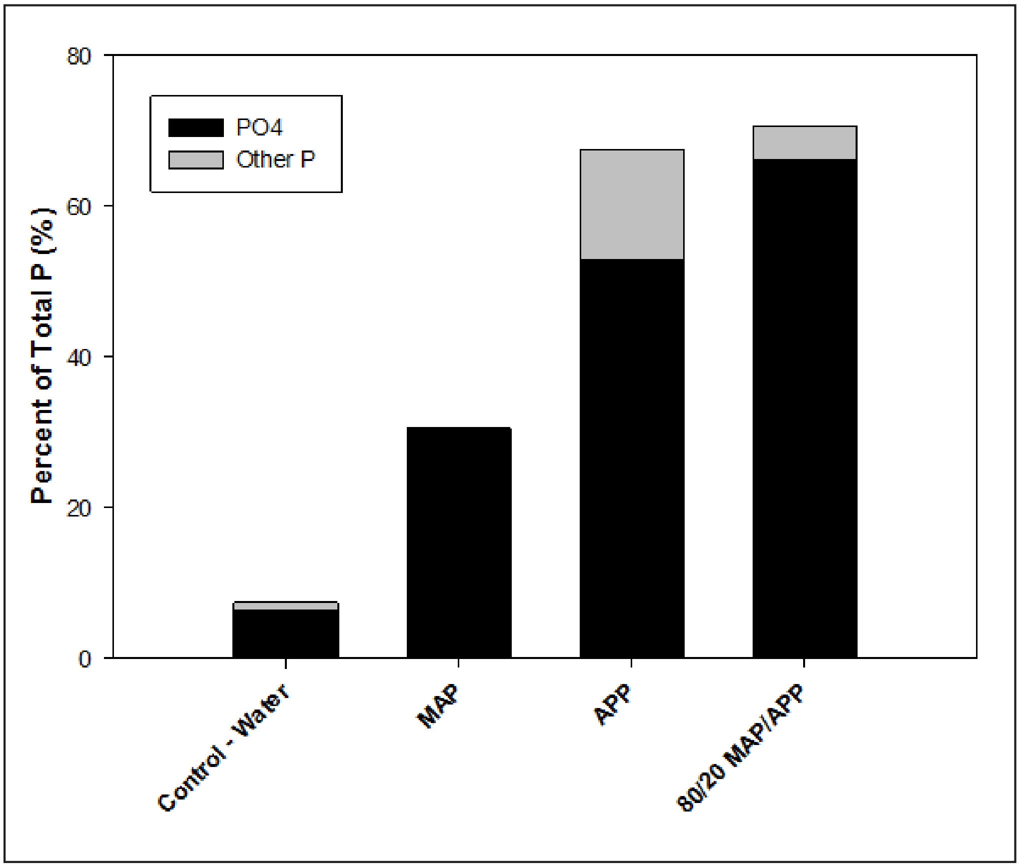


Figure 3. Resin extractable P as a percent of total P after sulfuric acid digestion of extract solution in the 0-8mm dish section.

Superior performance of APP relative to MAP was expected due to the extra hydrolysis step that polyphosphates require prior to their becoming available not only for plant uptake, but for chemical fixation as well; however, the superior performance by 80/20 was a curious finding. Previous studies, such as Lombi et al. (2006) and Pierzynski and Hettiarachchi (2016) confirm that the values obtained for MAP and APP are reasonable.

Digestion of resin P extraction reveals potential presence of polyphosphates. The increased lability found using the 80/20 blend was not anticipated but could be explained if calcium pyrophosphate or similar polyphosphate precipitates formed upon the addition of the fertilizer treatments. According to Lindsay (1979), OP solution activity is maintained at a higher concentration when more soluble calcium pyrophosphate is controlling solution activity instead of apatite-like P solids that would commonly be found in calcareous soils. Often the assumption is that PPs do not persist in soils very long but their presence in an incubation study such as this after four weeks is not unreasonable. To investigate whether soluble PPs were still present and were missed during the resin P analysis, the initial resin P extracts were digested to convert all extracted non-OP to OP that could then be measured colorimetrically. A limitation of the molybdate reactive P determined via Murphy and Riley (1962) is that the procedure only assesses OP concentration. Important to note is that the non-OP fraction includes PP as well as any organic forms of P that may be present. The results outlined in Figure 3 support the above explanation. The increase in OP in the APP and 80/20 treatments following digestion suggests that PPs are present in the soil solutions. A soluble PP mineral may be controlling P solution activity thus contributing to the significant increase in “plant available” P relative to the MAP treatment. The seemingly reduced performance of APP was confounded by the PP fraction remaining in solution that was overlooked by the initial round of analysis.

Treatment effects. The oxalate in the dark extraction procedure developed by Loeppert and Inskeep (1996) is designed to assess amorphous iron

Table 2. Bulk-XANES results expressing primary solid phosphorus species as a percent of the total.

Treatment	Dish Section	Ca-P	Clay adsorbed P	Fe adsorbed P	Al Adsorbed P	Red. X²
Control - Water	0-8	68	24	8	-	0.025
	8-15.5	72	7	21	-	0.005
MAP	0-8	68	-	22	10	0.005
	8-15.5	68	12	20	-	0.005
APP	0-8	46	25	29	-	0.015
	8-15.5	67	-	14	19	0.005
80/20 MAP/APP	0-8	44	15	41	-	0.009
	8-15.5	68	-	9	23	0.006

content of soil, primarily ferrihydrite, but in recent years some researchers are using the procedure to estimate the fraction of P associated with Fe and aluminum (Al) (Yan et al. 2016). Because calcium oxalates are highly insoluble, an ammonium acetate (pH = 5.5) pretreatment is employed to eliminate possible interference of the Fe estimation in calcareous soils. Phosphorus, naturally, is associated with some of the Ca removed, so quantification of the P in the pretreatment was necessary as well as in the ammonium oxalate extraction solution. Figure 4 suggests that treatment influences P partitioning. Soils receiving MAP appeared to favor the fraction dissolved by the oxalate treatment, while the APP and 80/20 blend, to a lesser extend, favored the pretreatment dissolved fraction. Baifan and Yichu (1989) found that similar ammonium acetate extractions selectively removed calcium associated P in addition to the water-soluble fraction. These results corroborate well with the resin extractable data as the pretreatment is a less chemically "aggressive" solution that removes a fraction that could be interpreted as more labile.

"Blending approach possesses tremendous potential to reduce total P inputs."

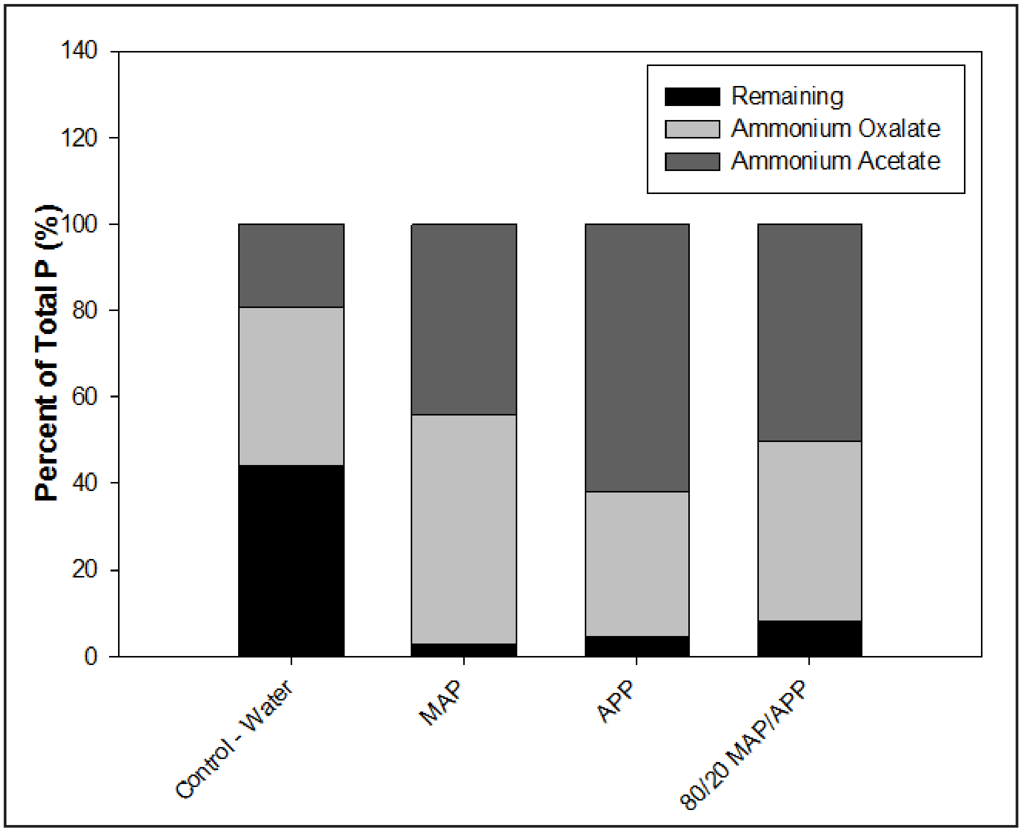


Figure 4. Oxalate extractable phosphorus is the 0-8mm dish section. Percentages expressed as portion of total phosphorus by aqua regia digestion.

Synchrotron investigation. Bulk-XANES (X-ray Absorption Near Edge Structure) analysis was completed to compliment and validate the information gathered through traditional wet chemical methods. This technique is useful in identifying the major P species present in each sample. As expected, the control soils were dominated by apatite, a highly insoluble Ca-P mineral, explaining the low resin extractability of the native P. Soils tested with MAP exhibited similar partitioning with the exception of a relatively large portion sorbed to ferrihydrite. This again supports the resin extractable P data in that approximately one third of the total P may be available to be used by crops. Phosphorus relegated to the apatite fraction was lessened when APP was involved. Both the APP and 80/20 blend treatments were found to contain greater proportions of sorbed P that is less tightly bound and thus more labile. In the 80/20 blend, a higher concentration seems to be associated with ferrihydrite as compared to the APP treated soil. Polyphosphates have been shown to possess a high affinity for iron, and the wet chemical investigation did insinuate that a portion of the P remaining was PP. Unfortunately, at this time, we do not possess a large library of PP mineral and sorbed species XANES spectra that would allow for more precise assessment of this fraction.

Digestion and resin extractable P results indicate that very little P diffused outside of the first section, therefore the XANES results (Table 2) for the 8-15mm sections more closely resemble the control soil. All treatments possessed between 67 and 72% calcium phosphate minerals. The best fit lines for APP and the 80/20 treatment revealed more Al adsorbed P, while the MAP and control P appear more closely associated with clay and Fe. Currently, no concrete evidence exists to explain this dichotomy, but given that significantly less MAP diffused into the second ring relative to the APP and 80/20 treatments, a PP presence effect is arguable. Additionally, the P in the APP treatments may be involved in weaker, outer-sphere associations and the MAP samples could have chemisorbed to Fe minerals via inner-sphere interactions that are significantly stronger, making P less labile.

Summing up

Small changes in P fertilization practices could save farmers money and reduce total P input requirements. Based on the results of this study, including small amounts of PPs when applying fluid MAP to calcareous soils, could potentially allow growers to apply less total phosphorus to agricultural systems without compromising plant performance. At this time, caution should be taken not to extrapolate the proposed mechanisms too far until future studies, at variable P rates in a wider array of calcareous soils, establish more incontrovertible evidence.

The lack of biological activity in this study may overestimate the amount of time PPs remain in soil. While temperature, moisture, pH, and many other abiotic factors influence PP hydrolysis rate, the presence of plants and the myriad of microbiota associated with the rhizosphere will also expedite the process for two reasons: 1) the concentration of PP will likely be greater thus increasing the total rate of conversion of PP to OP, and 2) plant root/microbial/mycorrhizal removal of OP from solution will drive greater dissolution rates to maintain solution OP activity. Although not assessed, microbial activity is surely taking place in the described incubation study albeit not to the extent that one would expect in an active root zone (Adesemoye and Kloepper 2009).

Even if PP does not persist more than four weeks, as was the case in this study, the potential benefit of using calcium polyphosphate precipitates as intermediates, to briefly maintain higher OP fluid activity early in the growing season, cannot be dismissed. Not only would this scenario possibly help mitigate P deficiency risks in cold soils of the early season, but the system allows for greater P diffusion from the POA creating conditions more conducive to nutrient sorption (more plant available) than precipitation (virtually plant unavailable). Enhanced nutrient movement also creates a greater fertilizer “footprint,” increasing the likelihood that crop roots encounter and exploit the P enriched zone.

In many ways, the 80/20 MAP/APP treatment combined the best attributes of MAP application (high OP, plant available P) and APP (prolonged temporal lability and greater diffusion) to create an ideal scenario to provide P nutrition. While more work is necessary, our group believes the blending approach possesses tremendous potential to reduce total P inputs to calcareous soils in the future, simultaneously saving grower capital, conserving a non-renewable resource, and protecting freshwater ecosystems.

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