

# What About Fluid P Fertilizers In Moderately Calcareous Soils?

*Do they excel?*

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**Summary:** Overall, in a controlled laboratory experiment on the 3 calcareous soils it did appear that fluid P fertilizer was superior over the P granular in terms of enhanced movement away from the point of application and/or remaining extractable. However, field studies on mild to moderately calcareous soils will be needed to gauge whether the laboratory results hold up under scrutiny in the field and actually enhance or influence plant growth.



The lack of soil phosphorus (P) availability in soil is one of the major reasons for less than optimal crop growth over the course of a growing season. When P fertilizer is added, it can rapidly undergo chemical transformations that make this macronutrient unavailable for crop uptake. It necessitates frequent or heavy applications of P to maintain crop productivity, which can be costly and also increase the potential for P runoff. This is a common problem in many agricultural areas of the world. The mechanisms responsible for decreased P availability in soils are quite complex and vary depending on soil mineralogy, pH, climate (such as soil moisture), and the form of P fertilizer added to the soil.

Calcareous soils present a unique challenge because we know the addition of granular P fertilizer to these soils can cause the rapid formation of insoluble calcium (Ca) P reaction products within and near the fertilizer application point. This greatly reduces the release of dissolved P of the fertilizer into the surrounding soil and also decreases the potential plant availability of applied fertilizer P.

The decrease in P solubility can be influenced by the form of P fertilizer added to highly calcareous soils, according to recent studies. The benefits of P supplied in fluid forms over conventional granular products in highly calcareous Australian soils have been demonstrated through field trials, x-ray, spectroscopic, and laboratory-based wet chemical analyses. The results suggest the use of fluid P fertilizer on the calcareous soils allows greater movement of P away from the point of application, thereby reducing the formation of Ca-P precipitates. These recent observations raise the question as to whether the observed behavior would extend to mild-moderately calcareous soils.

One approach to investigate whether mobility and lability are improved by the use of fluid over granular P fertilizer in calcareous soil is the use of a lab-based incubation study. This allows for a close look at possible reaction products formed in and surrounding the granule. Useful measurements on the incubated soil from the study would include total P added, a measurement of P mobility from the

point of application, resin extractability of P, which measures lability of the P fertilizer type added to the soil. Also included could be more sophisticated spectroscopy-based techniques, such as scanning electron microscopy (SEM) and energy dispersive x-ray (EDS), allowing for a close-up view of potential changes in fertilizer granule structure as well as elemental mapping of the granule to analyze the P reaction products in the granules and surrounding soil. Lastly, x-ray absorption near edge of structure (XANES) analysis to lend direct evidence of changes in P adsorbed or precipitation P formation as a result of P treatment

We hypothesize that there are differences in P diffusion and P reaction products in and around fertilizer granules and fluid fertilizer zones in mild to moderately calcareous soils, consequently resulting in differential plant-available P. We employed a combination of 1) wet chemical, 2) scanning electron microscopy combined with energy dispersive x-ray analysis, and 3) synchrotron-based x-ray techniques to identify chemical forms of APP-,

MAP-, and (DAP)-derived P in a highly calcareous Australian soil and two mildly calcareous soils from the U.S. (Idaho and Western Kansas).

Methodology

**Soils.** A five-week laboratory-based incubation experiment was set up that used three soils containing various amounts of free calcium carbonate [CaCO<sub>3</sub>] (none had a history of being fertilized): 1) a mildly calcareous Entisol soil collected from southwest Idaho, 2) a mildly calcareous Inceptisol soil collected from western Kansas, and 3) a highly calcareous Inceptisol soil collected from South Australia. The Kansas soil pH was 8.34 and soil texture a silt loam (SiL), with an effective CaCO<sub>3</sub> of 7.7 % total P 625 mg kg<sup>-1</sup>, and Mehlich P 15.6 mg kg<sup>-1</sup>. The Idaho soil pH was 8.02 and soil texture a sandy loam (SL), effective CaCO<sub>3</sub> 10.9%, total P 468 mg kg<sup>-1</sup>, and Mehlich P 31.8 mg kg<sup>-1</sup>. The Australian soil pH was 8.63, soil texture an SL, effective CaCO<sub>3</sub> 83.3%, total P 681 mg Kg<sup>-1</sup>, and Mehlich P 39.1 mg kg<sup>-1</sup>.

**Fertilizer.** Three P fertilizer sources were chosen for incubation: monoammonium phosphate (MAP), di-ammonium phosphate (DAP), and ammonium polyphosphate (APP). Monoammonium phosphate and DAP were added in granular form and APP was added as the fluid P source. The granular or fluid fertilizer containing an equivalent amount of P, approximately 9.8 mg P, and the nitrogen (N) balanced using urea, was placed in the center of petri dishes filled with one of the 3 soils at a moisture content equivalent to 60 percent of its maximum water-holding capacity.

**Treatments** totaled 4, including a control treatment. The 5 replicates of each treatment on the 3 soils were covered and incubated in petri dishes for five weeks at 25oC.

**Soil samples.** After five weeks, the soil was collected in 4 concentric rings from the central point of application: 0-7.5 mm, 7.5-13.75 mm, 13.75-25 mm, and 25-43.5 mm. The soil samples were analyzed for total P using aqua-regia digestion, pH (1:10) in water, resin extractable P using Meyers et al. [2005] for P extraction. P determination was completed using the Murphy Riley Methods.

**P mass.** The Percent P added was calculated by dividing the net increase of the total P mass for each dish ring

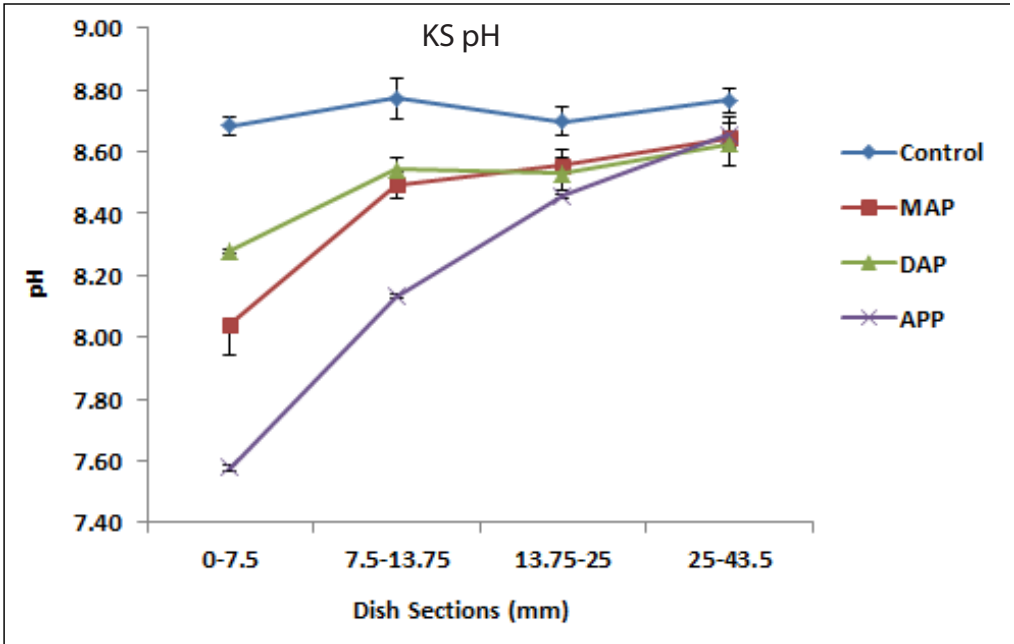


Figure 1. Soil pH: Kansas calcareous soil

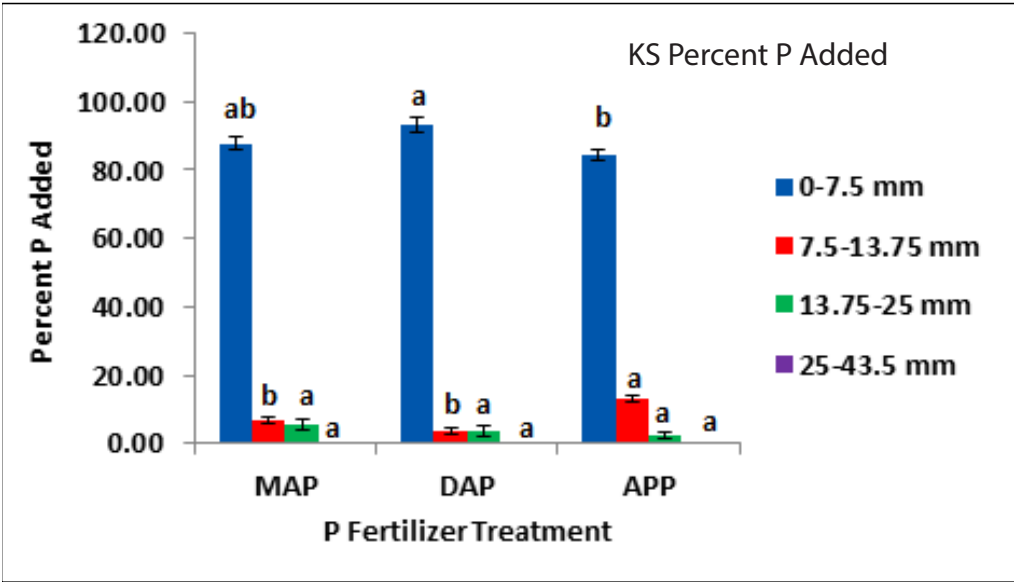


Figure 2. Kansas Percent P Added: Significantly more P added remained at the point of application for the DAP treatment than for APP treatment. For the second section, there was significantly more P fertilizer movement for APP than either granular treatment.

Table 1. P XANES data – Kansas Soil					
Soil P species (%)					
Section 1: 0-7.5 mm					
Treatment	pH	Calcium Phosphate	Alumina-Adsorbed P	Strengite	Reduced
					Chi-Square
Control	8.68	72.1	27.9	--	0.020
MAP	8.02	54.5	--	45.5	0.006
DAP	8.43	79.2	20.8	--	0.030
APP	7.70	47.5	22.1	30.4	0.010



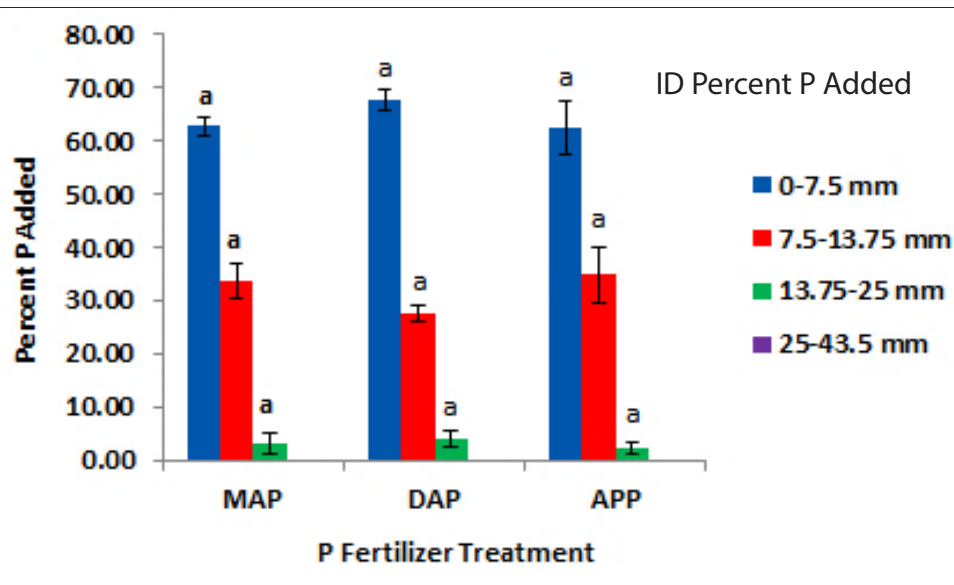


Figure 3. Idaho Percent P Added: There were no significant differences between the 3 treatments; however, DAP had more actual fertilizer P in the first section compared to the other treatments. Although there was enhanced P movement in the second section for APP it was not significant.

by the total P mass added to each dish and multiplying by 100. The net increase in the total P mass is the total P concentration in each dish ring minus the control P concentration and multiplying by the soil mass in that ring.

**Percent Resin P** was calculated in each dish section for each soil as resin extractable P concentration divided by total P concentration then multiplied by 100.

**Lab data** collected were analyzed with the Proc Mixed procedure using SAS software (SAS 9.2, 2008). The Bonferroni Pairwise Method was used for treatment comparison at a 0.05 level of significance

**Analysis.** The fertilizer products and soils were analyzed using Scanning Electron Microscope (SEM) connected with Energy-dispersive X-Ray spectroscopy (EDS). The 0-7.5 mm dish sections for all 3 research soils were analyzed further for reaction products formed during incubation using synchrotron-based P K-edge x-ray

## AU Incubated DAP granule Scanning Electron Microscopy/Energy Dispersive Spectroscopy

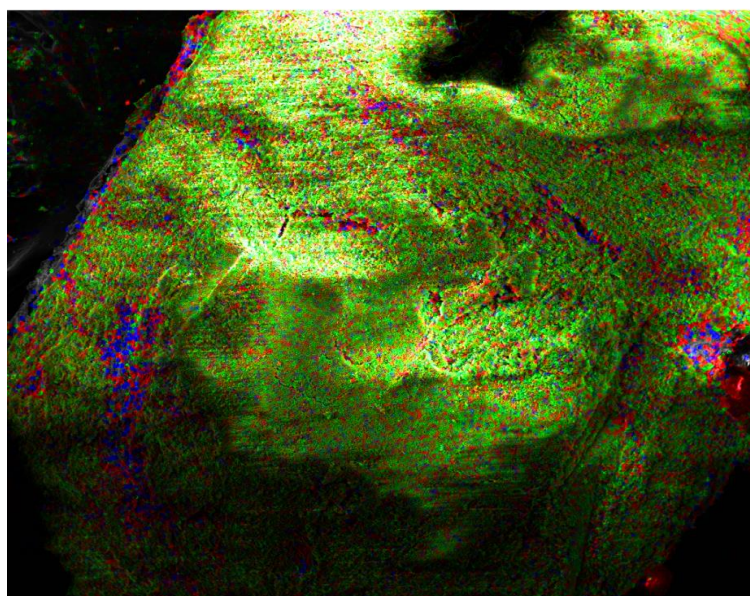
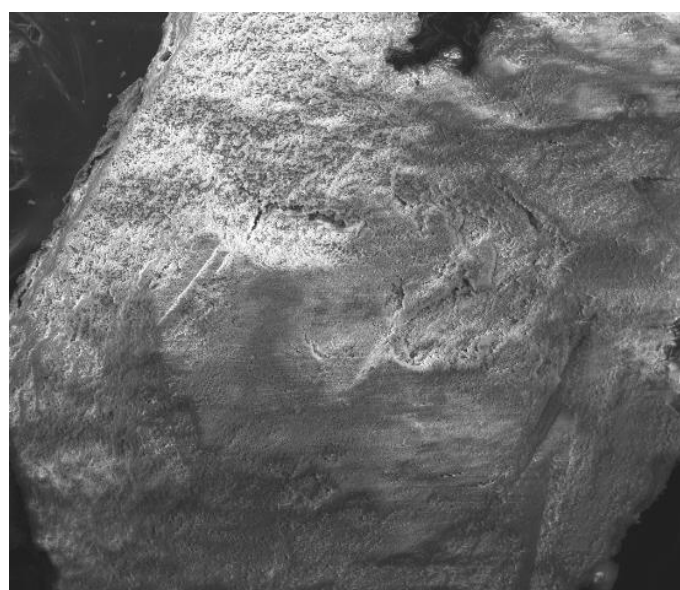
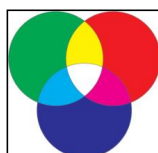


Figure 4: Elemental analysis of the inside of an incubated AU DAP granule using energy dispersive spectroscopy



Scanning electron micrograph of the inside of an incubated AU DAP granule

Red= Ca  
Green= P  
Blue= Fe



absorbance near edge of structure, or XANES spectroscopy. The Idaho soil analysis was performed at sector 9 BM-B, Advanced Photon Source Facility, Argonne National labs, Chicago, IL.

For the Kansas and Australian soils, it was performed at the Canadian Light Source Inc., Soft X-ray Micro-characterization Beamline (SXRMB) 06B1-1, Saskatoon, Saskatchewan, Canada.

Spectra for the P standards and the center section of the treatment samples (0-7.5 mm) were edge energy calibrated, background corrected and normalized. All spectra collected were analyzed by linear combination fitting (LCF) using IFEFFIT software (Newville, 2001).

Results

**pH.** For the Kansas soil (Figure 1), generally, the P treatments had significantly lower pH as compared to the control except in the third section that had been treated with MAP. Mono-ammonium P and DAP treatments were not significantly different from each other in the 7.5-13.75 mm section. The pH was lowest at the point of application for all P treatments and increased back to the pH of the control soil by the fourth dish section. This most likely was the result of the effect of acidification due to the nitrification of ammonium (NH<sub>4</sub>) contained in the P fertilizer or added as urea.

Overall, APP had the lowest pH for the 4 dish sections, suggesting greater diffusion or movement of NH<sub>4</sub> compared to the 2 granular fertilizers. The effects of the P treatments on soil pH results were very similar for the Idaho and Australian soils (data not shown).

**Percent P added.** Because each granule could potentially have slightly different amounts of P, we look at added P as a percent of the total added P in each section to understand fertilizer P diffusion. The greater the diffusion or P movement away from the point of application, the less the chance for the formation of P precipitates.

For the Kansas soil (Figure 2), most of the added P fertilizer remained close to the point of application with DAP having significantly less movement than APP from the 0-7.5 mm dish section. Phosphorus diffused into the 7.5-13.75 mm section for all 3 treatments and there was significantly more fertilizer P movement into this section for the fluid P

Table 2. P XANES – Idaho Soil					
Soil P species (%)					
Section 1: 0-7.5 mm					
Treatment	pH	Calcium Phosphate	Ferrihydrite-Adsorbed P	Vivianite	Reduced Chi-Square
Control	8.52	68.6	31.4	--	0.06
MAP	7.58	59.2	31.0	9.8	0.02
DAP	8.07	64.1	35.9	--	0.04
APP	7.38	27.8	48.2	24.0	0.04

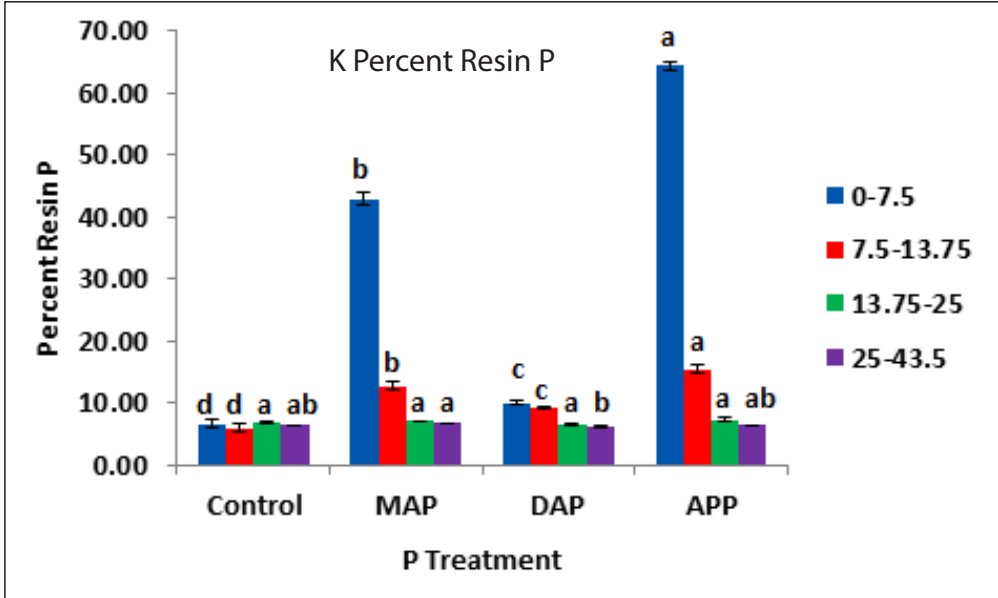


Figure 5. Kansas percent Resin P: The APP treatment had significant greater resin extractable P as a percentage of total P for the first two sections as compared to the MAP, DAP or Control treatments.

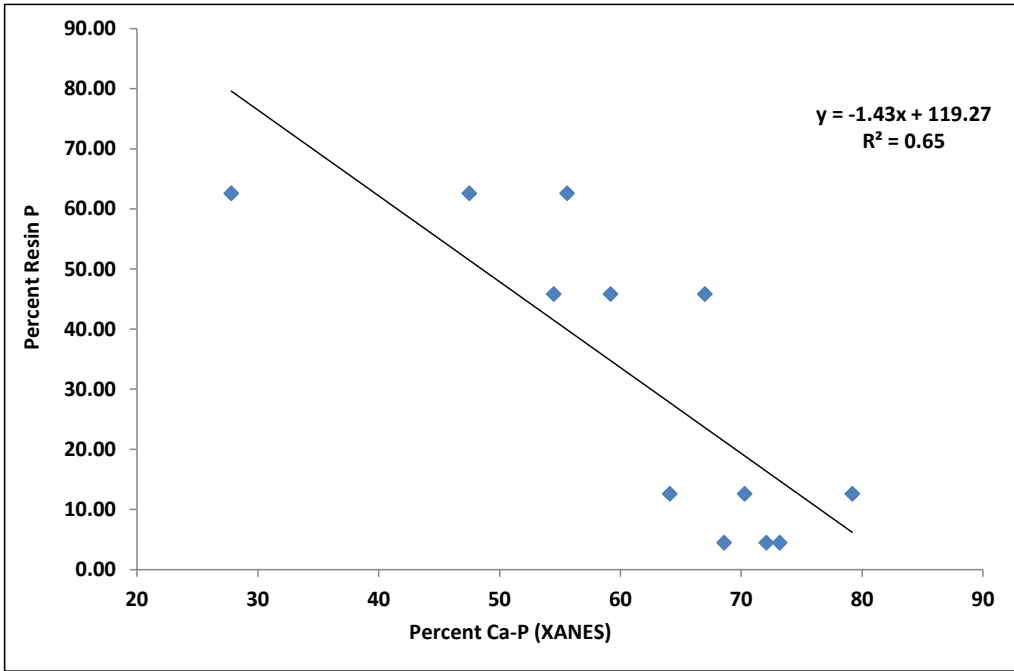


Figure 6. The relationship between Percent Resin P and the occurrence of Ca-P for all three soils.



treatment than for either granular fertilizer. The low P mobility was most likely due to the finer-textured soil.

For the Idaho soil (Figure 3) much of the P added remained in the first dish section for all treatments with no significant differences between them. There was P movement into the second dish ring for the 3 treatments with APP having slightly greater diffusion though there were not significant differences. The soil texture should not limit the P movement from the point of application in this soil.

For the Australian soil, significantly more fertilizer P remained in the center section for MAP than for the DAP or APP treatment. In the second section, both APP and DAP had significantly more P fertilizer than MAP, with APP having enhanced movement over the DAP treatment (data not shown). A spectroscopic image of the inside of an incubated Australian soil DAP granule (Figure 4) reveals the possible inward movement of Ca from the surrounding soil, prompting the formation of Ca-P reaction products as indicated by the yellow-colored areas along the inside edge of the granule. This evidence lends additional support for the lack of P diffusion from the point of application for P granular fertilizer in the calcareous soils.

**Percent Resin P** soil is used as an estimate of potential P available for plant uptake. The greater the percent resin P for a dish section, the greater the proportion of potentially plant available P for a particular treatment.

In the Kansas soil (Figure 5), the APP treatment had significantly more resin extractable P as a percentage of total P for the first and second sections as compared to the other two P treatments. Surprisingly, percent resin P for the center section for DAP was very low, suggesting very limited dissolution of the granule and/or plant availability. All P treatments were very similar to the control treatment for the third and fourth sections. Results for the Idaho soil were very similar to the Kansas results (data not shown).

For the highly calcareous Australian soil, there were no significant differences between the three P treatments, and MAP had slightly more percent resin P in the first section as compared to the two other treatments. However, for the second and third sections, APP had significantly

greater resin P extractability compared to the other P treatments (data not shown)

**XANES analysis.** In the Kansas soil (Table 1), the control soil suggests the presence of Ca-P species (72.1%) and alumina-adsorbed P (27.9%). These particular P solid phases are not uncommon to find in a calcareous soil, especially with a pH 8.7. The DAP treatment had a similar pH to the control but the percentage of Ca-P species (79.2%) was greater while alumina-adsorbed P (20.8%) was less. We could expect to see the presence of a small amount of aluminum-bound P in these higher pH soils. The MAP treatment had a lower percentage of Ca-P species (54.8%) and more strengite-like Fe-P than the DAP treatment near the point of application. The soil pH of 8.0 for the MAP treatment was lower than the DAP treatment. The APP treatment had the lowest pH (7.7) of all the treatments and had considerably lower Ca-P species (47.5%), alumina-adsorbed (22.1%), and a small amount of strengite-like Fe-P (30.4%). The prevalence of both Fe and Al associated P species with APP may explain, at least in part, the greater plant-available P compared to the granular P treatments.

For the Idaho soil (Table 2), the control treatment contained Ca-P species (68.6%) and ferrihydrite-adsorbed P (31.4%). These particular P solid phases would be common minerals found in a higher pH (8.5) calcareous soil. The MAP, and especially the DAP treatment, had higher percentages of Ca-P like species forms as compared to the APP treated soil. With APP having less Ca-P like species, there is an increase in Fe-P, either an adsorbed or precipitated species. Again, this gives an explanation of the increased percent resin P compared to the granular P treatments

For the Australian soil (Table 3), the control treatment indicates the presence of Ca-P species (74.1%) and alumina-adsorbed P (25.9%). At pH 8.7, it would be expected that much of the P found in the calcareous soil to be strongly associated with Ca-P species. The MAP treatment (pH 8.23) contained 67.0% Ca-P species with small amounts of crandallite-like P (15.2%) and alumina-adsorbed P (17.8%). This would not be uncommon in a calcareous, higher pH soil. The DAP treatment had a slightly lower pH of 8.12, and a somewhat similar percentage of Ca-P species (70.3%)

as compared to the control and MAP treatments, and had more alumina-adsorbed (29.8%). The APP treatment had the lowest pH of all the treatments and had much less Ca-P species (55.6%) and increased Al and Fe associated P (alumina-adsorbed P of 33.7% and goethite-adsorbed P of 9.4%). The decrease in precipitated Ca-P species and increase in Fe-adsorbed species appear to be associated with greater P movement away from the point of application plus more P remained in a potentially plant-available form.

It was useful to combine the results of percent resin P for the 3 soils with calcium-P speciation data (Figure 6). The fraction of the P that is resin extractable greatly decreases as the percentage of Ca-P increases. The relationship suggests that as added P fertilizer is converted to Ca-P species it may no longer be available for plant uptake. In addition, the P use efficiency would be low.

### Summing up

The 3 soils in this study had unusually high pH and were calcareous. With the addition of P fertilizer, either granular or fluid, the pH decreased near the point of fertilizer application from the control soil pH, most likely due to nitrification. We saw that with the fluid P fertilizer the soil pH was significantly lower than either granular fertilizer added and that change in pH was directly or indirectly responsible for the increased P solubility. With increasing distance from the point of application, soil pH slowly increased toward the pH of the control soil. In terms of fertilizer P diffusion, there was evidence of somewhat greater movement of P near the point of application for the Idaho soil and Australian soil compared to the Kansas soil. This most likely was due to the Kansas SiL texture adsorbing soil water, thereby decreasing P mobility.

For all 3 calcareous soils there was significantly more resin P as a percentage of the total P in the first and second dish sections for APP as compared to all other treatments.

The P speciation results strongly suggest the addition of P fertilizer promoted the formation of both adsorbed and secondary P mineral solid phases. For both Kansas and Idaho soils, the lower pH was coupled with a decrease in Ca-P speciation and an increase in adsorbed-P species and may be the reason for the significant increase in

percent resin P extractability for the APP treatment as compared to all other treatments. This observation was made on the Australian soil as well. The XANES data, combined with percent resin P, clearly showed the formation of Ca-P species negatively affected the potential plant availability.

Overall, in the controlled laboratory experiment on the 3 calcareous soils it did appear the fluid P fertilizer was superior over the P granular in terms of enhanced movement away from the point of application and remained resin extractable. However, field studies on calcareous soils will be needed to gauge whether the laboratory results held up under scrutiny in the field and actually enhance or influence plant growth.

Table 3. P XANES – Australia Soil						
Soil P species (%)						
Section 1: 0-7.5 mm						
Treatment	pH	Goethite-Adsorbed P	Calcium Phosphate	Crandallite	Alumina-Adsorbed P	Reduced Chi-Square
Control	8.70	--	74.1	--	25.9	0.004
MAP	8.23	--	67.0	15.2	17.8	0.004
DAP	8.12	--	70.3	--	29.7	0.002
APP	7.72	10.6	55.6	--	33.7	0.005

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