

# Can Soil Chemical Changes Influence Plant Growth?

What about mobility and lability of various P fertilizers on high P-fixing soils?

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**Summary:** There was evidence of fertilizer P diffusion to the second section with Brazil soil and up to the third section with Idaho soil. We found no differences in P diffusion away from the point of application between the three P sources (MAP, DAP, and APP) for either soil. Percent resin P results for Brazil soil indicated there was no statistical difference between the three P sources. Results for Idaho soil were different from Brazil soil. There was significantly greater percent resin P in the center section with the APP as compared with either MAP or DAP. Speciation results indicated that the addition of P induced the formation of P solid phases, including adsorbed as well as secondary P minerals. In calcareous soil, low pH and formation of less Ca-P species in the APP-treated soils may have been the reason for observed high-resin extractable P concentrations.



It has long been recognized that interactions between phosphorus (P) and soils result in a reduction in the availability of P for crop growth over time. This necessitates additional or excessive applications of P to maintain crop productivity, which can be costly and can result in environmental problems.

In many areas of the world, extensive weathering or a unique mineralogy have produced agricultural soils that are deficient in plant-available P. As a result, when P fertilizer is added it rapidly undergoes chemical transformations that make P unavailable for plant uptake.

Direct information from literature on high P-fixing soils and the associated mechanisms reducing P availability to plants is limited. A deeper understanding of these processes may help in developing improved management strategies and/or efficient fertilizer formulations leading to higher productivity on these soils.

The objectives of this research were to:

- Investigate the mobility and ability of various P fertilizers on two high-P fixing soils
- Identify the P reaction products formed within and around the point of fertilizer application.

## Methodology

**Site.** The five-week laboratory incubation-based experiment consisted of two different soils:

- An Oxisol collected from Rondonopolis, Brazil
- A calcareous Inceptisol soil collected from southwest Idaho.

Neither of the soils had a history of being fertilized, though the soil from Brazil had been under cultivation.

**Sources.** There were three P fertilizer sources used in the study:

- Monoammonium phosphate (MAP)
- Diammonium phosphate (DAP)

- Ammonium polyphosphate (APP). MAP and DAP were added as granules and APP was added as a fluid.

**Application.** MAP, DAP, and APP were each applied to the center of a petri dish filled with soil at a moisture content equivalent to 60 percent of its maximum water-holding capacity. Each P source added approximately 9.8 mg P/plate for a total of four treatments, including a control treatment not receiving P. The nitrogen (N) was balanced using urea. Five replicates of each treatment on both soils were covered and incubated in petri dishes for five weeks at 25°C.

**Sampling.** At the end of the incubation period, concentric rings of soil surrounding the fertilizer application point were removed corresponding to 0-7.5 mm, 7.5-13.75 mm, 13.75-25 mm and 25-43.5 mm from the point of P application.

Soil samples were analyzed for soil pH, total P, and resin extractable P.

Percent P added was calculated by dividing the net increase in total P mass in each ring by the total P mass added to each petri dish, multiplied by 100.

The net increase in total P mass is the total P concentration in a ring minus the native or control total P concentration, multiplied by the soil mass in that ring.

Percent Resin P was calculated as resin extractable P concentration divided by the total P concentration, multiplied by 100.

In addition, scanning electron microscopy-energy dispersive x-ray analysis was performed on residual granules of DAP and MAP after the incubation, and P K-edge x-ray absorption near-edge structure spectroscopy (XANES) analysis of bulk soil of the 0.75 mm section for each treatment was performed to determine fertilizer reaction products.

**Statistical analyses.** All data were analyzed using the Proc GLM procedure using SAS software (SAS 9.2, 2008). The Bonferroni Pairwise Method was used for comparison of all treatments at a 0.05 level of significance. Synchrotron-based bulk x-ray adsorption near-edge structure (XANES) spectroscopy analysis was performed at sector 9 BM-B, Advanced Photon Source, Argonne, IL to determine the chemical form of P reaction products. Spectra for the various standard compounds and soil samples were edge-energy calibrated, background corrected and normalized. The reduced XANES spectra for the samples were analyzed by linear combination fitting (LCF) using IFEFFIT software (Newville, 2001).

## Study overview

**pH.** For the Brazil soil, all treatments that received P had significantly higher pH as compared to the control treatment in the first three sections of the petri dish, with no difference at 35-43.5 mm from the point of P application (Figure 1). In general, the pH was highest at the point of P application and decreased to background levels by the fourth section. The pH increases were due to the dissolution of P fertilizer followed by chemisorption of dissolved P onto iron/aluminum oxides followed by release of hydroxyl ion and/or from the hydrolysis of urea added with MAP and APP treatments (for DAP urea was not added). Given the acidic nature of the native soil, further acidification due to the ammonium-N may not have occurred due to inhibition of the nitrification process.

For the Idaho soil, all treatments were significantly lower in pH as compared to the control treatment in all four sections of the petri dish (Figure 2). The pH, more acidic at the point of P application, increased out to the fourth section and most likely was the effect of acidification due to nitrification. The APP treatment had the lowest pH although it was not statistically significant from the MAP treatment in some sections.

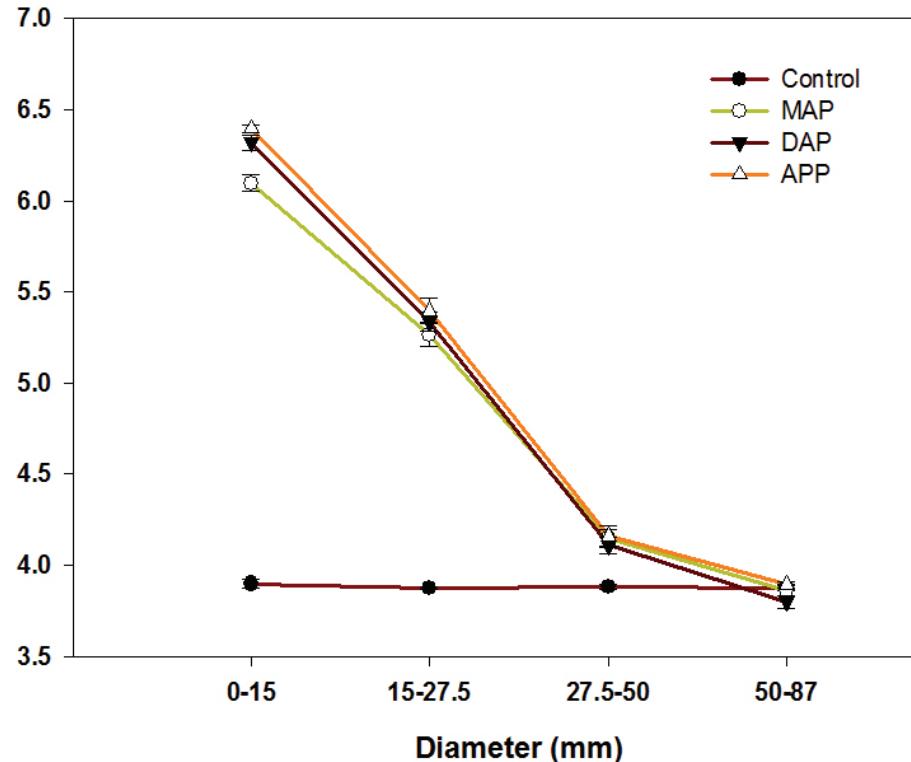


Figure 1. Soil pH- Brazil Acid Soil

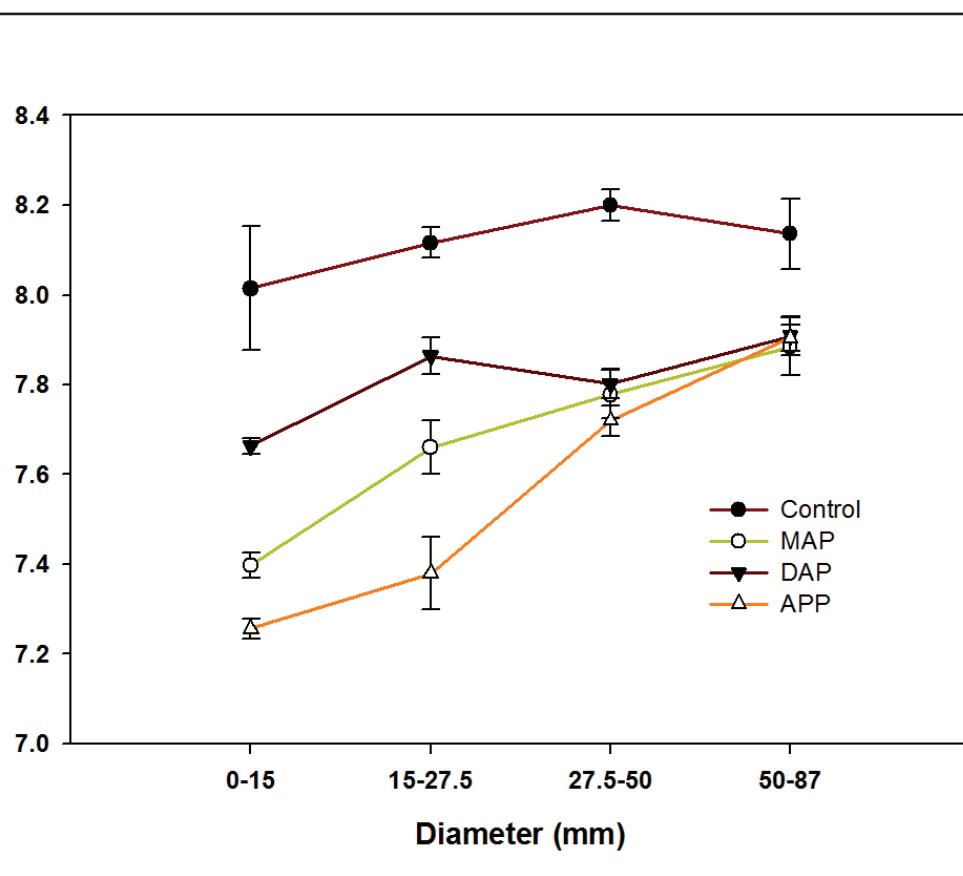


Figure 2. Soil pH- Idaho Calcareous Soil

**Percent P added.** For the Brazil soil (Figure 3), much of the P remained in the first two sections of the petri plates for all treatments. Most P remained close to the point of application and there were no significant differences between treatments in the 0-7.5 section. Phosphorus did diffuse into the second section (7.5-13.75 mm) for all 3 treatments. However, there were no significant differences between treatments in that section, either. High P fixation with aluminum and iron oxides and hydroxides, or forming solid phases with iron and/or aluminum, most likely prevented P movement into the outer two sections of the dish.

For the Idaho soil (Figure 4), the majority of the P remained in the center section of the petri dishes for all three treatments with no significant difference between them. MAP appeared to have greater diffusion into the second section than other treatments, though it was not significantly different from any other treatment.

**Percent Resin P.** Resin extractable P analysis is used as an estimate of plant available P in soils. Anion exchange membranes mimic P uptake by roots and is considered to be an acceptable method to assess labile P in the soil. Total soil P analysis is a measure of the many P forms that exist in soil samples. Calculation of percent resin P allows for normalization of the data when comparing treatments because of slight variations in the amount of P added to each dish and the possibility that the treatments can influence the diffusion distance for added P. High percent resin P means a greater proportion of the P in the soil is potentially available for plant uptake.

For Brazil soil (Figure 5), the center petri dish section for all three treatments had the highest extractable P though there were no significant differences between treatments. The second, third, and fourth dish sections contained significantly less resin extractable P for all treatments, with a small increase in the third and fourth sections of the dish.

Percent resin P results on the Idaho soil were more complex (Figure 6). The APP treatment had the greatest percent resin P in the center section when compared to either granular fertilizer treatment. It was clear that when P was applied as APP to Idaho calcareous soil, although it did not appear to enhance P movement further into other sections, APP helped to remain in potentially plant-available forms. DAP had significantly less labile P in calcareous soil than the MAP treatment. Moreover, there was a significant enhancement of resin extractable P levels in the 7.5-13.75 mm section for all treatments compared to the control treatment. The third and fourth sections had percent resin P values equivalent to the control treatment.

**XANES analysis.** Phosphorus was present as ferrihydrite-adsorbed P (64.1%), vivianite-

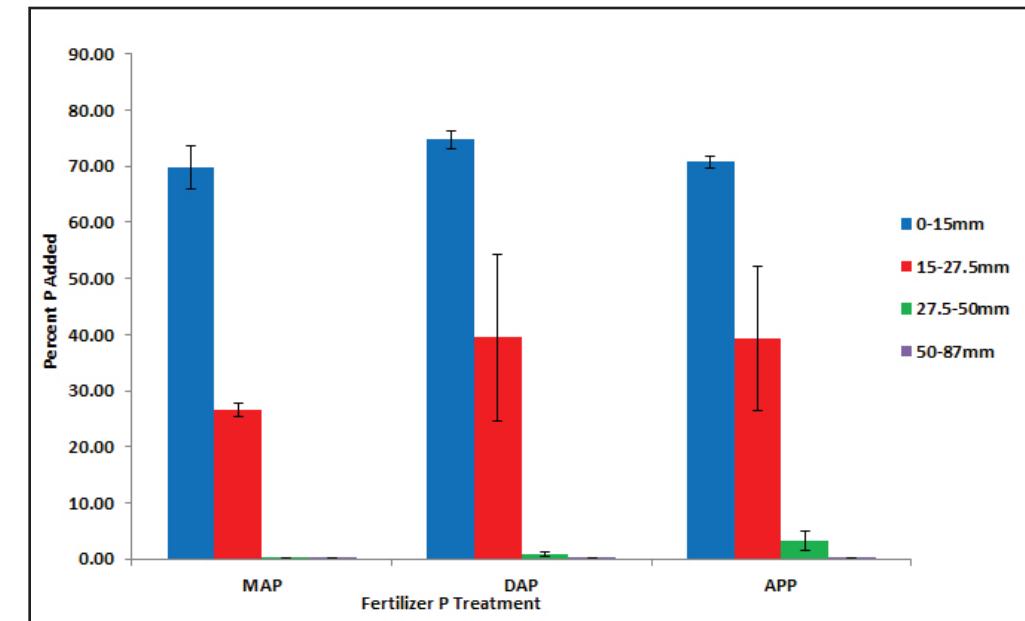


Figure 3: There were no significant differences between the treatments. Nearly all the fertilizer P added remained within the first two sections of the petri dish for all three P treatments.

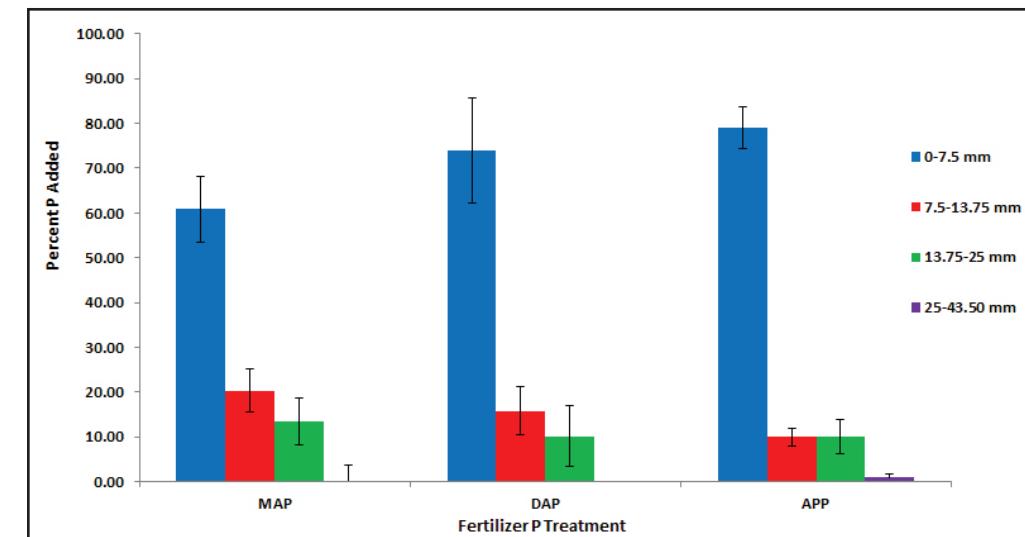


Figure 4: Though there were no significant differences between the three treatments APP had more actual fertilizer P in the first section compared to the other two treatments. Similarly, although there was enhanced fertilizer MAP movement in the second section it was not significant.

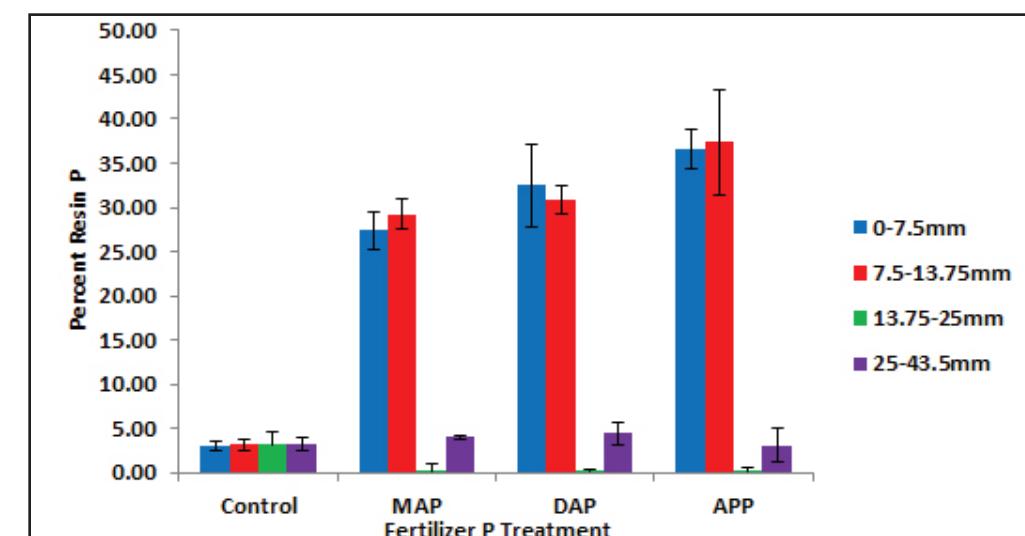


Figure 5: Though there were no significant differences between the three treatments, APP had more resin extractable P as a percentage of total P in the first section than the other two treatments. The first two sections of all P treated soils had significantly more resin extractable P compared to the control and the two remaining sections.

like Fe-P (21.9%) and aluminum phosphate-like Al-P (13.9%) in the Brazil control soil (Table 1). In contrast, no Al-P was observed in P-treated soils (center sections).

All P treatments resulted in the disappearance of aluminum phosphate and an increase in the amount of aluminum adsorbed P, ferrihydrite adsorbed P, or vivianite. The changes may be due to both the increased soluble P levels and increase in pH produced by the fertilizers.

The MAP treatment shows predominantly ferrihydrite adsorbed P and vivianite-like P.

DAP and APP contained alumina adsorbed P, which may be a less soluble P form; however, overall adsorbed-P concentration in DAP and APP treatments was significantly less than the MAP-treated soils.

There were no significant differences in resin extractable P between the APP and DAP-treated Brazil soils, although both had significantly higher resin extractable P than the MAP.

The XANES analysis of the control Idaho soil (Table 2) indicated the presence of

hydroxyapatite-like P (48.2%), ferrihydrite-adsorbed P (31.4%) and apatite-like P (20.4%). These P minerals would not be uncommon in a high pH calcareous soil.

MAP and DAP had a higher percentage of apatite-like P forms close to the fertilizer application point as compared to the APP treated soils. These fertilizer treatments had the highest pH at the center section of their respective plates as well.

APP had significantly less apatite-like P (Ca-P) and more Fe-P either as adsorbed or precipitated. Comparison of resin-extractable P data with XANES speciation results showed a negative correlation of Ca-P species with resin-extractable P, suggesting that Fe-P species in calcareous soils might be more available.

#### Summing up

The two soils used in this study had extreme pH, one being very acidic and the other alkaline. With the addition of granular or fluid P fertilizers, the pH values were modified to a level more favorable to higher P solubility. With increasing distance from the P application point, the soil pH either slowly increased or decreased toward its native pH.

There was evidence of fertilizer P diffusion to the second section with the Brazil soil and up to the third section with the Idaho soil. We have no evidence that there were differences in P diffusion away from the point of application between the three P sources for either soil.

The percent resin P results for Brazil soil indicated there was no statistical difference between the three sources. Results for the Idaho soil were different from the Brazil soil. There was significantly greater percent resin P in the center section with the APP (fluid fertilizer treatment) as compared with either MAP or DAP. MAP had significantly greater resin extractable P than DAP.

The speciation results indicated that the addition of P induced the formation of P solid phases, including adsorbed as well as secondary P minerals.

In calcareous soil, low pH and formation of less Ca-P species in the APP-treated soils may have been the reason for observed high resin extractable P concentrations.

Further study is needed under field conditions to see if the soil chemical changes can influence plant growth.

Table 1. P XANES data--Brazil Acid Soil

Soil P species (%)	Aluminum	Alumina	Ferrihydrite	Strengite	Vivianite	Red. Chi
Section 1: 0-7.5 mm						
Treatment	Phosphate	Adsorbed	Adsorbed			Square
Control	13.9			64.1	21.9	0.27
MAP				72.1	27.9	0.32
DAP		47.3			52.7	0.04
APP		43.6			56.4	0.02

Table 2. P XANES data--Idaho Calcareous Soil

Soil P species (%)	Apatite	Hydroxy	Aluminum	Ferrihydrite	Vivianite	Red. Chi
Section 1: 0-7.5 mm						
Treatment	Apatite	Hydroxy	Aluminum	Ferrihydrite	Vivianite	Red. Chi
Control	20.4	48.2		31.4		0.06
MAP	59.2			31.0	9.8	0.02
DAP	64.1			35.9		0.04
APP	27.8			48.2	24.0	0.04

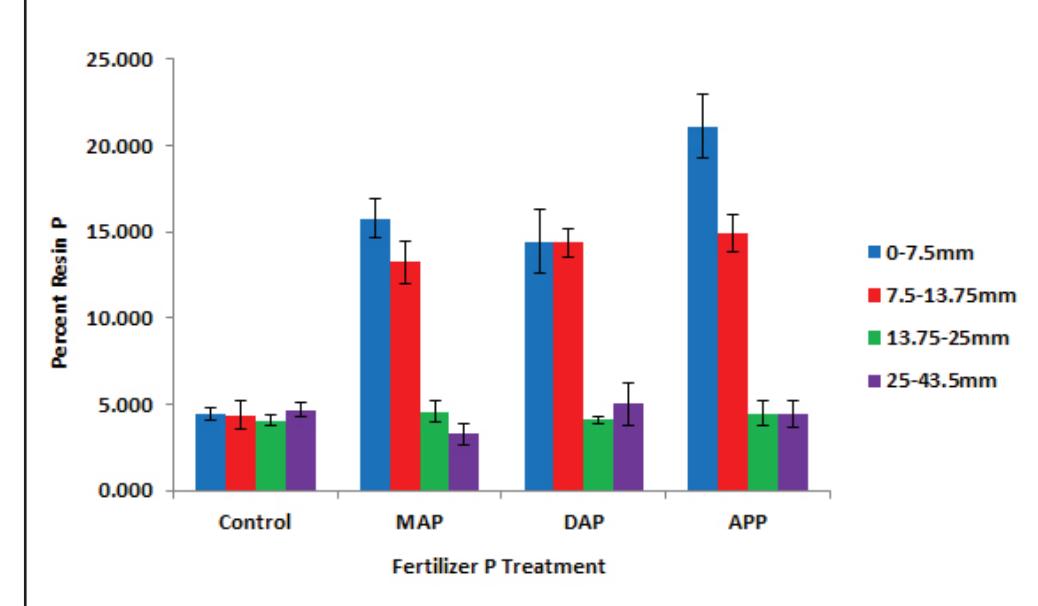


Figure 6: APP had significantly more resin extractable P as a percentage of total P as compared to the other two treatments. The first two sections of the petri dish for all treatments had significantly higher resin extractable P compared to the control and the last two sections.

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