

Determining The Yield Potential of APP In Varying Australian Soil Environments

Researchers design a series of experiments to investigate the hydrolysis and sorption of pyrophosphate.

Summary: Polyphosphate fertilizers have gained attention in Australian agricultural research due to significant yield increases with the application of ammonium polyphosphate (APP) as compared to granular orthophosphate (OP) fertilizer on highly phosphorus (P) fixing soils. In order to determine the potential of APP fertilizers to provide yield benefits in a range of soil environments, it is necessary to understand the chemistry of their behavior in the soil. Studies have shown that the sorption characteristics of pyrophosphate, the dominant polyphosphate in APP fertilizers, are quite different from that of orthophosphate. A series of experiments was designed to investigate the hydrolysis and sorption of pyrophosphate. Phosphorus sorption was found to be greater where P was added as pyrophosphate than when added as orthophosphate in all five soils, with varying effects on pH and metal concentrations in solution.

Polyphosphate fertilizers have recently shown significant yield benefits compared to traditional granular P forms on the calcareous soils of Eyre Peninsula, South Australia. APP fertilizers have unique chemistry compared to other inorganic P fertilizers, as the P in a polyphosphate fertilizer exists as more than one ionic species.

Several studies have been conducted to compare hydrolysis of pyrophosphate on a range of non-calcareous soil types. Most previous work on pyrophosphate hydrolysis has been conducted in temperate climates where soils are neutral or acidic and have higher organic matter contents and biological activity, factors known to promote pyrophosphate hydrolysis. Understanding the nature of hydrolysis reactions of pyrophosphate in Australian soil types is necessary in order to elucidate the mechanisms underlying the superior agronomic performance of polyphosphate fertilizer as compared to traditional P fertilizer on calcareous soil types.

Owing to the popularity of polyphosphate fertilizers in the U.S., several studies have been conducted to compare the sorption characteristics of

pyrophosphate and orthophosphate (the dominant P species in a polyphosphate fertilizer). The results of these studies suggest that pyrophosphate has different affinities for the bonding energies with various soil components as compared to orthophosphate, which could be due to the ability of pyrophosphate to solubilize organic matter, making soil mineral constituents available for sorption. No such study has been conducted on Australian soil types.

Hydrolysis

Figures 1 A and B show the quantification data for the study of hydrolysis of pyrophosphate in a highly calcareous (Warramboo) soil. Two methods of quantification are shown. The extraction technique using sodium hydroxide (NaOH, Figure 1 B) had a lower recovery than quantification using nuclear magnetic resonance (NMR) data (Figure 1A). There was a loss in recovery or observability over time for both quantification methods. For both quantification methods there was a decrease in the pyrophosphate concentration and an increase in the

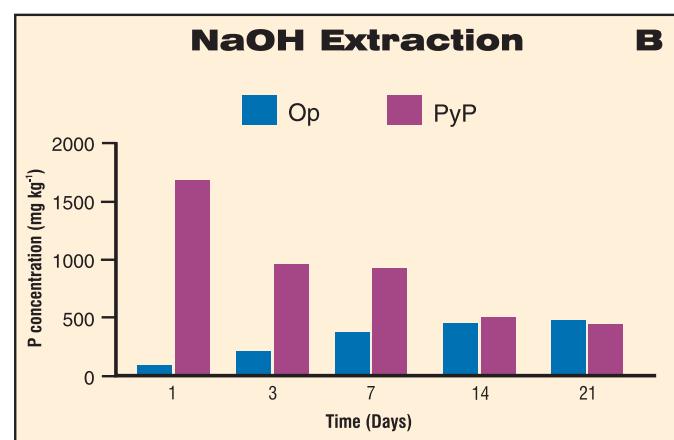
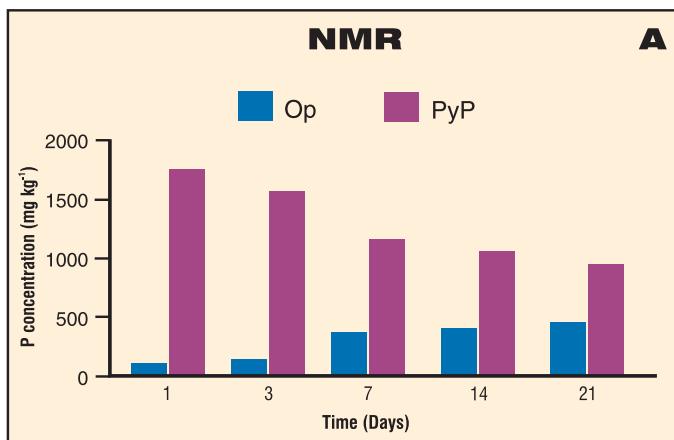


Table 1. Concentration of P as orthophosphate derived from hydrolysis of pyrophosphate (native P subtracted) and pyrophosphate (pyro-P) as determined by (A) NMR, and (B) 15 minute (1:10) 1 M NaOH extraction. (op=orthophosphate, PyP=pyrophosphate)

orthophosphate concentration over time. According to the NMR data (Figure 1A) the concentration of pyrophosphate decreases to approximately half of the original concentration added and is converted to orthophosphate, presumably by hydrolysis.

Soil spectra are obtained by direct polarization using P solid-state NMR. The native P spectra are for soil incubated one week at 75 percent of water holding capacity with no P added. After one day, the spectra show the pyrophosphate added and the distinct spinning side-band pattern that it has. Six spinning side bands are observable throughout the incubation and they remain in the same proportion of the central band for each P species throughout the incubation, suggesting that we were consistently measuring the same species.

After one day the peak for orthophosphate is very small and mostly represents the native P. As time progresses the orthophosphate peak grows as pyrophosphate hydrolyzes, and consequently the peak for pyrophosphate decreases. After 21 days of incubation, approximately half of the pyrophosphate peak remains and the orthophosphate peak has increased in size, including both native P and P that has hydrolyzed from pyrophosphate.

Due to the success of this technique for the study of hydrolysis of pyrophosphate, further investigations will look at other highly P fixing soil types and the biological and chemical causes of hydrolysis will be studied.

Soil	Fertilizer	Kf	n	R ²
Hamilton	OP	80.83	0.47	0.99
Hamilton	PyP	670.89	0.34	0.96
Warramboo	OP	52.88	0.52	0.97
Warramboo	PyP	671.19	0.34	0.96
OP=orthophosphate PyP=pyrophosphate				

Table 1. Freundlich sorption parameters for orthophosphate and pyrophosphate in Warramboo and Hamilton soils.

The work conducted on hydrolysis using NMR will be complemented by an isotopic double labeling technique currently being developed to investigate the potential availability of P supplied to the soil as pyrophosphate.

Sorption

Two soils were selected to demonstrate the relationships observed between P in solution and total P sorbed. The two soils selected were: 1) Warramboo of South Australia, a high pH, highly calcareous soil and 2) Hamilton of Victoria, a low pH soil with relatively moderate levels of total Fe and Al.

The sorption characteristics of both soils show that a greater amount of total P was sorbed when applied as pyrophosphate as compared to orthophosphate (Figure 2 A and B).

The Freundlich isotherm data (Table 1) shows a satisfactory fit for both the Warramboo and Hamilton P sorption data with a R² of 0.99 to 0.96 for orthophosphate and pyrophosphate, respectively. The Kf values in Table 1 indicate that there is a higher level of retention where pyrophosphate is added to both soils as compared to orthophosphate.

Further work in this study investigated the behavior of calcium, iron, and dissolved organic carbon (DOC) in solution (data not shown). The general trends indicated a significant decrease in the concentration of calcium in solution and an increase in the iron and DOC concentration in solution with the addition of pyrophosphate as compared to orthophosphate. The results of this study suggest that the greater performance of P supplied as APP in the field is not due to reduced sorption of pyrophosphate as compared to orthophosphate.

Conclusions

Pyrophosphate is able to persist in highly P-fixing Australian soil types with approximately half of the P added as pyrophosphate remaining as pyrophosphate after three weeks of incubation. Sorption data suggest that pyrophosphate is rapidly sorbed in these soil types. Work under way, investigating the potential availability of pyrophosphate using a double labeling technique, will further contribute to our understanding of the behavior of polyphosphates, particularly pyrophosphates in Australian soil types.

McBeath is a PhD student, Dr. McLaughlin is senior principal scientist, Dr. Smernik is research Fellow, and Dr. Bunemann is research Fellow, School of Earth and Environmental Sciences, University of Adelaide, South Australia; Dr. Lombi is senior research scientist who also works with Dr. McLaughlin (joint appointment), CSIRO Land and Dr. Holloway is principal research scientist, South Australian Research and Development Institute, Minnipa. □

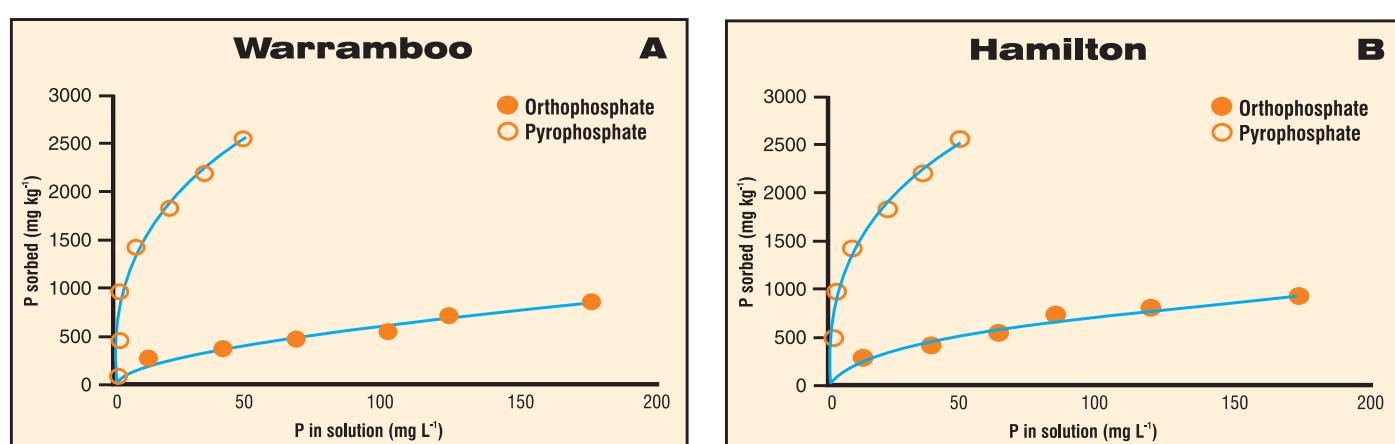


Table 1. P sorbed (mg kg⁻¹) vs. P in solution (mg L⁻¹) for Warramboo (A) and Hamilton (B) soils.