

Sorption of orthophosphate and pyrophosphate in Australian soils

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Abstract

Fluid forms of phosphorus (P) have been found to be much more agronomically efficient than granular forms on calcareous soils. In particular ammonium polyphosphates (APP) have shown significant crop yield benefits. Ammonium polyphosphate fertilisers have a unique chemistry compared to other orthophosphate fertilisers, with up to 60% of the total P in the APP fertiliser being in the form of polyphosphates. The dominant polyphosphate found in APP is pyrophosphate. The sorption characteristics of pyrophosphate as compared to orthophosphate have been studied in the U.S. and Canada where fluid fertilisers are more commonly used. However, this information is not available for Australian soils. To fill this gap, sorption of orthophosphate and pyrophosphate was investigated on several Australian topsoils. Here we report preliminary results suggesting that there is a significant difference between the sorption characteristics of orthophosphate and pyrophosphate in various Australian soils. On the range of soils studied P sorption was greater where P was added as pyrophosphate than when added as orthophosphate. In an alkaline soil type orthophosphate decreased soil solution pH whilst pyrophosphate increased soil solution pH. In an acidic soil type orthophosphate and pyrophosphate both increased soil solution pH.

Introduction

Polyphosphate fertilisers are widely used in the U.S. (Mortvedt *et al.* 1999) and have received attention more recently in Australia following significant yield benefits being achieved, compared to traditional granular phosphorus (P) forms, on the calcareous soils of Eyre Peninsula, South Australia (Holloway *et al.* 2003). Ammonium polyphosphate fertilisers have a unique chemistry, compared to other inorganic P fertilisers, as the P in a polyphosphate fertiliser exists as more than one ionic species. At the point of sale, approximately 30-40% of the fertiliser P is present as orthophosphate, 50-55% is present as pyrophosphate and the remainder exists as tripolyphosphate and more condensed forms of P. Due to the popularity of polyphosphate fertilisers 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 fertiliser) (Blanchar and Hossner 1969; Hashimoto *et al.* 1969; Mnkeni and MacKenzie 1985; Al-Kanani and MacKenzie 1991). The results of these studies suggest that pyrophosphates have different affinities for and bonding energies with various soil components as compared to orthophosphate. Mnkeni and Mackenzie (1985) suggested that these differences are due to the ability of pyrophosphate to solubilise organic matter, making soil mineral constituents available for sorption. However, no such study has been conducted on Australian soil types.

This paper will describe the results for a preliminary study of the sorption characteristics of orthophosphate and pyrophosphate on a selection of Australian soil types and discuss future experimentation.

Methods for Preliminary Study

Soil Characteristics

Surface soil samples (0-10cm depth) were collected from 5 agricultural sites across the Southern cropping region of Australia. The soils collected were: Wongan from Western Australia, Ulverstone from Tasmania, Birchip and Hamilton from Victoria and Warramboos from South Australia. Soil pH and EC were measured in a 1:5 soil:water extract (Rayment and Higginson 1992). Soil pH in 0.01 M CaCl₂ was measured in a 1:5 extract. Soil samples were digested in *aqua regia* and total P, Al, Fe and Ca were determined by inductively coupled plasma atomic emission spectroscopy (ICP- AES, Spectroflame Modula, Spectro).

Sorption Study

For each soil, P sorption was estimated by adding 8 concentrations of P solution (0, 5, 25, 50, 75, 100, 125 and 150 mg P L⁻¹) as sodium orthophosphate or sodium pyrophosphate in 0.01M KCl, with two drops

of toluene to inhibit microbial activity. The pH of these solutions was adjusted to 7.25, which is equivalent to the pH of a commercial polyphosphate fertiliser solution containing 100 mg P L⁻¹. The soil:solution ratio was 1:10 (4 g soil:40 mls solution). The suspensions were equilibrated by shaking in an end-over-end shaker for 24 hours (17 rpm). The samples were then centrifuged (1000 g) for 10 minutes. After centrifugation, 5 ml of the suspension was removed with a plastic syringe and filtered through a 0.2 µm Schleicher & Schuell membrane (Bertrand *et al.* 2003). This filtered solution was further centrifuged (450 g) for 20 minutes. The concentration of P, Al and Ca in the initial solution and filtered and centrifuged sample were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The total P sorbed (mg kg⁻¹) was calculated by subtracting the concentration of P remaining in solution after equilibration from the total concentration of P initially added. The P sorption data was then fitted to the Freundlich sorption isotherm in the following form.

Freundlich isotherm:

$$S = K_f C^n$$

Where S is P sorbed (mg kg⁻¹), K_f and n are empirical constants with n < 1 and C is the concentration of P in solution (mg P L⁻¹).

The pH of the equilibrium solution was also measured.

Results for Preliminary Study

Soil Characteristics

Characteristics of the five soils tested are presented in Table 1. Only one soil contained detectable levels of calcium carbonate (CaCO₃) with the Warramboos soil containing 77% CaCO₃ (w/w). The soil pH measured in calcium chloride (CaCl₂) ranged from 4.7 to 8.0 (the soil pH in water varied from 5.4 to 9.1).

Table 1: Soil Characteristics.

*T-trace

Site	State	pH (H ₂ O)	pH (CaCl ₂)	EC (dsm ⁻¹)	CaCO ₃ (%)
Ulverstone	Tas	5.59	5.00	0.26	T
Birchip	Vic	8.74	7.75	0.14	T
Hamilton	Vic	5.39	4.73	0.28	T
Warramboos	S.A.	9.12	7.98	0.12	76.72
Wongan	W.A.	6.26	5.07	0.02	T

The total concentrations of P, Al, Fe and Ca in the soil are reported in Table 2. The total P content of the selected soils varied from 0.01 to 0.09%. The range in soil Al, Fe and Ca is considerable across the range of soil types tested. The Warramboos soil from S.A. had the highest level of Ca by a factor of 27 to 608. Soils high in Al, tended to also be high in Fe. The highest value for total soil Al was 5.41% with a corresponding total Fe in soil of 7.82%.

Table 2: Total soil phosphorus (P), aluminium (Al), iron (Fe) and calcium (Ca) (% w/w).

Site	State	Total P (%)	Total Al (%)	Total Fe (%)	Total Ca (%)
Ulverstone	Tas	0.09	5.41	7.82	0.33
Birchip	Vic	0.03	3.77	2.60	0.68
Hamilton	Vic	0.04	2.51	2.75	0.15
Warramboos	S.A.	0.03	0.42	0.33	18.24
Wongan	W.A.	0.01	1.25	0.64	0.03

P sorption characteristics

Two soils were selected to demonstrate the relationships observed between P in solution (mg L⁻¹) and total P sorbed (mg kg⁻¹) where orthophosphate or pyrophosphate was added. At the same time the concentration of Ca and Al in solution (mg L⁻¹) were investigated. The two soils selected were Warramboos of South Australia, a high pH, highly calcareous soil and Hamilton of Victoria, a low pH soil with relatively moderate levels of total soil Fe and Al.

Warramboos soil

The sorption characteristics of the Warramboos soil when sodium orthophosphate and sodium pyrophosphate were added are shown in Figure 1 and Table 3. P sorption is greater when P is applied as pyrophosphate as compared to orthophosphate. Calcium in solution remains relatively constant with

increasing additions of sodium orthophosphate, but there is a considerable reduction in Ca in solution with increasing additions of sodium pyrophosphate.

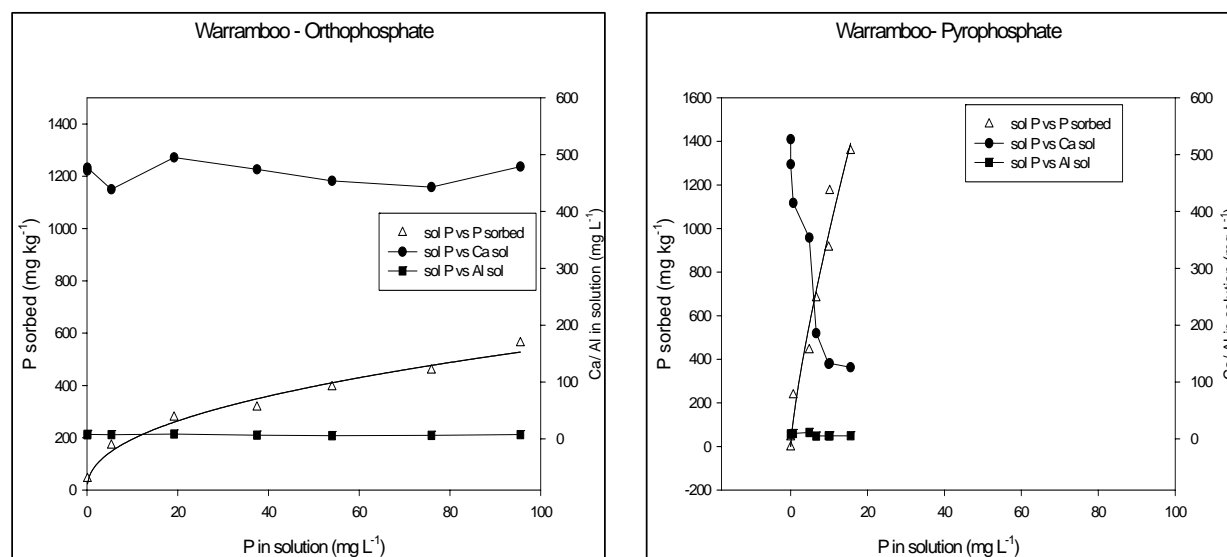


Figure 1. P sorbed (mg kg^{-1}) (Y1 axis) and Al/Ca in solution (mg L^{-1}) (Y2 axis) vs. P in solution (mg L^{-1}) for Warrambo soil treated with sodium orthophosphate and sodium pyrophosphate.

The Freundlich isotherm shows a satisfactory fit to the Warrambo P sorption data with a R^2 of 0.96-0.98 for ortho and pyrophosphate, respectively. The K_f value is an empirical constant where an increasing K_f is correlated to increased sorption. The K_f values in Table 3 indicate that there is a higher level of sorption where pyrophosphate is added to the Warrambo soil as compared to orthophosphate.

Table 3. Freundlich sorption parameters for Warrambo soil.

Soil	Fertiliser	K_f	n	R^2
Warrambo	Orthophosphate	70.40	0.44	0.98
Warrambo	Pyrophosphate	162.85	0.78	0.96

The relationship between soil solution pH and increasing additions of P as sodium orthophosphate (op) and sodium pyrophosphate (pyp) is shown in Figure 2. As increasing amounts of orthophosphate are added to the Warrambo soil, the soil solution pH decreases while as increasing amounts of pyrophosphate are added, the soil solution pH increases.

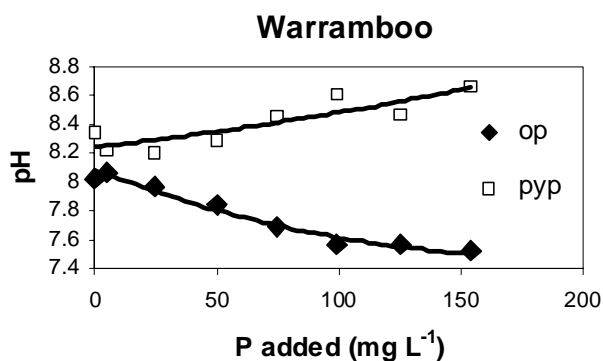


Figure 2. pH vs. P added (mg L^{-1}) as sodium orthophosphate (op) and sodium pyrophosphate (py p) in Warrambo soil.

Hamilton

The sorption characteristics of the Hamilton soil when sodium orthophosphate and sodium pyrophosphate were added are shown in Figure 3 and Table 4. Similar to the Warrambo soil, a greater amount of total P was sorbed when applied as pyrophosphate as compared to orthophosphate.

With increasing additions of P there was a significantly greater level of Al in solution when P was added as pyrophosphate as compared to when P was added as orthophosphate.

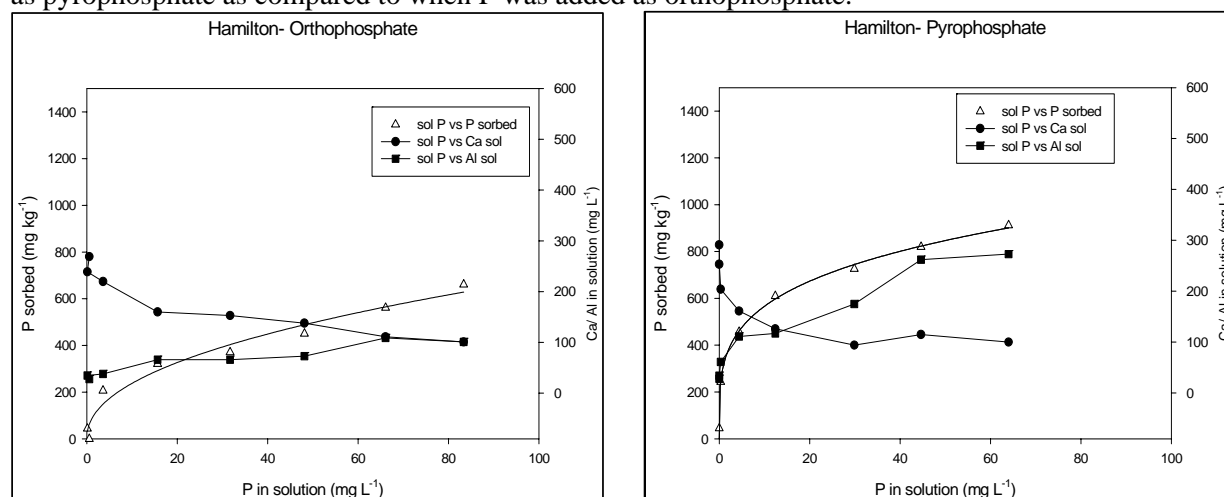


Figure 3. P sorbed (mg kg⁻¹) (Y1 axis) and Al/Ca in solution (mg L⁻¹) (Y2 axis) vs. P in solution (mg L⁻¹) for Hamilton soil treated with sodium orthophosphate (A) and sodium pyrophosphate (B).

The Freundlich isotherm shows a satisfactory fit to the Hamilton P sorption data with a R² of 0.97-0.99 for ortho and pyrophosphate, respectively. The K_f values in Table 4 indicate that there is a higher level of sorption where pyrophosphate is added to the Hamilton soil as compared to orthophosphate.

Table 4. Freundlich Sorption parameters for Hamilton soil.

Soil	Fertiliser	K _f	n	R ²
Hamilton	Orthophosphate	82.74	0.46	0.97
Hamilton	Pyrophosphate	317.84	0.25	0.99

The relationship between P added as sodium orthophosphate (op) and sodium pyrophosphate (pyp) and soil solution pH is shown in Figure 4. Soil solution pH increased with additions of P as both orthophosphate and pyrophosphate

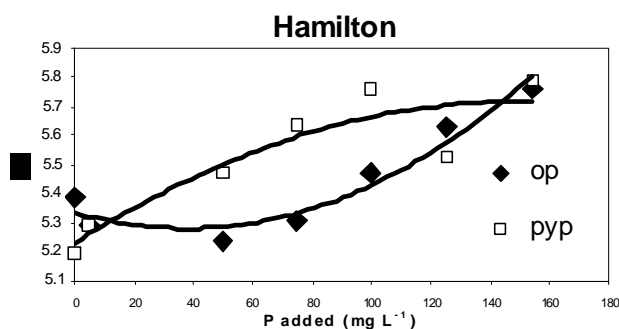


Figure 4. pH vs. P added (mg L⁻¹) as sodium orthophosphate (op) and sodium pyrophosphate (pyp) in Hamilton soil.

Discussion and Future Experimentation

For the Warrambo and Hamilton soils P sorption was greater where P was added as pyrophosphate as compared to orthophosphate. Increasing additions of pyrophosphate increased the soil solution pH in both soils, however increasing additions of orthophosphate increased the soil solution pH in an acidic soil but decreased the soil solution pH in an alkaline calcareous soil. At this stage, it is not clear why the soil solution pH appeared to be affected differently by orthophosphate as compared to pyrophosphate in the alkaline soil. This experiment will be repeated to investigate the potential reasons for these differences.

It is difficult to compare these data to other authors' results as previous studies have reported conflicting data with regard to the extent and of ortho- and pyro-phosphate adsorption reactions (Sutton and Larsen 1964; Hashimoto *et al.* 1969; Savant and Tambe 1979). However in general our findings are in agreement

with the work of Sutton and Larsen (1964) and Mnkeni and Mackenzie (1985) where a greater amount of P was sorbed when added to soil as pyrophosphate as compared to when added as orthophosphate. Al-Kanani and MacKenzie (1991) suggested that the wide range of methods and soil types used to test the P sorption relationship could partly account for the large variance in results between authors. Our data is preliminary and can only be regarded as indicative, as P determinations were obtained using ICP-AES that measures total aqueous P concentration. This does not enable the identification of the P species involved in the sorption of added pyrophosphate, where there may be some hydrolysis of pyrophosphate to orthophosphate during the equilibration period. Therefore, a further experiment will be conducted using ion chromatography that will enable speciation of orthophosphate and pyrophosphate. Amer and Mostafa (1981) suggested that the ratio of pyrophosphate to orthophosphate plays a very important role in the extent and type of P retention reactions in soil. It is therefore important to speciate the P in order to account for these differences.

Mnkeni and Mackenzie (1985) suggested that pyrophosphate is capable of solubilizing organic matter, which plays an important role in the sorption and hydrolysis reactions of pyrophosphate. Therefore, a measurement of dissolved organic carbon levels for the various treatments is required in order to attempt to quantify the effect of this interaction.

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