

Phosphorus chemistry around placement of dry and fluid fertilizers in acidic high P-fixing soils

Daniela Montalvo¹, Fien Degryse¹, and Mike J. McLaughlin^{1,2}

¹ Soil Science, Waite Research Institute, The University of Adelaide, PMB 1, Glen Osmond, SA 5064, Australia.

² CSIRO Land and Water, Sustainable Agriculture Flagship, Waite Precinct, PMB 2, Glen Osmond, SA 5064, Australia

INTRODUCTION

The management of P nutrition is still a challenge in acidic high P-fixing soils. In these soils, precipitation and adsorption reactions are the processes that remove P from solution reducing its availability to plants. The precipitation reactions occur at high P concentrations, in acidic soils Al and Fe are normally the cations involved in the reaction; whereas at low P concentrations, adsorption reactions into Al/Fe oxyhydroxides minerals predominate (Pierzynski et al., 2005).

The dissolution of granular fertilizers renders an acidic highly P concentrated solution, that when in contact with Al and Fe from the soil may precipitate in the form of Al and Fe phosphates (Havlin et al., 2006; Hedley and McLaughlin, 2005). If this is the case, it has been hypothesized that application of fluid P fertilizers may be beneficial as P is spread in a larger volume of soil therefore diminishing the formation of highly concentrated P environments. On the other hand, if P sorption is the predominant mechanism reducing P availability, then banding of P will be beneficial as it limits the contact of P with a large number of strongly P-sorbing sites.

The present study aimed to investigate the chemical reactions that limit fertilizer P availability. An experiment was conducted to evaluate the diffusion, lability, and solubility of a range of granular and fluid fertilizers applied in acidic high P-fixing soils.

MATERIALS AND METHODS

Air dried and < 2 mm sieved surface samples (0-10 cm) of soils from the orders Andisols (North and Chile), Oxisols (Greenwood and Redvale), calcic Inceptisol (Pt Kenny), and Alfisol (Monarto) were used in the present study (Table 1). The calcic Inceptisol is a soil rich in calcium carbonate which promotes precipitation of P with Ca and the Alfisol is a weak P-sorbing soil. These soils were included for comparison.

Table 1. Selected soil properties of the six soils used in the study.

Soil properties‡	Chile	North	Greenwood	Redvale	Pt Kenny	Monarto
Soil type	Andisol	Andisol	Oxisol	Oxisol	Calcic Inceptisol	Alfisol
pH _(1:5 in water)	5.30	5.72	5.87	6.40	8.44	7.09
Clay (%)	14	7	13	61	3	8
CaCO ₃ (%)	b.d.l.§	b.d.l.	b.d.l.	b.d.l.	28	b.d.l.
Al _{ox} (g kg ⁻¹)	42.8	42.0	17.3	2.34	0.241	0.345
Fe _{ox} (g kg ⁻¹)	16.7	8.19	4.14	2.22	0.098	0.325
Total P (mg kg ⁻¹)	1122	1549	157	128	375	84
Soluble P (mg kg ⁻¹)	0.22	0.58	0.17	0.02	0.96	0.62

‡U.S. soil taxonomy classification; particle size analysis by pipette method (McKenzie et al., 2002); CaCO₃ content (Martin and Reeve, 1955); ammonium oxalate extractable Al (Al_{ox}) and Fe (Fe_{ox}) (Rayment and Higginson, 1992); total P determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after soil sample digestion with *aqua regia* (Zarcinas et al., 1996).

§b.d.l.: below detection limit

Evaluation of chemical reactions around the application site of granular and fluid fertilizers

A 35 d Petri dish incubation experiment was performed following the methodology from Lombi et al., (2004). Briefly, Petri dishes (5.5 cm diameter and 1.1 cm height) were filled with soil to obtain a bulk density of 0.5 g cm⁻³ for the Chile soil, 0.7 g cm⁻³ for the North soil, 1.1 g cm⁻³ for the Greenwood, Redvale, and Kenny soils, and 1.3 g cm⁻³ for the Monarto soil. Soils were wetted to field capacity and after an equilibration time of 24 h the fertilizer treatments were placed at the center of the Petri dish and 3 mm below the surface. The fertilizer treatments included four granulars and three fluids. The granular sources were: single super phosphate (SSP; 0-8.8-0, (NPK)), triple super phosphate (TSP; 0-20-0), monoammonium phosphate (MAP; 10-22-0), and diammonium phosphate (DAP; 18-20-0). The fluids included a solution of technical grade MAP (TGMAP; 12-26-0) applied in a volume of 200 or 100 µL and a solution of ammonium polyphosphate (APP; 11-16-0) applied in a volume of 58 µL. In addition, a control treatment without fertilizer was included.

The fertilizer treatments were applied at the rate of 9.2 mg P per Petri dish. All treatments were replicated three times. At the end of the incubation period, two concentric soil sections inner (0–7.5 mm radius) and outer (7.5–27.5 mm radius) surrounding the fertilizer application point were removed using stainless steel cylinders to perform the chemical analysis. Subsamples of each soil section were assessed for total P and labile P determined by the isotopic dilution method. For this analysis, soil was weighed into a centrifuge tube and equilibrated with deionized water in a 1:10 soil:water ratio. The soil suspensions were equilibrated by shaking for 24. Thereafter, the suspensions were spiked with carrier free ³²P. The samples were centrifuged, the supernatants filtered through a 0.2-µm membrane filter, and filtrates analyzed for water soluble P by colorimetry (Murphy and Riley, 1962). The ³²P activity from the filtrates was measured by scintillation counting. Additionally, spiked solutions (without soil) were prepared and analyzed in parallel to the soil suspensions to determine the initially amount of radioactivity added. Labile P (E-value) was calculated according to Hamon and McLaughlin (2002) :

$$E = R \cdot \frac{C_s}{r} \cdot \frac{V}{W} \quad \text{Equation 1}$$

where E is the amount of isotopically exchangeable P (mg kg⁻¹), R is the amount of radioactivity added to the soil (Bq), C_s is the concentration of P in solution (mg L⁻¹), r is the amount of radioactivity (Bq) in solution after 24 h of exchange, V is the solution volume (L), and W the (equivalent dry) mass of soil (kg).

Additional Petri dishes were prepared following the as described procedure and at the end of the incubation time the residual fertilizer granules were removed from the Petri dishes, individually digested in *aqua regia* and their total element content analyzed by ICP-AES.

The experiment was a completely randomized design with a structure of fertilizer treatment × soil section. The ANOVA procedure was performed for data analysis using Genstat version 14 statistics package. Fisher's protected least significant difference LSD at 0.05 level was used to compare treatment means.

RESULTS AND DISCUSSION

The percentages of P recovered from the granular and fluid fertilizers in the inner soil section are shown in Table 2. For Chile, North, Greenwood, and Pt Kenny soils, more than 70% of added P from the granular fertilizers was recovered within 7.5 mm from the point of fertilizer application. In the Redvale soil, P from the granular fertilizers was equally distributed between the inner and outer soil sections. In the weak P-sorbing Monarto soil, around 30% of added P from the granular fertilizers was recovered in the innermost section. The limited mobility of P from granular

fertilizers in acidic and calcareous soils has been previously reported (Benbi and Gilkes, 1987; Lombi et al., 2004) and our results are in agreement with those findings. It has been shown that in non-calcareous soils, the key factors controlling the diffusion of P are amorphous Al and Fe oxides (Freese et al., 1992; Warren, 1994). It was likely that the restricted P diffusion in the Andisols and Oxisols was related to the presence of these compounds in the soils. In the calcareous soil, the limited mobility is most likely due to Ca-P precipitation. In contrast to the granular fertilizers, the application of fluid P resulted in more P diffusing to the outer soil section in all the soils. The differences observed between the fluid treatments were likely related to the injection volumes (200 vs. 100 vs. 58 μL).

The analyses of the granules extracted from the Petri dishes indicated that the content of Al and Fe in the residual granules did not significantly increase with respect to the control granules in all the soils. Furthermore, only a significant increase in the Ca content of MAP and DAP incubated in the Pt Kenny soil was observed. These results indicate that the possibility of precipitation of Al and Fe phosphates in the zone close to the granule in acidic soils is rather unlikely, which contradicts our initial hypothesis and supports the idea that in these soils strong adsorption rather than precipitation reactions limit fertilizer P diffusion and availability.

Table 2. Percentage of fertilizer P recovered in the inner soil section (<7.5 mm of fertilizer application site).

Treatment‡	% of added P recovered at <7.5 mm					
	Chile	North	Greenwood	Redvale	Pt Kenny	Monarto
SSP	72a	73b	83a	50ab	92a	35a
TSP	63a	81a	74ab	50ab	91a	36a
MAP	72a	80ab	82a	46b	84ab	26bc
DAP	69a	80ab	68bc	54a	76bc	28b
TGMAP 200 μL	26c	30e	21e	21d	36e	12d
TGMAP 100 μL	45b	41d	34d	17d	48d	14d
APP	47b	56c	60c	35c	72c	22c

‡SSP: single super phosphate

TSP: triple super phosphate

MAP: monoammonium phosphate

DAP: diammonium phosphate

TGMAP 200 μL : fluid technical grade MAP, applied in a volume of 200 μL

TGMAP 100 μL : fluid technical grade MAP, applied in a volume of 100 μL

APP: fluid ammonium polyphosphate, applied in a volume of 58 μL

Using the isotopic dilution method it was found that in all the P-sorbing soils circa 30% of P, averaged of all the granular treatments, remained in labile form after the incubation period (Figure 1). In the Andisols, there was no significant differences in the percentage of fertilizer labile P between MAP and FIMAP (applied at the volume of 200 μL) (Figure 1a,b); whereas in the Oxisols, significantly more P remained labile with MAP than with FIMAP (Figure 1c,d). In contrast to the acidic soils, in the calcareous Pt Kenny soil significantly more P (62%) remained isotopically exchangeable (labile) with FIMAP than with the granular counterpart (38%) (Figure 1e). As expected in the Monarto soil, there were no differences in terms of lability between the fertilizer treatments (Figure 1f). The lack of increase of labile P in the acidic soils fertilized with fluid P indicate that the effect of dilution of the P in a larger volume of soil may have prompted strong sorption reactions onto the Al and Fe oxyhydroxides removing P from the labile pool. However, in the calcareous soil, this dilution effect was advantageous likely by reducing opportunities to form Ca-P precipitates (Hettiarachchi et al., 2006).

The concentration of soluble P was significantly greater in the inner soil section compared to the outer soil section in all the soils. In the Andisols and Oxisols the increase in soluble P at > 7.5 mm from the point of fertilizer application was minimal with either granular or fluid fertilizer reflecting the strong P sorption capacity of these soils. In the Pt Kenny soil, a greater concentration of soluble P in the outer soil section (> 7.5 mm) was measured with the fluid than with the granular MAP (0.97 vs. 0.09 mg P L⁻¹) which is also consistent with the greater lability measured in this soil with the fluid MAP.

CONCLUSIONS

The results from this study indicate that the application of fluid P fertilizers in soils where adsorption reactions predominate is of little or no benefit. For these soils, the recommended P management strategy is banding the fertilizer to limit its contact with the soil, therefore reducing opportunities for strong adsorption reactions to occur. Unfortunately, in these strongly P-sorbing soils the recommended P fertilization demands the use of large amounts of P, thus becoming a strategy that is economically restrictive for many farmers. There is still much scope to improve the efficiency of P fertilizers in acidic high P-fixing soils.

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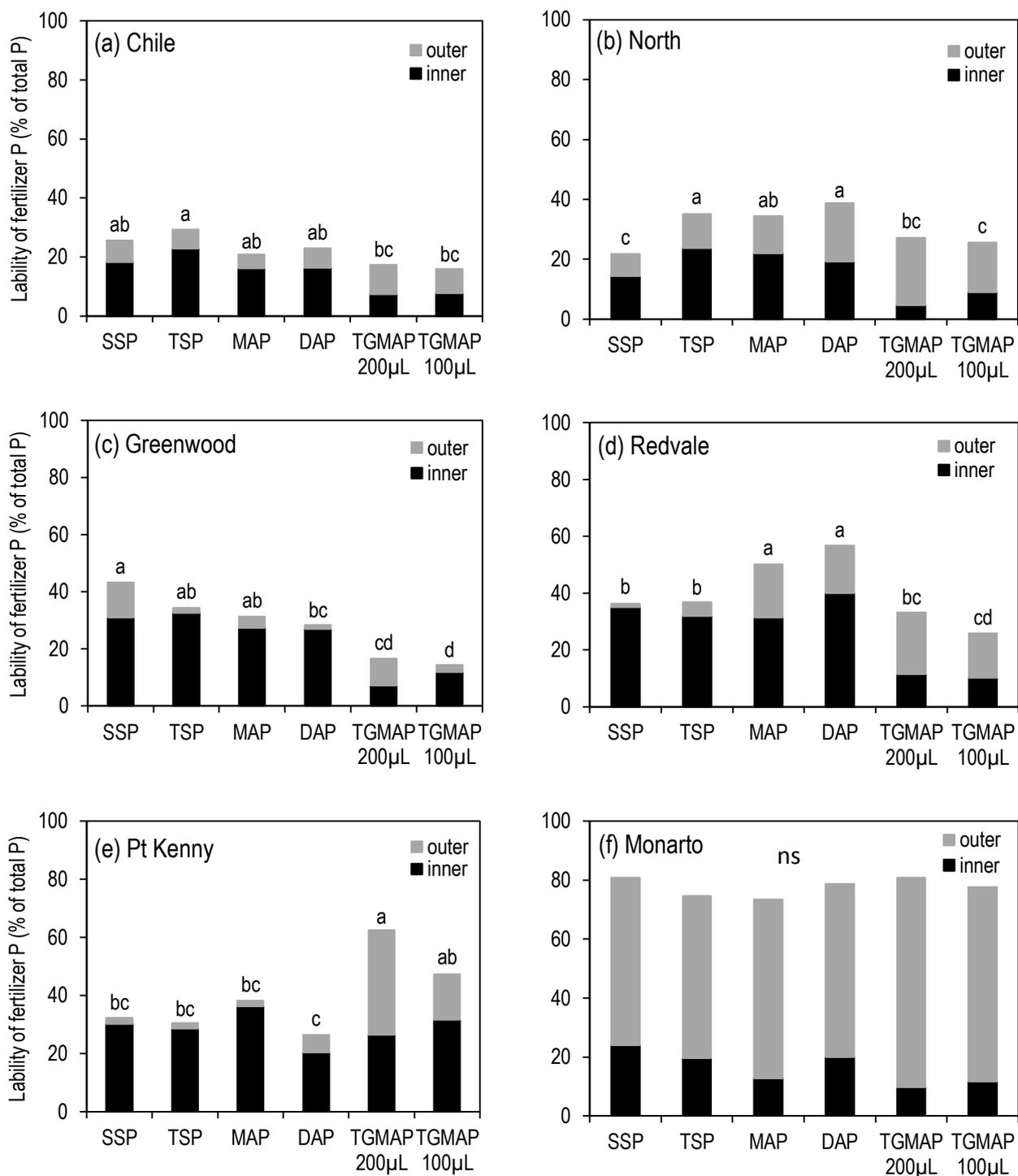


Figure 1. Percentage of fertilizer P remaining in labile form at inner and outer soil sections for (a) Chile, (b) North, (c) Greenwood, (d) Redvale, (e) Pt Kenny, and (f) Monarto soils. Different letters for each bar denote significant differences at $P \leq 0.05$ level. ns indicates no significant difference. For abbreviations see footnote Table 2.

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