

# **Visualization of phosphorus diffusion from granular and fluid fertilizers in non-calcareous highly phosphorus-fixing soils**

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## **INTRODUCTION**

Low phosphorus (P) availability is an important constraint for plant growth in soils with high P-fixing capacities. In these soils, large amounts of fertilizer are necessary to counteract low efficiency of P, as P can be rapidly and irreversibly converted to forms not available for plant uptake. There is an increasing interest in the improvement of fertilizer efficiency through reducing P fixation in soils. However, improvements can only be achieved when the behaviour of fertilizers in soils are clearly understood. Work in this regard has been undertaken in the calcareous alkaline soils of Australia where the chemical behaviour of granular and fluid P fertilizers has been investigated using direct methods (isotopic dilution with radiotracers) and non-destructive spatially resolved spectroscopic techniques. Results from these studies have led to the conclusion that fluid fertilizers outperform granular sources on these types of soils, due to a greater diffusion of P from the point of fluid P application (Lombi et al., 2004a; Lombi et al., 2006). It is not clear yet whether fluid fertilizers have beneficial effects in non-calcareous soils. The aim of this study was to investigate the diffusion of P from granular and fluid fertilizers applied to slightly acidic high-P fixing soils through the utilization of a simple and quick visualization method. Also a calcareous and a non-fixing soil were included for comparison.

## **MATERIALS AND METHODS**

### **Visualization of P diffusion**

Five surface (0-10 cm) soils (Table 1) from the following soil orders (U.S. Soil Taxonomy Classification): an Andisol from New Zealand (North-NZ), two Oxisols, one from Western Australia (Greenwood) and one from Queensland (Redvale), a calcic Inceptisol from South Australia (Pt. Kenny), and an Alfisol from South Australia (Monarto). Soils from the orders Andisol and Oxisol were selected because of their large content of minerals with high P affinities (e.g. Fe/Al oxides, hydroxides, and allophane). The calcic Inceptisol was included because of its high calcium carbonate content, which promotes P fixation through precipitation reactions of P with Ca. The Alfisol is a non-fixing soil and was included for comparison.

The soil samples were air dried and ground to pass a 2-mm sieve. Soil pH was measured in a 1:5 soil/deionized water suspension. Oxalate extractable Al ( $Al_{ox}$ ) and Fe ( $Fe_{ox}$ ) were determined using a 1:100 soil/oxalate extract, following the procedure described by Rayment and Higginson (1992). Diffusive gradient in thin films (DGT) devices assembly and deployment was performed according to the methodology of Mason et al. (2010). Total soil carbon content was measured using the procedure of Matejovic (1997). The  $CaCO_3$  content of the Pt. Kenny and Monarto soils was determined following the Martin and Reeve (1955) method. Soil texture was determined using the pipette method (McKenzie et al., 2002) after oxidation of

organic matter by hydrogen peroxide and destruction of carbonate by acetic acid. The sorption of P by the soils was determined using different P equilibrating solutions as described by Rayment and Lyons (2011).

Table 1. Selected chemical and physical properties of the soils used in the visualization study.

	North-NZ	Greenwood	Redvale	Pt Kenny	Monarto
Soil order	Andisol	Oxisol	Oxisol	Inceptisol	Alfisol
pH (H <sub>2</sub> O)	5.7	5.9	6.4	8.7	7.9
Al <sub>ox</sub> , mg/kg	42000	17300	2340	241	345
Fe <sub>ox</sub> , mg/kg	8190	4140	2220	98	325
P <sub>DGT</sub> , µg/L	16	6	b.d.l. <sup>†</sup>	33	11
Total C, %	8.5	4.4	1.0	2.8	1
CaCO <sub>3</sub> , %	<0.2	<0.2	<0.2	28	< 0.2
Clay, %	6.6	13.1	61.3	3	8.3
Freundlich <i>k</i> parameter ‡	2515	1402	983	92.7	8.64
Freundlich <i>n</i> parameter ‡	0.79	0.76	0.32	0.57	0.59

<sup>†</sup> b.d.l., below detection limit

<sup>‡</sup> Freundlich equation:  $s = k.c^n$ , with *s* (mg/kg) the P concentration on the solid phase and *c* (mg/l) the solution concentration in a water extract at L:S 10 l/kg. *k* is a measure of soils affinity to sorb P while *n* relates to the change in affinity with concentration.

Plastic Petri dishes (5.5 cm diameter and 1.1 cm height) were filled to obtain a bulk density of 0.7, 1.0, 1.2, 1.1 and 1.3 g/cm<sup>3</sup> for the North-NZ, Greenwood, Redvale, Pt Kenny, and Monarto soils, respectively and were wetted to field capacity using deionized water. The Petri dishes were closed, sealed with Parafilm and left to equilibrate overnight. The following day the Petri dishes were opened and fertilizer was placed at the exact centre of each Petri dish 3 mm from the surface. Fertilizer treatments included five granular and three fluid fertilizer sources. Three and four replicates were prepared for the granular and fluid treatments, respectively.

- Granular fertilizers: the granular products evaluated were the calcium phosphates: single super phosphate (SSP; 9% P), and triple super phosphate (TSP; 20% P), and the ammonium phosphates: monoammonium phosphate (MAP; 22% P), diammonium phosphate (DAP; 20% P), and MES-10 which is a product that contains 17.5% P in the form of monoammonium phosphate and 10% S (half as ammonium sulphate and half as elemental sulphur). The granules of each fertilizer were selected based on their weight in order to add 9.24 mg of P per Petri dish.
- Fluid fertilizers: 200 and 100 µL of a solution of technical grade MAP (TG-MAP), and 100 µL ammonium polyphosphate (APP; 16% P) were injected in the middle of each Petri dish. The rate of P added was the same as for the granular treatments (9.24 mg P per Petri dish).

After the application of the fertilizers the Petri dishes were closed, sealed with Parafilm, and incubated in dark conditions and room temperature. The Petri dishes were opened at days 7 and 35 after the fertilizer application, in order to carry out the visualization.

The visualization of P diffusion was performed following the method developed by Degryse et al. (in preparation). On the day of the visualization, previously prepared

Fe oxide impregnated filter papers (Chardon et al. 1996) (Whatman, No. 1, and 5.5 cm diameter) were wetted and immediately put in contact with the soil. After a 30 min deployment time the papers were removed from the soil and rinsed with deionized water to remove adhering soil particles. The P on the paper was visualized using a method modified from Cutting and Roth (1973). The papers were left to air dry before being scanned. The scanned images were analyzed with GIMP (v. 2.6.11) software for image processing. The images were converted to black-white binary images, based on a threshold colour value. The area of the black (high-P) zone was quantified using the histogram command, from which the radius was derived.

#### *Statistical analysis*

The radius of P diffusion was analyzed using the PROC GLM procedure Statistical Analysis System software (SAS Institute, 2003). Additionally, the Tukey's multiple comparison procedure was used to identify differences among treatment means at the 0.05 level.

## **RESULTS AND DISCUSSION**

### **Visualization of P diffusion**

The Andisol and Oxisol used in the present study were classified as slightly acidic, with a pH (in water) ranging from 5.7 to 6.4; whereas the calcic Inceptisol is an alkaline soil with a pH of 8.7. The strength of P sorption decreased in the order of North>Greenwood>Pt. Kenny>Monarto but was also concentration dependent (Figure 1).

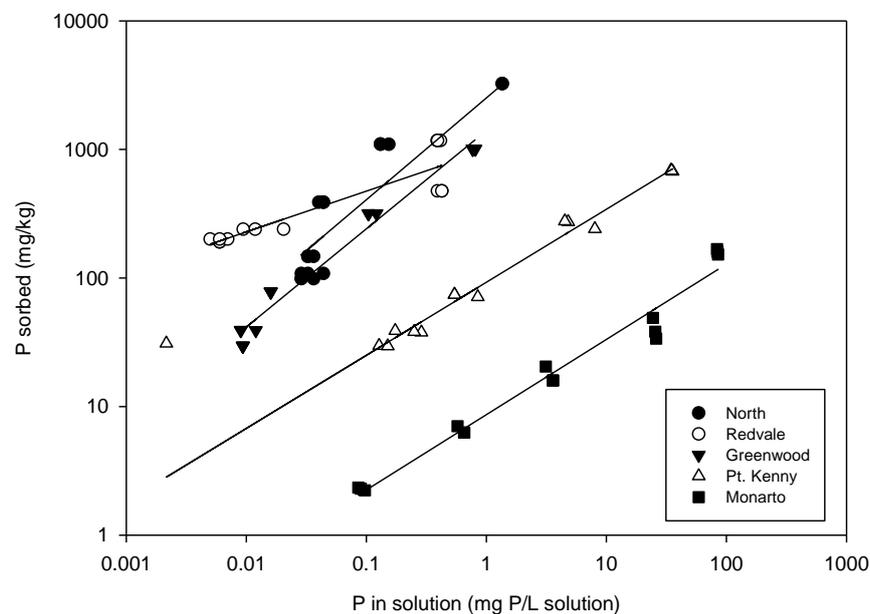


Figure 1. Sorption data for P applied as  $\text{KH}_2\text{PO}_4$  for the five soils, showing agreement with the Freundlich model (parameter values in Table 1), except for the North NZ soil.

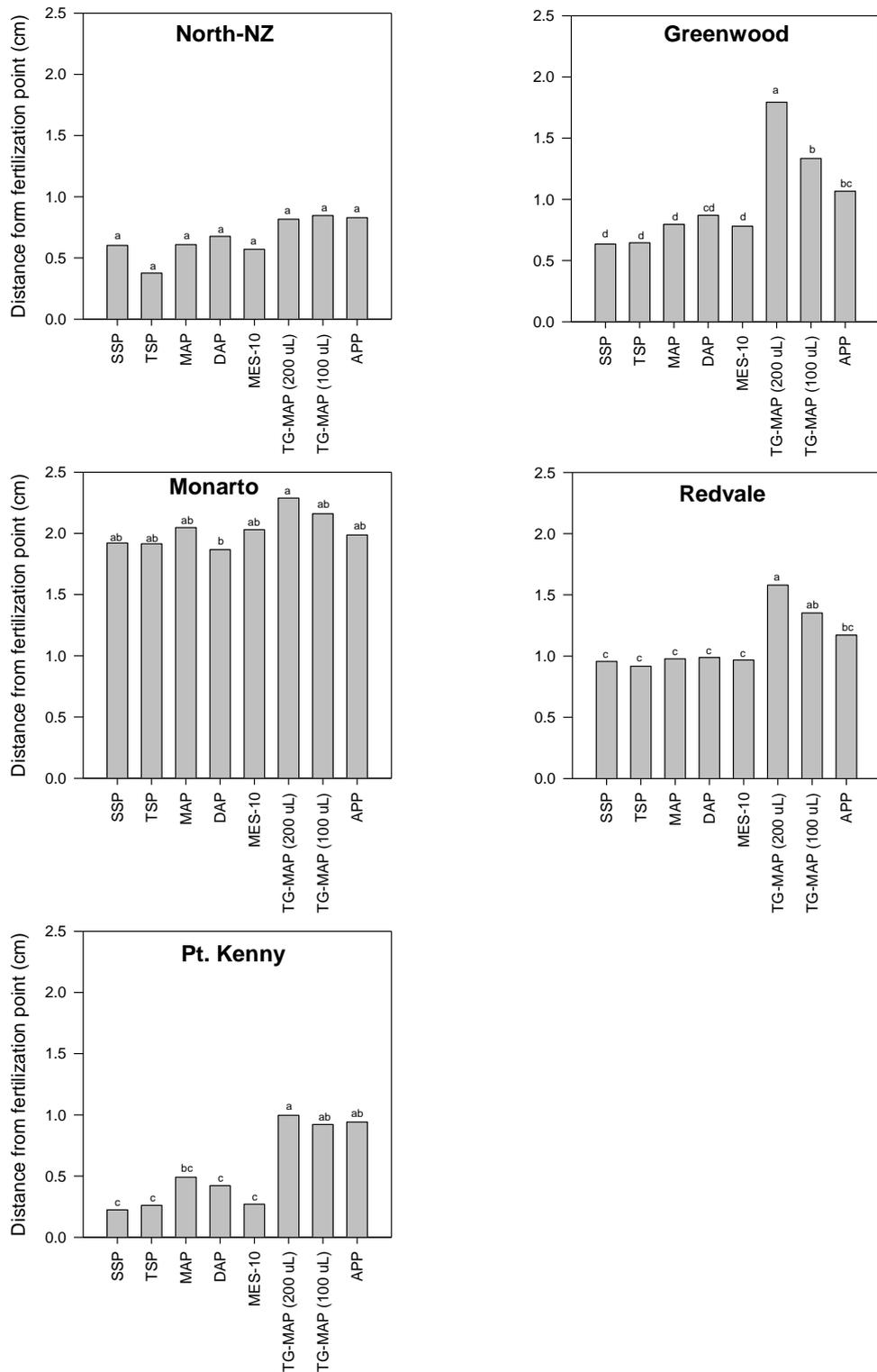


Figure 2. Diffusion of P from granular and fluid fertilizers as measured by the visualization technique.

The radius of diffusion of P from the point of fertilizer application at day 7 is shown in Figure 2. The faster diffusion of P in the Monarto soil (2.04 cm) compared to that of the other soils can be explained by the weaker P sorption in this soil. The calcic Inceptisol (Pt. Kenny) had the smallest radius of diffusion despite having a P sorption strength lower than the Oxisols and the Andisol.

A significantly greater diffusion was observed for the fluid fertilizers than for the granular fertilizers in the two Oxisols (Redvale and Greenwood) and in the calcic Inceptisol (Pt. Kenny), but not in the Andisol (North) and Alfisol (Monarto) soils.

The greater mobility of fluid P in a calcareous soil was previously observed by Lombi et al. (2004a), and was found to be related to the flow of soil moisture toward the hygroscopic fertilizer granule, limiting the diffusion of P outward which in turn favours precipitation of Ca-P species (Hettiarachchi et al., 2006; Lombi et al., 2006). The same physical and chemical processes may have limited the diffusion of P from the granular fertilizers in the Oxisols; however it is likely Al and Fe, and not Ca, were the key elements in these acidic soils limiting P diffusion.

Diffusion of P from the fluid fertilizers in the Andisol was not significantly better than the granular products, despite this soil having a highest P sorption capacity.

## CONCLUSIONS

Previously, fluid fertilizer P has been found to diffuse better through calcareous soils and lability of the fertilizer P is higher than for equivalent granular formulations (Lombi et al., 2004b), leading to higher agronomic efficiency for crop production (Holloway et al., 2001). The visualization experiment indicated that diffusion of P from fluid fertilizers may also be greater than equivalent granular fertilizers in non-calcareous soils. The two Oxisols used here exhibited strong P sorption and fluid P was more effective in diffusing through these soils than granular P. However, fluid P was not more effective in terms of diffusion in the Andisol, despite the strong P sorption in this soil – this is under further investigation.

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## REFERENCES

- Chardon, W.J., Menon, R.G., Chien, S.H. 1996. Iron oxide impregnated filter paper (Pi test): A review of its development and methodological research. *Nutrient Cycling in Agroecosystems* 46(1):41-51.
- Cutting, J.A., and T.F. Roth. 1973. Staining of phospho-proteins on acrylamide-gel electropherograms. *Analytical Biochemistry* 54:386-394.
- Hettiarachchi, G.M., E. Lombi, M.J. McLaughlin, D. Chittleborough, and P. Self. 2006. Density changes around phosphorus granules and fluid bands in a calcareous soil. *Soil Science Society of America Journal* 70:960-966.
- Holloway, R.E., I. Bertrand, A.J. Frischke, D.M. Brace, M.J. McLaughlin, and W. Sheppard. 2001. Improving fertiliser efficiency on calcareous and alkaline soils with fluid sources of P, N and Zn. *Plant Soil* 236:209-219.

- Lombi, E., M.J. McLaughlin, C. Johnston, R.D. Armstrong, and R.E. Holloway. 2004a. Mobility and lability of phosphorus from granular and fluid monoammonium phosphate differs in a calcareous soil. *Soil Science Society of America Journal* 68:682-689.
- Lombi, E., M.J. McLaughlin, C. Johnston, R.D. Armstrong, and R.E. Holloway. 2004b. Mobility and lability of phosphorus from granular and fluid monoammonium phosphate differs in a calcareous soil. *Soil Sci Soc Am J* 68:682-689.
- Lombi, E., K.G. Scheckel, R.D. Armstrong, S. Forrester, J.N. Cutler, and D. Paterson. 2006. Speciation and distribution of phosphorus in a fertilized soil: a synchrotron-based investigation. *Soil Science Society of America Journal* 70:2038-2048.
- Martin, A.E., and R. Reeve. 1955. A Rapid Manometric Method for Determining Soil Carbonate. *Soil Science* 79:187-198.
- Mason, S., A. McNeill, M. McLaughlin, and H. Zhang. 2010. Prediction of wheat response to an application of phosphorus under field conditions using diffusive gradients in thin-films (DGT) and extraction methods. *Plant and Soil* 337:243-258.
- Matejovic, I. 1997. Determination of carbon and nitrogen in samples of various soils by the dry combustion. *Communications in Soil Science and Plant Analysis* 28:1499-1511.
- McKenzie, N.J., K.J. Coughlan, and H.P. Cresswell. 2002. *Soil physical measurements and interpretation for land evaluation* CSIRO Publishing, Collingwood.
- Rayment, G.E., and F.R. Higginson. 1992. *Australian laboratory handbook of soil and water chemical methods* Inkata Press, Melbourne.
- Rayment, G.E., and D.J. Lyons. 2011. *Soil chemical methods-Australasia* CSIRO, Collingwood.