DISSOLUTION OF GRANULAR FERTILIZERS AND DIFFUSION/LABILITY OF P FROM FLUID AND GRANULAR FERTILIZERS IN ALKALINE AND CALCAREOUS SOILS OF SOUTHERN AUSTRALIA

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ABSTRACT

Unlike many soils in Europe and North America, many Australian soils are still responsive to additions of P fertilizer, especially alkaline and/or calcareous soils that dominate the low rainfall zone of southern Australia. Poor responses to granular fertilizers in these areas have recently stimulated a swing by grain growers towards the use of fluid formulations, often resulting in significant yield responses. Laboratory experiments examining P diffusion were undertaken to investigate the reasons for the poor efficiency of granular formulations such as triple superphosphate (TSP), mono- and diammonium phosphate (MAP and DAP) and the greater efficiency of the fluid products; liquid MAP (TGMAP), phosphoric acid (PA) and ammonium polyphosphate (APP) in alkaline soils. Diffusion of P from granular products was reduced in highly calcareous soils. In contrast P derived from liquid formulations not only diffused further from the point of application, but a greater proportion of the applied P remained in labile forms (as determined by isotopic dilution). While granules dissolved rapidly in these soils, P diffusion was limited, and an appreciable percentage of the applied P remained in the fertilizer granule (up to 18% for TSP). The yield advantages offered by fluid formulations in calcareous soils is likely due to this differential chemistry in the soil fertilizer band. Similar experiments in a noncalcareous (but alkaline) Vertisol, with low P retention capacity, found few differences between the chemical behaviour of P in granular and fluid products. Experiments to determine the soil characteristics associated with fluid P responsiveness (compared to granular P) indicated that high pH and high CaCO₃ content were certainly important, but that advantages in using fluid formulations may also be evident in some acidic Australian soils. This is now under further investigation.

INTRODUCTION

Australian soils are inherently low in total P and, at the same time, are able to sorb/fix P readily. Consequently, P fertilizers constitute one of the largest variable input costs for both dryland grain and pasture production for Australian farmers. Over the decades farmers have applied large quantities of P, but only a small fraction of the P applied is used by crops in the ear of application. Soils used for dryland cropping in southern Australia are often very calcareous or strongly weathered acidic soils.

Phosphorus fertilization in Australia has, until recently, not differed significantly from that used in the 1980's, when concentrated granular superphosphates and ammonium phosphates provided the major source of fertilizer P for cereal crops. In the USA, fluid ammonium polyphosphates were developed in the 1950's as an alternative form of P fertilizer. However, the majority of research studies investigating the agronomic efficiency of granular and fluid products, which were conducted in the USA in the 1960's and 1970's (Sutton and Larsen 1963; Khasawneh et al., 1974; 1979; Sample et al., 1979), did not reveal any particular advantages of using the higher-priced fluid formulations. However these studies were almost all conducted on acidic or neutral soils.

By contrast, there has recently been mounting evidence of the greater efficiency of fluid P fertilizers compared to granular P products in highly calcareous soils in southern Australia. For instance, Holloway et al. (2001) reported the results of field and pot trials comparing the performance of liquid and granular P fertilizers in calcareous soils Fluid (technical grade) monoammonium phosphate (TG-MAP) was 4 to 15 times as effective as granular monoammonium phosphate (MAP) in field trials. Several hypotheses have been proposed to explain these results ranging from a simple "placement" effect to changes in chemical and physical processes in the fertilizer band. According to the "placement theory", in highly calcareous and P-fixing soils the more uniform distribution of fluid fertilizers in comparison to granular products may result in a greater number of crop roots intercepting the applied fertilizer (Sleight et al., 1984; Jiapeng and Barber, 1986). This hypothesis is schematically represented in Figure 1.

Figure 1. Granular and fluid fertilizers distribution, P diffusion areas, and possibility of fertilizer interception by root crops in a non P-fixing and in a P-fixing soil.

Placement may indeed represent an important factor in fertilizer efficiency. However, experimental and theoretical evidences indicate that placement is not the key factor responsible for the differential efficiency of granular and fluid fertilizers in calcareous soils. For instance, a simple calculation reveals that the theoretical interspace between fertilizer granules along a row is not large enough to assume that crop roots will not intercept fertilizer P. Under Australian conditions, we can assume a fertilization of wheat with 10 kg P ha⁻¹ in the form of DAP granules, a weight of a single granule of DAP \approx 27 mg and a row spacing of 20 cm. With these assumptions the theoretical average distance between DAP granules along a row is only 1.23 cm. To further test the importance of the 'placement effect', Holloway et al. (2001) mixed different powdered granular (triple superphosphate, TSP; MAP and diammonium phosphate, DAP) and fluid fertilizers (orthophosphoric acid, PA; TG-MAP; ammonium polyphosphate, APP) homogeneously in the soil. In two soil types, a cracking clay and a grey calcareous soil, application of P with fluid fertilizers significantly increased wheat dry matter production compared to granular products.

These results suggest that physical and/or chemical soil processes controlling P availability in the fertilizer band, and hence plant uptake, may differ when granular and fluid sources of P are applied. In this work we investigated a) whether granular products dissolved completely in calcareous and alkaline non-calcareous soils; b) whether P solubility, diffusion and lability of P from fluid and granular sources differed in these soils, and c) which soil parameters controlled wheat responsiveness to P from fluid and granular sources.

MATERIALS AND METHODS

Diffusion, solubility and lability of P from fluid and granular fertilizers

A grey and a red brown calcareous sandy loam soil (Calcarosols) and a non-calcareous alkaline cracking clay (Vertosol) soil were collected in southern Australia, dried and sieved to < 2 mm. In previous field experiments on the two calcareous soils, fluid TG-MAP outperformed granular MAP fertilizers in terms of wheat grain yield and P effectiveness (Holloway et al., 2001). In contrast, preliminary results indicated that fluids and granular fertilizers preformed similarly in a field trial conducted in the non-calcareous alkaline soil (Armstrong et al., unpublished data).

The experimental set up was similar to that described by Lombi et al. (2004). Plastic Petri dishes were filled with dry soil to obtain a soil density of 1.2 -1.3 g cm⁻³. The soil was then wetted to field capacity. After equilibration overnight, four granular and three fluid fertilizer treatments, replicated four times, were prepared:

- Granular treatments: the four granular products tested included two commercial monoammonium phosphates (10:22:0) sourced from Australia and the USA (hereafter named MAP and MAP-US respectively), DAP (18:20:0) and TSP (0:20:0). The granules were selected based on their weight in order to add 8.8 mg P per Petri dish. One granule was placed in the centre of each Petri dish;
- Fluid treatments: commercial TG-MAP (12:26:0), APP (14:21:0) and PA (0:26:0) were used. Aliquots of TG-MAP, APP or PA containing 8.8 mg P were dissolved/diluted in/to 200 μl with distilled water (equivalent to less than 1% of the total water added to each Petri dish) and injected using a needle in the centre of each Petri dish.

After the treatments were prepared the Petri dishes were closed, sealed with Parafilm and incubated for 5 weeks. After equilibration, the Petri dishes were opened and concentric rings of soil, centered around the granule or the injection point, were removed using a series of plastic cylinders. These cylinders were driven into the soil one at a time, starting with the smaller one, and all soil inside the cylinder was removed. Samples of soil were collected between 0-7.5, 7.5- 13.5, 13.5-25.5 and 25.5-43 mm radius from the granule or injection point. A subsample of each soil section was digested and the total phosphorus measured by ICP-AES. Labile or isotopically exchangeable P (E-value) was measured using an isotopic dilution technique (Salcedo et al., 1991).

Granular fertilizers dissolution in high pH soils

For each of the granular treatments, additional Petri dishes were prepared using the same procedure as described above, each containing either a granule of MAP, DAP, or TSP. After 1, 3, 7 days and 2, 5, 8 weeks the granules were carefully extracted from the soil oven dried and weighed. Each fertilizer granule was individually digested with *aqua regia* and elemental composition measured by ICP-AES.

Soil parameters controlling P responsiveness of wheat to fluid and granular fertilizers

Surface soil samples were collected from twenty-nine sites in southern Australia, representing different soil types and cropping regions. They were thoroughly characterized and used for a pot trial. The P fertilizers tested were triple superphosphate (TSP), phosphoric acid (H3PO4), ammonium polyphosphate (APP) and a control of no P fertilizer. The amount of P applied to each pot was the equivalent of $12 \text{ kg } P$ ha⁻¹. Wheat plants were grown and harvested at mid to late tillering (four weeks of growth) by cutting the stem at ground level. Shoots were oven dried and the dry weight was recorded. Responses of plants to applied P either in fluid or granular form were compared to soil physical and chemical characteristics.

RESULTS AND DISCUSSION

Diffusion, solubility and lability of P from fluid and granular fertilizers

There was a significant interaction between soil type and fertilizer form on the distribution pattern of P derived from fertilizers (Lombi et al., submitted). In the two calcareous soils, the distribution of fertilizer P varied significantly between fluid and granular fertilizers but did not differ significantly between the red and grey Calcarosol. When granular forms of P were applied to these soils, between 77 and 98 % of the total fertilizer P was recovered from the two most central sections indicating that diffusion of P was mainly confined within 13.5 mm from the granules. In contrast, when fluid fertilizers were applied to the two calcareous soils the amount of fertilizer P remaining in the central section of the Petri dish was significantly lower compared to the granular products. In the calcareous soils, the largest amount of fluid fertilizer P was recovered from the 7.5-13.5 mm section. The distribution of fertilizer P from granular sources in the red calcareous soil is reported in Figure 2 (Lombi et al., submitted).

Figure 2. Percentage of P derived from fluid and granular fertilizer in soil sections collected at different distances from the point of fertilizer application.

In the alkaline non-calcareous Vertosol the distribution of P derived from fertilizer did not differ significantly between granular and fluid forms. The distribution pattern of fertilizer P was intermediate between that of fluid and granular fertilizers observed in the calcareous soils. Differences in P diffusion between the calcareous soils and the Vertosol may be explained by the contrasting physico-chemical characteristics of these two soil types, especially P sorption/fixation and texture (which influences the tortuosity of the soil pores).

Generally, solubility and lability of P in the calcareous soils was significantly greater for fluid compared to granular fertilizers. The difference between fluid and granular treatments is largely due to significantly larger P lability and solubility in the section 7.5 - 13.5 mm of the fluid treatments. As observed for the distribution of fertilizer P, differences in P solubility and lability between granular and fluid fertilizers were much less marked in the Vertosol. When averaged across the treatments, P solubility and lability were greater in the Vertosol than in the two calcareous soils. This result supports our hypothesis that fertilizer fixation processes might be less intense in this soil independent of the form of fertilizer applied.

Granular fertilizers dissolution in high pH soils

There was no significant difference in granule dissolution in the three soil types investigated (Lombi et al., submitted) During 5 weeks of incubation the weight of MAP and DAP granules decreased by 80 and 84 % respectively. By contrast, only 70 % of the TSP granules dissolved. As for the granule weights, the elemental composition of the exposed granules was similar across the three soils. The amount of P remaining in the MAP, DAP and TSP granules after 5 weeks corresponded to 13, 9.5 and 18 % of the total P initially present in the granules, respectively the residue remaining in the granules after 5 weeks probably reflects the effect of high soil alkalinity in preventing the dissolution of the citrate-soluble P fraction contained in the fertilizer granules. Phosphate is released quickly into the soil from fertilizer

granules. At the same time, the Ca content in MAP and DAP granules incubated in the soil increased over time, whereas it decreased in the TSP granules (which contain mainly monocalcium phosphate).

Soil parameters controlling P responsiveness of wheat to fluid and granular fertilizers

Wheat responded to P application on 70% of the 29 soils used. This response was not well correlated with methods commonly used to assess P availability such as Colwell extraction (Colwell, 1963). In fact, 37% of the fluid responsive soils had a Colwell P of ≤ 15 mg kg⁻¹ which is considered the threshold for P deficiency in wheat. Of the P responsive soils, 52% were significantly responsive to fluids compared to granular P. Among the soil characteristics pH was the more strongly correlated to the fluid response. As expected, soils with $pH > 8.0$ were responsive to fluids. However, good responses were also observed in some acidic soils (pH < 6.0). Few instances of fluid fertilizers outperforming granular products were observed for neutral pH soils (pH between 6.0 and 8.0). Differences in P buffer capacity could not explain when fluid products were more effective than granular P sources.

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