

The chemical nature of P accumulation in agricultural soils—implications for fertiliser management and design: an Australian perspective

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Abstract Many agricultural soils worldwide in their natural state are deficient in phosphorus (P), and the production of healthy agricultural crops has required the regular addition of P fertilisers. In cropping systems, P accumulates almost predominantly in inorganic forms in soil, associated with aluminium, calcium and iron. In pasture soils, P accumulates in both inorganic and organic forms, but the chemical nature of much organic P is still unresolved. The P use efficiency (PUE) of fertilisers is generally low in the year of application, but residual effectiveness is important, highlighting the importance of soil P testing prior to fertiliser use. With increasing costs of P fertiliser, various technologies have been sug-

gested to improve PUE, but few have provided solid field evidence for efficacy. Fluid fertilisers have been demonstrated under field conditions to increase PUE on highly calcareous soils. Slow release P products have been demonstrated to improve PUE in soils where leaching is important. Modification of soil chemistry around the fertiliser granule or fluid injection point also offers promise for increasing PUE, but is less well validated. Better placement of P, even into subsoils, also offers promise to increase PUE in both cropping and pasture systems.

Keywords P-use efficiency · Inorganic P · Organic P · Sorption · Precipitation · Fixation · Fertiliser placement

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Abbreviations

DAP	diammonium phosphate
DCPD	dicalcium phosphate dihydrate
EDTA	ethylenediamine tetraacetate
MAP	monoammonium phosphate
MCP	monocalcium phosphate
NMR	nuclear magnetic resonance
OM	organic matter
P	phosphorus
P _i	inorganic P
P _o	organic P
PUE	P use efficiency
RPR	reactive phosphate rock
TSP	triple superphosphate
XANES	x-ray absorption near-edge structure

Introduction

The main sources of phosphorus (P) in Australian agricultural soils are mineral weathering, atmospheric inputs, additions in irrigation waters, additions in urban, industrial and agricultural wastes, and additions in fertilisers. The relative importance of each of these sources varies according to climate, geology, and farming practices, but P additions in fertilisers often dominate all other sources, while P additions in urban, industrial and agricultural wastes may be significant in some localised areas (McLaughlin et al. 1992).

Australian agriculture has long been dependent on the use of fertilisers to improve crop production (Donald 1964), due mainly to the inherently low concentrations of both total P and available P in Australian soils (Wild 1958; Beadle 1962). Depletion of native P (and other nutrients) in Australian cropping soils at the end of the 19th century caused wheat yield to decline dramatically between 1870 and 1900, and this was reversed by the introduction of use of P fertilisers in the form of superphosphate, due to pioneering experiments at Roseworthy Agricultural College in South Australia reported in 1882 (Donald 1964). Use of superphosphate in cropping soils spread rapidly, and after World War 1 superphosphate became commonly used on pasture soils also. The widespread use of superphosphate, coupled with the introduction of pasture legumes, led to rapid increases in the agricultural productivity of Australian agricultural soils (Donald and Williams 1954). Use of P fertilisers was limited in the period around World War 2, which led to many studies of the residual value of previously applied P fertiliser (Trumble and Donald 1938; Anderson and McLachlan 1951), and a recognition that P applied to soils in previous years was available to subsequent crops, albeit at a lower efficiency than freshly applied. P. Use of P fertilisers in Australia continued to grow after World War 2, peaking in the 1970s at around 480 kt P/yr, with use dropping significantly in the late 1970s and early 1980s due to removal of fertiliser subsidies and increases in price of raw materials (McLaughlin et al. 1992). Since then, use of P in Australia has remained in the range 300–500 kt P/yr with cyclic fluctuations related to prices of fertiliser and commodity values. This P input can be compared to the annual removal of P in animal and plant products from agricultural land of ~120 kt

(McLaughlin et al. 1992). Hence for many (but not all) agricultural soils in Australia that receive P fertilisers, the net balance is positive and P accumulates in soil (Weaver and Wong 2011).

Accumulation of phosphorus in Australian agricultural soils

With the long history of P fertiliser use in Australia, and the historic excess of fertiliser P applied compared to P removal in harvested produce (McLaughlin et al. 1992), it is no surprise that there has been accumulation of P in most fertilised Australian agricultural soils (Williams 1950; Weaver and Wong 2011).

In pasture systems where removal of P in produce is low, addition of P (mostly as single superphosphate) has led to significant increases in soil organic matter content, total nitrogen, total P and sulfur (S) (Donald and Williams 1954; Williams and Donald 1957; Lewis et al. 1987; McLaughlin et al. 1990). In permanent pastures, much of this P accumulates in the top 2–4 cm of the soil profile (Table 1), making pasture species growing on these soils very susceptible to P deficiency induced by surface drying (Pinkerton and Simpson 1986). Similarly, McCaskill and Cayley (2000) observed 38% of applied P in a 17 year trial on a duplex soil near Hamilton in the surface 5 cm, with 80% ultimately recovered in the A horizons to 43 cm depth. The movement of P down a profile in a pasture is related to soil texture and buffer capacity, hence P distribution was greater down coarser textured profiles under similar environmental conditions in long-term trials in southern Australia (Russell, 1960). In more intensively fertilised pasture systems, such as dairy production, P may accumulate to a greater extent, and horizontal spatial variability of P may be high due to uneven return of P to soil in dung pads (Aarons et al. 2004). The camping effect on distribution of P within paddocks also affects the amount of available P recorded in soil tests. Cayley et al. (2002) observed a transient higher soil test P status in the early years of a long term trial at Hamilton as grazing pressure increased. The eventual transfer and increased cycling of P to camps ultimately reversed this trend, particularly with the higher P offtake in product, however it goes some way to explaining the observed claims of increased available P in pastures

Table 1 Concentrations of total P, inorganic P and organic P as determined by the ignition-extraction procedure of Walker and Adams 1958 in the topsoils of a range ($n=15$) of pasture sites in NSW and Victoria (from McLaughlin et al. 1990)

Depth (mm)	Total P (mg/kg)		Inorganic P (mg/kg)		Organic P (mg/kg)	
	Mean	Range	Mean	Range	Mean	Range
0–20	441 ^a *	192–821	105 ^a	38–243	336 ^a	143–579
20–40	282 ^b	145–545	65 ^b	30–165	217 ^b	108–404
40–60	213 ^c	83–381	51 ^c	20–124	162 ^c	63–278
60–100	167 ^d	48–278	38 ^d	7–94	129 ^d	41–208

* mean values followed by different superscripted letters are significantly different at $P \leq 0.05$

that are ‘cell-grazed’. This involves short-term, high impact grazing (and hence dung cycling) which anecdotally then increases available P in soil tests. Ultimately without P inputs though, this system will also run down.

In cropping and horticultural systems, P also accumulates but historically vertical and horizontal heterogeneity has been less than in pasture systems due to cultivation. However, the adoption of minimum till in the last 3 decades combined with the recent introduction of controlled traffic has led to increased spatial heterogeneity in some cropping systems with time (Vu et al. 2009). Significant amounts of P have accumulated in some soils due to a historic low P use efficiency (Bertrand et al. 2003; Bunemann et al. 2006; Vu et al. 2008; Weaver and Wong, 2011).

Reactions of phosphorus added to soil

Following addition of soluble P fertiliser to soil, a series of reactions occurs between P, soil constituents and non-P components of the applied fertiliser that remove P from the solution phase and make the P less bioavailable (Barrow 1973; Hedley and McLaughlin 2005). These may include both adsorption reactions on the surface of soil particles, diffusion reactions where surface P becomes incorporated into soil particles, as well as precipitation reactions that form new solids in the soil.

Adsorption reactions of soluble phosphorus

In acidic and neutral soils, there are fast and reversible surface-based sorption reactions and slower reactions

which move P below surfaces of aluminium (Al) and iron (Fe) oxides (Barrow 1991; Strauss et al. 1997). In alkaline soils, calcium carbonate (CaCO_3), or mixtures of CaCO_3 and Fe oxides, play a more important role in removing soluble P from soil solution (Cole et al. 1953; Ryan et al. 1985a). Sorption reactions occur in the zone of soil where the soil P concentration does not exceed the P sorption maximum of the soil, and the concentrations of Al, Ca, Fe, Mg, Si, P, and trace elements in soil solution do not exceed the solubility product of mineral phases of these elements (Ryden and Syers 1975; Hedley and McLaughlin 2005; Pierzynski et al. 2005).

An important factor determining the extent of sorption reactions, particularly in acidic and neutral pH soils, is the abundance and type of Al and Fe minerals present in the soil (Parfitt 1978; McLaughlin et al. 1981; Ryan et al. 1985a; Borggaard et al. 1990). Hydrous oxides of Al and Fe are the most abundant form of Al and Fe in soil, and therefore sorb more P than layer silicates and other crystalline forms of Al and Fe. Despite the importance of Al and Fe in reactions of P in acidic and neutral soils, recent spectroscopic evidence has indicated that a large proportion of soil P may be associated with Ca even in acidic soils (Beauchemin et al. 2003).

In alkaline calcareous soils, Ca is the dominant determinant of P solubility (Castro and Torrent 1998; Bertrand et al. 2003), although coatings of Al/Fe oxides on CaCO_3 surfaces may also be important in some situations (Ryan et al. 1985a; Ryan et al. 1985b; Samadi and Gilkes 1998). Free CaCO_3 in calcareous soils can absorb P ions at low solution P concentrations without precipitation of Ca phosphates (Freeman and Rowell 1981). Phosphorus replaces adsorbed water molecules, bicarbonate ions

and hydroxyl ions, with the amount of sorption controlled by the CaCO_3 specific surface area and the adsorbing strength dependent on the solubility of the compound formed (Cole et al. 1953; Sample et al. 1980). Sorption reactions are therefore key processes governing the efficiency of added P fertilisers, but where P concentrations are higher (e.g. around fertiliser granules or fluid injection points) precipitation reactions may also be important.

Precipitation of soluble phosphorus

Precipitation reactions involve the creation of new solid phases from ions in solution, and can be observed around fertiliser granules or injection zones for fluid fertilisers (Fig. 1) (Hedley and McLaughlin 2005).

In acidic and neutral soils, hydrous oxides of Al and Fe react with highly concentrated P solutions to

form Al-P or Fe-P mineral phases (Lindsay 1979; Sample et al. 1980; Hedley and McLaughlin 2005), but direct spectroscopic confirmation of the presence of crystalline variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) and strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) in soils is lacking (Sato et al. 2005), likely because the solid P phases formed are not stoichiometrically pure, nor are they highly crystalline (Sawhney 1973). In calcareous soils, the dominant reaction around fertiliser granules is precipitation to dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, DCPD) by surface rearrangement of amorphous phosphate into phosphate heteronuclei (Sample et al. 1980; Freeman and Rowell 1981). At lower soil P concentrations, hydroxyapatite forms ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and at high soil P concentrations, octocalcium phosphate forms ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) (Lindsay and Moreno 1959; Olsen et al. 1983). Recent investigations using synchrotron X-ray spectroscopy have yielded direct evidence for the presence of discrete mineral P forms in soils. Lombi et al. (2006) investigated solid P species in soil around monoammonium phosphate (MAP) fertiliser granules and liquid MAP injection zones, and suggested apatite-like compounds were more prevalent in the former (Lombi et al. 2006). An earlier and more detailed study by Beauchemin et al. (2003) using adsorbed P and mineral P standards confirmed that hydroxyapatite and octocalcium phosphate can indeed be identified in soils. In their soils, these two compounds comprised up to 85% of the total P. Hence, despite some reports asserting that P precipitation is not an important process in controlling P availability and hence fertiliser efficiency (Syers et al. 2008), recent direct spectroscopic evidence suggests the opposite (Beauchemin et al. 2003; Lombi et al. 2006; Ajiboye et al. 2008).

Dissolution of mineral phosphorus

Solid P fertilisers added to soils must undergo dissolution reactions in order to release nutrients into the soil solution. Solubilisation of granules of soluble P fertiliser is achieved by soil porewater, which is predominantly supplied by mass and capillary flow from the soil (Lawton and Vomocil 1954). This movement of water to the granule occurs in a direction opposite to that of dissolved P diffusion (Hettiarachchi et al. 2006), and hence slows or restricts the outward diffusion of P from

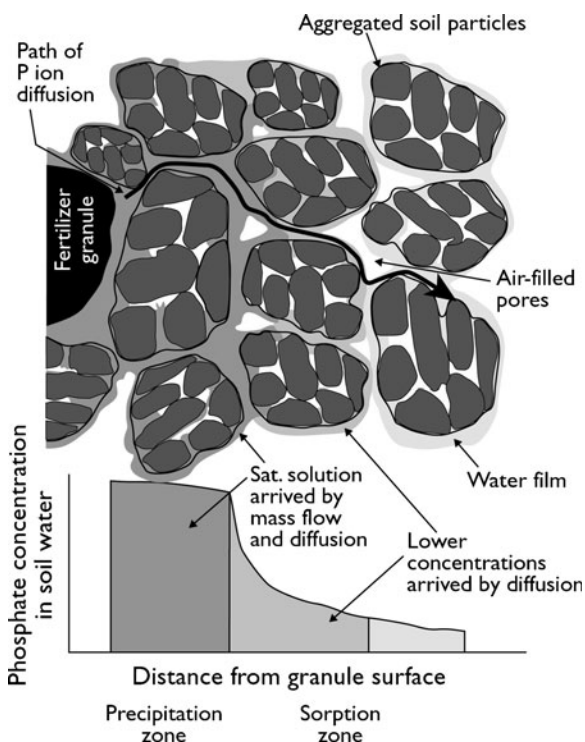


Fig. 1 Diagrammatic representation of the movement of phosphate by mass flow and diffusion from a granule of water soluble P fertiliser through water-filled and water-lined large micro-pores in a well aggregated soil. Note that the penetration of P into aggregates is incomplete due to the slow rate of P diffusion in smaller intra-aggregate micropores and discontinuous micropores (not to scale, from Hedley and McLaughlin, 2005).

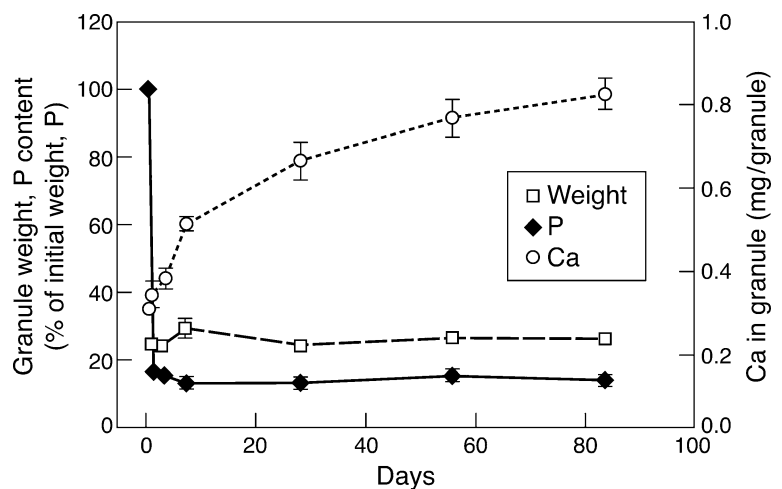
the granule, thus increasing the chances for P precipitation around the granule (Lombi et al. 2006). The solution around the granule is an almost saturated solution, with molar concentrations of P, and pH in this zone may be significantly higher or lower than the bulk soil depending on fertiliser composition (Sample et al. 1980). Movement of P in the saturated solution is driven by an osmotic potential gradient (Huffman and Taylor 1963; Hedley and McLaughlin 2005). The saturated solution does not remain in the granule, rather it is drawn out by matric suction supplied by the surrounding soil and comes into contact and reacts with soil minerals. The process of inward movement of solution continues until the concentration of solution is decreased by dilution or precipitation of the P such that there is no osmotic potential gradient (Huffman and Taylor 1963).

Phosphorus is released quickly from water-soluble P fertiliser granules with most of the P leaving the granule within days (Williams 1970; Williams 1971; Benbi and Gilkes 1987), although in some soils significant concentrations of P can remain in the granule (Benbi and Gilkes 1987). In a laterite and a podsol, 45% and 72%, respectively, of the P from the fertiliser granule dissolved within 4 weeks (Benbi and Gilkes 1987). In another study by Lombi et al. (2004), the addition of MAP granules to a calcareous soil led to an initial rapid dissolution and movement of P out of the granule (within 24 hr), after which the remaining 10–20% of applied P remained in the granules for up to 12 weeks (Fig. 2).

Organic phosphorus mineralisation and immobilisation reactions

Mineralisation is the transformation of organic P to inorganic P and is an important source of plant-available P in some soils. The reverse process, immobilisation, is where inorganic P is converted to organic P, and these two processes occur simultaneously (for reviews see Dalal 1977 and Guppy and McLaughlin 2009). Predicting when P will be released from, or incorporated into, soil OM is difficult, as the strong stoichiometry observed between C and N is not consistently seen with C and P (Kirkby et al. 2011). There are diverging views on the link between C cycling and P cycling (McGill and Cole 1981; Smeck 1985; Condrón and Tiessen 2005), and there have been many studies which have attempted to produce “critical” C:P ratios for organic materials added to soils (Enwezor 1967; White and Ayoub 1983). These have failed for several reasons. One is that much of the P in green or senesced plant material is actually inorganic P and not organic P (Bromfield and Jones 1972; Martin and Cunningham 1973), so that release of P is not a true mineralisation reaction brought about by microbial decomposition of OM, and hence does not require a critical C:P ratio. Secondly, unlike N, microorganisms are able to store inorganic P in their cells as condensed phosphates if availability is high (Khoshmanesh et al. 2002; Bunemann et al. 2008) so that release of inorganic P above a critical C:P ratio for microbial growth is variable.

Fig. 2 Change in granule weight of monoammonium phosphate and content of Ca and P with time in a Cal-cixerollic xerochrept (CSIRO, unpublished data)



The chemical nature of accumulated P in soils

Several techniques have been developed to determine P speciation in soils and there have been many studies directed toward determining the chemical nature of P accumulated in soil through P fertilisation. However, these efforts have not as yet generated a clear and consistent picture of the fate of fertiliser P added to the soil. One reason for this apparent failure is that there is no one fate of fertiliser P added to the soil, but rather a number of different fates, dependent on soil properties, environmental conditions and time. A second reason is that soil P speciation is generally quite difficult, and all of the techniques used have their limitations, as detailed below.

The simplest speciation of soil P is to determine the fraction of soil P in soil solution. This is often very small (μM concentrations) compared to P held on, or in, solid phases in soil (mmol/kg concentrations). Phosphorus on the solid phase and in soil solution can be further differentiated into inorganic P (P_i) and organic P (P_o). Inorganic P in soil solution is usually determined spectrophotometrically through the formation of the blue-coloured phosphomolybdenum complex (Murphy and Riley 1962). Organic P can be determined as the difference between total P, usually measured as inorganic P after digestion. However, there are drawbacks to this method. Organic P is overestimated when inorganic polyphosphates are present because they do not react with the molybdate reagent, and therefore are included in the organic P fraction (Dick and Tabatabai 1977). Additionally, organic matter can interfere with spectrophotometric determination of P_i .

Besides the differentiation of P_i and P_o in soil solution, solid-phase P in soils can be broadly separated into inorganic and organic P using chemical extraction before and after oxidation of organic matter by combustion (Saunders and Williams 1955; Walker and Adams 1958). This does have drawbacks however, in that the extractability of mineral P may be changed by the high temperatures. Perhaps the most widely used method for solid-phase soil P speciation is sequential chemical fractionation (Chang and Jackson 1958). Many variations exist, but the method developed by Hedley et al. (1982) is the most commonly used. It divides soil P into seven fractions: resin-P, bicarbonate-extractable P_i and P_o , hydroxide-extractable P_i and P_o , acid-extractable P and residual

P. The concept is that these fractions equate to P pools of decreasing lability (or increasing stability). Furthermore, at least in the case of P_i , the extracts have become associated with P_i sorbed to or contained within different minerals, with bicarbonate extractable, hydroxide extractable and acid extractable P_i linked to weakly sorbing sites, crystalline oxides/amorphous oxides and calcium phosphates, respectively (e.g. Cross and Schlesinger 1995; 2001).

There are over 100 papers that have used sequential fractionation to study the impact of land use and management (including P fertilisation) on P speciation, and the findings from these have recently been reviewed and analysed by Negassa and Leinweber (2009). They found that P fertilisation tended to increase the labile P_i fraction in temperate soils and the moderately labile P_i fraction in subtropical and tropical soils, whereas it generally had little effect on P_o fractions.

One of the simplest questions with regard to the effect of P fertilisation on speciation is whether fertilisation with P_i can result in accumulation of P_o . Williams and Donald (1957) reported a clear and linear increase in P_o when superphosphate was added to podzolic soils under pasture. This coincided with an increase in organic C, N and S and was attributed to a build-up of soil organic matter once P limitation was removed. However, rarely is there such a simple relationship of P_o with P_i addition, as discussed in the review by Dalal (1977). It is interesting to note however that efforts to increase C sequestration in soil (Lal 2004) will likely lead to greater immobilisation of fertiliser P into organic pools.

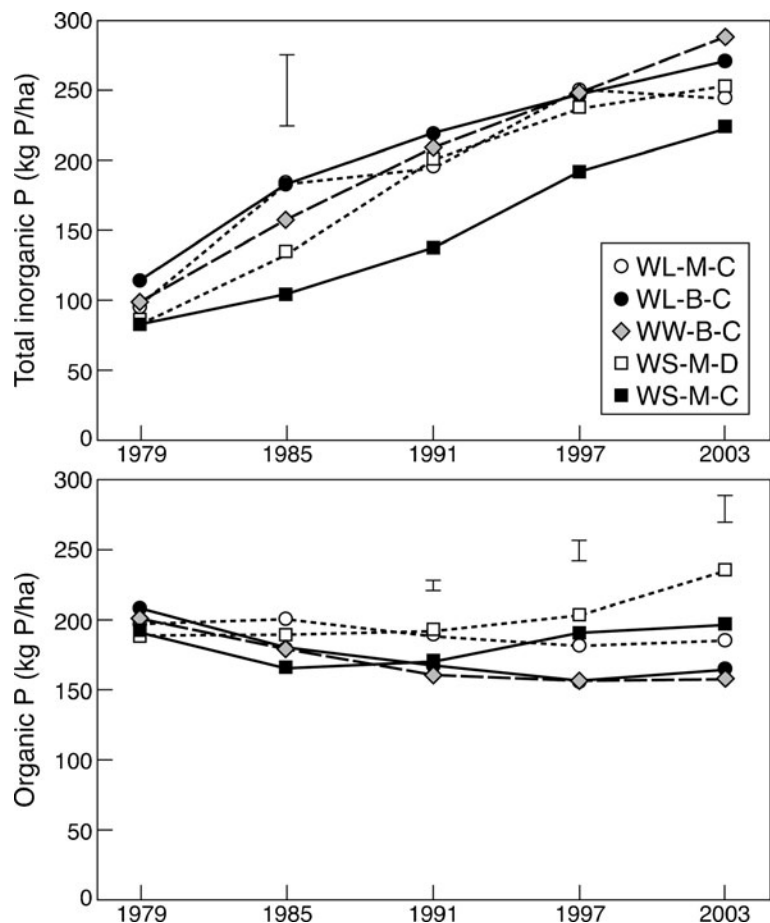
Long-term field trials offer the best assessment of the effect of P fertilisation on soil P speciation. Sequential extraction studies have been carried out at long-term trial sites at Rothamsted, Saxmundham and Woburn in the UK (Blake et al. 2003) and at Askov in Denmark (Guggenberger et al. 2000). In all cases, the addition of P mostly increased the labile and moderately labile P_i fractions. The only organic P fraction substantially higher for fertilised treatments was the most labile organic P fraction (resin OP) (Guggenberger et al. 2000). Oniani et al. (1973) measured organic and inorganic P in long term field trials at Rothamsted, Georgia (in the former USSR) and Ceylon. They reported large increases in inorganic P where superphosphate was added, but only minor or no increases in organic P. Similar results have been shown in long-term trials in Australia. Bunemann et

al. (2006) showed that over 26 years of P fertilisation on a long-term trial at Wagga Wagga, NSW, P predominantly accumulated in soil in inorganic forms (Bunemann et al. 2006) (Fig. 3). Note that organic P was high in these soils at the start of the experiment (double that of inorganic P), but organic P was estimated using the Saunders and Williams ignition method, a technique that Oniani et al. (1973) dismissed as overestimating organic P. This is discussed further below. Russell (1960) also demonstrated small increases in organic P fractions from large P additions in a long-term pasture trial. These increases were correlated with increased soil organic matter following P fertilisation; a similar result to that observed in a 30 year perennial forestry trial near Sydney (Turner and Lambert 1985). Conversely, Helyar et al. (1997) reported that more than half of the P accumulated over 18 years was organic P at a different site near Wagga Wagga, NSW. The contrast-

ing result to that of Bunemann et al. (2006) may be due to either lower P additions or the inclusion of pasture phases in the Helyar et al. (1997) study. Note that Helyar et al. (1997) also used the ignition method to determine organic P.

Guggenberger et al. (2000) found there was little difference in the ratio of P_i to P_o for soils fertilised with manure compared to those fertilised with similar amounts of mineral P fertiliser. Although this may sound surprising, it should be noted that the majority of the P in manure is usually in inorganic forms (McDowell and Stewart 2005). Thus, the term “organic fertiliser” used to refer to manure is somewhat of a misnomer when it comes to P speciation (Hedley and McLaughlin 2005). On the other hand, a sequential extraction study of soils from the long-term Palace Leas Hay Meadow Trial in the UK did find higher levels of microbial P (and readily extractable P) in soils fertilised with manure, than in

Fig. 3 Change in total inorganic P (top) and total organic P (bottom) over time in the top 10 cm of a Chromic Luvisol at Wagga Wagga (NSW) as a function of crop rotation and stubble management. The soil received 20 kg P/ha/yr and the treatments are: WL-M-C = wheat/lupin mulch cultivated; WL-B-C = wheat/lupin burnt cultivated; WW-B-C = wheat/wheat burnt cultivated; WS-M-D = wheat/clover mulch direct drill; WS-M-C = wheat/clover mulch cultivated (from Bunemann et al. 2006)



soils fertilised with mineral P, which in turn had higher levels of these P forms than unfertilised soils (Colvan et al. 2001).

The two main limitations of sequential fractionation are that it offers only very rudimentary chemical characterisation of P in the extracts (it is classified either organic or inorganic) and that the operationally-defined assignments to chemical species (e.g. the assignment of acid extractable P_i as Ca phosphate) are unproven and in all likelihood over-simplifications (Negassa and Leinweber 2009). Ignition methods to speciate accumulated P into inorganic and organic pools have also been criticised as grossly over-estimating organic P in soils (Oniani et al. 1973; Condron et al. 1990). More detailed chemical speciation of soil P can be achieved using spectroscopic techniques. For speciation of P_o in soil, solution ^{31}P NMR spectroscopy of NaOH-EDTA extracts is the most widely used and powerful technique. Unfortunately, it provides very little in the way of P_i characterisation (other than for condensed inorganic species such as pyrophosphate- and polyphosphate), since the main variation in soil P_i chemistry is in what it is sorbed to or precipitated as and this information is lost when P_i is extracted into solution. X-ray absorption near-edge structure (XANES) spectroscopy, a synchrotron-based technique, probably offers the best potential for directly characterizing P_i species in soil. On the other hand, XANES spectroscopy offers little in the way of P_o characterisation, since most P_o species produce very similar XANES spectra. Therefore, the best way to achieve the comprehensive characterisation of soil P chemistry required to understand what happens to P added to soil is most likely a combination of NMR and XANES spectroscopy, possibly in combination with sequential fractionation, as suggested by Negassa and Leinweber (2009).

Whereas there are many papers that have used sequential fractionation to assess the effect of P fertilisation on soil P chemistry, there are relatively few that have used spectroscopic techniques for the same purpose. Koopmans et al. (2004) used solution ^{31}P NMR to assess the effect on P speciation of 11 years of mineral or manure fertilisation of sandy pasture soils. Their results were consistent with those from sequential extraction studies, i.e. there was a large increase in P_i on fertilisation with either form of fertiliser, but little change in the amount or forms of

organic P, although it should be noted that the spectra they acquired were not of sufficient quality to provide detailed organic P characterisation. Consistent with the work of Donald and Williams (1954), a large percentage of the P accumulated in pasture soils is in organic forms, and using extraction methods and more recently NMR techniques, it appears a proportion of the organic P is in monoester forms (both *myo*- and *scyllo*- inositol hexakisphosphates) (Cosgrove and Tate 1963; Omotoso and Wild 1970; Turner et al. 2003; Turner et al. 2005). However, Smernik and Dougherty (2007) recently raised doubts regarding the accuracy of some published NMR data and suggest that monoester P concentrations in some soils have been overestimated (Smernik and Dougherty 2007). Even assuming NMR identification of monoester P has been accurate, up to 50% of the remaining organic P is in forms that are, to date, poorly identified (Turner et al. 2003). Recent improvements in NMR methodology offer the potential to distinguish subtle differences in P_o chemistry that have not been possible previously.

Even more recent than the application of solution ^{31}P NMR spectroscopy to the characterisation of P_o in P fertilised soils is the application of XANES spectroscopy to the characterisation of P_i . Beauchemin et al. (2003) demonstrated the potential of the technique and also discussed its limitations in a careful study of soils enriched in P through the long-term addition of mineral fertiliser or manure. They were able to distinguish between P_i in Ca minerals and P_i sorbed to Fe or Al hydroxides. Sato et al. (2005) used the same technique to also study soils amended with mineral fertiliser and/or manure for varying periods of time. They found P_i in unfertilised soils was mainly associated with Fe minerals, whereas P_i in soils that had a short history of fertilisation was associated with both Fe and Ca. Long-term fertilisation resulted in a dominance of Ca-associated P_i and an increase in more stable Ca-P forms.

To summarise, it would appear a large proportion of added P fertilisers in cropping systems will remain in the inorganic pool, sorbed or precipitated to Al, Ca and Fe. This is likely because of the localisation of added P in bands in soil, thus minimising the opportunity for microbial immobilisation and incorporation into soil OM (McLaughlin et al. 1988b). In pasture soils, organic P accumulates in tandem with inorganic P, likely because soil organic matter con-

centrations may increase under pastures, and also because there is a greater opportunity for added P to interact with available C (through surface broadcasting of fertiliser). In permanent pastures there is also a lack of soil disturbance which encourages the mineralisation of organic P. Hence, increasing P use efficiency (PUE) in cropping systems will need to target the minimisation of soil reactions that sorb or precipitate added soluble P. Likewise, releasing the “bank” of accumulated soil P in cropping systems should focus on mobilisation of inorganic P. In pasture systems, increasing PUE needs to focus not only on the inorganic reactions, but also must target reductions in the immobilisation of P in soil OM. Releasing P from the “P bank” in pasture soils should focus on both inorganic and organic forms, and it is imperative the chemical nature of the latter is characterised better (i.e. phytate or other forms) so that appropriate mechanisms can be targeted.

Measuring and managing PUE of fertilisers

Increasing the efficiency of added P to crop plants has been at the forefront of P nutrition research for decades. Improving management practices has been the main approach used to improve PUE. Best management practices involve the use of the right P source at the right rate, right time, and right place; coined the 4Rs principle (IPNI 2010).

There are several ways to measure PUE discussed in full by Syers et al. (2008), based on the methods for estimating N use efficiency (Cassman et al. 1998). These are the direct method (using isotope dilution or tracing), the difference method (comparing yield and/or P uptake with and without fertiliser), the partial factor productivity method (yield per unit P applied), the physiological efficiency method (yield increment as a function of increment of P uptake) and the balance method (P uptake divided by P applied). From the standpoint of fertiliser design and evaluation, PUE measured by the direct or difference methods are the most commonly used. Comparing the long-term efficiency of fertiliser P formulations is more time-consuming and difficult to measure as it requires evaluation against freshly added P for each crop cycle over several years. The balance method includes geogenic and residual P in the soil and hence PUE is higher when measured by this method (Syers

et al. 2008)—its drawback is that it assumes all residual P in the soil derives from previous fertiliser applications, which would not be true in many situations. Hence, to compare fertiliser formulations, PUE is best measured using isotope techniques (direct method), either by direct nutrient tracing or via isotopic dilution (Fried and Dean 1952; Larsen 1952), or by the difference method. Unfortunately, it is impossible to measure fertiliser PUE using the direct method over several years due to the short half-lives of P radioisotopes, and PUE for fertilisers must be examined using other methods. It is important to note that PUE measured by the direct method will be much lower than by other methods, as it does not account for the residual value of added P over several years.

Evaluation of the efficiency of P fertilisers using isotopic techniques under field conditions has been carried out in Australia mostly on alkaline soils, and has not been adequately studied on other soil types. For alkaline soils, two studies using isotope techniques have reported that the PUE was very low; less than 12 % in the year of application, with most P taken up by the plant coming from residual P, presumably from previous applications if we assume low concentrations of available geogenic P (McLaughlin et al. 1988a; Dorahy et al. 2008). This highlights the need for soil P testing to evaluate the availability of P from residual fertiliser applications (and from geogenic P). Why is the efficiency of added P so low in the year of application? Partly this is due to the volume of soil fertilised (i.e. banding), poor root interception and uptake of banded P, soil reactions which reduce P availability, and variable soil moisture in the field. Under glasshouse experiments where soil moisture conditions and root exploration are optimised, PUE determined by the direct method can be up to 60–70% in Australian soils (Bertrand et al. 2006).

Placement to improve PUE

Since P moves primarily to the root zone through diffusion and the P diffusion coefficients are very small in soil; ranging from 10^{-12} to 10^{-15} m²/s (Marschner 1995), a readily available supply of P in the nearby root zone is necessary to optimise plant uptake, especially during the most active growth period. Therefore, banding of P fertiliser near the

root zone is the best placement option for most cropping systems (Mitchell 1957; Sanchez et al. 1991). Banding will improve PUE where sorption reactions dominate, but where precipitation reactions are dominant, banding may actually reduce PUE. For pasture systems, broadcasting has been the predominant fertiliser placement method due to cost considerations, although subsurface placement has shown potential to increase PUE (Scott 1973), likely through interactions with soil water (see below).

Soil water plays a significant role in PUE through the interaction with soil chemical reactions, and the diffusion of P to the rhizosphere. Dry conditions may exacerbate P precipitation reactions with the solid phase in fertiliser bands by increasing the concentration of P around the point of application. When water is inadequate, P diffusion is also reduced due to reduced water-filled porosity and increased tortuosity of water-filled pores. Therefore, the efficiency of P use in soils with adequate water is much higher than in dry soils and the placement of P (i.e. surface or subsurface) may be critical in determining PUE (Scott 1973; Cornish and Myers 1977; Pinkerton and Simpson 1986; Jarvis and Bolland 1991; Officer et al. 2009). In any cropping season, soil moisture appears to markedly affect the availability of residual P in soil (Bolland 1999; Officer et al. 2009).

Deep placement in the subsoil may also increase PUE on some soils. Research in both southern and northern Australia has shown that enormous yield increases are possible when fertilisers are applied to infertile subsoils (Graham and Ascher 1993; Singh et al. 2005). Graham and Ascher (1993) measured 3.6-fold yield increases when N, P and trace element fertilisers were mixed into the subsoil, compared with surface fertiliser application. Residual benefits from subsoil fertilisation were measured for seven years. Similarly large increases in crop production were observed by Singh et al. (2005) in northern Australia. Unfortunately the difficulty of applying fertilisers to subsoils limits the use of this technology, but if effective subsoil fertilisers could be developed, large increases in crop production could be achieved in many soils.

Due to the low PUE of P applied to soil, it is reasonable to expect that foliar-applied P might have a higher PUE. In general, P uptake by leaves is either via cuticular pores or via the stomata. The dissociated species H_2PO_4^- , which dominates at pH 2–3, is

absorbed more readily than the undissociated form H_3PO_4 (Wittwer and Teubner 1959). However, the foliar application of acidic solutions may cause damage to leaf tissues. There is no consensus in the literature on the PUE of foliar application of P; it has been reported to either increase, decrease, or have no effect on P uptake in comparison to soil-applied P (Noack et al. 2010). Due to the low leaf area for foliar uptake early in the crop growth cycle, it is important to use soil-applied starter P at sowing for early growth and to replace P exported in the previous crop harvested (Silberstein and Wittwer 1951; Batten et al. 1986; Grant et al. 2001). Noack et al. (2010) hypothesised that in seasons with increased yield potential due to good late-season rainfall, a strategic top-up application of P may increase yield. Furthermore, there are cases where supplemental P in the foliar form could help to overcome P access issues, whereby P stratified in the drying topsoil is not readily available to roots. This strategy is only useful if the plant has access to adequate water to fulfil the yield potential created through improved P nutrition and is similar to tactical management strategies currently used for N fertilisers (Gooding and Davies 1992; Angus 2001). Further evaluation is required of the factors likely to affect the utility of using top-up foliar P applications in agricultural systems including identification of responsive soil types, optimum timing of fertiliser application, optimum fertiliser rates and effective formulations.

Linking P supply to plant demand

For optimal yield of most crops, a readily available P pool above the critical value is required to meet plant demand. Phosphorus demand differs for different crop species and even for different genotypes within species with most of the differences attributed to root architecture (Marschner 1995). Annual crops demand P earlier during their growth while perennial tree crops require P supplied slowly over several seasons (Benzian 1966; Johnson 1980; Rahmatullah et al. 2006). Therefore, for annual crops, fertilisers with high P solubility are essential in meeting the crop's P requirement. On the other hand, a slow release P fertiliser will be more suitable for slow growth perennial species. Furthermore, slow release P fertilisers may improve PUE of pastures growing in high-rainfall areas and/or on coarse-textured soils where

dissolved P can be lost via leaching (Yeates et al. 1984; Lewis et al. 1987).

Fertiliser formulations to improve PUE

At the outset it is worth highlighting that fertiliser design strategies have focussed on placing P in an available form in the soil and limiting the rate at which it reacts with soil constituents. The scientific literature suggests that PUE may be improved by technologies that either alter the pH around fertiliser granules (Owino-Gerroh and Gascho 2004), slow the release rate of P from fertiliser granules (Pauly et al. 2002) or increase P solubility (Holloway et al. 2001; Rudresh et al. 2005; Babana and Antoun 2006). The most applicable technology will depend on the source and speciation of the P source used and the main cause of poor PUE, which is soil dependent.

As soil pH has a major influence on the reactions that remove P from soil solution, methods have been developed to increase P solubility by modifying the pH around fertiliser granules. Elemental S (S^0) and ammonium salts have been co-granulated with phosphates to reduce soil pH on neutral and alkaline soils. Silicate compounds have been used to increase soil pH on acidic soils and reduce P retention by Al and Fe oxides. These technologies are not new. Elemental S has been co-granulated with phosphate fertilisers since the late 1940's (Mitchell et al. 1952). A net release of protons results from the oxidation of S^0 into sulfate, which may reduce soil pH and increase P solubility. Mitchell et al. (1952) found that S^0 co-granulated with dicalcium phosphate and MAP significantly increased fertiliser P uptake by wheat in the glasshouse using non-S responsive soils (Fig. 4).

However, there was no improvement in P availability under field conditions (Mitchell et al. 1952). Since then, there have been a large number of dual P and S^0 fertilisers made available to farmers, such as SF45 (Incitec Pivot Ltd.), Super M (Hi-Fert Pty Ltd.), Biosuper (Swaby 1975), Super and Sulfur (Clarkson et al. 1989), MicroEssentials (The Mosaic Company) and Granulock (Incitec Pivot Ltd.). However, most published studies have focussed on the nutritional value of S in these products, rather than the effect of S on P solubility (McLaughlin and Holford 1982; Clarkson et al. 1989; McCaskill and Blair 1989).

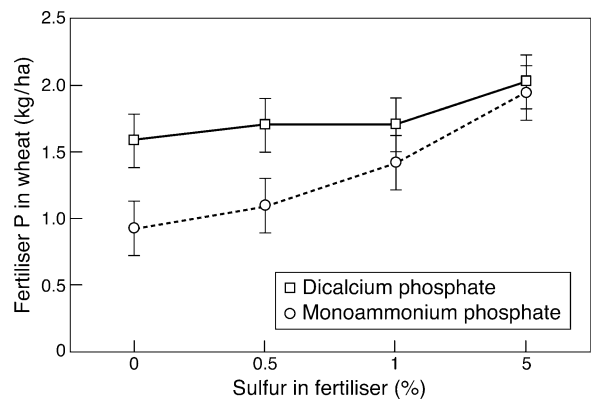


Fig. 4 Effect of elemental S on phosphate uptake by wheat (adapted from Mitchell et al. 1952)

Some studies have examined the effect of S^0 oxidation in improving P acquisition by crops, the earliest in Australia being with Biosuper (a mixture of rock phosphate, elemental S and S-oxidising bacteria). The earliest report of field trials using Biosuper was that by Fisher and Norman (1970), who evaluated the agronomic effectiveness of Australian sources of phosphate rock, and techniques to increase the agronomic effectiveness. Incorporating S^0 into the phosphate rock sources increased their effectiveness, and similar results have been obtained by others in Australia since (Jones and Field 1976; Friesen et al. 1987), in line with experiences overseas (for a review see Boswell and Friesen 1993). More recently, Evans and Price (2009) found that ground S^0 applied with ground phosphate rock increased Olsen-extractable P in 5 out of 11 soils compared with phosphate rock applied on its own. However, very high rates of S^0 were applied, up to 400 kg/ha. The lowest rate of S^0 (100 kg/ha) significantly increased Olsen P on four soils and decreased Olsen P on one site. The average increase in Olsen P was 0.9 mg P/kg with a S^0 application rate of 100 kg/ha, so the effects were not strong.

While incorporation of S^0 into insoluble sources of P seems to assist PUE from these products, effects of incorporation of S^0 into soluble P sources on PUE are less clear. In an elegant set of glasshouse experiments examining oxidation of S^0 co-granulated with ^{32}P -labelled diammonium phosphate (DAP) and triple superphosphate (TSP), Friesen (1996) found no effect of S^0 oxidation on recovery of fertiliser P by the maize plants. Hence, while oxidation of S^0 certainly appears to increase the release of P from rock

phosphates or partially acidulated phosphate rocks, the evidence for any increase in effectiveness of P from soluble P fertilisers is not strong and further research is needed in this area to verify under what conditions S^0 could improve PUE.

On alkaline and neutral pH soils, P solubility and plant uptake can also be increased by co-application of other salts. It has been known for some time that co-application of ammonium salts increases the solubility and effectiveness of P fertilisers. This has been attributed to both stimulation of root P uptake and to increases in solubility of the P (Starostka and Hill 1955; Bouldin and Sample 1958; Miller et al. 1970; Leikam et al. 1983). In glasshouse experiments Miller et al. (1970) showed that co-application of ammonium sulfate ($(NH_4)_2SO_4$) with monocalcium phosphate (MCP) increased the recovery of fertiliser by maize, and these authors were able to demonstrate a reduced precipitation of Ca-P compounds at the root surface when ammonium salts were co-located with the MCP, largely as a result of a rhizosphere pH reduction.

More recently, Rahmatullah et al. (2006) found a similar stimulation of P uptake from rock phosphate when ammonium-sulfate nitrate was co-applied, and attributed this to a pH reduction due to ammonium. Part of the effect of ammonium can be related to rhizosphere acidification as ammonium uptake leads to rhizosphere acidification (Grinsted et al. 1982), but it has also been suggested that nitrification of the ammonium can contribute to pH reduction. However, Faurie and Fardeau (1990) found little effect of nitrification of ammonium on labile P in calcareous soils, suggesting that any protons generated preferentially dissolved carbonates rather than calcium phosphates. If these results are generally applicable, then perhaps nitrification-induced pH changes affect P desorption rather than P dissolution (i.e. increase P availability without increasing the labile pool).

With sulfate salts, as well as localised acidification due to the added salt (Miller et al. 1970), in alkaline soils the complexation of Ca by sulfate can increase the solubility of P in the fertiliser band (Olatuyi et al. 2009). Hence S, as both elemental and the oxidised species, has the potential to affect the PUE from water-soluble fertilisers, particularly when combined with ammonium (as $(NH_4)_2SO_4$). Several fertiliser products are already on the market that provide S in either elemental and/or sulfate form in combination

with either single or triple superphosphate or ammonium phosphates, although the primary aim of incorporating S in either form is predominantly to supply S to plants rather than to affect PUE.

Silicon compounds have also been used to modify soil pH and reduce P retention in soils. Application of sodium silicate to an acidic sandy-clay soil reduced P sorption and increased P concentrations in maize shoots, from 0.55 mg/g to 0.91 mg/g (Owino-Gerroh and Gascho 2004). The authors concluded that P solubility was improved by an increase in soil pH and reduced precipitation with Al or Fe, rather than the substitution of silicates for phosphates on soil binding sites. Smyth and Sanchez (1980) also measured a reduction in P sorption to an acidic Oxisol following $CaSiO_3$ application, which was also associated with a small increase in soil pH. Duque and Samonte (1990) also claimed that $CaSiO_3$ increased PUE on an acidic clay soil. The effect was also associated with a small increase in soil pH, however statistics for fertiliser PUE were not provided in this study.

Slow release coatings may also increase PUE. Nyborg et al. (1998) simulated the effect of slow release P by making small periodic additions of P to soil. Compared to a large single addition of P, smaller periodic additions increased P uptake in barley by 12.2%, 25.8% and 19.4% when MAP, DAP and ammonium polyphosphate were applied, respectively. Subsequently, Pauly et al. (2002) coated MAP and DAP fertilisers with synthetic polymers to slow the rate of P release from the fertilisers. In barley, the slow release polymer significantly increased P uptake from MAP by 9.7% and 10% on the silty loam and sandy clay loam soil, respectively. However, the polymer did not increase the PUE of DAP.

Other studies have found no significant benefits from slow release coatings. Garcia et al. (1997) coated lignin and rosin onto DAP and triple superphosphate. The fertilisers were supplied to ryegrass grown on a highly calcareous soil. Phosphorus uptake from the DAP-treated soil was significantly higher than from TSP and the P-free control (Garcia et al. 1997). However, the coatings did not affect P uptake by ryegrass. Various other new polymers and coatings for water-soluble P fertilisers have been reported recently due to the interest in slow-release P fertilisers to reduce off-site P movement from soils (Wu and Liu 2008; Tyliczszak et al. 2009; Entry and Sojka 2010).

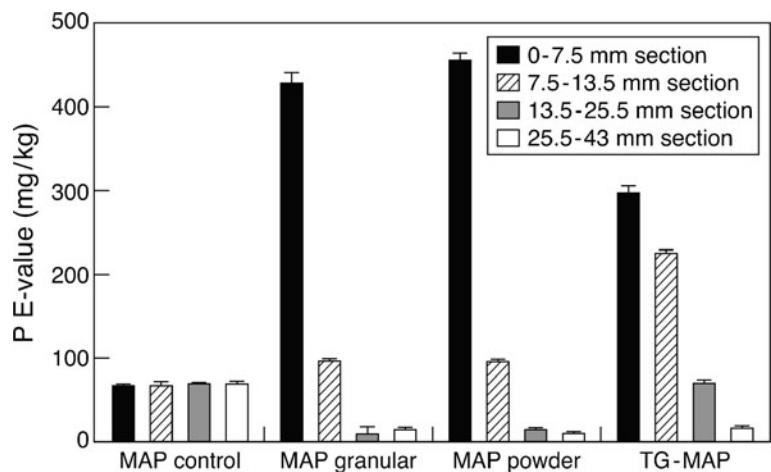
Sparingly soluble P sources, such as magnesium ammonium phosphate and reactive rock phosphates (RPRs), also have slow release characteristics. Chien et al. (2009) recently reviewed this topic. These compounds may be effective P fertilisers for slow growing perennial species and/or where soluble P is rapidly lost by leaching (Benzian 1966; Johnson 1980). In Australia the potential effectiveness of reactive phosphate rocks has been extensively reviewed (Bolland et al. 1988; Sale and Blair 1989; Bolland and Gilkes 1990; Lewis et al. 1997) and studied through a national series of field trials in the 1990s (Simpson et al. 1997). The outcome of this coordinated series of trials identified that soils where RPRs are likely to be equally or more effective as water-soluble fertilisers are those that are acidic ($\text{pH}_w < 6$) in high rainfall environments (850–1000 mm/yr), and therefore restricted mainly to pasture production systems in Australia (Sale et al. 1997). Sparingly soluble P fertilisers and RPRs are likely to be relatively ineffective when supplied to annual cropping systems where crops have a high P demand over a relatively short time period (Rahmatullah et al. 2006).

Recent studies have shown that fluid fertilisers can improve PUE on some soils. In southern Australia, Holloway et al. (2001) found fluid P fertilisers were more effective than granular fertilisers on calcareous soils. Fluid sources of P were up to 15 times more effective than granular sources at equivalent P application rates. Only slight yield responses to P were observed when granular fertilisers were used, even at application rates as high as 100 kg P/ha

(Holloway et al. 2001). Subsequently, Lombi et al. (2004) found that fluid P sources significantly increased P diffusion and availability (measured by isotope dilution) in calcareous soils compared to granular sources (Fig. 5). Soluble calcium from the soil diffused into granular fertilisers and precipitated P as apatite-like minerals (Lombi et al. 2004; 2006). The increased diffusion measured with fluid P reduced P concentrations at the point of application, which in turn reduced P precipitation (Lombi et al. 2006). To date, improvements in PUE from the use of fluid fertilisers have mainly been limited to calcareous soils and some alkaline non-calcareous soils (McBeath et al. 2005).

New fertiliser products and emerging manufacturing technologies also promise to improve PUE. A review of the patent and scientific literature reveals that a number of products have been designed to either enhance the efficiency of applied P or unlock P already retained in the soil. Two recent technologies that appear in the patent literature include the use of polymers to complex cations that might otherwise precipitate P following application to soil (e.g. US 6,515,090) and the use of silicon based compounds to reduce P fixation (e.g. WO 2005/097947). Polymers/polymeric organic acids to reduce P fixation around fertiliser granules are attracting much interest, with Avail™ (<http://www.chooseavail.com/>) and X10D™ (<http://www.nanochemsolutions.com/agriscience/index.shtml>) both claiming to reduce P retention by soil through complexation of Al, Ca, Fe and Mg, reducing precipitation reactions and hence increasing crop PUE. At present reports of effectiveness are mixed with both positive and negative

Fig. 5 Diffusion of labile P from granular MAP and fluid MAP (TG-MAP) away from the point of application on a grey calcareous soil (redrawn from Lombi et al. 2004). For each fertiliser vertical bars represent concentric rings of soil at increasing distance from point of fertilisation. Error bars represent the standard error of 5 replicates. Total available P from fluid MAP was significantly greater than granular MAP ($P \leq 0.05$)



findings in the scientific literature (Gordon and Tindall 2006; Cahill et al. 2010; Karamanos et al. 2010; Karamanos and Puurveen 2011), although at present the only peer-reviewed publication concluded no advantages were found using Avail™ (Karamanos and Puurveen 2011). Certainly it is important that the mechanism and effectiveness of these products be robustly evaluated (Chien et al. 2009).

Increasing availability of accumulated P reserves in soil

To this point we have addressed reactions of added P to soil systems, their form and strategies to increase the availability of those additions to plants in the short term. Here we address strategies to increase the availability, through fertiliser design, of added P after it has transformed to more recalcitrant soil P forms, be they inorganic or organic. Biological strategies, such as green manuring or addition of P-solubilising organisms to soil systems have been extensively reviewed elsewhere (Guppy and McLaughlin 2009; Simpson et al. 2011),

A comprehensive literature search revealed that very little mainstream research effort has addressed application of products that will increase the availability of existing recalcitrant P sources. However, internet (Google™) searching of this topic reveals enormous amounts of literature referring to products claiming to do just that. The quality and intent of the majority of this literature however is aimed at sales of said products, and to the extent that it is reviewed, is reviewed by marketing experts within those companies. They do raise questions regarding potential mechanisms of action of products that may effect increased availability of recalcitrant P sources, however detailed review of these mechanisms is difficult as they remain unsubstantiated speculation for the most part.

What product marketers have correctly identified is that in terms of available P resources, more than half of P in soil falls, under the numerous fractionation schemes devised, and in the majority of soil types, into forms that are difficult to extract chemically (Cross and Schlesinger 1995). Consequently, products that target existing P sources rather than adding new P sources into the soil have considerable potential. Whilst acid extractable P reserves are most likely insoluble inorganic P com-

pounds, it is less clear what proportion of the residual P pool in fractionation schemes is organic or inorganic and further research is needed to understand the nature of the residual P fractions prior to investing considerable effort in developing strategies to mobilise and render bioavailable this fraction. Certainly, the use of concentrated acids has been suggested to liberate P from the soil “bank” in calcareous soils (Ryan and Stroehlein 1979), but generally difficulty in handling and expense has prevented this from being a commercial reality.

Conclusions

Significant amounts of P have accumulated in agricultural soils, and this P is perhaps the most important source of P nutrition for crops in any one cropping/pasture season. Hence, prediction of the potential supply of accumulated P to crops by use of accurate soil testing is an important part of using P fertiliser effectively. In cropping systems, P accumulates predominantly in inorganic forms in soil, while in pasture soils organic P also plays a very important role. Surprisingly, the chemical nature of organic P is still open to question and recent spectroscopic research has questioned the dominance of inositol phosphate in some soils. Clearly, before we aim to improve the release of P from organic forms in soil, we need to understand its chemical nature.

The P use efficiency (PUE) of P fertilisers is generally low in the year of fertiliser application, but they continue to provide P to crops for several years, and this highlights the importance of soil P testing prior to making decisions on fertiliser use. With increasing costs of P fertiliser inputs, various technologies have been suggested to improve P efficiency, but few have provided solid field evidence for efficacy. Fluid fertilisers have been demonstrated to offer clear agronomic advantages for crops on highly calcareous soils and slow release products improve PUE in soils where leaching losses are important. Modification of soil chemistry around the fertiliser granule or fluid injection point appears to offer the most promise for increasing PUE in cropping systems.

The vertical stratification of accumulated P, particularly in pasture soils and increasingly in minimum till cropping soils, makes agricultural production very

sensitive to rainfall amount and distribution, as surface drying limits PUE. Better placement of P, even into subsoils, also offers promise to increase PUE in both cropping and pasture systems.

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