

## **FERTILIZER SELECTION FOR OPTIMAL ENVIRONMENTAL PERFORMANCE**

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### **Introduction**

#### ***Why is fertilizer selection important?***

Under good management practice where the principles of 4R Nutrient Stewardships are followed, phosphorus (P) exports attributable to recently applied fertilizer can be a relatively small proportion (i.e., <10%) of total P exports (see previous paper). However, particularly in New Zealand, where intensive pastoral agriculture has expanded into areas of increased risk for P exports, the adverse consequences of inappropriate selection of the form, placement, rate and timing of P fertilizer applications, are increasing. Fertilizer selection is important in situations where there is regular and frequent rainfall (McDowell 2010), poor soil P sorption (McDowell and Monaghan 2015), high hydraulic fluxes (Simmonds *et al.* 2015) or soil properties (e.g., acid soil pH) that result in the rapid dissolution of calcium phosphates (Simmonds *et al.* 2016).

#### ***So, what is this paper about?***

In this paper we examine some of the more common P fertilizers applied to pastures in Australasia, their reactions in soil and the principles for selecting formulations that will minimize P exports from three of the most common pasture-based grazing systems.

## Phosphatic fertilizers and their reactions with soil

### *What are the most common phosphorus fertilizers in Australasia?*

Some common P compounds in fertilizers and soil are presented in Table 1. Granular inorganic P fertilizers are often surface applied (i.e., broadcast onto pastures) and can be broadly classified as being: (i) water-soluble; (ii) partially water-soluble; and (iii) sparingly soluble. The most common water-soluble phosphatic fertilizers are single- and triple- superphosphate, together with mono- and di-ammonium phosphates.

**Table 1. Some common phosphate compounds in fertilizer and soil.**

Compound	Formula	Common name (Acronym)	Phosphorus concentration (%)	Water solubility
Monocalcium phosphate	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	Superphosphate (SSP / DSP / TSP)	Single 9 Double 18 Triple 21	High
Mono-ammonium phosphate	$\text{NH}_4\text{H}_2\text{PO}_4$	MAP	23	High
Di-ammonium phosphate	$(\text{NH}_4)_2\text{HPO}_4$	DAP	20	High
Di-calcium phosphate	$\text{CaHPO}_4$ $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	DCP (anhydrous) DCP	Variable	Low
Hydroxyapatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	Phosphate rock (PR)	Variable	Low

Adapted from (Nash and Halliwell 1999)

### *How is superphosphate made?*

Superphosphates are formed by the reaction of an acid with phosphate rock (PR). Where sulfuric acid is used, the resulting fertilizer is a combination of water-soluble monocalcium phosphate (MCP) and gypsum (calcium sulphate) commonly referred to as single superphosphate (SSP). Single superphosphate is the dominant form of P applied to pastures in Australasia.

The gypsum in SSP affects the physical properties of the granules and provides sulphur, another essential nutrient for plants. If phosphoric acid, rather than sulfuric acid, is reacted with the PR, a more concentrated MCP fertilizer is produced (triple superphosphate, TSP).

### *How are ammonium phosphates made?*

Ammonium phosphates are produced by reacting ammonia with phosphoric acid. The products formed depend on the molar ratios of reactants but are commonly mono- and di-ammonium phosphate (MAP and DAP). Ammonium phosphates are fully water-soluble.

### ***What are the different partially water-soluble fertilizers and how are they made?***

There are several partially water-soluble P fertilizers and their chemical properties vary considerably. Fertilizers in this group can be made by reacting anhydrous or aqueous ammonia with SSP or TSP, nitric acid with PR, or reactive PR with sulfuric acid or phosphoric acid to form partially acidulated phosphate rock fertilizers. This group also includes fertilizers made by mixing water-soluble compounds, such as SSP, with sparingly soluble compounds such as PR or lime. Sparingly soluble or slow-release P fertilizers include reactive PR, heat treated (calcined) PR and di-calcium phosphate formed by reacting hydrochloric acid with PR.

### ***Which phosphorus fertilizers will we be discussing here?***

This paper will focus mainly on the reactions of single superphosphate (SSP), di-ammonium phosphates (DAP) and phosphate rock (PR).

### ***What happens when phosphorus fertilizers are added to soil?***

A diagram representing the processes occurring when P fertilizers are added to soil is presented in Figure 1. A series of precipitation (i.e., formation of a solid from dissolved reactants) and adsorption (i.e., electrostatic attraction between a solid and chemical species which is akin to magnetic attraction) reactions explains P behaviour in soil. Precipitation/dissolution reactions dominate when there is a large change in the P concentration, when cation concentrations are high, and when soil pH is low or high, for example in the immediate vicinity of a fertilizer granule. Adsorption/desorption processes dominate when P concentration changes are small, solution cation concentrations are low, and where micro-surfaces are large, for example in clay soils.

### ***In water-soluble fertilizers how does the phosphorus leave the granules?***

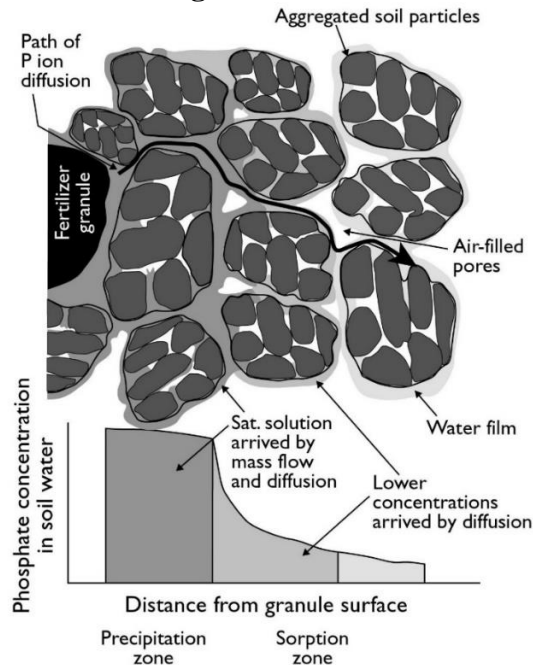
Even in quite dry conditions, water-soluble granular fertilizers absorb water on application to soil. Surface-applied SSP is initially wetted directly from rainfall or irrigation, by capillary uptake of water, and by vapour transfer from the soil or atmosphere due to the hygroscopic (i.e., water attracting) nature of the MCP. Similar processes would be expected to occur for DAP except that the absence of the gypsum carrier present in SSP would restrict the opportunities for capillarity. The high solubility of DAP would tend to enhance mass flow of soil water to the DAP granule once the wetting process has commenced by establishing a high osmotic gradient in the soil.

Factors affecting the entry of water vapour into water-soluble fertilizer granules include relative humidity, temperature, and the physical properties of the particles themselves such as size, shape and porosity, and surface oil coatings designed to improve handling. For hygroscopic uptake of water by SSP a relative humidity greater than 89% is generally considered necessary but is exceeded in most field soils. Water uptake and movement of phosphate out of SSP granules occurs rapidly (i.e., within hours). Recently a method to visualize P dissolution and diffusion from fertilizer granules *in situ* (i.e., in soil) has been developed, and has confirmed the reaction is fast and virtually complete within 24 hours (Degryse and McLaughlin 2014).

Coatings applied to water-soluble fertilizer granules affect moisture uptake and P dissolution. For example, sulphur coatings have been used to slow the release of orthophosphate thereby

increasing P efficiency, and to address other nutrient deficiencies. Polymer coatings have also been used in developing controlled release fertilizers.

**Figure 1. A diagram representing the movement of phosphate out of fertilizer granules and into soils.**



Adapted from (Hedley and McLaughlin 2005)

### ***What about low solubility phosphorus fertilisers such as rock phosphate?***

The low water solubility of PR lends itself to use in areas with considerable sub-surface drainage and poor soil P sorption, such as Western Australia or organic soils in New Zealand with a low anion storage capacity ( $ASC < 10$ ), where more water soluble fertilizers would not be retained in the root zone. However, a lack of quality rock and poor agronomic effectiveness in areas where the soil pH is 6 or greater and rainfall less than 800 mm, has limited market penetration in Australia. Similarly, use of PR for direct application to pastures is a very small proportion (4%) of the New Zealand market (McDowell *et al.* 2019).

Partially water-soluble superphosphates (e.g., the SuperSR<sup>®</sup> range of products from CSBP Fertilisers and lime-reverted SSP in New Zealand, often termed “Dicalcic phosphates”), which are basically di-calcium phosphate dihydrate formed by treatment of SSP with lime are sometimes used, but the agronomic efficiency of these products is usually greater than SSP only in situations where P leaching is significant (i.e., coarse textured soils in high rainfall environments) (Edmeades 2000).

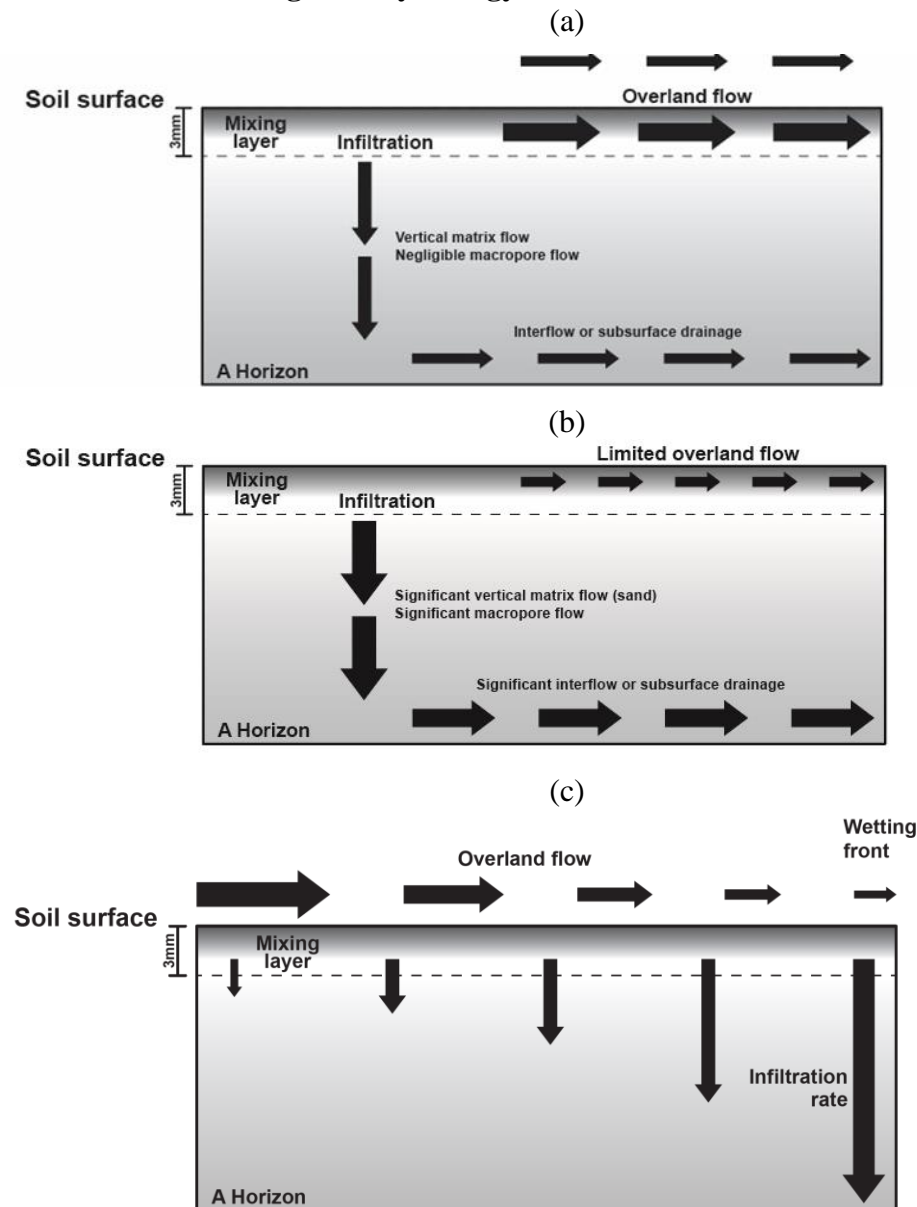
Polymer-coated products, while effective in slowing P release from water-soluble products, are generally too expensive for widespread use on pastures and tend to be used more in horticultural production systems on light textured soils, focussed mostly on decreasing losses of nitrogen (Morgan *et al.* 2009).

## Choosing the right fertilizer for your farm

### *How do you choose the best fertilizer when there are so many different farming systems?*

Due to the variability in farming systems, three model systems with varying hydrology will be used to demonstrate the principles for selecting fertilizers to minimize P exports soon after their application (Figure 2). Such systems are common to Australia and New Zealand, and, while recognising there are other options, discussion will be limited to the surface application of the mineral fertilizer compounds commonly used in pastoral systems.

**Figure 2.** Schematic representation of field-scale hydrology in selected farming systems: (a) overland flow dominant hydrology; (b) infiltration dominant hydrology including macropore flow to sub-surface drains; and (c) border-check irrigation hydrology.



### *Model System 1: Overland flow dominated hydrology*

In overland flow dominated systems (Figure 2a) with seasonal rainfall, basal (i.e., annual) applications of P fertilizers should be undertaken when the probability of overland flow is lowest, for example, late autumn in south-eastern Australia. Late autumn and early winter rainfall onto dry soil would be expected to transport dissolved P below the soil surface, lowering P concentrations in the mixing layer from where dissolved P exports originate. Moreover, by maximizing the time between fertilizer application and overland flow, retention reactions should also minimize the P exports (see our previous paper at this conference). Under those circumstances, fertilizer selection should be based on agronomic efficiency.

Fertilizer selection is likely to be more important where there is frequent (e.g., >50 overland flow events) and reliable (e.g., >4000 mm rainfall annually) year-round rainfall (McDowell 2010), the soils are hydrophobic (Simmonds *et al.* 2017), or there are accidental additions of fertilizer-P to stream channels from aerial applications in steeper country (McDowell *et al.* 2010). In those instances, sparingly soluble or slow release fertilizer could well be the most appropriate providing the agronomic objectives for its application are achieved.

In New Zealand the application of reactive PR has been shown to produce the same mass of pasture as TSP after three years, provided there is sufficient rainfall (> 800-mm) and the soil is < pH 6 to allow the PR to dissolve (Sinclair *et al.* 1990). The lag in the performance of PR, means that it cannot be used as a capital application of P to raise soil fertility quickly and must also be slowly introduced, increasing the proportion in the blend by a third each year.

While partially water-soluble fertilizers are probably the most appropriate form of P for applications in periods when overland flow is likely, that may not always be the case. For example, in south-eastern Australia formulations containing P (sometimes referred to as booster products) are used to stimulate short-term pasture production in early spring. If applications can be timed to avoid overland flow in the next 7 or more days, P exports from water-soluble P in booster products should be relatively minor. In that case the required rootzone P concentration could be achieved at a lower total P application rate than if partially water-soluble forms of P had been used. In addition, water-soluble P in booster products can help minimize the legacy effects (i.e., background exports) associated with increasing residual P in the soil-plant system. This is particularly true for very intensive systems where cattle traffic may enhance particulate P exports, that might include fertilizer solids, during vulnerable times of the year.

### *Model System 2: Subsurface flow dominated hydrology*

In sub-surface flow dominated systems (Figure 2b), the potential for P exports depends on the ability of the soil to remove P in-transit. Where macropore flow dominates, surface applications of P can result in significant P exports if drainage occurs soon after application. This is especially true where artificial drainage systems intercept vertical macropore flow and convey it to waterways.

Like systems where overland flow dominates, the timing of fertilizer application in relation to drainage is important in determining the most appropriate fertilizer formulation. Fertilizer formulation is of lessor but not negligible importance where application and macropore drainage are unlikely to coincide. Less soluble fertilizers may well be appropriate where they are applied to wet or dry, cracked soils. Fertilizer P could also be applied during pasture renewal where cultivation destroys macropores in the topsoil. However, the long-term effectiveness of

this strategy is questionable given that macropore flow is often restored by earthworm activity within a year of cultivation, pasture renovation is not usually an annual event, and cultivation may simultaneously increase erosion and particulate P exports in overland flow.

In systems where matrix flow predominates, P exports are largely determined by the P sorption capacity of the soil. For example, in New Zealand sub-surface drainage from runoff plots with varying anion storage capacity (ASC) (i.e., P sorption potential) were compared (McDowell and Monaghan 2015). Over an 18-month period, drainage from the plots was similar across all three sites (521–574 mm). Exports from a Podzol (55% ASC) that had been developed into pasture for ten years was 1.7 kg TDP/ha. However, the export of TDP leached to 35-cm depth from an Organic soil was 87 kg P/ha (approximately 89% of fertilizer-P added).

Mitigation measures tested in a New Zealand study included reduced P applications, applying alum (50 kg Al/ha) to improve the P sorption and applying low water-soluble reactive PR. Alum reduced exports by approximately a third, but that effect was likely to be transient as alum would be quickly leached from the soil, or converted into more crystalline and unreactive forms (McDowell 2015). The application of PR was marginally effective but did not lessen P exports when pH was < 5.5. Hence, it was concluded that P application rates should be decreased, and the intensity of the system lowered.

In Western Australian studies using sandy pasture soils, P in leachate from SSP and coastal superphosphate (equal parts SSP, PR and sulphur) were compared. Phosphorus was released more quickly from SSP than coastal superphosphate and increased P exports by 10-40%. However, in the long-term, non-water-soluble components of fertilizer contributed to P in leachate emphasising the need to consider the legacy effects of fertilizer P when selecting the most appropriate formulation.

Sub-surface pathways can also dominate the hydrology of irrigated pasture systems. Under spray irrigation the potential for overland flow should be minimal, but substantial P exports can occur via sub-surface flow, especially if the soil has a poor capacity to adsorb P or irrigation practice is poor.

In a study in Central Otago, New Zealand, P exported in sub-surface drainage was measured for three years under a uniform rate irrigation from a sandy textured soil (anion storage capacity < 20%) (McDowell 2017). Exports decreased by 70% following soil mapping and the recalibration of water application rates to match soil types beneath the irrigator. This example clearly shows the benefits of considering hydrology in combination with the 4Rs of nutrient stewardship, and the site-specific nature of P exports through sub-surface pathways.

While a wide range of factors bear consideration in selecting an appropriate fertilizer, where agronomically viable alternatives are available, water-soluble fertilizers are probably inappropriate for many systems with significant sub-surface drainage (e.g., macropore flow, poor soil P sorption).

### *Model System 3: Border-check irrigation*

Border-check irrigation, which is used to supplement natural rainfall, has a consistent pattern of hydrology (Figure 2c). While gradually being changed to spray irrigation, border-check irrigation was once common in both Australia and New Zealand. Border-check irrigation is characterized by high infiltration rates at the wetting front. Here water traverses dry soil but

infiltration rates decline rapidly behind the wetting front, back up the bay towards the water inlet. Tailwater (e.g., overland flow) from behind the wetting front enters drains at the foot of the bay, carrying with it predominantly dissolved P.

In border-check irrigation systems land managers control water inflow and outflows to and from their bays. It follows that the best way of lessening P exports from P fertilizer applied during the irrigation season is short watering (i.e., minimising drainage by not watering the final portion of the bay) and/or recycling tailwaters. However, some drainage (i.e., tailwater) from bays and farms is inevitable.

It is tempting to think that sparingly soluble or slow release fertilizers will minimize P exports from border-check irrigation. This is probably true if fertilizers are applied and irrigation occurs a week or two later. However, if high risk periods are avoided, New Zealand studies have shown that for soils receiving long-term applications of reactive PR, P exports in tailwater >60 days after application can be greater than from soils receiving the same (i.e., long-term) rate of P applied as SSP. As a result, annual P exports may be higher from reactive PR as compared to water-soluble P fertilizer (McDowell *et al.* 2003).

Water solubility is not the only factor to consider in selecting the most appropriate fertilizer for border-check irrigation systems. An Australian laboratory study examined the mobilization of P from individual fertilizer granules and showed that when applied to acidic soil, P was released more rapidly from DAP than SSP (Nash *et al.* 2003). That result was consistent with subsequent field trials where P concentrations in flow sampled immediately behind the true wetting front were lower for DAP than SSP. It was postulated that compared to SSP, P was rapidly released from DAP and infiltrated at the wetting front during irrigation, lowering the P concentration in the mixing layer and the quantity of P subsequently available for mobilization (Nash *et al.* 2004). In that study rainfall on recently irrigated pastures yielded the opposite result. That finding was attributed to a lack of infiltration (i.e., mass flow of P below the mixing layer) and the P from DAP being released more quickly into the mixing layer and mobilized in the wetting front. A more rapid release of P from ammoniated phosphates than SSP has been observed in other studies (Degryse *et al.* 2013). Especially in alkaline soils with high exchangeable calcium, SSP dissolution is delayed, and diffusion from the granule initially limited by a common ion effect. Such studies suggest that there will be soil-specific differences in the relative benefits of compounds within solubility classes (i.e., SSP and DAP).

## **Concluding comments**

There is little doubt that not following the 4R principles for P fertilizers can result in excessive P exports from grazing systems in Australasia. This paper has focused on the selection of appropriate compounds and formulations to minimize the associated risk to downstream water resources. Due to the variability in farming systems, three model systems with varying hydrology were used to demonstrate the principles for selecting fertilizers to minimize P exports soon after their application (Figure 2).

By understanding the processes responsible for P mobilization, and the pathways through which P may be exported, it should be possible to mitigate the short-term risks associated with fertilizer use through prudent selection of compounds and formulations, and optimizing their application in terms of rate, timing and placement (i.e., applying 4R nutrient stewardship). However, as demonstrated through 4R nutrient stewardship, understanding the attributes of



individual farming systems is the key to optimizing production and minimizing environmental impact.

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