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Erratum:

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The sentence on page 662 is incorrectly stated as: The effect of increased temperature causes the foliar spray to have an increased viscosity, which decreases surface tension and increases diffusion across the cuticle and stomata (Kirkwood 1999).

The correct sentence should read: The effect of increased temperature causes the foliar spray to have a decreased viscosity, which decreases surface tension and increases diffusion across the cuticle and stomata (Kirkwood 1999).

The following reference is incorrectly cited as: Fernandez V, Ebert G (2005) ‘Foliar iron fertilization – a critical review.’ (Aula Dei Experimental Station: Zaragoza, Spain)

The correct reference should be: Fernández V, Ebert G (2005) Foliar iron fertilisation – A critical review. *Journal of Plant Nutrition* **28**, 2113–2124.

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Potential for foliar phosphorus fertilisation of dryland cereal crops: a review

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Abstract. Although not commonly used in dryland cropping systems to date, foliar phosphorus (P) fertilisation may allow a tactical response to prevailing seasonal climatic conditions, with the added benefit of reduced input costs at sowing. However, variable outcomes have been reported from field trials predominantly conducted in the USA, and to a lesser degree in Australia. The effectiveness of foliar P is dependent on soil P status, soil water status, crop type, fertiliser formulation and prevailing climatic conditions. This review argues that the potential of foliar P fertilisation in Australian dryland cereal cropping could be enhanced by altering formulations for enhanced leaf penetration using adjuvants, and by accurately assessing the responsiveness of sites before application. This review demonstrates that it is important to use appropriate techniques such as isotopic labelling, to measure the efficacy and mode of action of foliar formulations.

Additional keywords: adjuvants, efficacy, formulations, liquid fertiliser, nutrient management, uptake.

Introduction

Fertiliser use efficiency is fundamental to effective crop production due to increasing input costs and risks associated with farming in an uncertain climate. Farmers are increasingly looking to optimise the amount of fertiliser applied and cost of fertiliser applications. Soil-applied fertilisers react in soils containing high levels of aluminium, calcium, and iron to form insoluble compounds which limit the effectiveness of soil-applied phosphorus (P) fertilisation strategies (Hedley and McLaughlin 2005).

Currently in Australian dryland cropping systems, almost all P fertiliser is supplied at sowing and this application strategy is not responsive to the climatic conditions of the season. In some cases the provision of all P fertiliser at sowing sets the crop yield potential higher than the subsequent prevailing climatic conditions support. In this scenario, the crop commits high amounts of energy to biomass production including the production of tillers, heads and ultimately grains per plant. If the crop is committed to a high number of grains per plant in low rainfall conditions, the crop will exhaust soil water reserves and these grains will not fill properly, resulting in poor quality light weight and pinched grain (Elliott *et al.* 1997; Grant *et al.* 2001).

It is important to apply some P to the soil at the beginning of the crop growth cycle to provide essential P for early growth and, if a maintenance fertilisation strategy is required, to replace P exported in previous crops (Batten *et al.* 1986). With low rates of P added to replace P exported in the previous grain crop there may be sufficient P reserves to grow crops to tillering, but in seasons of adequate rainfall, and therefore increased yield potential, a tactical top-up application of P may be required similar to management strategies currently used for nitrogen (N) (Gooding and Davies 1992; Angus 2001).

Foliar applications of P are the most effective way for a grower to supply P to crops late in-season, should there be a need to increase P supply to the crop. Foliar P can be applied directly to the plant and only when required, and this potentially provides increased fertiliser use efficiency (Silbertstein and Wittwer 1951; Dixon 2003; Girma *et al.* 2007). The use of soil-injected liquid fertilisers has become increasingly popular in Australia. In 2002 the Fertiliser Industry Federation of Australia started collecting sales figures for liquid fertilisers, which at the time were just under 150 000 t (Fertilizer Industry of Australia 2010). In 2009, this figure was more than 600 000 t, which constituted 16% of total fertiliser sales in Australia (Fertilizer Industry of Australia 2010). As the market for liquid fertilisers grows, foliar products using the same formulations will become readily available to growers.

Research to date on the effectiveness of foliar P application in cereals has not been systematic, with research occurring in temporally and spatially isolated pockets. The majority of the research has occurred in the USA (Barel and Black 1979*a*, 1979*b*; Sawyer and Barker 1994; Mosali *et al.* 2006; Girma *et al.* 2007) and only a small body of work has been published for plants grown in Australian dryland cropping systems (Bouma 1969; Alston 1979).

A number of studies have investigated the physiology of foliar P fertiliser uptake under controlled conditions, often using single droplets (Koontz and Biddulph 1957; Bouma 1969). These studies provide valuable information about the

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mechanisms for foliar fertiliser uptake and the rate and amount of nutrient absorbed and translocated in the plant.

A range of P formulations have been examined as potential foliar fertilisers (e.g. Silbertstein and Wittwer 1951; Garcia and Hanway 1976; Gray 1977; Alston 1979; Barel and Black 1979*a*; Parker and Boswell 1980; Harder *et al.* 1982; Mallarino *et al.* 2001; Ahmed *et al.* 2006). These studies demonstrated that the salt load, pH and nutrient mixture all had important effects on the efficacy of foliar P fertiliser. However, further research is required to develop effective formulations, to accurately assess the effectiveness of formulations, to determine what rates of product can be applied without damaging the crop through salt loading, and the optimum timing of application.

This review identifies the current state of knowledge in the field of foliar P nutrition. It outlines the research gaps and provides methodologies and approaches that can be used to adequately test the potential and fit of foliar P fertilisation in dryland agriculture in Australia.

Timing of in-season P applications

Different soil types, land use and climatic conditions make it difficult to pre-determine the quantity of P needed to grow a cereal crop throughout a given growing season. Batten *et al.* (1986) described the P requirement during the growth of wheat. It is common to only add P at the early stages of plant establishment, but with high yield potential crops can become deficient in P later in the growing season (Gray 1977). Plants deficient in P may present with stunted growth, a shorter period for grain filling, a reduced number of fertile tillers and reduced grain yield (Batten and Wardlaw 1987; Elliott *et al.* 1997).

When a plant progresses from the vegetative stage of growth to the reproductive stage of growth, photosynthate produced by the leaves is translocated to the developing seed, which has a higher P requirement (Gray 1977; Batten *et al.* 1986; Peng and Li 2005). In this phase the amount of photosynthate transported to roots reduces, and therefore root growth ceases and nutrient uptake decreases. As root growth ceases the nutrients that are required for seed growth must be translocated from other parts of the plant to the seed (Williams 1955; Gray 1977). Addition of P during this time may prolong the time before photosynthesis stops, delaying premature senescence of leaves, and provide further resources for seed growth.

Applying foliar P in early growth stages can increase the number of fertile tillers (Elliott *et al.* 1997; Grant *et al*. 2001). While this may result in an increased number of fertile tillers, it has not been well established that this early supply of foliar P can increase grain yield as well. Phosphorus applied to leaves may result in an early dry matter response but may not necessarily be supplying the P needed for a significant grain yield response. Several foliar applications may be required throughout the growing season to achieve this if not used in conjunction with soil-applied starter P (Silbertstein and Wittwer 1951).

Foliar fertiliser efficiency is controlled by the leaf area available to intercept the applied formulation. Early in the growing season the proportion of surface cover of the growing crop is often less than 50% (Scotford and Miller 2004). This halves the maximum possible efficiency of a foliar fertiliser, as the P that falls to the ground is not likely to contribute to plant P uptake due to both the low mobility of P (Hedley and McLaughlin 2005) and the very small concentrations of P reaching the soil surface.

Research into the best timing to apply this in-season 'top-up' P suggests that before anthesis is the optimal time, but this covers a large proportion of the total growing season. A higher supply of P between Zadoks (Zadoks *et al.* 1974) 31 and 47 (before heading) resulted in a higher grain yield compared with P added at Zadoks 91–92 (ripening) (Römer and Schilling 1986). Römer and Schilling (1986) proposed that the addition of P before the emergence of the head allowed the plant to produce a higher number of fertile heads per unit area resulting in a higher yield. This was compared with P-deficient crops that conserved sufficient P to sustain the survival of at least one fertile head on each plant. Mosali *et al.* (2006) identified Zadoks 32 as the optimum time for foliar P addition as it increased both P uptake and grain yield. Other studies (Batten *et al.* 1986; Rose *et al.* 2007) showed that P accumulation in wheat plants was highest before anthesis.

Field studies applying P after anthesis have resulted in more tiller dry matter but varying effects on P content in the grain and grain yield. Rose *et al.* (2007) noted a cessation of P uptake after anthesis (even when soil P was available) and concluded P supply after anthesis is not necessary for maximum grain yield of wheat. While the number of fertile tillers and grains has been determined before anthesis (Elliott *et al.* 1997), it appears that in some instances an application of P after anthesis does have the capacity to increase yield through increased grain fill. Benbella and Paulsen (1998) found that applications of P to wheat after anthesis increased yield while Gray (1977) reviewed several experiments that showed yield responses to foliar P applications after anthesis.

The Agriculture Production Systems Simulator (APSIM) has been used to develop an N fertiliser management decision making tool. Yield Prophet is an interface of APSIM that allows growers to forecast yield based on a number of soil, climate and crop parameters. The model allows growers to match N fertiliser inputs with the yield potential of their crop (Hochman *et al.* 2009). While APSIM does contain a module for P (soilP) it is not used to predict in-season P fertiliser requirements (Keating *et al*. 2003). However, APSIM can give an assessment of yield potential based on crop physiology and soil properties including soil water storage. When combined with diagnostic tools such as crop tissue P testing, APSIM predictions can potentially aid decisions about in-season P fertiliser application.

The key factors that control the optimal timing of foliar P applications are therefore:

(1) The physiological age of crop: the potential for yield improvement will decrease with increasing crop age (most likely diminishing beyond anthesis);
(2) The degree of P deficiency as determined by tissue testing: a crop that is very P deficient will have limited potential to overcome deficiency at low foliar P application rates, while a crop that is P sufficient will not be responsive; and
(3) Leaf area of crop: sets foliar P-uptake potential and depending on physiological age of crop sets photosynthetic potential for grain filling.

With detailed understanding of these three key factors there is an opportunity to model the interaction and predict when foliar P applications will be most effective.

Mechanisms of plant uptake of foliar nutrients

The processes that regulate the uptake of foliar substances have been studied in detail (Schönherr and Bukovac 1972; Kirkwood 1999; Eichert and Burkhardt 2001; Fernandez and Ebert 2005) as movement of nutrients into the plant through the leaf involves different mechanisms to nutrient transport into plant roots. Most notably, plant leaves have thicker cuticles, which are coated with a waxy layer making penetration of solutes difficult.

For foliar fertilisers to be utilised by the plant for growth, the nutrient must first penetrate the leaf surface before entering the cytoplasm of a cell within the leaf. Penetration of foliar nutrients occurs through the cuticle (Fig. 1), the stomata, leaf hairs (Fig. 2) and other specialised epidermal cells (Franke 1967). There is ongoing debate as to which of these penetration pathways plays the most important role in nutrient uptake (Wittwer and Teubner 1959; Buick *et al.* 1992; Kirkwood 1999; Eichert and Burkhardt 2001; Fernandez and Eichert 2009; Oosterhuis 2009).

There are several processes required for leaf penetration of solutes; the solute must adhere to the leaf surface and be retained to allow sufficient time to penetrate, the solute must diffuse through the cuticle, and there must be desorption from the cuticle into the phloem to transport nutrients to high growth areas (Kirkwood 1999).

Barriers to uptake

Epicuticular waxes are a barrier to the retention and penetration of foliar fertilisers into plant organs (Jenks and Ashworth 1999). Almost all plant surface waxes are hydrophobic and repel water-based sprays. The cuticle itself is a lipid layer making it wettable by oils but still only slightly permeable to both water and oils. The thinnest areas of the waxy layer are covering the stomatal pore (Currier and Dybing 1959). This is one reason why the timing of foliar sprays is often targeted to stomatal opening (Jenks and Ashworth 1999). Several studies (Jenks and Ashworth 1999; Kirkwood 1999; Eichert and Burkhardt 2001) have shown that

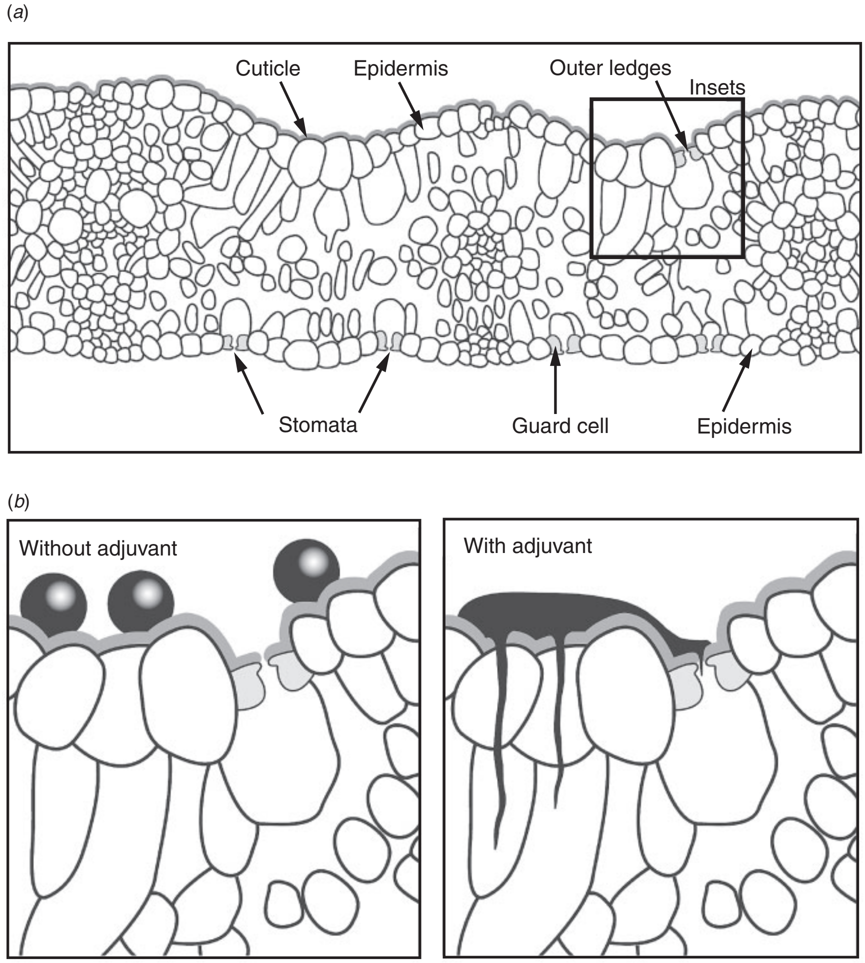

Fig. 1. (*a*) Cross-section of a wheat leaf, and (*b*) diagrammatic representation of the ability of foliar fertiliser to traverse the stomata and cuticle when there is adjuvant in the formulation to aid sticking, spreading and penetration of the fertiliser (adapted from www.fao.org/DOCREP/006/Y5146E/y5146e04.htm, accessed 22 June 2010).

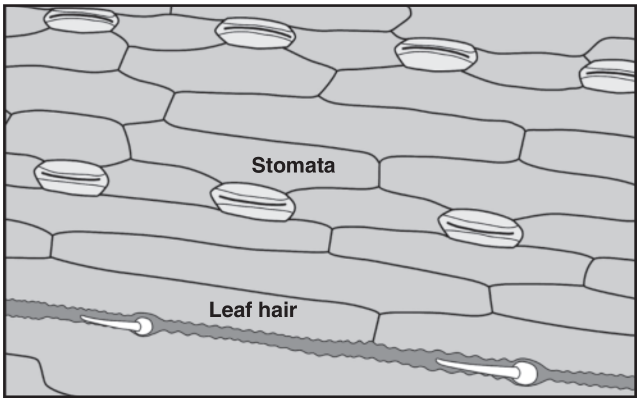

Fig. 2. Surface of wheat leaf showing stomata in two rows (top and middle) and two leaf hairs are seen at bottom of image (image redrawn from a Scanning Electron Microscopy image).

the chemical or physical removal of cuticular waxes increased the penetration of foliar-applied nutrients. Causing injury to leaves by light scouring also increased the penetration of nutrients (Swanson and Whitney 1953; Jenks and Ashworth 1999). This is due to the disruption of the waxy layer allowing solutes to move more freely into the leaf (Jenks and Ashworth 1999). However, the thickness of the waxy layer alone does not fully explain the inhibition of the permeability of foliar sprays.

Stomatal penetration

The epidermal layer is dotted with stomata which allow carbon dioxide exchange between the outside environment and photosynthetic cells (Marschner 1995). The stomatal pore is enveloped by two guard cells which regulate the opening and closing of the pore (Fig. 1*a*). Stomata also provide the major pathways for evaporative loss of water, exchange of gases during photosynthesis and for controlling the transport of water across the epidermis (Raven and Johnson 1999).

Accurately identifying and measuring stomatal uptake of chemicals applied to leaves has proven difficult. Currier and Dybing (1959) provided early evidence that stomatal penetration can be a major pathway for plants to absorb solutes in foliar sprays. Buick *et al.* (1992) showed that pretreatment of broad bean leaves with abscisic acid to close stomata resulted in diminished absorption of foliar-applied solution. This confirmed that stomatal penetration played a role in penetration and uptake. Similarly, other studies (Field and Bishop 1988; Eichert *et al.* 1998) have identified stomatal penetration and therefore it is important to consider this when applying foliar fertilisers.

Uranine has been used as a dye tracer to show the role stomata play as a pathway for solute uptake in leaves (Eichert *et al.* 1998; Kirkwood 1999; Eichert and Burkhardt 2001). With open stomata, 30 times more uranine penetrated through the epidermal strips than with closed stomata (Eichert *et al.* 1998). Penetration of the chemical was strongly correlated to the number of stomata penetrated and was higher below the rims of drying droplets compared with the entire drop-covered area (Eichert and Burkhardt 2001). Of the stomatal area covered by the droplet (10 µL) only a small proportion (10%) contributed to uptake and 42% of the applied dose penetrated the leaf (Eichert and Burkhardt 2001).

Recently, the size-exclusion limits of stomata in various leaves have been measured (Eichert and Goldbach 2008; Eichert *et al.* 2008). Eichert *et al.* (2008) studied the penetration of water-suspended hydrophilic particles of two different sizes (43 nm and 1.1 µm) into bean leaves. Penetration of the larger particles was never detected, whereas between 2 and 9 days the smaller particles occasionally penetrated the leaf. Stomatal pore lengths in the bean leaves were measured to be 25 µm with widths between 3 and 10 µm. Given these dimensions the 1.1 µm particles should have penetrated. The exclusion of the larger particles therefore indicates that uptake of the small particles does not take place by mass flow.

Penetration via the stomata has been well documented so it is important to consider the factors that control stomatal opening when applying foliar P fertilisers. Some of the main environmental factors that influence stomata opening are water stress, light and temperature (Currier and Dybing 1959; Sargent and Blackman 1965; Eddings and Brown 1967). Increases in foliar uptake rates have been documented after stomata have been opened by light. Hydration of the plant cuticle can improve penetration and conversely water stress can decrease penetration (Kirkwood 1999). When a leaf is hydrated the stomata are open to allow water vapour to emerge (Eichert and Burkhardt 2001), and this could allow the foliar spray to be transported across the epidermis at a faster rate. The opposite effect is expected under water stress as water stress in plants results in stomatal closure to prevent loss of fluids and this excludes penetration of fluids applied to the leaf surface (Currier and Dybing 1959).

The effect of increased temperature causes the foliar spray to have an increased viscosity, which decreases surface tension and increases diffusion across the cuticle and stomata (Kirkwood 1999). However, at these higher temperatures the solute may evaporate more quickly and so there would be a decrease in the available penetration time. A high temperature in the presence of increased humidity delays the drying of the applied droplets, prevents water stress and favours stomatal opening (Clor *et al.* 1962; Kirkwood 1999).

Non-stomatal penetration

Some researchers believe stomatal uptake plays a minor or negligible role compared with cuticle penetration of foliar-applied nutrients (Schönherr and Merida 1981; Schönherr 2006; Oosterhuis 2009). The cuticle is the first route available for penetration of solutes into leaves upon contact with the leaf, and the cuticle layer partially extends across the stomatal cavity forming cuticle ledges (Fig. 1). These cuticle ledges will therefore also interfere with the ability of the stomata to take up solutes (Dickison 2000).

The cuticle is a structurally complex waxy layer and, on the basis of urea and glucose absorption studies, Schönherr (1976) concluded that liquids could penetrate through cuticular pores up to 0.9 nm in diameter. Permeability of cuticles to ions is dependent on similar environmental factors to stomatal uptake. The pores are lined with a fixed negative charge and consequently cation movement along this diffusion potential is enhanced whereas anions are repelled from the pores (Tyree *et al.* 1990). Phosphorus formulations containing anionic species are not soluble in lipids as they are charged and cannot pass through the lipophilic pathway. Ionic species can only cross the lipid membrane if aqueous pores transverse the membrane (Schlegel *et al.* 2005). Aqueous pores within the plant cuticle arise by hydration of permanent dipoles and ionic functional groups (Schönherr 2006). Aqueous pores preferentially occur at cuticular ledges and at the base of trichomes (fine outgrowths such as hairs). In experiments by Schönherr (2006), pore radius ranged from 0.45 to 1.18 nm, with most having a diameter of less than 1 nm (Schönherr 1976). Solutes with a radius smaller than 1 nm should therefore have the capacity to penetrate the cuticular pores.

Research to date suggests that both stomata and the cuticle play a role in nutrient uptake. However, stomatal penetration appears to be more complex and dependent on more environmental factors than cuticular penetration. Currier and Dybing (1959) described stomatal penetration as quick and rapid, when it occurs, whereas cuticular penetration is a slower process. The charged nature of foliar P compounds will determine the ease by which they transverse the cuticle and stomata. Further investigation of the ability of P compounds to traverse these two uptake pathways will help identify the best foliar P products.

Measurements of foliar nutrient uptake

Isotopic techniques

While dye tracers are commonly used to probe the physiology of plant uptake of solutes, radioiosotopic tracers are a technique used for evaluating the transport of foliar P materials throughout the plant. For the study of foliar P uptake the tracers used are $^{32}P/^{33}P$ isotopic tracers. Early use of foliar ^{32}P was by Silbertstein and Wittwer (1951) and Swanson and Whitney (1953). Silbertstein and Wittwer (1951) momentarily dipped the first leaf of bean and squash plants into ^{32}P phosphoric acid (H_3PO_4) solution and found that it was rapidly absorbed with a higher fertiliser use efficiency but lower yield response than soil-applied P (where 50 times more soil P than foliar P was applied). Swanson and Whitney (1953) and Barrier and Loomis (1957) both applied a single 10-µL drop of ^{32}P beans and soybeans and found temperature influenced foliar fertiliser uptake rate, with the optimal uptake temperature being 30°C, which concurs with the previously discussed effect of increased temperature on increased stomatal penetration.

Koontz and Biddulph (1957) applied a range of ^{32}P-labelled fertiliser formulations to red kidney bean plants to determine the effect of spray volume, accompanying cation and wetting agents on uptake efficiency. Plants were harvested 24 h after application of the tracer. Plants were quickly dried and pressed and radioautographs provided evidence that ^{32}P was absorbed and translocated in seedlings. The highest volume (100 µL leaf^{-1}) sodium phosphate solution without wetting agent had the greatest efficacy. Three P application methods were also compared: vein injection, droplet and spray application. Spray application had the greatest uptake with ~60% of the solution applied absorbed and 34.5% of this was translocated out of the treated leaf into other plant parts. Importantly, the most practical application technique of spraying had the best efficiency, and the effect of spray volume and accompanying cation were measured, which will be discussed further in the section on formulations.

Barrier and Loomis (1957) used ^{32}P to track the movement of P into soybean leaves and found that 16% of the ^{32}P applied to the leaf was absorbed within 2 h. Of the absorbed ^{32}P, 66% remained in the leaf and the remainder was concentrated in the bud, in young growing leaves in the stem (above the leaves treated), and in the roots.

Bouma (1969) applied 10 µL of ^{32}P solution to the centre leaflet of the first (oldest) or second most expanded clover leaf. Bouma (1969) commented that the period of 2 days after application of ^{32}P probably extended far beyond the rapid initial uptake phase and it was unlikely that any of the P would have been available for further uptake. Goldstein and Hunziker (1985) added protoplasts (wheat leaf discs with the cell wall removed leaving just cell membrane) to a solution containing ^{32}P-labelled potassium phosphate (KH_2PO_4). At pH 5.8 protoplasts accumulated phosphate at 2.9 nM mg protein h^{-1}. The uptake rate of foliar P fertilisers is an important consideration when developing formulations adapted to variable climatic conditions (temperature, light and moisture) and isotopic tracers have provided an effective avenue to measure this.

These studies show the potential that isotopic tracing provides for investigating the penetration, rate of uptake and translocation of foliar-applied P in plants. The development of new formulations can be based on the insight gained into pathways for P translocation. The use of an isotopic tracer can provide a direct measure of the uptake efficiency of the foliar-applied fertilisers enabling researchers to rapidly screen a range of foliar P products.

Plant studies with foliar P solutions

Foliar applications of P have been tested on various agricultural crops such as soybeans (Garcia and Hanway 1976; Barel and Black 1979*b*; Syverud *et al.* 1980; Mallarino *et al.* 2001, 2005), clover (Bouma 1969, Bouma and Dowling 1976), wheat (Arif *et al.* 2006; Mosali *et al.* 2006) and corn (Harder *et al.* 1982; Giskin and Efron 1986; Girma *et al.* 2007). The objectives of such studies have been to identify the best formulation, rate, timing, crop type and sites. There is no one combination of these factors that will give the best possible outcome, however, it is important to note that an overwhelming number of studies have used sites with high fertility that were not requiring and therefore not responsive to additional P.

Benbella and Paulsen (1998) applied 0, 2.2, 4.4 and 6.6 kg P ha^{-1} as KH_2PO_4 foliar P at late anthesis in wheat, in two separate growing seasons, with three planting dates. There were significant grain yield responses (as compared with a nil control) for both the 2.2 and 4.4 kg P ha^{-1} rates but the rates did not differ from each other suggesting that the most efficient P application rate is 2.2 kg P ha^{-1}. In wheat crops Mosali *et al.* (2006) applied foliar KH_2PO_4 at 1, 2 and 4 kg P ha^{-1} comparing applications at Zadoks 32, Zadoks 47 and Zadoks 65 growth stages. The best response to foliar P was when it was applied during flowering (Zadoks 65) at 2 kg P ha^{-1}. Girma *et al.* (2007) had significant corn grain yield response to foliar P at 2 kg P ha^{-1} applied from eighth leaf through to tasseling growth stages.

Harder *et al.* (1982) reported that there were negative corn yield responses to multi-nutrient foliar treatments compared with the control. These applications were made very late in the season, ranging from 14 to 28 days after 75% silking. While yield was unaffected by foliar application, the P content of the corn grains was increased by 4.7% by foliar fertilisation.

Based on our review of the literature the most appropriate timing for application is at early pod development in soybeans (Gray 1977), from canopy closure to anthesis in cereal crops (Benbella and Paulsen 1998; Mosali *et al.* 2006; Girma *et al.* 2007) and early tasseling in maize/corn (Harder *et al.* 1982; Giskin and Efron 1986; Girma *et al.* 2007). The rate of application is dependent on crop requirement, crop type, number of applications, water volume and salt loading but in general 1.5–4 kg P ha^{-1} gave the best results (Benbella and Paulsen 1998; Mosali *et al.* 2006; Girma *et al.* 2007).

Plant studies with mixed nutrient foliar solutions

Mixed nutrient solutions have been tested in a number of studies (Garcia and Hanway 1976; Alston 1979; Ahmed *et al.* 2006; Arif *et al.* 2006). Arif *et al.* (2006) investigated the effect of applying numerous foliar applications of mixed nutrient solutions [N, P and potassium (K)] to wheat at tillering (Zadoks stage 26) and at booting (Zadoks stage 47) with one, two or three applications of the nutrient mix. While all treated sites produced higher grain yields compared with the control (1695 kg ha^{-1}), the maximum yield was achieved when two foliar applications of the nutrient mix were applied (2752 kg ha^{-1}).

Field experiments conducted by Giskin and Efron (1986) found foliar applications of N, P, K and sulfur (S) resulted in a significant uptake of N and P giving a 16.6% increase in grain yield. Ahmed *et al.* (2006) applied a foliar nutrient solution containing 9% P with 12% N, 8% K, 1% zinc, 2% iron, 1.5% manganese, 3% magnesium, 1.4% copper, 2.3% S and 0.05% boron at three different rates to two different wheat cultivars compared with a control treatment with no fertiliser. Plants in all treatments with the mixed nutrient solution had a higher plant P concentration than the control. Alston (1979), Strong (1982) and Gooding and Davies (1992) also reported increased grain yield with foliar application of N and P. In all of these mixed nutrient experiments it is difficult to infer the effect of the P due to the absence of complete factorial experimental designs and the possibility of both positive and negative interactions between nutrients.

Phosphorus responsiveness

A recurring issue in field studies of foliar P fertiliser is the selection of non-P responsive sites, which are often identified by the authors themselves. Many sites contain enough soil P to supply the plants till maturity and therefore no effect of foliar P is observed. Foliar applications of KH_2PO_4 to corn at 6–8 leaves, 12–14 leaves and 50% tasseling with 0–5 kg P ha^{-1} as foliar P and no starter fertiliser had little effect on corn yield (Sawyer and Barker 1994). The two sites had initial soil test values in the high–very high range and therefore responses to additional P could not be expected. Syverud *et al.* (1980) tested applications of potassium polyphosphate at 0, 5, 10 and 15 kg P ha^{-1} (each treatment applied in four separate doses). While this experiment was well designed in that it had a full factorial design, and tested all possible combinations of nutrients, the site had relatively high initial fertility and received 47 kg P ha^{-1} of starter P, and was therefore non-responsive to additional P added as foliar fertiliser.

Mallarino *et al.* (2001) reported very few responses to foliar NPK treatments largely due to the selection of sites with optimum or above-optimum soil P test values. In field experiments by Mosali *et al.* (2006), 50% of trials showed significant yield response to applied P. However, a response was expected by all plants treated with foliar fertiliser because the initial soil P tests were below 100% sufficiency. The best responses to foliar P were in soils with the lowest levels of soil P. Similarly in the studies of Girma *et al.* (2007), only 50% of trials showed significant yield response to foliar P corresponding with sites with the lowest levels of initial soil P. The reliability of soil P testing methodology is a critical issue for site selection and is under detailed investigation in Australia (Moody 2007; Mason and McNeill 2008). The diffusive gradient in thin films technique appears to offer much more reliable prediction of crop response to P addition over a wide range of soil types (Mason and McNeill 2008).

Green and Racz (1999) examined the effect of an N : P : K foliar solution with a composition of 7 : 6 : 7 applied at 0, 6.3, 13 and 18 kg P ha^{-1}. Experiments were established at two field locations using spring wheat. One site was unresponsive to foliar P application due to leaf tissue P concentrations above the critical value (0.3% w/w) for deficiency while the other site had leaf tissue P below the critical value and was responsive to 6.3 and 13 kg P ha^{-1} (average yield increase of 316 kg ha^{-1}).

Water stress and foliar phosphorus

Low soil moisture limits root access to P, as P needs to be in solution for uptake (dos Santos *et al.* 2004). While water may still be available in the subsoil, mineral nutrition can become the growth-limiting factor as nutrients are often stratified in the dry topsoil. Foliar work by Alston (1979) investigated the effects of soil water content and foliar fertilisation of N and P on wheat yield. The P was applied at a rate of 9–18 mg pot^{-1} as H_3PO_4, where 15 mg pot^{-1} is equivalent to 10 kg ha^{-1}). A grain yield increase was documented for plants with foliar applications although Alston (1979) attributed the response to the N applied. Alston (1979) commented that increasing grain yield after head emergence can be achieved by keeping the soil wet to enable nutrient uptake or by applying foliar fertiliser directly to the plant.

When bean plants were put under severe water stress their photosynthetic rate was significantly reduced and there was only a small effect of applied P on yield (dos Santos *et al.* 2004). This study found that addition of extra P as a foliar application was able to alleviate the effects of mild water stress (withholding water for 10–11 days at the pre-flowering stage). Compared with no P and low foliar P additions, the higher foliar P application had greater pod numbers and seed dry weight under water stress (dos Santos *et al.* 2004).

Data from Mosali *et al.* (2006) also suggested increases in grain yield that resulted from foliar P application, generally took place in seasons of water stress. This is likely due to reduced root-soil contact for nutrient exchange enhancing the benefits of foliar

P in lower rainfall areas and/or years. The application of foliar nutrients under water stress conditions requires careful consideration of stomatal opening and rate of fertiliser drying on the leaf before penetration is possible.

Foliar phosphorus formulations

The composition of the formulation is critical for the uptake of the P applied and important factors include pH by ionic composition interactions, P concentration, crop species and the presence of adjuvants. The development of a better understanding of the penetration pathway in plant leaves will also allow formulations to be optimised to increase penetration and uptake.

Ionic composition

A P fertiliser formulation with a low pH of 2–3, compared with a higher pH, has been shown to facilitate more rapid uptake by leaves (Tukey *et al.* 1961; Bouma 1969). Swanson and Whitney (1953) suggested that the role of pH in facilitating absorption may be due to the suppression of the dissociation of H_3PO_4, and the effect of pH on the permeability of the epidermal and adjacent tissues (Swanson and Whitney 1953). Bouma (1969) sprayed P-deficient clover plants every 2–3 days with 10–300 mM P solutions of H_3PO_4, with a solution pH adjusted to 2.5 and 5.0. The resulting leaf analysis 7 days after application showed that 23% of the pH 5.0 solution and 72% of the pH 2.5 solution was absorbed by the first trifoliate leaf. Similarly, H_3PO_4 (pH 2–3) had better penetration than other phosphate salts (pH 4–5) on bean leaves (Tukey *et al*. 1961). These studies suggest that lower pH solutions result in greater penetration of P. This is most likely due to the effect pH has on the P species in solution and the resultant ability to traverse the penetration pathway.

Koontz and Biddulph (1957) demonstrated the effect of the accompanying cation in the foliar P solution using compounds labelled with ^{32}P tracer. They showed that sodium phosphate (NaH_2PO_4) had the greatest uptake (60%) in bean plants, with decreasing absorption in the following order: $NaH_2PO_4 >$ dipotassium phosphate (K_2HPO_4) > tripotassium phosphate (K_3PO_4) = disodium phosphate (Na_2HPO_4) = ammonium phosphate $[(NH_4)_2HPO_4] > H_3PO_4 > KH_2PO_4 =$ trisodium phosphate (Na_3PO_4). The two compounds for which translocation was the highest, NaH_2PO and K_2HPO_4, did not crystallise on the leaflet as rapidly as the other formulations. They attributed the effectiveness of supplying P to the capacity of the accompanying cation to increase the retention of moisture on the leaf surface. Wittwer and Teubner (1959) suggested that the accompanying cation, in this case the mono-ammonium salt $[(NH_4)_3PO_4]$, applied to leaves at low pH values can maximise P absorption. This data highlights the fact that the accompanying cation and solution pH both require consideration when optimising formulations. The accompanying cation is particularly important when developing foliar P fertilisers that have the capacity to simultaneously provide other nutrients such as N, K, S and trace elements.

Phosphorus rate and foliar scorch

One of the major problems associated with foliar P nutrition has been the limited amount of a given P compound that can be applied without damaging the leaf through high nutrient loading (Koontz and Biddulph 1957; Gray 1977; Barel and Black 1979*a*, 1979*b*). The damage is predominantly a result of the nutrient imbalance under the fertiliser droplets rather than osmotic effects (Marschner 1995). If leaf 'burn' occurs, photosynthesis is reduced and there is a reduction in the transport of nutrients to the seed (Gray 1977; Fageria *et al.* 2009).

The appearance of leaf burn where foliar droplets have been applied has been observed in many studies (Barel and Black 1979*b*; Parker and Boswell 1980) and generally is not detrimental to the plant. However, some studies have resulted in leaf burn so severe that part or all of the leaf dies, causing a lower yield for foliar-applied treatments. A study using urea, KH_2PO_4 mix and ammonium polyphosphate mix was reported to significantly lower yield of soybeans compared with the control (Parker and Boswell 1980). This was due to considerable leaf injury through salt loading of the leaves, with P applied at 3, 6 and 9 kg P ha^{-1} but a corresponding N rate of 28, 56 and 84 kg N ha^{-1}. The decrease in yield was due to excessive salt loading from three successive applications of foliar fertiliser resulting in severe leaf burn.

In a study by Barel and Black (1979*b*) several times as much P could be added in polyphosphate compounds compared with the orthophosphate form. The maximum concentration of P tolerated in solutions of tri- and polyphosphates as sprays was 1.3% compared with 0.5% orthophosphate on corn leaves. Orthophosphate produced the lowest yield (even lower than the control), which may have been due to leaf damage after the first application.

A small amount of research has investigated the effect of foliar P formulations on different crop species. A large number of P compounds were applied to maize and soybean leaves, to determine the maximum amount that could be applied without damage to the leaves (Barel and Black 1979*a*, 1979*b*). In the first of two studies 32 different foliar P compounds were tested (Barel and Black 1979*a*). The most successful compound tested on maize was ammonium tripolyphosphate followed by ammonium polyphosphate and phosphoryl triamide. Soybeans were more sensitive to scorch tolerating 60–75% less compound than corn in most cases. This work highlights the different responses of crop species to the same P formulation. The leaf structure for each crop species varies (cuticle thickness, leaf hairs, etc.) and this will influence the sensitivity to P formulations. An experiment testing different crop species for the leaf scorch effect at different P application rates and climatic conditions is needed for the development of new formulations.

Adjuvants

Adjuvants are chemicals added to foliar fertilisers and other foliar-applied agrochemicals to enable them to efficiently diffuse through the cuticular membrane. Adjuvants can contain wetting, sticking and spreading agents. Since the cuticular membrane is composed of a lipophilic layer, the nature of the applied materials (hydrophilic or lipophilic) affects penetration. Adjuvants are capable of increasing retention time, lowering surface tension, adjusting pH and spreading foliar liquid over a larger leaf area compared with a foliar chemicals applied with no adjuvant (Fig. 1*b*) (Stein and Storey 1986; Stock and

Holloway 1993; Wiesman *et al.* 2002; Liu 2004; Singh and Singh 2008).

The most common adjuvant cited in research is Tween 20™ (Clor *et al.* 1962; Bouma 1969; Barel and Black 1979*b*; Syverud *et al.* 1980; Reuveni *et al.* 1996; Ahmed *et al.* 2006). Generally this adjuvant is added to foliar fertilisers at a concentration of 0.1% v/v. The majority of studies have considered it a suitable adjuvant to use as it is a solubilising agent of membrane proteins (Helenius *et al.* 1979).

Silicone-based non-ionic surfactants are recommended due to their ability to reduce surface tension and the contact angle of the spray solution (Knoche 1994; Singh and Singh 2008). Glyphosate is an anionic foliar-applied herbicide, therefore, studies of foliarly applied glyphosate are particularly relevant to anionic foliar P applications. Singh and Singh (2008) compared the translocation of ^{14}C-glyphosate combined with organosilicone (0.125% v/v) or conventional organic (0.5% v/v) adjuvants. Absorption of ^{14}C-glyphosate was greater when sprayed with organosilicone adjuvants than for conventional adjuvants on redroot pigweed leaves, reaching maximum absorption within 0.5–1.0 h after application. Maximum absorption for conventional adjuvants was not achieved until at least 24 h after application. Similar absorption differences between the organosilicaone and conventional adjuvants were observed for guinea grass. However, absorption in guinea grass took much longer for both adjuvant types illustrating that different plants have varying leaf wax, cuticle and stomatal structures that determine the effectiveness of the adjuvant.

Liu (2004) similarly monitored glyphosate uptake with various adjuvants. Results showed that ammonium sulphate [$(NH_4)_2SO_4$] improved glyphosate uptake when combined with non-ionic surfactants applied to wheat leaves. The combination of Triton X-100™ with 2% v/v $(NH_4)_2SO_4$ in solution increased glyphosate uptake compared with non-ionic surfactant (glycerol: 1 and 4% v/v), 6 h after wheat plants were treated. Bouma (1969) found that glycerol did not improve the effectiveness of foliar-applied H_3PO_4 but did improve KH_2PO_4 uptake.

Stein and Storey (1986) tested 46 adjuvants for leaf burn and foliar absorption of N and P by soybean leaves. The adjuvants were added at 0.05% (v/v) with foliar fertiliser N, P, K, S to the middle adaxial surface of the leaf. Drops were monitored for spread and the extent of foliar burn (rated 1–5). Two spray rates were used, 90 and 470 L ha^{-1}. Glycerol was the only adjuvant that significantly increased leaf P concentration over the unsprayed controls at 90 L ha^{-1}. If treatments were applied at the 470 L ha^{-1} numerous adjuvant/fertiliser combinations increased the P penetration. However, by increasing the spray rate, the phytotoxicity rating also increased with many adjuvants causing total cell necrosis. Therefore, identification of the optimal spray volume requires consideration of the most efficient uptake with minimal leaf damage. In a subsequent experiment Stein and Storey (1986) also found that the adjuvants Lecithin and Pluronic L-121™ (BASF Chemical Co., USA) significantly increased percentage of P and chlorophyll content over the control and foliar (no adjuvant) treatments.

Wiesman *et al.* (2002) tested Ferti-Vant™ (Fertilizer and Chemical Substances, Israel), which are fertilisers coated with an adjuvant containing emulsified oils, surfactants and food grade polysaccharides. Scanning Electron Microscopy images showed that Ferti-Vant™ had a greater spread of nutrients across citrus leaves and increased P % dry weight by 0.9% at day 6 and 0.05% day 12 compared with the control. In a related study, Chapagain and Wiesman (2006) investigated the use of four glycosidic saponins as adjuvants for the delivery of 2,4-dichlorophenoxyactic acid (2,4-D) to plant leaves. At an application concentration of 1% (w/v) all four saponins increased penetration compared with no adjuvant but Triton X-100™ increased 2,4-D penetration more than the saponin treatments.

While there have been a number of studies on the effect of adjuvants, the findings suggest that no single adjuvant, rate of adjuvant, or spray volume will simultaneously increase spread, delay drying and increase the permeability of the cuticle or the plasma membrane for all foliar fertiliser-plant combinations. The adjuvant and/or combination of adjuvants to be used requires careful consideration when developing a foliar fertiliser application plan.

Conclusions

Foliar P fertilisation has yet to be accepted as a reliable method of supplying P to plants. It is evident there are limitations to the amount of P that can be supplied to crops in foliar form due to solubility, efficacy and leaf burn considerations. Foliar P can also only be effectively absorbed by plants when leaf area is high, and with dryland cereal crops there is a requirement for P early in the life cycle to stimulate root growth and tillering. Hence foliar P will never substitute for P applied to soil either pre-plant or more commonly at sowing.

The disadvantage of all seasonal P being applied to soil at sowing is that a number of chemical reactions in soil can reduce effectiveness over time (Hedley and McLaughlin 2005), and forthcoming seasonal conditions (and therefore P requirement) are unknown. Yield potential can be compromised if P applied at sowing is too little in seasons with a high yield potential or if too much P is supplied in seasons of limited late-season moisture supply. In-season tactical applications of P to soil cannot be made effectively in dryland agriculture, due to the poor mobility of P in soil making topdressing ineffective. Foliar P fertilisers could fill this niche in dryland cropping in variable climates where a small tactical top up of P is required to achieve yield potential in seasons with favourable rainfall conditions and higher yield potential. However, the development of foliar P fertilisation strategies will only become a viable on-farm nutrient management technique if they are in-synchrony with in-season applications of other nutrients such as N.

There appears to be no ideal formulation which combines the correct form of P with the most effective adjuvant. It would appear that acidic P solutions are more effective than neutral or alkaline solutions. More effective adjuvants are needed to improve P absorption through the waxy leaf cuticle. In studies of effectiveness of foliar P fertilisers, it is important that appropriate experimental techniques are used; otherwise the interpretation of data is made difficult. We suggest that the following are key requirements for assessment of foliar P fertilisers:

(1) A P-responsive soil – confirmed by application of several rates of P to soil to ensure other factors are not more limiting;
(2) Foliar P fertilisers applied at the same rate on an elemental basis;
(3) Same spray rate (or drop size) and adjuvant if comparing P formulations, same P formulation if comparing adjuvants;
(4) Same timing of application (diurnal and growth stage) when comparing formulations or adjuvants;
(5) Good independent assessment of amount of nutrient applied; and
(6) Accurate assessment of foliar uptake and efficacy.

Much of the experimentation in the literature has not addressed all of the above requirements, and future research effort should focus on using these techniques to:

(1) Develop practical application methods for farming systems with appropriate formulation, timing and crop P requirements and yield potential identified;
(2) Identify suitable combinations of nutrients (in particular with N) and adjuvants;
(3) Better understand the physiology of foliar P leaf penetration and interaction with the membrane of the leaf using tracer techniques; and
(4) Assess the potential for foliar P to improve nutrient use efficiency under variable climatic conditions.

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