5. Years of practice – learning from the field

Experience gained from many years of grower applications as well as extensive controlled environment and field research trials has produced a wealth of valuable but frequently confusing data and information on the performance and efficacy of foliar fertilizers. This chapter is not intended to be a thorough review of field trials of foliar fertilizers since the majority of such trials do not attempt to explain their results in terms of physical, chemical or biological principles and therefore cannot be readily extrapolated beyond the specific context of the crop, location and methodology used in that particular trial. To make sense of field trials requires a sound understanding of the underlying principles as outlined in the previous chapters. This chapter will draw from field experience and integrate any established known principles to highlight the complexity and knowledge gaps in the use of foliar fertilizers in modern agriculture.

5.1. Spray application technology

Much of our current understanding of spray application techniques is based upon lessons learned with crop protection products such as herbicides, insecticides or fungicides, and there is little specific information available on foliar nutrient sprays. The information provided below has been obtained from spray application technology studies which can be generally applied to the performance of foliar fertilizer sprays.

The spray application technique is a key process influencing the effectiveness of a foliar fertilizer. The application process is complex and involves: the formulation of an active ingredient; atomization of the spray solution; transport of the spray to the target plant surface and droplet impaction; spreading and retention on the leaf surface; residue formation and penetration into the leaf (Brazee *et al.*, 2004). Application of a foliar treatment implies that the liquid is passed through a spray generating system to produce droplets which are commonly different types of pressure nozzles (Butler Ellis *et al.*, 1997). Spraying is inherently inefficient since not all the liquid droplets reach the plant target because of losses related to, amongst others, droplet reflection, run-off, spray drift and in-flight evaporation (Leaper and Holloway, 2002; Shaw *et al.*, 1997; Wang and Liu, 2007).

- The spraying technique strongly influences the performance of a foliar nutrient spray.
- Spray drift is a common problem associated with foliar spraying.

The characteristics of an agricultural spray nozzle are important criteria in the application of foliar sprays because of their ultimate effect on the efficiency of the application process. Droplet size and velocity affect the structure of the spray deposits as well as the drift of the droplets (Nuyttens *et al.*, 2009; Taylor *et al.*, 2004). Furthermore, droplet size may influence the biological efficacy of the applied formulation and also the environmental hazards associated with the treatment. Hence, the ideal nozzle-pressure combination will maximize the efficiency of spray delivery and in depositing an adequate dose to the plant target whilst minimizing off-target losses such as spray drift and equally important sprayer-user exposure to the latter (Nuyttens *et al.*, 2007).

Nozzles can deliver spray drops of different sizes depending on the size of the orifice, the shape of the nozzle and the pressure used (van de Zande *et al.*, 2008a). Spray quality classification systems that distinguish drop size distributions as fine, medium or coarse have been introduced in recent years as a means to predict spray drift potential, which is a matter of increasing environmental concern, particularly in the case of plant protection agro-chemicals (Hewitt, 2008; van de Zande *et al.*, 2008b). Such classification of sprays based on droplet size has enabled the identification of nozzles in relation to their efficacy and drift potential (van de Zande *et al.*, 2008a; van de Zande *et al.*, 2008b).

Spray drift is defined as the quantity of foliar spray that is deflected out of the treated area by air currents at the moment of spray application. Spray drift is affected by four main factors: weather conditions; spray application technique; characteristics of the surroundings; and physico-chemical properties of the spray liquid (De Schampheleire *et al.*, 2008). Droplet size is determined by the interaction between the spray technique (spray pressure and nozzle selection) and the physico-chemical properties of the spray liquid (De Schampheleire *et al.*, 2008).

Methods to limit spray drift have been implemented, such as using equipment that reduces the drift of the fine droplet component or that changes the droplet size distribution of the spray (Jensen *et al.*, 2001). Nowadays, there is an increasing interest in standardizing the protocols for testing the efficacy of spray drift reducing technologies as a means to ultimately minimize the chance for environmental pollution with agrochemicals (Donkersley and Nuyttens, 2011; Khan *et al.*, 2011).

Apart from the properties of the nozzle and of the solution, the characteristics of the plant canopy, as described in Chapter 4, will also affect the rate of retention, spreading, wetting and uptake of a foliar nutrient sprays. If leaves are wet from rain or dew, prior to application of foliar nutrients, the rate of retention may decrease (Zabkiewicz, 2002). Spray efficacy often depends on droplet size with better coverage being achieved by smaller droplets which are more likely to be retained by the leaf surface but equally are more prone to drift (Butler Ellis *et al.*, 1997; Tuck *et al.*, 1997).

Development of models to predict droplet size and spray performance under field conditions is difficult due to the many factors involved and to the complex nature of the agrochemical spray mixtures employed (Liu, 2004; Miller and Butler Ellis, 2000; Steiner *et al.*, 2006).

Electrostatic spraying technologies for agricultural applications have been developed in recent decades (Law, 2001) which have great potential for improving the performance of foliar-applied plant protection products but these have not yet been fully tested on foliar nutrient sprays. Droplet size is very much reduced by this technology giving better plant coverage but this method also increase the risk of spray drift as well as evaporation of the fine droplets from the plant surface particularly in arid and semi-arid climates. Additionally, in order to ensure that the plant surface is appropriately wetted as a prerequisite for the uptake of foliar-applied nutrients, a longer application time is required. This is in contrast to conventional spraying devices that deliver coarser spray droplets that represent a higher liquid volume deposited onto and wetting the plant surface.

5.2. Foliar formulations and application technology

Foliar nutrient sprays are often applied as mixtures in the sprayer tank with compatible adjuvants and/or agrochemicals according to the recommendations/specifications of the relevant product manufacturers. The performance of foliar fertilizers in combination with some adjuvants and/or plant protection products may differ from the nutrient spray when applied alone. Currently, there is no way to predict theoretically the relative efficacy of foliar-applied nutrient/adjuvant/agrochemical mixtures. The significance of formulating foliar nutrient sprays with adjuvants has been described in detail in Chapter 3.

The physico-chemical properties of the spray formulation may also influence the application process and the risk of spray drift (De Schampheleire *et al.*, 2008). Therefore changing the properties of the spray solution by addition of adjuvants may influence the mechanisms of spray formation and droplet performance on the leaf surface (Miller and Butler Ellis, 2000). Certain formulation additives can induce significant changes in the quality of the spray with effects on droplet size, velocity and structure (Butler Ellis *et al.*, 1997). Increasing the viscosity of the spray liquid decreases drift occurrence through the formation of larger droplets (De Schampheleire *et al.*, 2008). On the other hand the relationship between formulations having lower surface tension, droplet size and rate of drift is currently not fully understood (De Schampheleire *et al.*, 2008).

5.3. Biological rationale for the use of foliar fertilizers

The use of foliar fertilizers to overcome adverse soil physical and chemical properties, or field access issues, is well defined and many examples of its implementation are available. However, the use of foliar fertilizers to target specific biological demands including the prevention or avoidance of deficiencies that occur as a result of phenology-dependent mis-match between plant demand and soil supply, refered to hereon as 'transient deficiency', has received little attention. It is generally true that foliar fertilizers, since foliar-applied nutrients provide a quality, specificity and rapidity of response that cannot be reliably achieved with soil application. While there are very few published research papers that have clearly identified the occurrence of a critical but transient nutrient

deficiency that can be best corrected through foliar fertilization, there is both a clear scientific rationale as well as considerable global field experience to suggest that this phenomenon is of agronomic significance. In the following, the relationship between stage of plant growth and plant response to foliar fertilizer applications through an integrated analysis of field research experience and established biological principles will be addressed.

5.3.1. Role of crop phenology and the environment on plant response

A significant commercial justification for the use of foliar fertilizers is based upon the premise that they offer a specific advantage over soil fertilizers at certain crop phenological stages when high nutrient demand coincides with inadequate soil supply or poor within plant transport of essential nutrients. Good examples include periods of rapid fruit growth or grain fill; early spring growth in deciduous species when shoot growth occurs before adequate root nutrient uptake; or during rapid seedling growth when ambient air temperatures are favourable for growth but low soil temperature restricts nutrient uptake. Nutrient immobility may also result in deficiencies occurring even in a fertile soil when localized plant tissue demand exceeds the capacity for withinplant nutrient re-distribution.

The effect of crop phenology on response to foliar fertilization is complex and related to both physical and biological effects. Physical effects include changes in leaf structure and composition that may alter the penetration and subsequent utilization of foliar nutrients; and changes in canopy size and architecture which directly influence the surface area available to intercept the foliar spray.

Biological effects are:

- during flowering and fruit set in deciduous species with increases in demand for specific elements involved in critical plant functions e.g. B or Cu for pollen development and growth;
- restriction in soil nutrient uptake or transport due to senescence e.g. decreased N uptake following grain set in cereals;
- shoot demand occurring prior to root development e.g. flowering and fruit development in deciduous species or unfavorable root conditions e.g. cold or saturated soil in spring;
- decrease in root growth and activity due to shoot vs. root competition for carbohydrates and metabolites e.g. during fruit growth;
- limitation to within-plant transport or distribution of essential nutrients to critical plant organs e.g. Ca delivery to apple fruit.

 Table 5.1 Interactions between crop phenology and the environment can determine the usefulness of foliar fertilization through the following processes.

A limitation in soil nutrient uptake capacity occurs as a consequence of the environment or plant senescence that limits nutrient uptake by roots.	During early spring when many deciduous species flower and set fruit and soil temperatures or moisture regimes are unfavourable for soil nutrient uptake.	
	As a consequence of plant senescence limiting root activity.	
Periods of peak crop growth induces a nutrient demand that exceeds nutrient	Nutrient demand for rapid fruit growth or grain fill can exceed uptake capacity even in adequately fertilized soils.	
supply even in a well-fertilized soil.	Competition between roots and shoots during periods of high shoot demand can reduce carbohydrate allocation to roots and restrict root growth and metabolism and hence reduce nutrient acquisition.	
Plant architecture and organ development create local nutrient demand that exceeds capacity for within-plant nutrient delivery.	Limitations in transport of phloem-immobile elements to fleshy organs with inadequate vascular connectivity or low transpiration e.g. B or Ca deficiencies in fruits and fleshy organs and B, Cu, Fe, Zn deficiencies in reproduc- tive structures.	
	Nutrient depletion due to rapid withdrawal of mobile nutrients in leaves adjacent to large rapidly growing reproductive organs.	

In the following, selected examples in which unique environmental and phenological factors contribute to the efficacy of foliar fertilizers are provided.

5.3.2. Influence of the environment on the efficacy of foliar applications during spring

Unfavourable climate and soil environment frequently limit nutrient availability and uptake from soils. If these limitations coincide with periods of critical nutrient demand the application of foliar fertilizers may be beneficial and thus the plant phenology at the time of the environmental limitation is critical in determining the need for foliar fertilization. For example, unfavourable weather conditions during reproductive development can be economically devastating, while unfavourable conditions during vegetative stages may have little effect on productivity, especially if subsequent warm weather allows for 'catch up'.

The best documented examples of this phenomenon come from deciduous tree crops where spring time foliar fertilization is widely practiced. In the Mediterranean and colder climates, an unusually cool, wet spring can result in water-logging and root anoxia (low soil oxygen) which reduces nutrient uptake (Drew, 1988; Leyshon and Sheard, 1974; Robertson *et al.*, 2009) which can be partially alleviated by foliar nutrient sprays (Pang *et al.*, 2007). Dong *et al.* (2001) and Hogue and Neilsen (1986) noted that nutrient translocation from the roots of apple trees is restricted by low root temperatures during

anthesis. The occurrence of cool, wet springs, before the onset of warm conditions that favour rapid shoot growth and flowering, can result in a condition described as 'spring fever' which is generally believed to be caused by transient deficiencies of the immobile elements, B, Cu and Zn which are critical for bud break, pollen-tube development, flowering and vegetative expansion. It is generally observed that plants 'grow out' of the deficiency once conditions improve though considerable loss of yield is possible, especially with flowering species having reduced fruit set at the start of the growing season.

While all nutrients are required for new growth deficiencies of B and Zn are particularly critical because of their low mobility in most species and their essential roles in vegetative and reproductive growth (Marschner, 2012).

Boron plays an important role in pollen germination and pollen tube growth (Chen *et al.*, 1998; De Wet *et al.*, 1989; Jackson, 1989; Nyomora *et al.*, 2000; Perica *et al.*, 2001; Rerkasem and Jamjod, 2004; Robbertse *et al.*, 1990; Schmucker, 1934) and foliar sprays of B increase pollen-tube germination and fruit set in a number of tree species including almond (*Prunus amygdalus* L.) (Nyomora *et al.*, 1999), pear (*Pyrus communis* L.) (Lee *et al.*, 2009), olive (*Olea europea* L.) (Perica *et al.*, 2001), cherry (*Prunus avium* L.) (Wojcik and Wojcik, 2006) and apple (*Malus domestica Borkh.*) (Peryea *et al.*, 2003).

Table 5.2. Influence of B application on yield, and on bud and July leaf B of pistachio. Foliar B was applied in 1998 at the specified concentrations; soil applications were applied by hand during an irrigation cycle in July 1997. Yield and tissue nutrient was determined in 1998.

Foliar (Feb 1998)	Yield (ka in-shell splits tree ⁻¹)	Buds (ma E	Leaves (July) 3 kg ⁻¹)	
(mg B L ⁻¹)	()		(
0	8.6	35	170	
490	10.0 ¹	37	185	
1225	11.8 ²	39	171	
2450	9.5	41	210	
Soil (August 1997) (g B tree ⁻¹)				
12	8.6	35	172	
23	8.6	38	189	
35	9.1	44	201	
47	9.5	50	219	

¹ and ² denote significantly greater than control at 0.05 and 0.01% respectively.

The importance of phenology in crop response to B was illustrated in a series of experiments reported by Brown (2001) demonstrating that foliar B application can result in the correction of deficiency that is not responsive to soil B application (Table 5.2). Foliar applications of B to mature pistachio trees (Table 5.3) and walnut (Figure 5.1) resulted in a significant increase in fruit set and yield only when that application was made during the late dormancy stage (pistachio) or the early-leaf-out phase (walnut) immediately preceding flower opening (Brown, 2001). Applications made at any other time of the year, including soil applications, were ineffective at increasing yield. The benefit of foliar application was observed even with high leaf B values (>150 ppm B in pistachio and >35 ppm in walnut) and irrespective of soil B application. This indicates that adequate soil and leaf B status in the prior season does not ensure that optimal B will be present at flowering and that tree productivity can be impacted by localized transient deficiencies which respond well to properly timed foliar applications. In the region where these experiments were conducted, heavy winter rain and persistent wet fogs may have leached B from flower buds and facilitated crop response to the pre-flowering foliar sprays. Nevertheless foliar applications of B served a unique role in enhancing pistachio fruit set most likely by providing B directly to the emerging reproductive structures.

Application date	Growth stage	Yield ¹	July leaf B
		(kg)	(mg kg⁻¹)
28-Feb	Late dormant	64 ²	188
19-Mar	Early budbreak	52	188
3-Apr	Flowering	54	187
17-Apr	Leafing out	51	256 ²
8-May	Fully leafed out	52	468 ²

Table 5.3. Effect of application date of foliar B (1225 mg B L⁻¹) on yield and leaf B in pistachio.

¹All yields are fresh weight of fruit per tree.

² denotes significantly greater than control at 0.01%.

Similar responses to foliar B applications, immediately prior to flowering, were observed in olive (Perica *et al.*, 2001), walnut (Brown *et al.*, 1999c; Keshavarz *et al.*, 2011) and almond (Nyomora *et al.*, 1999). In almond, however, yield was maximized when the foliar B was applied in either September (postharvest) or February (immediately preceding flowering). The effectiveness of postharvest B applications in almond but not pistachio or walnut are a consequence of difference in B mobility in these two species (Brown and Hu, 1996). Boron is phloem-mobile in almond and applications made in August are rapidly translocated from leaves to developing buds for utilization in the springtime. In contrast, B is immobile in pistachio and foliar applications in August provided little or no B to the developing flower buds.



Figure 5.1. Effect of B deficiency on reproduction in walnut (*Juglans regia*). Walnut trees were treated with soil B applications (2 kg B ha⁻¹) in mid-summer in 1999, 2000 and 2001. In a sub-set of trees, foliar applications were applied at 400 ppm B in the final spray solution applied 14 days prior to pistillate flowering. Control trees received no soil or foliar B applications. Yields were as follows: Control: 1280 kg ha⁻¹; Soil Applications: 2060 kg ha⁻¹; Foliar Application: 4592 kg ha⁻¹ (Brown *et al.*, 1999c).

Zinc is a cofactor of over 300 enzymes and proteins and has an early and specific effect on cell division, nucleic acid metabolism and protein synthesis (Marschner, 2012). As a consequence of both the demand for Zn in growing tissues and springtime weather conditions many species exhibit Zn deficiencies early in the growing season. The responsiveness of many species (including walnut, pistachio, apple, avocado, pecan, macadamia) to foliar Zn is also greatest in the springtime (Huett and Vimpany, 2006; Keshavarz *et al.*, 2011; Peryea, 2007; Zhang and Brown, 1999a; Zhang and Brown, 1999b) in part because young leaf surfaces are more easily penetrated prior to full expansion (Zhang and Brown, 1999b). In many deciduous species Zn deficiency can have a marked effect on pollen production and physiology, floral anatomy and yield (Christensen, 1980; Pandey *et al.*, 2006; Pandey *et al.*, 2009; Sharma *et al.*, 1990; Swietlik, 2002).

Foliar-applied Zn generally exhibits a low degree of leaf penetration (1 to 5%) and limited phloem-mobility. The resulting effect that foliar Zn sprays have greatest efficacy on are the tissues that directly received the foliar spray (Christensen, 1980; Faber and Manthey, 1996; Huett and Vimpany, 2006; Keshavarz *et al.*, 2011; Peryea, 2007; Zhang and Brown, 1999a). The extent to which Zn is phloem-mobilevaries with crop phenology. Low but measurable Zn transport to non-sprayed tissues (including roots) has been observed in many tree species (Faber and Manthey, 1996; Neilsen *et al.*, 2005b; Sanchez *et al.*, 2006; Zhang and Brown, 1999a) while increasing evidence suggests that foliar Zn applied immediately prior to leaf senescence in grain crops can

significantly enhance grain Zn concentrations (Cakmak, 2008; Cakmak *et al.*, 2010; Ebrahim and Aly, 2004; Erenoglu *et al.*, 2002; Fang *et al.*, 2008; Haslett *et al.*, 2001; Kinaci and Gulmezoglu, 2007; Ozturk *et al.*, 2006; Zhang *et al.*, 2010).

Several researchers have suggested a synergistic effect of application containing both B and Zn. Combined B and Zn sprays applied during the pre-bloom stage in apple improved yield by 22 to 35% (Stover *et al.*, 1999). In walnut (Keshavarz *et al.*, 2011) three B and three Zn concentrations (0,174 and 348 mg L⁻¹ for B and 0,1050 and 1750 mg L⁻¹ for Zn) applied either independently or in combination showed that all B and Zn applications, and combinations, had a significant effect on reproductive and vegetative growth. Pollen germination, fruit set, vegetative growth, nut weight, kernel per cent, nut and kernel length and chlorophyll index were all highest when B and Zn were applied simultaneously at 174 and 1050 mg L⁻¹ concentrations respectively.

The relatively greater efficacy of springtime Zn sprays likely reflects the specific need for Zn during rapid vegetative and floral expansion, the high degree of phloem immobility and the relatively greater penetration of Zn into young rather than mature leaves. The high degree of Zn mobility observed in senescing wheat leaves and its effective transport to grain also suggest that plants have an inherent ability to transport Zn and that limitations to mobility are likely physical and not biological in nature.

There is a significant need for continued development of Zn materials and timings to increase Zn mobility and enhance the longevity of foliar Zn applications.

Nitrogen foliar application in the springtime shows variable results depending on species, the environment or the plant nutritional status at time of application, as well as formulation used. In citrus the response to foliar-applied urea is generally beneficial. A seven year trial with navel orange demonstrated that application of urea as the foliar N source, immediately preceding and during flowering and leaf expansion, at the rate of 0.23 kg urea-N tree⁻¹ split between two foliar applications, one in February and the second in late April to early May, were statistically equal to yields obtained with 0.45 or 0.91 kg N tree⁻¹ as ammonium nitrate applied to the soil (Sharples and Hilgeman, 1972). The importance of an adequate supply of N during the critical stages of fruit initiation and development for yield and good quality citrus fruit has been demonstrated by several researchers (Alva *et al.*, 2006a; Alva *et al.*, 2006b). Trees receiving foliar-applied urea in mid-January or mid-February, independent of soil N treatment, had significantly greater yield and fruit numbers per tree each year compared to the control trees receiving only soil N for three consecutive years (Ali and Lovatt, 1994).

Research in citrus has shown yield benefits of foliar sprays at bloom and postbloom, presumably from increased fruit retention during the two physiological drop periods during the spring-time (Rabe, 1994; Sanz *et al.*, 1987). Several authors have demonstrated that application of foliar urea during flower initiation-differentiation can alter flower performance (Ali and Lovatt, 1994; Chermahini *et al.*, 2011; Rabe, 1994). Single applications during fruit set and "June drop" were also efficient in increasing yield. In these trials, foliar urea increased leaf N content during the first 48 hours following treatment of 'Cadoux' clementine mandarin trees (*Citrus reticulate* Blanco) but this effect disappeared by the 30th day after treatment. Yield improvement was due to increased fruit number since fruit size was not affected by the urea spray. In agreement with these results, urea applied pre-bloom increased flower initiation and intensity of the clementine mandarin and reduced alternate bearing (El-Otmani *et al.*, 2000). In the majority of these trials, foliar N does not result in long term increases in tissue N levels and primarily acts to alter flower initiation/differentiation, fruit set and retention. These results may suggest that urea provides a physiological benefit that is more than a consequence of simply adding N in this form.

Phosphorus foliar fertilization provides beneficial effects for a number of fruit crops. Increased fruit set (Albrigo, 1999), fruit yield (Lovatt *et al.*, 1988) and fruit quality (Albrigo, 1999) have been reported in fruit trees in response to foliar P applications made near the bloom period or during the growing season.

Ensuring that plants are well supplied with all essential elements during the spring is essential for optimal productivity:

- Predicting the occurrence of spring-time nutrient deficiency is difficult.
- Environmental conditions can induce nutrient deficiencies in an unpredictable manner.
- In high-value crops prophylactic application of foliar nutrients is frequently advised.
- Some crop responses to foliar fertilizers are unexplained and may suggest a nonnutritional effect.

5.3.3. Efficacy of foliar applications for flowering and grain set in field crops

Foliar application of nutrients to cereal crops is increasingly used though it is still not a widely adopted practice. Numerous foliar fertilizer trials have been conducted in a variety of crops and growing conditions. The results have been highly variable, at times demonstrating substantial benefit from foliar applications while on other occasions showing no effect (Barraclough and Haynes, 1996; Freeborn *et al.*, 2001; Haq and Mallarino, 2005; Ma *et al.*, 2004; Ma *et al.*, 1998; Mallarino *et al.*, 2001; Schreiner, 2010; Seymour and Brennan, 1995; Tomar *et al.*, 1988) and sometimes negative effects. The reported negative effects of foliar applications can largely be explained by the direct effects of the foliar salts causing leaf burn thus reducing effective leaf area and photosynthate production (Barel and Black, 1979a; Bremner, 1995; Fageria *et al.*, 2009; Gooding and Davies, 1992; Haq and Mallarino, 1998; Kaya and Higgs, 2002; Krogmeier *et al.*, 1989; Parker and Boswell, 1980; Phillips and Mullins, 2004). Negative effects of the foliar application of B to open flowers have also been reported (Brown, 2001; Nelson and Meinhardt, 2011) and may be a consequence of the applied B disrupting the directionality of pollen tube growth and reducing effective fertilization (Dickinson, 1978; Robbertse *et al.*, 1990).

Research with foliar P formulations is illustrative of the challenges in interpreting the role of crop phenology and experimental protocols on foliar efficacy. Foliar applications of P have been used on various crops such as soybeans (Haq and Mallarino, 2005; Mallarino *et al.*, 2001; Syverud *et al.*, 1980), wheat (Batten *et al.*, 1986; McBeath *et al.*, 2011; Mosali *et al.*, 2006; Noack *et al.*, 2011), clover (Bouma, 1969; Bouma, 1975), maize (Girma *et al.*, 2007; Ling and Silberbush, 2002) and cereal crops (McBeath *et al.*, 2011; Noack *et al.*, 2011).

Syverud et al. (1980) found significant increases in the yields of maize and soybean from weekly sprays of polyphosphates, and low rates of foliar-applied P corrected midseason P deficiency in winter wheat and resulted in higher P use efficiency (Mosali et al., 2006). Foliar P application in early growth stages of wheat increased the number of fertile tillers (Grant *et al.*, 2001) but it has not been well established that this early supply of foliar P increases grain vield as well. Mosali et al. (2006) identified 'Zadoks 32' as the optimum growth stage for foliar P addition as it increased both P uptake and grain yield. Other studies (Batten et al., 1986; Hocking, 1994) showed that P accumulation in wheat plants was highest when applied before anthesis and a cessation of P uptake after anthesis was observed in wheat (Rose et al., 2007). Foliar application of 0, 2.2, 4.4 and 6.6 kg P ha⁻¹ as KH₂PO₄ at late anthesis in wheat (Benbella and Paulsen, 1998) suggested an optimal application rate of 2.2 kg P ha⁻¹. Similarly, foliar KH₂PO₄ applied to wheat at various vegetative growth and early reproductive stages was most effective when it was applied during flowering (Zadoks 65) at 2 kg P ha⁻¹ (Mosali et al., 2006), while in maize grain yield response to foliar P at 2 kg P ha⁻¹ was greatest when applied from the eighth leaf through to the tasseling growth stages (Girma et al., 2007). In general, the most appropriate timing for foliar P application is at early pod development in soybeans (Gray and Akin, 1984); from canopy closure to anthesis in cereal crops (Mosali et al. 2006; Girma et al. 2007); and early tasseling in maize (Girma et al., 2007; Giskin and Efron, 1986).

The response of various soybean cultivars to foliar N, P, K, S supply has been encouraging (Boote *et al.*, 1978) when applied during the seed-filling period (between growth stages R5 and R7). Foliar N supply to soybean was found to be an effective means to replenish N in the leaves and resulted in higher yields in contrast to soil fertilization alone (Garcia and Hanway, 1976). Foliar application of N in combination with P, K and S during the R4 to R7 development stages showed the best results (Haq and Mallarino, 1998; Poole *et al.*, 1983a; Poole *et al.*, 1983b). However, other studies did not reproduce these results (Boote *et al.*, 1978; Parker and Boswell, 1980) perhaps due to leaf damage and consequent loss of photosynthetic area from foliar fertilization and the background nutrient status of the plant. Foliar sprays have been shown to increase tissue N, P, K and S concentrations with no effect on yields (Boote *et al.*, 1978). Some nutrients, when applied as foliar fertilizers, may interact positively with other nutrients and may improve crop yields. For example, S applied alone as a foliar fertilization to soybean did not increase grain yield but when applied in a combination with N,P and K, the response was positive (Garcia and Hanway, 1976).

Increased yields from foliar sprays with N, P, K, S during the seed-filling period in bean plants have been reported (Neumann and Giskin, 1979). However, the response of *Vicia faba* L. and *Phaseolus vulgaris* L. to foliar N, P, K, S sprays led to inconsistent and even negative effects (Day *et al.*, 1979; Witty *et al.*, 1980) and Lauer (1982), while increased vegetative growth and quality due to Zn and N, P, K applications has been reported for musk-melon and a few other cucurbits (Lester *et al.*, 2010; Lester *et al.*, 2006).

In conclusion, the most appropriate timing for foliar application of macronutrients is at early pod development in soybeans; from canopy closure to anthesis in cereal crops; at early tasseling in maize; and at early flowering in cotton. However, while there are many cases of positive crop response to foliar applications of N, P, K and S there are several very well conducted trials in which no substantial benefits of foliar P or foliar fertilizer mixtures were detected (Haq and Mallarino, 2005; Leach and Hameleers, 2001; Mallarino *et al.*, 2001; Seymour and Brennan, 1995).

The diversity of field crop response to foliar fertilization suggests that there is a substantial influence of the environment (climate, soil conditions, nutrient status, stage of growth, conditions during application), species and formulation on crop response. Understanding the conditions that lead to a positive crop response remains a major challenge.

5.3.4. Foliar fertilization during peaks of nutrient demand

In the majority of crops, nutrient demand is at its peak during the maximum (grand) phase of vegetative development in annuals and during fruit and nut development in tree crops. During these phases as much as 40% of total annual nutrient accumulation can be acquired over a 10-day period (Figure 5.2) (Jones *et al.*, 2009). In almond, N demand is particularly high and during the first 60 days of growth it may exceed 180 lbs N acre⁻¹, whereas K demand maximizes later in the season and tends to overlap with periods of greatest demand for carbon (C) and during periods of limited new root production.

In many perennial high-value crops, foliar fertilizers should be applied during the period of highest nutrient demand under the premise that soil supply and root uptake may be inadequate to meet demands even with adequate soil-applied fertilizer. Evidence for this phenomenon is available for several species. French prune has a particularly high demand for K (up to 280 kg K ha⁻¹ year⁻¹) with much of this demand occurring during mid to late summer as fruits accumulate sugars. Southwick *et al.* (1996) in a comparative study of foliar versus soil K application with 'French' prune trees reported that foliar KNO₃ sprays given four times throughout the growing season corrected K deficiency and gave simiar or higher yields than soil applications. The rapid re-mobilization of K to the fruit from leaves reduced leaf K concentrations which resulted in leaf scorch (K deficiency symptoms) and shoot dieback in prune (Southwick *et al.*, 1996) and pecan trees (Sparks, 1986). This effect occurred even in soils with abundant available K suggesting that demand in leaves immediately adjacent to fruit



Figure 5.2. Patterns of nutrient accumulation as a percentage of total seasonal accumulation over the growing season for six field crops (Adapted from Jones *et al.*, 2009).

exceeds the capacity for replenishment from soil pools. Foliar sprays appear to provide a more rapid replenishment particularly in K and P fixing soils where diffusion rates may be inadequate to satisfy demand which is also exacerbated by the reduced new root production that occurs during summer in many tree species. Often during summer nutrient absorption by roots is also decreased in plants when under water stress and foliar application of nutrients offers the possibility of an alternative path for nutrient entry.

In pistachio, the primary periods of N accumulation coincide with the spring flush of growth and the nut fill period. Potassium accumulation followed the same pattern as N accumulation. This demand for nutrients can be supplied from re-distribution or from uptake. The high demand for K and N during fruiting years, particularly during early spring growth and nut fill, suggests that any reduction of root nutrient uptake during those periods could result in impaired fruit growth and yield (Rosecrance *et al.*, 1996; Rosecrance *et al.*, 1998b) The demand for nutrients by large crops (heavy fruiting) in pistachio can result in highly localized but pronounced nutrient deficiencies in leaves immediately adjacent to nut clusters even in well fertilized soils (Figure 5.3). A similar pattern of deficiencies can be observed in the spur leaves immediately adjacent to a fruit in almond (Figure 5.4).

Musk-melon (*Cucumis melo* L.) responds very well to foliar sprays of K (Jifon and Lester, 2009; Lester *et al.*, 2010; Lester *et al.*, 2006) as the fruit sugar content is directly related to K-mediated phloem transport of sucrose into the fruit and during rapid



Figure 5.3. Severe K and N deficiency in leaves immediately adjacent to a large nut cluster in pistachio (*Pistacia vera*). Deficiencies can occur even in heavily fertilized orchards and targetted foliar applications of KNO₃ effectively corrects these foliar symptoms (Brown, unpublished results).



Figure 5.4. Multi-element deficiencies in leaves immediately adjacent to two-fruited spurs (F2) of almond. Note the lack of apparent deficiencies in green leaves on non-fruiting (NF) neighbouring spur of the same tree (Brown unpublished).

musk-melon fruit growth when soil fertilization may be inadequate due to poor root absorption capacity. Under such conditions K supplementation through foliar sprays is very effective in improving fruit quality. Cotton has a very high K demand and is sensitive to conditions that limit K availability such as soil drought during the critical

Fertilizer	Boll load	Foliar nitrogen	Yield
(kg N ha ⁻¹)		(kg N ha⁻¹)	(kg seed cotton ha-1)
50	Low boll load	0	783 cdª
50	Low boll load	50	970 bc
50	High boll load	0	1035 b
50	High boll load	50	1258 a
100	Low boll load	0	776 d
100	Low boll load	10	782 bcd
100	High boll load	0	884 b
100	High boll load	20	1170 a

 Table 5.4. Influence of foliar-applied K at boll filling stage on boll load, leaf N and yield of cotton

 (Oosterhuis and Bondada, 2001).

^a Means within a column followed by the same letter are not significantly different at $P \le 0.05$.

demand periods. Peak demand for K is at the boll filling stage when higher boll load and potential yield results in greater demand (Gwathmey *et al.*, 2009; Mullins and Burmester, 1990). Late season foliar N application is also a standard practice in much of the world's cotton producting regions (Gerik *et al.*, 1998) and many studies demonstrate a benefit of foliar N applications even with high soil N rates (Bondada *et al.*, 1999; Oosterhuis and Bondada, 2001). As with K the benefits from late season foliar N applications are strongly dependent upon tissue sink strength and phenology of the crop (Oosterhuis and Bondada, 2001).

5.3.5. Postharvest and late season sprays

Late season (postharvest) foliar application of nutrients is a common practice in many deciduous tree species with the belief that nutrient status can be enhanced for the spring flowering period. However there are considerable differences in leaf health and longevity during the postharvest period which depends upon species and cultivar. Thus, early season cherry, grape, apricot and peach can experience a substantial period of full postharvest leaf function, while late species such as almond, pistachio, walnut, apple and pear have very little active postharvest leaf function. In general, evidence suggests that the advantages associated with foliage application of nutrients during the postharvest period are greatest with the phloem-mobile nutrients (N, K as well as B in species that readily transport B) though the potential benefit of all nutrient sprays is diminished as plants and trees approach leaf abscission. For the phloem-immobile nutrients, particularly Ca, Fe, Mn and Zn, there appears to be no advantage of supplying trees with these elements during the late post-harvest period (Faber and Manthey, 1996; Huett and Vimpany, 2006; Neilsen *et al.*, 2005b; Peryea, 2006; Peryea, 2007; Sanchez *et al.*, 2006).

Foliar-applied urea is commonly used to provide N to trees as they enter dormancy (Dong *et al.*, 2002; Dong *et al.*, 2005a; Sanchez and Righetti, 2005; Sanchez *et al.*, 1990; Shim *et al.*, 1972). Fall urea sprays increased total N of the dormant spur flower buds and fruit set of apple trees in the subsequent season (Guak *et al.*, 2004). Late season applications of urea are better tolerated than in-season sprays since phytotoxicity is less of a concern in senescing leaves. In peach, the phytotoxicity threshold for most of the growing season is attained by foliar-applied urea concentrations between 0.5 to 1.0% and consequently multiple sprays are required to meet tree demand. Concerns about phytotoxicity diminish prior to natural leaf fall when higher urea concentrations (5 to 10%) may be used (Johnson *et al.*, 2001). Tagliavini *et al.* (1998) and Toselli *et al.* (2004) also reported that peach leaves are able to take up a significant proportion of the N intercepted by the canopy from foliar sprays and Scagel *et al.* (2008) reported that fall urea application enhanced spring growth and as a result that spring fertilizer practices may need to be modified upwards to account for the increased uptake or demand of some nutrients.

5.3.6. Foliar fertilization and crop quality

Foliar fertilizers can be used to enhance crop quality both in terms of grain protein and Zn content (Cakmak, 2008; Cakmak *et al.*, 2010; Erenoglu *et al.*, 2002). In wheat

(*Triticum* sp.), several studies have shown that foliar sprays of N increased grain protein. Optimum timing for N sprays on wheat showed that post-pollination foliar N gave the highest grain protein (Blandino and Reyneri, 2009; Bly and Woodard, 2003; Gholami *et al.*, 2011; Pushman and Bingham, 1976; Varga and Svecnjak, 2006; Woolfolk *et al.*, 2002). The benefits of late season foliar applications are influenced by both cultivar and plant N status (Varga and Svecnjak, 2006).

Results of Dong *et al.* (2009) showed that pre-harvest application of Ca and B to 'Cara cara' navel orange (*Citrus sinensis* L. Osbeck) had significant effect on the crosslinked polymer network of the fruit segment membrane and the enzyme expression levels of polygalacturonase, pectinesterase and b-galactosidase were significantly reduced by pre-harvest application of Ca and B alone, or in combination. Such treatments increased contents of total dietary fibre, insoluble dietary fibre, proto-pectin and cellulose but decreased soluble dietary fibre and water-soluble pectin. 'Fortune' mandarin fruit showed positive effects from the Ca sprays in reducing peel disorder incidence (Zaragoza *et al.*, 1996{Ait-Qubahou, 2000 #1709}).

Pre-harvest sprays of Ca and K increased their mineral content in the fruit peel of 'Fortune' mandarin at harvest (El-Hilali *et al.*, 2004). Foliar spraying of trees with fertilizers containing N, Ca and K, four weeks before harvest, reduced significantly the appearance of peel disorders after storage at 4 and 8°C, and a pre-harvest spray with $Ca(NO_3)_2$ and KNO_3 improved the mineral content of fruit peel at harvest.

5.4. Impact of plant nutritional status on efficacy of foliar fertilizers

The nutritional status of a plant can have a significant effect on response to foliar fertilizer applications. These vary with plant species, the nutrient element and duration of the nutrient deficient condition. A persistent nutrient deficiency can reduce foliar absorption by altering leaf physical and chemical composition; by reducing canopy size; or by altering crop phenology. Short-term deficiencies can also result in enhanced absorption through increases in the activity of deficiency response mechanisms (uptake 'activators') or as a consequence of the relative abundance of unsaturated binding sites for deficient nutrients. Transport of nutrients from the application site may also be enhanced under deficiency conditions as a consequence of chemical potential gradients that favour nutrient movement from the site of absorption. In contrast, nutrient adequacy can favour foliar absorption by increasing new shoot growth and increasing canopy size thereby enhancing nutrient uptake as described earlier (Chapter 4.1.). In accordance with Liebig's Law of Minimum, crop response to enhanced supply of a single nutrient is maximized when all other essential elements are present in adequate amounts. The following text provides examples of each of these processes.

Marschner (2012) concluded that if the amount of any mineral nutrient in the leaves is extremely low then their ability to absorb this nutrient is limited because of irreversible changes in their tissues. This principle has been demonstrated recently in studies of Fe deficiency where it was shown that significant changes occur at the cuticular membrane level as a result of Fe chlorosis (Fernandez *et al.*, 2008b). Iron deficient plants had altered morphology and mechanical properties in the epidermis, the cell wall and the vascular bundles. Leaves were characterized by the occurrence of hydraulic problems (Eichert *et al.*, 2010; Fernandez *et al.*, 2008b) as a result of disruptions in cuticle formation caused by limited production of lipidic material which has also been suggested to occur in pear and peach chloroplast thylakoid membranes under Fe deficiency (Abadia *et al.*, 1988; Abadia, 1992; Abadia *et al.*, 2011; Monge *et al.*, 1993).

In citrus leaves, N deficiency induced an increase in epicuticular wax concentration (Bondada *et al.*, 2006; Bondada *et al.*, 2001) and an analogous response was observed in *Pinus palustris* needles with low N status which exhibited greater epicuticular wax concentrations than high N needles (Prior *et al.*, 1997). An increase in epicuticular wax reduces foliar absorption by reducing the transcuticular transport process and by increasing the proportion of long chain alkanes which alters epicuticular wax morphology as observed in 'Douglas' fir (Chiu *et al.*, 1992). Nitrogen deficiency can also affect uptake by reducing leaf expansion and shoot growth resulting in smaller leaves and stems with thicker cuticles and more epicuticular wax on a leaf area basis.

However a decrease in N absorption under N deficiency is not always observed since studies employing ¹⁵N-enriched urea undertaken by Klein and Weinbaum (1984) failed to establish a relationship between tree N status and foliar uptake of urea. They reported comparable absorption of foliar-applied urea by N-sufficient and N-deficient 'Manzanillo' olive plants and demonstrated a 17% greater retention of urea-N by N-deficient plants than those with adequate N status. In olive, N deficient plants take up more N by the leaves than those with optimal N content (Fernandez-Escobar et al., 2011). In citrus, N uptake from foliar urea decreased with increasing total shoot N content (Leacox and Syvertsen, 1995). Plant response to foliar sprays is also affected by K status as absorption of Rb (a K analog) by olive leaves was reduced in K-deprived and water-stressed plants compared to those cultivated in a K-rich medium (Restrepo-Diaz et al., 2008a). The K content in olive plants increased significantly as concentration of foliar KCl increased but only in plants cultivated in a low K (0.05 mM KCl) nutrient solution (Restrepo-Diaz et al., 2008a). This may occur as a result of changes in leaf cuticle as described earlier. The reduced absorption of foliar-applied Rb (K analog) by olive leaves under water stress may explain the irregular response of rainfed olive trees to foliar K application and could be related to water stress effects on leaf and canopy expansion (Arquero et al., 2006; Restrepo-Diaz et al., 2008a; Restrepo-Diaz et al., 2009; Restrepo-Diaz et al., 2008b), or reduced stomatal opening (Fischer and Hsiao, 1968).

Boron-deficient leaves were found to have significantly lower ¹⁰B absorption rates as compared to B-sufficient leaves (9.7% of the applied dose vs. 26to 32%) (Will *et al.*, 2011). Plants with no root B supply exhibited only 30% of the foliar B absorption as compared to plants grown under 10, 30 and 100 μ M B. The absolute amount of foliar-applied B moving out of the application zone was reduced in plants with 0 μ M root B supply (1.1% of the applied dose) and highest in those grown in 100 μ M B (2.8%). The limited foliar B absorption by B-deficient leaves was most likely caused by a reduced permeability of the leaf surface (Will *et al.*, 2011). In leaves of plants grown without B supply stomata were shrunken and closed which has been reported to reduce absorption of foliar-applied

solutes via the stomatal pathway (Eichert and Burkhardt, 2001; Eichert and Goldbach, 2008). Possibly, B deficiency also induced alterations in cuticular structure as has been reported for Fe deficiency in peach and pear trees (Fernandez *et al.*, 2008b). Several authors have quantified a proportionally greater mobility of foliar- and soil- applied B during plant reproductive stages under B-deficient conditions (Huang *et al.*, 2008; Liakopoulos *et al.*, 2009; Marentes *et al.*, 1997; Shelp, 1988; Shelp *et al.*, 1996). This effect may be a consequence of enhanced activity of B transporter channels under B deficiency (Miwa *et al.*, 2010); a result of enhanced phloem B transport from leaf to reproductive tissue under deficiency (Huang *et al.*, 2008; Will *et al.*, 2011); or a stimulation of polyol production that facilitates B transport (Liakopoulos *et al.*, 2009).

Though there is little work identifying an interaction between nutrient deficiency, crop phenology, crop canopy expansion and foliar absorption, it can be hypothesized that growth conditions that optimize leaf expansion, canopy development, reproduction, fruit growth and senescence will enhance foliar nutrient absorption and re-mobilization. Klein and Weinbaum (1984) observed that the partitioning of foliar-applied N appeared to be linked indirectly with the tree N status and transport out of leaves was increased in the more vigorously growing, high N trees. Furthermore, they concluded that, depending upon the tree N status, there may be uncoupling between the effects of the tree N status on leaf absorption of urea and the mobility of foliar-applied urea-N within the plant. Others (Sanchez and Righetti, 1990; Sanchez *et al.*, 1990; Tagliavini *et al.*, 1998) have shown that foliar N re-mobilization prior to natural leaf abscission was unaffected by the tree N status.

In apples, leaves with N content absorbed more N from sprays (Cook and Boynton, 1952) and responded better to Mg sprays (Forshey, 1963) as well as foliar applications in general (Swietlik and Faust, 1984). While the amount of ⁶⁵Zn absorbed by wheat leaves was not affected by the Zn nutritional status of the plants (Erenoglu *et al.*, 2002), the supply of supplemental N to wheat plants resulted in enhanced grain N and a significant enhancement of foliar ⁶⁵Zn transported to the grain and therefore an increase in grain Zn concentration (Cakmak *et al.*, 2010). Improved foliar absorption of nutrient elements in trees replete with all other nutrients likely occurs due to the overall better physiological status of the trees, as well as to the enhanced availability of an absorptive surface (bigger canopy) and the enhanced sink strength of developing organs.

The plant nutritional status has predictable but not necessarily predictive effects on crop response to foliar fertilizers.

- Plants with high nutrient status are less likely to respond to foliar fertilizers though the capacity for a plant to respond to a particular foliar nutrient application is dependent on an adequate status of all the other nutrients in the plant.
- The nutrient status can alter plant size and plant structure and hence have complex effects on crop response.

5.5. Source and formulation of nutrients for foliar spray

From a review of the available literature, it is clear that the source and formulation of foliar nutrient sprays affects absorption by leaves and differences in response are found among nutrients and plant species. The differences in response may be ascribed to the chemical form of the nutrient; its physico-chemical properties (molecular size, solubility, volatility, charge partition, hygroscopicity, and point of deliquescence); the accompanying ions; and the presence of various additives and adjuvants. The following review is limited to examples where general principles rather than product-specific results can be highlighted.

Foliar applications of urea, calcium nitrate and ammonium sulphate had similar effects in increasing N concentration in apple (*Malus domestica* Borkh) leaves (Boynton, 1954; Rodney, 1952). Urea is frequently used in foliar sprays in agriculture as it is rapidly and efficiently assimilated by plants and trees (Bi and Scagel, 2008; Bondada *et al.*, 2001; Cheng *et al.*, 2002; Chermahini *et al.*, 2011; Dong *et al.*, 2002; Dong *et al.*, 2005a; Gooding and Davies, 1992; Guvenc *et al.*, 2006; Johnson *et al.*, 2001; Laywisadkul *et al.*, 2010; Rosecrance *et al.*, 1998a; Shim *et al.*, 1972; Xia and Cheng, 2004; Yildirim *et al.*, 2007). The primary limitations in the use of urea are associated with the occurrence of leaf toxicity and fruit damage when rates exceed plant tolerance. Furthermore, toxicity and damage may also be associated with a higher biuret content of some ureas (Fisher, 1952; Gooding and Davies, 1992; Johnson *et al.*, 2001; Krogmeier *et al.*, 1989; Strik *et al.*, 2004; Witte, 2011).

Bowman and Paul (1992) showed comparable N absorption rates by ryegrass (Lolium perenne L.) leaves from foliar applications of urea, ammonium and nitrate N sources. This is in contrast with the majority of results that demonstrate a higher absorption rate of N by the leaves treated with urea compared with those treated with nitrate or ammonium forms (Reickenberg and Pritts, 1996; Swietlik and Faust, 1984; Wittwer et al., 1967). This phenomenon is related to the fact that the cuticular membrane is 10 to 20 times more permeable to urea than to inorganic ions (Yamada et al., 1964a; Yamada et al., 1964b) which is a consequence of the small uncharged nature of the urea molecule. Urea-ammonium nitrate has also been very effective as a foliar-applied N source to barley (Turley and Ching, 1986), while in soybeans there were no differences in the uptake rate of foliar-applied N in the urea, ammonium or nitrate forms (Morris, 1983). The absorption rate of ammonium ions into the leaves is faster than that for nitrate ions because the permeation of cations along the gradients of negatively charged sites in cuticular pores is enhanced. This has been verified in grapevines (Porro et al., 2006) where uptake from the NH,-containing treatments was higher than treatments containing NO₂.

The role of the POD in determining the efficacy of foliar fertilizers has been described in Chapter 4 and as stated salts used for foliar nutrition often have a low POD (Schönherr, 2001). Thus, $CaCl_2$ (33%), K_2CO_3 (44%), and $Ca(NO_3)_2$ (56%) should be more effective than K_2HPO_4 , KH_2PO_4 , KNO_3 , Ca-acetate, Ca-lactate, and Ca-propionate as the later are soluble only at humidity close to 100% (Schönherr, 2001). However, the increased phytotoxicity risk of low POD salts should not be overlooked. It is commonly accepted that, for most plant species, foliar-applied Mg is rapidly absorbed when present as chloride and nitrate salts (Allen, 1959; Neilsen and Hoyt, 1984) and Fisher and Walker (1955) reported that apple leaf Mg concentrations as a result of foliar applications of Mg in the form of nitrate, chloride, acetate and sulphate were increased by 71, 66, 32 and 8% respectively. When applied as MgCl₂, 90% of the applied Mg was absorbed by apple leaves even at a relative humidity of 30%, whereas MgSO₄ required a relative humidity of 80% for an increase in absorption (Neilsen and Hoyt, 1984). The response likely reflects the greater deliquescence of MgCl₂ compared to MgSO₄.

Prior studies on foliar Zn fertilization of various plants have shown relatively little translocation of foliar-applied Zn as ZnSO, or after chelation with a synthetic chelate such as EDTA (Chatzistathis et al., 2009; Neilsen et al., 2005b; Peryea, 2007; Swietlik and Laduke, 1991; Zhang and Brown, 1999a; Zhang and Brown, 1999b). In pea (Pisum sativum L.) only 25% and 75% of Zn applied as Zn-EDTA or ZnSO, respectively were recovered after removal of epicuticular waxes, and 8 to 10% was translocated from the treated tissues (Ferrandon and Chamel, 1988). In one of the only available studies on avocado (Kadman and Cohen, 1977) there was no translocation of ⁶⁵ZnCl, from spots applied to intact leaves even to adjacent parenchyma tissue. Amino acid chelates (metalosates) have been reported to be more effectively taken up and translocated than inorganic metal salts or the synthetic chelate EDTA in a variety of crops and trees (Hsu, 1986; Shazly, 1986). Foliar-applied ZnSO4, ZnO, and Zn metalosate with Zn at 5.4, 0.8 and 0.9 g L⁻¹ respectively, resulted in increased leaf Zn concentrations in avocado (Crowley et al., 1996). However, experiments with ⁶⁵Zn applied to leaves of greenhouse grown avocado seedlings (Persea americana Mill.) showed that <1% of Zn applied as ZnSO, or Zn metalosate was actually taken up by the leaf tissue and that there was little translocation of Zn into leaf parenchyma tissue adjacent to the application spots or into the leaves above or below those treated.

Zinc deficiency in rice can be corrected by the application of ZnSO₄ but application in chelated forms, such as Zn-EDTA, was found to be more efficient (Correia et al., 2008; Karak et al., 2006). In citrus plants, (Sartori et al., 2008) reported that ZnCl, was more efficient than ZnSO₄ in supplying Zn to the leaves though the former source may have caused toxicity symptoms in the leaves. The magnitude of the leaf Zn absorption appears to be dependent on the micronutrient source. When ZnSO₄ was the Zn source for orange trees, Zn absorbtion by leaves was small at 6% of the total applied (over 120 days). However, when the Zn source was the chloride, Zn absorption reached 92% of the total applied. When commercially available Zn-chelated products were used on orange trees, the absorption and translocation rates were no greater than inorganic Zn sulphate and chloride (Caetano, 1982; Santos et al., 1999). When foliar applications of Zn sulphate and chloride, or chelated compounds of EDTA or lignosulfonate, labelled with ⁶⁵Zn were compared on pea or bean leaves less than 7% of applied Zn was translocated from treated leaves to the other plant parts irrespective of Zn source (Ferrandon and Chamel, 1988; Sartori et al., 2008). In pecan and citrus, Zn(NO₃), alone, and in combination with urea and ammonium nitrate, raised leaf Zn level more than ZnSO₄ (Smith and Storey,

1979). There was no difference in the effectiveness of Zn compounds for foliar sprays applied to apples (Neilsen and Neilsen, 1994).

The efficacy of 11 commercially available Zn products applied in foliage of apple trees during post-bloom stage demonstrated that all of the Zn products increased leaf Zn concentrations to desirable levels (Peryea, 2006; Peryea, 2007). Leaf Zn concentration increased in the order: Zn phosphate < Zn oxide = Zn oxysulphate < chelated/organically complexed Zn < Zn nitrate. Because the inorganic Zn-based products usually are less expensive per unit of Zn, it may be less costly and just as effective to use a higher rate of an inorganic Zn product than use a lower rate of a more expensive but organically complexed product. On the other hand, the use of organically complexed Zn products at low rates may minimize release of the metal into the environment. Post-bloom sprays of Zn applied at lower rates and with these safer formulations are replacing dormant and postharvest inorganic salt-based Zn sprays (Peryea, 2007; Sanchez *et al.*, 2006). The relative effectiveness of the Zn-chelates, Zn-PHP, Zn-HEDTA, Zn-EDDHSA, Zn-EDTA, Zn-S, ZN-EDDS and Zn-EDTA-HEDTA sources to navy beans (*Phaseolus vulgaris* L.) was greatest with Zn-EDTA, Zn-EDTA-HEDTA, Zn-HEDTA and Zn-EDDHSA (Gonzalez *et al.*, 2007).

Most forms of B available for use in foliar fertilizer products are highly soluble and generally effective. In apple, the B products Mor-Bor 17, Solubor, Solubor DF, Spraybor, Borosol, Liquibor, N-Boron, and Solubor plus Coron showed little substantive difference (Peryea *et al.*, 2003). Furthermore, the chemical form of B in the product, its physical state and presence of additives had no consistent and substantive differential effects on B uptake. In a greenhouse study, there was a difference in tissue B concentration in cotton receiving foliar applications of different B sources, including boric acid and sodium borate, but there was no effect on tissue B concentration in soybean (Guertal *et al.*, 1996). The relatively small effect of source or formulation on foliar B fertilizers is likely a result of the small size and uncharged nature of undissociated boric acid which is the predominant chemical state of B at pH values of less than 8.2. Undissociated boric acid, similar to urea and glycerol, should pass easily through cuticular membranes.

Identifying superior and effective sources of foliar Fe fertilizers has been a significant challenge for foliar fertilizer practitioners (Abadia *et al.*, 2011; Fernandez *et al.*, 2009). While some authors report advantages of using Fe chelates over inorganic Fe salts (Basiouny *et al.*, 1970) others observed no benefit of the former over the latter which are cheaper (Alvarez-Fernandez *et al.*, 2004; Rombola *et al.*, 2000). In groundnut, Fe(II) sulphate was as effective as Fe(III)-EDTA and Fe(III)-citrate (Singh and Dayal, 1992) and Fe(II) sulphate was as effective as Fe(III)-DTPA in kiwi-fruit (Tagliavini *et al.*, 2000) while Fe(II) sulphate alone (9 mM Fe), or in combination with ascorbic, citric and sulphuric acids, was able to induce leaf re-greening in chlorotic pear (Garcia-Lavina *et al.*, 2002). In grape Fe sulphate was somewhat effective (Reed *et al.*, 1988) but not in peach. Similarly, several investigations observed variable physiological responses of Fe deficient plants to diluted acids and chelators such as citric acid (Alvarez-Fernandez *et al.*, 2004; Tagliavini *et al.*, 1998). Fernández and Ebert (2005) concluded that due to the chemistry of Fe(II) and Fe(III) in solution, as well as their instability in the presence of oxygen and pH dependency, it is better to apply Fe as foliar sprays as chelates than

as salts. However, when assessing the effect of several Fe compounds including Fesulphate and four Fe chelates (Fernandez *et al.*, 2006; Fernandez *et al.*, 2008a) it was shown that all compounds may efficiently re-green chlorotic leaves and increase foliar Fe concentrations provided that suitable adjuvants are added to the formulations. Concentration plays an important role in foliar Fe uptake with proportionally increased uptake occurring from lower concentrations in the treatment solution (Fernandez and Ebert, 2005).

Two Mn sources ($MnSO_4 \cdot H_2O$ and Mn-EDTA) were foliar applied at various concentrations (0, 200, 400, 800 and 1200 mg Mn L⁻¹) to Mn deficient 'Washington navel' orange trees (Papadakis *et al.*, 2005) and 170 days after the applications the mean Mn concentrations in the leaves treated with $MnSO_4 \cdot H_2O$ (200, 400, 800 or 1200 mg Mn L⁻¹) or Mn-EDTA (400, 800 or 1200 mg Mn L⁻¹) were significantly higher than those of the control leaves. It was concluded that $MnSO_4 \cdot H_2O$ was more effective than Mn-EDTA when applied at equal (Mn kg⁻¹) amounts. Similar results have been observed with apples (Thalheimer and Paoli, 2002), sugar beets (Last and Bean, 1991) and wheat (Modaihsh, 1997) with $MnSO_4$ being more effective than chelated Mn; while in lupin (*Lupinus augustifolia*) the two sources (Mn kg⁻¹) proved to be equally effective (Seymour and Brennan, 1995).

Nutrient formulations can have a profound effect on plant response to foliar fertilizers.

- The chemical and physical properties of the formulation alter the length of time that the nutrient remains hydrated and available for uptake on the leaf.
- The size of the functional nutrient molecule affects its cuticular penetration though currently it is not understood how this will predict response.
- It is unknown if a formulation alters within-plant efficacy of a nutrient or whether the differences in response are biological or simply physical in nature.
- There are literally thousands of commercially available nutrient formulations in the market and a vast number of ways in which they can be combined and applied.
- To compare and contrast effectively the different formulations it is essential that precise information be provided on the experimental methodology employed and formulation compositions applied.

5.6. Toxicity

Leaf damage can sometimes occur with foliar-applied fertilizers due to localized salt toxicity; the presence of toxic compounds and contaminants; solution pH; or direct elemental toxicity (Alexander and Schroeder, 1987). The expression of toxicity can vary depending upon the degree of localization of the deposited materials and can be influenced by the movement of the applied material into and within the leaf tissue. The two most common toxicity symptoms are: 1) isolated necrotic spots that occur when droplets dry and materials concentrate in discrete spots ('balling') and; 2) leaf margin and tip burn due to gravitational flow of spray material to these areas, or as a consequence

of internal re-distribution of the applied chemical through the transpiration stream to the leaf margins and tips. The occurrence of necrotic or marginal lesions can result in a reduction in the photosynthetic area of the leaves with consequent decrease in productivity (Harder *et al.*, 1982; Neumann, 1979) which can offset or negate the growth promoting effects of foliar fertilization.

A common symptom of toxicity following the application of foliar fertilizers is 'burning' or 'scorching' which may be a consequence of cell rupture due to large differences in osmotic pressure across the cell wall when highly concentrated fertilizer solution is applied to the leaf surface (Greenway and Munns, 1980). This type of foliar damage is generically described as leaf burn and is most prevalent with compounds of high salt index (Clapp, 2009). In this scenario, the rapid development of a solute concentration gradient across the cell membrane generates an osmotic potential difference resulting to the collapse of the cell due to the movement of water out of the plant cell (Majid and Ballard, 1990). The propensity for 'salt burn' is dependent upon the solubility and formation of charged species; the concentration of the applied fertilizer; and on environmental conditions (temperature, humidity, wind speed) that influence the rate of evaporation and hence the concentrating of foliar sprays on the leaf surface. As the concentration gradient is the driving force for the penetration through the leaf cuticle it is the first and most limiting barrier to foliar uptake of nutrients (Schönherr, 2001; Swietlik and Faust, 1984) and a key challenge for the use of foliar fertilizers is to balance the need for high solubility with the risks of 'salt burn'.

An additional factor is the potential damage caused by supplying high concentrations of salts with low points of deliquescence (POD's) as discussed in Chapter 4 and as suggested by Burkhardt (2010). Spraying nutrient salts with low POD's may lead to leaf burn under conditions favouring the process of foliar uptake. This toxicity may be a result of the osmotic damage caused by the easily ionizable and soluble salt or may reflect direct elemental toxicity from large concentrations of the nutrient elements or associated counter-ions entering the cellular space. Given the mechanisms that function to maintain cellular metal ion concentrations within very tight tolerances (Brown and Bassil, 2011) it is perhaps not surprising that rapid entry of elements following foliar fertilization might lead to toxic responses.

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 (Barel and Black, 1979a; Barel and Black, 1979b) though evidence suggests that the damage is predominantly a result of nutrient imbalance under the fertilizer droplets rather than osmotic effects (Marschner, 1995). The appearance of leaf burn has been observed (Parker and Boswell, 1980) but is not detrimental to the plant. However, some studies have resulted in severe leaf burn that results in part or all of the leaf dying which reduces yield following foliar-applied treatments. A study using urea, KH_2PO_4 and ammonium polyphosphate spray mixes was reported to lower significantly the yield of soybeans (Parker and Boswell, 1980) due to excessive salt loading from the three successive applications of foliar fertilizer resulting in severe leaf burn. 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 leaves (Barel and Black, 1979a; Barel and Black, 1979b). The best compounds (safest) for maize were $[(NH_4)5P_3O_{10}]$ followed by $[NH_4 PO_3]_n$ and then $PO(NH_2)_3$. Soybeans were more sensitive to scorch tolerating between 60 to 75% less compound than maize in most cases (Noack *et al.*, 2011).

There is still much uncertainty about the effects of low volume (water rate) applications on foliar absorption and the possible phytotoxic side effects due to the increased solute concentration. Increasing the concentration of the spray solution of different mineral compounds has been reported to improve leaf concentration of nutrients such as P, K, Mg and Cu (Swietlik and Faust, 1984) and Mn (Thalheimer and Paoli, 2002). The main reason for the observed increase of Mn and Mg uptake at reduced water volumes (rates) is the increased nutrient concentration in the spray droplets (Thalheimer and Paoli, 2002). In the case of Mn, and to a lesser extent of Mg, there was a general increase of foliar nutrient concentration as water volume decreased from 1500 L ha⁻¹ to 500 L ha⁻¹, whereas a further reduction to 300 L ha⁻¹ did not result in any further increment. This is likely because a threshold was reached when further increments in the concentration gradient are no longer effective for increasing cuticular penetration perhaps as a result of more rapid drying of the increasingly small droplets.

The role of salt-burn in defining the efficacy of foliar fertilizers is well illustrated by K. Potassium chloride is the most widely used source of soil-applied fertilizer K but its relatively high salt index of ~120 (Mortvedt, 2001) and its high POD of 86%, (Schönherr and Luber, 2001) limit its use as a foliar fertilizer particularly as the high POD increases the risk of crystallization following foliar sprays. The efficacy of six foliar K sources (KCl, KNO₃, MKP, K₂SO₄, KTS and a glycine amino-acid complexed K) on fruit quality parameters of field-grown musk-melon was assessed and phytotoxicity problems were not observed with any of the foliar K sources or concentrations used (Jifon and Lester, 2009) when the pH levels of spray solutions ranged from 6.5 to 7.7. Unbuffered solutions of the K sources tend to have alkaline pH levels that can cause leaf burn and this is more pronounced when applied during dry, hot weather conditions (Swietlik and Faust, 1984).

Salts present in foliar sprays can act synergistically to cause salt damage. Injury can be directly caused by foliar absorption and accumulation of salt in irrigation water and in foliar applications. Sprinkling with a solution of 10 meq C1 L⁻¹ caused leaf injury symptoms (Maas, 1982) but the degree of injury depended on the Ca:Na ratio as CaC1₂ alone was more toxic than NaC1, but at lower concentrations (1-3 meq L⁻¹) it reduced NaCl-induced leaf injury. The highly toxic effects of CaC1₂ solutions may have resulted directly from the marked accumulation of Ca²⁺ or indirectly from the ionic imbalance it caused. Since Na⁺ is generally far more permeable than Ca²⁺, and Cl⁻ is highly permeable, the application of CaC1₂ may induce a local charge imbalance as Cl⁻ fluxes greatly exceed Ca²⁺ fluxes into the leaf. However, the beneficial effects of low concentrations of Ca²⁺ are worth noting as a mixture containing 1 meq CaC1₂ and 24 meq NaC1 per liter was noticeably less toxic than 25 meq NaC1 L⁻¹. This was true despite slightly higher Ca²⁺, Na⁺ and Cl⁻ concentrations in the tissue itself. The rate of ion absorption as a function of salt concentration film on the leaf evaporates and the salt is concentrated. Injury appeared to be related to excessive accumulation of Cl⁻ or

Na⁺. The toxicity of NaCl solution may reflect a deficiency in Ca which is important for maintaining membrane integrity.

In addition to salt effect, there is increasing evidence to suggest that the rapid passage of nutrient ions from foliar fertilizer into the plant metabolic spaces can result in the disruption of normal metabolism. The potential for direct toxicity is greatest with foliar fertilizers that are rapidly assimilated into the leaf such as urea. A high penetration rate is a prerequisite for effective foliar nutrition and urea, due to its characteristics including its non-ionic nature, is usually taken up rapidly (Hill-Cottingham and Lloydjones, 1975). It is also believed that the burn observed depends upon the form of N fertilizer used and that urea is less likely to cause leaf burn than other N fertilizers because it has a lower salt index and is more rapidly absorbed into the leaf where it is subject to dilution and metabolism (Garcia and Hanway, 1976).

The leaf burn commonly observed after foliar fertilization of soybeans with urea results from accumulation of toxic amounts of urea in the soybean leaves rather than any salt effect, or from the formation of toxic amounts of ammonia through urea hydrolysis by leaf urease (Bremner, 1995; Krogmeier *et al.*, 1989). Most studies of foliar fertilization of soybeans during seed development have given disappointing results. For example, in the review of Gray and Akin (1984) foliar fertilization of soybeans usually led to a decrease in yield and, to some degree, of leaf-tip necrosis. Leaf-burn is partly responsible for the reduced yields observed after foliar fertilization (Poole *et al.*, 1983a; Poole *et al.*, 1983b) and leaf burn is increased by low humidity and high temperatures which leads to accumulation of very concentrated fertilizer solution on leaf surfaces (Garcia and Hanway, 1976).

Among the factors affecting leaf penetration of urea, its concentration in the spray solution plays a major part (Toselli et al., 2004). Leaf N uptake within 48 hrs was highest when urea was sprayed at the lowest concentration. However at the end of the study period (120 hrs) no differences in the percentage of intercepted N recovered in the leaves was recorded. The hygroscopic behaviour of urea which has a critical relative humidity of 70% (Glendinnig, 1999), and the alternating high and low air relative humidity, likely caused the swelling of leaf cuticle that promotes urea absorption (Eichert and Burkhardt, 2001). Repeated drying and wetting cycles are known to increase cuticle pore sizes and consequently cuticle penetration of water solutions. Thus, within a few days, the spray water volume does not substantially affect urea absorption. Once foliar-applied urea is absorbed by the leaves it is converted into ammonia by the enzyme urease, and then it is incorporated into glutamate by the enzyme glutamine synthetase (Witte, 2011). The effectiveness of urea as a foliar fertilizer can be enhanced, and its toxicity reduced, with the addition of Ni which is an essential component of the enzyme urease required for urea metabolism (Eskew and Welch, 1982; Gheibi et al., 2009; Krogmeier et al., 1991; Nicoulaud and Bloom, 1998).

In peach, the phyto-toxicity threshold is attained with foliar-applied urea concentrations of between 0.5 to 1.0% and as a consequence multiple sprays are required to supply tree demand. However phyto-toxicity diminishes prior to natural leaf fall when higher urea concentrations (5 to 10%) may be used (Johnson *et al.*, 2001). Furthermore, Tagliavini *et al.* (1998) also reported that peach leaves are able to take up

a significant proportion of the N intercepted by the canopy during sprays. Scagel *et al.* (2008) stated that when growers spray plants with urea in the fall then spring fertilizer practices may need to be modified to account for this.

Urea applied as foliar spray is absorbed rapidly and efficiently by leaves of most fruit crops (Johnson *et al.*, 2001). Studies have shown about 48 to 65% uptake and translocation efficiency of foliar applied urea to all other organs of the trees including roots (Tagliavini *et al.*, 1998). Foliar application of low-biuret (< 0.5%) urea is quite common on large scale citrus plantations to provide a supplemental supply of N without any phytotoxic effects (Albrigo, 2002). Therefore foliar application of urea to citrus is an efficient and cost-effective way to supply N, which greatly influences fruit quality and enhances fruit size, peel thickness, juice content and yield according to Agabbio *et al.* (1999) and and El-Otmani *et al.* (2002).

Direct ion effects are important factors in determining the toxicity of foliar fertilizers containing Zn, Cu, Fe and Mn which are generally not applied at high enough concentrations to result in salt burn. However, these can disrupt metabolism by virtue of a rapid increases in cellular concentrations of what are potentially toxic elements. Somnez (2006) reported that high levels of Cu application to leaves seriously disrupted normal plant growth resulting in a reduction of total yield, fruit number, dry root weight and plant height. Copper is a transition metal that participates in redox reactions and in excess causes overproduction of oxy-radicals believed to be its primary toxic effect in plant cells. Furthermore, Cu and the other essential transition metals can induce cell disturbances when present in toxic levels, and therefore each has a sophisticated internal homeostatic process that could be disrupted by excessive foliar applications (Brown and Bassil, 2011).

Though CuSO_4 has a high salt index (Tisdale and Nelson, 1975) and therefore a high tendency to cause osmotic burning it is generally not used as a foliar fertilizer at high concentrations. Copper is, however, frequently applied as a fungicide at concentrations well in excess of that required to satisfy nutrient demands and under these conditions it can cause toxicity (Majid and Ballard, 1990). Similarly, ZnSO_4 is frequently used in deciduous tree production (at rates as high as 20 kg ha⁻¹ in 100 L) in the early fall to defoliate trees to reduce over-wintering disease load. In this manner, the toxicity of ZnSO_4 is deemed beneficial though the environmental consequences of such a heavy metal load should be examined.

Foliar application of solutions containing high levels of B caused relatively small increases in leaf/plant B but had considerable negative effects on plant growth (Ben-Gal, 2007). The increased toxicity symptoms and decreased yields found in plants with overapplied B implies that the relative toxicity of B entering through the leaves is greater than that of B entering *via* the roots. This is possible since a greater percentage of total B in the leaves receiving foliar applications would exist in a soluble, intercellular form in contrast with the predominance of cell wall bound B in B-deficient plants (Hu and Brown, 1994). Soluble B has been reported to play an important role in occurrence of B toxicity (Wimmer *et al.*, 2003) as it is likely to be more involved in physiological processes (Brown *et al.*, 2002). Results of Nable *et al.* (1990) and Ben-Gal and Shani

(2002) imply that absolute B values in plant matter are not reliable for judging or predicting B damage.

The occurrence of toxicity following application of foliar fertilizers represents a major legal and financial threat to the foliar fertilizer industry and to grower productivity. The development of mechanisms to avoid toxicity while maintaining efficacy is, therefore, an issue of tremendous importance. The degree to which the presence of a toxicity symptom results in yield loss is poorly understood, frequently unpredictable and highly sensitive to crop type and foliar product used. Small blemishes on high value ornamental (flowers, foliage plants), or horticultural produce (peaches, cherries, melons, etc.), can result in complete loss of marketable crop, while quite severe toxicity on field crops may have little or no negative yield effect.

A variety of approaches have been used to reduce the toxicity of foliar fertilizers; the most important of which involve careful and diverse field-testing and controlled environment experiments to ensure that the product rates recommended and used are safe for all potential crops and production environments. Rate modification can be achieved through dilution and/or co-formulation with additives to optimize, amongst others, spray solution pH, reduce salt index or alter the distribution and drying rate of spray materials on the leaf surface. Care should be taken to ensure that the prevention of possible toxicity from a foliar spray does not result in a diminishment of the ability of the formulation to serve as an effective nutrient source.

Toxicity of foliar applications is an extremely important issue but poorly understood process.

- Toxicity may be the result of osmotic or direct elemental effects.
- Osmotic toxicity is the result of dehydration of cells due to the loss of water to an extracellular salt solution.
- Elemental toxicity occurs when an excess of an essential element or its counter-ion enters the metabolic space, a process which is also very poorly understood.
- The occurrence of elemental toxicity is an indication of excessive concentration of the formulation at providing nutrients to plant cells.

5.7. Conclusions

Given the great complexity and theoretical uncertainties governing foliar fertilization then field trials and controlled environment experimentation will continue to play a critical role in the adaptation of theory into field practice. Equally important is the recognition that results gained from field trials cannot be generalized without thought to the specific conditions that prevailed during the trial and the characterisitics of the crop used.

The observations and outcomes of field trial results cannot always be explained by known physical and chemical principles and that efficacy predicted on the basis of laboratory experimentation suggests that much remains to be learned. Regardless of this, the greatest likelihood of success in achieving optimum efficacy for foliar fertilization practices will inevitably be realized through application of sound physical, chemical and biological principles and understanding.

Certainties

- The occurrence of plant toxicity following foliar application is unacceptable for most growers and fertilizer manufacturers.
- For some crops, especially those with a high reliance on visual quality, there is zero tolerance to toxicity.
- The environment, crop and formulation all interact to influence the occurrence of toxicity.
- Toxicity can be the result of osmotic, elemental or metabolic perturbations.

Uncertainties

- Low to moderate levels of toxicity may indicate foliar nutrient efficacy, be transient in nature and hence, not a cause for concern.
- It is not known if foliar-applied nutrients behave in a similar manner as soil-derived nutrients once they enter the plant.
- It is unknown if foliar-applied nutrients can be re-translocated better than soil derived nutrients.
- It is unknown if the counter-ion, or other molecules present in the formulation along with the nutrient element, enter the leaf and have a perceptible metabolic effect on crop performance.

Opportunities

- There is a need for the development of a risk assessment approach to foliar fertilization that integrates the potential for occurrence of a transient but critical deficiency, with the likelihood of a positive outcome and the risk of a negative outcome (toxicity) based upon formulation, plant and environment conditions at the time of application.
- Methodologies, both experimental and model-based, are required to predict the performance as well as the potential for a foliar fertilizer to cause toxicity damage.
- Methodologies to measure the translocation of nutrients into the metabolic space are required.
- There is a need to demonstrate if molecules delivered (co-formulated) along with the appropriate nutrient elements provide any benefit to, or can harm, the plant.