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Fertilizer Industry
Association



Foliar Fertilization

Scientific Principles and Field Practices

V. Fernández, T. Sotiropoulos
and P. Brown

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Foliar Fertilization: Scientific Principles and Field Practices
V. Fernández, T. Sotiropoulos and P. Brown
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International Fertilizer Industry Association
28, rue Marbeuf
75008 Paris
France
Tel: +33 1 53 93 05 00
Fax: +33 1 53 93 05 45/ 47
publications@fertilizer.org
www.fertilizer.org
Twitter: fertilizernews

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About the book

Foliar fertilization is a widely used crop nutrition strategy of increasing importance worldwide. Used wisely, foliar fertilizers may be more environmentally friendly and target oriented than soil fertilization though plant responses to foliar sprays are variable and many of the principles of foliar fertilization remain poorly understood.

The aim of the book is to provide up-to-date information and clarification on the scientific basis of foliar fertilization and plant responses to it with reference to the underlying environmental, physiological and physico-chemical determinants. Information drawn from research, field trials and observational studies, as well as developments in formulation and application techniques, are discussed.

About the authors

Victoria Fernández

Forest Genetics and Ecophysiology Research Group, School of Forest Engineering, Technical University of Madrid (Universidad Politécnica de Madrid), Madrid, Spain.

Victoria Fernández holds a research tenure at the Technical University of Madrid, Spain. She gained a Bachelor of Science in Horticulture at University College, Dublin, Ireland and a PhD at Humboldt University of Berlin, Germany. For more than 12 years, Dr. Fernández has been implementing applied and fundamental research approaches to foliar fertilization as a means to improve the effectiveness of foliar sprays and has published various peer-reviewed articles in this regard. She is currently focusing on analyzing the physico-chemical properties of plant surfaces from an eco-physiological and agronomic viewpoint and also in relation to their interactions with foliar-applied agro-chemicals.

Thomas Sotiropoulos

Ministry of Rural Development and Food, Greek Agricultural Organization 'Demeter', Pomology Institute, Naoussa, Greece.

Thomas Sotiropoulos received a Bachelor of Science in Agriculture at the Aristotle University of Thessaloniki, Greece in 1993, a MSc in Plant Breeding and Plant Physiology in 1996 and a PhD from the same University in 1999. Dr. Sotiropoulos is currently an Associate Researcher in the Greek Agricultural Organization 'Demeter', Pomology Institute, Naoussa. His main interests include applied and fundamental research dealing with fertilization as well as cultivar breeding and evaluation, mainly on deciduous fruit trees. He has participated in several national and European research projects and published various peer-reviewed articles on the previous topics. He also served as a part time Professor in the School of Agriculture of the Aristotle University of Thessaloniki and the Alexander Technological Educational Institute of Thessaloniki.

Patrick Brown

Professor, Department of Plant Sciences, University of California, Davis, California, USA.

Patrick Brown received a Bachelor of Science (Hons) in agronomy and biochemistry at the University of Adelaide, Australia in 1984 and a PhD in agronomy and international agricultural development from Cornell University, USA in 1988. Dr. Brown is currently Professor of Plant Nutrition in the Department of Plant Sciences at the University of California, Davis. His research focusses on the role of micronutrients in plant growth and development and encompasses research from fundamental biology to field application and extension. Dr. Brown is author of 150 scientific articles, books and book chapters with significant contributions in the area of the physiology of boron, the role of nickel in plant biology and the mechanisms of elemental transport in plants. Current research focuses on the optimization of nutrient use in orchard crops and the development of decision support systems for growers. Dr. Brown has served as the Director of International Programmes at the University of California, Davis and as President of the International Plant Nutrition Colloquium, as well as frequently serving in an advisory role for governmental, industrial and grower organizations.

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List of abbreviations, acronyms, and symbols

ATP	Adaptation to Technical Progress (<i>as used in the book</i>)
B	boron
$B(OH)_3$ or H_3BO_3	boric acid
Ca^{2+}	calcium ion
$CaCl_2$	calcium chloride
$Ca(H_2PO_4)_2$	calcium phosphate
$Ca(NO_3)_2$	calcium nitrate
Cu	copper
DAFB	days after full bloom
EC	European Commission
EDDHSA	ethylenediamine-di-(2-hydroxy-5-sulfophenylacetate)
EDDS	ethylenediaminedisuccinate
EDTA	ethylenediaminetetraacetate
EU	European Union
Fe	iron
$FeCl_3$	iron chloride
$Fe(NO_3)_3$	iron nitrate
HEDTA	N-2-hydroxyethyl-ethylenediaminetriacetate
H_3PO_4	phosphoric acid
IDHA	iminodisuccinic acid

K	potassium
kg ha ⁻¹	kg per hectare
KCl	potassium chloride also known as muriate of potash (MOP)
K ₂ CO ₃	potassium carbonate
KH ₂ PO ₄	monopotassium phosphate
K ₂ HPO ₄	dipotassium phosphate
KM	potassium metalosate
KNO ₃	potassium nitrate
K ₂ SO ₄	potassium sulphate
KTS	potassium thiosulphate
lbs acre ⁻¹	pounds per acre
Mg	magnesium
mg kg ⁻¹	milligram per kilogram
mg L ⁻¹	milligram per litre
MgCl ₂	magnesium chloride
Mg(NO ₃) ₂	magnesium nitrate
MgSO ₄	magnesium sulphate
MKP	monopotassium phosphate
mM	millimole
Mn	manganese
mN m ⁻¹	miliNewton per meter
MnSO ₄	manganese sulphate
Mo	molybdenum
N	nitrogen
Na	sodium
Na ₂ B ₄ O ₇	borax
Na ₂ B ₈ O ₁₃	sodium-octoborate
NH ₄ H ₂ PO ₄	ammonium dihydrogen phosphate
(NH ₄) ₃ P ₃ O ₁₀	ammonium tripolyphosphate
Ni	nickel
nm	nanometer
P	phosphorus
³² p	phosphorus isotope
PHP	polyhydroxyphenylcarboxilate
PO ₄ ³⁻	phosphate
POD	point of deliquescence
PO(NH ₂) ₃	phosphoryl triamide
Q10	temperature coefficient
Rb	rubidium
S	sulphur
SEM	Scanning Electron Microscopy
µg cm ²	microgramme per square centimeter
µL	microlitre
µM	micromolar

US	United States (of America)
UV	ultra violet
Zn	zinc
ZnSO ₄	zinc sulphate
°	degree
°C	degree Celsius

List of terms

Uptake	The process of transport of foliar applied nutrients through the leaf cuticular surface into cellular space where they can affect plant physiology and metabolism.
Adsorption	The adherence of foliar applied nutrients to the leaf cuticular surface. At any time a portion of adsorbed nutrients may not be available for uptake into the cellular space where they can affect plant physiology and metabolism.
Absorption	The term absorption is used here to include both the uptake and adsorption of nutrients.

1. Introduction and scope

Foliar fertilization is an important tool for the sustainable and productive management of crops. However, current understanding of the factors that influence the ultimate efficacy of foliar applications remains incomplete. This book provides an integrated analysis of the principles, both physico-chemical and biological, known to influence foliar absorption and utilization by the plant, and reviews the available laboratory and field experimental results to provide insights into the factors that ultimately determine the efficacy of foliar applications. Advances in this field will require a sound understanding of the physical, chemical, biological and environmental principles that govern the absorption and utilization of foliar applied nutrients. The aim of this book is to describe in detail the state of knowledge on the mechanisms of uptake by plant organs (leaves and fruits) of surface-applied nutrient solutions, and to describe the environmental and biological factors and interactions that are key to understanding these processes. Empirical information gathered from foliar nutrient spray trials and field practices will be merged with physical, chemical and biological principles to arrive at a greater understanding of this technology, its potential, its weaknesses and its unknowns. The authors will also strive to illustrate the challenges facing this technology and the research and development required for its advancement. The goal of this book is to provide the reader with this understanding.

1.1. A brief history of foliar fertilization

The ability of plant leaves to absorb water and nutrients was recognized approximately three centuries ago (Fernández and Eichert, 2009). The application of nutrient solutions to the foliage of plants as an alternative means to fertilize crops such as grapevine agriculture was noted in the early 19th century (Gris, 1843). Following this, research efforts were applied to try and characterize the chemical and physical nature of the plant foliar cuticle, the cellular physiology and structure of plant leaves as well as focusing on potential mechanisms of penetration by foliar sprays. With the advent of firstly fluorescent and then radio-labelling techniques in the first half of the 20th century it became possible to develop more accurate methods to investigate the mechanisms of leaf cuticular penetration and translocation within the plant following foliar application of nutrient solutions (Fernandez and Eichert, 2009; Fernandez *et al.*, 2009; Kannan, 2010).

The role of stomata in the process of foliar uptake has been a matter of interest since the beginning of the 20th century. However in 1972 it was postulated that pure water may not spontaneously infiltrate stomata unless a surface-active agent to lower surface tension below 30 mN m⁻¹ is applied with the solution (Schönherr and Bukovac, 1972).

As a consequence of this, most investigations were subsequently carried out on cuticular membranes isolated from adaxial (upper) leaf surfaces of species in which enzymatic isolation procedures could be conducted, e.g. from poplar or pear leaves. Utilizing this system it was found that cuticles are permeable to water and ions as well as to polar compounds (Kerstiens, 2010). Furthermore the occurrence of two distinct penetration pathways in the cuticle, one for hydrophilic and another for lipophilic substances, has been suggested (Schönherr, 2006; Schreiber and Schönherr, 2009).

The proposition that stomata could also contribute to the foliar penetration process was re-assessed by Eichert and co-workers at the end of the 1990's and subsequently validated (Eichert and Burkhardt, 2001; Eichert and Goldbach, 2008; Eichert *et al.*, 1998; Fernandez and Eichert, 2009). At present the quantitative significance of this pathway and the contribution of other surface structures such as lenticels to the uptake of foliar applied solutions remain unclear.

Since its first recorded use in the early 19th century (Gris, 1843), foliar fertilization has been the subject of considerable controlled environment and field research and has become widely adopted as a standard practice for many crops. The rationales for the use of foliar fertilizers include: 1) when soil conditions limit availability of soil applied nutrients; 2) in conditions when high loss rates of soil applied nutrients may occur; 3) when the stage of plant growth, the internal plant demand and the environment conditions interact to limit delivery of nutrients to critical plant organs. In each of these conditions, the decision to apply foliar fertilizers is determined by the magnitude of the financial risk associated with the failure to correct a deficiency of a nutrient and the perceived likelihood of the efficacy of the foliar fertilization.

Furthermore foliar fertilization is theoretically more environmentally friendly, immediate and target-oriented than soil fertilization since nutrients can be directly delivered to plant tissues during critical stages of plant growth. However while the need to correct a deficiency may be well defined, determining the efficacy of the foliar fertilization can be much more uncertain.

2. Mechanisms of penetration into the plant

The processes by which a nutrient solution applied to the foliage is ultimately utilized by the plant include foliar adsorption, cuticular penetration, uptake and absorption into the metabolically active cellular compartments in the leaf, then translocation and utilization of the absorbed nutrient by the plant. From a practical perspective it is often difficult to distinguish between these processes though many trials using the term ‘foliar uptake’ often refer to an increase in tissue nutrient content without directly measuring the relative biological benefit of the application to the plant as a whole. This confusion and imprecision greatly complicates the interpretation of both controlled environment/laboratory and field experimentation and has undoubtedly resulted in inconsistent plant response and general uncertainty in predicting the efficacy of foliar treatments. Therefore the challenges facing practitioners of foliar fertilization and for researchers attempting to understand the factors that determine the efficacy of foliar fertilizers are great.

The aerial surface of the plant¹ is characterized by a complex and diverse array of specialized chemical and physical adaptations that serve to enhance plant tolerance to an extensive list of factors including unfavorable irradiation, temperatures, vapor pressure deficits, wind, herbivory, physical damage, dust, rain, pollutants, anthropogenic chemicals, insects and pathogens. Aerial plant surfaces and structures are also well adapted to control the passage of water vapor and gases, and to restrict the loss of nutrients, metabolites and water from the plant to the environment under unfavourable conditions. These characteristics of aerial plant surfaces that allow them to protect the plant from environmental stress and to regulate water, gas and nutrient exchange also provide the mechanisms affecting the uptake of foliar applied nutrients. Improvements in the efficacy and reproducibility of foliar fertilization requires knowledge of the chemical and physical attributes of plant surfaces and the processes of penetration into the plant.

Aerial plant surfaces are generally covered by a hydrophobic cuticle and very often possess modified epidermal cells such as trichomes or stomata. The outer surface of the cuticle is covered by waxes that may confer a hydrophobic character to the plant’s surface. The degree of hydrophobicity and polarity of the plant surface is determined by the species, chemistry and topography which are also influenced by the epidermal cell structure at a microscopic level. Like leaves, fruits are also protected by a cuticle

¹For simplicity we will use the term ‘aerial plant surfaces’ to mean the external surfaces of all above ground plant organs including stems, leaves, trunks, fruits, reproductive and other above ground organs that can be targeted for foliar application.

and may contain epidermal structures such as stomata² or trichomes³ that influence the transpiration pathway and contribute to its conductance of water (and nutrients) which are critical factor for fruit growth and quality (Gibert *et al.*, 2005; Morandi *et al.*, 2010).

A transverse section of a typical angiosperm leaf consists of a cuticle that covers the upper and lower epidermal cell layers enclosing the mesophyll as illustrated in Figure 2.1 with a microscopic image shown in Figure 2.2.E. Leaves differ in their structure between species but generally consist of palisade parenchyma near the upper epidermis and spongy parenchyma (also referred to as spongy mesophyll) between the palisade layer and the lower epidermis. There are large intercellular spaces among the mesophyll cells, especially in the spongy parenchyma (Epstein and Bloom, 2005). The epidermis is a compact layer with sometimes two or more layers of cells (Figure 2.2.F) and the principal features, related to nutrient and water transport, which characterize the epidermis are the cuticle and the stomata.

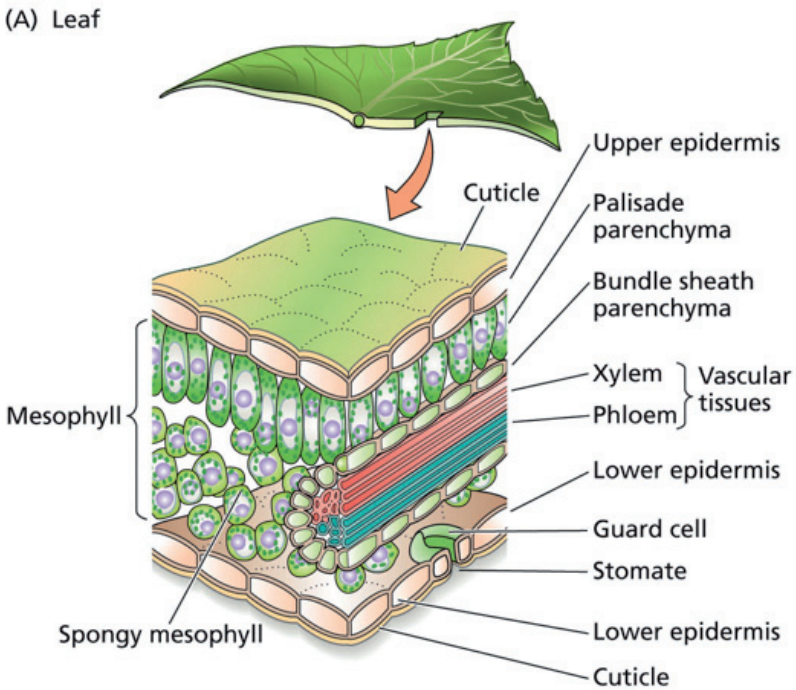


Figure 2.1. Typical structure of dicotyledonous leaf including vascular bundle in a leaf vein. (Reproduced with permission from Plant Physiology, 4th Edition, 2007, Sinauer Associates).

²Stomata are pores surrounded by 2 guard cells that regulate their opening and closure which are present at high densities in leaves and are responsible for gaseous exchange and controlling water transpiration through the plant.

³Epidermal cell hair or bristle-like outgrowth.

The surface topography and transversal structure of a peach leaf and a fruit using Scanning Electron Microscopy (SEM) and optical microscopy after tissue staining is shown in Figure 2.2. Both the peach fruit and leaf surface stained with auramine O is covered by a cuticle that emits a green-yellow fluorescence when observed under UV light (Figure 2.2. C and D). The leaf has a cuticle protecting the abaxial (lower) and adaxial (upper) leaf side and the trichomes on the peach fruit surface are also covered by a cuticle. On the abaxial peach leaf surface, stomata are present (approximately 220 mm⁻²) while only a few (approximately 3 mm⁻²) occur beneath the trichomes covering the peach fruit (Figure 2.2. A and B) (Fernandez *et al.*, 2008a; Fernandez *et al.*, 2011). A

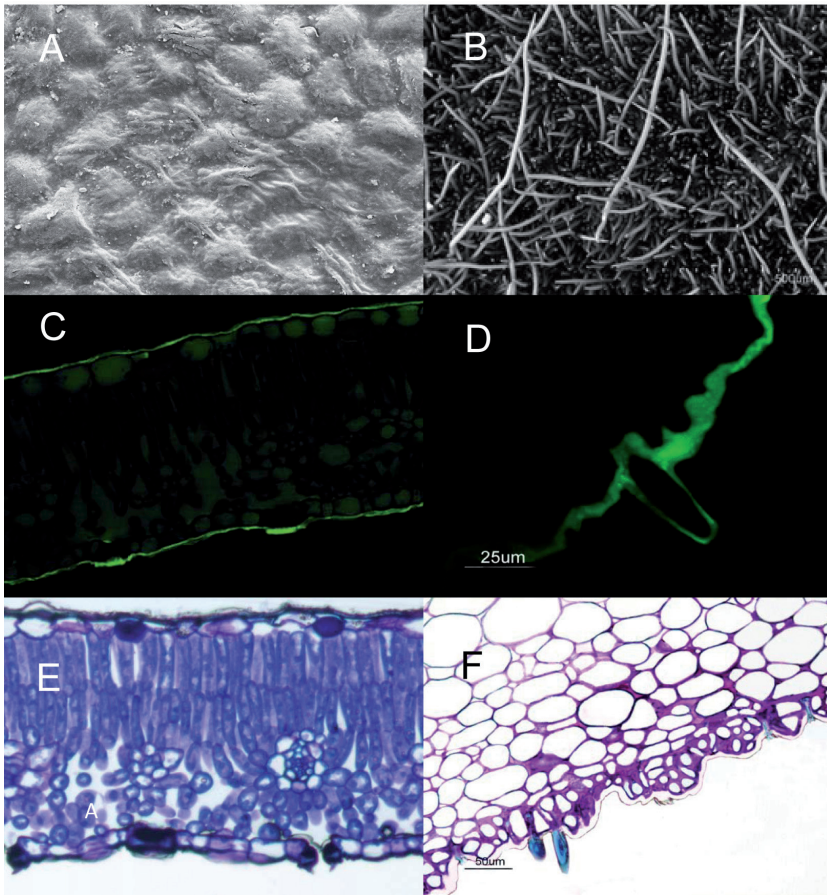


Figure 2.2. Micrographs of a peach leaf *versus* a peach fruit. Surface topography of a leaf (A) and fruit (B) observed by Scanning Electron Microscopy (SEM) (x400). Transversal sections of a peach leaf and a peach fruit after tissue staining with auramine O (UV light observation; C and D) and toluidine blue (light transmission; E and F) (micrographs A and B by V. Fernández; C and E by G. López-Casado; D and F by E. Domínguez).

layer of epidermal cells is observed beneath the abaxial and adaxial leaf cuticle and on top of the mesophyll cells (Figure 2.2. E). A multiserrate, disorganized epidermis with single-celled trichomes is found above the parenchyma cells and underneath the peach fruit surface (Figure 2.2. F).

When present in deciduous plant species, and always in evergreens, the leaves represent the majority of the total surface of the aerial part and will capture most of the spray applied and will also interact with rain water, fog or mist. While the primary function of the plant surface is to protect against dehydration, the permeability of plant surfaces to water and solutes may actually play a crucial eco-physiological role to absorb water under water-limiting conditions (Fernandez and Eichert, 2009; Limm *et al.*, 2009).

- All aerial plant parts are covered by a hydrophobic cuticle that limits the bi-directional exchange of water, solutes and gases between the plant and the surrounding environment.
- Epidermal structures such as stomata, trichomes or lenticels may occur on the surface of different plant organs and play important physiological roles.

2.1. Role of plant morphology and structure

The fundamental requirement for an effective foliar nutrient spray is that the active ingredient penetrates the plant surface so it can become metabolically active in the target cells where the nutrient is required. A foliar applied chemical may cross the plant leaf surface *via* the cuticle *per se*, along cuticular cracks or imperfections, or through modified epidermal structures such as stomata, trichomes or lenticels. The cuticle proves an effective barrier against the loss of water and yet, at the same time, it proves an equally effective one against the uptake of foliar applied chemicals. The presence of cuticular cracks or the occurrence of modified epidermal structures can contribute significantly to the rate of uptake of foliar nutrient sprays. The structure and composition of the plant leaf surface will be briefly described as a basis for understanding their role in the uptake and absorption of foliar applied nutrient sprays.

2.1.1. Cuticles and their specialized epidermal structures

The cuticle covering aerial plant parts is an extra-cellular layer composed of a biopolymer matrix with waxes embedded into (intra-cuticular), or deposited onto (epi-cuticular waxes), the surface (Heredia, 2003). On the inner side, a waxy substance called cutin is mixed with polysaccharide material from the epidermal cell wall, which is chiefly composed of cellulose, hemicellulose and pectin in a ratio similar to that found in plant cell walls. Therefore the cuticle itself can be considered as a 'cutinized' cell wall, which emphasizes the compositional and heterogeneous nature of this layer and its physiologically important interaction with the cell wall underneath (Dominguez *et al.*, 2011).

The cuticle matrix is commonly made of the bio-polyester cutin forming a network of cross-esterified hydroxy C_{16} and/or C_{18} fatty-acids (Kolattukudy, 1980). The composition of the biopolymer matrix may vary depending on the plant organ, species and genotypes, stage of development and growing conditions (Heredia, 2003; Kerstiens, 2010). While cutin is depolymerized and solubilized upon saponification, cuticles from some species may contain an alternative non-saponifiable and non-extractable polymer known as cutan, which yields a highly characteristic series of long chain n-alkenes and n-alkanes upon flash pyrolysis (Boom *et al.*, 2005; Deshmukh *et al.*, 2005; Villena *et al.*, 1999). Recently, Boom *et al.* (2005) determined the presence of cutan in cuticles of drought-tolerant species such as *Agave americana*, *Podocarpus sp.* or *Clusia rosea* and suggested that it might be a preserved biopolymer especially in xeromorphic (water storing) plants. Cutin is the only polymer present in cuticles of the fruits and leaves of many *Solanaceae* and *Citrus* species (Jeffree, 2006) whereas in *Beta vulgaris* cutan is the only polymer forming the leaf cuticular matrix (Jeffree, 2006). Variable proportions of cutin and cutan have been determined in cuticular membranes extracted from leaves of some plant species such as *Agave americana* (Villena *et al.*, 1999) and in some fruit types such as soft-fruit berries, apples and peppers (Jarvinen *et al.*, 2010; Johnson *et al.*, 2007).

The waxes present in the cuticle, either deposited onto, or embedded into, the cuticular matrix are mainly mixtures of long chain aliphatic molecules (mainly C_{20} - C_{40} n-alcohols, n-aldehydes, very long-chain fatty-acids and n-alkanes) and of aromatic (ring-chain) compounds (Samuels *et al.*, 2008). Wax composition has been observed to vary between different plant species and organs, the stage of development and the prevailing environmental conditions (Koch *et al.*, 2006; Kosma *et al.*, 2009).

As well as the cutin and/or cutan matrix and the waxes, variable amounts and types of phenolics may be present in the cuticle either in free form embedded in the matrix or chemically bound to cutin or waxes by ester or ether bonds (Karabourniotis and Liakopoulos, 2005). Hydroxycinnamic acid derivatives (e.g. ferulic, caffeic or p-coumaric acid), phenolic acids (e.g. vanillic acid) and flavonoids (e.g. naringenin) have been determined analytically in epicuticular wax and cuticle matrix extracts and observed by fluorescence microscopy (Karabourniotis and Liakopoulos, 2005; Liakopoulos *et al.*, 2001). Besides the major role of phenols in protection against biotic (microbes or herbivores) and abiotic (UV radiation, pollutants) stress factors, they are also involved in the attraction of pollinators (Liakopoulos *et al.*, 2001).

Many plant surfaces are pubescent⁴ to a greater or lesser degree as shown in Figure 2.3. for soybean, maize and cherry leaf adaxial surfaces. According to Werker (2000), trichomes are defined as unicellular or multicellular appendages which originate from epidermal cells only, and which develop outwards from the surface of various plant organs. Scientific studies on these epidermal structures began in the 17th century with emphasis being placed either on individual trichomes or on the collective properties of the trichome layer referred to as the indumentum (Johnson, 1975). Trichomes can grow on all plant parts and are chiefly classified as “glandular” or “non-glandular”. While “non-glandular” trichomes are distinguished by their morphology, different kinds of “glandular” trichomes are defined by the secretory materials they excrete, accumulate or

⁴A surface covered by trichomes.

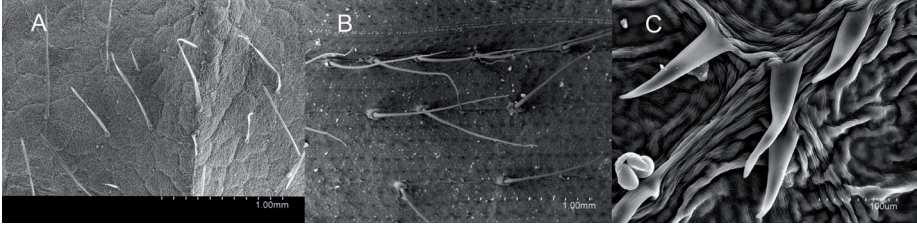


Figure 2.3. Adaxial surface of: (A) soybean; (B) maize; and (C) cherry leaf (Micrographs by V. Fernández, 2010).

absorb (Wagner *et al.*, 2004; Werker, 2000). “Non-glandular” trichomes exhibit a major variability in size, morphology and function and their presence is more prominent in plants thriving in dry habitats and usually on young plant organs (Fahn, 1986; Karabourniotis and Liakopoulos, 2005).

Stomata are modified epidermal cells that control leaf gaseous exchange and transpirational water losses. They are generally present on the abaxial leaf side but in some plant species (known as amphistomatic), including maize and soybean, they also occur on the upper leaf side (Eichert and Fernández, 2011). Stomata also occur in the epidermis of many fruits such as peaches, nectarines, plums or cherries though at lower densities compared to the leaves. Stomatal density, morphology and functionality may vary between different plant species and organs (Figure 2.4) and can be affected by

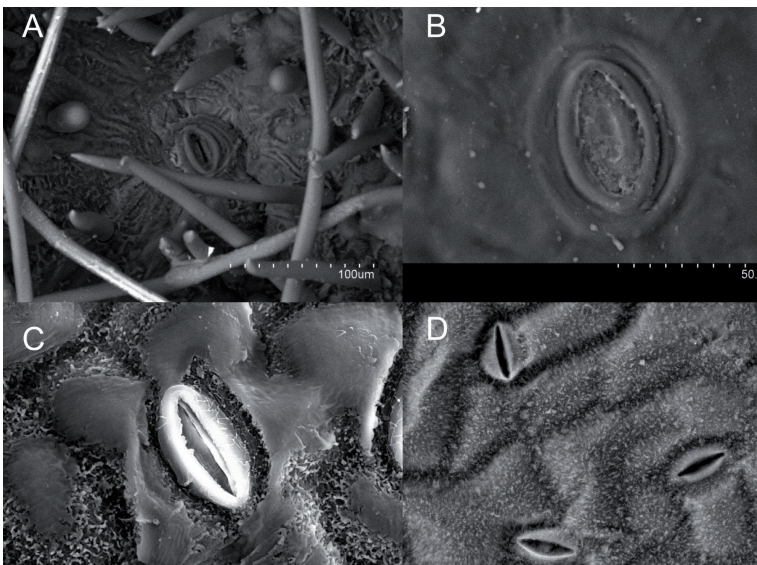


Figure 2.4. Scanning electron micrographs of stomata present on the surface of: (A) peach fruit; (B) cherry fruit; (C) rose abaxial leaf surface; and (D) broccoli abaxial leaf surface (Micrographs by V. Fernández, 2010).

stress factors such as nutrient deficiencies (Fernandez *et al.*, 2008a; Will *et al.*, 2011), or the prevailing environmental conditions such as light intensity and quality as illustrated by changes seen in plants growing in natural or artificial shade (Aranda *et al.*, 2001; Hunsche *et al.*, 2010).

Another example of epidermal structures that occur on plant surfaces are lenticels (Figure 2.5). Lenticels are macroscopic structures that may occur in stems, pedicels or fruit surfaces (e.g. they are present on the skin of fruits such as apple, pear or mango) once the periderm (cork) has formed. Their evolutionary origin has been linked to stomata, epidermal cracks and trichomes (Du Plooy *et al.*, 2006; Shaheen *et al.*, 1981).

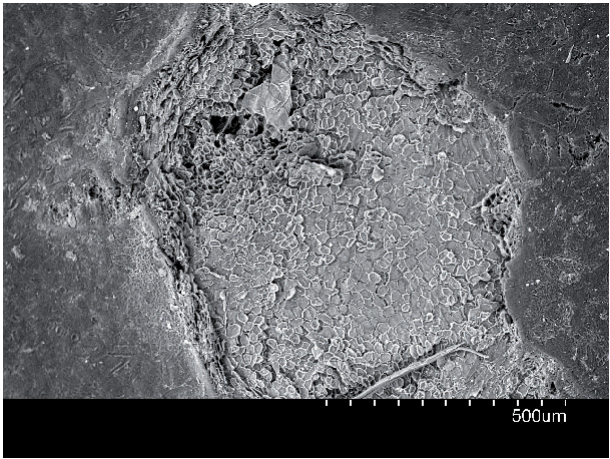


Figure 2.5. Scanning electron micrograph of a lenticel found on the surface of a “Golden Delicious” apple skin (Micrograph by V. Fernández, 2010).

The absorption of nutrient solutions by plant surfaces may occur via:

- The cuticle.
- Cuticular cracks and imperfections.
- Stomata, trichomes, lenticels.

2.1.2. Effect of topography: micro- and nano-structure of the plant surface

The topography of the plant surface, as determined by the composition and structure of the epi-cuticular waxes in glabrous (trichome-free) areas, or by the presence of trichomes or trichome layers in pubescent surfaces, will determine its properties and interactions with water, nutrient solutions, contaminants, micro-organisms, agrochemicals, etc.

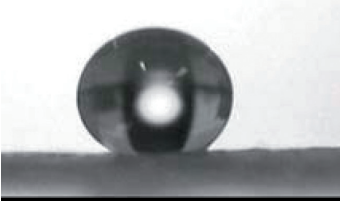
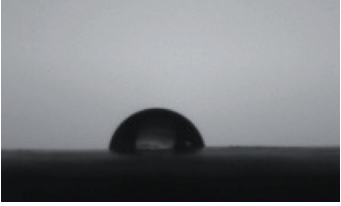


Plant organ and species	Average contact angle with pure H ₂ O (°)	Drop image
Adaxial side of <i>Eucalyptus globulus</i> leaf	140	
Adaxial side of <i>Ficus elastica</i> leaf	83	
'Calanda' Peach (<i>Prunus persica</i> L. Batsch)	130	
Apple (<i>Malus domestica</i> L. Borkh) fruit surface	84	

Figure 2.6. Average contact angles with pure water drops of the adaxial *Eucalyptus globulus* (A) and *Ficus elastica* (B) leaves; and peach (C) and apple (D) fruit surfaces (V. Fernández, 2011).

Plant surfaces have different degrees of wettability when in contact with water droplets as shown in Figure 2.6 for the leaves and fruits of four different plant species.

In the last decade, the water and contaminant repellent properties of plant surfaces with 'rough' topography have been described (Barthlott and Neinhuis, 1997; Wagner *et al.*, 2003) and different types of epicuticular waxes have been classified for several plant species (Barthlott *et al.*, 1998; Koch and Ensikat, 2008).

The presence of a micro- and nano-relief structures associated with the surfaces over the epidermal cells, and the chemical properties of the waxes deposited onto the leaf surface, may markedly increase its 'roughness' and surface area and will ultimately

determine the degree of polarity and hydrophobicity. Differences in surface polarity and hydrophobicity in relation to variable growing conditions, plant species, varieties and organs can be expected and these will have an influence on the effectiveness of foliar sprays. Fernández *et al.* (2011) examined the properties of a peach variety which is covered by a dense indumentum⁵ as a model system for a pubescent plant surfaces. The peach skin investigated was found to be very hydrophobic with contact angles for water higher than 130°. Properties such as the surface free energy, polarity, and work of adhesion of the peach leaf surface was determined by means of estimating the contact angle of three liquids - water, glycerol and di-iodomethane. This methodology has proved a valuable tool for the characterization of plant surfaces and should be further explored and exploited for scientific and applied purposes (Figure 2.6).

2.2. Pathways and mechanisms of penetration

The structure and chemistry of the plant surface will affect the bi-directional diffusion of substances between the plant, the leaf surface and the surrounding environment and hence and therefore the rate of uptake of foliar fertilizers. In the following sections, the most significant plant surface penetration pathways of chemical sprays will be described, with emphasis on the mechanisms of cuticular permeability and stomatal uptake.

2.2.1. Cuticular permeability

The cuticle consists of three layers (Figure 2.7), namely (from the external to the internal surfaces of the plant organ), the epicuticular wax layer (EW), the cuticle proper (CP) and the cuticular layer (CL) (Jeffree, 2006).

The EW layer is the outermost and most hydrophobic component of the cuticle. The CP that lies beneath the epicuticular waxes contains mainly cutin and/or cutan and is by definition free of polysaccharides (Jeffree, 2006). The CL is located under the CP and consists of cutin/cutan, pectin and hemicelluloses that increase the polarity of this layer due to the presence of hydroxyl and carboxylic functional groups. The middle lamellae and pectin layer (ML) is situated beneath the CL. Variable amounts of polysaccharide fibrils and pectin lamellae may extend from the cell wall (CW), binding the cuticle to the underlying tissue (Jeffree, 2006).

A gradual increase in negative charge from the epicuticular wax to the pectin layer creates an electrochemical gradient that may increase the movement of cations and water molecules (Franke, 1967). The intra-cuticular waxes limit the exchange of water and solutes between the plant and the surrounding environment (Schreiber and Schönherr, 2009), while the epicuticular waxes influence the wettability (Holloway, 1969; Koch and Ensikat, 2008), light reflectance (Lenk *et al.*, 2007; Pfündel *et al.*, 2006) and surface properties of the plant organ.

The lipophilic and hydrophobic nature of the structural components of the cuticle make it an effective barrier against the diffusion of hydrophilic, polar compounds. However, lipophilic and a-polar compounds may penetrate the hydrophobic cuticular

⁵A covering of trichomes.

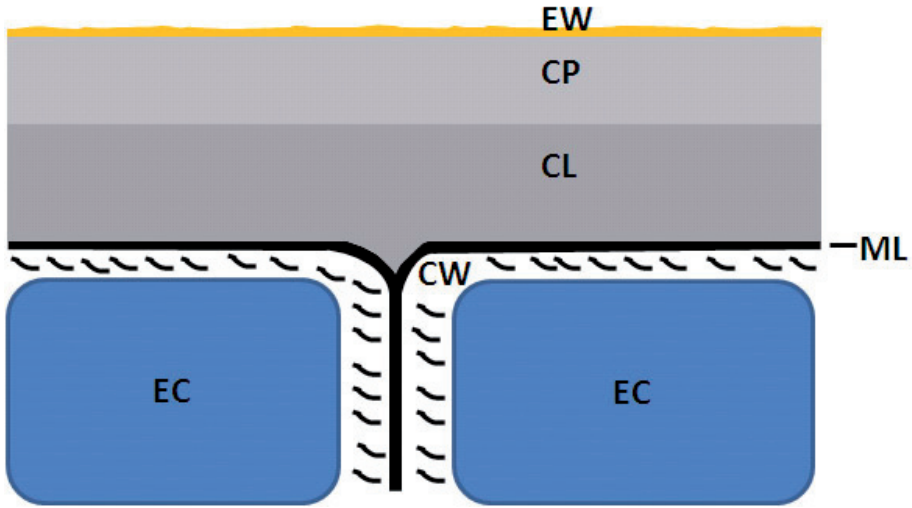


Figure 2.7. Schematic representation of the general structure of the plant cuticle covering two adjacent epidermal cells (EC) separated from each other by the middle lamellae and pectinaceous layer (ML) and the cell wall (CW). Epicuticular waxes (EW) are deposited onto the cuticle proper (CP) which is mainly composed of a biopolymer matrix and intra-cuticular waxes. The cuticular layer (CL) chiefly contains cutin and/or cutan and polysaccharides of the CW.

membrane at high rates compared to polar electrolyte solutions which have not had surface-active agents added to them (Fernandez and Eichert, 2009). Indeed, several studies provide evidence for the penetration of polar solutes through intact astomatous cuticles by direct and indirect means (Heredia, 2003; Riederer and Schreiber, 2001; Tyree *et al.*, 1992).

Experimental evidence has shown that plant cuticles are asymmetric membranes with a gradient of fine structure and waxes from the outer to the inner surface. Plant cuticles have a large inner sorption compartment consisting mainly of the biopolymer matrix (cutin and/or cutan) and a comparably smaller ($\leq 10\%$ of total volume) outer compartment where waxes predominate (Schönherr and Riederer, 1988; Tyree *et al.*, 1990).

The current state of knowledge on the mechanisms of penetration of polar solutes and apolar lipophilic substances through the cuticle will be briefly discussed in the following paragraphs.

The cuticle is an asymmetric membrane composed mainly of 3 layers:

- The epicuticular wax layer.
- The cuticle proper, chiefly made of cutin/cutan and intracuticular waxes.
- The cuticular layer, containing cutin/cutan and polysaccharide material.

Permeability of lipophilic, apolar compounds

The penetration of lipophilic⁶, apolar substances through the plant cuticle has been proposed to follow a dissolution-diffusion process (Riederer and Friedmann, 2006). This model implies that the movement of a lipophilic, apolar molecule from a solution deposited onto the plant surface into the cuticle precedes the diffusion of the molecule through the cuticle (Riederer and Friedmann, 2006). The diffusion of a lipophilic molecule has been proposed to be governed by partitioning and its penetration rate will be proportional to the solubility and mobility of the compound in the cuticle (Riederer, 1995; Schreiber, 2006). At a molecular level, both the dissolution and diffusion of a molecule in the cuticle can be viewed as passing into and between voids in the polymer matrix arising by molecular motion (Elshatshat *et al.*, 2007).

Taking into account Fick's first law, the diffusive flux (J ; molm⁻²s⁻¹) is related to the concentration gradient with solutes moving from regions of high to low concentration with a magnitude that is proportional to the concentration gradient (spatial derivative). According to the cuticular diffusion model, which has been thoroughly explained by Riederer and Friedmann (2006), the diffusive flux J is proportional to the mass transfer coefficient P (i.e. the permeance of the membrane; m s⁻¹) multiplied by the concentration difference between the inner and the outer sides of the cuticle:

$$J = P * (C_i - C_o)$$

where: C_i is the concentration (mol m⁻³) at the inner side of the cuticle and C_o is the concentration in the outer side of the cuticle.

Under certain experimental conditions, the mobility of a molecule can be predicted by calculating the permeance which is a value specific to a given molecule and a particular cuticular membrane (Riederer and Friedmann, 2006). The permeance (P m s⁻¹) is expressed as:

$$P = D * K * l^{-1}$$

where: D (m² s⁻¹) is the diffusion coefficient in the cuticle; K the partition coefficient which is the ratio between the equilibrium molar concentrations in the cuticle and in the solution at the cuticle surface; and l (m) which is the path length of diffusion through the cuticle. The diffusion path length may be tortuous and much larger than the cuticle thickness which is determined by the waxes embedded in the polymer matrix (Baur *et al.*, 1999; Schönherr and Baur, 1994) and by the spatial disposition of cutin and/or cutan molecules (Fernandez and Eichert, 2009). The diffusion coefficient D also depends on the temperature and fluid viscosity of the foliar nutrient solution and size of the chemical molecules it contains.

Methods to predict the mobility of lipophilic, apolar compounds through the cuticle of a few species that enable the enzymatic isolation of astomatous (adaxial) cuticles have been developed in recent decades (Riederer and Friedmann, 2006; Schreiber, 2006; Schreiber and Schönherr, 2009).

⁶Compounds which are soluble in oils, fats, or organic solvents.

Experimental evidence has shown that the cuticle is highly size selective (Buchholz *et al.*, 1998) and that it may act as a “molecular sieve”. The size of voids have been found to follow a log-normal distribution that may be in the same order of magnitude as some agrochemicals which may be limiting their diffusion through the cuticle (Schreiber and Schönherr, 2009).

Permeability of hydrophilic, electrolytes

The permeability of cuticles to solutes has been investigated using astomatous isolated cuticles using the same methodology used to assess the penetration of apolar, lipophilic substances (Schreiber and Schönherr, 2009). In the absence of surface-active agents solutions of ionic, hydrophilic⁷ compounds have generally been found to penetrate the cuticle at a lower rate compared to lipophilic, apolar compounds. This finding is probably explained by the lipophilic nature of the cuticular constituents as well as the ease with which lipophilic compounds will diffuse owing to their higher solubility in such media as compared to hydrophilics. However, some authors have suggested that the rate of penetration of electrolytes determined experimentally is too high to be explained by simple dissolution and diffusion in the cuticle and have proposed that hydrophilic solutes may penetrate through the cuticle *via* a physically distinct pathway, along what have been called “polar, aqueous or water-filled pores” (Schönherr, 2006; Schreiber, 2005; Schreiber and Schönherr, 2009).

It has been hypothesized that such pores may arise from the absorption of water molecules onto polar moieties located in the cuticular layer (Schönherr, 2000; Schreiber, 2005), such as unesterified carboxyl groups (Schönherr and Bukovac, 1972); ester and hydroxylic groups (Chamel *et al.*, 1991) in the cutin network; and carboxylic groups of pectic cell wall material (Kerstiens, 2010; Schönherr and Huber, 1977). However, no conclusive experimental evidence has been found so far to support the presence of such “aqueous pores” in cuticles as they are not visible or identifiable with current microscope technologies (Fernandez and Eichert, 2009).

However the size of the “aqueous pores” of a few plant species has been indirectly derived from permeability trials using astomatous, adaxial cuticles. Diameters of about 1 nm were calculated for de-waxed isolated citrus cuticles (Schönherr, 1976), and isolated ivy (*Hedera helix*) cuticles (Popp *et al.*, 2005). Furthermore, pore diameters ranging from 4 to 5 nm have been calculated from permeability trials carried out with intact coffee and poplar leaves (Eichert and Goldbach, 2008).

- Lipophilic, apolar compounds have been proposed to penetrate cuticles by a solution-diffusion process.
- The mechanisms of penetration by hydrophilic, polar compounds are not fully elucidated yet.

⁷ Water miscible/soluble compounds such as mineral salts, chelates or complexes.

Permeability of stomata and other plant surface structures

The potential contribution of stomata to the penetration of leaf-applied chemicals has been a matter of controversy for many decades (Dybing and Currier, 1961; Schönherr and Bukovac, 1978; Turrell, 1947) and is still not fully understood (Fernandez and Eichert, 2009). Early studies aimed at assessing the process of stomatal uptake suggested that it may occur *via* infiltration i.e. the mass flow of foliar-applied solutions into the leaf interior through the open stomata (Dybing and Currier, 1961; Turrell, 1947; Middleton and Sanderson, 1965). However, Schönherr and Bukovac (1972) showed that the spontaneous infiltration of an open stoma by a foliar-applied aqueous solution could not occur in the absence of an external pressure or a surface-active agent that could lower the surface tension of the solution below a certain threshold (set to 30 mN m⁻¹). Subsequently, many studies have provided evidence for increased uptake rates of plant surfaces where stomata are present, especially when the prevailing experimental conditions were favourable to the opening of the stomatal pores (Eichert and Burkhardt, 2001; Fernandez and Eichert, 2009). Investigations carried out on leaves containing stomata only on the abaxial leaf surface demonstrated higher foliar penetration rates through the abaxial as compared to the adaxial side (Eichert and Goldbach, 2008; Kannan, 2010). Since this observation contradicts the premise of Schönherr and Bukovac (1972) that the higher penetration rates associated with stomatal opening could not be due to the mass flow through the stomatal pores unless the solution's surface tension is below 30 mN m⁻¹, several different hypotheses have been proposed to explain these subsequent observations. For instance, the higher penetration rates in the presence of stomata have been attributed to the increased permeability of the peristomatal cuticle and the guard cells (Sargent and Blackman, 1962; Schlegel and Schönherr, 2002; Schlegel *et al.*, 2005; Schönherr and Bukovac, 1978) but no conclusive evidence supporting this has been forthcoming so far (Fernandez and Eichert, 2009).

The direct contribution of stomata to the process of penetration by foliar-applied aqueous solutions in the absence of surface-active agents has been subsequently re-assessed (Eichert *et al.*, 1998) in investigations on stomatal uptake performed with water-suspended hydrophilic particles (43 nm and 1 µm diameter respectively) using confocal laser scanning microscopy which demonstrated that the treatment solution passed through the stomata by diffusing along the walls of the stomatal pores (Eichert and Goldbach, 2008). This process was reported to be slow and size selective since particles with a diameter of 1 µm were excluded while the 43 nm particles passed into the pores.

The mechanisms of solute movement into fruits has received only limited investigation though several studies have estimated the permeability of apples to Ca solutions either with intact fruits (Mason *et al.*, 1974; Van Goor, 1973), fruit discs (Schlegel and Schönherr, 2002) or isolated cuticular membranes (Chamel, 1989; Glenn and Poovaiah, 1985; Harker and Ferguson, 1988; Harker and Ferguson, 1991). Schlegel and Schönherr (2002) reported a major contribution of stomata and trichomes to the uptake of surface-applied Ca-containing solutions during the early developmental stages of fruits. However after June drop the disappearance of stomata and trichomes

and the sealing of the remaining scars by cutin and waxes may significantly reduce the permeability of fruit surfaces.

There have been a few instances of the assessment of the contribution of trichomes or lenticels on fruits to the process of uptake of surface-applied nutrient solutions. Harker and Ferguson (1988) and others (Glenn and Poovaiah, 1985; Harker and Ferguson, 1991) suggested that lenticels in mature apples were preferential sites for the uptake of Ca solutions through the fruit surface though this possibility has not been assessed in detail so far.

- Stomata may play a major role in the absorption of nutrient solutions applied to the foliage.
- The mechanisms of stomatal penetration by pure water are not yet fully elucidated but recent evidence points towards a process of diffusion along the stomatal pore walls.
- Addition of certain surfactants to the nutrient solution formulation leads to the infiltration of stomata (Chapter 3).

2.3. Conclusions

The state-of-the-art concerning the process of uptake of solutions by plant surfaces has been described in Chapter 2. Plants are covered by a hydrophobic cuticle that controls the loss of water, solutes and gases to the environment though conversely it also prevents their unrestrained entry into the plant interior. The structural and chemical features of the plant surface render it difficult to wetting and therefore permeation by a surface-applied polar nutrient solution. In the light of the current state of knowledge, the following certainties, uncertainties and opportunities for the application of foliar fertilizers can be addressed.

Certainties

- Plant surfaces are permeable to nutrient solutions.
- The ease by which a nutrient solution may penetrate into the plant interior will depend on the characteristics of the plant surface, which may vary with organ, species, variety and growing conditions, and on the properties of the foliar spray formulation applied.
- Plant surfaces usually possess a hydrophobic coating provided by the epicuticular waxes.
- The micro- and nano-relief associated with the structure of the epidermal cells, and the epicuticular waxes deposited onto the surface, together with the chemical composition of these waxes, will determine the polarity and hydrophobicity of each particular plant surface.

- Epidermal structures such as stomata and lenticels, which can be present on the leaves and fruits surfaces, are permeable to surface-applied solutions and may play a significant role in its uptake.
- Apolar, lipophilic substances have been found to cross cuticles via a solution-diffusion process.

Uncertainties

- The mechanisms of cuticular penetration of polar, hydrophilic compounds (i.e. those relating to the uptake of aqueous foliar fertilizers) are currently not fully understood.
- The contribution of the stomatal pathway to the foliar uptake process should be further elucidated as well as the role of other epidermal structures such as trichomes and lenticels.
- Improving the effectiveness of foliar fertilizers will require a better understanding of the contact phenomena at the interface between the liquid (i.e. the foliar fertilizer formulation) and the solid (i.e. the plant surface).
- The effectiveness of foliar nutrient treatments will improve once the mechanisms of foliar uptake are better understood.

Opportunities

- Multiple scientific experiments and applied studies carried out in the last century have shown that plant surfaces are permeable to foliar nutrient fertilizers.
- This permeability presents the opportunity to supply nutrients to plant tissues and organs, by passing root uptake and translocation mechanisms which may limit the nutrient supply of the plant under certain growing conditions.
- Foliar fertilization has great potential and should be further explored and exploited in the future.

3. Physico-chemical properties of spray solutions and their impact on penetration

The absorption of foliar-applied nutrients by the plant surface involves a series of complex processes and events. The main processes involved include formulation of the nutrient solution; the atomization of the spray solution and transport of the spray droplets to the plant surface; the wetting, spreading and retention of the solution by the plant surface; the formation of a spray residue onto the surface; and the penetration and distribution of the nutrient to a (metabolic) reaction site (Young, 1979). The above events are interrelated and overlap in that a change in one usually has an effect on the others, and each process is affected by plant growth stage factors, environmental conditions and application parameters (Bukovac, 1985).

The properties of the spray formulations are crucial in determining the performance of foliar fertilizers, especially since most of the conditions at the time of treatment cannot be fully controlled. Foliar nutrient sprays are generally aqueous solutions containing mineral element compounds as active ingredients. The physico-chemical characteristics of the specific nutrient compound in aqueous solution, such as its solubility, pH, point of deliquescence (POD) and molecular weight will have a major influence on the rate of absorption of the element by the leaf. However, an array of additives that may modify the properties of the fertilizer solution are often included in the formulations with the aim of improving the performance of nutrient sprays. The rate of retention, wetting, spreading and rainfastness of a nutrient foliar spray is governed by the physico-chemical properties of the formulation which can contain chemical compounds with different characteristics that may interact with each other when they are together in aqueous solution.

When an aqueous solution is applied to a leaf, initially there is a high rate of penetration which decreases with time resulting from the drying of the applied solution (Sargent and Blackman, 1962). This drying is influenced by the prevailing environmental conditions and by the formulation of the applied foliar spray solution.

In the following sections, the principal physico-chemical properties of a fertilizer formulation that may affect and improve its performance will be described in theoretical and applied terms.

- Water is the usual matrix of foliar nutrient sprays.
- Plant surfaces are hydrophobic to a greater or lesser degree and the contact area of pure water drops can be limited depending on the characteristics of the surface.
- The prevailing environment will affect the physico-chemical properties and performance of the formulations on the leaf surfaces.

3.1. Factors determining spray retention, leaf wetting, spreading and rate of penetration

Plant responses to foliar fertilizers may be affected by the properties of the spray solution, which determine the success in achieving the absorption and translocation of the applied nutrients into plant organs. While the process of absorption of leaf-applied solutions is complex and currently remains unclear (Chapter 2), the properties of the formulations are associated with strict chemical principles well as by the prevailing environmental conditions (e.g. relative humidity and ambient temperature) at the time of treatment. An account of the principal physico-chemical factors in relation to the foliar application of nutrient solutions will be provided in the following sections.

3.1.1. Concentration

In Chapter 2 it was shown that the current cuticular diffusion models are based on Fick's first law and relate the diffusive flux to the concentration gradient between the outer and the inner parts of the plant surface. The concentration of a nutrient present in a foliar spray will always be significantly higher than the concentration found within the plant organ. Therefore, a concentration gradient will be established when a nutrient solution is applied onto the plant surface and this will potentially lead to the diffusion of the nutrient across the surface. Higher penetration rates in association with increased concentrations of several applied mineral elements have been reported in studies performed with isolated cuticles (Schönherr, 2001) and intact leaves (Zhang and Brown, 1999a; Zhang and Brown, 1999b). However, the relationship between concentration of the applied solution and foliar penetration rates is currently not fully understood. A negative correlation between increasing Fe-chelate concentrations and the penetration rate through isolated cuticles and intact leaves, expressed as a percentage of the amount applied, has been observed (Schlegel *et al.*, 2006; Schönherr *et al.*, 2005). A similar negative correlation has been reported for foliar-applied K (Ferrandon and Chamel, 1988) and other elements (Tukey *et al.*, 1961). It is hypothesized that the decrease in relative penetration rates with higher K concentrations may be due to a progressive saturation of the uptake sites (Chamel, 1988). As an alternative hypothesis, Fe-salts and chelates may reduce the size of the hydrophilic pathway by inducing the partial dehydration of the pores in the cuticle (Schönherr *et al.*, 2005; Weichert and Knoche, 2006a; Weichert and Knoche, 2006b).

The ideal concentration range of mineral nutrient solutions for foliar application should be selected according to factors such as the kind of nutrient (e.g. macro- or micro-nutrient), plant species, plant age, nutritional status and weather conditions (Kannan, 2010; Wittwer and Teubner, 1959; Wojcik, 2004), and all of these will ultimately be limited by the need to avoid phyto-toxicity.

3.1.2. Solubility

Before applying a foliar spray formulation, it is crucial that the compounds it contains are appropriately dissolved or suspended. Foliar fertilizers are commonly dissolved or suspended in water and contain as active ingredients chemical compounds as salts,

chelates or complexes of mineral nutrients. The solubility of a chemical compound in a specific solvent (usually water) at a given temperature is a physical property which can be altered through use of additives. The highest limit of the solubility of a substance in a solvent is referred to as the saturation concentration where adding more solute does not increase solution concentration. Water solubility of the applied substance is a key factor for foliar uptake, since absorption will occur only when the applied compound is dissolved in a liquid phase on the plant surface that will subsequently diffuse into the plant organs.

3.1.3. Molecular weight

The size of the nutrient molecule in solution will affect the rate of penetration of a foliar fertilizer as a consequence of the mechanism of cuticular absorption. It has been suggested that water and solutes cross the cuticle *via* aqueous pores (Schönherr, 2006) or in an aqueous continuum (Beyer *et al.*, 2005), and a few studies have estimated the *radii* of such pores by indirect means. The *radii* of cuticular aqueous pores has been estimated at approximately 0.3 to 0.5 nm in leaves and 0.7 to 1.2 nm in fruits of some species (Beyer *et al.*, 2005; Luque *et al.*, 1995; Popp *et al.*, 2005; Schönherr, 2006). However, larger pore radii between 2 and 2.4 nm have been calculated for the cuticle of coffee and poplar leaves by Eichert and Goldbach (2008). Several experiments with different solutes and cuticular membranes have shown that the process of cuticular permeability is size-selective with high molecular weight (larger) compounds being discriminated against low molecular weight molecules (Schreiber and Schönherr, 2009).

Recent evidence (Eichert and Goldbach, 2008) suggests that the foliar uptake pathway is less size selective than would be predicted by the cuticular penetration route of entry which may indicate that there is a stomatal pathway (Chapter 2). However the process of stomatal uptake is also size-selective since particles with a diameter of 1 μm did not enter the stomatal pore whereas particles of 43 nm diameter did penetrate into the stomata (Eichert and Goldbach, 2008).

3.1.4. Electric charge

Salts are electrolytes and will dissociate into free ions when dissolved in water with the final solution being electrically neutral. Anions and cations present in aqueous solution will be hydrated or solvated to different degrees depending upon their physico-chemical characteristics. The same phenomena will apply for nutrients supplied as chelates or complexes since with few exceptions most of these compounds are not neutral and will therefore be ionized when dissolved in water. For example, many of the Fe-chelates available on the market are negatively charged (Fernandez and Ebert, 2005). At a pH > 3 plant cuticles are negatively charged (Schönherr and Huber, 1977) and cell walls have charges corresponding to dissociated weak acids (Grignon and Sentenac, 1991). Consequently uncharged or electron-charged compounds and anions can penetrate the leaf and are translocated in the apoplast⁸ easier than positively-charged complexes or cations.

⁸ Non-living, extracellular space surrounding the living cells (i.e. the symplast).

However, when applying salts or chelates or complexes, the latter two being formed by mixing metal salts with ligands accompanied with their own corresponding ions, the anions and cations present in solution can penetrate into the leaves. The nature of the anions and cations in the foliar applied solution will have physiological significance and must be considered when designing a foliar spray formulation.

3.1.5. Solution pH

Since plant cuticles are poly-electrolytes, their ion exchange capacity will be altered with pH fluctuations (Chamel and Vitton, 1996). Cuticles were shown to have iso-electric points around pH 3 and when solution pH values are higher than this they will render the cuticle negatively charged and the cuticular carboxyl groups will then readily bind positively charged cations (Schönherr and Bukovac, 1972; Schönherr and Huber, 1977).

While it is clear that the pH of the spray solution alters penetration there is no consistency in plant response and it appears that the pH of the solution alone is not that predictive of penetration and is influenced more significantly by the nutrient being applied and the plant species being treated. In most of the scientific reports on foliar fertilization usually no reference is made to the pH of the nutrient spray solution applied to the foliage which is a critical oversight particularly in the case of pH unstable mineral elements such as Fe. Cook and Boynton (1952) recorded the greatest absorption of urea by apple leaves in the pH range 5.4 to 6.6. Furthermore the highest uptake rates by citrus leaves after foliar urea treatment were recorded when the pH of the solution was kept between 5.5 to 6.0 (El-Otmani *et al.*, 2000). Working with Fe compounds, Fernandez *et al.* (2006) and Fernandez and Ebert (2005) observed that pH values around 5 were optimal for foliar uptake of Fe-containing solutions. Blanpied (1979) showed that maximum Ca absorption by apple leaves occurred when the solution pH ranged from 3.3 to 5.2. However, Lidster *et al.* (1977) reported the highest Ca absorption rates by sweet cherry (*Prunus avium* L.) fruits when CaCl₂ solution of pH 7 was applied. Reed and Tukey (1978) observed maximum P absorption by chrysanthemum leaves when the solution pH was between 3 to 6 for Na-phosphate and between 7 to 10 pH for K-phosphate.

Frequently foliar spray salts dissolved in pure water will alter spray solution pH and some formulations may have extreme pH values and hence will affect the uptake process of by the foliage. For instance the majority of Fe(III)-salts are very acidic while 1% CaCl₂ or 8% K₂SO₄ have pH values above 9.

3.1.6. Point of deliquescence

The processes of hydration and dissolution of a salt are determined by its point of deliquescence (POD) which is a physical property associated with a compound at a given temperature (Schönherr, 2001). Deliquescent salts are hygroscopic substances (i.e. capable of trapping water from the surrounding environment) and will dissolve once a critical relative humidity threshold has been attained. The point of deliquescence is defined as the relative humidity value at which the salt becomes a solute. Thereby, the lower the point of deliquescence of a salt is, the sooner it will dissolve upon exposure to ambient relative humidity (Fernandez and Eichert, 2009). When ambient relative

humidity is higher than the point of deliquescence of the foliar applied compound, the substance will dissolve and will be available for absorption by the leaf. The effect of relative humidity on the solution or crystallization of salts has been assessed in studies carried out with cuticular membranes and intact leaves and could be better explored following the experimental practices used in aerosol research (Fernandez and Eichert, 2009). Similarly, the physiological effects associated with the deposition of hygroscopic aerosol particles onto plant surfaces are currently not fully understood, but it is considered that such particles may either act as leaf desiccants or promote increased uptake rates (Burkhardt, 2010).

3.2. Environment

Environmental factors such as relative humidity and temperature will play a role with regard to the performance of a foliar sprays and the uptake of leaf-applied solutions. Environment can also alter foliar spray efficacy through its influence on the biology of the plant - a process that will be discussed in Chapter 4.

The most relevant environmental factors affecting the performance of solutions when sprayed to the foliage will be described, considering that under field conditions, continuous interaction between such factors will result in different physiological and physico-chemical responses and effects. The effect of the environment on foliar uptake-related phenomena will be discussed in more detail when describing the biological factors affecting the efficacy of foliar fertilization in Chapter 4. Here the two environmental factors that most directly affect the performance of foliar nutrient sprays are temperature and relative humidity.

Relative humidity is a major factor influencing foliar uptake of nutrient sprays since it affects the permeability of the plant surface and the physico-chemical responses to applied compounds. At high relative humidity permeability may be increased due to cuticular hydration and the delayed drying of the salts deposited onto the plant surface following the application of a foliar spray. Salts with points of deliquescence above the prevailing relative humidity in the phyllosphere⁹ will theoretically remain as solutes and leaf penetration will be prolonged.

Temperature will affect various physico-chemical parameters of the foliar spray formulation such as its surface tension, solubility, viscosity or point of deliquescence. In general, increasing temperature range (e.g. from 0 to 40°C) under any field conditions will increase solubility of the active ingredients and adjuvants, but will decrease viscosity, surface tension and the point of deliquescence. In addition, high temperatures will speed the rate of evaporation from the spray solutions deposited onto the foliage reducing the time until solution dryness occurs when leaf penetration can no longer occur.

Other environmental factors such as light intensity or precipitation may also affect the performance of foliar nutrient sprays. For instance, several Fe(III)-chelates are known to be degraded by exposure to sun-light. On the other hand, the occurrence

⁹ The aerial part of plants that can serve as a habitat for microorganisms.

of precipitation shortly after the application of a foliar spray may rapidly wash-off the treatment. As a consequence, weather forecasts should be taken into consideration prior to foliar spray applications to avoid conditions that can reduce humidity or increase drying speed such as high winds, heavy rain or extremes of temperature at the time of foliar application.

3.3. Formulations and adjuvants

Commercial foliar nutrient sprays are generally composed of at least two major components, namely: the active ingredient(s) and the inert material(s) or adjuvant(s). Adjuvants help to improve the spreading (wetting) and persistence (sticking) of the active ingredient(s) or mineral element(s) on the leaf surface as well as promote the rate of uptake and bioactivity of the mineral element(s) applied. Limitations to the foliar uptake of applied mineral elements has led to the widespread use and continuous search for adjuvants that improve the performance of spray treatments. In the following paragraphs information on the active ingredients and adjuvants will be provided.

3.3.1. Mineral compounds applied as foliar sprays

A preliminary distinction should be made concerning the application of either macro- or micro-nutrients, the latter being supplied at lower rates and concentrations and often being unstable when applied as inorganic salts. An account of the most common mineral element carriers according to recent articles is shown in Tables 3.1 and 3.2. The foliar fertilizer industry is characterized by a large number of proprietary products that are frequently derived from common salts which can be occasionally mixed in novel ratios and/or with addition of compounds that serve to ‘complex, chelate or bind’ and/or adjuvants that can ‘enhance’ efficiency of uptake.

Table 3.1. Macro-nutrient carriers normally used in foliar spray formulations.

Macronutrient	Common element compounds	References
N	Urea, ammonium sulphate, ammonium nitrate	Zhang <i>et al.</i> (2009); Fageria <i>et al.</i> (2009)
P	H ₃ PO ₄ , KH ₂ PO ₄ , NH ₄ H ₂ PO ₄ , Ca(H ₂ PO ₄) ₂ , phosphites	Noack <i>et al.</i> (2011); Schreiner (2010); Hossain and Ryu (2009)
K	K ₂ SO ₄ , KCl, KNO ₃ , K ₂ CO ₃ , KH ₂ PO ₄	Lester <i>et al.</i> (2010), Restrepo-Díaz <i>et al.</i> (2008)
Mg	MgSO ₄ , MgCl ₂ , Mg(NO ₃) ₂	Dordas (2009a), Allen (1960)
S	MgSO ₄	Orlovius (2001), Borowski and Michalek, (2010)
Ca	CaCl ₂ , Ca-propionate, Ca-acetate	Val and Fernández (2011); Wojcik <i>et al.</i> (2010); Kraemer <i>et al.</i> (2009a,b).

Table 3.2. Micro-nutrient carriers normally used in foliar spray formulations.

Micronutrient	Common element compounds	References
B	Boric acid (B(OH) ₃), Borax (Na ₂ B ₄ O ₇), Na-octoborate (Na ₂ B ₈ O ₁₃), B-polyols	Will <i>et al.</i> (2011); Sarkar <i>et al.</i> (2007), Nyomora <i>et al.</i> (1999)
Fe	FeSO ₄ , Fe(III)-chelates, Fe-complexes (lignosulphonates, glucoheptonates, etc.)	Rodríguez-Lucena <i>et al.</i> (2010a, 2000b); Fernández <i>et al.</i> (2008b); Fernández and Ebert (2005); Moran (2004)
Mn	MnSO ₄ , Mn(II)-chelates	Moosavi and Ronaghi (2010), Dordas (2009a), Papadakis <i>et al.</i> (2007), Moran (2004)
Zn	ZnSO ₄ , Zn(II)-chelates, ZnO, Zn-organic 'complexes'	Amiri <i>et al.</i> (2008); Haslett <i>et al.</i> (2001), Moran (2004); Zhang and Brown (1999).

Until the 1970's, the foliar micronutrient fertilizer market was dominated by products based on inorganic compounds particularly sulphates (Moran, 2004). During the 1980's a wide variety of micronutrient 'chelates' and 'complexes' (e.g. synthetic chelates using EDTA, glucoheptonates, polyols, amino-acids, or lignosulphonates, among many other types) were offered as an alternative to the application of inorganic compounds.

The recommended rates at which foliar fertilizers are used are highly variable and are usually based on the specific plant species being treated. As previously described the physico-chemical properties of the active ingredients, e.g. molecular size, solubility or point of deliquescence, will influence the rate of uptake by foliage. In general, synthetic chelates are much larger and have higher points of deliquescence than the inorganic mineral salts commonly used as active ingredient carriers. While some materials are recommended on the basis of rigorous controlled environment and extensive field trials, many frequently utilize rates designed to merely ensure safety and satisfy cost concerns. Optimal concentration rates for the many and varied foliar fertilizers available for different crops are currently lacking and future research efforts should focus on trials to establish clear concentration thresholds for foliar-applied nutrient solutions.

Foliar-applied nutrient solutions could be phytotoxic due to their high osmotic potential and pH by affecting important physiological processes such as photosynthesis and/or stomatal opening (Bai *et al.*, 2008; Elattal *et al.*, 1984; Fageria *et al.*, 2009; Kluge, 1990; Swietlik *et al.*, 1984; Weinbaum, 1988). These effects can be a critical factor for consideration when spraying macro-nutrient fertilizers to the foliage.

3.3.2. Formulation additives: adjuvants

General information

As described in Chapter 2, plant surface topography may vary between plant species and varieties, organs and growing conditions. The presence, chemistry and topography of epicuticular waxes and epidermal structures such as trichomes may render the surface difficult to wet. Under such circumstances, the proper wetting, spreading

and penetration of foliar fertilizers may require the addition of co-formulants such as surface-active agents (adjuvants) that modify the properties of the spray solution. Numerous foliar and cuticular uptake studies have shown the improved efficacy of formulations containing adjuvants that act by enhancing the wetting, spreading, retention, penetration and humectant properties of foliar sprays as compared to pure mineral element solutions applied alone. Therefore the formulation of mineral element solutions with adjuvants can have a significant effect on the uptake and bioactivity of the nutrients supplied to the foliage though this may also decrease or increase the phytotoxicity risk associated with the nutrient active ingredients applied. This implies a fine-tuning of the nutrient active ingredients and the adjuvant compounds and their relative concentration which is necessary to develop a foliar nutrient formulation that provides reproducible plant uptake responses without plant damage.

Adjuvants can be defined as any substance included in a formulation or which is added to the spray tank that modifies the nutrient active ingredient activity or the spray solution characteristics (Hazen, 2000). They are generally classified as; (i) activator adjuvants (e.g. surface active agents) which increase the activity, penetration, spreading and retention of the active ingredient or; (ii) utility adjuvants (e.g. acidifiers) that modify the properties of the solution without directly affecting the efficacy of the formulation (Penner, 2000).

Although there are many commercially adjuvant co-formulants on the market (Table 3.3) there is considerable confusion concerning the classification of such compounds and their purported mode of action (Green and Foy, 2000).

Adjuvant names are usually related to the major properties they confer upon the spray formulations to which they are added. However the categorization and distinction between activator and utility adjuvants is rather subjective and currently lacks standardization. For instance, adjuvants described as ‘penetrators’, ‘synergists’ or ‘activators’ may increase the rate of foliar uptake through different chemical or physical mechanisms though the general principle of enhanced spray absorption is the same. Adjuvants described as “buffering agents” or “neutralizers” are generally chemical systems that adjust and stabilize spray solution pH; while other surfactants may be referred to as “detergents”, “wetting agents”, or “spreaders”; but again for both types the general principles are the same. There are several adjuvant types usually referred to as stickers that increase solution retention and rainfastness and some of these may also prolong or retard the process of solution drying when included in foliar sprays.

Humectants are compounds with water-binding properties which can be either organic, such as carboxy-methyl cellulose (Val and Fernandez, 2011), or inorganic, such as CaCl_2 . Their presence in the formulation lowers the point of deliquescence (POD) and prolongs the process of solution drying which is especially important to increase the efficacy of foliar sprays in arid and semi-arid growing regions. Some types of “surface-active” agents or “utility” adjuvants such as stickers or humectants can also act to increase the rate of retention and rain fastness of foliar applied formulations (Blanco *et al.*, 2010; Kraemer *et al.*, 2009b; Schmitz-Eiberger *et al.*, 2002) which can be particularly important in regions of high rainfall or where frequent overhead irrigation is employed. Typical examples of stickers and humectants are latex and soy lecithin

Table 3.3. Example of adjuvants available on the market classified according to their purported mode of action.

Adjuvant name on label	Proposed mode of action
<i>surfactant</i>	lowering surface tension
<i>wetting agent</i>	equivalent to "surfactant"
<i>detergent</i>	equivalent to "surfactant"
<i>spreader</i>	equivalent to "surfactant"
<i>sticker</i>	increasing solution retention; rainfastness
<i>retention aid</i>	increasing solution retention; rainfastness
<i>buffering agent</i>	pH buffering
<i>neutraliser</i>	pH buffering
<i>acidifier</i>	lowering pH
<i>penetrator</i>	increasing the rate of foliar penetration (e.g. by 'solubilizing' cuticular components)
<i>synergist</i>	increasing the rate of foliar penetration
<i>activator</i>	increasing the rate of foliar penetration
<i>compatibility agent</i>	improving formulation compatibility
<i>humectant</i>	retarding solution drying by lowering the formulation's point of deliquescence (POD) on the leaf
<i>drift retardant</i>	better spray targeting and deposition on foliage
<i>bounce and shatter minimizer</i>	better spray targeting and deposition on foliage

both of which can significantly improve the retention of foliar sprays on leaves and are frequently included in commercial formulations of many plant protection products although there is an apparent lack of sound information concerning the effectiveness of such adjuvants when used with foliar fertilisers.

The reasons underlying this are that considerable research efforts have been made in recent decades to develop adjuvants for foliar spray formulations which enhance the performance of pesticides and herbicides while less attention has been paid to developing products specific for foliar nutrient sprays. Adjuvants are usually marketed separately and may contain single compounds (e.g. "surface-active" agents alone) or are sold as mixtures of surfactants, lecithin, synthetic latex, vegetable oils, tallow amines or fatty acid esters that confer a spectrum of the desired properties outlined previously when included in a foliar-applied solution.

As a consequence since most commercial adjuvant products have been devised for their application in combination with plant protection products to facilitate their performance when applied to the foliage, their suitability for combination with foliar nutrient sprays, which are normally hydrophilic solutes, cannot be *a priori* assumed and should therefore always be empirically tested. For foliar nutrient sprays it is critical that the treatments are not phytotoxic to leaves and plants since their value and marketability

can be compromised by crop damage caused by such treatments. Unfortunately it is not currently possible to predict theoretically the performance of any active ingredient whether a herbicide, a pesticide or a mineral nutrient element in combination with a particular adjuvant (Fernandez *et al.*, 2008a; Liu, 2004).

Surfactants

Surface-active agents or surfactants are the most widely-used type of adjuvant in foliar spray formulations. One of the first examples of these compounds being added to foliar nutrient sprays was in the first half of the 20th century with the use of the ionic surfactant Vatsol in combination with Fe compounds (Guest and Chapman, 1949).

One method used to assess the effect of a surfactant is to measure the contact angle with a paraffined microscope slide and the drop shape by the pending drop method comparing the surface tensions of pure water (A and B) with a 0.1% organosilicon surfactant solution (C and D) as shown in Figure 3.1.

These measurements were carried out at 25°C and the contact angles (Figure 3.1 A and C) for water and a 0.1% organosilicon surfactant solutions were approximately 95° and 45° respectively giving calculated surface tensions of approximately 72 and 22 mN

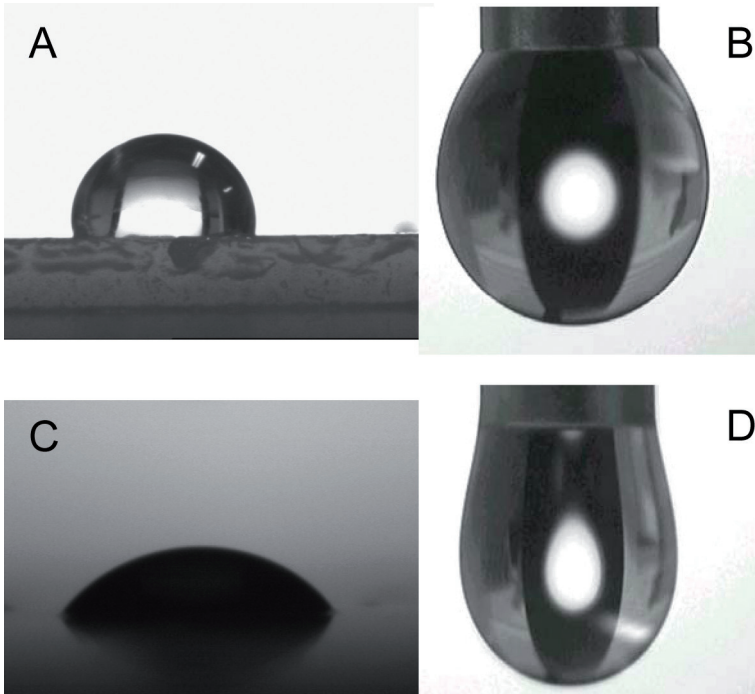


Figure 3.1. Contact angles (A and C) and pending drops used to calculate the surface tension (B and D) of distilled water (A and B) and a 0.1% organosilicon (C and D) distilled water solution (V. Fernández, 2011).

respectively. This experimental system demonstrates how the addition of a surfactant to a pure water solution lowers its surface tension and increases dramatically the area of contact between the liquid and the solid (in this case a paraffined surface) by lowering the contact angle.

Surfactants are large molecules consisting of a non-polar, hydrophobic portion attached to a polar, hydrophilic group (Cross, 1998; Tadros, 1995). It is important that the ends of the hydrophobic and the hydrophilic parts of the surfactant molecule are far away from each other so that they can react independently of each other with surfaces and solvent molecules (Cross, 1998). The hydrophobic part of the surfactant interacts weakly with water molecules while the polar or ionic head group interacts strongly with these so rendering the surfactant molecule water soluble.

Surface active agents are characterized by the abrupt change in their physical properties they undergo once a certain concentration has been reached. These changes in solubility, surface tension, equivalent conductivity or osmotic pressure are due to the association of surfactant ions or molecules in solution to form larger units. These associated units are called micelles and the concentration at which this association takes place is known as the critical micelle concentration. Each particular surfactant molecule has a characteristic critical micelle concentration value for a given temperature and concentration.

The mechanisms of action of surfactants when applied to the foliage are very complex and are only partially understood (Wang and Liu, 2007) although possible modes of surfactant action have been suggested by Stock and Holloway (1993) and include: increasing the effective contact area of deposits; dissolving or disrupting epicuticular waxes; solubilizing agrochemicals in deposits; preventing or delaying crystal formation in deposits; retaining moisture in deposits; and promoting stomatal infiltration. However, it is now known that surfactants can also alter the diffusion of substances *via* cuticular solubilization or hydration and that they can also affect the permeability of the plasma membrane. Therefore surfactant composition and concentration are key factors influencing the performance of foliar sprays (Stock and Holloway, 1993).

The hydrophilic portion of a surfactant can be non-ionic, ionic or zwitterionic, accompanied by counter-ions in the last two cases. When present in a foliar spray formulation the polarity of the hydrophilic part of a surfactant may determine factors such as the occurrence of interactions between the surfactant and the active ingredients or the contact properties between the spray solution and each particular plant surface.

Non-ionic surfactants

Non-ionic surfactants are widely used in foliar sprays as they are theoretically less prone to interact with other polar components of the formulation. The most common hydrophilic polar group in non-ionic surfactants is that based on ethylene oxide (Tadros, 1995) with the organosilicons, alkyl phenol ethoxylates, alkyl-polyglucosides, fatty alcohol ethoxylates, polyethoxylated fatty acids, ethoxylated fatty amines, alkanolamides or sorbitan esters belonging to this group of surfactants.

An example of a non-ionic surfactant molecule is shown in Figure 3.2.

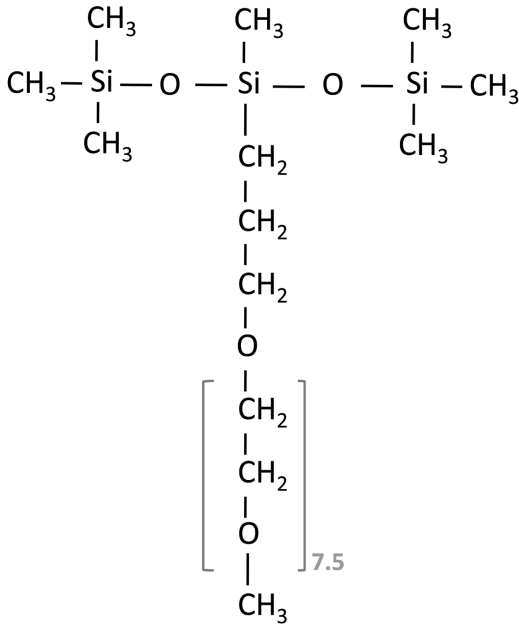


Figure 3.2. Molecular structure of the non-ionic surfactant, Silwet® L-77.

According to Stock and Holloway (1993) the addition of non-ionic surfactants with low ethylene oxide contents, which are good spreaders with their low surface tensions, will favour the uptake of lipophilic pesticides; while conversely uptake of hydrophilic pesticides is improved by surfactants with higher ethylene oxide units and therefore poor spreading properties. However, conflicting evidence concerning the effect of high and low ethylene oxide containing surfactants suggests that ethoxylated surfactants may enhance the uptake of both hydrophilic and lipophilic compounds by different mechanisms as yet not fully clarified (Haefs *et al.*, 2002; Kirkwood, 1993; Ramsey R. J. L., 2005). For example, low ethylene oxide-content surfactants that enhance uptake of lipophilic compounds were found to alter the physical properties of cuticles and to be more phytotoxic. By contrast, surfactants with higher ethylene oxide contents appear to increase cuticular hydration and to be less phytotoxic (Coret and Chamel, 1993; Ramsey, 2005; Uhlig and Wissemeier, 2000). Surfactants with either large hydrophobic groups or long hydrophilic chains, or both, have been reported to be less phyto-toxic because of their lower water solubility and hence, slower rate of foliar uptake (Parr, 1982). Studies performed with Ca-containing compounds (CaCl₂ and Ca-acetate) in combination with ethoxylated rapeseed oil surfactants with different ethylene oxide contents (Kraemer *et al.*, 2009a; Kraemer *et al.*, 2009b; Schmitz-Eiberger *et al.*, 2002) showed that they can affect the rate of cuticular permeability of Ca *via* the distribution of the active ingredient in the droplet and the rain-fastness of the formulations. Organosilicon, non-ionic surfactants, also known as super-spreaders, are a group of

chemicals containing alkylsiloxane groups as the hydrophobic moiety (Knoche, 1994). Owing to their low surface tension (well below 30 mN m^{-1} and generally between 20 to 25 mN m^{-1}) such surfactants are known to promote stomatal infiltration (Knoche, 1994; Schönherr *et al.*, 2005; Stevens, 1993) and increase leaf wetting and spreading that reduces solution retention by the foliage due to the formation of a thin liquid film and increased run-off by the spray solution. The effect of nutrient foliar sprays containing organosilicon surfactants has been assessed in several foliar uptake studies (Fernandez *et al.*, 2008a {Horesh, 1981 #1568}; Horesh and Levy, 1981; Neumann and Prinz, 1975; Neumann and Prinz, 1974) and a high phytotoxicity-risk due to increased penetration rates has often been observed suggesting that such compounds should be used with caution (i.e. at lower concentrations and/or by reducing the active ingredient dose) to avoid leaf burn and potential defoliation.

In spite of being non-ionic, several investigations showed that this type of surfactant (e.g. containing organosilicons, alcohol ethoxylates or triglyceride ethoxylates) can interact with mineral element ions present in foliar nutrient solutions and alter their performance by salting-in or salting-out of surfactant molecules or resulting in the formation of polymers (Fernandez and Eichert, 2009; Knoche, 1994; Uhlig and Wissemeier, 2000). The interaction of mineral nutrient compounds with surfactants may lead to the loss of surface tension as has been observed for the organosilicon surfactant Silwet® L-77 in the presence of ferric-citrate (Knoche *et al.*, 1991; Neumann and Prinz, 1975). On the other hand, the interaction between the divalent cations Ca^{2+} and Mg^{2+} (supplied as CaCl_2 and MgSO_4) and surfactant molecules reduced the phytotoxicity of 0.1% Triton® X-100 and Genapol® C-80 when applied to *Euphorbia pulcherrima* leaves and bracts (Uhlig and Wissemeier, 2000).

Ionic surfactants

Ionic surface-active agents are widely used in formulations devised for cleaning purposes such as detergents, shampoos or washing powders but they are of limited relevance in agriculture since most nutrients are delivered as ionized compounds (e.g. nutrient salts) which may interact and bind to the ionic surfactant molecules and thereby alter their surface-active performance.

The hydrophilic portion of an ionic surfactant can be either anionic or cationic. Anionic surfactants may possess one or more functional groups which become(s) ionized in solution and generate the negatively-charged organic ions responsible for lowering surface tension. This group of surfactants is probably the most widely used and includes various chemical compound groups such as alkyl-sulphates, alkyl-phosphates and alkyl-polyether sulphates and also paraffin-, olefin- and alkylbenzene-sulphonates and sulphate esters. The sulphate ester groups (C-O-S) attaching the hydrophilic head to the surfactant is easily hydrolysed to the corresponding alcohol and sulphate ion by dilute acids while the stronger C-S bond of sulphonate groups is much more stable and will be broken only under extreme chemical conditions (Cross, 1998).

Cationic surfactants have one or more functional groups which becomes ionized in solution to generate positively-charged organic ions and therefore they are incompatible with anionic surfactants. The most representative cationic surfactants are based on

quaternary ammonium, alkyl-ethoxylate-ammonium or alkyl pyridinium compounds which have been found to have anti-microbial properties (Badawi *et al.*, 2007).

Zwitterionic or amphoteric surfactants

This kind of surface-active agents contains both anionic and cationic head groups and can be anionic, cationic or non-ionic depending on the pH of the solution. These surface-active agents are milder as compared to other surfactants and are often used in cosmetics and 'soft' household chemicals in combination with other additives. Examples of commonly used zwitterionic surfactants are alkyl-betaines and lecithin and there are a number of commercially available adjuvant mixtures which use soya lecithin as the major ingredient.

- Mineral element carriers can be applied alone or in combination with a variety of adjuvants that may improve the contact properties, rate of absorption and surface distribution of the active ingredient(s) when applied to the foliage. Surfactants are an important and widely used group of adjuvants that reduce the surface tension of nutrient solutions as well as generally improve their wetting and spreading onto the plant surface.
- Some adjuvants like surfactants, penetration synergists, stickers and humectants may increase the rate of uptake, retention and retard the rate of drying of foliar nutrient sprays.

3.4. Conclusions

In this chapter the current state of knowledge about the physico-chemical properties of foliar nutrient spray formulations and of the factors which can affect such properties has been provided. Since plant surfaces are hydrophobic to a lesser or greater degree depending on the plant species, organ and growing conditions, pure water (unformulated) solutions are limited in their uptake by the foliage. Therefore it is important to formulate foliar sprays with appropriate forms of nutrients and adjuvants to take into account these physico-chemical properties and limitations so that the overall efficacy of foliar fertilizers can be optimized.

With this current knowledge base, the following certainties, uncertainties and opportunities for the application of foliar fertilizers can be addressed.

Certainties

- There is abundant empirical and scientific evidence to demonstrate that to varying degrees pure water and formulated nutrient solutions can be taken up by plant foliage.

- The hydrophobic character of plant surfaces impairs the rate of uptake of pure water nutrient solutions compared to formulations containing additives that reduce surface tension, increase retention and humectancy.
- While higher nutrient concentration solutions can be supplied without adjuvants their efficacy will be lower compared to foliar spray treatments co-formulated with adjuvants and furthermore they may also be more phytotoxic to leaves.
- Environmental factors such as relative humidity and/or ambient temperature will affect the physical properties and performance of a foliar fertilizer formulation and these should be taken into consideration before applying spray treatments under field conditions.

Uncertainties

- The physico-chemical parameters that govern foliar uptake are poorly understood.
- Interactions between nutrients and adjuvants occur and are not fully understood.
- While the performance of a particular nutrient carrier can be improved by addition of surfactants and/or other additives, it is currently not possible to determine accurately which adjuvant or additive will be most effective, or to determine the optimum rates of their addition, without empirical testing.

Opportunities

- Increased understanding of the mechanisms of nutrient penetration into leaves will provide better targets for the development of foliar fertilizer formulations with improved efficacy and safety.
- Improved understanding of the properties of formulation additives, their interactions with nutrients and their effects on leaf structure and chemistry will also help improve the efficacy and reproducibility in performance of foliar sprays.
- The addition of humectants to foliar fertilizer formulations helps to prolong the process of solution drying which can improve the efficacy of the spray treatments especially in arid and semi-arid regions.

4. Environmental, physiological and biological factors affecting plant response to foliar fertilization

4.1. Introduction

The response of plants to the foliar application of nutrients varies not only between species and cultivars but also depends upon the plant's phenology, the physiological status and the environment in which the plant is growing. Understanding these responses is key to optimizing the efficacy and reproducibility in performance of foliar fertilizers (Kannan, 2010; Marschner, 2012; Weinbaum, 1988).

The physical and physiological characteristics of a plant can alter the efficacy of foliar fertilization in two ways; differences in canopy surface area and the characteristics of the plant surface have a quantitative impact on the amount of applied nutrient that penetrates the surface barriers; while differences in physiological processes (uptake, storage and retranslocation) alter both the immediate and long-term biological efficacy of the nutrient once it has entered the plant.

The environment also influences the efficacy of foliar fertilizers through direct effects on the physico-chemical properties of the spray on the leaf surface (Chapter 3), and by affecting biological processes in the plant over both the immediate and long-term. The immediate conditions of light, temperature and humidity at the time of foliar application affect plant metabolic status and hence may directly influence absorption processes across the leaf surface and from within the internal leaf spaces. Environmental conditions following application can determine the persistence of the treatments on leaf surfaces and affect nutrient redistribution within the plant following their absorption. Over a longer time frame, the environment in which a plant is growing can alter the efficacy of foliar fertilisers through its effect on leaf surface characteristics, the size and composition of the canopy, and its effect on plant nutrient status, morphology and physiology. These interactions are summarized in Table 4.1.

The complexity of the possible interactions between the environment and the biology of the plant on the efficacy of foliar applications greatly complicates the conduct and interpretation of field research and hence their agronomic efficacy. Historically, there have been relatively few studies of nutrient foliar applications that have directly characterized the environmental determinants of uptake integrated with the physiological basis of the observed plant response and consequently this has limited the development of broadly applicable, biologically-based guidelines for the use of foliar fertilizers in diverse crops.

Table 4.1. The physical structure and physiology of the leaf and the plant canopy interact with the local environment affecting retention, absorption and utilization of foliar-applied fertilizers.

Leaf age, leaf surface, leaf ontogeny, leaf homogeneity and canopy development	Physical structure of the leaf affects spray retention	hairs, trichomes, surface architecture stomatal distribution and density presence of discontinuities (lenticels, cracks...)
	Chemical composition of the leaf affects penetration, distribution, absorption and 'availability' of foliar-applied nutrients	cuticle thickness, cuticle composition apoplast binding and complexation
	The physiological state of the leaf at the time of spraying affects nutrient assimilation and mobilization	leaf expansion and source/sink status leaf senescence and remobilization
Plant architecture and metabolic status	Canopy architecture and phenology have a quantitative effect on spray retention and penetration	canopy size and leaf age distribution new growth, presence of leaf or floral buds, presence of reproductive structures
	Plant metabolic activity and crop phenology affect uptake and remobilizations	shoot and root growth activity alters demand and source:sink dynamics metabolic status of plant affects availability of substrate and energy for absorption and assimilation
Short- and long-term environmental interactions	Temperature, light, humidity	immediate effects on energy and metabolites required for nutrient absorption, metabolism and transport long-term effects on physical and chemical properties of leaf and plant
	Plant nutrient status alters leaf structure and physiology and may alter leaf assimilation of foliar applied nutrients	
	Biotic and abiotic stress (pests, temperature, water)	

The purpose of this chapter is to review the existing literature on the role of the environment and biology in foliar fertilization efficacy and to use this information to identify common principles and knowledge gaps.

4.2. Leaf age, leaf surface, leaf ontogeny, leaf homogeneity and canopy development

There is considerable evidence from field and laboratory studies that leaf and plant age can have a significant impact on the efficacy of foliar application of nutrients. These effects may reflect differences in ultrastructure, chemical and physical properties and metabolic state of the leaf as described earlier, but may also be a result of differences in the physiological status of the plant which acts to alter the availability of energy and substrate for absorption and assimilation as well as the rate at which absorbed nutrients are translocated out of the leaf (Weinbaum, 1988). When interpreting field studies that show an effect of leaf age on efficacy of foliar fertilization it is critical to consider possible confounding effects of environment (temperature, light, humidity) that generally vary coincident with plant and canopy development and consequently act to reduce the surface area available for spray retention.

A number of studies have shown that rates of uptake of applied chemicals by leaves declines with leaf age from initiation to full expansion (Sargent and Blackman, 1962; Zhang and Brown, 1999b). This may also be followed by a period of increasing permeability as mature leaves begin to senesce. For example, uptake of N from ^{15}N labelled urea and KNO_3 on a per unit leaf area of *Citrus paradisi* L. cv. Redblush was 1.6 to 6 fold greater for two month old leaves than for six month old leaves. In studies using isolated cuticles of Marsh grapefruit (*Citrus paradisi* Macfad), transcuticular movement of urea decreased as leaf age increased from three to seven weeks, but permeability increased in cuticles from leaves older than nine weeks (Orbovic *et al.*, 2001). In these studies, cuticle thickness, weight per area and the contact angle of urea solution droplets increased as leaves aged.

Though most researchers have focused on N in these studies, the effect of leaf age on foliar absorption has been observed for other elements. Walker (1955) reported a higher P absorption by young apple leaves than old ones; and immature pistachio and walnut leaves absorbed 55 and 25% more Zn than fully expanded leaves (Zhang and Brown, 1999b). Olive plants sprayed with three KCl concentrations (0.2 and 4%) showed a positive linear response to increasing leaf K applications and that foliar K uptake was higher in young than in mature leaves of olive and French prune (Restrepo-Diaz *et al.*, 2009; Southwick *et al.*, 1996).

Many researchers in diverse crops and environments have made the observation that the gross quantity and composition of the cuticle and the epicuticular waxes varies with leaf development, and have hypothesized that this variation with age influences foliar uptake (Hull *et al.*, 1975; Leece, 1976; Rhee *et al.*, 1998; Riederer and Friedmann, 2006; Swietlik and Faust, 1984; Zhang and Brown, 1999b). While correlations between absorption and gross changes in cuticles clearly occur, this is not sufficiently mechanistic to be considered causal. The difficulty in interpreting the role of gross cuticular characteristics on foliar absorption is illustrated by the contrast in foliar absorption by diverse species whose leaves frequently exhibit gross differences in cuticle structure, wax percentages and composition but these differences are poorly predictive of foliar absorption capacity.

To better understand the relationship between cuticle composition and foliar absorption as affected by leaf age, Riederer (1995) analyzed the change in specific waxes in *Fagus sylvatica*. In this species, the distribution of aliphatic¹⁰ wax constituents, within the maximum range of C₂₈ and C₅₂ (number of carbon atoms), shifted within 20 days after bud expansion to a large single maximum of C₂₈ waxes when the leaf reached final size (Riederer and Friedmann, 2006). Unfortunately, the physiological relevance of these changes was not determined. During leaf expansion of *Prunus laurocerasus*, the average chain length of alcohols and fatty acids of epicuticular waxes increased from C₂₄ to approximately C₃₂ (Bringe *et al.*, 2006; Jetter and Schaffer, 2001) which altered the wettability of cuticles (Chapter 2). In apples, this coincided with the decrease in height of cuticular ridges or 'wrinkles' (about 0.8–1.0 µm in height in youngest leaves), especially above the lumen of epidermal cells (Bringe *et al.*, 2006). In leaves and fruits of citrus, the same shift in wax composition during leaf expansion was observed and was coincident with a corresponding decline in wax concentration per unit of leaf area (Freeman *et al.*, 1979). During ontogenesis of peach leaves, the individual wax mass as well as the composition of major components (triterpenes and alkanes), and the average chain lengths of alcohols increased with leaf ontogenesis while the absolute amounts of alcohols largely remained constant or slightly increased (Bukovac *et al.*, 1979).

The cuticular wax of the adaxial surface of apple leaves was analyzed under controlled growth conditions for their chemical composition, micro-morphology and hydrophobicity just as the leaf unfolded (Bringe *et al.*, 2006). With increasing leaf age, the hydrophobicity of the adaxial leaf surface decreased significantly. The contact angles of solutions with the leaf surface also decreased with age, facilitating the absorption of solutes. The amount of apolar cuticular wax per unit area was lower in older than in young leaves. A similar effect was detected for the ester fraction: the C₄₀:C₅₂ ratio was approximately 1:1.1 for the youngest leaf, and changed to 1:5 for the oldest one. These changes decreased the hydrophobicity of adaxial leaf surfaces and were associated with a decrease in the total amount of extractable surface waxes as well as modifications in the composition of wax compounds. The accumulation of OH-functional groups also seems to play an important role in increasing leaf wettability with leaf age. This effect may be explained by the increased polarity of the mature surface due to the accumulation of hydroxyl groups (Fernandez *et al.*, 2011). In agreement with Bringe *et al.* (2006), Hellmann and Stosser (1992) observed no consistent effect of leaf age or cultivar on total wax mass in apple (*Malus domestica* Borkh), while the proportion of alkanes and esters decreased during leaf ontogenesis and primary alcohols increased.

The conflicting results on the effect of leaf age on foliar absorption that are reported by different researchers are certainly a consequence of the species and the environment in which the experiments were conducted. The difference in response between field and laboratory research is striking. Bringe *et al.* (2006) observed that, in all stages of leaf development for apples grown in the laboratory, the wax mass of adaxial cuticles of the leaves remained low (10–15 µg cm⁻²) as compared to about 280 µg cm⁻² (total wax mass) and 76 µg cm⁻² (epicuticular waxes) for apple leaves grown in the field (Hellmann and Stosser, 1992). The conclusions derived from research focused on one leaf surface or

¹⁰Organic compounds with an open chain structure, for instance, n-alkanes

species must also be considered with caution; in *P. laurocerasus* total cuticular waxes on the adaxial ($280 \mu\text{g cm}^{-2}$) were much less than on the abaxial ($830 \mu\text{g cm}^{-2}$) leaf surface (Jetter and Schaffer, 2001), and significantly greater than amounts detected for field grown *Malus domestica* (Hellmann and Stosser, 1992) which are 30 times greater than total cuticular waxes in laboratory grown *Malus domestica*. The differences in cuticular wax between these field and laboratory grown plants is a result of integrated differences in many factors including temperature, humidity, UV light, dust, mechanical strain, leaf phenology and other biotic and abiotic stresses.

- Leaf cuticular composition changes with leaf age and varies with species and the environment.
- Changes in leaf cuticular composition corresponds with changes in efficacy of foliar-applied fertilizers.
- It is not currently possible to predict how changes in leaf cuticular composition will alter the efficacy of foliar-applied fertilizers.
- With these uncertainties, empirical testing of foliar fertilizers is essential to ensure efficacy and safety.

It is well documented that the abaxial leaf surface takes up mineral nutrients more rapidly than the adaxial surface. According to Hull (1970), the greater nutrient absorption by the abaxial leaf surface results from the presence of a thinner cuticular membrane and a large number of stomata. Fernández *et al.* (2008) observed that adaxial cuticles isolated from pear leaves were thicker in contrast to abaxial ones, though the significance of abaxial cuticle characteristics in the uptake of foliar-applied fertilizers is currently unclear and requires further investigation. The theory that abaxial cuticles are thinner and therefore uptake will be more rapid has been inadequately validated as the majority of studies have been conducted with adaxial cuticles to avoid the complexities associated with the presence of stomata. Schlegel and Schönherr (2002) examined four plant species and observed that, during the first 24 hours, the absorption of Ca^{2+} by the abaxial leaf surface was much higher than that of the adaxial. In contrast, Boynton *et al.* (1954) concluded that both leaf surfaces differ only in the rate of nutrient absorption and not in their total absorption capacity. This conclusion was based on the observation that urea absorption by the abaxial leaf surface was rapid within the first 24 hours and then decreased rapidly. The adaxial leaf surface absorbed urea steadily for seven days after which the rate of this absorption was similar to the abaxial leaf surface (Boynton, 1954). Leaf surface influenced Zn adsorption but not Zn absorption in pistachio and had no effect on either Zn adsorption or absorption in walnut (Zhang and Brown, 1999a).

In addition to changes in leaf cuticle composition, the number of trichomes and the composition of the exudates also change with leaf development (Valkama *et al.*, 2004). Density of both glandular and non-glandular trichomes decreased drastically with leaf expansion although their numbers per leaf remained constant or decreased

as they were shed (Schönherr and Schreiber, 2004). These results suggest that the final number of trichomes in a mature leaf is established early in development. Therefore the functional role of trichomes is likely to be most important at the early stages of leaf development when density is highest. However, since changes in trichome number occur simultaneous with changes in cuticular waxes, it is difficult to directly quantify the contribution of trichome density to foliar absorption as the leaf ages.

At the whole plant level, differences among species in patterns of leaf development, canopy expansion and bearing habit also affect the homogeneity of the leaf canopy by altering the leaf population at a given age at any point in time. For example, in peach (*Prunus persica* L. Batch) the canopy is borne mainly on long shoots with shoot growth and leaf expansion continuing throughout the growing season (Gordon and Dejong, 2007). On the other hand, the canopy of apple (*Malus domestica* L.) and almond (*Prunus amygdalus* L.) trees consists mainly of short shoots and development of the leaf canopy is essentially complete within a month (Lakso, 1980). There is also a distinct difference between evergreen and deciduous trees, with evergreen trees (eg. *Citrus* sp. *Olea europea*) maintaining their leaves for more than a year with growth occurring in flushes during discrete periods. In many annuals, including the major cereal crops, plant growth and leaf expansion continues from first leaf expansion through flowering until seed set, at which time leaf senescence commences in the oldest leaves and progresses to the youngest leaves.

Young trees growing under high levels of fertility and water availability show a longer period of shoot extension and persistence of the leaf canopy (Ramos *et al.*, 1984) while conversely total canopy area and size of leaves is adversely affected by nutrient deficiencies or water deficit (Chabot and Hicks, 1982). Variability in light intensity and spectral distribution within the canopy may also result in non-uniformity of the foliage within the canopy. The distribution of light within the canopy may be influenced by various cultural practices such as tree spacing, rootstocks and pruning (Jackson and Palmer, 1980). Also, leaf senescence is delayed in exposed compared to shaded parts of the canopy.

The uptake and redistribution of foliage-applied nutrients varies with the heterogeneity of leaves (Weinbaum, 1988). Experiments on foliar applications of urea in both almond (Weinbaum, 1988) and olive (Barranco *et al.*, 2010) made in June/July, or later, had a greater response than April applications. Fisher (1952) and Barranco *et al.* (2010) interpreted this effect as a result of a greater leaf area available for urea absorption. The export of N from foliage-applied urea to immature leaves is reduced when applied early in the season because of a greater incorporation of N into leaf protein in developing foliage. In contrast, N applied in the late season does not stimulate protein formation and shows increased mobility to other plant parts as leaf senescence occurs (Klein and Weinbaum, 1984). The effect of leaf age on the absorption and transport of foliar-applied nutrients can be directly attributed to the stage of leaf transition from being a sink for photosynthates produced in mature tissues to then becoming a source of photosynthates for newly developing sinks.

“The transition from sink to source status is one of the key events in leaf development. When a leaf is about half grown it stops importing phloem-mobile nutrients from the rest of the plant and begins to export its own products of photosynthesis. This shift in transport direction, which is largely irreversible, involves major changes in the way metabolites are transported to and from the leaf mesophyll through plasmodesmata and via transporters. The import of nutrients ceases when plasmodesmata in large veins are lost or narrowed preventing phloem-unloading. Export begins when the minor veins mature and begin to unload sugars and other compounds into the phloem. The uni-directional nature of loading is a consequence of sucrose transporter orientation in the plasma membrane of phloem cells, or of the trapping of raffinose family sugars in those species that load through plasmodesmata.” (Turgeon, 2006)

In view of leaf ontogeny, leaves are not physically or physiologically capable of exporting nutrients until after they have matured and likewise old leaves are incapable of importing nutrients following maturation. This view is consistent with older literature in which radioactive ^{32}P was applied as a foliar treatment to bean leaves of sequentially younger age and the transport of the applied labelled P monitored 48 hours later by placing plants on X-ray films (Figure 4.1). The application of ^{32}P to mature leaves (A and B) resulted in rapid transport of the labelled P containing products to young developing leaves and roots. With application to successively younger leaflets (C), transport out of the treated leaf is reduced and restricted to the nearest sink tissue (apical shoot meristems) with no ^{32}P transported to root; while application to immature leaves (D) resulted in 100% retention of the labelled P in the treated leaf. While the timing with which leaves transition from sink to source varies between species and environments, the effect of this transition on the ability of leaves to export foliar-applied nutrients is a general principle that should be considered when designing and interpreting foliar applications.

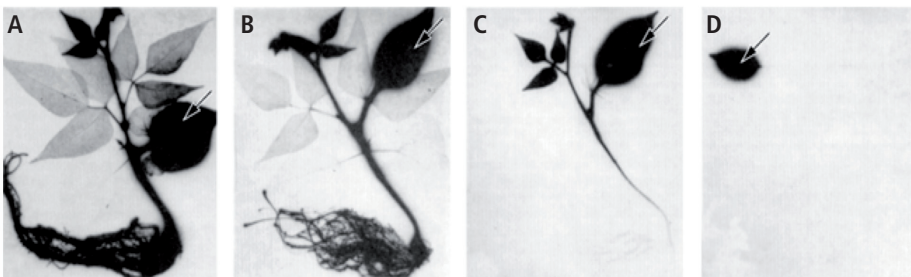


Figure 4.1. ^{32}P was applied to the indicated leaf (arrow) by immersion. 24 hours after exposure, plants were placed on X-ray film and the distribution of the labelled P was illustrated.

Collectively these results illustrate the difficulty in interpreting studies of leaf age, leaf cuticular structure and plant phenology on foliar absorption. In the absence of biotic and abiotic factors, it is apparent that (at the single leaf scale) the proportion of cuticular waxes on a leaf area basis decreases with time as leaves expand more quickly than new cuticular matter is synthesized. In field conditions, this pattern may be reversed as light, temperature, humidity, mechanical stresses and other abiotic and biotic factors stimulate cuticular synthesis while restricting leaf expansion. The complexity of the interactions between leaf age and foliar absorption are further complicated by simultaneous changes in leaf metabolism and nutrient export that occur during development, as well as patterns of crop phenology which determine leaf age distribution, canopy architecture and relative competition between organs. It is also very difficult to compare results from diverse experiments since true physiological leaf age is highly dependent on growth conditions and simultaneous changes in deposition of cuticular materials, leaf expansion and the accumulation of mechanical and biotic stresses (pathogens and herbivory) which all act to alter foliar absorption capacity. When rapid leaf export of a phloem mobile nutrient is occurring care should be taken to ensure quantification of the rate of absorption by measuring both nutrient recovery in the treated area as well as in sink organs.

- The influence of leaf age and the environment on the efficacy of foliar applications is complex and currently no universal principles can be discerned.
- Leaves of diverse species exhibit gross differences in cuticle structure, wax percentages and composition but these differences are poorly predictive of foliar absorption capacity.
- The effect of leaf age on the absorption and transport of foliar-applied nutrients can be directly attributed to leaf transition from a sink for photosynthates to a source of photosynthates for newly developing sinks.
- At the whole plant level differences in patterns of leaf development, canopy expansion and bearing habit affect the homogeneity of the leaf canopy and hence alter the population of leaves of a given age at any point in time.
- The rates of uptake of applied chemicals by leaves declines with leaf age from initiation to full expansion and may increase again during leaf senescence.

4.3. Plant species and variety

While there have been a large number of reports that demonstrate differences in foliar absorption between species, very few of these studies have identified the mechanism underlying them. Klein and Weinbaum (1985) examined urea absorption by the leaves of olive (*Olea europea* L.) and almond (*Prunus dulcis* Mill. D.A. Webb) and found that olive absorbed 15 times more urea than almond per unit leaf area. Amongst fruit trees, examples of varietal differences in response to foliar N application have been seen for

peach, plum, apple and citrus. Van Goor (1973) showed significant differences in Ca^{2+} absorption by apples of different varieties, with 'Cox's Orange Pippin' absorbing five times more Ca^{2+} than 'James Grieve'. Wojcik *et al.* (2004) indicated that an increase in apple fruit Ca^{2+} concentration as a result of foliar Ca^{2+} application depended on variety. For example, 'Idared' apples took up less Ca^{2+} than 'Jonagold' and 'Gloster'.

The mechanism by which species differ in response to foliar sprays was investigated by Picchioni *et al.* (1995) who showed that the rate of B absorption by apple leaves was two to three times higher than that of pear, plum and sweet cherry. Genotypic differences in shoot leaf surface characteristics, among the species tested, was found to influence greatly the amount of solution retained per unit leaf area. Leaf retention varied between species, with apple retaining significantly more B on a leaf area basis than pear, plum and sweet cherry (Figure 4.2). On average, apple shoot leaves retained, absorbed and exported at least twice as much labeled B per unit leaf area as prune and pear shoot leaves; and three to four times as much as sweet cherry shoot leaves. These differences in the quantity of B absorbed by the leaves and the amount of B exported from the leaves (Figure 4.3) may be attributed to the occurrence on the apple leaves of abundant epidermal hairs that help retain the applied solution (Picchioni and Weinbaum, 1995). These observations are in agreement with others (Brewer *et al.*, 1991; Fernandez *et al.*, 2011; Hesse and Griggs, 1950) who found a significant influence of trichomes upon the degree of surface wetting of the different plant surfaces.

The rate at which a nutrient is removed from the leaf in the phloem will also influence tissue nutrient levels observed hours or even days following foliar application. Boron application in apple and almond, for which there is a substantial remobilization of applied B out of the leaves and movement into fruiting tissues (Picchioni and Weinbaum, 1995), generally results in a lower long-term leaf B concentration than the application of an equivalent treatment to pistachio or walnut in which B is immobile. This difference in relative mobility of B is the result of the formation of specific B-sorbitol compounds in apple and almond but not in walnut or pistachio (Brown and Shelp, 1997). Therefore under these circumstances leaf tissue analysis for B content performed hours or even days after foliar treatment will result in the false conclusion that walnut and pistachio absorbed more B than apple or almond.

Differences in rate of re-mobilization of absorbed nutrients may also explain differential response of species to Fe-chelates. Schlegel *et al.* (2006) reported that penetration of Fe-IDHA into stomatous leaf surfaces differed among plant species. The decrease in slopes with time was most conspicuous with apple and grapevine leaves. Penetration plots were linear with broad bean and Madagascar jasmine but not with the other species tested. The previous authors suggested that if Fe-chelates accumulate under the cuticle and are not translocated rapidly then rate constants would decrease with time.

Species difference in utilization of foliar nutrients is undoubtedly related to the physical and chemical composition of the leaf surface. For example, the recovery and absorption of applied Zn by walnut was less than pistachio (Zhang and Brown, 1999b). This low effectiveness is associated with a highly hydrophobic cuticular wax layer in

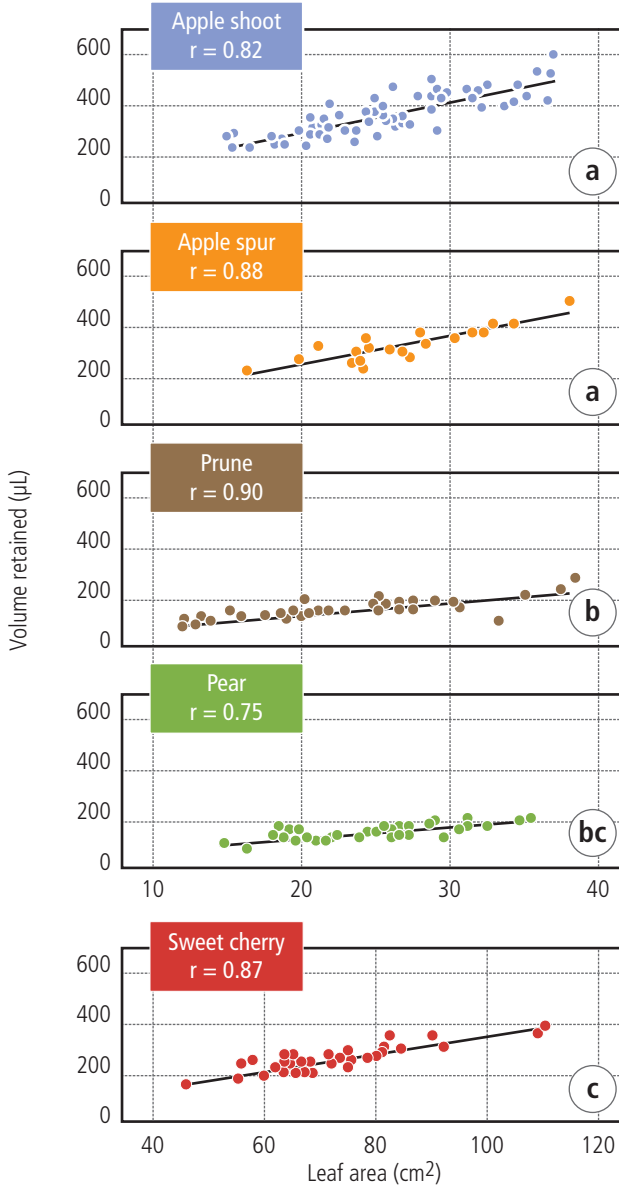


Figure 4.2. Relationship between leaf area per single leaf and the total volume of B treatment solution (1000 mg B/liter + 0.05% Triton X-100) retained per leaf. Cultivars from top: 'Red Delicious' Apple, 'French' prune, 'Bartlett' pear and 'Bing' sweet cherry. All data correspond to shoot leaves unless specified. Regression lines with the same letter have slopes that are not significantly different at $P=0.05$. Each correlation coefficient is significant at $P=0.01$ (Adapted from Picchioni and Weinbaum, 1995).

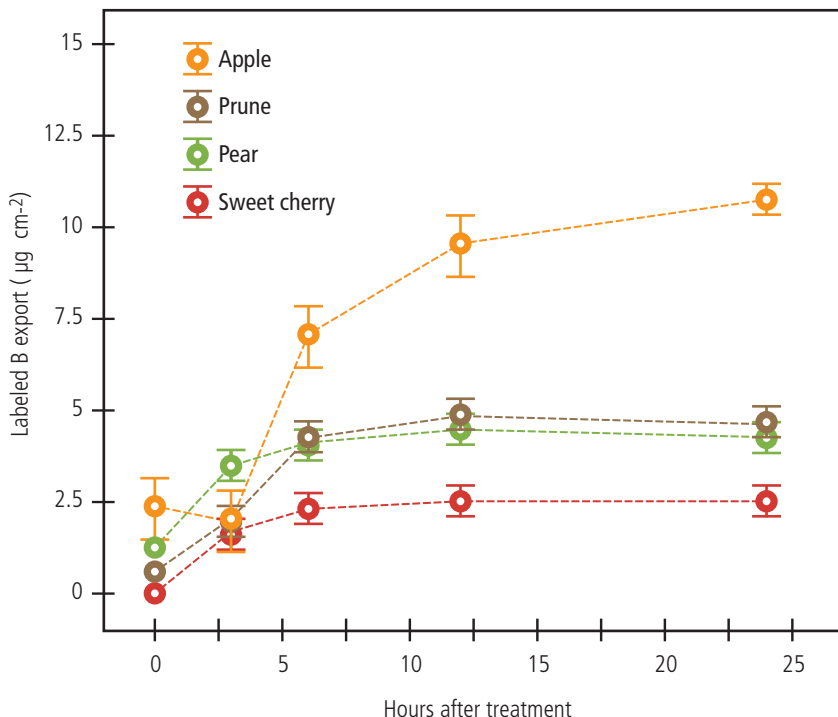


Figure 4.3. Export of foliar-applied, labelled B by shoot leaves expressed as absolute quantity. Time 0 h refers to 15-20 min following application (when the leaf had visibly dried). Export was calculated as the difference between the quantity of labeled B uptake and the quantity of labeled B measured in the leaf tissue extract at each time period ($\mu\text{g cm}^{-2}$). Cultivars are shown in Figure 4.2. Each value is the mean \pm standard error of five tree replicates of two leaves on a single shoot (Adapted from Picchioni and Weinbaum, 1995).

walnut, which limits Zn penetration, and a high capacity for fixation of the cationic Zn to exchange sites in the cell wall and cuticle (Zhang, 1999).

Leaf longevity can also account for species difference in response to foliar fertilizers with evergreen trees such as citrus, banana, coffee and cacao plants being more efficient in their utilization of soil-derived and foliar-applied leaf nutrients because of their longer leaf life; and the cycles of leaf wetting and drying enhances the recycling of nutrients through the autumn fall and decomposition process (Aerts and Chapin, 2000).

Species differ remarkably in their response to foliar fertilizers as a consequence of differences in:

- Canopy architecture and distribution of leaves of different age.
- Leaf retention and absorption of foliar sprays.
- The rate of remobilization of applied nutrients.

4.4. Effect of the environment on efficacy of foliar-applied nutrients

Light, humidity and temperature can each affect foliar absorption in several ways: 1) through direct effects on the spray solution prior to leaf absorption (Chapter 3.2.); 2) through effects on the leaf developmental processes discussed above (Chapter 4.2); and 3) by altering photosynthesis, stomatal opening, respiration, leaf expansion and sink activity and consequently changing energy and metabolite availability for the uptake, assimilation and subsequent transport of foliar nutrients.

4.4.1. Light

Chemical ion uptake by leaves can be directly influenced by light as a result of physical and chemical changes in the cuticle and also from the direct involvement of light on the energy and metabolite availability on the uptake and assimilation of foliar-applied nutrients (Abadia, 1992; Alvarez-Fernandez *et al.*, 2004; Hundt and Podlesak, 1990; Jacoby, 1975; Muhling and Lauchli, 2000; Nobel, 1969; Nobel, 1970; Rains, 1968; Raven, 1971; Swader *et al.*, 1975).

The amount and composition of synthesized waxes and their arrangement on the surface is directly influenced by light including photosynthetically active radiation (Cape and Percy, 1993; Takeoka *et al.*, 1983), as well as by UV-B radiation (Barnes *et al.*, 1996; Bringe *et al.*, 2006). The thickness of the cuticle and the amount of cuticular waxes in various plant species was found to be higher on those grown under high rather than low light intensities (Macey, 1970; Reed and Tukey, 1982) and the development of secondary wax structures is increased by higher light intensities (Hull *et al.*, 1975). The influence of light is cumulative with exposure and Leece (1978) demonstrated that the seasonal build-up and development of secondary wax structures on the abaxial surface of plum leaves (*Prunus domestica* L.) positively corresponded with increasing light intensity. Leaves of apple trees grown outdoors can synthesize up to three times more cuticular wax per surface area as compared to the same species grown in the greenhouse (Hunsche *et al.*, 2004) and as much as 30 times greater than those grown under low light intensity and high humidity plant culture conditions (Bringe *et al.*, 2006).

Numerous researchers have also shown stimulatory effects of light on short-term absorption of nutrients (Bowen, 1969; Christensen, 1980; Nobel, 1969; Rains, 1968) while others have demonstrated that light does not affect absorption (Rathore *et al.*, 1970; Zhang and Brown, 1999b). Jyung *et al.* (1965) and Shim *et al.* (1972) showed positive relationships between light intensity and ability of apple and bean (*Phaseolus vulgaris* L.) leaves to take up urea, Rb and PO_4 . Rains (1968) demonstrated increased uptake of K^+ by corn/maize (*Zea mays* L.) leaf slices in light; an effect that was seen under even low-light conditions and could be reversed with the addition of metabolic inhibitors. In corn/maize the light level required to maximize K absorption was significantly lower than that required for photosynthesis (Rains, 1968); while in tomato much higher light levels were required to maximize K absorption which was rapidly decreased in the dark and by inhibitors of photosynthesis and metabolic uncouplers as shown in Figure 4.4

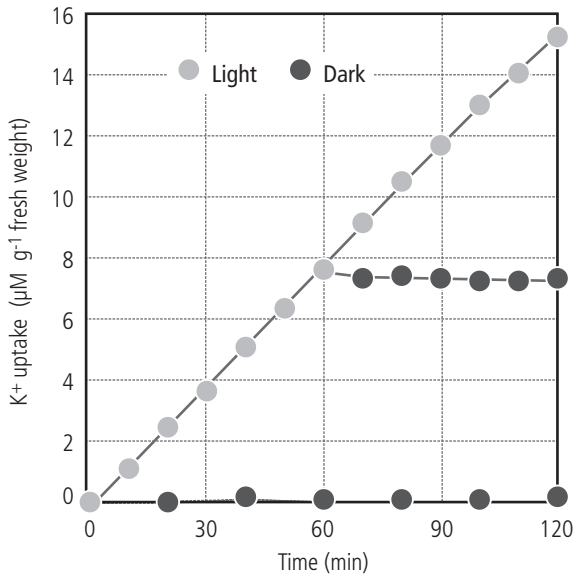


Figure 4.4. Effect of light and dark periods on uptake of K into leaf slices of tomato (Adapted from Nobel, 1969).

(Nobel, 1969). Schlegel and Schönherr (2002) reported that rates of CaCl_2 penetration from apple and pear leaf surfaces in the light were higher than in the dark.

While a positive effect of light on uptake of foliar applied elements has been frequently reported, many examples exist where light, metabolic inhibitors or reduced temperatures had no effect on nutrient absorption or transport (Rathore *et al.*, 1970; Zhang and Brown, 1999b). In pistachio and walnut Zn absorption at high concentrations (7.5 to 15 mM) was not affected by light or metabolic inhibitors (Zhang and Brown, 1999b) which supports earlier reports on Zn absorption in bean (*Phaseolus vulgaris*) (Rathore *et al.*, 1970). Zhang and Brown (199b) interpreted this result as evidence that Zn absorption was mostly determined by an ion exchange and/or diffusion process rather than a metabolically active one.

A direct effect of light on foliar absorption may also occur if the spray compound is unstable in the light. Several authors have demonstrated that Fe^{3+} chelates are UV-labile (Albano and Miller, 2001a; Albano and Miller, 2001b; Albano and Miller, 2001c) and as a consequence Schönherr *et al.* (2005) concluded that foliar penetration of chelated Fe preferentially occurs during the night and therefore foliar applications during the late afternoon are recommended. The potential for photochemical or temperature dependent degradation of foliar sprays exists for many commercial products and should be verified before widespread adoption. However, application of sprays under dark conditions may in turn limit uptake rates since the stomatal pathway may not be involved in the absorption process due to stomatal closure during the night.

The reported differences on the effect of light in short-term uptake of foliar-applied nutrients are likely to be the result of several interacting factors. At the cellular level the transmembrane transport, regulation and assimilation of most nutrients is directly or indirectly influenced by the metabolic status of the cell so light deprivation would be expected to reduce uptake. The only exception among the essential plant elements may be B, which is uncharged at normal pH, and sufficiently permeable through both leaf cuticle and cellular membranes to be absorbed and assimilated spontaneously into molecules of biological and metabolic importance. The finding that Zn absorption does not respond to the presence or absence of light may simply reflect a lack of sensitivity of the methodology employed or could be a consequence of the relatively small metabolic demand that (passive) Zn uptake would have on whole cell energetics which likely reflects the significant binding of Zn to cell wall materials by non-metabolic diffusion and exchange processes. The contrasting results obtained with the macronutrients, N, P and K, likely reflect the proportionally lower cell wall binding and the predominance of active uptake and transport processes for these more mobile elements. It is also probable that applications of relatively low concentrations of micronutrients do not represent a substantial metabolic cost while supplying higher concentrations of the macronutrients presents a significant metabolic cost for uptake and assimilation especially in experimentation using excised leaf slices.

4.4.2. Temperature

Temperature can influence foliar absorption through its effect on the rate of drying of the spray application; the nutrient solution physico-chemistry; as well as its impact on leaf cuticles; and on plant metabolism, ion uptake and assimilation. The most immediate effect of high temperature is increasing the drying rate of the spray droplets which will directly reduce absorption. However, increased absorption by leaves over prolonged high temperatures has been recorded in several species (Cook and Boynton, 1952). This may be the result of the high temperature during leaf development altering the amount and composition of synthesized waxes and their arrangement on the surface (Baker, 1974; Reed and Tukey, 1982) which then influences absorption (Norris, 1974). Reed and Tukey (1982) claimed that under conditions of persistent high air temperature surface wax components adopt a vertical configuration and hence their leaf surface coverage decreases which consequently allows increased nutrient absorption. Lurie *et al.* (1996) reported that even slight alterations in the molecular configuration of surface waxes can significantly affect nutrient absorption rate. Temperature will also have a direct effect on the rate of leaf development and hence influence foliar absorption through effects on leaf phenology and sink:source relations (Chapter 4.1.).

Over a short period, the prevailing temperature during and immediately following foliar application has varied effects depending on species and mineral element applied. In pistachio, Zn absorption after application ranged from 9 to 14% as the temperature increased from 8 to 31°C over a 24 hour period. Within the same temperature range Zn absorption in walnut only increased from 4 to 6% (Zhang and Brown, 1999b). The temperature coefficient (Q₁₀) is perhaps the most classical of all indices for separating active and passive uptake processes by plant tissues (Zhang and Brown, 1999b).

According to Wittwer and Teubner (1959) the Q10 for active nutrient uptake processes in plants is usually above 2. The average Q10 of between 1.2 to 1.4 for Zn absorption observed by Zhang and Brown (1999b) is consistent with a Q10 of 1.2 as reported by Rathore *et al.* (1970). This lack of a strong temperature dependence suggests that foliar Zn absorption was largely non-metabolic dominated by ion exchange and/or diffusion processes. Furthermore lower Zn uptake by leaves under lower temperatures has also been attributed to an increased viscosity of the aqueous ambient solution which probably results in a decreased rate of diffusion of Zn ions (Rathore *et al.*, 1970). The slight temperature dependence observed in these experiments is in contrast to the strong temperature dependence reported by Bowen (1969) who found a Q10 of >2.5 using sugarcane leaf slices. In Marsh grapefruit (*Citrus paradisi* Macfad.) the permeability of isolated leaf cuticles to urea within the first 4 to 6 hours after application increased as temperature was raised from 19 to 28°C but there was no further increase at 38°C (Orbovic *et al.*, 2001).

Further evidence that the effects of temperature on cuticular penetration are not due to changes in metabolism has been presented (Schönherr, 2001; Schönherr *et al.*, 2005; Schönherr and Luber, 2001). When temperature increased from 15 to 30°C rates of penetration of Ca and K did not increase (Schönherr, 2001); and in the range of 15 to 35°C the rate constants of penetration of chelated Fe³⁺ did not depend on temperature (Schönherr *et al.*, 2005). In field situations temperature will interact with humidity to affect the physico-chemical characteristics and solubility of deposited materials.

4.4.3. Humidity

As with light and temperature, humidity can affect multiple processes that ultimately influence the rate of foliar absorption of aerial applied fertilizers. The key processes affected by humidity are 1) the reaction of the foliar application during aerial transport and once deposited on the plant surface 2) the effect of humidity of leaf cuticle structure and stomatal function and 3) the effect of humidity on leaf metabolism and transport processes. In the short term the effect of humidity on nutrient absorption by leaves is primarily related to the rate of drying of droplets during aerial transit to the plant surface and their persistence once deposited on the plant surface (Gooding and Davies, 1992). High relative humidity favors uptake as it delays rapid solution drying which can lead to crystallization on the leaf surfaces (Gooding and Davies, 1992). Additionally, high air humidity causes the swelling of the cuticular membrane which favors the absorption of hydrophilic compounds (Schönherr and Schreiber, 2004) (Chapter 3). Therefore humidity at the time of foliar application affects the velocity of penetration by two independent mechanisms: a) swelling of the cuticle; and b) dissolution of salt as related to the point of deliquescence (POD) which is defined as the relative humidity value at which the salt becomes a solute (Chapter 3.1.4.). Over longer time frames (days to weeks) the amount and composition of synthesized waxes and their arrangement on the surface is influenced by relative humidity which consequently may alter the rate at which foliar applications can penetrate the plant surface (Baker, 1974). Post absorption humidity can have general effects on plant responses to foliar nutrients by affecting xylem and phloem transport processes. Eichert and Goldbach (2010) reported that,

at high relative air humidity, B applied to the cotyledons of *Ricinus communis* L. was transported to hypocotyls and roots; whereas at low relative humidity no translocation of B was detectable. It is concluded that ambient air humidity influences phloem mobility of B *via* its effect on the xylem flow rate; if the xylem flow rate is low or interrupted then foliar-applied B becomes modestly mobile.

Various studies have demonstrated the effect of humidity on physico-chemical properties of different spray solutions and their interactions with plant surfaces (Schönherr and Schreiber, 2004) (Chapter 3). In their classical earlier work, Wittwer and Bukovac (1959) showed that the uptake of P by bean leaves was doubled when the treated surface was kept moist compared with similar treatments in which leaf surfaces were allowed to dry. Salts with points of deliquescence (POD's) above the prevailing relative humidity, when applied in the leaves, theoretically remain as solutes and leaf penetration is prolonged. This principle has been clearly demonstrated in isolated cuticular membrane studies of Ca, K and Fe compounds under varied humidity regimes

Table 4.2. Point of deliquescence (POD) of various salts (Schönherr, 2002).

Compound	POD (%)
CaCl ₂ · 6H ₂ O	33
Ca(NO ₃) ₂ · 4H ₂ O	56
MgCl ₂ · 6H ₂ O	33
Mg(NO ₃) ₂ · 6H ₂ O	56
MgSO ₄	90
Zn(NO ₃) ₂ · 6H ₂ O	42
ZnSO ₄	90
KCl	86
KNO ₃	95
K ₂ SO ₄	98
K ₂ CO ₃ · 2H ₂ O	44
K ₂ HPO ₄	92
KH ₂ PO ₄	95
NH ₄ NO ₃	63
Ca-propionate · H ₂ O	95
Ca-lactate · 5H ₂ O	97
Ca-acetate	100
FeCl ₃ · 6H ₂ O	44
Fe(NO ₃) ₃ · 9H ₂ O	54
Mn(NO ₃) ₂ · 4H ₂ O	42
MnCl ₂ · 4H ₂ O	60

membrane penetration followed first order kinetics. When humidity is above the POD the salt residue on the cuticle dissolves while penetration ceases when humidity falls below the POD. Above the POD there is often a linear increase in penetration as humidity increases, though the exact nature of this relationship is mineral salt and species specific (Schönherr, 2001; Schönherr and Luber, 2001).

Anomalies in the relationship between humidity, POD and penetration can be the result of undisturbed layers at the leaf surface which would increase effective humidity on the leaf surface. High humidity may also alter stomatal opening and have non-linear effects on aqueous pore formation (Schlegel *et al.*, 2005; Schlegel *et al.*, 2006; Schönherr, 2006). Van Goor (1973) demonstrated that an increased penetration of Ca^{2+} through the cuticular membrane of apple fruit correlated with decreasing air humidity in the period of time just after application. This phenomenon is explained by an increase in droplet Ca^{2+} concentration resulting from their drying and the consequent increase in the concentration gradient for diffusion. However, despite initial enhanced absorption dynamics at low air humidity the final uptake rates of nutrients from salts of low hygroscopicity are decreased because of rapid salt crystallization once humidity drops below the POD (Wojcik, 2004).

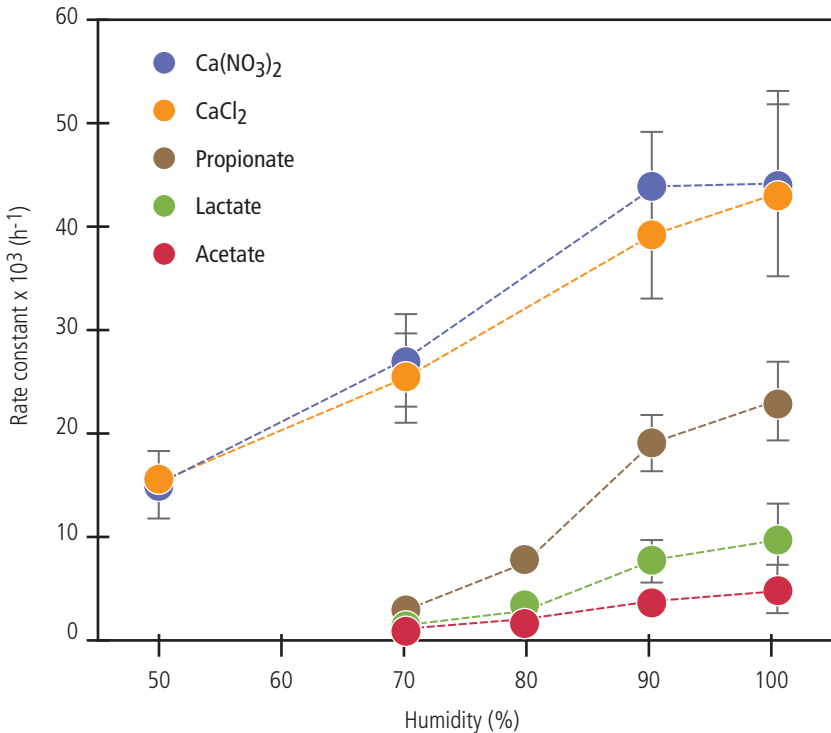


Figure 4.5. Influence of humidity and anions on penetration of Ca salts through isolated cuticles of apple fruit (Adapted from Schönherr, 2001).

While it is clear that the POD of the foliar applied chemical and the humidity during the application period have an important effect on penetration, knowledge of the POD alone is often insufficient to predict the efficacy of a mineral salt as a foliar fertilizer. For example, the apparent ease of penetration of $\text{Ca}(\text{NO}_3)_2$ or CaCl_2 (Figure 4.5) demonstrated by Schönherr (2001) and Schönherr and Luber (2001) does not explain the great difficulty many growers have encountered in correcting field Ca deficiencies; and there are many reports of formulations with purported efficacy that an analysis of POD alone would not support. While a POD less than ambient humidity is required for uptake to occur, it is not always a guarantee since many other factors (e.g. associated with plant physiology or the prevailing environmental conditions) may hinder the absorption process under field conditions. Efficacy of salts with a high POD can be enhanced through the use of adjuvants with humectant properties (Chapter 3). In addition, and as suggested by Burkhardt (2010) for hygroscopic aerosols deposited onto plant surfaces, salts with low POD's may either act as desiccants or simply increase nutrient uptake rates. Consequently, salts with low PODs may be more effective but may be more likely to cause phytotoxicity.

In summary, humidity influences foliar absorption primarily through its effect on droplet size and persistence on the leaf surface in the liquid state. Humidity also alters leaf cuticular composition, its physical and chemical characteristics and has direct effects on leaf physiology and transport processes.

Light, humidity and temperature can affect foliar absorption: 1) through direct effects on the spray solution prior to leaf absorption; 2) through effects on the leaf development processes; and 3) by altering photosynthesis, stomatal opening, respiration, leaf expansion and sink activity which consequently changes energy and metabolite availability involved in the uptake, assimilation and subsequent transport of foliar applied nutrients.

- Light and temperature influence foliar absorption primarily through their effects on the physical and chemical characteristics of the foliar solution as well as the development of the cuticle.
- Direct effects of light or temperature on leaf metabolism influencing foliar fertilizer efficacy are not highly significant.
- Humidity alters both leaf structure and the rate at which foliar fertilizer solutions dry on leaf surfaces.

4.5. Summary of the effects of the environment on plant response to foliar fertilization

Over longer periods (weeks) the environment in which a plant develops can alter the cuticle and other physical characteristics of leaves as well as crop phenology and metabolism. Environmental stress has been observed to either enhance foliar uptake,

through the disruption of leaf cuticular integrity, or reduce uptake and utilization, by impairing leaf expansion, sink activity and metabolism. In the shorter term (hours or days) optimal environmental conditions maximize photosynthetic activity, stomatal opening and metabolic performance of crops and therefore enhance the potential for uptake, translocation and the plant response to foliar-applied nutrients. This effect is greatest for nutrients that are readily permeable; are applied in metabolically significant quantities; and are rapidly assimilated by the plant. For such nutrients unfavourable environmental conditions (especially low light or sub-optimal temperatures) may limit the availability of adequate energy and metabolic substrates to drive the uptake, transport and assimilation processes. Examples of fertilizer nutrient sources that may be impacted by sub-optimal environmental conditions are urea and other soluble and permeable macronutrient formulations of N, P, K, S and Mg. For elements that interact strongly with the cuticle and cell wall components and are applied at concentrations that would not be expected to represent a substantial energetic or metabolic cost (predominantly the micronutrients) for their absorption, a direct effect of temperature on metabolic processes (and hence absorption) is unlikely. In this case any effect of the environment is likely to be a result of physical and not biological influences.

In addition to its direct effects on metabolic absorption and transport processes, temperature determines the pattern of droplet drying and leaf surface distribution, which also has a direct effect on the efficacy of foliar applications (Chapters 2 and 3). Ultimately, it is the combination of effects of environment on the plant prior to foliar application and on the biology of the plant during and post-absorption that determine its impact on the efficacy of foliar fertilization.

4.6. Nutrient mobility and transport

The efficacy of foliar nutrient sprays depend not only on the absorption of the nutrients but also on the transport of these nutrients to other plant parts like fruit, grains, young leaves, etc. (Bukovac and Wittwer, 1957). Knowledge of the ability of an element to be transported from the site of application can provide insight into the longevity and potential nutritional impact of foliar application on non-sprayed tissues. Non-sprayed tissues include roots, new growth that develops after spray application, and tissues that were not directly in contact with the spray solution. This includes internal tissue of fruit, dormant buds, enclosed reproductive tissues (such as wheat ears within the leaf sheath) as well as vascular and storage tissues.

While the ability of an element to be transported from the site of application to other plant parts (roots, storage tissues, reproductive organs) increases the potential for the whole plant to benefit, it must be emphasized that transport from the site of application is not essential for foliar efficacy. Indeed, it is likely that most Zn, Mn, Ca and Fe sprays are local in their effect with only very limited transport out of the sprayed tissues. Nevertheless, these sprays may still have a significant local benefit and even a relatively small transport out of treated leaves and tissues may have a short-term, critical benefit to the plant. Development of foliar fertilizers and application techniques

that optimize transport of nutrients from site of application remain one of the most important challenges to the industry. Currently, there is only limited information to suggest that foliar-applied nutrients are transported differently or have a different physiological impact than soil-derived nutrients. Similarly, while it has been shown that the chemical form in which a nutrient is applied can influence its rate of absorption, it has not been confirmed if the nutrient provided can then influence the transport of the absorbed nutrient from the site of application. These are questions of great importance to the science and practical field application of foliar fertilizers.

Marschner (1995) classifies nutrients into three groups with regard to their phloem mobility: highly mobile (N, P, K, Mg, S, Cl, Ni); intermediate or conditionally mobile (Fe, Zn, Cu, B, Mo); and low mobility (Ca, Mn). Furthermore, Epstein and Bloom (2005) also classify nutrients with regard to their phloem mobility (Table 4.3). The former authors classify B as having high or low mobility depending on species as described by (Brown and Hu, 1998).

The plant species and phenological stage have critical effects on the mobility of all elements but these are particularly important for the intermediate or conditionally mobile ones.

In particular the mobility of micronutrients within plants is an important characteristic that determines plant growth and survival under conditions of limited nutrient availability. Three factors combine to determine the overall phloem mobility of a nutrient: a) the ability of the nutrient to enter the phloem; b) the ability of the nutrient to move within the phloem; and c) the ability of the nutrient to move out of the phloem into sink tissues.

The degree of mobility of a particular element occurs to varying degrees throughout the plant's life and this may vary significantly between species. The developmental stages that affect micronutrient mobilization include seed germination, vegetative and reproductive growth, leaf senescence and the onset of new growth in perennial species. Nutrient mobilization during flower and seed formation as well as following seed germination are the most critical phases. Indeed mobilization of stored nutrients during seed germination, particularly in infertile and arid soils, is important for supplying

Table 4.3. Classification of nutrients with regard to their phloem mobility (Epstein and Bloom, 2005).

Mobile	Intermediate or conditional mobility	Low mobility
Potassium	Sodium	Calcium
Nitrogen	Iron	Silicon
Sulfur	Zinc	Manganese
Magnesium	Copper	Boron (species dependent)
Phosphorus	Molybdenum	
Boron (species dependent)		
Chlorine		

micronutrients to the young seedlings prior to their developing a sufficient root system to enable significant soil uptake. During leaf senescence, re-mobilization of nutrients from the leaves to the reproductive tissues represents an important source of nutrients for the fruits and seeds. Recent evidence suggests that the nutrient content of the seeds can be enhanced using appropriate well-timed foliar applications with subsequent benefits for human consumption (of 'treated' grain) and subsequent (following planting out) seed germination (Cakmak *et al.*, 2010; Dordas, 2006; Ozturk *et al.*, 2006).

In general, there is low potential for re-mobilization of foliar absorbed nutrients until the potential binding sites for that element within the leaf are saturated, thus nutrient deficiency can reduce nutrient mobility since there will be many unsaturated binding sites to be filled (saturated). Nutrient mobility may also be low until the structural integrity of the leaf begins to decline during senescence thereby releasing previously tightly bound nutrients. This effect is particularly prominent for nutrients that are found in permanent structures such as the cell wall which exhibit low turnover rates for elements including some micronutrients e.g. Zn, B and Cu. When grown in deficient or marginally adequate levels of nutrient supply, more than 90% of the micronutrients, Cu, Zn and B, are present within permanent structures particularly the cell wall (Brown and Bassil, 2011; Brown *et al.*, 2002; Zhang and Brown, 1999a). In species with limited B mobility (Brown and Hu, 1998) foliar applications of B are most effective at enhancing translocation when B is sufficient in the tissue at the time of application (Hanson, 1991; Leite *et al.*, 2007; Will *et al.*, 2011). A similar response was hypothesized for Zn (Erenoglu *et al.*, 2002; Zhang and Brown, 1999a) with optimum re-translocation of applied Zn to grain being observed when a combination of soil and foliar Zn was used. Furthermore during grain development in wheat Cu-sufficient flag leaves lost more than 70% of their Cu compared to only 20% in Cu-deficient plants (Hill *et al.*, 1979a; Hill *et al.*, 1979b). This relationship between nutrient status and re-mobilization does not occur with the more mobile elements N, P, K, S, Mg, B (in polyol producing species), Cl, and Ni since a small portion of the cellular content of these elements is associated with permanent structures and each of these elements is also phloem mobile. In general, deficiency of N, P, K, Mg and S enhances senescence and speeds nutrient re-mobilization.

The mobility of micronutrients has a significant effect on the occurrence, expression and correction of deficiencies. Phloem mobile elements can move from organs of relative abundance to growing tissues so that plants do not immediately exhibit nutrient deficiency or depressed plant growth when the demand for a particular nutrient is higher than its uptake rate. Understanding the precise mechanism of phloem mobility is important as it can provide a basis for the selection, or genetic engineering, of plants with enhanced phloem mobility. Improved tolerance to a short-term micronutrient deficiency has recently been demonstrated for B (Brown *et al.*, 1999). Knowledge of the chemical form in which nutrients are transported in the phloem is important when developing foliar fertilizer formulations that mimic the natural plant process. The development of polyol-based fertilizers for transport of B as well as those based on amino acids have been rationalized on this understanding though scientific proof of transport of the element in its esterified form is not yet available.

Any discussion of phloem transport must recognize that transport is strongly affected by plant genotype and various external and internal factors though a few broad

generalizations may be made. Nitrogen, P, K, Ni, Mg, S, Cl and B in polyol transporting species (Brown and Bassil, 2011) are thought to be phloem mobile in all species with transport rates determined by local leaf nutrient status and source:sink relationships. The elements Ca, B (in polyol non-transporting species) and Mn are immobile in the vast majority of plants except in a few species (Ca and Mn are mobile in lupin) and during senescence in some (Brown and Shelp, 1997; Graham *et al.*, 1988; Jeschke *et al.*, 1987). The intermediate or conditionally mobile elements (Zn, Fe, Cu and Mo) can be immobile or relatively mobile depending on phenology and supply which will be discussed later.

The typical ranges for components of xylem and phloem saps in higher plants are given in Table 4.4.

Because of the generally high mobility of N, P, K, Ni, Mg, S and Cl little discussion of species or phenology-specific re-mobilization will be presented here. Nitrogen, K, P,

Table 4.4. Comparison of concentrations of organic and inorganic solutes in the phloem (stem incision, pH 7.9-8.0) and xylem (tracheal, pH 5.6-5.9) exudates of *Nicotiana glauca* (Marschner, 2012).

	Phloem	Xylem (mg L ⁻¹)	Ratio phloem/xylem
Dry matter	170-196	1.1-1.2	155-163
Sucrose	155-168	nd	
		(µg mL ⁻¹)	
Amino compounds	10,808	283	38.2
Nitrate	nd ¹	na ²	
Ammonium	45.3	9.7	4.7
K	3,673.0	204.3	18.0
P	434.6	68.1	6.4
Cl	486.4	63.8	7.6
S	138.9	43.3	3.2
Ca	83.3	189.2	0.44
Mg	104.3	33.8	3.1
Na	116.3	46.2	2.5
Fe	9.4	0.60	15.7
Zn	15.9	1.47	10.8
Mn	0.87	0.23	3.8
Cu	1.20	0.11	10.9

From Hocking, 1980b.

¹nd: not detectable

²na: not available

S, Mg, Ni, Cl and B (in polyol producing species) are highly mobile in the phloem with transport driven mostly by source:sink relationships and tissue senescence. Phloem mobile nutrients frequently follow a circuitous path through the leaves (Figure 4.6) and are preferentially mobilized from the leaves to the fruit *via* the phloem rather than proceeding directly to sink tissues and fruit in the transpiration stream (Jeschke and Hartung, 2000).

Phloem mobility can become particularly high during seed maturation in annual plants with the majority of nutrients being supplied by re-translocation from the leaves to the seeds (Neumann, 1982). The extent of re-mobilization is highly element specific (Table 4.5) with a large percentage of final seed nutrient content being derived from leaf re-mobilized nutrients and not from 'new' uptake (Marschner, 2012). In many species the N requirements of developing seeds exceed the supply capacity of the roots and the resulting N deficit triggers catabolism (breakdown of leaf proteins) and the transfer of the resulting N and other nutrients to the seed. Catabolism of leaf protein also has a positive effect on the availability of Cu and Zn for re-mobilization to reproductive tissues (Hill *et al.*, 1979b; Kutman *et al.*, 2011).

Factors that influence the relative re-mobilization of the poorly mobile phloem elements have the greatest relevance to studies on the efficacy of foliar applications.

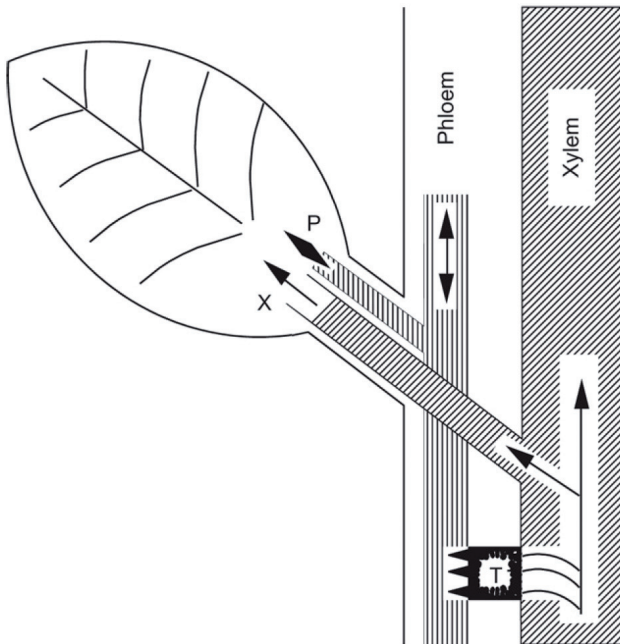


Figure 4.6. Schematic diagram of long distance transport in xylem (X) and phloem (P) in a stem with a connected leaf; and xylem-to-phloem transfer mediated by a transfer cell (T) (Marschner, 2012).

Table 4.5. Re-mobilization of nutrients in a pea crop between flowering and ripening (Marschner, 2012).

	N	P	K	Mg	Ca
	Content in stems and leaves (kg ha ⁻¹)				
Harvest					
June 8 (flowering)	64	7	53	5	31
June 22	87	10	66	8	60
July 1	60	7	61	8	69
July 12 (ripening)	32	3	46	9	76
	Increase or decrease after June 22 (%)				
	-63	-73	-30	+10	+21
	In seeds (% of total shoot content)				
	76	82	29	26	4

Based on Garz, 1966.

Calcium is generally immobile in the phloem as a consequence of its low concentration in cytoplasm and phloem of between 0.1 to 10 μM (White and Broadley, 2003) as well as the negative impact of Ca on phloem sieve callose formation and plugging (Marschner, 2012). Phosphate is the major anion in the phloem sap and the translocation of cations such as Ca^{2+} , which form phosphates of low solubility, are limited in the sieve tubes by the solubility product of the phosphate salt. Many physiological disorders of fruits are associated with low Ca levels and because of its phloem immobility foliage-applied Ca is not re-distributed from sprayed leaves to the fruit (Swietlik and Faust, 1984). Because of the importance of Ca on the storage quality of fruits and vegetable, and as a consequence of the prevalence of Ca deficiency disorders, there has been considerable research effort on methods to enhance fruit Ca content (Blanco *et al.*, 2010; Koutinas *et al.*, 2010; Kraemer *et al.*, 2009b; Lotze *et al.*, 2008; Neilsen *et al.*, 2005a; Peryea *et al.*, 2007; Val and Fernandez, 2011). Evidence for the very low degree to which Ca is re-mobilized from sprayed leaves to fruits is provided in numerous publications and it is generally accepted that multiple sprays as well as the concurrent application of Ca to leaves, stems and fruit are required. Early season sprays appear to be more effective than late season sprays (Lotze *et al.*, 2008; Peryea *et al.*, 2007) probably as a consequence of different leaf characteristics, or benefits of direct spray application to young fruits, or because it provides the time available for multiple applications. Though evidence suggests that the choice of Ca formulation can affect the amount of Ca in the fruit it is not clear if this is a result of enhanced absorption or better transport (Lotze *et al.*, 2008; Rosen *et al.*, 2006).

Iron is generally considered to be an intermediately mobile nutrient in higher plants and can be re-translocated in small amounts from the old leaves to the younger ones (Abadia *et al.*, 2011; Fernandez *et al.*, 2006; Fernandez *et al.*, 2009). A typical concentration of Fe in the phloem is $9.4 \mu\text{g ml}^{-1}$ which is too low to supply plant demand (Hocking, 1980) and the pH of the phloem is about 7.8-8.0 which favours Fe^{3+} insolubility (Mass *et al.*, 1988). This suggests that mechanisms must exist to actively load the phloem and that Fe must be present in a complexed form (Palmer and Guerinot, 2009; Waters and Sankaran, 2011; White and Broadley, 2009). The degree of mobility of Fe clearly varies with species, stage of plant growth and Fe supply amongst other factors (Garnett and Graham, 2005; Shi *et al.*, 2011). Garnett and Graham (2005) observed very high levels of Fe and Cu, and moderate levels of Mn and Zn, re-mobilization during shoot senescence and grain filling in wheat. These results contrast with field studies in which very little Fe or Mn re-mobilization was observed (Hocking, 1994; Pearson and Rengel, 1994). Examples of limited mobility of foliar-applied Fe in both herbaceous plants and citrus shoots towards new, expanding leaves is a function of several factors, but most importantly the specific Fe source (Abadia, 1992; Abadia *et al.*, 2011; Fernandez *et al.*, 2009). In this regard, some reports have suggested a better plant translocation of Fe chelates versus inorganic salts (Basiouny and Biggs, 1976; Basiouny *et al.*, 1970; Fernandez and Ebert, 2005; Fernandez *et al.*, 2009).

Zinc is frequently more mobile than either Mn or Fe in most species (Nowack *et al.*, 2008; Zhang *et al.*, 2010) and Swietlik (2002). Longnecker and Robson (1993) suggested that Zn movement out of old leaves coincides with their senescence and the re-mobilization of Zn from the flag leaf to the grain in wheat has been confirmed (Herren and Feller, 1994). In subterranean clover (*Trifolium subterraneum*) total Zn in leaves and petioles decreased as the reproductive structures accumulated Zn (Riceman and Jones, 1958; Riceman and Jones, 1960). Application of ^{65}Zn labelled fertilizer to 'Pera' orange demonstrated that after 120 days 14% of the total absorbed Zn was translocated from the applied leaves to other plant parts (Sartori *et al.*, 2008). In other studies utilizing citrus species (Swietlik and Laduke, 1991) found limited or no evidence of Zn movement from sprayed leaves using ^{65}Zn isotope.

These results suggest that significant Zn re-mobilization can occur in some species during normal growth and in many species during senescence. Zinc concentrations in the phloem sap range from 3 to $170 \mu\text{M}$ (White and Broadley, 2009) and under conditions of normal supply only a small portion of Zn can be supplied *via* the phloem. While Zn re-mobilization in the phloem appears to be possible the quantity appears to be limited to about 5 to 20% across all experiments. The very limited re-translocation of Zn observed following foliar applications can be attributed to either the poor penetration or the high binding capacity of leaf tissues for Zn (Zhang and Brown, 1999a), but does not imply that phloem mobility was limited (Figure 4.7).

Manganese is generally considered to have low mobility in most species but can be influenced by the supply of Mn in the growth medium (Brown and Bassil, 2011). Early studies concluded that Mn has intermediate mobility with less mobility than P and



Figure 4.7. Zinc is highly immobile in pistachio trees. The right side of this tree received foliar fertilizer at the rate of 10 kg ZnSO₄ per 500 litres applied to drip in September (early post-harvest) with a hand gun sprayer each year for five years. The left half of the tree received no foliar applications. Repeated Zn applications effectively (but inefficiently) corrected deficiency on the sprayed right side. However, no significant benefit of the Zn applications was perceived on the un-sprayed left side (Courtesy Kiyoto Uriu).

more mobility than Ca. Experimental evidence by Romney and Toth (1954) showed that radioactive ⁵⁴Mn can be partially translocated from leaves when foliar applied. In addition Nable and Loneragan (1984) used ⁵⁴Mn and demonstrated that the isotope remained in the cotyledons and old leaves with little or no Mn exported from them and limited re-mobilization or re-translocation of Mn from mature leaves. MnSO₄ foliar sprays were applied by Swietlik and Laduke (1991) for four years in 'Valencia' orange (*Citrus sinensis* Osbeck) and 'Ruby Red' grapefruit (*Citrus paradisi* Macf.) resulting in a very small but measurable increase in Mn in new leaves of 2 to 5 ppm. Hocking *et al.* (1977) reported variation in Mn accumulation among various lupin species with the concentration in *Lupinus albus* L. being consistently higher than that of *Lupinus angustifolium* L. and the differences were also expressed in the relative extent to which the species mobilize Mn from pods to seeds. In wheat Mn contents increased throughout the entire leaf life and did not even decline during senescence (CF and Graham, 1995; Pearson and Rengel, 1994; Pearson *et al.*, 1995). Everett and Thran (1992) also reported that mobilization of Mn from leaves was limited as evidenced by the increase in amount of Mn in the needles of pinyon (*Pinus monophylla*) with time. However there is evidence to suggest that Mn is mobile in the phloem of *Ricinus communis* (Van Goor and Wiersma, 1976).

Molybdenum exhibits high phloem mobility in soybean, rice and bean (Brown and Bassil, 2011; Kannan, 1986) but lower mobility in many other species (Masi and Boselli, 2011; Williams *et al.*, 2004). Bukovac and Wittwer (1957) reported that Mo has intermediate mobility and observed that in Mo-sufficient plants there was re-mobilization from leaves during flowering and pod filling; while in Mo-deficient plants content increased or remained constant in leaves which suggests that there was no or little re-mobilization (Jongruaysup *et al.*, 1994; Jongruaysup *et al.*, 1997).

Boron is a unique element in that phloem B mobility is strongly species- dependent (Brown and Bassil, 2011; Brown and Shelp, 1997). In most plant species, B is largely xylem transported and exhibits marked immobility once deposited in the leaf. It is suggested that this immobility is a consequence of either the incompatibility of B with the phloem or 'solute' trapping in which the high trans-membrane mobility of B favors the movement of any B in the phloem back to the less concentrated xylem stream (for discussion see Brown and Bassil, 2011; Brown *et al.*, 2002; Brown and Shelp, 1997). Limited phloem mobility may occur in certain species under conditions of low B supply (Huang *et al.*, 2008; Shelp *et al.*, 1996; Stangoulis *et al.*, 2001; Stangoulis *et al.*, 2010), perhaps suggesting that deficiency induced transporters are up-regulated.

In contrast to the majority of plants, re-mobilization of B from mature leaves can easily take place in species that primarily transport polyols (sugar alcohols) and foliar B applications have long been known to be an effective means of enhancing bud and flower concentrations resulting in increased fruit set and yield in *Malus*, *Prunus*, *Olea*, *Coffea* and *Pyrus* species. Using ^{10}B , Brown and Hu (1996) demonstrated that re-mobilization of B can occur when B forms esters with a sugar alcohols (e.g. sorbitol, mannitol, dulcitol) which are stable when sugar alcohol to B ratios exceed 100:1. Plants where B is mobile are far less susceptible to transient shortages of B since foliar-applied B can be re-mobilized and supply untreated tissues. This principle that phloem mobility impacts susceptibility to deficiency and enhances plant response to foliar fertilizers is equally relevant for all elements.

Phloem immobility increases susceptibility to short-term nutrient withdrawal but can be corrected with foliar fertilization. Wild type tobacco, in which B is immobile, and transgenic tobacco containing a gene that induces phloem B mobility, were grown in nutrient solutions containing adequate B for 38 days (Figure 4.8). B in the rooting medium was removed on day 39 and the oldest mature leaf of both cultivars was supplied with daily spray application of foliar B at 250 ppm. Within 24 hours of B removal from the rooting media wild type tobacco plants rapidly exhibit B deficiency symptoms including abortion of flowers, inhibition of shoot elongation and chlorosis (Figure 4.8a). Transgenic tobacco, in which B is mobile, did not exhibit B deficiency due to enhanced ability to translocate B from old to young tissue (Figure 4.8b) (Brown *et al.*, 1999a).

At normal pH values B is present as the uncharged low molecular weight borate molecule (H_3BO_3) with a relatively high cuticle and membrane permeability which is readily absorbed by leaves (Picchioni and Weinbaum, 1995). Therefore all species show a rapid uptake of B into the sprayed organ. However in species that transport polyols

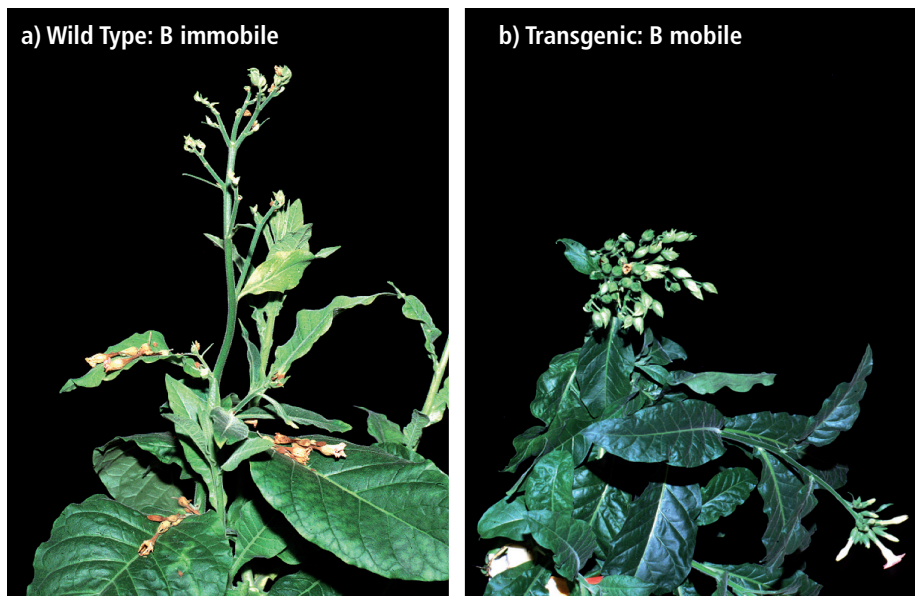


Figure 4.8. Boron is immobile in the natural 'Wild Type' cultivars of tobacco (a) and highly mobile in transgenic (b) cultivars into which the gene for sorbitol production has been inserted (Brown *et al.*, 1999). Plants were grown for 45 days with adequate boron then transferred to boron free media for 72 hours. After 72 hours, significant boron deficiency, including flower abscission was observed in wild-type but not in transgenic cultivars. The phloem mobility of boron in the transgenic species prevented the occurrence of deficiency by allowing for re-use of previously acquired B.

foliar applications of B are also rapidly transported out of the leaf in the phloem stream and move toward sink tissues including roots, young expanding leaves, reproductive organs and fruits, thus demonstrating the relevance of phloem mobility of crop response to foliar fertilization.

Phloem mobility has a profound effect on the ability of plants to absorb, translocate and benefit from foliar fertilizers and therefore it has an important role in determining their efficacy.

Phloem-immobile nutrients:

- Foliar application of phloem-immobile nutrients only benefit the tissues that directly receive the foliar spray.
- Measurement of nutrient status in sprayed leaves may be problematic due to the presence of residues from un-absorbed nutrients on the leaf surface.
- While development of foliar nutrient formulations with greater mobility is a worthwhile endeavor, a more immediate need is to maximize the efficacy of these materials on the sprayed tissues.

Phloem-mobile nutrients:

- Foliar application of mobile nutrients has the potential for systemic and long-term benefit.
- Limitations to the quantity of nutrient that can be applied and rapid dilution of the applied nutrients from mobilization within the plant reduce the potential benefit of foliar sprays of phloem-mobile nutrients.
- Therefore measuring the impact and benefit of phloem-mobile foliar nutrients is complicated by their mobility and dilution within the plant.

For both mobile and immobile nutrients the most relevant role of foliar sprays is to prevent immediate and transient deficiencies that cannot be addressed quickly by soil applications.

4.7. Conclusions

This chapter has highlighted the complex interactions between the environment, plant species, growth stage and conditions and timing of application on the efficacy of foliar fertilizers. While there are very few specific 'rules' that can be applied to every specific situation an understanding of the general principles that affect foliar fertilization will help make more informed decisions.

Certainties

- Species differ markedly in the characteristics of their leaf surfaces and prediction of crop response to any formulation is currently impossible.
- The environment affects every aspect of foliar fertilization; from physical and chemical reactions of spray materials; to plant architecture; to leaf cuticular composition; and fate of the nutrients once they enter the plant.
- Plant phenology also has a large effect on leaf cuticular composition and therefore the efficacy of foliar fertilization.

- Phloem mobility has a profound effect on the manner in which foliar nutrients are utilized by treated plants.

Uncertainties

- Current knowledge of the factors that determine plant cuticular composition and response to foliar application is insufficient to predict, or manipulate, plant response to a foliar application.
- It is an unknown if foliar-applied nutrients, once they enter the cellular space, are more or less 'available' or mobile than soil acquired nutrients.

Opportunities

- Improved understanding of the principles that govern the movement of foliar-applied nutrients through the cuticle into the living leaf cellular spaces is essential to the development of improved foliar fertilizer formulations and practices.

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 agro-chemicals (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, referred to hereon as 'transient deficiency', has received little attention. It is generally true that foliar fertilizers are more expensive per unit compared to an equivalent quantity of soil-applied 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 within-plant 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.

<p>A limitation in soil nutrient uptake capacity occurs as a consequence of the environment or plant senescence that limits nutrient uptake by roots.</p>	<p>During early spring when many deciduous species flower and set fruit and soil temperatures or moisture regimes are unfavourable for soil nutrient uptake.</p> <p>As a consequence of plant senescence limiting root activity.</p>
<p>Periods of peak crop growth induces a nutrient demand that exceeds nutrient supply even in a well-fertilized soil.</p>	<p>Nutrient demand for rapid fruit growth or grain fill can exceed uptake capacity even in adequately fertilized soils.</p> <p>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.</p>
<p>Plant architecture and organ development create local nutrient demand that exceeds capacity for within-plant nutrient delivery.</p>	<p>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 reproductive structures.</p> <p>Nutrient depletion due to rapid withdrawal of mobile nutrients in leaves adjacent to large rapidly growing reproductive organs.</p>

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) (mg B L ⁻¹)	Yield (kg in-shell splits tree ⁻¹)	Buds (mg B kg ⁻¹)	Leaves (July)
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.

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

Application date	Growth stage	Yield ¹ (kg)	July leaf B (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

¹All yields are fresh weight of fruit per tree.

²denotes 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.

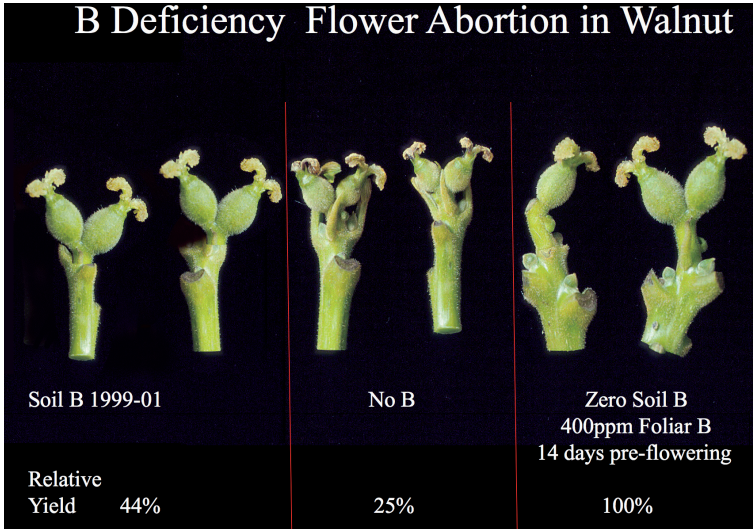


Figure 5.1. Effect of B deficiency on reproduction in walnut (*Juglans regia*). Walnut trees were treated with soil B applications (2 kg B ha^{-1}) in mid-summer in 1999, 2000 and 2001. In a sub-set of trees, foliar applications were applied at 400 ppm B in the final spray solution applied 14 days prior 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-mobile varies 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; Nielsen *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 post-bloom, 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 reticulata* 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 non-nutritional 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 mid-season 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 yield 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).

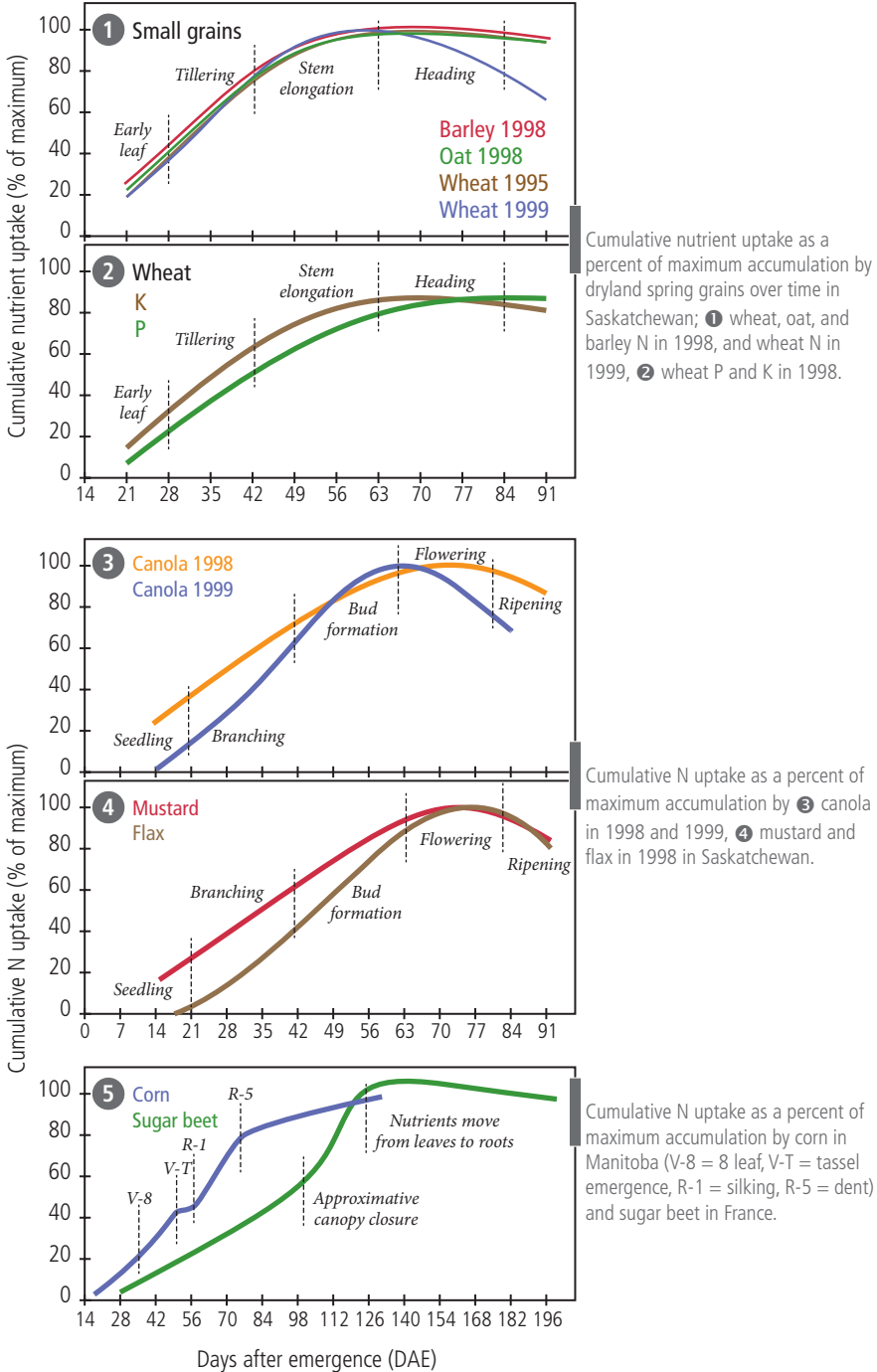
In conclusion, the most appropriate timing for foliar application of macronutrients is at early pod development in soybeans; from canopy closure to anthesis in cereal crops; at early tasseling in maize; and at early flowering in cotton. However, while there are many cases of positive crop response to 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 similar 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



Cumulative nutrient uptake as a percent of maximum accumulation by dryland spring grains over time in Saskatchewan; 1 wheat, oat, and barley N in 1998, and wheat N in 1999, 2 wheat P and K in 1998.

Cumulative N uptake as a percent of maximum accumulation by 3 canola in 1998 and 1999, 4 mustard and flax in 1998 in Saskatchewan.

Cumulative N uptake as a percent of maximum accumulation by corn in Manitoba (V-8 = 8 leaf, V-T = tassel emergence, R-1 = silking, R-5 = dent) and sugar beet in France.

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 targeted foliar applications of KNO_3 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-fruited (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

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).

Fertilizer (kg N ha ⁻¹)	Boll load	Foliar nitrogen (kg N ha ⁻¹)	Yield (kg seed cotton ha ⁻¹)
50	Low boll load	0	783 cd ^a
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

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

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 producing 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 cross-linked 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 $\text{Ca}(\text{NO}_3)_2$ 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. 26 to 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 μM B. The absolute amount of foliar-applied B moving out of the application zone was reduced in plants with 0 μM root B supply (1.1% of the applied dose) and highest in those grown in 100 μM 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 ^{65}Zn 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 ^{65}Zn 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_4 -containing treatments was higher than treatments containing NO_3 .

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 $\text{Ca}(\text{NO}_3)_2$ (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 $MgCl_2$, 90% of the applied Mg was absorbed by apple leaves even at a relative humidity of 30%, whereas $MgSO_4$ required a relative humidity of 80% for an increase in absorption (Neilsen and Hoyt, 1984). The response likely reflects the greater deliquescence of $MgCl_2$ compared to $MgSO_4$.

Prior studies on foliar Zn fertilization of various plants have shown relatively little translocation of foliar-applied Zn as $ZnSO_4$ 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 $ZnSO_4$ 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 $^{65}ZnCl_2$ 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 $ZnSO_4$, 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 ^{65}Zn applied to leaves of greenhouse grown avocado seedlings (*Persea americana* Mill.) showed that <1% of Zn applied as $ZnSO_4$ 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 $ZnSO_4$ 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 $ZnCl_2$ was more efficient than $ZnSO_4$ 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 $ZnSO_4$ was the Zn source for orange trees, Zn absorption 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 ^{65}Zn 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, $Zn(NO_3)_2$ alone, and in combination with urea and ammonium nitrate, raised leaf Zn level more than $ZnSO_4$ (Smith and Storey,

1979). There was no difference in the effectiveness of Zn compounds for foliar sprays applied to apples (Nielsen and Nielsen, 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 Fe-sulphate 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 ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 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 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (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 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 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 $[(\text{NH}_4)_5\text{P}_3\text{O}_{10}]$ followed by $[\text{NH}_4\text{PO}_3]_n$ and then $\text{PO}(\text{NH}_2)_3$. 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 Cl L⁻¹ caused leaf injury symptoms (Maas, 1982) but the degree of injury depended on the Ca:Na ratio as CaCl₂ alone was more toxic than NaCl, but at lower concentrations (1-3 meq L⁻¹) it reduced NaCl-induced leaf injury. The highly toxic effects of CaCl₂ 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 CaCl₂ 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 CaCl₂ and 24 meq NaCl per liter was noticeably less toxic than 25 meq NaCl 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 increases rapidly as the solution 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 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 over-applied 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 characteristics 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.

6. Regulatory and environmental considerations

In this chapter a brief account of the status of foliar nutrient sprays within the existing fertilizer regulation will be provided with emphasis on the environmental impact associated with foliar fertilization.

6.1. Regulatory matters

This overview of current fertilizer legislation has been written based upon discussions with Prof. Juan José Lucena (Universidad Atónoma de Madrid). Currently, within the European Union (EU) and the United States (US) there are no specific regulations for foliar fertilizers other than those developed for fertilizers as a whole. Regulations governing fertilizers vary between countries and states and there are currently no general or standard protocols agreed upon for chemicals to be designated as fertilizers. For example, there are many products currently certified as fertilizers in the United States that are not yet permitted for use in the European Union. This is particularly true in the realm of products acceptable for use in organic agriculture. A consequence of these disparate guidelines is that manufacturers must approach registration separately and agriculturalists must validate the efficacy of all products in each jurisdiction. For instance, the terms ‘complex’ or ‘chelate’ are widely used throughout the industry but as there is no requirement that these terms be used in accordance with their true chemical meaning the occurrence of these terms on material or product labels should be interpreted with caution.

In the EU, regulation (EC) N° 2003/2003 and its subsequent technical amendments known as ATP's (Adaptations to Technical Progress) are used to approve fertilizers that comply with these conditions. Since 2003 a number of amendments (with a fifth and sixth to appear shortly) have been approved and subsequently implemented with the aim of promoting the effectiveness and purity of fertilizers as well as the standardization of products and analytical techniques to assess their quality. China, India, Australia and some other countries have regulations in place to ensure quality and efficacy of fertilizers to greater or lesser degrees. In the US, regulations mandate that fertilizer labels accurately reflect nutrient contents and meet the standards for heavy metal contamination only. Currently, there are no US regulations that require a demonstration of effectiveness of a fertilizer product as a nutrient source.

The European fertilizer legislation complies with the legal requirements established in all European countries but it may be superseded by national fertilizer regulations that may allow or disallow the use of nutrient compounds not regulated by the

European Union. The regulation of fertilizers within the European countries enables the occurrence of “legal windows” to introduce products that may otherwise not be allowed by Regulation (EC) N° 2003/2003 and its consequent ATP’s.

6.2. Environmental and food quality considerations

Generally speaking, and when applied alone the environmental impact of foliar fertilizers is lower than that of most soil-applied fertilizers and leaf-applied plant protection products primarily because amounts applied are lower and the risk of soil or water contamination is minimized. However, since agricultural sprays are often supplied as agrochemical mixtures that may include foliar nutrients and plant protection products together, care should be taken to avoid environmental contamination. In Chapter 5, the technology of foliar application was discussed and referred to the rising concern about spray drift from plant protection products which is leading to the gradual implementation of control policies in many areas of the world as described by Hewitt (2008) and van de Zande *et al.* (2008a). These restrictions may impact upon the use of foliar fertilizers both by limiting their use in tank mixes with other agrochemicals and indirectly by affecting public perception of field spraying activities in general.

Foliar nutrients may benefit the environment by enhancing the efficacy of plant protection chemicals. The synergistic effect of mineral nutrients when applied in combination with plant protection products has been shown in several investigations (Dordas, 2009; Elattal *et al.*, 1984; Moustafa *et al.*, 1984; Simoglou and Dordas, 2006). In addition, the plant protection effects of several foliar-applied macro- and micro-nutrient solutions, including silicon based compounds, has been described, especially in relation to the control of fungal diseases (Dordas, 2009; Reuveni and Reuveni, 1998a; Reuveni and Reuveni, 1998b). Recently, Deliopoulos *et al.* (2010) reviewed the existing literature to analyze the effect of 34 inorganic salts (chiefly bicarbonates, phosphates, silicates, chlorides and phosphites) that were reported to reduce the severity of 49 fungal diseases in 35 plant species, and concluded that they were generally less effective in controlling fungal diseases than conventional fungicides and therefore cannot fully replace them. However, it was suggested that application of inorganic salts in a disease management strategy may enable a reduction in the number of conventional fungicide applications required (Deliopoulos *et al.*, 2010), and the supply of nutrients may improve the tolerance or resistance mechanisms of the host plant to pathogens (Dordas, 2009). Balanced nutrition is clearly an essential component of any integrated crop protection programme (Datnoff, 2007) but more research is required to fully realize the potential of foliar mineral element sprays as tools to reduce the effect of biotic stress in plants.

Phosphite has been recognized to have antifungal properties but there is controversy concerning the potential of this chemical to provide P to plants (Lovatt, 1990). Recently, it has been suggested that it should not be classified as a foliar fertilizer due to the high phytotoxicity risk from its application (Ratjen and Gerendas, 2009).

- Foliar fertilizers are often applied alone and as such they have a low environmental impact.
- When supplied in combination with plant protection products problems associated with spray drift may occur.
- Foliar fertilizers may have a synergistic effect when applied together with fungicides or pesticides.
- Several foliar-applied inorganic compound solutions have been reported to limit the effect of biotic stress in plants.

There are only a few studies reporting the occurrence of foliar spray residues and subsequent damage to marketability and safety of horticultural commodities. Application of in-season P-based foliar fertilizers to apple trees led to the occurrence of P-acid residues in apples at the time of harvest (Malusa and Tosi, 2005; Tosi and Malusa, 2002). Cheng and Crisosto (1994) showed that high concentrations of surface Fe and Al contaminants, in combination with abrasion (as may occur to the fruits during transportation), induced 'skin-inking' of peach and nectarine. In the light of these observations, Crisosto *et al.* (1999) recommended avoiding the application of foliar-nutrient sprays containing heavy metals particularly Fe but to a lesser degree Al and Cu in decreasing order for inducing fruit 'skin-inking' within 22 days before harvest.

- In general, and when applied alone, foliar fertilizers are not prone to cause food safety risks or produce marketability problems.

The beneficial effect of applying nutrients as foliar sprays in terms of improved effectiveness and limited environmental pollution as compared to soil-applied fertilizers has been illustrated by several authors (Kannan, 2010). Johnson *et al.* (2001) suggested that supplying N to peach trees using a combination of soil and foliar N fertilizers leads to optimal plant responses and limited environmental pollution risks. This approach has also been supported by others (Dong *et al.*, 2002; Dong *et al.*, 2005b) who demonstrated the effectiveness of foliar applications of urea in autumn as a strategy to increase tree N storage and to limit NO₃-N leaching problems associated with soil N fertilization. Stiegler *et al.* (2011) measured minimal NH₃-N volatilization losses when urea was applied to the foliage of actively growing turf grass. The authors highlighted the potential for minimizing N losses to the environment and increasing application efficiency through the use of foliar N fertilization on high-density golf courses. A similar efficacy relationship between foliar and soil K fertilization was demonstrated in rainfed olive trees grown in arid and semi-arid regions (Restrepo-Diaz *et al.*, 2009) in order to avoid problems associated with low K root uptake under limited soil moisture conditions. Similarly, a benefit of foliar P nutrition in dry-land cereal crops may occur when soil surface layers become dry thereby reducing the efficacy of surface P applications (Noack *et al.*, 2011).

- Foliar fertilization has a lower environmental risk in contrast to soil applications.
- Nutrients are delivered to target organs by spraying.
- A combination of foliar and soil treatments can help to increase nutrient uptake efficiency and limit soil pollution, particularly with elements such as N and/or P.

6.3. Conclusions

In this chapter, the regulation of foliar fertilizers and the potential environmental and food quality risks have been evaluated. In light of the current knowledge and understanding, the following certainties, uncertainties and opportunities for the regulation and risk potential of foliar fertilizers can be addressed.

Certainties

- There are currently no specific regulations governing foliar fertilizers.
- Products are classified according to a list of active ingredients allowed as fertilizers.
- When applied alone foliar fertilizers have a low environmental impact.
- Fertilizer/plant protection product mixtures are often applied to the foliage with the consequent spray drift and pollution risk.
- Certain nutrient element compounds can have a synergistic effect when applied together with fungicides or insecticides.
- Some nutrient element compounds can have a plant protection effect (e.g. fungicidal) when sprayed to the plants.
- Foliar nutrient fertilizers applied alone generally do not represent food safety risks.
- Many reports provide evidence for the lower environmental impact of foliar sprays as compared to soil treatments.

Uncertainties

- Since there are currently no specific regulations for foliar fertilizers it is difficult to standardize the many foliar fertilizer products available on the market.
- The process of introducing new foliar fertilizers in the market is complex.
- The effects of combined fertilizer/plant protection products cannot be predicted *a priori*.
- Several reports provide evidence for the beneficial effect of spraying nutrient element solutions to the foliage as a tool to control plant disease but the mechanisms involved are currently not fully understood
- The use of foliar fertilizers as a complementary strategy to reduce soil applications and pollution has not been fully exploited in agricultural production.

Opportunities

- By introducing regulations specifically for foliar fertilizers it might be possible to standardize and categorize the commercially available products and better focus scientific research and field practices to improve the overall performance and efficacy of foliar nutrient sprays.
- Knowledge of the synergistic effect of certain plant nutrient compounds when applied together with plant protection products may help to optimize the concentration of agrochemicals applied to plants and therefore reduce their environmental impact
- The beneficial effect of foliar-applied nutrients in reducing plant biotic stress should be further elucidated and implemented in agriculture.
- The low food safety and environmental risk of foliar-applied fertilizers have proven advantageous for agricultural and horticultural production.
- As a complementary strategy to soil treatments foliar nutrient sprays can help reduce nutrient run-off and leaching from soils and thus reduce contamination of water tables.

7. Perspectives of foliar fertilization

Foliar fertilization has been widely adopted in modern crop management where it is used to ensure optimal crop performance when nutrient supply from the soil is inadequate or uncertain. Foliar fertilizers offer specific advantages over soil fertilizers when plant demand for nutrients exceeds the capacity for root nutrient uptake; when elemental mobility within the plant limits delivery to tissues; and when environmental conditions limit the effectiveness or prevent the application of nutrients to the soil. In many risk-averse, high-value production systems foliar fertilizers are marketed as 'insurance' to minimize the potential impacts of unpredictable nutrient deficiencies.

The supply of nutrients by foliar fertilization represents a significant cost (per kg of applied element) and requires careful consideration of the relative benefit over conventional soil fertilizer applications. Determining the cost:benefit ratio of foliar fertilizers is not trivial and requires a realistic assessment of the economic risk of a nutrient deficiency occurring; quantification of the biological efficacy of the foliar fertilizer; and consideration of the full costs of the application (such as spraying). While it is relatively straightforward to estimate application and yield-lost costs it is much more difficult to determine: 1) the likelihood of an economically relevant nutrient deficiency occurring during the growing cycle; and 2) the biological efficacy of the foliar fertilizer applied. Given the widespread use of foliar fertilizers and the cost of these practices it is remarkable that there are very few examples where the economic viability of foliar fertilizers has been critically assessed. This is at least partially a consequence of the difficulty in knowing accurately the true risk of an economically important nutrient deficiency occurring and the uncertainty as to the effectiveness of the foliar materials used as a solution in treating the effects of the deficiency. The goal of this book is to provide insight into these two uncertainties so that more informed decisions can be made and improved practices can be developed.

As illustrated in the preceding chapters there is a good deal of complexity in determining if plants in a given environment have the potential to experience a nutrient demand that cannot be adequately provided by soil nutrients. Equal complexity exists in predicting if a given foliar application will adequately supply the required nutrients in a timely manner. Regardless of these complexities a fundamental understanding of the principles of foliar fertilization will minimize uncertainty and help improve the efficacy of foliar fertilization in modern crop production.

The factors that govern plant 'demand' for foliar fertilizers and the factors that govern the ability of a foliar formulation to 'supply' nutrients are summarized by the following:

Demand: foliar fertilization is applicable if any of the following situations prevail:

- Plant demand exceeds the capacity of the root to absorb the nutrient. This occurs when:
 - Soil conditions limit nutrient solubility or delivery to the root as a consequence of unfavorable pH or chemical composition of the nutrient; excess soil concentrations of competing ions; unfavorable conditions for root growth; or soil environmental conditions that limit nutrient uptake (unfavorable temperature, moisture or oxygen content).
 - A limitation in uptake capacity as a consequence of plant phenology such as during early spring when many deciduous species flower and set fruit during periods of unfavorable soil temperatures.
 - During periods of peak nutrient requirement such as rapid fruit growth when demand for nutrients can exceed the ability of roots to supply adequate nutrients even in a well-fertilized soil.
- When localized within-plant demand exceeds the capacity for within-plant nutrient re-distribution.
 - This commonly occurs in the vicinity of large fruit and nut clusters, or during grain fill or storage tissue development, and is related to both the highly localized demand for elements (notably N and K) or as a consequence of low phloem mobility of certain elements (notably Ca and B).
 - Within-plant element mobility can also be limited if flowering precedes leaf expansion and thereby limits xylem nutrient transport.
 - Periods of drought or high humidity can also limit both transpirational xylem flow as well as restrict the delivery of phloem-immobile nutrients.
- When plant demand cannot be satisfied due to:
 - Field conditions, application costs or growth stages that prevent the use of soil applications.
 - A perceived need for nutrient ‘insurance’ to minimize the potential risks of unpredictable nutrient deficiencies.

Supply: the efficacy of foliar fertilization is determined by:

- The physical and chemical characteristics of the fertilizer which determines the total quantity of nutrient that can be delivered and the compatibility of that nutrient with other chemicals.
- The characteristics of the species and the environment in which it is grown.
- The use of additives (surfactants, humectants, spreader/stickers, etc) and the method of application.
- The environment at the time of, and following, foliar application.
- The ability of the nutrient to penetrate into the cytoplasmic volume which is influenced by species; leaf type and age; chemical characteristics of the fertilizer; environmental conditions; and application method.

- The phytotoxicity of the foliar fertilizer mixture which limits the concentration of nutrient that can be applied.
- The mobility of the applied nutrient within the leaf that is determined by its relative phloem mobility, species characteristics, leaf age and immobilization of the element at the site of application.

Ultimately, the decision to use foliar fertilizers requires consideration of each of these demand and supply factors balanced against the relative costs. In circumstances where the soil-type, cropping system or the environment prevent soil application of the required nutrients then foliar fertilization represents an essential practice and as a consequence the primary challenge must be to develop foliar formulations and application methods that are as efficacious and economical as possible. However the majority of foliar fertilizers are not applied under circumstances where soil application is impossible but are rather being applied under the presumption that foliar application is superior to soil application. It is also probably true that the uncertainty of knowing the demand for foliar fertilizers, or the efficacy of a formulation, results in growers utilizing foliar fertilizers inefficiently; either applying them when they are not required; or failing to apply them when they are. In such scenarios which likely represent a large percentage of the conditions under which foliar fertilizers are utilized the challenge is not only to develop foliar formulations and application methods that are as effective and economical as possible, but also to develop methodology to predict if and when nutrients may become limiting and unresponsive to soil applications.

Foliar fertilization, as currently practiced, is both a science and an art and for those who ascribe to the 'spray and pray' philosophy it also resembles a faith. For the science of foliar fertilization to be optimized there is a substantial need to understand the factors that govern the efficacy of foliar fertilizers and to develop formulations and application methods that maximize the chance of beneficial response.

7.1. Conclusions

In this book, we have provided an integrated analysis of the physical, chemical and biological principles known to influence the absorption and utilization of foliar fertilizers by the plant and have reviewed the available laboratory and field results to provide insights into the factors that ultimately determine the efficacy of their application. Our goal was to provide an integrated analysis of what is known and what remains to be discovered toward reaching the goal of optimizing the utilization of foliar fertilizers in modern crop production. The factors that determine the efficacy of foliar fertilization are complex and encompass aspects of physics, chemistry, environment, biology and economics as well as intangibles such as risk aversion and ease of management. While some of the fundamental principles governing the use of foliar fertilizers are well understood there is far more about their technology that remains to be resolved or is yet to be discovered.

Certainties, uncertainties and opportunities

Previous chapters have identified the facts that are known (certainties); those that are unknown or unclear (uncertainties); and the opportunities that exist to improve the practice of foliar fertilization by optimizing our understanding of the factors that govern plant demand for foliar fertilizers as well as the factors that govern the ability of a foliar formulation to supply nutrients. The most important uncertainties that are constraining the utility of foliar fertilizers are as follows:

With regard the factors that govern the ability of a foliar formulation to 'supply' nutrients current knowledge of the following critical processes is inadequate:

- The mechanisms of cuticular penetration of polar, hydrophilic compounds are largely unknown.
- The contribution of the stomatal pathway and other epidermal structures such as trichomes and lenticels, to foliar uptake has not been adequately investigated.
- We have poor understanding of the contact phenomena between the foliar fertilizer formulation and plant surface.
- The role of surfactants, humectants, spreaders/stickers and other additives is not well understood and hence there is no mechanism to predict plant response without empirical testing.
- The factors that affect plant cuticular composition and plant response to foliar application are poorly understood and current knowledge is insufficient to predict or manipulate plant response to a foliar application.

With regard the factors that govern plant demand for foliar fertilizers current knowledge of the following critical processes is inadequate:

- The occurrence and importance of 'transient' or other nutrient deficiencies that cannot be prevented by soil fertilization has not been adequately investigated.
- It is unknown if foliar applied nutrients, once they enter the cellular space, are more or less metabolically available than soil acquired nutrients.
- The mechanism of toxicity of foliar fertilizers is not well understood.
- It is unknown if foliar-applied nutrients can be re-translocated more efficiently than soil derived nutrients.
- The significance of the counter-ion, or other molecules present in the formulation, in the metabolism or transport of nutrient elements following passage into the living cell is unknown.
- The influence of foliar sprays on shoot-to-root signalling and subsequent root growth and nutrient uptake from the soil has not been adequately investigated.

There are clear opportunities to improve the efficacy, or extend the utilization, of foliar fertilizers:

- There is potential to use supplemental foliar fertilizers with soil-applied fertilizers to provide more environmentally friendly, target-oriented and efficient fertilization.

- The full potential of foliar nutrient sprays as a complementary strategy to improve the quality characteristics of crops has not been fully researched.
- The permeability of plant surfaces to nutrient solutions offers the opportunity to supply nutrients to sink organs, bypassing root uptake and translocation mechanisms that limit the nutrient supply of the plant under certain growing conditions.
- There is increasing evidence showing that nutrient deficiencies can damage plant structure and limit responsiveness to subsequent nutrient availability.
- The addition of humectants to the foliar nutrient formulations to prolong the process of solution drying improves the efficacy of the treatments especially in arid and semi-arid areas.
- There is a need for the development of a risk assessment approach to foliar fertilization which would integrate the potential for occurrence of a transient but critical deficiency with the likelihood of a positive outcome and balance these with the risk of a negative outcome based upon formulation, plant and environment conditions at the time of application.
- Methods, both experimental and model-based, are required to predict the potential for a foliar fertilizer to cause toxicity damage.
- More importantly there is a need to better coordinate foliar timing and formulation to match critical periods of plant demand where foliar application may have a specific advantage.

In Chapters 2 to 4, the mechanisms of foliar uptake of nutrient sprays in association with plant structure and function were described in detail. The characteristics of the plant surface as a barrier for the entry of water and solutes were described and remarked on the generally hydrophobic character of the lipid coating covering the epidermis, namely the cuticle. The importance of providing nutrients in formulations that may facilitate the process of foliar uptake was subsequently highlighted and developed. In order to ensure the effectiveness of foliar nutrient sprays, one of the key factors that can actually be controlled, and that may radically change the performance of a particular nutrient compound, is the addition of suitable adjuvants. Efforts should be made to improve the physico-chemical properties of nutrient spray formulations to ensure the effectiveness and reproducibility of treatments under different environmental conditions. For instance, foliar applications in arid and semi-arid areas may be hindered by the rapid drying of spray solutions after treatment, and the addition of humectants may significantly increase the rate of uptake of foliar-applied nutrients.

Research and development in the area of foliar fertilizer formulations may increase the market and improve the quality, performance and effectiveness of foliar treatments. Apart from improving the rate of uptake of foliar nutrient fertilizers research efforts should focus on analyzing the physiological effect of foliar-applied nutrients on plant metabolism and signalling. In addition, the role of plant stress physiology relating to the effectiveness of foliar-applied nutrients is still not clear and should be elucidated, since foliar sprays are often used to overcome nutrient deficiencies that are more common in arid and semi-arid areas with high pH, calcareous or saline soils.

Other key factors influencing the effectiveness of foliar nutrient sprays are the mode and timing of application. For instance to improve uptake treatments should be sprayed when stomata are open and the improvement and development of more efficient spraying technologies will increase the efficacy of nutrient sprays when applied to the foliage.

In summary, foliar fertilization is already established as a normal practice in many cropping systems. The full potential of this technology has not been fully realized due to an inadequate understanding of the principles involved. There are clear knowledge gaps that hinder the development of improved foliar fertilization strategies. However, there is also a good deal of information on the mechanisms of uptake, plant physiology, physico-chemistry and formulation that has not been fully applied. Foliar fertilization is likely to play an increasing role in maintaining crop nutrient status under a variety of environmental situations when soil supply of nutrients is inadequate, and during periods of peak nutrient demand when delivery of soil-applied nutrients may be inadequate.

Ultimately the goal should be to improve the ability to predict the likelihood of an economically relevant nutrient deficiency occurring during a crop growth cycle and to optimize the timing and biological efficacy of the foliar fertilizer applied. With this information on hand, a rational cost/benefit analysis can be performed and an informed decision made. Furthermore analyses such as these will result in better focus of research efforts which will undoubtedly result in improved foliar fertilizer formulations and their practical application.

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