Foliar nutrition of crops:

Facts, Myths and Perspectives

Foliar fertilisers are increasingly used in agriculture and new commercial products are continuously released by fertiliser companies as a result of the increasing demand. There is indeed abundant evidence showing the beneficial effects of applying foliar fertilisers as a complementary strategy to soil treatments in terms of improved plant metabolism, yields and quality of crops. However, the current lack of scientific knowledge on many factors associated with the effectiveness of foliar treatments limits the reproducibility of the results after spraying fertilisers to different crops under different growing conditions. Additionally, the limited transfer of technical know-how from the scientific foliar uptake community to the agricultural sector supports the exiting "spray and pray" attitude when applying a foliar treatment to a crop (i.e., anything may happen). Thereby, and in light of the current foliar fertilisation scenario, the following questions are raised: (i) which foliar fertilisation facts are currently clear for researchers?, (ii) which kind of traditional believes are not helpful to ensure the effectiveness of a foliar treatment?, and (iii) what is the future of foliar fertilisation? Dr Victoria Fernández, from the Forest Genetics and Eco-physiology Research Group, School of Forest Engineering at the Technical University of Madrid, has the story for New Ag International.

She tackles the answers to some of these questions in scientific and applied terms, stressing the great market potential and usefulness of foliar nutrient sprays as a more target-oriented, sustainable and environmentally-friendly complementary fertilisation method.

DESPITE THE FACT that plant leaves are organs largely specialised for photosynthesis, evidence that they could absorb water and nutrient solutions applied on to them was gained more than one and a half centuries ago. Scientific trials on the mechanisms of foliar nutrient solution penetration into the foliage carried out during the last 50 years showed that no metabolically-active processes seem to be involved, which yields the term "uptake" not fully correct when referring to foliar fertilisation. However, due to the widespread use of foliar "uptake" in relation to the application of agrochemical sprays, such term will also be employed in this article as a synonym of foliar "penetration" or "absorption" that better describe the process taking place which is largely driven by concentration gradients between the plant surface and its interior.

Basic and applied research efforts during the last 50 years led to a better understanding of the key factors affecting the efficacy of foliar sprays and to the application of foliar fertilisers, chiefly as an alternative means of delivering nutrients to the plants under situations such as e.g., when the nutrient demand exceeds the root absorbing capacity and when soil conditions limit nutrient availability (e.g., in the presence of high pH, calcareous soils).

Variable penetration rates may be obtained in relation to the application of different element compounds and formulations on to the surface of various crops species and varieties. However, foliar nutrient sprays are supplied at higher concentrations as compared to soil treatments, but they may have a lower environmental impact since nutrients are direct delivered to the organs where they are required following the implementation of suitable foliar fertiliser programs.

In recent years, the potential of foliar fertiliser treatments as a sustainable tool to improve yields and quality of horticultural and field crops subjected to abiotic stress (e.g., drought and nutrient deficiencies) has been recognised, and continuous efforts are made by the industry to improve the performance of foliar nutrient formulations. Additionally, an array of plant physiological (e.g., stomata opening or plant water and nutrient status) and environmental factors (e.g., light, relative humidity

or temperature) are known to affect the efficacy of foliar sprays.
The mechanisms of foliar penetration directly affect the performance of surface-applied agrochemicals and for instance, many of biostimulant products shown in the first World Congress on Biostimulants in Agriculture recently held in Strasbourg (November 2012), were applied as foliar sprays. The question whether products such as e.g., foliar fertilisers, biostimulants or nano-plant protection products and fertilisers may penetrate into the foliage after foliar application, remains a crucial pre-requisite to obtain positive plant responses to the treatments. But, what is the state-of-the-art on foliar uptake mechanisms in relation to the polarity and hydrophobicity of the active ingredient molecules, the properties of plant surfaces and last but not least, the major environmental and plant physiological factors involved?

PLANT SURFACES: A HETEROGENEOUS PHYSICAL-CHEMICAL SCENARIO

Most aerial plant parts such as fruits, leaves and stems, are covered by an extra-cellular layer named the cuticle. This is a lipid-rich membrane largely composed of waxes (epi-and intra-cuticular), a polymer matrix of cutin (polyester network of hydroxy- C16 and/or C18 fatty acids) and/or cutan (and insoluble and more apolar polymer present in the cuticles of some species and organs), and variable amounts of polysaccharides and phenols. There is limited information on the chemical composition of the cuticle of most of plant species and for instance, hundreds of compounds can be extracted from a single cuticle, which can be classified as e.g., waxes, cutin monomers, fatty acids or phenols. The thickness of the cuticle may vary among species/varieties, organs and growing conditions (e.g., stress or environmental factors) and for higher plant leaves can be within a range of 0.5 to 14 μm. Furthermore, no relationship between the ultra-structure (as determined in transversal cuticle sections observed by transmission electron microscopy) and chemical composition of the cuticles has been established so far.

Major surface topography variations have been observed among plant species, which also influence the rate of wettability, hydrophobicity and retention of foliar-applied solutions1. Micro- and/or nano-scale roughness associated with the topography of epidermal cells (including trichomes, papillae or stomata), epicuticular waxes or cuticular folds may lead a high degree of hydrophobicity and even to super-hydrophobicity (contact angles >150º). But crop plants are not free from having a high degree of hydrophobicity and drop repulsion, and water contact angles between 130 and 150 º can be measured e.g., on peach fruit, wheat or cabbage upper leaf surfaces. In contrast, the surface of other crops such as pepper fruits, pear or maize upper leaf sides may be wettable and have water contact angles between 70 to 90 º (contact angle estimations and scanning electron micrographs by V. Fernández; Figure 1). The contact angles of water or agrochemical drops with plant surfaces determine the area of liquid which is in direct touch with the plant organ and therefore the higher this may be, the greater will be the zone were foliar uptake may occur. Thereby and in addition to possible adhesion or repulsion of drops (as determined by the work of adhesion), pure water solutions deposited on to peach fruit, wheat and cabbage leaf surfaces (Fig1, A-C) will initially have a lower chance to be absorbed as compared to the more wettable pepper fruit, pear and maize leaf surface were penetration may take place more readily (Fig. 1 D-F).
Taking into account the chemical heterogeneity and potential micro- and nano-topography and transversal section of the cuticle it can be concluded a priori that the process of uptake of leaf-applied solutions is neither simple to char-

acterise nor to take place, and that efforts must be made to modify the properties of the agrochemical formulation for improving contact phenomena between the liquid and the plant surface.

FOLIAR UPTAKE: A BOTTLENECK FOR THE EFFECTIVENESS OF FOLIAR SPRAYS

Agrochemical sprays are generally heterogeneous mixtures of chemicals dissolved in water as a matrix. The active ingredients of foliar fertilisers are essential elements salts, complexes, chelates or compounds, which are ionisable or present charges (e.g., as observed in many micronutrient chelates) in water solution. Unformulated fertiliser solutions will have a high surface tension (approximately within the range of pure water), which will lead to higher contact angles between the spray drops and plant surfaces. Once additives such as adjuvants are added to the formulations, the physical-chemical properties of the mixture will change, and complex surface phenomena between spray drops and plant surfaces may occur, ultimately facilitating the foliar uptake process.

Therefore, foliar fertiliser active ingredients will be highly polar and hydrophilic, but adjuvants such as surfactants, humectants or stickers may have predominant apolar components in their molecular structure and are more hydrophobic. The cuticle is chiefly made of compounds having important apolar components such as waxes and cutin and molecules, which yield it a rather hydrophobic membrane. Hence, agrochemicals having a dominant apolar component will be more soluble in plant surfaces and may cross the cuticle more easily1. Since water may account for more than 95% of a fertiliser spray, the mechanisms of penetration for water and electrolytes will apply for the uptake of such agrochemicals by plant surfaces. While there is abundant evidence showing

Table 1: Major factors affecting plant responses to foliar fertilisers

Environmental factors	Formulation factors	Plant related factors
• Light	• Point of deliquescence (humectancy)	• Surface topography and chemistry
• Relative humidity	• Solubility	• Plant phenological state
• Temperature	• Rate of retention	• Circadian and metabolic rhythms (stomatal opening, xylem flux, etc.)
• Wind speed	• pH, electrical charge	• Kind of organs treated (e.g., fruits or leaves)
• Rain, fog	• Molecular size	• Plant nutrient and water status
	• Ease to be metabolically incorporated	• Incidence of potential stress factors

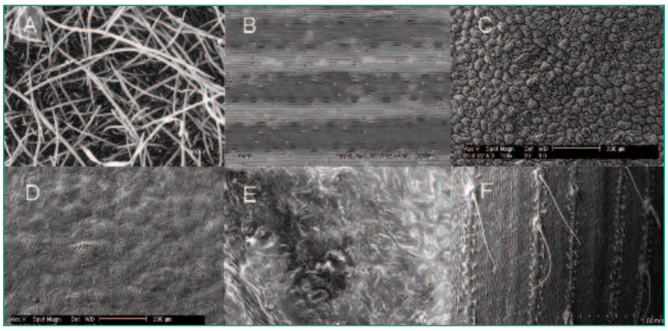

Figure 1. Surface topography of fruits and leaves of agricultural crops observed by scanning electron microscopy: A) peach fruit cv. Calrico (x100), B) upper side of wheat leaf cv. Axe (x100), C) upper side of cabbage leaf (x100), D) bell pepper fruit (x100), E) upper side of pear leaf (x400), and F) upper side of maize leaf (x50). Source V. Fernandez

that water and solutes can cross the cuticle of several species, the actual mechanisms of penetration are currently not fully understood and require further investigation. However, surface-applied agrochemicals have also been found to be absorbed via stomata, cuticular cracks and imperfections, trichomes, lenticels and other potential epidermal structures. While the stomatal foliar uptake pathway was neglected for decades, current evidence suggests its importance both when applying unformulated and formulated foliar spray solutions.

SCIENTIFIC FACTS AND FICTION

Aware that the mechanisms of cuticular penetration of water and solutes remain unclear and that the cuticle is a rather hydrophobic membrane, efforts should be made to improve the contact phenomena between the spray formulations and plant surfaces, and also to take advantage of stomatal opening. Many plant physiologists, biologists and even agronomists still consider plant surfaces as impervious to surface-deposited solutions, despite there is an important body of literature providing evidence for the process foliar uptake. The stomatal pathway has been especially disregarded during the last decades and consideration of plant metabolic rhythms (i.e., circadian rhythms) which may rule stomatal aperture at least in temperate zones of the world, may help raising the rate of uptake and translocation of foliar fertilisers.

On the other hand, foliar fertilisers have been traditionally used to cure nutrient deficiencies in crop plants and recent evidence suggests that such leaves may not be so permeable to leaf-applied solutions. For instance, we have observed a disruption of stomatal opening in iron-chlorotic leaves and boron-deficient leaves, which may limit the rate of uptake of foliar fertilisers, as observed to occur after boric acid foliar application. While there are many reports showing the physiological improvement of deficient plants after fertiliser spraying, there is some evidence suggesting that structural damages inherent to plant growth under nutrient deficiencies cannot be cured by applying foliar nutrient treatments. Hence and despite the traditional use of foliar fertilisers as a tool to cure nutrient deficiency symptoms in plants, wouldn't it be better to supply mineral element sprays to the foliage as routine complementary treatments for avoiding the development of nutrient deficiencies in crops? The implementation of routine spraying programs containing lower fertiliser concentrations may help to preserve the plant nutrient status while ensuring an optimal use of the resources, since increased uptake rates and metabolic responses may be expected from healthy plants.

Many nutrients traditionally applied as foliar sprays such as calcium, iron, zinc, or manganese have a limited mobility and many factors associated with the process of mineral element translocation within the plant in different species remain unclear. Hence, foliar sprays may act as contact fertilisers in relation to many elements and species and we cannot expect miracles or systemic responses after the application of a foliar fertiliser to a crop, since there are some obvious functional and structural constrains.

Similarly, complete reliance on foliar fertilisers to meet the nutrient demand of crops cannot be achieved especially in the case of macro-nutrients, which are required at higher concentrations. However, foliar fertilisation can be a complementary, sustainable and cost-effective method to preserve the quality, yields and nutrient status of crops during the entire growing season.

Given the rather apolar and hydrophobic nature of plant surfaces, it is likely that most leaf applied chemicals such as fertilisers, biostimulants or nano-particles are not taken up via the foliage unless, care is taken to apply the treatments under favourable conditions. For instance, light is known to stimulate stomatal opening and low relative humidity and high temperature will shorten the process of drying of the spray solutions, hence decreasing the chance of foliar penetration to occur (Table 1). Hence, the lack of response or major effects associated with foliar treatments in many reports may be due to foliar uptake failures or to the increased root uptake rate of treatments after spraying plants to run-off.

Additional issues such as spraying technology and drop size will also affect the rate of uptake of foliar fertilisers, but also considering the major role of plant physiological factors and the prevailing environmental conditions at the time of treatment. The factors affecting the effectiveness of foliar nutrient sprays (Table 1) are many and cannot be considered in isolation. For instance, light will promote stomatal opening, but may affect the stability of iron-chelate formulations when applied on to plant surfaces. Increased temperatures will lead to a rapid spray solution drying, but may also modify the physical-chemical properties of the formulation (e.g., surface tension, solubility or point of deliquescence). Having a low point of deliquescence (i.e., the relative humidity at which a compound traps enough water from the environment and becomes a liquid) is not the sole requisite to ensure the success of a foliar fertiliser and such property should be modulated to lower the phyto-toxicity risk of the treatment which can otherwise cause leaf burn when applied under certain favourable conditions.

MERGING KNOWLEDGE TO IMPROVE THE PERFORMANCE OF FOLIAR NUTRIENT SPRAYS

Nowadays, there no doubt about the increased use of foliar fertilisation in agriculture and horticulture, in parallel to the on-going efforts of fertiliser producers to develop products with optimised properties for better plant responses. However, when applying a foliar treatment there is an array of factors that lay beyond the physical-chemical properties of the fertiliser formulations and the effectiveness of treatments may vary among plant species/varieties grown in a different area of the world. The prevailing water pH, temperature, humidity and plant surfaces properties in different plant production locations may play a significant role concerning the performance of foliar nutrient sprays and there is a fair room for human decision-making mistakes when applying the treatments (e.g., applying them under low relative humidity, high temperatures, at high wind speeds or when stomata are closed).

Nevertheless, the transfer of knowledge and technical know-how from the scientific to the agricultural sector may contribute to increase plant responses to foliar sprays, via the development of effective fertiliser programs in accordance with plant physiological aspects, and also by improving fertiliser formulations and spraying technologies. But some scientists are still far away from the field and fail to understand the needs and the reality of crop plants, which is a prerequisite to improve the current "spray and pray" situation. Therefore, by merging the different scientific and applied knowledge of farmers, consultants, agrochemical producers and plant scientists it is in our hands to improve the performance of foliar nutrient sprays and to make the most out of this use.

Foliar Fertilization: Scientific Principles and Field Practices

The International Fertilizer Association (IFA) edited the book titled: "Foliar Fertilization: Scientific Principles and Field Practices", with the aim of providing a general overview of foliar fertilisation for a broad readership ranging from farmers to agricultural consultants and scientists. The authors are the researchers Dr. Victoria Fernandez (Technical University of Madrid, Sapin), Dr. Thomas Sotiropoulos (Greek Agricultural Organization 'Demeter', Pomology Institute, Naoussa , Greece) and Prof. Dr. Patrick Brown (University of California, Davis, USA). By merging their different kinds of expertise and backgrounds concerning foliar fertilisation in different areas of the world, they give a complete overview of this fertilisation technique which is based on the existing scientific and applied knowledge on foliar fertilisation.

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. The book describes 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 is merged with physical, chemical and biological principles to arrive at a greater understanding of this technology, its potential, its weaknesses and its unknowns.

The continuous exchange of information with Patrick Heffer (IFA), the IFA editorial committee, and with many people from the agro-chemical and scientific sector made it possible to develop this book, which may ultimately contribute to improve the effectiveness of the treatments by clarifying some of the major factors involved.

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