4

Foliar Nutrition: Current State of Knowledge and Opportunities

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Abstract

The effectiveness of foliar nutrition is affected by numerous endogenous (related to leaf anatomic structure) as well as exogenous (nutrient concentration, soil type, pH) and environmental factors. Simultaneous application of foliar nutrition with plant growth and development biostimulators enables the increase of crop yield and the improvement of its quality. A significant trend in functional food production is plant biofortification with mineral nutrients – mainly Ca, Mg, microelements, and biogenic trace elements. Foliar nutrition can be used as a method of increasing crop level of these elements. Citrus plants, despite its thick cuticle layer of leaves, respond relatively well to foliar nutrition due to a high number of stomata on the lower leaf surface accompanied by a greater amount of cuticle pores (easing nutrient absorption) than any other epidermal cells. Foliar application treatments, when properly planned and conducted, may stimulate the flowering, increase yield, and improve nutritional and postharvest quality of citrus fruits.

Keywords

Foliar nutrition • Biostimulation • Biofortification • Point of deliquescence • Crop nutritional quality • Postharvest quality • Nutrient deficiency • Water quality

4.1 Introduction

"Feed the plants, not the soil." This statement represents one of the current views on plant mineral nutrition both by soil fertilization and foliar application. In the historical context of the development of plant nutrition science (since ancient times through the classic studies by Justus von Liebig in nineteenth century), the idea of plant fertilization through foliar application stood in strong opposition to commonly approved theories on plant mineral nutrition based on mineral uptake by roots. It is worth to mention that historical origins of foliar nutrition of citrus plants date back to 1844 (Srivastava and Singh 2003). Since the mid-twentieth century, a dynamic increase in the number of studies on foliar nutrition has been noted which contributed to the development and, consequently, implementation of agricultural recommendations for foliar fertilization in the cultivation of numerous crops.

In many works, plant treatment of supplying mineral nutrients by spraying is described as "foliar fertilization," "foliar nutrition," "foliar feeding," or "foliar application." A correct usage of any of these terms depends on the type and number of applied compounds. In common practice, "foliar nutrition" is mostly used although not always it is related strictly to mineral nutrient application. It should be emphasized that nutrients supplied by spraying are absorbed not only by leaves but also other green aerial parts of plants covered by epidermis (petioles, shoots, fruits) as well as scales which cover buds.

Foliar nutrition cannot replace or eliminate the natural way of nutrient uptake by plant roots. In general, foliar

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application of mineral elements is not so effective as to cover total nutritional requirements of plants – even after foliar spraying with easily remobilized mineral elements (Marschner 1995; Michałojć and Szewczuk 2003; Starck 1997). It mainly results from restrictions in applying increased doses of mineral nutrients or its insufficient translocation from leaves to roots. Nevertheless, depending on plant species, a significant portion of plant requirements for mineral nutrients (mainly microelements) can be covered by foliar nutrition (Szewczuk and Michałojć 2003a).

Foliar fertilization is most commonly used for: supplying nutrient deficiency, improving nutritional status of plants and, thus, increasing crop yield and its quality. However, depending on plant species, environmental factors, and agrotechnique, this treatment can be applied for other purposes, such as mitigating the negative effects of stress conditions – drought, frost damages, etc.

Not only mineral elements can be supplied by plant spraying but also nutritional compounds (i.e., simple sugars, disaccharides), amino acids, peptide chains, organic acids, growth regulators and stimulators. The whole spectrum of organic compounds present in seed or marine algae extracts is applied with fertilizers. In such a case, "plant biostimulation" should be mentioned rather than "foliar nutrition."

Recently, a particular attention is put on plant biofortification with mineral nutrients, especially those characterized by insufficient distribution in food chain (soil–plant–consumer). This impaired transfer results in a deficient level of such macro- and microelements as Ca, Mg, Fe, Zn, Cu, I, and Se in the diet of many people in the world (Dayod et al. 2010; Hirschi 2009; White and Broadley 2009). In many cases, foliar application is considered the quickest and highly cost-effective method of its introduction into plants and, as a consequence, in human diet and animal fodder.

It needs to be mentioned that significant differences exist in the possibility of conducting foliar nutrition and its efficiency in the cultivation of annual (mono- and dicotyledonous), biennial, and perennial plants, as well as C3 and C4 plants. These dissimilarities result from differences in leaf anatomy, physiological and biochemical processes, and cultivation period – 1, 2, or many years. The efficiency of foliar treatment depends on numerous endo- and exogenous factors.

In spite of considerable progress in foliar nutrition research, still many problems are encountered related to the development of agricultural recommendations for conducting this treatment especially in the range of improving its efficiency, plant biostimulation, balancing reduced soil fertilization with foliar application, as well as adjusting current foliar nutrition programs for newly obtained cultivars.

To sum up, it can be stated that foliar nutrition is the fastest method of introducing mineral nutrients in the aerial parts of crop plants when compared to any other technique of soil fertilization, including fertigation.

4.2 Endogenous Factors Affecting Nutrient Absorption by Leaves and Other Aerial Parts of Plants

When endogenous factors are considered, the absorption efficiency for nutrients applied foliarly depends on the thickness of the cuticle covering epidermal cells (green shoots, lower and upper leaf surfaces) as well as the number of cuticular pores and ectodesmata (*syn*. ectoteichodes) located in this layer. Additionally, it is related to the distribution of trichomes and stomata in leaves accompanied by the highest occurrence of cuticle pores (Franke 1961; Kannan 2010; Marschner 1995; Michałojć and Szewczuk 2003).

4.2.1 The Cuticle

The cuticle protects above-ground parts of plants against excessive transpiration, pests, and infections as well as prevents leaching of particular compounds from leaves by precipitation. Cuticle thickness is species-dependent, but leaf position on the stem is also of significance. Citrus and coffee plants are characterized by a particularly thick leaf cuticle. What is more, leaves grown in the shade have thinner cuticle layer than those exposed to full sunlight (Marschner 1995).

The cuticle consists of three layers: (a) external – top coating of wax, (b) the cuticle proper – middle layer of cutin embedded with wax, and (c) inner layer composed of cutin and wax blended with carbohydrates (pectin, cellulose, etc.) – cuticular (cutinized) layer contacting cell walls. The cuticle proper is covered with a wax layer composed of highly polymerized saturated and unsaturated esters, ketones, fatty and hydroxy fatty acids, as well as alcohols (Fageria et al. 2009; Franke 1967, 1971; Holloway 1971; Michałojć and Szewczuk 2003; Weaver 1972). Waxy substances are of apolar–lipophilic character. Cutin, a main component of the middle part of the cuticle, contains numerous hydrophilic groups defining its polarity. The presence of carbohydrates in the most inner layer of cuticle furtherly increases its polar and hydrophilic character. As a consequence of described physicochemical properties of these three layers (differences in electrochemical potential), a distinct polarity gradient occurs which is mainly responsible for ion transport through cuticle (Komosa 1990; Michałojć and Szewczuk 2003; Schönherr 2006). Franke (1967) indicates that across the cuticle, polar substances soluble in water (cations, anions) are transported by "hydrophilic path," while apolar compounds soluble in lipids through "lipophilic path."

Open spaces can be formed in the cuticle layer favoring the process of intercuticular penetration. Its mechanism is based on the diffusion of organic and inorganic ions as well as undissociated molecules (Franke 1986; McFarlane and

Berry 1974; Norris and Bukovac 1972). Polar characteristics of cuticle and pectin layer, which is a part of an outer cell wall, determined mainly by its negative charge due to the presence of –OH and –COOH groups enable cation sorption (Franke 1986; Michałojć and Szewczuk 2003). Additionally, negative charge of these layers contributes to more efficient translocation of apolar molecules (*i.a.*, urea) and cations rather than anions. For that reason, a lower efficiency is observed for foliar nutrition with mineral nutrients in anion forms (NO_3^-, $H_2PO_4^-$, Cl^-, HPO_4^{2-}, SO_4^{2-}, $B_4O_7^{2-}$, MoO_4^{2-}, BO_3^{3-}) than with cations (NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, Cu^{2+}, Cu^+, Zn^{2+}). Rate of cation permeation through the cuticle declines with increasing valency. For both types of ions, cations and anions, nutrient translocation from the outer to the inner parts of leaves (influx) is greater than in the opposite direction – efflux. However, these differences are less distinct for organic molecules (Yamada et al. 1964).

The above-described mechanism of mineral nutrient absorption by epidermis of aerial parts of plants differs from processes occurring in roots. Typical antagonistic and synergistic interactions between cations and anions noted for the root uptake can also be assigned for foliar nutrition. Its strength and occurrence depend, however, on a dose and concentration of nutrients – particularly in the case of multielement fertilizers used for foliar nutrition. Due to a huge disproportion in macro- and micronutrient concentration in such fertilizers, it is recommended to use chelated forms of the latter ones which eases its absorption by leaves.

The efficiency of nutrient absorption is also dependent on the contact angle of liquid drop on leaf and stem epidermis surface. The lower the angle and more thorough the coating of epidermis surface by droplets of solution, the better translocation of dissolved nutrients into plant cells is observed. The value of the angle can be successfully decreased by the application of adjuvants and surfactants which reduce surface tension of liquid droplets (Komosa 1990; Michałojć and Szewczuk 2003).

Amide nitrogen in the form of urea [apolar organic compound $–CO(NH_2)_2$] undergoes the fastest transport across the cuticle. Foliar application of urea, even in low concentrations, hydrates the cuticle making its absorption (as well as other mineral nutrients) more effective (Marschner 1995; Michałojć and Szewczuk 2003; Smoleń and Sady 2008a). In the studies conducted by Bondada et al. (2006) on isolated grapefruit (*Citrus paradisi* Macf.) cuticle, maximum penetration rate of urea occurred approx. 40 min after droplet application, and the rate was about 2% of the amount applied per hour. Total urea penetration averaged approx. 35% and tended to decrease with increased cuticle weight until the cuticles were 6 months old. In comparison, in bean leaves (characterized by a relatively thin cuticle), 50% of foliarly applied urea was absorbed within 1–4 h (Wittwer and Teubner 1959).

4.2.2 Cuticular Pores and Ectodesmata – Stomata and Trichomes

Numerous models of nutrient transport across the cuticle have been described (Srivastava and Singh 2003). Basically, besides a direct penetration through this layer, mineral nutrients can be absorbed by cuticular pores and ectodesmata syn. ectoteichodes (Kannan 2010; Marschner 1995; Michałojć and Szewczuk 2003).

Relatively little is known on nutrient absorption through ectodesmata (Franke 1971). Kannan (2010) informs that ectodesmata were demonstrated in epidermal walls of mesophytic plant species. Michałojć and Szewczuk (2003) indicate that nutrient transport across the cuticle occurs in regions contacting with ectodesmata. There is no clear information in the literature whether these regions overlap with the distribution of cuticular pores and ectodesmata, in particular, plant species.

Cuticular pores, depending on its size, are permeable to compounds of various molecular weights, such as mineral nutrients, chelated microelements, and sugars (Marschner 1995). Studies conducted by Schönherr (2006) revealed that aqueous pores in plant cuticles arise by hydration of permanent dipoles and ionic functional groups. Aqueous pores preferentially occur in cuticular ledges, at the base of trichomes, and in cuticles over anticlinal walls and its radii range from 0.45 to 1.18 nm. Translocation of ionic compounds can be fairly rapid, and ions with molecular weights of up to 800 g mol^{-1} can penetrate cuticles that possess aqueous pores with time.

Generally, the number of cuticle pores in stomata (guard and subsidiary cells) and trichomes exceeds its level in other epidermal cells. Thus, the density of stomata and trichomes on leaf surface (adaxial and abaxial) affects the efficiency of the uptake of mineral nutrients supplied by plant spraying (Komosa 1990; Marschner 1995). A significant role of stomata cells and trichomes in the absorption of nutrients applied through foliar nutrition results from a great number of ectodesmata in these cells. Trichome-related absorption decreases with the level of its cutinization and leaf aging (Komosa 1990). Leaves of citrus plants are characterized by several times higher stomatal density than observed in other plants (Table 4.1). In such a case, it may be stated that despite a relatively thick cuticle layer, foliar nutrition of these plants can be more successful than in other crop species.

Basic physiological role of stomata is to regulate gas exchange between plant and atmosphere. Nutrient uptake through stomata depends on its density (rather than the degree of stomatal opening), value of surface tension of applied liquids (solutions of lower tensions are more readily absorbed), and the morphology of stomatal cells. According to Marschner (1995), rate of mineral uptake through stomata is higher at night, when these structures are closed, than

Table 4.1 Number of stomata (stomata density) per unit area of adaxial and abaxial side leaves

Plant	Number of stomata (mm^{-2}) Adaxial side	 Abaxial side	References
Citrus group			
Citrus plants – average	n.d.	400–700	Spiegel-Roy and Goldschmidt (1996)
Red Bush grapefruit	n.d.	477.9	Graham et al. (1992)
Marsh grapefruit	n.d.	438.9	Graham et al. (1992)
Swingle citrumelo	n.d.	498,3	Graham et al. (1992)
Valencia sweet orange	n.d.	654.2	Graham et al. (1992)
Orlando tangelo	n.d.	542.3	Graham et al. (1992)
Sour orange	n.d.	359.3	Graham et al. (1992)
Cleopatra mandarin	n.d.	530.5	Graham et al. (1992)
Others species			
Alfalfa	169	138	Piskornik (1994)
Apple tree	0	290–400	Piskornik (1994)
Arabidopsis	250	350	Coupe et al. (2006)
Bean	40	281	Piskornik (1994)
Cabbage	141	226	Piskornik (1994)
Cherry	0	250	Piskornik (1994)
Coffee	n.d.	138.8–184.4	Pompelli et al. (2010)
Corn	52	68	Piskornik (1994)
Geranium spp.	n.d.	7.75	Schletz (2008)
Lime	n.d.	370–420	Meinder and Mansfield (1968)
Oat	25	23	Piskornik (1994)
Pea	101	216	Piskornik (1994)
Peach	0	225	Piskornik (1994)
Soybeans	81–170	242–385	Ciha and Brun (1975)
Sunflower	58	156	Piskornik (1994)
Tomato	12	130	Piskornik (1994)
Wheat	50.7–57.5	34.9–39.7	Mohammady (2011)

n.d. not detected

during day when stomata are open. Studies conducted by Eichert et al. (2002) confirmed that stomata can be an important pathway for the uptake of foliar applied substances. In the case of *Sedum telephium* leaves, uptake rates increased by a factor of 1.5–36 when compared with leaves kept in darkness prior to the foliar application. Additionally, frequency of stomata per leaf surface reduces with increasing ploidy level (Beck et al. 2003).

Stomata number on leaf surface is not a constant value. According to Graham et al. (1992), stomatal density on leaves of various citrus species changes in relation to cultivation conditions – in field or greenhouse. Nevertheless, irrespective of cultivation site, this index was lower for leaves of full expansion than in leaves of two-third expansion.

Shaded leaves are usually greater in size and have thinner cuticle layer than leaves growing in full sunlight. Interesting is the total stomatal area calculated for both types of leaves as it affects the effectiveness of foliar nutrition – expressed as rate of nutrient absorption by leaves. Results of the studies conducted by Pompelli et al. (2010) indicated that coffee leaves exposed to full sunlight were characterized by higher stomatal density (184.4 mm^{-2}) than leaves grown at 50% of reduction in solar irradiation (138.8 mm^{-2}). However, with a significantly higher total leaf area, shaded leaves had a comparable stomatal area to full-sunlight leaves – 377.2 μm^2 and 374.7 μm^2, respectively. It therefore can be concluded that leaves developed in full sunlight as well as shaded ones take up mineral nutrients by leaves at a similar level while the efficiency of this process is the resultant of the following factors: cuticle thickness, stomatal density, and stomatal area.

Gas exchange occurring through stomata enables the uptake of mineral nutrients present in the atmosphere in gaseous forms. This applies mainly to SO_2, NH_3, and NO_2 which are rapidly included in metabolic pathways in mesophyll cells in leaves. The amount of nutrients absorbed in such way is difficult to estimate. The concentration of mentioned gases in the air depends on the degree of industrialization and transportation (emission of SO_2 and NO_2), agricultural technology (crop fertilization, livestock farming – ammonia emission), as well as microbiological processes occurring in soil. The excessive level of these gases in the air, particularly of SO_2, can induce plant damages (Malhotra and Hocking 1976).

To sum up, the efficiency of nutrient uptake by leaves is mainly dependent on leaf area (which relates to its developmental stage) as well as the number of stomata and trichomes along with cuticle pores accompanying these two types of cells.

4.2.3 Cell Wall and Cell Membrane

Apart from the cuticle, other barriers in nutrient uptake by aerial parts of plants are cell wall and cell membrane. Mineral nutrients and more complex compounds are transferred across cell wall through interfibrillar spaces and ectodesmata. The sole mechanism of nutrient transport in cell wall is based on diffusion. Donnan free space (DFS) (also called apparent free space AFS) plays a crucial role in cation sorption and translocation with diffusion (Komosa 1990). During nutrient absorption from leaf surface into deeper layers, cations are easily transported in this area, while anions are removed (Marschner 1995).

Nutrient translocation across cell membrane into cytoplasm is mainly regulated by the active mechanism with the use of protein carriers or ion pumps (Komosa 1990; Michałojć and Szewczuk 2003). Mineral nutrients transported into cytoplasm are utilized in various metabolic pathways. Further, they can be transported in ionic or organic form. Distribution of nutrients between mesophyll cells in leaf and into phloem and xylem occurs mainly by plasmodesmata, protein carriers, or ion pumps.

4.2.4 Leaf Growth and Development, Plant Age

Foliar fertilization requires higher leaf area index (LAI) for absorbing applied nutrient solution in sufficient amount (Fageria et al. 2009). However, young developing leaves (characterized by low LAI value) are a significant acceptor of mineral nutrients and photosynthetic products. Mineral nutrients applied at that stage of leaf development rapidly permeates through the cuticle. Mature leaves with the highest photosynthetic productivity remain the source of photosynthetic products for other parts of the plant. At that stage, compounds applied through foliar nutrition are translocated from leaves to shoots, flowers, fruits, and roots along with assimilates. In each development stage or phenologic phase, plant requirements toward particular mineral nutrients vary significantly. During early growth and leaf development, plants need higher nitrogen levels. In further stages, depending on plant species, increased requirements toward phosphorus are noted for flowering and seed setting while appropriate potassium and/or calcium nutrition is crucial for fruit growth and development. These variations in nutrient demands result from the changes in the dynamics of metabolic processes and plant productivity. The amount and proportion of applied mineral nutrients should be adjusted to particular development stages. What should also be taken into consideration is the efficiency of foliar nutrition of annual, biennial, and perennial plants (Magdziak and Kołodziej 2003), as well as trees and shrubs.

Efficiency of foliar nutrition decreases during leaf senescence. This process is characterized by remobilization of endogenous mineral nutrients from leaves to shoots. At the same time, higher rate of nutrient leaching from leaf surface by aqueous solutions (rain, fog, etc.) is observed as permeability of cell membranes for mineral nutrients significantly increases (Marschner 1995).

To sum up, if for certain nutrients foliar application at an early growth stage of citrus plants leaves is recommended, it is therefore necessary to reach a compromise between early application and allowing the crop to attain a leaf area large enough for the absorption of large amounts of nutrients (Srivastava and Singh 2003).

4.2.5 Leaf Turgor

Leaf turgor undergoes diurnal changes caused by direct influence of exogenous environmental factors – light, temperature, wind – affecting physiological and biochemical mechanisms regulating water relations in plants.

Leaves maintained at full turgor – during the morning and evening hours – present the highest ability to absorb and metabolize mineral nutrients applied foliarly. High temperature combined with light intensity and wind decreases leaf turgor, negatively affecting the rate of biochemical and physiological processes in plants. Leaves with lower turgor values are more prone to exhibit midday depression of net photosynthesis. This may result in weakened absorption and metabolism of mineral nutrients applied in the early morning hours particularly in hot and sunny days. Foliar nutrition is the more effective, the longer leaves maintain high turgor. If foliar application is conducted in the morning hours, it is achieved in cloudy days with moderate temperature and high air humidity.

4.2.6 Soil Fertilization, Nutritional Requirements of Plants, Nutritional Status of Plant vs. Efficiency of Foliar Nutrition

Soil applications of fertilizers are mainly done on the basis of soil tests, whereas foliar nutrient applications are mainly conducted on the basis of visual foliar symptoms or plant tissue tests. Hence, correct diagnosis of nutrient deficiency is fundamental for successful foliar fertilization (Fageria et al. 2009).

Szewczuk and Michałojć (2003a) inform that foliar nutrition gives better results if plant cultivation is conducted on soil with optimal pH value and level of mineral nutrients. Nevertheless, efficiency of foliar nutrition, particularly in the aspect of its influence on crop yield and its quality, is directly related to nutritional status of plant. Generally, the better is nutritional status of plant (mainly achieved by nutrient uptake from soil), the lower is the efficiency of mineral nutrient supplementation by foliar application (Wójcik 2004). It is a consequence of simple relations described by the classic Liebig's law of the minimum and Shelford's law of the tolerance. In plants with high nutritional status, additional foliar supplementation of mineral nutrients increases its leaf concentration to the level of "luxury consumption." In that case, a significant increase of crop yield or improvement of its quality should not be expected, and thus, this treatment is not economically justified. Adversely, additional foliar application of mineral nutrients is considered cost-effective if it is conducted to obtain crops biofortified with elements (particularly micro- and trace elements) that are deficient in the diet of human populations living in particular environments.

Foliar application of excessive doses of nutrients (in relation to plant requirements) may induce some negative effects on plant organisms. Toxicity of mineral nutrients applied foliarly can be observed irrespective of current nutritional status of plants as nutrients can be introduced in such forms (speciations) that cause plant damages even if applied in relatively low concentrations, *i.a.*, I^- and SeO_4^{2-} when compared to IO_3^- and SeO_3^{2-}.

A completely different aspect that should be considered together with foliar nutrition is the problem of mineral deficiency. Particular species of annual, biennial, perennial plants as well as trees and shrubs differ with respect to macro- and micronutrient requirements and therefore exhibit various tolerance toward nutrient deficiency (Szewczuk and Michałojć 2003b). It is important for microelements as its assimilation from soil is insufficient due to low level in soil, inappropriate pH, antagonistic interactions with other elements, soil humidity, or organic matter content.

If deficiency of a nutrient occurs in plants, its supplementation through foliar application will be more rapid than through soil fertilization (Marschner 1995). Foliar absorption of mineral nutrients is from 8 to 20 times more efficient than soil application. Nevertheless, such high efficiency is not commonly achieved in agricultural practice (Kuepper 2003).

It needs to be underlined that in many cases, nutrient deficiency in above-ground parts of plant (leaves, shoots, fruits) is brought about by impaired translocation, as for P and Ca (from roots or within leaves and fruits) rather than its low concentration in soil. A perfect example is symptoms of Ca deficiency noted in annual plants (tip burn) or citruses (blossom-end rot of citrus). Physiological causes of Ca deficiency in particular plant groups are complex and result not only from strongly acidic properties of soils but also disturbances in water relations – and therefore difficulties in Ca translocation to outer parts of leaves or fruit skin. In citrus plants, symptoms of calcium deficiency are usually associated with strongly acidic soils and climatic conditions characterized by numerous cloudy or rainy days. What is of particular importance, in many cases, these symptoms become visible only during postharvest storage. Foliar nutrition with Ca may prove to be efficient in mitigating and counteracting these physiological diseases. In this aspect, interesting are the results obtained by Xie and Zhang (2004) in citrus cultivation and foliar application of phosphorus which undergoes a relatively slow absorption by leaves. In these studies, an average of 24 h after treatment, the leaf retained 74.8% of original amount of ^{32}P applied, but fruit rind only retained 47.4% of the total ^{32}P applied. Within 72 h after application, the leaf exported 1.61 μmol g^{-1} dry weight tissue, whereas the rind exported 0.143 μmol g^{-1} dry weight tissue of the initial amount of ^{32}P applied. Some ^{32}P was transported into the adjacent fruit 5 days after the application of ^{32}P.

A significant issue in modern agriculture is the need of improving nitrogen utilization from mineral fertilizers mainly in order to control its loss from soil. Soil application of lower N doses may decrease crop yield, although this can be compensated by additional foliar nutrition. This relation was confirmed for annual, biennial, and herbaceous perennial plants (Rydz 2001; Jodełka et al. 2003; Wojciechowska et al. 2005; Smoleń and Sady 2008c). According to the reports of Rożek et al. (2000), Rydz (2001), and Wojciechowska et al. (2005), the efficiency of foliar nutrition is dependent on soil, climate, fertilizer type, and the amount of nitrogen used. In trees and shrubs, application of foliar nutrition for mentioned purpose seems less effective. It is the consequence of a limited amount of nitrogen that can be delivered foliarly when compared to nutritional requirements of this plant group.

4.3 Exogenous and Environmental Factors Affecting the Efficiency of Foliar Nutrition

Srivastava and Singh (2003) presented the list of the most important exogenous and environmental factors affecting foliar fertilization: light, temperature, wind, time of day, photoperiod, humidity, amount and intensity of precipitation, drought, osmotic potential of growing medium (or soil water), and nutrient stress. To factors associated with spray solution, quality of water used for foliar nutrition, nutrient concentration, and pH of working solution can be included. Each of these exogenous factors (particularly environmental ones) has a direct influence on physiological and biochemical processes in plants, at the same time impacting the efficiency of foliar nutrition. Effects induced by some of these factors have been discussed in the previous section.

If plant spraying is carried out in bright sunlight, droplets of working liquids on leaf surface act as miniature lenses and by focusing sun radiation cause leaf burn and necrosis. At high temperature, loss of plant turgor is observed which reduces the rate of biochemical reactions and impairs the absorption of applied compounds. What is more, with rising air temperature, relative humidity drops rapidly which increases the rate of water evaporation. As a consequence, nutrient penetration through the cuticle is significantly slowed down. Additionally, rapid drying of droplets increases the final concentration of nutrients on the leaf surface posing a risk particularly if highly concentrated fertilizers are applied. Therefore, in the conditions of high sunlight and temperature, plants may be unable to effectively take up and utilize compounds supplied through foliar spraying (Marschner 1995; Starck 1997; Kujawski 2005).

It should be emphasized that at elevated temperatures occurring together with increased intensity of solar radiation and length of daytime, significant changes are noted in the structure of cuticle waxes (transition to vertical configuration) and coverage of the leaf surface with these compounds. Such modifications improve nutrient absorption by leaves (Komosa 1990). Marschner (1995) informs that, in contrast to roots, the uptake of mineral nutrients by green parts of the plant is stimulated by light. Additionally, the rate of nutrient absorption by leaves is higher during daytime than at night which is a direct consequence of circadian rhythms of metabolic processes. Nevertheless, droplets of working liquid applied on leaf surface dry quicker during the day than in the evening hours.

With reference to the information presented above, it should be mentioned that there are also different opinions on the optimal timing of foliar application. Szewczuk and Michałojć (2003a, b) as well as Kujawski (2005) recommend to conduct this treatment during the late afternoon or evening hours, while Fageria et al. (2009) suggest the afternoon hours when air temperature is low (after 2–3 p.m.). Application of foliar nutrition in the evening hours contributes to a prolonged wetting of the plant surface favoring bacterial and fungal infections – if foliar nutrition is not combined with plant protection treatment. Additionally, active ingredients and formulas of fungicides might reduce the rate of nutrient absorption in leaves (Schönherr 2002).

In the context of discussed influence of light and temperature on the cuticle wax structure and stimulation of nutrient uptake by light (Komosa 1990; Marschner 1995), it seems unreasonable to conduct foliar nutrition in the afternoon and evening hours. After the sunset, the wax structure may return to its original shape, and most of metabolic processes slow down which, in consequence, may decrease the absorption rate and the efficiency of utilization of mineral nutrients supplied with foliar application. Nevertheless, for nutrients applied foliarly, ion uptake rate is higher at night (when stomata are closed) than during day (Marschner 1995).

A key factor affecting nutrient absorption by aboveground green parts of the plant is the drying time of working liquid droplets on leaf and shoots epidermis. A reduction in liquid evaporation from plant surface can be achieved by the application of humectants or antievaporants. Some of these chemicals are included in commercial foliar fertilizers or surfactants and adjuvants.

Rates of penetration are greatly affected by humidity over cuticles and hygroscopicity of salts (Schönherr 2002). Utilization of mineral nutrients supplied by foliar application is never 100% effective – even for urea, which is relatively easily translocated across the cuticle (Bondada et al. 2006). After droplet drying, a significant amount of applied compounds remains on epidermis surface as "dry deposit" – salt crystals or organic sediments (amino acids, saccharides, etc.). These solid-state forms can be redissolved in water vapor from humid air. The possibility of rehydration is determined by the point of deliquescence (POD) of the salt and humidity over the salt residue (Table 4.2). POD is defined as that humidity over a saturated solution containing solid salt. When humidity is above POD, the salt residue on the cuticle dissolves, while below, a solid residue is formed and penetration ceases (Schönherr 2002). In the case of foliar application of a mixture of various compounds (multielement fertilizers), ionic strength of the solution significantly changes (as well as cation–anion interactions) depending on the concentration of particular salts. As a consequence, values of POD are also different and difficult to determine experimentally. Generally, values of POD are not affected by temperature (Kolthoff et al. 1969).

Compounds with POD values above 90% are characterized by low ability of rehydration by air humidity. In such a case, efficiency of its absorption will be mainly influenced by the duration of leaf wetness after foliar application. Rehydration of dry deposit on leaf surface occurs also due to fog, dew, or small rainfall (short-time drizzle). Efficiency of the process depends on the solubility of dry deposit components and the amount of water supplied with precipitations. Intensive leaf wetting by rain, on the other hand, is responsible for the leaching of endogenous mineral nutrients from leaves as well as removal of dry deposit from endodermis. In the studies conducted by Bondada et al. (2006), simulation of rehydration of urea deposit on grapefruit leaves with water stimulated additional penetration of about 1%; however, this was not significant.

Potassium fertilizers (KNO_3 and KCl, in particular) have high values of POD, but foliar nutrition of citrus plants with K compounds gives satisfactory results in increasing yield and improving fruit quality (Srivastava and Singh 2003). It is more likely related to a large number of stomata and cuticular pores on citrus leaves facilitating nutrient absorption

Table 4.2 Characteristics of selected salts and organic compounds containing one or two mineral nutrients with respect to POD in the aspect of its applicability for foliar nutrition

Mineral nutrients	Salt/compound	POD (%)[a]	Assessment of salt/compound applicability for foliar nutrition
N	$CO(NH_2)_2$ – urea	n.d.	Very good
	NH_4NO_3	63	Average
N and P	$(NH_4)_2HPO_4$, $NH_4H_2PO_4$	n.d.	Average
P	H_3PO_4	n.d.	Average
K	$K_2CO_3 \cdot 2H_2O$	44	Good
K and Cl	KCl	86	Small
K and N	KNO_3	95	Small
K and P	K_2HPO_4	92	Small
	KH_2PO_4	95	Small
K and S	K_2SO_4	n.d.	Average
Ca	$CaCl_2 \cdot 6H_2O$	33	Very good
	Lactate of calcium	95	Small
	Acetate of calcium	100	Small
Ca and N	$Ca(NO_3)_2$	56	Very good
Mg and S	$MgSO_4 \cdot H_2O$	n.d.	Good
Mg and Cl	$MgCl \cdot 6H_2O$	33	Very good
Mg and N	$Mg(NO_3)_2 \cdot 6H_2O$	56	Good
Fe	$FeSO_4$	n.d.	Very good
	$FeCl_3 \cdot 6H_2O$	44	Good
	$Fe(NO_3)_3 \cdot 9H_2O$	54	Good
Mn	$MnSO_4$	n.d.	Very good
	$Mn(NO_3)_2 \cdot 4H_2O$	42	Very good
	$MnCl_2 \cdot 4H_2O$	60	Average
Zn	$ZnNO_3 \cdot 6H_2O$	42	Good
B	$Na_2B_4O_7 \cdot 10H_2O$ (borax)	n.d.	Good
Mo	Na_2MoO_4	n.d.	Very good
	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	n.d.	Very good

n.d. not detected

[a]POD – Point of deliquescence by Schönherr (2002)

from these fertilizers. It should be mentioned, however, that the influence of foliar K application on citrus yield is dependent on the current state of plant nutrition with K (and N) as well as potassium level in soil (Srivastava and Singh 2003). Studies conducted by Schönherr and Luber (2001) revealed that penetration of potassium salts ($5\ g\,l^{-1}$) across *Citrus* leaf cuticular membranes is higher than through pear leaves. It was demonstrated that K_2CO_3 was best suited for foliar applications as rates of penetration were large at 50% humidity and higher, while for other salts (KNO_3 and KCl), humidity was required to be 90–100% for maximum rates of penetration.

Air humidity not only affects the droplet drying or POD but also influences the rate of nutrient penetration across cuticular membrane, which generally increases with higher values of air humidity – as a direct consequence of a greater turgor (Schönherr 2001; Schönherr and Luber 2001).

A significant parameter determining the effectiveness of foliar nutrition is pH of applied solution. Marschner (1995) suggests that leaf damages are less severe if pH of sprayed solution is low – unfortunately, this author did not provide precise values. Komosa (1990) informs that nutrient absorption is higher with pH between 3 and 4. For particular compounds (mineral fertilizers), maximum rate of its absorption is noted at various pH values. What is more, with pH changing from acidic to alkaline, higher plant toxicity of increased concentration of foliarly applied NH_4^+ ions is observed. Results of the studies conducted by Schönherr (1976) revealed that average size of isolated pores of *Citrus aurantium* did not depend on pH, but the number of pores increased with pH from $5 \cdot 10^{10}$ (at pH 3) to $16 \cdot 10^{10}$ (at pH 9) per cm^2 of cuticular membrane. In further work, Schönherr (2002) points out that the main factor affecting the swelling of cuticular membrane, and thus the rate of salt penetration, is not solely pH but also air humidity. Zekri and England (2010) inform that the optimum pH of solutions for foliar nutrition of citrus plants should be between 5.0 and 7.5. If pH of spray solution is above or below critical values, leaf absorption of nutrient is poor, and the solution can cause leaf and fruit burn.

To sum up the discussion of the influence of exogenous and environmental factors on the efficiency of foliar nutrition treatments, it should be emphasized that low temperatures (particularly within the root zone) more strongly affect nutrient uptake by roots than leaves (Komosa 1990). In those conditions, application of foliar nutrition can improve nutrient status of plants.

4.4 Aims and General Rules for Foliar Nutrition

Foliar nutrition treatment is mostly considered an additional supplementation of mineral nutrients. In common practice, together with foliar supplementation of mineral nutrients, various compounds of biostimulation effect on plant growth and development are also applied. These compounds, apart from growth promotion, can improve nutrient absorption from leaves or its utilization in plants.

Currently, foliar nutrition with minerals can be combined with the application of marine algae (Durand et al. 2003; Mugnai et al. 2008) or seed extracts (Cwojdziński et al. 1996; Barczak and Cwojdziński 1998; Barczak et al. 2007) which are rich in natural plant metabolites such as sugars, amino acids, organic acids, phytohormones, peptide chains, etc. Additionally, for foliar biostimulation purposes, products of enzymatic hydrolysis of plant tissues or meat industry wastes (which contain large amounts of amino acids and peptide chains) may be applied. For that reason, a boundary between classic foliar nutrition and plant biostimulation – gaining more and more recognition – gets blurred. The issue whether foliar biostimulation can be considered as “foliar nutrition” should also be taken into discussion (see also Sect. 4.6).

In agricultural practice as well as in scientific research, foliar nutrition is applied for various purposes (Fageria et al. 2009; Smoleń and Sady 2008a, b; Smoleń and Szura 2008a, b; Smoleń and Ledwożyw-Smoleń 2011) including supplementation of mineral nutrient deficiency in plants, improvement of nutritional status of plants, counteracting or mitigating stress effects, growth stimulation (biostimulation), and crop quality control, as well as plant biofortification. In Table 4.3, general rules for foliar nutrition with respect to achieving desired goals are presented.

Table 4.3 Basics and general practical rules of foliar nutrition

Aim	Practical notes on foliar nutrition
Supplementation of nutrient deficiency	Nutrients should be applied in chemical forms easily taken up by plants. Apolar molecules (such as urea) are absorbed the quickest, and cation uptake is fastest than of anions
	Even if applied in low doses, urea hydrates the cuticle easing the absorption of urea itself as well as other mineral nutrients. For the improvement of the efficiency of foliar nutrition (with nutrients other than nitrogen), it is recommended to add 0.2–0.4% solution of urea into the working solution (apart from adjuvants and surfactants). It is particularly advised for plants with thick cuticular layer on leaves
	In the case of micronutrient deficiency, it is recommended to introduce chelated forms of these microelements – molybdenum and boron are the only micronutrients that are not chelated
	The number and frequency of foliar nutrition treatments depend on the intensity of deficiency symptoms – the maximum recommended fertilizer dose should never be exceeded
Improvement of nutritional status of plants	The optimal time for foliar nutrition shall be the stage of intensive plant growth and development which is related to the highest photosynthetic productivity and biomass increase
Counteracting and mitigating stress effects	Foliar nutrition with multielement fertilizers – also containing amino acids and sugars – is highly recommended. Fertilizers with biostimulators may be used if its application is advised by manufacturers to mitigate the effects caused by stress factors
	In the case of long-term low intensity of photosynthetically active radiation (PAR), it may be recommended to mix 0.5–2% solution of sugars (sucrose) or biostimulators containing sugars with the working solution. Sugars are the additional source of energy needed for the incorporation of mineral nutrients into organic compounds in metabolic processes responsible for plant growth and development
Biostimulation – growth stimulation and crop quality management	Prior to the application of fertilizers containing biostimulators, one should get acquainted with the rules of its usage. It is necessary to confirm whether a biostimulator can be applied together with plant protection products
	Recommended doses of biostimulators should never be exceeded as it may lead to various unfavorable effects. Application of these products should be conducted strictly according to manufacturer’s recommendations
Biofortification	Plant biofortification concerns, among others, plant enrichment in microelements and/or trace elements. Practical notes of foliar biofortification of particular species are yet to be developed as they require conducting thorough vegetative experiments

4.4.1 Supplementation of Mineral Nutrient Deficiency in Plants

Insufficient nutrient status of plants is revealed by the development of physiological diseases on plant organs. The need of supplementing nutrient deficiency can result from incorrectly performed soil fertilization or impaired uptake of nutrients by roots. This is basically the main cause of physiological diseases observed on annual or biennial plants. In plantations of fruit trees and shrubs as well as perennials plants, soil depletion in mineral nutrient in subsequent years of cultivation most commonly contributes to the development of deficiency symptoms in plants. Impaired translocation of mineral nutrients from roots to above-ground parts of plants, especially fruits (as in the case of calcium), should not also be neglected.

4.4.2 Improvement of Nutritional Status of Plants

Foliar nutrition treatments can serve as an efficient method of improving the level of mineral nutrient utilization and, in consequence, plant fitness (Elmer et al. 2007) and yield (Biesiada and Kołota 1998). Higher nutritional status of plants can enhance its resistance to pathogen infection. What should also be emphasized is that poor plant nutrition is not always manifested by visible symptoms of deficiencies.

4.4.3 Counteracting or Mitigating Stress Effects

Environmental stress can seriously affect plant mineral nutrition on each step from nutrient uptake by roots through its transport to upper parts of plants to the mechanism of mineral metabolism processes. Stress factors can be related to the following:

- High air temperature often considered together with excessive light intensity
- Osmotic stress resulting from water deficit in soil – drought, salinity
- Excessive soil humidity due to long-term rainfalls and increased groundwater levels
- Long-term drop of air temperature below the range optimal for plant growth and development
- Long-term exposure to low levels of photosynthetically active radiation – noted mainly in the greenhouse production but also in the field cultivation of annual and biennial plants
- Frost damages of flowers, leaves, and young shoots of biennial, perennial plants, as well as trees and shrubs

A detailed description of the influence of particular stress factors on physiological and biochemical mechanisms of plants related to mineral nutrition is beyond the scope of foliar nutrition *sensu stricte*. Plants have developed natural mechanisms, protecting them from many of environmental stresses. Nevertheless, these defense processes require large amounts of metabolic energy for the synthesis of protective proteins during drought or heat stresses. It is worth to mention that foliar nutrition is considered the fasted method improving plant regeneration during these particular conditions.

4.4.4 Growth Stimulation (Biostimulation) and Crop Quality Control

In this place, it is necessary to make a distinction between the application of biostimulators *sensu stricte* and fertilizers containing compounds known for its biostimulative action (see also Sect. 4.6). In many countries, due to imperfect legal regulations, numerous "fertilizers" with a negligible amount of mineral nutrients and a relatively high concentration of stimulative compounds are introduced in the market.

The possibility of managing nutritional or postharvest quality of crop is a topic relatively rarely taken up in the research. It should be emphasized that foliar application of mineral nutrients, often simultaneously with plant biostimulation, allows to achieve the intended goal, for example, a reduction of nitrate level in crop (Smoleń and Sady 2008a, b, 2009; Smoleń and Ledwożyw-Smoleń 2011). Within the potential for crop quality management, it is crucial to obtain reproducible results which can be reached only through the development and experimental testing of foliar nutrition regimes. The first step, however, should be a thorough analysis of nutrient requirements and the specificity of biochemical and physiological processes occurring in particular plant species.

4.4.5 Plant Biofortification

Biofortification is defined as such a process that increases the content of biogenic elements such as Ca, Mg, Cu, Fe, Zn, I, or Se in edible parts of crop plants. As a result, improvement of consumer's health is expected to occur. Increased accumulation of biogenic elements in plants can be achieved through application of agronomic, genetic, or transgenic strategies (Dayod et al. 2010; White and Broadley 2009). Foliar application is one of the most efficient methods of plant enrichment in these elements and, thus, incorporation of its additional amounts into the food chain – human diet or animal fodder. What needs to be taken into consideration is the fact that either of mentioned elements, if applied excessively or in inappropriate chemical form, can become toxic for plants inducing growth inhibition, leaf chlorosis, and necrosis or, in extreme cases, plant death. Overall, such strategies are applicable to specific crops and mineral scenarios but cannot be universally applied as a strategy to boost the nutritional quality of foods (Hirschi 2009). Studies conducted by Machado et al. (2005) on citrus genomics allowed to state that the knowledge accumulated so far on metabolic pathways in citrus plants makes possible to begin biofortification programs focusing on the enhancement of the nutritional quality of citrus fruits and its derivatives.

In agricultural practice, depending on a current situation in crop cultivation and the course of climatic conditions, realization of the above-mentioned goals (listed from 1 to 5) will require the application of fertilizers differing with its composition, proportion of macro- and microelements, as well as containing stimulative compounds of various modes of action.

4.5 Influence of Foliar Nutrition on Physiological and Biochemical Processes in Plants

Foliar supplementation of mineral nutrients primarily improves nutritional status of above-ground parts of plants. Molecular, physiological, and biochemical influence of this treatment on plant organism, however, goes beyond the mineral nutrition of plants. It is particularly relevant for foliar application of biostimulators or fertilizers with stimulative compounds. A cascade of molecular and biochemical processes is activated, and the signals of these changes (of a chemical character – phytohormones, sugars, etc.) are transduced from leaves to other aerial as well as underground parts of the plant. The potential range of these interactions is broad, and even with the current progress in analytical techniques, it is not possible to conduct a global assessment of these relations. What can be performed is only evaluation of the influence exerted by foliar nutrition or biostimulation on selected molecular, biochemical, and physiological processes in controlled conditions – in phytotron experiments. Exogenous environmental factors additionally affect plant response to these treatments. It is repeatedly observed that if crop cultivation is conducted in field conditions, obtained results differ from those coming from experiments with controlled conditions. From a practical point of view, the latter ones are more informative as they provide a balanced description of foliar nutrition influence on plant metabolism, growth, and development, as well as crop yield and its quality.

Depending on the type, form, and concentration of applied nutrients (macro-, micro-, and trace elements), as well as plant development stage and environmental factors, foliar nutrition (or biostimulation) can contribute to the following:

1. Regulation of molecular and biochemical processes related to the metabolism of particular nutrients – its chemical reduction and incorporation into organic compounds
2. Induction or silencing of genes encoding transport proteins for mineral nutrients as well as those responsible for direct regulation of active transport of nutrients across cell membranes
3. Enhanced transport of exogenous mineral nutrients (applied foliarly) to roots, shoots, fruits, and seeds or its temporary deposition in sprayed leaves
4. Biosynthesis of phytohormones and transduction of chemical signals to other parts of the plant in order to regulate molecular and metabolic pathways related with mineral nutrition or other physiological processes in plants
5. Direct or indirect increase/reduction in the rate of active nutrient uptake by roots dependent on the current nutritional status of leaves – particularly in the case of nitrogen
6. Regulation or stimulation of enzymatic processes – mineral elements playing the role of enzyme activators/cofactors
7. Depending on nutrient (biostimulator) concentration – positive or negative influence on the intensity of physiological processes in plants – photosynthesis, cellular respiration, etc.

The complexity of above-mentioned interactions will be briefly presented in the example of selected steps of the metabolism of foliarly applied nitrogen along with foliar application of Ni, Mo, sucrose, cytokinins, salicylic acid, or exogenous amino acids.

The rate of uptake and penetration of various nitrogen forms into the cytosol of leaf cells is as follows: N–NH_2 (amide form) > N–NH_4 > N–NO_3. This order varies, however, from this described for uptake preference of roots.

The amide nitrogen from urea is not directly included into the metabolic path of this element in plant. The ammonium nitrogen, being the result of urea hydrolysis by the urease enzyme, is incorporated into simple organic compounds (Marschner 1995). Nickel is a cofactor for this enzyme, so urease activity, and therefore urea hydrolysis, strongly depends on Ni level in plants (Nicoulaud and Bloom 1998; Gheibi et al. 2009), simultaneous foliar nutrition of urea and nickel (Krogmeier et al. 1991), or foliar application of multi-element fertilizers containing this element. A positive interaction has been noted for citrus nutrition with nickel and urease activity which, in consequence, increases flowering and percentage of fruit set (Malavolta et al. 2006; Malavolta and Moraes 2007). Srivastava and Singh (2003) inform that the mechanism of flower development – flowering induction in citrus plants is related to NH_4^+ level in leaves as well as arginine biosynthesis – can be indirectly stimulated by foliar application of urea.

Ammonium ions occur in plant cells as a product of the reduction of NO_3^- (taken up both by roots and leaves through foliar nutrition) to NO_2^-, which process is catalyzed by nitrate reductase (NR). The next step is NO_2^- reduction to NH_4^+ by nitrite reductase (NiR) (Campbell 1999). Assimilation of ammonium nitrogen (taken up by roots or applied foliarly) takes place in GS-GOGAT cycle in chloroplasts. The crucial role in nitrogen assimilation process plays the alpha-oxoglutarate (created in the Krebs cycle) which is transformed by GDH to glutamine, which in turn enters GS-GOGAT cycle (Tischner 2000; Masclaux-Daubresse et al. 2002). Thus, the efficiency of the nitrogen assimilation process will be higher with greater photosynthetic productivity (Masclaux-Daubresse et al. 2002).

The process of NO_3^- reduction is under the control of numerous exo- and endogenous factors (Campbell 1999). Plants have the ability to accumulate relatively high levels of NO_3^- in leaves but not NH_4^+, which tends to be toxic in excessive concentrations. With a low photosynthetic productivity, the process of NO_3^- reduction and NH_4^+ assimilation is also inhibited. Another reason for a decreased rate of NO_3^- reduction is the accumulation of simple organic forms of nitrogen–glutamine and other amino acids. It basically hampers the active root uptake of nitrate and ammonium ions mediated by NO_3^- and NH_4^+ transport proteins – due to feedback regulation. It is worthy to mention that gene families encoding transport proteins for these two types of ions are divided into two systems: HATS – high-affinity transport system and LATS – low-affinity transport system (Forde 2000; Forde and Cole 2003; Gansel et al. 2001; Howitt and Udvardi 2000; Orsel et al. 2002). Some of genes belonging to HATS-NO_3^-, HATS-NH_4^+, LATS-NO_3^-, and LATS-NH_4^+ are expressed mainly in roots, others are ubiquitous in all (aerial and underground) parts of the plant (Forde and Cole 2003). Taking this into consideration, excessive foliar treatments with reduced forms of nitrogen (N–NH_2 and N–NH_4) but particularly amino acids (or mixtures containing peptide chains) may decrease the rate of nitrogen uptake by roots and, consequently, lower level of nitrogen nutrition expressed as N total content in plants (Wierzbińska 2009).

It needs to be underlined that a positive effect on NO_3^- reduction in leaves, and thus crop yield and its biological quality, was revealed for foliar application of molybdenum as NR cofactor (Williams et al. 2004), cytokinins (Campbell 1999), or sucrose (Kováčik 1999).

Interesting is the influence of exogenous sucrose applied foliarly on nitrogen metabolism. As reported by Marschner (1995), compounds with small molecule mass, for example, sugars (sucrose), do not penetrate through cuticular layer, and their assimilation takes place in the cuticular pores. Sucrose is transported between parenchymal cells of leaf with the participation of transporter proteins on the basis of sucrose/H^+ symport (Shakya and Sturm 1998; Starck 2003). The endogenous sucrose created in the process of photosynthesis in parenchymal cells along with exogenous sucrose (from foliar nutrition) is then transported by phloem to the acceptors, such as young developing leaves or storage roots (Starck 2003). Starck (2003) informs that sugar also plays the role of signal substance that indirectly informs cells or individual structures about the level of supply and demand for the photosynthetic products. Sugars together with hormones participate in the transduction of signals on the level of gene expression. Foliar application of sucrose was shown to decrease the level of NO_3^- (Kováčik 1999; Smoleń et al. 2010; Smoleń and Sady 2012). Reduction of nitrate content was obtained after spraying plants with an extract derived from *Lupinus angustifolius* seeds (Cwojdziński et al. 1996; Barczak et al. 2007; Barczak and Cwojdziński 1998). According to Cwojdziński et al. (1996), this extract, apart from nutritional components, proteins, and sugar, most probably contained dihydrozeatin (cytokinin). Another phytohormone belonging to the cytokinin group is benzyl adenine (BA). The physiological role of cytokinins is, apart from the others, connected with the regulation of biochemical processes by controlling enzyme activity (Borkowska 1997). Endo- and exogenous cytokinins are included to the group of factors stimulating NR activity (Yu et al. 1998).

In the study by Yaronskaya et al. (2006), exogenous cytokinins caused an increase in the content of alpha-linolenic acid (syn. 5-aminolevulinic acid – ALA; a direct precursor of chlorophyll) in barley seedlings, while in the research by Liu et al. (2006), they elevated chlorophyll level in *Spirodela polyrrhiza*. As a result, the application of exogenous cytokinins may result in a greater assimilative potential of plants, which in turn can indirectly contribute to better assimilation of nitrogen to organic compounds and N uptake by plants (Smoleń et al. 2010; Smoleń and Sady 2012). Still, it should be mentioned that cytokinins together with amino acids are involved in the feedback regulation of N uptake and metabolism in plants (Dluzniewska et al. 2006; Forde and Cole 2003).

Endogenous salicylic acid (SA) is considered a hormone-like substance, which plays an important role in the regulation of plant growth, development, and a variety of physiological processes in plants (Klessig and Malamy 1994). The study by Fariduddin et al. (2003) revealed a positive effect of exogenous salicylic acid on dry mass, net photosynthetic rate, and efficiency of carboxylation in *Brassica juncea*. A favorable effect of SA on the activity of NR was indicated by Jain and Srivastava (1981), Miguel et al. (2002), and Fariduddin et al. (2003).

In the summary, it is worth to add that simultaneous foliar application of nitrogen (in the form of urea), sucrose, Mo, BA, and SA can produce different effects that application of a single compound: urea, sucrose, BA, or SA (Smoleń et al. 2010; Smoleń and Sady 2012; Wierzbińska 2009).

4.6 Plant Biostimulation

An interesting trend in foliar nutrition of plants is the enrichment of fertilizers with substances of biostimulation activity (*syn.* stimulators, bioactivators, growth stimulants) for plant growth and development as well as selected metabolic processes. These compounds can be foliarly applied separately or together with mineral nutrients.

What are biostimulators? They mean inorganic and organic substances or its mixtures positively affecting plant development or other physiological processes in plants. One of the requirements for biostimulators is that they pose no risk for human, animal, or natural environment due to its application. Depending on legislation in a particular country, various classification of this group of compounds is provided. It is often that substances of stimulative character are included into the formulation of fertilizers for foliar nutrition, soil fertilization, or products designed for the nutrient solution preparation in the hydroponics.

The following substances can be included to this group: organic acids occurring in plants (salicylic acid, ALA syn. aminolevulinic acid, etc.), vitamins, amino acids, low-molecular-weight polypeptides, extracted phytohormones, phenolic compounds, sugars (mono-, di-, oligosaccharides), and many other organic compounds. They are obtained due to complex technological processes basing on extraction, enzymatic treatments, or microbiological processes. Taking into consideration the source, biostimulators can be divided into the following groups:

- Naturally occurring compounds – plant extracts
- Extracts from marine organisms – mainly phytoplankton
- By-products from the meat (food) industry wastes
- Synthetic organic compounds – products of chemical or pharmaceutical industry

In the case of biostimulators obtained from plant or animal tissues, they contain numerous organic and inorganic compounds naturally occurring in these organisms (Cwojdziński et al. 1996; Barczak and Cwojdziński 1998) and exhibit a broad spectrum of the physiological and biochemical influence on plants. The composition of the extracts is strictly dependent on raw material quality. Adversely, if biostimulators are derived from the extract by selective separation processes, as for several marine bioactive substances (MBS): N PRO (Durand et al. 2003), EXT1116, NA9158 and 251104 (Mugnai et al. 2008), or glycine betaine (Zamarreño et al. 1997), a stable composition and concentration of active substances can be achieved.

In many countries, plant biostimulation is gaining popularity. However, it should never be forgotten that plants are autotrophic and have the ability of synthesizing amino acids, vitamins, and organic acids. Among the skeptics on biostimulation, a question of the usefulness and the basic rule of this treatment arises. The answer is not simple as the group of biostimulators includes preparations containing compounds and substances (natural or synthetic) which, among others:

- Enhance plant growth and development through increasing the efficiency of soil fertilization or foliar nutrition with mineral elements
- Improve the functioning of physiological and biochemical processes in plant tissues
- Provide additional protection against unfavorable environmental conditions
- Increase plant resistance to diseases and pathogens

Plant biostimulation was shown to improve growth and development, quantity and quality of fruit yield (Basak and Mikos-Bielak 2008) also in citrus plants (Caronia et al. 2010; Fornes et al. 1995; Koo 1988; Santana et al. 2006).

Foliar application of biostimulators can be particularly effective during unfavorable environmental or stress conditions. Biostimulation efficiency (as well as for foliar nutrition *sensu stricte*) may be low if the treatment is conducted in near-optimum conditions (soil and environmental) additionally when manufacturer's recommendations are not followed. In such conditions, physiological changes in plants, regulated by environmental and endogenous factors (*i.a.*, phytohormones), proceed optimally.

It can be stated that, to a certain degree, plant biostimulation can be considered an alternative to genetically modified crops. A properly designed biostimulation strategy may allow to a controlled use of "native" genetic information in order to activate selected metabolic processes. The planning of foliar biostimulation program requires detailed information on chemical composition of applied substances as well as a thorough knowledge of the regulation and mechanism of individual biochemical and physiological processes in plants. The more complex is the composition of biostimulators (or fertilizers with these substances), the more difficult it is to predict the final result of its application. The reason is the complexity of plant reaction due to the simultaneous use of numerous stimulative compounds and mineral nutrients.

Another question of concern is the safety of plant biostimulation. A major disadvantage is that excessive frequency of treatments as well as application of too high doses may deregulate metabolic processes in plants. Many compounds used for biostimulation play an "indirect information role" in biochemical and physiological responses of plants. As a consequence of inappropriate application of biostimulators, a blockage, weakening, or change in the intensiveness of various processes may occur. That situation is particularly dangerous in the cultivation of fruit plants with excessive application of growth regulators (phytohormones *sensu stricte*). In such a case, a "complex dependence effect" may be noted which is characterized by, *i.a.*, impaired growth or flower and fruit setting due to discontinuation of several-year-long foliar spraying with exogenous growth regulators. A question arises whether the same reaction may be observed for foliar biostimulation. For that reason, plant biostimulation should be conducted strictly according to manufacturer's recommendations or be based on the results of independent scientific research – best if carried out in multiple growing seasons.

In the summary, it should be emphasized that foliar biostimulation of plants means the application of the compounds much larger than mineral nutrients. Thus, the efficiency of its absorption by leaves is lower, and the key factor affecting the rate of this process is the duration of leaf surface coverage by droplets of a working solution.

4.7 Foliar Nutrition vs. Crop Nutritional and Postharvest Quality Control

A separate issue is the influence of foliar application on nutritional, postharvest, and processing quality of crop yield. This problem is relatively complex, and the assessment of the effect of foliar nutrition on particular crop species requires consideration of various quality parameters (Biesiada and Kołota 1998; Berbeć et al. 2003; Jabłoński 2002). Depending on the crop, these characteristics include the level of nutritional and health-promoting compounds (*i.a.*, vitamins, antioxidants, essential oils), as well as those negatively affecting the consumer's health (*i.a.*, nitrates, heavy metals, mycotoxins). Significant is the fact that simultaneous foliar application of two or more mineral nutrients may lead to diverse results with respect to yield quality which can be modified by environmental conditions (Sugier 2003; Rożek et al. 2000; Rydz 2001; Wojciechowska et al. 2005). Thus it is difficult to propose the general relations between foliar nutrition and the quality of various crops.

Implementation of agricultural recommendations for foliar application of fertilizers in order to improve (in a repeatable manner under varying climatic conditions) not only the quantity but also the quality of crop yield needs conducting numerous vegetation experiments. An important aspect in ensuring the nutritional and processing value of yield is an appropriate selection of fertilizer composition for particular crops and cultivars. Development of the composition of specialty fertilizers designed for a single crop species should include both nutritional requirements as well as the level of those compounds (mainly microelements, *i.a.*, Cu, Mn, and Zn) that are introduced with plant protection products (Szewczuk et al. 2003).

Foliar nutrition – particularly when combined with the application of biostimulators or growth regulators – can be used for the management of plant growth and crop quality, such as the reduction of nitrate level in edible parts of plants (Smoleń and Sady 2009). Development of a program for crop quality management requires a thorough knowledge on mechanisms and regulation of key physiological and biochemical processes in plants. This is the only basis for a proper selection of biostimulators or its combination with growth regulators, the application of which should affect the above-mentioned processes in the most selective way. The efficiency of the strategy so developed should always be verified in vegetation experiments.

The issue of the improvement of postharvest quality of yield through foliar nutrition also falls within the scope of this field. By means of properly prepared and conducted programs of foliar nutrition and/or biostimulation, it is possible to positively affect yield suitability for storage. These treatments, if conducted during the preharvest period, may naturally protect fruits from skin damages, evaporation, fungal (Elmer et al. 2007), bacterial, or physiological diseases, as well as delay senescence during storage. For the improvement of the quality and postharvest stability of citrus fruits, foliar nutrition with K and Ca can be applied. Skin damages observed on citrus fruits during storage are mainly caused by potassium deficiency (Achilea et al. 2002). It is confirmed that foliar application of Ca reduces skin discoloration in citrus fruits (Crisosto et al. 1997, 2000).

4.8 Agrotechnique – Foliar Nutrition in Practice

Foliar application of nutrient solutions makes salt concentrations on a leaf surface higher than those of soil solutions (Wójcik 2004). It is possible due to the coverage of the aerial parts of plants with the cuticle not found on roots. This layer is, at the same time, a natural barrier to the transmission of mineral nutrients and other compounds applied foliarly. Despite this, nutrient absorption through leaves can be from 8 to 20 times more efficient than its uptake by roots (in optimal conditions). However, this rate of efficiency is rarely achieved in practice (Kuepper 2003). It is caused by quick evaporation of liquid droplets from epidermis surface, various thickness of the cuticle in particular species, or droplet drift from the cuticle.

Increase of the efficiency of nutrient absorption can be achieved by the use of adjuvants and surfactants which reduce the surface tension of working liquid as well as the application of humectants and antievaporants (Fernández et al. 2006; Komosa 1990; Michałojć and Szewczuk 2003; Srivastava and Singh 2003). Some practical advice on foliar nutrition treatment is included in Table 4.3.

A significant factor affecting the efficiency of foliar nutrition is the chemical and microbiological water quality. Water used for foliar nutrition purposes should contain the lowest level of mineral nutrients. It is confirmed that water from rivers, lakes, wells, etc., may have high amounts of mineral nutrients due to its leaching from soils – particularly in agricultural areas and around greenhouse farms (Breś 2009, 2010).

Foliar fertilization should be physiologically balanced containing all main and secondary plant nutrients and essential trace elements (Fritz 1978). With high concentration of mineral nutrients in water, it is possible to lower the dose of fertilizers applied foliarly – by adjusting the final level of nutrients in the working solution. An indirect indicator of high mineral content in water is the measurement of electrical conductivity (EC). EC values above 1.0–1.2 mS cm^{-1} inform

Table 4.4 Water EC values in relation to its salinity

Water quality[a]	EC (mS cm^{-1})	Salinity (mg dm^{-3})
Very high	0.3	<200
High	0.3–0.7	200–500
Sufficient	0.7–1.2	500–1,000

[a]The classification of water quality for hydroponics may serve as approximate information on its applicability for foliar nutrition

that water may contain relatively high amount of nutrients in a total number exceeding 1 g of salt dissolved in 1 dm^3 (Table 4.4). In the common practice, even when planning experiments with foliar nutrition of plants, an issue of nutrient content in water is usually neglected – except for dissolution of fertilizers or biostimulators in distilled water. Application of distilled water in vegetation experiments is, however, troublesome to perform, not to mention the practical foliar nutrition in large plantations, orchards, etc. In such cases, the effect of foliar application of fertilizers will be the result of the interaction between nutrients introduced with fertilizers and cations/anions previously present in water.

Another significant problem related to chemical quality of water is its hardness. High water hardness, and more precisely carbonate hardness (resulting from the presence of HCO_3^- anions and Ca^{2+}/Mg^{2+} cations), causes white spots on leaf surface due to drying droplets of working solution – this may negatively affect photosynthesis. Calcium content in hard waters exceeds the level of 120–140 mg dm^{-3} and that amount can be of significance when balancing the level of nutrients applied foliarly – for a comparison, 0.5% w/v water solution of $Ca(NO_3)_2$ contains approximately 950 mg Ca·dm^{-3}. The process of Ca absorption by leaves may be impaired by too high pH of hard waters (mainly neutral or slightly alkaline). A decrease of water (working solution) pH by HNO_3 neutralizes HCO_3^- anions which can improve Ca absorption by leaves. Nevertheless, this treatment does not affect the total water hardness but only lowers the carbonate one. An issue of optimal pH level for the working solutions is discussed in Sect. 4.3. It is worth to mention that the solubility of phosphorus fertilizers in hard water may be significantly lowered by the precipitation of calcium phosphates.

Water used for foliar nutrition should be free from potential plant and human pathogens. In the case of its presence, water disinfection should be performed, but the application of products containing chlorine should be avoided. Spraying with chlorinated water may cause some developmental disorders or even kill beneficial microorganism colonizing leaf surfaces. High levels of chlorine are also unfavorable for plant growth. If chlorine is used for water disinfection, it is highly recommended to leave water in open containers for 12–24 h in order to remove chlorine by its natural evaporation (Kuepper 2003). Other methods of water disinfection (thermal, ozone, iodine, or selenium application) are either relatively expensive or potentially dangerous for plants due to excessive concentration of iodine or selenium in water. Sometimes it is recommended to use 35% solution of hydrogen peroxide in an approximate dose of 500 ml per 100 dm^3 of water. Foliar application of H_2O_2 (depending on a dose) may cause various effects on plants – from the enhancement of antioxidant status (when applied in low concentrations) to the increase of oxidative stress and occurrence of symptoms resembling a hypersensitive response when applied in high doses (Gechev et al. 2002).

When preparing working solution, powdery or granulated fertilizers should be totally dissolved so as not to clog sprayer nozzles. Solubility of solid fertilizers is affected by water temperature. Most of solid fertilizers, when dissolved, cause the drop of solution temperature – it is particularly observed for urea but also ammonium, potassium, and magnesium nitrates. Therefore it is advised to first dissolve liquid products (diluting of concentrated solutions in water is an exothermic process) and then powdery or granulated fertilizers. Calcium and sulfate fertilizers should never be mixed in high concentrations (risk of gypsum precipitation) as well as calcium and phosphate ones – as calcium phosphate may be the product. Fertilizer solutions must be prepared directly prior to its application to prevent the occurrence of unfavorable chemical reactions. In the case of simultaneous application of chemical plant protection products with foliar nutrition, they should be introduced into sprayers after dissolving fertilizers.

The efficiency of foliar application largely depends on the coverage of leaves with working solution – basically its lower surface where the highest number of stomata is located (Table 4.1). Leaf coverage with droplets is higher if the working solution is strongly atomized so important may be the overall functioning of the sprayer.

Additional significant factor affecting the efficiency of foliar nutrition is leaf turgor which depends on soil humidity, light intensity, air temperature, and humidity, as well as wind (Sect. 4.2.5). Therefore, it is recommended to conduct foliar nutrition in cloudy days with a moderate air temperature and high relative humidity.

The optimal solution would be to perform foliar application few days after rain or field irrigation – particularly during dry and hot season. A significant improvement of leaf turgor as well as metabolic activity of plant may be thus obtained. When it is not possible to irrigate the plantation, an alternative may be to spray plants with pure water 1 or 2 days before foliar nutrition treatment (depending on the current soil humidity and weather conditions). It is advised to use 50–100% higher amounts of water for spraying and further foliar nutrition than the standard applied. This strategy is recommended for foliar biostimulation of annual plants (Smoleń and Ledwożyw-Smoleń 2011). It can be assumed that in the case of citrus plants, such proceedings may be equally effective. Application of pure water temporarily increases leaf turgor and, consequently, activates metabolic processes. In a certain sense, this treatment is a kind of plant "preparation" for a proper foliar application of mineral nutrients and/or biostimulators in unfavorable environmental conditions caused by drought and high temperatures. Positive impacts of such a strategy observed in practice (Smoleń and Ledwożyw-Smoleń 2011) are most likely related to a "memory effect" in plants (Goh et al. 2003).

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