Foliar Application: from Plant Nutrition to Biofortification

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It is well known that, sustainable agriculture is an important part of sustainable development. This sustainable agriculture should lead to achieve food security and maintain the biodiversity of natural ecosystems. Sustainable agriculture also should have definitely a global perspective. The conservation of both soil and water resources, therefore, is considered an essential prerequisite as well as the efficient use of mineral and organic fertilizers. This could be achieved by improving agro-technology and better understanding of the essential processes in soils. Foliar application of agrochemicals including fertilizers should be improved seeking for the sustainability of agriculture. The present review will focus on the effects of foliar application of nutrients for plant nutrition and its biofortification. Proper timing of foliar application, endo-, exogenous and environmental factors affecting foliar nutrition, influence of mineral fertilizer nutritional quality of staple food crops and finally nano-foliar nutrition as well as postharvest quality of crops will be also highlighted.

Keywords: Foliar nutrition, Postharvest management, Nano foliar application, Agrotechnology, Biofortification.

Introduction

It is well known that, plants use different inorganic nutrients in addition to CO2 and water for their growth and production. Most of these nutrients inherently exist in soil and can get depleted under different conditions. So, soil application of nutrients is necessary and it is the most common practice in soil fertilization, but it has many limitations with respect to the nutrients bioavailability for plants. The nutrients such as phosphorus (P), potassium (K) and most of the micronutrients, their availability in soil solution is relatively low, because they are mainly fixed on the soil complex as insoluble forms. Otherwise, the more soluble nutrients such as nitrogen (N) are easily leached down the soil profile. What is lost through leaching reaches the aquifer and pollutes the groundwater (El-Ramady 2014; El-Ramady et al. 2014a, b, 2015, 2016a). As well known also, leaves can absorb nutrients as a natural process by which plants obtain additional nutrients from rainwater. This principle is utilized in agriculture by spraying the foliage with dilute solutions of the

desired nutrients. Therefore, foliar fertilization is generally recommended for supplying additional N, magnesium (Mg) and micronutrients as well as P, K and sulphur (S).

The importance of nutrients for plant nutrition was and still one of the crucial studies for plant biological sciences. So, several books, reviews and articles have been published about these significant nutrients (e.g., Sonneveld and Voogt 2009; Marschner 2011; Srivastava 2012; Benton 2012; Barker and Pilbeam 2015). Additionally, these studies included roles of nutrients in plant nutrition and then changed to the plant biofortification towards crop production (Singh et al. 2016; Bouis and Saltzman 2017; Díaz-Gómez et al. 2017). The biofortified crops include mainly zinc (Barrameda-Medina et al. 2017), iron (Vasconcelos et al. 2017), iodine (Gonzali et al. 2017), selenium (Bañuelos et al. 2015; Ros et al. 2016; El-Ramady et al. 2016a, b; Bañuelos et al. 2017; Li et al. 2017; Sharma et al. 2017), manganese (Ullah et al. 2016), folate (Strobbe

and Van Der Straeten 2017), vitamin E (Mène-Saffrané and Pellaud 2017), etc.

Several ways could be used in delivering nutrients for plants including soil and foliar or spraying methods. Foliar application could be considered one of the most common methods, which used to deliver the needed nutrients to plants in adequate concentrations and improve plant nutritional status as well as increase the crop yield and its quality (Smoleń 2012). Foliar application also could be used for different purposes including mitigating the negative damages of many stresses (e.g., heat, drought, frost, etc) and spraying different plant nutritional compounds (i.e., simple sugars, disaccharides), growth regulators and stimulators, amino acids, peptide chains, pesticides and nanomaterials (Smoleń 2012; Shalaby and El-Ramady 2014; Simões et al. 2017). However, the fertilizer management is very important due to its roles in plant growth and development or plant physiology and its biochemistry as well as controlling plant diseases (Table 1; Dordas 2009).

Therefore, the foliar application of nutrients for plant nutrition will be reviewed as well as some information concerning this process including factors affecting foliar application, impact of mineral fertilizer on nutritional quality of staple food crops and finally nano-foliar nutrition.

History of foliar nutrition

Foliar fertilization is defined as the foliar spray or application of one or more essential plant

mineral nutrients on above-ground plant parts in order to supply traditional soil applications of fertilizers (Sabbe and Hodges 2009). A large number of nutrient fertilizers are soluble in water that may be applied directly to the aerial portions of plants (Fig. 1). The applied nutrients can enter the leaves either through many steps by penetrating the cuticle or entering through the stomata (Fig. 2) before entering the plant cell where they can be used in metabolism (Oosterhuis and Weir 2010). With regard to the historical origin of foliar nutrition or foliar feeding, it has been documented as early as 1844 (Pace 1982), when an iron sulfate solution was sprayed as a possible remedy for "chlorosis sickness". Foliar fertilization, recently, has been widely used and accepted as an essential part of crop production like horticultural crops. Several benefits of foliar feeding have been well documented (e.g., El-Fouly et al. 2011). Foliar application also is characterized by a technique of feeding plants by applying liquid fertilizer directly to their leaves. This process has been known for many years with the ability of plants in uptake essential nutrients through the leaves, where plant stomata of these leaves are usually faster in their nutrient uptake comparing with soil application (Smoleń 2012).

It is clear that nutrients reach the leaf cells, after penetrating the cuticle and are further transported to other parts through plasmodesmata (Fig. 3). Some micronutrients are not as freely mobile as the major nutrient elements such as N, P, or K. The age of the leaf and pH of spray liquid

TABLE 1. Essential plant nutrients, forms taken up and their typical concentration in plants (adapted from Roy et al. 2006; Kabata-Pendias 2011; El-Ramady et al. 2014a)

Nutrient (symbol)	Essentiality established by	Forms absorbed	Typical concentration in plant
Magazantianta	scientist		dry matter
Macronutrients			
Nitrogen (N)	de Saussure (1804)	NH ₄ ⁺ , NO ₃	1.5 %
Phosphorus (P, P ₂ O ₅)	Sprengel (1839)	H ₂ PO ₄ -, HPO ₄ ²⁻	0.1–0.4 %
Potassium (K, K_2O)	Sprengel (1839)	K ⁺	1–5 %
Sulphur (S)	Salm-Horstmann (1851)	SO ₄ ²⁻	0.1-0.4 %
Calcium (Ca)	Sprengel (1839)	Ca ²⁺	0.2–1.0 %
Magnesium (Mg)	Sprengel (1839)	Mg^{2+}	0.1-0.4 %
Micronutrients			
Boron (B)	Warington (1923)	H ₃ BO ₃ , H ₂ BO ₃	6–60 μg/g (ppm)
Iron (Fe)	Gris (1943)	Fe ²⁺	50–250.μg/g
Manganese (Mn)	McHargue (1922)	Mn ²⁺	20–500.μg/g
Copper (Cu)	Sommer, Lipman (1931)	Cu ⁺ , Cu ²⁺	5–20.μg/g
Zinc (Zn)	Sommer, Lipman (1931)	Zn ²⁺	21–150.μg/g
Molybdenum (Mo)	Arnon & Stout (1939)	MoO ₄ ²⁻	below 1.µg/g
Chlorine (Cl)	Broyer et al. (1954)	Cl-	0.2–2 %
Nickel (Ni)	Eskew et al. (1983)	Ni ²⁺	10 – 100 mg/kg



Fig. 1. Some photos for foliar application used in Italy (Photos by M. Fari, Debrecen, Hungary).

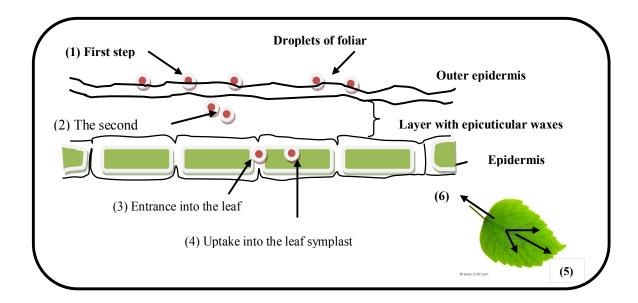


Fig. 2. Different steps of nutrient uptake by leaves (adapted from Roemheld and El-Fouly, 1999). These following steps could be summarized as follows: (1) Wetting of the leaf surface with fertilizer solution; (2) penetration across the outer epidermal cell wall; (3) entrance into the leaf apoplast; (4) uptake into the leaf symplast; (5) Distribution within the leaf; and (6) transport out of the leaf.

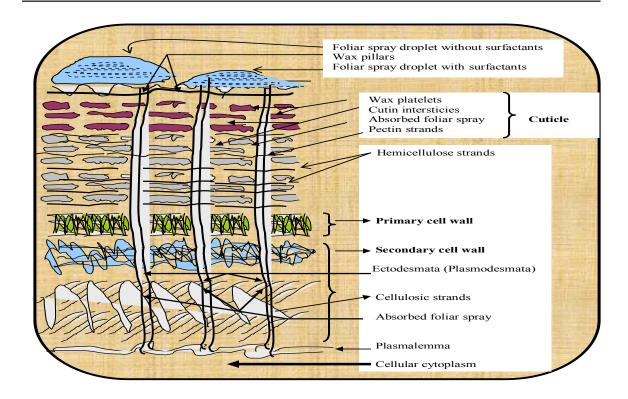


Fig. 3. Cross-section of exudated cuticle and outer cell walls of the upper epidermis (adapted from Voet and Ashmead 1999).

are important for foliar absorption. The absence of plasmadesmatic connections between the guard cells and the epidermal cells is also important (Kannan 2010). It is worth to mention that, foliar fertilization feeds the plants not the soils. This previous statement considered one of the most important approaches for plant mineral nutrition through foliar application as reported by Justus von Liebig in the 19th century. Therefore there are many words could be described the supplying mineral nutrients such as "foliar nutrition" or "foliar fertilization" or "foliar feeding," or "foliar application" (Smoleń 2012).

Role of foliar fertilization

Foliar fertilization has the ability to improve the efficiency and rapidity of utilization of a nutrient urgently required by the plant for maximum growth and yield (Oosterhuis 1995). Foliar applications of nutrients also can provide for a more rapid material utilization and permits the correction of observed deficiencies in less time than can be accomplished by soil applications. The main advantage of foliar fertilization is the immediate uptake of applied nutrients. Under problems of soil fixation, foliar fertilization is the most effective ways of fertilizer placement

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and usually necessitates using smaller quantities of nutrients comparing with soil application. The most important use of foliar nutrition is the application of micronutrients in small amounts as well as macronutrients (e.g., nitrogen, phosphorus, or potassium) without causing any phytotoxicity (Oosterhuis and Weir 2010). Foliar fertilization also could be used under farming conditions as (1) a quick remediation for unexpected deficiencies, (2) for late supply of N during advanced growth stages, (3) as a preventive measure against unsuspected (hidden) deficiencies, and (4) to overcome fixation of nutrients in soils e.g. Cu, Fe, Mn and Zn.

It could be concluded that, foliar nutrition has some potential benefits such as:

- (1) Supplying nutrients during peak periods of demand when an immediate response is needed.
- (2) Providing plants with certain nutrients like zinc and iron, that may not be readily available for root uptake.
- (3) Providing a nutrient source during periods of stress when soil applications are not practical.

- (4) Controlling nutrient losses in conditions with high potential loss.
- (5) Allowing flexibility in supplying nutrients related to improving the quality of the harvest.
- (6) Giving a nutritional boost to plants at the same time that other foliar chemicals are being applied, thereby minimizing application expenses (Mikkelsen 2008).

Soil fertilization versus foliar nutrition

Soil application of fertilizers is 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). It is confirmed that, foliar nutrition gives better results if plant cultivation is conducted on soil with optimal pH value and level of mineral nutrients (Szewczuk and Michałojć 2003a, b). In case of high nutritional status of plants, additional foliar supplementation of mineral nutrients may increase its leaf concentration to the level of luxury consumption, therefore a non-significant increase of crop yield and its quality would be expected. Whereas, additional foliar application of mineral nutrients could be considered cost-effective if it is conducted to obtain crops biofortified with micro- and trace elements, that are deficient in human diet living under certain environments (Smoleń 2012). If deficiency of nutrients occurs in plants, its supplementation through foliar application will be more rapid than through soil fertilization. Foliar uptake of mineral nutrients is ranged from 8 to 20 times more efficient than soil application. Nevertheless, such high efficiency is not commonly achieved in agricultural practice

(Smoleń 2012).

Proper timing of foliar applications

The timing of foliar sprays, particularly in regard to growth stage, could be considered critical in relation to the optimum efficacy of the foliar treatment, and more attention should be given to it (Alexander 1986). The effectiveness of foliar nutrition is affected by numerous endogenous (related to leaf anatomical 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. Environmental factors include time of day, humidity, temperature and wind speed influence the physical and biological aspects of foliar applications. Plant tissue permeability is an important factor in absorption of nutrients into the plant: warm, moist and calm conditions favor highest tissue permeability, conditions found most often in the late evening hours, and occasionally in the early morning hours. Table 3 summarized meteorological conditions favoring foliar applications (MWL 1994). Rainfall within 24 to 48 hours after a foliar application may reduce the application effectiveness, as not all nutrient materials are immediately absorbed into the plant tissue (Tables 2 and 3).

It could be concluded that, the most important exogenous and environmental factors affecting foliar fertilization include light, temperature, wind, time of day, photoperiod, humidity, amount and intensity of precipitation, drought, osmotic

 $TABLE\ 2.\ Meteorological\ conditions\ favoring\ foliar\ applications\ (adapted\ from\ MWL\ 1994)$

Time of Day Late evening; after 6 p.m. or early morning; before 9 a.m.

Temperature $65 - 85 \, ^{\circ}\text{F}; 70^{\circ} \, \text{ideal} \, (21 \, ^{\circ}\text{C})$

Humidity Greater than 70% relative humidity

Temperature/Humidity Index 140-160

Wind Speed less than 5 mph

TABLE 3. Rates of nutrients	absorption or entry	into the plant leaf tissue	(adapted from MWI 1994)

Nutrient	Time for 50% absorption
Nitrogen (as urea)	1/2 – 2 hours
Phosphorus	5-10 days
Potassium	10 – 24 hours
Calcium	1-2 days
Magnesium	2-5 hours
Sulfur	8 days
Zinc	1-2 days
Manganese	1-2 days
Iron	10-20 days
Molybdenum	10 – 20 days

potential of growing medium (or soil water), and nutrient stress. When endogenous factors are considered, the uptake 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.

Foliar nutrition and postharvest quality of crop

One of the most important beneficial of foliar application beside the nutritional status of plants is postharvest and processing quality of crop yield. This is a relatively complex problem concerning assessment of the effect of foliar nutrition on particular crop species, where it requires some considerations related to various quality parameters (Sumathi and Shivashankar 2017). These characteristics or parameters may include the level of nutritional and healthpromoting compounds i.e., antioxidants, vitamins, essential oils, as well as those negatively affecting the consumer's health i.e., nitrates, heavy metals, mycotoxins. These criteria definitely differ from the conventional to organic production of crops (Mditshwa et al. 2017). Therefore, the farming system, the appropriate fertilizers and crop cultivars are the most factors controlling these criteria or the nutritional and processing value of yield (Smoleń 2012; Hendricks et al. 2015).

Foliar nutrition combined with applied biostimulators or growth regulators could 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 proper program for crop quality management definitely requires a thorough knowledge on different mechanisms and

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regulations of key biochemical and physiological processes in plants. Thus, this is the general rule for selecting proper biostimulators or their combination with growth regulators. Therefore, the improvement of postharvest quality and crop yield using foliar nutrition could be considered one of the most issues in the field of plant nutrition (Zhu et al. 2016). The proper programs of foliar nutrition and/or biostimulation should also have positive effects on yield and its storage. It is noticed that, applications of these biostimulators during the pre-harvest 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 (Favaro et al. 2017). 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. It is confirmed that foliar application of Ca reduces skin discoloration in citrus fruits (Smoleń 2012; Singh and Khan 2012; Gimeno et al. 2014).

Therefore, it could be concluded that, the influence of foliar application on nutritional, postharvest, and processing quality of crop yield is relatively complex. The assessment of the effect of foliar nutrition on particular crop species requires consideration of various quality parameters. A good program for foliar nutrition for crops enhances the harvested crop and ensuring suitable post harvesting crops.

Foliar nutrition as an agrotechnique for biofortification

It is well known that, the industrialization has been penetrated all our life fields including the agriculture through the agro-technological packages, producing high-input and high-output agro-systems. Foliar application was and still one of the most important agro-technological tools, where most new formulations or biostimulators or pesticides or nano-fertilizers or else could be applied. This agrotechnique could be considered a promising tool in plant biofortification (Ahmadi-Rad et al. 2016; Davarpanah et al. 2016; Li et al. 2016; Saltzman et al. 2016; Ding et al. 2017; Vasconcelos et al. 2017). Concerning plant biofortification, it could be defined as producing different staple foods containing in their edible parts higher content of bioavailable minerals (Fe, Cu, Zn, Ca, Se, I, etc.), and some nutritional compounds such as folate (Olivares et al. 2015; Strobbe and van der Straeten 2017), thiamin or vitamin B1 (Goyer 2017), vitamin B6 (Fudge et al. 2017), provitamin A (Halilu et al. 2016; Giuliano 2017) and vitamin E (Mène-Saffrané and Pellaud 2017). The plant biofortification mainly is used in micronutrient malnutrition or enriching plants with desirable nutrients or against hidden hunger (El-Ramady et al. 2016b; Singh et al. 2016; de Valença et al. 2017; Díaz-Gómez et al. 2017). This biofortification process also could cover several strategic or staple crops such as rice (Boldrin et al. 2013; Shivay et al. 2016; Chen et al. 2017; Gontia-Mishra et al. 2017), wheat (Shaikh and Saraf 2017), maize (Halilu et al. 2016; Liu et al. 2017; Sharma et al. 2017), barley (Bityutskii et al. 2017), beside other crops like Brassica sp. (Barrameda-Medina et al. 2017), pea (Poblaciones and Rengel 2016), common bean (Ram et al. 2016), potato (Kromann et al. 2017; White et al. 2017) and sweet potato (Laurie et al. 2015).

Therefore, the biofortification is a process in which some desirable nutrients can be provided for plants in a sustainable and cost effective manner. This process can be used in delivering some nutrients (Fe, I, Zn, Ca, Se, etc.) and some vitamins (A, E, B1, B6, etc.) as well as folate for food crops. This approach also can be achieved through agronomic (fertilization), genetic engineering or plant breeding (Singh et al. 2016). Foliar application is a promising tool in delivering the previous minerals and vitamins as well.

Nano foliar application

There are many compounds including nutrients, pesticides, biostimulators, nanomaterials, etc could be applied through foliar or spraying on plants. Nanofertilizers are the most important group among these previous compounds. Nanofertilizers could be considered a kind of fertilizers more effective comparing with conventional fertilizers. These nanofertilizers have the ability to improve the nutrition of plants, to enhance the efficiency use of nutrition and to protect cultivated plants from different environmental stresses (Wang et al. 2015; Belal and El-Ramady 2016; El-Ramady et al. 2016a; Shalaby et al. 2016; Chhipa 2017; Khan and Rizvi 2017; Sarlak and Taherifar 2017). Nanofertilizers also can provide growing plants with one or more of nutrients and support growth and development of plants (Liu and Lal 2015). Foliar application of nanofertilizers on plants is controlled by the same factors controlling the foliar nutrition of normal nutrients beside the particular characterizations of nanoparticles. Several studies have been published regarding nano foliar application on plants including plant nutrition and its protection (e.g., Larue et al. 2014; Wang et al. 2015; Davarpanah et al. 2016; Hong et al. 2016). There are many nanonutrients could be applied for plant nutrition through foliar spraying such as nanosilica (Wang et al. 2015, 2016), nano-selenium (Golubkina et al. 2012), CuO nanoparticles (Hong et al. 2016), nano zinc (Davarpanah et al. 2016), sulphur nanoparticles (Salem et al. 2016), Fe2O3 nanoparticles (Alidoust and Isoda 2013), etc as well as foliar plant protection like silver nanoparticles (Larue et al. 2014), and titanium dioxide (Choi et al. 2015).

There is a great role of nanoparticles or nanomaterials in plants under different challenging environments, as confirmed in many studies (Hatami et al. 2016; Khan et al. 2017). The right reason for this behavior of nanoparticles includes different unique characteristics such as the ability of nanoparticles to engineer electron exchange and the large surface area as well as the high surface reactive capabilities (Hatami et al. 2016). The most important consideration should be taken into account for nano foliar application is the characterization of applied nanoparticles including size of particles as well as the plant leaves structure (pore sizes in cell walls). It is reported that, the size of leaf pores in cell walls is around 20 nm and then the transfer of nanoparticles greater than 20 nm in diameter will be impeded (Dietz and Herth 2011). Therefore, the uptake of nanoparticles and its translocation or transformation and accumulation in plants is very important issue concerning plant nano foliar

nutrition. Furthermore, it is also reported that, nanoparticles have the ability to enter different plant tissues through either root tissues (via soil application) or aboveground organs (via foliar application) including trichomes, stomata, cuticles and stigma, as well as through wounds and root junctions (Shukla et al. 2016; Ruttkay Nedecky et al. 2017; Tripathi et al. 2017; Zuverza-Mena et al. 2017). In general, when different nanoparticles could be applied on plant leaf surfaces, they can enter through the stomata pores (openings) or through trichome bases moving towards various plant tissues (Hatami et al. 2016). Therefore, further studies are needed for more details concerning the foliar of nanomaterials on plants for plant nutrition and/or plant protection. These studies should include the behavior, uptake, translocation and transformation as well as phytotoxicity of these nanomaterials on plants.

Conclusion

Foliar application is considered an agrotechnique. It could be used it in delivering different agro-chemicals including fertilizers, pesticides, biostimulators and some soil amendments as well as nano-agro-chemicals (nanofertilizers, nanopesticides, etc.). efficiency of foliar process is mainly controlled with the characterization of plant leaves, the agro-chemicals, and the environmental conditions including weather factors. Therefore, the proper timing of foliar applications mainly also depends on these previous factors. No doubt that, foliar applications have several benefits including the quality of harvested crops during pre- and postharvest, production biofortified food crops and plant nutrition as well as its protection. Day by day, there are new tasks for foliar applications will be discovered like nano foliar application.

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