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Review Article

Enhancing the efficiency and sustainability of foliar fertilization in agriculture

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Abstract

When considering foliar fertilization, many questions arise about the differences between chelation, complexation, and their efficiency in supplying nutrients to plants. How efficiently are chelated and complexed nutrients absorbed by plants? Are chelates and complexes absorbed by plants? How do they perform in foliar and soil applications? Do they exhibit greater efficiency when compared to pure inorganic fertilizers? and, which ones are the best: soluble, sparingly soluble, or insoluble inorganic fertilizers? Although many people believe chelation and complexation are similar, some differences must be considered when choosing products to better supply plants with nutrients, avoid problems with tank mixtures, and enhance plant nutrition efficiency. The same is true for the vast variety of inorganic sources of fertilizers available for agriculture. They do not behave the same. For instance, inorganic water-soluble fertilizers such as nitrates, sulfates, and chlorides present different performances and should be chosen not only based on their nutrient concentration, availability, and price. All this information will assist farmers and technicians in better defining and selecting products to improve sustainability, efficiency, and achieve better results.

Keywords: Biological organisms; sparing solubility; nutrient supplementation; soil moisture; biological and chemical interaction; combination of products.

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Introduction

Soluble vs. sparingly soluble and insoluble inorganic fertilizers: What to consider? Plants can only absorb, assimilate, and utilize nutrients, whether through roots or leaves, if they are present in a soluble form, meaning they are soluble in water (Gaige, Rowe, & Jurin, 2020). Most oxides, carbonates, and hydroxides have minimal or low availability to plants (Prochnow, Casarin, Stipp, 2010). These types of fertilizers, with a few exceptions, exhibit sparing solubility or insolubility in water and require extended periods to solubilize due to pH variations and/or the presence of biological organisms in soils (Majaron et al., 2022).

When applied through foliar fertilization, sparingly soluble and insoluble fertilizers are not absorbed by plants. Consequently, these fertilizers accumulate on the leaf surface, creating a physical barrier against pathogens, insects, and adverse environmental conditions (Thabet et al., 2021; Derbalah et al., 2022). This explains why calcium carbonates ($CaCO_3$), oxides (CaO), and silicates (Ca_2O_4Si), when applied via foliar sprays, are recommended for protecting plants from sunburn and acidic rainfalls (Silva et al., 2022) rather than as effective sources of calcium (Ca^{2+}). The same is true for copper oxides (CuO), hydroxides ($Cu(OH)_2$), and oxychlorides ($Cu_2(OH)_3Cl$), which function as contact fungicides and bactericides rather than as copper sources for plants (Franco, Goes, & Pereira, 2020).

Therefore, for rapid and efficient foliar nutrient supplementation, it is essential to use water-soluble organic and/or inorganic fertilizers (Gaige et al., 2020). Chlorides, nitrates, and sulfates are the most common sources of inorganic water-soluble fertilizers available for agricultural use (Prochnow et al., 2010; Macedo et al., 2021). These fertilizers are industrially produced through acid/base reactions of insoluble/sparingly soluble fertilizer sources, such as carbonates and oxides, with hydrochloric, nitric, and sulfuric acids, respectively (Table 1) (Reidies, 2000; Rodrígues & Zea, 2015; Xiao, Zou, Ding, Peng, & Chen, 2020).

Sulfate-based fertilizers (SO_4^{-2}) stand out as the most widely used foliar fertilizers in agriculture (World Integrated Trade Solution [WITS], 2021), not because they are the best, but because they are usually they are usually the cheapest, safer and the easiest to use/handle. Consequently, agricultural industries and companies often promote sulfates as the primary fertilizer option for farmers (WITS, 2021; Ministry of Industry, Foreign Trade and Services [COMEX STATS], 2022) (Table 1).

According to Table 1, on a per-point (%) basis of nutrients, nitrates are among the most expensive fertilizers, typically followed by chlorides and sulfates. Although chlorine-based fertilizers may be economically more attractive than nitrates and offer prices similar to sulfates, there are numerous issues associated with their use as plant fertilizers, particularly through foliar applications (Zehler & Kreipe, 1981).

Efficiency and Sustainability of Foliar Fertilization in Agriculture

Soil vs. Foliar nutrition

Providing nutrients to plants via foliar fertilization is a complex task (Fernández, Sotiropoulos, & Brown, 2013). While plants can only absorb and utilize water-soluble substances through their roots and leaves (Gaige et al., 2020), nutrient supplementation through these different pathways should be based on different aspects and implemented in distinct ways.

The first factor relates to moisture, which is consistently present in soils. As a result, most soluble nutrients are solubilized and can be easily transported to and absorbed by roots over time (Havlin, Tisdale, Nelson, & Beaton, 2014). In other words, plants have ample time to absorb these nutrients from the soil solution. However, chemical interactions may convert soluble nutrients into insoluble particles over time, as seen in the interactions of phosphates with iron, aluminum (when pH is below 5.5), and calcium (when pH is above 7.0) (Johan, Ahmed, Omar, & Hasbullah, 2021).

Compared to foliar fertilization, soil nutrition offers a greater opportunity for nutrient absorption over time. Furthermore, in soils, intensive biological and chemical interactions can solubilize nutrients that were once insoluble (Majaron et al., 2022), thereby buffering nutrients in solution.

Table 1. Global trade in key raw materials and the costs associated with the production of inorganic soluble fertilizers.

<table>
<tr><th colspan="3">World's Exports in 2021[1]</th><th rowspan="2">Solubility at 20 °C (mol L^{-1})</th><th rowspan="2">Nutrient amount</th><th rowspan="2">Price (US$) per mol</th><th rowspan="2">Price (US$) per Kg of Nutrient</th></tr>
<tr><th>Product</th><th>Quantity (million tons)</th><th>Average Price per ton (US$ FOB)</th></tr>
<tr><td>Sulphuric Acid</td><td>14.41</td><td>99.81</td><td>Miscible</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Nitric Acid</td><td>1.66</td><td>248.50</td><td>Miscible</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Hydrochloric Acid</td><td>2.55</td><td>138.80</td><td>Miscible</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Zinc Oxide</td><td>0.84</td><td>2164.62</td><td>Insoluble</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Magnesium Carbonate</td><td>1.53</td><td>46.58</td><td>$4.6x10^{-3}$</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Manganese Dioxide</td><td>0.13</td><td>1580,14</td><td>Insoluble</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Calcium Carbonate</td><td>3.78</td><td>237.93</td><td>$6.1x10^{-5}$</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td></td><td colspan="2">Industrial Reaction</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Zinc Sulphate</td><td colspan="2">$ZnO + H_2SO_4 \leftrightarrow ZnSO_4 + H_2O$</td><td>3.331[6]</td><td>36%[2]</td><td>0.185</td><td>2.876</td></tr>
<tr><td>Zinc Nitrate</td><td colspan="2">$ZnO + 2HNO_3 \leftrightarrow Zn(NO_3)_2 + H_2O$</td><td>6.195[5]</td><td>22%[5]</td><td>0.207</td><td>3.170</td></tr>
<tr><td>Zinc Chloride</td><td colspan="2">$ZnO + 2HCl \leftrightarrow ZnCl_2 + H_2O$</td><td>28.983[6]</td><td>42%[4]</td><td>0.186</td><td>2.874</td></tr>
<tr><td>Magnesium Sulphate</td><td colspan="2">$MgCO_3 + H_2SO_4 \leftrightarrow MgSO_4 + H_2O + CO_2$</td><td>2.916[6]</td><td>17%[2]</td><td>0.013</td><td>0.577</td></tr>
<tr><td>Magnesium Nitrate</td><td colspan="2">$MgCO_3 + 2HNO_3 \leftrightarrow Mg(NO_3)_2 + H_2O + CO_2$</td><td>4.686[6]</td><td>9%[5]</td><td>0.035</td><td>1.527</td></tr>
<tr><td>Magnesium Chloride</td><td colspan="2">$MgCO_3 + 2HCl \leftrightarrow MgCl_2 + H_2O + CO_2$</td><td>5.921[6]</td><td>11%[5]</td><td>0.014</td><td>0.628</td></tr>
<tr><td>Manganese Sulphate</td><td colspan="2">$MnO_2 + 2H_2SO_4 \leftrightarrow MnSO_4 + 2H_2O + SO_4^{-2}$</td><td>4.165[6]</td><td>32%[2]</td><td>0.014</td><td>2.718</td></tr>
<tr><td>Manganese Nitrate</td><td colspan="2">$MnO_2 + 4HNO_3 \leftrightarrow Mn(NO_3)_2 + 2H_2O + 2NO_3^-$</td><td>7.767[6]</td><td>22%[4]</td><td>0.016</td><td>3.054</td></tr>
<tr><td>Manganese Chloride</td><td colspan="2">$MnO_2 + 4HCl \leftrightarrow MnCl_2 + 2H_2O + 2Cl^-$</td><td>5.872[6]</td><td>27%[4]</td><td>0.014</td><td>2.760</td></tr>
<tr><td>Calcium Sulphate</td><td colspan="2">$CaCO_3 + H_2SO_4 \leftrightarrow CaSO_4 + H_2O + CO_2$</td><td>0.014[3]</td><td>23%[3]</td><td>0.033</td><td>0.846</td></tr>
<tr><td>Calcium Nitrate</td><td colspan="2">$CaCO_3 + 2HNO_3 \leftrightarrow Ca(NO_3)_2 + H_2O + CO_2$</td><td>7.386[6]</td><td>17%[4]</td><td>0.055</td><td>1.373</td></tr>
<tr><td>Calcium Chloride</td><td colspan="2">$CaCO_3 + 2HCl \leftrightarrow CaCl_2 + H_2O + CO_2$</td><td>6.713[6]</td><td>27%[3]</td><td>0.034</td><td>0.854</td></tr>
</table>

[1] WITS, 2021.
[2] based on its monohydrate form.
[3] based on its dihydrate form.
[4] based on its tetrahydrate form.
[5] based on its hexahydrate form.
[6] based on its anhydrous form.

Conversely, foliar nutrition is far more intricate. Firstly, foliar nutrition is typically administered as a combination of different products, including oils, pesticides, adjuvants, and fertilizers (both soluble and insoluble). For example, in Brazil, over 90% of all farmers mix between two to five products in the same tank mixture, and alarmingly, over 70% of these farmers are unaware of the outcomes or consequences of these mixtures (Gazziero, 2015).

Secondly, foliar sprays are increasingly applied with lower volumes of spraying medium and micrometric droplets to achieve greater agronomic and economic efficiency, improved plant surface coverage, and environmental friendliness (Ahmad, Khaliq, Qiu, Sultan, & Ma, 2021). Consequently, the use of oils and other adjuvants to extend the droplet's lifespan on the leaf, break water tension, and reduce spray drift becomes essential but can also pose a risk to the plant and the effectiveness of products (Pierce, McBeath, Priest, & McLaughlin, 2019; Song et al., 2022).

Thirdly, most of these applications are conducted during the day, with varying temperatures, air moisture levels and winds. Because of the timing and climatic conditions during application, plants have limited time to absorb the compounds applied to their leaves before the sprayed medium dries out. This increases the risk of issues such as leaf scorch due to the accumulation of dried salts on leaves, which can reach toxic levels and cause osmotic damage (Fernández et al., 2013).

Fourthly, the mixture of different products with nutrients without proper protection (chelation or complexation) may lead to tank reactions. These reactions can diminish the performance of products and, in extreme cases, result in clogs in the sprayer system (Machado et al., 2020), leading to financial losses for farmers and exacerbating environmental problems.

All of these factors make efficient foliar nutrition a challenging task compared to soil nutrition.

The mechanisms of foliar uptake

The absorption and translocation of nutrients following penetration of the leaf cuticle follow mechanisms similar to those of root absorption and translocation (Taiz, Zeiger, Moller, & Murphy, 2014). In other words, nutrients enter the xylem through roots, while in foliar nutrition, nutrients directly access the phloem (Du et al., 2020).

Although there are ongoing debates on how nutrients enter plants through their leaves, it is widely accepted that nutrient penetration follows a concentration gradient and most commonly occurs through the leaf cuticle rather than directly through stomata (Schreiber & Schönherr, 2009). Stomata do not allow the entry of substances with a surface tension greater than 30 $mN.m^{-1}$ (Fernández et al., 2013); thus, they are not ideal portals for substances to enter plants.

In addition to being hydrophobic and negatively charged (Fernández et al., 2013), the leaf cuticle contains numerous hydrophilic cracks, pores, and pathways that are permeable to water and small substances, such as nutrients and organic molecules (Figure 1). These hydrophilic pathways, estimated to be found at a density of 10^{10} pores/cracks cm^{-2}, present pores with a diameter of less than 1 nm, allowing the entry of low molar mass molecules, including nutrients (0.05 to 0.44 nm), free amino acids (0.34 to 1.12 nm), and other small organic natural molecules. Larger molecules such as synthetic chelates (EDTA ~ 1.23 nm) are hindered from entering (Schönherr, 2006). Cations and neutral-charged molecules are absorbed more quickly compared to anions (Schreiber & Schönherr, 2009).

Problems affecting foliar nutrition efficiency

Deciding which source of foliar fertilizer to use is not an easy task, and it should rely on aspects other than only nutrient concentration, availability, and price. Nutrient concentration and its solubility are tricky aspects that are usually not considered by technicians and farmers, who tend to choose highly concentrated and cheaper products for foliar fertilization. For instance, let's suppose a farmer is offered two different products at the same price to supply zinc to plants: a liquid-concentrated suspension of zinc oxide (insoluble) with an average of 700 g L^{-1} of zinc, and a liquid-concentrated solution of zinc nitrate (highly soluble) with an average of 200 g L^{-1} of zinc. Which one would the farmer be inclined to choose?

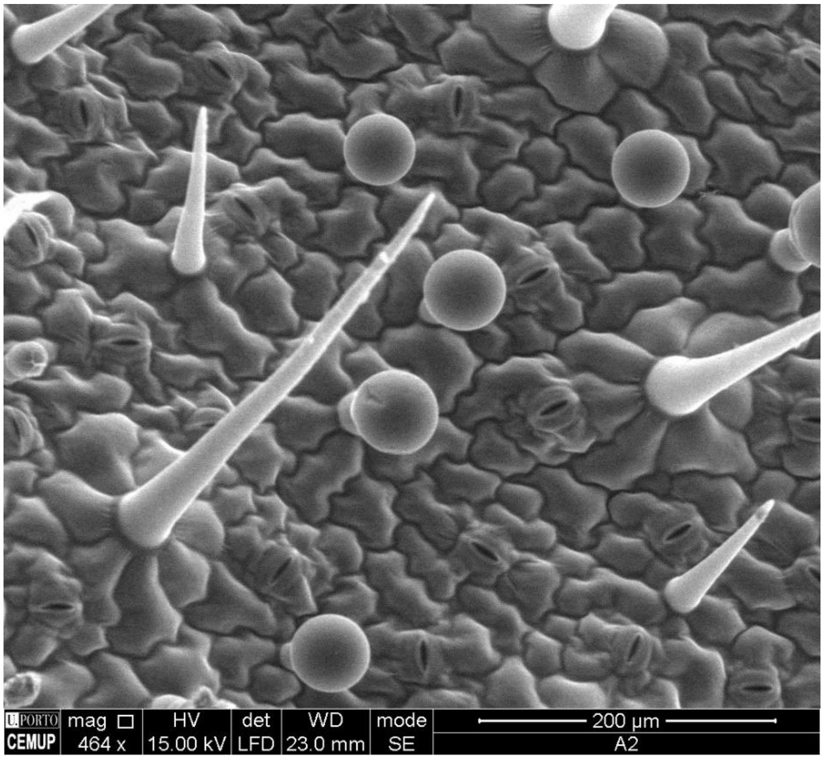

Figure 1. Leaf stomata, pore/crack and trichome density seen from the abaxial side of the leaf. **Source:** Pissarra (2018).

Liquid fertilizers that present high density and high nutrient concentration (% w/w) are usually composed of insoluble inorganic fertilizers such as oxides, carbonates, and hydroxides (Hippler, Boaretto, Quaggio, Azevedo, & Mattos, 2015), as mentioned before. It makes these products very inefficient in quickly supplying nutrients to plants, as they demand time to be solubilized, absorbed, and used (Majaron et al., 2022).

The final pH of a solution is another important aspect to be considered. As a rule of thumb, the perfect pH for the uptake of most nutrients ranges from 5.0 to 6.0 (Fernández et al., 2013). However, it is essential to know which fertilizer will be used and with which products it will be mixed, especially when dealing with pesticides. Glyphosate, for instance, has its performance increased when applied through a spraying medium with a pH lower than 4.0 (Machado et al., 2020). Conversely, fungicides, such as the commercial product named FOX SC325®, work better at a pH ranging from 5.5 to 7.0.

Leaf charge and its interactions with nutrients must also be considered to increase the efficiency of foliar nutrition. Leaf surfaces are negatively charged at pH greater than 3.0 (Fernández et al., 2013). In these conditions, cations are easily retained and accumulate over the leaf, which might favor the occurrence of leaf scorch (Schreiber & Schönherr, 2009) and reduce the absorption of these nutrients (Jacob, Afify, Shanab, & Shalaby, 2022). To avoid such problems, industries improve the safety and efficiency of foliar fertilizers by protecting these cations with organic natural or synthetic stable molecules, neutralizing their positive charge, and facilitating leaf absorption in some cases.

This protection helps to reduce possible interactions between nutrients and other products added to the tank mixture, avoiding problems of efficiency with varying pH (Jacob et al., 2022). For instance, if cationic nutrients such as Ca, Mg, Fe, Cu, and Mn are not well protected, the possibility of undesirable reactions with phosphorus and sulfur occurs, leading to 1) the formation of insoluble substances (precipitates), 2) a decrease in nutrient absorption (Sousa, Marouelli, Coelho, Pinto, & Filho, 2011), and 3) in extreme cases, problems with tank mixtures (Gazziero, 2015).

The molar mass and size, as well as the point of deliquescence of a fertilizer, are other important aspects to be considered to increase foliar nutrition efficiency (Schreiber & Schönherr, 2009). The smaller and lighter the molecule, the more probable and faster it will be absorbed by the plant (Schönherr, 2002; Nielsen, Steele, Forster, & Zabkiewicz, 2005). Molecules approaching the size of a leaf cuticle pore are highly hindered from absorption (Führ & Sauerbeck, 1967).

When analyzing the root uptake of different chemicals by different crops, Lamshoeft et al. (2018) reported a limited absorption of substances with a molar mass heavier than 390 g mol^{-1}. For leaf uptake, Schreiber and Schönherr (2009) demonstrated that citrus membranes were almost 100% impermeable to raffinose, a molecule with a molecular radius of 0.65 nm, a volume of 421.7 Å^3, and a molar mass of 595 g mol^{-1}. However, Citrus membranes were permeable to berberine sulfate, with a molar mass of 769 g mol^{-1} and a volume of 292.9 Å^3. This shows that molar mass alone does not indicate how fast and probable a molecule will be absorbed. Molar volume and size are also important aspects influencing nutrient uptake.

The point of deliquescence (PoD) indicates, for a given temperature and pressure, the air moisture needed for a fertilizer to dissolve and become a liquid. Therefore, the lower the PoD of a substance, the faster it will hydrate and be absorbed by the plant. This is an important aspect regarding foliar fertilization as it allows nutrient absorption by the plant even after the water droplet used to apply the fertilizer dries out (Fernández et al., 2013).

As mentioned before, foliar fertilization is carried out with ever-increasing lower volumes of water and small-size droplets, causing a faster dry out of the sprayed medium. Nutrient absorption by the plant is more efficient when nutrients are supplied through leaves using fertilizers with a lower PoD. In general, for soluble inorganic fertilizers, chlorides usually present the lowest PoD and molar mass, followed by nitrates and sulfates (Table 2).

Environmental conditions and the use of adjuvants with the spraying medium also impact the efficiency of foliar nutrition. Environmental conditions such as wind, temperature, and air moisture affect the application of the spraying medium and the absorption of nutrients by the plants (Fageria, Barbosa Filho, Moreira, & Guimarães, 2009). Moments of the day with lower temperatures (avoid temperatures above 28 °C), light winds (3 – 15 km h^{-1}), good sunlight incidence, and air moisture above 45% are the best conditions for the foliar application of products (Figure 2) (Schönherr, 2002; Australian Government Bureau of Meteorology [AGBM], 2004). Air moisture also affects the physiology of the plant, facilitating and/or making absorption more difficult as it interferes with the turgidity of the cells, the opening of the stomata (guard cells), and the permeability of the cuticle (Fernández et al., 2013).

Adjuvants such as surfactants, wetting agents, spreaders, detergents, penetrators, neutralizers, acidifiers, stickers, and others are tools that can be used by farmers to help increase the efficiency of products and the penetration of nutrients into plants (Ahmad et al., 2021).

Different sources of soluble inorganic fertilizers and their performance over plants

As shown in Table 2, chlorine-based fertilizers usually present a lower PoD compared to other inorganic soluble fertilizers. Nevertheless, all soluble inorganic fertilizers present a molar mass lighter than 390 g mol^{-1}, consequently, easily absorbed by plants (Lamshoeft et al., 2018).

The molar mass of a substance weakly affects its PoD and solubility; however, it negatively affects its salt index (Table 4), showing that the higher the molar mass, the lower its salt index and solubility. Nevertheless, the salt index and the solubility are tightly correlated with each other (Table 3 and Table 4). This is a tendency for the most used inorganic soluble fertilizers in agriculture, where the absorption efficiency usually follows the specific order $Cl_2^{-2} > (NO_3)_2^{-2} > SO_4^{-2}$ (Jacobs & Timmer, 2005).

Table 2. Molar mass and point of deliquescence of common inorganic fertilizers containing K^+, Ca^{+2}, Mg^{+2}, Mn^{+2}, and Zn^{+2} in agriculture.

Source	Molar mass (g mol^{-1}) [1]	Point of deliquescence [2] (%) (25 °C)
…Cl	35.45	-
…NO_3	62.00	-
…Cl_2	70.90	-
…SO_4	96.06	-
…$(NO_3)_2$	124.01	-
NH_4NO_3	80.04	63
$(NH_4)_2SO_4$	132.14	80
KCl (anhydrous)	74.55	86
K_2SO_4 (anhydrous)	174.26	98
KNO_3 (anhydrous)	101.10	95
$CaCl_2 \cdot 6H_2O$	110.98	33
$CaSO_4 \cdot 2H_2O$	136.14	99
$Ca(NO_3)_2 \cdot 4H_2O$	164.09	56
$MgCl_2 \cdot 6H_2O$	95.20	33
$MgSO_4$ (anhydrous)	120.36	90
$Mg(NO_3)_2 \cdot 6H_2O$	148.31	56
$MnCl_2 \cdot 4H_2O$	125.83	60
$MnSO_4 \cdot 1H_2O$	150.99	82
$Mn(NO_3)_2 \cdot 4H_2O$	178.94	42
$ZnCl_2$ (anhydrous)	136.28	< 0.5
$ZnSO_4$ (anhydrous)	161.47	90
$Zn(NO_3)_2 \cdot 6H_2O$	189.39	42

[1] molar mass is expressed considering all the compounds in their anhydrous form.
[2] PoD is expressed considering the compound in its hydrated or anhydrous form (as shown in the “Source” column).

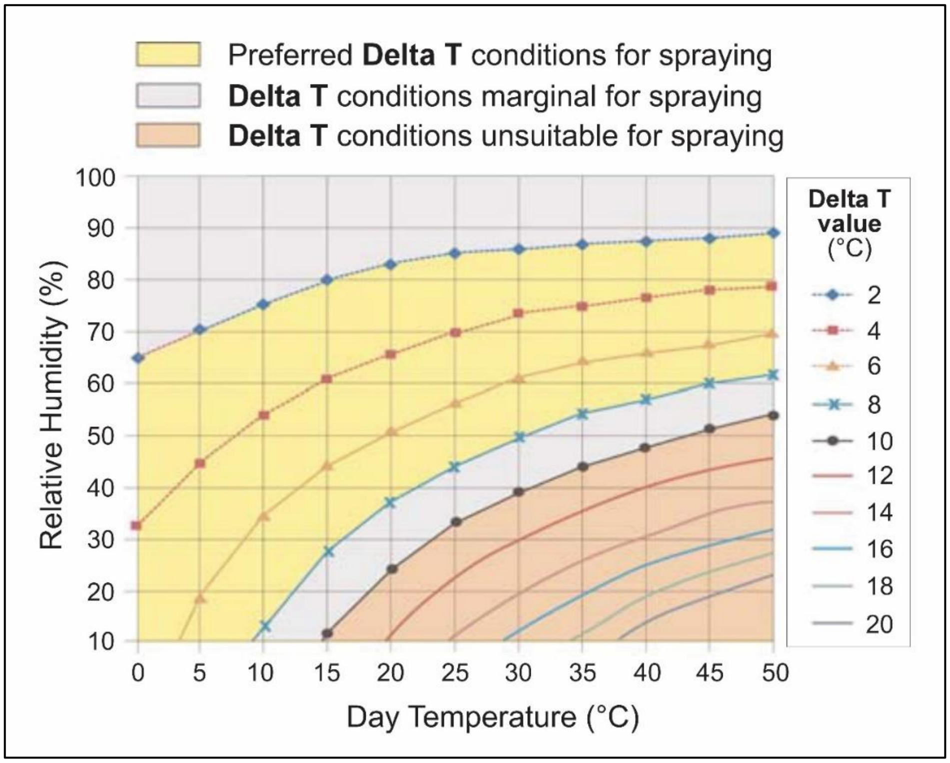

Figure 2. Suitable temperature and air moisture (Delta T) for product spraying.
Source: Australian Government – Bureau of Meteorology (AGBM, 2004).

Table 3. Salt index and solubility of Ammonium, Calcium and Potassium Chloride, Nitrate, and Sulfate fertilizers.

Source	Salt Index (%) [1]	Solubility at 20 °C (mol L^{-1}) [2]
NH_4NO_3	105	23.987
$(NH_4)_2SO_4$	69	5.706
KCl (anhydrous)	116.1	4.587
K_2SO_4 (anhydrous)	42.6	0.635
KNO_3 (anhydrous)	69.5	3.125
$CaCl_2$ (anhydrous)	82	6.712
$CaSO_4 \cdot 2H_2O$	8	0.015
$Ca(NO_3)_2 \cdot 4H_2O$	65	7.386

[1] Salt Index (%) is expressed considering the compounds in their hydrated or anhydrous form (as shown in the “Source” column).
[2] all solubilities are expressed considering the compounds in their anhydrous form.

Table 4 indicates that the higher the solubility of a substance, the higher its salt index and the lower its PoD. Therefore, one could predict how efficiently a substance may be absorbed by a plant by knowing one of these parameters. Nitrates and chlorides are also monovalent ligands, which facilitate plant absorption.

Guedes (2012) compared the absorption and accumulation of different inorganic sources of zinc fertilizers ($ZnSO_4.7H_2O$, $ZnCl_2$, $Zn_3(PO_3)_2$) applied in equal concentrations (700 mg Zn L^{-1}) to citrus trees. The author showed that the most efficient fertilizer was chloride, followed by phosphite and sulfate.

Table 4. Pearson's correlation (r) among molar mass (g mol^{-1}), point of deliquescence (PoD) (%), salt index (%), and solubility (mol L^{-1}) of common inorganic soluble fertilizers in agriculture.

	Molar mass	PoD	Salt index	Solubility
Molar mass	-	-0.0617	-0.6161	-0.2234
PoD		-	-0.4262	-0.6547
Salt Index			-	0.5465
Solubility				-

Fu et al. (2016) analyzed three different sources of zinc fertilizers ($ZnSO_4.7H_2O$, $ZnCl_2$, and Zn $(NO_3)_2.6H_2O$) and three different concentrations (50, 100, and 150 mg Zn L^{-1}) on citrus. These authors showed that zinc chloride was +222.20% and +46.95% more efficient than sulfate and nitrate, respectively. Zinc nitrate was +119.24% more efficient than sulfate.

Gaige et al. (2020) demonstrated the differences in the uptake of three different sources (Oxides, Sulphates, and EDTA) of micronutrients (Mn, Zn, and Cu) applied via soil (Top Soil and Top Soil + Sand) to maize plants. In Top Soil application, sulfate was the best option followed by EDTA and then oxides. For Top Soil + Sand, sulfate was the best choice for Cu and Zn, while EDTA showed to be the best option for Mn.

Assessing zinc absorption of three different fertilizers ($ZnSO_4.7H_2O$, $Zn(NO_3)_2$, and Zn-EDTA) via foliar fertilization on citrus trees for 4 years, Boaretto et al. (2023) demonstrated that nitrates were +113% and +214% more efficient than sulfate and EDTA, respectively. These authors had to decrease the concentration of zinc nitrate applied to plants to half of the dose used in the fourth year of the experiment due to leaf scorching. Sulfates showed to be 47% more advantageous than Zn-EDTA via foliar fertilization.

Regarding the total amount of manganese applied to tomato fruits, Zandonadi, Burkhardt, Hunsche and Cunha (2018) showed that manganese sulfate and nitrate were +3% and +21% more efficient, respectively, in supplying manganese to plants when compared to the control. These authors demonstrated that manganese nitrate was 700% superior in efficiency than manganese sulfate.

When foliar applied in citrus for two consecutive years, calcium nitrate at a 1.0% concentration was 13.2% more efficient than calcium chloride at the same concentration (Sheikh, Zaeid, & Khafagy, 2007). This difference in efficiency was closely correlated to the difference in their solubility (mol L^{-1}) (Table 1).

For foliar application of potassium in olive plants, Bahamonde Pimentel, Lara, Bahamonde-Fernández and Fernández (2022) did not encounter any difference in efficiency when potassium chloride, nitrate, and sulfate were used. This might be probably because all these sources have a high PoD, which may have affected the absorption of the nutrient (Table 2).

The drawbacks of chlorine-based fertilizers to plants

While chlorine-based fertilizers are known for their efficiency in providing nutrients to plants through foliar fertilization (Guedes, 2012; Fu et al., 2016; Boaretto et al., 2023), they are not commonly used for this purpose. But why?

Every cation must have a counterion to neutralize its charge (Schreiber &

Schönherr, 2009). For the most used water-soluble inorganic fertilizers, this counterion is either sulfur (sulfates), nitrogen (nitrates), or chlorine (chlorides). Nitrogen and sulfur are primary and secondary macronutrients to plants, whereas chlorine is classified as a micronutrient. Moreover, their requirements by plants follow the specific order: N > S > Cl (Table 5) (Havlin et al., 2014).

Table 5. Average concentration of macro and micronutrients in vascular plants and their uptake forms through roots and leaves.

Classification	Nutrient	Available form for plant uptake	Adequate concentration mg.kg^{-1} of Dry Matter)
Macronutrients	Carbon	CO_2	450000 (45%)
	Oxygen	O_2, H_2O, CO_2	450000 (45%)
	Hydrogen	H_2O	60000 (6%)
	Nitrogen	NO_3^-, NH_4^+	15000 (1.5%)
	Potassium	K^+	10000 (1.0%)
	Phosphorus	$H_2PO_4^-$, HPO_4^{-2}	2000 (0.2%)
	Calcium	Ca^{+2}	5000 (0.5%)
	Magnesium	Mg^{+2}	2000 (0.2%)
	Sulfur	SO_4^{-2}	2000 (0.2%)
Micronutrients	Chlorine	Cl^-	100 (0.01%)
	Iron	Fe^{+3}, Fe^{+2}	100 (0.01%)
	Boron	H_3BO_3	20 (0.002%)
	Manganese	Mn^{+2}	50 (0.005%)
	Zinc	Zn^{+2}	20 (0.002%)
	Copper	Cu^+, Cu^{+2}	6 (0.006%)
	Nickel	Ni^{+2}	0.1 (0.00001%)
	Molybdenum	MoO_4^{-2}	0.1 (0.00001%)

Therefore, using large volumes of fertilizers based on chlorine easily raises the chances of causing toxicity to plants, including chlorosis, necrosis, and growth reduction. Excessive chlorine in plants may affect nitrogen and phosphorus uptake, causing symptoms of deficiency for these nutrients. It may also affect the chloroplasts, causing an intense Oxygen Reactive Species (ROS) production, damaging the photosystem II, and decreasing CO_2 fixation. Other consequences of excessive chlorine in plants have to do with reduced mitochondrial and enzyme functioning, causing the synthesis of ROS and reducing cell respiration. Cell membranes and the apoplast are also considerably affected (Geilfus, 2018; Hasanuzzaman & Fujita, 2022). Turhan and Özmen (2021) demonstrated that excessive chlorine caused a decrease in the total soluble solid content in pepper plants.

Testing foliar applications of potassium fertilizers (KCl and K_2SO_4) in soybeans, Adhikari, Dhungana, Kim and Shin (2020) showed that KCl lowered the total polyphenol content, the DPPH radical scavenging potential, and the total flavonoid content in normal growing conditions of soybean plants when compared to the use of K_2SO_4. These authors also reported a decrease of 62.8% in total chlorophyll content (mg L^{-1}) caused by KCl.

The yield and the fruit quality of pepper plants grown in different salinity (NaCl or $NaSO_4$) were considerably affected. At higher salt concentrations, NaCl caused yield and fruit quality reductions when compared to $NaSO_4$. At lower salt concentrations, NaCl was more effective at increasing plant yields, probably because this source has a higher solubility and a greater potential to reduce the osmotic potential of plants, allowing the uptake of greater quantities of water and nutrients (Navarro, Garrido, Carvajal, & Martinez, 2002). Moreover, at lower rates, chlorine is classified as beneficial for plant development (Havlin et al., 2014).

For pineapple growth and yield, fertilization with K_2SO_4 was more efficient and less aggressive to plants than KCl. At higher rates of potassium application, the use of K_2SO_4 allowed higher plant biomass and yield. The negative effects of KCl were linked to the toxicity caused by excessive amounts of chlorine in plants (Teixeira, Quaggio, Cantarella, & Mellis, 2011).

For sweet basil, using the fertilizers $CaCl_2$ and $Ca(NO_3)_2$ at a final concentration of 6.5 mM in a hydroponic solution, and varying the ratio between NO_3^{-2} and Cl^-, Corrado et al. (2020) demonstrated that the ratio of 80:20 (NO_3^{-2}:Cl^-) promoted an increase in fresh root biomass of 61.4% when compared to the ratio 20:80 (NO_3^{-2}:Cl^-). These authors linked this decrease in biomass accumulation due to the antagonistic relationship between NO_3^{-2} and Cl^-, and the toxicity caused by excessive chlorine in plants.

Nitrogen and Sulfur toxicities have also been reported in plants (Castro, Kichey, Persson, & Schjoerring, 2022; Xu, Liu, Ma, & Wu, 2022), although the chances of having these problems are much lower because their requirements by plants, as macronutrients, are greater (Havlin et al., 2014). Usually, toxicity caused by nitrates and sulfates is more linked to their solubility and the metal cations that accompany these ligands. Copper, for instance, when applied in equal amounts via a nitrate-based source was more toxic than the same amount applied via sulfate (Mohanapriya, Senthilkumar, Sivakumar, Dineshkumar, & Subbhuraam, 2006). As nitrates are more efficient than sulfates for foliar/root absorption, similar concentrations of cations applied through these different sources cause different levels of toxicity (Boaretto et al., 2023).

Chelation vs. Complexation: Turning inorganic into organic fertilizers and changing their efficiency

Techniques to turn inorganic into organic fertilizers deal with industrial reactions of inorganic water-soluble salts and organic compounds in a procedure called complexation and/or chelation (Tewari, Pareek, Pachauri, & Pandey, 2018).

Chelation and complexation are based on the use of synthetic and/or natural organic compounds (also inorganic for complexation) (Table 6) to create “protections” to metal cations and avoid their interaction with other ions present in a solution (Jacob et al., 2022). These techniques are usually performed for metal cations classified as micronutrients. Nevertheless, macro-cationic metals such as calcium, potassium, and magnesium may also be complexed or chelated.

These procedures aim to 1) protect nutrients and other ions present in solution in a mechanism of “grasping and holding” the metal cation; 2) avoid problems with antagonistic reactions when increasing the ionic strength of a solution; 3) avoid nutrient reduction/oxidation; 4) balance out the ionic charge of a substance to facilitate absorption; 5) avoid problems of tank mixtures; 6) raise fertilization efficiency; 7) reduce problems with leaf scorch; 8) improve nutrient translocation within the plant;

and, 9) hinder the formation of precipitates and insoluble molecules (Tewari et al., 2018; Neocleous, Nikolaou, Ntatsi, & Savvas, 2020; Jacob et al., 2022).

A chelating agent is any polydentate molecule that creates two or more bonds to the metal cation, forming a cyclic compound (ring) to "fully" envelop it. Chelation is a type of complexation that can be performed using natural (lignosulfonates, citric acid, glycine, humic/fulvic acid, etc.) or synthetic organic compounds (Tewari et al., 2018). However, industries usually perform these reactions with synthetic chelates such as EDTA, DTPA, PDTA, and EDDHA because of their higher standardization, stability, availability, and price (Sekhon, 2003).

Conversely, a complexing agent is any chemical molecule that can bind to metal cations through single or multiple bonds without creating a ring-like structure. Usually, complexation involves more than one complexing agent to create a stable complex with the metal cation. Complexing agents can be classified as natural inorganic (nitrates, chlorides, sulfates, phosphates, etc.) or organic (glutathione, monoethanolamine, etc.) compounds (Tewari et al., 2018).

Because in complexation, nutrients are not fully enveloped, their protections are weaker compared to chelation. However, in both situations, some conditions may drastically affect the stability of these protections. These conditions include pH variations (higher or lower pH may affect the complex stability depending on the complexing/chelating agent used), temperature (lower stability as temperature increases), the presence of cationic metals with greater stability constant (cation displacement to form a more stable complex), and the solution's ionic strength (Sokhanvarian, 2012; Dow Chemical Company [DCC], 2021).

Although both techniques bring many benefits, their efficiency varies a lot. Zn-EDTA was the least efficient for the foliar application of zinc in citrus plants. Pure zinc nitrate and sulfate were +214% and +47% more efficient than Zn-EDTA (Boaretto et al., 2023). Conversely, humic-stabilized nano-ferrihydrite (FH) particles were 70 to 75% more effective than Fe-EDTA via foliar fertilization in wheat (Zimbovskaya et al. 2020).

This demonstrates that although chelation and complexation provide many benefits to industry and agriculture, they can't be considered similar due to the vast number of differences related to these agents (Tewari et al., 2018) and their different efficiency in providing nutrients to plants. Some of these differences have to do with the size and molar mass of the molecules (Table 5), and how plants recognize and assimilate them (Jeppsen, 1999; Stacey, 2007; Marschner, 2012).

The problems associated with synthetic chelates for foliar nutrition

The first chelating agent to be synthesized was NTA in 1862 (Nowack & Briesen, 2005). However, the word "chelate" was only presented to the scientific community in the 1920s by Morgan and Drew (1920). Because their fate is still not yet completely understood, synthetic chelates have been a subject of big discussion in the scientific community. These chelates, such as EDTA, DTPA, PDTA, and others, demand a long time to be degraded and thus accumulate in the environment. One of the reasons why their use in some countries is drastically restricted (Oviedo & Rodriguez, 2003).

For the food/feed industry, the use of synthetic chelates has also been narrowed as its consumption was associated with many side effects such as low blood pressure, abnormal calcium levels in the body, lower levels of magnesium and potassium in the bloodstream, fatigue, intestinal inflammation, among others (Institute for Health and Consumer Protection [IHCP], 2004; Evstatiev et al., 2021).

Table 6. Key organic molecules for metal cation chelation/complexation in agriculture. All molecular sizes consider the substance in their anhydrous form (not hydrated).

	Molar mass (g.mol^{-1})	Approximate molecular size (nm)*			Surface area (nm)^{2}*	Volume (Å)^{3}*
		Axle a	Axle b	Axle c		
Synthetic						
Group of the Aminopolycarboxylic Acids						
Nitrilotriacetic acid (NTA)	191.14	0.93	0.89	0.79	3.63	152.7
Ethylenediamine tetraacetic acid (EDTA)	292.24	1.23	1.16	0.79	5.20	240.1
Hydroxyethyl ethylenediamine triacetic acid (HEDTA)	278.26	1.23	1.17	0.79	5.21	241.8
Propylenediamine tetraacetic acid (PDTA)	306.29	1.36	1.24	0.79	5.55	257.6
Diethylenetriamine pentacetic acid (DTPA)	393.37	1.34	1.42	0.96	6.72	329.2
Ethylenediamine-N, N'-bis((2-hydroxyphenyl) acetic acid [o,o] (EDDHA)	360.39	1.11	1.56	1.22	6.18	312.5
Group of the Hydroxylamine Compounds						
N, N-Diethyl-N'-hydroxy-1,2-ethylenediamine	132.20	0.92	0.57	0.80	3.47	145.9
N,N-Bis(2-hydroxyethyl)glycine	163.17	0.93	0.88	0.75	3.71	149.9
Group of the Amines and Polyamines						
Ethylenediamine	60.10	0.71	0.63	0.42	2.37	71.4
Diethylenetriamine	103.17	0.98	0.82	0.43	3.30	119.3
Triethylenetetramine	146.23	1.18	0.56	0.76	3.90	160.9
Tetraethylenepentamine	189.30	1.58	1.23	0.41	5.17	204.1
Natural						
Group of the Hydroxycarboxylic Acids						
Tartaric acid	150.08	0.72	0.81	0.13	2.93	113.9
Citric acid	192.12	0.95	0.86	0.69	3.48	149.0
Gluconic acid	196.16	0.86	0.84	0.79	3.68	164.1
Heptagluconic acid	226.18	1.21	0.66	0.61	4.04	189.7
Group of the Hydroxyamine Compounds						
Monoethanolamine	61.08	0.71	0.60	0.42	2.29	67.4
Diethanolamine	105.14	0.97	0.79	0.43	3.13	111.0
Triethanolamine	149.18	0.72	0.79	0.80	3.51	152.6
Group of the Poliols						
Sorbitol	182.17	0.86	0.85	0.76	3.60	164.8
Mannitol	182.17	0.87	0.81	0.92	3.68	162.3
Dulcitol	182.17	0.75	0.90	0.87	3.61	162.6
Glycerin	92.09	0.76	0.64	0.47	2.63	85.9
Group of other natural compounds						
Lignosulfonates	488.52	1.39	1.64	0.87	7.05	397.6
Humic substances						
Humic acids	227.17	0.93	0.77	0.74	3.67	179.2
Fulvic acids	308.24	1.19	1.10	0.58	4.75	237.5
Algae extract						
Carrageenan[1]	505.57	1.19	0.88	0.71	4.33	234.8
Alginate[1]	370.26	1.35	0.96	0.76	5.32	288.6
Laminarin	504.40	1.81	1.16	0.76	7.15	414.9
L-Amino acids[3]						
Glycine	75.03	0.61	0.60	0.52	2.19	65.8
Alanine	89.09	0.64	0.61	0.58	2.44	82.7
Valine	117.07	0.68	0.80	0.71	2.95	117.5
Leucine	131.17	0.58	0.89	0.83	3.31	134.2
Isoleucine	131.17	0.68	0.90	0.71	3.28	132.7
Serine	105.09	0.58	0.77	0.63	2.56	90.8
Threonine	119.11	0.68	0.78	0.64	2.82	107.8
Tyrosine	181.18	0.83	1.03	0.69	3.69	161.8
Phenylalanine	165.19	0.83	0.94	0.69	3.57	154.3
Tryptophan	204.22	1.05	0.86	0.70	3.93	180.3
Aspartic acid	133.10	0.86	0.69	0.58	2.91	109.4
Glutamic acid	147.12	0.94	0.72	0.59	3.22	125.5
Glutamine	146.14	1.01	0.70	0.59	3.26	128.5
Asparagine	132.11	0.83	0.85	0.53	2.95	111.0
Lysine	146.18	0.99	0.96	0.59	3.71	145.2
Arginine	174.20	1.07	1.08	0.60	3.96	158.0
Histidine	155.15	0.70	0.86	0.72	3.29	135.5
Cysteine	121.01	0.57	0.82	0.69	2.78	102.6
Methionine	149.21	1.02	0.78	0.59	3.49	135.4
Proline	115.13	0.67	0.79	0.58	2.83	106.8

[*] Calculated with the use of VEGA ZZ software using the 3D molecule structure provided by PubChem (https://pubchem.ncbi.nlm.nih.gov) and ChemSpider (http://www.chemspider.com)

[1] Considering kappa-carrageenan and potassium alginate.

For agriculture, problems related to the use of synthetic chelates are more focused on their efficiency. It is believed that plants recognize synthetic chelates as alien organisms, and therefore, their absorption is hindered by either roots or leaves (Figure 3) (Jeppsen, 1999; Stacey, 2007; Marschner, 2012).

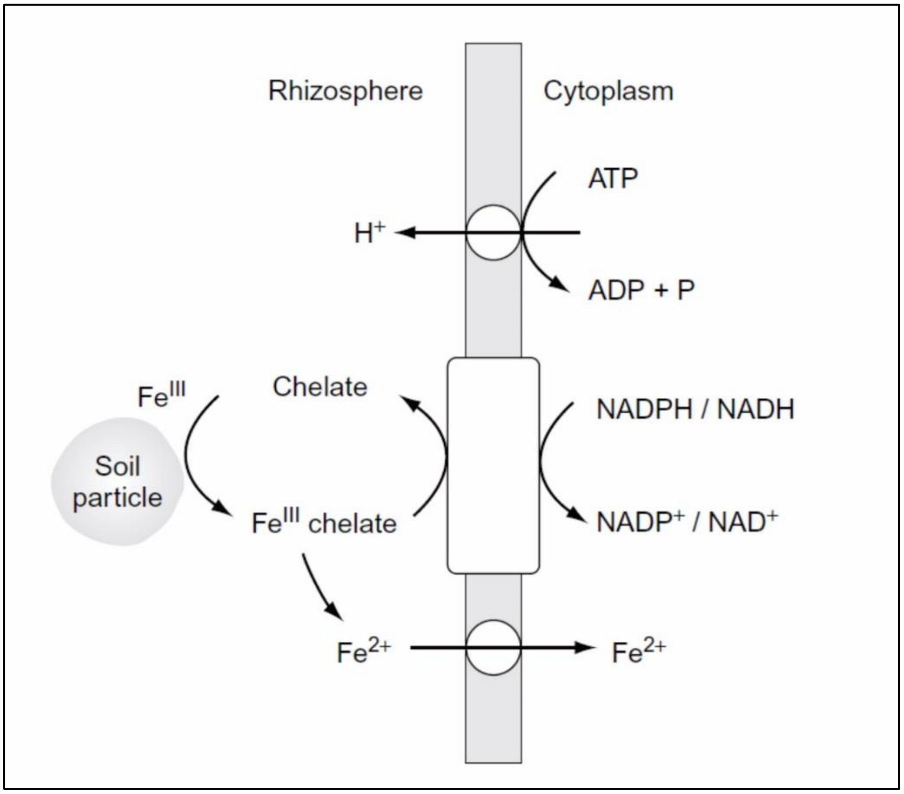

Figure 3. Schematic diagram showing the behavior of synthetic Fe-chelates for root absorption.
Source: Marschner, 2012.

When a nutrient chelated with a synthetic molecule is applied via foliar fertilization, it settles on the leaf surface, and the plant has to "steal" the nutrient in its ionic form from the chelate, leaving the chelate behind (Marschner, 2012). This is a process that demands time, and as foliar-applied solutions dry out very quickly, the probability for lower rates of nutrient absorption and for salt accumulation over leaves exists, leading to cell damage and leaf scorch (Salisbury & Ross, 1992), as mentioned before.

The same happens for the application of synthetic chelated nutrients in soils. The chelate binds to the root, the plant exchanges protons with the chelate, the cation is absorbed, and then, the chelate is released back into the soil solution to chelate other nutrients (Marschner, 2012), i.e., it is not absorbed by the plant.

Nevertheless, as moisture in soils is "constantly present," plants will have time to exchange protons with chelates and absorb the nutrients from it. This explains why the efficiency of synthetic chelates, in soils, is much better than via foliar applications. Assessing different sources of zinc via fertigation over four years, Boaretto et al. (2023) showed that Zn-EDTA allowed an accumulation, in citrus leaves, of +11% and +17% higher compared to pure zinc nitrate and sulfate, respectively.

Evaluating Zn-EDTA and $ZnSO_4$ absorption via roots of soybean seedlings using in vivo X-ray fluorescence (XRF) and X-ray absorption spectroscopy (XANES), Montanha et al. (2020) did not find any evidence that EDTA was absorbed by the plants. Conversely, sulfate was absorbed by the plant; however, its absorption did not follow Zinc absorption. This goes in accordance with Schreiber and Schönherr (2009), who demonstrated that cations and neutral molecules are faster absorbed if compared to anions. Montanha et al. (2020) demonstrated that zinc was absorbed in its ionic form. Zinc sulfate absorption was 10-fold higher than Zn-EDTA.

Which one is better: Chelation or Complexation?

As described before, chelation is a type of complexation performed with an organic compound to "fully" envelop the metal cation and create a ring-like structure around it. Complexation with complexing agents is based on the use of one or more compounds to create bonds to the metal cation without forming a ring-like structure (Tewari et al., 2018). Therefore, complexation forms weaker protections to the metal cation and is more easily broken with varying conditions (Sokhanvarian, 2012; DOW, 2021).

Deciding on which organic or synthetic molecules to use for foliar fertilization is just as hard as choosing the best source of inorganic soluble fertilizer to use. Yet, applying complexed or natural chelated nutrients via foliar fertilization is far more efficient than using synthetic chelates. However, the risk of having tank reactions increases considerably.

The access to key information about the different complexes/chelates and fertilizers available in the market eases the process of understanding and choosing one source over another. For foliar fertilization, the best option is the use of foliar fertilizers complexed or chelated by organic natural molecules. While for soil fertilization, synthetic chelates are preferred. In Table 7, a list of advantages and disadvantages is presented for both options.

Table 7. Pros and cons of complexing and chelating agents in foliar and soil applications.

Parameter	Complexation		Chelation	
Substance type	Organic	Inorganic	Organic	Organic
Source	Natural	Natural	Natural	Synthetic
Environmental degradability	High	High	High	Low
Plant absorption	Yes[1]	Yes	Yes[1]	No
Source of other nutrients provided by the complexing/chelating agent	Yes	Yes[2]	Yes	No
Molecular stability	Medium	Low	High	High
Resistance to pH variation	Low	Low	Medium	High
Foliar fertilization performance	High	High	High	Low
Soil fertilization performance	Low	Low	Medium	High
Probability of leaf scorch	Low	High	Low	Medium
Tank mixture problems	Medium	High	Low	Low

[1] depending on the molar mass and molecular size.
[2] the main complexing agents are: NO_3^-, Cl^-, SO_4^{-2}, PO_4^{-3}.

Final Comments

The best option for farmers to increase plants' nutritional performance via foliar fertilization is by using products with nutrients protected by natural organic molecules. Although these products are usually more expensive, they present a lower probability of causing tank mixture problems when compared to the use of pure inorganic fertilizers such as nitrates, chlorides, and sulfates.

In the case of soil fertilization, and because moisture is "constantly present" in soils, the use of synthetic-chelated nutrients tends to help farmers achieve higher crop quality and yields. The reason why this happens is that in soils there are intensive chemical and biological interactions that may cause metal cations to become insoluble. Therefore, the use of a strong chelating agent, such as EDTA, EDDHA, DTPA, etc., is essential to prevent these cations from reacting with different substances and becoming not accessible to plants.

For farmers not willing to spend extra money for the acquisition of organic-protected nutrients, the best choice for foliar fertilization is to go for nitrates, followed by sulfate, and only then chlorides, as demonstrated before. The use of chlorides is only recommended when other sources are not available.

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