

Technical bulletin ICL

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Foliar nutrition:
Do all sources have the
same efficiency?





1. Introduction

With the discovery in the 19th century that nutrients can be absorbed by plant leaves (Mayer, 1874), foliar nutrition became an important strategy to improve crop nutrition. Over the years, foliar nutrition has evolved along with the development of new technologies and currently, supplying nutrients through leaves is considered a consolidated technique.

The success of foliar nutrition depends on the technologies used in the sources and their interaction with environmental and physiological factors of the plant, and related to the compatibility of the spray mixture with other active ingredients. Thus, this technical bulletin seeks to bring information to light about the main sources available in the market and their interactions in the production system.

2. Nutrient sources for foliar nutrition

2.1 Types of sources and their origin

Nutrient sources for foliar nutrition can be classified as inorganic, organic complex and synthetic chelate. Inorganic sources are metal salts such as sulphate, chloride and nitrate (water-soluble) and oxides and carbonates (insoluble or poorly soluble in water). These inorganic sources can be found naturally in nature or produced industrially through calcination and/or acidulation. Based on Figure 1, it is possible to observe that to transform an insoluble or low-solubility inorganic source (oxide) into a water-soluble inorganic source (metal salts), the rock needs to be attacked with strong acids, i.e., for solubilization of an oxide, the medium must be acidic (low pH).

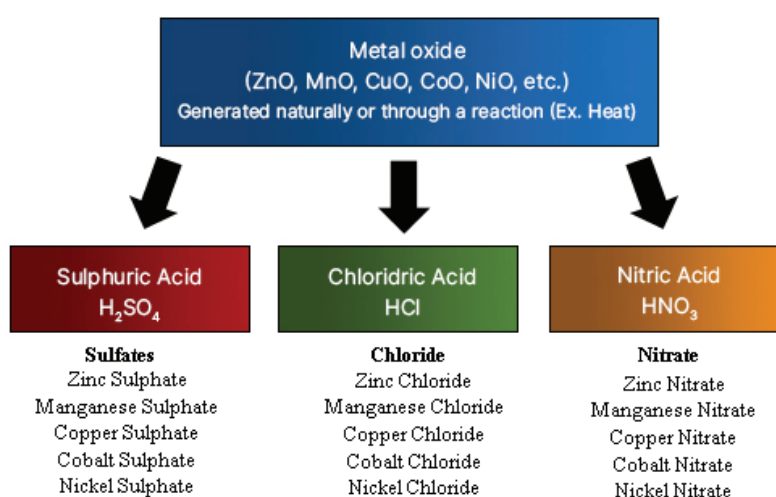


Figure 1. Solubilization of oxides in soluble sources (Sulphates, Chlorides and Nitrates) using sulfuric acid, hydrochloric acid and nitric acid, respectively.



Organic complexes are produced by the reaction of metal salts with organic by-products of the cellulose industry, especially lignosulfonate (LS). As it is organically derived, lignosulfonate may have different physical and/or chemical characteristics depending on the material used in the pulp industry as well as the extraction method used (Barbora, 2018; Benedicto et al., 2011), as can be seen in Table 1. The chemical composition of the LS shown in Table 1 is highly variable, with LS content ranging between 390 and 835 (unit), which consequently can provide different binding stabilities with the associated nutrients and, mainly, the possibility of incompatibility in the tank.

Table 1. Chemical characteristics of different lignosulfonates (LS). (Adapted from Benedicto et al., 2011).

| Characteristics | Unit | LS 1 | LS 2 | LS 3 | LS 4 | LS 5 | LS 6 |
|-----------------|---------------------|-------|------|------|------|------|------|
| pH | - | 3.6 | 4.3 | 6.8 | 4.7 | 3.5 | 2.3 |
| LS content | g kg ⁻¹ | 835 | 587 | 559 | 653 | 504 | 390 |
| Organic S | g kg ⁻¹ | 55 | 51 | 45 | 57 | 45 | 55 |
| -OH phenolics | g kg ⁻¹ | 19 | 19 | 18 | 18 | 31 | 18 |
| -COOH | g kg ⁻¹ | 26 | 35 | 77 | 67 | 63 | 58 |
| M _w | g mol ⁻¹ | 25732 | 6275 | 7550 | 7903 | 6259 | 4975 |

As noted above, the existing variability of lignosulfonates makes it impossible to determine a unique stability constant for this micronutrient-complexing agent (Table 2). This characteristic makes use of this type of product in foliar nutrition risky, since if it is mixed with other products with high Log K such as Glyphosate can make the spray solution incompatible. DID YOU KNOW? The stability constant of lignosulfonate with micronutrients may vary according to the raw material and extraction method used (Barbora, 2018; Benedicto et al., 2011).

Table 2. Stability constant (Log K) between different chelating agents and micronutrients (Clemens et al., 1990; Lundager Madsen et al., 1978).

| Chelating agent | Log K | | | | | |
|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | Cu ²⁺ | Co ²⁺ | Fe ²⁺ | Mn ²⁺ | Ni ²⁺ | Zn ²⁺ |
| Glyphosate | 11.9 | 7.2 | 6.9 | 5.5 | 8.1 | 8.7 |
| AMPA | 8.1 | 4.6 | - | 3.6 | 5.3 | 4.9 |
| Gluconate | 3.6 | - | 1.0 | - | - | 1.7 |
| Glycine | 8.6 | 5.1 | 4.3 | 3.7 | 6.2 | 5.4 |
| Citrate | 10.9 | 6.3 | 6.1 | 5.0 | 6.6 | 6.1 |
| HEDTA | 17.4 | 14.4 | 11.6 | 10.7 | 17.0 | 14.5 |
| EDTA | 20.5 | 18.2 | 16.0 | 15.6 | 20.1 | 18.2 |
| DTPA | 21.1 | 1.8 | 16.5 | 15.1 | 19.6 | 18.3 |
| EDDHA | 23.9 | - | 14.3 | - | - | 16.8 |
| Lignosulfonate | x | x | x | x | x | x |



In turn, synthetic chelates originate from the combination of a chelating agent that contains donor atoms or groups (ligands) that can combine with a single metal ion to form a cyclic structure called a chelate. Although there are several synthetic chelates, the best known are those originating from ethylenediaminetetraacetic acid (EDTA).

It is important to point out that each source mentioned above has different characteristics (solubility, molecular size, electrical charge and deliquescence point) that interfere with the absorption, translocation of nutrients and, consequently, the efficiency of foliar nutrition.

2.2 Solubility of sources and absorption by plants

Source water solubility is an essential factor for foliar absorption, since absorption will only occur when the nutrient is dissolved in a liquid phase (Fernández et al., 2013). The importance of the solubility of the source used in foliar nutrition is shown in the study carried out by Li et al. (2019). In this study, the authors applied two solutions to the surface of a leaf, one containing a soluble source ($ZnSO_4$) and the other a source of low solubility (Zn oxide). After a certain time, the amount of Zn absorbed by the leaves was quantified using X-ray micro-fluorescence (w-XRF). The results of this work demonstrate that the sources of greater solubility increased the Zn content (more intense colors) in the leaf tissue after 3 hours (Figure 2 A) and 3 days (Figure 3 B). The authors also observed that sources of low solubility (Zn oxide) even at the nanometer scale (size smaller than 100 nm) were less absorbed than sources of higher solubility ($ZnSO_4$) after 6 and 24 hours of exposure (Figure 3).

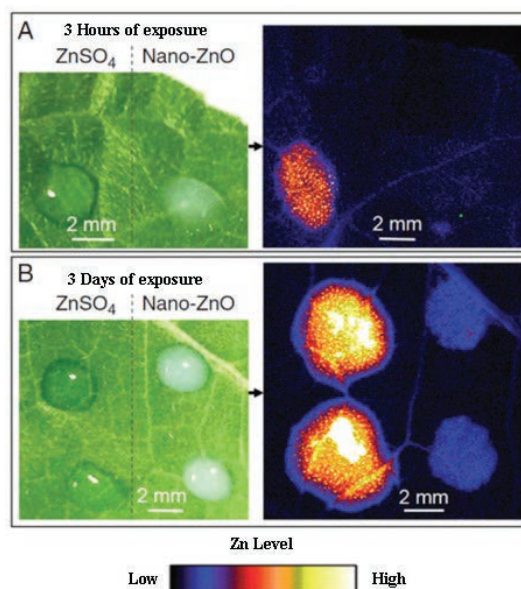


Figure 2. Comparison of foliar absorption of nano-ZnO and $ZnSO_4$ after exposure for 3 hours (A) or 3 days (B) (Adapted from Li et al., 2019).

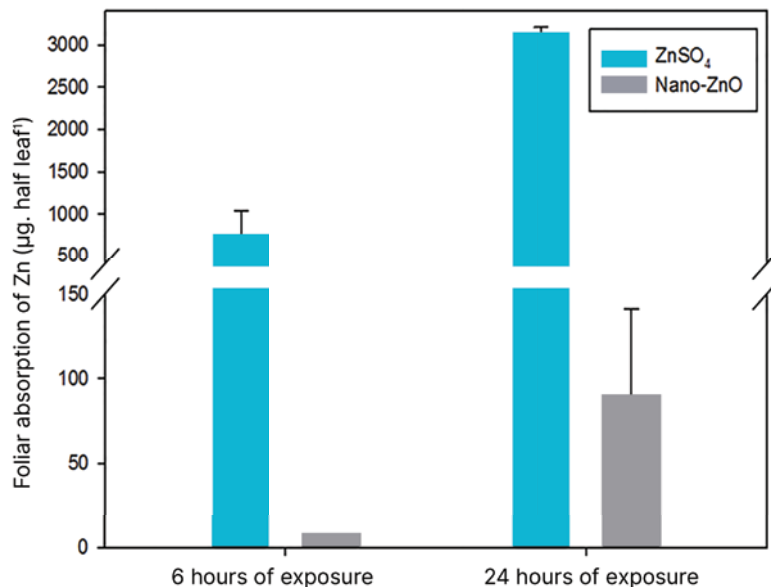


Figure 3. Comparison of foliar absorption of Zn between different sources using inductively coupled plasma mass spectrometry (ICP-MS). (Adapted from Li et al., 2019). **IMPORTANT:** Foliar absorption of Zn from soluble sources can be up to 92 times greater than Zn in the form of nanoparticulate oxide after 6 hours of exposure (Li et al., 2019).

Did you know? Brazilian legislation, through Normative Instruction No. 39, of August 8, 2018, allows fertilizers with a physical concentrated suspension containing nutrients with low water solubility for foliar application to be registered (MAPA 2018).

IMPORTANT: Although the source used on the product label is not indicated, products with a high concentration of the nutrient and high density generally come from insoluble sources such as oxides and carbonates.

2.3 Molecular size

The size of the molecule present in the foliar fertilizer must also be taken into account, since this characteristic affects the possibility and speed of cuticular absorption. **IMPORTANT:** Although absorption of particles up to 2.4 nm is possible through aqueous pores in the cuticle, and up to 43 nm through the stomata (Eichert and Goldbach, 2008), larger particles are segregated and cannot be absorbed (Schreiber; Schönherr, 2009). In this sense, Gomes et al. (2020) characterized thirteen fertilizers containing concentrated suspensions (insoluble sources) marketed in Brazil and observed that the average particle size of these fertilizers was much greater than 100 nm (Figure 4). According to these same authors, foliar absorption of these fertilizers is unlikely, since the particle size is greater than the exclusion limit observed for the stomatal and cuticular pathways (Gomes et al., 2020).

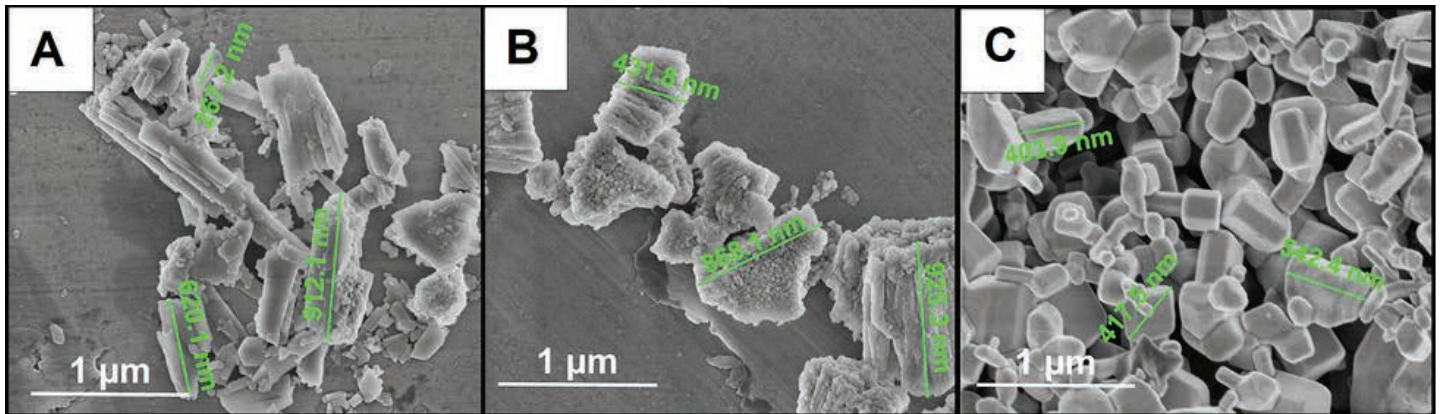


Figure 4. Scanning electron microscopy images highlighting the particle diameter of fertilizers containing CuO (A), MnCO₃ (B) and ZnO (C) (Adapted from Gomes et al., 2020).

2.4 Electrical charge and translocation

For penetration and translocation of nutrients to occur, they must cross the negatively charged leaf cuticle (Schönherr and Huber, 1977). Thus, uncharged species and anions can penetrate the leaf and move within the leaf tissue more easily than positively charged cations (Fernández et al., 2013). In this sense, the chelated nutrient (EDTA) with a neutralized electrical charge has a greater capacity to be absorbed and translocated to other organs of the plant. To verify the importance of electrical charge, Tian et al. (2015) performed an experiment where Zn translocation was evaluated. In this study, the authors sprayed leaves with Zn-Chelate (EDTA) and Zn-Sulphate. After a certain time, samples of vascular tissue where there was no spraying were collected and the Zn content was determined using X-ray micro-fluorescence (μ -XRF). The authors observed a higher concentration of Zn in the vascular bundle of the petiole (region with a more reddish color) with Zn-Chelate (EDTA) in relation to Zn-Sulphate (Figure 5). Such results evidence the greater capacity of translocation of nutrients in the form of chelate (EDTA) in relation to other sources.

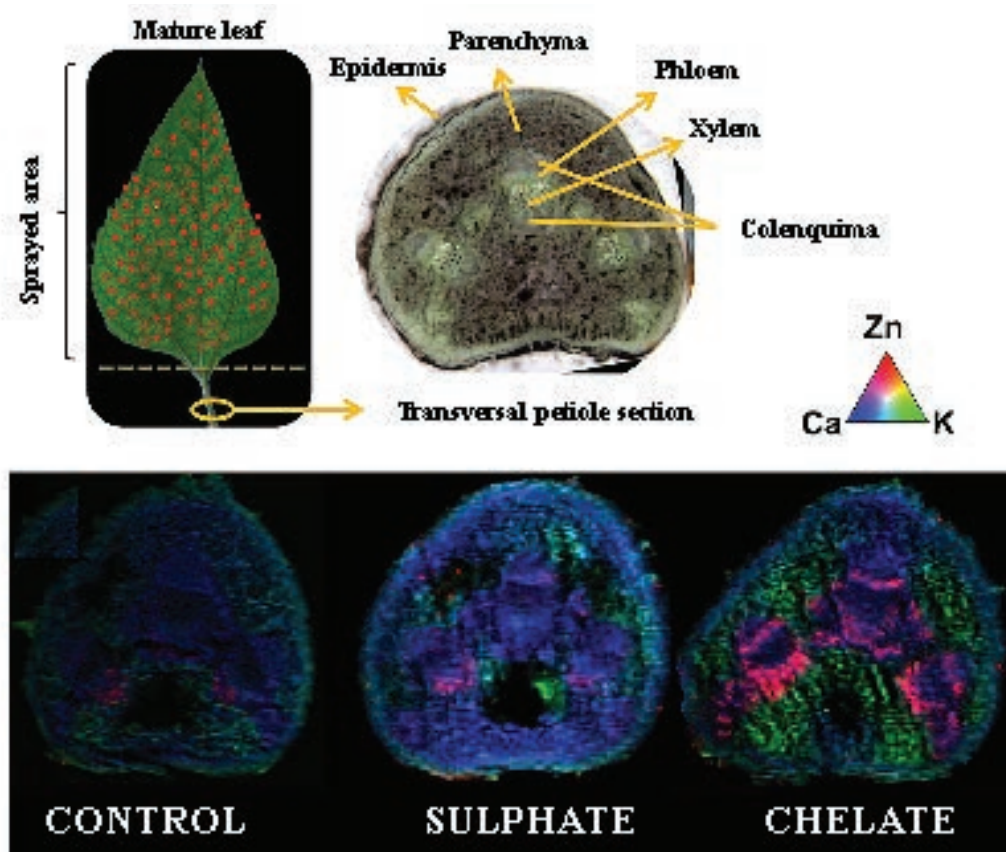


Figure 5. Zn concentration (Red) in the vascular bundle of the petiole without Zn application (Control), after foliar application of Zn-Sulphate and Zn-Chelate (EDTA) (Adapted from Tian et al., 2015).

2.5 Point of deliquescence

The processes of hydration and dissolution of salts are determined through the point of deliquescence (PD). The point of deliquescence is defined as the relative humidity value at which the salt becomes a solute. Thus, when the relative humidity of the air is above the point of deliquescence of the source, the applied compound will dissolve and become available to be absorbed by the leaf. The point of deliquescence is variable according to the source, however additives can be used to reduce this index and improve source efficiency. An example of this can be seen in the work of Alexander and Hunsche (2016), who used surfactants to improve the absorption of Mn-EDTA and Zn-EDTA in an environment of high relative humidity (90%). It is worth mentioning that the addition of surfactants in chelates is necessary, especially in conditions of low relative humidity, where the efficiency of chelates without surfactants is drastically reduced.

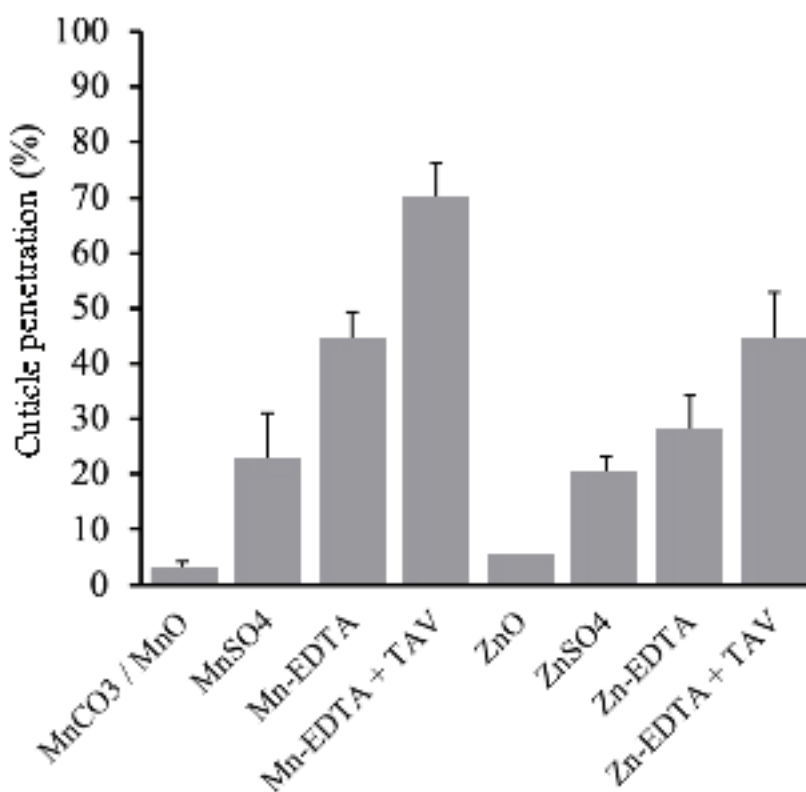


Figure 6. Cuticular penetration (%) of different sources of Mn and Zn with and without surfactants (TAV) (Plus) (Adapted from Alexander & Hunsche, 2016).

2.6 Safety and compatibility

In addition to the characteristics related to absorption and translocation, there is a great variability of sources regarding safety and compatibility in the mixture with other pesticides (Table 3). This feature is very important since the spray mixture makes it possible to reduce operating costs while maintaining the efficiency of both foliar nutrition and active ingredient.

Table 3. Concentration, solubility and compatibility in a tank of manganese sources (Adapted from Good Practices for Efficient Use of Fertilizers, IPNI).

| Manganese sources | % Mn | Solubility | Tank compatibility |
|-------------------------------|-----------|-------------|--------------------|
| Oxide - MnO | 41-68 | Not soluble | Compatible |
| Carbonate - MnCO ₃ | 31 | Not soluble | Compatible |
| Sulphate - MnSO ₄ | 26 - 30.5 | Soluble | Not compatible |
| Chloride - MnCl ₂ | 17 | Soluble | Not compatible |
| Chelate - Mn-EDTA | 13 | Soluble | Compatible |



An example of spray mixture incompatibility can be seen when the base sources of sulphate ($MnSO_4$) and chloride ($MnCl_2$) are mixed with glyphosate. Such mixing reduces the efficiency of the active ingredient and forms precipitates and lumps in the solution. Bernards et al. (2015) carried out a study to verify the effect of foliar fertilizers on herbicide glyphosate absorption by plants. The authors observed that after 48 hours, the amount of glyphosate absorbed by the plants varied from 70% using Mn-EDTA to 25% using Mn with lignosulfonate and $MnSO_4$ (Figure 7).

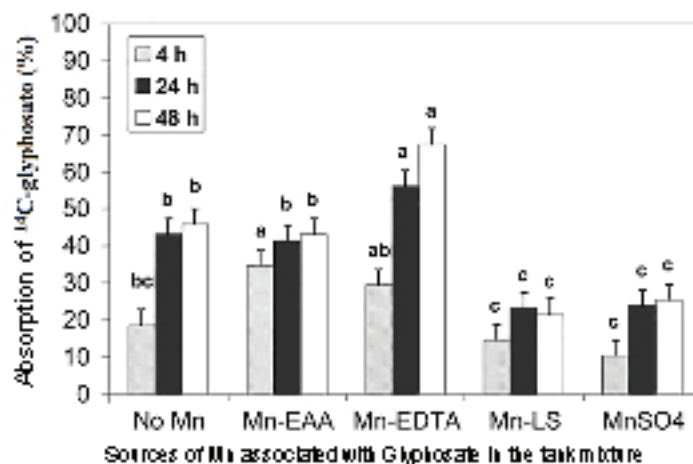


Figure 7. ¹⁴C-glyphosate absorption (%) with different Mn sources in the tank mixture (Adapted from Bernards et al., 2005).

In addition to reducing the efficiency of the active ingredient as shown above, some sources can destabilize the solution, forming precipitates and lumps in solution (Figure 8) that clog the sprayer's filtration system, compromising the flow of the nozzles, reducing the efficiency of foliar nutrition and the useful life of the nozzles, in addition to reducing operational efficiency.

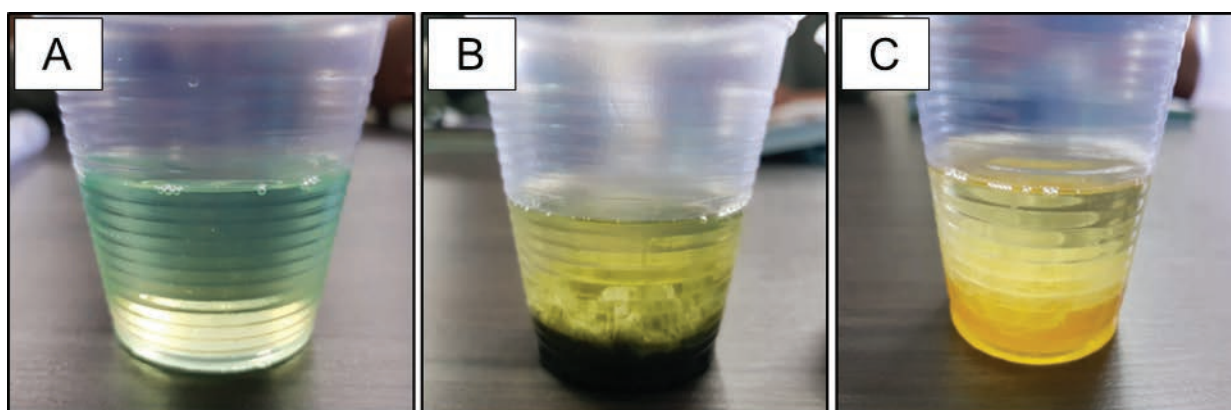


Figure 8. Kellus Manganese (Mn-EDTA) + Glyphosate (A), Lignosulfonate-Mn + Glyphosate (B), and Mn Chloride + Glyphosate (C). Source: Vinícius Faria.



Thus, selecting sources for foliar nutrition that are soluble in water, with characteristics that allow a high penetration and translocation of nutrients inside the plant, in addition to the compatibility with other active ingredients in the tank mixture, provides safety to the farmer and is key to successful foliar nutrition.

Discover the Kellus line

Foliar fertilizer technology developed for agriculture with 100% protected nutrients (chelate + additives). The **Kellus** line improves crop nutrition, ensuring adequate absorption of nutrients by the leaves, has high nutrient mobility within the plant and maximum physiological response. In addition, the **Kellus** line provides compatibility and safety when mixed with other active ingredients in the tank.



Benefits

- Precision nutrition: achieving very high efficiency at low doses applied
- Smaller volume of product to be transported and stored
- Lower volume of packaging generated for disposal
- Very high translocation: reaching action sites throughout the plant
- Safe application in mixtures with any pesticide in the sprayer tank
- Maximum physiological activity of plants for maximum productive potential
- Activation of plant defense systems



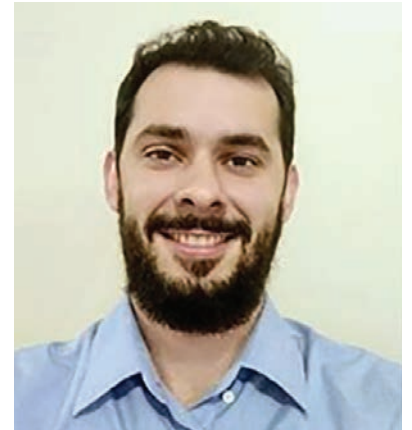
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