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Analysis of Nutrients in Foliar Fertilizers

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***Abstract*: The use of fertilizers is necessary to increase productivity, food quality and environmental and economic sustainability. Foliar fertilization is an extremely important tool, it is friendlier to the environment, with a more immediate and targeted response to the plant's nutrition objective when compared to soil fertilization. However, some fertilizers do not contribute to the development of a plant. For this, it is necessary to assess whether the contents are in accordance with the product labels. Thus, the aim of this study was to evaluate the levels of different nutrients in foliar fertilizers in order to compare the results obtained with the labels. For this, 5 commercially acquired fertilizers were evaluated for macro and microelements contents through analytical quality control techniques and the results indicated that all evaluated fertilizers were in accordance with the contents shown on the labels. This way, ensuring greater security for its buyers and applicators in vegetables.**

Keywords: Fertilizers, macronutrients, micronutrients, planting, vegetables.

INTRODUCTION

Agriculture is one of the most important Brazilian economies, the sector's revenue, considering the 2019/2020 harvest, had an increase of 22.3% from the previous harvest, thus reaching R$ 582 billion (CNA, 2020).

According to Sordi (2020), the use of fertilizers is necessary to increase productivity, food quality and environmental and economic sustainability, in addition to providing better soil quality and allowing the maintenance of soil fertility. Nutrients to be absorbed by the plant without the use of fertilizers need to go through a mineralization process before being absorbed, as with the use of fertilizers the nutrient will already be in the form the plant needs to absorb.

The use of fertilizers includes knowing the characteristics of the soil, the plant and the relationship between the plant and the soil so that it is possible to choose the best fertilizer, the best source of nutrients, the correct amount of application, the frequency of application, fertilizer in powder or liquid, application time, seeking maximum fertilizer application efficiency (VIÉGAS, 2020).

Foliar fertilization is an extremely important tool, it is friendlier to the environment, with a more immediate and targeted response to the plant's nutrition objective when compared to soil fertilization. In addition, through the foliar application of fertilizers, nutrients can be provided in the vegetative, reproductive and plant growth periods (FERNÁNDEZ; SOTIROPOULOS; BROWN, 2015).

Currently on the market there is a large offer of foliar fertilizers composed of macro and micronutrients, which can be supplied individually or in a set with two or more nutrients. Macronutrients are the elements most needed for plant development, the most important being nitrogen (N), phosphorus (P) and potassium (K). The other macronutrients calcium (Ca), magnesium (Mg) and sulfur are also essential for the plant and are considered secondary macronutrients. Micronutrients are the elements that the plant needs in small amounts, such as boron (B), chlorine (Cl), molybdenum (Mo), zinc (Zn), copper (Cu), manganese (Mn), iron (Fe) and silicon (Si) (MIRANDA, 2010).

Quality control within the fertilizer industries is necessary so that it is possible to guarantee that the contents mentioned on the labels are correctly delivered to customers and that the final product does not present non-compliance (VIÉGAS, 2020).

With this information, the general objective of this work is to validate the macro and micronutrient contents of mineral and organomineral foliar fertilizers presented on the labels of the selected fertilizers. compare the laboratory results with the contents of the following nutrients: total organic carbon (TOC), nitrogen (N), phosphorus (F), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe) and zinc (Zn) in 5 foliar fertilizers.

This proposal is justified since some fertilizers are not causing the expected effects on certain vegetables. Also, why the Ministry of Agriculture, Livestock and Supply (MAPA) establishes some parameters that must be analyzed in agricultural products.

THEORETICAL REVIEW

Fertilizers are mineral or organic compounds that help the plant develop, they provide the nutrients needed to germinate and thus produce leaves, flowers, seeds and fruits. The use of fertilizers and other agricultural techniques are very important to increase productivity (MIRANDA 2010).

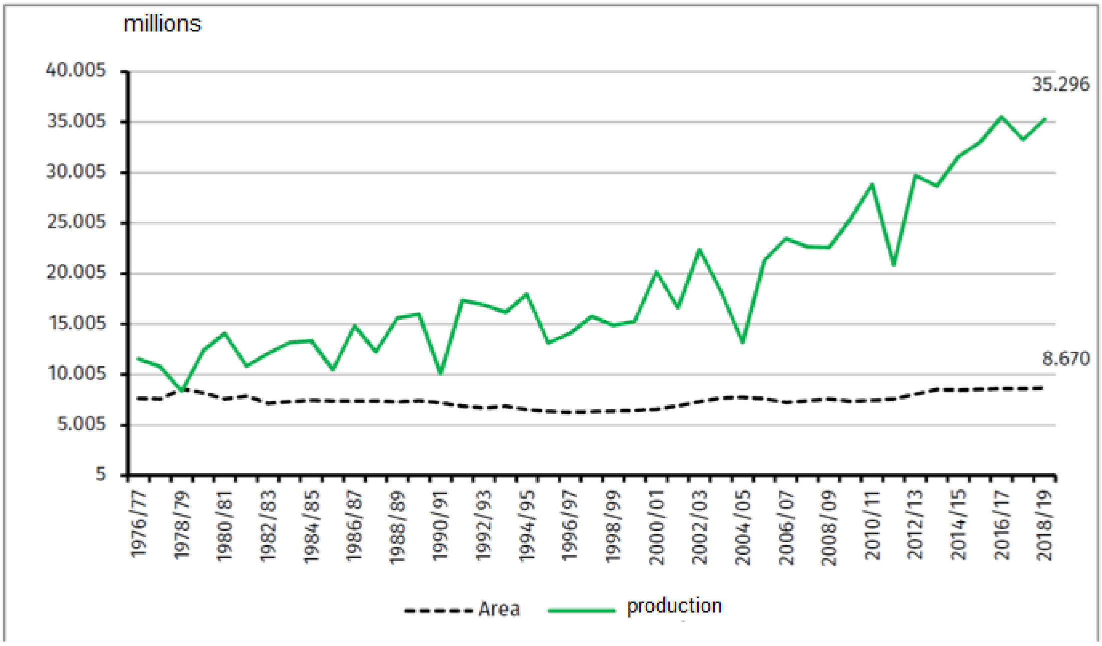
According to Oliveira (2019), chemical or mineral fertilizers have been used since the Neolithic period, at that time animal ashes and manure were used as a source of nutrients for plants. Around 8,000 BC, in China there was already the use of fertilizer produced from animal and vegetable waste. However, it was only in the Middle Ages that fertilization came to be considered a business.

In 1842 was born the famous and widely used nitrogen (N), phosphorus (P) and potassium (K) through the researches of Justus von Liebig, considered the father of modern agriculture, who reported that plant nutrition occurred due to mineral elements in the soil and thus the manure was replaced by chemical compounds. From this moment on, the era of chemical fertilizers began, with the first fertilizer factory in England appearing in 1843. Over the years, the use of foliar fertilizers has become common, as they allow the supply of nutrients more quickly than through methods involving root fertilization (SORDI, 2020).

In Brazil, the history of fertilizers began around 1895 in the region of Campinas, a large coffee producer at the time, but convincing farmers to pay and use a product they apparently did not need was a major challenge. Thus, on April 13, 1967, the National Association for the Diffusion of Fertilizers (ANDA) was founded, whose objective was to convince producers of the cost-effectiveness of using fertilizers. Currently, Brazil is one of the biggest powers in the world in food production and one of the biggest consumers of fertilizers in the world, striving each year for greater productivity and better quality of soil, plants, seeds and fruits (MICHELLON, 2011).

Within the state of Rio Grande do Sul, the main crops in terms of amount of planted area and production are soybean, rice, corn and wheat, when it comes to production value, tobacco, grape and Apple. Figure 1 shows the growth of planted area and grain production in the state.

Figure 1 - Advances in planted area and production in Rio Grande do Sul - 1976 – 2019.



Source: Adapted from FEIX, LEUSIN JÚNIOR (2019).
Note 1: area measured in thousands of hectares and production measured in thousands of tons.
Note 2: Data for the 2018/2019 harvest were estimated in June 2019.

Analyzing the market for foliar fertilizers in Rio Grande do Sul, it is seen that in all these cultures, from small to large producers, the technique of foliar fertilization is already used, in Rio Grande do Sul the cultivation of grapes, apples, peaches, among others that are part of the horticultural group, are the ones that use foliar fertilizers the most (ABISOLO, 2020).

FLUID FERTILIZERS

According to Alberto (2017), fluid or foliar fertilizers are nutritive compounds composed of macronutrients, micronutrients and amino acids that are applied to the leaves, aerial parts of plants. They are generally more effective than soil-applied fertilizers in solving acute feeding problems because they deliver these components ready for plant uptake. Other advantages of foliar fertilizers are quick response, lower doses and applications can be lined up through the soil. to help complement food on the floor and through the sheet.

MAPA, according to Normative Instruction 39, classifies fertilizers in relation to their composition, which can be simple minerals, complex minerals, organic, organominerals and biofertilizers. Due to its physical nature, for solids it can be powder or granules, and for liquid, solution or suspension. And it is also classified in relation to the mode of application, being via soil, via foliar, via hydroponics, via fertigation and via seed (BRASIL, 2018).

Normative Instruction 39 (BRASIL, 2018) determines that the composition of nutrients is presented in percentage (%), which can be classified as follows: primary macronutrients, secondary macronutrients, micronutrients. In addition to nutrients, foliar fertilizers can contain chelating agents, complexing agents, surfactants/surfactants, among other additives to obtain a fertilizer with better absorption in the plant.

According to Alcântara and Porto (2019), the use of foliar fertilizers for products that contain amino acids is highly viable, as there was a 38% increase in productivity. Franco (2020) applied organomineral foliar fertilizers together with mineral foliar fertilizers with polymers and observed an agronomic efficiency of 26.04%, in addition to presenting better results for the percentage of P and K recovered from the soil and translocated to the aerial part of the plant, due to reduced phosphorus fixation and potassium leaching.

For Minikowski (2018), the application of foliar fertilizers containing N, P, sulfur (S), manganese (Mn), boron (B), copper (Cu) and amino acids presents positive results for the development of soybean, increasing the mass of leaves and pods, consequently increasing productivity. Peloso (2020) obtained positive results indicating an increase in production in relation to the application of different foliar fertilizers in the coffee crop.

Nicchio et al (2020) carried out a study of the foliar application of P, K and silicon (Si) in the development, production and quality of sugarcane ratoon, and obtained a positive result related to the increase of nutrients in the aerial part of the plant, and the average sugar production was considered above the ideal value, in addition to obtaining an increase in the quality of the crop.

Foliar fertilization allows for the correction of a nutrient deficiency with an immediate and more targeted response when compared to soil fertilization, due to the fact that nutrients are supplied during the critical phases of plant development. Thus, the use of foliar fertilizers is a widely used crop nutrition strategy of growing importance on a world scale (FEIX; LEUSIN JÚNIOR, 2019).

PLANT ABSORPTION MECHANISMS

The process for using a foliar-applied nutrient solution can be divided into the following steps: leaf adsorption, cuticular penetration, absorption within cell compartments that are metabolically active and translocation and use of the nutrient that was absorbed (VELLAME; RABBIT; TOLENTINO , 2012).

The plant surface area has a complex and diverse set of chemical and physical adaptations that increase the tolerance against irradiation, temperatures, vapor pressure deficit, physical damage, dust, rain, among others. In addition to this feature, the plant surface controls the passage of water vapor and gases, the absorption of nutrients when applied via the leaves and, when under unfavorable conditions, control the loss of water and nutrients to the environment. (SCHWAMBACH; NEPHEW 2014).

The absorption of solutes by the leaf surface is restricted due to the presence of the cuticle and the wax layer, these two layers have several functions, the main one being to reduce the loss of water and nutrients. The pores present in the cuticle are of the order of 1 nm in diameter and are permeable to ions and soluble substances that are below this diameter and impermeable to substances above it, an example being iron complexes. For cations, they can be retained in the leaf cuticle due to negative charges present in pectins, cutins and waxes. The stomata are important access routes for ions, but absorption through them depends on the opening and density and the number of stomata present (SCHWAMBACH; SOBRINHO 2014).

The rate of absorption depends on the age of the leaf, the nutritional status of the plant and the mobility of the element. In relation to leaf age, the younger the leaf, the greater the ability to absorb ions due to greater metabolic activity, thinner cuticles, greater absorption speed and greater demand for nutrients (VEDOVATO; FINAMORE, 2016).

For the nutritional status of the plant, for example, when they are deficient in K they can absorb this element twice as quickly through the leaves as through the roots, so when deficient the best way to correct it is by foliar application (BISSANI; GIANELLO ; CAMARGO; TEDESCO, 2008).

Regarding nutrient mobility, those that are known as mobile move easily and deficiency symptoms are presented in old leaves. Elements with variable mobility depend on leaf senescence, which is directly linked to N deficiency. For nutrients with conditional mobility, they depend on additives or surfactants that allow better translocation within the plant structure. The Table 1 shows which elements are within each category for mobility (KERBAUY, 2004).

Table 1 - Differences in nutrient mobility in the phloem.

Mobility high	Mobility medium	Mobility conditional
N, K, P, Mg e Cl	S, Fe, Zn, Cu, Mo e Ni	Ca, B e Mn

Source: KERBAUY, 2004.

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MACRO AND MICRONUTRIENTS

Plants need seventeen elements to develop and complete their life cycle, which are carbon (C), oxygen (O), hydrogen (H), N, K, P, Ca, Mg, Mn, chlorine (Cl), S, B, Zn, Fe, molybdenum (Mo), nickel (Ni) and Cu. The C, O and H are absorbed by the plant through the air so they are considered organic nutrients, the rest of the seventeen nutrients are absorbed by the plant through the roots and leaves and these are considered mineral nutrients (FERREIRA, 2011).

The classification with macro and micronutrients refers to the concentration in the plant, macronutrients are presented in percentage (%) and micronutrients in part per million (ppm). Nutrients classified as macronutrients are: C, H, O, N, P, K, Ca, Mg and S, and N, P and K are the ones that are present in greater amounts in the plant, being considered the primary macronutrients. The rest of the nutrients, namely, Bo, Cl, Cu, Fe, Mn, Mo, Zn, Na, Si and Co, are classified as micronutrients (MIRANDA, 2010).

According to Epstein and Bloom (2004), each nutrient has its specific function within the plant, for example, the N applied to the vine has a great impact on the vegetative growth of the plant, on productivity and on the chemical aspects of the grape and its must, the N is linked to the most important physiological processes of the plant, namely photosynthesis, respiration, ionic absorption of other nutrients, growth, among others. P helps in the formation of phosphate in metabolism allowing the transfer of energy within the plant. The main function of Ca is to be part of the plant cell wall, being very important in the germination of grains and in the movement of grease in the plants (BLANK; OLIVEIRA; ARRIGONI-BLANK; FAQUIN, 2006).

K regulates the entry of CO2, maintains the amount of water in the plant and activates various enzymatic systems. Mg stands out in participating in chlorophyll and in activating a large number of enzymes. The B permeabilizes the cell walls allowing a better absorption of nutrients and greater resistance to drought (BLANK; OLIVEIRA; ARRIGONI-BLANK; FAQUIN, 2006).

In relation to Cu, this metal has many functions, from photosynthesis to helping plant uniformity. Organic Fe compounds are present in electron transfer. The main functions of Mo are the activation of nitrogenase enzymes and the reduction of nitrates in the plant. Zn helps in the metabolism of carbohydrates, proteins, phosphates and in the formation of auxins, in addition to being a stabilizer of cellular components. Mn accelerates the germination and root system of the plant (EPSTAIN; BLOOM, 2004).

METHODOLOGY:

The selected fertilizers are shown in Table 2 with their respective nutrients and classification. All of them were acquired from a commercial in the region of Vale do Taquari, RS.

Table 2 - Fertilizers chosen to be analyzed.

Sample identification	Classification	Nutrient(s) to be evaluated
Sample 1	Mineral foliar fertilizer	K
Sample 2	Mineral foliar fertilizer	S e K
Sample 3	Mineral foliar fertilizer	P e K
Sample 4	Mineral foliar fertilizer	Ca
Sample 5	Organomineral Fertilizer	N; P; K; Ca; Mg; S; B; Cu; Fe; Mn; Mo; Zn; COT

Source: the Author (2021).

The 5 fluid fertilizers were purchased directly from the manufacturing industry and the nutrient analyzes were analyzed at Univates' chemistry laboratories and, in some cases, at Tecnovates and third parties. For comparison of results, data presented on product labels and in analysis reports provided by the production company that were carried out in outsourced laboratories were used.

Methodology for N validation in mineral and organomineral fertilizers for foliar application

For the analysis of N in mineral and organomineral fluid fertilizers, the Raney alloy macromethod was used, which consists of the ammonification of all non-ammoniacal forms of nitrogen, as described in chapter II, method 1.1 of the Manual proposed by MAPA (BRASIL, 2017) .

Methodology for P validation in mineral and organomineral fertilizers for foliar application

In the phosphorus analysis, a spectrophotometric method of molybdovanadophosphoric acid was used, which consists of a strong acidic and hot chemical attack in order to extract its phosphorus content. of ammonium, whose absorbance is measured at 400-420 nm (GALDINO, 2003).

Methodology for K and Ca validation in mineral and organomineral fertilizers for foliar application

The flame photometric method is based on the solubilization of potassium and calcium and measuring their emission in a flame photometer (BRASIL, 2017). For this it was necessary to use a flame photometer located in the chemistry laboratory of Univates, previously calibrated with standard solutions of K and Ca.

Methodology for Mg validation in mineral and organomineral fertilizers for foliar application

The method indicated by MAPA (BRASIL, 2017) for the determination of Mg in mineral fertilizers was the spectrometric method by flame atomic absorption and is described in chapter II, method 5.3 of the manual prepared by MAPA. For this it was necessary to send the samples to laboratories specialized in these analyses.

Methodology for S validation in mineral and organomineral fertilizers for foliar application

The analysis of sulfur in foliar fertilizers was based on the extraction of sulfur and precipitation as barium sulphate and after quantification of this precipitate, this method is called the gravimetric method of barium sulphate, for its realization the described reagents, equipment, procedures and calculations will be used in chapter II, method 6 of the manual prepared by MAPA (BRASIL, 2017) for analysis of nutrient content in fertilizers. This analysis was carried out in the chemistry laboratories of Univates.

Methodology for B validation in mineral and organomineral fertilizers for foliar application

For the analysis of boron, the spectrophotometric method of azomethine-H was used, where, in an aqueous solution of azomethine-H, it dissociates into 4-amino-5-hydroxy-2,7-naphthalenesulfonic acid and salicylic aldehyde, where, under conditions controlled, allows the determination of boron by UV-visible spectrophotometry at 410 nm. This methodology is described in chapter II, method 7 of the manual prepared by MAPA (BRAZIL, 2017).

Methodology for validation of micronutrients in mineral and organomineral fertilizers for foliar application

For water-soluble micronutrients such as Co, Cu, Fe, Mn, Mo, Ni and Zn, MAPA (BRASIL, 2017) indicates in chapter II, method 8, the methodology used and its respective reagents, equipment and calculations. For this analysis, the flame atomic absorption spectrometry method was used, which is based on the solubilization of micronutrients in water and determination of their concentration by atomic absorption spectrometry. These analyzes were performed in third-party laboratories.

Methodology for validation of TOC in organominerals for foliar application

According to Bezerra and Barreto (2011), the volumetric method of potassium dichromate for TOC analysis is suitable for organomineral and organic fertilizers. This method is based on wet oxidation of the organic carbon contained in the sample with excess potassium dichromate and concentrated sulfuric acid to promote external heating, the residual dichromate is determined by standard ammonium ferrous sulphate titration method.

For this methodology, a set for digestion with heating under reflux was necessary, containing a digester with heating plates for 6 tests or similar, and the heating must be individual with condensers and supports for fixation. It must also contain reaction flasks, which can be flasks for distillation or Erlenmeyer flasks with a ground mouth to make the connection with the condensers. These analyzes were performed in third-party laboratories.

RESULTS AND DISCUSSION

Table 4 shows the results obtained in the analysis of nutrients in each sample and also the values presented on the labels and reports provided by the producing industry.

Table 4 - Results obtained and presented on the label and report.

Sample identification	Nutrient	Value on label	Valeu on report	Results obtained
Sample 1	K_2O	32%	30%	29,99%
Sample 2	K_2O	25%	25%	25,47%
	S	25%	25,4%	24,87%
Sample 3	P2O5	30%	31,2%	32%
	K_2O	20%	20%	20,96%
Sample 4	Ca	12%	12,12%	12,47%
Sample 5	N	5%	5,3%	5,2%
	P2O5	8%	8,8%	8,33%
	K_2O	8%	8%	9,19%
	B	0,4%	0,55%	0,63%
	Ca	0,8%	0,86%	0,92%
	S	1%	1,51%	1,1%
	Cu	0,1%	0,11%	0,12%
	Fe	0,1%	0,14%	0,15%
	Mn	0,4%	0,4%	0,47%
	Mo	0,05%	0,06%	0,06%
	Zn	0,4%	0,41%	0,048%
	Mg	0,6%	0,61%	0,083%
	COT	6,5%	6,75	7,2%

Source: the Author (2021).

With these data, it can be seen that the results obtained are consistent with the information presented in the label and report provided by the producing industry. Thus being able to deliver a product with quality assurance. Some differences between values may be due to differences in equipment, calibration and analyst errors.

As already seen, it is of great importance for the fertilizer to supply the necessary minerals for the cultivation of certain vegetables. Several examples can be cited in scientific articles.

Santis et al (2020) evaluated the performance of Fe, Cu and Zn micronutrients at different concentrations in tomatoes, with the aim of determining the supplemental effect of the micronutrients. When the plant is deficient in these micronutrients, it has a limit of absorption via the leaves, in addition to interfering with the vitamin C produced by the plant. The authors found positive results where the applied micronutrients increased the quality of tomatoes, especially in parameters such as total soluble solids, pH and firmness, in addition to improving the vitamin C index, productivity and absorption index via the leaves.

Silva et al (2018) carried out a study on the application of foliar fertilizer, composed of the macronutrients N and K2O and TOC, on carrots in order to assess whether the fertilizer can weaken the toxicity of the herbicide Metribuzin. As a result of the application of fertilizer together with pesticide, there was an increase in total yield and a decrease in forked carrots. With this result it is possible to observe that the application of foliar fertilizers is not only for plant deficiencies, but also to help in situations where pesticides cause phytotoxicity.

Santos et al (2019) carried out a study on the importance of applying foliar fertilizers based on the evaluation of the application rates and times in dwarf cashew seedlings. A fertilizer with N, P_2O_5, K_2O, B, Cu, Fe, Zn and EDTA was used, at a dosage of 2.5 g/L. In this study, he obtained positive results, with an increase in the root, leaf and total dry mass, and the author considers that during the application period, the cashew tree needs more nutrients, thus allowing a greater use of the nutrients delivered by the fertilizer.

From these studies, it is possible to observe that it is extremely important that fertilizers deliver nutrients in the concentration mentioned on the label, so it is always necessary to analyze fertilizers before marketing them.

CONCLUSION

From the analyzes carried out, it was possible to compare and guarantee the quality of the fertilizers, providing the correct contents that were highlighted on their labels. Given the nutritional importance that is necessary for macro and micronutrients to be available for plant development.

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