Soil micronutrients: dynamics, availability, and fertilization management

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ABSTRACT

Micronutrients (B, Cu, Fe, Mn, Zn, and Mo) are generally required in small quantities and perform various metabolic functions in plants. In the soil, their availability can be affected by several factors, such as pH, texture, organic matter content, and the concentration of other elements. The way these factors interact can influence the absorption of micronutrients by plant roots. Once absorbed by the roots, the transport of micronutrients is affected by the way they are complexed and the available concentration in the soil solution. The deficiency of micronutrients causes various visible symptoms in plants, including chlorosis, deformation, necrosis, and reduced growth, which can be corrected with proper fertilizer management. This chapter provides updated information on the dynamics of micronutrients in soil and plants, the factors influencing their availability, and fertilization recommendations for these nutrients.

Keywords: Absorption, Chlorosis, Deficiency, Necrosis, Transport.

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INTRODUCTION

In recent decades, micronutrients have been used more routinely in fertilization practices. Of the sixteen essential nutrients for plants, seven are micronutrients: boron (B), copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), molybdenum (Mo), and chlorine (Cl). Although plants generally do not require large quantities of these nutrients, the absence of any one of them in the soil can limit plant growth. This study will not address Cl.

The functions of micronutrients are divided between being constituents of prosthetic groups and activators of enzymatic reactions. Without micronutrients as activators, the enzymatic system in plants would be simply an inert mass of proteins (Gupta et al., 2008; Andrade et al., 2021).

The reasons for the inclusion of fertilizers containing micronutrients in fertilization plans can be summarized as follows:

a) Expansion of the agricultural frontier: intensive agrosilvopastoral exploitation in the Cerrado region, characterized by soil with poor chemical properties and high acidity, leading to nutrient deficiencies. Correcting acidity aims to raise the pH and make Ca and Mg bases available. Increasing the pH reduces the availability of cationic micronutrients, so their addition through fertilizer management must be anticipated.

b) Crop productivity: high crop yields lead to significant nutrient export and sometimes the depletion of reserves, especially micronutrients in soils. These deficiencies are increasingly documented in research (Resende, 2005; Abreu et al., 2007).

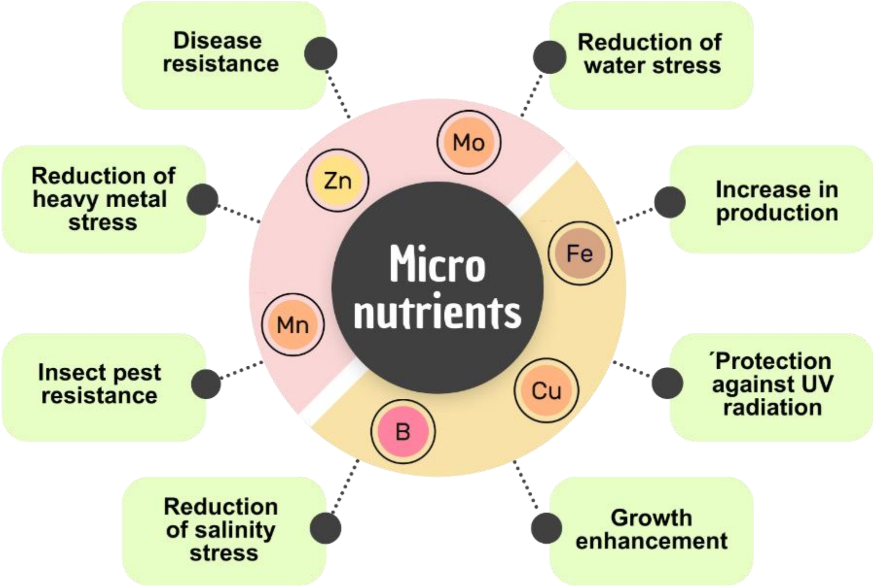
c) Fertilizer purity: current NPK fertilizer production processes remove impurities, excluding micronutrients that were indirectly supplied.

d) Nutritional specificity: certain crops have specific micronutrient requirements; for example, legumes and plants in the Brassicae family require B and Mo. Cereals show greater responses to Zn and Cu, and beet to Mn (Khaliq et al., 2019; Andrade et al., 2021).

e) Soil management: soil erosion and long-term cultivation result in the removal of micronutrients from the soils.

Figure 1 highlights the main roles of micronutrients in plants. The symptoms caused by the lack or excess of these nutrients in plants, at tissue levels, are a useful guide to establishing the deficiency or toxicity of an element. Therefore, it is important to know the distribution of micronutrients in different plant organs (Gupta et al., 2008). Some essential micronutrients and heavy metals in excess can result in toxicity to crops (Khaliq et al., 2019).

Figure 1. Plant responses to soil micronutrients under biotic and abiotic stresses.



Source: Author (2024).

DYNAMICS OF MICRONUTRIENT

Soils exhibit significant variations in micronutrient content. A comprehensive analysis shows that the abundance of these micronutrients primarily varies with the parent material (Table 1). However, even when the parent material is the same, the action of different weathering agents, such as moisture and temperature, can result in soils with distinct characteristics. Additionally, the effects of various climatic conditions, both current and past, on soil composition are evident.

Table 1. Micronutrient contents in some igneous and sedimentary rocks.

Element	Igneous rocks		Sedimentary rocks		
	Granite	Basalt	Limestone	Sandstone	Shale
	--- mg dm^{-3} ---				
Fe	27,000	86,000	3,800	9,800	47,000
Mn	400	1,500	1,100	10 - 100	850
Cu	10	100	4	30	45
Zn	40	100	20	16	95
Mo	2	1	0.4	0.2	2.6
B	15	5	35	100	100

Source: Silva et al. (2006)

The relative stability of minerals present in soils also illustrates how micronutrient levels can vary according to the weathering stage. Soils formed under more advanced weathering conditions may have a different mineralogical composition, reflecting variations in the levels of micronutrients essential for plant development.

FACTORS INVOLVED IN DYNAMICS OF MICRONUTRIENTS IN SOIL AND PLANTS

Soil texture

Soil texture influences the dynamics of micronutrients for plants, as these elements can associate with the solid phase of the soil. The energy with which micronutrients associate with the solid phase varies among them, causing differential mobility between micronutrients in the soil system (Table 2). Zn and Mn generally have very low mobility, while B is extremely mobile in the soil profile. Thus, for the first two, transport in the soil solution is essentially by diffusion. For Cu, the process of root interception assumes some importance, while for B, mass flow is the main means of transport (Rehman et al., 2018).

Table 2. Different forms of micronutrient mobility in soil.

Nutrient	Forms (%)		
	Root interception	Mass flow	Diffusion
B	3	97	0
Cu	70	20	10
Fe	50	10	40
Mn	15	5	80
Mo	5	95	0
Zn	20	20	60

Source: Camargo (2006).

The transport of micronutrients in the soil is important for aspects associated with fertilizer use and the understanding of deficiency symptoms, such as those of B and Mo, which are frequently observed in dry seasons. In the case of B, its transport to the root region depends on a water potential gradient resulting from plant transpiration, a process that decreases during dry periods (Landi et al., 2019). For Zn, initially, the establishment of a necessary concentration gradient is required, but it is not sufficient for the establishment of diffusive flow, which requires a good soil moisture content. Therefore, it is common to observe the disappearance of deficiency symptoms of these micronutrients after the first rains. However, if the rains are more intense, B deficiency may recur due to its high mobility in the soil and possible leaching, a phenomenon that does not occur with Zn (Rengel, 2015; Rehman et al., 2018).

B leaching allows us to infer about the importance of organic matter in its maintenance, as it complexes this micronutrient through radicals and organic groups like a diol group. Therefore, all soil management and conservation practices that lead to the maintenance of organic matter are beneficial for the availability of micronutrients to plants (Landi et al., 2019).

Clayey soils can adsorb part of the B, which is in the anionic form $H_2BO_3^-$ or $B(OH)_4^-$, making this nutrient unavailable for plant absorption (Chatterjee and Bandyopadhyay, 2017). In the case of Zn, soils with higher levels of iron and aluminum oxides are more affected due to their affinity for these colloids. On the other hand, Cu has a greater affinity for organic matter, being more adsorbed in organic soils (Andrade et al., 2021).

The ionic transformation of micronutrients is a relevant process, as it determines whether the nutrient will be more or less available for plant absorption (Abreu et al., 2007). Table 3 presents a summary of the absorbed forms of these micronutrients and their mobility within the plant. It is important to note that, except for B, all micronutrients are incorporated into the plant in the same form they are absorbed. Additionally, except for Mo, these micronutrients are considered immobile within the plant (Raij, 2011). Due to this immobility characteristic, the deficiency of these nutrients tends to manifest first in young leaves, where the demand for nutrients is higher during the initial stages of development.

Table 3. Forms of absorption, incorporation and mobility of micronutrients in soil.

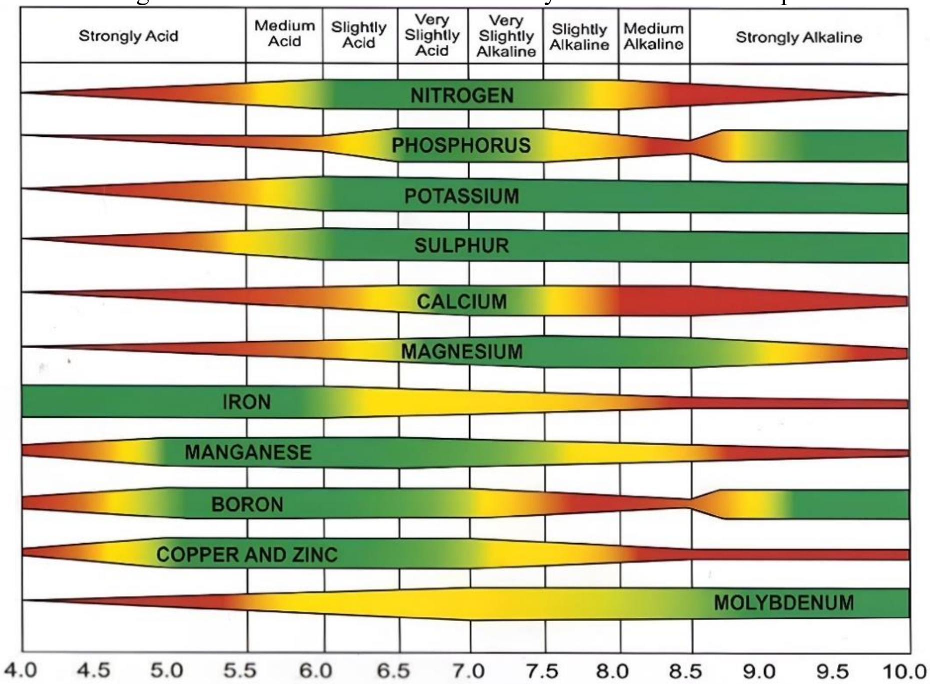
Nutrient	**Absorbed form**	**Incorporated Form**	**Mobility**
B	H_3BO_3	-	Immobile
Cu	Cu^{2+}	Cu^{2+}	Immobile
Fe	Fe^{2+}, Fe-Chelate	Fe^{2+}	Immobile
Mn	Mn^{2+}	Mn^{2+}	Immobile
Zn	Zn^{2+}	Zn^{2+}	Immobile
Mo	MoO_4^{2-}	MoO_4^{2-}	Mobile

Source: Dechen et al. (2018).

Soil pH

Soil pH significantly affects the availability of micronutrients due to the transformation from soluble to insoluble forms in the soil. The exception is Mo, which follows the opposite path (Figure 2). Under acidic pH conditions, some micronutrients can become sufficiently soluble to be toxic to plants. Mn, for example, can inhibit root growth in some acidic soils. Proper liming of these soils, to raise the pH close to 6.5, reduces the risk of toxicity (Mascarenhas et al., 2013).

Figure 2. Variation in nutrient availability as a function of soil pH.



Source: Agroadvance (2023).

Increases in soil pH above 6.0 induce the hydrolysis of hydrated Cu, which can lead to strong adsorption of Cu by clay and organic matter charges. Thus, the solubility of Cu^{2+} depends on the soil pH and decreases 100 times for each unit increase in pH (Fageria et al., 2002; Fonseca et al., 2010). The surface application of lime, at the correct rates in a no-tillage system, does not necessarily lead to micronutrient deficiencies (Moreira et al., 2017).

At higher pH levels, the form of H3BO3 most absorbed by the plant is minimized in solution, reducing absorption by the roots (Abreu et al., 2007; Dechen et al., 2018). The availability of Zn and Cu is affected by pH, decreasing by 100 to 1000 times for each unit increase. pH values above 6.0 strongly increase the adsorption of ions to soil colloids, affecting their availability (Abreu et al., 2007; Khaliq et al., 2019). In relation to pH, each unit increase causes a reduction in Fe availability by 1000 times and Mn by 100 times.

Unlike other micronutrients, Mo availability increases with rising pH due to the predominant form of MoO_4^{2-}, an anion absorbed by plants. Its greatest availability occurs in alkaline soils and is negatively affected by high levels of organic matter and iron and aluminum oxides, which are less impactful than the increase in pH (Chatterjee and Bandyopadhyay, 2017).

High doses of acidity correctives (over-liming) can cause drastic changes in the environment, reducing productivity due to unbalanced nutrition from micronutrient deficiencies. It is noted that, generally, considering technical, operational, and economic aspects, it is more challenging to correct the conditions resulting from over-liming than the conditions often found in acidic soils (Carneiro et al., 2018).

Soil organic matter content

The activity of microorganisms can promote changes in organic matter content and, thus, in the availability of micronutrients, either through the supply of these nutrients in response to mineralization or by decreasing their complexation (Oliosi et al., 2016). Due to the number of active sites, organic matter has a high capacity to complex micronutrients, especially cationic ones in soils with corrected acidity. Organic matter is also the main source of B, interfering with its availability to plants. Dry environments hinder the supply of B from organic matter through reduced mineralization due to decreased soil microbiological activity (Abreu et al., 2007; Dechen et al., 2018).

Oxidation-reduction potential

The availability of Fe and Mn is affected by the oxidation-reduction potential and pH of the soil. Since the forms absorbable by plants of these nutrients are Fe^{2+} and Mn^{2+}, moisture is necessary to ensure the greater presence of these ions in the form absorbable by plants (Khaliq et al., 2019). In the case of Fe, the transformation from Fe^{3+} (insoluble form) to Fe^{2+} (soluble form) occurs at an oxidation-reduction potential of -185 mV, while Mn^{4+} (insoluble form) changes to Mn^{2+} (soluble form) at an oxidation-reduction potential of 200 mV, causing Mn toxicity to occur much faster than Fe toxicity (Andrade et al., 2021).

The decrease in the oxidation-reduction potential of the environment is of great practical importance. For example, plants cultivated in lowland areas (wetlands) may suffer toxicity from Mn and Fe due to the increase in the availability of their reduced and, consequently, mobile forms (Mn^{2+} and Fe^{2+}). In the specific case of rice cultivation, this toxicity can be mitigated as rice plants possess aerenchyma, which allows the conduction of oxygen from the aerial part to the roots. Thus, under field conditions like those mentioned, the observation of a brownish-red coloration, indicating the presence of iron in the oxidized form (Fe^{3+}) on the surface of rice plant roots, is common. Additionally, there is a change from Mn^{2+} to the less active oxidized form (Mn^{4+}).

Soil use and management

Regarding the influence of soil use and management on the availability of micronutrients, in addition to the considerations already mentioned, the issue of soil compaction can be raised (Oliosi et al., 2016). There has been an increasing trend of compacted soil layers in areas with intensive agricultural exploitation. Besides aspects or factors associated with often inadequate agricultural mechanization (mainly soil preparation), the addition of inputs such as lime in high doses and repeated applications account for a large part of the compaction problems observed. In compacted layers, low oxidation-reduction potential may even occur, sufficient to cause Mn toxicity.

STUDY OF MICRONUTRIENTS

BORON

The function of B in plants is represented in the differentiation of meristematic cells. The consensus is that its main function is related to the structure of the cell wall and the substances associated with it (Chatterjee; Bandyopadhyay, 2017). The variation in plant tissues is broad, with generally higher values in dicotyledons than in monocotyledons (Gupta et al., 2008). It is present in soil solutions with a pH below 8, mainly as undissociated boric acid (H_3BO_3), the primary form taken up by roots, and it dissociates to $B(OH)_4^-$ only at higher pH values (Abreu et al., 2007; Raij, 2011).

B deficiency is a widespread nutritional disorder. Under conditions of high precipitation, B is easily leached in the form of H_3BO_3. The availability of B decreases with increasing soil pH, particularly in calcareous soils and those with high clay content (Abreu et al., 2007). Availability also decreases drastically under dry conditions, likely due to reduced B mobility through mass flow to the roots and the polymerization of boric acid (Resende, 2005; Dechen et al., 2018).

Symptoms of B deficiency in shoots are noticeable in terminal buds or the youngest leaves, which become discolored and may die. Internodes become shorter, giving plants a thick or rosette appearance (Figure 3). The deficiency is mainly found in the younger plant tissues (Dechen et al., 2018). Chlorosis can occur in mature leaves, as well as deformed leaf blades. Dropping of buds, flowers, and developing fruits are also symptoms of deficiency. With B deficiency, cells may continue to divide, but the structural components are not differentiated (Gupta et al., 2008). B is not mobile in plants, and a continuous supply is necessary at all growth points (Chatterjee; Bandyopadhyay, 2017).

Figure 3. Symptoms of B deficiency in maize plants (*Zea mays*).

Source: IPNI (2019).

COPPER

Cu is present in plants in a complexed form. Like other potentially toxic heavy metals, excess Cu binds to phytochelatins and sulfur-containing peptides (Khaliq et al., 2019). Cu in solution is present as cuprous (Cu^{+}) and cupric (Cu^{2+}). Cuprous Cu is easily oxidized to cupric Cu and, therefore, is only found in complexed forms (Abreu et al., 2007). Cu is an activator of various enzymatic systems in plants and functions in electron transport and energy capture by proteins and oxidative enzymes. It may play a role in the production of vitamin A. Deficiency interferes with protein synthesis (Raij, 2011; Dechen et al., 2018).

The native Cu supply has rarely been recognized as needing supplementation; however, in some tree plantations grown on organic soils or sands, supplementation may be required (Gupta et al., 2008). Cu can be toxic at low levels, so the need must be clearly established before replenishment (Andrade et al., 2021).

Symptoms of Cu deficiency include: i) Leaves may be chlorotic or deep blue-green with curled margins (Figure 4); ii) The bark of trees is often rough and blistered, and gum may ooze from cracks in the bark; iii) Flowering and fruiting may not develop in annual plants and may die at the seedling stage; iv) Stunted growth.

Figure 4. Symptoms of Cu deficiency in maize plants (*Zea mays*).

Source: IPNI (2019).

IRON

Fe is necessary for chlorophyll formation in plant cells. It serves as an activator for biochemical processes such as respiration, photosynthesis, and symbiotic nitrogen fixation (Gupta et al., 2008). Fe deficiency can be induced by high levels of Mn or high lime content in soils (Raij, 2011). Fe is absorbed by plants as ferrous ions (Fe^{2+}) or ferric ions (Fe^{3+}), with the latter in smaller quantities. The function of Fe in plants depends on the rapid transitions between its two oxidation states in solution (Abreu et al., 2007). Plants store Fe as ferritin, a protein that encapsulates ferric iron.

In aerobic soil conditions, Fe is largely insoluble as a constituent of oxides and hydroxides and tends to bind to organic chelates. Thus, the concentration of free Fe in soil solution is extremely low in most soils, and plants use mechanisms to mobilize Fe and make it available for root absorption (Resende, 2005; Abreu et al., 2007). Some of these mechanisms are not specific to Fe absorption. Roots expel protons and organic acids into the soil, lowering the pH of the rhizosphere, increasing Fe solubility and availability.

There are two specific mechanisms for the absorption of this nutrient (Khaliq et al., 2019). The first mechanism (characteristic of dicotyledons and non-grass monocotyledons) acidifies the rhizosphere through proton extrusion. Ferric iron is reduced to ferrous iron by reductase enzyme at the plasma membrane. The reduced iron is transported across the membrane by a specific ion transport system. The second mechanism (characteristic of maize, barley, and oats) involves the extrusion of siderophores by roots. In this case, reduction to ferrous iron does not occur (Dechen et al., 2018; Andrade et al., 2021).

Symptoms of Fe deficiency include: i) Interveinal chlorosis of young leaves (the veins remain green except in severe cases) (Figure 5); ii) Branch necrosis; iii) In severe cases, death of branches or entire plants.

Figure 5. Symptoms of Fe deficiency in maize plants (*Zea mays*).

Source: IPNI (2019).

MANGANESE

Mn acts as an enzyme activator in growth processes and aids Fe in chlorophyll formation. It is part of the system where water is split, and O_2 is released. Another protein of which Mn is an integral constituent is superoxide dismutase, common in aerobic organisms (Dechen et al., 2018). The function of this enzyme is to provide protection against free oxygen radicals formed, converting this highly toxic free radical into hydrogen peroxide (H_2O_2), which is then decomposed into water (Resende, 2005).

High Mn concentration can induce Fe deficiency. Mn is primarily absorbed as Mn^{2+}, the reduced form (Abreu et al., 2007). Tree crops can exhibit deficiencies in this nutrient; however, the requirements for this element are not commonly recognized (Raij, 2011). Some authors suggest that Mn additions can increase grain production (Khaliq et al., 2019; Andrade et al., 2021).

Symptoms of Mn deficiency include: i) Interveinal chlorosis of young leaves (gradation from pale green color with darker coloration near the veins) (Figure 6); ii) Development of gray spots (oats), interveinal white streaks (wheat), or interveinal brown spots and streaks (barley).

Figure 6. Symptoms of Mn deficiency in maize plants (*Zea mays*).

Source: IPNI (2019).

ZINC

Zn acts as a component of enzymes or as a functional, structural, or regulatory cofactor for a large number of enzymes. More than 80 Zn-containing proteins have been reported (Andrade et al., 2021). The accumulation of amino acids and amides in plants demonstrates the importance of Zn for protein synthesis. Zn is a component of RNA polymerase and constitutes ribosomes, being essential for their structural integrity. The decrease in protein content in Zn-deficient plants also results in increased RNA degradation in affected cells (Gupta et al., 2008). Unlike other metal ions such as Cu, Fe, and Mn, Zn is a divalent cation (Zn^{2+}) that does not undergo valence changes and, therefore, does not have redox activity in plants. High concentrations of divalent cations such as Ca^{2+} can inhibit Zn absorption (Abreu et al., 2007; Dechen et al., 2018).

Several experimental results indicate that P-Zn interactions exist in plants, including the inhibition of Zn translocation from roots to shoots and physiological inactivation of Zn within the shoots (Khaliq et al., 2019). P-Zn interactions in the soil occur through root infection with vesicular-arbuscular mycorrhiza, increasing the uptake rate of this nutrient. This mycorrhizal infection is decreased by an increase in P supply. Although the connection between Zn deficiency and P toxicity is not well understood, there is substantial evidence that Zn affects P metabolism in roots and increases the permeability of root cell plasma membranes to P and Cl (Raij, 2011).

Zn deficiency is widespread in plants grown in highly weathered acidic soils and is often associated with Fe deficiency (Resende, 2005). Low Zn availability in high-pH calcareous soils results primarily from Zn adsorption to clay or $CaCO_3$ (Abreu et al., 2007). Additionally, Zn uptake and translocation to the shoot are strongly inhibited by high bicarbonate concentrations.

Symptoms of Zn deficiency in plants include: i) Reduced stem length and shortened internodes (Figure 7); ii) Reduced fruit bud formation; iii) Mottled leaves with interveinal chlorosis; iv) Branch necrosis after the first year.

Figure 7. Symptoms of Zn deficiency in maize plants (*Zea mays*).

Source: IPNI (2019).

MOLYBDENUM

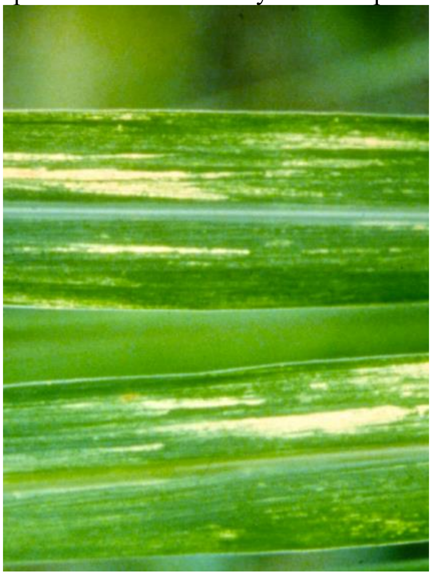
Although Mo is a metal, it occurs in aqueous solution primarily as the molybdate anion, MoO_4^{2-} (Abreu et al., 2007). Molybdate is relatively mobile in plants, and higher concentrations can be found in the roots than in the leaves when supplies are limited. The requirement for Mo is the lowest among minerals, except, in certain species, for nickel (Dechen et al., 2018). The functions of Mo as a nutrient for plants are related to the valence changes it undergoes as a metallic component of enzymes.

Research shows that only a few enzymes contain Mo in plants. Still, in higher plants, two Mo-containing enzymes, nitrogenase and nitrate reductase, are of vital importance in agricultural production (Gupta et al., 2008). All biological systems fixing N_2 require nitrogenase. Each nitrogenase molecule contains two Mo atoms associated with Fe. For this reason, the growth of plants that depend on N_2 fixation is stimulated by the application of Mo in deficient soils (Chatterjee and Bandyopadhyay, 2017).

Liming can increase the availability of Mo to the point of luxury consumption, which can become dangerous for ruminants, which are sensitive to excessive concentrations of Mo (Abreu et al., 2007). Plants generally have a wide range of acceptable Mo concentrations. The high concentration of Mo in seeds, although not toxic, ensures adequate seedling growth and a higher final grain yield. There is an inverse relationship between the Mo content of the seed and the yield response to added Mo fertilizer (Raij, 2011; Chatterjee and Bandyopadhyay, 2017).

Symptoms of Mo deficiency include: i) Interveinal chlorosis (Figure 8); ii) Short stature and lack of plant vigor; iii) Marginal scorching and cupping or curling of leaves.

Figure 8. Symptoms of Mo deficiency in maize plants (*Zea mays*).



Source: IPNI (2019).

AVAILABILITY OF MICRONUTRIENTS IN SOIL

Studies on the determination of total micronutrients in soils are limited. In most soils, the total micronutrient content is not related to what is potentially available to the plant (Raij, 2011). However, the total content indicates the relative abundance of B and Mo and can be useful in determining their potential for plant absorption (Resende, 2005). A summary of total micronutrients in Brazilian soils, as reported by various authors, is presented in Table 4.

Studies conducted by Chatterjee et al. (1976) in the main soils of the northern plains of India showed that available Mn and Fe were not related to their total contents. Similar relationships were reported by Kanwar and Randhawa (1974) in most soils of India. As expected, the total Fe content in the soil was high, ranging from 5.6 to 45.6 mg g^{-1}, and the total Mn content in the soil ranged from 107 to 1600 mg kg^{-1}. Compared to Fe and Mn, total Cu contents in the soil were low, ranging from 8 to 50 mg kg^{-1}. The Zn content in soils of northern India ranged from 13 to 384 mg kg^{-1} but showed no relationship with the available fraction in the soil profiles examined. In Brazilian soils, Mn contents have ranged from 20 to 3000 mg kg^{-1}, and Fe from 10 to 100 mg g^{-1}. For Cu, the contents have ranged from 10 to 80 mg kg^{-1}, while Zn does not exceed 300 mg kg^{-1} (Abreu et al., 2007; Andrade et al., 2021).

Table 4. Ranges of availability considered adequate in the interpretation of soil analysis for micronutrients according to different authors.

Literature	**B**	**Cu**	**Fe**	**Mn**	**Zn**
	---------- **mg dm^{-3}** ----------				
Raij et al. (1996)	0.21 - 0.6	0.3 - 0.8	5.0 - 12.0	1.3 - 5.0	0.6 - 1.2
Alvarez V. et al. (1999)	0.36 - 0.6	0.8 - 1.2	19.0 - 30.0	6.0 - 8.0	1.0 - 1.5
Galrão (1999)	0.3 - 0.5	0.5 - 0.8	-	2.0 - 5.0	1.1 - 1.6
Sousa and Lobato (1998)	0.5	0.5	-	5.0	1.0
RS Fertility Commission (1994)	0.1 - 0.3	0.2 - 0.5	-	-	0.2 - 0.5
Value ranges	0.1 - 0.6	0.2 - 1.2	5.0 - 30.0	1.3 - 8.0	0.2 - 1.6

Source: Resende (2005).

The B content of soils ranged from 4 to 630 mg kg^{-1} in soils of India (Kanwar and Randhawa, 1976). The total B content in some Argisols of eastern Canada ranged from 70 to 116 mg kg^{-1} (Gupta et al., 2008). In Brazilian soils, the contents ranged between 7 and 80 mg kg^{-1} (Abreu et al., 2007; Andrade et al., 2021). A study conducted on 108 soil samples showed a positive correlation between total B and hot-water soluble B, suggesting that total B can be used to some extent as an index of availability.

Of all micronutrients, total Mo is found in the smallest quantities, ranging from 0.05 to 3.2 mg kg^{-1} in soils of India (Chatterjee et al., 1976). In humid regions, the total Mo content in soils is about 2 mg kg^{-1}, and in Brazil, it has not exceeded 5 mg kg^{-1} (Abreu et al., 2007; Andrade et al., 2021). Although no real data are available showing the relationship between total and available Mo in soil, the total Mo in soil is an important reserve. Gupta et al. (2008) showed that soils containing very low amounts of Mo were not able to meet the nutrient needs of crops, even when sufficiently limed. This was not the case in soils that contained higher total Mo.

FERTILIZATION RECOMMENDATIONS

There are positive, null, and negative effects of micronutrient application, with a high degree of local specificity in terms of soil and crops. This demonstrates that broad and standardized recommendations are not the ideal strategy when aiming for the rational supply of micronutrients (Resende, 2005).

In general, to achieve good results, the management of micronutrient fertilization needs to be more refined than that adopted for macronutrients, due to the greater complexity inherent in the behavior of the former in the soil and plant. Soil analysis is the reference for sizing the application of micronutrients in areas that have never been fertilized (Abreu et al., 2007). From then on, supplementary fertilization should be confirmed through foliar analysis (Sousa, 1998).

Soil analysis has the advantage of allowing the evaluation of soil fertility and the adoption of corrective measures before planting. However, it is not advisable to manage fertilization solely based on soil analysis, which sometimes leads to dubious interpretations and recommendations. As previously mentioned, soil analysis for micronutrients is subject to interferences, and its interpretation has not yet been satisfactorily perfected (Resende, 2005; Abreu et al., 2007). In the case of Zn, for example, the critical level for maize is 1 mg dm^{-3} when the pH is around 6.0 and increases with rising pH (Galrão, 2002). The critical level of Cu is also usually higher in soils with high organic matter content. Therefore, leaf analysis of the crop is highly recommended for a more accurate diagnosis of the nutritional status of the production, which ultimately reflects the efficiency in fertilization management.

Due to the lack of detailed information for local conditions, the so-called "safety fertilization" is still widely used. For the Cerrado region, for example, safety fertilization consists of broadcasting and incorporating doses of 4.0-6.0 kg of Zn; 3.0-6.0 kg of Mn; 0.5-2.0 kg of B; 1.0-4.0 kg of Cu; and 0.2-0.4 kg of Mo per hectare every four or five years. The residual effect of this fertilization is sufficient for four or more crops, especially for Cu and Zn (Sousa, 1998; Galrão, 2002).

Although foliar fertilization is a routine practice for perennial crops when combined with the application of pesticides, for annual crops, the best method of micronutrient application is via soil. In this case, foliar fertilization is recommended when no soil application was made or if it was insufficient (Galrão, 1998). Thus, foliar fertilization should be supplementary to soil application, with its residual effect being small or nil. According to Lopes (1999), foliar sprays of Zn in maize, Mn in soybeans, and Mo in beans can yield good results compared to no application of these micronutrients. Foliar fertilization done with phytosanitary treatments is more cost-effective

(Volkweiss, 1991). Micronutrients can also be supplied via seed (mainly Co and Mo) or by soaking seedling roots in solutions containing the desired nutrients (Resende, 2005). There are a variety of mineral fertilizers available on the market that can be used as sources of micronutrients (Table 5).

Table 5. Information on different sources of micronutrients (B, Cu, Fe, Mn, Zn and Mo).

Source	Formula	Content (%)
B		
Borax	$Na_2B_4O_7 \cdot 10H_2O$	11
Boric Acid	$B(OH)_3$	17
Sodium Pentaborate	$Na_2B_{10}O_{16} \cdot 10H_2O$	18
Ulexite	$Na_2CaB_5O_9 \cdot 8H_2O$	8 - 15
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	10
Cu		
Copper Sulfate	$CuSO_4 \bullet 5H_2O$	25
Copper Chelate, EDTA	Na_2Cu EDTA	13
Copper Sulfate Monohydrate	$CuSO_4 \cdot H_2O$	35
Ammonium Copper Phosphate	$CuNH_4PO_4 \cdot H_2O$	32
Copper Oxide	CuO	75
Cuprous Oxide	Cu_2O	89
Fe		
FTE BR-9	-	6
FTE BR-10	-	4
FTE BR-12	-	3
BR-12 Extra	-	3
FTE BR-13	-	2
NaFe EDTA	-	5 - 14
Mn		
Manganese Sulfate	$MnSO_4 \cdot 3H_2O$	26 - 28
Manganese Chloride	$MnCl_2 \cdot 4H_2O$	25
Manganese Carbonate	$MnCO_3$	40
Manganese Dioxide	MnO_2	63
Manganese Oxide	MnO	41 - 68
Zn		
Zinc Sulfate (hydrated)	-	23 - 35
Zinc Sulfate (basic)	-	55
Zinc Oxide	-	50 - 80
Zinc Oxysulfate	-	Variable
Zinc Chloride	-	24
Zinc Nitrate	-	18

Mo		
Sodium Molybdate	$Na_2MoO_4 \cdot 2H_2O$	39
Ammonium Molybdate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	54
Molybdenum Trioxide	MoO_3	66

Source: IPNI (2019).

The variation in molecular formulas, the various contents, and the high quantity of micronutrients make it difficult for the farmer to decide, resulting in generalized fertilizations (Andrade et al., 2021). This is the main reason for the occurrence of deficiency symptoms in crops, although less frequently than with macronutrients.

It is not a simple task to compare results obtained from different experiments testing sources, doses, and methods of micronutrient application. Many published studies do not describe the area's history (initial availability level and previous applications of micronutrients, use of pesticides with micronutrients in their composition, etc.), the characteristics of the fertilizers, the application procedures, and other information that can greatly influence the occurrence and magnitude of responses (Raij, 2011). Thus, there are controversial results, making it difficult to draw consistent conclusions about the efficiency of micronutrient fertilization.

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