

MICRO-ELEMENTS

in Agriculture

EYAL RONEN outlines the importance of micro-elements, their availability problems and possible solutions through chelates.

The increase in cultivation intensity with the increasing demand for higher yields with better quality has resulted in increasing demand for micro-elements. Plant productivity has increased along the years due to genetic development and selection of high yielding cultivars. These cultivars with intensive cultivation methods were found to remove higher quantities of micro-elements from the soil, leading to deficiencies occurring in many soils. In this article I will review micro-elements, their importance, the problems affecting their supply, and ways to overcome these availability problems.

Plants require water, air, light, suitable temperature, and 16 nutrients to grow. Plants absorb carbon, hydrogen and oxygen from air and water. The other 14 nutrients come from the growing medium/soil.

Soil nutrients are divided into two groups according to their demanded quantity by the plants. The macronutrients are those that are demanded in relatively high levels. In the group of macro-elements we can distinguish between two sub groups, major ones and secondary ones. The nutrients nitrogen (N), phosphorus (P) and potassium (K) are referred as the major macro-elements, and calcium (Ca), magnesium (Mg), and sulfur (S) are the secondary ones.

The micronutrients, which are needed only in trace amounts, are iron (Fe), manganese (Mn), boron (B), zinc (Zn), copper (Cu), molybdenum (Mo), chloride (Cl), sodium (Na), nickel (Ni), silicon (Si), cobalt (Co) and selenium (Se). Within this group of nutrients two definitions exist. The 'essential mineral elements' (or mineral nutrients); this term was proposed by Arnon and Stout (1939). They concluded three criteria must be met for an element to be considered essential. These criteria are:

1. A plant must be unable to complete its life cycle in the absence of the mineral element.
2. The function of the element must not be replaceable by another mineral element.
3. The element must be directly involved in plant metabolism.

These criteria are important guidelines for plant nutrition but exclude beneficial mineral elements.

The 'beneficial elements' are those that can compensate for toxic effects of other elements, or may replace mineral nutrients in some other less specific functions such as the maintenance of osmotic pressure. The omission of beneficial nutrients in commercial production could mean that plants are not being grown to their optimum genetic potential but are merely produced at a subsistence level.

Different divisions exist and in certain references some nutrients might be considered essential, although they only serve as such for certain plant species.

As the science of chemistry progresses and the analytical techniques improve, *Table 1* might extend to include mineral elements that are essential in very low concentrations (ppb).

Table 1. Essential of mineral elements for higher and lower plants.

| Classification | Element | Higher plants | Lower plants |
|-----------------------------|-------------------------------|---------------|----------------------------|
| Macronutrients - major | N, P, K | + | + |
| Macronutrients - secondary | Ca, Mg, S | + | + (exception Ca for fungi) |
| Micronutrients - essential | Fe, Mn, Zn, Cu, B, Mo, Cl, Ni | + | + (exception B for fungi) |
| Micronutrients - beneficial | Na, Si, Co, Se | +/- | +/- |

Table 2. Discovery of micronutrients for higher plants.

| Element | Year | Discovered by |
|------------|------|----------------------------|
| Iron | 1860 | J. Sachs |
| Manganese | 1922 | J. S. McHague |
| Boron | 1923 | K. Warington |
| Zinc | 1926 | A. L. Sommer & C.B. Lipman |
| Copper | 1931 | C.B. Lipman & G. Mackinney |
| Molybdenum | 1938 | D.I. Arnon & P.R. Stout |
| Chlorine | 1954 | T.C. Broyer <i>et al.</i> |
| Nickel | 1987 | P.H. Brown <i>et al.</i> |

The importance of micro-elements

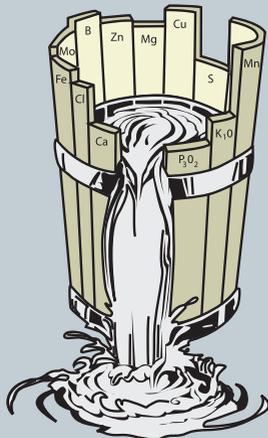
The importance of micro-elements in plant nutrition is high and they should not be neglected although they are needed in minor quantities. This understanding was developed in 1840 by the German chemist, Freiherr Justus von Liebig, who made a major contribution to the science of agriculture and biological chemistry. He determined the 'Law of the Minimum', which describes the effect of individual nutrients on crops.

Liebig's Law of the Minimum, often simply called Liebig's Law, is a principle developed in agriculture that states that if one of the nutritive elements is deficient or lacking, plant growth will be restricted and not in its full potential even when all the other elements are abundant. Any deficiency of a nutrient, no matter how small the amount needed, it will hold back plant development. If the deficient element is supplied, growth will be increased up to the point where the supply of that element is no longer the limiting factor. Increasing the supply beyond this point will not be helpful, as some other elements would then be in minimum supply and become the limiting factor. Liebig used the image of a barrel to explain his law. The capacity of a barrel with staves of unequal length is limited by the shortest stave, so a plant's growth is limited by the nutrient in shortest supply.

Table 3. Micronutrients role in plant nutrition.

| Element | Taken form | Functional contributions | Average concentration in tissue (ppm) |
|------------|---|--|---------------------------------------|
| Iron | Fe ²⁺ /Fe ³⁺ | <ul style="list-style-type: none"> Promotes formation of chlorophyll Enzyme mechanism which operates the respiratory system of cells Reactions involving cell division and growth | 100 |
| Manganese | Mn ²⁺ | <ul style="list-style-type: none"> Predominant in metabolism of organic acids Activates the reduction of nitrite and hydroxylamine to ammonia Role in important enzymes involved in respiration and enzyme synthesis Activator of enzyme reactions such as oxidation/reduction, hydrolysis Direct influence on sunlight conversion in the chloroplast | 50 |
| Zinc | Zn ²⁺ | <ul style="list-style-type: none"> Formation of growth hormones (auxin) Seed and grain formation Promotes maturity Plant height Protein synthesis Transformation and consumption of carbohydrates | 20 |
| Boron | B(OH) ₃ or as H ₂ BO ₃ ⁻ (Depends on pH) | <ul style="list-style-type: none"> Protein synthesis Formation of plant hormones Promotes maturity Increase in flowering set Affects nitrogen and carbohydrate metabolism Water relation in plant | 20 |
| Copper | Cu ²⁺ | <ul style="list-style-type: none"> Enzyme activator Major function in photosynthesis Major function in reproductive stage Function in respiratory enzymes Indirect role in chlorophyll production Increases sugar content Intensifies colour Improves flavour in fruits and vegetables | 6 |
| Molybdenum | MoO ₄ | <ul style="list-style-type: none"> Essential for nitrogen fixation Essential for nitrate reduction Essential for plant growth | 0.1 |
| Chlorine | Cl ⁻ | <ul style="list-style-type: none"> Activator for the enzyme that releases oxygen from water during photosynthesis Regulating turgor pressure and growth of cells and is important in drought resistance (stomata gate cells aperture) Counter ion to the positively charged 'cations' in the cell. | 100 |

* Nickel will not be reviewed since it has minor importance in agricultural practices.



Plant nutrient uptake

Plants absorb nutrients only from the liquid solution phase of the soil. The problem with micro-elements is their limited solubility and therefore their limited presence in the solution.

The uptake from the soil solution is done in three major ways: root interception, mass flow and diffusion.

Root interception - as roots proliferate through the soil they also move into spaces previously occupied by soil containing available nutrients, for example, absorbed by clay particles. Root surfaces may thus intercept nutrients during this displacement process (Barber, 1984).

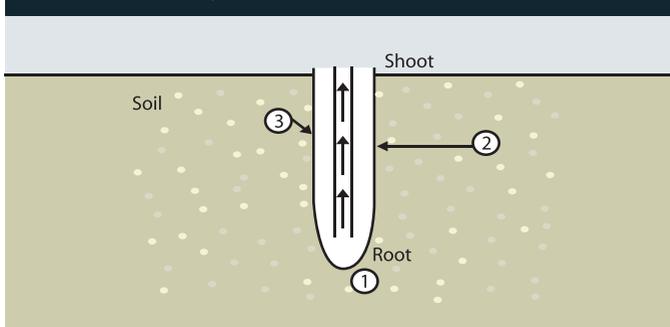
Mass flow - is movement of water and dissolved nutrients, which is driven by the transpiration gradient.

Diffusion - is movement of nutrients according to the gradient from high concentration to low concentration.

In diffusion, the soil moisture content has a major effect as well as the presence of other ions - both factors may increase the diffusion coefficient (De) of the micro-elements and may increase their uptake.

Diffusion is considered the major uptake route for micro-elements, especially when their concentration is limited in the soil solution.

Figure 1. Schematic presentation of mineral element movement to root surface. (1) Root interception (2) Mass flow (3) Diffusion (o) available nutrients.



The contribution made by mass flow to total supply differs between mineral nutrients and between plant species due to differences in transpiration rate or uptake rate of a particular mineral nutrient, or both these factors.

In soil, a gradient is created when the uptake rate of ions exceed the supply by mass flow. The depletion profile develops with time and depends mainly on the balance between uptake by roots, replenishment from soil and mobility of ions by diffusion. Ion mobility is defined by diffusion coefficient, which is fairly uniform for different ions on homogenous medium such as water, and differ in non-homogeneous soils such as aerated soil.

Lack of availability

In soil, micro-elements are not always present in the solution and their availability is restricted due to several factors, which mainly limit their solubility. The main factors determining the level of soluble micronutrients in soil solution are:

- Oxidation-reduction reactions and the pH.
- The complex bond affinity described as 'stability constant = K_{ma} ,' often referred as Log K (MA) , which is a more convenient way of describing the same thing.

Table 4. Solubility constants of different metals in the soil.

| Metal | Log K (MA) |
|------------------|------------|
| Fe ²⁺ | -13.7 |
| Fe ³⁺ | -37.8 |
| Mn ²⁺ | -13.4 |
| Cu ²⁺ | -19.0 |
| Zn ²⁺ | -16.6 |
| Ca ²⁺ | -12.2 |

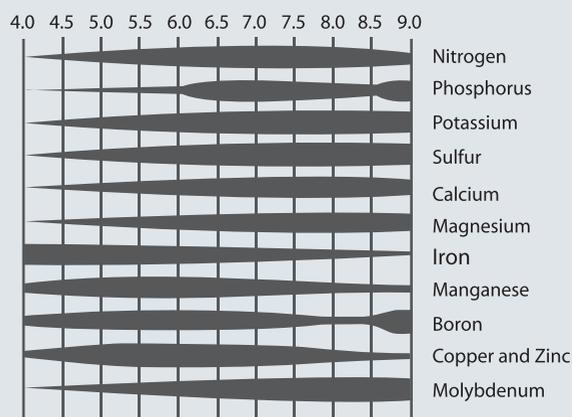
The factors restricting the availability will be reviewed in the following paragraph.

Soil solution pH

Among the different factors affecting the availability of micro-elements, soil solution pH is the major one. Soil pH is determined by a measurement of the hydrogen ion concentration reflected as a negative logarithm's (-log). When clay colloids are captured by basic ions such as Ca²⁺, Mg²⁺ and K⁺, the greater the alkalinity of the soil. Soils formed under low rainfall conditions tend to be basic with soil pH readings around and over 7.0.

The pH has many effects, mainly on nutrients solubility and their ionic form. At different levels of pH some nutrients may be deficient while others might reach high concentrations to cause toxicity. At high basic pH, most micro-elements will suffer from availability problems (Figure 2). Most plants would prefer to grow within the pH range of 6 to 6.5 that will assure high availability of most demanded nutrients.

Figure 2. Plant nutrient availability in regards to changes in the soil solution pH.



Plant nutrient interactions

Some of the interactions interfere and damage the availability of micro-elements. Some of the interactions are soil interactions, and some are happening in plant tissue due to excessive concentrations in the tissue.

Interactions with macro-elements

Zinc-Phosphorus - high levels of available P induce zinc deficiency (Thorne, 1957; Stuckenholtz *et al.*, 1966). Several explanations exist: soil interaction with the creation of Zn₃(PO₄)₂; P-Zn antagonism in the roots affecting the zinc translocation; 'dilution' effect in the plant tissue due to high growth rate that exceeds the uptake rate; physiological effect due to interference of P in the plant Zn metabolic function.

Zinc-Nitrogen - high levels of nitrogen induce zinc deficiency (Camp & Fudge, 1945; Ozanne 1955). Explanations exist: increased growth rate with marginal supply of Zn; change in soil solution pH due to different nitrogen source; Zn retention in the roots as N-Zn protein complex.

Iron-Phosphorus - excessive supply of P and an increase of the P/Fe ratio (Watanabe *et al.*, 1965) inactivates iron (Biddulph & Woodbridge *et al.*, 1952). Explanations are not fully clear and relate to possible competition of P for Fe with the roots; plant capacity to absorb and hold Fe in a soluble, mobile form decrease as the P tissue concentration increase; Fe-phosphate precipitate on or in the roots.

Copper-Phosphorus - Heavy or prolonged applications of phosphorus result in phosphorus and copper interactions (Bingham, 1963; Spencer, 1966). A significant decrease in Cu leaf concentration was observed at increasing P applications (Bingham & Garber, 1960).

Molybdenum-sulfur - plants Mo uptake is reduced by S (Stout *et al.* 1951). It is explained as direct competition between two equivalent anions of the same size; another explanation suggests inhibition of Mo utilization within the plant occurring at low levels of Mo (Reisenauer, 1963).

Zinc-Magnesium - An increase of soil pH, followed the use of $MgCO_3$, causes interaction between Zn and Mg within the plant and in the soil (Seatz, 1960).

Boron-Calcium - Boron toxicity can be alleviated by increasing concentrations of Ca. Plants grow normally only when a certain balance exists in the uptake of Ca and B, expressed in equivalent weights of the two elements (Jones and Scarseth 1944).

Interactions with micro-elements

Zinc-Iron - the metabolic functioning of Fe in plants is connected in a way with the supply of Zn (Rosell and Ulrich, 1964). Mechanisms remain unclear, yet one of the suggestions insinuates that the addition of Zn increases growth and leads to a marked reduction in Fe concentration in the plants.

Iron - Manganese - Fe and Mn are interrelated in their metabolic functions, with the effectiveness of one determined by the proportionate presence of the other. Fe chlorotic plants were observed in different crops when soils contained large amounts of available Mn. Epstein and Stout (1951) suggested that Mn interfered with the transport of Fe from the roots to the shoots.

Iron - Molybdenum - Two effects of Mo and Fe are suggested - one beneficial and one detrimental. The mechanisms are not clear. Fe-Mo interactions were observed and it was suggested that Mo accentuated Fe deficiency due to the formation of Fe-Molybdate precipitate in the roots (Gerloff, Stout and Jones, 1959). It was suggested that Mo could interfere with the reduction of Fe in solid phase compounds. In another situation, at marginally adequate level, Mo enhanced Fe uptake, and at higher levels depressed Fe uptake (Berry and Reisenauer, 1967).

Copper-Iron - In several crops and mainly citrus, Fe chlorosis was produced due to high concentration of Cu in the nutrient solution (Chapman, Liebig and Vanselow, 1940).

Copper-Molybdenum - antagonism of Cu and Mo in plants was suggested (Giordano, Koontz and Rubins, 1966). Some evidence was found to show that Cu interfered with the role of Mo in the enzymatic reduction of NO_3^- . Deficiency of one was developed

because of the high application rate of the other, and increasing the rate of the antagonist reduced toxicity.

Copper-Zinc - zinc was found to induce copper deficiency in several crops. The mechanism is not clear, yet the relation was found to a greater extent in coarse-textured soils (Gilbery, Greathead and Cartell, 1970).

Low soil organic content effects

Plants grown on soils with low organic content have a higher tendency to develop different micro-element deficiencies. Organic matter in the soil has the ability to form stable complexes with metal ions; accordingly, when organic matter in the soil is low, plants may suffer from it by showing different deficiencies. Two groups can be defined in the organic complexes formed in the soil:

1. Complexes formed due to micro-organism activity - organic acids, polyphenols, amino acids, peptides, proteins and polysaccharides.
2. Complexes formed in secondary synthesis reactions - humic acid and fulvic acids.

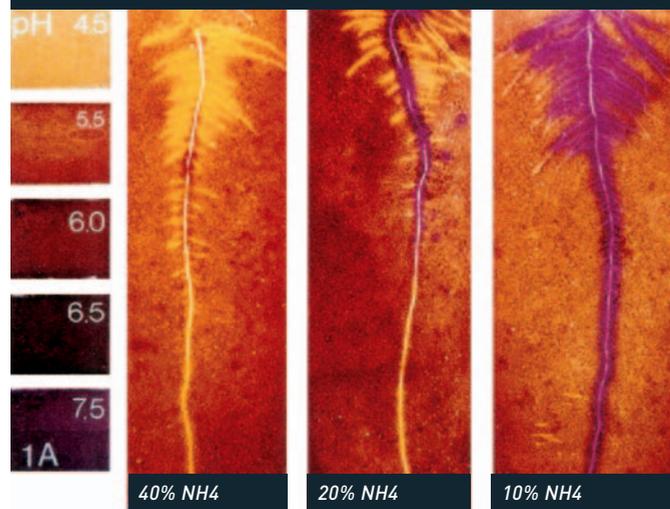
Plant strategies to overcome availability problems

In nature, plants that suffer from availability problems to the extent of deficiency have developed different mechanisms to overcome the situation and utilize micro-elements and phosphorus as macro element from the soil.

Controlling the rhizosphere pH - several factors may effect the change in the rhizosphere pH as follows:

- Change in the root pH can be induced by an imbalance in the cation/anion uptake ratio and corresponding with this, differences in net release of H^+ and HCO_3^- (or OH^-). The form of nitrogen has the most prominent effect on the cation/anion uptake ratio and rhizosphere pH in both annual and perennial species (Romheld and Marschner, 1983; Rollwagen and Zasoski, 1988). Ammonium diet will result in acidification of the rhizosphere that will increase the solubility and uptake of micro-elements, while nitrate diet will result in alkalinity of the rhizosphere.

Figure 3. Root rhizosphere changes influenced by different nitrogen forms (Romheld & Marschner, 1983).



- Excretion of organic acids that may be produced by microbial activity stimulated by the release of organic carbon from roots, and CO₂ production by the roots and rhizosphere micro-organisms. The CO₂, which is dissolved in the soil solution, is the one that affects rhizosphere pH greatly.
- Soil pH buffering capacity will determine the impact of the above changes. The soil buffer capacity is mainly dependent on the initial soil pH and the organic matter content. The lowest buffer is at pH 6 and increases in both directions up and down (Schaller and Fischer, 1985).
- Nutritional status of the plant also has its effect on rhizosphere pH. In specific element deficiency, like in the cases of iron or zinc deficiency, localized pH reduction will be confined to the apical root zones.

Root exudates - the exudates are defined by their molecular weight - there are low molecular ones (LMW) and high molecular (HMW).

- HMW - include mucilage and ectoenzymes.
- LMW - include organic acids, sugars, phenolics and amino acids (phytosiderophores).

In the group of HMW, mucilage consists of polygalacturonic acid, which can mobilize micro-elements from the soil clay surfaces (Nagarajah *et al.*, 1970). Mucilage may be of importance to micronutrient uptake from dry soils (Nambiar, 1976).

In the group of LMW, organic acids, phenolics and amino acids play a dominant role in acquisition of micro-elements from the soil. The importance of organic acids is of lowering the pH in the rhizosphere, chelation of the micro-elements, and of lowering the Ca²⁺ concentration by chelation and formation of soluble salt such as calcium-citrate. Major acids involved are:

- Malic acid - acquisition of Mn²⁺ (Jauregui & Reisenauer, 1982).
- Citrate, phenolics, amino acids (piscidic acid) - acquisition of Fe³⁺ and mobilization of manganese and zinc.

The efficiency of root exudates is effected by the distribution of microbial populations along the root axis.

Proteoid root-forming plant species - mineral supply can strongly affect the growth, morphology and distribution of root systems in the soil profile. In certain plant species formation of root clusters is the plant response to micro-elements and phosphorus deficiency. The best root cluster formation strategy exists in the Proteaceae (Lamont, 1982 Vorster and Jooste, 1986), although it exists also in species of Myricaceae, leguminous trees and annual legumes. Proteoid roots are dense clusters of determinate lateral roots. Their strategy is the increase in the root surface and increased excretion of organic acids and/or phenolics.

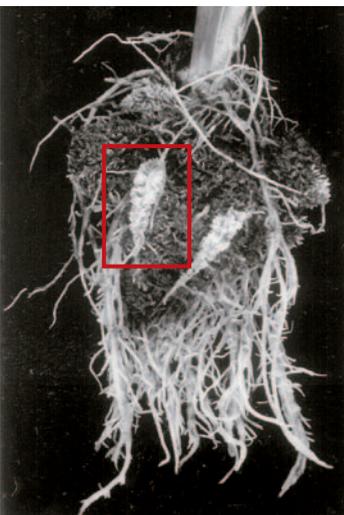
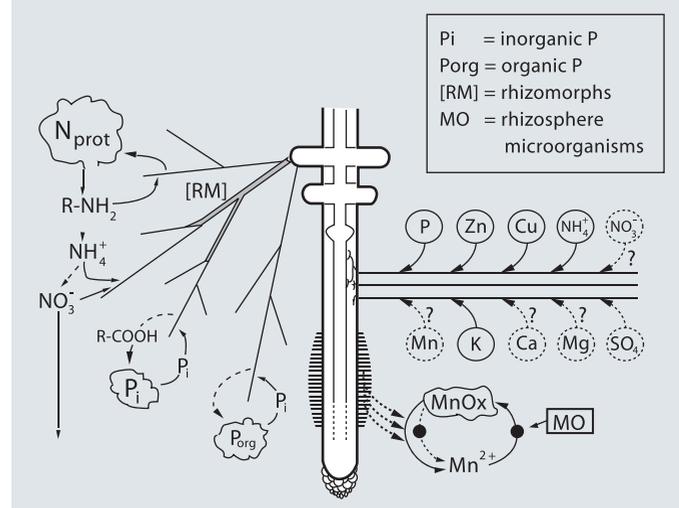


Figure 4. Proteoid root clusters, squared in red (Lamont, 2003)

Root mycorrhiza - Many plant species, including most agricultural crops, have endotrophic mycorrhiza of which 'vesicular arbuscular mycorrhiza' (VAM) is the predominant type of fungal infection. The fungus has mycelium that actually penetrates cells in the root cortex and these are connected to an external mycelium in the root rhizosphere and soil. The micro-elements uptake is increased due to fine hyphae that can enter pores within the soil that are too small for root hairs to enter. The fungi increase the uptake of Co, Mo, Cu and Fe. The benefits of mycorrhizal associations in the uptake of micronutrients have been studied less than those for P, but it was found that the uptake of Zn and Cu are usually larger in plants with VAM than in those without (Kothari *et al.*, 1990).

Figure 5. Nutrient uptake dynamics of mycorrhizal roots (Marschner & Dell, 1994).



The fertilizer industry's solution

Chelation solution

As shown before, plants have developed different strategies to overcome availability limitations of micro-elements, yet it needs to be clear that these mechanisms have high energy cost for the plants. In intensive cultivation practices, wasting energy is a luxury plant cannot afford. The whole of plant resources should be directed for higher productivity and quality yields.

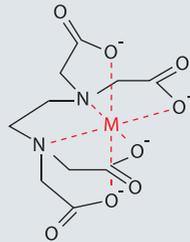
The fertilizer industry has found a solution to micro-elements availability. For the past 20-25 years it has been recognized that many of the micronutrient requirements of plants could be supplied by special complexes containing metals, referred to as 'chelates'.

Chelation originated from the Greek word, *chelè*, (meaning lobster claw). Chelation is the process of reversible binding (complexation) of a binding molecule, referred also as ligand, chelant, chelator or chelating agent to a metal ion, forming a metal complex, known as the chelate (Fig. 6). The term is generally reserved for complexes in which the metal ion is bound to two or more atoms of the chelating agent, although the bonds may be any combination of coordination or ionic bonds. The chemical connection is done by a ligand. Ligand is an atom, ion, or molecule that donates one or more of its electrons through a coordinate covalent bond to, or shares its electrons through a covalent bond with, one or more central atoms or ions.

Figure 6. Metal EDTA chelation.

Basic description of metal-chelate stability equation:

M Metal
A Agent
K Stability constant
MA Chelate

$$M + A = MA ; K = \frac{MA}{M + A}$$


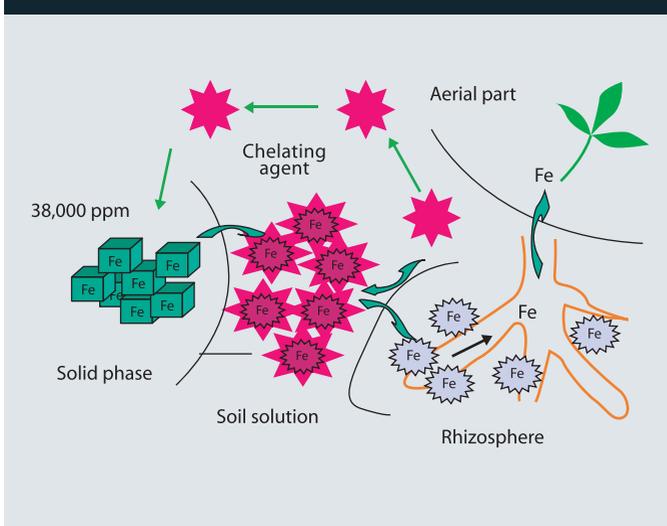
The use of inorganic salts (metal-sulfates) is not a preferred option in intensive agriculture, because they can easily form insolubles that precipitate with inorganic ions such as phosphate, sulfate, carbonate and hydroxide. Once the metal ion has precipitated, it is no longer available to the plant. This reaction can take place even at the stock solution tank, prior to fertigation, and cause filters to block. The chelate serves as protection to the metal ion, prevents its reaction with the environment, and keeps it highly soluble and in a form that plants can absorb, even at a pH that would naturally cause them to precipitate.

There are many forms of chelates, yet they differ from one another by their strength and their capacity to stabilize and hold the metal through different conditions (mainly pH).

Chelates, metal release mechanism

The synthetic chelates do not penetrate the root. The metal leaves the chelate on the root surface before the root takes it up. The citric acid inside the plant is the natural organic chelate in the transport of iron and other metals in the plant.

Figure 7. Release mechanism of metal (Fe) from the chelating agent; chelate "Iron shuttle effect".



Chelate stability

There are various factors that affect the stability of the metal chelate; some are related to the metal ions, some to the chelating agent, and some to the environment.

Stability is expressed by stability constants; its simple form is as follows:

The stability constant is reflecting the strength of the chelate; high value for K means more stability of the chelated metal to the non-chelated one. K is often expressed in logarithms (Log) due to the figures high order of magnitude.

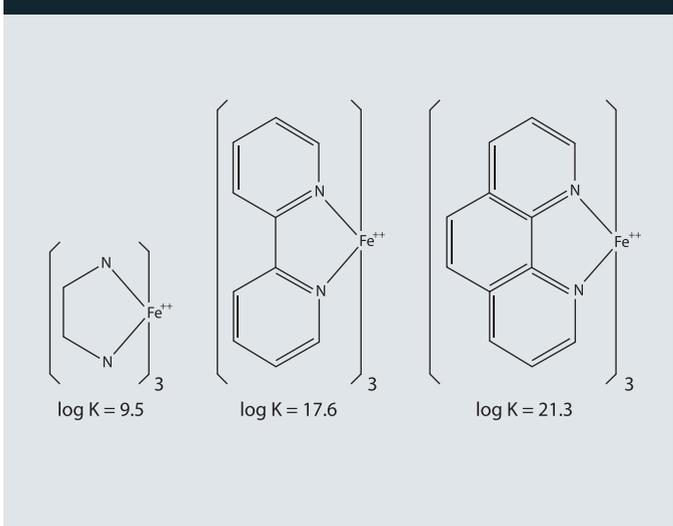
The metal ion effects

- Size of the metal ion - for metal ion of the same family and having the same charge, stability increases as the size of the metal ion decreases. Calcium forms more stable chelate than Strontium.
- Charge of the metal ion - the stability increases with increasing charge of the metal ion. Fe³⁺ is more stable than Fe²⁺ in most cases.
- Electro-negativity of the metal ion - electro-negativity is the atom ability to attract electrons to it in a covalent bond (cooperative bond). Stability increases as electro-negativity increases as follows: (eV units) Cu (1.9) > Fe (1.8) > Zn (1.6) > Mn (1.5) > Ca (1.0).

The chelating agent effects

- Number of rings - stability increases with more rings formed between the metal ion and the chelating agent.
- Donor atom - no consistency exists and the stability changes for the different ions between the different electron donors (ligand group). For example, zinc shows higher stability with this order S > N > O, while for Ca ions no significant difference exists between these three donors.
- Resonance stabilization - stabilization effect caused by certain organic compounds referred as aromatic compounds. In these aromatic rings, the electronic bonds enjoy de-localization, so the single and double bonds jump from one atom to another continuously and, therefore, there is no polarity and the stability of the compound increases. Chelating agents that have more of these aromatic rings enjoy higher stability.

Figure 8. Resonance effect of aromatic rings on the stability (Log K) of chelated Fe²⁺.



- Steric effect - relate to possible positive or negative interference in space between atoms of the ligands. If atoms are brought too close together, there is an associated cost in energy due to overlapping electron clouds (Pauli or Born repulsion), and this may affect the molecule's preferred shape (conformation) and reactivity. In conclusion, different configurations in the space have different stability levels.
- Entropy consideration - in nature, all things have a tendency to reach the most stable energetic state ('steady-state'). When free energy exists (enthalpy), materials are unstable; on the other hand, more stable materials have high entropy. Entropy is a thermodynamic state or property that measures the degree of disorder or randomness. More positive entropy makes the free energy more negative and K (stability constant) more positive, higher chelate stability. The formation of chelate produce large positive entropy. Entropy described by ΔS (cal./°c) is used to describe stability of EDTA (ethylenediaminetetraacetate) for different metals (25°C): +55 (Cu²⁺) = +55 (Zn²⁺) > +42 (Cu²⁺) > +41 (Mn²⁺) > +32 (Mg²⁺).

The environmental effects

Some of these factors have minor importance and are only reviewed here briefly, since they do not have any practical implementations.

- Temperature - Increase in the temperature generally results in a decrease of the stability constant.
- Dielectric point - Stability constant generally increase with the decrease in dielectric constant of the solvent.
- Ionic strength - stability constant decrease with an increase of the ionic strength.

- Competing complexes - presence of organic complexes might compete with the chelation by forming a higher stability complex with the metal (polycarboxylic acids). In a solution, the metal having the highest stability constant with the chelating agent will be the first to be chelated.
- pH effect - hydrogen ions can successfully compete with metal ions for the chelant where the metal complex stability is low. At low pH, more hydrogen ions are present in the solution and there are more possibilities of exchange of the metal. In EDTA, Fe and Cu have a high stability constant and they remain unaffected by the low pH. At high pH (8-9) exist other exchanges, mainly with calcium - at these pH, EDTA becomes very weak chelate and need to be replaced. Effective chelation within the pH of 8-12 is achieved by the use of aminopolycarboxylic types.

Chelation forms

There are many forms of chelates that exist in the agricultural market. Most of them have an organic basis, yet there are some inorganic ones like different polyphosphates. In this part of the article I will shortly review the differences between the major chelation groups.

One of the convenient ways to describe the stability of the different chelates is through stability diagrams. The diagrams describe the equilibria of the chelate with different metals in the presence of certain ions in the soil solution that threaten the stability of chelation.

In soil, four cations can form strong competition, and stable enough to exist in equilibrium with the free ligand and the free



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Table 5. Common chelation forms.

| Abbreviation | Name | Formula |
|--------------------------------|--|--|
| EDTA | Ethylenediaminetetraacetic acid | C ₁₀ H ₁₆ O ₈ N ₂ |
| DTPA | Diethylenetriaminepentaacetic acid | C ₁₄ H ₂₃ O ₁₀ N ₃ |
| CDTA | Cyclohexanediaminetetraacetic acid | C ₁₄ H ₂₂ O ₈ N ₂ |
| EDDHA | Ethylenediaminedi-Q-hydroxyphenylacetic acid | C ₁₈ H ₂₀ O ₆ N ₂ |
| HEDTA | Hydroxyethylenediaminetriacetic acid | C ₁₀ H ₁₈ O ₇ N ₂ |
| NTA | Nitrilotriacetic acid | C ₆ H ₉ O ₆ N |
| EGTA | Ethyleneglyco-bis(2-aminoethylether)tetraacetic acid | C ₁₄ H ₂₄ O ₁₀ N ₂ |
| CIT | Citric acid | C ₆ H ₈ O ₇ |
| OX | Oxalic acid | C ₂ H ₂ O ₄ |
| P ₂ O ₇ | Pyrophosphoric acid | H ₄ P ₂ O ₇ |
| P ₃ O ₁₀ | Triphosphoric acid | H ₅ P ₃ O ₁₀ |

cations of its kind: Ca²⁺, Mg²⁺, Al³⁺ and Fe³⁺. H⁺ is not neglected as it is represented by the change of pH. For the formation of the diagrams, cation concentration was determined according to the most common conditions in non-alkaline soils. Through this evaluation three groups can be identified:

EDTA, DTPA, CDTA, EDDHA

This group share high specificity for iron (Fe³⁺), but also for Ca²⁺ from a certain pH. In reference to iron chelation with increasing pH, the order of stability is decreasing as follows:

EDDHA > DTPA > CDTA > EDTA

It should be stated that EDDHA has high selectivity to Fe³⁺ over a wide pH range of 4 to 9; unfortunately, this effective chelate can be formed only with iron and not with other essential micro-elements.

HEDTA, NTA, EGTA, CIT and OX

This group share relatively lower specificity for iron (Fe³⁺) and general lower stability. These chelates show high affinity to Al³⁺ at low pH, and to Ca²⁺ as the pH rises. In reference to iron chelation with increasing pH, the order of stability is decreasing as follows:

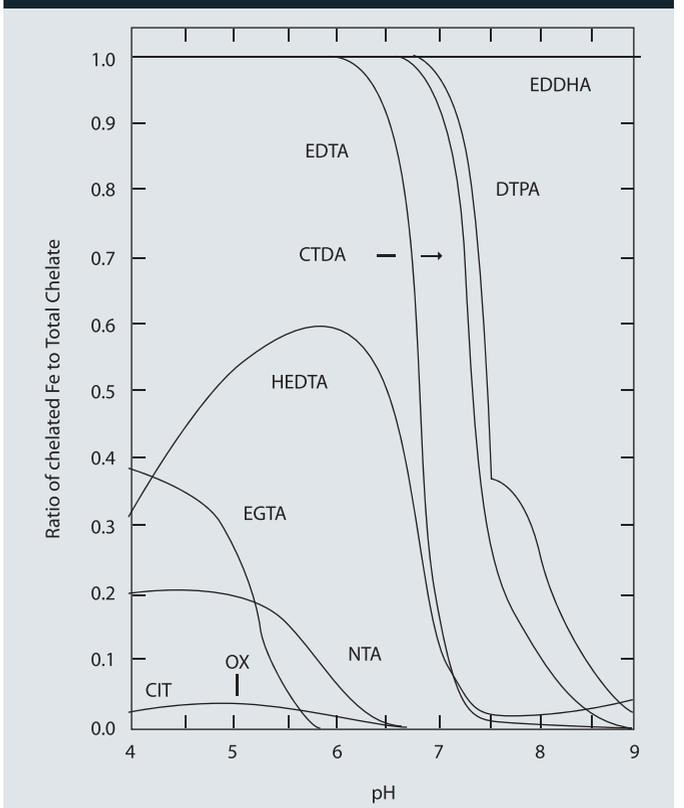
HEDTA > NTA > CIT > EGTA > OX

P₂O₇, P₃O₁₀

Reliable stability constants for these chelating agents with iron do not exist.

Iron is of great importance, as for most crops; among all micro-elements it is the most needed. A summary of the stability of the different chelates is expressed in *Figure 9*.

Figure 9. Comparison of Fe-chelate stabilities in soil solution.



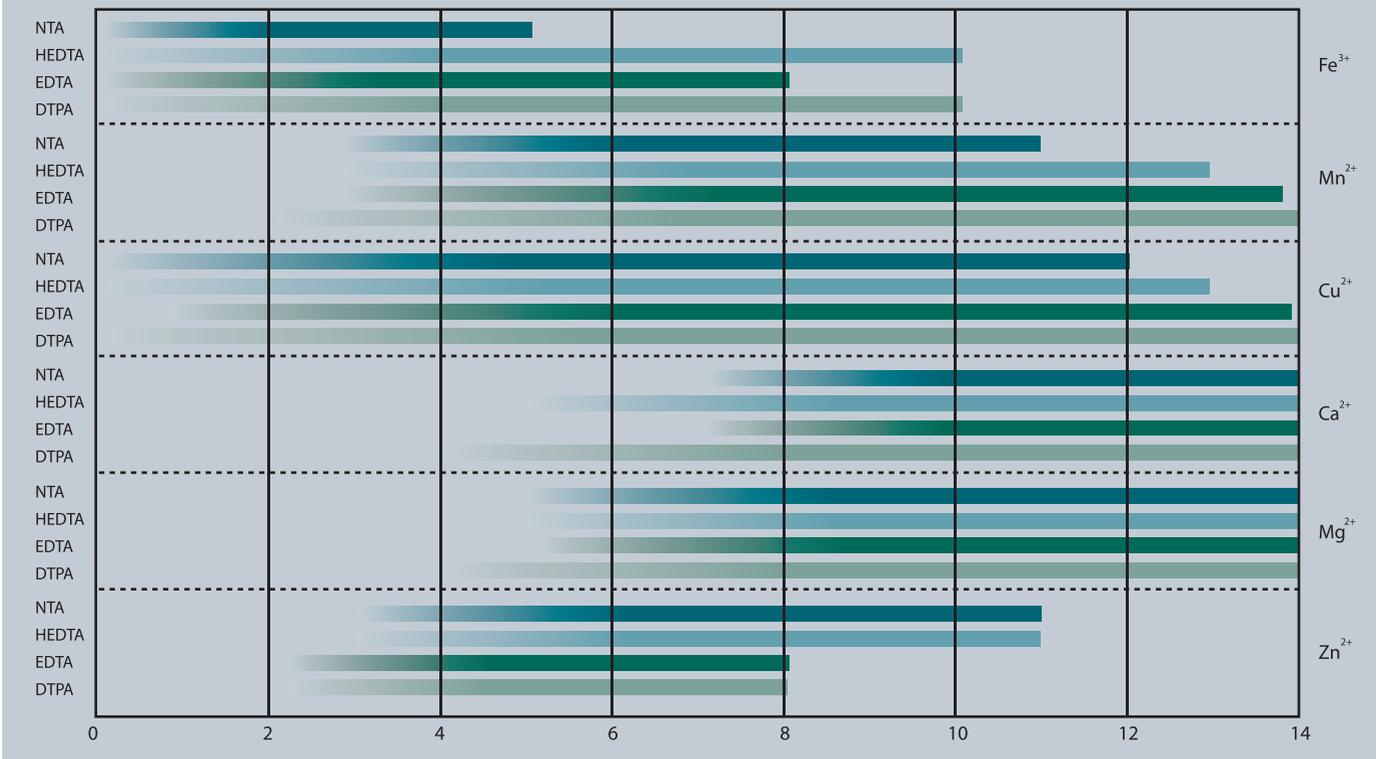
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Figure 10. Proximate summary of common chelate stability with different ions.



Another simple description that summarizes the different chelates stability with different ions appears in *Figure 10* and includes only the major ones used today in agriculture for the chelation of all ions.

Chelation compositions

Many compositions may exist in the fertilizer market, yet the most suitable one to satisfy most crop needs is the one that favours iron, followed by relatively half ratio of the manganese, relatively quarter ratio of the zinc, and one part of a tenth copper. Other compositions will be either answering crop specific needs or solving specific soil conditions, which induce specific micro-element deficiency.

Summary

The importance of micro-elements in overall plant nutrition cannot be neglected. Plant performance is crucially dependent on adequate supply of all elements including those that are demanded in relatively small quantities. Although in nature plants have succeeded in developing different techniques to assure sufficient supply of micro-elements, in intensive growing methods where plants are pushed to their productivity limits, relying on the plant to feed by itself is not a good option.

It was emphasized that supplying these elements through chelated forms is the right and only reliable way that will assure availability of these elements. Chelates may not be the perfect solution, yet as of today they are well understood and already proven to be more efficient than using metal sulfate forms.

About the author

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