

Chelating Agents

The three main classes of micronutrient sources are inorganic, synthetic chelates and organic complexes. A chelate describes a kind of organic chemical complex in which the metal part of the molecule is held so tightly that it cannot be 'stolen' by contact with other substances, which could convert it to an insoluble form. Chelating agents are organic molecules that can trap or encapsulate certain metal ions like Ca, Mg, Fe, Co, Cu, Zn and Mn and then release these metal ions slowly so that they become available for plants to take them up.

A chelate refers to a ring system that results when a metal ion combines with two or more electron donor groups of a single molecule. Actually unidentate water molecules, which are coordinated with a metal ion, are replaced by the most stable bi-, tri or poly dentate groups of the chelating agent. This results in the ring formation. Metals bound in chelate rings have essentially lost their cationic characteristics. In this form they are less prone to precipitation in some chemical reactions. This is the characteristic feature that makes these compounds useful in agriculture. The plant availability of certain micronutrient fertilizers reduces by transformation of the added micronutrient into forms that plants are unable to absorb. For example, if the inorganic iron salt (iron sulphate) is supplied to some soils, much of the iron is transformed into forms that are not readily assimilated. They are converted to 'plant unavailable' forms. This problem can be overcome by using chelates.

There are many naturally occurring chelating agents that are products of organic matter decomposition such as organic acids, amino acids, ligninosulfonates, ligninipolycarboxylates, sugar acids and derivatives, phenols, poly flavonoids, siderophores and phyto siderophores. Many chelating agents have been developed synthetically. Both classes of chelating/complexing agents increase micronutrient solubility.

One of the most important characteristics of chelating agents used is the relative stability of various metal chelates, especially if one is considering synthetically developed chelates. In other words, it is the degree of affinity of a given agent for a metal. From the stability constant data the ability of one metal to compete with another can be estimated. Stability of micronutrient chelate bonded generally determines 'plant availability' of the applied micronutrient. An effective chelate relationship is one in which the rate of substitution of the chelated micronutrients for cations already in the soil is low, thus maintaining the applied micronutrient in the chelated form for length of time sufficient to be absorbed by the plant roots. Some chelating agents used for the production of synthetic micronutrient chelates are

- Ethylene diamine-tetra-acetic acid (EDTA)
- N-(hydroxyethyl) ethylene-diamine-triacetic acid (HEEDTA): also known as EDTA-OH .
- Diethylene-triamine penta-acetic acid (DTPA)
- Ethylene-diamine-di-(o-hydroxyphenylacetic acid)

- (EDDHA): also known as N, N'-Ethylene-bis-2(o-hydroxyphenyl)- glycine (EHPG)
- Ethylene di amine di (o-hydroxy-p-methylphenyl) acetic acid (EDDHMA)
- Ethylene-diamine-di-(5-carboxy-2-hydroxyphenyl) acetic acid (EDDCHA)
- Nitrilo-tri-acetic acid (NT A)
- Glucoheptonic acid
- Citric acid

Advantages of Chelates over Tradition Forms

The chelated forms of micro nutrients have a number of advantages over more traditional forms of trace elements such as oxides and sulphates:

1. Much lower quantities are necessary compared to inorganic compounds because they are completely assimilatable by crops. Chelates are thus cost effective even though they are a little more expensive.
2. Chelates are much more easily absorbed by plant roots or leaves because chelates are of organic nature. The chelation process removes the positive charge from the micro nutrients allowing the neutral or slightly negatively charged chelates to slide through the pores on the leaf and root surface more rapidly. Since these pores are negatively charged, positively charged micro nutrients would normally be 'fixed' at the pore entrance would be difficult to be assimilated by plants. When neutral chelated micronutrients are used there would be no such restriction barriers.
3. Chelates are more easily translocated within the plant as their action is partly systemic.
4. Chelates are easily assimilated within the plant system.
5. The chances of 'scorching' of crops while using chelates is less because they are organic substances.
6. Under alkaline conditions, chelated iron, zinc, manganese and copper is a better way to provide micronutrients to a crop.
7. Chelates are compatible with a wide variety of pesticides and liquid fertilizers, as chelates do not react with their components. Most chelates can be mixed with dry mixes and liquid fertilizers.
8. Chelates are not readily leached from the soil as they adsorb on to the surface of soil particles.

Corrections of Iron Deficiency by Chelates

Iron deficiency-induced chlorosis is a widespread nutritional disorder in many crops, in particular when the soil is alkaline or calcareous. It has been found that in the alkaline soils, where Fe solubility and availability to plants are extremely low, adding soluble Fe salts is not

very effective, unless the soluble Fe is in a form that does not react with the soil system and yet can be readily assimilated by plants. There are two alternatives available to deal with iron deficiency. These are (i) soil application of iron chelates and (ii) foliar sprays containing chelated iron. If the soil pH is alkaline, chelates must be preferred to inorganic salts. There are a number of commercially available chelating agents, which differ considerably in their stability. The effectiveness of chelates in alkaline soils is related to their stability at various pH values of soil. For example, EDDHA is selective for Fe only over a pH range of 4 -

9. This selectivity makes EDDHA a much better Fe source for calcareous soils compared to EDTA, which chelates Fe primarily at pH <6.3: above pH 6.8 EDTA reacts with Ca²⁺, making it an ineffective chelate in soils with high pH. DTPA chelates Fe up to a pH of about 7.5: above this pH Ca²⁺ binds to this chelate. The application of micronutrient chelate fertilizers to soil or as foliar spray have their own advantages. Some advantages of foliar application are the lower application rates needed, immediate effect on the crop, feasibility of uniform application even when using small amounts and no build-up of harmful levels.

Thus they serve as a good supplement to soil application as well as a mid-course correction and practical method for tree crops. On the other hand, advantages of soil application include: application of deficient micronutrient right at the beginning of the crop cycle with generally no injury to plants, provide residual benefits to crops that follow the current one, no sprayer needed and skilled labour not essential. In case of soil application, it is important to have adequate water supply to wash the chelates down into the soil up to the extent of the spread of the root system. At higher soil pH levels, soil CaH is present in high concentrations and can displace Fe³⁺ from less stable chelates giving rise to Ca-chelates and precipitated Fe-oxide thus rendering the Fe unavailable.

Iron chelates in commercially produced soluble fertilizers are degraded by light. Therefore, proper storage of fertilizer stock solution in opaque containers should be followed to check degradation of iron chelates. Solid forms of the fertilizer are not influenced by light. Recently, a new Fe (II)/Fe (III) chelator with a complex stability between Fe-citrate and Fe-EDTA has been reported. Its high resistance to photo-reduction makes it a promising technique for future use in the remedy of iron chlorosis.

Application of Micronutrient and Competition

In citrus cultivation, application of about 10-20 g Fe/tree in chelate form has proved satisfactory. Fe(II)-humic acid complexes provide iron to wheat plant under adverse soil conditions and provides stimulation to crop growth. The application of FeEDDHA and Fe-sugar acid chelates at 7 mg Fe/litre resulted in re-greening of leaves in iron-deficient plants. The application of ligninosulfonates or lignino-polycarboxylates resulted in better chlorosis recovery of cotton than application of EDDHA. The result appears to fit into a general pattern of competitive chelation. Chelating agents, from which iron has been released and under conditions favorable to chelation of Mn, compete with plant roots for Mn. Chelating agents have the ability to keep iron sufficiently in solution to provide enough iron at the root surface to effect competition with manganese. The nature of Fe-Mn interactions in peanuts depends on the source of the applied Fe. The addition of Fe chelate

(Fe-EDDHA) is known to reduce Mn uptake in peanut plants. But, when Fe was applied as FeSO_4 it did not affect Mn uptake by plants.

Chelates in Zn Nutrition

Organic zinc fertilizer sources are the chelates of EDTA, NTA and HEDTA. Other organic sources include Zn-ligninsulfonate, Zn-polyflavonoid and by-products of the wood pulp industry. Solubility and plant availability of zinc from zinc sulphate is a great problem under certain soil conditions. Almost 85-90% of soil-applied zinc is rendered unavailable to the plant due to its fixation in different forms. The most common source of zinc in chelated form is Zn-EDTA ($\text{Na}_2\text{Zn-EDTA}$), which contains about 12% Zn. Chelated-Zn dissociates to only a very slight degree and being negatively charged moves easily like other anions in soils of high pH and reaches the vicinity of the roots. Organic-chelated zinc sources generally have been reported as superior to inorganic zinc sources. Only about half as much Zn was required for corn and beans if Zn-EDTA was the source rather than ZnSO_4 . Zn-chelates are effective for rice production and zinc uptake by corn plants was higher for Zn-EDTA on a calcareous silt loam than for zinc sulphate.

Potential for Mn and other Chelates

Mn is mainly transported as Mn and not as an organic-complex. Chelated-Mn reactions in soil are quite different from chelated-Zn reactions. Mn-chelates when applied to the soil are usually ineffective because of high level, of available iron in our soils. Fe replaces the Mn in soil applied Mn chelates. Thus, Mn-chelates are effective only when used as liquid fertilizer formulation and hydroponics. Foliar application of Mn is frequently recommended in calcareous organic soil. Mn containing fungicides such as Maneb have also proved effective for correcting Mn deficiency in fruit trees and other crops.

Seed treatment with EDTA-Zn and EDTA-Co increased sugar accumulation in tillering nodes, improved field germination and increased yield in winter wheat. Application of Cu chelates with different amino acids increased chlorophyll content, grain yield, amino acid content and the uptake. It also influenced the distribution of Cu, Zn and Mn in roots, grain and straw. Water-soluble chelates of degraded and hydrophilised Larch tannin with Fe, Mn, Zn and Cu ions increased leaf production by 20- 25% in apple (tested with mixed and Zn-chelated micronutrients) and 26.5% in Ginkgo biloba (tested with mixed chelated micronutrients).

Amino Acid Chelates of Micronutrients

True amino acid chelates are emerging as state-of-the-art technology for delivering selected micro nutrients with maximum bioavailability, tolerability and safety. These are chelated mineral products specifically designed for application on plants. They are unique because the micronutrients are chelated with amino acids. The advantages of using these chelated micronutrients are that the amino acid ligands surround and protect the micro nutrients from adverse interactions - typically those that take place in soil solution, in the presence of soil or on leaf surfaces. Natural amino acids are used to chelate the micronutrients and hence they are rapidly absorbed, translocated and metabolized by plants. Moreover, they are very small molecules and are absorbed and translocated within the plant similar to other

small nitrogen containing molecules. All of them are completely soluble in water and consequently are available for absorption by the plants.

The leaves of most plant as well as primary cell wall serve as a barrier against the absorption of free metal ions. Metals completely chelated with amino acids are neutral in charge. They are neither attracted to nor repulsed from negatively charged surfaces of the leaf. Therefore, they freely pass through this barrier. When the amino acid chelates reach the cell membrane, they are recognised by the mechanisms of absorption organic N. As a result, entire amino acid chelate is taken into the cell very rapidly and efficiently.

On the other hand, natural complexing agents such as ligninosulfonates, humates, fulvates and long-chain hydrolysed proteins are large and complex. Because of their large size, the chances that any of these molecules actually chelating a micronutrient are less. These natural chelates are however, broken down by soil microorganisms into much smaller units for absorption into the cells of the plants. Therefore, such natural complexes /chelates do not offer all the benefits of true amino acid chelates. However, because of its efficient absorption, much lower doses of true amino acid chelates need to be applied to the crops. True amino acid chelates are available as Zn, Fe, Mn, Cu and B complexed forms.

Recent Trends

New generations of chelates are being developed and the application strategy and technology are changing with time. Recently, emphasis is being laid on sugar based chelating agents to make micronutrients more effective. Such chelated micronutrients contain no EDTA chelates (EDTA has been found to be toxic in some cases after releasing the required micronutrient).

It is suggested that chelating agents such as sugar acid derivatives, condensed tannins and gluco-heptonates could be used as substitutes for the traditionally used EDT A for preparing chelated micro nutrients. A few recent reports suggest that the combined use of humate and metal chelates seems to have a greater potential rather than metal chelates only.