

## Metal Chelates in Plant Nutrition

E. J. HAERTL

The Dow Chemical Co.,  
Midland, Mich.

Experimental work on the control of metal nutrition in plants with synthetic chelating agents is described. As in higher plants, chelated iron can be used to augment the iron nutrition of lower forms of plant life. The use of divalent metal chelates to correct recognized specific deficiencies has been open to question because their application to growing plants has not always resulted in a decided increase of the metal in the tissues of the treated plant. The author is of the opinion that the correction of a micronutrient (metal) deficiency is not wholly due to increasing metal content of plant tissue. It may be equally dependent upon an efficacious metal balance in the tissues which, apparently, can be improved through the use of certain synthetic chelating agents. The commercial use of these materials in fertilizer depends upon an adequate interpretation of their behavior.

THE RECOGNITION of chelation as an important factor in the metabolism of living organisms has shed a new light on the importance of metals in physiology. The close association between metals and natural chelating agents such as enzymes, certain proteins, organic acids, and other organic compounds has helped to interpret the function of metals in metabolism. The development and manufacture of synthetic chelating agents by industry has contributed toward the solution of many problems involving the role of metals in physiology. Much of the research work done in the past has been academic in nature. It is only within the past 10 years that experiment station workers and industry have attempted to utilize this information in the field. The practical applications of synthetic chelating agents and their metal chelates have, in many instances, proved to be beneficial. There are, at present, a number of synthetic chelating agents on the market, and it is now up to the manufacturer and experiment station workers to supply the necessary use information to the grower. This paper briefly reviews the practical uses of the principal chelated metals—iron, zinc, manganese, and copper and discusses current research of interest in this field.

The common synthetic chelating agents now being manufactured and sold are EDTA, ethylenediaminetetraacetate; HEDTA (EEDTA, HEEDTA, HOEDTA) *N*-hydroxyethyl ethylenediaminetriacetate; DTPA, diethylenetriaminepentaacetate; EHPG (EDDHA) *N,N'*-ethylenebis-2-(*o*-hydroxyphenyl)glycine. The properties of these specific chelating agents, as metal carriers in agricultural practice, were adequately described by Chaberek and Martell (2).

### Chelated Iron

The use of chelated iron to correct iron deficiencies in susceptible crops and under various conditions has been demonstrated in numerous experiments. The mechanism by which plants use chelated iron is not well understood and is being investigated. Tiffin and Brown (78), using tagged chelating agents, presented evidence that the iron chelates of EHPG, DTPA, and EDTA dissociate at the surface of the root releasing their iron for absorption. The amount of chelating agent absorbed, under their experimental conditions, was relatively small. Wallace (79), to the contrary, indicated that tagged iron EDTA applied to the roots of soybean, *Pyra-cantha*, and rough lemon resulted in higher concentrations of EDTA than iron in the leaves and stems of the plants. Simons *et al.* (16) further substantiated the idea of dissociation of the iron chelate at the surface of the root by studies on soybeans using FeEHPG. However, they maintained that the iron chelates with lower stability constants for iron are better sources of iron in nutrient culture of soybeans. Krauss and Specht (9) reported that chelated iron behaves in a similar manner in the nutrition of the alga, *Scenedesmus*—i.e., the iron content of the algal cell is increased, but no marked increase occurs in the absorption of chelating agent. Some work has been done along this line in Michigan. Schelske (73, 74) described the efficiency of iron chelate (FeHEDTA) as a source of iron for the growth of phytoplankton.

Versenol (registered trademark of The Dow Chemical Co.) iron chelate, FeHEDTA, was added to the water of Blind Lake in Michigan, a marl lake with a pH between 8.4 and 8.6, at

concentrations varying from 0.02 p.p.m. up to 2.0 p.p.m. of iron. At the time of the experiment (late spring of 1959), the surface water tested at 57 p.p.b. The response measured by the gross increase in uptake of  $C^{14}$  showed over a 50-fold increase at a concentration of 0.02 p.p.m. of iron and a 160-fold increase at a concentration of 2.0 p.p.m. of iron.

To determine if the previous results had practical applications, Sand Lake in the vicinity of Traverse City, Mich. (75) was treated on July 27, 1959, with Versenol 120 and ferrous sulfate. The amount of material applied resulted in concentrations of above 584 p.p.b. of Versenol and 72 p.p.b. of iron. This amount of chelating agent was sufficient to chelate slightly more than the amount of iron added. Four days after the treatment, the gross rate of  $C^{14}$ -uptake increased 3.3-fold, and 5 days after treatment sixfold. On the 10th day after treatment the lake was fertilized, which resulted in approximately a 60-fold increase in rate of gross uptake of  $C^{14}$ . The low concentrations of chelating agent used in these experiments apparently lends credence to the idea that the chelating agent serves as a carrier and source of iron.

The use of chelated iron to correct iron deficiency (i.e., chlorosis) in certain crops has been limited to geographic areas where chlorosis is a problem. However, beneficial effects of chelated metals may also be noted under conditions where a specific metal may not be deficient to the extent of causing chlorosis, yet may limit the growth of plants. In other words, is there a need for the use of chelated metals in fertilizers applied to apparently normal crops? Figure 1 illustrates the effect of adding Versenol 120 (HEDTA) and ferrous sulfate to



Figure 1. Effect of adding Versenol 120 and ferrous sulfate to cotton growing in sandy loam of Brownfield, Tex.

Left, control with regular fertilizer treatment; right, plant with fertilizer treatment plus 26 pounds of Versenol 120 and 8.8 pounds of ferrous sulfate per acre

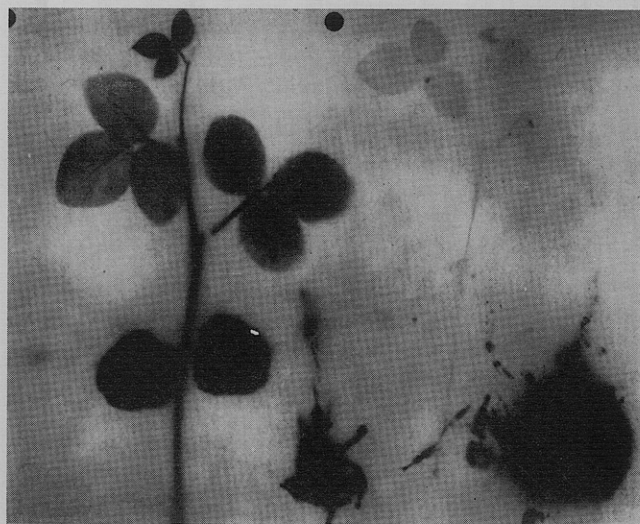


Figure 2. Autoradiogram of normal soybean plants

Left, roots treated with Versenol 120 and  $Fe^{59}$ ; right, roots treated with  $Fe^{59}Cl_3$

Table I. Translocation of Radioactive Phosphorus Applied to the Primary Leaf of Soybean (12)

Solution in Which Plants Were Grown	C.P.M. per Plant Part				% of Total C.P.M. of Each Plant Part			C.P.M./Gram per Plant Part		
	R <sup>a</sup>	St <sub>1</sub> <sup>a</sup>	St <sub>2</sub> <sup>a</sup>	Total	R	St <sub>1</sub>	St <sub>2</sub>	R	St <sub>1</sub>	St <sub>2</sub>
-Fe	27 <sup>b</sup>	15	7	49	56	30	14	180	180	300
1X (2 p.p.m. Fe as FeHEDTA)	560	45	270	875	64	5	31	3300	410	2700
10X (20 p.p.m. Fe as FeHEDTA)	1150	35	340	1525	75	2	23	6240	220	1450

<sup>a</sup> R = Root; St<sub>1</sub> = first trifoliolate leaf; St<sub>2</sub> = second trifoliolate leaf.

<sup>b</sup> Each value is the average of eight plants.

cotton growing in sandy loam of Brownfield, Texas. The average increase in fresh weight of the plant tops was 20%. Addition of 15 pounds of ferrous sulfate to the acre, without chelating agent, resulted in no increase in fresh weight.

Figure 2 demonstrates some results obtained by Penner (12) using Versenol 120 (HEDTA) in solution cultures. The absorption of iron in the chelated form by the healthy plant is clearly demonstrated over the absorption of  $Fe^{59}$  in the inorganic form. Table I summarizes information about the translocation of radioactive phosphorus applied to the primary leaf of soybean plants. The chelated iron was supplied to the roots of the plant. The significant point is that under adequate iron nutrition it is possible for foliar applied phosphorus to be translocated readily to other parts of the plant.

#### Chelated Zinc

Increasing recognition is being given to the role of heavy metal chelates other than iron in areas where deficiencies

are recognized. This is particularly true in regard to chelated zinc. Since zinc, manganese, and copper are ordinarily in the divalent form, their metal chelates have a lower stability constant than that for ferric iron. This has led to speculation as to their efficiency in supplying the metals to growing plants when applied to the soil. As a result, particular emphasis has been given to foliar applications of these metal chelates. The results of foliar applications, in many instances, have not been too successful in comparison with the use of the inorganic forms of the metals. This is particularly true if the correction of a metal deficiency is measured by an increase in the amount of metal in tissues. In many instances where iron chlorosis has been corrected by applications of iron chelate, the root analysis shows a decrease in iron content, very little change in the stem iron content, and slight to large increases in leaf tissue. In other words, the correction of a metal deficiency may not be entirely a quantitative problem. DeKock and Mitchell (3) illustrate this point with their work on the divalent metal chelates. Mustard

plants grown with 4 p.p.m. of zinc from zinc sulfate and 2 p.p.m. of Fe from ferric chloride contained over 2940 p.p.m. of zinc in the leaf. With the same concentrations of zinc and iron in the form of EDTA, the leaf concentration of zinc was only 240 p.p.m. Regardless, the plants treated with the inorganic salts averaged 7 cm. in height and were severely chlorotic. Those treated with the metal chelates were 30 cm. in height and dark green in color. Similar results were obtained in their experiments involving copper. Work by Guinn (5), who experimented with iron, copper, manganese, and zinc in the nutrition of the cotton plant, produced similar results. Table II shows the effect of chelated iron plus complexing agents in nutrient culture on the growth and dry weight of leaves and roots of cotton plants. The citrate and tartrate applications can be considered the controls since both of these materials are not as powerful chelating agents as the synthetic forms. The use of HEDTA and EDTA show decided increases in the dry weights of both leaves and roots.

Table III shows the effect of the chelat-

**Table II. Oven Dry Weights of Leaves and Roots and Ratios of the Weights of Leaves to Roots as Influenced by Source of Iron and Complexing Agent in the Nutrient Solution<sup>a</sup>**

Iron Source	Complexing Agent	Weight in Grams		Leaves Weight/Roots Weight
		Leaves	Roots	
Fe EDTA	Na <sub>3</sub> citrate	17.70	3.28	5.40
Fe EDTA	NaK tartrate	18.00	3.51	5.13
Fe HEDTA	Na <sub>3</sub> citrate	17.31	3.19	5.43
Fe HEDTA	NaK tartrate	17.61	2.94	5.99
Fe citrate	Na <sub>3</sub> citrate	5.52	1.66	3.33
Fe citrate	NaK tartrate	6.10	1.79	3.41

<sup>a</sup> Averages of three replications.

**Table III. Concentrations of Iron, Copper, Manganese, and Zinc in the Leaves of 29-Day-Old Cotton Plants as Influenced by Source of Iron and Complexing Agent in the Nutrient Solution<sup>a</sup>**

Source	Complexing Agent	Concentration, $\mu\text{G. per Gram}$			
		Iron	Copper	Manganese	Zinc
Fe EDTA	Na <sub>3</sub> citrate	98	8.1	62	26
Fe EDTA	NaK tartrate	80	8.2	54	28
Fe HEDTA	Na <sub>3</sub> citrate	90	8.0	62	24
Fe HEDTA	NaK tartrate	96	7.4	56	21
Fe citrate	Na <sub>3</sub> citrate	56	9.8	100	54
Fe citrate	NaK tartrate	51	9.9	106	43

<sup>a</sup> Averages of three replications.

ing agents on the iron, copper, manganese, and zinc content of the cotton plants. The controls show less iron but more copper, manganese, and zinc than those treated with the synthetic chelating agents. Also, the greatest dry weight was not associated with the highest iron content. This was produced in the culture containing iron EDTA and sodium potassium tartrate.

It would appear, from the previous absorption data, that the correction of zinc deficiency in plants could not be effectively accomplished through the application of chelated zinc. This would be particularly true if the correction were dependent entirely upon the increase of zinc in the plant tissue. However, Benson *et al.* (7) reported the correction of zinc deficiency in peach and sweet cherry trees through the application of chelated zinc. These corrections were brought about through soil applications and persisted in their effect for well over a year. Their data indicate that the correction of zinc deficiency, through applications of chelated zinc, did not always result in increased zinc content of the leaf tissues. Further, they stated that the leaf zinc content does not indicate deficiency since untreated trees with symptoms contained as much zinc as untreated, normal appearing trees. Ionic zinc is rapidly fixed in many soils, whereas anionic zinc in the chelated form is much more mobile. Leonard *et al.* (10) demonstrated this mobility of chelated zinc in their studies on zinc deficiency in citrus. Therefore, chelated zinc is more mobile in the soil and more efficient in bringing zinc into closer contact with deep-rooted plants.

Chelated zinc has corrected zinc deficiency in more shallow-rooted field crops. Less than 1/4 pound of elemental zinc, applied in the chelated form to zinc-deficient corn growing in Nebraska, corrected zinc deficiency. In many areas in this state, terracing or grading had exposed an extremely zinc-deficient subsoil. Corn, grown in this soil, manifests serious symptoms of zinc deficiency in the early stages of growth.

As much as 14 pounds of elemental zinc in the ionic form has been recommended for treatment of corn growing under these conditions, yet 1/4 to 1 pound, as a chelated metal, has achieved the same desired effect.

Zinc deficiency (rosette formation) in pecan trees has been recognized for quite some time. Zinc-deficient pecan trees in New Mexico have been treated successfully with Versenol zinc chelate (ZnHEDTA). To reduce the cost of treatment with preformed zinc chelate, the treatment used here was a soil application of a liquid solution made from Versenol 120 (HEDTA), zinc sulfate, and water. This treatment proved to be effective in correcting the zinc deficiency and stimulating growth, whereas treatment with zinc sulfate alone was ineffective.

Leonard *et al.* (10) reported greater mobility for chelated zinc in soils than for inorganic forms of zinc such as zinc sulfate. Inorganic forms of zinc become more available with a decrease in pH. They successfully corrected zinc deficiency in citrus through applications of zinc sulfate in combination with calcium chloride to acid sandy soils. However, at pH 6 and higher the zinc chelates become a more effective source of zinc for the growing plant. In most areas where zinc deficiency is a serious problem, the soil pH is usually around neutral or alkaline in reaction.

#### Chelated Manganese

The recognition of the problem of manganese deficiency in plants is not, apparently, as widespread as that of iron and zinc deficiencies. It is recognized in certain areas of the country, particularly in states bordering the Great Lakes, and as a result, not much research has been devoted to investigation of chelated manganese as a means of correcting manganese deficiency. Recognition of manganese as an important factor in the nitrogen metabolism of living organisms may, in the future, provide a field wherein chelated manganese may prove to be

useful. It is possible to prevent the symptoms of manganese deficiency from appearing in beans grown on certain Michigan soils by the addition of chelating agent and manganese salt to liquid fertilizer applied at the time of planting. Ordinarily, one or two sprays of manganese sulfate applied during the growing season will correct manganese deficiency.

#### Chelated Copper

The incidence of copper deficiency in plants is not so widespread as that of iron and zinc deficiencies. In a few instances, copper chelate has been used successfully in treating recognized copper deficiency. Guinn (5), described some interesting results using chelated copper in the nutrition of cotton plants. The use of chelated copper, as a source of copper in nutrient culture, reduced the uptake of copper by the cotton roots. Nonetheless, in all instances where chelated copper was used as a source of copper, the growth response was much greater than with copper in the inorganic form. Maximum growth response was obtained with both iron and copper in the chelated form. Contrary to the accepted views about the stability of chelated iron in relation to the other divalent metals—zinc, copper, and manganese—Guinn pointed out that, due to the more rapid hydrolysis of iron, it is possible for copper and zinc, and to a lesser extent, manganese, to displace iron in the chelate molecule. This provides an explanation for the effective use of chelated iron in correcting the heavy metal toxicities (copper, zinc, and manganese) since their chelates are not as readily absorbed as the metals in the ionic form. This reaction has been observed in the formulation of fertilizers with chelating agent and metal salts. Analyses of these fertilizers showed chelation of copper and zinc in excess of the estimated amount in the presence of iron.

The importance of micronutrient balance in plant nutrition cannot be over-emphasized. In many instances

analyses of chlorotic plant tissue show an excess usually of manganese or copper. Stout (17) calculated a theoretical micronutrient element requirement of growing plants. This ratio of about 20 parts iron, 10 parts manganese, and 3 parts zinc to 1 part copper places iron in excess of the other micronutrients. Considering the reactions of synthetic chelating agents with metals in the inorganic form, it would appear that the combination of chelating agent and metal salts would be of distinct benefit in fertilizer applications.

### Magnesium Chelate

Koukkari (8), in a study on apple seedlings grown in magnesium-deficient soil, reported some interesting results on the use of the chelating agent  $\text{Na}_3\text{-HEDTA}$  in combination with the salts of various metals. His observations show that the chelating agent in combination with the metals had a distinct effect upon the nutrition of the plant. Eggert (4) reported a correction of magnesium deficiency in apple seedlings through the use of Versenol in combination with dolomitic limestone. Leaf analysis of the treated plants showed an increase in magnesium uptake and a decrease in both iron and manganese uptake. In the treatments, growth response was associated more with the reduction in manganese uptake than with the change in status of either magnesium or iron. Possibly, excess manganese in acid soils may interfere with the utilization of both magnesium and iron. From these results, the use of a synthetic chelating agent in combination with metal salts has a distinct effect upon the absorption and translocation of metal resulting in an improved micronutrient balance.

### Soil Microorganism Relationships

Considering the extensive research that has been done on plant chlorosis, very little attention has been paid to the importance of the soil microflora in relation to this problem. Nicholas (17), in his review of minor mineral nutrients, pointed out the importance of metals in critical enzymes associated with the metabolism of soil microorganisms. Both molybdenum and iron are needed by both free-living and nodule bacteria for nitrogen fixation. The reduction of both nitrate and nitrite is associated with both iron and copper. The process of nitrification, associated with *Nitrosomonas* and *Nitrobacter*, depends upon the presence of metals, particularly iron. In the process of ammonification, the reduction of hydroxylamine is dependent upon the presence of manganese. It is apparent that the nitrogen cycle in the soil requires the presence of certain metals. The chelates of these metals undoubtedly would have a

distinct effect upon these important nitrogen changes. In addition, the phosphate cycle and the potassium cycle in soils are influenced by the presence of metals. It is conceivable that some of the growth response obtained through the use of synthetic chelating agents may be due to their effect upon the metabolism of soil microorganisms.

### Discussion

The controversial subject, in regard to the mechanism whereby synthetic metal chelates are utilized in plant metabolism, does not detract from the fact that they have proved to be beneficial in the treatment of some metal deficiencies and for stimulation of growth. The concept of the chelating agents acting as stable transport mechanisms for metals in the soil to the surface of the root apparently holds true for iron in some instances but has not been demonstrated, as yet, for other divalent metals. The concept of the chelate molecule being absorbed by the root and translocated in the plant appears to be substantiated by the work of Weinstein *et al.* (20) and Hale and Wallace (6). It would appear that any changes in enzymatic activity brought about by treatment with chelating agent would involve the absorption and translocation of the chelating agent in the living plant. Hill-Cottingham and Jones (7) offer an explanation which reconciles both of these views. When a plant is deficient in iron and treated with iron chelate, the iron chelate dissociates at the surface of the root, thereby increasing the iron content of the root. When a plant is not deficient in iron and is treated with iron chelate, both the iron and the chelating agent are absorbed in equal amounts. This may explain why some treatments with chelated iron may not be manifested by a distinct growth response until 6 to 8 weeks after treatment regardless of the fact that the plant begins to take up iron immediately after application. Non-chlorotic ornamental plants will very often show a growth response to applications of chelated iron in a very few days after treatment. The value of synthetic chelates in the metabolism of growing plants has been recognized by many research workers. Their general use in agriculture has been retarded by misconceptions regarding their cost and the economics of their use.

A hope has been expressed by many research workers that industry will be able to produce better synthetic chelating agents in the future. Industry is well aware of the cost associated with use of synthetic chelate materials in fertilizers. Chelating agents are no different than any other chemical or commodity in that expanded use with increased

volume would undoubtedly have some effect on price. The synthetic chelating agents now offered for agricultural use are standardized materials with recognized performance. Their use in fertilizer is beneficial and in most instances brings about returns in excess of their cost. There is always the possibility that new and better synthetic chelating agents will be produced in the future. However, when one considers the research, synthesis, production, and development necessary to put a complex chemical of this type on the market, it will be necessary to expand the agricultural use of the present chelating agents far in excess of that now being sold.

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