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CHELATES

As Aids in Combating Plant Malnutrition

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SUMMARY

Chelates are relatively new aids in combating plant malnutrition. They are organic chemicals which have the capacity to envelop certain elements (nutrient metal ions, in their agricultural application) and to keep them water-soluble under conditions in which they would otherwise become insoluble.

Chelated metal treatments applied to the soil or as foliage sprays have proved advantageous in supplying iron and zinc to some plants damaged for want of these essential nutrients.

The Agricultural Research Service is among agencies that are investigating the role of chelates in plant nutrition and their agricultural uses. Current research includes work with experimental chelates as well as chelates now on the market.

Practical chelated metal treatments are necessarily developed to suit a specific plant in a specific soil situation. Recently, for example, a spray treatment employing a chelate combined with iron and manganese has been developed which improves the greening and fruit yield of pear trees grown on clay adobe soils of southern Oregon--where iron deficiency has posed a serious problem for pear growers.

At present costs, chelates are practical primarily for treating crop trees, ornamentals, and other high-value plants. ARS applied chelate research is focused mainly on crop trees, though some work is being done to test the effectiveness of these substances for combating nutrient metal deficiencies in other plants.

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Agricultural Research Service

CHELATES AS AIDS IN COMBATING PLANT MALNUTRITION

Organic chemicals known as chelates (pronounced kee-lates) are relatively new aids to plant growers in protecting plants against deficiencies of certain metal nutrients, notably iron and zinc. The most characteristic distress sign of a plant deficient in one of these metals is a yellowing and fading of foliage. This symptom, termed chlorosis, indicates that the plant is developing too little of the vital green coloring material, chlorophyll.

Iron and zinc deficiencies in plants are common causes of low yields and other disappointments to growers--not because the soil is necessarily lacking in iron or zinc, but because the metal is in a form not readily available to plants. Older methods of treating metal-deficient plants have been only partly successful. Chelates offer a new approach to combating this type of plant malnutrition, with some distinct successes already to their credit.

The name chelate was coined from the Greek word "chela," meaning claw, to describe chemicals (both natural and synthetic) that have a peculiar capability of enveloping certain elements. This claw-like grip is actually an electrical force. When the right chelate is combined with a metal, such as iron, the electrical force causes the metallic particles, known as ions, to remain soluble in water and protects them from further chemical and physical changes. Metals in water-soluble form are most readily available to plants for nutritional use.

Natural chelate materials occur in soils, but they are sometimes not sufficiently stable, effective, or abundant enough to keep some nutrient metal in soluble form for plant needs. The chelates that are being used in agriculture are relatively stable synthetics made from organic compounds. A successful chelate treatment is shown in Figure 1.

Prior to the 1950's, synthetic chelates were most familiar to chemists who required a metal-stabilizing agent in certain analytic and industrial processes. Some efforts were made to apply these chemicals to plant research but results were not encouraging.

The first strong evidence that synthetic chelates would be useful to agriculture was presented in 1951 when scientists at the University of California reported that application of a chelate combined with iron (chelated iron) could overcome iron deficiency in plants grown in a nutrient solution. Shortly thereafter, practical field use was demonstrated by scientists of the Florida Citrus Experiment Station who applied chelated iron to citrus trees, with strikingly good results, to correct a mineral imbalance that damaged trees on acid sandy soils.

Figure 1.--These soybean plants of a single variety were grown experimentally in several calcareous soils--kinds of soils in which many plants become chlorotic due to failure to take up adequate iron in useful form. The plants at left, not treated, produced yellowed, chlorotic leaves. The plants at right, given chelate treatment, developed normally green foliage.

Since then, research to determine specific uses and limitations of chelates and chelated metals among various agricultural crops has expanded rapidly.

Chelated metals are expensive and their prospect for becoming less costly are unpredictable. Consequently, they are practical, at present, primarily for treating crop trees, ornamentals, and other high value plants. However, it is possible that some chelated metal treatments may be developed that can be used economically in row-crop farming.

PLANT DEFICIENCIES THAT CHELATES COMBAT

The Leading Symptom--Chlorosis

Metal nutrient deficiencies in plants that chelates combat are evidenced by chlorosis as the leading symptom.

Chlorosis--a Greek word "chloros," meaning green, merged with a suffix "osis," indicating disease--describes a yellowing and fading of foliage and is a warning that the plant is de-

veloping too little of its vital green coloring material, chlorophyll. Veins are the last part of the leaf to fade.

Chlorotic plants develop additional symptoms of distress, varying to some extent with the plant species and the growing conditions. Among these further symptoms are mottled leaves, meager bud development, and dieback of twigs and even large branches. A combination of symptoms often points plainly to a specific nutrient which the plant lacks.

As chlorotic plants weaken, their yields of flowers, fruit, or other expected products may become disappointing in quantity and quality. A serious chlorosis may kill a plant. In ornamentals and turf, the disfigured foliage is in itself cause for concern.

Plants may become chlorotic for want of essential nutrients other than metals, but the specific deficiencies discussed here are limited to those which the chelates are helping to overcome. Chelates used in agricultural research have been most effective in keeping iron and zinc water-soluble, and therein lies their most promising value to growers. Of the nutrient metal deficiencies that damage plants, a lack of soluble iron is the hardest for plant growers to correct; zinc perhaps second.

Causes of Plant Chlorosis

Tracing the originating and contributing causes of a plant chlorosis in order to provide suitable treatment generally reveals a chain of imbalances in the soil.

Chlorotic plants are sometimes growing in soil that is naturally poor in the nutrient they lack. This simple chain of cause and effect, however, occurs infrequently.

Far more often, plants are starved for a metal although growing in soil abundantly supplied. In this paradoxical state, physical and chemical influences in the soil are so great as to prevent the plants from getting even their small requirements of the needed metal.

Following are adverse conditions which most frequently start chlorosis or make it more serious:

- * A soil may be naturally overstocked with some mineral. Calcareous soils, for example, have accumulated lime and other elements in their formation, and these elements interfere with nutrient iron to such an extent that many species and varieties of plants become chlorotic in these soils.
- * Overwatering or sudden heavy rains may launch physical and chemical changes in naturally calcareous soils, decreasing the soluble iron supply.

- * Irrigation water or other water supplies may have a high content of calcium or sodium bicarbonate, which tend to interfere with the solubility of iron.
- * Long use of fertilizers or pesticides may build up trouble-making deposits of certain minerals in a soil. This has occurred in some of Florida's acid, sandy soils long planted to citrus. Several years ago, ARS scientists analyzed some of these soils and also feeder roots and leaf tissues of iron-chlorotic citrus trees grown in the soils. They found that excessive copper prevented the foliage from getting requirements of iron. They have advised that in this situation growers make minimum use of fertilizer and pesticide sprays containing copper.

TREATING PLANT CHLOROSIS

Chelated metals, like other plant nutrient supplements, are temporary remedies for controlling deficiencies. Unless the initial cause of the deficiency can be corrected, a chelated metal treatment needs to be renewed when effectiveness wanes.

In developmental work, chelates are frequently compared experimentally with older treatments for chlorosis, to learn whether a chelated metal shows some advantage in effectiveness, economy, or convenience over other possible treatments.

Older Treatments for Chlorosis

Farmers have fought chlorosis in valuable trees for many years with increasing success but not to their entire satisfaction. Few resort any longer to the crude process of driving iron nails into ailing fruit trees in hope of improving yields. Research long since provided more practical treatments, such as iron salts in sprays, injections, and soil applications. These old research-based treatments often give reasonably good returns and are still the most economic controls for some chloroses. These treatments are effective for periods from a few weeks to several years. Their repetitive use, especially in large-scale planting, calls for much time-consuming labor and the treatments are not helpful to some chlorotic plants.

Some Types of Chelates Employed

Chelates have already been produced from varied combinations of chemicals, and additional formulas with agricultural promise continue to be developed. Plant research includes work with some chelates that are still in an experimental stage as well as work to extend the usefulness of chelates that have been put on the market.

Long chemical names of chelates are frequently abbreviated for convenience. Here are abbreviations and full names of four of the chelates used in ARS experiments:

EDTA -- Ethylenediamine tetraacetic acid
HEEDTA -- Hydroxyethyl ethylene diaminetriacetic acid
DTPA -- Diethylene triamine pentaacetic acid
EDDHA -- Ethylene diamine di(o-hydroxyphenol acetic acid)

Of these four, EDTA and HEEDTA are most effective in making iron and zinc available to plants in acid and slightly alkaline soils. DTPA and EDDHA are more effective than EDTA and HEEDTA in calcareous soils. EDDHA is not currently on the market.

Evaluating a Chelating Treatment

In plant research, whether a chelated metal treatment is found practical and advantageous depends on a combined evaluation of answers to these questions:

- * What yield increase or other benefit does a plant show after treatment?
- * How long is one treatment helpful?
- * Does the treatment damage the plant by toxicity?
- * What does the treatment cost? (A relatively expensive treatment may be economical if one application is sufficiently effective and lasting.)

Some General Findings

Since chelate treatments are tailored to suit specific soil-plant situations, the following general statements are not directions for use, but will give some idea of current ranges of practical applications and results to expect.

Strength. Application of a small amount of chelated metal is the invariable rule for plant safety and economy. Overdosages can be toxic to plants and the margin of safety is sometimes small.

Spray solutions are likely to be made with 1 to 5 pounds of chelated metal in 100 gallons of water. Soil applications for trees range from a few ounces to as much as 8 pounds of chelated metal around each tree; field applications, 20 to 400 pounds per acre, depending on the plant and the chelate employed. For ornamentals, a teaspoon of chelated metal per plant is often enough.

Soil application vs. spray. Chelated metal in a spray is likely to be cheaper and easier to apply than a soil treatment. Soil application, on the

Figure 2.--The pronounced image of this soybean plant on X-ray film is due to emanations from radioactive iron. The chlorosis-susceptible soybean was able to absorb the radioactive iron from a calcareous soil after the soil was treated with a chelate, DTPA. The image of roots, stems, and leaves shows that the iron was taken up and distributed evenly and amply throughout the plant.

other hand, is likely to be more lasting. Soil application is safer than spray for plants, such as azaleas, which have delicate tissues that can be easily damaged by the spray. In experimental work thus far, a few plants have indicated inability to absorb and utilize a soil-applied chelated metal.

Effectiveness. The first signs of plant response to a chelated metal treatment are the improved greening of developing leaves, and perhaps an increase in bud development. When treated plants are in the active growing stage, such signs generally appear within a week or two. Benefit from a single treatment may continue for as brief a time as a month or as long as several years, depending on the soil-plant situation.

SOME RESEARCH ADVANCES

The ARS is among public and private agencies making efforts to learn more about the role of chelates in plant nutrition and to develop ways of using them to advantage. Following are examples of work conducted by ARS scientists alone or in cooperation with a State agricultural experiment station or with support of another Federal agency.

Radioactive Isotope Studies

Atomic techniques--used in place of the ponderous work of analyzing plant tissues--are providing much clear and direct information on nutritional difficulties that bring about plant chlorosis, and on the effects of chelating treatments. In such experiments, a selected isotope--radioactive iron, for example--is applied to the soil of a potted plant. The extent to which the radioiron is taken up by the plant can be learned by placing an X-ray film over the plant in the dark. Radio-emanations expose the film, and the higher the concentration of the tagged iron in any part of the plant, the lighter the image will appear in the autoradiograph. A faint image means that little of the iron is present, and here the plant is chlorotic.

A number of greenhouse studies at the Agricultural Research Center with support from the Atomic Energy Commission have dealt with effects of iron, with and without chelate aid, on plants grown in calcareous soils. A variety of soybean that is highly susceptible to chlorosis in calcareous soils has been used as a test plant in much of this work. The isotope used has been sometimes radioactive iron and sometimes a chelate tagged with radioactive carbon.

An autoradiograph of a soybean plant that took up radioiron effectively by aid of a chelate is shown in Figure 2. The evenly pronounced image indicated that ample radioactive iron reached all parts of the plant.

Without a chelate, the same soybean plant variety grown in the same soil got almost no benefit from a radioiron supplement. The tagged iron

produced a faint image of roots and lower stems on an autoradiograph, and practically no image of foliage. This indicated that the supplemental iron did not remain available for plant growth but was changed in the soil to an unavailable form.

Different chelates and different rates of treatment have been used in the isotope studies of test plants. The outward appearance of plants and corresponding inner signs have been observed when increasing amounts of a chelate-and-iron treatment improved the greening of plants up to the point where overdosage produced toxic symptoms. The variable effect of the nature of the soil has been shown by applying the same chelate-and-iron treatment to a number of different calcareous soils. The same treatment, which alleviated chlorosis in the test plant in some soils, was less effective in other soils, and caused the plant to show toxic damage in still other soils.

Wheatland milo used in isotope experiments has given evidence that a plant species may be unable to utilize chelated iron. This variety of milo was found to be susceptible to iron chlorosis in two calcareous soils. When a treatment of radioactive iron chelated with DTPA was tried for these plants, they did not improve appreciably in above-ground growth. Dark autoradiographs explained the failure of the Wheatland milo plants to improve: they did not absorb and transport worth-while amounts of the chelate-protected iron.

Chelated Metal Treatments for Crops

Pears. A practical chelated metal spray treatment has been developed which improves the greening and fruit yields of iron-chlorotic pear trees grown on clay adobe soils of the Rogue River Valley in Oregon. This work has been done cooperatively by scientists of the Oregon Agricultural Experiment Station and the ARS.

Pear growers in this area have fought chlorosis in the past by injecting iron citrate into trees. The practice was time-consuming and trees showed damage after repeated injections.

In the chelate experiments, 1,500 pear trees were given various chelated metal treatments over several years. The greatest benefit to the trees without toxic damage was obtained with a spray containing the chelate DTPA compounded with both iron and manganese. The role of the manganese is not clearly understood. Nevertheless, with manganese added to the iron the amount of chelate itself could be doubled without toxic effect and, therefore, one treatment could do the work of two. The spray recommended contains 1 pound of iron-DTPA and 1 pound of manganese-DTPA to 100 gallons of water, applied at the rate of 300 gallons per acre. The spray gives best results when applied in the first half of the growing season: first treatment when spur leaves are three-fourths grown; the second, about 2 weeks later. Two are likely to be sufficient, although severely

chlorotic pear trees could be given a third treatment after a 2- or 3-week interval.

Peaches and Sweet Cherries. Encouraging results are being obtained in Washington State with soil-applied chelated zinc as possible replacement for zinc sulfate sprays for zinc-deficient peach and sweet cherry trees. In this cooperative research of the Washington Agricultural Experiment Station and the ARS, peach and sweet cherry trees have taken up through their roots worth-while amounts of either zinc-EDTA or zinc-HEEDTA. The best time for these soil treatments has proved to be in spring. Zinc chelates applied in sprays have been less successful--in fact, not so beneficial as zinc sulfate sprays.

In further cooperative experiments with Washington State at the Tree Fruit Experiment Station at Wenatchee, a chelated zinc treatment has been developed which overcomes arsenic toxicity of peach trees in soils where apples or pears have previously grown. Until recent years, arsenical insecticides sprayed on apple and pear trees caused so much arsenic to be deposited in the soil that young peach or other stone fruit trees planted later in these soils developed serious leaf damage and in some instances lost all of their leaves. Zinc sulfate has heretofore been the best treatment known, although its protective value is low in calcareous soils. Some growers have resorted to bringing virgin soil to old apple and pear lands to assure a favorable start for stone fruits.

A spray containing 2 pounds of zinc-EDTA in 100 gallons of water is the most effective and economical treatment yet found for overcoming this arsenic toxicity in peach trees. The spray has been most effective when applied in 3 treatments at 3-week intervals, starting in mid-June.

Apples. Adding a zinc chelate spray to other treatments for zinc-deficient apple trees may enable Pacific Northwest growers to correct stubborn conditions of zinc deficiency. In this area, where zinc deficiency of apple trees is common, many growers can correct it by spraying trees with a zinc sulfate solution in the autumn after harvest, or a similar spray in the spring just before trees start growth. When a single spray is ineffective, spraying at both seasons corrects the condition in most cases, but not in all.

In limited trials, considered only preliminary, ARS scientists at Wenatchee, Wash., have obtained complete correction of serious zinc deficiency in apple trees by first spraying trees with zinc-EDTA in the growing season and following with zinc sulfate spray at the customary times, in autumn and the succeeding spring.

In other experiments at Wenatchee, soil applications of chelated zinc have been tried as possible replacements for zinc sulfate sprays in treating zinc-deficient apple trees, but without success. The soil-applied chelating treatments that failed to improve the apple trees were the same treatments that did benefit peach and sweet cherry.

Citrus. Soil applications of chelated iron give promise that lime-induced iron chlorosis may be reduced to a minor problem in the propagation of young grapefruit trees on calcareous soils in the Rio Grande Valley in Texas. Some desirable rootstocks on which Texas grapefruit can be developed have demonstrated weak resistance to iron chlorosis on these soils.

In these experiments, cooperative with the Texas Agricultural Experiment Station, soil-applied iron compounded with either DTPA or HEEDTA has benefited young grapefruit trees growing on Cleopatra rootstock. Young trees on sweet orange rootstock responded best to iron compounded with one of the newer chelates, EDDHA. The work is preliminary. Cost of chelate treatments has not been determined.

In the Coachella Valley in California, ARS scientists are comparing iron chelate treatments with iron sulfate, soil applied, as chlorosis protection for citrus. The trifoliolate orange is being used as a test plant because it is particularly susceptible to iron chlorosis in calcareous soils of this area. These experiments indicate that the effective life of some chelated iron compounds in a calcareous soil may be as long as a year and a half, whereas zinc sulfate may be effective as long as 3 years. Thus far, iron sulfate has given more overall benefit in lastingness and effectiveness than the chelates tried. However, as new chelates are being developed, a chelated iron treatment may yet be found advantageous for citrus in this type of soil.

Blueberries. Preliminary experiments with blueberries indicate that these acid-loving plants can be grown successfully in mildly acid or even neutral soils, if chelated iron is applied to enable the bushes to get adequate water-soluble iron.

Pecans. ARS scientists are making comparative tests of zinc chelate and zinc sulfate treatments for zinc-deficient pecan trees in Louisiana and Texas. Both types of treatment have corrected the deficiency symptoms in one orchard for a period of 3 years and may prove even more lasting. Zinc deficiency is responsible for the malnutrition disease known as pecan rosette, which weakens pecan trees and reduces their yields. From 10 to 30 pounds of zinc sulfate per tree in acid soil areas, and 100 to 200 pounds per tree in heavy alkaline or neutral soils may be required to correct rosette. A chelated metal treatment might be advantageous if cheaper initially or more lasting. Rough figuring has indicated that a pound of chelated metal might have to do the work of 20 pounds of zinc sulfate to keep the initial price of one treatment comparable.

For comparative tests, zinc chelate has been applied to the soil around selected trees as water solutions at rates of 1/2 to 8 pounds of chemical per tree, while other trees have been given 20 pounds of zinc sulfate.

In acid soils, some nearly neutral, 1/2 to 2 pounds of the chelated zinc have corrected the zinc deficiency in some young pecan trees up to

1-1/2 feet in diameter, but larger trees have required 4- or 8-pound treatments. In one test area, at Shreveport, La., large zinc-deficient trees that were given either 4 or 8 pounds of zinc chelate in 1954 recovered fully in 1955 and so far have not required further treatment. Meanwhile, other trees given 20 pounds of zinc sulfate have shown similar good and lasting response.

In alkaline soils, where pecan rosette is particularly hard to combat, even the 8-pound treatment with chelated zinc has not entirely corrected the condition, but has been more effective than 20 pounds of zinc sulfate.

In soils where chelated zinc is effective, benefit may be relatively lasting. Hence, several years will elapse before it is known how frequently treatment must be renewed, and thus whether it would pay to use chelated zinc to replace zinc sulfate for pecans in such soils or not.

CHELATED IRON FOR ORNAMENTAL PLANTS

Chelated iron is being increasingly used by nurserymen and gardeners to combat chlorosis in azaleas, roses, rhododendrons, and other ornamentals. Marked helpfulness of chelated metal treatments for such plants has been established in some growing situations. Where results remain uncertain, some growers are making their own small-scale tests.

ARS horticulturists have not included ornamentals in chelate research projects, but have gained some practical knowledge by applying chelated iron to ornamentals, chiefly azaleas, at the National Arboretum. The following information on azaleas would apply also to rhododendrons and gives some indication of how chelated metal may benefit other ornamentals.

Iron chlorosis in azaleas may be due to varied common causes: too much or too little water; a soil that is poorly aerated from compactness or lack of organic matter; a soil containing excessive lime which has leached from cement in a nearby building or wall; or a soil type that is by nature unfavorable to the acid-loving azalea plant. Azaleas normally get their iron requirement from moderately acid soils of 4.5 to 5.5 pH in the acid-alkaline scale. Azaleas grown in alkaline soils become so deficient in iron that remedial treatment is difficult and in calcareous soils treatment may be futile.

If the cause of an iron deficiency of azaleas cannot be corrected by adjusting the water supply, mulching, or resetting plants in a more favorable soil, chlorosis-susceptible azaleas can be kept supplied with iron by conservative treatments with chelated iron such as iron-DTPA or EDTA. It is essential to keep treatment conservative to avoid risk of burning these delicate plants.

The safest method of applying the chelated iron to azaleas is to sprinkle a mild solution--made with 1/4 to 1 pound of the chelated metal to 100 gallons of water--on the soil around the plants.

From the standpoint of azalea protection, the above mentioned method combines three safety features: mildness, liquid form, and soil application. By contrast, if dry chelated metal is applied to soil around azaleas, some heavy deposits may reach the shallow roots and burn them.

If azaleas are seriously chlorotic, several mild soil treatments are better than one strong application.

If seriously chlorotic azaleas need speedy help to survive, a spray treatment may be used. Directions for use ordinarily accompany commercial chelated metal products. A spray applied to azaleas should be kept within the lower range of recommended strength to avoid or minimize burning foliage, especially if plants are young or grown in greenhouse conditions.

The most advantageous time to apply chelated iron to azaleas is in the active growing stage. An initial small treatment at the start of active spring growth may be followed by a second treatment, if it seems needed, perhaps a month later. Small plants are most likely to need this follow-up treatment. Applying the chelated metal to azaleas in autumn is helpful only to large woody plants.

If azalea plants which have been normally green show some yellowed foliage in winter and early spring, there is no cause for immediate concern. Temporary yellowing limited to these seasons is not unusual in azaleas, and such plants are not deficient in iron. Their roots are taking up iron and the nutrient metal will reach the leaves in due time for active growth needs.

MUCH RESEARCH WORK AHEAD

Despite advances thus far, the controlled use of chelates in agriculture and the knowledge of how chelates work are still in early stages of development.

Some of the chelates that have proved beneficial for certain chlorotic plants may have wider usefulness--which can be determined only by continued tests in additional soil-plant situations. Also, the introduction of new types of chelates could re-open the possibility of using a chelated metal where those tried in the past were not promising.

Even more basic help to plant growers in overcoming plant malnutrition may come through use of chelates in studies of plants' nutrition processes and problems. Major questions about chelates and plant chlorosis that are not yet clearly answered include:

- * How do chelates function in plants?
- * What is the metabolic fate of a chelate in plant tissue?

- * What causes some chelated metal treatments to be harmful to plants?
- * What biochemical principles account for striking differences in some plant species and varieties--some able to resist chlorosis in adverse growing conditions, others weakly susceptible?
- * How can chlorosis-resistance be developed and used to strengthen the line of defense against nutrient deficiencies of plants?