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9. ABSTRACT

There are 20 elements thought to be essential in the growth of plants. Some plants need all of them, and all plants need most of them. These nutrient elements are often divided into four categories: (1) macronutrients (nitrogen, phosphorus, potassium); (2) secondary (calcium, magnesium, sulfur); (3) micronutrients (copper, zinc, iron, maganese, boron, and molybdenum); and (4) functional (chlorine, sodium, silicon, cobalt, vanadium). The micronutrients are called micro or minor only because they need be present in trace amounts--not because they are less essential than the other nutrients. Problems with micronutrients have become of increasing concern in the past 20 years, as increased crop production and fertilizer practices have left soils bereft of their natural micronutrients. This is particularly true of highly leached, weathered acid soils; soils with very high pH; soils heavily fertilized with macronutrients only; soils that have had their surfaces removed through erosion or leveling; and organic soils. The symptoms of micronutrient deficiency show up in the leaves of plants. With iron, terminal leaves first show yellowing between the veins; as severity increases, the entire leaf turns yellow. With manganese, there is gradual fading of green color along outer edges of leaves. With zinc, rosetting of the terminal growth of larger plants occurs. With copper, terminal leaves grow shorter. With molybdenum, leaves turn mottled yellow between veins, and the leaves often curl upward. With boron, symptoms vary greatly from plant to plant. Programs for correcting micronutrient deficiencies use a trial-and-error approach, because of the lack of quick, routine, and reliable soil tests. Often in cases of suspected micronutrient deficiency, a "shotgun" approach is used; a fertilizer mixture is applied which contains all of the micronutrients. Foliar sprays containing micronutrients are also used, but these entail a risk of injuring the plant foliage.

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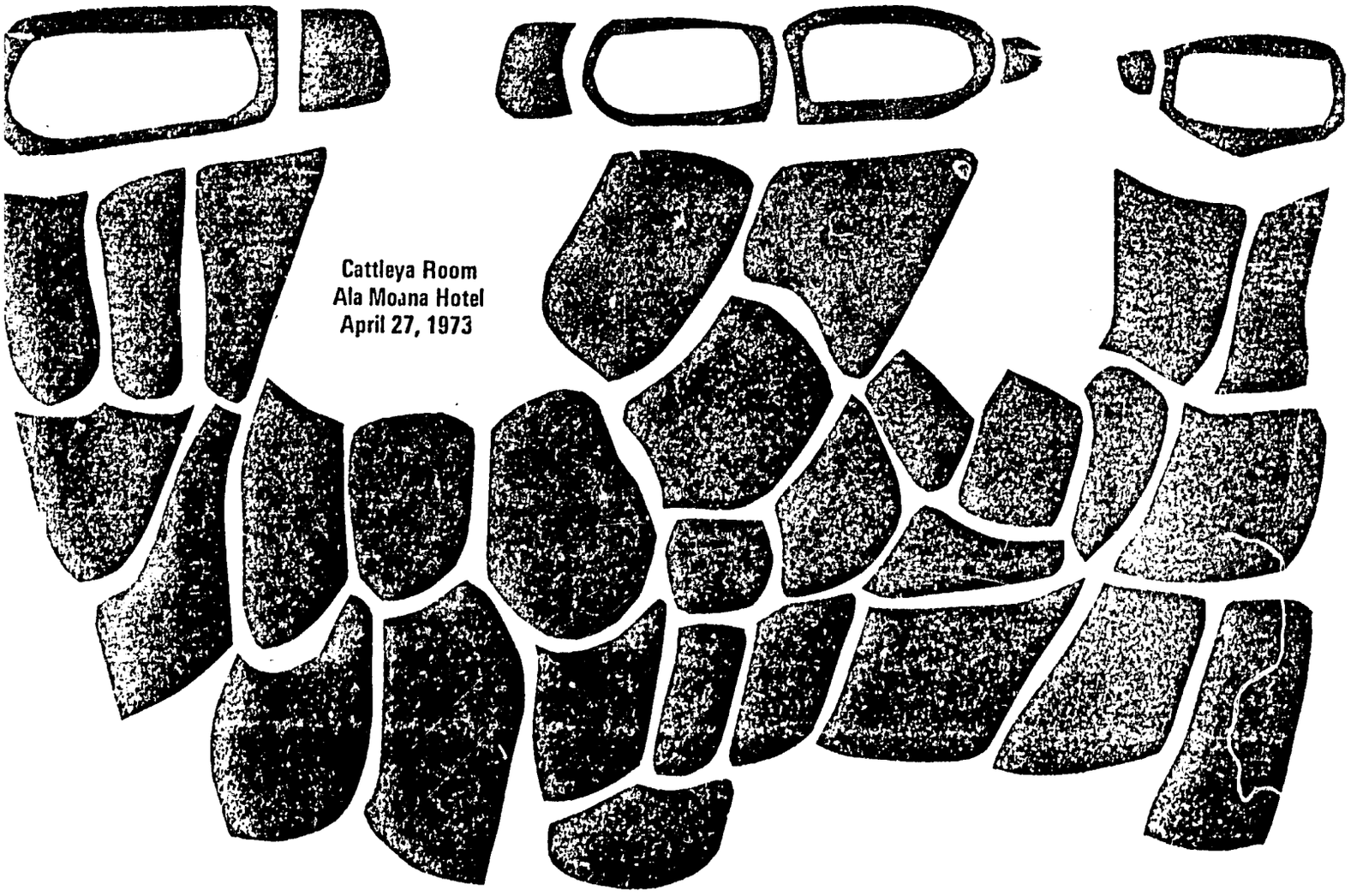

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CORRECTING MICRONUTRIENT PROBLEMS

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There are 20 elements that are thought to be essential or functional in the growth of plants. All of these elements are not required by all plants but all are needed by some plants. The plant will take up carbon, hydrogen, and oxygen from carbon dioxide and water. The remaining 17 elements are considered mineral nutrients and are ordinarily taken from the soil by the plant roots.

The nutrient elements are often divided into the following four categories: 1) macronutrients (also called "primary" or "major" nutrients) - nitrogen, phosphorus, and potassium; 2) secondary - calcium, magnesium, and sulfur; 3) micronutrients (also called "minor" or "trace" elements) - copper, zinc, iron, manganese, boron, and molybdenum; and 4) functional - chlorine, sodium, silicon, cobalt, and vanadium. Sometimes confusion arises because categories or nutrients "overlap"; for example, iron may be placed in the secondary group and chlorine with the micronutrients. For the purpose of this paper, I will restrict myself to the micronutrient category as given above.

The term "micronutrients" is today being encouraged to be used more than the term "minor elements" because the latter term connotates that the minor elements play a minor or less essential role than the macronutrient and secondary nutrient elements. In fact, the micronutrients are just as important as the macronutrients in the health and growth of plants. It is only that micronutrients are needed only in small or "trace" quantities.

Micronutrients have become of increasing concern during the past 20 years or so. This has been due to several reasons: 1) in some cases crop removal of the micronutrients has lowered their concentration in the soil below that required for normal growth; 2) improved crop varieties and fertilizer practices have greatly increased the level of production, causing the micronutrient removal; 3) the trend toward high analysis fertilizers has tended to eliminate the use of impure salts which formerly contained some micronutrients; and 4) man's increased knowledge of plant nutrition has helped in the diagnosis of micronutrient deficiencies which heretofore may have gone unnoticed. Undoubtedly, one can keep adding to this list of reasons. Most of these reasons will be directly related to the increasing demand that the farmer places on the soil in his quest for increased food and fiber production, coupled with shrinking agricultural lands.

Before helping to correct micronutrient problems, it is necessary that we first recognize some of the problems and their contributing factors. In discussing these problems, applications to Hawaii situations will be made whenever possible.

Areas and Causes of Micronutrient Deficiency

Except for iron, micronutrient elements are found in small amounts in most soils. Their availability to plants is often very low. Therefore, even though the removal by plants is small compared to the macronutrients, the cumulative effects of intensive crop production may rapidly deplete the original limited reserves. Some of the general situations where micronutrients are most likely to be a problem are: 1) highly leached, weathered acid soils; 2) very high pH (alkaline) soils; 3) soils which have been intensively cropped and heavily fertilized with macro-

nutrients only; 4) soils which have their surfaces removed through erosion or land-leveling; and 5) organic soils. In Hawaii, micronutrient deficiency is usually associated with one or more of the first four situations.

Strongly leached, acid soils tend to be low in micronutrients because acid leaching has removed much of the small quantity of these elements originally present. In soils where the surface has been removed and where the subsoil is exposed, the deficiency problem usually becomes more acute because much of the micronutrients are held in the naturally chelated form in the soil organic matter. Organic matter is, of course, much higher in the surface than in the subsoil. Table 1 shows vegetative yield and zinc concentration data on corn grown in a greenhouse test, using surface soil and subsoil from a zinc-deficient area of Paaloa soil (now classified as Tropohumults formerly Humic Latosol) in Helemano, Oahu, with and without the addition of zinc sulfate. You will note that growth (as measured by yield) was better and concentration status higher in the corn plants grown in the surface soil than in the subsoil.

High pH (alkaline) and calcareous conditions can bring about a deficiency in five (copper, zinc, iron, manganese, and boron) of the six microelements concerned. In Hawaii, a high pH situation is usually associated with coastal soils derived from coral parent material. A good example is iron deficiency found in sugarcane growing in Ewa near the beach area. Under acid conditions where the concentration of one or more of these five microelements may be high enough to be toxic to plants, liming will reduce the solubility of these ions. In the case of molybdenum, an opposite situation prevails as far as the effect of pH is concerned; that is, acid soil conditions have a depressing effect on the availability of this element. Molybdenum deficiency has been found in certain acid soils in Hawaii; e.g., alfalfa has responded to the application of molybdenum in the Wahiawa soil (now classified as a Eutrustox, formerly a Low Humic Latosol) at the Poamoho Station (Younge and Takahashi, 1953).

The oxidation state of a soil affects the valence status of three micronutrients: iron, managenese, and copper. The lower-valence states (or reduced states) are encouraged by low oxygen and high moisture conditions. High pH generally favors oxidation, while low pH favors reduction. The oxidized states of iron, manganese, and copper are generally much less soluble than the reduced states at pH values common in most soils. A combination of high pH, good drainage, and aeration in the soil sometimes causes deficiency of available iron and manganese. In Hawaii, iron deficiency is also found in acid soils under well-drained conditions, even in the presence of high amounts of total iron. This situation arises because soluble iron is rendered insoluble in the presence of higher valence oxides of manganese. Sanford (1969) presented the following oxidation-reduction reaction to show this conversion:

$$\underset{\text{Soluble Fe}}{2\,Fe^{+2}} + \underset{\text{Insoluble Mn}}{Mn^{+4}} = \underset{\text{Insoluble Fe}}{2\,Fe^{+3}} + \underset{\text{Soluble Mn}}{Mn^{+2}}$$

"Pahala blight" of sugarcane at Pahala, Island of Hawaii, has served as a classic example of manganese deficiency. With manganese, the problem in some of the Oxisol in Hawaii is one of excessive amounts (Sherman and Fujimoto, 1946). In the latter situation, liming the soil would likely be the most practical method in decreasing manganese availability in most situations. Reports on copper deficiency have been increasingly noted in recent years in the Islands. Hori (1970) reported

"soft onion", a disorder which was eliminated by the application of copper at Kula, Maui. Olney (1969) reported response to copper application with some agricultural and ornamental crops of Hawaii.

The application or the presence of large quantities of certain elements can reduce the availability of several of the micronutrients. Excessive phosphates often cause lowered iron and zinc uptake. Table 2 illustrates this situation with zinc, using corn grown in zinc-deficient Hoolehua (ψstropepts formerly Low Humic Latosol) soil (Island of Lanai), with and without high rates of phosphorus. You will note that zinc concentration keeps decreasing as the rate of phosphorus goes up in both no-zinc and 27-pound-zinc treatments. Heavy nitrogen fertilization may intensify copper deficiency. Excess copper may, in turn, together with high manganese and zinc, adversely affect molybdenum uptake. Boron deficiency is known to be accentuated by high potassium and calcium. Since micronutrients are required in small amounts, control of the quantities added is highly essential in maintaining nutrient balance.

Recognizing Micronutrient Deficiency Symptoms

Unless severe, micronutrient deficiencies are not easily detectable. One may find it necessary to evaluate growth and yield in considering the possibility of a micronutrient deficiency. Symptoms also vary from plant to plant. Furthermore, young plants displaying deficiency symptoms may outgrow these symptoms with time. This is especially true of marginal cases of deficiency. What this usually means is that, as the plant matures, there is a larger distribution of roots which, in turn, means greater accessibility to the available micronutrient. When deficiencies are severe, however, plants often exhibit characteristic symptoms. The following are some of the symptoms associated with deficiency in:

1. Iron. Terminal leaves first show yellowing between the veins, with veins remaining green. As severity increases, entire leaf turns yellow. Leaves are also much smaller than normal. Plants are spindly and weak.

2. Manganese. At first there is gradual fading of green color along outer edges of leaves. Fading moves up between major lateral veins, with veins and areas next to them remaining dark green. In severe cases, light-green color may become gray or whitish. Sometimes small necrotic spots develop on leaves.

3. Zinc. Rosetting of the terminal growth of larger types of plants occurs. This condition is also called "little leaf". Interveinal areas of leaves become mottled yellow, extending to the edge. Veins and areas next to them remain green. Plants are stunted in severe cases.

4. Copper. Terminal leaves grow short distances. There is a dieback of growing tips in severe cases. Rosetting often precedes dieback. Leaves are curled and become rolled in certain plants. In some mild cases, only edges of upper leaves dry up and plant takes on a lighter color.

5. Molybdenum. There is a mottled yellowish color between veins and around the margin of the leaf. Tissue in affected areas may die, leaving dead spots between veins and a scorched rim around the leaf margin. Leaves often curl upward, giving cupped appearance. Plant is stunted in severe cases.

6. Boron. Symptoms vary greatly from plant to plant. In some the top leaves turn red or yellow. Boron-starved plants may become stunted and appear bushy.

The color slides presented in the talk will help to illustrate these symptoms. As much as possible, examples are those of local crops and situations.

Corrective Measures

A program of corrective measures for micronutrient deficiencies is quite heavily based on a "trial and error" approach. This is because soil and plant testing and recommendations for the microelements is still more of an empirical art than a science. The lack of quick, routine and reliable soil tests, plus the lack of good interpretative data for many crops, particularly to cover various stages of growth, handicaps a recommendation program. Of late, theses needs are being increasingly recognized at the national level, as evidenced by such publications as "Soil Testing and Plant Analysis. Part I. Soil Testing. Part II. Plant Analysis", (1967) and "Micronutrients in Agriculture" (1972). These comprehensive publications resulted from two symposia sponsored by the American Society of Agronomy.

Micronutrient fertilization to correct deficiencies can be done from different approaches and methods. To cope with these differences, fertilizer manufacturers have come up with many kinds and types of fertilizers. Micronutrients can be applied: 1) as a single microelement fertilizer, 2: in a combination mixture of microelements, or 3) as a supplemental addition in a macronutrient or primary fertilizer mixture. Micronutrients can also be applied to the soils, sprayed on the plants, or applied in the irrigation water. They can also be used as the inorganic salts or as the chelated, fritted, or other forms. Let us discuss some of these corrective measures.

One way to correct micronutrient problems is to use the "shotgun mixture" approach. In this approach the idea is to have insurance against any deficiency arising by using a fertilizer mixture which contains all the micronutrients. Quite often the grower is forced to take this approach for lack of a better way. If enough interpretative soil and plant data are available, however, this approach is not recommended because this practice may risk upsetting the balance of plant nutrients in the soil. It, of course, is also wasteful if the element(s) is not needed, or it may even contribute to toxicity. Wherever possible, it is better to establish that a deficiency does exist and then to determine the effective rate to apply.

Micronutrients can be applied to the soil (broadcasted, drilled in, or in the irrigation water), or to the plant as a foliar spray. Soil application may be more desirable, practical, and economical in many situations. Under certain conditions, e.g., in an orchard where the trees are so large that movement of a spray rig becomes almost impossible, soil application may be the only practical method of application. Another advantage of soil application is that a heavier rate can be applied at a time so that frequency of applications can be reduced. Table 3 gives recommended rates from two sources. You will note that Sauchelli's recommended rates are lower than those of Buckman and Brady. I am inclined to go along with the latter rates under most Hawaii conditions. Commonly used inorganic carriers are listed in Table 5 to supply the desired microelements. There are, of course, other carriers that may be used in place of those listed. Whatever is used, however, it is important that we note the chemical formula because this will determine the percentage

of microelement found in the compound which, in turn, determines the required amount necessary to provide the desired microelement weight. For example, if Zn $SO_4.7H_2O$ (molecular weight of 287) is used as the carrier, this means that it contains 22.8 percent zinc, and it further means that it will take 4.4 pounds of Zn $SO_4.7H_2O$ to provide 1 pound of zinc. Now, if we were to use Zn $SO_4.H_2O$ (molecular weight of 179) the zinc percentage will be 36.4 and it will take 2.7 pounds of this carrier to provide the comparable 1 pound of elemental zinc.

Foliar spray is becoming more popular today. The biggest advantage is that micronutrients can be conveniently included in sprays with macronutrients and other materials, such as insecticides. Numerous examples of responses to iron, manganese, and zinc have been found and, to a lesser extent, copper, boron, and molybdenum. The recent developments in sprinkler irrigation raises the possibility of greater incorporation of micronutrients (and macronutrients) into spray-irrigation programs. Wetting agents may increase effectiveness of these sprays for most crops. Enough pressure should be supplied in the sprayer so that a fine mist can be obtained to give good coverage on the foliage. Suggested foliar application rates are given in Table 4.

Risk of injury to plant foliage sometimes accompanies foliar feeding of nutrients. There are suggested concentrations of micronutrient sprays in Table 6. The concentrations in this table should be modified, depending on local conditions, kinds of plants, stage of plant growth, and other factors. For example, spraying during midday will risk greater foliar injury than during morning hours. A hot, dry spell also intensifies this risk. Young seedlings are likewise more susceptible to injury than older established plants. Sometimes it is necessary to take stock of one's disease and pest sprays because occasionally some of these materials already contain a micronutrient, e.g., bordeaux mixture, is made up of copper sulfate and lime.

The use of chelates of iron and zinc for soil and plant applications and to a lesser extent of manganese and copper has been steadily increasing in recent years. To give you an idea of the increasing popularity and availability of chelates, Sauchelli (1969) lists five main synthetic chelating agents that are now available for agricultural and horticultural use, based on the following acids:

EDTA: Ethylenediaminetetraacetic acid.
HEEDTA: Hydroxyethylethylenediaminetriacetic acid.
DTPA: Diethylenetriaminepentaacetic acid.
EDDHA: Ethylenediamine di-*o*-hydroxyphenylacetic acid.
APCA: Amino polycarboxylic acid.

EDTA and HEEDTA have proved most effective in making iron and zinc available to plants in acid to slightly alkaline soils. DTPA and EDDHA are suitable for use in calcareous soils.

A chelate is an organic compound which combines with and protects metallic cations, including iron, zinc, manganese, and copper. These metals lose their usual ionic characteristics and, therefore, are less likely to take part in reactions with other soil constituents. The protected cations are not as subject to precipitation and other reactions; consequently, the desired metallic element remains in solution for longer periods of time, which increases its availability to the plant. Since chelated micronutrients do not behave as cations and are less reactive in both fertilizer and soil, they can be effectively incorporated into many

fertilizers that would render inorganic sources unavailable to plants. Because of these aforementioned properties, many micronutrients, especially iron and zinc, are more effective than the inorganic forms. Figure 1 shows the results of a greenhouse test with corn on the effectiveness of chelate vs. sulfate sources of zinc. The data show that vegetative yields were greater at 20- and 40-pound rates when the source was chelate as compared to the sulfate source. On the minus side of chelates is their higher cost as compared to the inorganic salts. When, however, they are compared on the basis of effectiveness, they appear quite competitive on a per acre, net cost basis (Sauchelli, 1969). Chelating agents are decomposed by sunlight (Sauchelli, 1969) and thus this becomes an important consideration in a spray program.

In additon to the inorganic salts and chelates, frits and polyflavonoids are coming into the market as sources of micronutrient fertilizers. Both of these types are classified as the slowly available type of carriers. In frits, the microelements are held in a matrix of finely ground glass particles. Micronutrients are released in the soil as the matrix disintegrates, and control over the rate of release is made possible by varying the hardness of the glass and its particle size. Polyflavonoids are byproducts of the wood pulp industry. They are water-soluble complex materials of high molecular weight. They are nonphytotoxic but are less biologically stable than are synthetic chelates. Because of these properties they are more useful as foliar sprays than as supplements to soil-applied fertilizers.

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Table 1. Vegetative yield and zinc analysis of corn grown in surface and subsoil (Paaloa Silty Clay)

Treatment	Surface soil	Subsoil
No Zn		
Veg. yield (g/pot)	22	10
Zn (ppm)	25	16
18 lb. Zn		
Veg. yield (g/pot)	33	23
Zn (ppm)	38	29

Table 2. Effect of phosphorus and zinc on the zinc Content (ppm) of corn grown in Hoolehua Soil (average of three replicates)

lb/acre	P, lb/acre 0	430	1308	Sig. diff. for Zn treatments
0	14.3	10.3	7.0	
27	37.3	27.3	18.7	7.2
Sig. diff. for P treatments				8.9

Table 3. Common micronutrient fertilizer rates for soil application

Micronutrient	lb/acre (expressed as the element) Buckman and Brady[1]	Sauchelli[2]
Iron	15 - 50	0.5 - 10.0
Manganese	15 - 30	0.3 - 20.0
Zinc	5 - 50	0.35 - 20.0
Copper	2 - 50	1.2 - 25.0
Boron	5 - 30	0.25 - 10.0
Molybdenum	1 oz - 2	0.02 - 0.4

Table 4. Micronutrients to apply as sprays. (High volume: 50-150 gal/acre)[3]

Micronutrient	lb/acre (expressed as element)
Iron	4 - 12
Manganese	1 - 2
Zinc	0.3 - 0.7
Copper	0.3 - 0.5
Boron	0.1 - 0.5
Molybdenum	0,05 - 0.1

1/Buckman, H. O. and Brady, N. C. 1969. The Nature and Properties of Soils. The Macmillan Company. New York.

2/Sauchelli, V. 1969. Trace Elements in Agriculture. Van Nostrand Reinhold Co. New York.

3/Wittwer, S. H. 1967. Foliar Application of Nutrients. Plant Food Review. Vol. 13, No. 2, p. 14

Table 5. Commonly used carriers to supply micronutrient elements and the amounts needed to supply a pound of the micronutrient element.

Micronutrients	Form used by plant	Symbol of form	Commonly used carrier1/	Chemical formula	% micronutrient element in carrier	Pounds of carrier needed to give 1 lb. of element
Iron	Cation	Fe^{++}	Iron sulfate	$Fe\ SO_4.7H_2O$	20.1	5.0
Manganese	Cation	Mn^{++}	Manganese sulfate	$Mn\ SO_4$	36.4	2.8
Zinc	Cation	Zn^{++}	Zinc sulfate	$Zn\ SO_4.7H_2O$	22.8	4.4
Copper	Cation	Cu^{++}	Copper sulfate	$Cu\ SO_4.5H_2O$	25.4	3.9
Boron	Anion	$B_4O_7^{--}$	Sodium tetraborate ("borax")	$Na_2B_4O_7.10H_2O$	28.3	3.5
Molybdenum	Anion	MoO_4^{--}	Sodium molybdate	Na_2MoO_4	46.3	2.2

1/Other carriers may, of course, be used to supply the desired micronutrient element. It is also important to note the chemical formula of a carrier (e.g., "zinc sulfate" can be marketed as: 1) $Zn\ SO_4.7H_2O$; 2) $Zn\ SO_4.H_2O$; or 3) $Zn\ SO_4$), since the chemical formula will determine the values in the two right columns.

Table 6. Suggested concentrations of micronutrient sprays

Micronutrient	Carrier	lb/100 gal water
Iron	Iron sulfate	1 - 10
Manganese	Manganese sulfate	3
Zinc	Zinc sulfate	2
Boron	Sodium tetraborate ("borax")	0.5
Molybdenum	Sodium molybdate	0.2
Copper	Copper sulfate	2

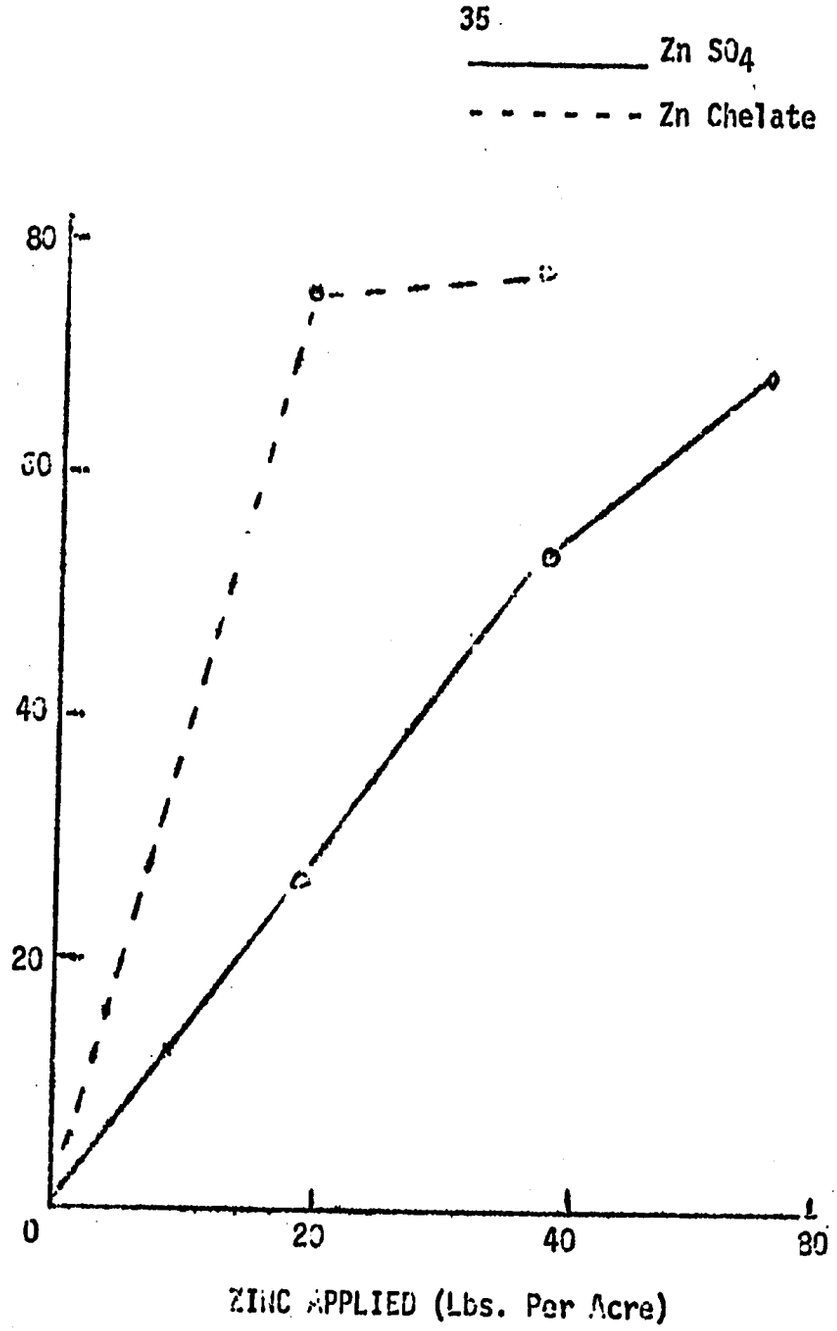

Figure 1. Effect of two sources of zinc on dry matter yield of corn. 1/

1/Md. T. Ahmed. A study on the effect of chelates and chelating agents in releasing zinc and other micronutrients in Hawaiian soils. M.S. Thesis 1969, University of Hawaii. Honolulu. HI.