## CHAPTER 10

# Micronutrients

A number of elements that are required by plants in very small quantities are known as micronutrients or *trace* elements. This term usually applies to elements that are contained in plant tissues in amounts less than 100 mg/kg. Although trace elements have been known to affect plant growth for many years, they have been studied intensively since 1950. When other growth factors kept yields at relatively low levels, seldom did micronutrients limit growth and yield. But with the advent of modern fertilizer technology, irrigation, and new varieties, came very high yield potentials. Micronutrient supplies in soils that were adequate for 40, 50, or even 100 bushels of corn per acre were not adequate for yields of 200 or more. Thus, the need to study soil fertility from the micronutrient standpoint became more pressing.

Our ability to study micronutrients has always been closely tied to our analytical capabilities. Although colorimetric methods have existed for many of the micronutrients, they were laborious and often subject to a variety of interferences. When atomic absorption spectrophotometry became common in the early 1960s, it lent itself well to determinations of the trace metals Zn, Cu, Mn, and Fe, as well as other trace metals, such as cadmium and nickel which are potentially toxic. Inductively coupled plasma emission spectrographs gave us the ability to analyze for many elements at the same time, thus greatly reducing the cost of analysis.

## 10.1 CLASSIFICATION OF MICRONUTRIENTS AND TRACE ELEMENTS

The micronutrients that are essential for plant growth are zinc, copper, iron, manganese, boron, molybdenum, and chlorine. Others such as vanadium, sodium, nickel, cobalt, and silicon may have some function in plant growth. It is obviously very difficult to purify all growth media to the point of proving essentially for a trace element. Consequently, others may be added to this list at a later date. The term *trace element* may be more applicable in the discussion of certain metals that are essential for animal growth or in fact toxic to either plants or animals.

Certain trace elements are essential for animal growth and generally are furnished to the animals (including human beings) by the plant material consumed. Included in this list would be cobalt, chromium, selenium, iodine, and perhaps tin and nickel. Other elements are known to be toxic to plants, animals, or both. These include mercury, lead, and cadmium. For many others, the levels will determine the toxicity or beneficial nature of the element. For example, chromium, which is required in very low levels for animal growth, may enhance plant growth under some conditions. But chromium can be quite toxic to both plants and animals if present in very high levels.

A complete discussion of all trace elements is beyond the scope of this text.* We will focus here on the identification of soils and cropping systems that are likely to be infertile because of micronutrient deficiencies. We will also discuss how to identify and correct the deficiencies. The elements covered will be Zn, Cu, Fe, Mn, B, and Mo.

### 10.1.1 Essential Micronutrients

Of the six essential micronutrients that we will discuss, four — Cu, Zn, Mn, and Fe — exist as cations in soils and two — B and Mo — exist as anions or uncharged molecular species. The discussion will reflect these differences. A general diagram reflecting the different pathways that micronutrients may take in soils is given in Figure 10.1.

The importance of a particular pathway will depend on the micronutrient and the particular soil. Each may be added to the soil's pool of soluble micronutrients by weathering of minerals, by mineralization of organic matter, or by addition as a soluble salt. Once in the soil as a soluble nutrient, the micronutrient may undergo a number of reactions. Many of the micronutrients will readily precipitate in soils. A given micronutrient may be absorbed by a plant or microorganism. Crop harvest obviously removes micronutrients from the system. Micronutrients are also incorporated into humus, which is formed as plant residues are digested by microorganisms. This process immobilizes micronutrients just as it does other nutrients.

Adsorption of micronutrients, either by soil organic matter or by clay-size inorganic soil components, is an important mechanism of removing micronutrients from the soil solution. Finally, micronutrients may leach from soils. But generally, leaching is a minor component of the mechanisms by which micronutrients are removed from the soil solution.

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* For those interested, *Applied Soil Trace Elements*, B.E. Davies (Ed.), 1980, and *Micronutrients in Agriculture*, No. 4, J.J. Mortvedt et al. (Eds.), SSSA, Madison, WI, are recommended.

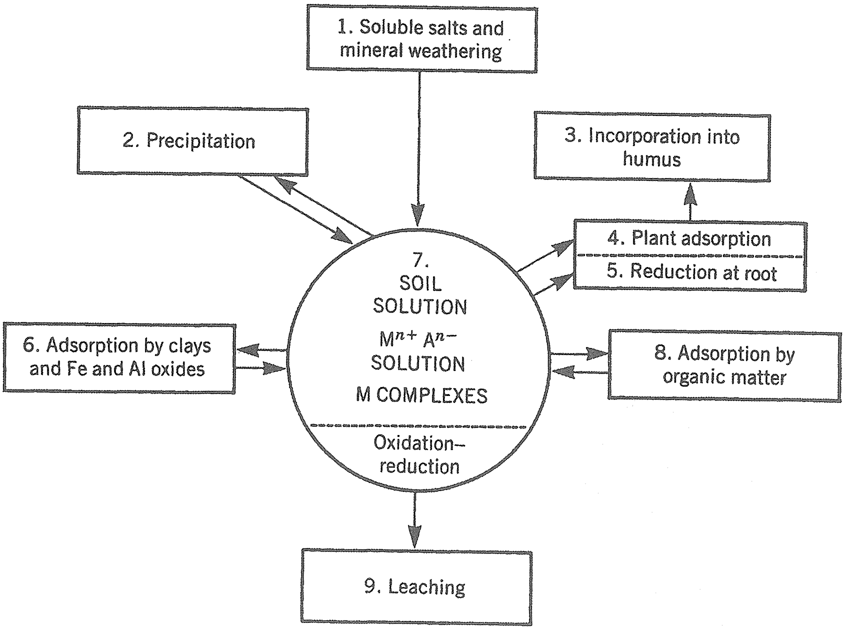

**Figure 10.1** The general cycle for micronutrients in soils.

## 10.2 COPPER AND ZINC

Both Cu and Zn occur in the earth's crust primarily as sulfide minerals. Igneous rocks contain larger amounts of Cu and Zn than do sedimentary rocks, and both elements concentrate more in basalt than in granite. The earth's crust contains on the average 55 ppm Cu and 70 ppm Zn. Soils commonly vary in total elemental content from 2 to 100 ppm Cu and from 10 to 300 ppm Zn.

### 10.2.1 Copper

Except for copper's occurrence in certain primary minerals, it is bound stronger by adsorption, principally by organic matter, as shown by reaction 8 in Figure 10.1, than by precipitation. Thus, profile distributions of Cu tend to follow the organic matter distribution, with higher concentrations in the surface horizon. These distributions reflect increases in Cu in horizons that have accumulated organic matter (as in spodic horizons). It has been shown that carboxyl and phenol groups are important as the functional groups binding Cu to soil organic matter. Copper is more strongly bound by organic matter than other metals, with the exception of Fe and Al.

The role of organic matter in Cu chemistry is also indicated by analysis of the soil solution. Greater than 99% of the Cu in the soil solution is complexed by organic matter. This complexing is of great importance in maintaining adequate

Cu in solution for plant utilization. Of the inorganic forms of Cu, $Cu^{2+}$ is the major ion form if the solution pH is less than 6.9. The major ion pair is $Cu(OH)_2^0$ if pH is above 6.8. Although $CuOH^+$ does form, it is never significant relative to the other two species.

Deficiencies of Cu are not commonly found in mineral soils. Organic soils (Histosols) containing little ash are more likely to be deficient. When organic soils are deficient, any one of a number of Cu carriers are satisfactory. Some of the common carriers are listed in Table 10.1. The initial application of Cu should be banded at the rate of 6 pounds/acre. Because Cu accumulates in soils, no additional amount need be added for crops that respond little to Cu after 20 pounds/acre has been applied over a period of years. This amount needs to be doubled for highly responsive crops.

**Table 10.1 Examples of Copper Carriers**

| Carrier | Formula | Percent Cu |
|---|---|---|
| Basic copper sulfate | $xCuSO_4 \cdot yCu(OH)_2$ | 13–53 |
| Copper sulfate | $CuSO_4 \cdot H_2O$ | 35 |
| Cupric ammonium phosphate | $Cu(NH_4)PO_4 \cdot H_2O$ | 32 |
| Copper EDTA chelate | $Na_2CuEDTA$ | 13 |
| Copper HEDTA chelate | NaCuHEDTA | 9 |
| Copper frit | Frit | 40–50 |
| Cupric oxide | CuO | 75 |
| Cuprous oxide | $Cu_2O$ | 89 |
| Copper chloride | $CuCl_2$ | 17 |

*Source:* Robertson, Warncke, and Knezek, 1981.

If Cu deficiency is found during the growing season, foliar sprays can be used at one-half to one pound Cu per acre, dissolved in 30 gallons of water. Common carriers for this purpose are $CuSO_4$ and CuO. Chelated forms of Cu are well adapted to foliar application. The Cu chelates used at sprays should be applied at the rate of about 35 g Cu/acre dissolved in 30 gallons of water.

### 10.2.2 Zinc

Much data has accumulated indicating a decrease in solubility of Zn with increasing pH. But precise identification of a solid phase which controls Zn solubility has been difficult. However, Zn uptake by plants declines rapidly as pH increases (Figure 10.2). Of the inorganic Zn species in soil solution, $Zn^{2+}$ is the predominant one for pH less than 7.7, and $ZnOH^+$ is the predominant species for pH between 7.7 and 9.1. The ion pair $Zn(OH)_2^0$ is only important for pHs above 9. Organic matter does complex Zn in soil solution, but the percentage of the Zn that is complexed varies over a considerable range, from 28 to 99 with a mean of 60 for 20 soils, according to one study.

The importance of organic matter in maintaining available Zn in soils is often illustrated by Zn deficiency, which appears in areas where the surface soil has been removed, either by leveling in preparation for irrigation or during the

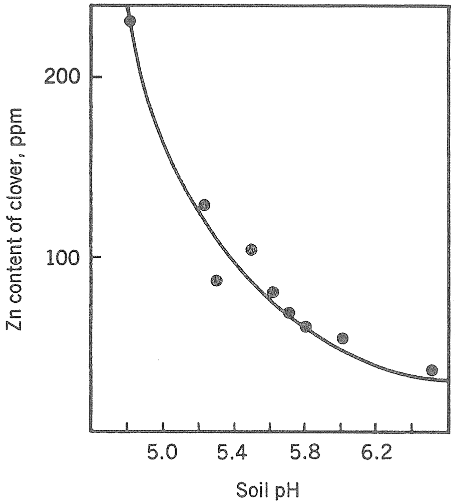

**Figure 10.2** The relation between the zinc content of clover and soil pH.

installation of tile drainage lines. Here the effect may also be due to increased pH, since removal of the surface layer very often exposes calcareous B and C horizons.

High levels of P in soils have been known to intensify Zn deficiency in a number of crops. It was particularly noticeable in rotations of navy beans, a crop susceptible to Zn deficiency, followed by sugar beets, a crop that responds to high levels of P fertilization. Data illustrating this are given in Table 10.2.

**Table 10.2 Interaction of Phosphorus and Zinc with Navy Bean Yield**

| | | Yield of navy beans, bushels/acre | | |
|---|---|---|---|---|
| Zinc, pounds/acre | Carrier | No extra P | 174 extra P | 696 extra P |
| None | — | 30.8 | 20.0 | 8.8 |
| 4.0 | Zinc sulfate | 39.1 | 39.8 | 34.6 |
| 4.0 | Residual (1 yr) | 29.7 | 24.3 | 12.1 |

*Source:* Judy, Lessman, Rozycka et al., 1964.

The exact cause of the Zn-P antagonism has been difficult to determine. But several factors are important from a soil fertility standpoint. The Zn-P antagonism occurs on calcareous soils and may be related to Fe availability. Moreover, this relationship may not be a soil relationship but one within the plant itself. Applications of Zn will readily overcome the P-induced Zn deficiency. The Zn applications show a considerable residual effect, indicating that total available Zn in the soil is very important in preventing Zn deficiency (Table 10.3).

The experiment was initiated in 1965, but severe drought in the summer of 1965 eliminated yields that year. Residual Zn was very effective in increasing yield, not only through the three years recorded here but for several additional years. The lower yield for the 3 pounds/acre of Zn banded yearly for this site

**Table 10.3 Effect of Residual Zinc on Yield of Pea Beans**

| Zinc, pounds/acre | Carrier | Time of application | Crop yield, bushels/acre 1966 | 1967 |
|---|---|---|---|---|
| None | — | | 4.2 | 0 |
| 3.0 | $ZnSO_4$ | Yearly | 17.1 | 3.7 |
| 25 | $ZnSO_4$ | 1965 | 19.9 | 19.0 |
| 122 | Clinker | 1965 | 17.7 | 18.6 |

*Source:* Brinkerhoff et al., 1966, 1967, and Vinande et al., 1968.

shows that this rate of Zn was not adequate for this very Zn-deficient soil. Other data have shown that banding Zn is a satisfactory method of supplying it if sufficient quantity is used.

Carriers for Zn are given in Table 10.4. Inorganic carriers have been satisfactory for correction of Zn deficiency. If the less-soluble forms of Zn such as ZnO are used, they should be finely ground. There is considerable evidence that the less soluble carriers should be broadcast and incorporated into the soil, whereas the soluble carriers, such as $ZnSO_4$ and Zn chelates, should be banded with starter fertilizer at planting time. Rates of 3 to 4 pounds/acre of Zn as inorganic carriers band applied with a starter fertilizer each year are satisfactory. Chelated material may be applied at one-fifth the rate of the inorganic carriers. A single broadcast application of 25 pounds of Zn/acre appears to be adequate for many years.

**Table 10.4 Examples of Zinc Carriers**

| Carrier | Formula | Percent Zn |
|---|---|---|
| Zinc sulfate | $ZnSO_4 \cdot H_2O$ | 36 |
| Zinc oxide | ZnO | 78–80 |
| Zinc carbonate | $ZnCO_3$ | 52–56 |
| Zinc EDTA chelate | $Na_2ZnEDTA$ | 14 |
| Zinc HEDTA chelate | NaZnHEDTA | 9 |
| Raplex zinc | ZnPF | 10 |

*Source:* Robertson and Lucas, 1976.

Considerable success has been obtained by incorporating Zn in starter fertilizers. For example, ZnO incorporated into ammonium polyphosphate becomes soluble and available to plants. Although trace elements, such as Zn, have been found to be beneficial in stabilizing APP liquid fertilizers, we must question the use of high-P starter fertilizer as a carrier of Zn in field situations in which the Zn deficiency is induced by high-P soil levels.

## 10.3 MANGANESE AND IRON

To a certain extent, Mn and Fe have similar chemistries in soils. Both will exist in more than one oxidation state: $Fe^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Mn^{3+}$, $Mn^{4+}$; consequently, both are affected by drainage conditions of the soils. Both are precipitated as oxides and hydroxides, but Fe forms far less soluble compounds. The total concentration of Mn and Fe in soil solution is increased by complexing with colloidal organic matter.

### 10.3.1 Manganese

In well-aerated, high-pH soils, Mn is expected to precipitate as $MnO_2$ and is removed from solution as shown by reaction 2 of Figure 10.1. But as pH decreases, $MnCO_3$ becomes the more stable phase. Here a paradox develops since high $CO_2$ levels develop in soils when drainage is poor, which decreases the solubility of Mn due to precipitation of $MnCO_3$. But on the other hand, poor aeration favors the reduction of $Mn^{4+}$ to $Mn^{2+}$ and reduced Mn compounds are more soluble.

Soluble Mn is thought to be in the form of $Mn^{2+}$ but it has been shown that 80 to 90% of the Mn in soil solution is complexed with organic matter. Steam sterilization reportedly makes Mn more soluble because it reduces and hydrates Mn compounds. It is true that steam sterilization releases Mn, but the reason appears to be that steam alters the functional groups on organic matter. We do not know whether altering the functional groups releases more colloidal organic matter to soil solution, which is capable of chelating Mn, or whether it reduces the soils ability to adsorb Mn (Table 10.5).

**Table 10.5 Effect of Steam Treatment on Change in Mn Fractions of a Houghton Muck**

| Mn added ppm | Time before extraction days | Steam treatment | Change in Mn extracted, ppm | | |
|---|---|---|---|---|---|
| | | | Water | Exchangeable | Easily reducible |
| 0 | — | 5 hours | 3.0 | 18 | −8.5 |
| 800 | 0 | none | 49 | 324 | 107 |
| 800 | 35 | none | 0 | 0.4 | 216 |
| 800 | 35 | 5 hours before extraction | 50 | 342 | 101 |
| 800 | 35 | 5 hours before Mn addition | 28 | 299 | 138 |

*Source:* Calculated from data of Kozakiewicz and Ellis as given in *Applied Soil Trace Elements,* 1980, Brian E. Davies, Ed., John Wiley & Sons, New York.

The availability of Mn in the field has always been difficult to predict. A number of reasons may account for this. Since Mn solubility is related to oxidation-reduction reactions in the soil, the availability of Mn is closely related to weather. Cool temperatures may slow down the mineralization of organic Mn. On the other hand, cool temperatures associated with high levels of rainfall in early spring may keep more Mn available due to reduction of Mn oxides.

There is an interaction between Mn and Fe. High levels of available Fe in organic soils or high levels of organic matter in sands may lead to Mn deficiency because of the high ratio of Fe to Mn within the plant. This ratio is particularly important since certain chelated Mn carriers will actually make the situation worse rather than correcting Mn deficiency. Data in Table 10.6 shows that the application of as little as one pound Mn per acre as MnEDTA actually reduced the yield of soybeans by about 50%. Similar data were observed for onions. The reason is that the soil had high levels of available Fe and low levels of available Mn. The Mn added as the chelate readily dissociated and was apparently rendered unavailable, leaving the chelate to complex more Fe, thereby increasing the available Fe.

**Table 10.6 Interactions Between Manganese Carriers, Soil pH and Yield of Soybeans**

| Mn treatments | | Planting time fertilizer | Yield of soybeans, bushels/acre | |
|---|---|---|---|---|
| Mn, pounds/acre | Carrier | | pH 6.4 | pH 7.5 |
| 0 | None | Acid | 19.2 | 22.1 |
| 10 | $MnSO_4$ | Acid | 30.8 | 30.1 |
| 1 | MnEDTA | Acid | 17.2 | 24.1 |
| 0 | None | Neutral | 19.2 | 24.0 |
| 10 | $MnSO_4$ | Neutral | 23.7 | 30.9 |
| 1 | MnEDTA | Neutral | 10.9 | 13.4 |

*Source:* Rumpel et al., 1967.

A number of Mn carriers may be used to correct Mn deficiency as shown in Table 10.7. Manganese sulfate has been the most satisfactory material for most situations. The inorganic carriers MnO and Mn frit are not water-soluble carriers and must be finely ground to be satisfactory; finer than 100-mesh is essential and finer than 300-mesh is desirable. MnEDTA is not satisfactory for organic soils and sands high in organic matter that may contain a high ratio of available Fe to Mn.

**Table 10.7 Examples of Manganese Carriers**

| Carrier | Formula | Percent Mn |
|---|---|---|
| Manganese sulfate | $MnSO_4 \cdot 3H_2O$ | 26–28 |
| Manganous oxide | MnO | 41–68 |
| Manganese frit | Frit | 35 |
| Manganese EDTA chelate | MnEDTA | 12 |
| Various other organic Manganese complexes | Mn-organic | 5–12 |

*Source:* Robertson and Lucas, 1976.

The recommended rate of Mn application when Mn deficiency is suspected varies with soil pH and mineral content. Generally, if soil pH is above 6.5, from 4 to 8 pounds/acre of Mn is recommended for mineral soils. If pH is from 6.0 to 6.5, from 4 to 6 pounds of Mn is adequate. In all cases the Mn should be band-placed at planting time for best results. For organic soils, if soil pH is above 6.4 an application of from 4 to 16 pounds of Mn/acre is recommended, depending upon the severity of the deficiency. If the pH is from 5.8 to 6.4, then 4 to 12 pounds of Mn per acre is recommended. Foliar sprays with Mn may also be used if they are compatible with other spraying programs or if the Mn deficiency appears after the crop is planted.

### 10.3.2 Iron

Few, if any, soils are deficient in total Fe since the total Fe content of soils varies from 1,000 to 10,000 ppm. But the solubility of Fe in soils may be limited by the low solubility of Fe hydroxides and Fe oxides in the pH range in which crops are grown.

Soil conditions which lead to Fe deficiency in plants include pHs above 7.0, low moisture content, and low organic matter content. These conditions are encountered in the more arid western states of the U.S. When Fe deficiency is seen in other areas, for example in the north-central region of the U.S., it is normally associated with removal of the surface soil and exposure of calcareous subsoils. In these areas, iron-inefficient species, pin oaks for example, may exhibit severe Fe deficiency.

Because of the very limited quantity of $Fe^{3+}$ ions in the soil solution of calcareous soils, it is obvious that organic matter must play a significant role in keeping Fe in soil solution by forming very strong Fe-organic matter complexes. Plants then obtain Fe from these complexes by reducing the $Fe^{3+}$ to $Fe^{2+}$ at the root surface, as shown in reaction 5 of Figure 10.1, and thereby freeing the Fe from the organic complex.

The rate of reduction of ferric to ferrous iron has been found to be greatly increased when a plant is under Fe stress. Staining techniques have been developed to reveal the location of active Fe-reducing sites (Bell et al., 1988). Figure 10.3 shows that the active sites in tomato plants are on the younger root hairs located either on lateral or near the tip of the primary root. As is evident, the plants that are grown without Fe and with P added show much more of the staining. A high magnification of lateral root hairs confirms that the site of the reduction is on the root hair and not on the epidermal cells between the root hairs (Figure 10.4). The dark staining indicates intense activity on these root hairs of an Fe-stressed plant. The plant's ability to respond to Fe-deficient conditions by becoming able to reduce $Fe^{3+}$ at the root surface is remarkable and undoubtedly accounts for the rather low number of soils that produce plants with an Fe deficiency in the field, even under calcareous conditions.

Correcting an Fe deficiency is very difficult because it is caused by chemical conditions within the soil and not from low total Fe content. If soluble Fe is added to the soil, it is very quickly precipitated and then is not available to plants. Consequently, treatment of the deficiency must be limited to acidification of the soil, thereby solubilizing some of the Fe present. It is also possible to add Fe as a chelate that is so stable that it does not dissociate in the soil. Spraying plants with a soluble Fe source is another possible Fe treatment.

The chelates FeEDDHA and FeHEDTA are satisfactory under many soil conditions. Soluble carriers are useful for spraying Fe-deficient plants. Some information about these carriers is given in Table 10.8.

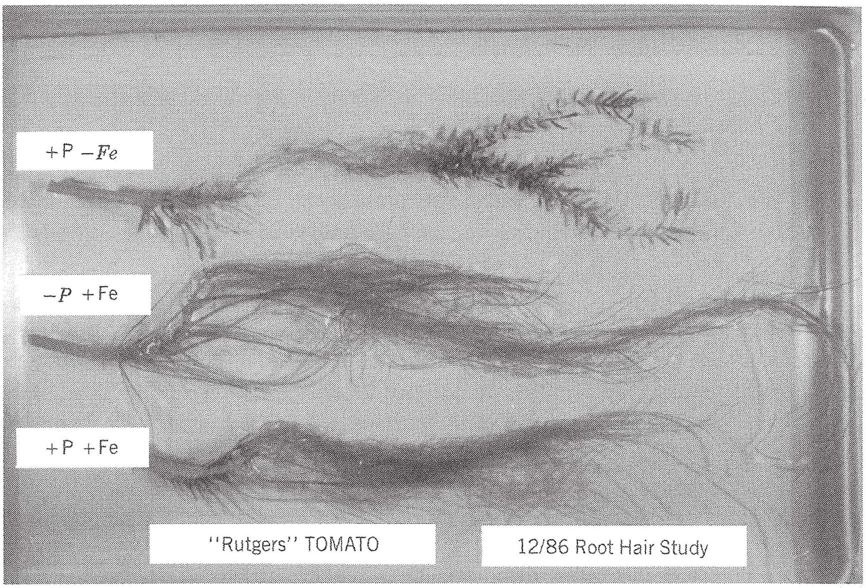

**Figure 10.3** Tomato roots showing the location of iron reduction sites in response to iron stress in plants. Notice the staining of the lateral roots (darker areas) on the −Fe plants. (Photograph courtesy P. F. Bell and R. L. Chaney. University of Maryland, the USDA, Beltsville.)

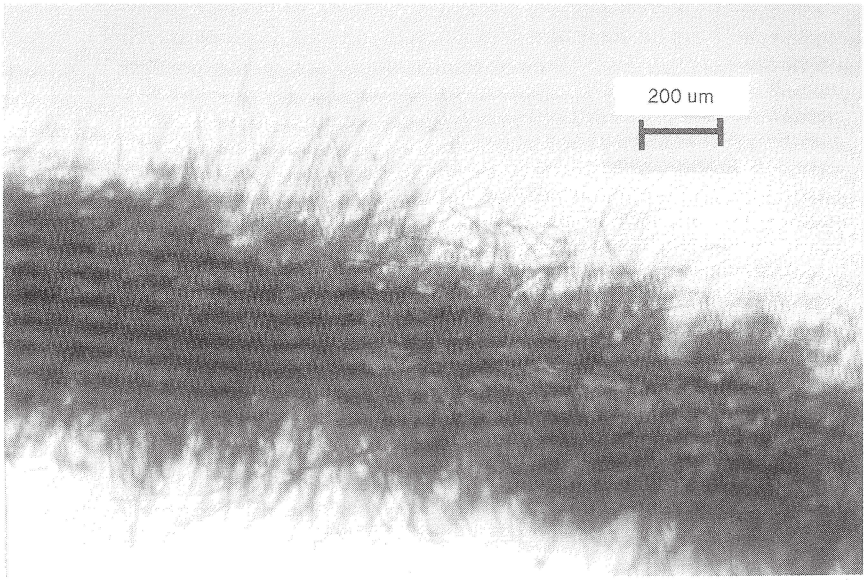

**Figure 10.4** A close-up of iron-stressed lateral root hairs. Notice the staining on the root hairs but not the epidermal cells between the root hairs. (Photograph courtesy P. F. Bell and R. L. Chaney. University of Maryland, the USDA, Beltsville.)

**Table 10.8 Examples of Iron Carriers**

| Carrier | Formula | Percent Fe |
|---|---|---|
| Ferrous ammonium phosphate | $Fe(NH_4)PO_4 \cdot H_2O$ | 29 |
| Ferrous sulfate | $Fe_2(SO_4)_3 \cdot 4H_2O$ | 23 |
| Fe chelates | FeEDTA | 9–12 |
| | FeHEDTA | 5–9 |
| | FeEDDHA | 6 |

*Source:* Robertson, Warncke, and Knezek, 1981.

## 10.4 BORON AND MOLYBDENUM

Boron and molybdenum are unique micronutrients because they exist in the soil as either anions or uncharged molecules. Because they take these two forms, their chemistry in the soil and factors that affect their availability are quite different from those of the other micronutrients. Both B and Mo, however, are much more strongly adsorbed by soils than other anions, such as $Cl^-$ or $NO_3^-$.

### 10.4.1 Boron

Boron exists as undissociated $H_3BO_3$ or as the anion $B(OH)_4^-$ in soils and in soil solution. Either form should be mobile in the soil solution. But both forms are adsorbed strongly by either Fe or Al hydroxides. Freshly precipitated Fe or Al hydroxides are known to adsorb much more B than the hydroxides that have aged and crystallized. The bonding is through the hydroxyls at the surface of the precipitated Fe or Al hydroxides. Hence, the more crystalline the hydroxides, the fewer the number of exposed hydroxals per unit weight of hydroxide. Micaceous clay minerals also adsorb B. Magnesium hydroxides and coatings of other minerals that contain Fe, Al, or Mg hydroxides will adsorb B.

Boron deficiency is often accentuated when soil contains little moisture. Consequently, symptoms of B deficiency will very often be observed during dry periods, but after the soils are brought back to field capacity by rain, the new growth will not show B deficiency.

In addition to deficiencies of B, toxicities must also be considered. Boron may be added in irrigation waters or in sludges and wastewaters. Toxicities are very crop dependent; thus, beans may show severe toxicity, whereas sugar beets, under the same conditions, will not show toxicity. A number of B carriers are shown in Table 10.9.

### 10.4.2 Molybdenum

Concentrations of Mo in soils are very low. Its availability is generally limited by adsorption of $MoO_4^{2-}$ rather than by precipitation. Hydrous Fe oxides and hydroxides are known to adsorb Mo strongly, which undoubtedly explains why Mo deficiencies most often occur on very acid soils. In fact, liming alone will

**Table 10.9 Examples of Boron Carriers**

| Carrier | Formula | Percent B |
|---|---|---|
| Borax | $Na_2B_4O_7 \cdot 10H_2O$ | 11 |
| Boric acid | $H_3BO_3$ | 17 |
| Sodium pentaborate | $Na_2B_{10}O_{16} \cdot 10H_2O$ | 18 |
| Sodium tetraborate | $Na_2B_4O_7$ | 20 |
| Sodium tetraborate pentahydrate | $Na_2B_4O_7 \cdot 5H_2O$ | 14 |
| Boron frits | Frits | 10–17 |

*Source:* Robertson, Lucas, and Christenson, 1981.

generally correct Mo deficiency. But in certain areas of the world where lime is not available, a few ounces per acre of Mo will substitute for many tons of lime.

Carriers for Mo are listed in Table 10.10. Usually about one-eight to one-quarter pound/acre of Mo is adequate to correct Mo deficiency. Since this small quantity of Mo is very difficult to spread evenly, it is better to incorporate Mo with other fertilizer or to use it as a seed coating.

**Table 10.10 Examples of Molybdenum Carriers**

| Carrier | Formula | Mo, percent |
|---|---|---|
| Ammonium molybdate | $(NH_4)_6Mo_7O_{24} \cdot 2H_2O$ | 54 |
| Sodium molybdate | $Na_2MoO_4 \cdot 2H_2O$ | 39 |
| Molybdenum trioxide | $MoO_3$ | 66 |

*Source:* Robertson, Warncke, and Knezek, 1981.

## 10.5 TRACE ELEMENTS THAT MAY BE TOXIC

A number of the micronutrients and other trace element may be toxic to plants, to animals, or to both. There are soils that naturally have large quantities of what are usually trace elements, for example Se. These soils may pose a threat because of this naturally high level of a particular trace element. The number of acres affected naturally is rather few, but in the case of Se, many soils in the western U.S. naturally contain large quantities.

Manufacturing processes have left waste materials that have high levels of many elements including Zn, Cu, Cd, Ni, Cr, Hg, Pb, and others. A few of these will be discussed to illustrate problems and questions which may come up when sludge is utilized as part of a soil fertility program.

Either municipal sludge or sludge generated as a waste product of industry may be available for disposal on land or for recycling on agricultural land to obtain benefit from one or more components of the waste material. The question that arises is whether we can safely use the waste material and obtain a benefit from it. Several rules should be followed before using a waste product. It must be analyzed to determine its exact composition. Normally N in sludges will be similar to N in manure in availability and may be used to advantage. Phosphorus and other nutrients, if needed by the soil, may also be beneficial. Occasionally micronutrients such as Zn may be needed, and sludges can furnish those.

Sludges or waste material will contain other trace metals that are not needed by crops and are potentially toxic. Here the question is how much can be applied to soils before they become a problem. Guides for soil loading have been defined and then redefined as more research data becomes available. Early guides for soil loading based on soil CEC were issued. These and more recent guides are given in Table 10.11. Loading with Pb is much more restricted under the newer guidelines. The other metals are much less restricted. State and local regulations may be more restrictive than the EPA guidelines.

**Table 10.11 Total Amount of Metals Suggested for Agricultural Soils Treated with Sewage Sludge**

| | Maximum amount of metal, pounds/acre Soil Cation Exchange Capacity (me/100g) | | | 503 Cumulative loading rate pounds/acre |
|---|---|---|---|---|
| Metal | less than 5 | 5–15 | >15 | |
| Lead | 500 | 1,000 | 2,000 | 270 |
| Zinc | 250 | 500 | 1,000 | 2,520 |
| Copper | 125 | 250 | 500 | 1,350 |
| Nickel | 50 | 100 | 200 | 380 |
| Cadmium | 5 | 5 | 5 | 35 |

*Source:* Jacobs, 1981. 503.13 CFR amendments to title 40, Feb. 19, 1993.

Certain metals, such as Zn, are not particularly toxic to plants or animals. Consequently, the soil can tolerate a considerable loading with little problem. For example, 503 CFR allows 2,520 pounds/acre cumulative loading of Zn. A heavy loading of Zn and other metals should be accompanied with pH control to maintain pH above 6.5, which will minimize the solubility of the metal. It should also be noted that certain crops may be susceptible to high soil Zn levels.

Other metals, Cd in particular, must be restricted because they are potentially toxic. Cd is a known carcinogen. Furthermore, it readily moves from the soil to the plant root and is easily absorbed by plants. Thus, even relatively low levels in soils becomes a threat to people consuming the food grown on that soil. Very careful control of applications of Cd are essential. The Environmental Protection Agency initially took a very conservative view and restricted Cd to 4.5 pounds/acre total loading. After extensive research, this has been extended to 35 pounds/acre. Lead, although very toxic if consumed, is strongly held by soils and does not solubilize and move readily plant into roots. This means that Pb and Hg may be applied to soils in larger quantities than Cd.

Chromium presents an interesting case. The form used in industry is generally $Cr^{+6}$. In this form, Cr combines with oxygen and exists as $Cr(OH)_4^{2-}$, which is toxic to both plants and animals. Since it is an anion, it is mobile in the soil. If $Cr(OH)_4^{2-}$ is applied to the soil, it can move out of the rooting zone and to the groundwater. But soils have the ability to reduce $Cr^{6+}$ to $Cr^{3+}$. This reduction is favored by a high content of organic matter and a low soil pH. Once reduced, the Cr is held as an exchangeable ion and also precipitated as the very insoluble $Cr_2O_3$. In this form, it is not available to plants.

## 10.6 METHODS OF EVALUATING SOIL FERTILITY FOR MICRONUTRIENTS

The soil fertility for micronutrients can be evaluated by soil sampling, extraction of an "available" or labile fraction, and analyzing the extract. Also, plant analysis is well adapted to evaluating the micronutrient availability in soils.

### 10.6.1 Soil Testing for Micronutrients

Deficiencies of micronutrients are related to plant species, climate, and soil chemical properties, such as pH and organic matter content, in ways that have made it very difficult to develop a single soil extractant for all micronutrients. Perhaps the most universally used extractant for micronutrients and other nonessential trace metals is the DTPA test developed by Norvel and Lindsay (1978). The extract consists of 0.005 M DTPA (diethylene triamine pentaacetic acid), 0.1 *M* triethanolamine, and 0.01 *M* $CaCl_2$ with a pH of 7.3. The DTPA is a strong complexing agent for heavy metals, particularly $Zn^{2+}$ and $Cu^{2+}$. Although this test has been widely shown to correlate well with available Zn in soils, it has been less successful in measuring other available micronutrients.

Some extractants that have been used successfully for micronutrients are listed in Table 10.12. For best evaluation and recommendations, they must be coupled with soil pH, soil type and local yield correlation studies.

**Table 10.12 Extractants for Micronutrients for Soil Testing**

| Trace | Soil Extractant |
|---|---|
| Zn | DTPA<br>0.1 N HCl |
| Mo | Calcium phosphate |
| Cu | 0.1 N HCl |
| B | Hot water |
| Mn | Phosphoric acid<br>0.1 N HCl |
| Fe | DTPA |

### 10.6.2 Tissue Testing for Micronutrients

Micronutrient deficiencies may be diagnosed by analyzing the plant tissue. The methods will vary widely with the particular crop and growing conditions. Generally, a certain plant portion is selected (e.g., ear leaf for corn) and a certain stage of plant growth is used. The tissue is collected and analyzed, and the values obtained are compared with values obtained from high-yielding plants. Some data are given in Table 10.13 as general guidelines for the micronutrients.

**Table 10.13 General Guidelines for Evaluating Micronutrient Content in Mature Leaves**

| Micronutrient | Concentration in leaves, mg/kg<br>Deficient | <br>Sufficient |
|---|---|---|
| B | <15 | 20–200 |
| Cu | <4 | 5–20 |
| Zn | <20 | 25–150 |
| Fe | <50 | 50–250 |
| Mn | <20 | 20–500 |
| Mo | <0.1 | 0.5–5 (?) |

*Source:* Jones, 1972.

## 10.7 MICRONUTRIENT DEFICIENCY SYMPTOMS

Deficiency symptoms have been used for a long time to identify deficiencies in the field. This has particularly been true for trace element deficiencies. But a number of factors make this practice difficult and at times less than desirable. It must be recognized that when a nutrient deficiency symptom appears on a plant, there has already been a loss in yield for that year's crop. Correcting the deficiency may be important for that year's crop, even though a yield reduction is expected, and it is important to identify what deficiency to expect in subsequent years. Trace element deficiencies are often related to climatic growing conditions, and these may change from year to year. If growing conditions are not taken into consideration, conclusions about yield responses to applied trace elements can become erratic.

Deficiencies in plants most often are manifested in growth irregularities, so that distinguishing between two or more deficiencies may be difficult. In addition, other factors that affect growth, such as weather, chemical damage, and pest damage to crops, may also give similar symptoms. For these reasons, it is important to obtain all possible information from the grower before attempting to diagnose a deficiency by plant symptoms. Once a tentative identification is made, it should be verified by treatment with the element in which the plant is assumed to be deficient. Table 10.14 has been given to help summarize factors which may help to identify a particular deficiency symptom.

Since many deficiency symptoms are similar, identifying where the deficiency occurs may be very important. Some trace elements, such as Mo, are relatively mobile in plants. When the element becomes deficient in the soil, the Mo in the plant is translocated from the old to the new tissue and the deficiency symptoms appear first on the old tissue. On the other hand, if the element, Fe for example, is not mobile in the plant, then the deficiency appears first on the new growth of the plant.

**Table 10.14 Guide to Nutrient Deficiency Symptoms for Micronutrients**

| Trace element | Plant mobility | Deficiency symptoms | Associated growth changes |
|---|---|---|---|
| Zn | Partially mobile | Light interveinal tissue in older leaves. Abnormal shaped leaves. Shortened internodes of broadleaf crops. | Iron accumulates at nodes. Delayed maturity. |
| Mo | Yes | General yellowing, with some mottling and cupping of older leaves. | Stunted growth. |
| Cu | No | Youngest leaves become "olive" and stunted. | Iron accumulates in nodes. |
| B | No | Unusual brittleness of stems, cracking of stems, thickening, curling, and chlorosis of leaves. | Slow growth. Death of terminal tissue. |
| Fe | No | Very light yellow to white on new growth. Veins are green. | New growth is severely retarded. |

### 10.7.1 Zinc

Zinc deficiency is perhaps one of the easiest to recognize under field conditions. It most often occurs on calcareous soils and soils that have high levels of phosphate, either as residual or as a current P application. In general, the Zn deficiency appears early in the growing season and is caused by either cool weather or by the restricted rooting zone of plants. Zinc deficiency is also commonly associated with particular crops and, in fact, with particular varieties. For example, when grown on the same soil and in the same rotation, navy beans may show a severe Zn deficiency when sugar beets show no Zn deficiency and do not give a yield response to Zn. Sanilac beans may show a severe deficiency of Zn when Saginaw beans grown side by side give relatively little response to Zn. The same observation can be made about toxicity. Sanilac beans are much more susceptible to Zn toxicity than Saginaw beans if Zn levels are excessive in soils. It is common to find this differential susceptibility to Zn deficiency in different varieties of navy bean, corn, and probably other crops. Breeding to reduce plant susceptibility to Zn deficiency has been successful.

The outward appearance of Zn deficiency is light interveinal tissue. For dicot crops such as navy beans, this disorder appears first in the older leaves and to a lesser degree in younger leaves. The light interveinal tissue takes on the appearance of striping in corn and does not usually affect the older leaves, but rather appears first on leaves of intermediate age. In corn and sorghum, the plants will have shortened internodes (Figure 10.5) and darkened nodal tissue, indicating accumulation of Fe at the nodes. As Zn deficiency develops, the shapes of leaves often become abnormal, particularly in crops such as beans and fruit trees (Figure 10.6). This symptom is very useful in separating Zn deficiency from Mn deficiency since Mn deficiency does not result is abnormal shaped leaves. Delayed

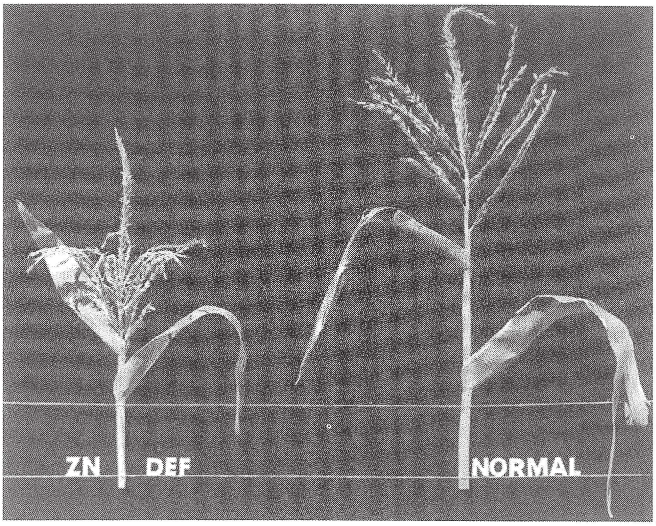

**Figure 10.5** Zinc-deficient corn (left) showing shortened internodes.

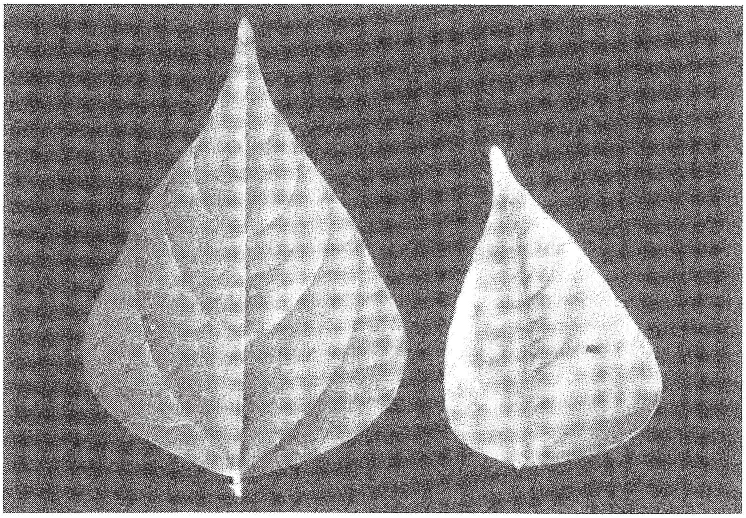

**Figure 10.6** Zinc-deficient bean leaf (right) showing light interveinal tissue and an abnormal leaf shape.

maturity is also characteristic of Zn deficiency. The field results with navy beans in Michigan revealed a Zn deficiency so severe that there was essentially no yield.

### 10.7.2 Molybdenum

The deficiency of Mo may affect legume and nonlegume plants quite differently. Mo is required by *Rhizobia* for fixation of $N_2$. Consequently, a Mo deficiency in a legume plant may be manifested as a N deficiency. It then appears as light color and stunting in plants.

Field symptoms of Mo deficiency in the U.S. have most often been observed on vegetable crops. The youngest leaves are most often affected. They become mottled and their leaf margins are narrow. The leaves will elongate abnormally and in cauliflower they are often twisted, leading to the common term *whiptail* applied to the deficiency symptom. Sometimes the leaves may take on a cupping appearance.

### 10.7.3 Manganese

Manganese deficiency often appears as interveinal chlorosis. Unlike what happens with Zn deficiency, leaves appear normal except for color and show no abnormal leaf shape. If Mn deficiency develops when the plant is very young, the deficiency may be very uniform in both young and older leaves. If the deficiency develops after the plant is much larger, however, it will be much more prevalent on the young leaves. This distribution is uneven, because Mn is only slightly mobile in the plant. In Mn-deficient bean plants, the tissue between the veins becomes increasingly lighter in color. But the veins remain dark green, making this Mn deficiency easy to distinguish from N deficiency (Figure 10.7).

Small grains quite often show Mn deficiency. Generally, a grey oval-shaped spot develops on the edge of a new leaf. The grey spot will enlarge until it covers much of the leaf and takes on a yellow appearance. The tip of the leaf will remain green during this process. Manganese deficiency in corn and grain sorghum appears as interveinal chlorosis, usually on the youngest leaves. It may be similar to Fe deficiency, but Mn deficiency usually appears on soils with high organic matter content, whereas Fe deficiency seldom occurs on these soils.

On certain vegetable crops, such as broccoli, Mn deficiency causes the leaf surface to lose its waxy coating. This is quite apparent when comparing deficient plants with plants sufficient in Mn.

### 10.7.4 Copper

Because Cu is not translocated in the plant, the deficiency symptoms appear on the new growth. For small grains and corn, the leaves appear olive or yellowish green in color, and often leaves fail to unroll as they emerge. Often the leaf tips will appear as though the plants have been frost damaged, and there will be some flags. A *flag* is a wilted or dead leaf or a branch with such leaves on an otherwise healthy-appearing plant.

### 10.7.5 Boron

Boron deficiency symptoms are seldom observed except for sensitive crops, such as legumes, sugar beets, and some vegetable crops. In alfalfa, the deficiency is shown by yellowing of the leaves and by restriction of the terminal growth.

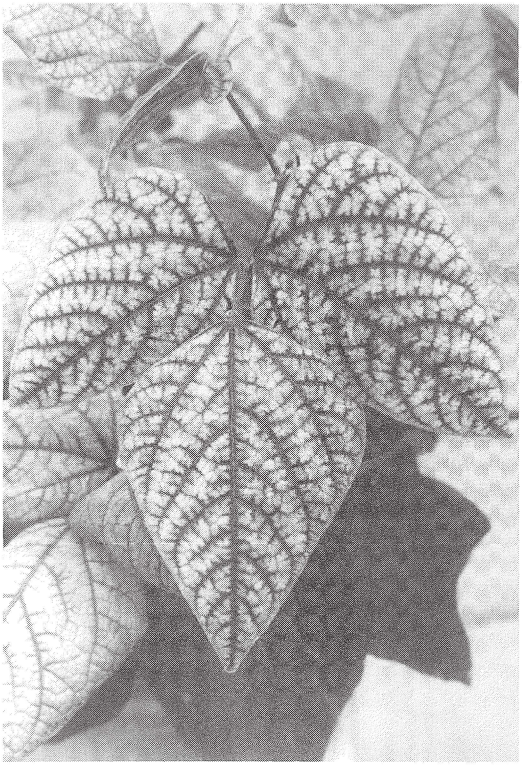

**Figure 10.7** Manganese-deficient bean plant grown in a greenhouse.

This restriction gives very short internodes and offers a method of separating B deficiency from insect damage, which may give similar visual symptoms, but with normal node lengths. Boron-deficient sugar beets develop cross-checked petioles and misshapen leaves. The leaf blades grow uneven on two sides of the plant and more in the horizontal direction than in the vertical direction. When the deficiency is severe, the terminal growth or apical meristem tissue dies and the roots may develop heart rot.

### 10.7.6 Iron

Iron is the least mobile of the micronutrients in plants. When the deficiency appears, it is on the new growth and may be very severe. The plant leaves will first appear yellow interveinally with green veins. But when the deficiency is severe, the entire area may appear white (Figure 10.8). It can be demonstrated that Fe is very immobile by placing a local spot of Fe solution on the surface of a deficient leaf and observing that the leaf will develop a green color in that area only.

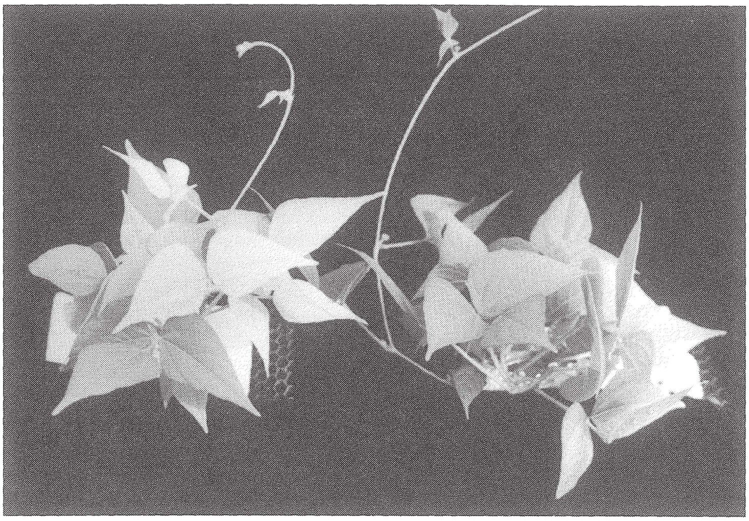

**Figure 10.8** Iron-deficient bean plants showing severe chlorosis on the new growth.

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