as a nutrient. Very likely many organic compounds formed from soil organic matter chelate, or complex, metal ions, such as Fe, Cu, and Mn. Many of these organic compounds may be readily destroyed by micro-organisms.

The characteristics of a satisfactory chelating agent for soil applications are: The chelated metal ion is not easily replaced by other metals; the metal-ion complex is stable against hydrolysis in all kinds of soil; the chelating agent is not decomposed by soil micro-organisms; the chelate is water soluble and not easily fixed in the soil colloidal fraction; the metal ion is available to the plant at the root surface and after it enters the plant; the chelating agent is not toxic to plants; and the chelating agent is available to the grower.

Ivan Stewart and C. D. Leonard, of the Florida Citrus Experiment Station at Lake Alfred, corrected iron chlorosis in citrus trees by adding iron chelate, Fe-EDTA (iron-ethylenediamine tetraacetic acid) to an acid, sandy soil. Their investigations have stimulated research on the practical importance of metal chelates for the correction of iron deficiency in many countries.

The chelating agents that have been used in soils to test their effectiveness in correcting iron chlorosis are ethylenediamine tetraacetic acid (EDTA), hydroxethyl ethylenediamine-tricetic acid (HEEDTA), diethylenetriamine pentaacetic acid (DTPA), cyclohexane trans 1,2-diaminotetraacetic acid (CDTA), and an aromatic aminopoly-carboxylic acid (APCA). The relative effectiveness of these chelates in making iron available at pH 7, in decreasing order, is: CDTA, APCA, DTPA, HEEDTA, EDTA.

Fe-APCA has been the most satisfactory chelate used thus far on alkaline calcareous soils. Ten pounds to the acre corrected chlorosis in greenhouse studies with soybeans. As much as 1,000 pounds an acre was not toxic. Fe-DTPA has been the next most satisfactory chelate. Fe-HEEDTA and Fe-EDTA have been good sources of iron on acid soils, but were ineffective on alkaline calcareous soils. The higher cost of producing Fe-APCA limited its practical use in 1957.

Less expensive chelates having some of the characteristics of APCA were being produced and tested in the field. APCA was the least toxic of the chelates tested. Several companies produce Fe-DTPA and Fe-EDTA.

It is important to understand the metabolic fate of chelates in plants, since the compounds, if they persist in plant fluids, may affect the mineral metabolism of the plant and other growth processes. The effect of very small applications of APCA on the mineral metabolism of soybeans suggests that this compound may have a favorable physiological effect besides its capacity to chelate iron in the soil.

Zinc and Soil Fertility

Lloyd F. Seatz and J. J. Jurinak

Zinc is essential for plants and animals. Many of our major farm regions contain areas that do not have adequate quantities of available zinc to support normal plant growth.

Zinc deficiencies in the field were first observed in Florida in 1927 on crops growing in peat soils. Zinc was used in the 1930's to cure nutritional difficulties in citrus in Florida and California. Deficiencies on other tree crops, such as pecans and tung, were encountered later in Florida and along the gulf coast. Corn and other crops on the Coastal Plain of the Eastern States have since been found to suffer from too little zinc.

Deficiencies also are common on
Calcareous (limestone) and noncalcareous soils throughout the West, particularly for cherries, apples, peaches, pears, apricots, citrus, and walnuts. Zinc deficiency in field crops in the West has increased since 1950. Regions affected include the Columbia Basin in Washington and the Sacramento Valley in California. The highly phosphatic soils of central Tennessee and Kentucky when heavily limed have also produced zinc-deficient crops, particularly corn and Sudangrass.

Several reasons can be offered.

Increased fertilization has produced larger yields, which have tended to remove larger amounts of available zinc from the soil than formerly. Other soils, naturally low in zinc, may develop zinc deficiencies when they are brought under cultivation. The Columbia Basin in Washington is an example of this type of area.

Two factors govern the ability of a soil to provide enough to a growing plant—the total supply of zinc in the soil and its availability to the plant. Zinc-deficiency disease therefore may be caused by a naturally low zinc fertility level or by fixation processes, which retain, or fix, zinc in a form that the plant cannot utilize.

Most soils in the United States usually have more than enough zinc for the requirements of normal plant growth, but crops may have zinc-deficiency disease. Thus the major problem is one of availability.

Occasionally the total supply of zinc in the soil—as in regions that support an intensive cropping program and that have strongly weathered and coarse-textured soils of low inherent fertility—may be the limiting factor.

Chemical tests are used to determine the ability of the soil to supply zinc to plants. Zinc is extracted from the soil with reagents and the results are compared with crop response or deficiency. Acidified potassium chloride solution, 0.1 normal hydrochloric acid, 0.04 normal acetic acid, and acidified ammonium acetate have been used as the extracting agents, but the most promising for both acid and calcareous soils is dithizone.

This method was introduced in 1951 by Ellsworth Shaw and L. A. Dean, of the Department of Agriculture. When dithizone-extractable zinc from a soil sample is less than 0.4 to 0.5 parts per million, symptoms of zinc deficiency can be expected from crops growing in that soil.

Biological methods based on the sensitivity of the fungus *Aspergillus niger* to zinc have been used with some success. The bioassay technique of determining the ability of soil to supply zinc takes about 8 days for incubation and analysis. The actual working time to analyze one sample is less than with chemical methods.

The concentration of zinc is highest in the surface soil and declines with depth. The reason lies in the uptake of zinc from the subsoil by plants and its translocation to the leaves. When the leaves fall and decay, zinc is released from the plant tissues and is fixed in the surface soil. The continuation of this fixation process near the surface depletes the subsoil of zinc and increases the possibility of deficiency to deep-rooted perennials, as fruit trees.

Many soil factors are associated with the deficiency of zinc in plants. One of the first factors to be correlated with deficiency was soil reaction, or soil pH. It was observed that less zinc was taken up after lime was put on an acid soil. The reduced availability of zinc, as the pH of the soil is increased, is generally attributed to the formation of insoluble zinc hydroxide, although undoubtedly other factors related to the adsorptive and exchange properties of the soil exert some influence on zinc availability as the pH of the system is altered by liming.

It is commonly thought that zinc availability is at a minimum in the soil pH range of about 5.5 to 7.0. Zinc is readily available at lower pH values. As the reaction rises above pH 7, the situation becomes more complex.
Evidence from experiments suggests that the positively charged zinc ion may be converted to a negatively charged zincate complex. The conversion would tend to reduce further the solubility of zinc in alkaline soils, where the predominance of calcium ion would favor the formation of very insoluble calcium zincate. The effect of possible zincate formation on zinc availability has not been established. The data, however, indicate that care must be exercised when attempting to define the chemical nature of the zinc ion in alkaline soils.

Adsorption studies in comparatively simple systems indicate that the clay fraction of the soil exerts a strong attractive force for zinc ions. A part of the attraction is related to the similarity in size and charge between magnesium and zinc ions. The similarity allows zinc ion to react with the clay mineral lattice, where it may substitute or possibly exchange for magnesium in the clay mineral, thus making it relatively unavailable. Inferences based on the knowledge of the electronic structure, small size, and charge of zinc ion allows one to predict that zinc will be tenaciously adsorbed by clay and other soil minerals. And indeed, at low concentrations, the zinc ion manifests itself in such a fashion.

The influence of excess soil phosphate on the availability of zinc has not been clearly defined. Excess phosphate has been associated with low availability of zinc in the major fruit regions of the West. The indiscriminate use of phosphate fertilizers in orchard management is not recommended there. Many soils of Kentucky and Tennessee that support crops suffering from zinc deficiency have a high content of native phosphate. These examples support the contention that zinc interacts with the phosphate radical to form an insoluble zinc phosphate complex, and so lowers its availability. Soils of the citrus regions of Florida, however, have not shown an increase in soil fixation of zinc within the limits of ordinary phosphate applications.

Attempts were made at Washington State Agricultural Experiment Station in 1953–1954 to induce zinc deficiency in field corn and beans by a heavy application of phosphate fertilizer. The phosphate treatments did not alter their uptake of zinc.

The detrimental effects of phosphate fertilization on zinc uptake may be due to the depressing action of the calcium ion in superphosphate. No conclusive evidence has shown this to be the case, but the apparent contradiction of various workers as to the effect of phosphate on zinc nutrition supports the view that the interaction is not a simple zinc-phosphate relation but that other factors must exert an influence.

Zinc ion has also been shown to be strongly adsorbed on commonly occurring lime minerals. The minerals are calcite (calcium carbonate), dolomite (calcium-magnesium carbonate), and calcian-magnesite (magnesium carbonate with calcium impurity).

The lime minerals containing magnesium carbonate exhibited a greater adsorptive capacity for zinc ion because of the compatibility of zinc ion with the magnesium carbonate crystal lattice. Thus, if the available zinc present in the soil is near the critical level, the presence of appreciable amounts of lime minerals may present an additional hazard to proper zinc nutrition of plants. Zinc deficiency could well be worsened in soils of semiarid and arid regions where these minerals are widely distributed, and zones of lime accumulation can be found frequently within the root zone of crops. The practice of land leveling for irrigation may increase the importance of zinc adsorption on lime minerals by bringing the zone of lime accumulation nearer the surface.

The effect of liming with calcitic and dolomitic limestone on acid soils thus lowers zinc availability by increasing soil pH; it may also increase temporarily the adsorptive capacity of the soil for zinc. The ability of the lime minerals to increase the adsorptive
capacity of any given soil, whether acid or alkaline, for zinc ions would probably be important only in soils of coarse texture where clay is not the dominating fraction of the soil.

Deficiency of zinc in California has been associated with soils of a high content of organic matter. Symptoms have been observed in spots that formerly were corrals or barnyards. In soils of average organic matter content, however, the destruction of the organic fraction has little influence on the amount of zinc extracted from the soil—an indication that the organic fraction in most soils does not affect greatly the availability of zinc. In organic soils, or soils where an appreciable portion of the adsorptive capacity derives from the organic complex, however, the organic fraction would have a more vital part in making zinc available.

**Zinc Deficiency** in plants causes several abnormalities in structure.

The palisade cells of leaves from most affected plants are larger and are transversely divided, rather than columnar, as in normal leaves. Zinc deficiency therefore may lead to cell enlargement rather than to cell differentiation. Other abnormalities may be a reduction in the number of chloroplasts, the absence of starch grains, the presence of oil droplets in the chloroplasts, the presence of calcium oxalate crystals, and the accumulation of phenolic materials in the leaves. These changes in chemical composition indicate that zinc is related to normal metabolism of carbon within plants.

The roots of zinc-deficient plants are also abnormal. Tomato roots may have a series of swellings with whorls of root hairs near the root tip. Secondary roots may develop later in them. Cell structure is also deranged; cells even in the meristematic, or actively growing, region may be enlarged, and an irregular arrangement with many air spaces may occur among the cells. Older tissue becomes necrotic and has flaky masses of exfoliated cells. The metabolic products of the root cells also are abnormal. Tannin, fats, and calcium oxalate crystals are present in abnormally large amounts. Starch is absent.

Zinc is also related to seed production in several plants. A threshold value of zinc has been established for peas and beans below which the plants produce only small, seedless pods. When plants are supplied zinc in concentrations above this value, the pods are larger and contain seeds.

Zinc may be translocated from other parts of the plant to the seeds at maturity, because the viability of the seeds is not affected by the concentration of zinc supplied the plants.

Zinc seems to be distributed fairly well within the plant. The concentration varies with the amount of available zinc in the soil, the kind of plant, the part of the plant sampled, and the stage of growth. Differences in varieties and in environmental factors probably affect the zinc content. Generally the zinc content of normal plants is higher than that of zinc-deficient plants grown in a similar environment, although a considerable overlap seems to exist.

E. Archibald and F. B. Wann, of Utah State University, have discovered that the limiting value for the zinc content of the leaves of several fruit trees (below which the development of zinc deficiency may be expected) is 0.0123 percent. Normal leaves contained between 0.0123 and 0.0345 percent of zinc. A critical value for tung is reported to be 0.0010 percent of zinc. Other research workers have reported that the percentage composition of zinc in the leaves of normal plants is considerably lower than the above values—as low as 0.0004 percent of zinc in normal leaves of some plants.

Frank Viets and his coworkers in Washington reported values ranging from 10.5 to 32.7 p.p.m. of zinc, with an average of 16.86 for selected parts of several crops that were growing on a normal area without zinc deficiency. In an area where crops showed a zinc deficiency, the values varied from 9.3 to 22.5 p.p.m., with an average of 15.44
When the crops were fertilized with zinc, the average content of the crops became 22.58 and 18.34 p.p.m.

Both the tops and roots of corn at several sampling dates did not show great or consistent differences in zinc concentration between normal and zinc-deficient plants. The total zinc uptake, however, was much greater for normal plants than for zinc-deficient plants, indicating greater growth for the normal plants.

P. R. Stout and G. Pearson, of California, discovered that plants very low in zinc have a higher concentration of zinc than larger plants that also are deficient in zinc. When zinc was added to the culture solution, the amount of internodal to nodal and embryonic tissue increased, and the zinc concentration of the entire plant dropped. The concentration in the plant again increased when more zinc was added.

The zinc concentration in actively growing parts of plants is higher than in older tissue. Zinc tends to accumulate in and around the primary veins of the leaf blade in actively growing corn leaves. The highest zinc concentration in cornstalks is at the node; concentration falls off quite rapidly both above and below the node. In oats, 20 to 30 percent of the zinc in the plant is in the leaves, mainly in the chloroplasts. Zinc is bound to the protein material in the chloroplasts along with their colored pigments.

A deficiency of zinc in a plant may affect its content of other elements. Leaves of corn plants that show zinc deficiency have more potassium and phosphorus than leaves of normal plants.

Zinc is a necessary component of several enzyme systems, which regulate various metabolic activities within plants. It is a part of the enzyme carbonic anhydrase, which regulates the equilibrium between carbon dioxide, water, and carbonic acid. It also functions as a part of two enzymes, dehydropeptidase and glycylglycine dipeptidase, which have a part in specific aspects of protein metabolism.

Zinc also is needed for the formation of auxins, which are growth-promoting substances in plants. Because one of the symptoms of zinc deficiency is a failure of the stem tissue between the nodes to elongate, resulting in rosetting, it was thought that zinc deficiency might be related to a low content of auxin. This phase of the function of zinc in plants has been studied by F. Skoog and his associates at the University of Wisconsin. They learned that plants deficient in zinc were low in auxin. The auxin content of the plants increased when zinc was applied. Further investigation showed that zinc seems to limit the production of one of the compounds that serves as a building block in the formation of the complex auxin compound.

Zinc is associated with water relations in plants. High osmotic pressures resulting from zinc deficiency are due to reduced water uptake, which was restricted by the failure of cell walls to grow because of lack of auxin.

The observation that zinc deficiency does not develop so readily in mild sunlight as it does in bright sunlight may be associated with auxin activity. Plants grown under blue light exhibit zinc deficiency symptoms more readily than those grown under red light. Light of high intensity and of short wavelengths inactivates auxin.

Plants differ in their ability to extract zinc from the native soil supply. Crops that followed crotalaria as a cover crop in Florida exhibited zinc deficiency, but crops that followed a cover crop of native weeds did not. Analysis of the plants showed that the weeds accumulated much more zinc from the limited soil supply than the crotalaria did.

Dr. Viets and his coworkers studied the relative ability of 26 different crops to utilize native soil zinc. They classified the plants in three groups.

In the very sensitive group (plants that cannot get enough zinc from the soil) are beans, soybeans, corn, hops, grapes, lima beans, flax, and castor beans. The mildly sensitive group includes
potatoes, tomatoes, onions, alfalfa, sorghum, Sudangrass, sugar beets, and red clover.

Insensitive plants are peppermint, the cereals, peas, asparagus, mustard, carrots, safflower, and grasses.

Zinc deficiency of trees is known as rosette, mottle leaf, little leaf, and yellows. The terms tend to describe the usual symptoms of zinc deficiency although such symptoms are not always brought about by too little zinc.

The deficiency in citrus is usually known as mottled leaf. Affected leaves have irregular chlorotic areas between the leaf veins. The leaves may be normal in size in the early stages of the disease, but new leaves as they develop become progressively smaller. Rosetting does not usually occur in citrus.

Pecans that get too little zinc have a bronzing of the leaves and rosettes of small leaves on shortened branches. Yellowish mottled areas appear on young leaves. They turn reddish brown on older leaves and may die and cause many small holes in the leaf.

The disease is called little leaf or rosette in deciduous fruit trees, such as apple, cherry, peach, apricot, and plum. Rosetting occurs, and dense clusters of small, yellowish leaves grow at the end of twigs that are bare of normal lateral leaves. The internodes are shortened. Little leaf produces small, chlorotic, narrow leaves. Chlorotic mottling progresses inward from the margin in the interveinal tissue. Considerable dieback of the branches occurs in severe stages of little leaf. The number of blossoms and fruits set usually is greatly reduced, and fruits that are produced are of poor quality.

A typical symptom of lack of zinc in most field crops is chlorosis of the interveinal tissue, particularly of the lower leaves. The younger leaves in severe cases may also be chlorotic. The lower leaves may turn brown to purple and die. The internodes may become short, and the plants are stunted. In severely affected corn the bud may become almost white.

Zinc deficiency disease usually can be cured by applying zinc to the plants in an available form.

Application of zinc-containing materials to the soil either as a soluble salt or in a chelated form is a common way. The effectiveness of soil applications is determined by how strongly the soil fixes the applied zinc. For that reason the application of soluble zinc salts may not be effective on soils with a high zinc-fixing capacity. Sometimes band placement of the zinc-containing fertilizer has increased its effectiveness.

The use of zinc chelates is an effective way of providing zinc to plants under high soil-fixing conditions. The chelating agent is made up of complex molecules capable of reacting with the zinc and combining it into the complex molecular structure. The zinc therefore is not fixed by the soil and remains in a soluble and available form to the plants. Often applications of chelated zinc have corrected deficiencies where applications of soluble salts, such as zinc sulfate, have not been effective.

Foliar sprays have been effective in correcting zinc deficiency, particularly on tree crops. For citrus a single spray of a solution containing about 5 pounds of zinc sulfate per 100 gallons of water corrected zinc deficiency for 1 to 3 years. Foliation injury is reduced by adding 2 to 3 pounds of hydrated lime, soda lime, or lime sulfur to the spray. Wetting and adhesive agents sometimes have given a beneficial effect at low concentrations. Sprays applied just before flush growth give a longer effect than those applied before dormancy.

Concentrated sprays of 25 pounds of zinc sulfate to 100 gallons of water are effective on apples and pears when applied as a dormant spray just before the buds open. Zinc dusts have been less effective than sprays.

Grapes are usually treated by daubing the freshly cut pruning wound with a solution containing 2 pounds of zinc sulfate to a gallon of solution.

Sometimes, especially on sweet cher-
ries and walnuts, when sprays are not effective, injections of zinc-containing materials are helpful. Zinc-coated nails and pieces of galvanized iron may be driven into the trunk and the main branches. Another means of injecting zinc into the tree has been to bore several holes into the trunk about 3 inches apart and to pack 2 to 3 grams of zinc sulfate into each hole. The holes are then filled with wax.

Field crops usually are fertilized with zinc fertilizers in the row or in bands slightly below and to the side of the seed at the time of planting. Top-dressing and sidedressing with zinc salts after the crop is growing have not been satisfactory. Fertilizer manufacturers in some areas add zinc sulfate to the mixed fertilizer so that farmers can apply the necessary fertilizer elements in one operation without having to mix zinc sulfate with the fertilizer.

Zinc sulfate sprays have also been satisfactory on field crops when the spraying is done early in the season before serious deficiencies arise.

Many crops are affected by a deficiency of boron in the soil. Sugar beets, alfalfa, and clovers are the most commonly affected of the agronomic crops. Celery, beets, cauliflower, apples, grapes, pears, walnuts, sunflowers, and asters are a few of the many vegetable, fruit, nut, and ornamental crops that may suffer from too little.

**Boron was first used as a fertilizer about 400 years ago when borax (then called Tincal or Tincar) was shipped from central Asia to Europe. Not until 1915, however, was boron suggested as an essential element for plant growth, when P. Mazé of France made this suggestion as a result of his work with corn grown in nutrient solutions. Katherine Warington, at the Rothamsted Experimental Station in England, provided the first proof in 1923 that boron was an essential element. An inadequate supply of boron in the soil was shown to be the cause of heart rot and dry rot of sugar beets and mangolds in Germany by E. Brandenburg in 1931.

L. G. Willis and J. R. Piland, of the North Carolina Agricultural Experiment Station, were among the first in the United States to show that legumes, especially alfalfa, responded to borax fertilizer. The two agronomists published the results of their research in 1938. Boron deficiencies have been reported since then in 41 States and for 90 or more crops.

Most of the boron in soils is in the form of the highly insoluble mineral tourmaline. The total boron content of the soil varies between 20 and 200 pounds in the plow depth of an acre. The total boron content of the soil is not a reliable guide to the adequacy of boron for crop growth, because less than 5 percent of the total may be available for the use of plants. The determination and measurement of the available forms of boron have been of concern since 1931.

**Available boron occurs in two broad forms, inorganic and organic.**

**Boron and Soil Fertility**

Darrell A. Russel

The modern American kitchen contains enough boron to produce 16 tons of alfalfa hay. This boron is in the enamel in freezers, stoves, refrigerators, sinks, dishes, and glassware.

But many thousands of acres of agricultural soils in the United States contain only enough available boron to produce a ton or two of alfalfa hay. That amount is the equivalent of the boron in an iron cookstove, an icebox, and a good set of china dishes.