SOILS AND FERTILIZERS
MODULE 10
MICRONUTRIENT FERTILIZERS; BEHAVIOR OF MICRONUTRIENTS IN SOILS

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1. General considerations
   a. Micronutrients include manganese (Mn), zinc (Zn), copper (Cu), iron (Fe), and boron (B), which are more available (soluble) at lower soil pH (< 6.5), and molybdenum (Mo) and chlorine (Cl), which are more available at higher soil pH.
   b. Native Florida soils are low in micronutrients.
   c. When micronutrients are applied to soil or plants, it is often with a "shotgun" mix of two or more.
   d. Micronutrient levels are not usually measured in routine soil analysis.
   e. One major reason that soils should not be overlimed is that micronutrient deficiencies can be induced; use of high-pH irrigation water can also have the same effect over time, thus the pH of soils irrigated with this water needs to be monitored on a regular basis.
   f. Some soils which have a native alkaline pH, (such as soils containing shell, rock, or marl) cannot be practically acidified; these soils are notorious for causing micronutrient deficiencies of plants; can apply micronutrient chelates to combat this problem and keep the nutrients in a form which can be taken up.
   g. Most micronutrient fertilizers are either inorganic salts, synthetic chelates, or organic complexes.
   h. The word **"chelate"** comes from a Latin word meaning "claw"; Synthetic chelates are large organic molecules that have "holes" inside of them where the micronutrient atom resides, thus the chelate holds it like a claw.
   i. Some synthetic chelates include EDTA, HEDTA, DTPA, EDDHA; these will hold different ions with different stabilities, depending on the ion and the soil pH; for example, EDDHA will be more stable with Fe^{3+} than with any other ion (e.g. Ca^{2+}, Mg^{2+}, H^{+}, Al^{3+}) at any pH.
   j. DTPA is also used as a soil extractant for micronutrients. It is the best micronutrient extractant for use with a "normal" low-CEC soil; however, the amounts extracted from Florida soils are so low that the slightest contamination during the extraction (e.g. from the containers or stoppers) will make the results inaccurate; a Mehlich-1 extraction gives fairly reliable results for Mn, Zn, and Cu.

2. Manganese (Mn)
   a. Taken up by plants as Mn^{2+}. Mn deficiency is expressed as interveinal chlorosis.
   b. The positive ionic charge of Mn influences its solubility tremendously, e.g. Mn^{2+} vs. Mn^{3+}; increasing charge will decrease solubility.
   c. If a soil is flooded for a long time, reducing conditions (absence of oxygen) develop, and the solubility of Mn increases; upon drying of the soil, can get Mn toxicity; this toxicity usually occurs at a pH of less than 5.2 in soils containing fine-textured particles.
   d. Soil organic matter can form insoluble or soluble complexes with Mn^{2+}.

e. Mn deficiency is most often observed in high pH soils or very sandy soils. Can be corrected through foliar sprays.
f. Sources of manganese:
   i. Manganous sulfate, $MnSO_4$ (32% Mn).
   ii. Manganous oxide, MnO (33 to 37% Mn).
   iii. Tecmangam (trade name), $MnSO_4 + MgSO_4$ (29% Mn).
   iv. Chelated manganese - The chelating agents commercially used today have a stronger affinity for other cations such as Fe than for Mn, thus if there is iron in the soil, the result of adding chelated Mn will be chelated iron and unchelated Mn (i.e. the expense of having chelated Mn in a fertilizer has been wasted).
   v. Repeated use of the fungicides manzate and maneb has resulted in a buildup of Mn in some soils.

3. Iron (Fe)
   a. Taken up by plants as Fe^{2+}.
   b. Although the total iron in a soil may be as high as 7 to 25% by weight (present as iron oxides and hydroxides), its solubility is often very low, especially at high pH. Iron deficiency can occur even if a lot of total iron is present.
   c. The solubility of Fe in the soil is very dependent on soil pH. As pH <u>increases</u>, Fe solubility <u>decreases</u>.
   d. The positive ionic charge of Fe also affects its solubility in the soil; Fe^{2+} exists in acid, flooded soil, while Fe^{3+} exists in well-aerated soil (poor drainage favors reducing conditions).
   e. Plants do not accumulate <u>Fe^{3+}</u> in their tissues; they accumulate and transport Fe in the <u>Fe^{2+}</u> form.
   f. Soluble organic complexes react with Fe in the soil solution, creating natural chelates that increase the amount of available Fe.
   g. Certain plants like azaleas are very sensitive to Fe deficiency; this is often seen around the foundation of houses where the soil has a very high pH and the Fe is tied up; can either foliar spray with $FeSO_4$, apply iron chelate, or replace the soil around the plant.
   h. Plants differ in their ability to take up soil Fe. This differential ability is caused by a genetically controlled adaptive process that responds to Fe deficiency or stress. For example, sour orange rootstock may experience sufficient Fe nutrition in a given soil, whereas Swingle citrumelo may not.
   i. Iron deficiency is expressed as a yellowing of the plant (chlorosis); it is the most difficult deficiency to correct in the field.
   j. Sources of iron:
      i. Iron sulfate, $FeSO_4$ (19% Fe) This material should not be used on high pH soils because the Fe will be immediately rendered unavailable.
      ii. Chelated iron - Agents like EDTA, HEDTA; these are expensive but very effective in soils below pH 7; DTPA chelate is effective up to about soil pH 7.5; if the soil is calcareous, the only effective iron chelating agent is EDDHA; one example of this is Sequestrene-138 (trade name).

4. Copper (Cu)
   a. Taken up by plants as Cu^{2+}.
   b. Most copper deficiencies will be seen on organic soils or soils that have never been cropped before (e.g. new land just put into production).
   c. Soils that have been used for citrus or vegetables over several years will show an accumulation of copper from the use of fungicides, and Cu fertilization is not needed.
   d. Organic matter complexes Cu very quickly (takes it out of solution). Cu is more strongly bound to organic matter than is any other micronutrient.
   e. Most common source of Cu for application to soil is copper sulfate, $CuSO_4$ (25 to 35% Cu).
   f. The availability of Cu to plants can be controlled by regulating the soil pH; very acidic soils may have enough soluble copper to cause copper toxicity; liming these soils will eliminate the toxicity by precipitating the Cu into a solid form (the copper is still present in the soil, it just is not soluble at higher pH).
   g. Applications of nitrogen fertilizer at high rates can aggravate Cu deficiency (in citrus, this is called ammoniation).

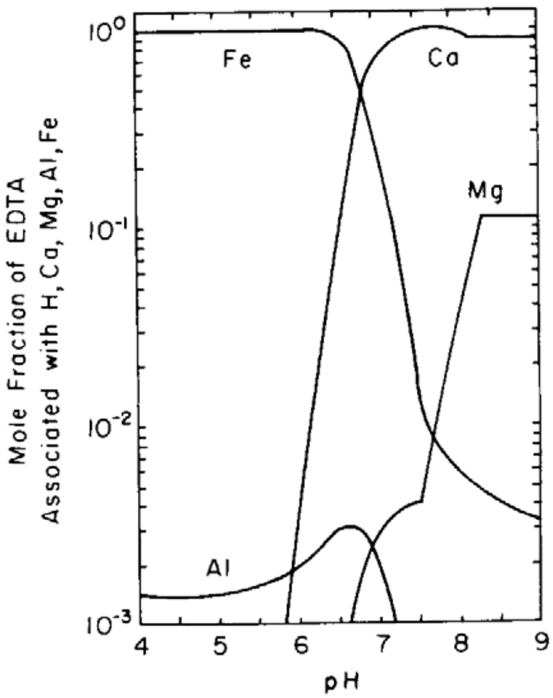
5. Zinc (Zn)
   a. Taken up by plants as Zn^{2+}.
   b. Most deficiencies of Zn are seen with high soil pH, but can occur anywhere; can see deficiency symptoms on young leaves of plants such as citrus even on acidic soils, but in many cases the symptoms will disappear as the leaf matures.
   c. Soil phosphorus levels can affect Zn availability; if the P:Zn ratio in the soil is greater than 150:1, can get Zn deficiency; the deficiency occurs because the Zn precipitates in the roots as a zinc-phosphate complex.
   d. Soil organic matter can form insoluble or soluble complexes with Zn^{2+}.
   e. Zn deficiency, which is expressed by short leaf internodes and small leaves, can be corrected with foliar sprays.
   f. Sources of zinc:
      i. Zinc sulfate, $ZnSO_4$ (22 to 36% Zn). This material is the form of Zn most commonly used.
      ii. Zinc oxide, ZnO (50 to 80% Zn). Less water-soluble than zinc sulfate.
      iii. Zinc chelates (EDTA, HEDTA, DTPA). 8 to 14% Zn.

6. Boron (B)
   a. Required by plants at approximately 2 lbs per acre; could get B toxicity at 4 lbs per acre (narrow range between sufficiency and toxicity). The only way that B can become toxic is through over-fertilization.
   b. Present in soils as a negatively charged ion (BO_3^-), thus it leaches readily in sandy soils.
   c. The calcium content of the plant affects B nutrition; plants with high Ca need a greater amount of B in order for it to be mobile.
   d. Sources of boron:
      i. Borax (sodium tetraborate, $Na_2B_4O_7$). Used in dry fertilizer. 11 to 21% B.
      ii. Solubor (highly concentrated, completely soluble, used in solutions) 20% B.

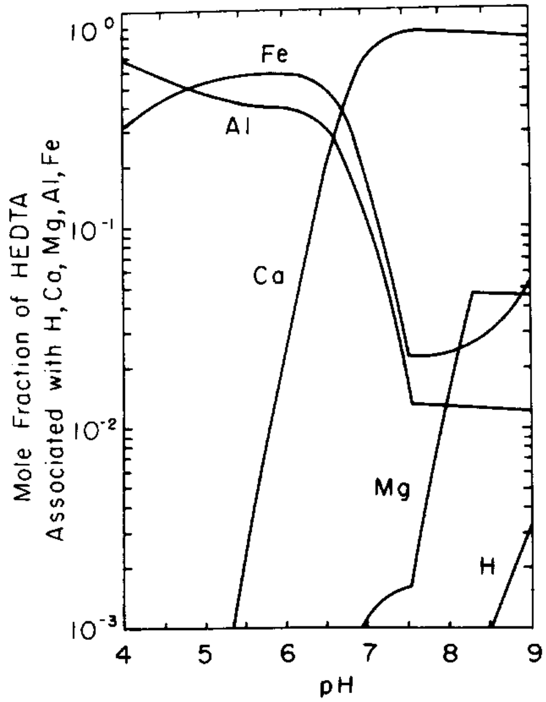
7. Molybdenum (Mo)
    a. A micronutrient that increases its solubility as the soil pH increases; found in soil as part of soil OM, adsorbed by clays and Fe/Al compounds, and within the structure of primary minerals.
    b. Not normally applied to crops except legumes, where it may be applied at about 2 oz per acre (legumes need Mo for nodule formation).
    c. Do not want to mix Rhizobia inoculum with Mo before application; a high concentration of Mo will kill the Rhizobia.
    d. Excessive amounts of Mo are toxic; Toxicity has been seen on citrus in Florida.
    e. Sources of molybdenum:
        i. Ammonium molybdate (54% Mo).
        ii. Sodium molybdate (39% Mo).

8. Chelates
    a. Metal chelates are defined as cyclic structures of a metal atom and an organic component, in which the two components are held together with varying degrees of strength, varying from loose to strong.
    b. Metal chelates are **soluble in water**.
    c. Chelates are also referred to as **sequestering** agents.
    d. Synthetic organic chelates that are important in agriculture include EDTA, HEDTA, DTPA, EDDHA, citric acid, and glucoheptanate.
    e. The mechanism of metal/chelate absorption and utilization by plants is not well understood.
    f. When applied to soils, chelates have the ability to sequester their surrounded metal ion from their insoluble forms in the soil. It is possible to correct micronutrient deficiency by applying chelates directly to the root zone in soils which would normally tie up the non-chelated form of the micronutrient.

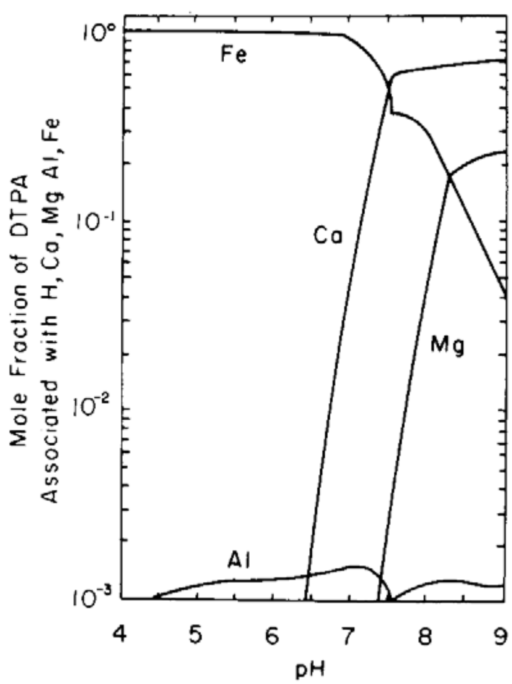
9. Summary of micronutrients
    a. Water-soluble forms
        i. Water-soluble forms of Zn and Cu are almost non-existent in the soil.
        ii. Water-soluble forms of Mn and Fe are very small in well-aerated neutral soils; low pH and poor aeration can markedly increase Mn and Fe solubility, but these conditions have little effect on Zn and Cu solubility.
    b. Exchangeable forms - Zn and Cu, small amounts; larger amounts of Mn (can use a measure of exchangeable Mn to predict availability).
    c. Adsorbed, chelated, or complexed ions.
    d. Micronutrient cations in secondary clay minerals and insoluble metal oxides.
    e. Micronutrients within primary minerals.
    f. Micronutrient anion pools:
        i. Chloride and boron - found in primary minerals and water-soluble forms.
        ii. Molybdenum - adsorbed (similar to phosphate and sulfate) and precipitated with oxides of iron and aluminum.



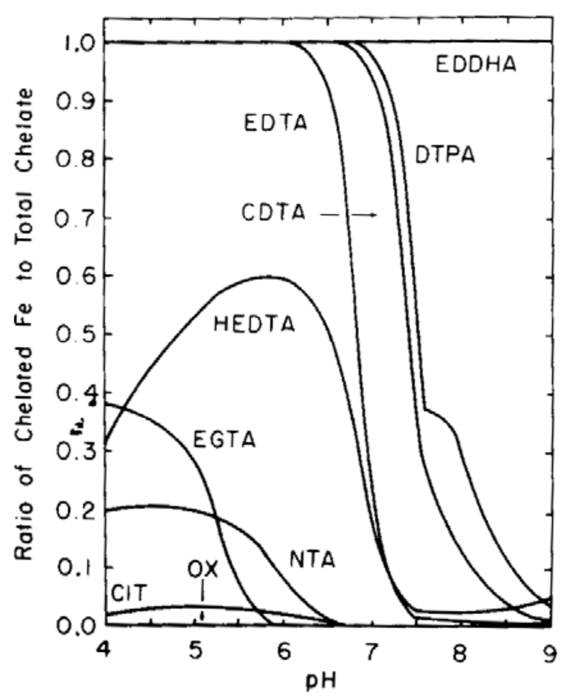
Stability diagram for EDTA in equilibrium with H^+, Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} in soil solution.



Stability diagram for HEDTA in equilibrium with H^+, Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} in soil solution.



Stability diagram for DTPA in equilibrium with H^+, Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} in soil solution.



Comparison of Fe-chelate stabilities in soil solution.