Title: Overview of Micronutrients and Focus on Fe and Mn
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Overview of Micronutrients and Focus on Fe and Mn
Micronutrients: Essential Elements Required in Small Concentrations (ppm) in Plants

- **Cationic micronutrients:** Fe, Mn, Cu, Zn.

- **Other micronutrients:** B, Mo, Cl.
<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Range in Soils, lb/A</th>
<th>Estimated Removal, lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>20 - 200</td>
<td>0.06</td>
</tr>
<tr>
<td>Copper</td>
<td>2 - 400</td>
<td>0.05</td>
</tr>
<tr>
<td>Iron</td>
<td>10,000 - 200,000</td>
<td>0.10</td>
</tr>
<tr>
<td>Manganese</td>
<td>100 - 10,000</td>
<td>0.08</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>1 - 7</td>
<td>0.03</td>
</tr>
<tr>
<td>Zinc</td>
<td>20 - 600</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Similarities of Cationic Micronutrients

• All carry + charges
• Fe and Mn undergo oxidation/reduction reactions in soils and plants.
• All can form chelate complexes with organics.
• All tend are more soluble under acid conditions.
Soil reactions that govern the solubility of cationic micronutrients

- oxidation-reduction (Fe, Mn only)
- chelation (all)
- adsorption (all)
- precipitation (all)
The Cationic Micronutrients Are More Available at Acid pHs
Iron Nutrition in Plants

- Principle absorbed form: ferrous iron (Fe\(^{2+}\))
- Relatively immobile in plants
- Typical plant tissue concentrations: 100 ppm = _____ mg/kg = ______ %
Biochemical Functions of Iron

• Structural component of porphyrin molecules
  – leghemoglobin (protects nitrogenase from oxygen)
  – cytochromes (energy transfer)
Biochemical Functions (cont.)

- Fe-S proteins
  - ferredoxin (electron transfer in photosynthesis)

- Enzyme systems
  - nitrogenase ($N_2$ fixation)
Iron Deficiency Symptoms

• Interveinal chlorosis of upper leaves
• Twig or branch dieback
Progression of Fe Deficiency
Iron Deficient Orchard in Calcareous soils-Jordan
Interveinal Chlorosis in Fe-Deficient Wheat
Iron Mineralogy

- **Abundance:** 4th most abundant element in earth’s crust.
- **Primary minerals that contain Fe** include biotite.
Secondary Fe Minerals

Pyrite: FeS
Siderite: FeCO₃
Hematite: Fe₂O₃
Goethite: FeOOH

most common Fe oxides in soil
Soil Solution Iron

- $\text{Fe}^{2+}$, $\text{Fe}^{3+}$ ions,
- various Fe hydroxy species, such as $\text{Fe(OH)}^{2+}$,
- various Fe chelates, such as iron citrate.
Reduction/oxidation (redox)

**Reaction**

\[
\text{Fe(OH)}_3 + e^- + 3H^+ = \text{Fe}^{2+} + H_20
\]

- **Acidity**
- **Waterlogging**

oxidized (3+)

reduced (2+)

aerated conditions

anaerobic
Fe Mineral Stability Diagram

Log Fe in sol’n

FeOOH

amorphous Fe(OH)$_3$

Fe$_2$O$_3$

increasing Fe in solution

pH
Mineral Stability of Reduced Iron Minerals

The graph shows the relationship between the pH and the concentration of Fe$^{2+}$ in solution. The x-axis represents the pH values ranging from 3 to 9, and the y-axis represents the log of Fe$^{2+}$ concentration in solution, ranging from -6 to -24. The arrow indicates an increase in reducing conditions with increasing Fe$^{2+}$ in solution.
As soil pH decreases, Fe solubility ____________.

As reducing conditions increase, Fe solubility ____________.
Chelation with soluble organic molecules increases Fe solubility

Fe oxides

$Fe^{3+}$

$Fe^{2+}$

Ionic concentrations are maintained, and chelated Fe increases
Synthetic Fe Chelate: EDDHA

Highly soluble complex (increases, decreases?) solution Fe
Metallic Cation (M) Chelation
With 2 Citrate Molecules

Soluble chelate
(increases, decreases?) M availability
Humic Acid-Clay-Metallic (M) Micronutrient Complex

Insoluble complex (increases, decreases?) M Availability
Factors in Fe deficiencies

- low total Fe content
  - coarse texture
  - low OM

- low Fe solubility
  - solution Fe decreases by 100 to 1000 x for every increase in one pH unit
Fe Fertilizer Sources

• soil applied ferrous sulfate ($\text{FeSO}_4$) has limited success due to rapid oxidation to ferric form in the presence of oxygen.

• Foliar ($\text{FeSO}_4$):
  – mild: one application of 2-3% ($\text{FeSO}_4$) at 10-30 gal/A
  – severe: every 2-3 weeks
Fe Fertilizer Strategies (cont.)

- Injected FeSO$_4$ into tree trunks and limbs
- Iron chelates as soil or foliar amendments
- Soil acidification: be able to describe how this will increase Fe availability!
Manganese Nutrition in Plants

• Absorbed form: As with Fe, the most reduced form is absorbed by plants ($\text{Mn}^{2+}$)
• Typical plant tissue concentrations: 50 ppm
• Relatively immobile in plants
Manganese Functions in Plants

- Enzyme activator
- Required in chlorophyll formation
Mn Deficiency Symptoms

- Interveinal chlorosis
Mn Deficiency in Wheat: Interveinal White Streaks
Mn Deficiency in Ornamentals

Interveinal chlorosis - Mn African Violet in Gerbera

Mn deficient Nasturtium + Mn
Interveinal Chlorosis and Brown Speckling in Mn Deficient Soybean
Brown speckling on the underveins of Mn toxic soybean
Bark Measles of Mn Toxicity in Apple Trees
Secondary Soil Mn Minerals

- pyrolusite (MnO$_2$)
- manganite (MnOOH)
Soil Mn

- Total Mn in soils ranges from 20 to 3,000 ppm in soil.
- Solubility usually controls availability.
- pH and redox reactions govern solubility.
The Mn$^{2+}$ concentration increases 1000 fold for each pH unit decrease.

\[ \text{MnO}_2 + 2\text{H}^+ = \text{Mn}^{2+} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \]

oxidized | reduced
---|---
(4+) | (2+)

aerated conditions | anaerobic

acidity | waterlogging
Based on these reactions, what management will increase Mn availability to plants??
## Effect of waterlogging and liming on Mn status of alfalfa

<table>
<thead>
<tr>
<th>Lime Waterlogging</th>
<th>Soil pH</th>
<th>Shoot Dry wt g/pot</th>
<th>Mn Conc. mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 4.8</td>
<td>3.1</td>
<td>426</td>
</tr>
<tr>
<td>0</td>
<td>+ 5.2</td>
<td>1.2</td>
<td>6067</td>
</tr>
<tr>
<td>2.5</td>
<td>0 6.4</td>
<td>5.7</td>
<td>99</td>
</tr>
<tr>
<td>2.5</td>
<td>+ 6.7</td>
<td>3.0</td>
<td>957</td>
</tr>
</tbody>
</table>
Manganese deficient wheat from over-liming an Atlantic Coastal Plain soil
Manganese deficient soybean from over-liming an Atlantic Coastal Plain soil
Mn Fertilizers

- MnSO$_4$ soil or foliar
- MnO
- MnEDTA
- Mn fertilizer rates range from 1 to 25 lb Mn/A