BIOL 695

MANGANESE

Chapter 14
MENGEL et al, 5th Ed

Mn OXIDATION STATES IN SOIL

- Mn can exist in the oxidation states:
  - Mn^{0+} Mn^{2+} Mn^{3+} Mn^{4+} Mn^{6+} Mn^{7+}
  - Mn^{2+} and Mn^{4+} are most common
- Mn^{2+} soluble and can be toxic
  - Low pH
    - Water logged soil $\Rightarrow$ anaerobic
    - Steam sterilization kills Mn oxidizing microorg $\Rightarrow$ Mn tox

Mn NODULES

$$Mn^{2+} \underset{+e^-}{\overset{-e^-}{\longleftrightarrow}} Mn^{3+} \underset{+e^-}{\overset{-e^-}{\longleftrightarrow}} Mn^{4+}$$

$$\underset{+2e^-}{\overset{-2e^-}{\longleftrightarrow}} Mn^{6+} \underset{+e^-}{\overset{-e^-}{\longleftrightarrow}} Mn^{7+}$$

Influenced by microbes & anaerobic soil conditions

TETRAVALENT Mn INSOLUBLE

- Mn^{4+} is insoluble $\Rightarrow$ Mn deficiency
  - High pH
    - Soil aeration
    - Microbial activity
- Mn plays important role in redox rea'ns
- Fig. 14.1 text Oxid'n - Red'n Cycle for Mn

UPTAKE

- Mn^{2+} lower uptake than Ca^{2+} & Mg^{2+}
- Active
- Mg^{2+} depresses Mn^{2+} uptake
- Mn^{2+} depresses Fe^{2+} uptake
- Plants supplied with NH_4-N took up more Mn^{2+} than NO_3-N fed plant

Mn RELATION TO OTHER IONS

- Ionic radius of
  - Mg^{2+} 0.065 nm
  - Mn^{2+} 0.075 nm
  - Ca^{2+} 0.099 nm
- Mn^{2+} can substitute or compete with these ions.

Mn CONTAINING ENZYMES

- Mn^{2+} activates IAA Oxidase
- Reduced IAA $\xrightarrow{\text{IAA Oxidase}}$ Oxidized IAA
  (Active) (Inactive)
- Mn deficient plants have toxic levels of IAA
- "Mn toxicity may relate to IAA defic"

WATER SPLITTING

- Mn protein in Photosystem II
- Role in water splitting system
  - Fig 14.3 on page 578 text

$$2H_2O \overset{Mn^{+4}\ Mn^{+3}}{\Rightarrow} O_2 + 4H^+ + 4e^-$$

NITRATE REDUCTASE

- Mn cofactor for NR (1970)
- $NO_2^- \longrightarrow NH_4^+$
- Evidence - NO_3^- Accum in Mn^{2+} def pl
- BUT due to shortage of red equiv in chloroplasts and neg feedback reg'n resulting in lower demand for red'd N in new growth of Mn def plant, then NO_3 accum. No evidence of direct Mn^{2+} role (1985)

ELIMINATION OF SUPEROXIDES

- Superoxide dismutase (MnSOD)
  - Present in all aerobic organisms
    - Plays essential role in survival of organ if presence of oxygen
- $O_2 + e^- \Rightarrow O_2^-$ (Superoxide)

$$O_2^- + O_2^- + 2H^+ \xrightarrow{SOD} H_2O_2 + O_2$$

$$2\,H_2O_2 \longrightarrow 2H_2O + O_2$$

Mg CAN SUBSTITUTE FOR Mn

- Mg^{2+} 50 - 100 times > Mn^{2+} in cell
- Mn^{2+} necessary in cases where more effective than Mg^{2+}
- Activation of chloroplast RNA polymerase req's 10 x greater Mg^{2+} than Mn^{2+}

ABSOLUTE REQ'MT FOR Mn^{2+}

- Bundle sheath chloroplasts of C4 plants where oxaloacetate acts as carbon shuttle.
  - Decarboxylation catalyzed by
    - PEP carboxykinase which has absolute requirement for Mn^{2+}

Mn^{2+} ROLE IN O_2 EVOLUTION

- Decrease in Mn^{2+} only small effect on chlorophyll or leaf dry wt.
- But O_2 evolution drops by 50%
- When Mn def becomes more severe
  - Chlorophyll content decreases & not reversible.
  - Caused by inhib of lipid synthesis

CHO & LIPIDS

- Mn deficiency has severe effect on non structural CHO
  - Largest effect in roots
- Depress of lipid content in chloroplasts
  - Role of Mn in synthesis of lipids
  - Coupling of C_2 units
  - Mn increases lipids, reduces protein
  - Shift from linoelic to oleic

CELL DIVISION & EXTENSION

- Cell elongation responds better to Mn than cell division
  - Mn def plant roots have small nonvacuolated cells
- Inhibition of root growth in Mn defic plants caused by lack of CHO
- Mn essential to root growth

Mn DEFICIENCY

- Soils derived from material low in Mn
- Highly leached tropical soils
- Common in high pH soil
- Containing free carbonates
  - Soils high in OM esp prone to defic
- Corrected by soil or foliar $MnSO_4$ app
  - Soil treatment is best

Mn DEFICIENCY SYMPTOMS

- Soaking seed in $MnSO_4$ improves growth in Mn deficient soils.
- Peaches are susceptible to low Mn
- Critical Mn conc 10 - 20 ppm leaves
- Interveinal chlorosis in younger leaves of dicots
- "Gray speck" on older cereal leaves

Mn TOXICITY

- Wide range of concentrations
- Symptoms are brown speckles on mature leaves
  - Less distance in high light vs low lt
  - Brown specks contain oxidized polyphenols + MnO_2
  - Preceded by callous indicating toxic Mn^{2+} on Plasma Membrane & + Ca^{2+} influx

Mn TOXICITY INDUCES DEFIC

- Beans - interveinal chlor & necrosis
  - Combined with deformed young leaves, typical of Ca deficiency
  - Induced deficiencies of Fe, Mg, Ca
    - Mn toxicity countered by
      - High supply of Mg

INDUCED Ca DEFICIENCY

- Acropetal Ca transport mediated by basipetal IAA transport.
- Toxic Mn levels $\Rightarrow$ IAA oxidase $\Rightarrow$ Less IAA $\Rightarrow$ Less Ca transport
- Aggravated by high light intensity
  - Loss of apical Dominance
    - "Witches broom"

STEAM STERILIZATION

- Of media is opposite reaction
  - It is a reducing reaction
  - Steam kills oxidizing bacteria
  - Media under water as steam condenses & oxygen is lost
  - Decaying OM Sucks up the O_2
  - Mn analysis: 80 ppm in greenhouse media. Mn^{2+} in media highly toxic