BIOL 695

COPPER

Chapter 16
MENGEL et al, 5th Ed

GENERAL

- Transition element
  - Similar to Fe
    - Forms stable complexes
    - Easy electron transfer

    - $Cu^{2+} + e^{-} \Leftrightarrow Cu^{+} - e^{-}$

TERMINAL OXIDATION

- Cu^{+} unstable
- Most Cu functions based on
  - Enzymatically bound Cu in redox
  - Terminal oxidation in cells catalyzed by Cu not Fe
- Cu has high affinity for peptide & sulfhydryl groups

Cu IN SOIL

- H^{+} replaces Cu^{2+} and $CuOH^{+}$ more easily than most ions.
  - Does lime increase or decrease the availability of Cu?
- Cu strongly bound to OM.
  - Thus Cu found in upper part of soil
    - Where appl'd as fert or in OM

Cu DEFICIENCY

- Occurs primarily on humus rich soil which strongly binds Cu^{2+}
  - Stronger bond than Mn^{2+} & Zn^{2+}
- Chelates prevent adsorption to soil particles
- Cu complexes with mol wt < 1000 more available than those > 5000

UPTAKE & TRANSLOCATION

- Cu content of plants 2-20 ppm
  - 1/10 of Mn content
- Active uptake
- Cu & Zn inhibit uptake of each other
- Cu not readily mobile in plant
  - If plenty of Cu - it moves
  - If Cu deficient - it does not move

Cu PROTEINS

- Blue Proteins
  - Without oxidase activity
    - Plastocyanin
    - One electron transfer
- Non-blue Proteins
  - Peroxidases
  - Mono and diphenols

Cu PROTEINS

- Multi-copper Proteins
  - At least 4 Cu atoms / molecule
    - Which act as oxidases
      - Ascorbate oxidase
      - Diphenol oxidase
  - $2AH_2 + O_2 \Rightarrow A + HO$
  - Cytochrome oxidase (Fe-Cu) Protein catalyzing terminal oxidation in mitochondria.

PLASTOCYANIN

- 50% of Cu in chloroplasts bound in plastocyanin
  - 1 Cu atom / molecule
  - Component of electron transfer chain of photosystem I
- Cu defic $\Rightarrow$ PS I drastic reduction
  - Chlorophyll not affected
- PS I more affected by Cu defic than PSII

SUPEROXIDE DISMUTASE

- Detoxification of superoxide radicals O_2^-
- CuZnSOD Mol Wt. ~32 kDa
  - 1 Cu & 1 Zn atom at active site connected to a histidine N
  - Cu atom involved in detoxification of O_2^- generated in photosynthesis
- CuZnSOD controls peroxidation of membrane lipids
  - Thus involved in senescence

ASCORBATE OXIDASE

- Oxidizes ascorbic acid to dehydroascorbic acid
- Contains 4 Cu atoms / molecule
  - Operates 4-electron red $O_2 \Rightarrow H_2O$
- Ascorbate Oxidase activity (AOA) decreases in Cu defic & sensitive indicator Cu nutritional status.

RAPID FIELD TEST FOR Cu

- Simple colormetric field test for AOA dev for diagnosis of Cu deficiency.
- Results close to Cu cont. of leaves.
- Resupplying Cu to deficient plants
  - Restores AOA in very young lvs
  - Thus enzyme synthesized only in young leaves

ASCORBATE OXIDASE ACTIVITY

- In contrast to plastocyanin
  - Activity can be restored in mature leaves on resupplying Cu.

DIAMINE OXIDASE (DO)

- Polyamine oxidase are flavoproteins
  - Catalyze degradation of polyamines e.g.
- Spermidine $\Rightarrow$ Putrescine + H_2O_2 + NH_3
  (triamine) (diamine)
- DO in widespread in legumes & other
- Restoration with Cu confined to young leaves.

LIGNIFICATION OF WOUNDS

- DO in apoplasm of epidermis & xylem of mature tissue where funct
  - H_2O_2- delivery system for peroxidase activity for:
    - Lignification & suberization
    - DO increases in lignification of wounded areas (graft healing)

PHENOL OXIDASES (PhO)

- Two functions
  - 1) Hydroxylate monophenols to diphenols
  - 2) Oxidize diphenols to *o*-quinone
    - Dihydroxyphenylalanine (DOPA) activity

LIGNIN SYNTHESIS

- Polyphenol oxidases involved in biosynthesis of lignins
  - Formation of brown melanotic substances when tissues wounded
  - Active as phytoalexins (PLX)
    - Inhibit spore germination & fungal growth

DISEASE RESISTANCE

- Within few hrs post infection:
  - Signal transmitted to non-infected leaves which increase their phenol synthesis
    - Cu & B: profound influence on synthesis & binding of phenols
- Neg corr between inc N & phytolexin & Downy Mildew on grapes

Aspergillus niger

- **Black spores - Ample supply of Cu**
- **Light brown - Mild Cu deficiency**
- **White spores - Severe Cu deficiency**
- **Obvious deficiency symptom**

Chrysanthemum Flowering

- **Cu Defic - polyphenol oxidase decline**
  - **Delay in flowering & maturation**
  - **IAA oxidase & peroxidase also low**
- **Regeneration in tissue culture favored in Cu deficient plants. WHY?**

POLLEN FORMATION

- Cu deficiency - low CHO
  - Impaired pollen formation & fertiza
  - Depressed nodulation
  - Accumulation of AA & NO_3
    - No evidence for protein synthesis role for Cu
- N appl'n accentuates Cu deficiency
  - High N content - apply Cu fertilizer

RETRANSLOCATION OF Cu

- N effect on Cu availability & mobility
  - sequesters more Cu to AA & protein in mature leaves
  - decreases rate of retranslocation of Cu from older leaves
- Impaired retranslocation to new leaves (leaf deformation)

LIGNIFICATION

- Impaired lignification of cell walls
  typical anatomical change Cu def
  - Distortion of young leaves
  - Twisting of stems & twigs
  - Increased lodging of cereals
- Decr in lignin with mild Cu defic thus
  indicator of Cu nutritional status

POLLINATION

- Cu defic affects reproduction more
  than vegetative growth
- Lack of lignin in anther cell walls
  causes soft tapetum $\Rightarrow$ no rupture
  - Lack of starch in pollen
  - Induced pollen sterility in
    microsporogenesis

COPPER DEFICIENCY

- Stunted growth
- Distorted young leaves
- Necrosis of apical meristem
- Bleaching of young leaves (White Tip)
- Summer die back in trees
- Auxiliary shoots - caused by death of apical meristem

TREATMENT

- Wilting of young leaves > insufficient lignification of xylem vessels.
- Foliar applications of Cu (Caution)
- Soil appl of inorganic salt, oxides or Cu chelates

COPPER TOXICITY

- Critical toxicity above 20-30 $\mu g\ g^{-1}$
- May induce Fe deficiency
- Chlorosis result of Tox Cu on lipid peroxidation $\Rightarrow$ destruction of memb
- High Cu inhibits roots > shoots
  - Because roots are site for excessive Cu storage

SOURCES OF Cu POLLUTION

- Toxic Cu from fungicides used in grape vineyards
- Air Pollution
- City Waste
- Sewage sludge
- Swine & poultry slurries high in Cu

MECHANISMS OF Cu TOLERANCE

- **Exist in *metallphytes* special ecotype**
- **Ectomycorrhiza may have central role**
- **Excluder type (no uptake)**
- **Includer type (tolerance mechanisms)**
  - **Compartmentation as soluble or insoluble complexes**
    - **Within cytoplasm or vacuole**