BIOL 695

IRON

Chapter 13
MENGEL et al, 5th Ed

Micronutrient Cycling

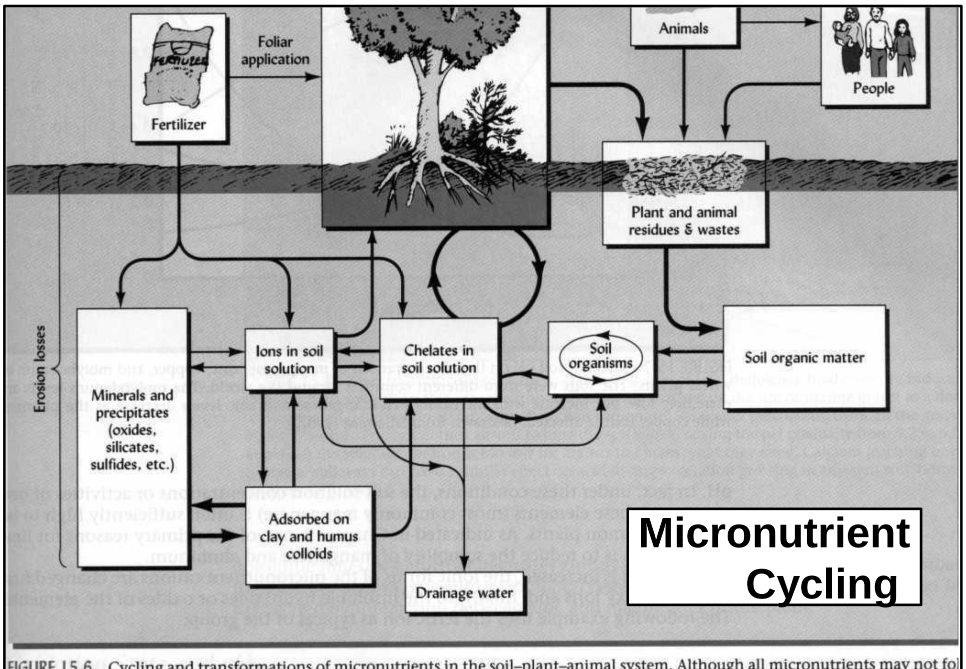


FIGURE 15.6 Cycling and transformations of micronutrients in the soil–plant–animal system. Although all micronutrients may not follow each of the pathways shown, most are involved in the major components of the cycle. The formation of chelates, which keep most of these elements in soluble forms, is a unique feature of this cycle.

SOIL Fe

- Primary minerals
  - Hematite (Fe_2O_3)
  - Magnetite (Fe_3O_4)
  - Siderite ($FeCO_3$)
- Secondary Oxides
  - $Fe(OH)_3 \cdot nH_2O$ - hydrous Fe oxides
  - $Fe(OH)_3$ - Fe oxide
  - Fe_2O_3 (hematite)

SOIL Fe

- Soluble Fe < < < Total Fe
- Soluble inorganic forms

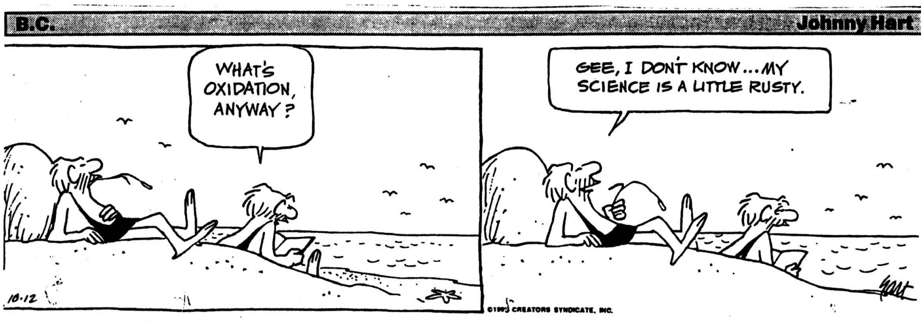
  Fe^{3+}

  $Fe(OH)_2^+$

  $FeOH^{2+}$

  Fe^{2+}

OXIDATION DEFINED



HIGH pH - LOW Fe UPTAKE

- Fe^{3+} activity decr 1000 fold each pH unit
  $Fe^{3+} + 3OH^- \Leftrightarrow Fe(OH)_3$ solid
- Under anaerobic cond red'n favored:
  $Fe(OH)_3 + e^- + 3H^+ \rightarrow Fe^{2+} + 3H_2O$
  - Thus red'n of Fe^{3+} to Fe^{2+} assoc with:
    - Consumption of H^+
    - Increase of pH

AERATION OXIDIZES Fe

- $Fe^{2+} + 3H_2O \rightarrow Fe(OH)_3 + e^- + 3H^+$
  - Oxidation of Fe^{2+} to Fe^{3+}
  - Fall in pH
- Higher levels of Fe^{2+} (of the soluble Fe) in deeper, less well aerated soil layers

LEACHING

- Fe forms organic complexes (chelates) [plant or soil]
  - In excessively leached
    - Poorly drained soils
    - Fe is mobilized from upper horz
    - Re-deposited in lower profile

UPTAKE AND TRANSLOCATION

- Fe^{2+} and Fe chelates
  - available to plants
- Fe^{3+} not available (Fig. 13.1 M&K)
- Thus absorption of Fe by roots depends on
  - Ability of roots to reduce Fe^{3+} to Fe^{2+} in rhizosphere

PHYTOSIDEROPHORES

- Strategy I
  - Dicots & non-graminaceous monocots
  - Characterized by 2 components of Fe deficient plants:
    - Increased reducing capacity
    - Enhanced net excretion of protons

STRATEGY I

- **May be characterized by Reducing compounds**
  - **Chelating compds like phenolics**
- **Root responses related changes in**
  - **root anatomy in formation of transfer structures in root cells.**
- **Increase of plasma membrane bound reductase in rhizodermal cells (R)**

STRONG EXCRETION OF PROTONS

- **Occurs under Fe deficiency**
  - **Caused by higher activity of**
    - **Plasma membrane proton efflux pump**
      - **NOT the reductase (R)**

STRATEGY II (GRAMINACEOUS)

- **Release of Phytosiderophores**
  - **Fe deficieny-induced enhanced release of non-proteinogenic AA**
  - **Release follows diurnal rhythm**
  - **Suppressed by resupply of Fe**

PHYTOSIDERPHORES

- **Such as mugineic acid**
  - **Forms stable complexes with Fe^{3+}**
- **Second component**
  - **Highly specific transport system (Tr) present in plasma membrane**
    - **Tr transf Fe^{3+} Phytosiderophores into cytoplasm**

Fe^{3+} REDUCTION

- At outer plasmalema mediated by
  - Electrons from within cell via
    - Cytochrome, or
    - Flavin compound
- Fe chelates supplied at low levels
  - Fe separates from chelates
    - Fe in, chelate out

Fe UPTAKE IS ACTIVE

- Fe in stem 30x > Fe in ambient sol'n.
- Uptake influenced by other cations
  - Heavy metals that induce Fe defic
    - Mn^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, K^{+}, Zn^{2+}
- Fe efficient species are able to lower pH of nutrient medium. Is this imp?

NO_3^- DEPRESSES; NH_4^+ INCREASES Fe UPTAKE

- **WHY? (H^+ in soil & efflux from root)**
- **Major form of Fe translocation in xylem is ferric citrate**

BIOCHEMICAL FUNCTIONS

- **Forms chelates**
- **Valence changes**
  - $Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$
- **Fe is part of cytochrome system**
  - **Only 0.1% in cytochrome**
  - **Remainder in Ferric phosphoprotein, PHYTOFERRITIN**

PHYTOFERRITIN

- **Protein shell**
  - **Interior ~ 5000 Fe^{3+} atoms**
- **High in dark-grown leaves (~50%)**
  - **Rapidly disappears when de-greens**
  - **Remains low in green leaves**
- **When Fe applied to Fe-deficient plants**
  - **Fe in phytoferritin increases rapidly**

Fe STORAGE

- **Phytoferritin not confined to chloroplasts**
  - **Also in xylem & phloem**
  - **Abundant in seeds**
  - **Rapidly degrades with germination**
  - **Storage for Fe in nodules**

80% Fe IN CHLOROPLASTS

- Fe associated with chlorophyll synthesis
- ^{59}Fe corresponds to green part of tomato plant (Plate 13.1 M&K)

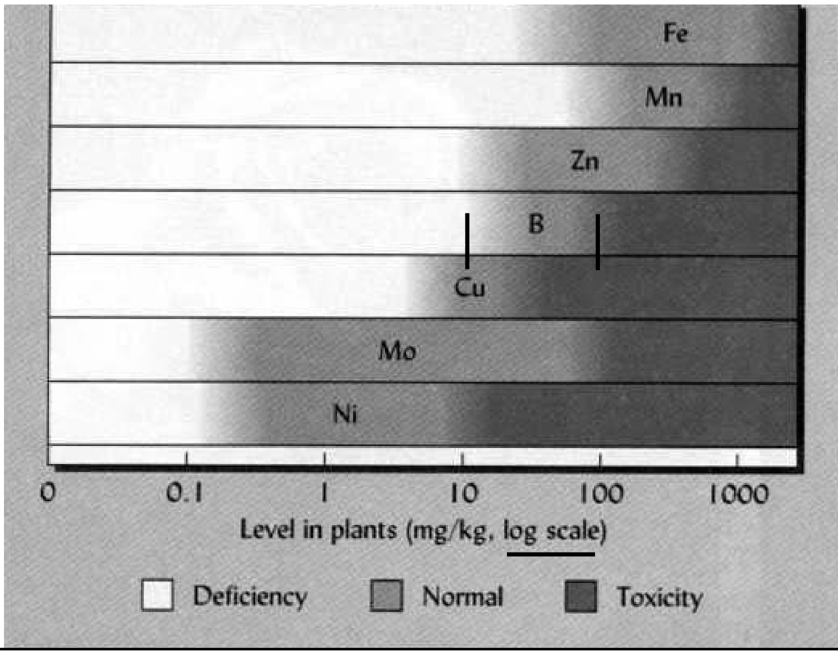
DEFICIENCY

- Both Fe & Mg deficiency characterized by failure of chlorophyll production
- Does deficiency appear in same part of plant? Why or why not?
- Chlorosis is interveinal - fine pattern.
  - Dark green veins on yellow backgr
  - Later - white

MORPHOLOGICAL CHANGES

- In root tips due to enlargement of cortex
  - Intensifies develop'mt of root hairs
- Cu & Zn may replace chelated complexes of Fe
- High PO_4^- and Ca^{2+} depresses Fe uptake
- High pH + aeration $Fe^{2+} \rightarrow Fe^{3+}$

DEFICIENCY, NORMAL & TOXICITY LEVELS



Fe AVAILABILITY

- P/Fe Ratio higher in deficient tissue
  - Shift to Fe^{3+}
  - Not available even high in nutrition analysis.
- 100 ppm Fe normal in green tissue
  - Much higher in most soils
- Plants require ~ 0.5 ppm Fe in soil

Fe AVAILABILITY

- Total in soil commonly 2% (20,000 ppm).
  - Thus problem is availability
- At normal pH, inorganic Fe levels below plant requirement
  - Soluble Fe-organic complexes are necessary

Fe AVAILABILITY

- **Alpha keto glutaric acid excreted from root tip, solubilizes Fe**
- **Chelate conc of 10^{-6} to 10^{-7} adeq**
- **Only root tips can absorb Fe**
- **Fe deficiency more common in calcifuge plants Azalea, rhododendron, *Vaccinum***

LIME INDUCED CHLOROSIS

- **Deficiency in high pH-calcareous soils**
- **Conditions aggravated by:**
  - **High HCO_3^- causing increased pH**
    - **Immobilizes Fe**
  - **NO_3-N rather than NH_4-N**
  - **Poor aeration - $CO_2 \Rightarrow HCO_3^-$**

MORE ON CHLOROSIS

- Ca & Fe compete for same binding site on chelating compound
- Fe-phosphates may ppt external to root. Excess P interferes with mobility of active Fe.
- High Mn may compete for enzymes.
- What other factors induce Fe-chlor?

Fe FERTILIZERS

- Fe salts not effective in soil because of conversion to oxides.
- Foliar $FeSO_4$ superior to chelates.
- Fe chelates more effective in soil than foliar.
- NH_4 fertilizer may increase Fe abs.