GEOL 408/508

CALCIUM, MAGNESIUM and TRACE ELEMENTS

Chapter 15

Brady and Weil, Rev. 14th Ed.

CALCIUM AND MAGNESIUM AS PLANT NUTRIENTS

Calcium:

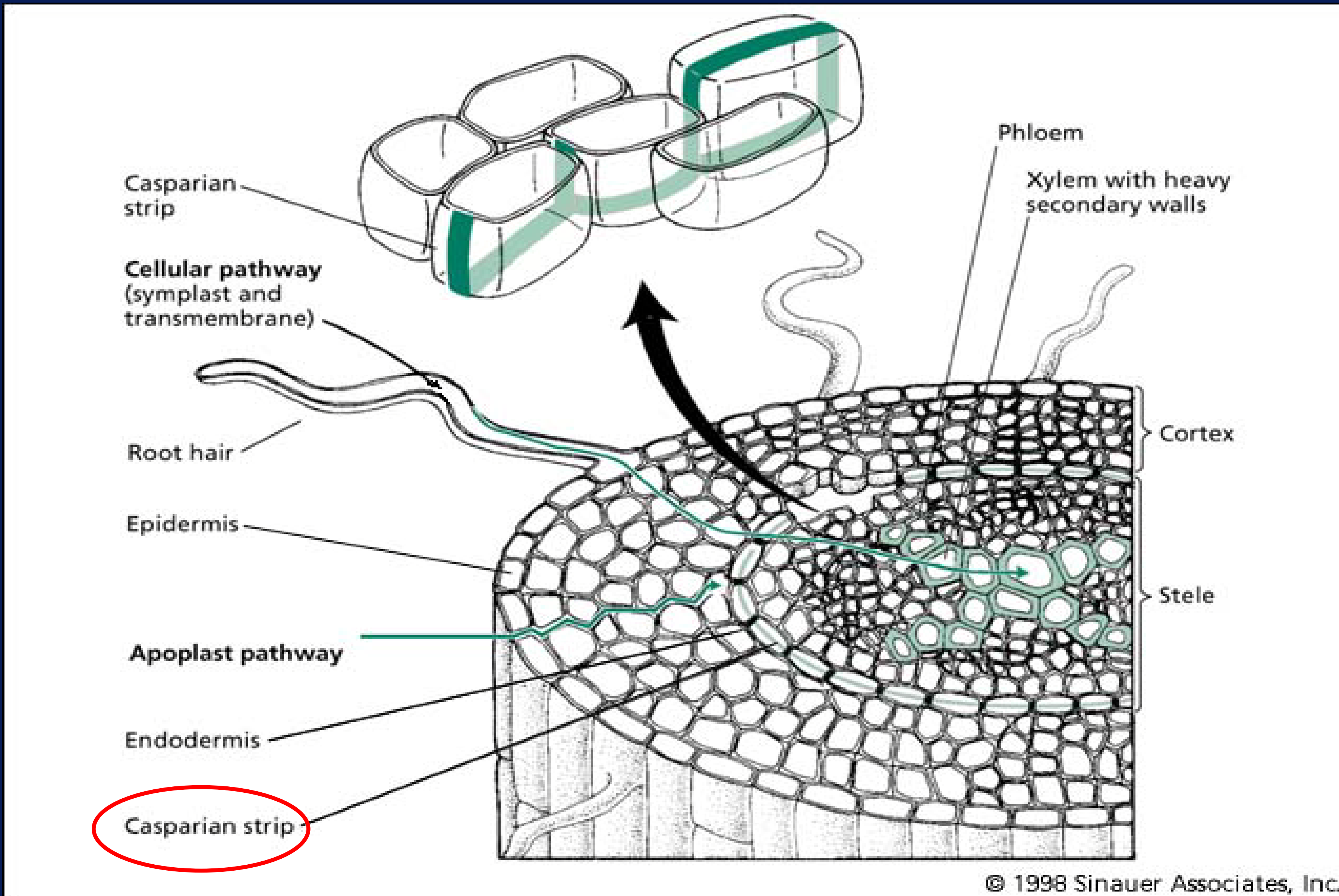
Ca uptake

- K^+ uptake 10 times more efficient than Ca^{2+} uptake.

- Low Ca^{2+} uptake because only absorbed by young roots prior to Casparian strip formation
  - Anything that reduces root growth reduces Ca^{2+} absorption.

    What are they?

RADIAL ROOT TRANSPORT



CALCIUM AND MAGNESIUM AS PLANT NUTRIENTS

Calcium:

Ca uptake:

- **Dependent on transpiration steam.**
  - **Ca^{2+} transport controlled by humidity.**
  - **BER (blossom end rot) cause**
    - **Drought**
    - **Water logged soil**
    - **NH_4^+ application**
    - **High salt concentration**
    - **Low temperature**

CALCIUM AND MAGNESIUM AS PLANT NUTRIENTS

Calcium:

Ca uptake:

- Growing points receive preferential amounts of Ca compared to older leaves even with less transpiration.
- Once Ca^{2+} in older leaves, cannot be mobilized to growing tips.
- Why doesn't Ca^{2+} move out?
  - No Ca^{2+} movement in phloem
    - Tissue supplied by phloem sap (fruit) has less Ca^{2+} than leaves.

CALCIUM AND MAGNESIUM AS PLANT NUTRIENTS

Calcium - deficiency:

- Reduction in growth of meristem
- Necrosis in leaf margins in advanced stage
- Becomes soft due to cell wall dissolution
- Brown suberian accum in intracellular spa and in transport tissue / affect transpiration
- Not usual in soil but can occur in artificial media
- Apple bitter pit
  - Surface pitted with small brown necrotic spots
- Tomato and watermelon blossom end rot

Ca DEFICIENCY IN TOMATO

Upward cupping of leaves, marginal necrosis and terminal tissue in calcium-deficient tomato plant.

BLOSSOM-END ROT OF TOMATO CAUSED BY CALCIUM DEFICIENCY

Ca DEFICIENCY IN TOMATO

Blossom-end rot of tomato caused by calcium deficiency.

Ca DEFICIENCY IN APPLE FRUIT

Calcium deficiency (bitter pit) in 'Northern Spy' apple fruit.

CALCIUM AND MAGNESIUM AS PLANT NUTRIENTS

Magnesium:

Roles in plant:

- Mg^{2+} central ion in chlorophyll
- Proportion of total Mg bound in chlorophyll depends on Mg supply:
  - 6 - 25% of total Mg in chlorophyll
  - 5 - 10% in cell wall pectates
  - Small amount in vacuoles
- Mg^{2+} bound in chlorophyll might be as high as 50% in low light.
- Chlorophyll takes precedence over other functions
  Content depends on availability of Mg^{2+}

CALCIUM AND MAGNESIUM AS PLANT NUTRIENTS

Magnesium:

Deficiency symptons:

- Mg^{2+} mobile, thus deficiency is where?
  Enhances protein degradation
  Other pigments also affected
- Interveinal yellowing - chlorosis
- Confused with virus yellowing
- May appear withered as in K deficiency
- Stiff & brittle leaves
- Leaves abscise prematurely

MAGNESIUM DEFICIENCY IN TOMATO

Yellowing and white chlorotic and necrotic interveinal tissue of older tomato leaves caused by Mg deficiency.

MAGNESIUM DEFICIENCY IN CHRYSANTHEMUM

Interveinal chlorosis of lower leaves in chrysanthemum caused by magnesium deficiency.

CALCIUM AND MAGNESIUM AS PLANT NUTRIENTS

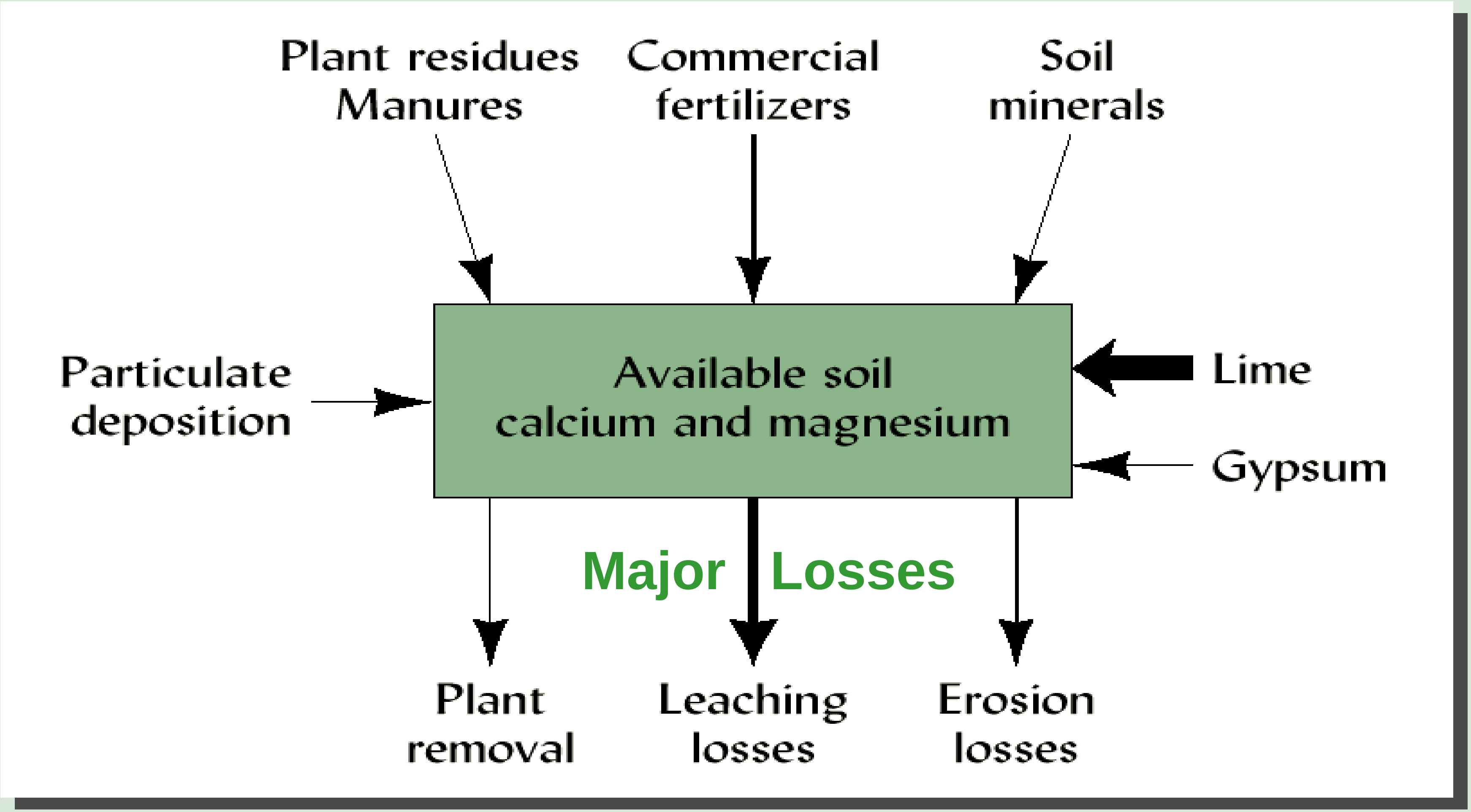
Ratio of calcium to magnesium:

- Mg is held less tightly and therefore leaches more easily than Ca

- Exchangeable Mg:Ca ratio in soil is usually from 1:4 to 1:12

- Acceptable ratio for good plant growth appears to be from 1:1 to 1:15 (Mg:Ca)

Ca & Mg EQUILIBRIA IN SOILS



Important ways by which available calcium and magnesium are supplied to and removed from soils (Figure 15.5).

DEFICIENCY VERSUS TOXICITY

More concern with micronutrients than with macronutrients for deficiency - sufficiency - toxicity ranges

- Macronutrients have wide sufficiency range
- Micronutrients have narrow sufficiency range
- May find problems with:
  - Cu, Zn - industrial sludges, swine manure, long-term use of $CuSO_4$ fungicide (problem when vineyards are converted to other uses)
  - B, Mo - poorly drained alkaline soils, irrigation water

DEFICIENCY VERSUS TOXICITY

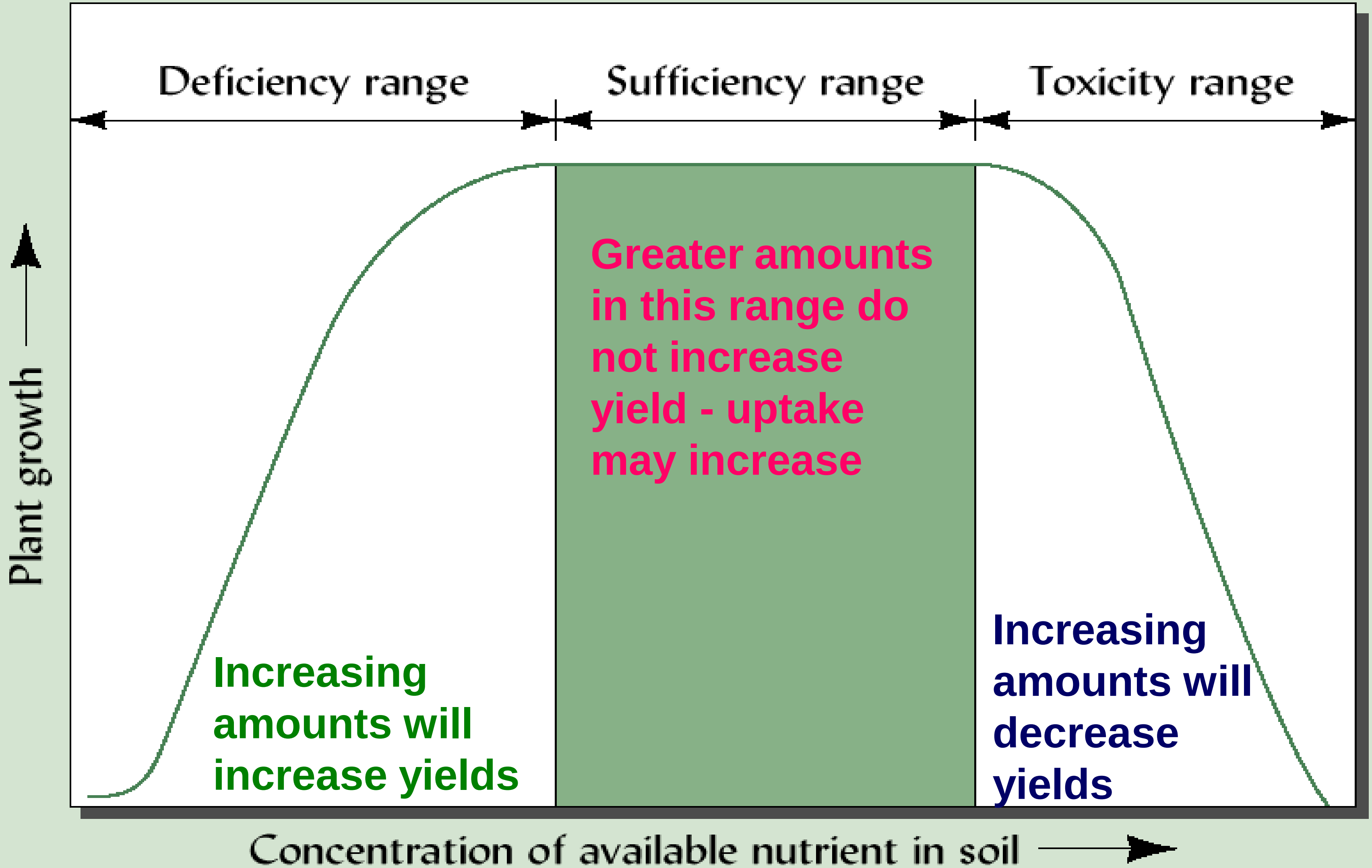
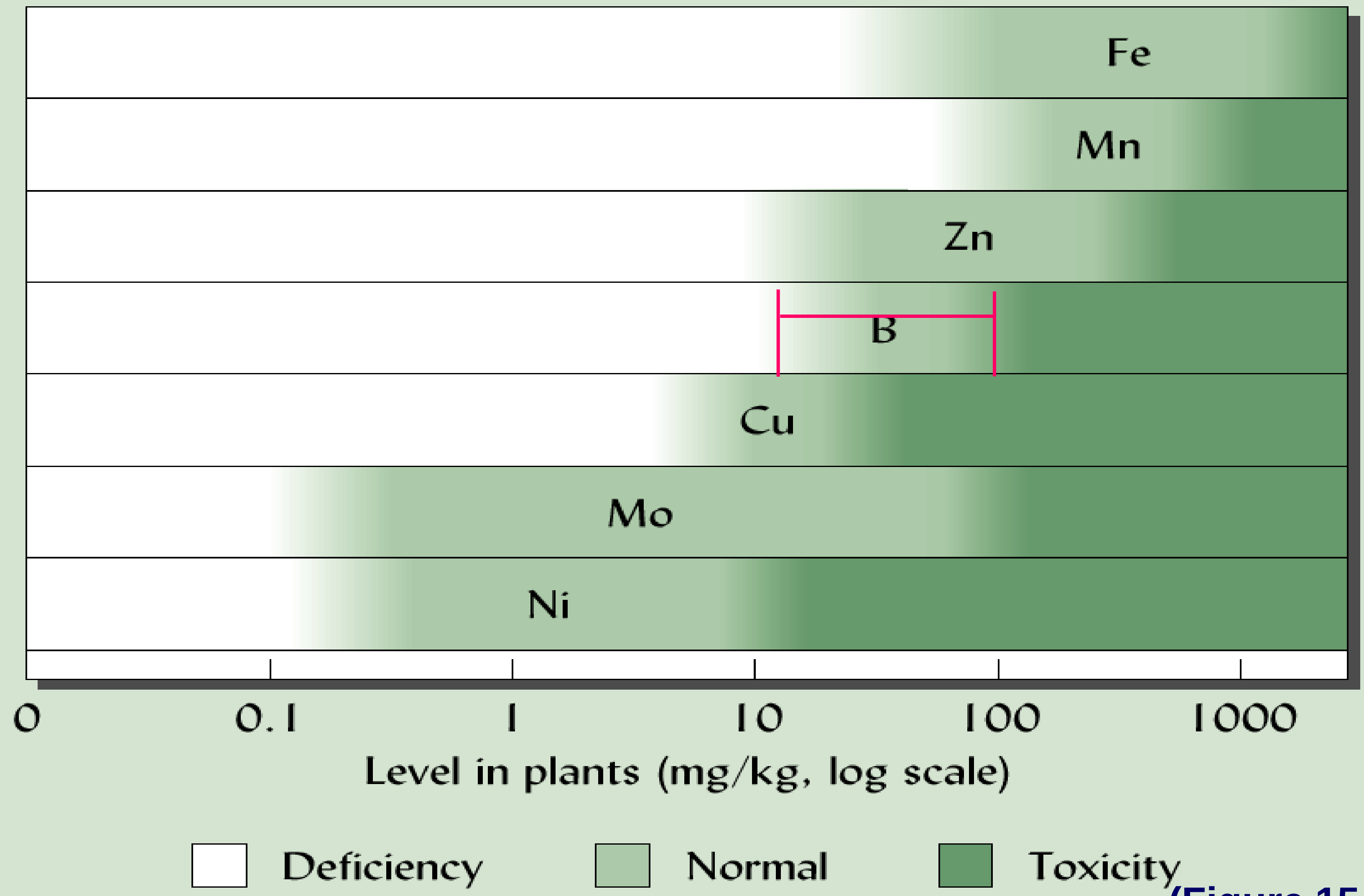


Figure 15.6)

DEFICIENCY, NORMAL & TOXICITY LEVELS IN PLANTS



(Figure 15.8)

ROLE OF THE MICRONUTRIENTS

Mn - enzyme activation; photosynthesis processes

B - enzyme activation; sugar translocation

Cu - enzyme activation; photosynthetic electron transp

Zn - enzyme activation; auxin synthesis for cell elong’n

Mo - nitrate reduction enzymes; N fixation

Cl - Photosynthetic oxygen evolution

Fe - Enzyme activation; redox reactions

Ni - component of enzymes such as urease

Co - essential for N fixation (for Rhizobium spp.)

SOURCE OF MICRONUTRIENTS

Inorganic forms:

- Original source is primary minerals
- Many are present in a variety of secondary minerals, such as oxides, clay minerals, other silicates
- See Text, Table 15.2
- Some from atmosphere: Cl, SO_4

Organic forms:

- Several micronutrients are complexed by humus
- Degree of availability from humus is variable

Forms in solution:

- Cationic forms: Fe, Mn, Cu, Zn, Ni, Co
- Anionic forms: Cl, B, Mo

MICRONUTRIENT CYCLE

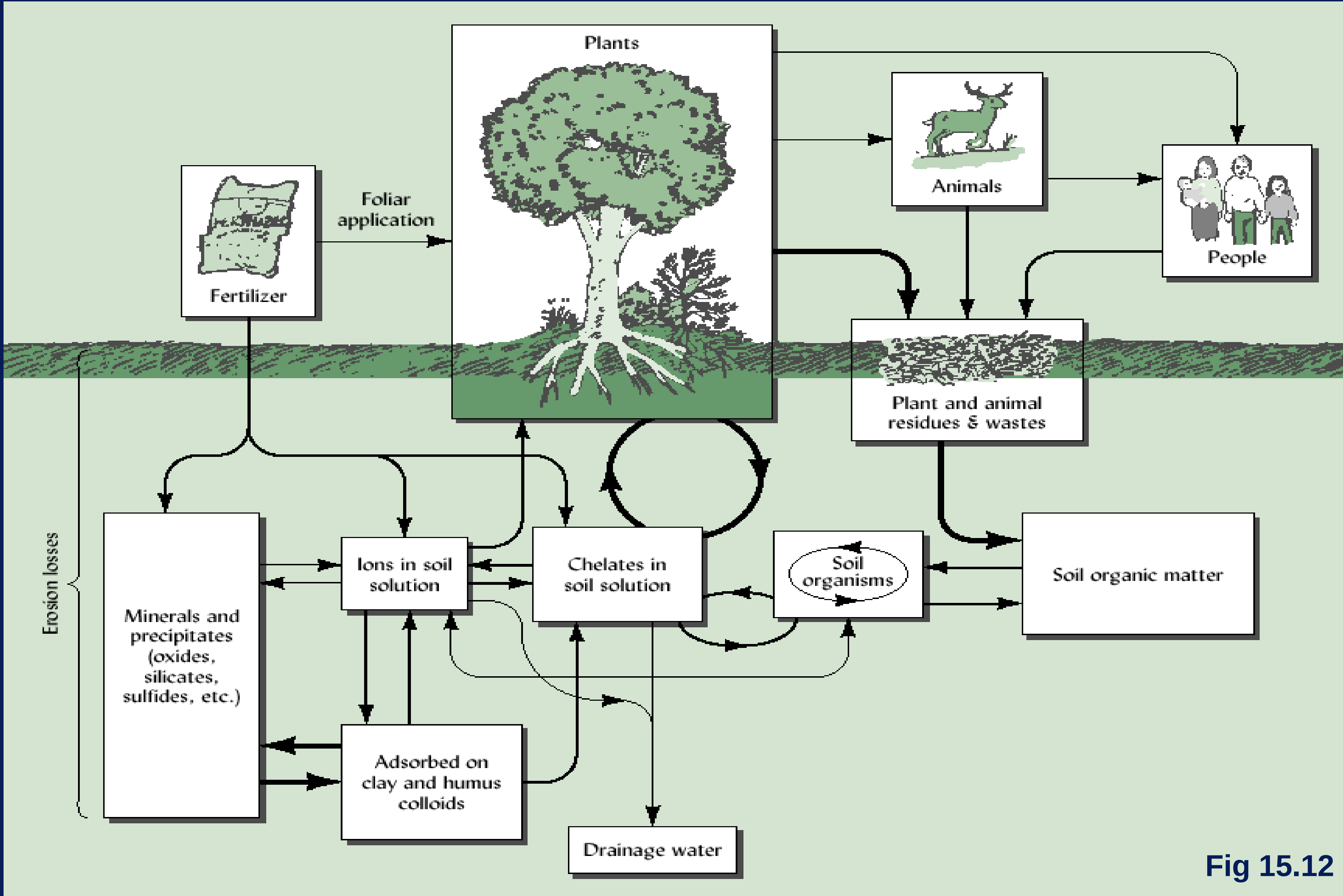


Fig 15.12

GENERAL CONDITIONS CONDUCIVE TO TRACE ELEMENT DEFICIENCY/TOXICITY

- Leached, acid, sandy soils: deficient in most micros
- Organic soils: often deficient; content depends on source material at time of soil formation
- Intensive cropping: deficiencies likely; especially when high levels of N-P-K only fertilizers applied
- Extremes of pH: at low pH, the cationic forms are most avail, may be toxic; Mo is unavailable
  - at high pH, cationic forms least avail; Mo avail high
- Eroded soils: topsoil with humus removed; subsoil may have higher pH
- Parent materials: deficiency or toxicity may be f'n of PM
- Waste disposal: tr ele's may not have been monitored

FACTORS INFLUENCING AVAILABILITY OF TRACE ELEMENT CATIONS

Soil pH:

- Most soluble under acid conditions and are converted to hydroxyl forms as pH increases

  $Fe^{3+} \rightarrow Fe(OH)^{2+} \rightarrow Fe(OH)_2^{+} \rightarrow Fe(OH)_3 \downarrow$

- Overliming leads to deficiency of Fe, Mn, Zn, Cu, B
- Zn availability may be be further reduced by high-Mg liming materials

Oxidation state and pH:

- Fe, Mn, Ni & Cu are more soluble in reduced forms
- Possible toxicity of Fe & Mn in anaerobic soils

FACTORS INFLUENCING AVAILABILITY OF TRACE ELEMENT CATIONS - 2

Oxidation state and pH:

Interaction of soil reaction and aeration:

- $Fe(OH)_3$ precipitates at pH 3-4
- $Fe(OH)_2$ precipitates at pH ≥6

• Mn toxicity may occur in some soils under heavy irrig'n

• Well-oxidized calcareous soils may be deficient in Fe, Mn, Zn

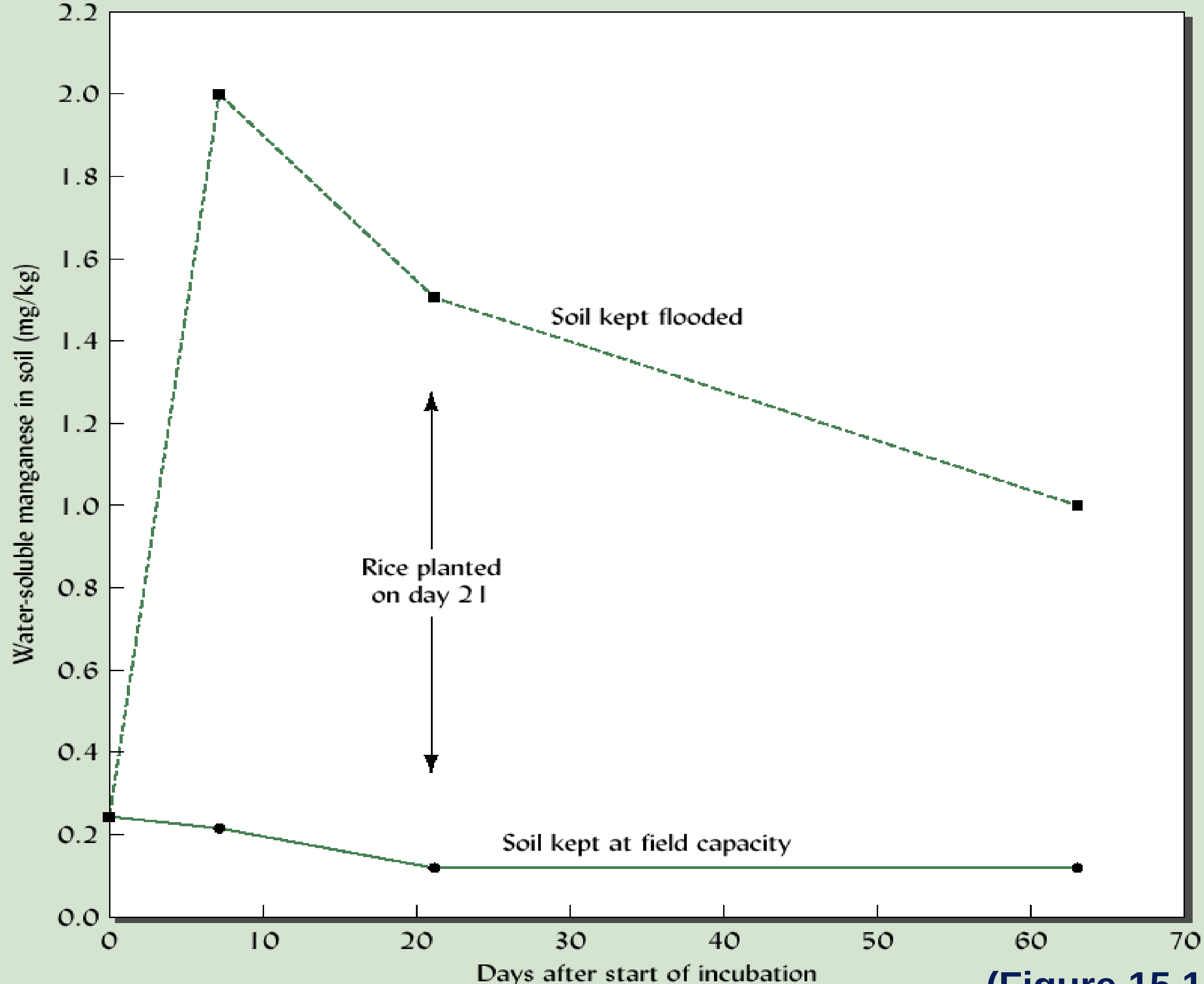
• Mo toxicity in livestock possible with high pH soils

Other inorganic reactions:

- may be tightly bound to silicate clays (inner sphere sorption)
- cations may occur in xal structure of silicate clays
- some cations may form insol compounds with PO_4

INTERACTION OF SOIL REACTION AND AERATION

Effect of flooding on the amount of water-soluble Mn in soils.



(Figure 15.15)

FACTORS INFLUENCING AVAILABILITY OF TRACE ELEMENT CATIONS - 3

Lime-induced chlorosis:

- especially common for Fe deficiency
- over-liming or bicarbonate-containing waters

Organic matter:

- may tightly bind trace metals in slowly avail forms
- may cause deficiencies of Cu, Mn
- may have temp deficiency after adding fresh OM

Role of mycorrhizae:

- aids in uptake of micronutrients
- may protect plant from excessive uptake of trace elements
- several tree seedlings grow on metal-contaminated sites only when roots have mycorrhizae

ORGANIC COMPOUNDS AS CHELATES

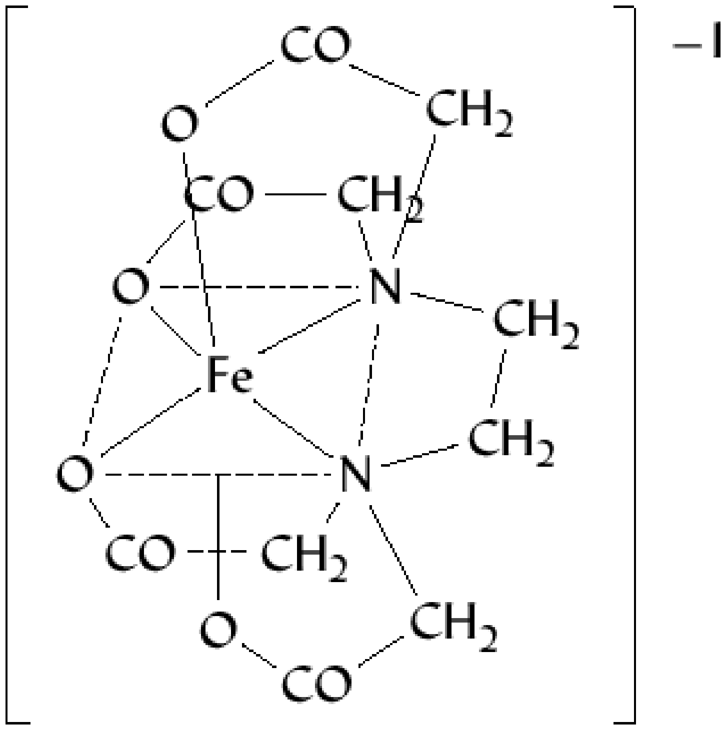
Chelate: an organic compound having two or more atoms capable of binding with the same ion, forming a ring

- Many natural and synthetic chelates
- Chelated cations are protected from precip'n reactions
- Especially important for Fe nutrition (used for all micros)
- Most plant roots will remove Fe from chelate at outside of root; others will absorb chelate, remove Fe, excrete chelate

Stability of chelates:

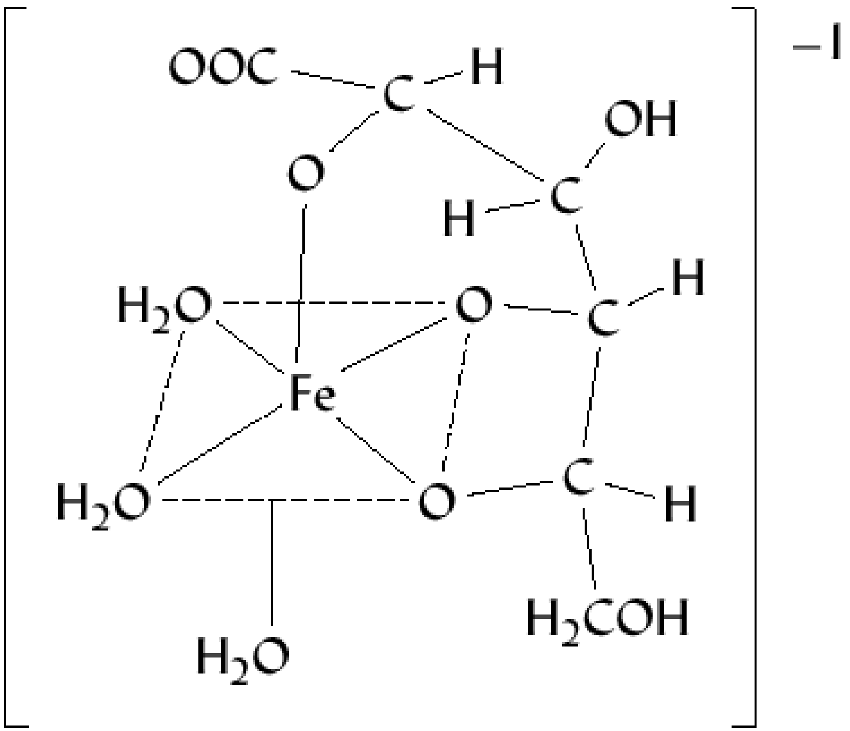
- stability varies for different chelates (see Table 15.4)
- use this value to determine which element will be most stable; which will replace which
- chelated forms are $$$; use for high value crops

ORGANIC COMPOUNDS AS CHELATES



Fe (III) EDTA

(*a*)



Fe(III) gluconate

(*b*)

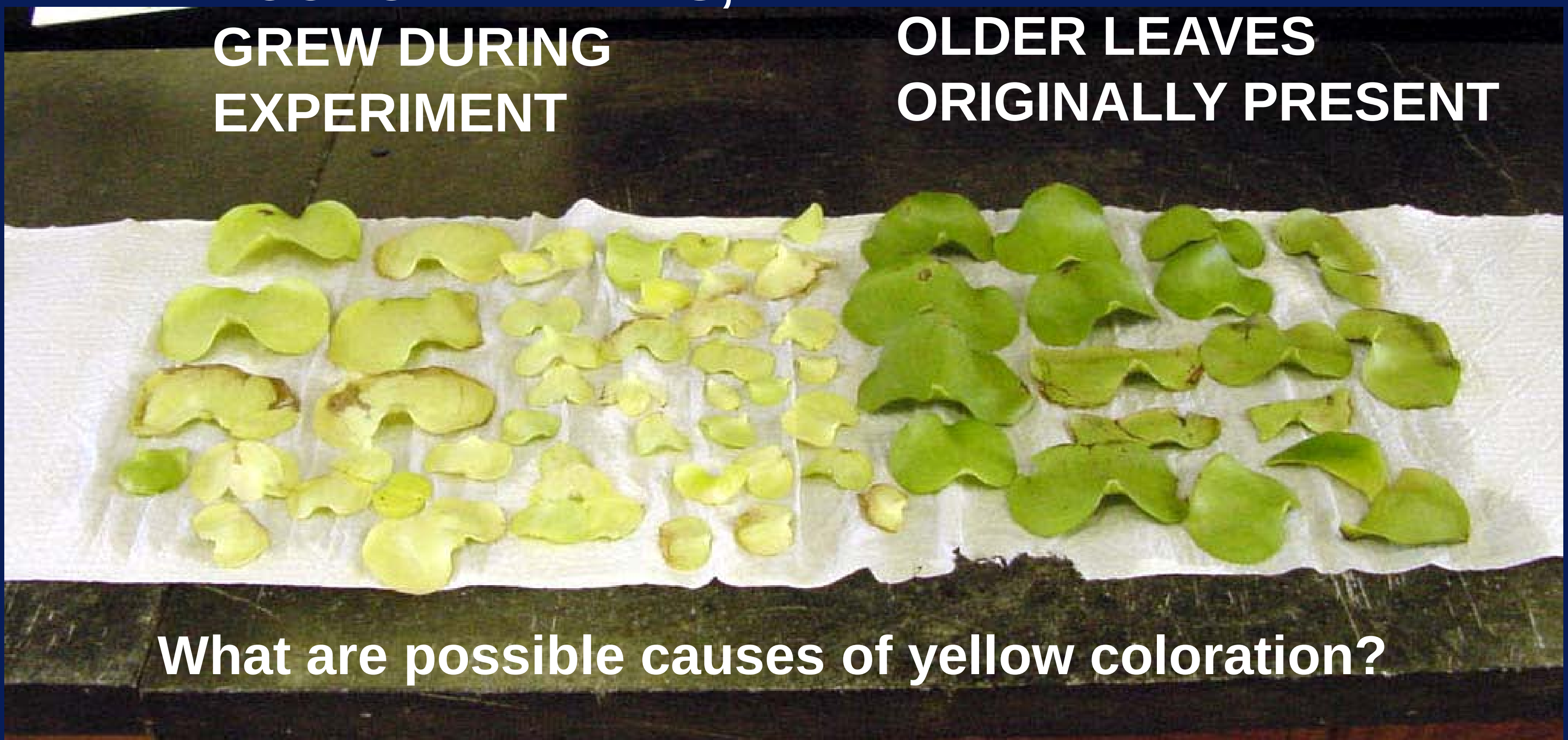
(Figure 15.21)

HYDROPONIC EXPERIMENT WITH WATER HYACINTHS

Designed to Determine N Uptake;

All Tmts Exhibited Yellowing

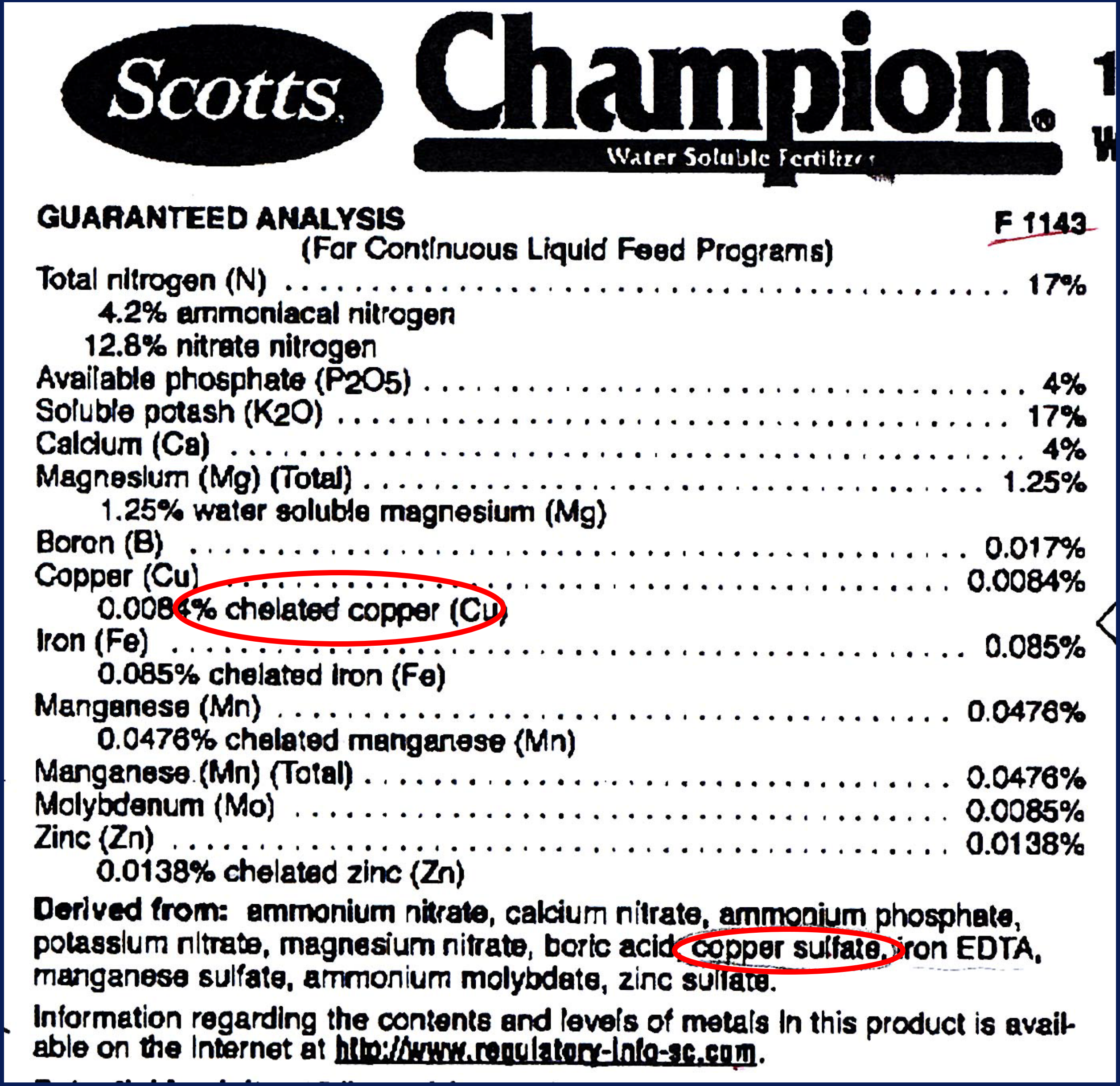
OLDER AND YOUNGEST LEAVES FROM 200 PPM N TMT



FERTILIZER LABELS: TRUE OR FALSE

What are the forms of Cu, Fe, Mn and Zn in the fertilizer?

What were the forms of Cu, Fe, Mn and Zn after solubilization of the fertilizer?



Scotts Champion® Water Soluble Fertilizer

GUARANTEED ANALYSIS F 1143

(For Continuous Liquid Feed Programs)

Total nitrogen (N)	17%
4.2% ammoniacal nitrogen	
12.8% nitrate nitrogen	
Available phosphate (P_2O_5)	4%
Soluble potash (K_2O)	17%
Calcium (Ca)	4%
Magnesium (Mg) (Total)	1.25%
1.25% water soluble magnesium (Mg)	
Boron (B)	0.017%
Copper (Cu)	0.0084%
0.0084% chelated copper (Cu)	
Iron (Fe)	0.085%
0.085% chelated iron (Fe)	
Manganese (Mn)	0.0476%
0.0476% chelated manganese (Mn)	
Manganese (Mn) (Total)	0.0476%
Molybdenum (Mo)	0.0085%
Zinc (Zn)	0.0138%
0.0138% chelated zinc (Zn)	

Derived from: ammonium nitrate, calcium nitrate, ammonium phosphate, potassium nitrate, magnesium nitrate, boric acid, copper sulfate, iron EDTA, manganese sulfate, ammonium molybdate, zinc sulfate.

Information regarding the contents and levels of metals in this product is available on the Internet at http://www.regulatory-info-sc.com.

STABILITY OF EDTA COMPLEXES

Fe^{+3}EDTA >> CuEDTA > ZnEDTA > Fe^{+2}EDTA > MnEDTA

If there was Fe^{+3}EDTA in the fertilizer what would happen upon solubilization of the fertilizer?

If there was NO Fe^{+3}EDTA in the fertilizer what would happen upon solubilization of the fertilizer?

If there was Fe^{+2}EDTA in the fertilizer what would happen upon solubilization of the fertilizer?

How would you test the hypothesis that the availability of Fe was affected by its displacement by the other micronutrients?

HYACINTH GROWTH IN 17-4-17 FERTILIZER WITH AND WITHOUT EXTRA EDTA

Plants after 1 week growth in nutrient solutions

AVAILABILITY OF THE TRACE ELEMENT ANIONS

Chlorine:

- common form is Cl^{-1}; highly water soluble
- may become excessive in poorly drained saline soils
- generally no nutritional problems
- may reach toxic levels with high rates of KCl app'ln

Boron:

- one of the most commonly deficient micronutrients
- very soluble at low pH; leached from sandy soils
- may bind with Al in OH's at high pH
- very strongly bound by humus (major reservoir)
- uptake may be reduced during drought periods

AVAILABILITY OF THE TRACE ELEMENT ANIONS

Molybdenum:

- soil pH is most important factor influ'ng availability
- avail at high pH; sorbed to oxides at low pH
- liming generally increases availability
- phosphate generally improves availability
- sulfate reduces Mo uptake by plants

Selenium:

- not essential for plants; essential for animals
- several ionic forms; redox sensitive
- selenates (SeO_4^{2-}) most soluble; prominent in high pH, well-aerated soils; generally most toxic
- some plants, in assoc'n with bacteria & fungi will uptake Se and release it as a volatile comp'd
  - used in phytoremediation

AVAILABILITY OF THE TRACE ELEMENT ANIONS

Other trace elements:

Arsenic:

- some studies have shown plant & animal essentiality
- major concern over ground-water contamination by As in Bangladesh, India, China, Chile & Slovakia
- some areas of western US have high levels
- use Fe oxides & plants to remove from water

Chromium:

- essential for humans in trace amounts; toxic in higher levels
- wastes from steel, pigment, tannery industries
- found as [Cr(III)] & [Cr(VI)] - most soluble, mobile
- to remediate, reduce to [Cr(III)]

ARSENIC IN GROUNDWATER IN USA

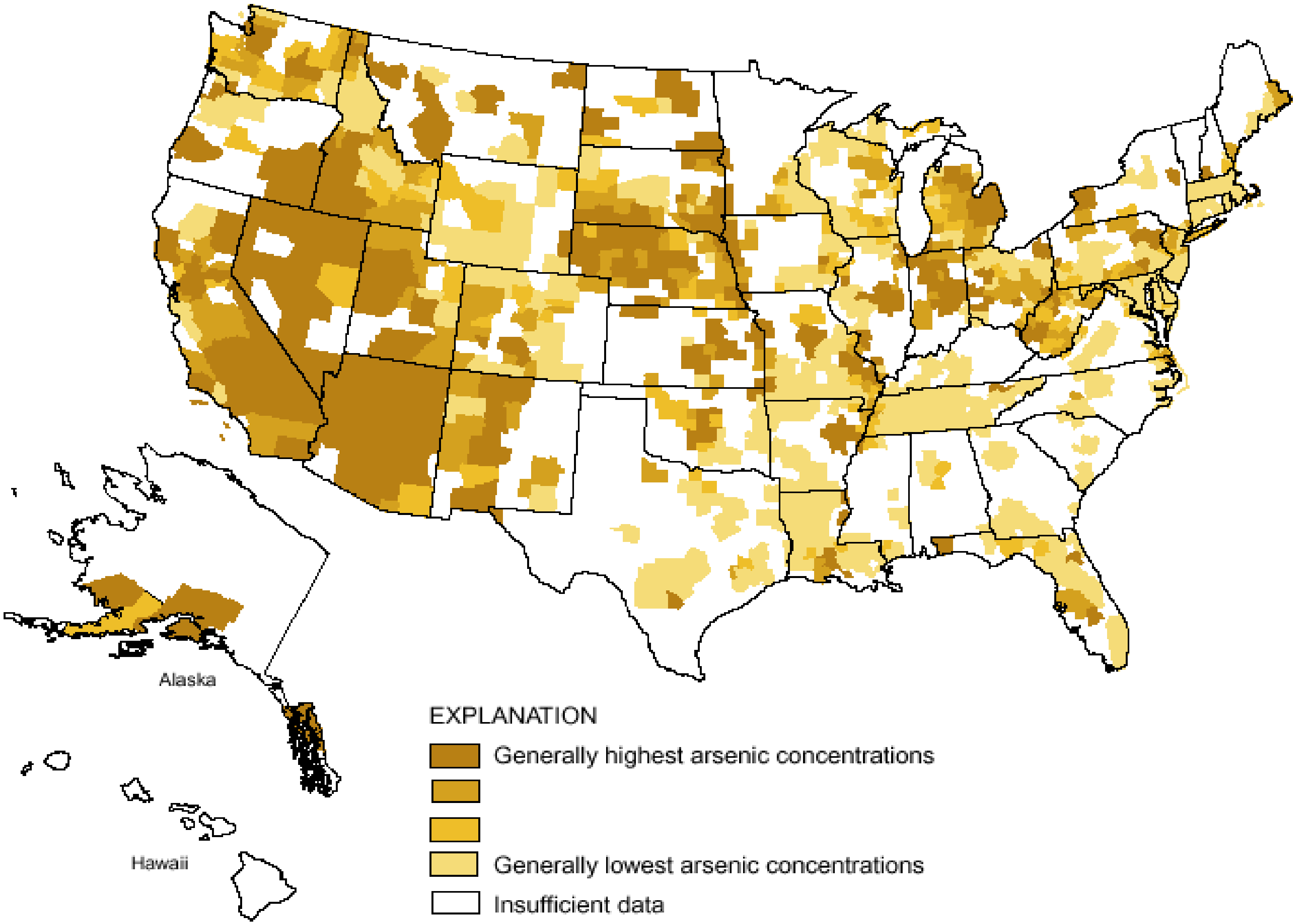


Figure 3. *Counties with arsenic concentrations exceeding possible new MCLs in 10 percent or more of ground-water samples.*

AVAILABILITY OF THE TRACE ELEMENT ANIONS

CCA wood preservative:

- Chromated copper arsenate (CCA) is used to preserve lumber for outdoor use
- Commonly called “salt-treated” lumber; has greenish color
- As leaches from lumber into soil and may reach relatively high concentrations
- Mobility is especially high in sandy soils
- Potentially a problem in playground areas where CCA treated wood is present
- May be concern for veggie gardens with CCA border
- Being replaced with Cu-NH_4 based treatment

NEED FOR NUTRIENT BALANCE

- Nutrient balance is difficult to maintain for micronutrients
- Many plant processes depend upon multiple elements
- Mn & Mo needed for N assimilation
- Zn & P for optimum use of Mn

Antagonism & synergism: (see Table 15.10)

- Antagonistic effects:
  - Cu toxicity reduced by adding Fe & P fertilizers
  - liming may induce deficiencies but may reduce toxicities of other trace metals
- Synergistic effects:
  - B enhances uptake of Fe & Cu
  - P enhances uptake & plant utilization of Mo

TRACE ELEMENT CLEANUP AND METAL HYPERACCUMULATORS

Hyperaccumulators are plant species that accumulate metal concentrations to very high levels in their tissues (<0.1% or > 1%, depending upon metal)

- Use to reduce metal contamination in soils
- Grow successive crops, harvesting and disposing of tissue; or recovering metals from tissue
- Phytoremediation is use of higher plants to remove chemical pollutants
- Presently, most hyperaccumulators have low biomass, making their use impractical
- Genetic engineering being used to improve accumulators

SOIL MANAGEMENT AND MICRONUTRIENT NEEDS

Changes in soil acidity:

- very acid soils: toxicities of Fe & Mn; deficiencies of P & Mo - correct by liming & fertilizer additions

• Very general guide: pH of 6-7 in medium textured soils should supply adequate levels of micronutrients

Soil moisture:

- improve drainage of acid soils will lessen availability of Fe & Mn

- increase moisture to increase availability of Fe & Mn in acid soil but not in alkaline soil

- poor drainage increases availability of Mo to point of possible toxicity

SOIL MANAGEMENT AND MICRONUTRIENT NEEDS

Fertilizer applications:

- micronutrient deficiencies unlikely where sufficient OM is returned to soils
- commercial fertilizers are more frequently used
- may be impractical to apply sufficient OM
- foliar sprays may be used in difficult situations
- applications are becoming increasingly necessary due to increased production and higher purity in filler materials in N-P-K fertilizers
- plant nutrient requirements vary widely (Table 15.12) - must match requirements in crop rotations

SOIL MANAGEMENT AND MICRONUTRIENT NEEDS

Plant selection and breeding:

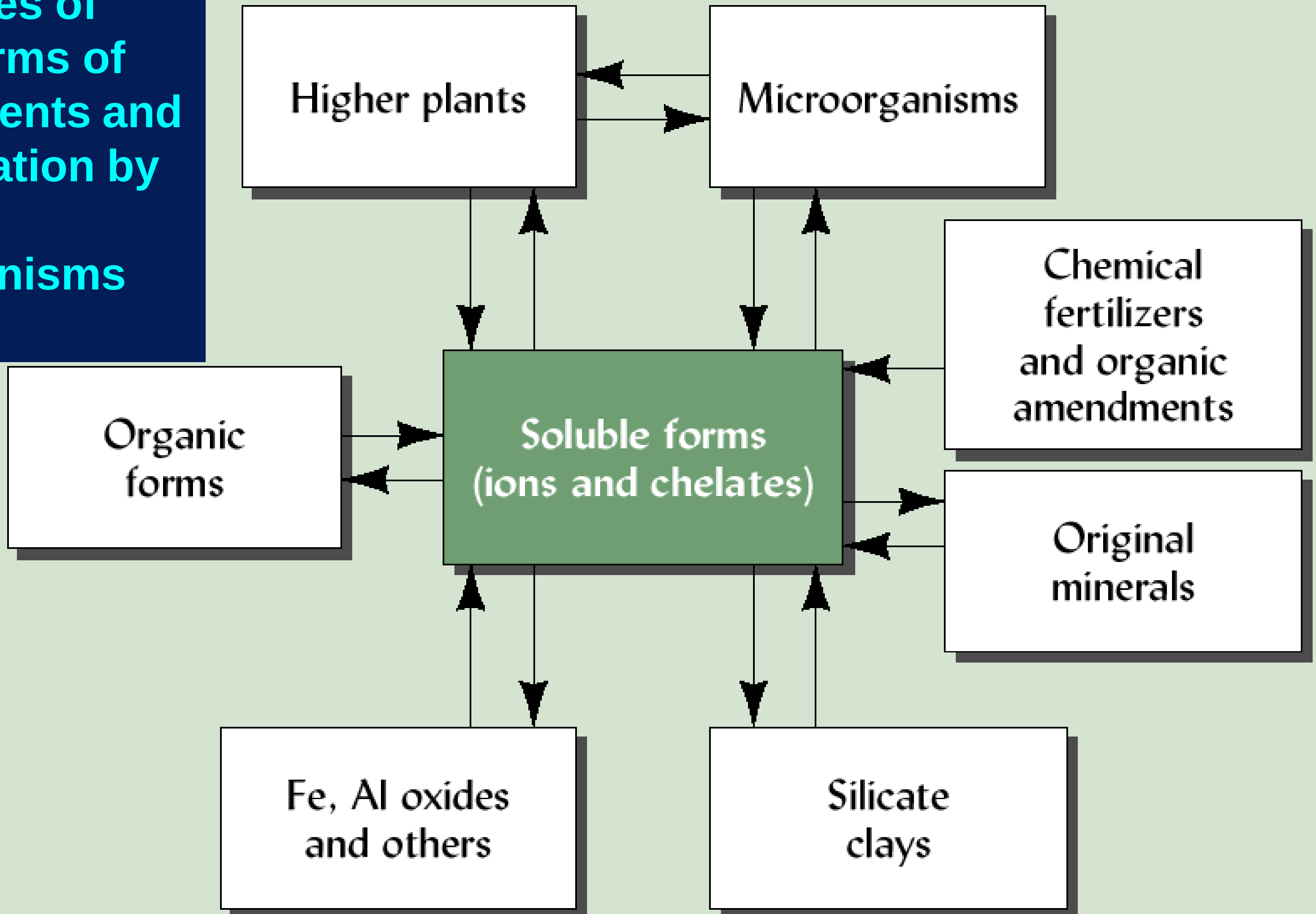
- choice of crops can often alleviate deficiency problems
- may be able to use plant selection & breeding to reduce element requirements or provide tolerance
- need to develop crops with balanced nutrient content for human nutrition

Worldwide management problems:

- less information available in developing countries
- as more N-P-K fertilizers are used, there will be more need for micronutrient fertilization
- must also watch for problems of toxicity - both from natural sources & chem pollution

MICRONUTRIENT AVAILABILITY

Soil sources of soluble forms of micronutrients and their utilization by plants and microorganisms



(Figure 15.31)