Plant Micronutrients and Heavy Metals

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Ecological Agriculture

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Outline

- What are micronutrients?
- Availability
- How to manage them
- What are heavy metals?
- How are they bound to the soil
- Food chain
  - Plant uptake of heavy metals
  - Animal uptake
- Reducing heavy metal contamination

Renewed interest in micronutrients

- Exportation from soils with high yields
- High-analysis fertilizers have decreased trace nutrient “contaminants”
- Ability to diagnose plant deficiencies
- Increasing evidence that food grown on deficient soils doesn’t meet human nutritional goals although plants don’t suffer
- Some are being applied to soils with heavy metals at levels that cause animal toxicity

TABLE 15.1 Functions of Several Micronutrients in Higher Plants

Micronutrient	*Functions in higher plants*
Zinc	Present in several dehydrogenase, proteinase, and peptidase enzymes; promotes growth hormones and starch formation; promotes seed maturation and production.
Iron	Present in several peroxidase, catalase, and cytochrome oxidase enzymes; found in ferredoxin, which participates in oxidation-reduction reactions (e.g., NO_3^- and SO_4^{2-} reduction and N fixation); important in chlorophyll formation.
Copper	Present in laccase and several other oxidase enzymes; important in photosynthesis, protein and carbohydrate metabolism, and probably nitrogen fixation.
Manganese	Activates decarboxylase, dehydrogenase, and oxidase enzymes; important in photosynthesis, nitrogen metabolism, and nitrogen assimilation.
Nickel	Essential for urease, hydrogenases, and methyl reductase; needed for grain filling, seed viability, iron absorption, and urea and ureide metabolism (to avoid toxic levels of these nitrogen-fixation products in legumes).
Boron	Activates certain dehydrogenase enzymes; facilitates sugar translocation and synthesis of nucleic acids and plant hormones; essential for cell division and development.
Molybdenum	Present in nitrogenase (nitrogen fixation) and nitrate reductase enzymes; essential for nitrogen fixation and nitrogen assimilation.
Cobalt	Essential for nitrogen fixation; found in vitamin B_{12}.

Orders of magnitude difference in micronutrient need

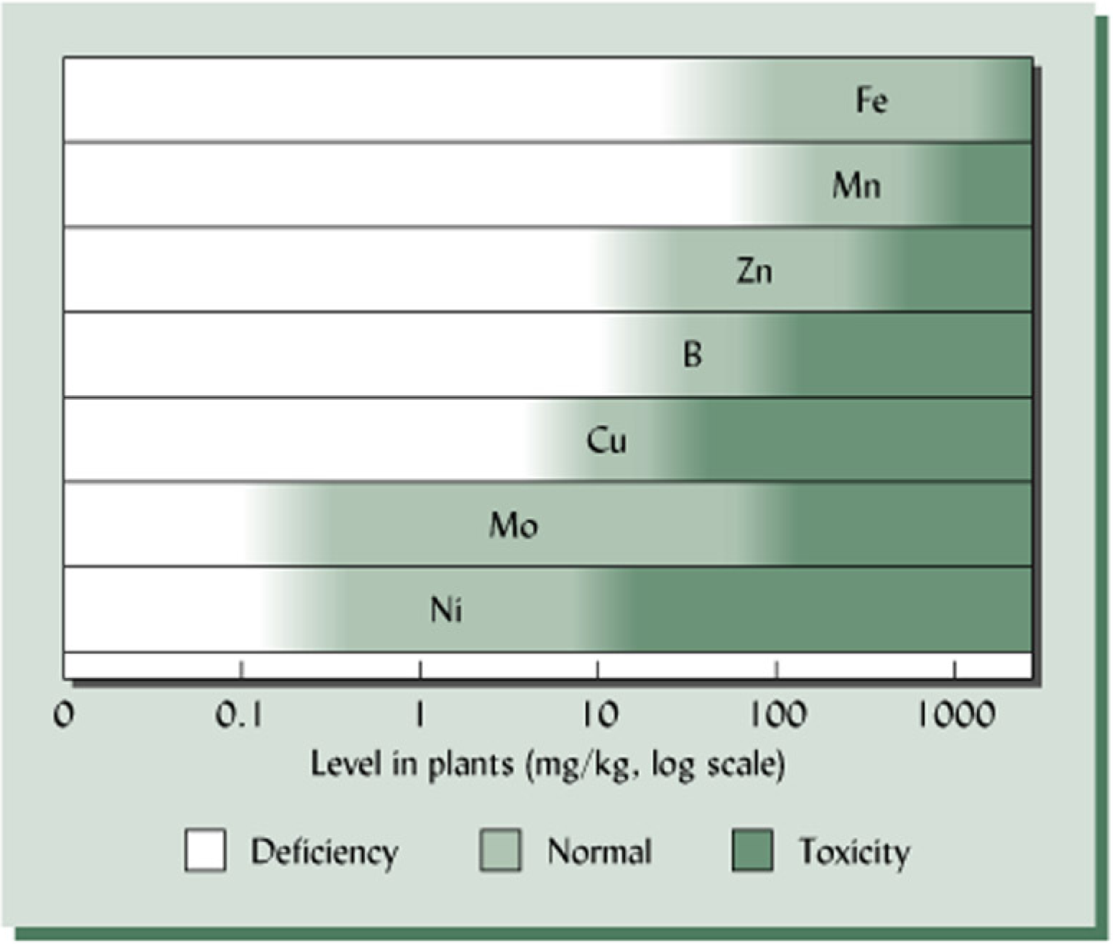
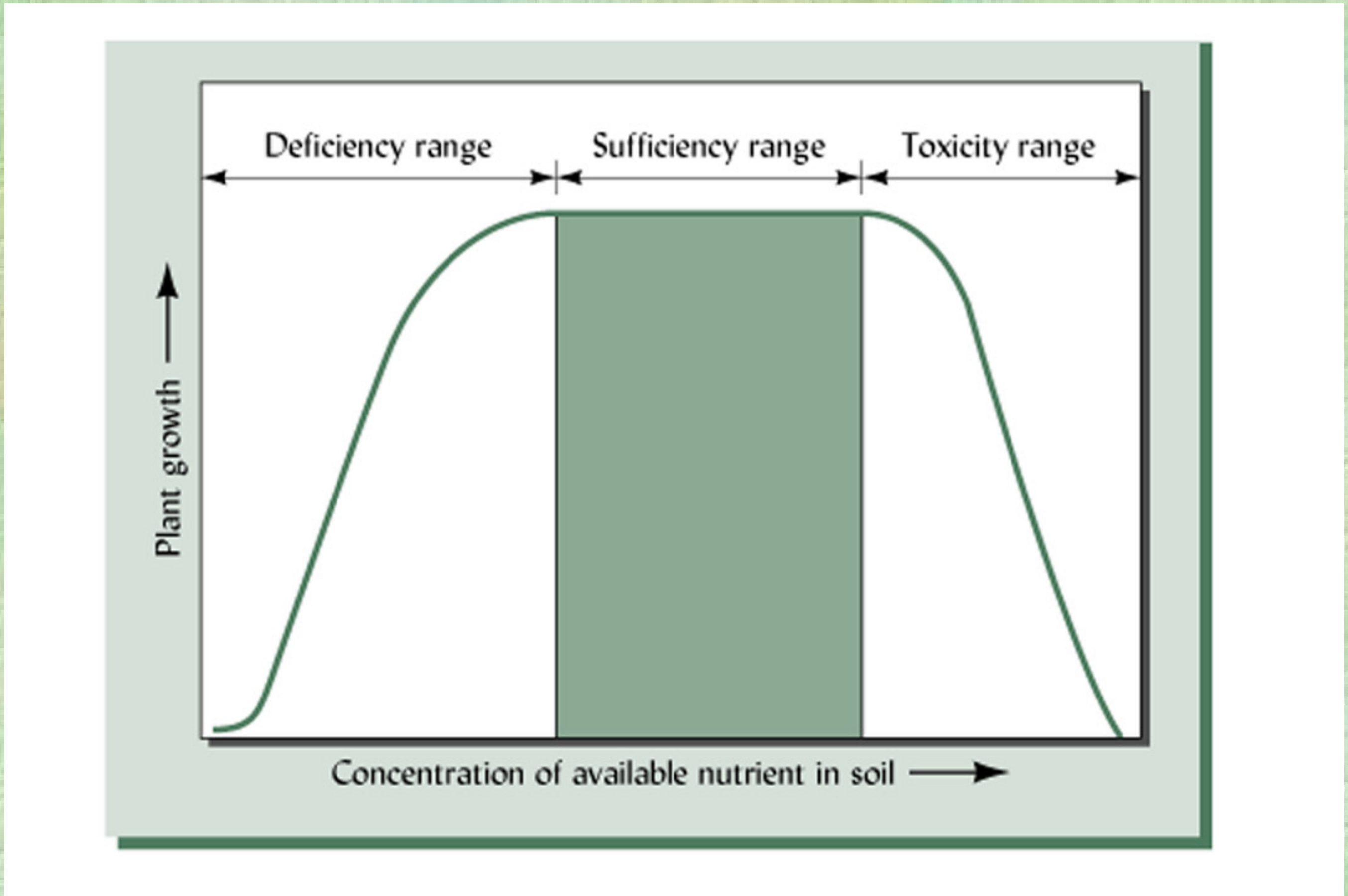


Figure 15.3

Deficiency vs. toxicity
Micronutrients can be toxic at high concentrations (heavy metals)



Zinc deficiency: Symptoms on new tissue

PLATE 53 Zinc deficiency on peach tree. Note whorl of small, misshaped leaves.

PLATE 54 Zinc deficiency on sweet corn. Note broad whitish bands.

Boron deficiency

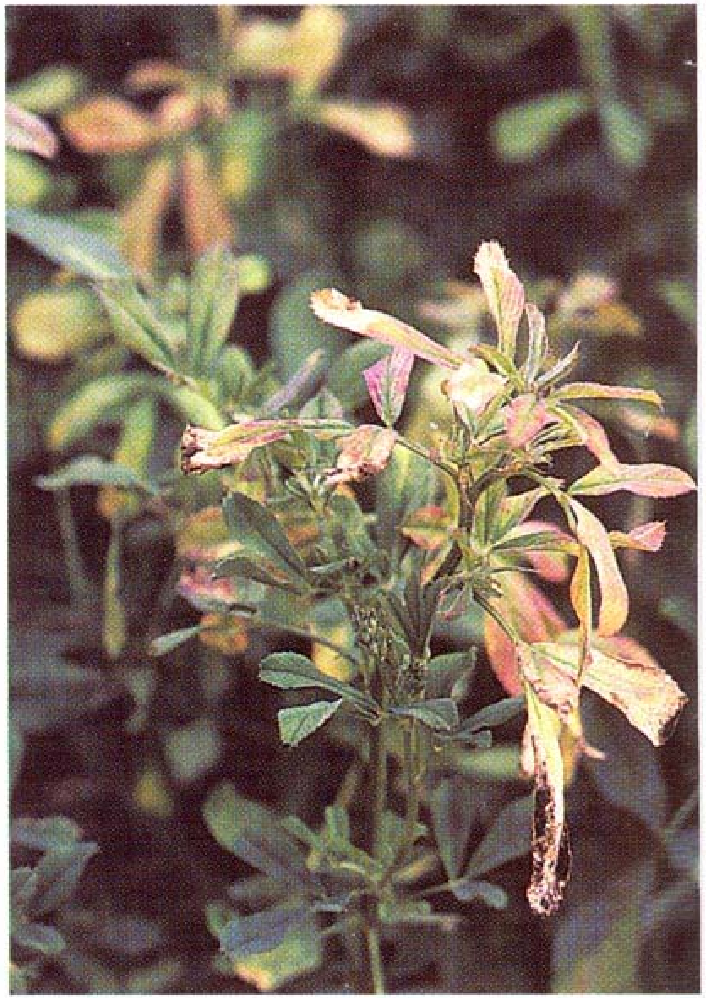


PLATE 56 Boron deficiency on alfalfa. Note reddish foliage.

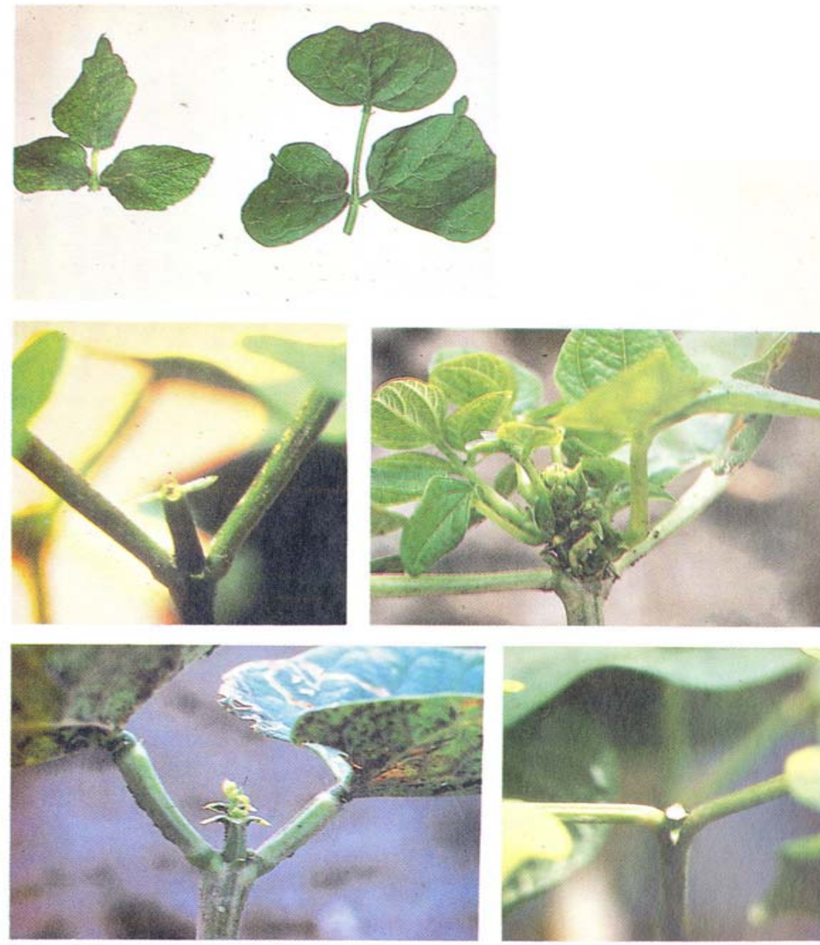
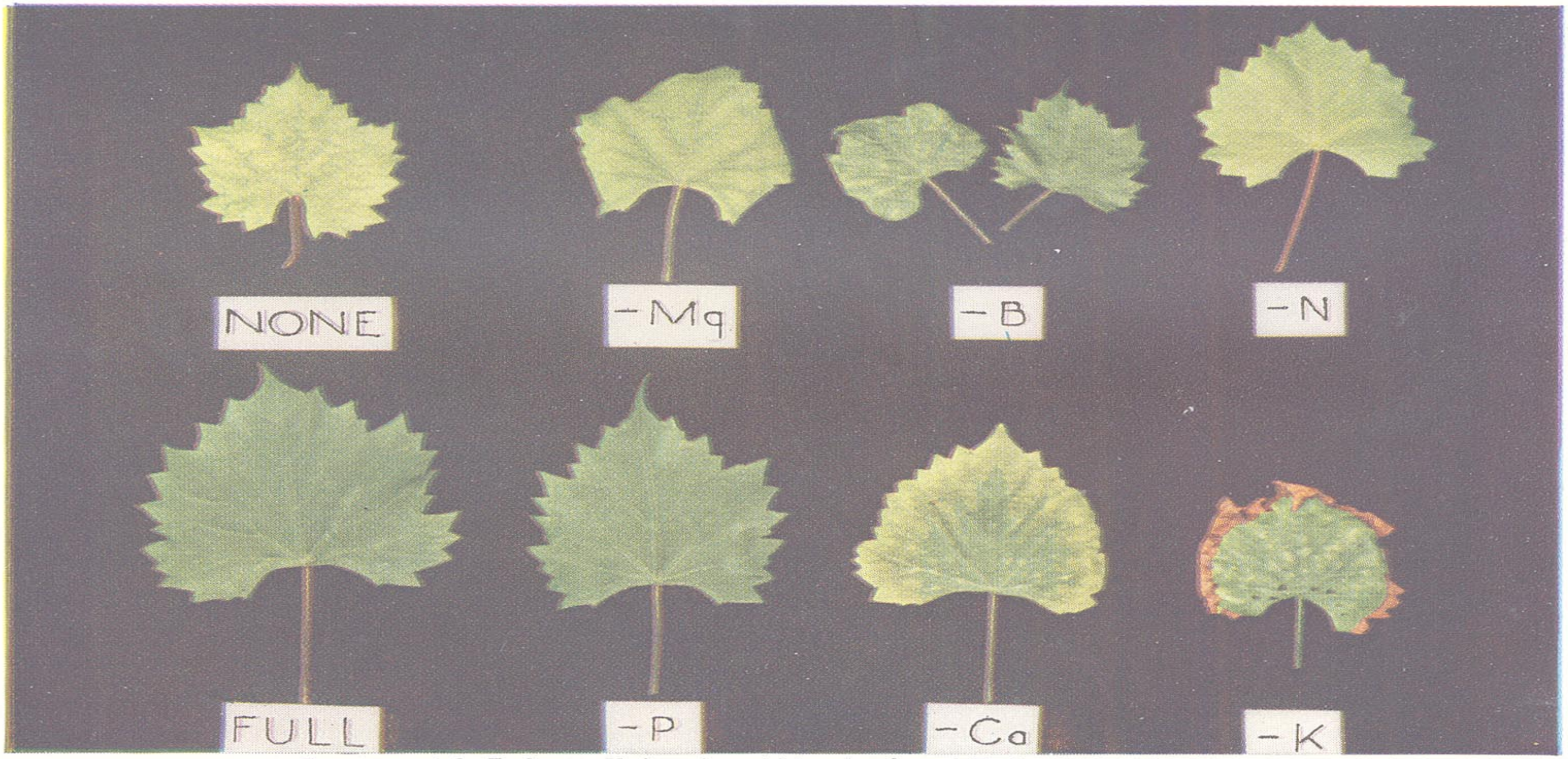


Figure 236. Symptom complex caused by boron deficiency.

Bean Production Problems in the Tropics. Centro Internacional de Agricultura Tropical.

Nutrient deficiencies in grape



Courtesy of L. E. Scott, University of Maryland, and T. B. Hagler, Alabama Polytechnic Institute

Plate 16.—Leaves of the Hunt muscadine grape when grown in sand culture supplied with nutrient solutions lacking the elements as indicated in the picture.

Hunger Signs in Crops, A Symposium. 1949. 2nd ed. The American Society of Agronomy, Washington, D.C.

TABLE 15.3 Forms of Micronutrients Dominant in the Soil Solution

Micronutrient	*Dominant soil solution forms*
Iron	Fe^{2+}, $Fe(OH)_2^+$, $Fe(OH)^{2+}$, Fe^{3+}
Manganese	Mn^{2+}
Zinc	Zn^{2+}, $Zn(OH)^+$
Copper	Cu^{2+}, $Cu(OH)^+$
Molybdenum	MoO_4^{2-}, $HMoO_4^-$
Boron	H_3BO_3, $H_2BO_3^-$
Cobalt	Co^{2+}
Chlorine	Cl^-
Nickel	Ni^{2+}, Ni^{3+}

From data in Lindsay (1972).

OH^- form dominant in alkaline soils

Micronutrient cycling, not volatile

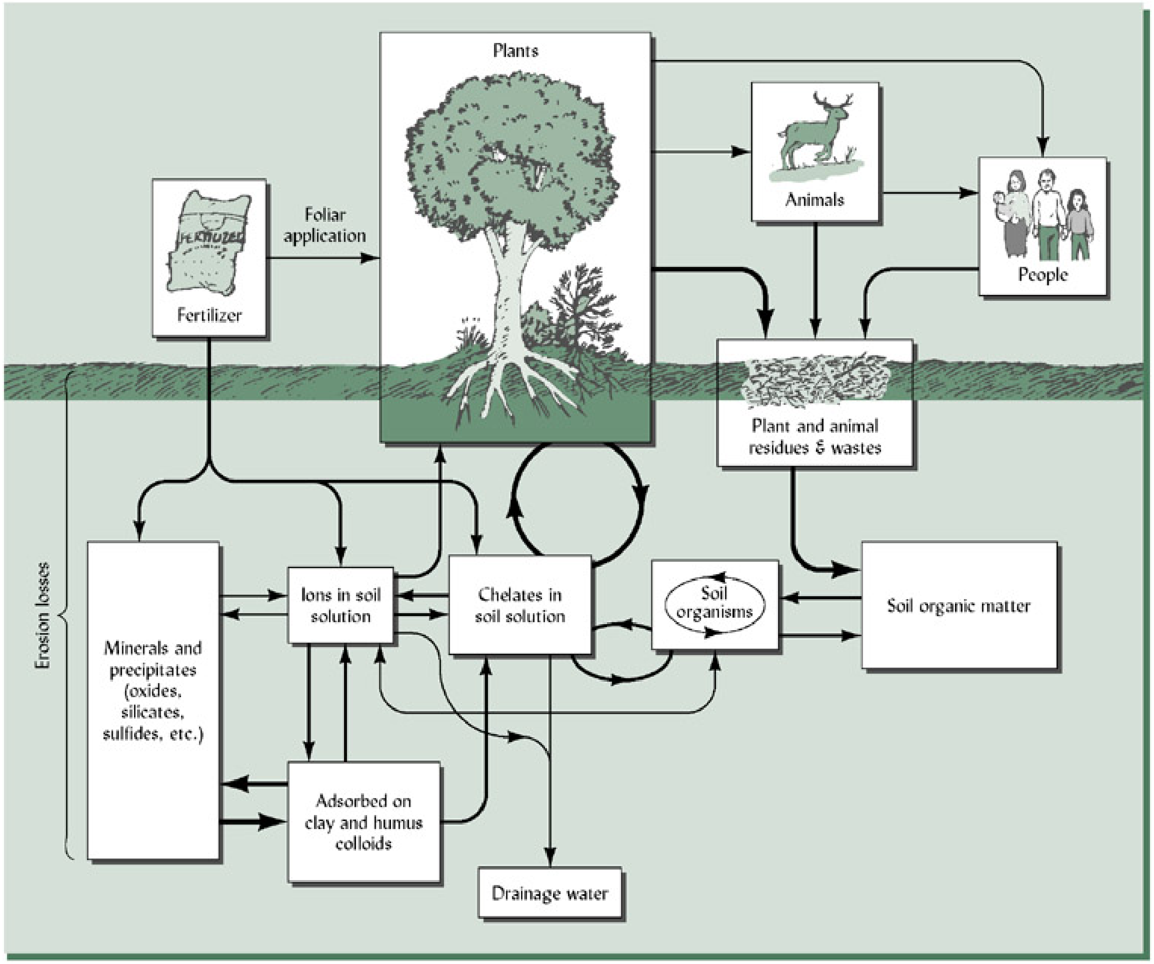


Figure 15.6

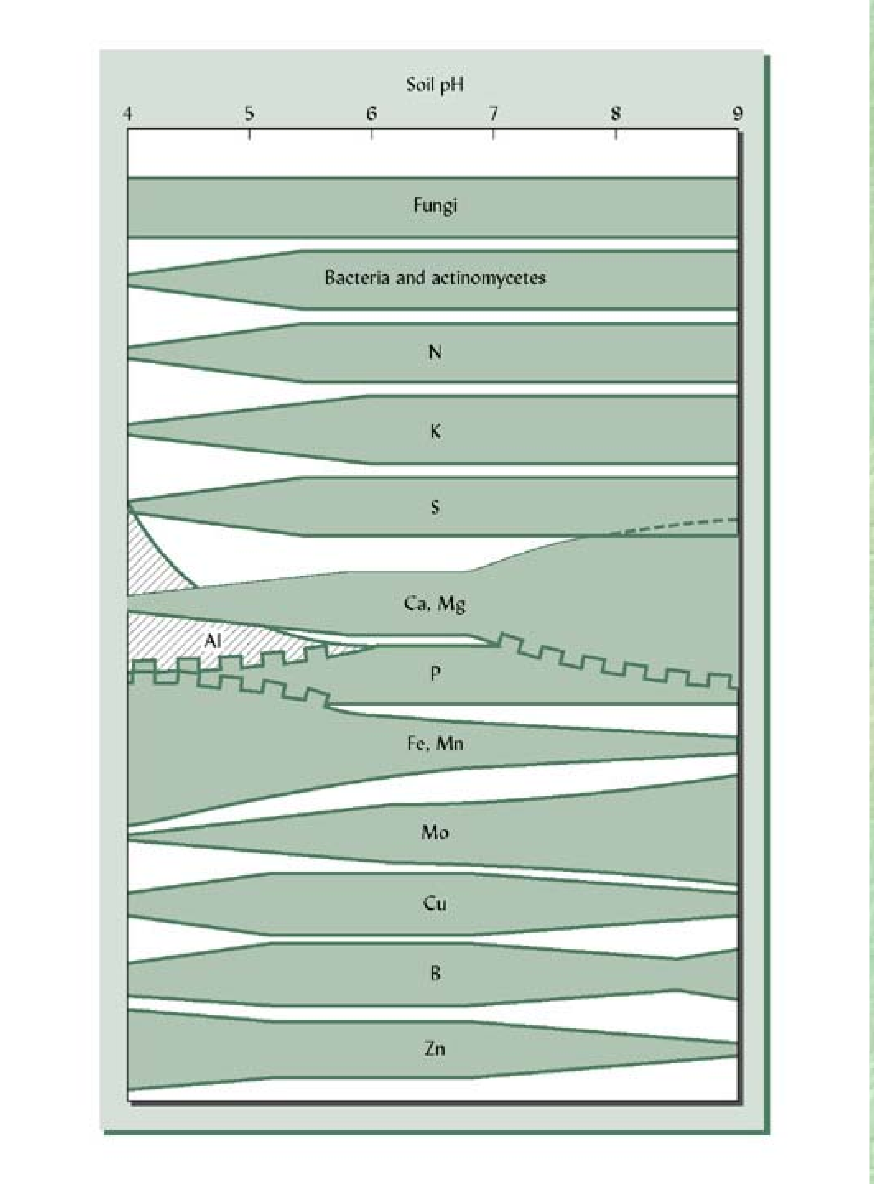
Conditions conducive to deficiencies

- Parent Material
- Leached, sandy acid soils
- Organic soils, esp. Cu is a problem
- Intensive cropping
- pH extremes– low Mo def, Mn toxic
  high pH- Fe, Mn, Zn, B, Cu unavailable
- Eroded

Availability influenced by:

- pH, e.g. lime induced Chlorosis
- Oxidation state and pH- Fe, Mn, Ni, Cu occur in more than one valence state, depends on aeration
- Interaction of pH and aeration (degree of oxidation):
  - Fe, Mn toxic at low pH, reduced form (flooded or wet conditions)
  - At high pH the hydroxide form of Fe, Mn precipitates out but Mo can be toxic
  - Certain plants less sensitive to low Fe, Mn because lower pH and secrete compounds that reduce the Fe
- Other inorganic reactions, e.g. Fe precipitated by PO_4^{-2}
- OM, organic compounds as chelates
- Role of mycorrhizae- in uptake/EM protect excess

pH and micronutrients



Iron deficiency: interveinal chlorosis

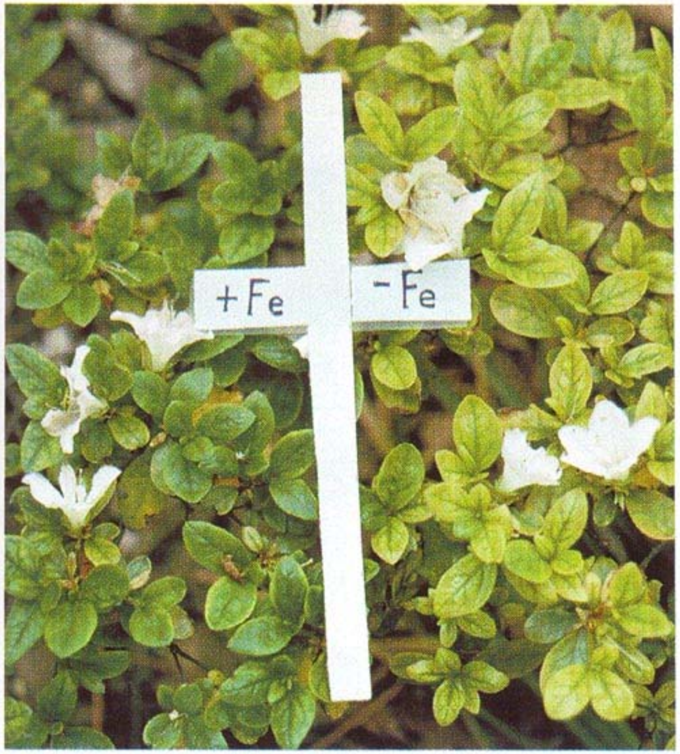


PLATE 45 This iron-deficient azalea was sprayed with $FeSO_4$ on one side 3 days before being photographed. Soil pH higher than 5.5 can induce such iron deficiency.

PLATE 63 Iron deficiency causes yellowing with sharply contrasting green veins on the younger leaves. Rose growing in soil with pH 6.8.

Fe deficiency in sorghum

PLATE 55 Eroded calcareous soil (Ustolls) with iron-deficient sorghum.

Iron deficiency of bean

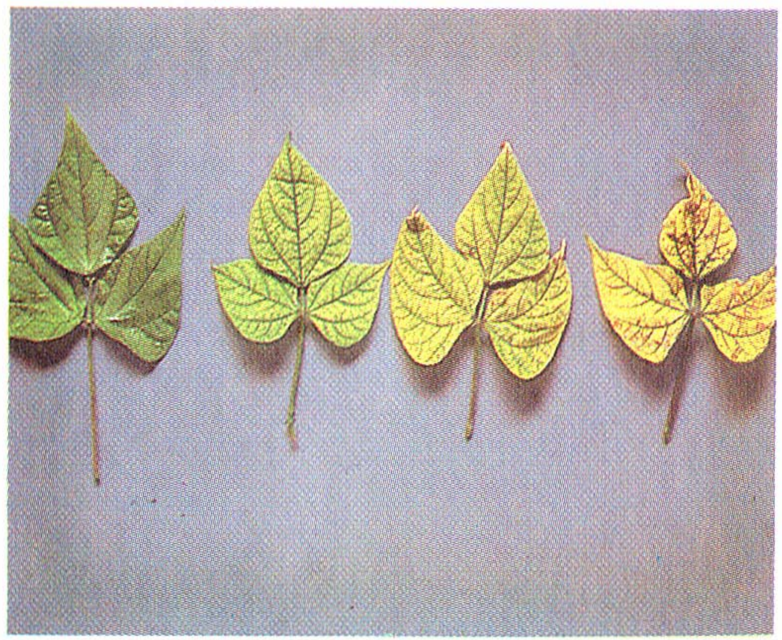
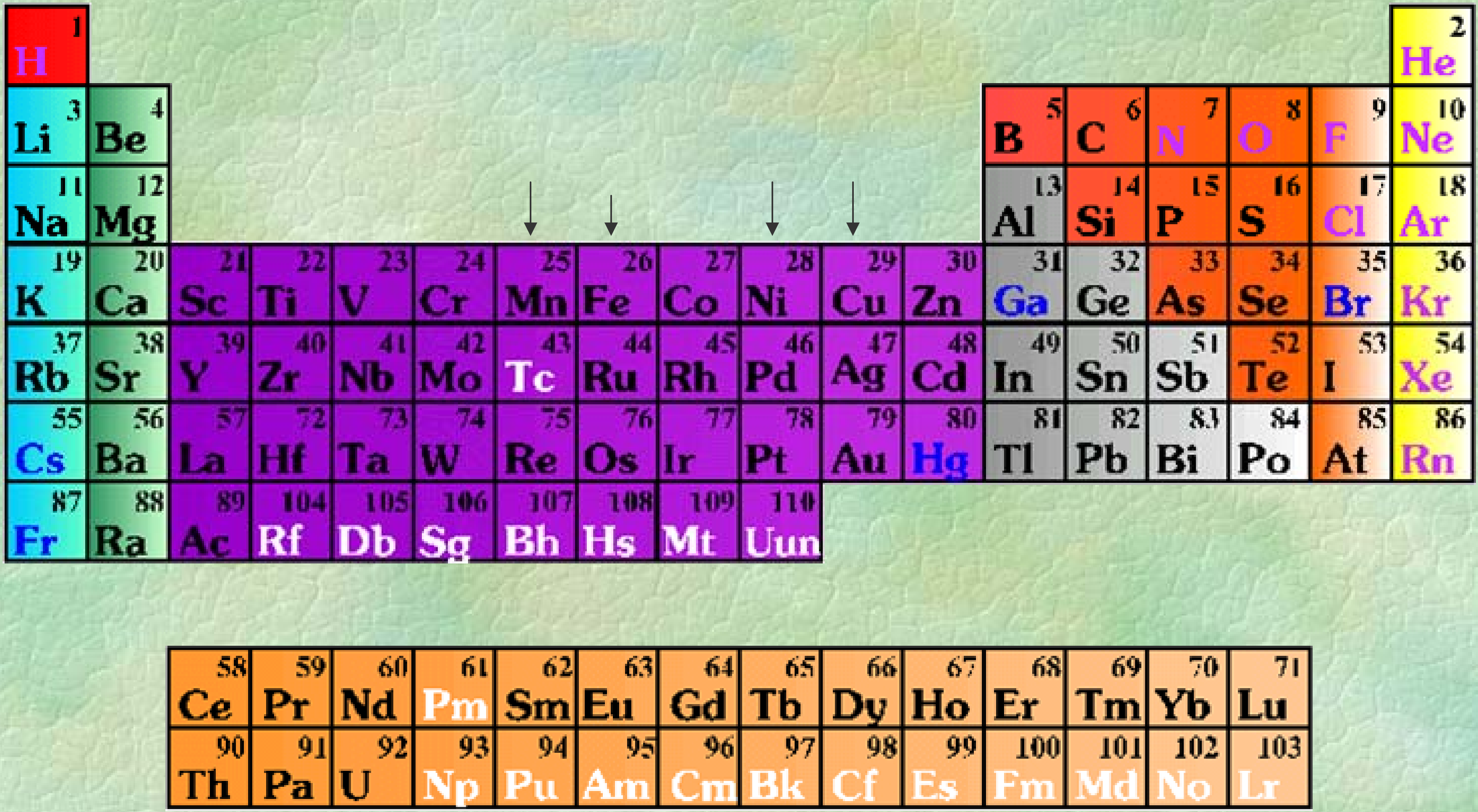


Figure 250. Symptom complex in young leaves, caused by iron deficiency.

Yellow chlorosis (yellowing) between green veins

Periodic table of the elements: redox rxns in soil



Oxidation/Reduction

- OIL RIG (oxidation is loss OIL/ reduction is gain RIG) or LEO/GER
- $O_2 + 4Fe^{+2} + 4H^+ \rightarrow 4Fe^{+3} + 2H_2O$
- $4 Fe^{+2} \rightarrow 4Fe^{+3} + 4e^-$ (iron gives up electrons)
- $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (oxygen accepts electrons)

- **Fe^{+2} (ferrous, more soluble) oxidized to Fe^{+3} (ferric, less soluble) and O_2 is being reduced (gaining elections)**
- **At low pH (high acidity) oxidation of Fe takes place because oxygen needs H to accept electrons**

Mn^{+3} available under reducing conditions

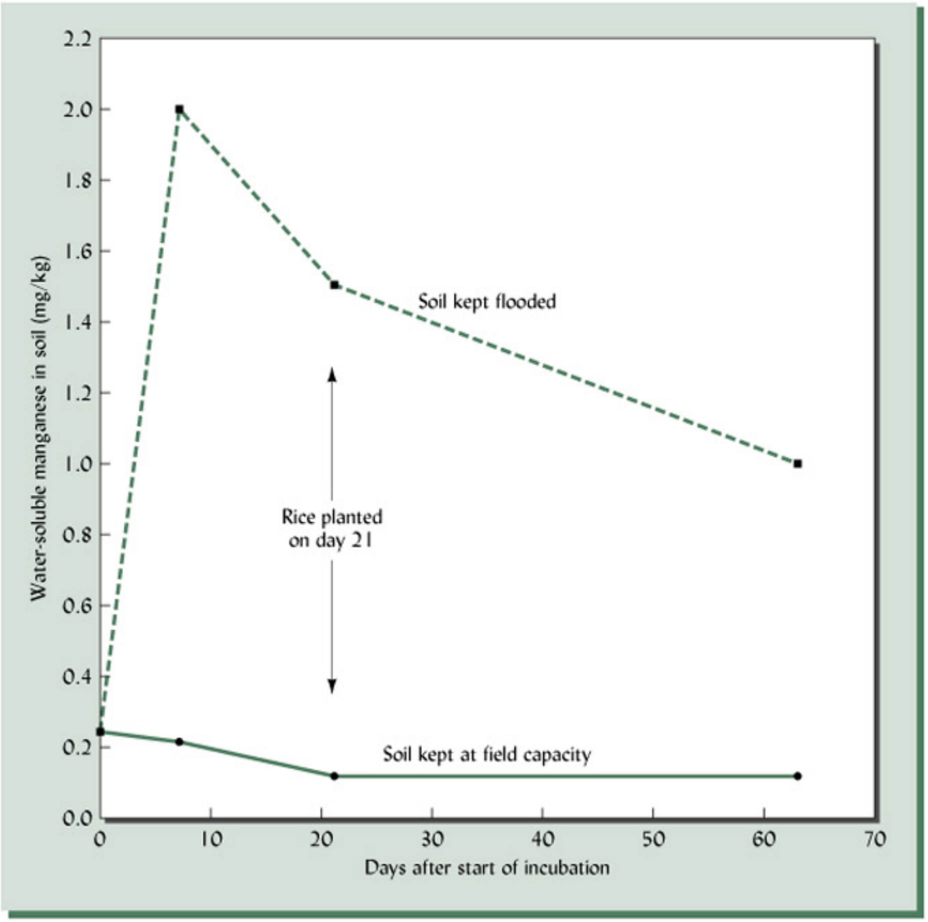
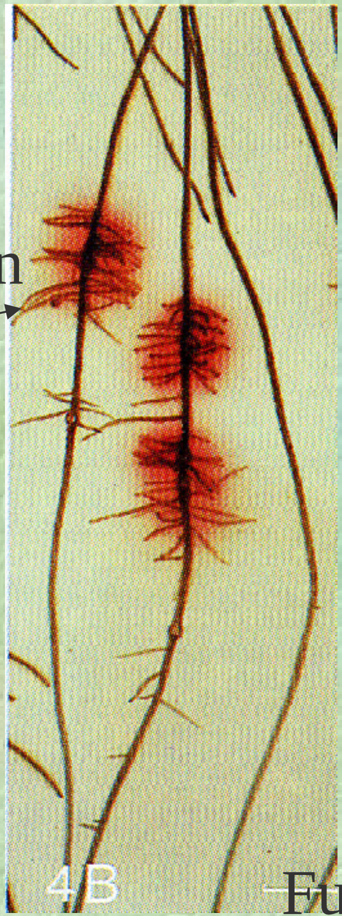


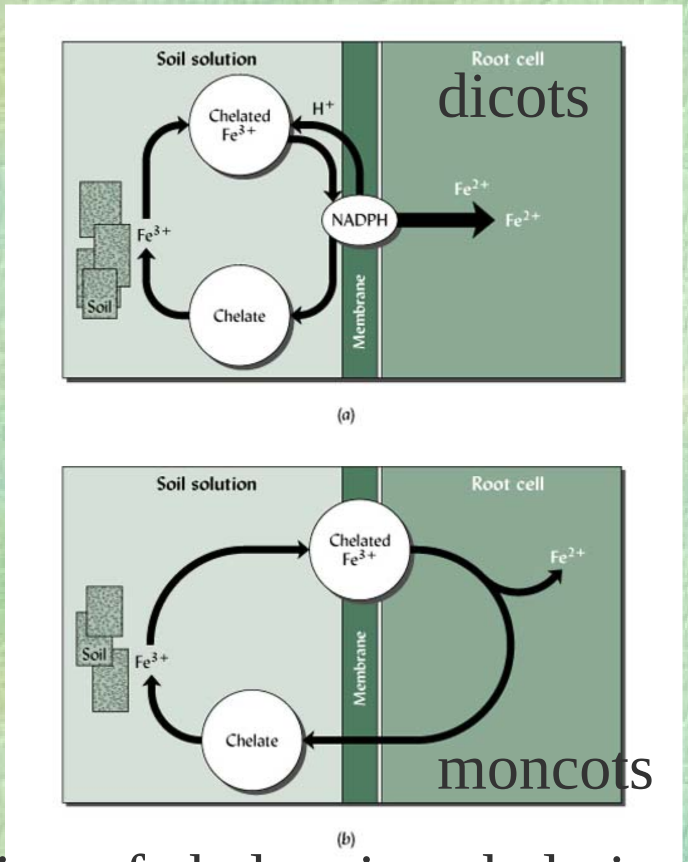
Figure 15.9

Acidification/chelation of lupine rhizosphere for iron uptake

Marschner et al. 1986

Fe^{+3} reduction to Fe^{+2}





Function of chelate is to help ion remain available, diffuses to soil And then reduced at root surface

Chromium, Cr

- Trace amounts are essential but excess are carcinogenic
- Cr^{+3} (reduced) and Cr^{+6} (oxidized)
- Cr^{+3} not available at pH 5.5 wet (anaerobic)
- Cr^{+6} contamination of ground water with mutagen, movie Erin Brockavich

Micronutrient interactions are highly complex and emphasize need for nutrient balance

TABLE 15.5 Some Antagonistic (Negative) and Synergistic (Positive) Effects of Other Nutrients on Micronutrient Utilization by Plants[a]

The occurrence of so many interactions emphasizes the need for balance among all nutrients and avoidance of excess application of any particular nutrient.

	Elements decreasing utilization		*Elements increasing utilization*	
Micronutrient	*Soil and root surface reactions*	*Plant metabolic reactions*	*Soil and root surface reactions*	*Plant metabolic reactions*
Fe	B, Cu, Zn, Mo, Mn	Mn, Mo, P, S, Zn	B, Mo	
Mn	Fe, B	Fe	B	
Zn	Mg, Cu, B, Fe, P	Fe, N	N, B	Fe, Mg
Cu	B, Zn, Mo	P, N	B	
B	Ca, K			N
Mo	S, Cu	S	P	P
Ni	Ca, Fe	Fe, Zn		

[a] Summarized from many sources.

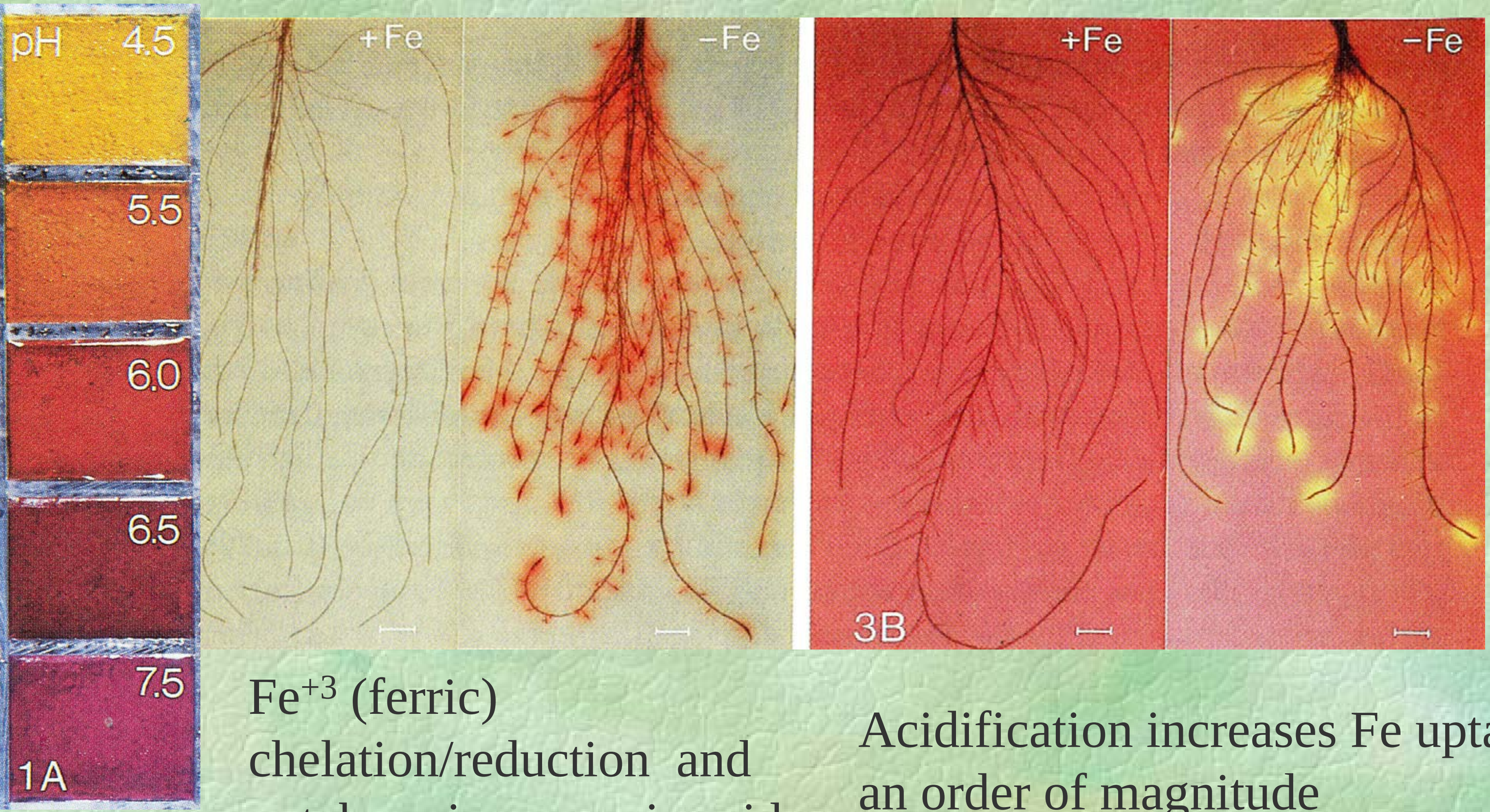
Iron deficiency induced enhancement of manganese reduction

MnO_2 reduced

Peanut in calcareous soil with low available Fe

Marschner et al. 1986

Fe-deficiency induced acid secretion in rhizosphere of cucumber (high pH)



Fe^{+3} (ferric) chelation/reduction and uptake using organic acids

Acidification increases Fe uptake an order of magnitude

Common plants/micronutrient deficiency

TABLE 15.8 Plants Known to Be Especially Susceptible or Tolerant to, and Soil Conditions Conducive to, Micronutrient Deficiencies

Plants which are most susceptible to deficiency of a micronutrient often have a relatively high requirement for that nutrient and may be relatively tolerant to levels of that nutrient that would be high enough to cause toxicity to other plants.

Micronutrient	*Common range in rates recommended for soil application[a], kg/ha*	*Plants most commonly deficient (high requirement or low efficiency of uptake)*	*Plants rarely deficient (low requirement or high efficiency of uptake)*	*Soil conditions commonly associated with deficiency*
Iron	0.5–10.0	Blueberries, azaleas, roses, holly, grapes, nut trees, maple, bean, sorghum, oaks	Wheat, alfalfa, sunflower, cotton	Calcareous, high pH, waterlogged alkaline soils
Manganese	2–20	Peas, oats, apple, sugar beet, raspberry, citrus	Cotton, soybean, rice, wheat	Calcareous, high pH, drained wetlands, low organic matter, sandy soils
Zinc	0.5–20	Corn, onion, pines, soybeans, beans, pecans, rice, peach, grapes	Carrots, asparagus, safflower, peas, oats, crucifers, grasses	Calcareous soils, acid, sandy soils, high phosphorus
Copper	0.5–15	Wheat, corn, onions, citrus, lettuce, carrots	Beans, potato, peas, pasture grasses, pines	Histosols, very acid, sandy soils
Boron	0.5–5	Alfalfa, cauliflower, celery, grapes, conifers, apples, peanut, beets, rapeseed, pines	Barley, corn, onion, turf grass, blueberry, potato, soybean	Low organic matter, acid, sandy soils, recently limed soils, droughty soils, soils high in 2:1 clays
Molybdenum	0.05–0.5	Alfalfa, sweet clover, crucifers (broccoli, cabbage, etc.), citrus, most legumes	Most grasses	Acid sandy soils, highly weathered soils with amorphous Fe and Al

[a] The lower end of each range is typical for banded application; the higher end is typical for broadcast applications.

How can you know positively?

- Plant tissue analysis

Where is the organic farm with respect to available micronutrients?

A & L WESTERN AGRICULTURAL LABORATORIES

REPORT NUMBER
05-095-059

PORTLAND OFFICE • 503-968-9225
10220 S.W. Nimbus Ave., Bldg. K-9 • Portland, OR 97223
Client No: 3972

SEND TO: BLACK LAKE ORGANIC NURSERY & GARDEN
4711 BLACK LAKE BLVD.
OLYMPIA, WA 98512

GROWER: MELISSA BARKER TESC FARM

SUBMITTED BY: GARY KLINE

GRAPHICAL SOIL ANALYSIS REPORT

DATE OF REPORT: 04/08/2005 LAB NO: 59845 SAMPLE ID: 2 South Field PAGE: 2

RATING	ORGANIC MATTER %	NITROGEN NO_3-N ppm	PHOSPHORUS WEAK BRAY ppm	PHOSPHORUS $NaHCO_3$-P ppm	POTASSIUM K ppm	MAGNESIUM Mg ppm	CALCIUM Ca ppm	SODIUM Na ppm	SULFUR SO_4-S ppm	ZINC Zn ppm	MANGANESE Mn ppm	IRON Fe ppm	COPPER Cu ppm	BORON B ppm		POTASSIUM K %	MAGNESIUM Mg %	CALCIUM Ca %	SODIUM Na %
TEST RESULTS	12.8	10	121	118	146	87	1112	9	1	3.1	3	43	1.6	0.6		5.3	10.2	79.4	0.5

ECe dS/m	CEC meq/100g	EX. LIME	pH
0.2	7.0	L	6.7

LOW — AVERAGE — HIGH
INCREASING SALINITY →

ACIDIC — BASIC
← INCREASING NEED FOR LIME

BUFFER pH: 6.7

SOIL FERTILITY GUIDELINES

CROP: VEGETABLES RATE: lb/acre

DOLOMITE (100 score)	LIME (100 score)	GYPSUM	ELEMENTAL SULFUR	NITROGEN N	PHOSPHATE P_2O_5	POTASH K_2O	MAGNESIUM Mg	SULFUR SO_4-S	ZINC Zn	MANGANESE Mn	IRON Fe	COPPER Cu	BORON B	REFER TO BACK
				70		90	10	30						ALL

COMMENTS
SHOOT GROWTH: Excessive shoot growth reduces sunlight penetration into the lower canopy, which reduces the productivity of lower fruiting wood and may encourage disease. Avoid excessive nitrogen.
PLEASE REFER to previous comments for remaining report.

Darcy L. Peebles
DARCY PEEBLES, CCA

Equivalencies: ppm = ug/mL

A & L WESTERN LABORATORIES, INC.

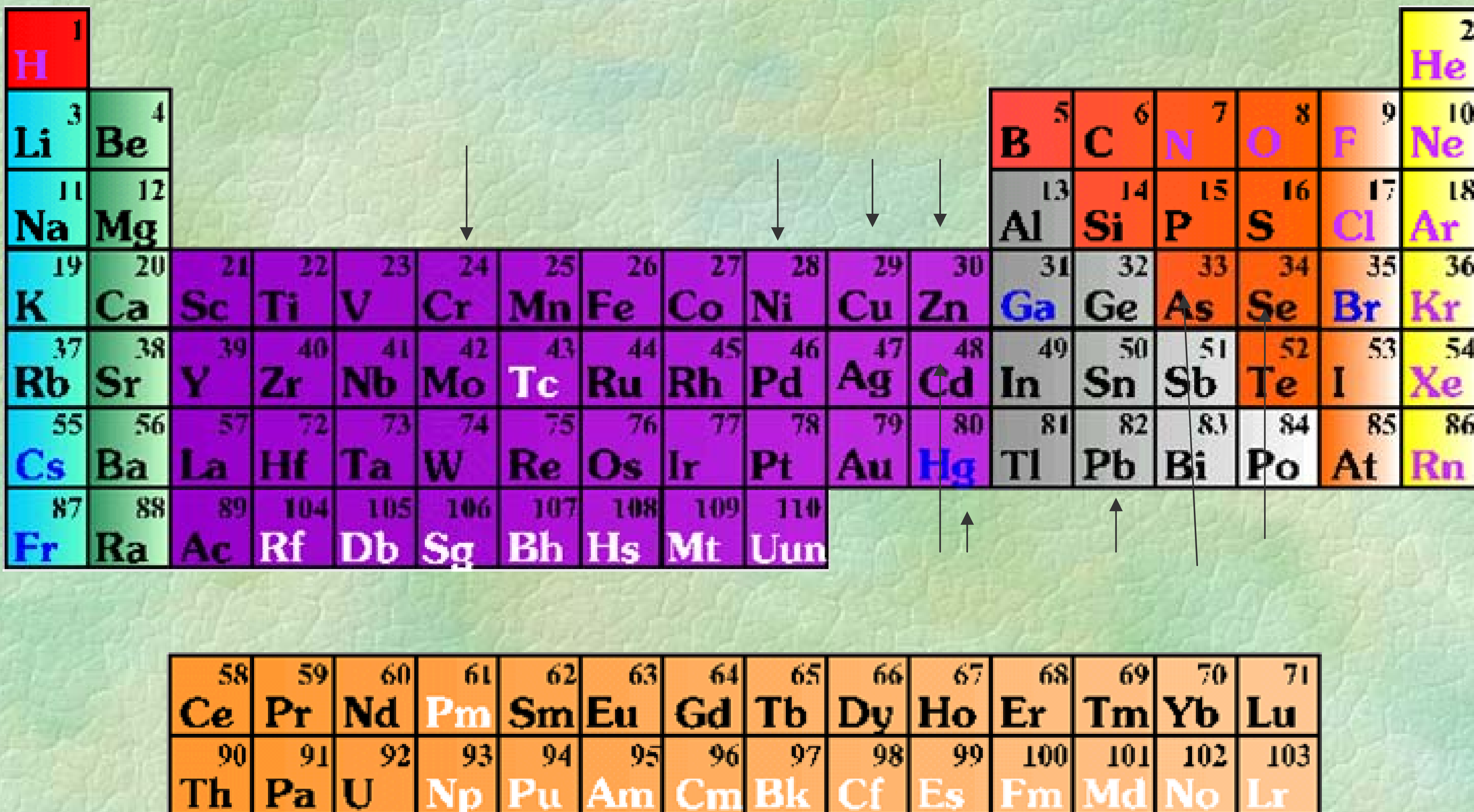
How to provide micronutrients

- Maintain balance
- **On-farm recycling**
  - **Plant residues**
  - **Compost**
  - **Manures**
- Off-farm inputs
  - Form of nutrient is important in terms of availability to plant and leachability
  - Read labels, analysis for other heavy metals

What is a heavy metal?

- Loose definition- specific density > 4-7 g/cm^3
- Usually associated with toxicity in plants (including micronutrients that produce toxicity symptoms) or animals (Se, Hg, Pb, As)
- "trace metal" metals in ppm concentrations in earth's crust

Periodic table of the elements
Problem heavy metals with arrows



Why are heavy metals impt in org ag?

- Use of high heavy metal containing wastes in fertilizers, esp. micronutrient fertilizers
- Sewage sludge application, current or past
- Smelter emissions and trash incineration on land
- Use of fish fertilizers (mercury)
- Use of lead arsenate pesticide on orchards in W WA and conversion to other crops and developed land*
- Use of high Cd, Pb containing rock phosphate
- Use of CCA treated fence posts

How’d they get into the soil?

- Most in deposits in earth where safe
- Generally natural low levels in soil
- By mining, smelting and concentrating metals they have become more toxic to the biosphere
- Have spread where humans come into contact with them
- “The toxicity of inorganic contaminants released into the environment every year is now estimated to exceed that from radioactive and organic sources combined. A fair share goes to contaminating soil. ”--Brady and Weil 2000, p818

Contamination vs. pollution

- “Contamination” is above the background
- “Pollution” means concentration above some level which is deemed safe
- **Pollution levels are not agreed upon and depend on who (child or adult), where (soil, water, air), over what time (8 hrs or chronic), workplace vs. public**
- Variability in action levels, recommended exposure limits

Some heavy metals and their environmental and physiological effects

TABLE 18.7 Sources of Selected Inorganic Soil Pollutants

Chemical	*Major uses and sources of soil contamination*	*Organisms principally harmed*[a]	*Human health effects*
Arsenic *	Pesticides, plant desiccants, animal feed additives, coal and petroleum, mine tailings, detergents, and irrigation water	H, A, F, B	Cumulative poison, cancer, skin lesions
Cadmium *	Electroplating, pigments for plastics and paints, plastic stabilizers, batteries, and phosphate fertilizers	H, A, F, B, P	Heart and kidney disease, bone embrittlement
Chromium	Stainless steel, chrome-plated metals, pigments, refractory brick manufacture, and leather tanning	H, A, F, B	Mutagenic; also essential nutrient
Copper	Mine tailings, fly ash, fertilizers, windblown copper-containing dust, and water pipes	F, P	Rare; essential nutrient
Lead *	Combustion of oil, gasoline, and coal; iron and steel production; solder in water-pipes; paint pigment	H, A, F, B	Brain damage, convulsions
Mercury *	Pesticides, catalysts for synthetic polymers, metallurgy, and thermometers	H, A, F, B	Nerve damage
Nickel	Combustion of coal, gasoline, and oil; alloy manufacture; electroplating; batteries; and mining	F, P	Lung cancer
Selenium	High Se geological formations and irrigation wastewater in which Se is concentrated	H, A, F, B	Rare; loss of hair and nail deformities; essential nutrient
Zinc	Galvanized iron and steel, alloys, batteries, brass, rubber manufacture, mining, and old tires	F, P	Rare; essential nutrient

[a] H = humans, A = animals, F = fish, B = birds, P = plants.
Data selected from Moore and Ramamoorthy (1984) and numerous other sources.

Canadian HM in soil stds also consider others Co, Mo, not Cr!

The Fertilizer Loophole in 1976 RCRA- Reduce, Recycle, Reuse

- Toxic waste can be called “fertilizer” if it includes 1% or more of a plant nutrient, or “liming material” if it is alkaline.
- Regulators only check for the labeled chemicals, not other elements or toxins

Some industrial wastes with arsenic, cadmium, lead, mercury, dioxins, etc., are “recycled” through ordinary fertilizer without testing, standards or disclosure.

Federal control of toxic chemicals			
	Testing	**Standards**	**Disclosure**
Pesticides	YES	YES	YES
Sewage sludge	YES	YES	YES
Fertilizers	NO	NO	NO

Wilson 2002

Wastes in Fertilizers

- Materials:
  - Industrial ashes
  - Acids
  - Slag
  - Tailings
- Industries:
  - Steel
  - Copper
  - Brass
  - Galvanizing
  - Electronics
  - Chemicals
  - Mining
  - Cement kiln
  - Gypsum
  - Nuclear
  - Coal combustion

Duff Wilson 2002

Government and industry’s position

- For government
  - Dual role: regulation and promotion
  - Dilution is the solution to pollution
- For industry
  - Save money on waste disposal
  - Save money on raw material for fertilizer
  - **It’s legal. Topsoil has become the legal repository for wastes no longer allowed as emissions to air or water**

Wilson 2002

Four heavy metals

- Mercury (Hg)
- As (Arsenic)
- Pb (Lead)
- Cd (Cadmium)

Mercury (Hg) ppm

- Background level
  - ~0.03 U.S. agricultural soils
  - 0.07 Washington state
- Products
  - 12 Ironite
  - 3 granular zinc
  - 1.8 Terrene-Greens
  - 0.6 NuLife
- Found in fish emulsion, bioaccumulated from Hg in waste and from burning coal

Source: Wash. Dept. of Agriculture

Duff Wilson 2002

Arsenic: Source

- Has been used for centuries (China 900 AD)
- Many different forms of arsenate (200),e.g CaAs
- Form influences mobility and toxicity
- Mined with other minerals esp. Au, Cu, Sn and mined, from mine waste or tailings
- Natural or mine waste in water
- Found in hydrothemal deposits

As- sources and background levels

- Essential in small quantities to plants and animals
- Occurs naturally in soil and water (may be toxic in water, e.g. Bangladesh and India)
- High As in upper end of Cascade Valleys in WA, may be high in volcanic soils and hot springs
- Present in coal burning and dusts from cement manufacture
- Smelter- especially within one mile
- Sprayed in WA state as insecticide on apples for codling moth until 1950, forest thinning to 1960s
- May be near Chromated Copper Arsenate treated timber- get $25 test kit from Environmental Working Group

Arsenic (As) ppm

- Background level
  - **~6 U.S. agricultural soils**
  - **7 Washington state**
- Products
  - 4,400 Ironite
  - 989 Boronat
  - 86 Nulife
  - 48 Nutrilime
  - 18 Diammonium phosphates

Arsenic and human health

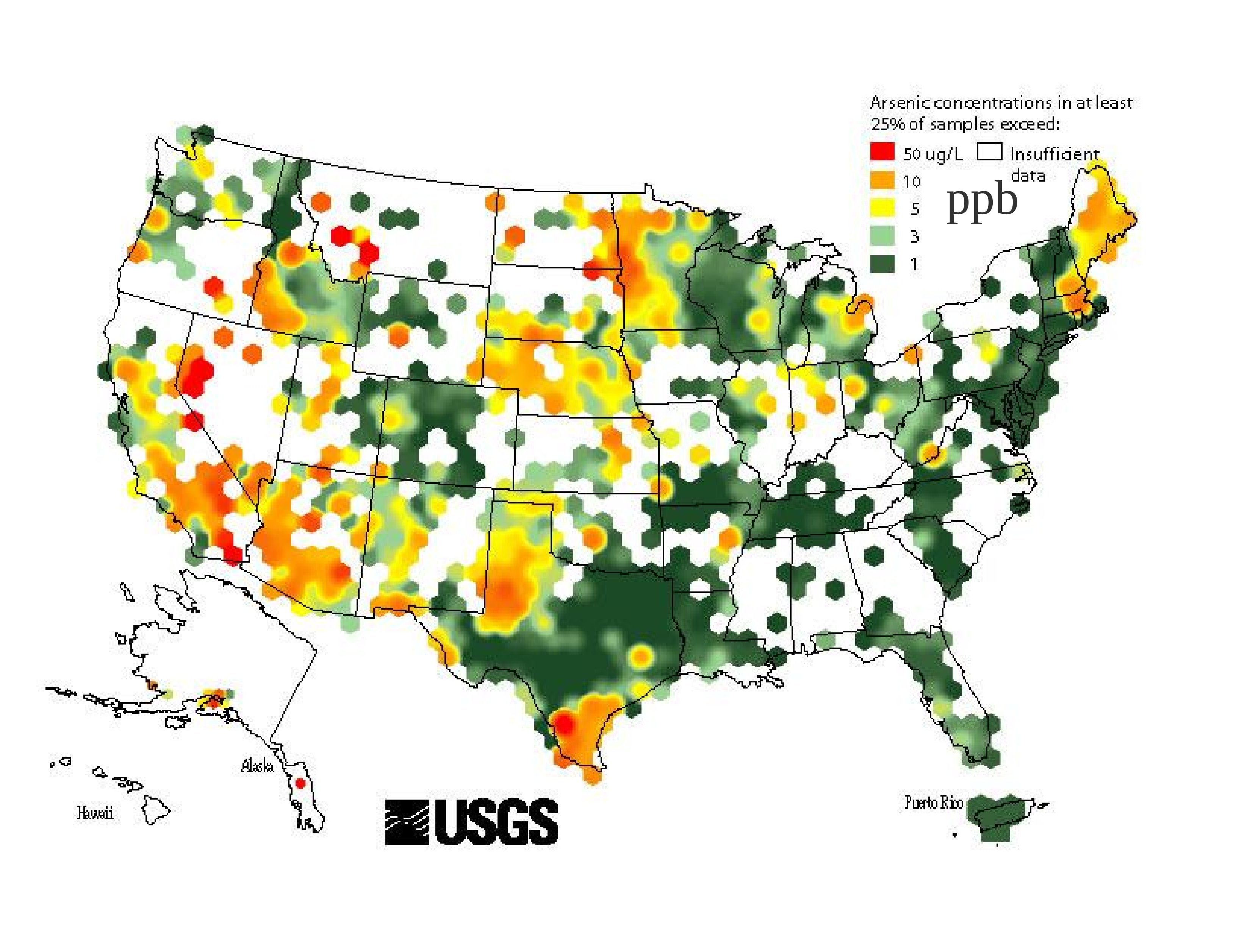
- Food and water major source of exposure for US citizens (NewYorkTimes)
- High concentrations: Internal bleeding and death
- Known to cause cancer: lung, skin, liver, kidney; reproductive damage
- Causes arsenic keratosis

  of skin

As- regulation

- Permissible level in water (Bush changed to WHO levels of .01 ppm)- 0.01 ppm or 10 ppb
- **Permissible level in soil in out-of-print WSU extension bulletin states: 25 mg/kg (ppm) is ‘probably not affecting plant growth’**
- Residential soil cleanup - 250 mg/kg
- Children should be < 37 ppm, adults with occasional exposure to 175 mg/kg acceptable
- **Chronic exposure is of concern, e.g in gardening**
- Symptoms in humans depend on individual susceptibility, form of As in soil, difficult to predict

Arsenic in drinking water in US



As behavior in soil and plants

- Background level in soil
  - **~6 ppm U.S. agricultural soils, but 7 Washington state**
  - **Vashon-Maury Soil samples 2.3 - 460ppm (<2mm sieved)**
  - **Due to location downwind from ASARCO smelting**
- More soluble and mobile in soil than Pb, so may have leached, increases in flooded, wet soils
- Redistributed through tillage, but usually only in subsoil if soil is sandy
- If high phosphate in soil may displace As to leach
- As in soil can be 10-1000x higher in soil than plant
- Can be high enough to stunt plants and reduce yield-- binds to energy exchange apparatus

Lead (Pb)

- Sources of lead in soil include: former roadways <100ft., PbAs pesticide, smelter, within 20 ft of buildings, < 1 mile for smelter or fossil fuel electrical power plants or cement manufacturing
- Background level in soil in ppm
  - **11 U.S. agricultural soils**
  - **17 Washington state,**
  - **Vashon-Maury Island 5.3-1300ppm**
- Lead in soil usually not high enough to affect the plant growth because highly bound to the soil unless pH is low (acid)

Lead (Pb) ppm

- Fertilizer Products that contain lead
  - 29,400 Frit Industries
  - 20,000 Bay Zinc
  - 2,770 Ironite
  - 2,491 NuLife
  - 350 Nutrilime
  - **153 Terrene-Greens Natural Organic**
  - 140 Vigoro

Cadmium (Cd) ppm

- Background level
  - 0.2 ppm U.S. agricultural soils
  - 1 ppm Washington State
  - 0-15ppm Vashon-Maury soil samples
- Cadmium in wheat grain related to soil salinity, esp. chlorides, uptake as CdCl
- Fertilizer Products
  - 4,506 Whatcom Farmers Co-op
  - **739 wood ash**
  - 500 Stoller
  - 275 Blu-Min Zinc
  - 153 DAP
  - 101 Ortho Superphosphate
  - **97 Walt's Organic**

Cadmium (Cd) ppm

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  - 275 Blu-Min Zinc
  - 153 DAP
  - 101 Ortho Superphosphate
  - **97 Walt's Organic**
  - **340 Rock P from Western States**

Cd- Sources of exposure

- Food- major source of non-occupational exposure, esp. wheat and potatoes
- Incineration- 71% Pb and 88% Cd due to plastics (***vinyl*** and other) in waste stream
- Cd in fertilizer and food is regulated much more strictly by Canadians and Europeans
- Now same as Canada 4 kg/ha max acceptable cumulative addition, 0.089 kg/ha max annual addition (Fert. Reg Act 1997)
- Canada and Aust. have fertilizer “truth in labeling”, ie the package is labeled– don’t need to go to a website

Cd has increased in soils due to P fertilizer use

- In Columbia basin and around the world where high Cd P is applied-- even where low Cd P is applied
- 10% in exchangeable pool in Canadian prairie vs. 1% in Brady and Weil!
- Concentrated on clays and organic matter

Phosphate fertilizers as source of Cd, Pb, As: Western states to 340 mg/kg Cd

J.R. Simplot’s phosphate mine near ID/WY border

Limits in sewage sludge and metal additions for WA

TABLE 18.9 Regulatory Limits on Inorganic Pollutants (Heavy Metals) in Sewage Sludge Applied to Agricultural Land

			Cumulative pollutant loading rates, kg/ha		
Element	*Maximum concentration in sludge, USEP,[a] mg/kg*	*Annual pollutant loading rates, USEPA, kg/ha/yr*	*USEPA*	*Germany*	*Ontario*
As	75	2.0 0.33 WA	41		28
Cd	85	1.9 0.089 WA	39	3.2	3.2
Cr	3000	150.0	3000	200	240
Cu	4300	75.0	1500	120	200
Hg	57	0.85 0.022 WA	17	2	1.0
Mo	75	—	—	—	8
Ni	420	21	420	100	64
Pb	840	15 2.2 WA	300	200	120
Se	100	5.0	100	—	3.2
Zn	7500	140	2800	400	440

[a] U.S. Environmental Protection Agency (1993).

Brady and Weil, 2000 and Labno,2001

Soil applied sewage sludge: Pb stays in soil, all others 40-60% lost (20-80%?)

TABLE 18.12 Forms of Six Heavy Metals Found in the Ap Horizon of a Metea Sandy Loam (Typic Hapludalfs) in Michigan That Received 870 Mg/ha (Dry Weight) of a "Dirty" Sewage Sludge Over 10 Years

The sludge application rate far exceeded that required to supply nitrogen to the crops grown, suggesting that the purpose was disposal rather than utilization. The sludge was incorporated into the soil between 1977 and 1986, prior to the implementation of source reduction programs to reduce the metal contents of most sewage sludges. The data are for soil samples taken 4 years after the last sludge application. The soil CEC was 7 $cmol_c$/kg, the organic matter content was 7%, and the pH was 6.9.

		Metal Content, mg/kg					
Forms in Soil	*Solubility*	*Cd*	*Cr*	*Cu*	*Pb*	*Ni*	*Zn*
Exchangeable and dissolved	Most	—	<1	4	<4	62	520
Acid soluble (carbonates, some organic)	↓	3	38	140	19	170	1940
Organic matter		<1[a]	200	56	35	31	89
Fe and Mn oxides		<1	331	96	28	180	370
Residual (very insoluble sulfides, etc.)	Least	<1	48	11	99	24	56
Total of all forms		≈4.5	617	307	≈181	467	2975
		Metal Content, kg/ha[b]					
Totals							
Total measured in Ap horizon		≈12	1728	859	≈507	1308	8330
Total content in sludge applied		21	3000	1800	480	2100	11300
Apparent recovery, %		≈60	58	48	≈106	62	74

[a] Numbers preceded by < indicate that the level present was less than the lowest concentration detectable by the analytical method used.
[b] The conversion from mg/kg to kg/ha assumes a bulk density of 1.4 Mg/m^3 and a sampling depth of 20 cm. Metal concentration data from Berti and Jacobs (1996). See also McBride, et al. (1999) for further evidence of sludge-borne metal mobility in soils.

Brady and Weil, 2000

Reduction of HM in sewage sludge 1976 to 1990

TABLE 18.8 Median Pollutant Concentrations Reported in Sewage Sludges Surveyed Across the United States in 1976 and 1990 and in Uncontaminated Agricultural Soils and Cow Manure

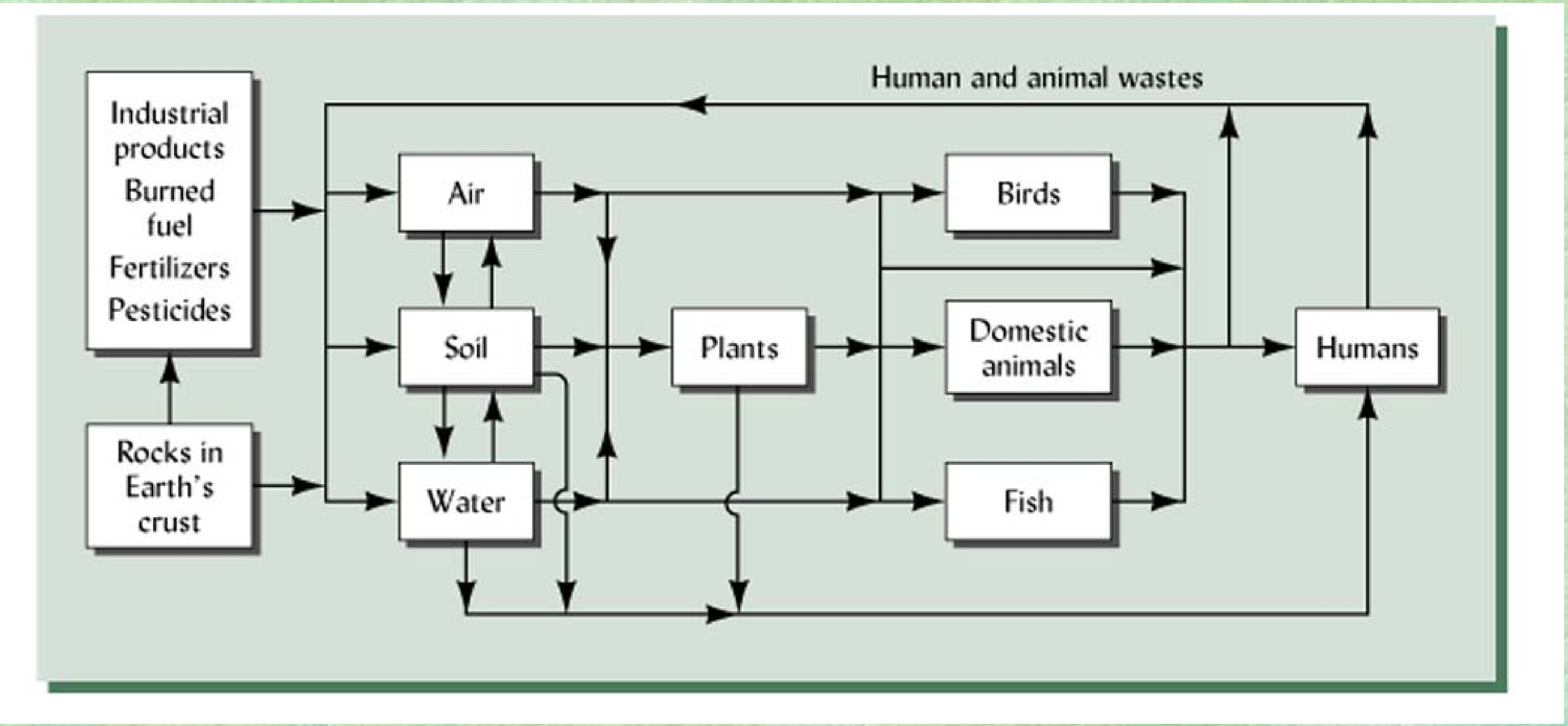
	Concentration, mg/kg dry weight			
Pollutant	*Sludges surveyed in 1990*[a]	*Sludges surveyed in 1976*[b]	*Agricultural soils*[d]	*Typical values for cow manure*
As	6	10	5.2	4
Cd	7	260	0.20	1
Cr	40	890	37	56
Cu	463	850	18.5	62
Hg	4	5	0.06	0.2
Mo	11	—	—	14
Ni	29	82	18.2	29
Pb	106	500	11.0	16
Zn	725	1740	53.0	71
PCB	0.21	9[c]	—	0

[a] Data from Chaney (1990).
[b] Data from Sommers (1977).
[c] 1976 PCB value is median of cities in New York; from Furr, et al. (1976).
[d] Median of 3045 surface soils reported by Holmgren, et al. (1993).

[d] Median of 3045 surface soils reported by Holmgren, et al. (1993).

Brady and Weil, 2000

Heavy metals in the food chain: soil to plant



Brady and Weil, 2000

Plant uptake

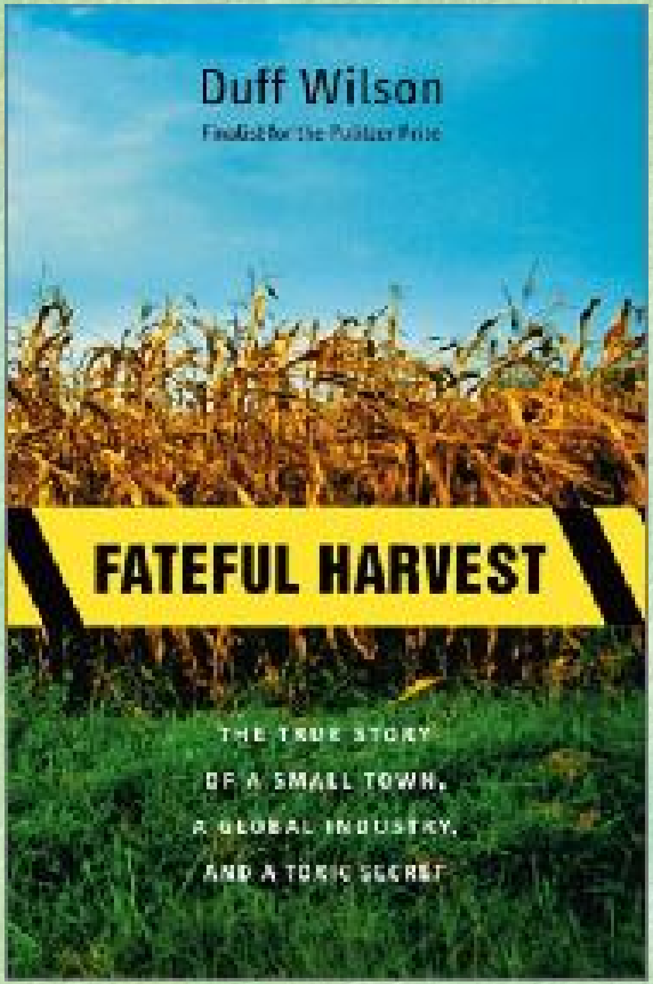
Element	**Crop**	**Uptake**
As	Root crops	Roots
Cd	Leafy veges *Grains*, *tuber*	Roots, tuber *leaves*
Pb	Fruits, grains	Surface *or in tuber*

Concentration of Pb and As in plants

- Roots > leaves> fruits and seeds
- Root skin is higher than inner flesh--
- Roots absorb but do not transport Pb
- Apples and apricots contain low Pb and As
- Haven’t found any regulations on As in food
- Organic As may be less toxic than inorganic compounds of As; Organic As may be predominant in fruits and vegetables, although inorganic As more common in grain

Duff Wilson's expose

- Patti Martin from Quincy WA is protagonist
- WA legislature creates database
- Finances research
- Lawsuit against EPA, now heard was lost



Feds not moving to regulate (USDA or EPA), States regulation

- Texas (1998) biosolids dose of 9 chemicals
- Washington (1998): Canadian standards on 9 toxic chemicals – 45-year doubling dose
  - 63 product stop sales, 46 denied, 25 changed recommended application rates
  - 96% passed
  - **Website:http://agr.wa.gov/PestFert/Fertilizers/ProductDatabase.htm**
- California (2002): ppm limits on 3 chemicals. Arsenic, 4-3-2. Cadmium, 6-5-4. Lead, 20

Duff Wilson 2002

Message

- Exact relationship between soil and plant depends on soil type, climate, management, chemical form, plant species and variety
- It is complicated and data is lacking
- Other countries have been able to regulate despite this-- why not US?

International Pb and Cd limits in foods-- no established US limits

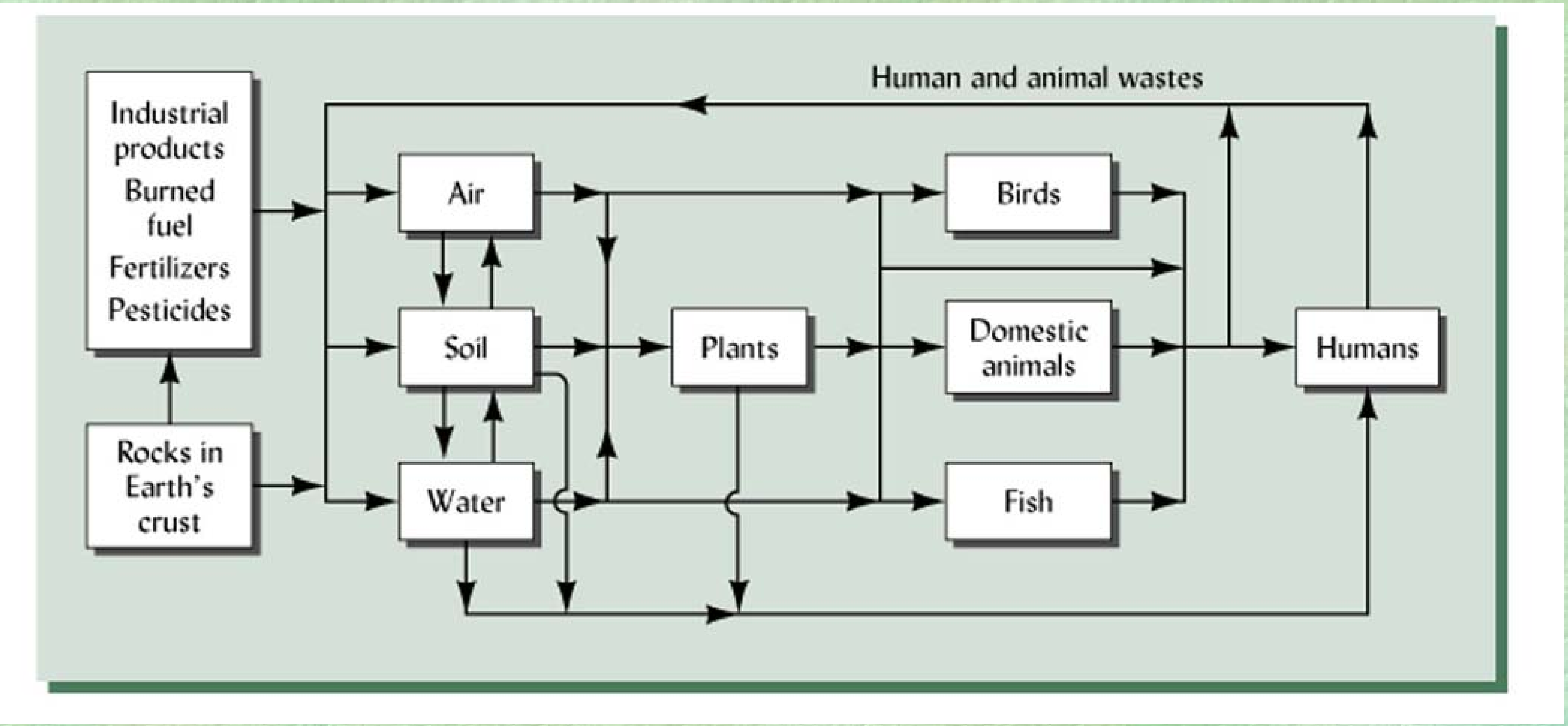
Table 1. Worldwide monitoring values and limits for Cd and Pb limits in foods.

Commodity [a]	Country	Cd (mg/kg)	Pb (mg/kg)	Citation
Cereal and oilseeds	FAO	0.1*		Hart et al., 1998
wheat	Germany	0.1	0.1	Lubben and Sauerbeck, 1991
Wheat	Australia	0.1		Oliver et al., 1997
Wheat grain	EU	0.1		Gavi et al, 1997 [b]
Potato	Australia	0.05	1.5	McLaughlin et al., 1996
Potato	Denmark	0.06 ***		McLaughlin et al., 1994
Potato	Netherlands	0.1		De Boo, 1990
Potato	UK		2 **	Thomas et al., 1972

a = concentrations reported as dry weights except for tubers.
b = "safety limit"
* proposed
** fresh or dry weight basis not specified.
*** "monitoring limit"

Labno 2001

Heavy metals in the food chain: Plants to animals



Brady and Weil, 2000

HM in earthworms after application of sewage sludge- concentrate Cd, Zn

TABLE 18.10 The Effect of Sewage Sludge Treatment on the Content of Heavy Metals in Soil and in Earthworms Living in the Soil

Note the high concentration of cadmium and zinc in the earthworms.

	Concentration of metal, mg/kg			
	Soil		*Earthworms*	
Metal	*Control*	*Sludge-treated*	*Control*	*Sludge-treated*
Cd	0.1	2.7	4.8	57
Zn	56	132	228	452
Cu	12	39	13	31
Ni	14	19	14	14
Pb	22	31	17	20

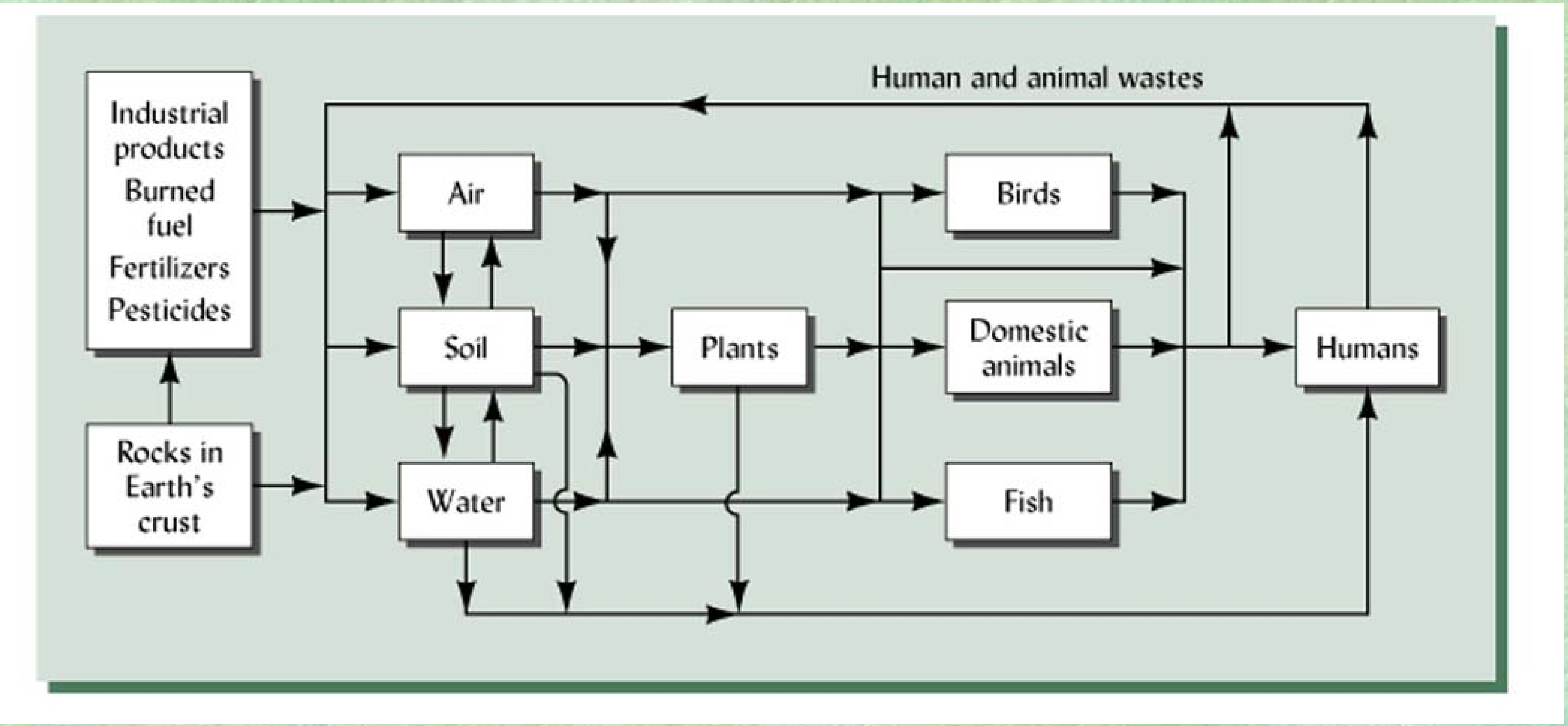
From Beyer, et al. (1982).

Brady and Weil, 1999

Cd uptake in snails

- New (2002) evidence from France, Renaud Scheifler of University of Franche-Comte
- Snails took up 12% of Cd from supposedly bound fraction of smelter soil with high Pb and As

Heavy metals in the food chain: Soil to animals



Brady and Weil, 2000

Animal uptake of soil-- not via plant!

- Up to 30% of diet is soil for sheep, goats
- Up to 18% for cattle
- Depends on management how much the animals get soil
- Direct ingestion of soil particles may increase uptake of HM

How can we manage Pb and As contaminated soil soils?

- Test soil
- Add organic matter (test to make sure low in Pb and As)
- Keep pH high with lime (check to make sure not contaminated with Pb and As or others)
- Add phosphate to bind with lead (TSP lowest), but may increase plant uptake of As. Rock P may have Cd.
- Biological remediation

Organic matter binds heavy metals (make sure OM not contaminated) --the case of Cr

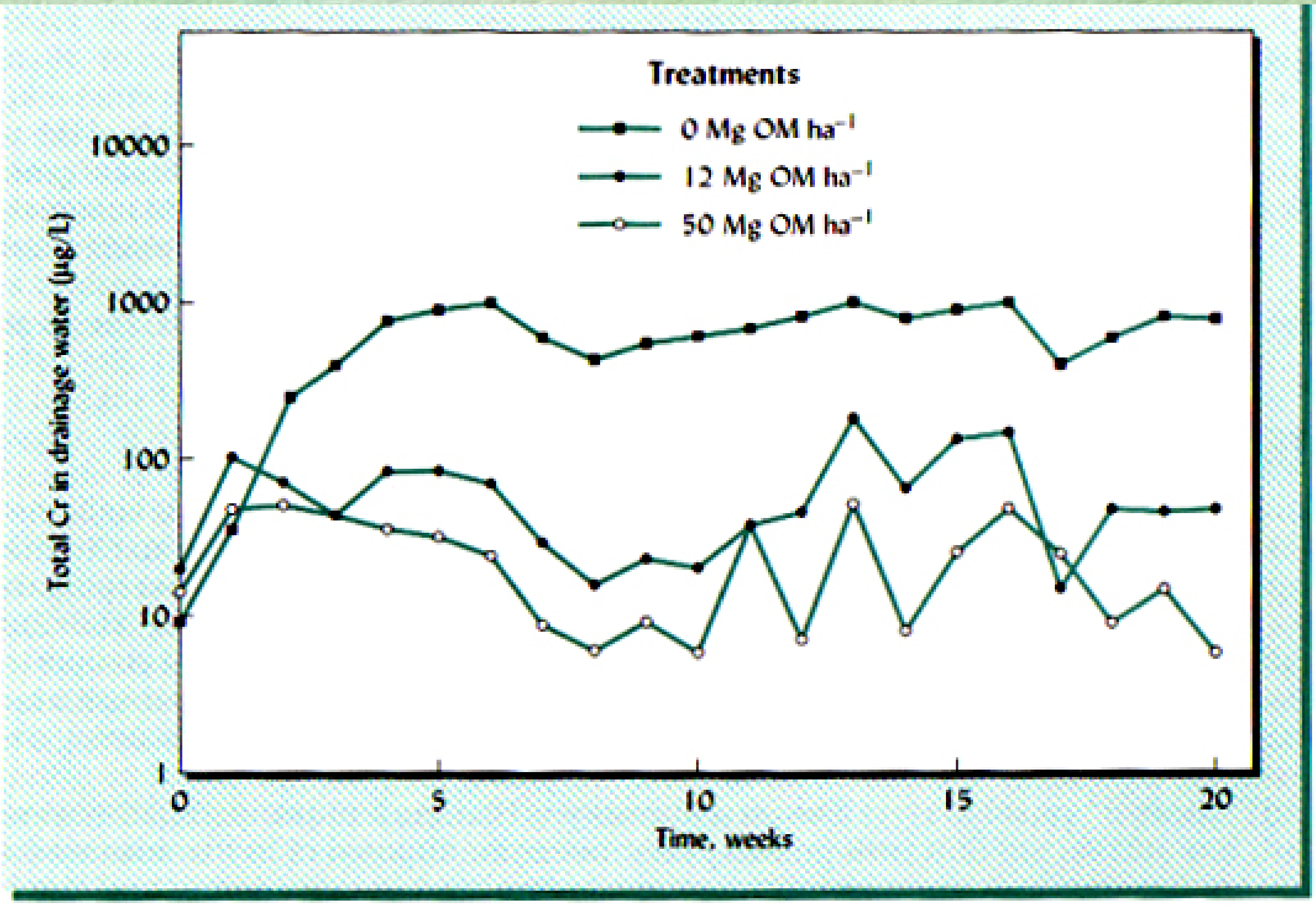


FIGURE 18.14 Effect of adding dried cattle manure (OM) on the concentration of chromium in drainage water from a chromium-contaminated soil. Oxidation of the manure caused the reduction of toxic, mobile Cr^{6+} to relatively immobile Cr^{3+}. Note the log scale for Cr in the water. The coarse-textured soil was a Typic Torripsamment in California. [Adapted from Losi, et al. (1994)]

Brady and Weil, 1999

Add lime (make sure source not contain heavy metals)

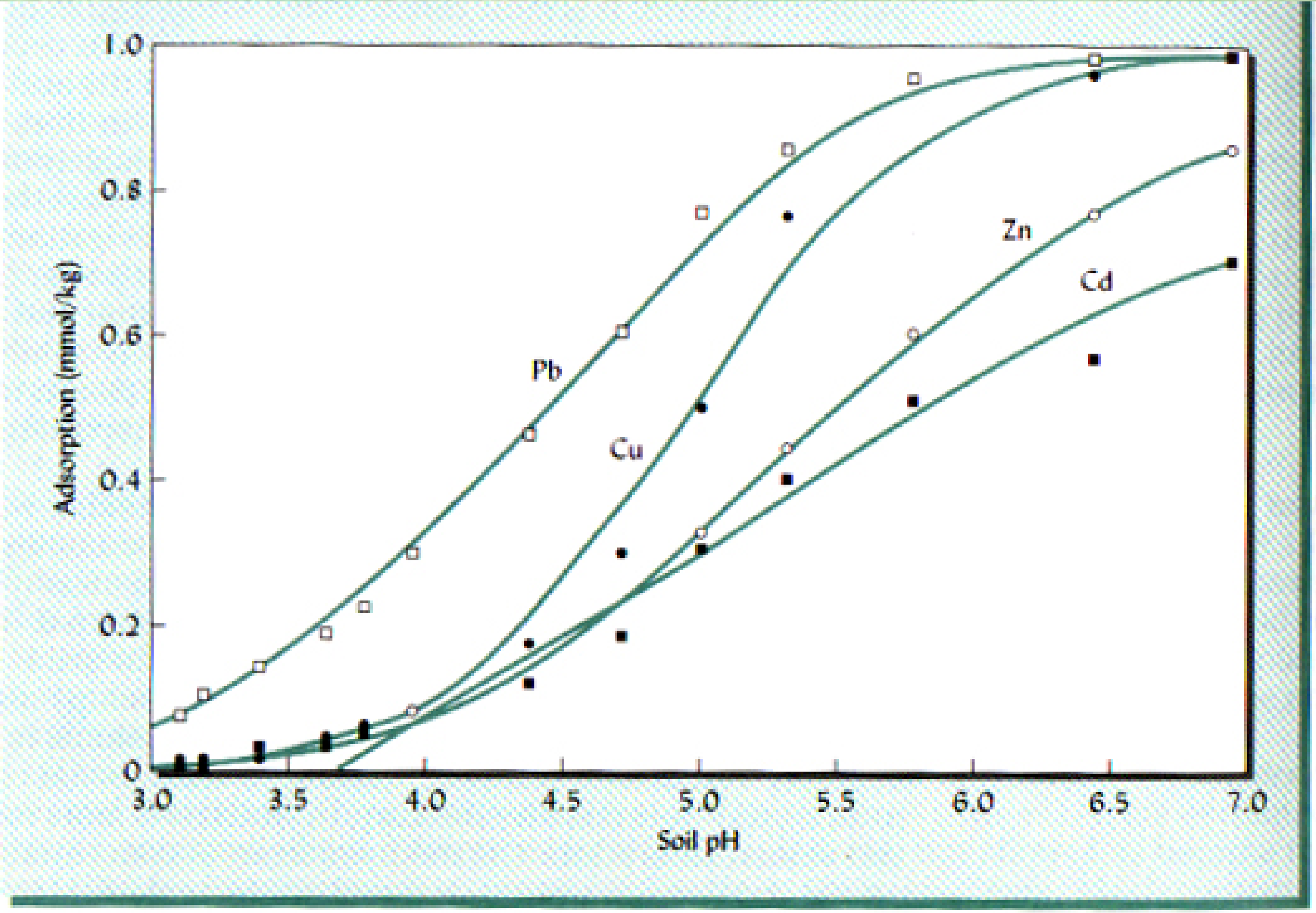


FIGURE 18.21 The effect of soil pH on the adsorption of four heavy metals. Maintaining the soil near neutral provides the highest adsorption of each of these metals and especially of lead and copper. The soil was a Typic Paleudult (Christiana silty clay loam). [From Elliot, et al. (1986)]

Brady and Weil, 2002

Phytoremediation

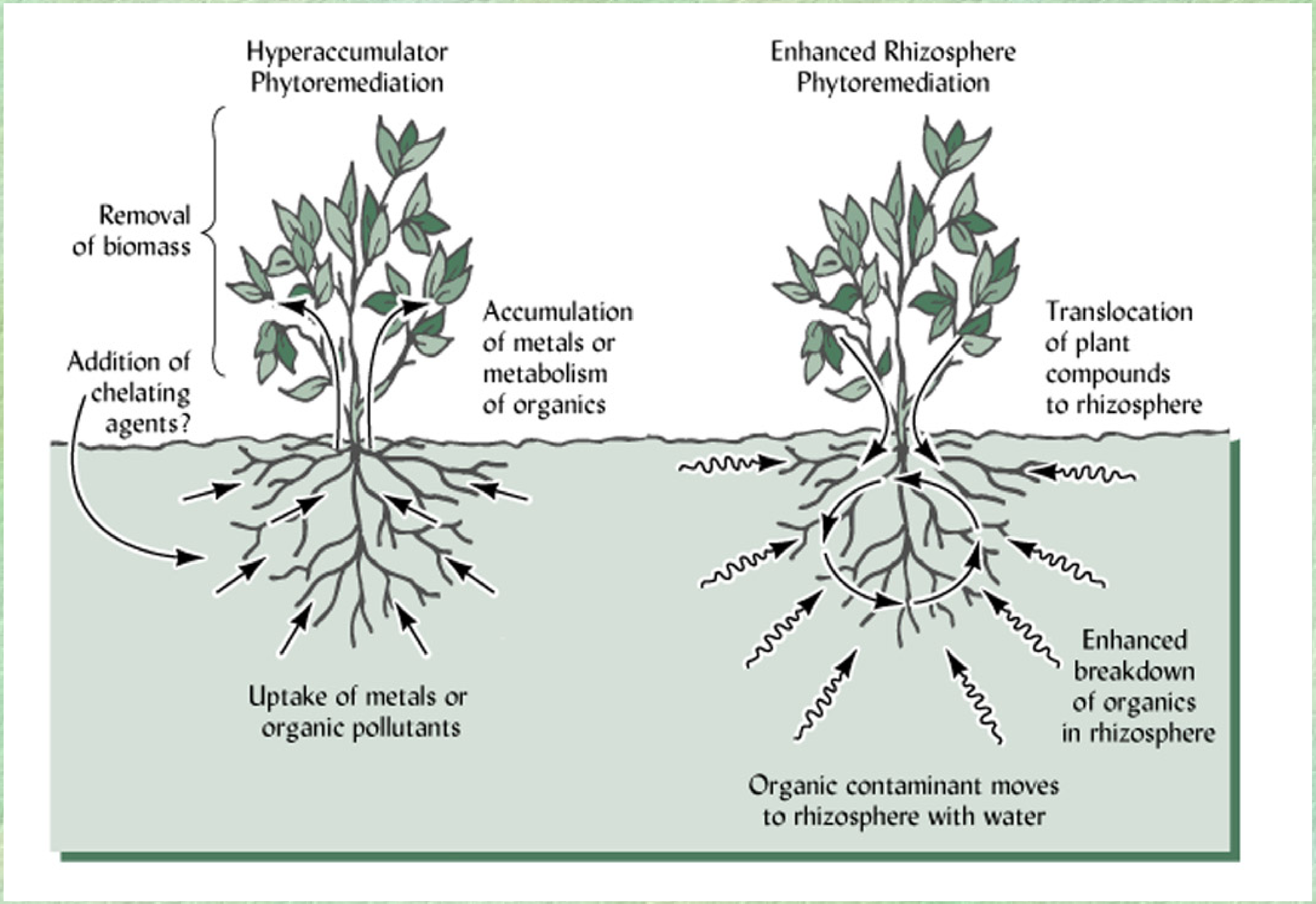


Figure 18.16

Table 15.6 Metal Accumulators have been found widely

Metal	% in leaf	Taxa	Families
Cd	>0.01	1	1
Co	>0.1	28	11
Cu	>0.1	37	15
Pb	>0.1	1	6
Mn	>1.0	9	5
Ni	>0.1	317	37
Zn	>1.0	11	5

Plant "hyperaccumulation"

FIGURE 18.15 *Thlaspi caerulescens*, a zinc and cadmium hyperaccumulator plant growing in smelter-contaminated soil near Palmerton, Pa. This plant has been reported to accumulate up to 4% zinc in its tissue (dry weight basis). Research with such plants aims at developing technology to biologically remove and recover metals from heavily contaminated soils. (Photo by H. Witham; courtesy of R. Chaney, USDA)

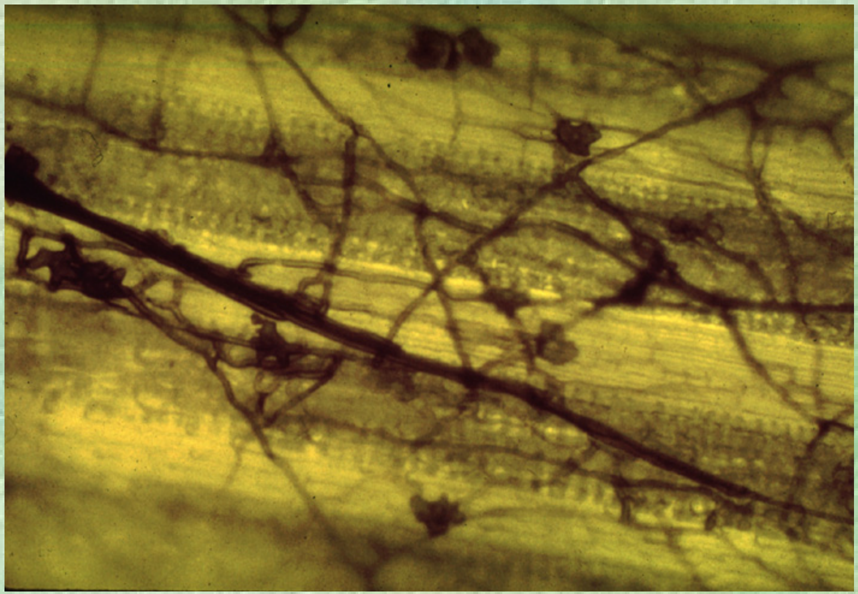
Hyperaccumulator

- Plant tissue concentrations of 4% Zn can be used as ore-- *Thalpsi*
- Brake fern *(Pteris vittata)* can accumulate As
- As accumulating fern available from Raintree nursery, ‘Victory’ or ‘Moonlight’ fern (from China to FLA)
  - Can accumulate 2000x more than most plants
  - $20 soil analysis: www.edenspace.com
  - Send plant -- As used in glass
  - Developing Pb, Cr, Ur extractors

- Pb- add chelators, solubilize lead and plant can take it up
- Genetic engineering
  - moving genes into canola (rapeseed) and Indian mustards to accumulate heavy metals!!
  - Is this systems thinking?

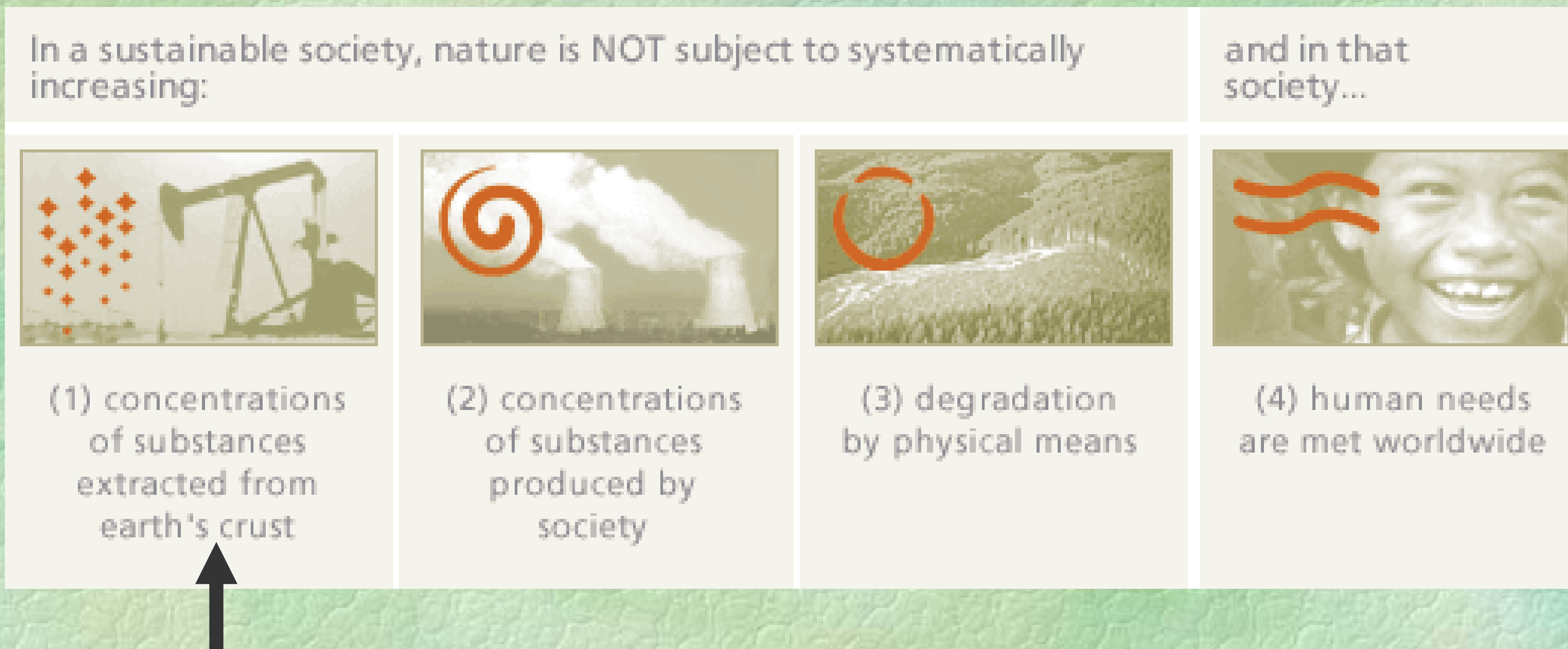
Bioremediation/accumulation by fungi

- Fungi can accumulate from mine tailings and contaminated soil, then collect fruiting bodies and ash
- Will not break down like hydrocarbons



The Natural Step addresses problem of mined products, and system is used by some industry, communities

www.naturalstep.org



Summary and conclusions

- Micronutrients can be deficient, adequate or toxic depending on concentration
- Availability can depend on pH, soil aeration, OM, interactions with other nutrients
- Soil contamination from previous agricultural practice is of continuing concern-- in using/buying land ask AND test:
  - Inorganic fertilization: micronutrient application (form)
  - Organic: rock P, fish emulsion
  - Sludge application history
  - Pesticide use (PbAs, Cu)
- Know your products/check web- including organic
- Maintain pH and OM at optimum levels if suspect heavy metals

Study Questions

- Ch 15 #3, 5, 6, 7, 8, 9, 10
- Ch 18 #3, 4, 5

References

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- **Website:http://agr.wa.gov/PestFert/Fertilizers/ProductDatabase.htm**