GEOL 408/508

SOILS AND CHEMICAL POLLUTION

Chapter 18

Brady and Weil, Rev. 14th Ed.

TOXIC ORGANIC CHEMICALS

Environmental damage from organic chemicals:

- xenobiotics are artificially synthesized compounds
- many are toxic to living organisms & resistant to biological decay
- many are contaminants in industrial & municipal wastes applied to or spilled on soils
- pesticides are the most widespread organic pollutants associated with soils

The nature of the pesticide problem:

- **Benefits of pesticides:**
  - help control mosquitoes and other vectors of human disease
  - herbicides make conservation tillage much more effective; aided in erosion control
  - reduce food spoilage from production to consum'n

TOXIC ORGANIC CHEMICALS - 2

The nature of the pesticide problem, continued:

- **Problems with pesticides:**
  - widespread use = contamination of surface & groundwater
  - organisms other than targets may be killed: natural enemies of targets or other beneficial
  - overall crop losses to insects, diseases & weeds is about the same as before pesticides were used

- **Alternatives to pesticides:**
  - "organic farming" which does not use synthetic chemicals; emphasizes soil OM & biological interactions to manage agroecosystems
  - may use natural biol pest control; crop rotation & diversification, pest-resistant cultivars,etc

TOXIC ORGANIC CHEMICALS - 3

The nature of the pesticide problem, continued:

- **Nontarget damages:**
  - most pesticides reach the soil because they miss the target insect of plant leaf
  - aerial appl'n to forests: 25% on foliage; <1% on target insect; 30% to soil; ≈50% lost to atmos or runoff
  - frequent nontarget organism damage; beneficial insects & soil organisms
  - chemicals may undergo biological magnification; example of DDT
  - suggestion of human endocrine imbalance due to traces of pesticides in environment

KINDS OF ORGANIC CONTAMINANTS-1

Industrial organics:

- gasoline components (BTEX) from spills or LUSTs
- solvents used in manufacturing, TCE; also TNT
- PCBs are especially troublesome (& toxic):
  - used in lubricants, hydraulic fluids, transformer insulators, other applications
  - essentially do not decay; persistent globally

Pesticides:

- **Insecticides:**
  - chlorinated hydrocarbons (e.g., DDT): very persistent, low biodegradability; toxic to birds & fish; now essentially banned
  - organophosphates: generally biodegradable; very toxic to humans
  - carbamates: gen. biodegrad; low mammalian tox.

LEAKING UNDERGROUND STORAGE TANK REPLACEMENT

Fig 18.2

KINDS OF ORGANIC CONTAMINANTS-2

Pesticides, continued:

- **Fungicides:**
  - used mainly to control diseases of fruit & veg crops
  - used as seed coatings to protect against seed rots; (problems in 3rd world countries when seed grain is consumed by humans)
  - protect fruits & vegs from decay; wood from rot

- **Herbicides:**
  - quantity of herbicides used in US exceeds that of all other pesticides combined
  - there are triazines, substituted ureas, carbamates, sulfonylureas, others; are somewhat selective
  - glyphosate (Roundup) is nonselective; some crops have been given a gene to confer resistance

KINDS OF ORGANIC CONTAMINANTS-3

Pesticides, continued:

- **Rodenticides:**
  - used to protect grain in storage; in homes
  - various minor uses
- **Nematocides:**
  - not as widely used as herbicides & insecticides
  - some are water soluble, not sorbed by soil & leach into groundwater
  - others are toxic to virtually all biological life in soil
  - CH_3Br has been banned due to its adverse effects on the soil environment & atmosphere

BEHAVIOR OF ORGANIC CHEMICALS IN SOIL

In the soil, organic chemicals may:

(1) vaporize without chemical change

(2) be sorbed by soils

(3) move in soil solution & leach out of the soil profile

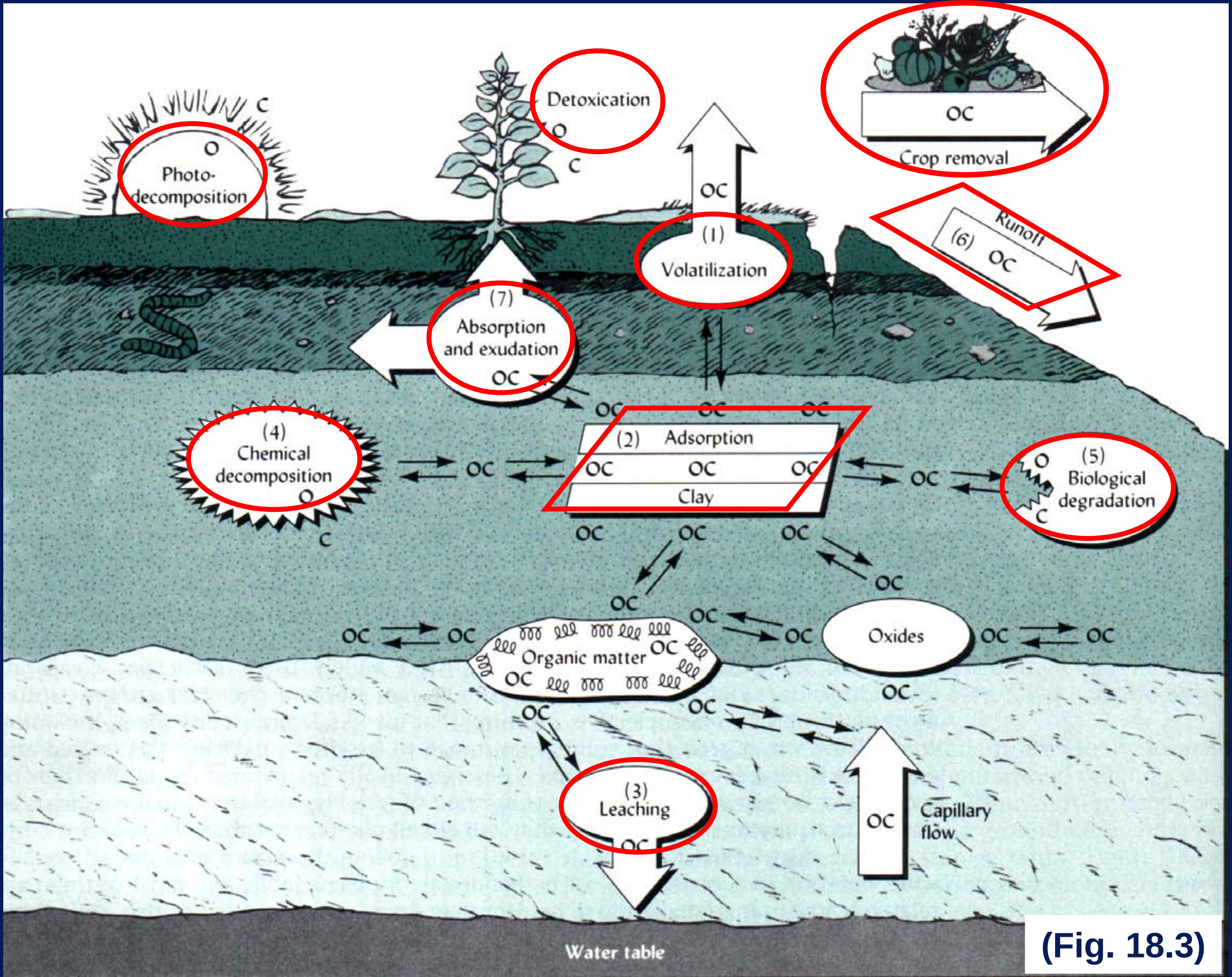
(4) undergo chemical reactions within or on surface

(5) be degraded by soil microorganisms

(6) wash into surface waters via surface runoff

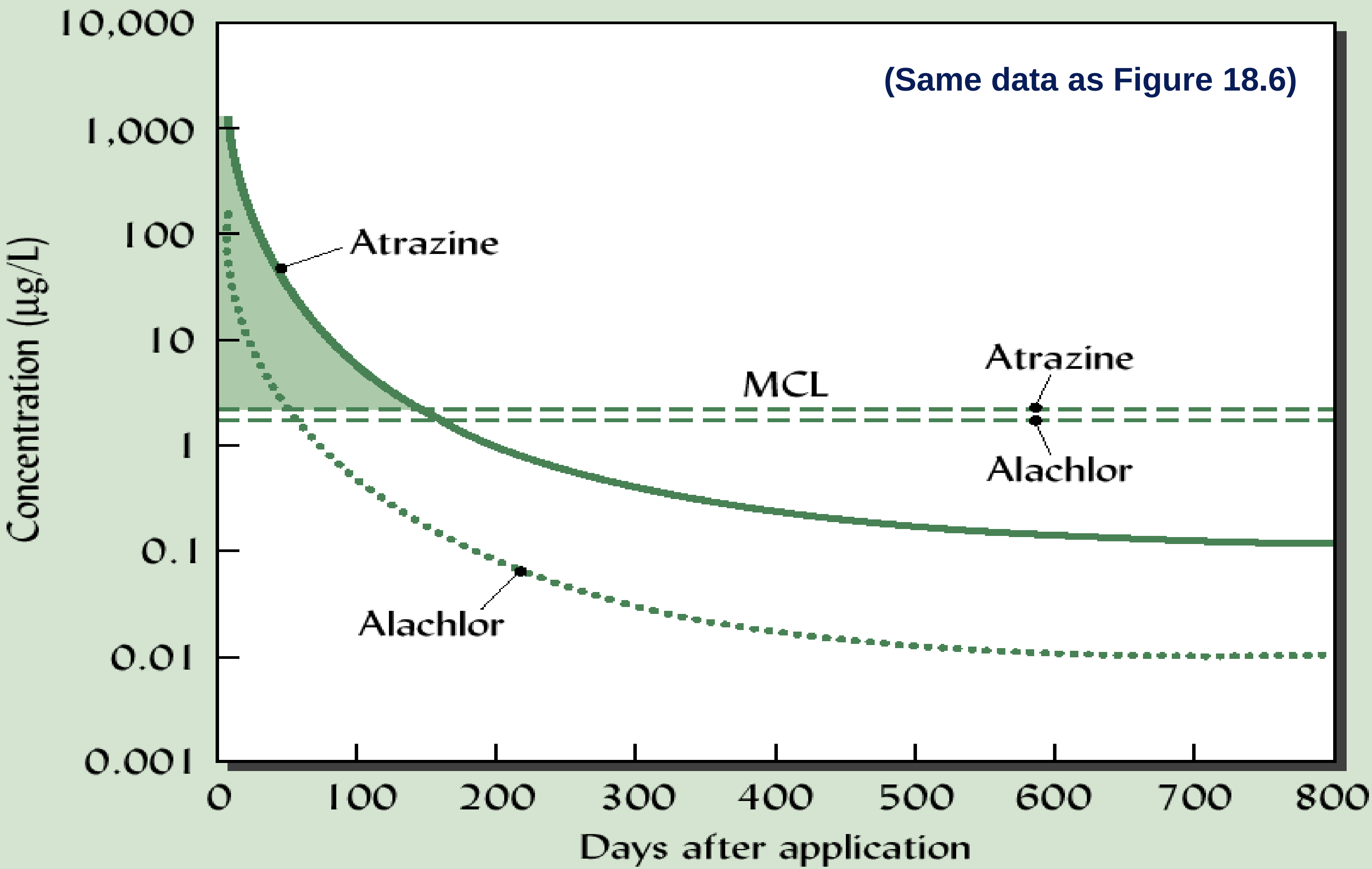
(7) be taken up by plants/soil animals & biomagnified

DISSIPATION OF ORGANIC CHEMICALS IN SOILS

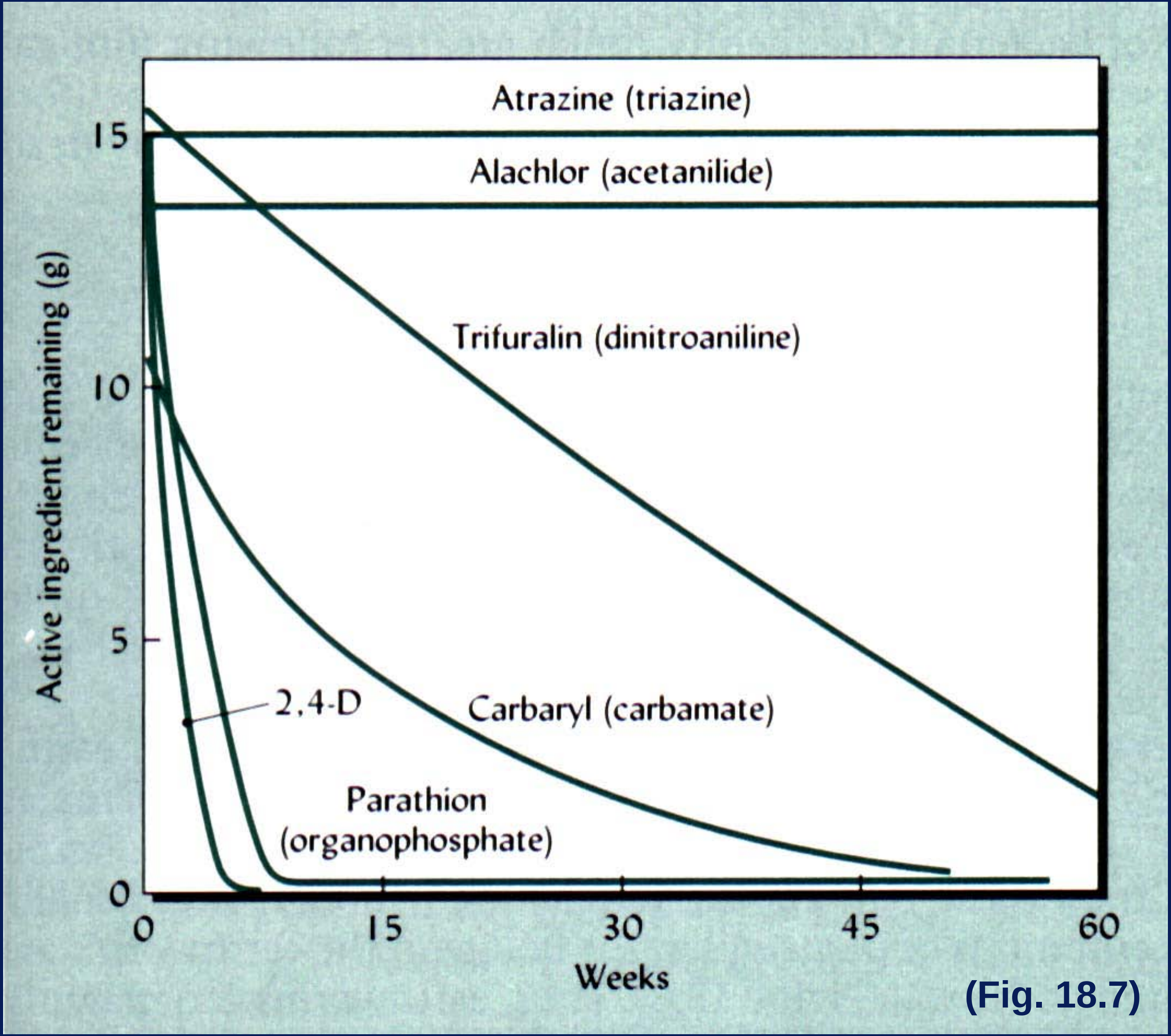


(Fig. 18.3)

CONCENTRATION OF TWO HERBICIDES IN RUNOFF



DEGREDATION OF HERBICIDES AND INSECTICIDES



(Fig. 18.7)

EFFECTS OF PESTICIDES ON SOIL ORGANISMS - 1

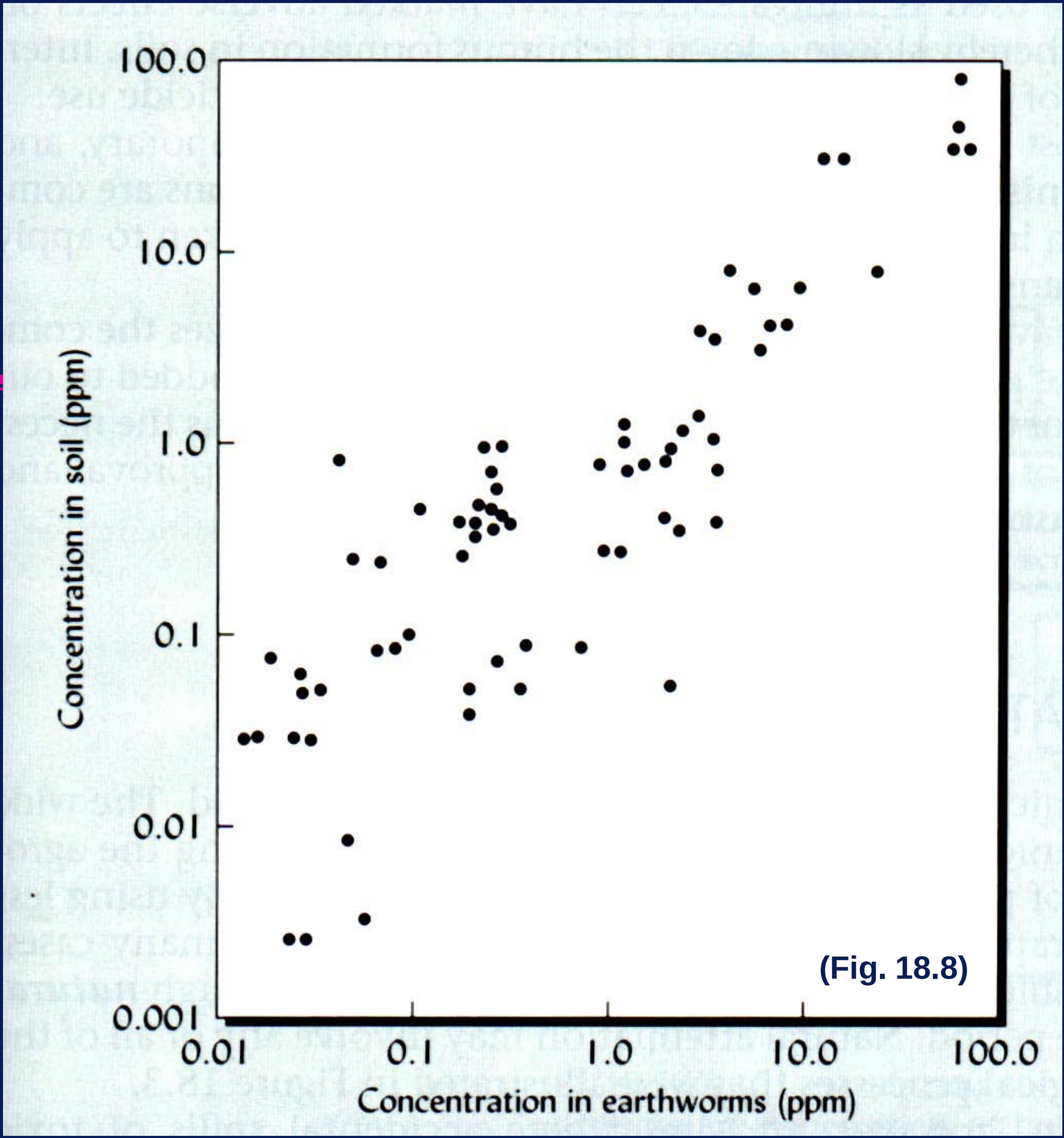
Fumigants:

- used on difficult to control pests; for general sterilization; kills much more than target organisms
- may take up to two years for overall population to recover; generally much less for microflora

Effects on soil fauna:

- nematodes not generally affected; mites more sensitive; springtails vary in sensitivity
- earthworms:
  - little affected by most pesticides
  - exceptions: carbamates are very toxic
  - pesticide conc. in earthworms are closely related to conc in soil (Fig. 18.8)

PESTICIDE LEVELS IN SOILS AND EARTHWORMS



Note that the concentration in the earthworm is approximately the same as in the soil; there is little or no bioaccumulation.

EFFECTS OF PESTICIDES ON SOIL ORGANISMS - 2

Effects on soil microorganisms:

- overall levels of bacteria are not too seriously affected
- nitrification & N fixing bacteria may be adversely affected
- some pesticides may enhance N fixation by reducing activity of predatory organisms
- fungicides obviously affect fungi & actinomycetes - other than targets
- most negative effects are temporary

REMEDIATION OF SOILS CONTAMINATED WITH ORGANIC CHEMICALS

Soil ecosystems may recover from pesticides by natural attenuation

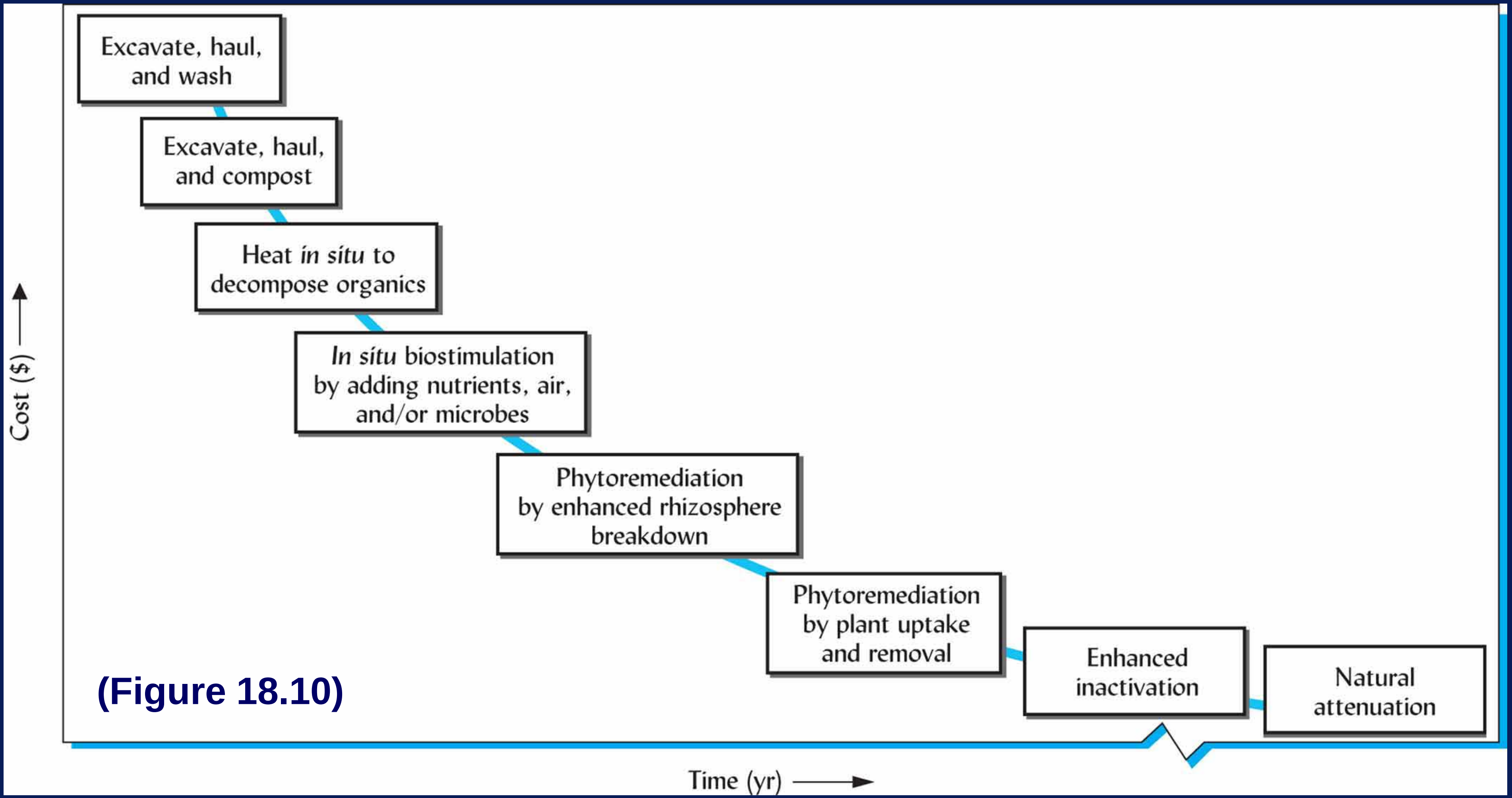
More severe problems arise from accidental spills of illegal disposal of organic chemicals

Need to consider clean-up speed, standards, costs (Fig 18.10)

Physical and chemical methods:

- ***Ex situ*** **treatment:**
  - remove soil and heat or flush with water or air to remove volatile organics
  - effective bit expensive method; destroys organisms
- ***In situ*** **treatment:**
  - decontamination: flush with water, surfactants, air; may use vacuum, heat
  - sequestration (binding); stabilization

REMEDIATION METHODS FOR CONTAMINATED SOILS



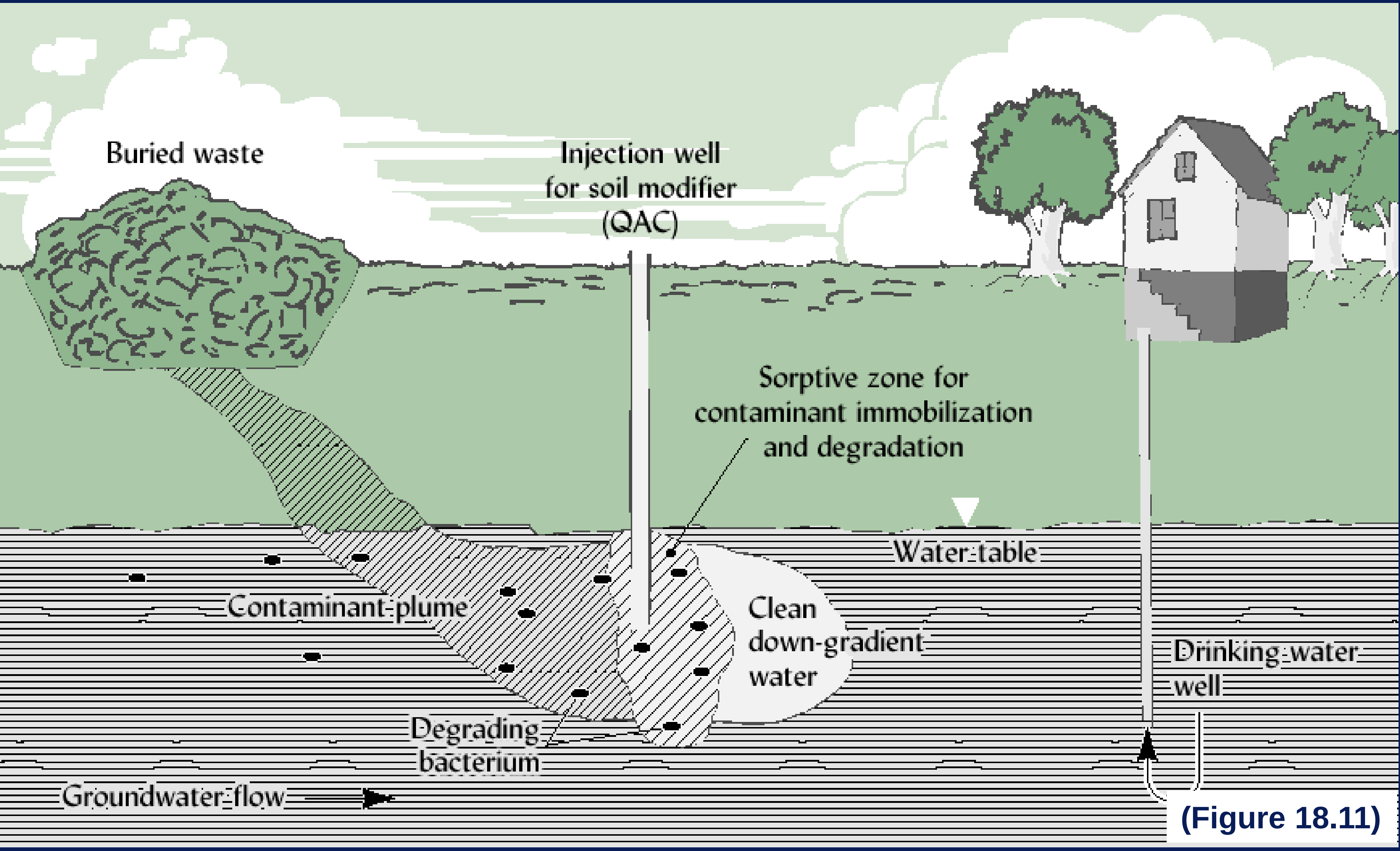
(Figure 18.10)

REMEDIATION OF SOILS CONTAMINATED WITH ORGANIC CHEMICALS - 2

Physical and chemical methods, continued:

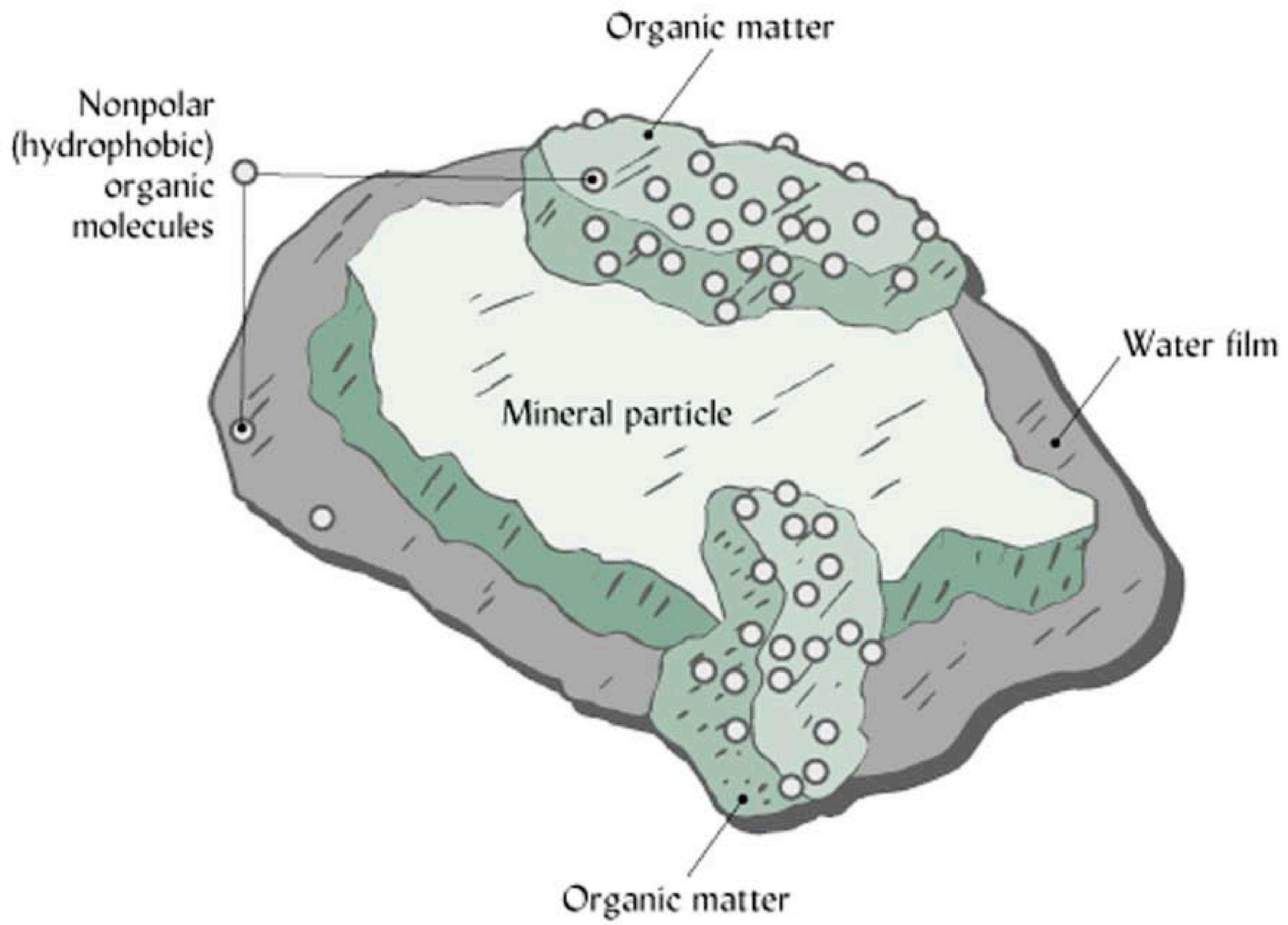
- **Organoclays:**
  - add a surfactant such as a quaternary ammonium compound (QAC), $(CH_3)_3NR^+$, to a clay particle
  - these clays will attract nonpolar organic compounds (Fig 18.12)
  - can inject QAC into the zone of groundwater flow to stimulate formation of organoclays (Fig 18.11)
- **Distribution coefficients, K_d:**
  - ratio of sorbed contaminant to that in solution (text)
  - K_d for nonpolar organics on untreated clays is low
  - K_d for organoclays much higher for nonpolar compounds
  - K_{oc} is often better for organic compounds

USE OF QAC AND BIOREMEDIATION



(Figure 18.11)

HYDROPHOBIC ORGANIC SORPTION TO SOIL PARTICLES



(Fig 18.12)

REMEDIATION OF SOILS CONTAMINATED WITH ORGANIC CHEMICALS - 3

Bioremediation:

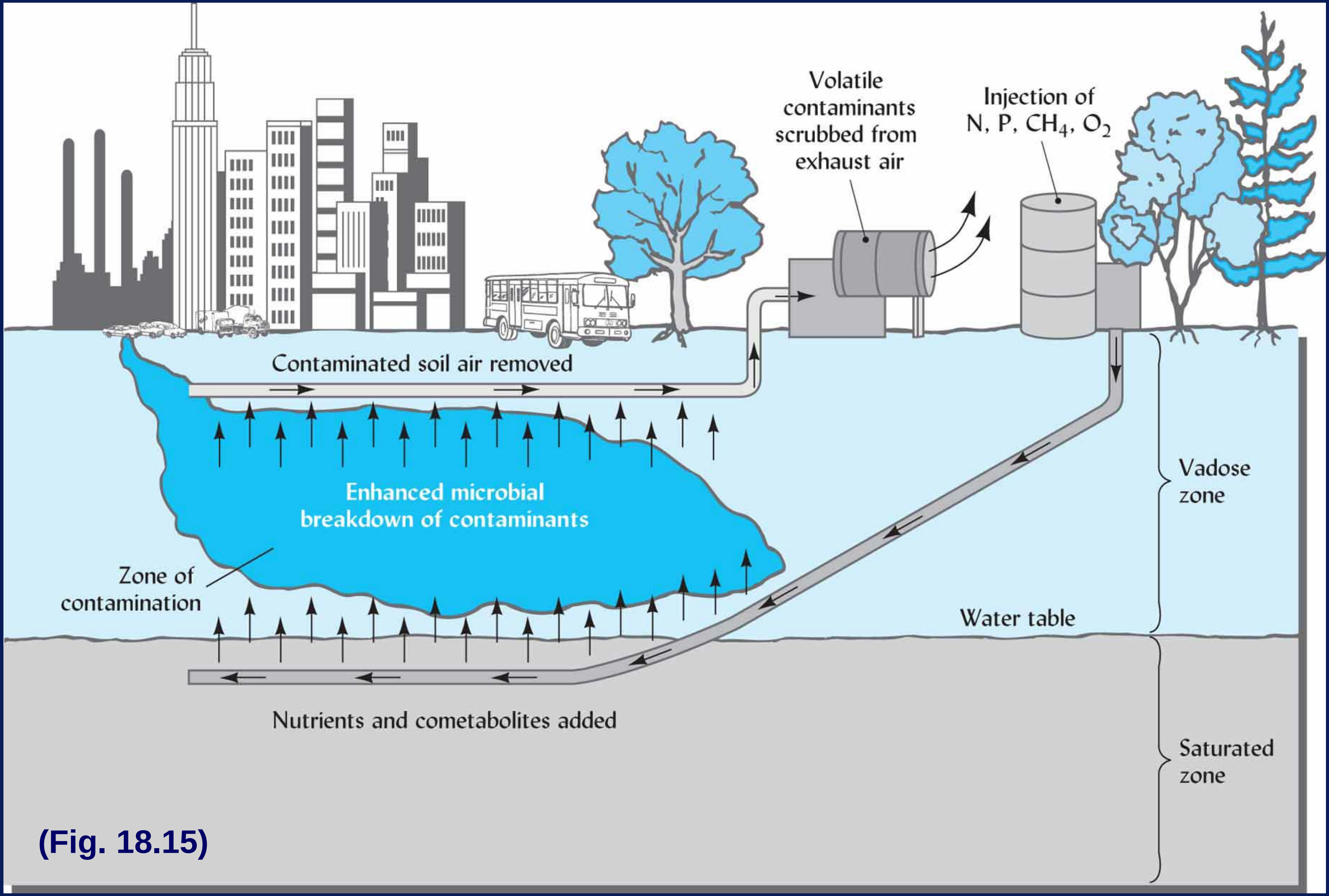
Process that uses enhanced plant and/or microbial action to degrade organic contaminants

Bioaugmentation introduces microbes to a soil system
- is increasing in use; maybe more in future

- **Biostimulation:**
  - assist naturally occurring microbial populations
  - this is most often used process
  - add fertilizers (N,P), O_2, co-substrate
  - may use oil-based fertilizer

- **Alaskan oil spill cleanup:**
  - an oil soluble fertilizer was used on beaches
  - much degraded within a few weeks; best results with most available N (Why was not more used?)

IN SITU BIOREMEDIATION OF VOC CONTAMINATION



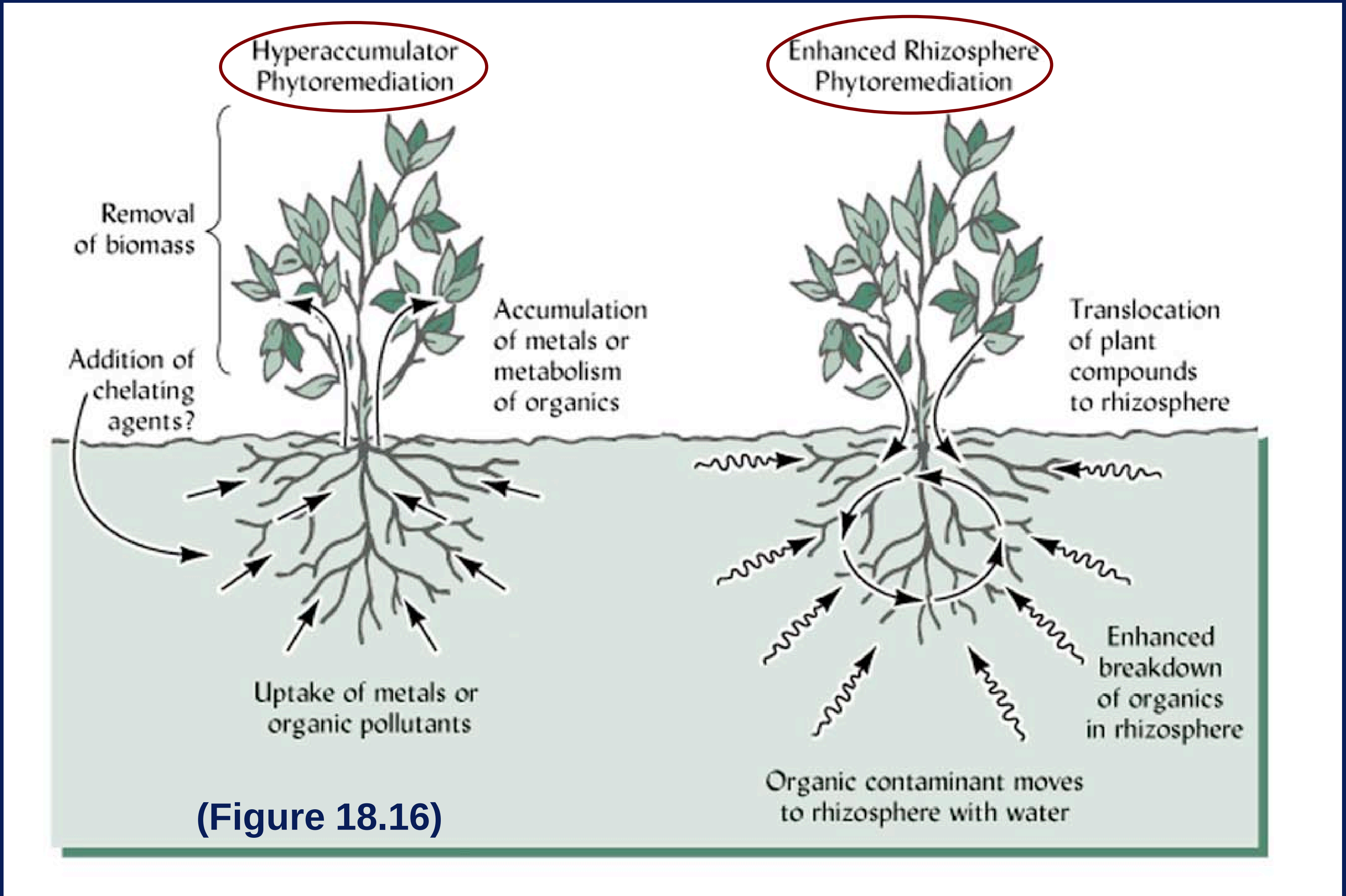
(Fig. 18.15)

REMEDIATION OF SOILS CONTAMINATED WITH ORGANIC CHEMICALS - 4

Phytoremediation:

- use of higher plants in contaminant removal
- hyperaccumulating plants will uptake and accumulate high concentrations of contaminants
- plants are harvested and disposed; metals recovered (?)
- enhanced rhizosphere remediation is where root exudates stimulate bacteria that will degrade contaminants
- used for metals, TNT, PAHs, other organic
- obviously, very species dependent
- especially advantageous with large areas of moderately contaminated soils; takes relatively long time

TWO APPROACHES TO PHYTOREMEDIATION



(Figure 18.16)

REMEDIATION OF SOILS CONTAMINATED WITH ORGANIC CHEMICALS - 5

Bioavailability of sorbed and/or complexed chemicals:

- many chemicals that are bound by OM or inorganic colloids are protected from microbial attack or are unavailable to plants
- bioavailability usually decreases with time
- these chemicals are not likely to move into groundwater
- are held in inter layer positions of silicate clays or are complexed very strongly by other colloids

CONTAMINATION WITH TOXIC INORGANIC SUBSTANCES

Greatest problems from: Hg, Pb, As, Cd, Cu, Zn, Cr, Mo, Mn, Se, F, B

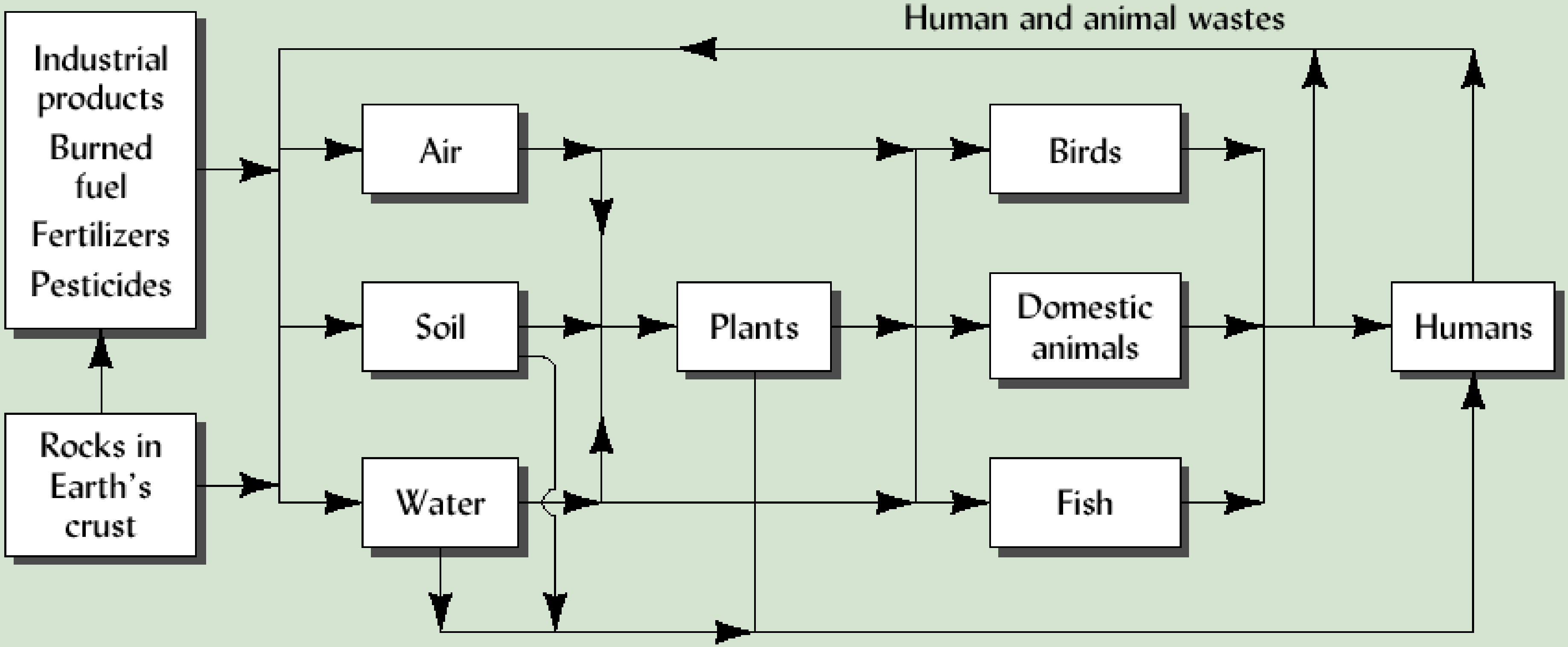
Sources and accumulation:

- burning of fossil fuels, smelting, metal fabrication, etc., release atmospheric contaminants
- Pb, Ni, B are (were) in gasoline
- borax: detergents, fertilizers & forest fire retardants
- Cd, Cu, Mn, Ni, Zn: limestone & superphosphate
- As: insecticide on cotton, fruit crops, lawns

Concentration in organism tissue:

- food chain: soil → plant → animal → human (Fig 18.20)
- bioaccumulation or biomagnification by fish, wildlife and humans
- now: restrictions in fish & wildlife consumption

TRACE METAL CYCLING IN THE ECOSYSTEM



(Fig 18.20)

POTENTIAL HAZARDS OF CHEMICALS IN SEWAGE SLUDGE

- **Source reduction programs:**
  - require industries to pretreat wastewater prior to discharge
  - HRSD one of first POTW systems to require this
  - result is biosolids with much lower levels of contaminants (note Table 18.8)
  - levels of most toxic metals have decreased;Cu less
- **Regulation of sludge application to land:**
  - EPA now recognizes Class I biosolids that can be applied to croplands; must calculate annual & cumulative loadings (Table 18.9)
  - note that cumulative loading rates for other countries are generally lower than for USA
  - major use problem is public acceptance

POTENTIAL HAZARDS OF CHEMICALS IN SEWAGE SLUDGE

- **Toxic effects from sludge:**
  - uncertainties in nature of organics and cumulative nature of metals (in spite of 20 years of data!)
  - note bioaccumulation of metals in earthworms (Table 18.10); from high metal sludge
  - need to be assured that plant contents of metals are not excessive (esp for Cd, Cr, Pb)
  - some grains in USA cannot be exported to Europe due to Cd levels (exceed Europian but not US standards)
  - must take care about direct ingestion of biosolids - grazing animals, children; dust

REACTIONS OF INORGANIC CONTAMINANTS IN SOILS

Heavy metals in sewage sludge:

- some may be relatively mobile when fresh material is added to soils (organic complexes ?)
- mobility/availability decreases with time (Table 18.12)
- mostly immobile & unavailable at pH >6.5

- **Forms found in soils treated with sludge:**

Water soluble - soil solution
Exchangeable - Adsorbed to surfaces
Carbonate - carbonates & hydroxides
Easily reducible - Mn oxides
Moderately reducible - amorphous Fe hydroxides
Organic-sulfide - difficult to distinguish between
Acid extractable - use conc (HNO_3) acid
Residual or matrix bound - use HF + $HClO_4$

REACTIONS OF INORGANIC CONTAMINANTS IN SOILS

Chemicals from other sources:

- As accumulated in orchard soils; sorbed to Fe & Al oxides
- can have toxicity to some plants & earthworms
- Pb from leaded gasolines, paint (chips & dust)
- Pb is generally unavail to plants but soil and paint chips are ingested by children
- B from irrigation water, power plant fly ash - relatively available & mobile in acid soils
- F in atmos from industrial processes; may be deposited onto vegetation (local problems)
- Hg from industrial processes; in effluents and in many food/cosmetic products (Red dye 24)
- CH_3Hg formed in anaerobic conditions; accumul. by fish - toxic to humans

PREVENTION AND ELIMINATION OF INORGANIC CHEMICAL CONTAMINATION

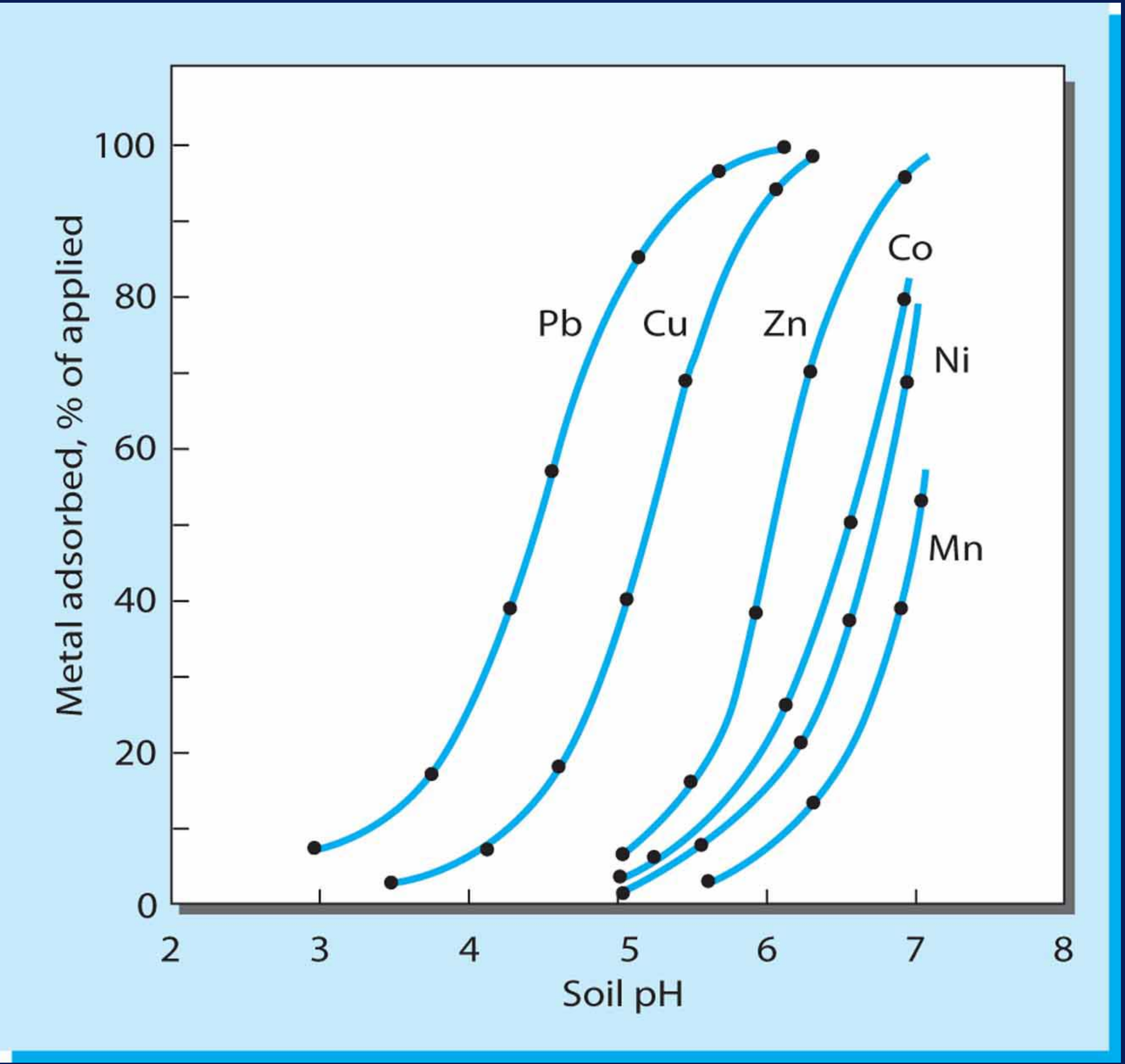
Reducing soil contamination:

- reduce aerial inputs from industry & vehicle exhausts
- better monitoring of all materials applied to soils

Immobilizing the toxins:

- lime soils to pH >6.5 to immobilize trace metals
- drain wet soils to oxidize certain metals; however, the sulfide form of most trace metals is very insol
- reduced form of Cr (Cr^{+3}) is less toxic form; OM is very effective in reducing Cr (Cr^{+6} to Cr^{+3})
- phosphate additions will reduce avail of several cations but has opposite effect on As
- take care with plants grown on metal- contam. soil; more metal transl. to leaves than fruits/seeds

EFFECT OF SOIL pH ON SORPTION OF SIX METALS



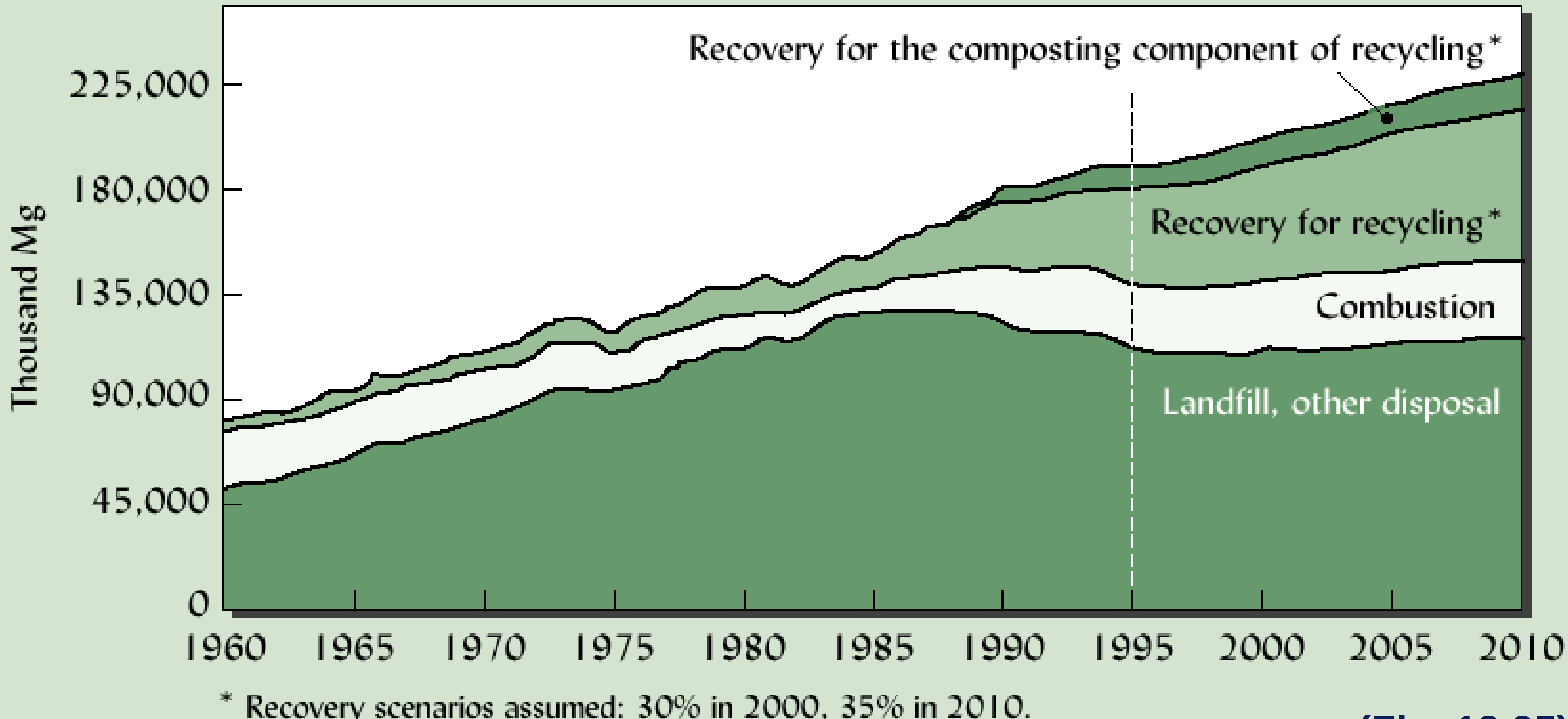
(Figure 18.23)

LANDFILLS

The solid waste problem:

- too much waste, too few disposal sites
- need much more waste reduction & recycling
- about 70% of material going to LFs is organic in nature & could be composted
- need to separate different types of recyclables
- much toxic waste from households are placed in municipal landfills - need for stringent control on construction and long-term monitoring

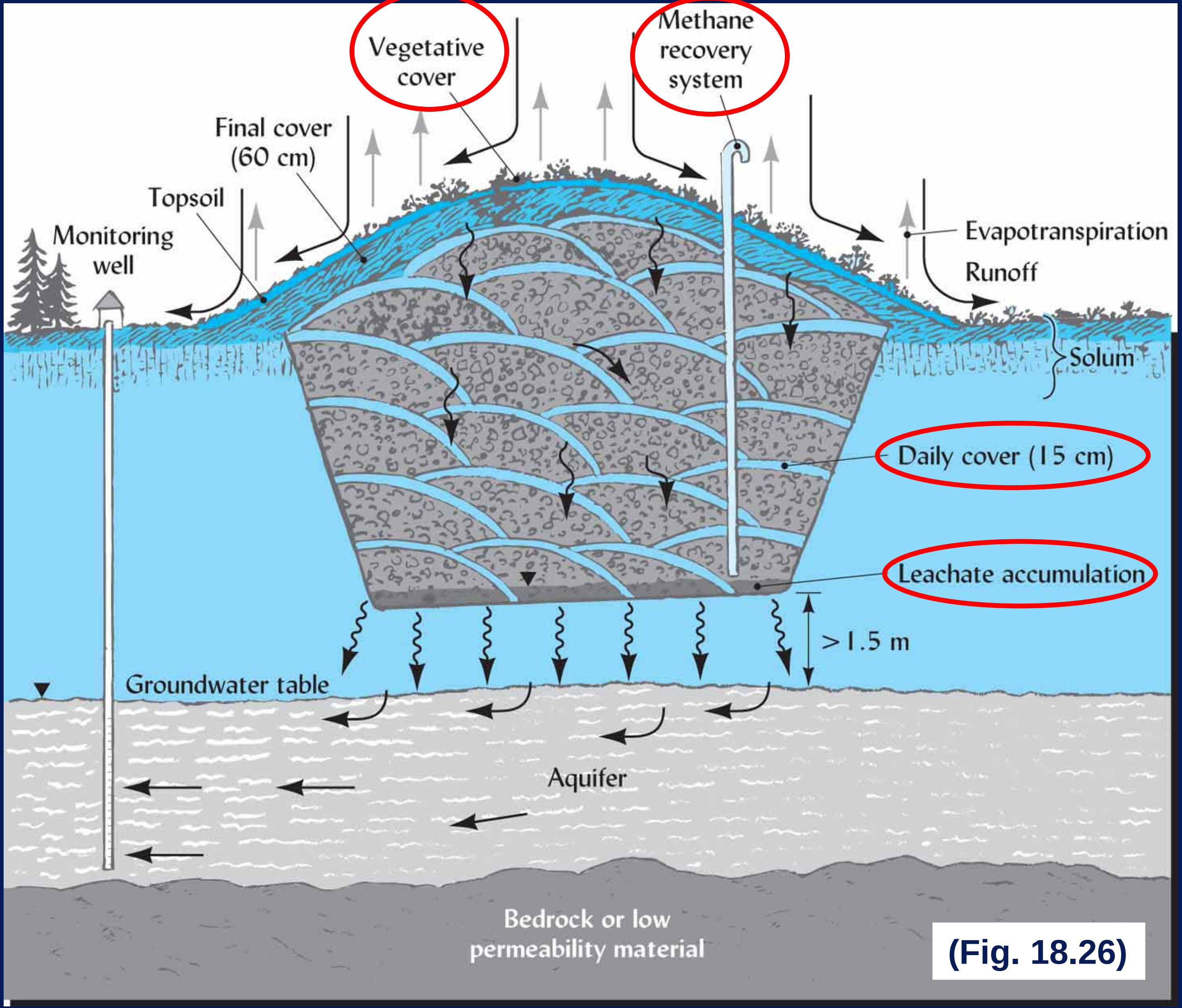
TRENDS IN MUNICIPAL SOLID-WASTE MANAGEMENT



(Fig. 18.25)

NATURAL ATTENUATION LANDFILL

Soils:
- mod perm
- high CEC
- soil for cover
- 1.5 m depth to ground water

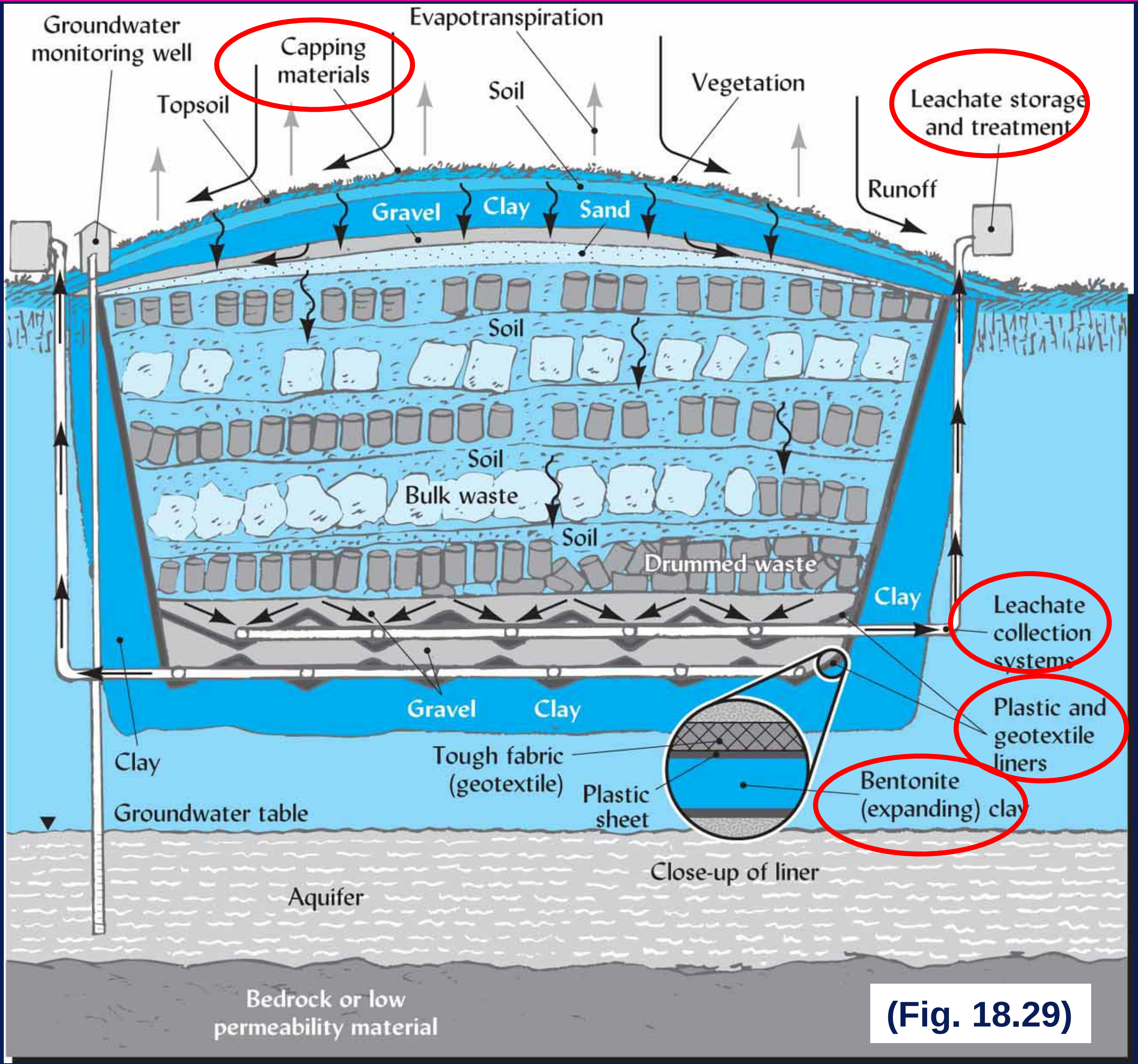


(Fig. 18.26)

CONTAINMENT OR SECURE LANDFILL

- used for hazardous wastes
- common type for most LFs of today

What's missing in this LF??



(Fig. 18.29)

LANDFILLS

Environmental impacts of landfills:

- major concern is contaminants in leachate reaching groundwater
- significant subsidence in older landfills
- methane gas is produced by anaerobic decomp. and is a considerable hazard:
  - if not collected will cause explosion hazard
  - may seep into basements of houses
  - may rupture cover/liner and provide path for leachate

RADIONUCLIDES IN SOIL

Radioactivity from nuclear fission:

- several radioisotopes released during atomic weapons testing
- two are of significance: ^{137}Cs and ^{90}Sr
- generally less of these isotopes than the naturally occurring ^{40}K

- **Strontium 90:**
  - Sr behaves similarly to Ca; some concern of uptake by forages, cattle & into milk
  - very small amounts in most soils
- **Cesium 137:**
  - Cs is similar to K but is less available in many soils
  - fixed in clays as is K, but more strongly held
- **Iodine 131:**
  - short half-life; problems at Chernobyl; thyroid prob

RADIONUCLIDES IN SOIL

Radioactive wastes:

- major problems at weapons manufacturing & processing plants; power plants
- more minor problems from research & medical labs
- elements of concern: Pu, U, Am, Cm, Cs

• **Plutonium toxicity:**

- ^{239}Pu is highly toxic to humans & is intensively radioactive
- immobile in soils, not taken up by plants
- oily liquid wastes carry Pu as does dust
- half-life = 24,400 years

• **Low-level wastes:**

- wastes from a wide variety of sources
- usually placed in shallow landfills
- concern with leaching of elements

RADON GAS FROM SOILS

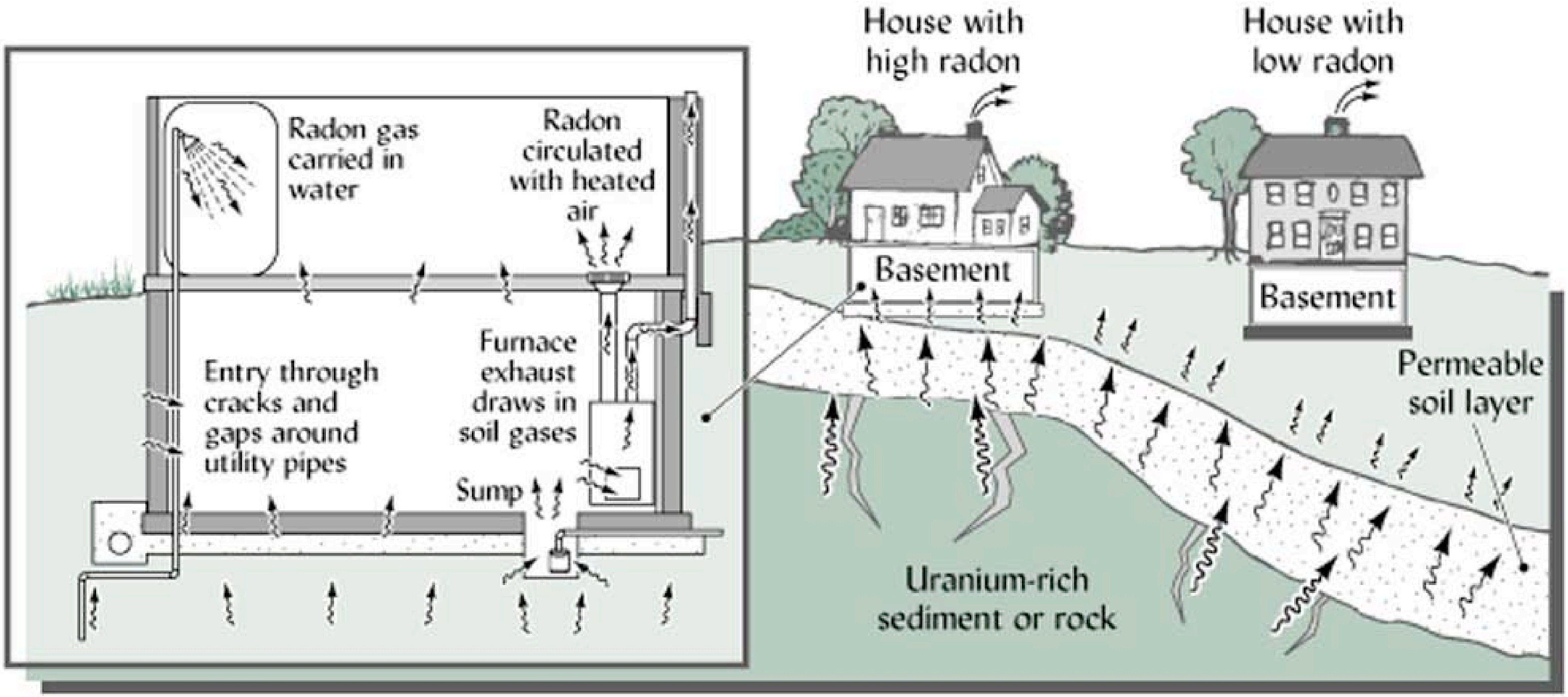
Health hazard:

- known to cause lung cancer
- deaths from Rn 10-50X more numerous than those from contaminants in drinking water
- Rn $\rightarrow$ Po isotopes; tend to sorb to dust particles which are inhaled; Po is α-emitter

Radon accumulation in buildings (Fig 18.32):

- $^{238}U \rightarrow Ra \rightarrow Rn$ - from rocks, soils, waters
- most problems where granites are near surface
- distance from source & soil permeability important
- diffusion greatest in coarse, dry soils
- Rn enters buildings through cracks, unsealed openings (utility pipes, etc.)
- accumulates in houses that are tightly sealed and where windows are rarely opened

RADON GAS FROM SOILS - 2



(Fig. 18.32)

RADON GAS FROM SOILS - 3

Radon testing and remediation:

- **Testing:**
  - first test uses a charcoal canister that sorbs Rn for specified period (3 days)
  - if positive for Rn, use alpha-track detector

- **Remediation:**
  - seal cracks, openings (for low concentrations)
  - may need to provide extra ventilation in house
  - may need to provide subslab ventilation by using perforated pipes