Lecture Note

Soil and Groundwater Pollution

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Ⅱ. Site Investigation, Evaluation, Remediation

1) Contamination Investigation - Source Analysis (HW, Ch.4)
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Ⅲ. Special Topic: Applied Ecological Engineering

1) Ecological Engineering (Ch.3-6)
2) Case Study: Ecological Restoration Examples

(Texts)
- EPS: Environmental and Pollution Science (2nd Ed), I.L.Pepper, C.P.Gerba, M.L.Brusseau, 2006, Academic Press
- HW: Hazardous Wastes-Sources, Pathways, Receptors (2nd Ed), R.J. Watts, 1998, John Wiley & Sons
- Ecological Engineering-Bridging Between Ecology and Civil Engineering, 2005, Hein Van Bohemian, Aeneas Technical Publishers

(Lecture 1)

EPS Ch 3. Physical-chemical characteristics of water

- Unique properties of water
  - polarity
  - universal solvent

- Gases in water
  - oxygen; DO
  - carbon dioxide <-> bicarbonate <-> carbonate (-> precipitates)

- Oxidation-reduction reaction
  - oxidation-reduction potential (ORP) or redox potential (1 volt = 1 *Eh*)
  - measures the tendency for a solution to either gain or lose electrons
  - higher (lower) ORP -> easily gain (lose) electrons
  - effect on bioavailability of metal ions (and nutrients)
    - . Fe(III)-phosphate <-> Fe(II) + phosphate
    - . Hg <-> methyl-Hg

- Water in the subsurface (groundwater): Supplement 1
  - hydraulic head, soil-water potential
  - Darcy's law
  - hydraulic conductivity (*K*)

(Lecture 2)

EPS Ch 2. Physical-chemical characteristics of soils and the subsurface

- Soil
  - weathered end product
  - soil-forming factors: parent material, climate, living organisms, topography, time
  - surface soil vs. subsurface soil
  - unsaturated zone (vadose zone, capillary fringe) vs. saturated zone
  - water movement; nonspontaneous vs. spontaneous
  - solid phase, gas phase, liquid phase
  - aggregation, structure

- Solid phase
  - 95-99% inorganic, 1-5% organic matter
  - soil texture; clay, silt, sand (soil textural triangle)
  - pore space; filled with gas, liquid
  - interaggregate pores vs. intraaggregate pores
  - cation exchange capacity (CEC)
  - soil pH
  - soil organic matter (SOM)

- Gas phase
  - N2 >>>> O2 >> CO2
  - soil respiration; aerobic vs. anaerobic
  - soil moisture; O2 availability

- Liquid phase
  - water; polar
  - field capacity (water-holding capacity)

- Basic physical properties
  - bulk density (ρ_b, dry soil mass/total volume, g/cm^{-3})
  - porosity (*n*, void volume/bulk volume, unitless)
    - . sand < silt < clay
    - . packing arrangement, grain size distribution
    - . when saturated soil, porosity = water content

- Soil water content
  - gravimetric water content; mass (θ_g)
  - volumetric water content; volume (θ_v)

- Soil temperature
  - temperature → reaction rate
  - surface; fluctuate
  - subsurface; relatively constant

(Lecture 3)

EPS Ch 5. Biotic Characteristics of the Environment

- Major groups of microbes; virus, bacteria, fungi, algae, protozoa
  - dominant culturable soil bacteria; Arthrobacter, Streptomyces, Pseeudomonas, Bacillus…

- Bacteria
  - 0.1-2 μm, single-celled, no nuclear membrane
  - genetic exchange; conjugation, transformation, transduction
  - abundant, diverse, ubiquitous, (e.g.) 10^{5-7} cells/ g-subsurface soil, 10^{9-10} cells/ g-surface soil
  - main removal mechanism of pollutants in soil

- Mode of nutrition (energy, carbon source)
  - autotrophic; chemoautotrophic, photoautotrophic
  - heterotrophic; chemoheterotropic, photoheterotrophic

- Types of electron acceptors
  - aerobic (O_2)
  - denitrifying (NO_3^-)
  - sulfate-reducing (SO_4^{2-})
  - anaerobic (CO_2)

- Ecological classification
  - *K*-selected organisms; under eutrophic env, (e.g.) rhizobacteria
  - *r*-selected organisms; under oligotrophic, rapid growth, (e.g.) pollutants-degrading bacteria

- Biological generation of energy; energy stored as ATP
  - photosynthesis; E needs to be provided (negative ΔG) by sunlight
  - respiration
    - aerobic heterotrophic respiration; negative ΔG, *Pseudomonas, Bacillus*…
    - aerobic autotrohphic respiration; negative ΔG, *Nitrosomonas, Nitrobacter…*
    - facultative anaerobic, heterotrophic/autotrophic respiration
    - anaerobic heterotrophic respiration
    - fermentation

- Soil as an environment for microbes
  - biotic stress;
    - competition for nutrients, water, growth factors…
    - inhibitory or toxic substances by other microbes (e.g.) antibiotics
    - predation
  - abiotic stress;
    - light
    - soil moisture, soil temp, pH, texture
    - soil carbon, nitrogen…
    - Soil redox potential; +800 mV ～ -300 mV (Table 5.5), *Eh*-pH diagram (Fig. 5.12)

- Activity and physiological state
  - viable and culturable (i.e., CFU, plate counting)
  - viable but unculturable

- *indigenous vs. introduced*
- *ecological niche*

(Lecture 4)

HW Ch 2. Common Hazardous Wastes: Nomenclature, Industrial Uses, Disposal Histories

1. Introduction to Organic Chemistry (p. 48)

: organic compounds; mainly C, H but O, N, P, S, and halogens (Cl, Br,..) also

1) Carbon bonding
   a) ionic bonding; donation of a valence electron from an electropositive atom to an electronegative atom (e.g., NaCl, $MgCl_2$,...)
   b) covalent bonding;
      - occurs when two atoms share valence electrons
      - usually N, O, C, S, or Si is involved (e.g., H_2O, NH_3, H_2S,...)
      - the bonds of organic compounds are covalent!

◎ Polarity, nucleophilic attack, and degradation (p. 51)

① polarity due to the differences in electronegativity between atoms

② unequal distribution of electron clouds --> partial charges --> polarity (e.g.) compare the electron clouds of H_2 and H_2O

③ chemical reaction:
- low electron density (i.e., electron poor region of a chemical) allows attack by nuclephiles (such as H_2O, OH^-), (e.g.) parathion

④ biological reaction:
- biological degradation rates are lowered by electron-poor areas of organic compounds, (e.g.) pentachlorophenol

2) Nomenclature of organic compounds (p. 51)

- a) aliphatic hydrocarbons; alkanes (radical forms; alkyl groups), alkenes (PCE, TCE..), alkynes
- b) aromatic hydrocarbons;
  - - monoaroatics (phenolics, BTEX,...)
  - - polyaromatics (PAHs,...)
- c) isomers; same chemical formulas but different structural configurations
  (formed from 4-carbon aliphatic compounds)
- d) IUPAC (International Union of Pure and Applied Chemists) nomenclaure vs. conventional name
  (e.g.) CH_2Cl_2; 1,2-dichloromethane, methylene chloride

◎ Aromatic compounds (p. 63)

① resonance structure (alternating single and double bonds between C atoms)
② π-bonds between aromatic compounds (stacking of aromatic rings possible!)
③ more stable than alkenes (e.g., benzene vs. cyclohexene)
④ substitution reaction for benzene and addtion reaction for cyclohexene

- e) Nomenclature of benzene derivatives (p. 64)
- f) Polycyclic Aromatic Hydrocarbons (PAHs, p. 68)
  ; incomplete combustion of organic compounds, heavier fractions of petroleum products, cigarette smoke, blackened barbecued food,...

2. Petroleum Products (p. 77)

1) UST (Underground Storage Tank) leakage
2) aliphatic and aromatic hydrocarbons
3) BTEX (Benzene, Toluene, Ethylbenzene, Xylenes)
4) TPHs (Total Petroleum Hydrocarbons)
5) Characteristics of petroleum products (Table 2.11, Table 2.12)
6) Gasoline additives;
    - Pb (leaded vs. unleaded)
    - oxygenates (e.g., methyl *tert*-butyl ether, MTBE)

3. Nonhalogenated Solvents (p. 81)

1) Hydrocarbons
2) Ketones
3) Alcohols and Esters

4. Halogenated Solvents (p. 85)

: an important class of environmental contaminants
(volatile, mobile, dense, moderate soluble, less degradable)

- halogenation of hydrocarbons --> lower flammability, higher density and viscosity --> improved solvent properties (for degreasing and cleaning)
- <u>methane derivatives</u>; methylene chloride (dichloromethane), chloroform (trichloromethane), carbon tetrachloride (tetrachloromethane)
- <u>derivatives of ethane, ethene (ethylene)</u>; 1,1,1-trichloroethane (TCA), trichloroethylene (trichloroethene, TCE), perchloroethylene (tetrachloroethene, PCE)

5. Pesticides (p. 90)

1) Insecticides
   a) organochlorine insecticides;
      - highly lipophilic, recalcitrant, bioconcentrated, chronic toxicity
      - most banned nowadays but present in the environment as residues
        (e.g.) DDT, methoxychlor, lindane, aldrin, dieldrin,...
   b) organophosphorus esters;
      - less persistent (days to weeks), less adverse effects, more degradation, but, higher acute toxicity than organochlorine insecticides, (e.g.) parathion, malathion,...
   c) carbamate esters;
      - widely used along with organophosphorus esters
      - moderately labile in the environment, low acute toxicity, (e.g.) carbaryl, carbofuran, aldicarb,...

2) Herbicides (generally less persistent and chronically toxic than organochlorines)
   a) acid amides; alachlor, propanil,,...
   b) aliphatics; glyphosate, methyl bromide,...
   c) phenoxy herbicides; 2,4-D (2,4-dichlorophenoxy acetic acid), 2,4,5-T (2,4,5-trichlorophenoxy acetic acids)
   d) substrate ureas; diuron, linuron (persist in soils for up to a year)
   e) triazines; atrazine (strongly sorb but mobile also, found in aquifers)

3) Fungicides
   a) pentachlorophenol (PCP); wood preservative and insecticide also
   b) ethylene dibromide (1,2-dibromoethane, EDB); soil fumigants

6. Explosives (p. 104)

: aliphatic or aromatic structure with substituted nitro (-NO_2) groups
- aliphatic nitrate esters; nitroglycerin
- nitramines; RDX (cyclotrimethylenetrinitramine), HMX (cyclotetramethylenetetranitramine)
- nitroaromatics; TNT (2,4,6-trinitrotoluene), picric acid (2,4,6-trinitrophenol)

7. Industrial Intermediates (p. 109)

- phthalene esters; plasticizers or softners (e.g., phthalic acid)
- chlorobenzenes, chlorophenols;
  . 2,4-dichlorophenol in the manufacture of 2,4-D
  . 2,4,5-trichlorophenol in the manufacture of 2,4,5-T
- anilines; in the synthesis of inks, dyes, frugs, photographic developers
- hexachlorocyclopentadiene; in the synthesis of aldrin, dieldrin, chlordane,,,,

8. Polychlorinated Biphenyls (p. 114)

- heat-stable nonflammable oils once used extensively as transformer and hydraulic fluids
  (--> high persistence and toxicity)
- banned in 1979, but still present in the environment
- biphenyl molecule with chlorine substitution up to 10 positions
- congeners; 207 products possible, (e.g.) Aroclor 1221, Aroclor 1232,...

9. Polychlorinated dibenzodioxins and dibenzofurans (PCDDs, PCDFs; p. 116)

- not intentionally manufactured chemicals
- trace impurities formed during the manufacture, chlorination or combustion of other organic compounds
- collectively called "(chlorinated) dioxins", derivatives of dibenzo-*p*-dioxin
- 75 possible congeners

◎ Generation of dioxins and their toxicities

① In the course of manufacturing 2,4,5-T (i.e., trichlorophenol + chloroacetic acid), two molecules of trichlorophenols may dimerize to form 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD)

② Chlorinated dioxins are produced during (incomplete) combustion at low-to-moderate temperatures, even from innocuous materials such as firewood (like PAHs)

③ 2,3,7,8-TCDD is the most toxic (--> Toxic Equivalent Factor, TEF 1.0)

④ Other dioxins' toxicities are expressed based on a reference TEF of 1.0

10. Metals and Inorganic Nonmetals (p. 119)

- semantic definitions of heavy metals;
  i) elements with atomic numbers greater than iron, ii) metals with densities greater than 5.0 g/cm^3
- what about Al (atomic number 13)?; regarded as a heavy metal
- another definition; metals cause adverse biological (=toxic) effects

1) Arsenic (As)
  a) present as anionic forms in solution
  b) arsenite AsO_3^- (As^{3+}); under reduced conditions, most toxic
  c) arsenate AsO_4^{3-} (As^{5+}); under aerobic conditions, less toxic
  d) extensively used in agriculture (weed control, insecticidal ingredients,...)

2) Cadmium (Cd)
  a) always found as Cd^{2+}
  b) highly toxic and accumulative

3) Chromium (Cr)
  a) highly toxic, stable, soluble; Cr^{6+}(chromate CrO_4^{2-}, dichromate $Cr_2O_7^{2-}$)
  b) insoluble form in water; Cr^{3+} (low toxicity)

4) Lead (Pb)
  a) low water solubility and strong tendency to sorb and exchange on solids
  b) less mobile in the environment

5) Nickel (Ni)

6) Mercury (Hg)
  a) three forms possible; elemental, inorganic, organic
  b) Hg^0 present as a liquid at room temperature
  c) Hg^0 for porosity measurement (e.g., Mercury porosimeter)
  d) bioconcentration (in fish); methyl mercury (CH_3Hg^+)
  e) volatilization and global recycling; dimethyl mercury (CH_3HgCH_3)
  f) $HgCl_2$; biocide (used to sterilize environmental samples)

7) Cyanides (-CN)
  a) inorganic nonmetal anions
  b) HCN; highly toxic, acute poison

8) Asbestos
  a) a group of six mineral fibers (hydrated magnesium silicates)
  b) nonflammable, strong, resistant to acids
  c) indoor air pollution
  d) toxic only through inhalation (not from dermal contact, ingestion,..)
    --> "route of exposure" is important!!!

11. Nuclear Wastes (p. 127)

(Lecture 5)

HW Ch 3. Common Hazardous Wastes: Properties and Classification

1. Common Concentration Units (p. 155)

1) SI vs Non-SI units (SI; International System of Units)
2) conversion of ppm to concentration

2. Water Solubility (p. 160)

1) definition; "maximum (saturation) concentration of a substance that will dissolve in water in a given temperature"
2) soluble vs. insoluble (filtration through 0.45-μm pore sized membrane)
3) polar (hydrophilic) vs. nonpolar (hydrophobic); Table 3.5
    (e.g.) water vs. hexane
4) controls the environmental fate of waste chemicals
    a) inversely proportional to sorptivity, bioaccumulation, volatilization from aqueous solutions
    b) influence biodegradation, photolysis, chemical oxidation,...
5) determined by intermolecular attractive forces between solute-solvent molecules
    a) van der Waals force
    b) hydrogen bonding (mainly with -OH, $-NH_2$ groups)
    c) dipole-dipole interaction (by electronegativity difference)
6) related to the size and structure of a chemical
    a) functional groups may or may not affect
    b) molecular volume (halogens increase m.v. -> decrease water solubility)
    c) Table 3.1

7) water solubilities of weak organic acids (bases)
  - a) basic (ionized) form is more soluble than acidic (unionized) form
  - b) [ionized forms] $\propto$ water solubility
  - c) pH vs. pKa (pH where [unionized forms] = [ionized forms])
    - pH < pKa ; protonated (acidic, unionized form)
    - pH > pKa ; deprotonated (basic, ionized form)
  - d) solubility change depending on pH
  - e) *Handerson-Hasselbalch* equation (Fig. 3.1)
    - calculates the degree of acidic dissociation at a given pH
  - f) fraction of unionized acid (α);
    - **$\alpha = (1 +)^{-1}$** (Ka = ; acid dissociation constant)
    - used to correct transport models; ionized forms are miscible in water -> no retardation (p. 281)

8) acidity of chlorophenols with higher chlorine substitution (Table 3.2)
  - a) Cl- is a highly electronegative element
  - b) more Cl- on the ring -> proton(s) more easily released -> higher acidity

3. Density and Specific Gravity (p. 167)

- density; ratio of mass to volume (g/mL, kg/m^3)
- specific gravity; a compound's density to that of water (1.0 g/mL at 4°C)
- (aliphatic) hydrocarbons are lighter than water
- substitution of a chlorine atom on a hydrocarbon increases its density (density; H < C < Cl)
- influence contaminants' fate and remediation technology selection (esp. in groundwater); Table 3.6
- metals are more dense than water

4. Light and Dense Nonaqueous Phase Liquids (p. 170)

; NAPL(s) as a continuous source in the subsurface system

1) LNAPL (Light Nonaqueous Phase Liquid) / Fig. 3.2 (a)
   a) floats on groundwater surface → easily detected
   b) aliphatic hydrocarbons, BTEX, nonhalogenated solvents,...

2) DNAPL (Dense Nonaqueous Phase Liquid) / Fig. 3.2 (b), Example 3.4
   a) sinks into the bottom of subsurface system (fractures, pores,...)
   b) form pools, lenses
   c) halogenated solvents,...

3) dissolution
   a) transfer of a compound from its insoluble phase into the water
   b) generally rate-limiting step in degradation (remediation) of a contaminant
   c) rate of dissolution [(mg/L)/min] = $K \cdot (C_s - C)$
      K (min^{-1}); mass transfer coefficient (from NAPL to water phase)
      C_s (mg/L); contaminant water solubility
      C (mg/L); contaminant concentration at a site

4) effective solubility
   a) solubility of the mixtures of NAPLs
   b) usually less than the water solubility of a single compound
   c) effective solubility of compound *i* (mg/L)
      $S_i^e = X_i S_i \gamma_i$
      X_i = mole fraction of compound *i* in the NAPL mixture
      S_i = water solubility of compound *i* found in literatures
      γ_i = correction factor that normalizes solubility based on field conditions and water chemistry

5. Flammability Limits (p. 177)

(Lecture 6)

EPS Ch 6. Physical Processes Affecting Contaminant Transport and Fate

- Contaminant transport and fate in the environment

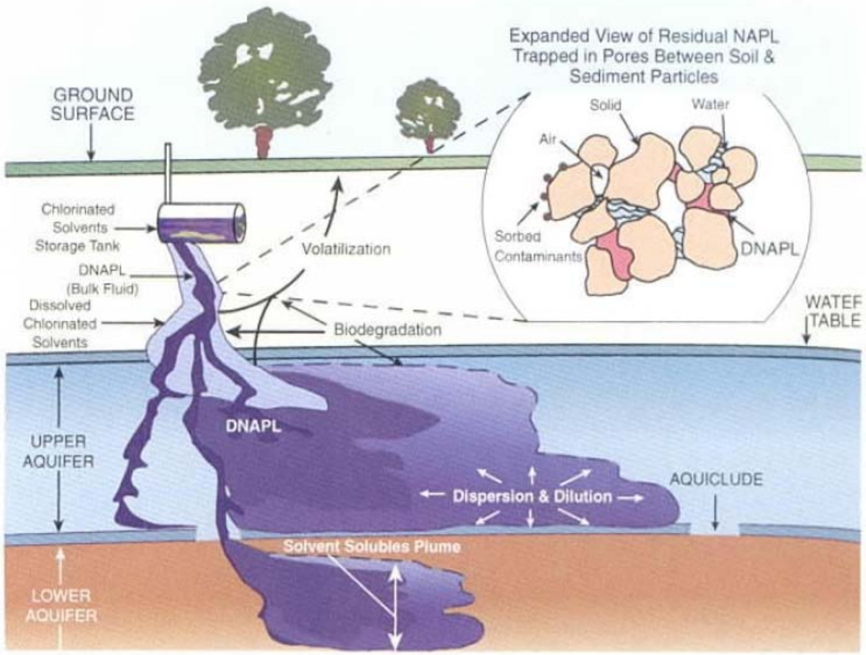


Figure 6.1 Disposition of organic liquid spilled into the subsurface. Schematic of chlorinated solvent pollution: dense nonaqueous phase liquids migrate downward in the subsurface, and serve as a source of contamination for groundwater. Also shown are natural attenuation processes. *DNAPL*, Dense nonaqueous phase liquid; *NAPL*, nonaqueous phase liquid. From U.S. EPA, 1999.

"The health risk posed by a contaminant to humans is a function of ***its pollution potential*** *as well as its toxicity"*

✓ advection

✓ dispersion
  - mechanical dispersion
  - molecular diffusion

✓ mass transfer
  - volatilization/evaporation
  - sorption
  - dissolution

✓ transformation
  - biological
  - chemical

- Dispersion

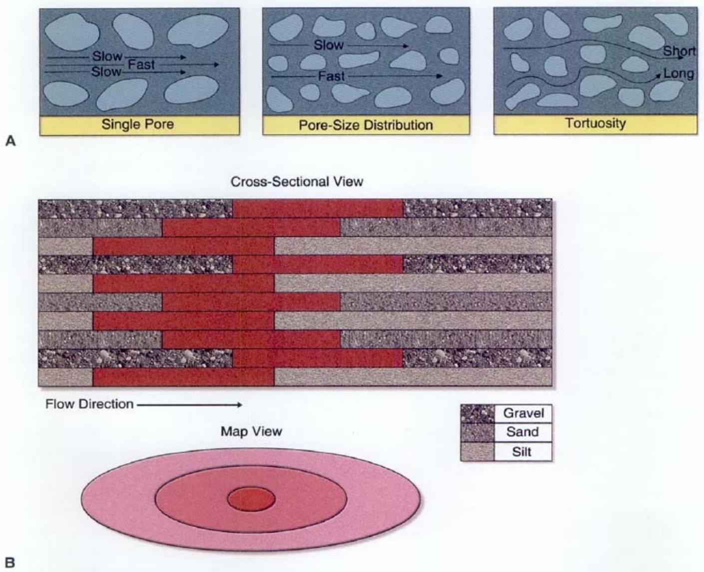


Figure 6.3 Processes causing dispersion (spreading of a pulse or plume) as a result of non-uniform fluid flow: (A) pore scale; (B) field scale.

- Breakthrough curves

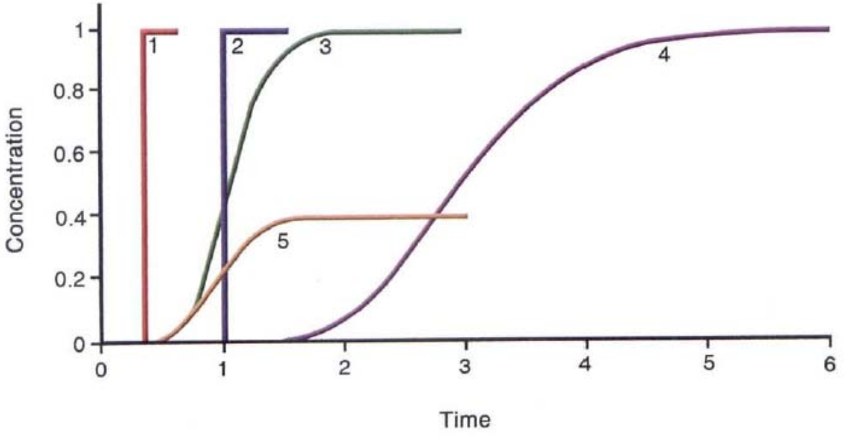


Figure 6.6 Simple examples of breakthrough curves as affected by the four transport and fate processes. Case 1: Advection (larger fluid velocity, *v*); Case 2: Advection (smaller *v*); Case 3: Advection (smaller *v*) and Dispersion; Case 4: Advection (smaller *v*), Dispersion, and Retardation; Case 5: Advection (smaller *v*), Dispersion, and Transformation. The input concentration is equal to 1 concentration unit.

- Spatial distribution of contaminant plume

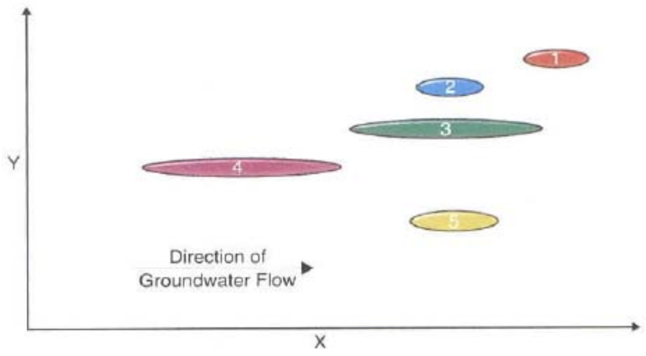


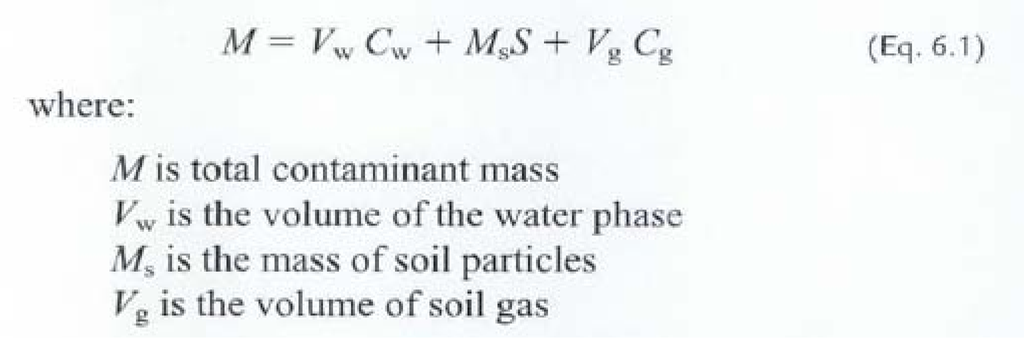
Figure 6.5 Simple examples of spatial distributions of contaminant plumes as affected by the four transport and fate processes. Case 1: Advection (larger fluid velocity, *v*); Case 2: Advection (small *v*); Case 3: Advection (smaller *v*) and Dispersion; Case 4: Advection (smaller *v*), Dispersion, and Retardation; Case 5: Advection (smaller *v*), Dispersion, and Transformation. The plumes are drawn with a single contour representing the detectable concentration. The plumes all originated at the $x = 0$ plane.

✓ Advection-dispersion model

$$R\left(\frac{\partial C}{\partial t}\right) = -v_i\left(\frac{\partial C}{\partial t}\right) + D_i\left(\frac{\partial^2 C}{\partial i^2}\right)$$

✓ What about **“transformation term”** is incorporated???
→ advection-dispersion-reaction equation (ADRE)

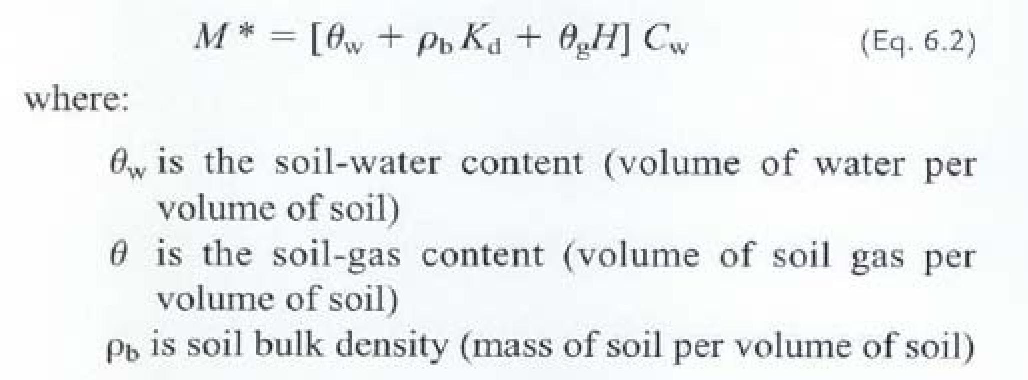
- Estimating phase distributions of contaminants



$$M = V_w C_w + M_s S + V_g C_g \qquad \text{(Eq. 6.1)}$$

where:

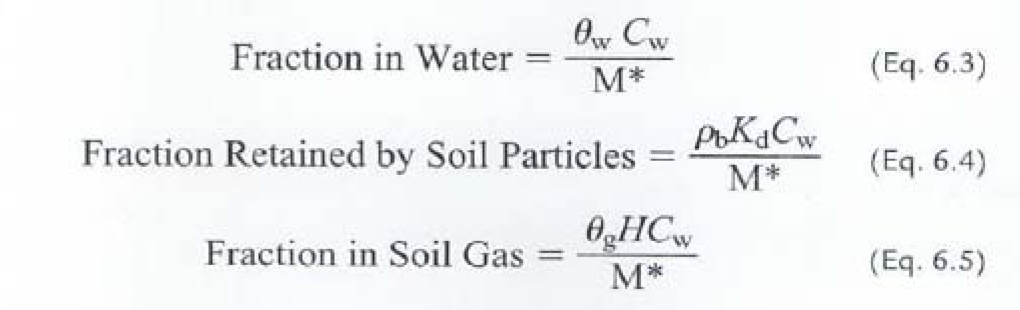
M is total contaminant mass
V_w is the volume of the water phase
M_s is the mass of soil particles
V_g is the volume of soil gas



$$M^* = [\theta_w + \rho_b K_d + \theta_g H]\, C_w \qquad \text{(Eq. 6.2)}$$

where:

θ_w is the soil-water content (volume of water per volume of soil)
θ is the soil-gas content (volume of soil gas per volume of soil)
ρ_b is soil bulk density (mass of soil per volume of soil)

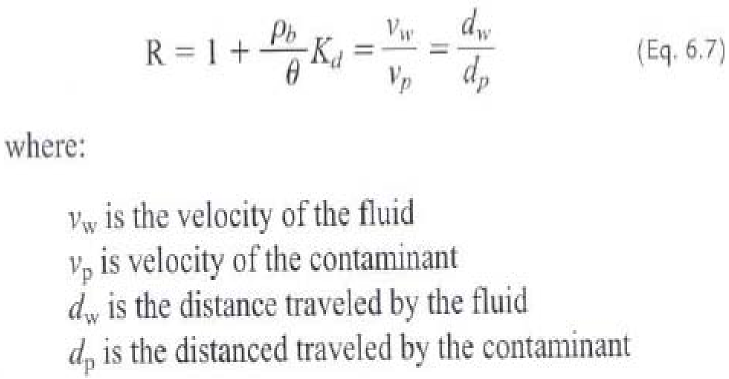


$$\text{Fraction in Water} = \frac{\theta_w C_w}{M^*} \qquad \text{(Eq. 6.3)}$$

$$\text{Fraction Retained by Soil Particles} = \frac{\rho_b K_d C_w}{M^*} \qquad \text{(Eq. 6.4)}$$

$$\text{Fraction in Soil Gas} = \frac{\theta_g H C_w}{M^*} \qquad \text{(Eq. 6.5)}$$

- Retardation factor



$$R = 1 + \frac{\rho_b}{\theta} K_d = \frac{v_w}{v_p} = \frac{d_w}{d_p} \qquad \text{(Eq. 6.7)}$$

where:

v_w is the velocity of the fluid
v_p is velocity of the contaminant
d_w is the distance traveled by the fluid
d_p is the distanced traveled by the contaminant

$$R = \frac{\text{groundwater velocity}}{\text{contaminant velocity}}$$

$$\frac{\text{dissolved conc + adsorbed conc}}{\text{dissolved conc}}$$

(Lecture 7)

HW Ch 8. Contaminant Release and Transport from the Source

- Contaminants distributions are commonly quantified using sampling and analysis schemes because monitoring data are more reliable and thus preferred.
- However, in some cases, values obtained from prediction models are still useful.

1. The Controlling Processes in Contaminant Release and Transport: Sorption, Volatilization, Transformation (p. 405)

a) atmospheric and subsurface transport (Fig. 8.1)

- major contaminants' trnasport through the subsurface and atmosphere
- once released from the source, contaminants experience sorption, volatilization, and transformation

b) conceptual pathway analysis (Example 8.1)

2. Mass Transfer of Contaminants in the Atmospheric and the Subsurface (p. 408)

1) Mass balance

a) expressions

▶ change in storage of mass = mass transported IN - mass transported OUT
+mass PRODUCED by sources - mass ELIMINATED by sinks

▶ rate of change in storage of mass = mass transport rate in - mass transport rate out
+mass production rate by sources - mass elimination rate by sinks

▶ rate of mass accumulation within the system boundary
= rate of mass flow into the system - rate of mass flow out of the system
-/+rate of reaction within the system (* rate = mass per time [M/T])

☞ *If storage does not change with time the left-hand sides are zero → steady state*

b) described by a general mass flux vector

$$\frac{\partial m}{\partial t} = \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}$$

J; the mass flux vector in the x, y, or z direction
m; contaminant mass per unit volume
t; time

c) differences between atmospheric and subsurface definitions of mass

- volume of air; total volume of the sample
- in the subsurface; "porosity" and "retardation" concepts included

$m = C$ (atmosphere)
$m = n \bullet R \bullet C$ (subsurface)

2) Two important phenomena of movement

a) advection (i.e., wind; pore-water velocity)
b) dispersion
c) flux $J = J_{adv} + J_{disp}$

3) Advective flux

a) mainly resulting from bulk, large scale movement of a medium (e.g.) wind blows, water flows,....

b) so, transported at the same velocity as the fluid

- macroscale view; center of mass of chemical moves by advection
- microscale view; Fickian transport occurs at the same time

c) convection; often vertical advection (but, considered almost a similar term)

d) flux density (*J*)

- mass of chemical transported across an imaginary surface of unit area per unit of time

$$\boldsymbol{J = C \cdot V}$$

J; advective flux (mg/m^2-sec) [M/L^{2}T] / C; contaminant conc. (mg/m^3) [M/L^3]
V; fluid velocity (m/sec) [L/T]

- in groundwater, V is pore-water velocity

$$\boldsymbol{J = C \cdot (n v_p)}$$

n; porosity (i.e., n_e) / v_p; seepage (pore-water) velocity (m/sec)

4) Dispersive flux

a) "all of the mass transfer exclusive of advection"

b) Turbulent diffusion ("eddy diffusion")

- resulting from random mixing of air or water by eddies
- carries mass in the direction of decreasing chemical concentration (e.g.) dye blob injected into a river
    - important in surface water and air **(not considered in the subsurface)**
    - use Fick's first law to describe

$$J = -nD \cdot \left(\frac{\partial C}{\partial x}\right)$$

J [M/L^{2}T]; dispersive flux in the x direction
n; porosity
D; turbulent diffusion coefficient
C [M/L^3]; chemical concentration
x [L]; distance over which a concentration change is considered

c) (mechanical) dispersion (hydraulic dispersion)

- fluctuations in the velocity field at scales smaller than advection
- groundwater flow;
  - . no eddies present due to its low velocity
  - . but still random detours exist, causing mixing chemicals
- transport of a chemical from regions of higher to lower concentration
- use Fick's first law to describe

$$J = -nD_{\mathrm{mech}} \cdot \left(\frac{\partial C}{\partial x}\right)$$

J $[M/L^2T]$; dispersive flux in the x direction
n; porosity
D_{mech}; mechanical dispersion coefficient
C $[M/L^3]$; chemical concentration
x [L]; distance over which a concentration change is considered

- related to the <u>tortuous path</u> of water through the subsurface solids
- tortuosity of flow paths and contaminant concentration result in the longitudinal mixing of contaminants

d) molecular diffusion

- random movement of chemicals due to local concentration gradient
- lower flux density compared to other Fickian transport processes
- use Fick's first law to describe

$$J = -nD_{\mathrm{mole}} \cdot \left(\frac{\partial C}{\partial x}\right)$$

J $[M/L^2T]$; dispersive flux in the x direction
n; porosity
D; molecular diffusion coefficient
C $[M/L^3]$; chemical concentration
x [L]; distance over which a concentration change is considered

- not related to advective, dispersive, or turbulent motion but dependent on contaminants' molecular properties (primarily, size) and temperature

e) hydrodynamic dispersion
- the spreading of a tracer beyond the region expected to the average flow alone
- the macroscopic outcome of the actual movements of individual tracer particles through the pores and the various physico-chemical phenomena that take place within the pores
    - $\boldsymbol{J_{disp} = J_{mech} + J_{mole}}$
    - $\mathbf{D = D_{mech} + D_{mole}}$

※ Transport in total: $\boldsymbol{J = J_{adv} + J_{dis}}$

※ One-dimensional situation is considered, flow is **anisotrophic**
- flow direction vs. perpendicular to flow,
- homogeneous medium vs. heterogeneous medium,
- time

5) The advection-dispersion equation
- for the subsurface transport; characteristics of the medium

$$\mathrm{R}\left(\frac{\partial C}{\partial t}\right) = -v_i\left(\frac{\partial C}{\partial t}\right) + \mathrm{D}_i\left(\frac{\partial^2 C}{\partial i^2}\right)$$

- analytical methods
- numerical methods

3. Atmospheric Transport Following Volatilization Releases (p. 413)

4. Subsurface Transport of Contaminants (p. 421)

1) Subsurface transport and exposure
  a) migration through the unsaturated zone to groundwater
  b) exposure routes
    - subsurface contamination; volatilization, leaching to groundwater
    - groundwater; drinking water wells, other uses

2) Nature of the subsurface environment (Fig. 8.12)
  a) vadose zone
    - subsurface region where the pore-water pressure is less than atmospheric pressure
    - pore-water pressure increases linearly with depth
    - water present as a thin film on solid surfaces
    - consists of solid particles, water (i.e,. volumetric water content) and air (i.e., empty pore space)
    - unsaurated zone;
  b) saturated zone
    - boundary of water table; pore-water pressure = atmospheric pressure
    - below the water table where the pore spaces are filled with water
    - pore-water pressure is greater than atmospheric, and increases linearly with depth
  c) more terms
    - capillary fringe; an area where the upward movement of water from the saturated zone due to surface tension and capillary forces
    - aquifer; a saturated permeable geologic unit that can transmit sufficient water under ordinary hydraulic gradients
    - aquitard; the strata that are less permeable than an aquifer
    - <u>unconfined aquifer;</u>
    - <u>confined aquifer;</u>

d) porous and heterogeneous; most important subsurface properties!!!

e) Darcy's Law
  - an empirical mathematical description between the flow rate of a fluid through a porous medium and the head gradient (basis for advection in groundwater)

f) hydraulic conductivity
  - a parameter that describes the ease with which a fluid passes through porous media
  - a function of a fluid and a medium (Table 8.2)

g) pore-water velocity (seepage velocity)
  - the velocity that accounts for the cross-sectional area / related to porosity of a medium

4.1. Development and use of groundwater transport equations

a) factors influencing subsurface transport (rates) of contaminants
  - media; characteristics of subsurface
  - fluid; flow (rate) of groundwater
  - interactions; sorption, transformation, volatilization,...

b) assumptions
  - the media are characterized by constant density and viscosity
  - the media are isotrophic, the flow is incompressible, and the system is saturated

c) many models are available
  - one-, two-, three-dimensional flow
  - pulse contaminant input and continuous contaminant input
  - presence or absence of transformation reactions
  - BUT, limited by estimation of parameters such as dispersion coefficient, transformation rate,...

d) one-dimensional advection-dispersion equations
  - simple models relatively accurate for simple systems
    (e.g.) soil columns, landfill leachate migration,...
  - a pulse input with or without transformation
  - a continuous input with or without transformation

1) Pulse model

- a) describes a pulse input of contamination such as hazardous materials spill
- b) derived with zero background concentration at the beginning (x = 0)
- c) a pulse input model without transformation;

  at a distance x downgradient and time *t*

$$C(x,t) = \frac{M}{\sqrt{4\pi D'_x t}} \bullet \exp\left[-\frac{(x - v'_x t)^2}{4D'_x t}\right]$$

M; the mass spilled per cross-sectional area (g/m^2)
D'_x; D/R (m^2/day)
D_x; dispersion coefficient in the x direction
x; distance from the source (from the point of spill)
v'_x; v/R (m/day)
v_x; pore-water velocity in the x direction
R; retardation factor

- d) a pulse input equation with transformation

$$C(x,t) = \frac{M}{\sqrt{4\pi D'_x t}} \bullet \exp\left[-\frac{(x - v'_x t)^2}{4D'_x t}\right] \bullet e^{-k't}$$

k'; k/R (day^{-1})
k; first-order transformation rate constant (day^{-1})

- e) estimation of downgradient concentration from a source with transformation (Example 8.4)

2) Plume model

a) describes a continuous input from a source (e.g., landfill)

b) a plume input equation without transformation

$$C(x,t) = \frac{C_0}{2}\left[\mathrm{erfc}\left(\frac{x - v_x' t}{2\sqrt{D_x' t}}\right) - \exp\left(\frac{v_x'}{D_x'}\right)\cdot\mathrm{erfc}\left(\frac{x + v_x' t}{2D_x' t}\right)\right]$$

C(x,t); contaminant conc. at point x and time t (mg/L)
erfc; the complementary error function

under most conditions, the right-hand term becomes negligible,

$$C(x,t) = \frac{C_0}{2}\left[\mathrm{erfc}\left(\frac{x - v_x' t}{2\sqrt{D_x' t}}\right)\right]$$

c) estimation of downgradient conc from a surface impoundment without transformation (Example 8.5)

3) Advection-Dispersion-Reaction Equation (ADRE)

a) from the advection-dispersion equation

$$R\left(\frac{\partial C}{\partial t}\right) = -v_i\left(\frac{\partial C}{\partial t}\right) + D_i\left(\frac{\partial^2 C}{\partial i^2}\right),$$

ADRE can be derived to account for transformation through the addition of a new term for first-order degradation (at a distance x and time *t*)

$$\frac{\partial C}{\partial t} = \frac{D}{R}\left(\frac{\partial^2 C}{\partial x^2}\right) - \frac{v}{R}\left(\frac{\partial C}{\partial x}\right) - \frac{k}{R}C$$

C; contaminant conc. in the aqueous phase (mg/L)
R; retardation factor (1+•K_d)
D; groundwater dispersion coefficient (m^2/day)
v; pore-water velocity (m/day)
k; first-order degradation rate constant (day^{-1})

b) effect of retardation on contaminant profile (Fig. 8.13)
c) effect of transformation on contaminant profile (Fig. 8.14)
d) an analytical solution to the ADRE equation (Eq. 8.35, p. 431)
- one-dimensional contaminant transport with transformation (Example 8.6)
  - → used to estimate the time required for a relative contaminant concentration to reach a distance downgradient
- development of a contaminant profile in groundwater (Example 8.7)
  - → used to estimate a contaminant conc. profile as a function of time at a set distance (or as a function of distance at a set time)

4.2. Contaminant Transport in the Vadose Zone

a) vadose zone
- may be less than a meter to hundreds of meters deep
- higher organic matter, more metal oxides, more microbial activity

b) contaminants can move in the vadose zone
- as a solute in the water phase
- as a separate, immiscible NAPL phase
- as a gas resulting from volatilization

c) percolation rate
- increases as a function of porosity
- ranges from cm/h to cm/yr (*recall infiltration rate!!!*)

(Lecture 8)

EPS Ch 7. Chemical Processes Affecting Contaminant Transport and Fate

- Basic properties of inorganic contaminants

1) Speciation
   - pH, redox status
   - metal solubility
   - surface charge of minerals
   - adsorption(<-> desorption)
   - precipitation(<-> dissolution)

2) Aqueous phase activity and concentration
   - effective conc (or activity) ≠ concentration
   - activity coefficient (γ_i)
     . approach 1 only in a very dilute solution
   - Ionic strength (I)
   - activity coefficient

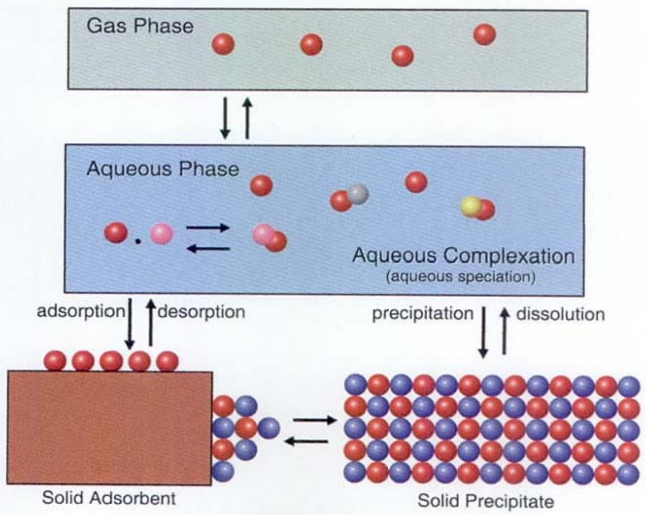


Figure 7.1 Disposition of inorganic contaminants in the environment is controlled by aqueous-phase complexation reactions, precipitation-dissolution reactions, and sorption-desorption reactions.

$$I = \tfrac{1}{2} \textstyle\sum_i [i]\, Z_i^2 \qquad \text{(Eq. 7.2)}$$

$$\log \gamma_i = -0.512 Z_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right] \qquad \text{(Eq. 7.4)}$$

● Ion hydration and hydrolysis

1) Ion hydration
  - ions dissolved → hydrated
  - ionic potential (Z/r)
  - small ionic potential → hydrated cations,
  - high ionic potential → hydrolysis → insoluble oxides(hydroxides), soluble oxyanions

2) Ion hydrolysis
  - breaking of O-H bonds in water molecules that are attached to the ions
  - proton dissociation
  - depends on pH

$$\mathrm{Pb(H_2O)_6}^{2+}\ (aq) \leftrightarrow \mathrm{PbOH(H_2O)_5}^{+}\ (aq) + \mathrm{H}^{+}\ (aq) \quad \text{(Eq. 7.5a)}$$

$$\mathrm{Pb}^{2+}\ (aq) + \mathrm{H_2O}\ (l) \leftrightarrow \mathrm{PbOH}^{+}\ (aq) + \mathrm{H}^{+}\ (aq) \quad \text{(Eq. 7.5b)}$$

$$\mathrm{PbOH}^{+}\ (aq) + \mathrm{H_2O}\ (l) \leftrightarrow \underline{\mathrm{Pb(OH)_2}^{0}\ (aq)} + \mathrm{H}^{+}\ (aq)$$
$$K_{h2} = 10^{-9.4} \quad \text{(Eq. 7.7)}$$

→ lead hydroxide (insoluble) at high pH
→ . precipitation → limited transport
  . low bioavailability → low risk

- Aqueous phase complexation reactions

  - metal-ligand complex
    - . cation; central metal group
    - . coordinating anion; ligand

  - stability constant (K_{stab})

$$Hg^{2+}\ (aq) + Cl^{-}\ (aq) \leftrightarrow HgCl^{+}\ (aq)$$

$$K_{\mathrm{stab}} = 10^{6.7} \quad \text{(Eq. 7.10)}$$

    - . mobility; $HgCl^{+} > Hg^{2+}$

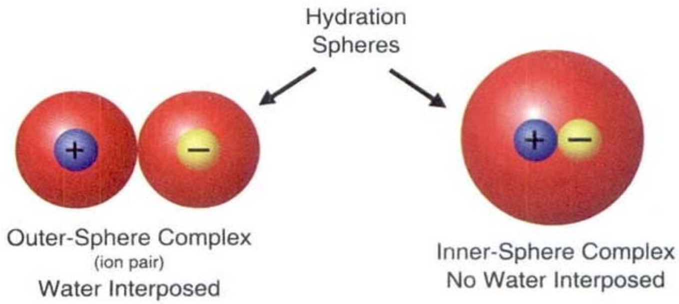


Figure 7.4 Aqueous phase complexation of inorganic ions can result in the formation of outer-sphere or inner-sphere complexes.

- Precipitation-dissolution reactions

$$Cr(OH)_3\ (s) + 3\ H^{+}\ (aq) \leftrightarrow Cr^{3+}\ (aq) + 3\ H_2O(l) \quad \text{(Eq. 7.11a)}$$

$$K_{dis} = \frac{(Cr^{3+})(H_2O)^3}{(Cr(OH)_3)(H^{+})^3} = 10^{12} \quad \text{(Eq. 7.11b)}$$

$$K_{so} = \frac{(Cr^{3+})}{(H^{+})^3} = 10^{12} \quad \text{(Eq. 7.11c)}$$

→ solubility product constant (K_{sp})

● Basic properties of organic contaminants

1) Phase transfer

2) Dissolution
- "likes dissolves likes"
- miscibility with water

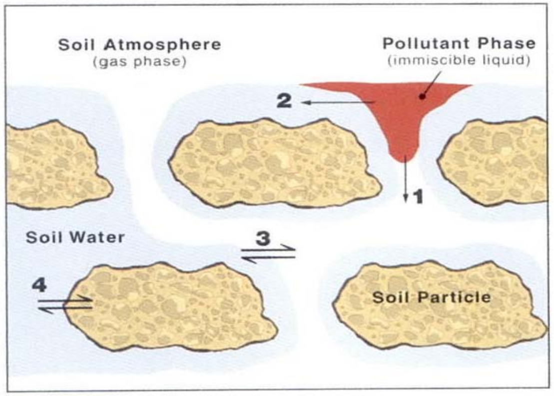


Figure 7.5 Phase transfer of pure pollutant with water and air phases: (1) evaporation, (2) solubilization, (3) volatilization, (4) sorption. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

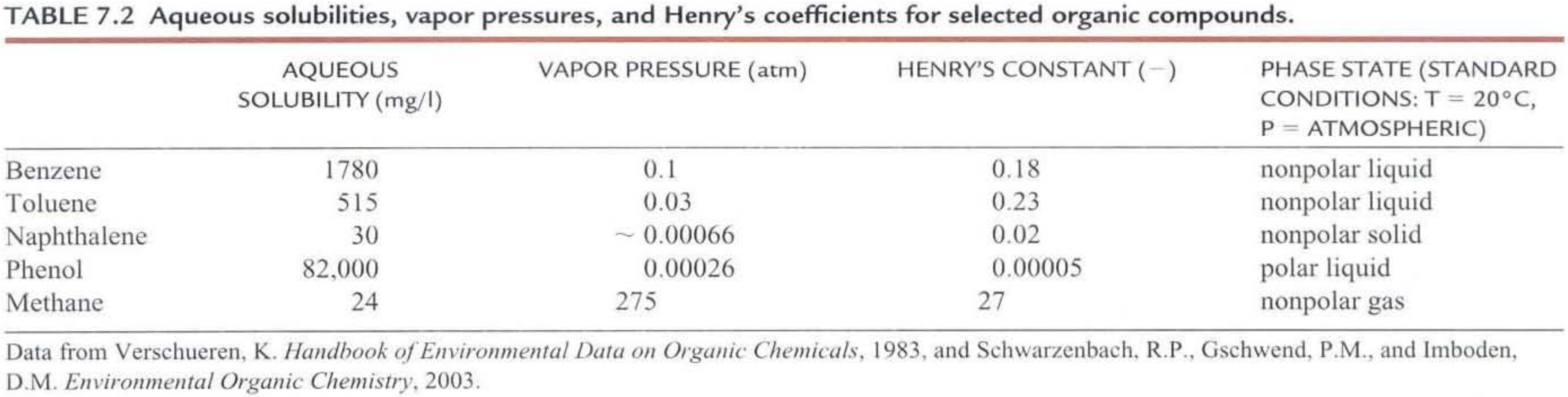


TABLE 7.2 Aqueous solubilities, vapor pressures, and Henry's coefficients for selected organic compounds.

	AQUEOUS SOLUBILITY (mg/l)	VAPOR PRESSURE (atm)	HENRY'S CONSTANT (–)	PHASE STATE (STANDARD CONDITIONS: T = 20°C, P = ATMOSPHERIC)
Benzene	1780	0.1	0.18	nonpolar liquid
Toluene	515	0.03	0.23	nonpolar liquid
Naphthalene	30	~ 0.00066	0.02	nonpolar solid
Phenol	82,000	0.00026	0.00005	polar liquid
Methane	24	275	27	nonpolar gas

Data from Verschueren, K. *Handbook of Environmental Data on Organic Chemicals*, 1983, and Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M. *Environmental Organic Chemistry*, 2003.

3) Evaporation
- transfer from the pure liquid (or solid) to the gas phase
- vapor pressure
  - . an index of the degree to which a compound will evaporate
  - . a measure of "solubility" of a compound in air
- governed by chemical-chemical interactions, temperature

● Volatilization

- transfer of contaminant molecules between water and gas phases
- Henry's law; $C_g = H \cdot C_w$ (at equilibrium)

● Multiple-component organic phase

- NAPL
- transfer of individual components of a multiple component into water; Raoult's law; $C^i_w = X^i S^i_w$

● Sorption

1) Inorganics
  - surface complex
  - cation exchange capacity (CEC) – exchangeable
  - adsorption mainly on clay minerals (as well as soil organic mater)
  - PZC (point of zero charge)
    . the suspension pH at which a surface has a net charge of zero

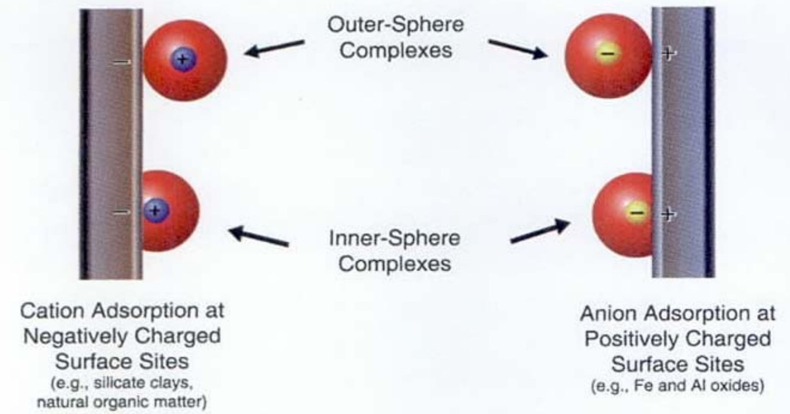


Figure 7.6 Mechanisms of inorganic contaminant adsorption: Outer-sphere and inner-sphere surface complexation.

2) Organics
  - "hydrophobic effect"
    . expulsion of a nonpolar compound from water
    . mainly on soil organic matter
    . distribution (partitioning) coefficient; K_d (K_p)

TABLE 5.5. Point of Zero Charge (pzc) of Minerals[a,b]

Material	pzc
α-Al_2O_3	9.1
α-$Al(OH)_3$	5.0
γ-AlOOH	8.2
CuO	9.5
Fe_3O_4	6.5
α-FeOOH	7.8
α-Fe_2O_3	6.7
"$Fe(OH)_3$" (amorphous)	8.5
MgO	12.4
δ-MnO_2	2.8
β-MnO_2	7.2
SiO_2	2.0
$ZrSiO_4$	5.0
Feldspars	2–2.4
Kaolinite	4.6
Montmorillonite	2.5
Albite	2.0
Chrysotile	>10

BOX 5.2. Partitioning Coefficients

A partitioning mechanism is usually suggested from linear adsorption isotherms (C-type isotherm, Fig. 5.6), reversible adsorption/desorption, a small temperature effect on adsorption, and the absence of competition when other adsorptives are added, i.e., adsorption of one of the adsorptives is not affected by the inclusion of a second adsorptive.

A partition coefficient, K_p, can be obtained from the slope of a linear adsorption isotherm using the equation

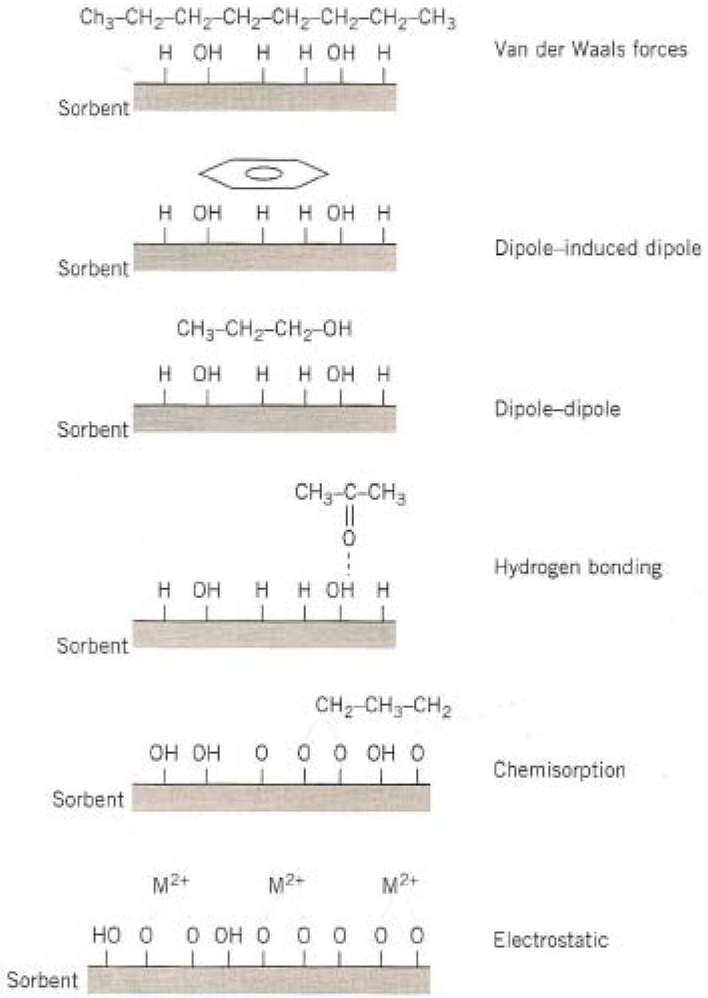
$$q = K_p C, \qquad (5.2a)$$

where q was defined earlier and C is the equilibrium concentration of the adsorptive. The K_p provides a measure of the ratio of the amount of a material that is adsorbed to the amount that is in solution.

Partition mechanisms have been invoked for a number of organic compounds, particularly for NOC and some pesticides (Chiou *et al.*, 1977, 1979, 1983).

A convenient relationship between the K_p and fraction of organic carbon (f_{oc}) in the soil is the organic carbon–water partition coefficient, K_{oc}, which can be expressed as

$$K_{oc} = K_p / f_{oc}. \qquad (5.2b)$$



3) Sorption isotherm

- relationship between the conc of sorbed contaminant and the conc of dissolved contaminant
- at the same temperature, in equilibrium
- Freundlich isotherm; $C_{sorb} = K_f C^n_w$
- *n*
  - . a measure of nonlinearity
  - . Indicates ‘sorption mechanism’
- Langmuir isotherm

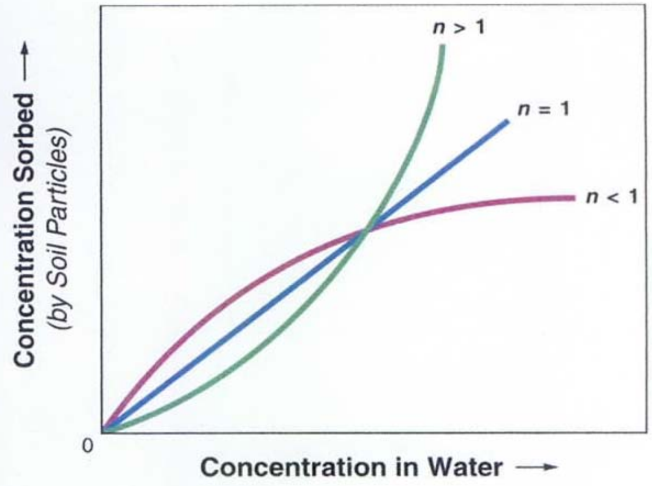


Figure 7.8 Sorption isotherms used to describe the relationship between sorbed concentrations and aqueous concentrations of a contaminant; linear (n=1) and nonlinear isotherms are shown. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

● Abiotic transformation mechanisms

$$\text{R-X} + \text{H}_2\text{O} \rightarrow \text{R-OH} + \text{X}^- + \text{H}^+ \qquad \text{(Eq. 7.20)}$$

2) Oxidation-reduction reactions

- heterotrophic respiration
- electron acceptors
  - . nitrate
  - . Mn(Fe) oxides
  - . sulfate…

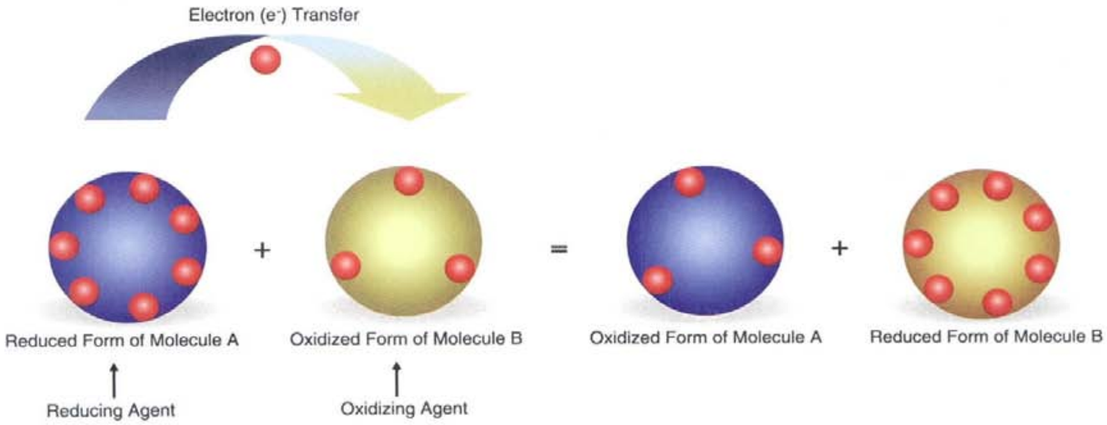


Figure 7.9 A full oxidation-reduction reaction involves the transfer of electrons from one species (the *reducing agent*) to another (the *oxidizing agent*).

3) Photochemical reactions

4) Radioactive decay

● Transformation rates

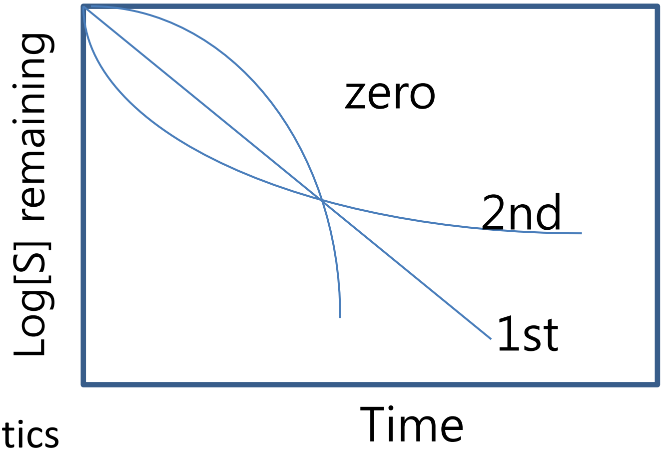
- reaction kinetics
  - . zero order rxn; constant amount is lost per unit time, all substrates are available
  - . first order rxn; exponential decrease of in initial conc, half-life (independent of initial conc)
  - . second order rxn; half-life (dependent of initial conc)
  - . pseudo-first order rxn; widely employed in the env.

    R = k[A][B]

    when [A] is in large excess amount, k[A] = k’

    → R = k’[B]

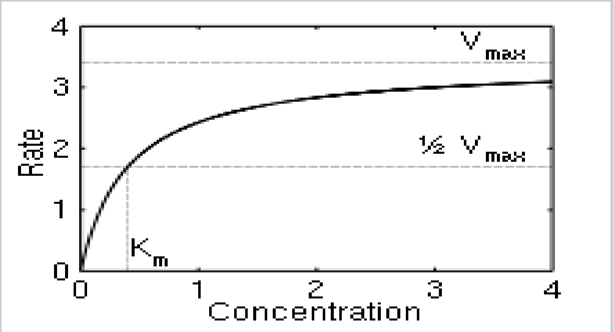
    half-life = 0.693/k’



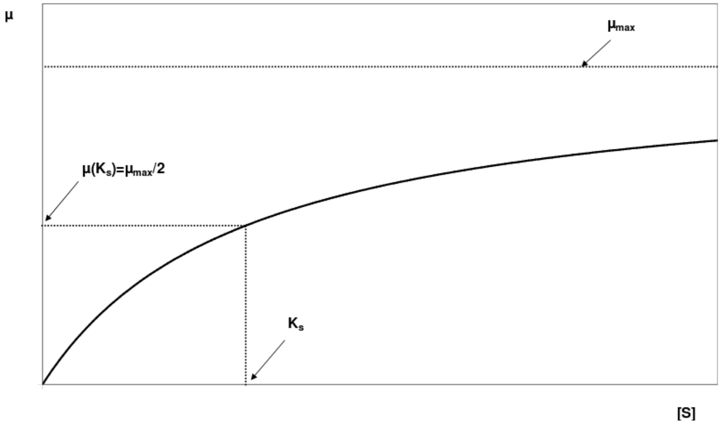
- saturation kinetics
  - . surface catalysis (enzyme) reaction; Michaelis-Menton kinetics
  - . bacterial growth; Monod equation

Enzyme reaction $v = \frac{d[P]}{dt} = \frac{V_{\max}[S]}{K_m + [S]}$

Bacterial growth $\mu = \mu_{\max}\frac{S}{K_s + S}$



An example curve with parameters V_{max} = 3.4 and K_m = 0.4.



(Lecture 9)

EPS Ch 8. Biological Processes Affecting Contaminant Transport and Fate

- Biodegradation
  - breakdown of organic compounds through microbial activity
  - pollutants as substrates (food – C & E source)
  - when biodegraded into CO2 and H2O → mineralization
  - a set of enzymatic activity
  - cometabolism; partial degradation, no benefit (C &E)

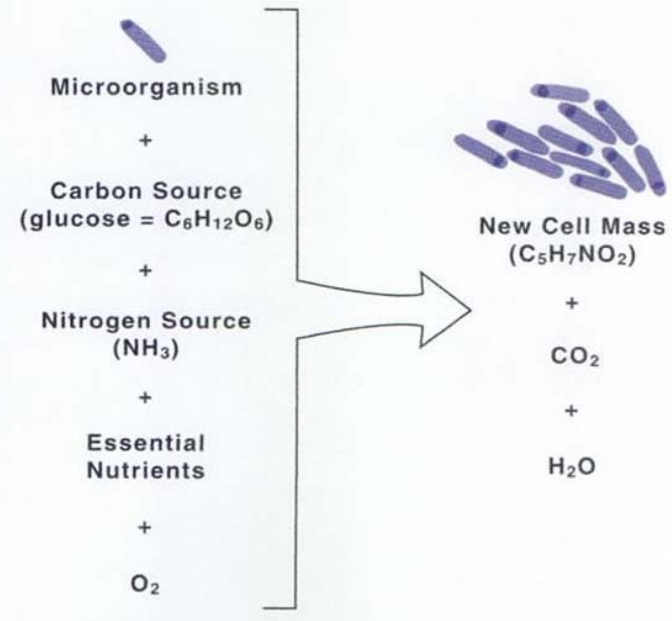


Figure 8.1 Aerobic mineralization of an organic compound. From *Pollution Science* © 1996 Academic Press, San Diego, CA.

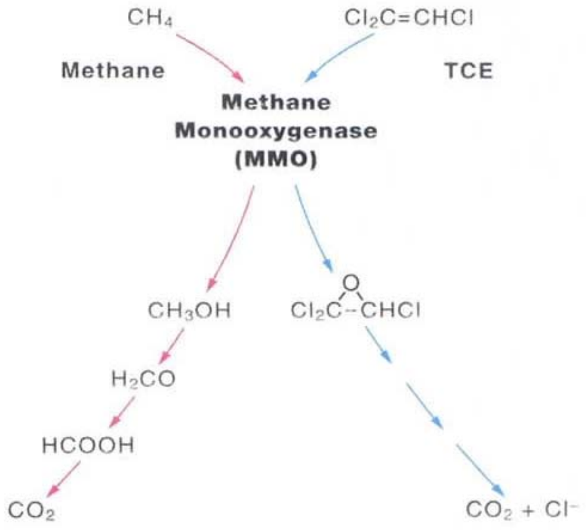


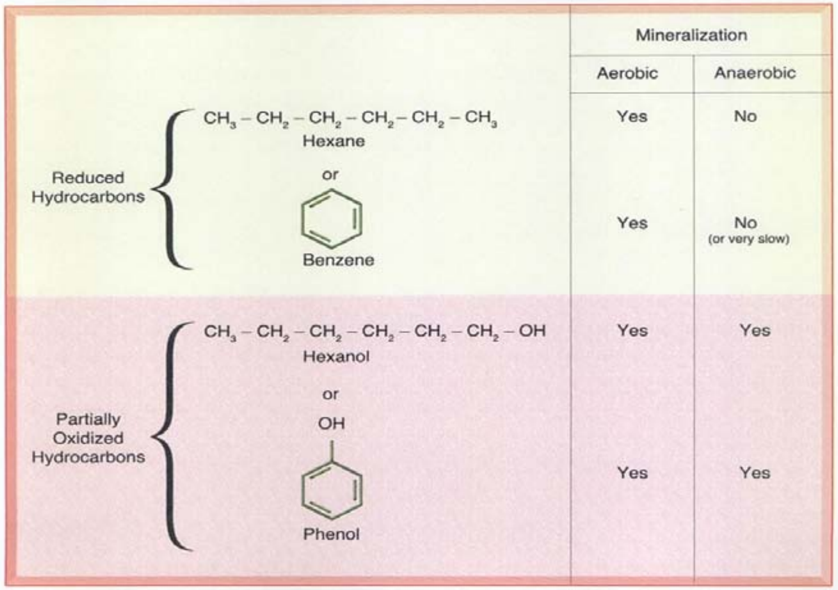
Figure 8.3 The oxidation of methane by methanotrophic bacteria. This is catalyzed by the enzyme methane monooxygenase. The same enzyme can act nonspecifically on TCE. Subsequent TCE degradation steps may be catalyzed spontaneously, by other bacteria, or in some cases by the methanotroph. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

● Environmental effects on biodegradation

1) Terminal electron acceptor (TEA)

- oxygen; highest energy generation → faster biodegradation
  - ✓ addition of oxygen; can improve biodegradation rates

- rule of thumb; reduced C ←→ oxidized C
  - ✓ TPH stable under anaerobic conditions
  - ✓ TCE stable under aerobic conditions



		Mineralization	
		Aerobic	Anaerobic
Reduced Hydrocarbons	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ Hexane	Yes	No
	or Benzene	Yes	No (or very slow)
Partially Oxidized Hydrocarbons	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-OH$ Hexanol	Yes	Yes
	or OH Phenol	Yes	Yes

Figure 8.8 The effects of oxidation on the biodegradability of aliphatic compounds. Hydrocarbons with no oxygen, such as hexane, are only degraded aerobically, while the addition of a single oxygen atom (hexanol) enables both aerobic and anaerobic degradation to occur.

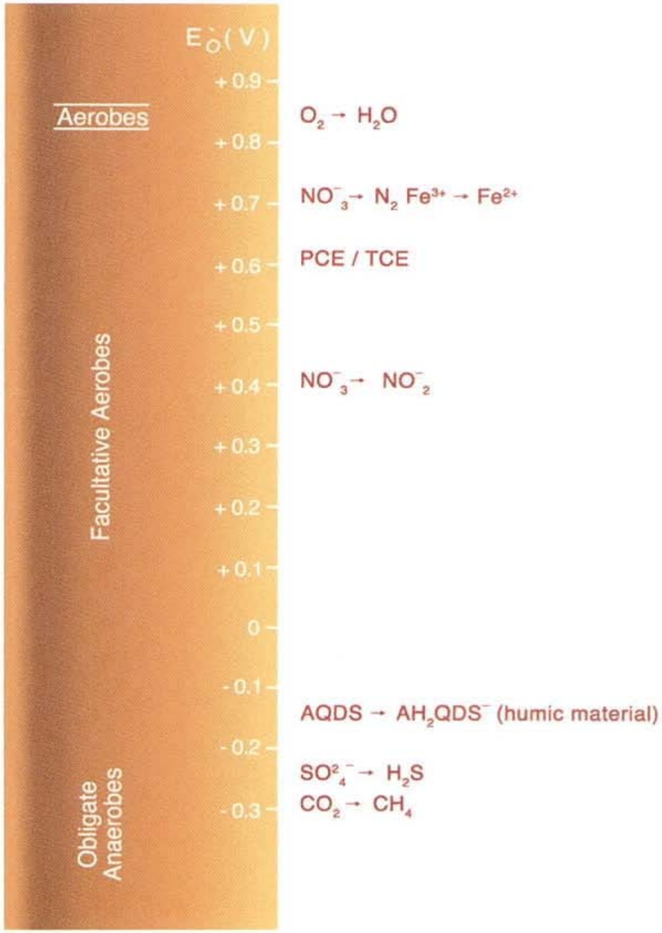


Figure 8.6 Terminal electron acceptors over a range of redox potentials. The electron tower shows the various terminal electron acceptors (TEAs) used under aerobic (oxygen) and anaerobic (all others) conditions. Note that the higher the place on the electron tower, the more energy that will be produced for metabolism and growth. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

2) Microbial population and soil organic matter content

- cultural bacterial numbers; ca. 10^6 – 10^9 CFU/g-soil
- decrease with depth by > 2 orders of magnitude
- mainly due to oxygen and nutrients (SOM and trace minerals)

✓ "Number of bacteria" participating in biodegradation is important

- population growth; acclimation
- acquisition of required metabolic activity; adaptation

3) Nitrogen and phosphorous

- may act ac limiting factors
- C:N:P → 100:10:1

4) Pollutant structure

- intrinsic property of p ollutants; "recalcitrant"

✓ matrix and time effect; "persistent"

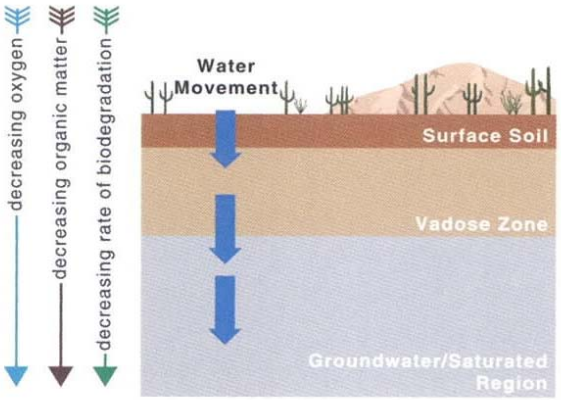


Figure 8.5 Contamination in different ecosystems. There are three major locations where contamination can occur in terrestrial ecosystems: surface soils, the vadose zone, and the saturated zone. The availability of both oxygen and organic matter varies considerably in these zones. As indicated, oxygen and organic matter both decrease with depth, resulting in a decrease in biodegradation activity with depth. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

● Aerobic biodegradation

- mainly use preexisting pathways; similar to naturally occurring compounds

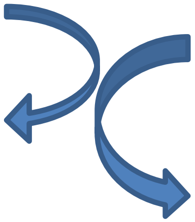
1) Aliphatic hydrocarbons

CH_3-$(CH_2)_n$-CH_3 → CH_3-$(CH_2)_n$-CH_2OH → CH_3-$(CH_2)_n$-CHO

→ CH_3-$(CH_2)_n$-$COOH$ → β-oxidation (C_2-removal)

→ TCA cycle

→ $CO_2 + H_2O$ + NADH



NAD^+

ADP

ATP

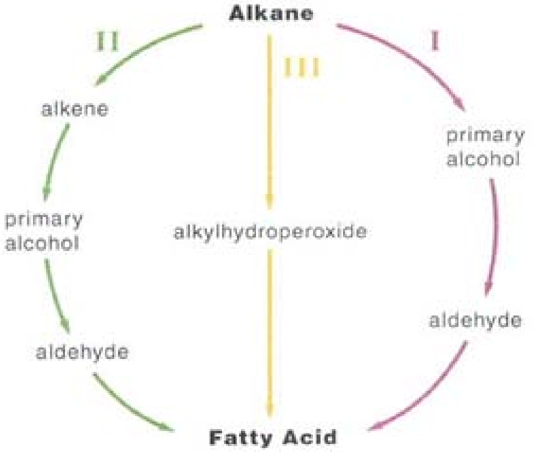


Figure 8.10 Aerobic biodegradation pathways for aliphatic

2) Aromatic hydrocarbons

- low solubility & high sorption
  → low biodegradation
  low bioavailability
- "dioxygenase"

3) Alicyclic hydrocarbons

- saturated carbon chains

✓ single isolate

✓ consortium (mixed culture)

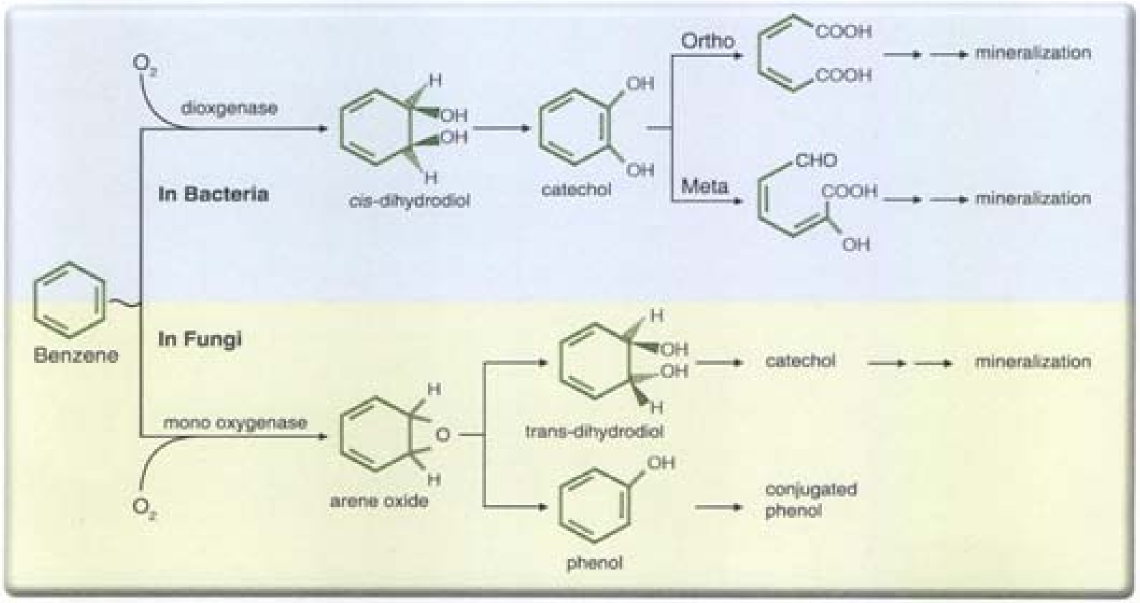


Figure 8.12 Aerobic biodegradation pathways of aromatic compounds in bacteria and fungi.

● Anaerobic biodegradation

- anaerobic respiration; use TEA (i.e., Fe/Mn, NO_3^-, SO_4^{2-}, CO_2) other than oxygen is used

1) Aliphatic hydrocarbons
   - reductive dehalogenation

2) Aromatic hydrocarbons
   - benzoate

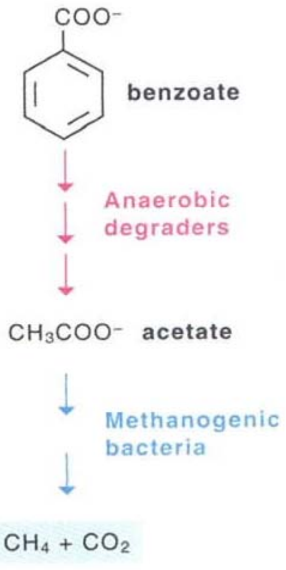


Figure 8.18 An example of an aerobic food chain. Shown is the formation of simple compounds from benzoate by a population of anaerobic bacteria and the subsequent utilization of the newly available substrate by a second anaerobic population, the methanogenic bacteria. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

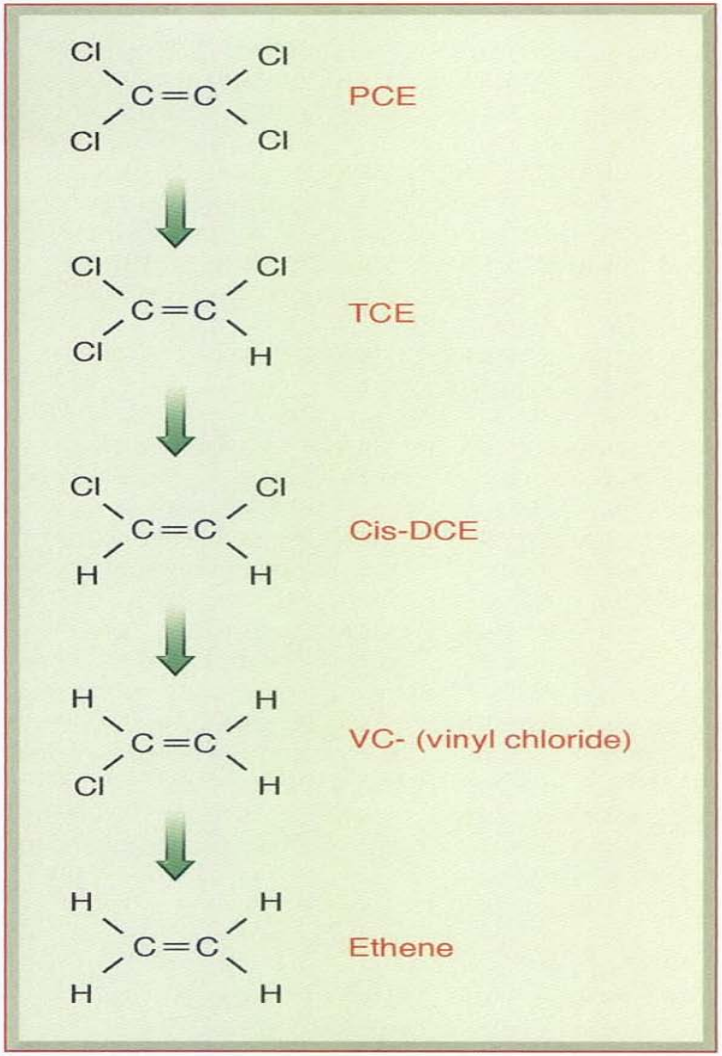


Figure 8.15 Halorespiration of perchloroethene (PCE). There are a number of anaerobic halorespiring microbes that can dehalogenate PCE to either TCE or DCE. Recently, there even has been one microbe described that can completely dechlorinate PCE to ethene!

- Transformation of metals
  - oxidation/reduction
  - complexation
  - alkylation

  - valence change
    - ✓ $Cr^{6+} \rightarrow Cr^{3+}$
    - ✓ $As^{3+} \rightarrow As^{5+}$

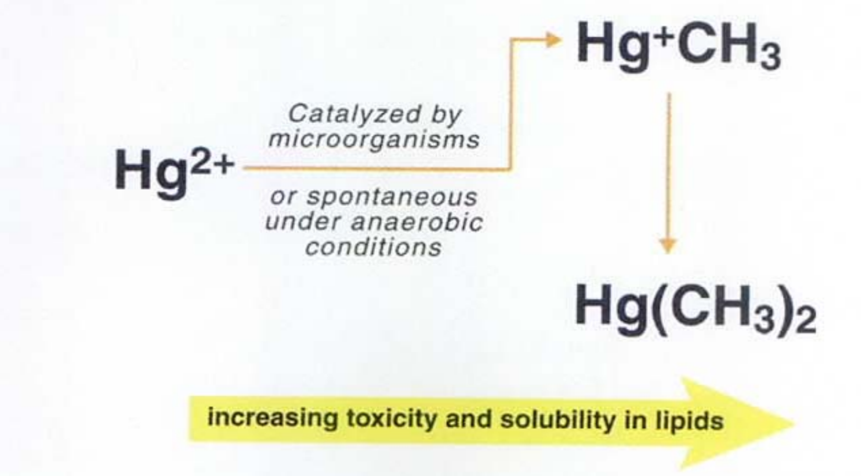


Figure 8.19 Microbial alkylation of mercury. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

(Lecture 10)

HW Ch 4. Source Analysis

1. Materials Balances and Waste Audits (p. 212)

2. Hazardous Waste Site Assessments (p. 216)

- Hazardous wastes sites must be assessed to determine the extent of contamination before cleanup is initiated.

(a) Phase I assessment

- to confirm the suspicions of the presence of hazardous wastes
- involves documents and paper research including a chemical inventory evaluation, interviews with current and former personnel and neighbors, regulatory agency record searches and interviews, and title searches and reviews of historical ownership,...
- on-site inspection also required (i.e., to find clues of contamination)
- to determine the need for further investigation, not to determine whether a site is contaminated or not

(b) Phase II assessment

- to confirm or deny the presence of hazardous wastes at the site
- includes a detailed evaluation of pathways and potential receptors
- extensive sampling and analysis around source areas

(c) Phase III assessment

- conducted if Phase II assessment shows that the site is contaminated
- to detail the extent of contamination in terms of the area, volume, and concentrations
- more extensive sampling and analysis around the source and adjacent areas (i.e., soil, subsurface, groundwater)
- to provide criteria for an appropriate remedial design

4. Source Sampling (p. 219)

- one of the most important procedure
- generally use statistical methods to minimize sampling errors
- sampling errors mainly from heterogeneous media
- sampling errors are usually greater than analytical errors

5. Source Sampling Procedures and Strategies (p. 229)

6. Sampling away from the Source (p. 232)

- often a prerequisite before designing remediation systems and documenting their effectiveness during operation

7. Priority Pollutant and Sample Analyses (p. 241)

- among a list of 129 chemicals, 114 organics, 13 metals, 1 mineral, and 1 inorganic nonmetal
- organics; extraction through simple solvent shaking or Soxhlet apparatus (continuous solvent flushing with heat)
- analysis; GC/FID (EDC...), HPLC, AA (Atomic Absorption) spectrophotometer, ICP (Inductively Couple Plasma)
- US EPA Method 600 series (for aqueous samples), 8,000 series (for soils and sludges); Table 4.3

(Lecture 11)

ESP Ch 14. Risk Assessment

- Risk assessment
  - the process of estimating both probability that an event will occur and the probable magnitude of its adverse effects
  - provides an effective framework for determining relative urgency of problems and the allocation of resources to reduce risks
  - human risk assessment, ecological risk assessment

✓ *de minimis* level of risk

✓ acceptable risk

- depends on population
  - . size/age/health conditions…
- for carcinogens, general range of $10^{-4} - 10^{-6}$
- for noncarcinogens, HI = 1

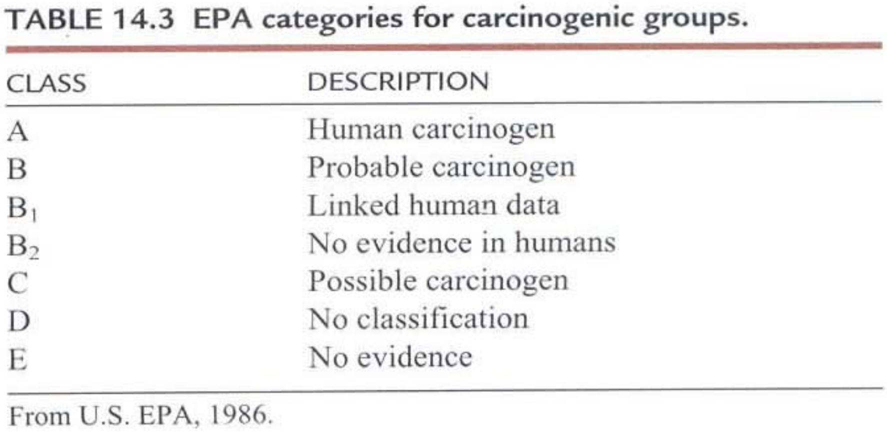
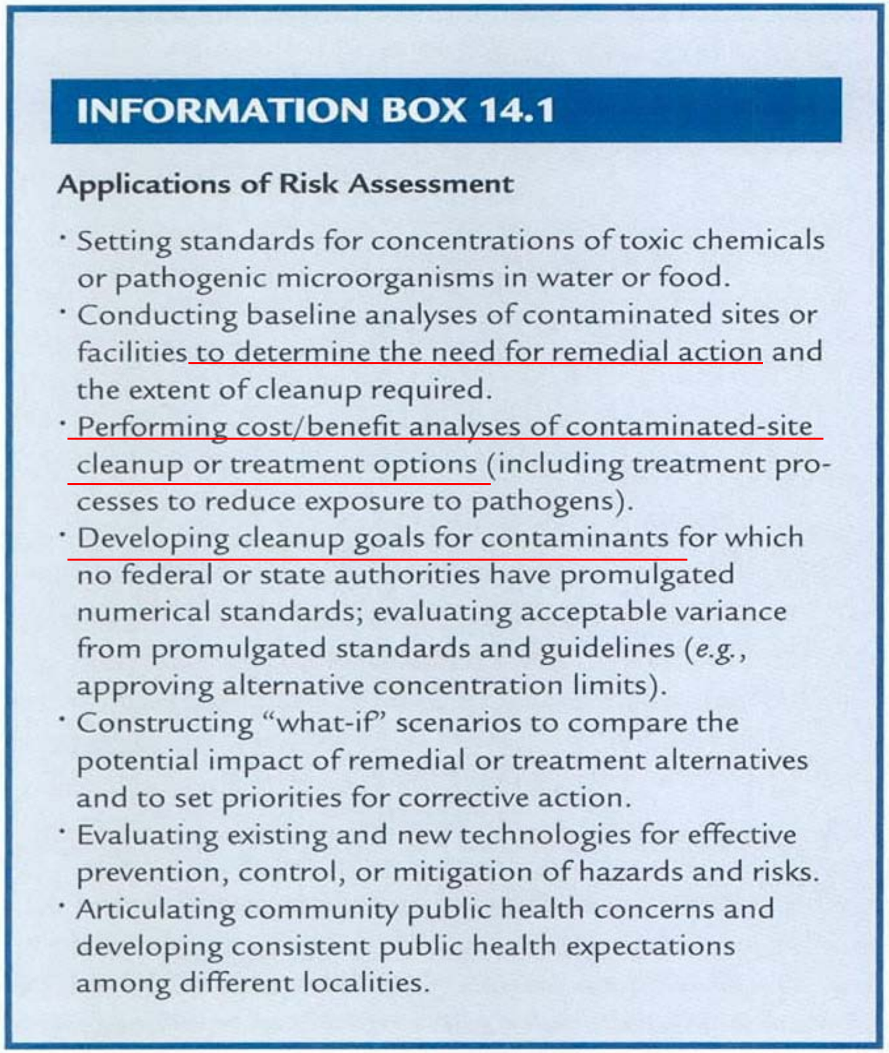


TABLE 14.3 EPA categories for carcinogenic groups.

CLASS	DESCRIPTION
A	Human carcinogen
B	Probable carcinogen
B_1	Linked human data
B_2	No evidence in humans
C	Possible carcinogen
D	No classification
E	No evidence

From U.S. EPA, 1986.



INFORMATION BOX 14.1

Applications of Risk Assessment

- Setting standards for concentrations of toxic chemicals or pathogenic microorganisms in water or food.
- Conducting baseline analyses of contaminated sites or facilities to determine the need for remedial action and the extent of cleanup required.
- Performing cost/benefit analyses of contaminated-site cleanup or treatment options (including treatment processes to reduce exposure to pathogens).
- Developing cleanup goals for contaminants for which no federal or state authorities have promulgated numerical standards; evaluating acceptable variance from promulgated standards and guidelines (*e.g.*, approving alternative concentration limits).
- Constructing "what-if" scenarios to compare the potential impact of remedial or treatment alternatives and to set priorities for corrective action.
- Evaluating existing and new technologies for effective prevention, control, or mitigation of hazards and risks.
- Articulating community public health concerns and developing consistent public health expectations among different localities.

● Risk assessment process

(1) Hazard identification

- a review of all relevant biological and chemical information bearing on whether or not an agent poses a specific threat
- site investigation (contamination levels…)

(2) Exposure assessment

- the process of measuring intensity, frequency and duration of exposure to an agent
- exposure routes; ingestion, derma contact, inhalation
- exposure pathway
  - . from source to receptors
  - . affected by interactions between pollutants and environmental media (soil, water, aquifer…)
- exposure factors

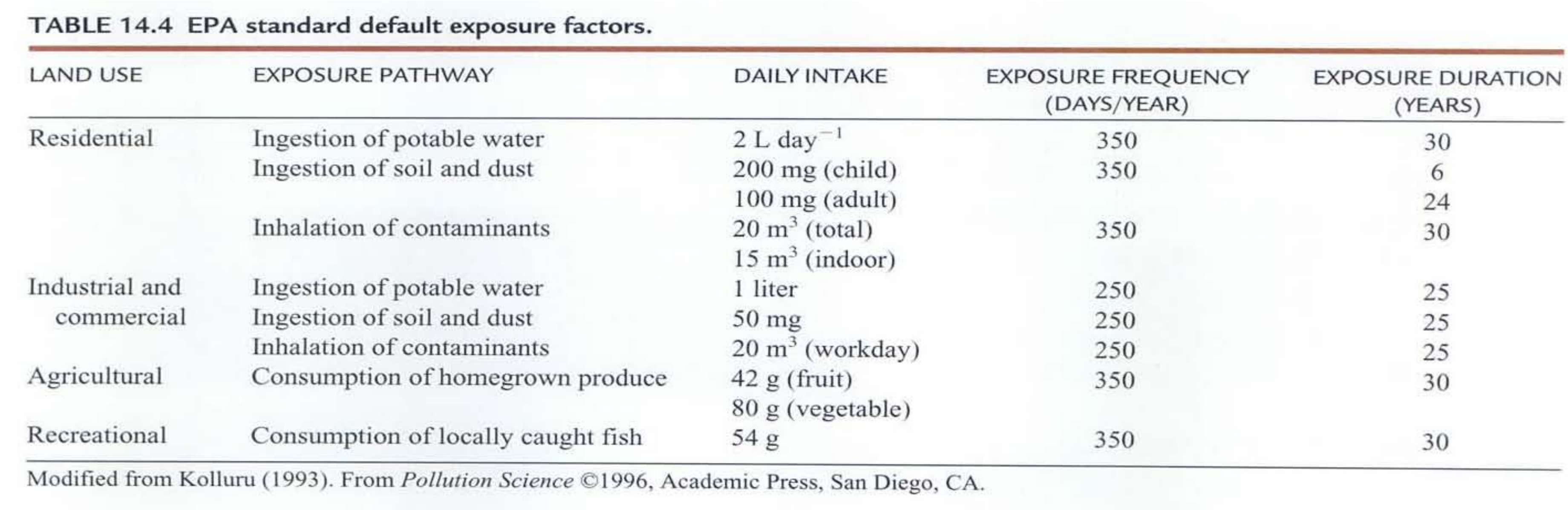
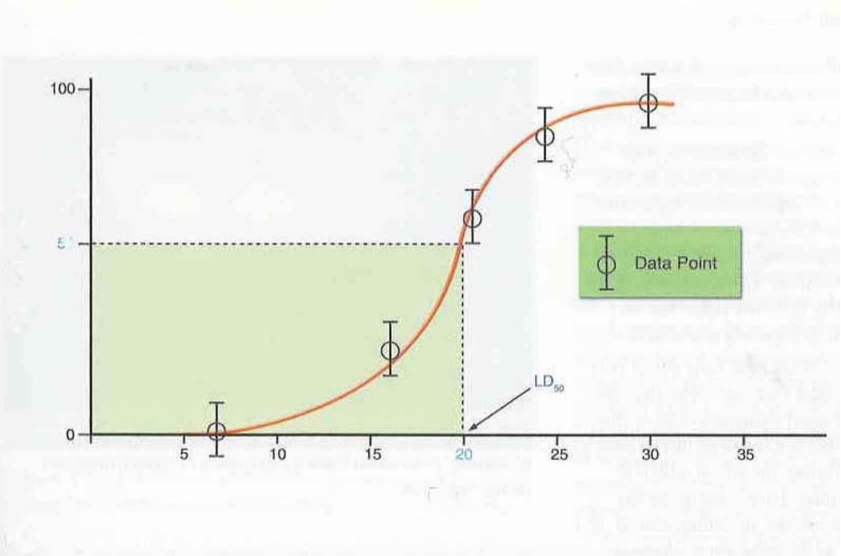


TABLE 14.4 EPA standard default exposure factors.

LAND USE	EXPOSURE PATHWAY	DAILY INTAKE	EXPOSURE FREQUENCY (DAYS/YEAR)	EXPOSURE DURATION (YEARS)
Residential	Ingestion of potable water	2 L day^{-1}	350	30
	Ingestion of soil and dust	200 mg (child)	350	6
		100 mg (adult)		24
	Inhalation of contaminants	20 m^3 (total)	350	30
		15 m^3 (indoor)		
Industrial and commercial	Ingestion of potable water	1 liter	250	25
	Ingestion of soil and dust	50 mg	250	25
	Inhalation of contaminants	20 m^3 (workday)	250	25
Agricultural	Consumption of homegrown produce	42 g (fruit)	350	30
		80 g (vegetable)		
Recreational	Consumption of locally caught fish	54 g	350	30

Modified from Kolluru (1993). From *Pollution Science* ©1996, Academic Press, San Diego, CA.

(3) Dose-response assessment
- need quantitative toxicity data
  - . mainly from animal experiments
  - . IRIS (US EPA)
- acute, subchronic, chronic toxicity
- dose-response relationship
  - . generally, sigmoid-type curve
  - . dose; mg-chemical/kg-body weight/day
  - . response; mortality…



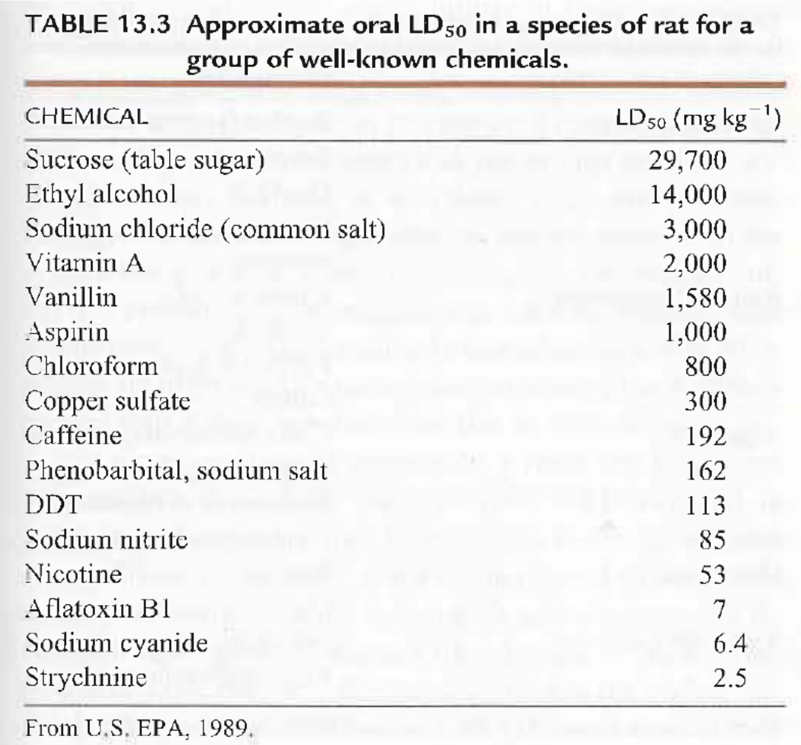


TABLE 13.3 Approximate oral LD_{50} in a species of rat for a group of well-known chemicals.

CHEMICAL	LD_{50} (mg kg^{-1})
Sucrose (table sugar)	29,700
Ethyl alcohol	14,000
Sodium chloride (common salt)	3,000
Vitamin A	2,000
Vanillin	1,580
Aspirin	1,000
Chloroform	800
Copper sulfate	300
Caffeine	192
Phenobarbital, sodium salt	162
DDT	113
Sodium nitrite	85
Nicotine	53
Aflatoxin B1	7
Sodium cyanide	6.4
Strychnine	2.5

From U.S. EPA, 1989.

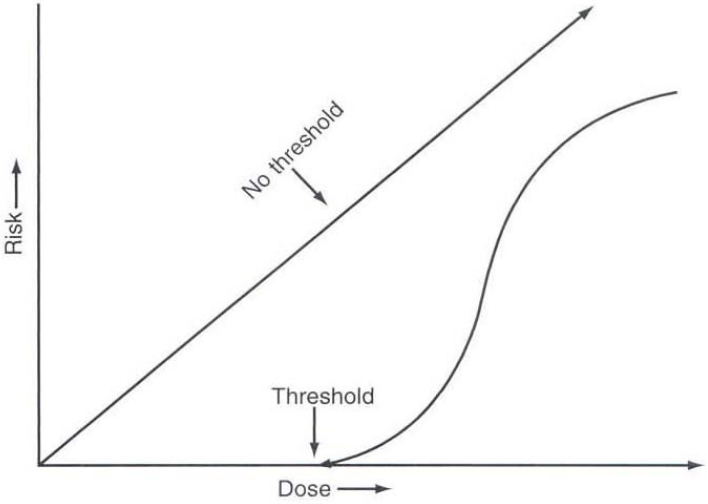


Figure 14.3 Relationship between a threshold and nonthreshold response.

▶ Surrogates vs. human

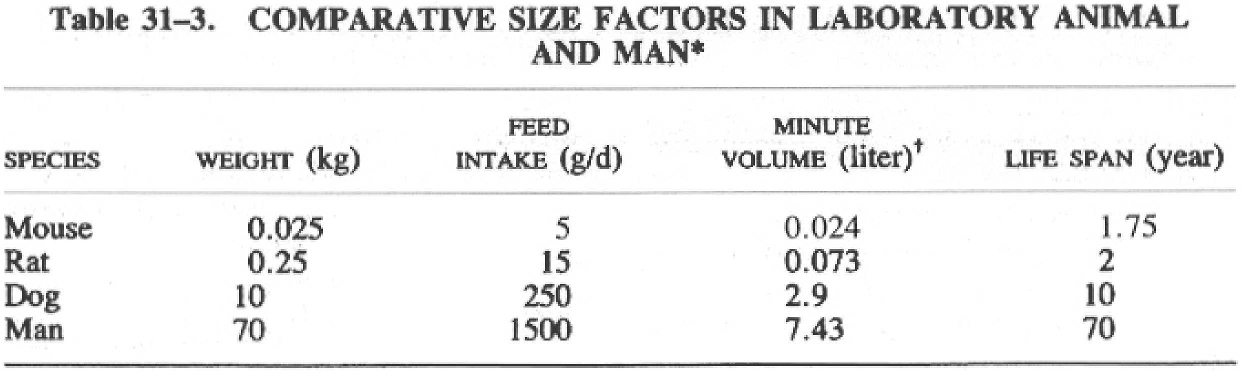


Table 31–3. COMPARATIVE SIZE FACTORS IN LABORATORY ANIMAL AND MAN*

SPECIES	WEIGHT (kg)	FEED INTAKE (g/d)	MINUTE VOLUME (liter)†	LIFE SPAN (year)
Mouse	0.025	5	0.024	1.75
Rat	0.25	15	0.073	2
Dog	10	250	2.9	10
Man	70	1500	7.43	70

▶ dose vs. dosage

- dose; the total mass of chemical to which an organism is exposed
- dosage; the chemical dose normalized for body weight, surface area,..

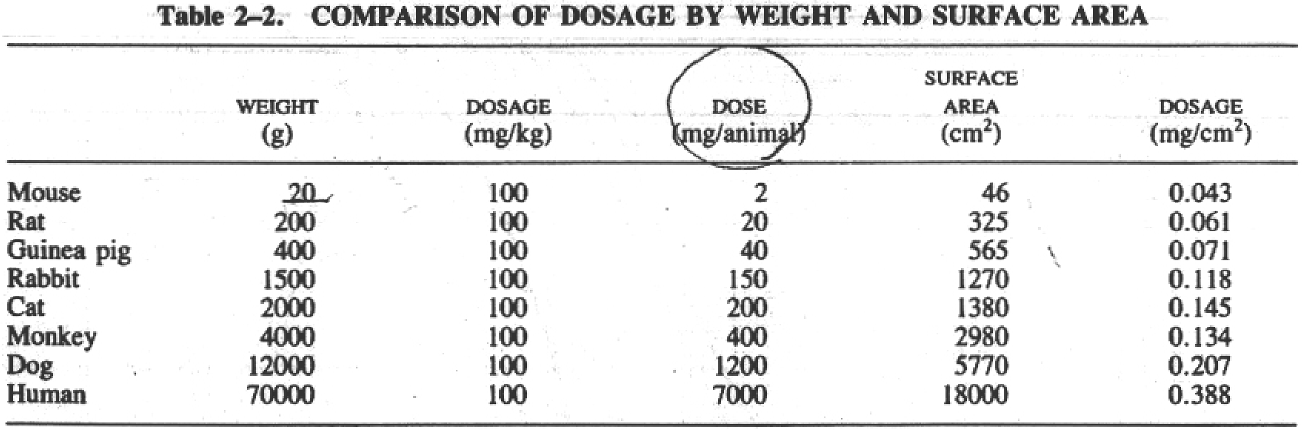


Table 2–2. COMPARISON OF DOSAGE BY WEIGHT AND SURFACE AREA

	WEIGHT (g)	DOSAGE (mg/kg)	DOSE (mg/animal)	SURFACE AREA (cm^2)	DOSAGE (mg/cm^2)
Mouse	20	100	2	46	0.043
Rat	200	100	20	325	0.061
Guinea pig	400	100	40	565	0.071
Rabbit	1500	100	150	1270	0.118
Cat	2000	100	200	1380	0.145
Monkey	4000	100	400	2980	0.134
Dog	12000	100	1200	5770	0.207
Human	70000	100	7000	18000	0.388

- for carcinogens
  - linear multistage model (USEPA)
  - slope factor (SF), cancer potency factor (CPF)
  - risk by a lifetime average dose (AD) of 1 mg/kg/day
  - lifetime risk = AD * SF (70 years)

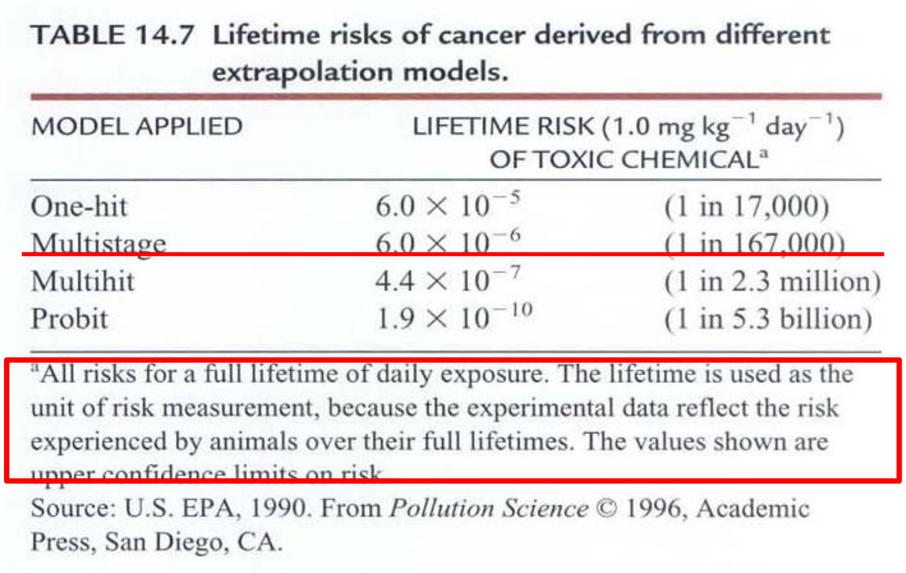


TABLE 14.7 **Lifetime risks of cancer derived from different extrapolation models.**

MODEL APPLIED	LIFETIME RISK (1.0 mg kg^{-1} day^{-1}) OF TOXIC CHEMICAL[a]	
One-hit	6.0×10^{-5}	(1 in 17,000)
Multistage	6.0×10^{-6}	(1 in 167,000)
Multihit	4.4×10^{-7}	(1 in 2.3 million)
Probit	1.9×10^{-10}	(1 in 5.3 billion)

[a] All risks for a full lifetime of daily exposure. The lifetime is used as the unit of risk measurement, because the experimental data reflect the risk experienced by animals over their full lifetimes. The values shown are upper confidence limits on risk.

Source: U.S. EPA, 1990. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

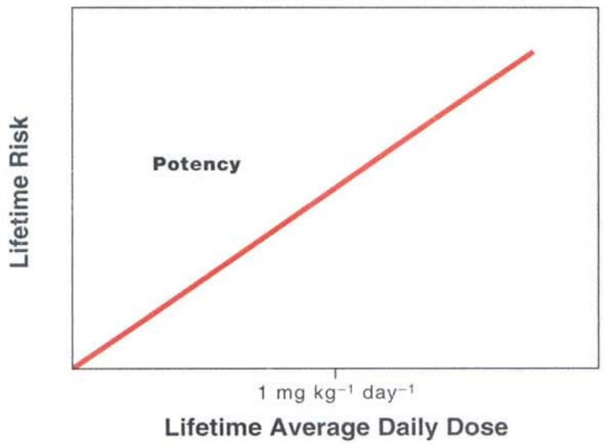


Figure 14.5 Potency factor is the slope of the dose–response curve at low doses. At low doses, the slope of the dose–response curve produced by the multistage model is called the potency factor. It is the risk produced by a lifetime average dose of 1 mg kg^{-1} day^{-1}. Adapted from U.S. EPA, 1990. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

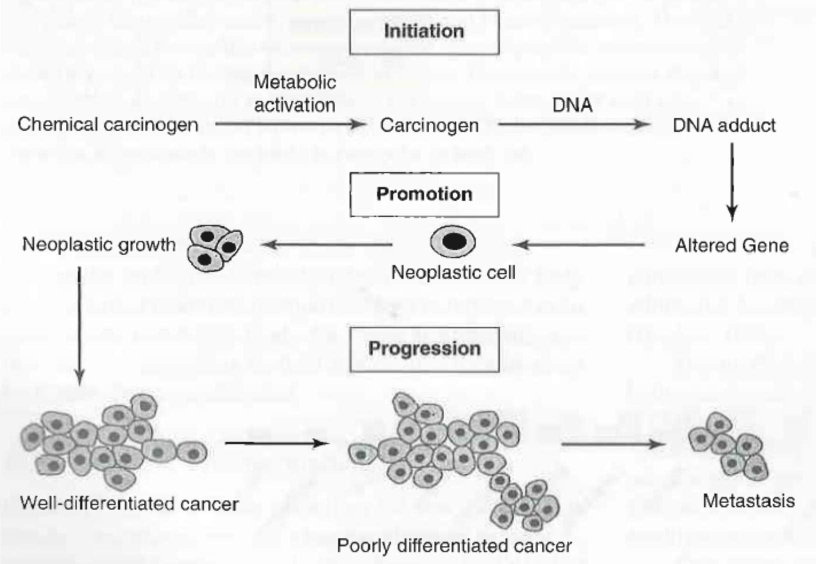


Figure 13.12 The three steps in cancer development. From Sullivan J.B. and Krieger G.R, (1992) *Hazardous Materials Toxicology: Clinical Principles of Environmental Health.* Williams and Wilkins, Baltimore, MD.

- for noncarcinogens
  - . assumes “threshold”
  - . reference dose (RfD)
  - . unit; mg/kg/day

$$\mathrm{RfD} = \frac{\mathrm{NOAEL}}{\underbrace{\mathrm{VF}_1 \times \mathrm{VF}_2 \ldots \times \mathrm{VF}_n}_{\text{uncertainty factors}}} \qquad \text{(Eq. 14.2)}$$

- individual sensitivity
- extrapolation to humans
- extrapolation from high dose to low dose
- professional judgement…

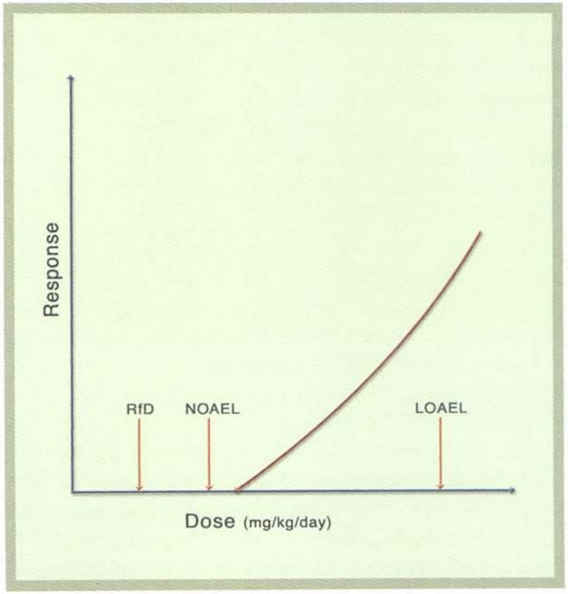
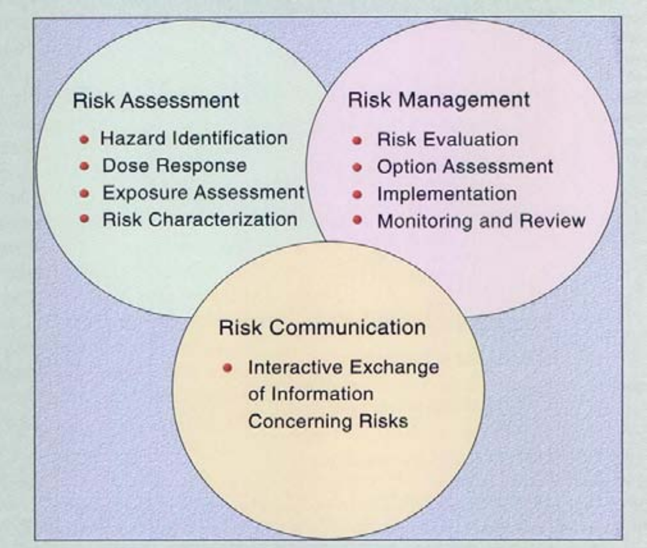


Figure 14.6 Relationships between RfD, NOAEL, and LOAEL for noncarcinogens.

(4) Risk characterization
- excessive lifetime risk = exposure * toxicity
- carcinogenic risk
- noncarcinogenic risk

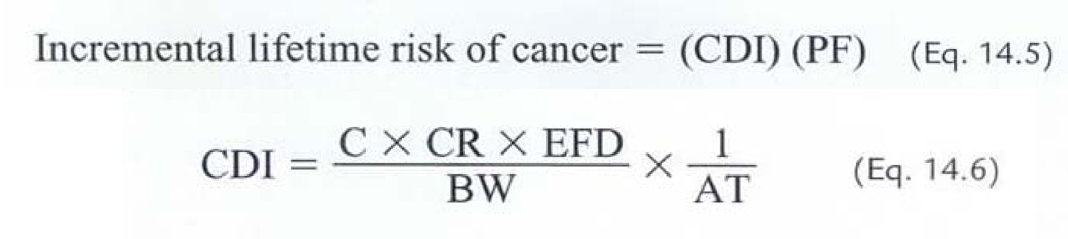
✓ uncertainty analysis
- sensitivity analysis
- Monte Carlo simulation

✓ record of decision (ROD) – “site-specific”
- site investigation
- risk assessment
- remediation goals
- remediation technologies,,,



Structure of risk analysis.

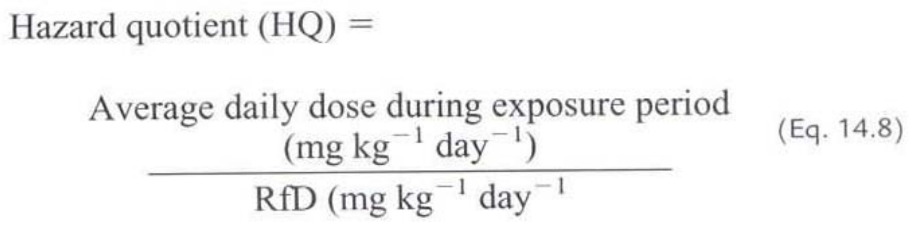
- Carcinogenic risk calculation



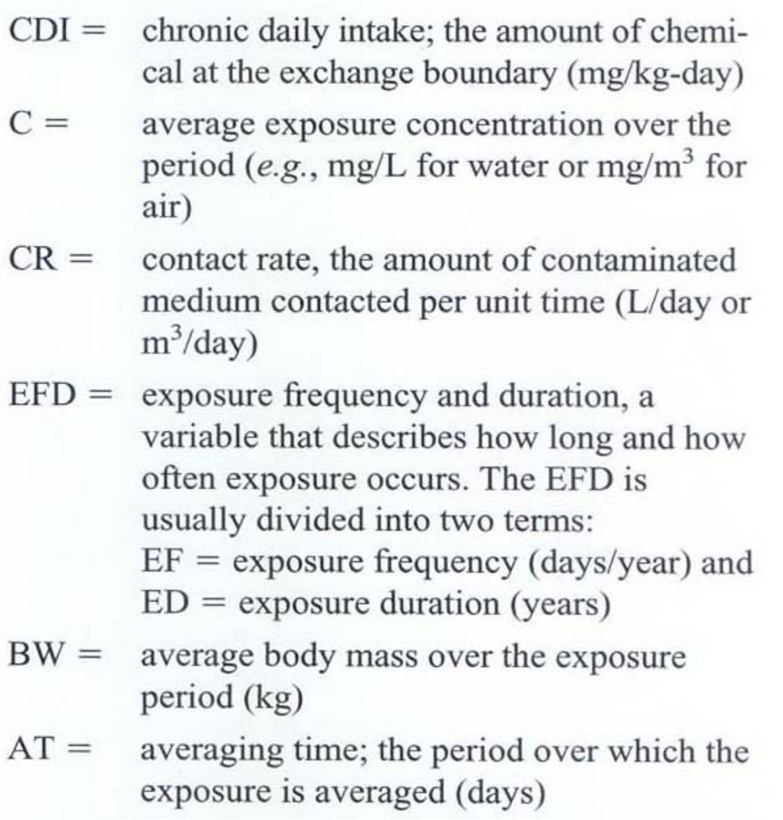
$$\text{Incremental lifetime risk of cancer} = (\text{CDI})\,(\text{PF}) \qquad \text{(Eq. 14.5)}$$

$$\text{CDI} = \frac{\text{C} \times \text{CR} \times \text{EFD}}{\text{BW}} \times \frac{1}{\text{AT}} \qquad \text{(Eq. 14.6)}$$

- Noncarcinogenic risk calculation



$$\text{Hazard quotient (HQ)} = \frac{\text{Average daily dose during exposure period } (\text{mg kg}^{-1}\,\text{day}^{-1})}{\text{RfD } (\text{mg kg}^{-1}\,\text{day}^{-1}} \qquad \text{(Eq. 14.8)}$$



CDI = chronic daily intake; the amount of chemical at the exchange boundary (mg/kg-day)

C = average exposure concentration over the period (*e.g.*, mg/L for water or mg/m^3 for air)

CR = contact rate, the amount of contaminated medium contacted per unit time (L/day or m^3/day)

EFD = exposure frequency and duration, a variable that describes how long and how often exposure occurs. The EFD is usually divided into two terms:
EF = exposure frequency (days/year) and
ED = exposure duration (years)

BW = average body mass over the exposure period (kg)

AT = averaging time; the period over which the exposure is averaged (days)

▶ Ecological risk assessment (ERA)
- much more difficult and time-consuming
- needs lots of database regarding biota and toxicity
- food chain vs. target species

[참고]

Biotransformation of toxicant in body

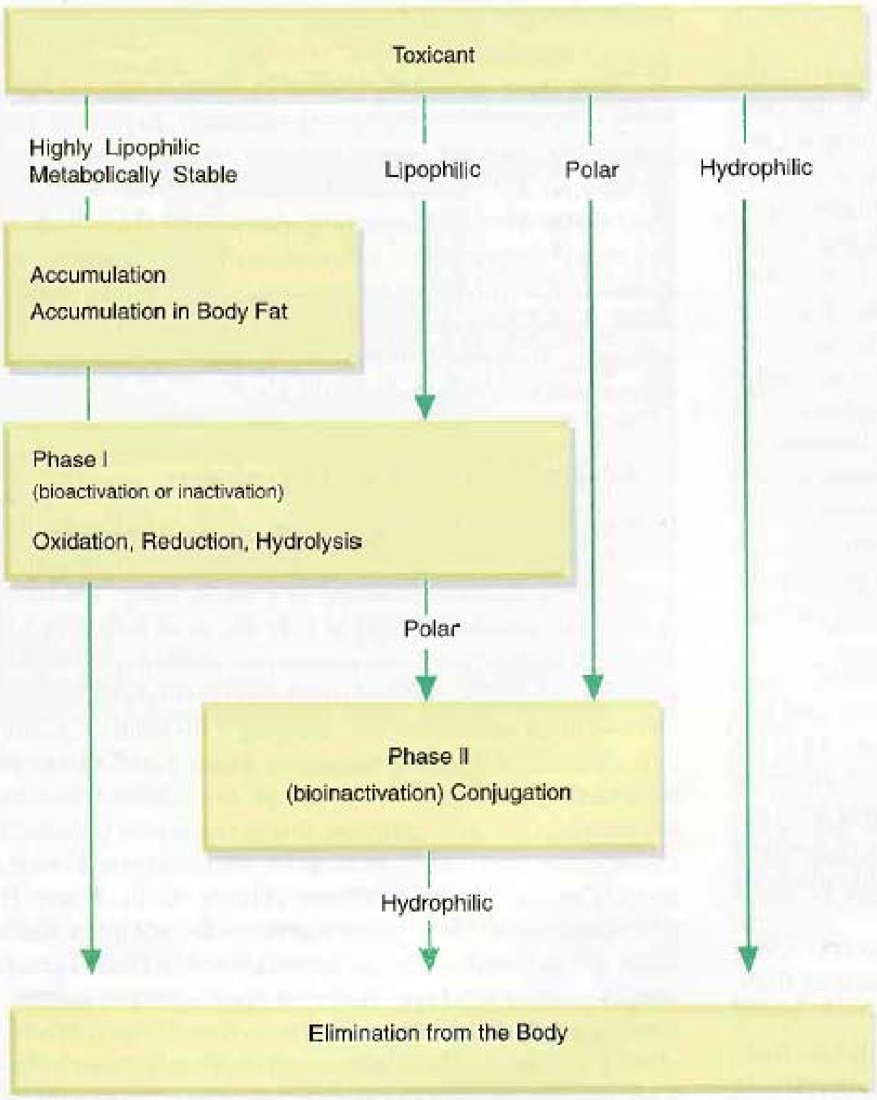


Figure 13.9 The various steps of biotransformation. This figure gives a general overview of biotransformation, showing Phase I and Phase II reactions.

Routes of Pb exposure in the environment

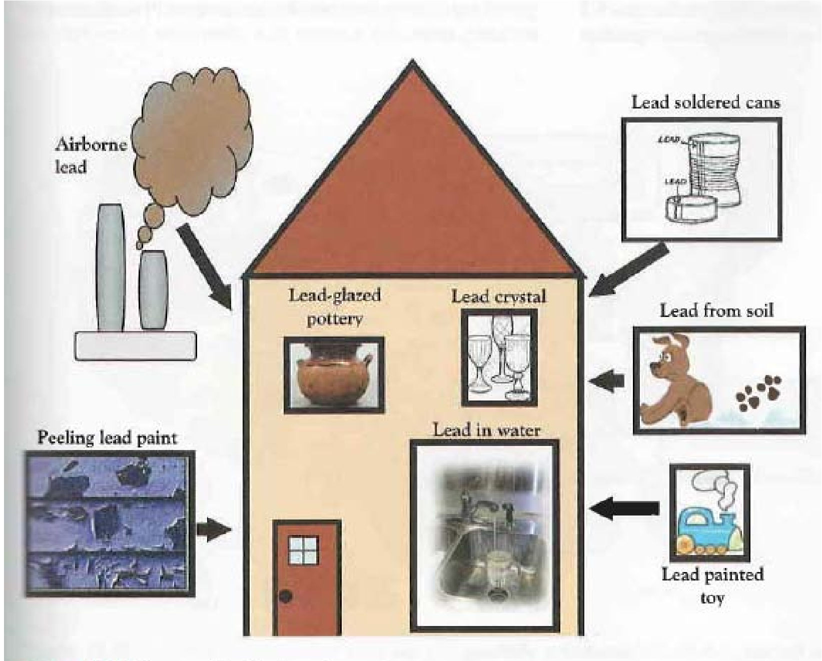


Figure 13.18 Sources of lead in the environment.

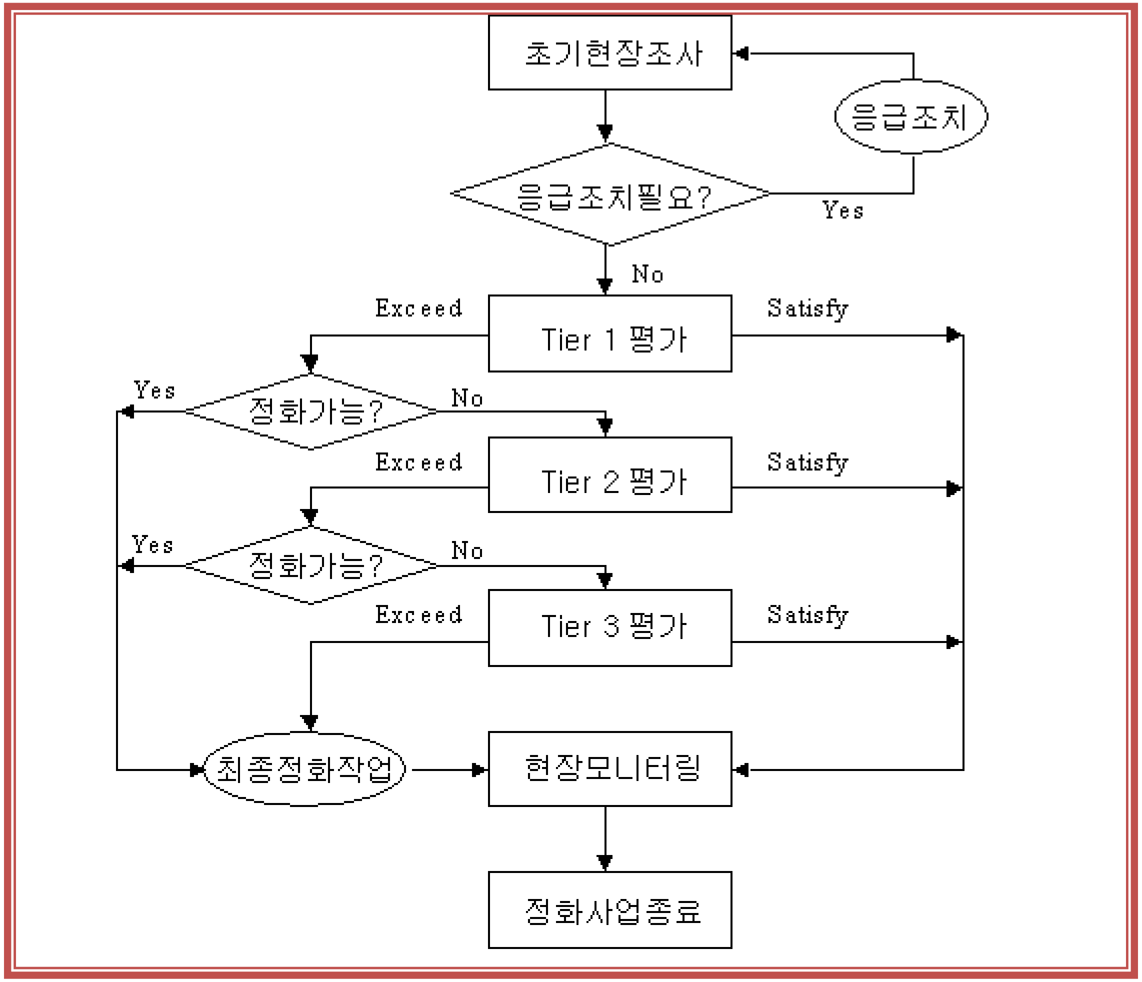
▶ <u>How to deal with "risk"?</u>

(example)

"During a shower, toxic chemicals are released from the water, exposing the person to chemicals that may be up to 100 times greater than normal exposure."

- ✓ *Is there a risk in showering?*
- ✓ *Should individuals be afraid of shower?*

RBRS (Risk-Based Remediation Strategy) 를 이용한 환경관리



Tier 1: 보수적 기본값을
이용한 위해성평가
(→ RBSL)

Tier 2: 오염현장 특수성을
반영한 위해성평가
(→ SSTL)

Tier 3: Tier 2보다 세분화된
위해성평가
(ERA 포함)

기존규제농도 vs. 오염농도
↓
RBSL/SSTL vs. 오염농도

General procedure

Site characterization

↓

Conceptual Site Model

↓

Target risk & Clean-up goal

↓

Site-specific remediation

○ **Extensive soil, hydrogeological survey**

○ Site-specific CSM

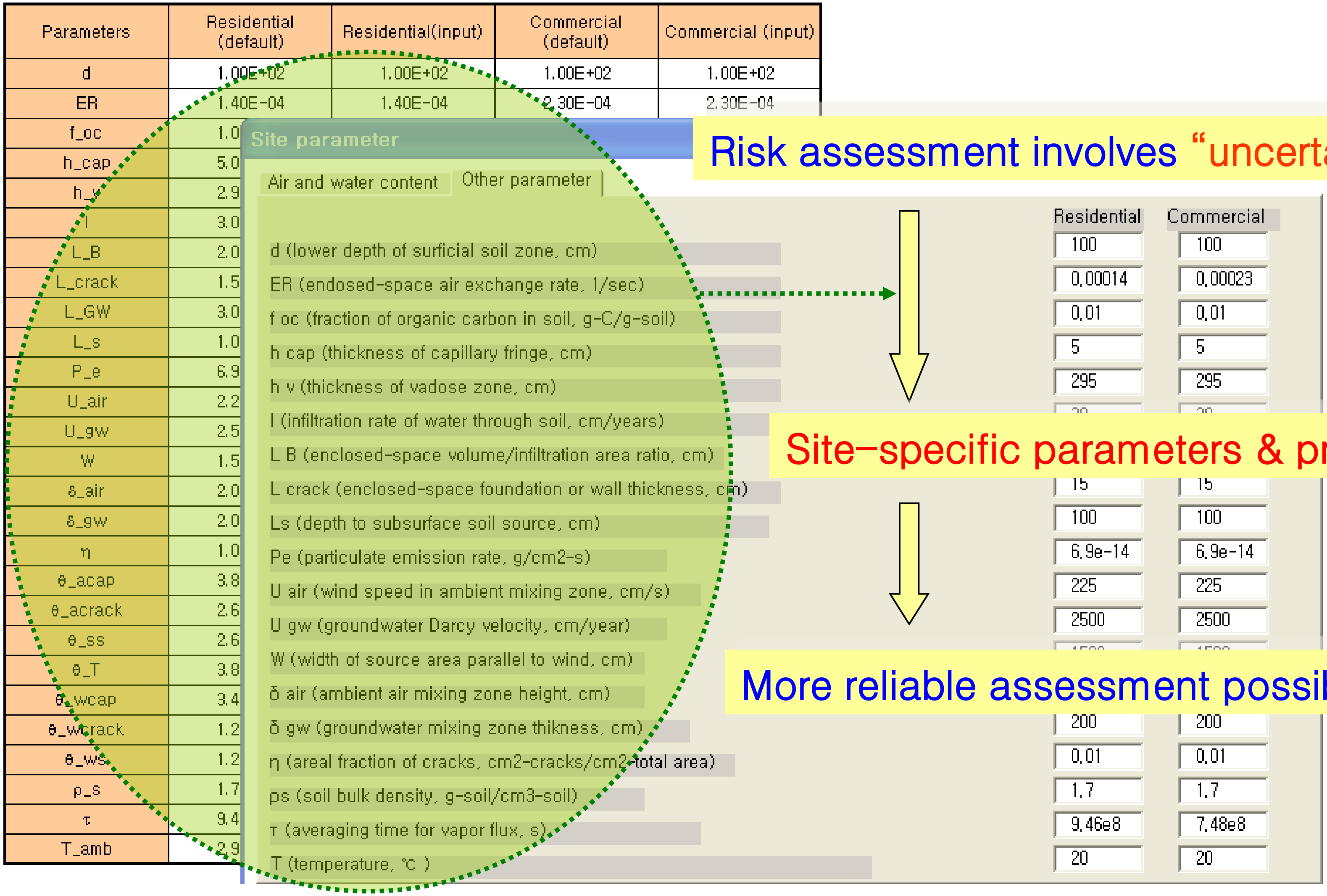
- Source identification
- Pollutants migration
- Potential exposure routes
- Potential receptors
- Land use

○ Control effective exposure pathways

○ **Remediation area**

○ **Available technology**

1. Site characterization



Parameters	Residential (default)	Residential(input)	Commercial (default)	Commercial (input)
d	1.00E+02	1.00E+02	1.00E+02	1.00E+02
ER	1.40E-04	1.40E-04	2.30E-04	2.30E-04
f_oc	1.0			
h_cap	5.0			
h_v	2.9			
I	3.0			
L_B	2.0			
L_crack	1.5			
L_GW	3.0			
L_s	1.0			
P_e	6.9			
U_air	2.2			
U_gw	2.5			
W	1.5			
δ_air	2.0			
δ_gw	2.0			
η	1.0			
θ_acap	3.8			
θ_acrack	2.6			
θ_ss	2.6			
θ_T	3.8			
θ_wcap	3.4			
θ_wcrack	1.2			
θ_ws	1.2			
ρ_s	1.7			
τ	9.4			
T_amb	2.9			

Site parameter

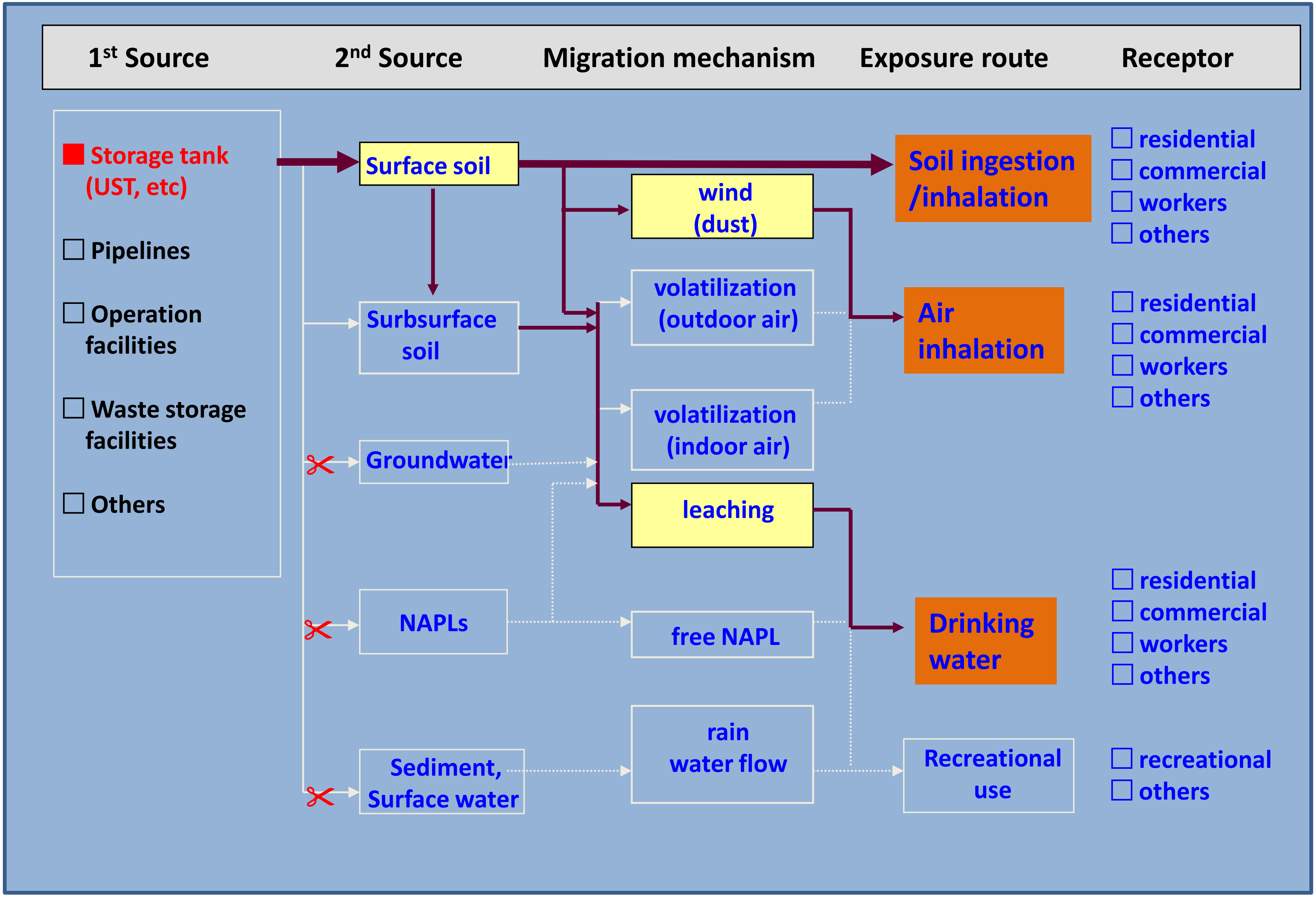
	Residential	Commercial
d (lower depth of surficial soil zone, cm)	100	100
ER (endosed-space air exchange rate, 1/sec)	0.00014	0.00023
f oc (fraction of organic carbon in soil, g-C/g-soil)	0.01	0.01
h cap (thickness of capillary fringe, cm)	5	5
h v (thickness of vadose zone, cm)	295	295
I (infiltration rate of water through soil, cm/years)	[illegible]	[illegible]
L B (enclosed-space volume/infiltration area ratio, cm)	[illegible]	[illegible]
L crack (enclosed-space foundation or wall thickness, cm)	15	15
Ls (depth to subsurface soil source, cm)	100	100
Pe (particulate emission rate, g/cm2-s)	6.9e-14	6.9e-14
U air (wind speed in ambient mixing zone, cm/s)	225	225
U gw (groundwater Darcy velocity, cm/year)	2500	2500
W (width of source area parallel to wind, cm)	[illegible]	[illegible]
δ air (ambient air mixing zone height, cm)	[illegible]	[illegible]
δ gw (groundwater mixing zone thikness, cm)	200	200
η (areal fraction of cracks, cm2-cracks/cm2-total area)	0.01	0.01
ρs (soil bulk density, g-soil/cm3-soil)	1.7	1.7
τ (averaging time for vapor flux, s)	9.46e8	7.48e8
T (temperature, ℃)	20	20

Risk assessment involves “uncertainty”

Site-specific parameters & predictions

More reliable assessment possible!

2. Conceptual site model: An example



1st Source | 2nd Source | Migration mechanism | Exposure route | Receptor

■ Storage tank (UST, etc)
☐ Pipelines
☐ Operation facilities
☐ Waste storage facilities
☐ Others

Surface soil
Surbsurface soil
✂ Groundwater
✂ NAPLs
✂ Sediment, Surface water

wind (dust)
volatilization (outdoor air)
volatilization (indoor air)
leaching
free NAPL
rain water flow

Soil ingestion /inhalation
Air inhalation
Drinking water
Recreational use

☐ residential
☐ commercial
☐ workers
☐ others

☐ residential
☐ commercial
☐ workers
☐ others

☐ residential
☐ commercial
☐ workers
☐ others

☐ recreational
☐ others

3. Exposure route identification

○ Air: inhalation of indoor/outdoor air

○ Groundwater: groundwater ingestion

inhalation of pollutants volatilized from groundwater

○ Subsurface soil: leaching to groundwater

inhalation of pollutants volatilized from subsurface

○ Surface soil: soil ingestion, dermal contact, particle inhalation

Target Clean-up Levels

- $\mathrm{TCL}_{\mathrm{air}}$ ($\mathrm{mg/m^3}$)
- $\mathrm{TCL}_{\mathrm{groundwater}}$ (mg/L)
- $\mathrm{TCL}_{\mathrm{subsurface\ soil}}$ (mg/kg)
- $\mathrm{TCL}_{\mathrm{surfice\ soil}}$ (mg/kg)

오염농도에 따른 발암위해성 산정 (예)

◆ 벤젠으로 오염된 토양으로부터 주거지 실내공기의 흡입으로 인해 성인이 입게 되는 위해성의 산정

현장상황

. 오염물질; 벤젠 (발암성)

. 수용체; 성인

. 노출경로; 주거지 실내공기 흡입으로 인한 노출

입력변수

. 벤젠오염농도; 1 μg/m^3

. 벤젠의 $SF_{inhalation}$; 0.029 kg–day/mg

. 실내공기흡입률; 15 m^3/일

. 노출기간; 30 년

. 노출빈도; 350 일/년

. 평균기간; 70 년

. 체중; 70 kg

$$\text{발암위해성} = \frac{(1\ \mu g/m^3) * (350\ \text{일/년}) * (30\ \text{년}) * (15\ m^3/\text{일}) * (0.029\ kg\text{–}day/mg)}{(70\ kg) * (70\ \text{년}) * (365\ \text{일/년}) * (1{,}000\ \mu g/mg)} = 2.55 \times 10^{-6}$$

목표위해성에 따른 정화수준 산정 (예)

♦ 벤젠으로 오염된 토양으로부터 주거지 실내공기의 흡입으로 인한 위해성으로부터 성인을 보호하기 위한 목표정화수준의 산정

현장상황

. 오염물질; 벤젠 (발암성)

. 수용체; 성인

. 노출경로; 주거지 실내공기 흡입으로 인한 노출

입력변수

. 목표위해성; 10^{-6}

. 벤젠의 $SF_{inhalation}$; 0.029 kg−day/mg

. 실내공기흡입률; 15 m^3/일

. 노출기간; 30 년

. 노출빈도; 350 일/년

. 평균기간; 70 년

. 체중; 70 kg

$$\text{목표정화수준} = \frac{(10^{-6})*(70\ \text{kg})*(70\ \text{년})*(365\ \text{일/년})*(1{,}000\ \mu\text{g/mg})}{(350\ \text{일/년})*(30\ \text{년})*(15\ \text{m}^3/\text{일})*(0.029\ \text{kg−day/mg})} = 0.39\ \mu\text{g/m}^3$$

주요노출인자 기본값 (1)

토지이용용도별

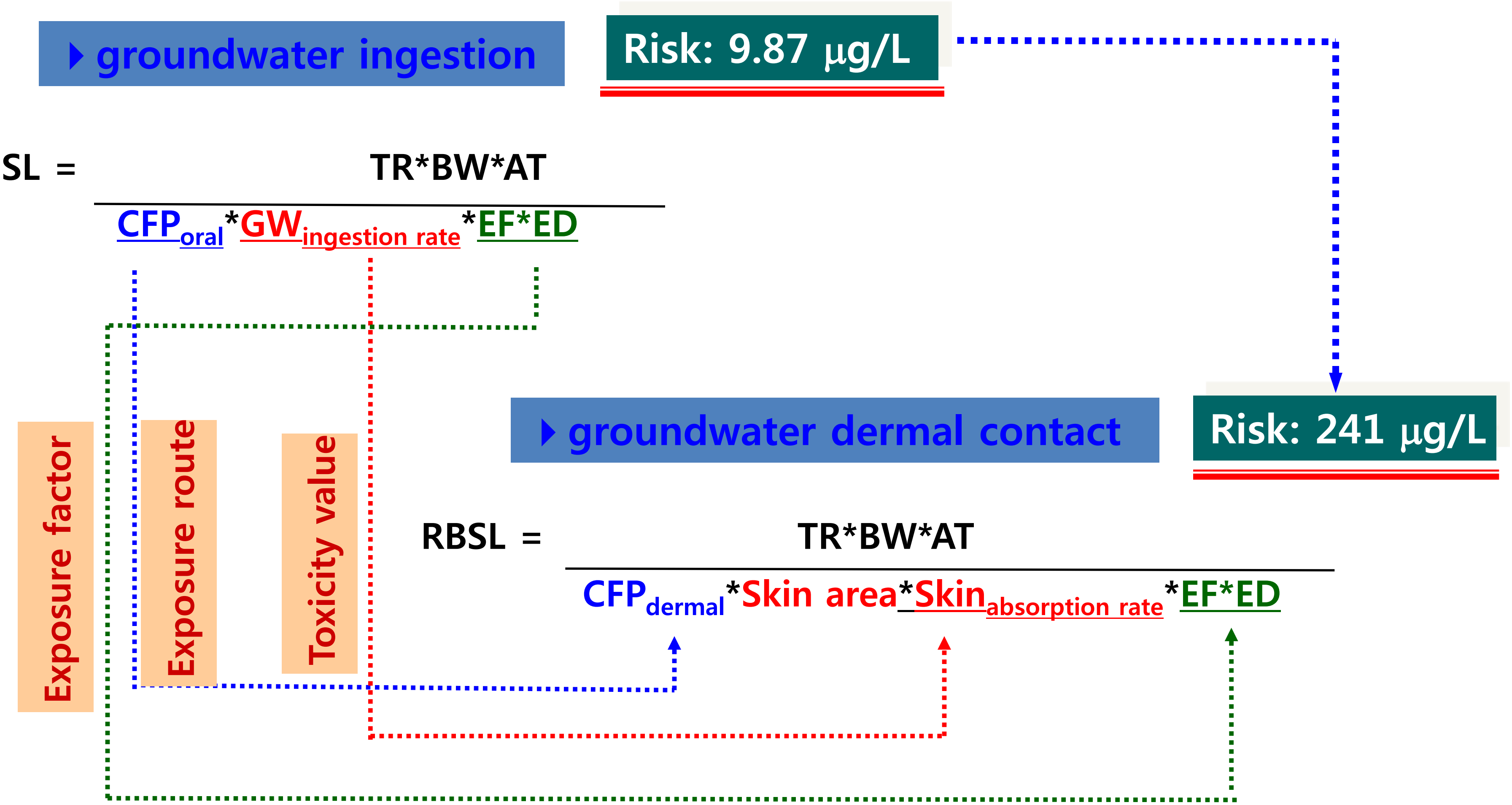
Parameters	Definition (units)	Residential	Commercial/ Industrial
ATc	발암성물질에 대한 평균노출기간 (years)	70 (73.5)	70
ATn	비발암성물질에 대한 평균노출기간 (years)	30	25
BW	성인평균체중 (kg)	70 (60.0)	70
ED	노출기간 (years)	30	25
EF	노출빈도 (days/years)	350 d/yr	250 d/yr
IR_{soil}	토양 섭취률 (mg/day)	100	50
IR_{air} (indoor)	일일 실내공기 흡입률 (m^3/day)	15	20
IR_{air} (outdoor)	일일 실외공기 흡입률 (m^3/day)	20	20
IR_w	일일 물 섭취량 (L/day)	2 (1.26)	1

주요노출인자 기본값 (2)

토지이용용도별

Parameters	Definition (units)	Residential	Commercial/ Industrial
M	토양-피부접촉계수 (mg/cm^2)	0.5	0.5
SA	피부표면적 (cm^2/day)	3160	3160
RAF_d	피부를 통한 흡수계수, BTEX/PAHs	chemical-specific	
RAF_o	섭취를 통한 흡수계수	1	1
LFsw	토양-지하수 용출 계수 ($mg/L\text{-}H_2O)/(mg/kg\text{-}soil$)	chemical-specific	
VF	휘발계수 토양-공기 ($mg/m^3\text{-}air)/(mg/kg\text{-}soil$) 지하수-공기 ($mg/m^3\text{-}air)/(mg/L\text{-}H_2O$)	chemical-specific	

Risk variation by exposure routes (e.g., benzene)



- groundwater ingestion

Risk: 9.87 µg/L

$$RBSL = \frac{TR*BW*AT}{CFP_{oral}*GW_{ingestion\ rate}*EF*ED}$$

- groundwater dermal contact

Risk: 241 µg/L

$$RBSL = \frac{TR*BW*AT}{CFP_{dermal}*Skin\ area*Skin_{absorption\ rate}*EF*ED}$$

수돗물과 생수...


DILBERT
OUR SAFETY DEPARTMENT HAS TESTED OUR DRINKING WATER AND FOUND NO PROBLEM.
THEN WHY DO YOU ONLY DRINK BOTTLED WATER?
BECAUSE THAT'S WHAT THE SAFETY DEPARTMENT DRINKS.
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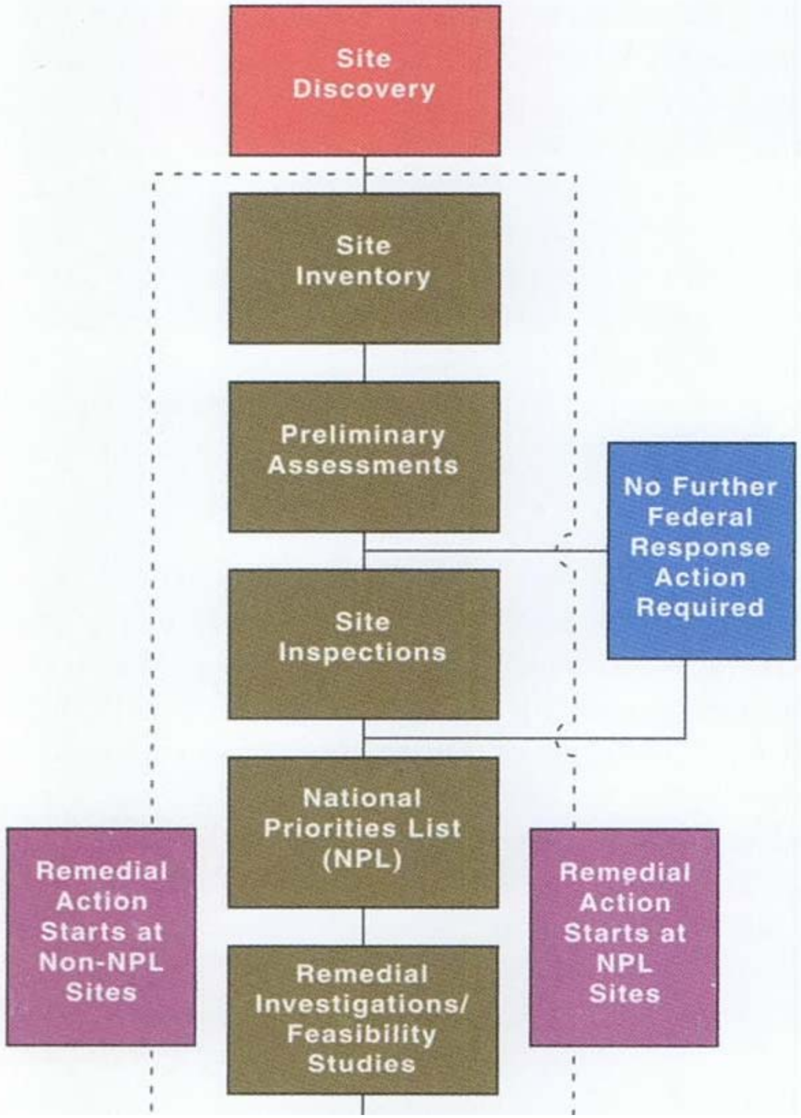
(Lecture 12)

ESP Ch 19. Soil and groundwater remediation



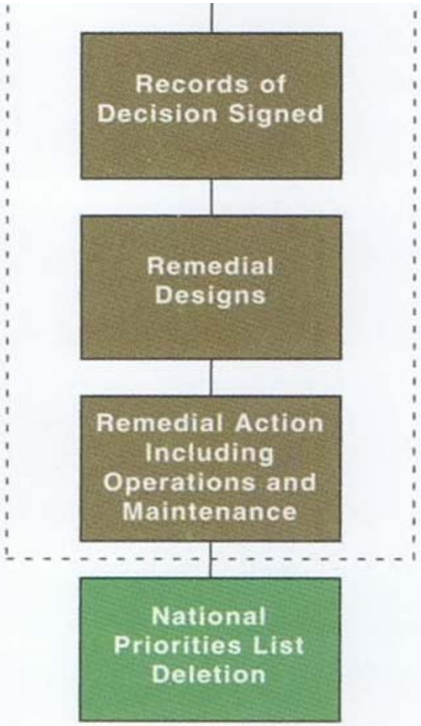


Figure 19.1 The Superfund process for evaluating and remediating a hazardous-waste site. Adapted from U.S. EPA, 1998. From *Environmental Monitoring and Characterization* © 2004, Elsevier Academic Press, San Diego, CA.

- Site characterization
  - type, location, amount
  - NAPL (free product) present?
  - remedial options

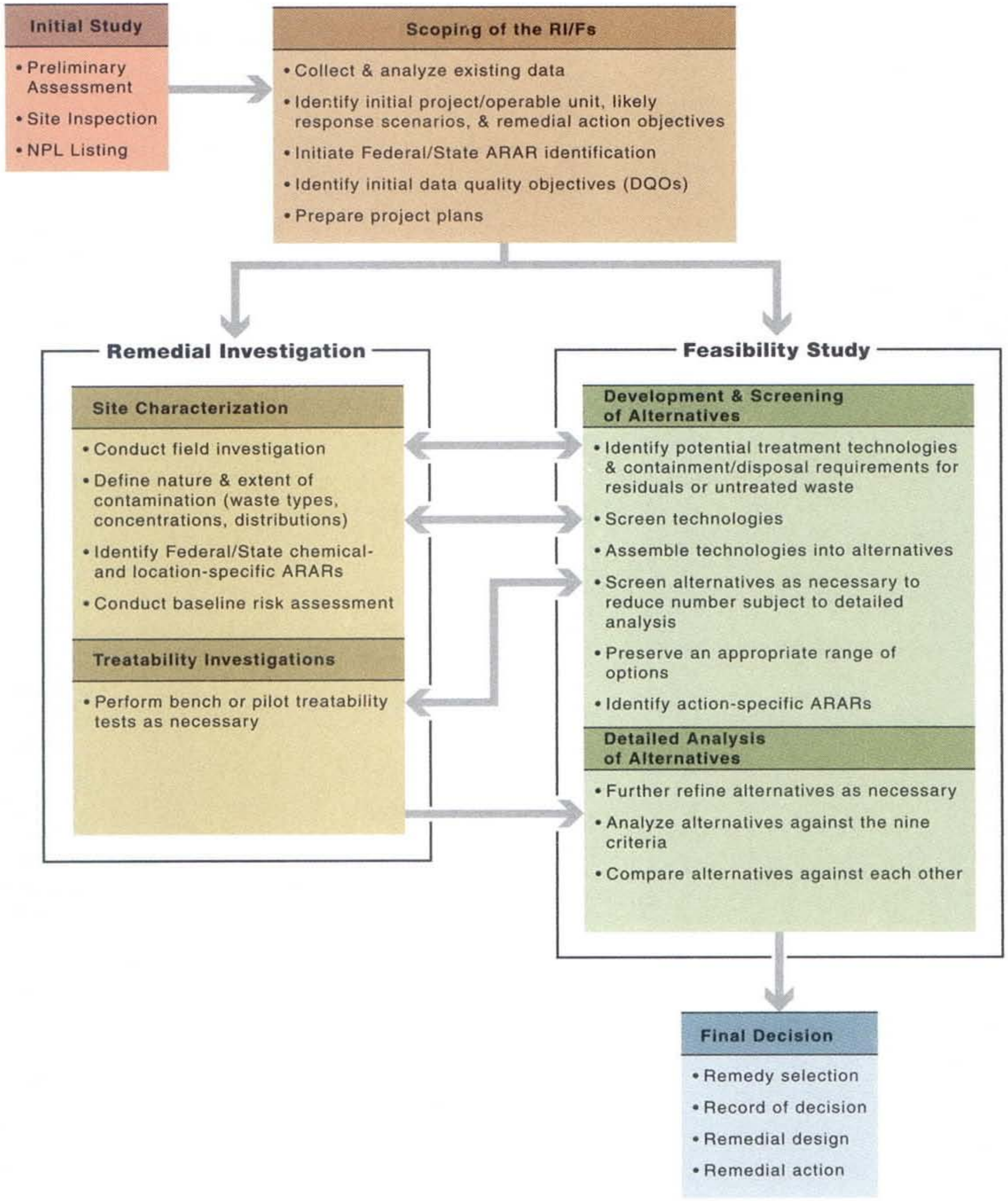


Figure 19.2 The remedial investigation/feasibility study process (RI/FS). Adapted from U.S. EPA, 1998. From *Environmental Monitoring and Characterization* © 2004, Elsevier Academic Press, San Diego, CA.

- Remediation technologies
  - principles: containment, removal, treatment

✓ Containment technologies
  - physical barrier
  - hydraulic barrier
  - immobilization (solidification/stabilization)…

✓ Removal technologies
  - excavation
  - pump-and-treat
  - soil vapor extraction (SVE); permeability
  - air sparging,

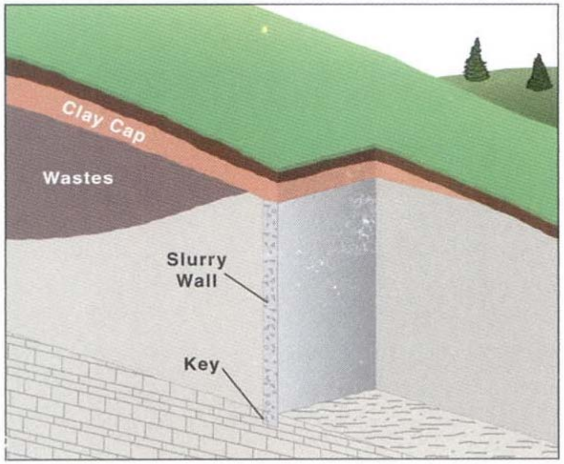


Figure 19.3 Physical containment of a groundwater contaminant plume with the use of a slurry wall. From *Environmental Monitoring and Characterization* © 2004, Elsevier Academic Press, San Diego, CA.

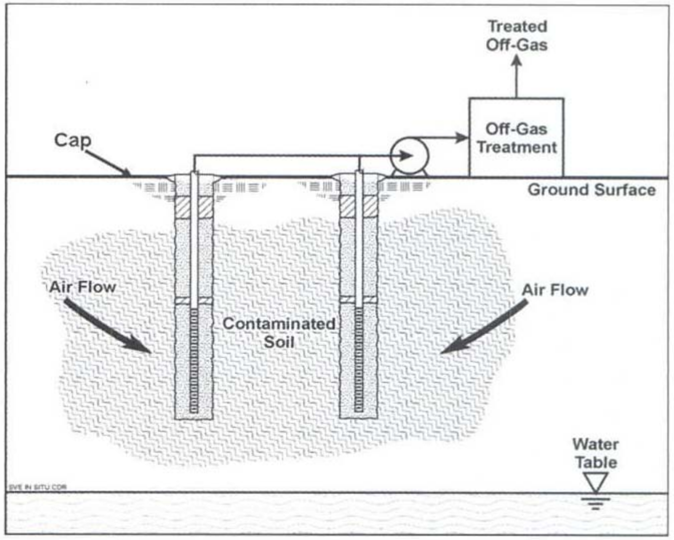


Figure 19.6 Schematic of a soil venting system for remediation of volatile organic contamination in the vadose zone. Image courtesy of U.S. Navy. http://enviro.nfesc.navy.mil/erb/restoration/technologies/remed/phys_chem/phc-26.asp.

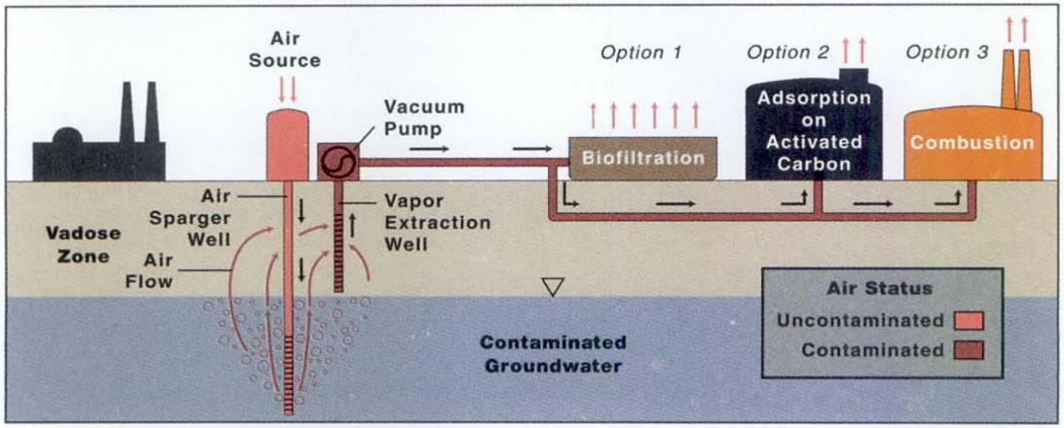


Figure 19.8 Air sparging to remove volatile contaminants from the saturated zone. The contaminated air extracted from the system can be treated above-ground using a number of different methods. Adapted from National Research Council, 1993. From *Environmental Monitoring and Characterization* © 2004, Elsevier Academic Press, San Diego, CA.

- *In situ* treatment
  - bioremediation
  - chemical treatment: Fenton’s reagent…

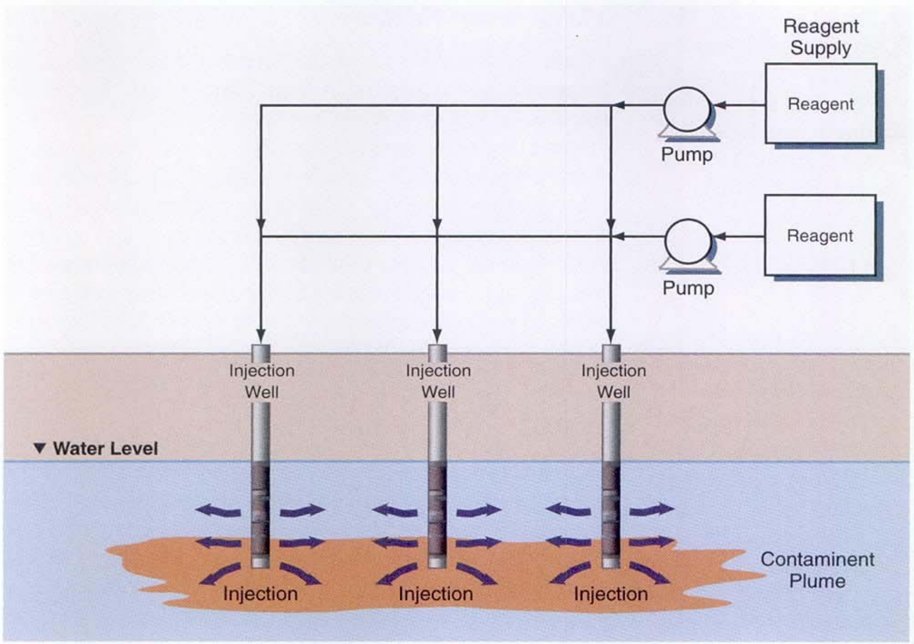


Figure 19.10 *In situ* remediation of a contaminated saturated zone using biological or chemical methods. Image courtesy of the U.S. Navy.

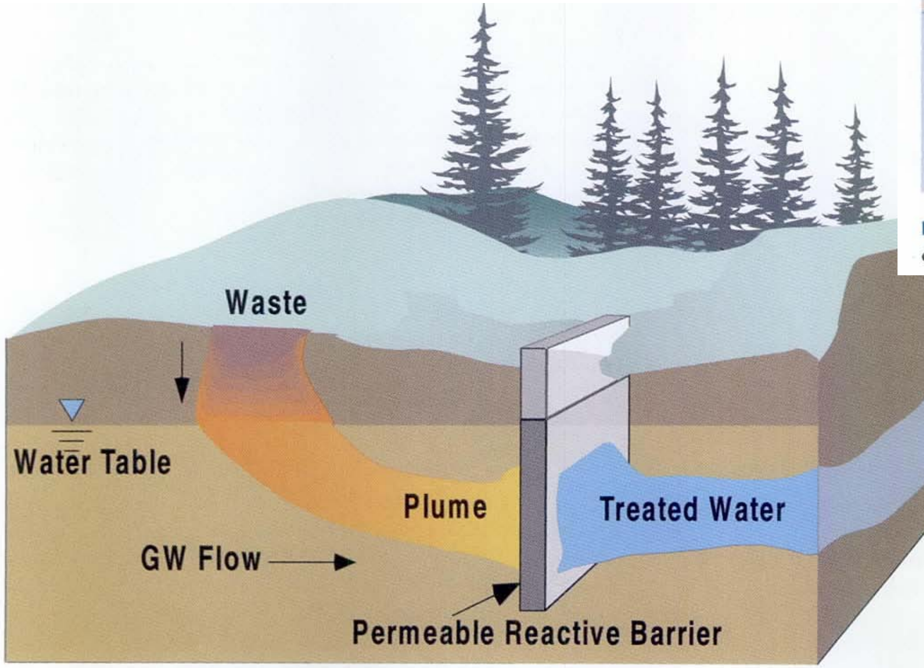


Figure 19.11 *In situ* treatment of a groundwater contaminant plume using a permeable reactive wall. Photo courtesy of US EPA. (EPA/600/R-98/125 September 1998; http://www.clu-in.org/download/rtdf/prb/reactbar.pdf)

- Others
  - soil washing
  - magnetic separation
  - electrokinetic treatment…

- Phytoremediation
  - accumulation; hyperaccumulators
  - stabilization
    - . root exudates
    - . rhizobacterial activity
  - plants as hydraulic barriers

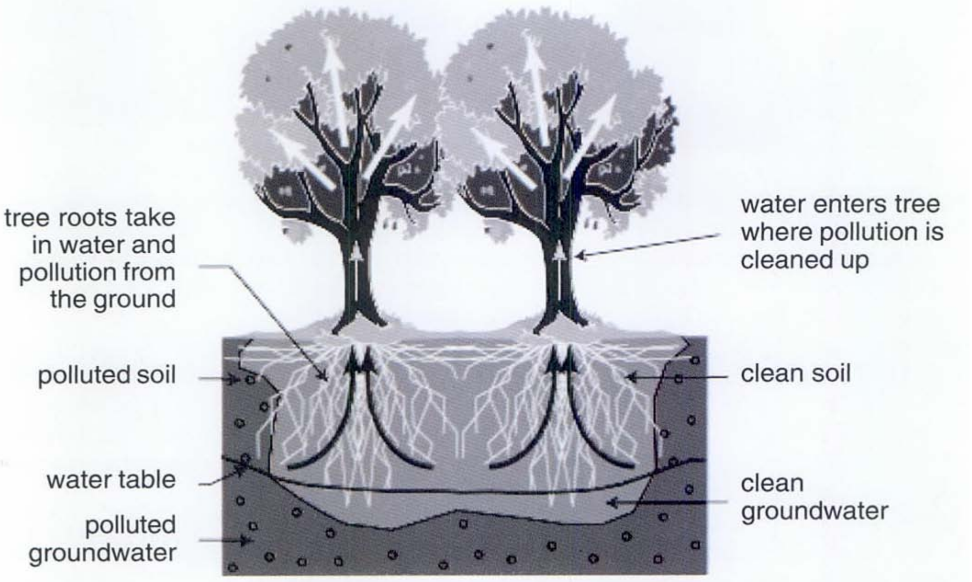


Figure 19.12 Use of plants for phytoremediation. Image courtesy of the US EPA. (http://clu-in.org/download/citizens/citphyto.pdf; EPA 542-F-01-002 April 2001)

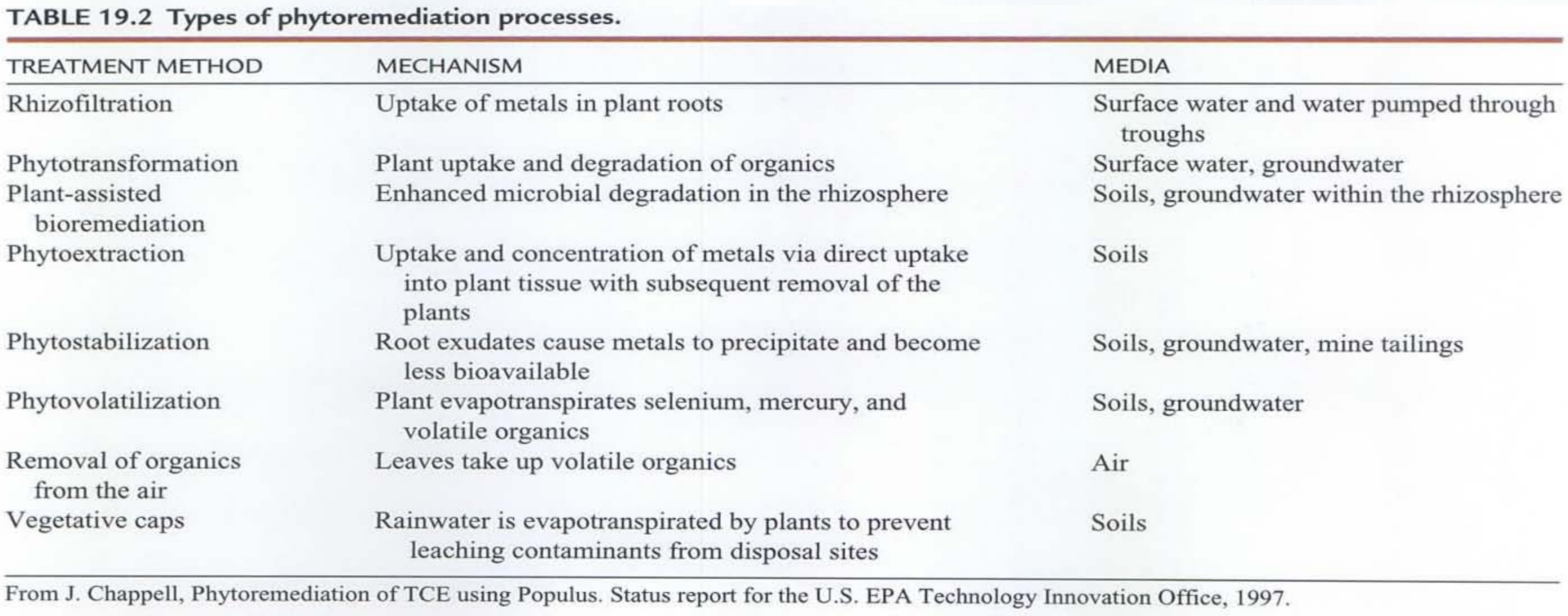


TABLE 19.2 Types of phytoremediation processes.

TREATMENT METHOD	MECHANISM	MEDIA
Rhizofiltration	Uptake of metals in plant roots	Surface water and water pumped through troughs
Phytotransformation	Plant uptake and degradation of organics	Surface water, groundwater
Plant-assisted bioremediation	Enhanced microbial degradation in the rhizosphere	Soils, groundwater within the rhizosphere
Phytoextraction	Uptake and concentration of metals via direct uptake into plant tissue with subsequent removal of the plants	Soils
Phytostabilization	Root exudates cause metals to precipitate and become less bioavailable	Soils, groundwater, mine tailings
Phytovolatilization	Plant evapotranspirates selenium, mercury, and volatile organics	Soils, groundwater
Removal of organics from the air	Leaves take up volatile organics	Air
Vegetative caps	Rainwater is evapotranspirated by plants to prevent leaching contaminants from disposal sites	Soils

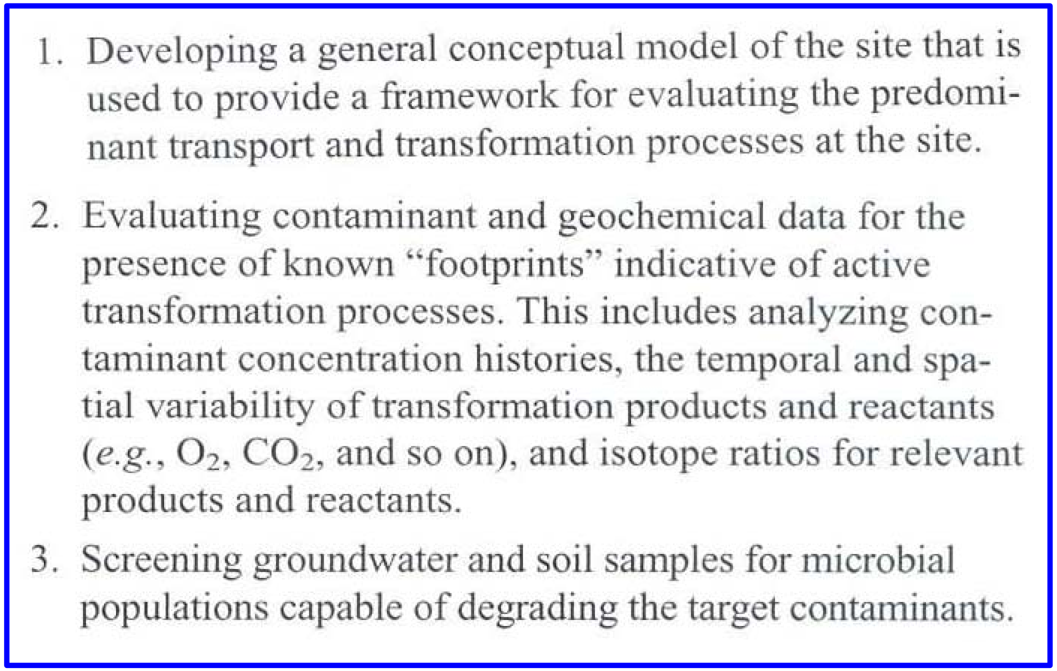
From J. Chappell, Phytoremediation of TCE using Populus. Status report for the U.S. EPA Technology Innovation Office, 1997.

- Monitored natural attenuation (MNA)
  - restricted application only where appropriate and needed
  - prerequisites
    - . “Are MNA process occurring at the site?”
    - . “Is the magnitude and rate of MNA sufficient to accomplish the remediation goal?”

✓ long-term site monitoring is important

✓ geochemical indicators

✓ be protective to human health and the environment



1. Developing a general conceptual model of the site that is used to provide a framework for evaluating the predominant transport and transformation processes at the site.
2. Evaluating contaminant and geochemical data for the presence of known “footprints” indicative of active transformation processes. This includes analyzing contaminant concentration histories, the temporal and spatial variability of transformation products and reactants (*e.g.*, O_2, CO_2, and so on), and isotope ratios for relevant products and reactants.
3. Screening groundwater and soil samples for microbial populations capable of degrading the target contaminants.

■ Monitored Natural attenuation (MNA)

"needs to show favorable processes are ongoing at the site“

- plume management technique - usu. for ground water remediation
- rationales
  - ground water (aquifer) contaminated by DNAPLs -> residual NAPLs
    → limitation of conventional means (e.g., pump-and-treat)
  - plumes; relatively short, not expanding, and little or no risk

<u>* Plume life cycle</u>

. <u>expanding</u>: residual source present. mass flux of contaminants exceeds assimilative capacity of aquifer

. <u>stable</u>: insignificant change. remediation processes are controlling plume length

. <u>shrinking</u>: residual source nearly exhausted. remediation processes significantly reduce plume mass

. <u>exhausted</u>: average plume conc. very low (e.g., 1 ppb) and unchanging over time

- key factors determining applicability
  . plume stability
  . required time frame...
  . site information (monitoring factors for MNA)…

- Attenuation processes
  1) dispersion;
    a. mixing process caused by
      - ground water movement (velocity variations) in porous media
      - aquifer heterogenicities (--> flow velocity and path)
    b. results in sharp edge and dilution of solutes at the edge
  2) sorption; represented by retardation factor
  3) degradation; biotic and abiotic (hydrolysis of chlorinated solvents...)
  4) dilution

❖ <u>insignificant factors</u>
  a. diffusion
    - molecular mass transfer by concentration gradients
    - can occur in the absence of velocity
    - only a factor in the case of very low velocities (tight soil, clay liner) or of mass transfer involving very long time periods
  b. volatilization
  c. advection; movement of contaminants along with flowing ground water

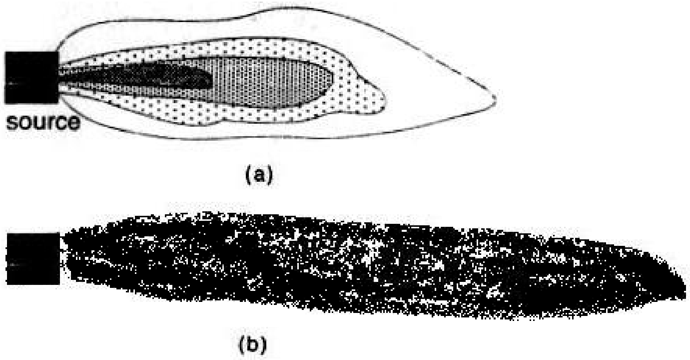


Figure 6.3 (a) Advection and dispersion. (b) Advection only.

- Geochemical indicators
  - a. consumption of electron acceptors used for oxidative reactions (e.g., dissolved oxygen, nitrate, sulfate in the plume area...)
  - b. production of metabolic by-products (e.g., ferrous iron, methane, c-DCE, VC, ethene...)
  - c. presence of appropriate redox/microbial environments (e.g., dissolved hydrogen...)

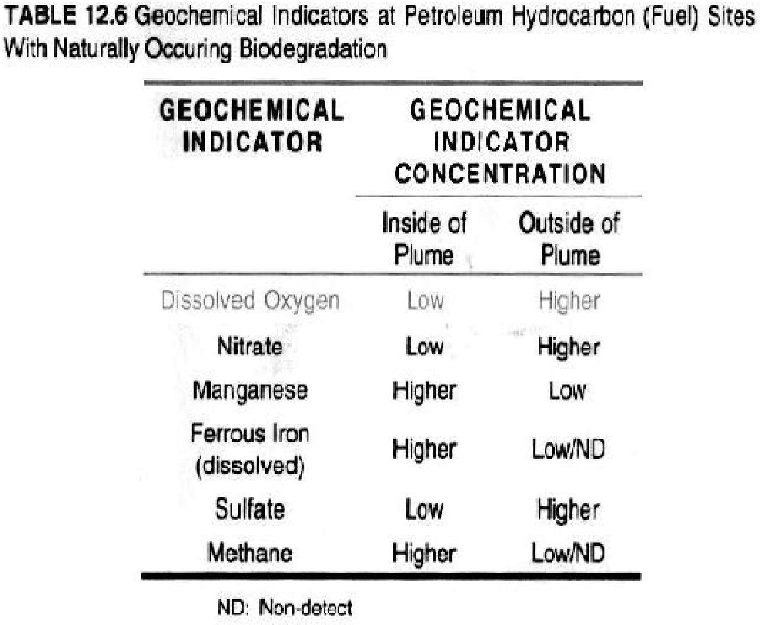


TABLE 12.6 Geochemical Indicators at Petroleum Hydrocarbon (Fuel) Sites With Naturally Occuring Biodegradation

GEOCHEMICAL INDICATOR	GEOCHEMICAL INDICATOR CONCENTRATION	
	Inside of Plume	Outside of Plume
Dissolved Oxygen	Low	Higher
Nitrate	Low	Higher
Manganese	Higher	Low
Ferrous Iron (dissolved)	Higher	Low/ND
Sulfate	Low	Higher
Methane	Higher	Low/ND

ND: Non-detect

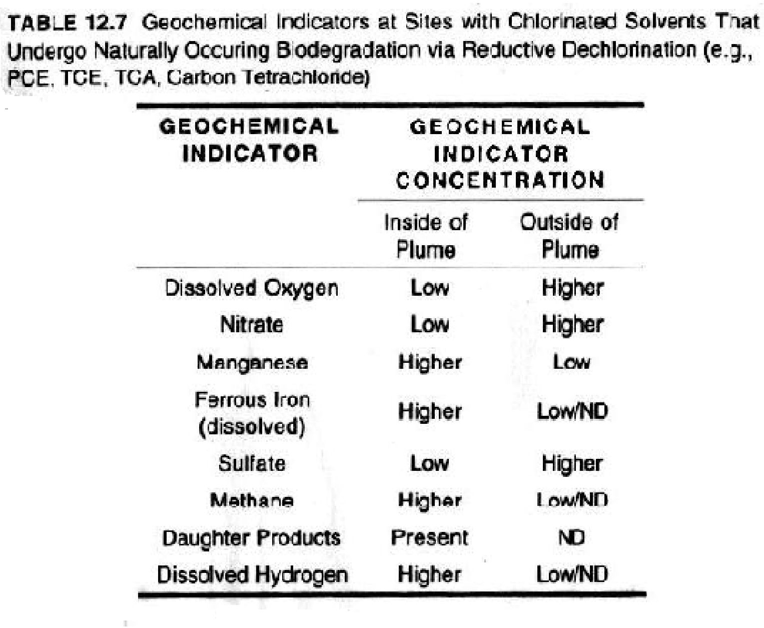
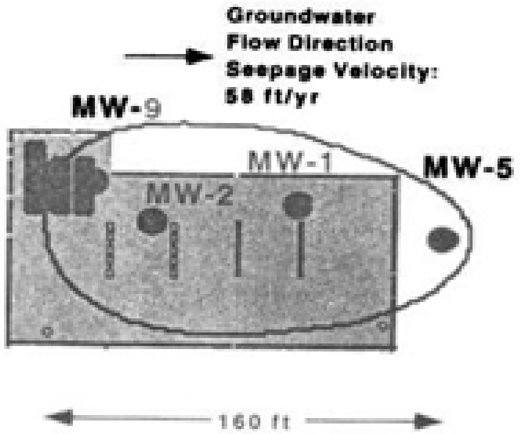


TABLE 12.7 Geochemical Indicators at Sites with Chlorinated Solvents That Undergo Naturally Occuring Biodegradation via Reductive Dechlorination (e.g., PCE, TCE, TCA, Carbon Tetrachloride)

GEOCHEMICAL INDICATOR	GEOCHEMICAL INDICATOR CONCENTRATION	
	Inside of Plume	Outside of Plume
Dissolved Oxygen	Low	Higher
Nitrate	Low	Higher
Manganese	Higher	Low
Ferrous Iron (dissolved)	Higher	Low/ND
Sulfate	Low	Higher
Methane	Higher	Low/ND
Daughter Products	Present	ND
Dissolved Hydrogen	Higher	Low/ND

- Attenuation rate calculation
  a. bulk attenuation rate (*k*); just indicates whether conc. declines or not...
  b. biodegradation rate (λ); attenuation rate model FATE V...

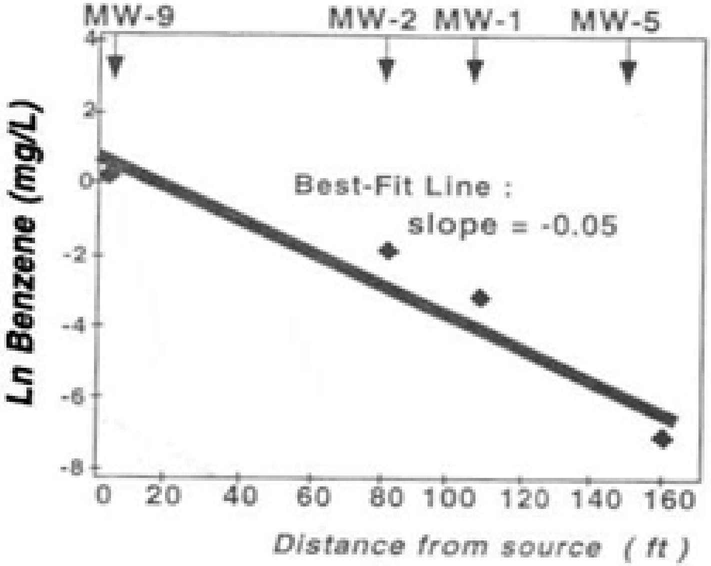
- Risk-based corrective action (RBCA); developed by ASTM (1995)
  a. identification of applicable risk factors on a site-specific basis
  b. identification of potential mechanisms for exposure
  on a site specific basis



➢ <u>SSTL = RBEL x NAF</u>
SSTL; site-specific target level
NAF; natural attenuation factor (rate; *k*)
RBEL; risk-based exposure limit at POE
(usu. standard level..)
POE; point of exposure

✓ if, measured or calculated
source conc. > SSTL-> remediation required

✓ if not, no further action required (based on RBCA)
→ monitoring!!!



(*K* = -slope*seepage velocity)

Summary: Remediation technologies

행정간행물등록번호
11-1480000-000841-01

오염토양 정화방법 가이드라인

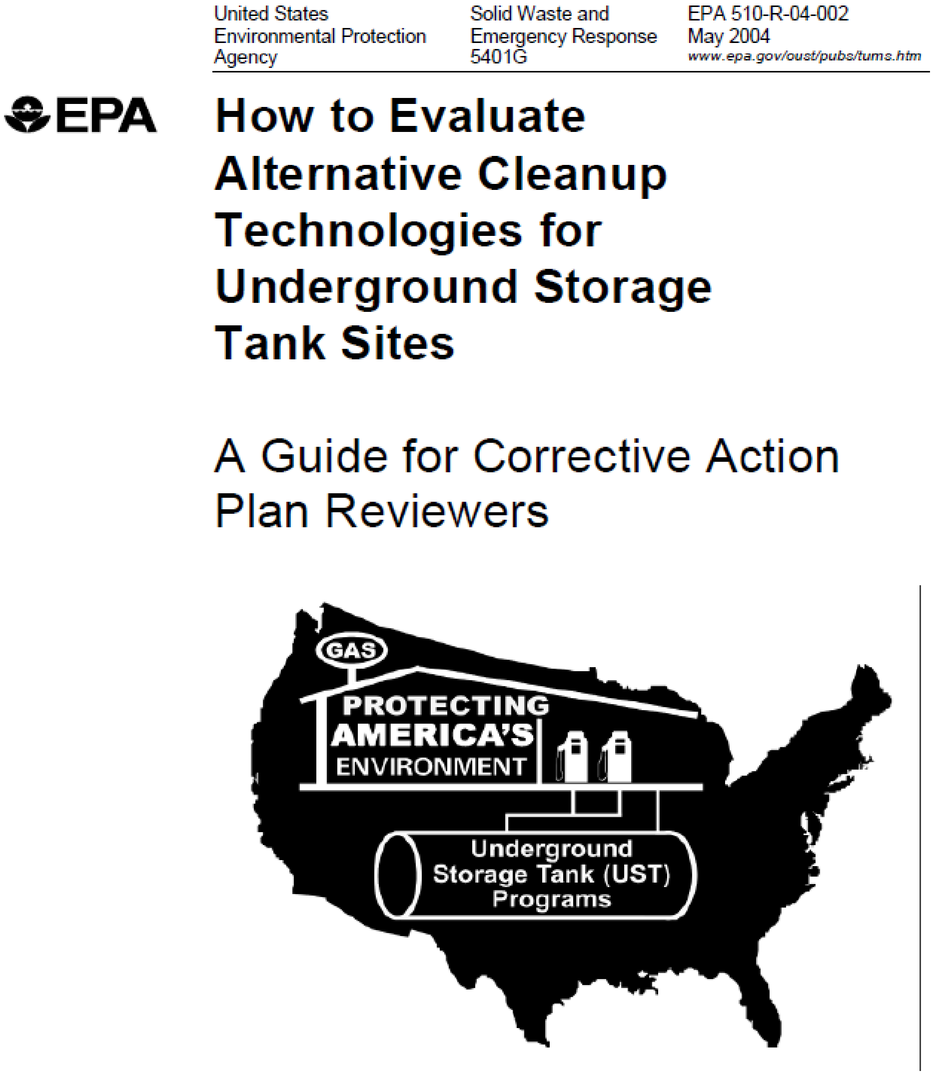
2007

오염토양 정화방법 가이드라인

2007

환경부

mev 환경부



United States
Environmental Protection
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EPA 510-R-04-002
May 2004
www.epa.gov/oust/pubs/tums.htm

EPA

How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites

A Guide for Corrective Action Plan Reviewers

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오염지역 정화 및 복원기술 (1)

1) 생물학적 정화기술 (개요)

정의 및 원리

- (미)생물의 오염물질 분해 능력을 이용하여 오염토양 또는 지하수를 처리하는 기술
- 가수분해, cleavage, 산화, 환원, 탈수소화, 탈염소화, dehyrrohalogenation, 치환 등의 효소 촉매반응
- 공대사(Cometabolism) : 다른 물질을 분해하는 미생물의 효소에 의하여 우연히 일어나는 분해과정으로 탄소원이나 에너지원으로 이용되지 않음
- 전자수용체에 따라 호기성(O_2), 혐기성(NO_3^-, SO_4^{2-}, CO_2), 발효(유기물)로 구분

장단점

장점	단점
현장처리(In-situ/On-site) 가능	일부 오염성분의 난분해성
오염성분의 궁극적 제거	처리효과가 부지 특성의 영향 받음
비교적 저렴	처리/사후 감시기간이 김
타 기술과 연계 용이	미지/독성 중간물질 생성 가능성
부지/토양 특성변형 최소화	기술의 신뢰성에 대한 인식문제
주민 친화성 양호	기술 집약적

오염지역 정화 및 복원기술 (2)

2) 생물학적 정화기술 (원리)

효소촉매반응 Enzyme Reaction

- **Hydrolysis** : Exoenzyme에 의해서 이루어지는 반응. 물이 첨가되어 유기물분자가 간단한 형태로 끊어지는 반응
- **Cleavage** : 탄소-탄소의 단일/이중결합이 끊어지는 반응.
- **Oxidation** : Electrophilic form을 이용하여 유기물이 분해되는 반응
- **Reduction** : Nucleophilic form이나 직접적인 전자전달을 이용하여 유기화합물이 분해되는 반응
- **Dehydrogenation** : 수소 원자 2개를 잃음으로써 두 개의 전자와 두 개의 수소를 잃는 산화환원반응
- **Dechlorination** : 염소계 화합물이 전자수용체로 이용되어 염소가 떨어지고 수소원자가 붙는 반응
- **Dehydrohalogenation** : 유기화합물로부터 수소원자와 염소 원자가 떨어지는 반응
- **Substitution** : 한 원자가 다른 원자로 치환되는 반응

공대사 Cometaboilsm

- 어떤 기질을 분해하는 미생물의 효소가 낮은 기질특이성 때문에 에너지 생산이나 탄소 동화 등의 생장 과정과 관계없이 다른 기질 전환
- 오염물의 분해, 독성 감소 가능
- 염소계 지방족화합물, 다환성 방향족 화합물 등의 주요 분해기작

전자수용체 Electron Acceptor

호기성	산소 O_2
혐기성	Nitrate (질산) NO_3^- Sulfate (황산) SO_4^{2-} Carbon dioxide (이산화탄소) CO_2
발효	기질을 전자공여체와 전자수용체로 동시에 이용하며 지극히 혐기적인 조건에서 발생

오염지역 정화 및 복원기술 (3)

(참고) 생물학적 정화기술 적용사례

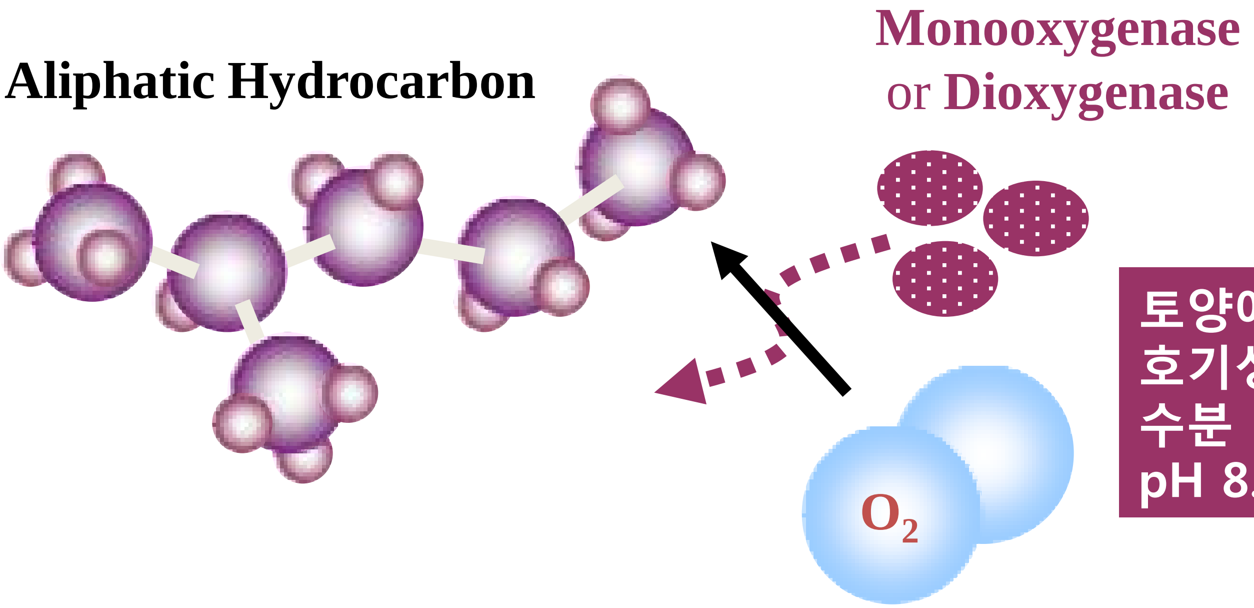
생물정화 대상오염물질 (미국)	
유류	29%
크레오소트류	29%
용매류	16%
기타 (살충제 등)	26%

Superfund 정화기술 적용사례 ('94)	
생물학적 정화	9% (원위치 4%, 지상 5%)
소각	30%
고형화/안정화	26%
SVE	17%
열탈착	6%
토양세척	6%
기타 (탈염화 등)	6%

오염지역 정화 및 복원기술 (4)

3) 생물학적 정화기술 (주요오염물의 분해 ①)

① Aliphatic Hydrocarbons 지방족 탄화수소



토양에 분해 미생물 多
호기성 분해
수분 50% 이상
pH 8.5 이하

종류 : Alkanes, Alkenes, Alcohols, Aldehydes, Ketones, Acids

분해되는 정도

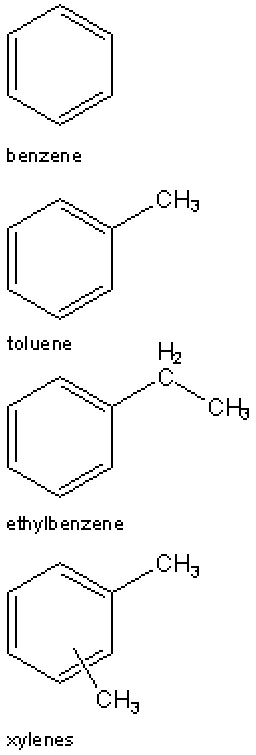
- Long Chain (C9 이상) > Short Chain
- Straight Chain > Branched Chain
- Saturated Hydrocarbons > Unsaturated Hydrocarbons

오염지역 정화 및 복원기술 (5)

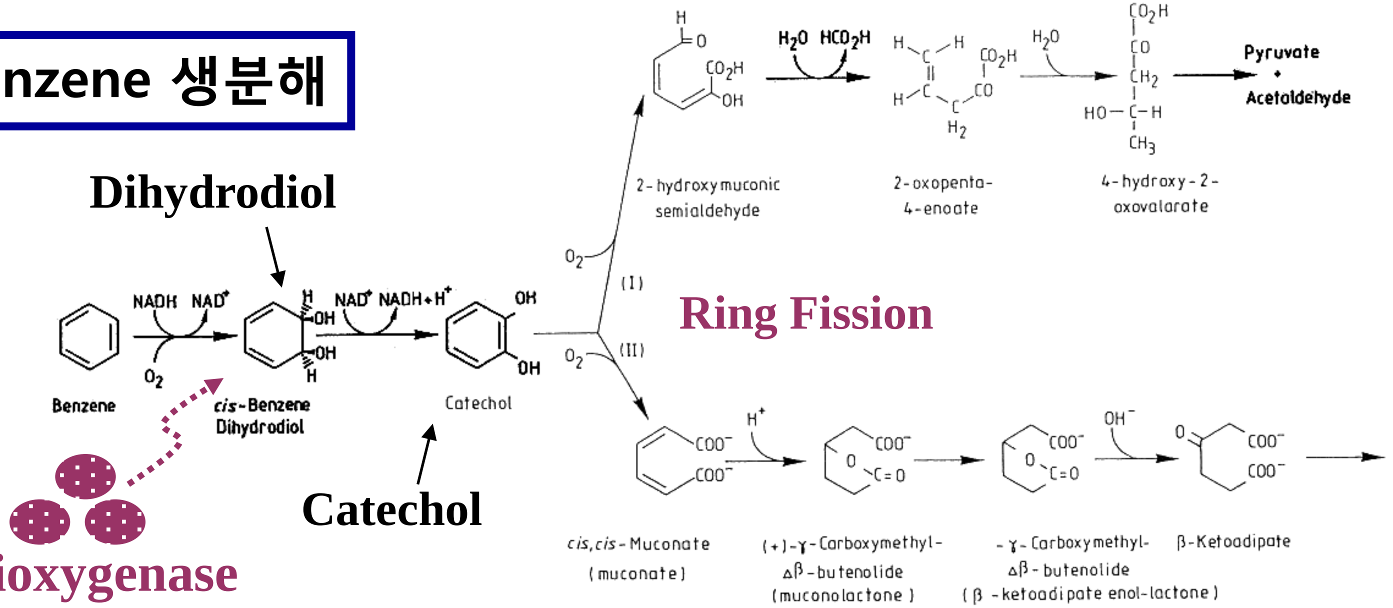
3) 생물학적 정화기술 (주요오염물의 분해 ②)

② Aromatic Hydrocarbons 방향족 탄화수소

BTEX



Benzene 생분해



Dihydrodiol

Catechol

Ring Fission

Dioxygenase

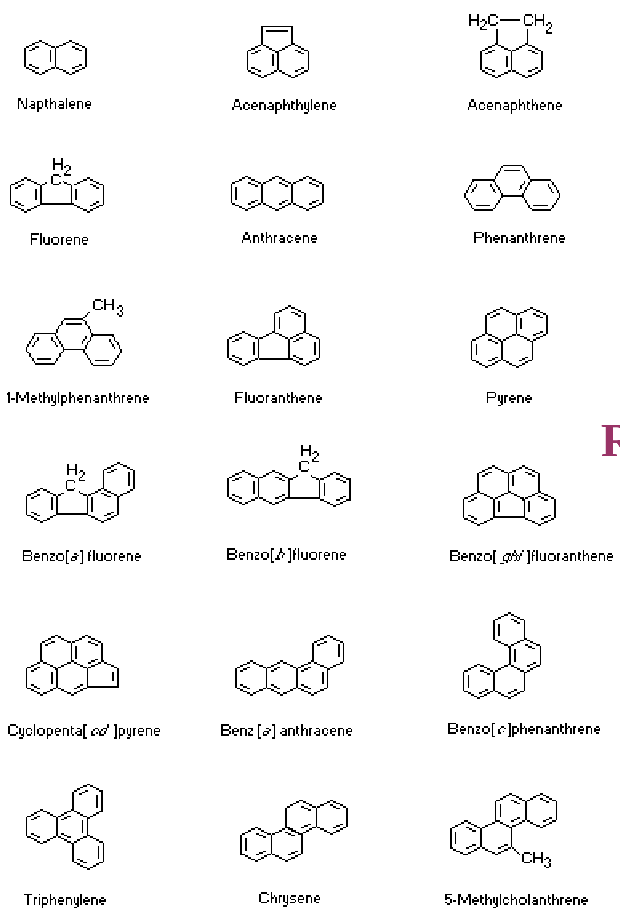
- 치환기의 위치, 수, 종류에 따라 분해성 차이
- 호기성 분해
- 탈질, 망간환원, 철환원, 황산염환원, 메탄생성 등 혐기조건에서도 분해
- 전자수용체의 이용가능성과 산화환원전위에 따라 결정

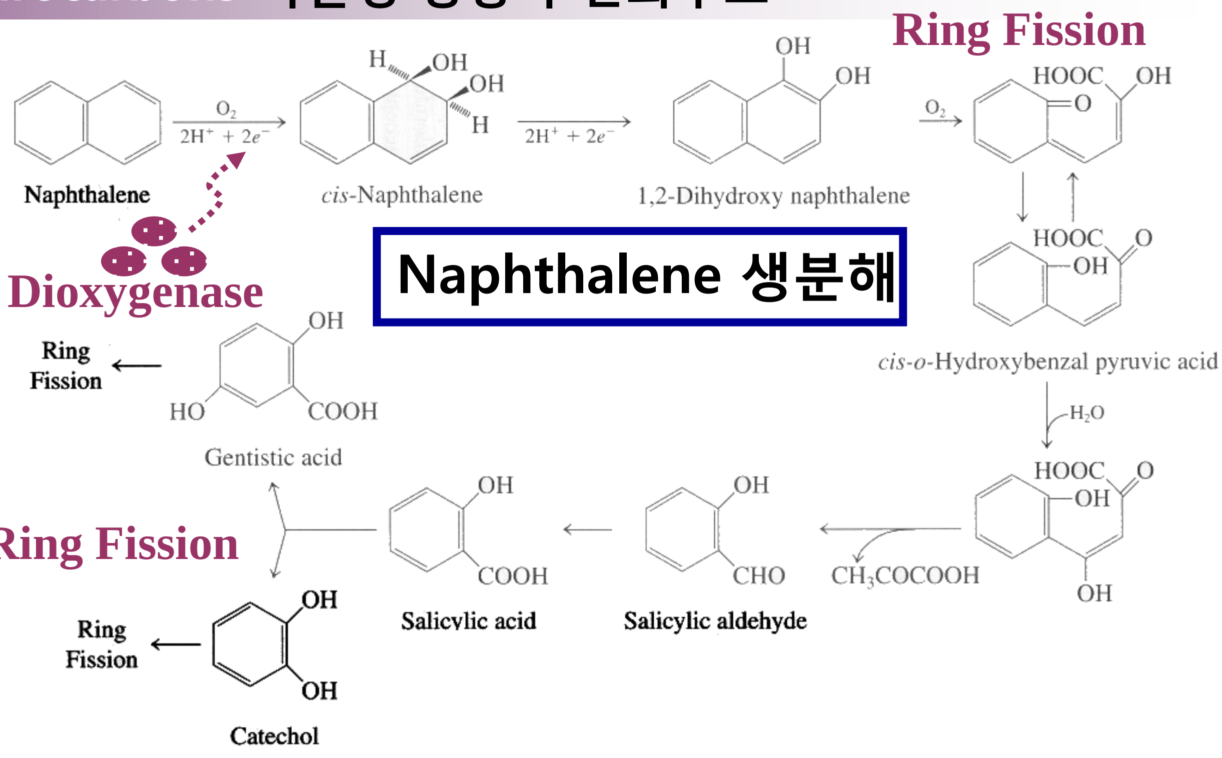
오염지역 정화 및 복원기술 (6)

3) 생물학적 정화기술 (주요오염물의 분해 ③)

③ Polycyclic Aromatic Hydrocarbons 다환성 방향족 탄화수소

Figure 1. Structural formulae of polycyclic aromatic hydrocarbons covered in this monograph



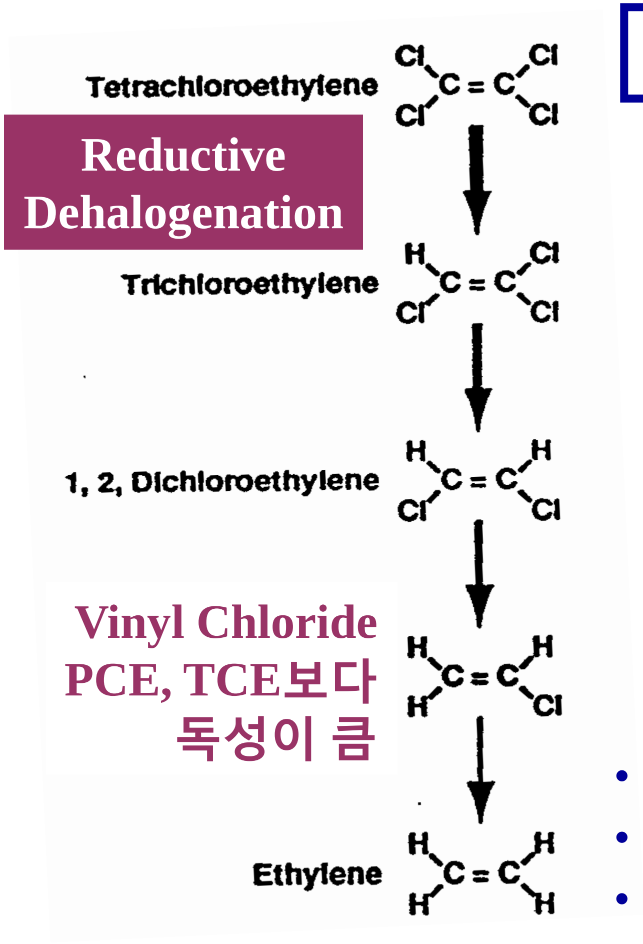


- 벤젠고리와 치환기의 수, 종류, 위치에 따라 분해성 차이
- 2~3 rings : 호기성 분해 & 혐기성 분해, 비교적 빠른 속도
- 4 rings 이상 : 큰 분해저항성 가짐
- 용해도 낮을수록 벤젠고리, 치환기 복잡할수록 분해 어려움

오염지역 정화 및 복원기술 (7)

3) 생물학적 정화기술 (주요오염물의 분해 ④)

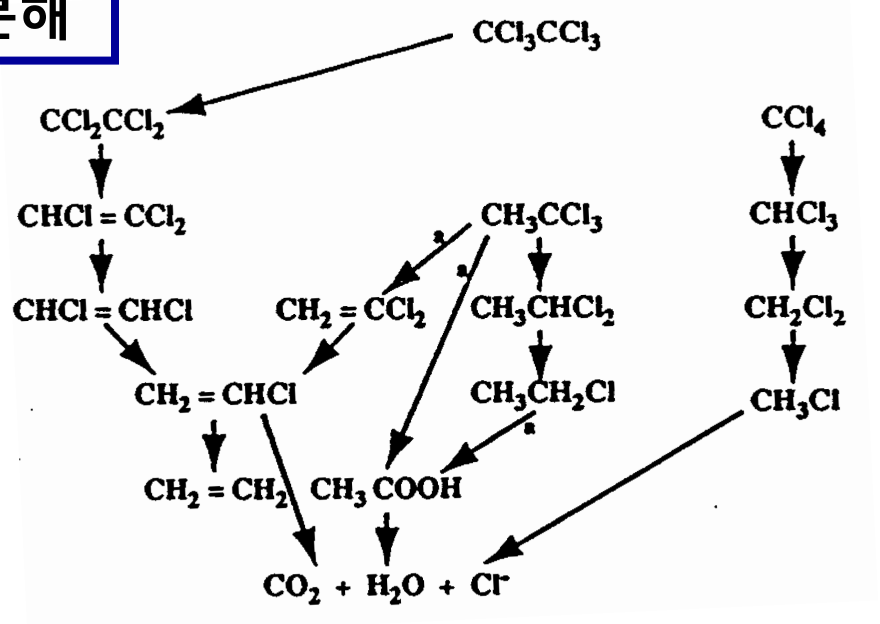
④ Chlorinated Aliphatic Hydrocarbons 염소계 지방족 탄화수소



Reductive Dehalogenation

Vinyl Chloride PCE, TCE보다 독성이 큼

PCE, TCE 생분해

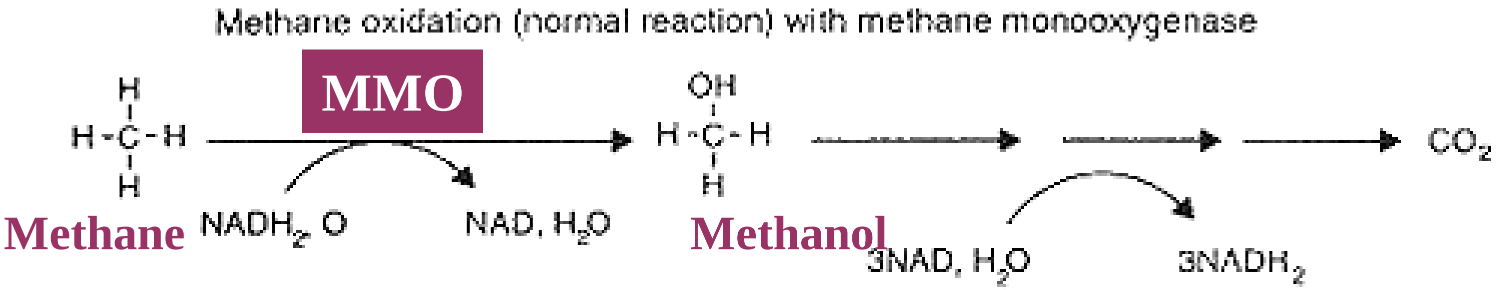


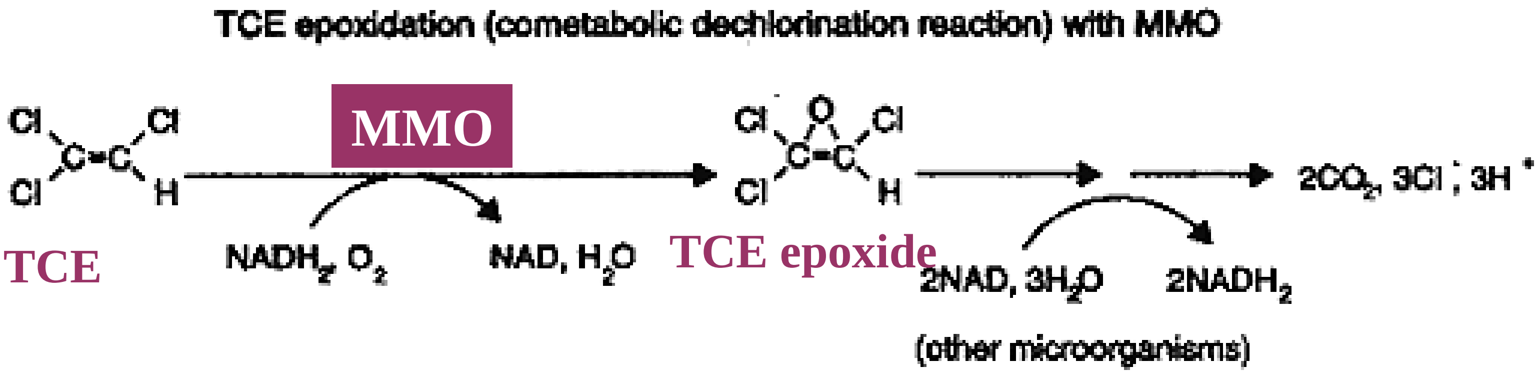
- 에너지원으로 산화/ 호기조건에서 공대사/ 혐기적 탈염소화
- 대부분 공대사에 의존
- (호기) Oxygenase, Dehalogenase, Hydrolytic dehalogenase

오염지역 정화 및 복원기술 (8)

3) 생물학적 정화기술 (주요오염물의 분해 ④)

(참고) Cometabolism of TCE by Methane Monooxygenase



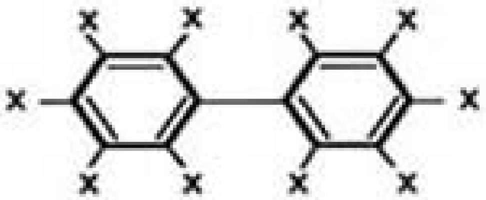


- Methanotrophic Bacteria가 생성하는 MMO의 기질특이성 부족으로 TCE 공대사가 일어남
- 메탄농도가 높으면 MMO에 대하여 TCE와 메탄이 경쟁할 수 있음
- PCE는 많이 산화된 상태이므로 공대사에 의해서도 분해되지 않음. 환원으로만 분해 가능

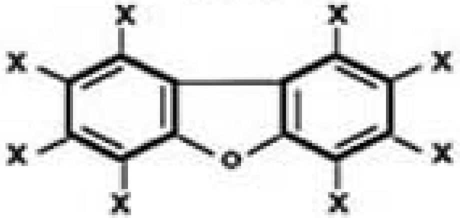
오염지역 정화 및 복원기술 (9)

3) 생물학적 정화기술 (주요오염물의 분해 ⑤)

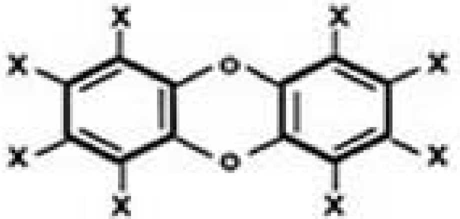
⑤ Chlorinated Aromatic Hydrocarbons 염소계 방향족 탄화수소



POLYCHLORINATED BIPHENYLS (PCBs)



POLYCHLORINATED DIBENZOFURANS (Furans)



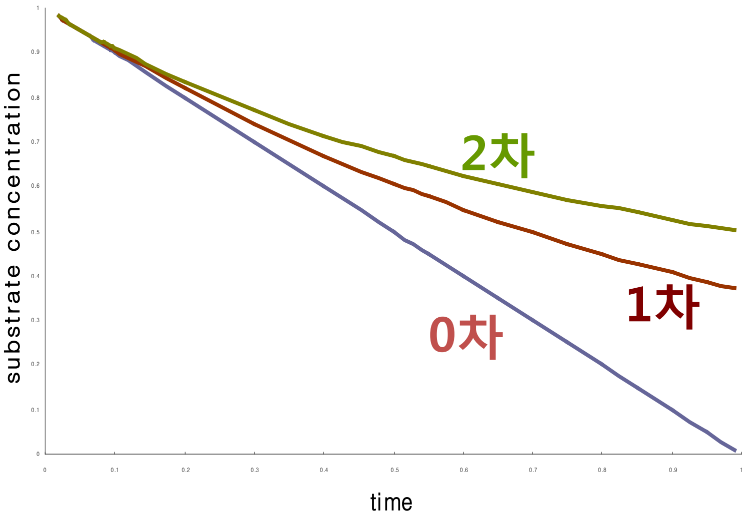
POLYCHLORINATED DIBENZODIOXINS (Dioxins)

X = Chlorine or Hydrogen

- 정화대상물질 - Chlorophenol, Chlorobenzene, Chloroaniline, PCBs, Pesticdes
- PCBs : Polychlorinated Biphenyls, 탄소와 염소의 무게비로 구분하며 용해도가 작아서 지하수보다는 토양오염
- 염소의 치환특성, 수, 위치에 의해 분해도 결정
- 호기조건에서 공대사(cometabolism)에 의해 분해
- 혐기조건에서 탈염소화(dechlorination)에 의해 분해 – 메탄생성 조건에서 효율적

오염지역 정화 및 복원기술 (10)

4) 생물학적 정화기술 (Kinetics & Rates)



- **Thermodynamics**
  - 반응(분해)의 가능성 문제
  - 과학자의 영역

- **Kinetics**
  - 반응(분해)속도의 문제
  - 농도, 미생물, 환경조건의 영향
  - 공학자의 영역

$$-\frac{dC}{dt}=k$$

0차 반응: 모든 기질이 이용가능한 상태. 대수적 감소

$$-\frac{dC}{dt}=kC$$

1차 반응: 속도가 기질농도에 비례

$$-\frac{dC}{dt}=kC^2$$

2차 반응: 실제와 가장 비슷/"유사일차반응"

오염지역 정화 및 복원기술 (11)

5) 생물학적 정화기술 (환경조건의 영향)

미생물

- Bacteria
  호기성 vs. 혐기성
  독립영양 vs. 종속영양
- 토양입자표면에 붙어있음
- 지표 가까이에 많이 존재

영양분

- C, H, O, N이 95%, P, Ca 등이 3.5%
- Bacteria 화학식
  $C_5H_7O_2N$
- 질소, 인 등이 부족
- 미생물사멸로 원소순환
- Growth factor 필요

온도

- 온도가 증가할수록 생화학반응속도 증가
- 최적온도
  Psychrophile(15±5℃)
  Mesophile(25~40℃)
  Thermophile(40℃이상)

pH

- 세포기능, 세포막을 통한 물질이동, 효소반응의 평형, 세포 내 에너지 생산 등에 영향
- 자연환경 pH 5~9
- 일반적으로 최적 6.5~7.5

수분

- 오염물질의 생물학적 이용성, 기체 전달, 오염물질의 위해성, 미생물의 움직임과 생장, 미생물 종의 분포에 영향
- 중력수 비율, FC로 측정

산화환원전위

- EH로 표현
- (+)는 산화환경, (-)는 환원환경
- 오염물의 분해여부 결정
- 특정 산화제/환원제의 농도가 미생물 대사 활성에 영향

오염지역 정화 및 복원기술 (12)

6) 생물학적 정화기술

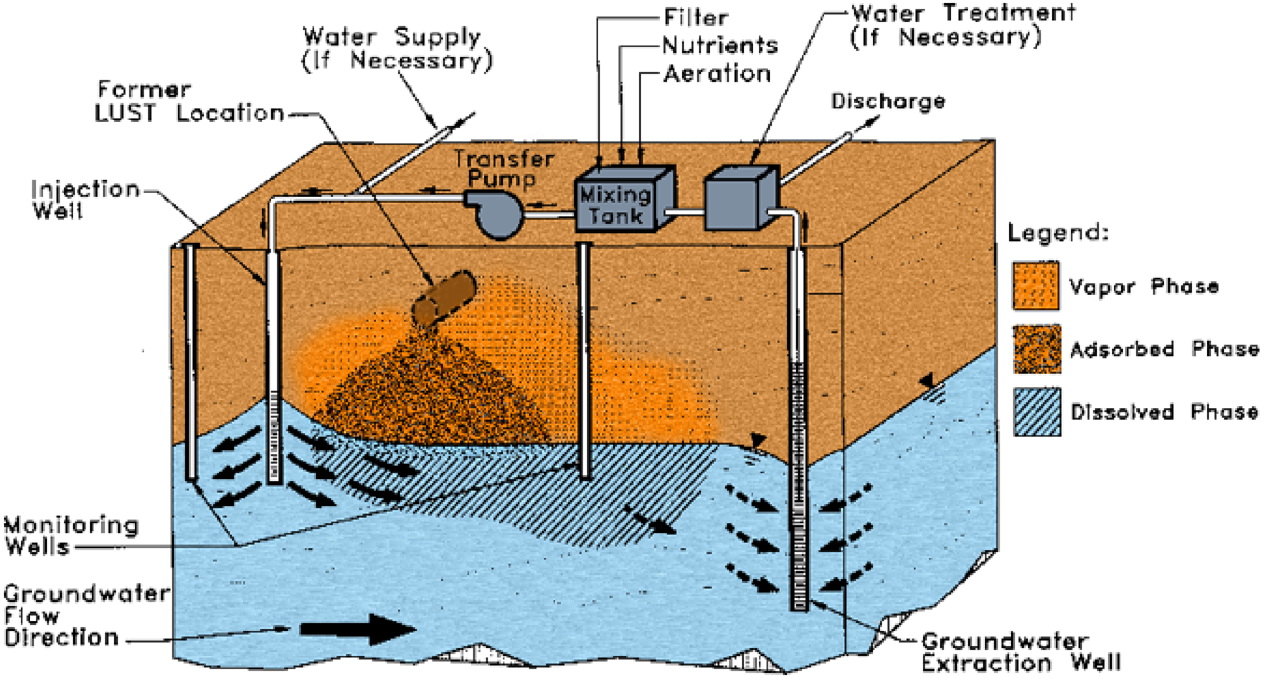
① Biodegradation 생분해법

개요

지중에 존재하는 오염물질을 분해하는 능력을 가진 미생물을 이용하여 토양 및 지하수 내의 유기오염물질을 분해하는 기술

처리물질

유류 탄화수소, 용매, 살충제, 기타 유기물



영향인자

오염물의 흡착성, 화학적 반응성, 생분해 가능성, 오염물의 농도, 오염물질과 미생물의 접촉 여부, 토양의 특성과 성상, 산화환원전위, 미생물 활성에 영향을 미치는 독성물질의 존재 여부

오염지역 정화 및 복원기술 (13)

6) 생물학적 정화기술

① Biodegradation 생분해법

Biostimulation

산소 공급

→ 공기 주입: 저비용, 적용 용이, 낮은 산소전달률

→ 산소 주입: 고비용, 높은 산소전달률

산소발생물질 공급

→ 과산화수소: 취급 용이, 자체독성

→ MgO 등 산소발생물질 주입

→ 산소 녹아있는 물

전자수용체 공급

→ 질산: 탈질 활성화, 혐기조건 지역까지 정화가능, 질산나트륨 오염기준 및 독성 고려 필요

영양분 공급

→ 질소, 인, 칼륨, 마그네슘 등 양분 공급: 주입구 주변 biofouling 가능성, pH 변화 주의

1차 기질공급

→ 아세테이트, 에탄올 등 공급: 혐기적 공대사능 향상, 환원적 탈염소화 촉진

기타

→ 메탄, 암모니아 등 영양염류 기체로 공급: CAH 공대사능 향상

→ 혐기화: 설탕 주입

Bioaugmentation

미생물 공급

→ 토착미생물 개체군을 지상에서 성장시킨 것이나 대상 오염물질을 분해할 수 있는 미생물을 토양에 접종

→ ubiquity principle & 자생미생물의 오염물질 분해효소 증진

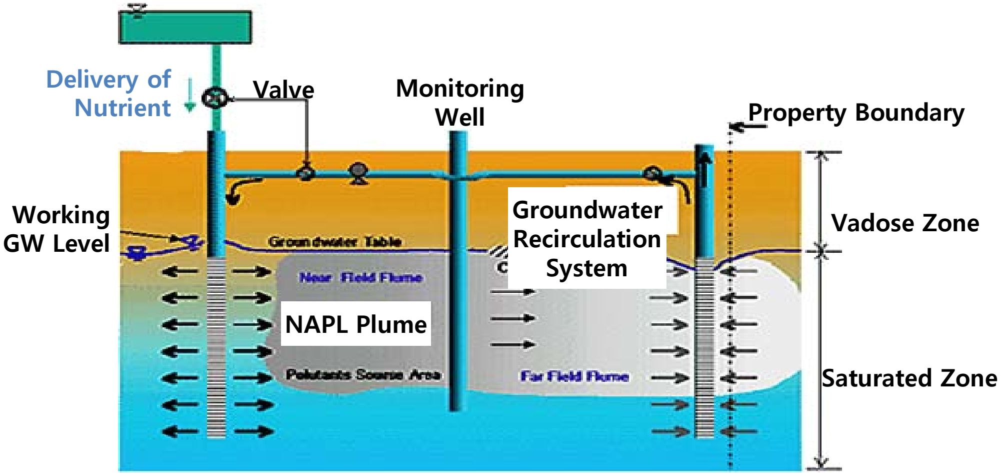
→ 주입미생물 이동, 분포 및 현장적응도 문제

오염지역 정화 및 복원기술 (14)

6) 생물학적 정화기술

② Bioventing 생물학적 통풍법

개요	오염된 불포화지반에 산소를 공급함으로써 토양에 함유된 유류 탄화수소 생분해를 활성화하는 기술
처리물질	유류 탄화수소, 비염소계 용매, 살충제 등 유기화합물질
영향인자	오염물의 생분해성, 충분한 산소, 토양의 pH와 온도, 통기성, 수분함량 및 영양분
설계 및 운전	현장지질조건 고려한 관정의 수와 위치 설계 토양함수비와 영양분에 대한 정기적 모니터링 필요



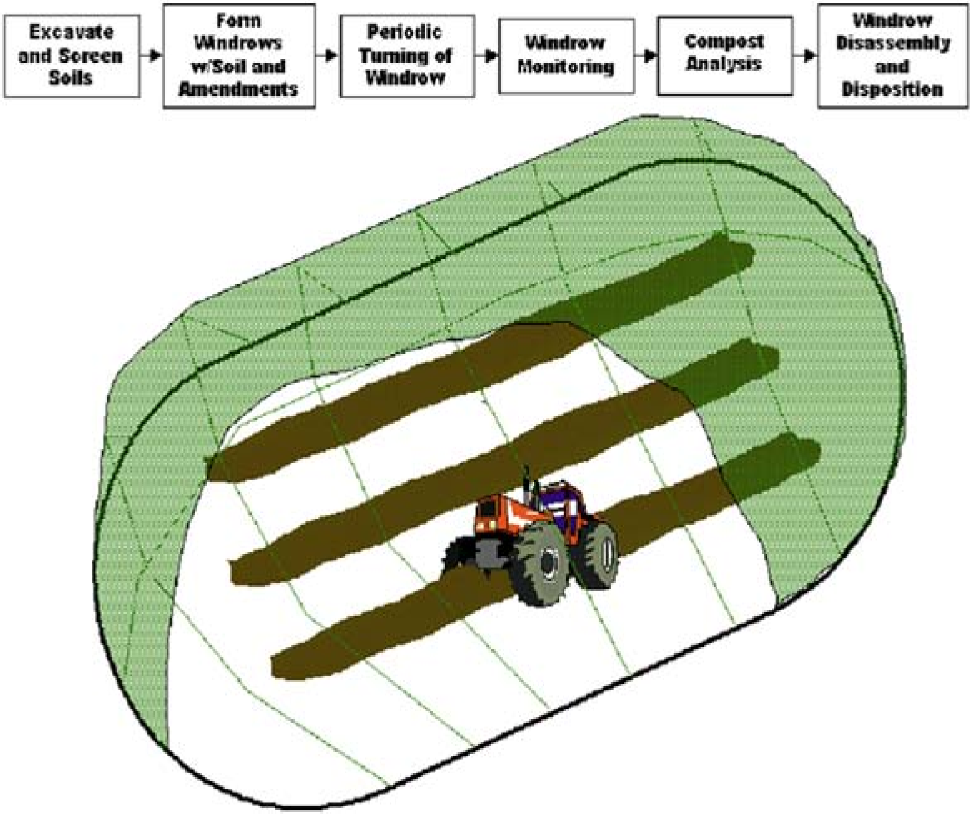
장점	낮은 압력으로 충분한 산소공급 가능 미생물 분해 외에도 휘발성 물질 제거 가능 무기물 흡착, 흡수, 응집, 농축 가능
단점	포화대에서는 Air Sparging 등 병행 필요 방출가스 처리시설 필요 무기물 분해 어려움

오염지역 정화 및 복원기술 (15)

6) 생물학적 정화기술

③ Composting 퇴비화

개요	미생물에 적정조건을 제공함으로써 혐기성 분해 또는 발효를 이용하여 오염물질을 생물학적 분해
처리 물질	유기물 또는 생분해 가능한 물질
영향 인자	오염물질의 농도, 토양의 형태, 영양분, 미생물의 분해능력
한계	넓은 부지 필요 팽화재 사용으로 전체 부피 증가 중금속 분해 불가능

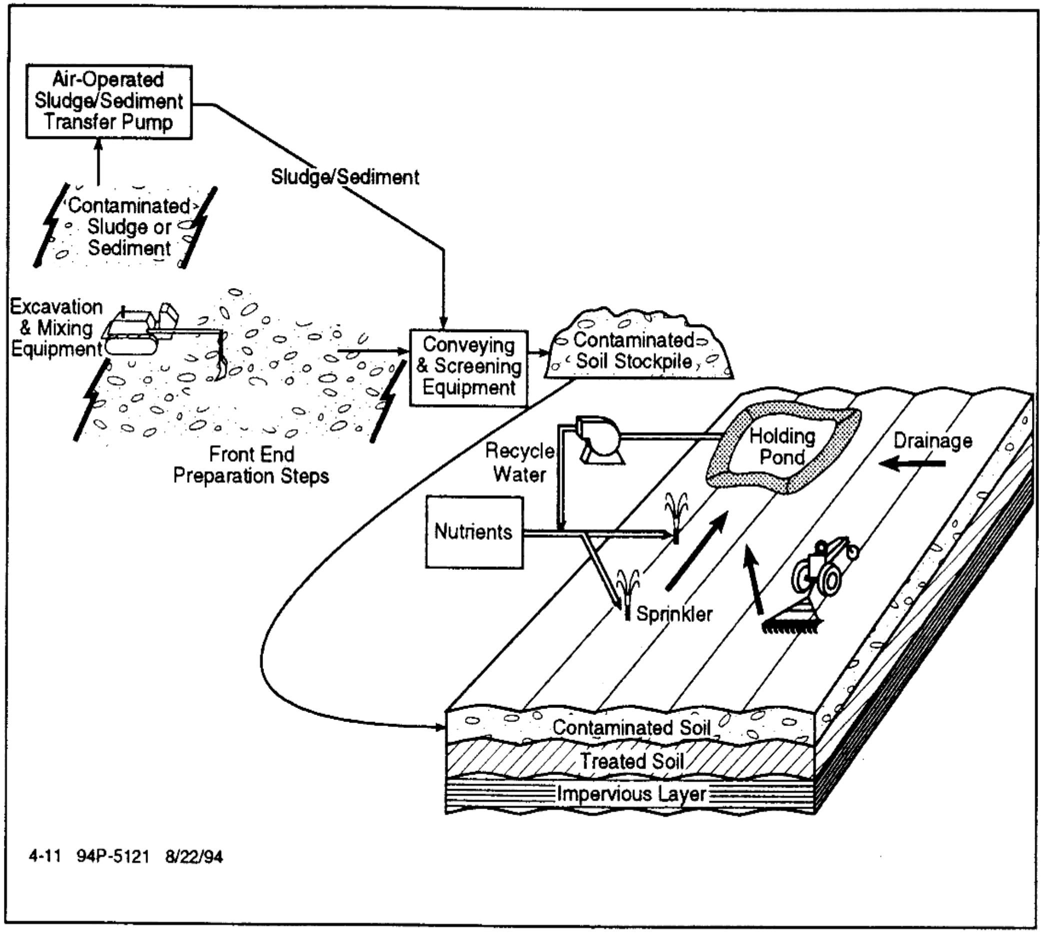


오염지역 정화 및 복원기술 (16)

6) 생물학적 정화기술

④ Controlled Solid Phase Biological Treatment

개요	토양을 굴착하여 토양개선재와 혼합하고 침출수처리장치, 폭기장치를 설치하여 생분해를 활성화하는 공법
처리물질	유기물 또는 생분해 가능한 물질
한계	토양굴착 필요 (비용) 각종 장치 설치 필요 넓은 부지 필요 긴 처리기간



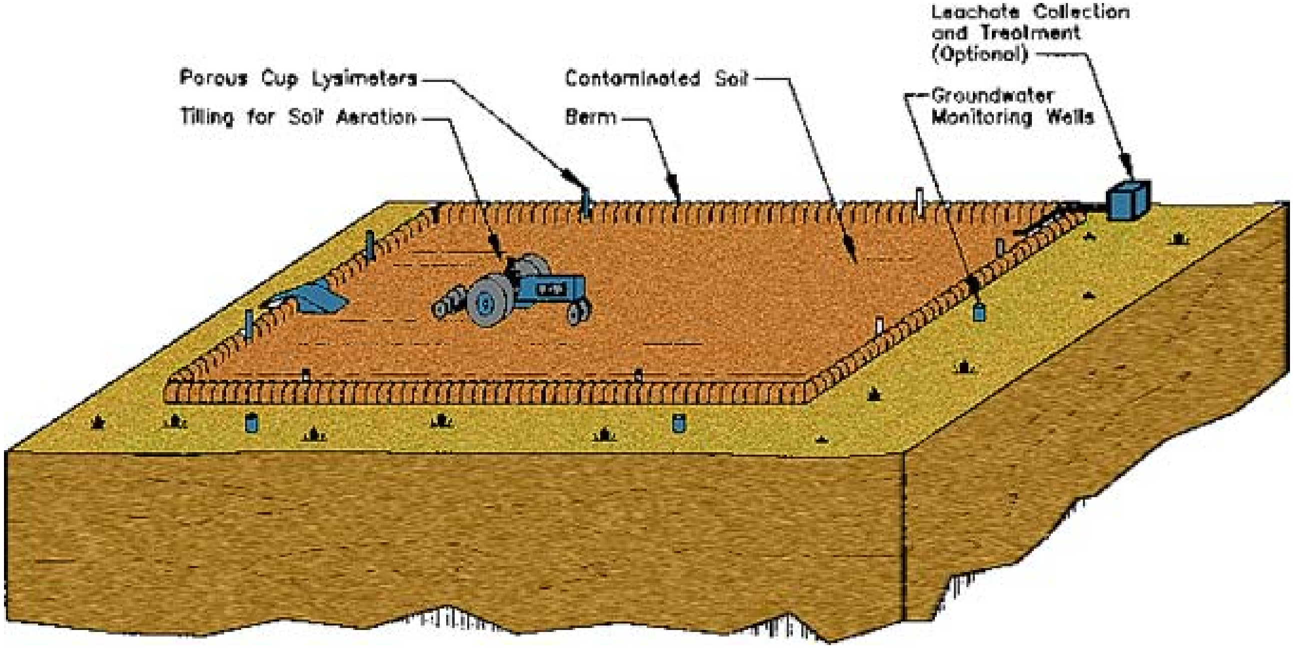
오염지역 정화 및 복원기술 (17)

6) 생물학적 정화기술

⑤ Landfarming 토양경작법

개요

오염토양을 굴착하여 정기적으로 혼합해 줌으로써 호기적 생분해를 유도하는 공법



처리물질

유류 탄화수소
살충제

영향인자

오염물질의 농도와 독성
무기물질의 존재 여부
토양의 유기물 함량

한계

시설 설치를 위한 넓은 부지 필요
배출가스 정화시설 필요
상대적으로 긴 정화기간
중금속 등 무기물 분해 불가능

오염지역 정화 및 복원기술 (18)

6) 생물학적 정화기술

⑥ White Rot Fungus

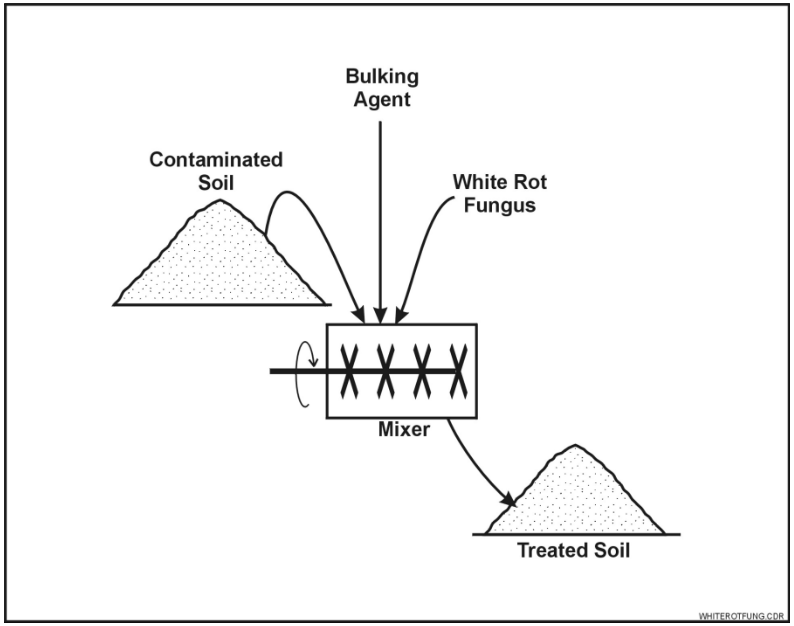
개요

리그닌을 분해하는 효소를 가진 미생물을 이용하여 다양한 유기물질을 분해하는 공법

처리물질

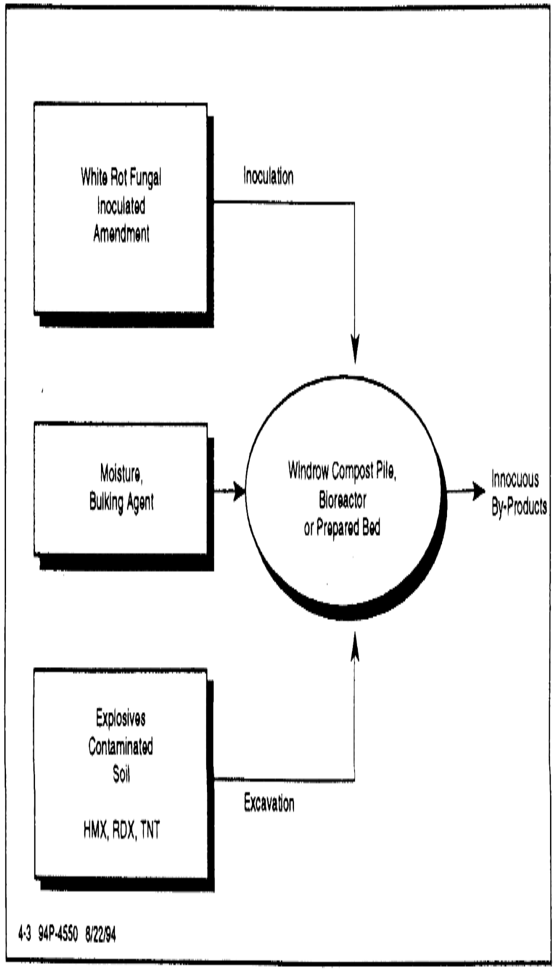
TNT, RDX, HMX 등 폭약류

DDT, PAHs, PCBs, PCP 등 유기오염물



영향인자

- 오염물질의 농도
- 토착미생물군의 박테리아 수
- 오염물질의 화학적 흡착
- 다른 오염물질이나 토양 특성



오염지역 정화 및 복원기술 (19)

7) 물리화학적 정화기술

① Air Sparging 공기분무법

개요	휘발, 생분해를 이용하여 포화대 내의 용해상, 자유상, 흡착상 오염물질 정화하는 기법
처리물질	헨리상수 10^{-5} atm-m^3/mole 이상 증기압 0.5~1.0 mmHg 용해도가 낮은 물질 (BTEX, PCE, TCE 등은 저효율) 호기성 생분해가 잘 일어나는 물질
영향인자	대수층 종류 (자유면 vs. 피압) 토양 종류 (입도분포/ 균질 vs. 불균질) 지하수면 깊이, 투수성, 통기성 pH, 온도, 산소, 수분함량, 영양분 유기탄소 함량 오염물의 휘발성, 용해도 및 생분해성

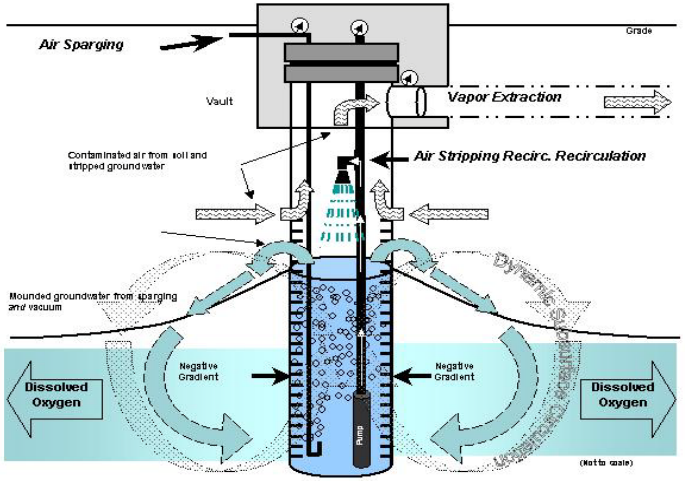


FIGURE 3-15
ART IN-WELL STRIPPER TREATMENT SCHEMATIC
RIVERFRONT SUPERFUND SITE
OPERABLE UNIT 1 FS

SOURCE: ADuTECH ENVIRONMENTAL, INC.

한계	피압대수층, 낮은 투수성 지반 불가능 불균질 매질에 적용 어려움 오염물 확산가능성, channeling 현상 주변구조물의 안정성에 영향 휘발성 큰 오염물 적용 어려움 두께 1ft 이상의 NAPLs 효율 낮음

오염지역 정화 및 복원기술 (20)

7) 물리화학적 정화기술

① Air Sparging 공기분무법

사전조사

- 오염물의 종류, 위치, 분포양상
- 대수층 종류, 지하수면 깊이, 토양의 종류와 특성 등 수리지질학적 조건
- 불균질성에 따른 air plume 분포양상
- 주입률에 따른 air channel 분포 양상
- Pilot test (압력, 용존산소량, 지하수면, 오염물 농도 변화 관측)
- 공기 분포 양상 및 영향반경
- 오염물의 휘발률과 산소공급률

설계요소

- 목표정화수준 및 정화시간
- 주입형태 (continuous vs. pulsed)
- Standard vs. Site specific design
- 오염물질 종류
- 주입정, 추출정, 관측정 위치 및 개수
- 주입정의 clogging 여부

타 기술과 병행

Horizontal Trench Sparging

오염지대 깊이가 30ft 이하일 때 낮은 투수성 지반에 적용

In-Well Air Sparging

공기주입에 비적합한 지역에서 casing을 이용, 공기흐름 형성

Biosparging

생분해만을 목적으로 하여 포화대에 낮은 유속으로 공기 주입

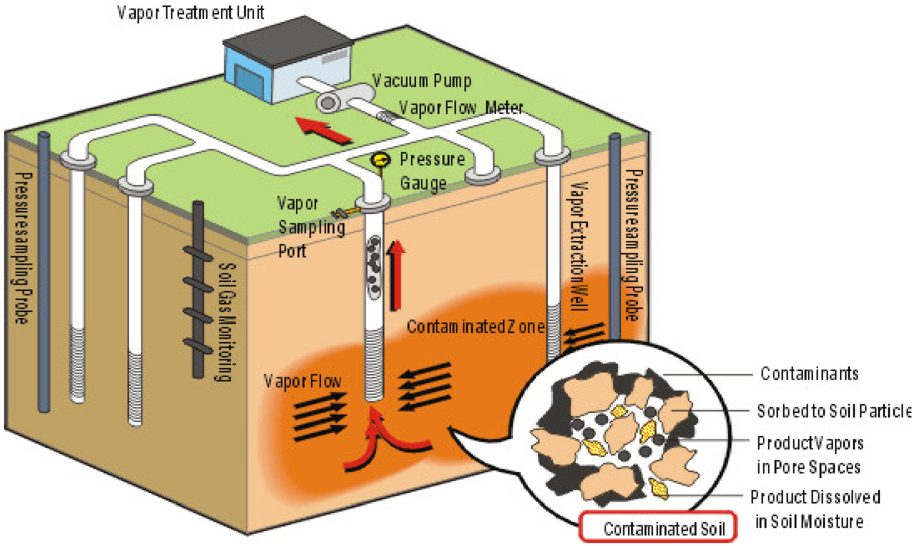
Vapor Recovery via Trenches

얕은 지하수대, 작은 입자로 구성된 지역에 갇힌 증기 제거

오염지역 정화 및 복원기술 (21)

7) 물리화학적 정화기술

② Soil Vapor Extraction (SVE) 토양증기추출법



개요	VOC/SVOC로 오염된 불포화대에 주입정과 추출정을 설치하고 깨끗한 공기를 지중에 넣은 뒤 진공압을 이용해 공기를 빨아들임으로써 휘발성 오염물질이 공기와 섞여 배출되도록 하는 공법
처리물질	불포화대의 휘발성 NAPL 지중에 잔류하거나(trapped), 자유 상태(free-product)로 존재하는 NAPL
장점	추가로 주입되는 시약이 없음 부작용이 거의 없음 설치 용이, 비용 저렴, 신속 일반굴착보다 깊이 정화 공기 주입을 통한 생분해 활성화 접근하기 어려운 지역에 적용 가능
한계	증기압 0.5mmHg 이하 오염물 부적합 균질/투수성 불포화 지반에 적용 가능 점토지반에서는 파쇄공법 병행 필요 중금속, DNAPL, PCBs, Dioxins 부적합 Bioventing 등으로 추가 정화 필요 방출가스 처리시설 필요

오염지역 정화 및 복원기술 (22)

7) 물리화학적 정화기술

② Soil Vapor Extraction (SVE) 토양증기추출법

사전 조사

오염물 휘발성, 증기압, Henry 상수
오염물 공기/물 분리계수, 용해성
오염물 분포 깊이, 형상, 면적
지반 공기투과성, 투수성, 공극률
유기탄소함유량, 함수비, 입도분포
지반과 지역 내로의 접근성

영향 인자

오염물 농도, 휘발성, 분포 및 면적, 적용 가능한 대수층 깊이, 토양 형태와 성분, 수분/유기물 함량, 공기투과도, 충분한 산소와 영양분의 존재 유무

설계 요소

공기 추출률/량, 영향반경을 고려한 추출정의 수, 간격과 형상, 세정시간, 방출가스 처리, 지하수위 변동의 영향을 고려한 스크린 범위 결정, 물 침투 제어

타 기술과 병행

SVE 적용 전 사전 양수

지하수위 저하로 SVE를 통한 정화영역 확장

표면에 불투수성 장벽 설치

공기의 순환주기가 너무 짧아지는 것을 방지

공기 송풍기 설치

송풍기로 공기 및 오염물질의 흐름을 원활하게 유도

Air Sparging

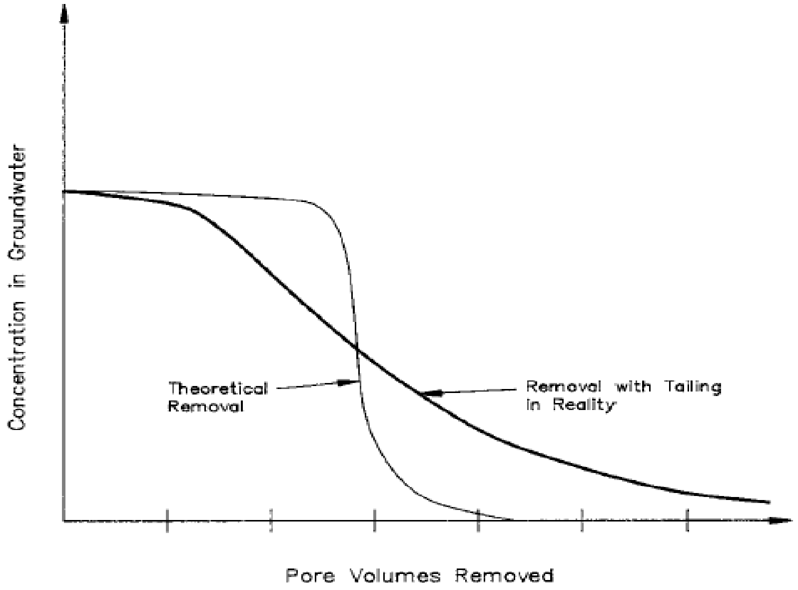
지하수대 상부의 오염물질을 휘발시켜 함께 정화처리

오염지역 정화 및 복원기술 (23)

7) 물리화학적 정화기술

③ Pump and Treat (P&T) 양수처리법

개요	오염지역에 추출정을 설치, 오염된 지하수를 진공펌프로 양수하여 물리화학적 혹은 생물학적 처리를 거쳐 정화한 후 다시 지하수로 유입시키는 순환과정
장점	안정한 NAPL 활성화로 효율적 제거 지하수위 저하로 불포화대에 남은 LNAPL에 타 기술 적용 지하수위 경사에 따른 LNAPL 추출 용이 DNAPL pool 직접 제거 용이 적용초기에 오염물 신속히 제거 가능
한계	지하수위 저하를 위한 다수의 추출정 필요 비균질, 저투수성 지반에서 비효율적 Tailing Effect로 타 기술과 병행 필요



Tailing Effect

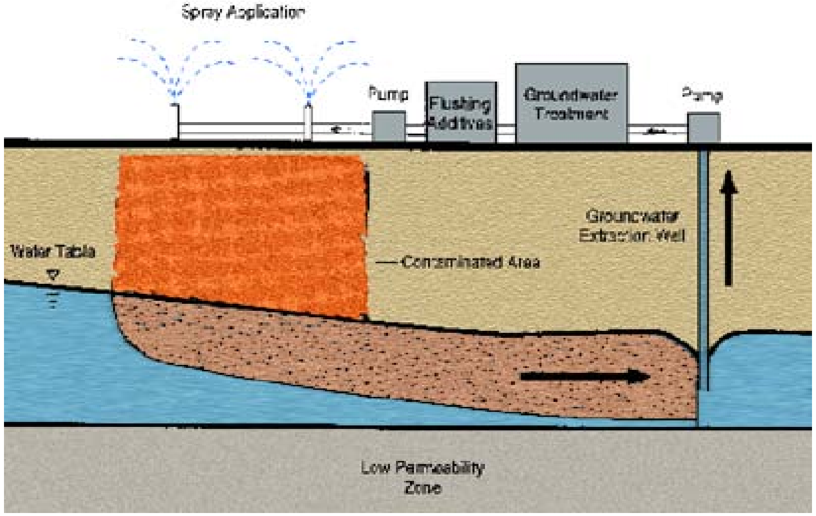
지하수대 간극수에 용해되어 있는 오염물과 달리 토양입자에 흡착되거나 간극속에 갇힌 용해되지 않은 상태의 오염물이 장기간 배출되지 않는 현상

오염지역 정화 및 복원기술 (24)

7) 물리화학적 정화기술

④ Soil Washing / Flushing 토양세척/수세법

개요	물이나 다른 수용체 또는 비수용액과 같은 적절한 용매를 사용하여 지반 내 오염물질을 씻어내는 방법
처리 물질	SVOC, 중금속 등과 특정 VOC, 유류오염물, 살충제, 방사능 오염물을 포함한 무기물, 광범위한 유기 및 무기오염물
사전 조사	오염물의 농도, 특성, 깊이, 형상, 면적, 세척용매와 지반 사이 오염물의 분리성, 지반의 특성에 미치는 세척액의 영향, 시스템설치와 침수에 대한 현장 적합성, 지역 내 특수지반의 유량과 흐름방향, 지반과 지역의 접근성
영향 인자	세척용액과 오염물의 접촉, 오염물에 따른 적절한 용액의 선정, 오염물의 지반흡착계수, 지반의 투수계수



장점	성공 시 추가공정 불필요, 오염물의 영구적 제거, 투수성 지반에 적합, 중간정도의 비용
단점	세척용액의 독성, 오염물 확산 가능, 계면활성제 토양부착으로 공극 감소, 토양/계면활성제 상호작용으로 오염물 유동성 감소

오염지역 정화 및 복원기술 (25)

7) 물리화학적 정화기술

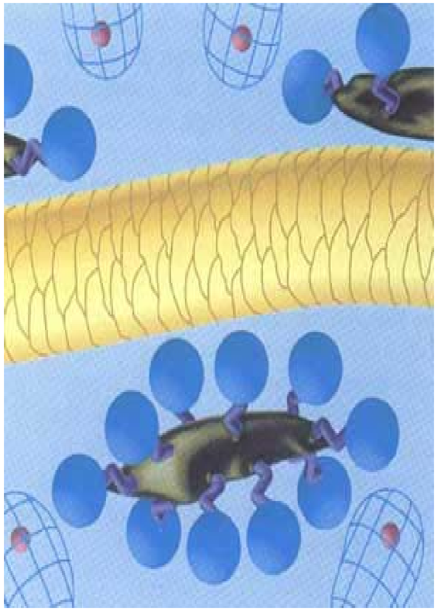
④ Soil Washing / Flushing 토양세척/수세법

ex-situ Soil Washing

오염토양을 굴착하여 부순 다음
세척제로 오염물 분리 후 정화된
토양은 현장에 되돌리는 방법
사질토+휘발성 오염물에 적합
휴믹물질 많으면 전처리 필요
고농도 오염물 전처리 필요
세척유출수 응집제 필요
굴착 및 후처리 필요

in-situ Soil Flushing

오염지역에 세척용액을 주입, 추출정/배수관으로 배수 후 추출된 오염수를 처리하여 정화지역에 재순환
오염물 용해, 유제형성, 세척용액과 화학반응
세척용액 집수시설 필요



세척제

계면의 자유에너지를 낮추고 성질을 변화시켜 오염물을 토양으로부터 분리, 용해시키는 역할, 정화작업에 악영향을 미칠 수 있으므로 신중하게 선택

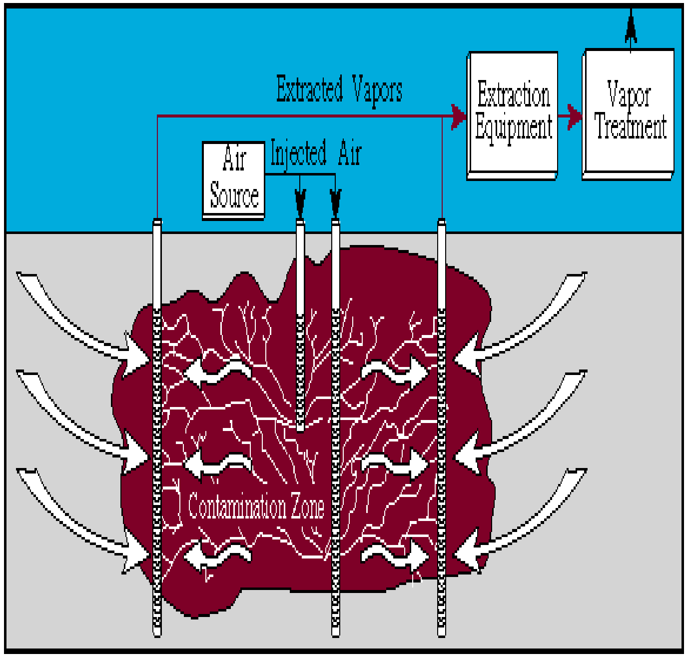
세척용액	대상오염물
물	수용성 물질
산성용액	금속, 염기성 유기물질
염기성용액	금속, 페놀, 킬레이트 화합물
계면활성제	흡착된 소수성 유기오염물

오염지역 정화 및 복원기술 (26)

7) 물리화학적 정화기술

⑤ Hydraulic and Pneumatic Fracturing 수압/공기 파쇄공법

개요	저투수성 지반에 압축공기나 액체를 오염지역에 주입하여 기존 균열을 확장하고 2차 균열망과 Channel 형성하여 투수성과 영향반경을 증가시킴으로써 타 정화공법의 효율을 증대시키는 기술
공정 과정	목적심도까지 시추 → 원하는 fracture 지점에 injector설치 → Packer로 1~2ft를 밀폐 → 밀폐된 공간에 압축공기 약 30초 간 주입 → 다음 지점 injector 설치 및 위 과정 반복 Fracture cycle은 약 15분, 하루 한 개의 시추공에 15~20 fracture 생성
영향 인자	Injection flow rate, 토양의 점착력, 인장강도, 상재압, 토양입자 크기, 토양 액소성 한계, 일축압축강도, 점성, 주입기체/액체의 종류
장점	투수성 증가로 인한 SVE 영향반경 증가, 산소/영양분 등 공급으로 미생물분해 촉진, 철을 주입함으로써 CAHs 환원적 탈염소화 유도, 유리화법/동전기에서 전극으로 사용가능

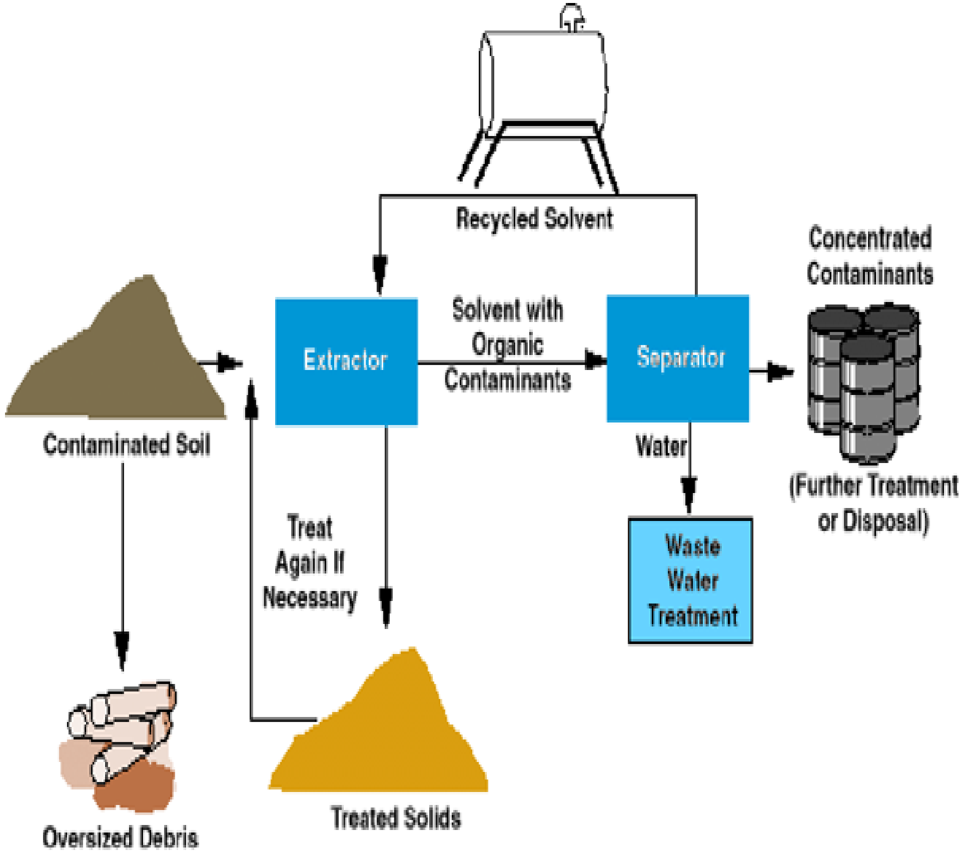


오염지역 정화 및 복원기술 (27)

7) 물리화학적 정화기술

⑥ Solvent Extraction 용매추출법

개요	오염물질을 분해하지는 않지만 토양, 슬러지, 퇴적물질로부터 오염물질을 분리시켜 부피를 감소시키며 유기화학물질을 용매로 사용하는 공법
처리물질	PCBs, 휘발성 유기물질, 할로겐 용매, 유류와 같은 유기오염물질
영향인자	토양의 입경, pH, 분배계수, 양이온 치환능력, 유기물 함량, 수분 함량 금속, 휘발성 물질, 점토, 복합오염물질의 존재 여부
한계	수분함량이 높으면 공정에 악영향, 청정제/유화제 존재 시 추출반응에 악영향, 추출용매 독성, 고분자 유기물질과 친수성 물질에 부적합

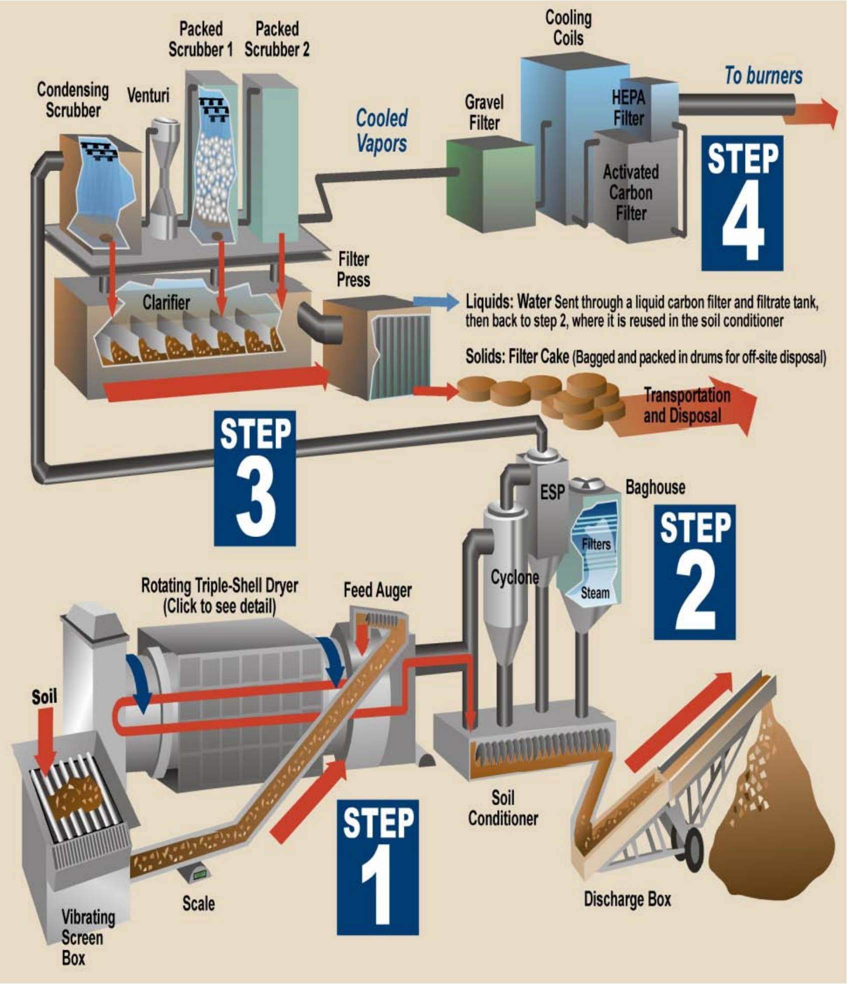


오염지역 정화 및 복원기술 (28)

7) 물리화학적 정화기술

⑦ Thermal Desorption 열탈착공법

개요	토양에 열을 가해 오염물을 증발시켜 가스를 발생시킨 후, 가스를 처리장치로 수집하여 처리하는 공법
처리 물질	HTTD: 금속(수은 등) 처리 가능 Coal tar, 목재, creosote, (SVOCs, PAHs, PCBs, 농약 등VOCs) LTTD: 가능비염소계 휘발성 유기화합물, 연료, (SVOCs)
영향 인자	토양 점착력, 입도분포, 함수비, 열 용적율, 유기물 농도, 오염물 농도, 끓는 점 범위, 증기압, 열에 대한 안정성, Dioxins 발생 가능성
설계 인자	현장위치와 조건, 오염물의 수직적 분포에 따른 고려사항, 목표정화수준, 탈수여부, 처리된 토양의 처리문제

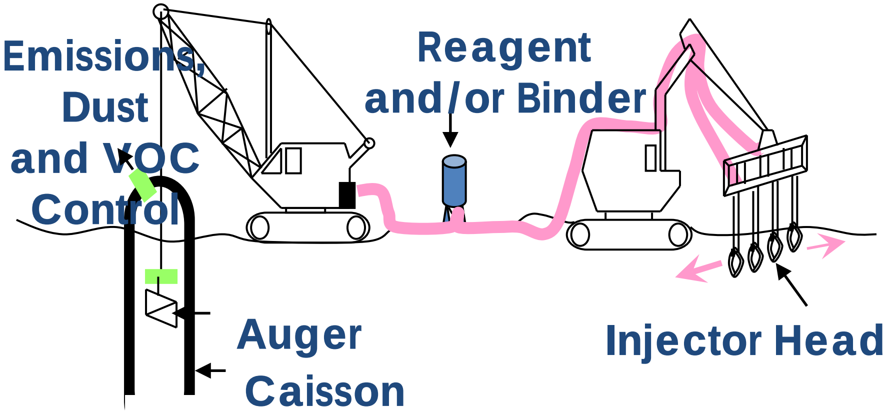


오염지역 정화 및 복원기술 (29)

7) 물리화학적 정화기술

⑧ Solidification/Stabilization 고형화/안정화

개요	화학적, 물리적인 처리를 통해서 유동성을 감소시킴으로써 위해성을 낮추는 오염처리방법
처리물질	방사능 물질을 포함한 무기물질
영향인자	토양의 입경, 수분 함량, 중금속 농도, 황 함유량, 유기물 농도, 압축강도, 투수성, 토양의물리화학적 특성
한계	In-Situ: 깊이에 따라 특정 장치 설치 필요, ex-situ에 비해 시약 주입/혼합이 어려움, 처리효율 확인 Ex-Situ: 부피 증가(유기물 부피의 2배까지), 휘발성유기물질은 고정화되지 않음. 혼합되면 처리시간이 길어짐



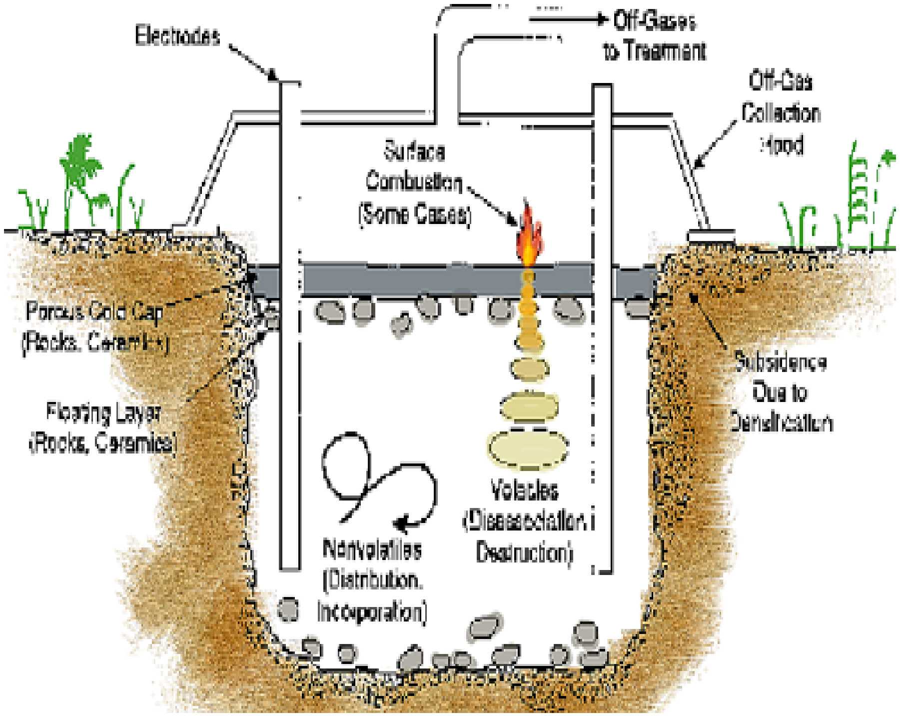
ex-situ	*in-situ*
물리적으로 안정한 상태의 물질 내에서 고형화하나 안정화제를 첨가하여 화학반응에 의해 오염물질의 유동성을 감소시키는 방법 후처리 필요	오염지역에 약품을 주입하여 고형화(이동성 감소), 안정화(독성물질 이동성감소 및 처리)

오염지역 정화 및 복원기술 (30)

7) 물리화학적 정화기술

⑨ Vitrification 유리화

개요	오염토양 및 슬러지를 전기적으로 용융시킴으로써 용출특성이 매우 적은 결정구조로 만드는 공법
처리물질	VOCs, SVOCs, Dioxins, PCBs
영향인자	토양의 입경, 수분 함량, 유기물 함량, 밀도, 투수성, 물리화학적 특성, 입도분포
한계	가스로부터 입자나 다른 오염물을 제거하는 방출가스 처리 장치 필요 자갈비가 20%가 넘으면 부적합 재오염 방지수단 필요 오염물 확산 가능 유리화물질 제거 후 토양 재이용 가능



오염지역 정화 및 복원기술 (31)

7) 물리화학적 정화기술

⑩ Chemical Oxidation/Reduction 화학적 산화/환원

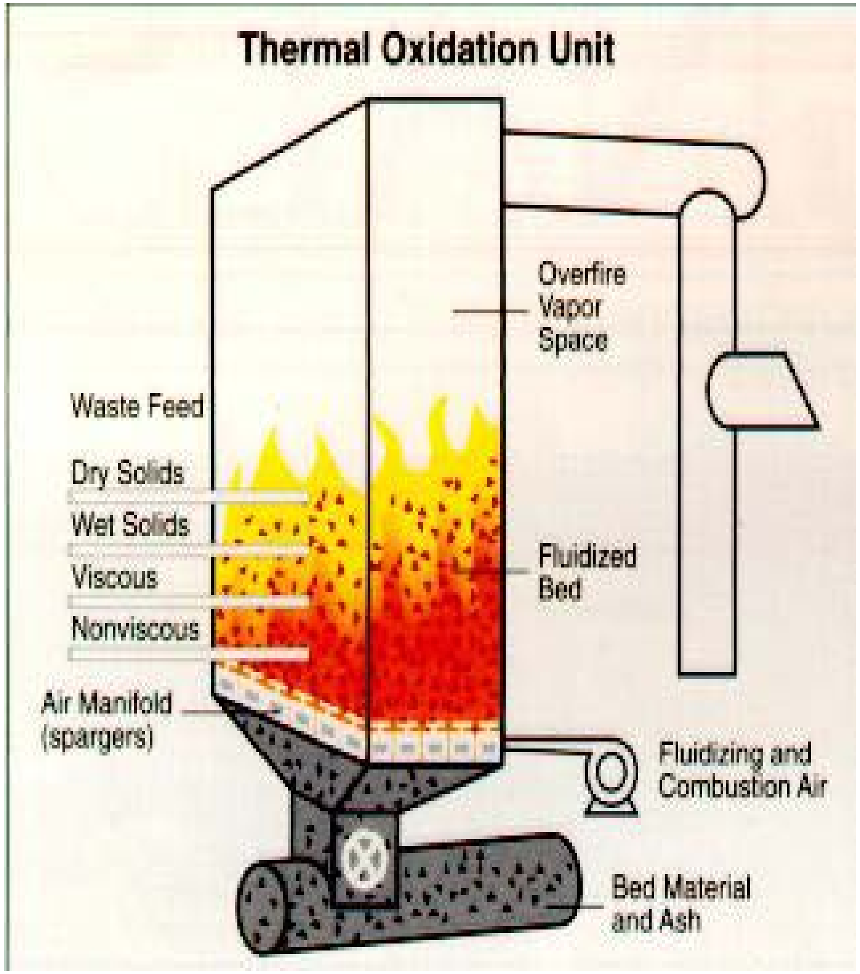
개요	오존, 과산화수소, 차아염소산염, 그리고 이산화염소 등을 이용하여 오염물질을 화학적으로 더 안정하고, 유동성이 없으며, 비활성 물질로 변화시키는 반응을 이용하는 공법
처리물질	주로 무기오염물을 대상 VOCs, SVOCs, 유류 탄화수소 등의 비염소계 물질에는 비효과적
한계	오염물질과 사용된 시약에 따라 불완전산화 혹은 중간물질이 형성될 수 있음 시약이 많이 필요하므로 오염물질의 농도가 높을 때는 비경제적 토양에는 기름과 그리스 성분이 적어야 함
영향인자	토양의 수분 함량, 알칼리 금속, 부식토 함량, 총 유기할로겐화합물 오염물질의 종류와 형태, 토양입자의 입경, 용매의 용해도 오염물의 농도 구배 약품의 종류

오염지역 정화 및 복원기술 (32)

7) 물리화학적 정화기술

⑪ Incineration 소각

개요	산소를 공급하여 유기물질을 연소/분해하는 열적으로 파괴하는 공정, 토양 내의 유해유기오염물을 871~1,204℃의 고온으로 소각하여 이산화탄소, 수증기, 황화수소, 할로겐화 수소로 분해
처리물질	폭발성 물질, 염소계 탄화수소, PCBs , Dioxins
한계	불완전연소로 중금속, 독성 재 생성 가능 오염토양 투입량에 따라 소각로의 크기가 커지므로 처리비용 증가 금속은 염소, 황과 반응하여 유해물질 생성 가능, 가스정화장치 필요 저온에서 Na, K 재를 형성하고 점착성이 강한 입자를 형성하여 덕트를 막히게 함

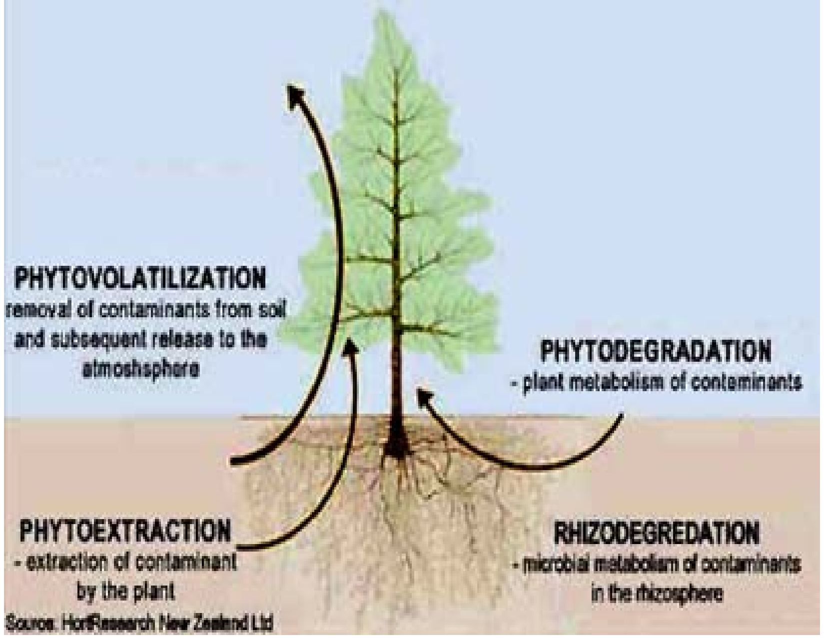


오염지역 정화 및 복원기술 (33)

8) 기타 정화기술

① Phytoremediation 식생정화법

개요	오염 토양/지하수 정화를 위하여 식물 이용하는 방법으로 대부분의 정화는 식물 뿌리가 뻗는 부분의 토양층인 rhizosphere에서 발생
처리 물질	중금속, 과잉 영양분(질산, 암모니아, 인산), 소수성 오염물(BTEX, 염소계 유기용매, PAHs, nitrotoluene, ammunition wastes), 제초제, 유기용매, 동위원소
장점	비용 저렴, 미관상 장점 오염물 누출 최소화, 토양 안정화
한계	적절한 기후조건, 장기간의 공정관리 필요 뿌리보다 깊은 곳의 오염물 추출 불가능



Source: HortResearch New Zealand Ltd

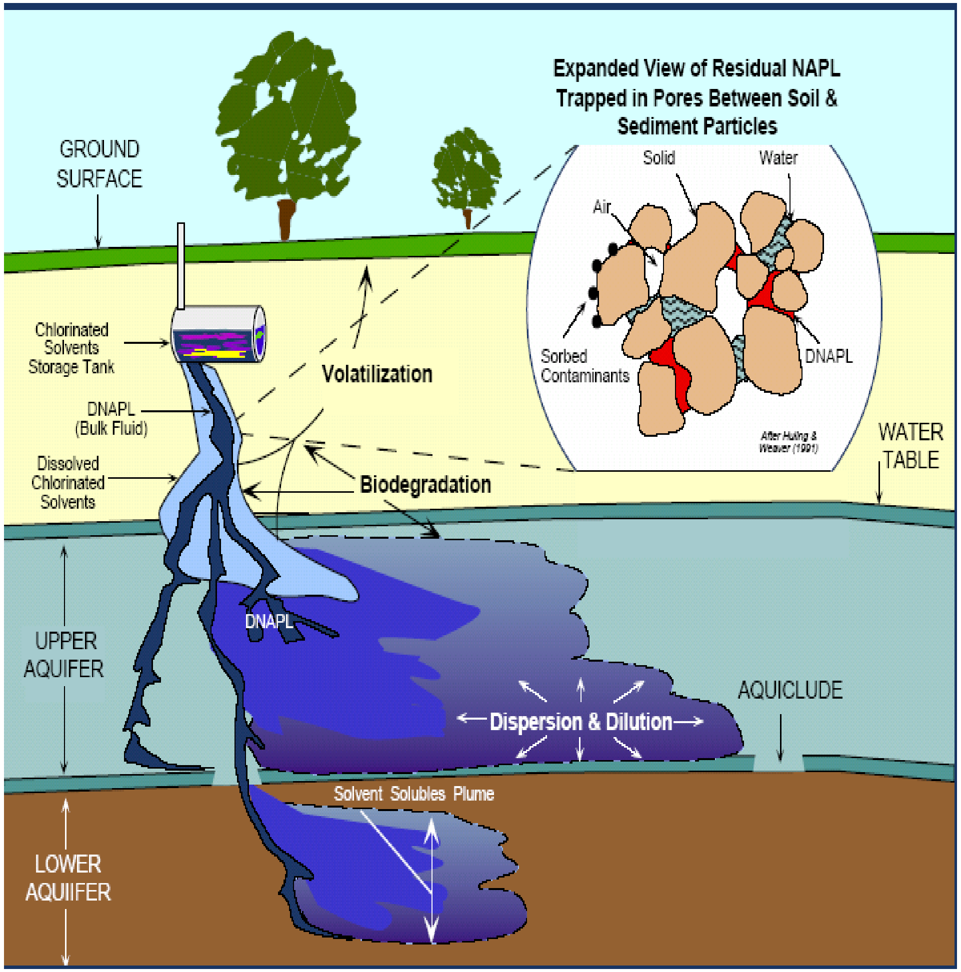
설계 및 운전	대상 오염물의추출, 흡수, 화학적 분해에 적합한 식물의 종 선택 오염물이 궁극적으로 제거되는 것이 아니므로 식물 소각 등 후처리 필요

오염지역 정화 및 복원기술 (34)

8) 기타 정화기술

② Monitored Natural Attenuation 자연저감법

개요	오염물의 자연적인 정화나 이동 지체를 이용하는 방법. 방치와는 다른 개념. 다른 적극적인 정화방법에 비교하여 합리적인 시간 내에 목표정화수준에 도달할 수 있는 자연저감과정
주요기작	미생물 분해, 분산, 희석, 흡착, 휘발, 방사성 붕괴, 화학적/생물학적 안정화, 변형, 파괴
적용여부판단	Protocol: 작업에 관련된 규약, MNA를 적용하기 위해 고려해야 할 사항 Pattern: 오염물의 상황과 형태에 따른 MNA 사용 여부 판단
장점	비용경제적, 장비 등이 거의 불필요 감시 강도에 따른 유연한 시공비



오염지역 정화 및 복원기술 (35)

8) 기타 정화기술

③ Permeable Reactive Barrier 투수성 반응벽체

개요

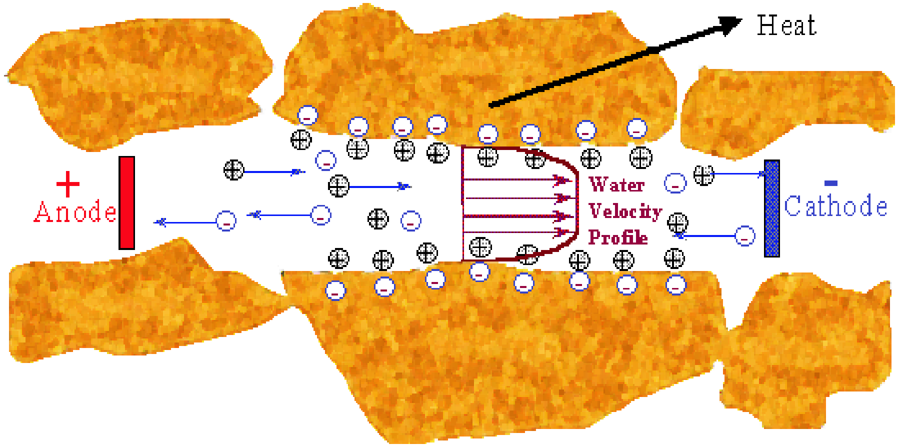
오염된 지하수가 흘러가는 곳에 오염물을 처리할 수 있는 수직 투수성 반응벽체를 설치하여 오염지하수가 벽체를 통과하면서 생물학적 또는 화학적으로 분해되도록 하는 현장 구조물

오염물질	오염원	구성요소	반응물질	반응기작
염화유기물	공단지역, 주유소, 정유공장 등의 산업시설 및 군사시설	TCE, PCE	Fe^0, GP dust, HRM Sludge	탈염소화
		PCBs	Pd/Fe Bimetal, Nanoscale Fe	촉매적 탈염소화
영양염류	매립지 침출수, 축산폐수	T-N, Ammonia	Zeolite	이온교환, 흡착, 철에 의한 탈질
	축산폐수	T-P	Wastelime, SM Slag	흡착 및 침전
중금속	산업 및 군사시설, 폐광산 산성폐수	Cr6+	HRM Sludge, SM Slag	환원
		Cd, Hg, Mn, As, Cu, CN, Pb	Zeolite, SM Slag	이온교환, 흡착
황산염	폐광산 산성폐수	Sulfate	AlOH, SM Slag, Wastelime	침전, 중화

오염지역 정화 및 복원기술 (36)

8) 기타 정화기술

④ Electrokinetics 동전기법



개요	지층 속에 전극을 설치한 후 전류를 가하여 지층의 물리.화학적 및 수리학적 변화를 유도한 후 전도현상을 일으켜 오염물질을 이동 추출.제거하는 기술 전기삼투 / 전기이동 / 전기영동
처리 물질	중금속, 핵종, 페놀, TCE, 톨루엔, 기타 유기 및 무기물
물질 이동 기작	전기삼투 흐름에 의한 간극수 이류 (advection) 외적으로 제고 또는 내적으로 생성된 수위차에 의한 간극수 이류 (hydro-potential) 농도경사에 의한 확산 (diffusion) 전기경사에 의한 이온이동 (migration)
영향 인자	점토의 완충능력, 양이온 교환능력, 유기물 함량, 포화대 내 점토광물 표면의 전하밀도, 양이온 물질의 특성과 농도, 유기질/탄산염의 존재, pH