Advanced Redox Technology (ART) Lab
고도산화환원 환경공학 연구실

http://artlab.re.kr

Water Pollution-5
-Groundwater

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What Is Groundwater?

√ **It is water stored underground in aquifers**

- Layers of sand, silt, clay, and/or rock
  - store, transmit, and yield water via the pores and cracks within the soil/rock.

- Not giant underground caves filled with water
  - 1 ft^3 of loose sand will hold ≈ 2 gallons (1 m^3 holds 270 L)
  - 1 ft^3 of cracked sandstone will hold ≈ 1 quart (1 m^3 holds 33 L)

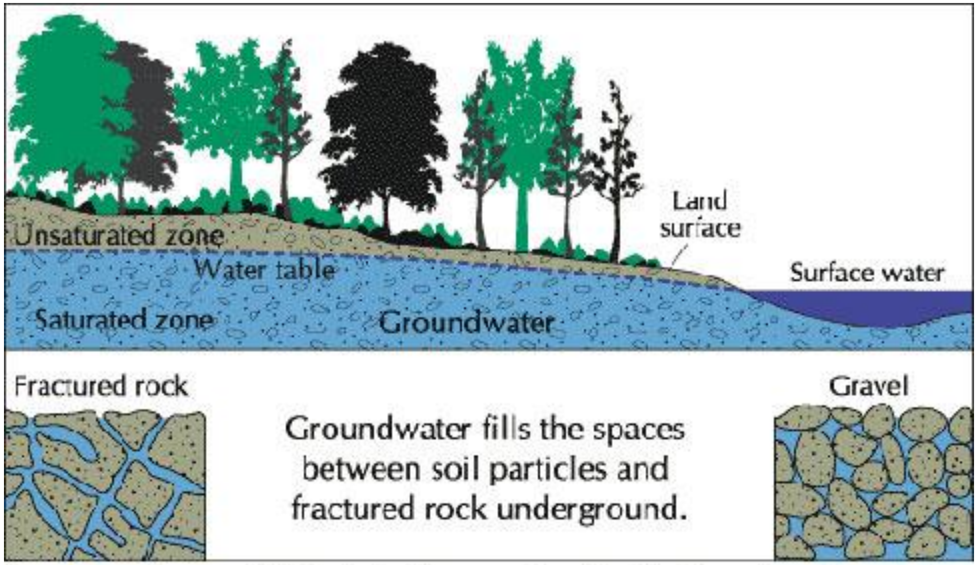
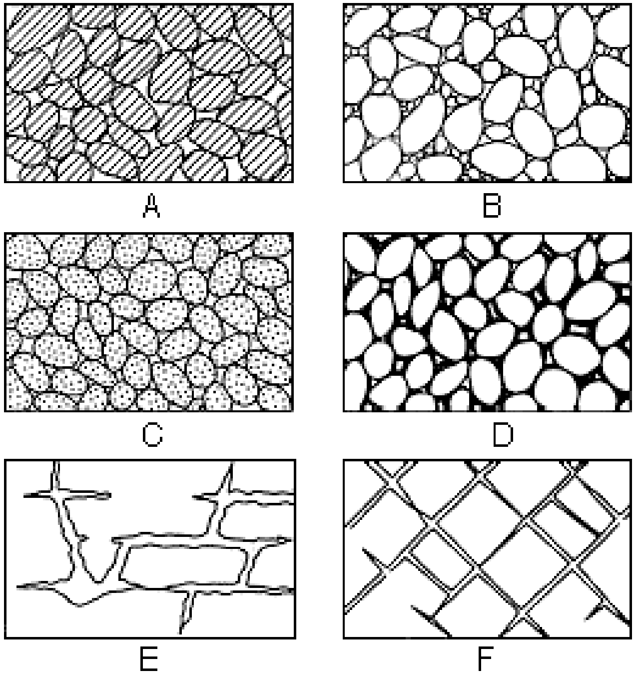


Image compliments of US Geological Survey, adapted by The Groundwater Foundation.

What Is Groundwater?

Better sorted (uniform particle size distribution) = higher porosity because smaller particles do not fill the pores



A, Well-sorted sedimentary deposit with high porosity;

B, poorly sorted sedimentary deposit with low porosity;

C, well-sorted sedimentary deposit with porous pebbles, so that the deposit as a whole has a very high porosity;

D, well-sorted sedimentary deposit with porosity diminished by the deposition of mineral matter in the interstices;

E, rock rendered porous by solution;

F, rock rendered porous by fracturing.

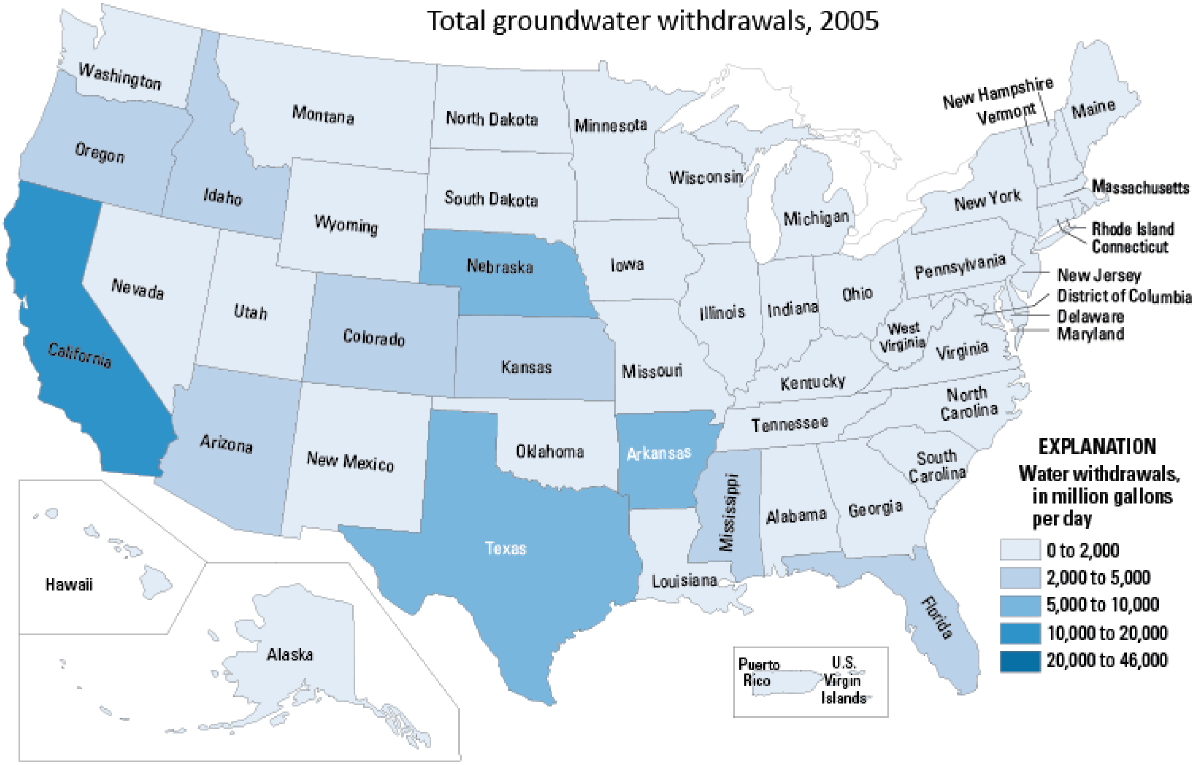
Groundwater Use

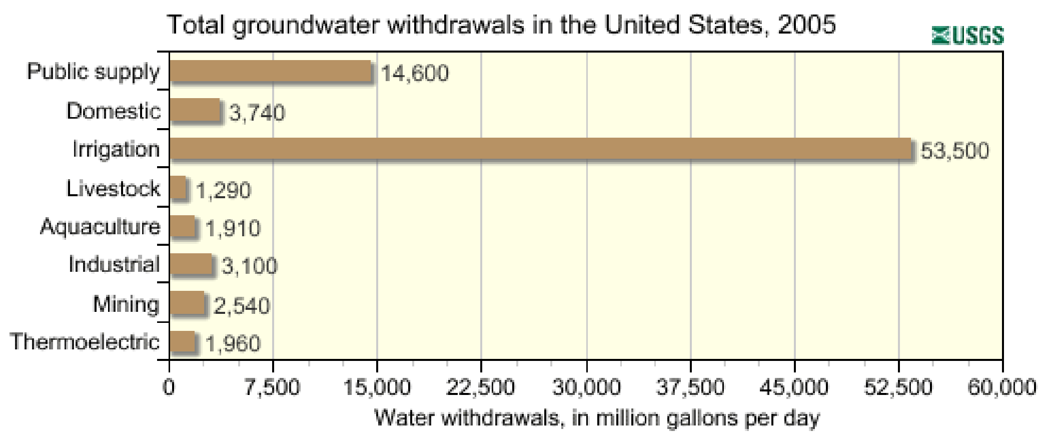
- Groundwater is **<u>98%</u>** of all freshwater available on earth
  - about 4,000 BC: 100-ft deep wells were hand-dug in the Middle East

- 1/3 of drinking water supply in the US is groundwater.
  - 67% irrigation, 20% industrial, 13%domestic

- Groundwater use has tripled in the past 40 years, and **50% of the US population drink groundwater.**

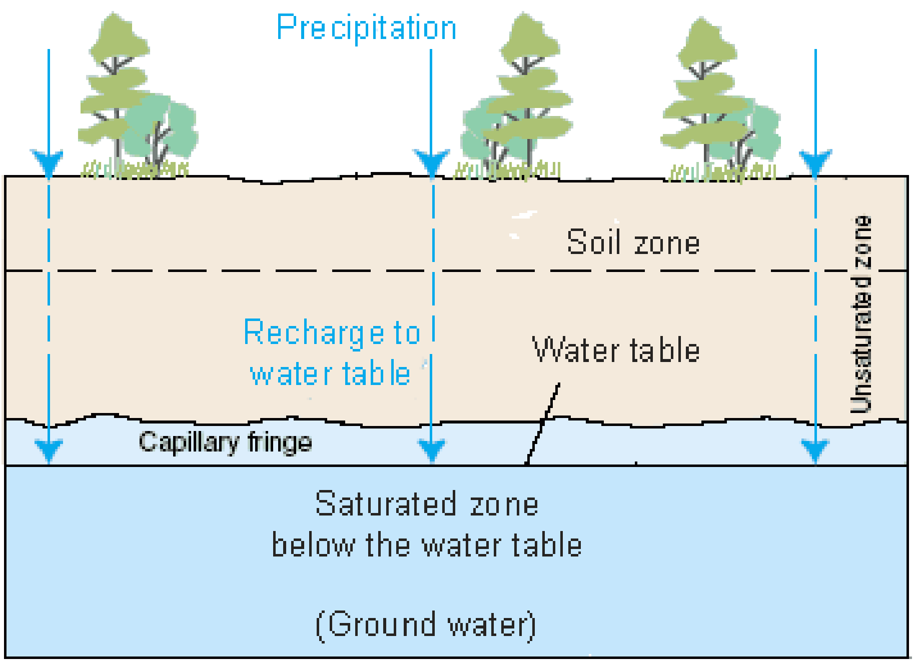
Groundwater Use





Terminology

- Unsaturated (vadose) zone – air and water in the crevices. This water is not usable to humans, but plants can draw on it.
- Saturated zone – all the spaces around the soil are filled with water (no air present) - this water is called groundwater.
- Water table – upper boundary of saturated zone (phreatic surface)
- Confining bed – aquitard, aquiclude – impermeable layer/ flow barrier.
- Aquifer – saturated layer that water can flow through easily.



Types of Aquifers

- Perched water
  - confining layer or aquitard in the middle of an unsaturated zone
- Unconfined aquifer
  - aquitard present below the saturated zone
- Confined aquifer
  - confining layer above and below the aquifer

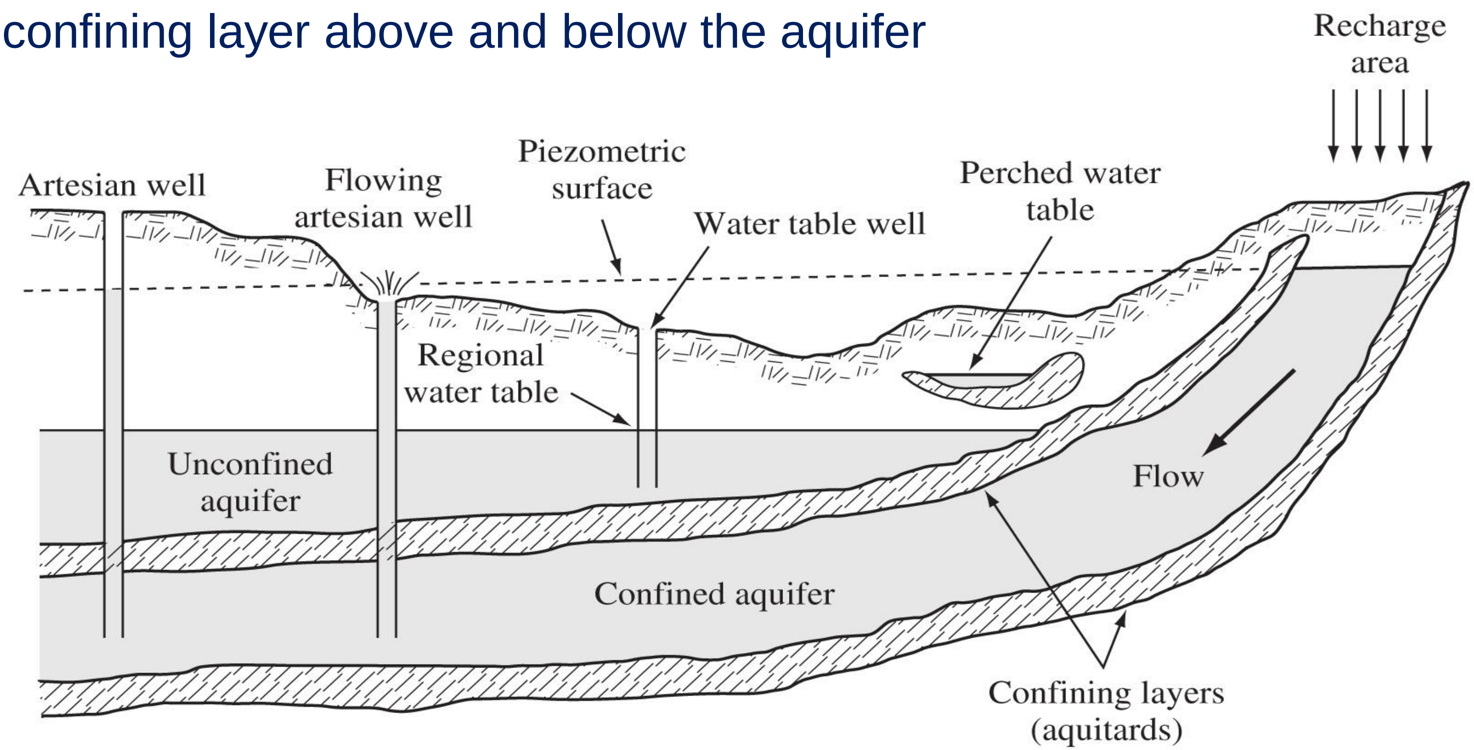


Figure: 05-27

Types of Wells

- Water table well – drilled into an unconfined aquifer
  - Water is at level of the water table
- Artesian well – tapped confined aquifer
  - Water may rise to above the regional water table
- The level an artesian well will rise to is called the piezometric surface

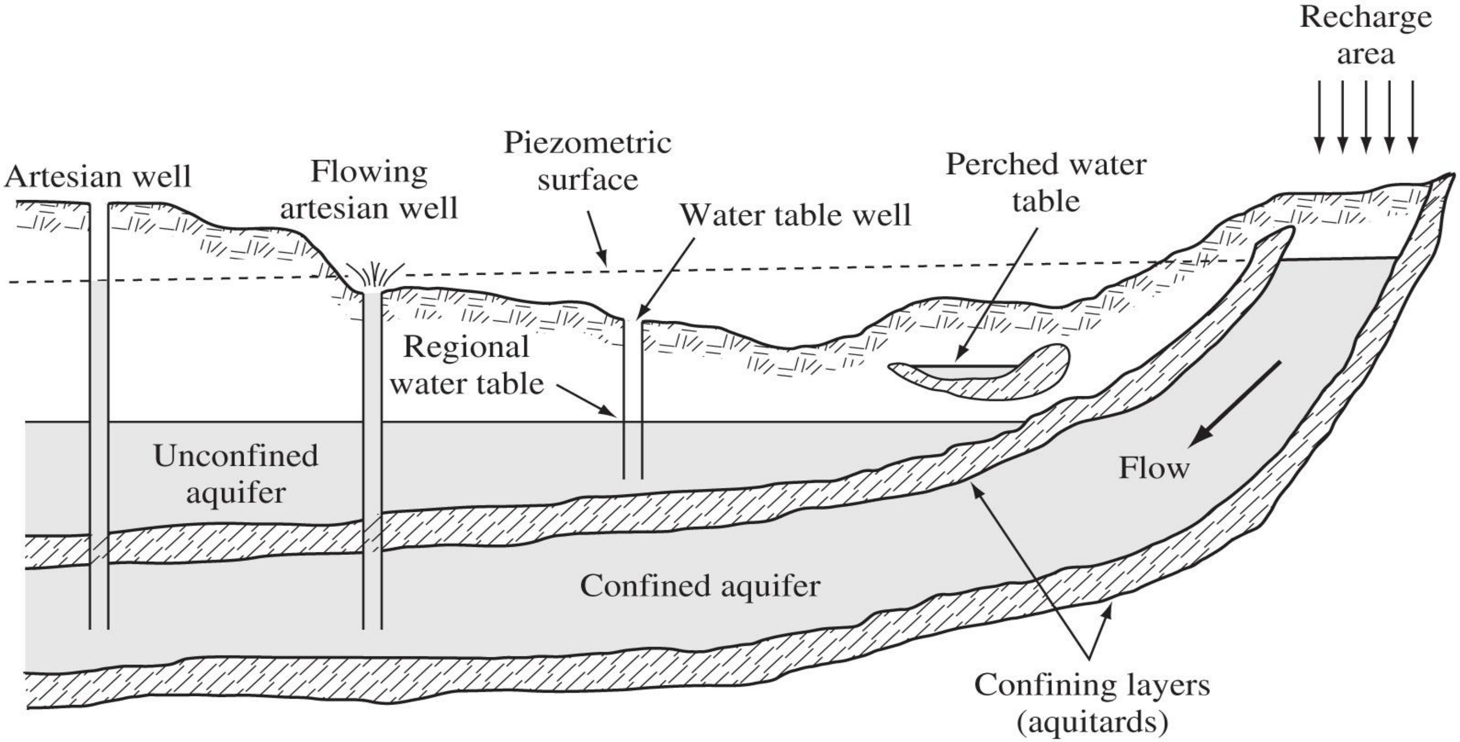


Figure: 05-27

Aquifer Properties

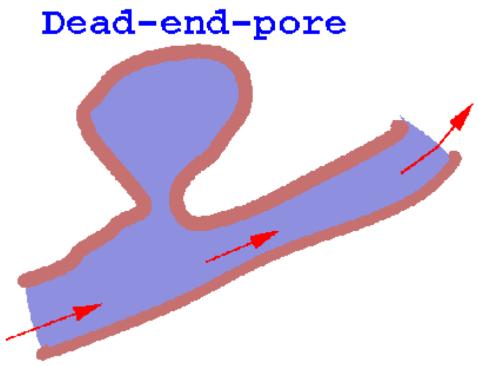
- **Porosity**

  Ratio: volume of voids to total volume of material

$$Porosity\ (\eta) = \frac{V_{voids}}{V_{solids} + V_{voids}} = \frac{V_{voids}}{V_{\text{total volume of material}}}$$

Volume of water stored = V_{voids} = porosity * volume of material

- **Specific yield** (unconfined aquifer)
  - volume of water available per unit area per unit decline in water table



Volume of water available = specific yield * volume of material

Hydraulic Gradient

- **Hydraulic head**
  - Distance from datum to water table (or piezometric surface for confined aquifers, Units: ft-H_2O, or m-H_2O

    (potential energy per unit weight)

- **Gradient**
  - Slope of the water table (or the potentiometric surface elevation - e.g., water table for unconfined aquifers) - unitless
  - decreases as groundwater flows due to head loss

$$\text{Hydraulic Gradient} = \frac{\text{Change in Head}}{\text{Horizontal distance}} = \frac{h_2 - h_1}{L} = \frac{dh}{dL}$$

Hydraulic Gradient

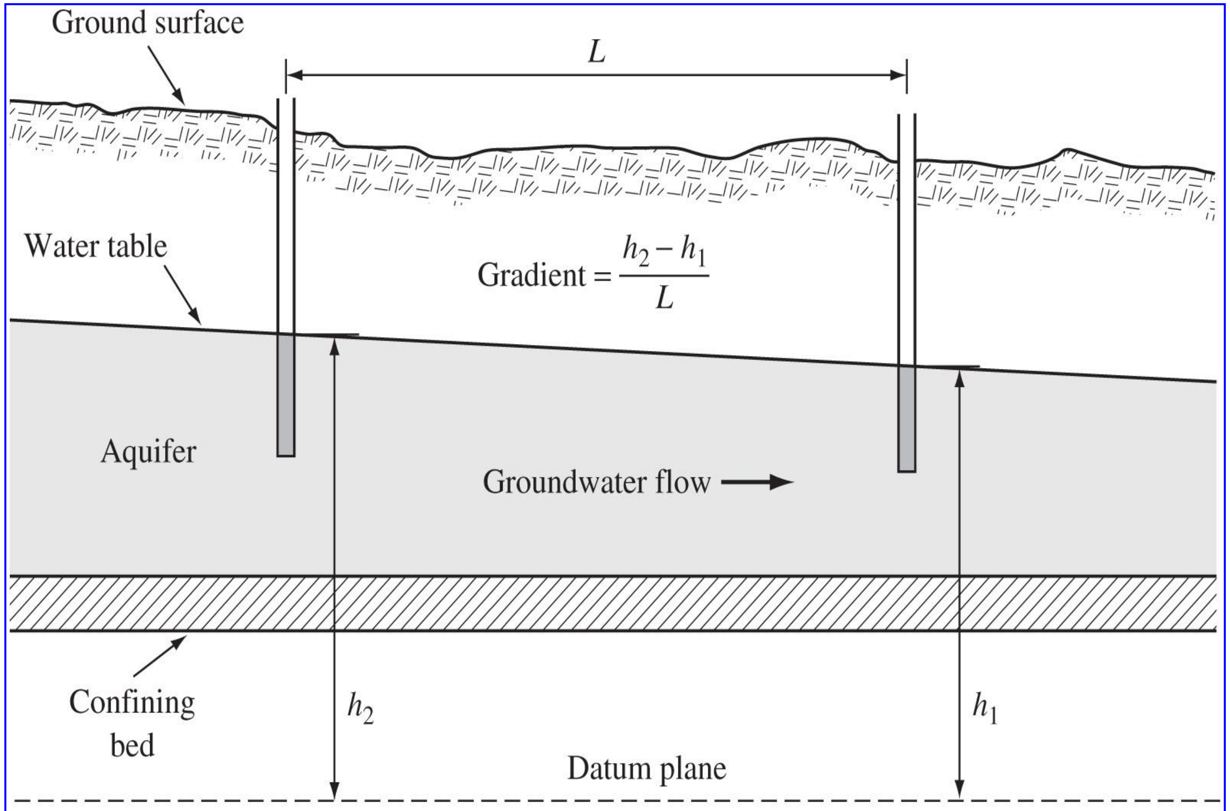
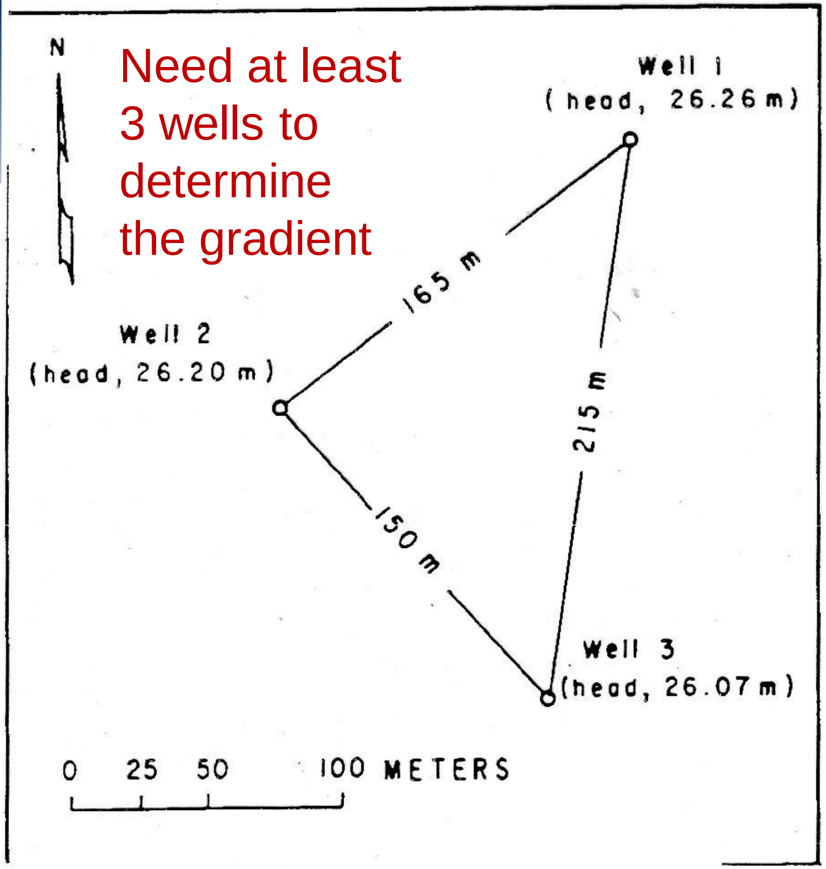
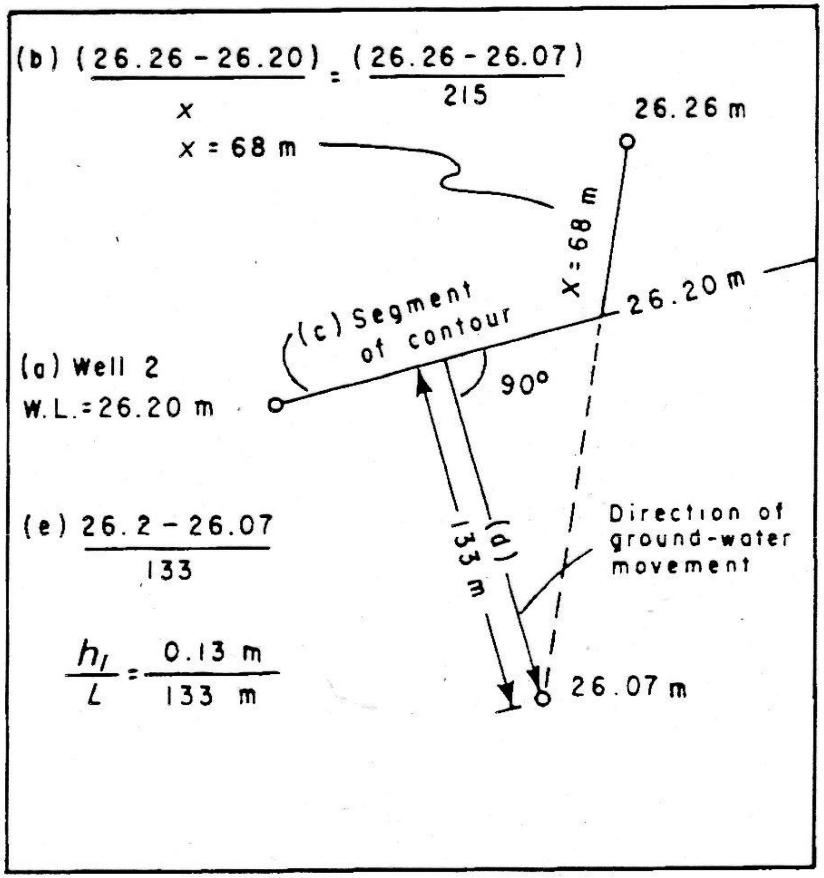


Figure: 05-28

$$\text{Hydraulic Gradient} = \frac{\text{Change in Head}}{\text{Horizontal distance}} = \frac{h_2 - h_1}{L} = \frac{dh}{dL}$$





a) Identify well with the intermediate water level (that is, neither the highest head nor the lowest head).

b) Calculate the position between the well having the highest head and the well having the lowest head at which the head is the same as that in the intermediate well.

c) Draw a straight line between the intermediate well and the point identified in step *b* as being between the well having the highest head and that having the lowest head. This line represents a segment of the water-level contour along which the total head is the same as that in the intermediate well.

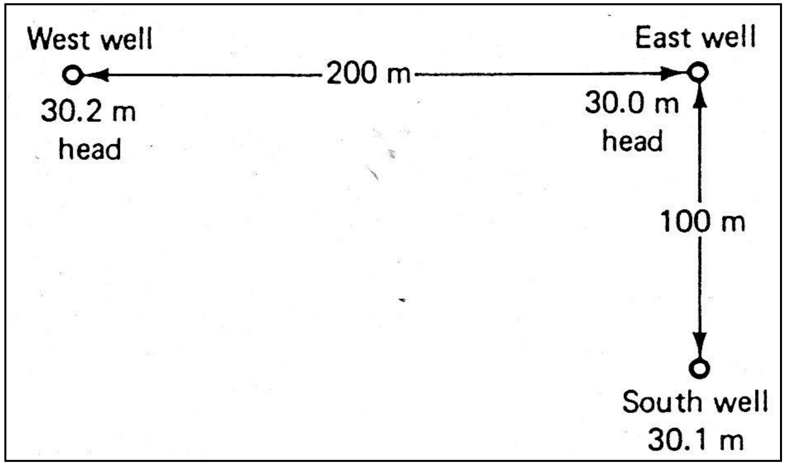
d) Draw a line perpendicular to the water-level contour and through either the well with the highest head or the well with the lowest head. This line parallels the direction of groundwater movement.

e) Divide the difference between the head of the well and that of the contour by the distance between the well and the contour. The answer is the hydraulic gradient.

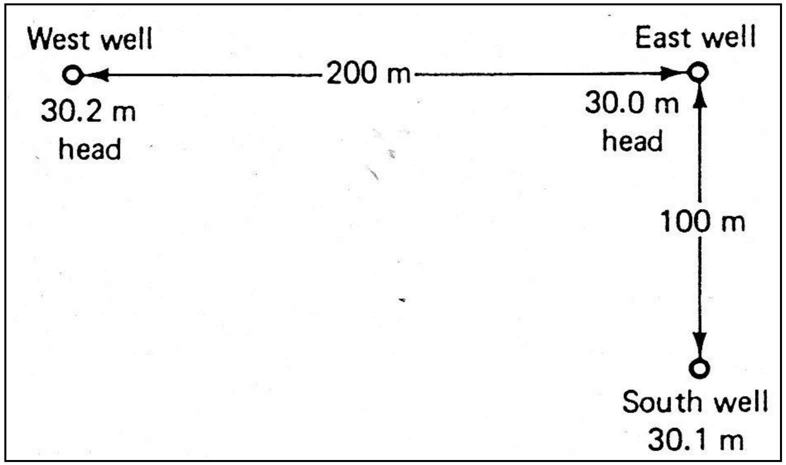
Example

- Two wells are drilled 200 m apart along an east-west axis. The west well has a total head of 30.2 m and the east well has a 30.0 m head. A third well located 100 m due south of the east well has a total head of 30.1 m.

Find the magnitude and direction of the hydraulic gradient.



Example (solution)



Groundwater Hydraulics

✓ Darcy's Law

- Groundwater flow rate is proportional to:
  - hydraulic gradient
  - hydraulic conductivity
  - cross-sectional area

$$Q = KA\frac{dh}{dL}$$

Where, Q : flow rate (m^3/day)

A : cross sectional area (m^2)

dh/dL : hydraulic gradient

K – hydraulic conductivity (m/day)

Groundwater Hydraulics

- ✓ Darcy Velocity (v)

$$v = K \frac{dh}{dL}$$

- ✓ Average linear velocity (v')

  (seepage velocity)

$$v' = \frac{v}{\eta}$$

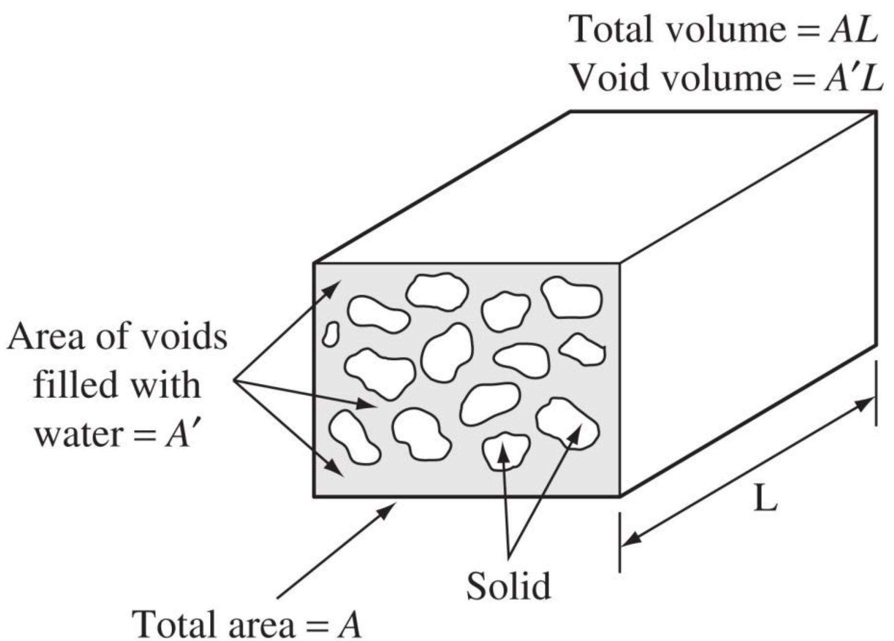


Figure: 05-33

The real groundwater velocity is considerably faster than the Darcy velocity

Hydraulic Conductivity (K)

- Hydraulic conductivity (coefficient of permeability)
  - indicates how easily water can flow through material
- K values range widely
  - least permeable clays and granite: K= 0.0004 m/d
  - most permeable gravel: K = 4,100 m/d
- Aquifer classification:
  - homogenous (uniform) – same K throughout
  - heterogeneous (non-uniform) – different K's
- Directionality:
  - isotropic : K is uniform in every direction
  - anisotropic : K is different in different directions

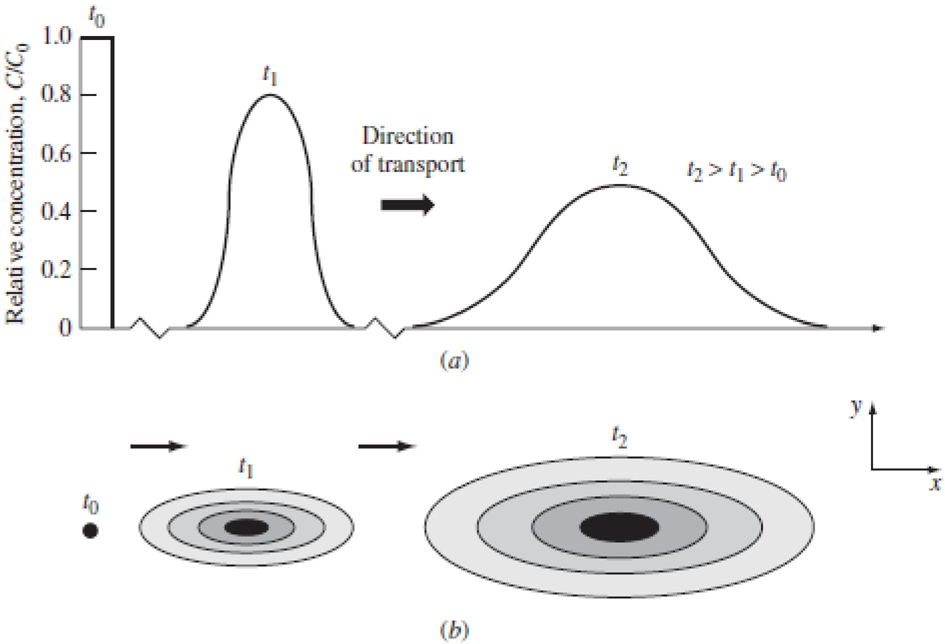
Contaminant Transport

- The assumption that the contaminant travels as plug flow without spreading (dispersion) is not realistic.

- In reality there is dispersion.

- Dispersion occurs both along and normal to flow direction.

- Caused by velocity variation (Net effect = dilution)

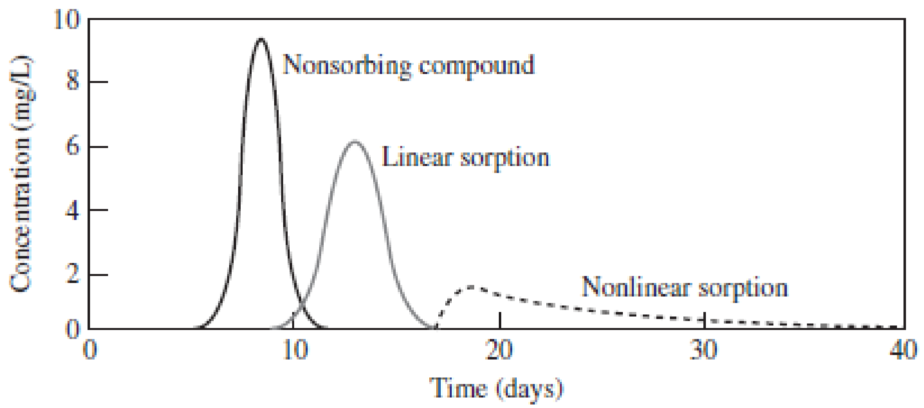


Retardation Factor

- Along with the dispersion of pollutants we need to consider retardation of organic pollutants – (caused by sorption)
- Retardation factor (R_f) – accounts for the fact that some materials are absorbed more strongly to particles than others, and migrate slower than water
- v_s = linear (pore) velocity of retarded substance

$$R_f = \frac{v'}{v_s} \geq 1$$

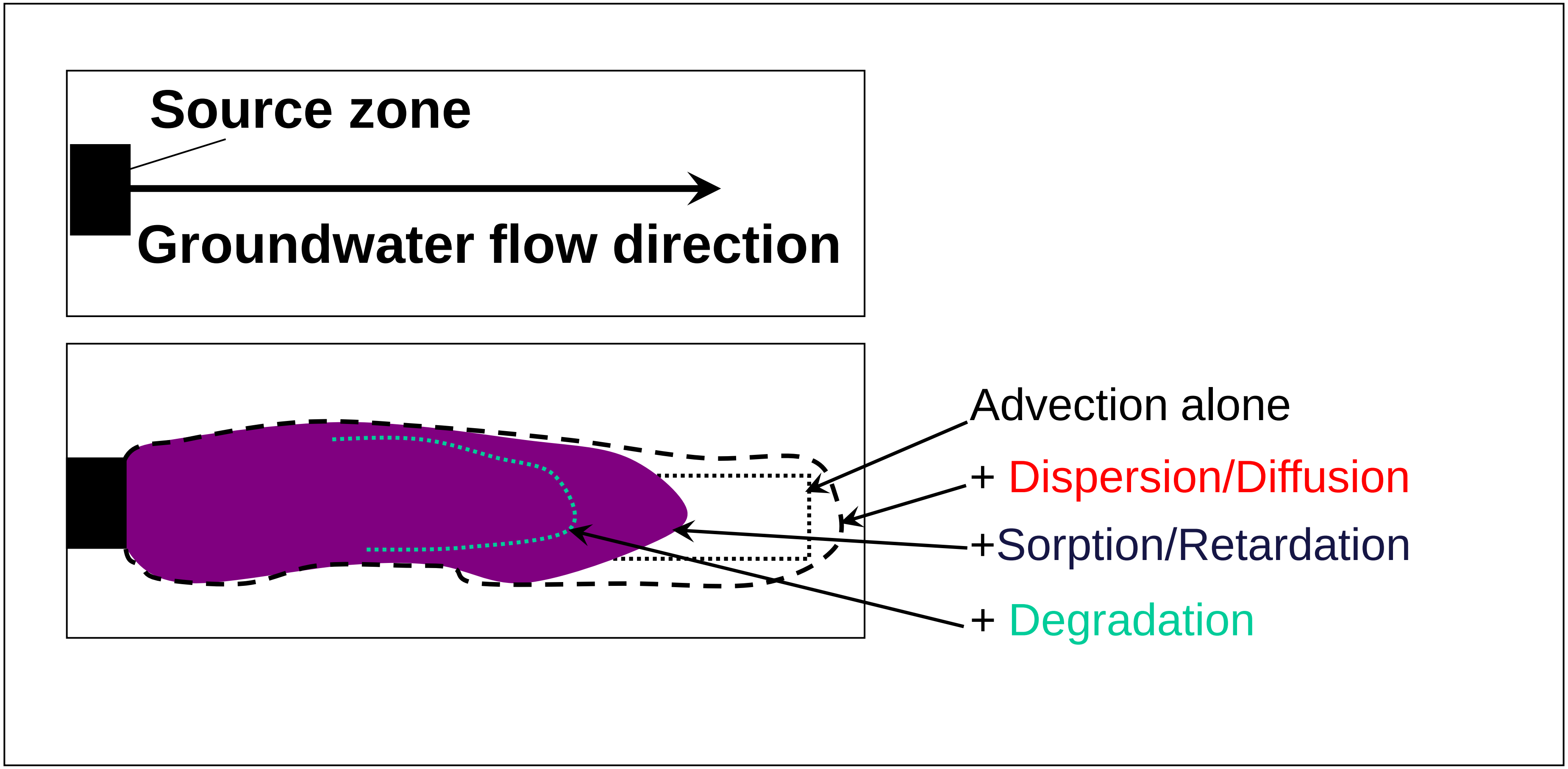
- R_f depends on the type of chemical and the aquifer matrix (larger for hydrophobic pollutants and higher organic carbon in aquifer material)



Fate and Transport of Pollutants in Aquifers

- Advection (bulk flow)
- Dispersion (dilution)
- Sorption (retardation & reduced bioavailability)
- Volatilization (in vadose zone)
- Chemical transformations
- Biotransformations
- Plant uptake

Transport Processes of Pollutants in Aquifers



Importance of Volatilization

- Henry's Law:

$$H = \frac{\text{concentration in air}}{\text{concentration in water}}$$

- Examples

Hazardous substance	$H\left(\frac{\text{atm-m}^3}{\text{mole}}\right)$
vinyl chloride	2.4
carbon tetrachloride	0.023
tricloroethylene	0.0088
benzo(a)pyrene	0.0000049

Which contaminant tends to remain in water?

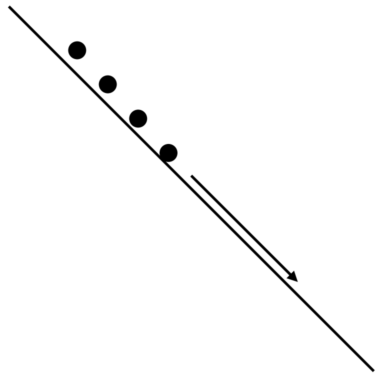
Which contaminant tends to escape to atmosphere?

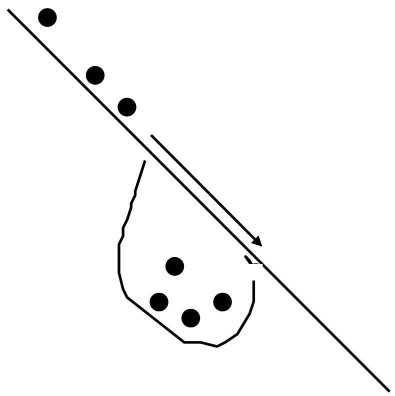
Which contaminant is easier to remove by air stripping?

Importance of Sorption

- Retards migration velocity of contaminants in aquifers (R)

No Sorption	With Sorption "trap"
100 balls reach end during a given time, Δt	Balls do not reach end until sorption trap is filled. Maybe only 10 reach end during the same time, Δt



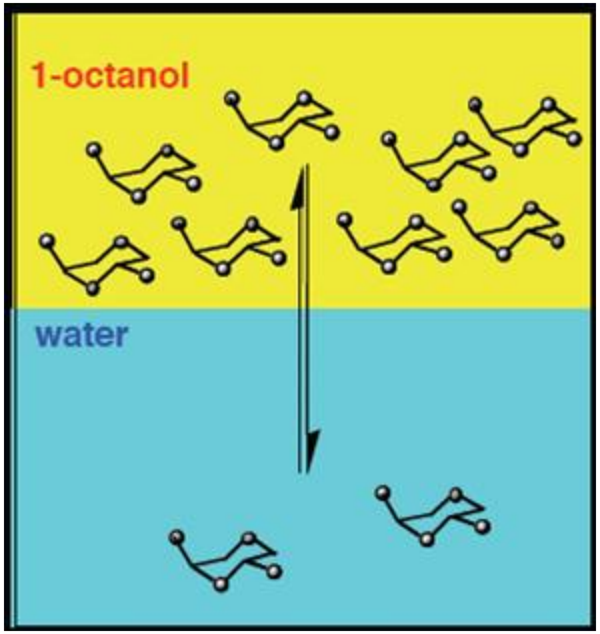


- The tendency of a pollutant to sorb to the aquifer material depends on various factors, and increases with
  - the organic matter content of the soil
  - the hydrophobicity of the substance

Importance of Sorption

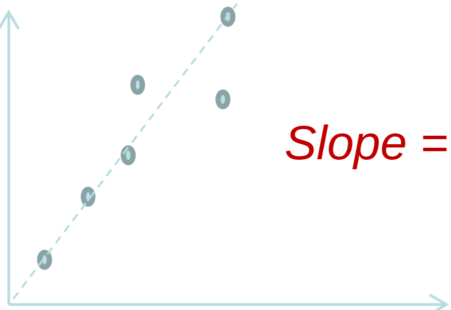
- The hydrophobicity of a substance is generally indicated by the "octanol/water partitioning coefficient" (K_{ow}):

$$K_{ow} = \frac{\text{concentration in octanol}}{\text{concentration in water}}$$



- K_{ow} can be correlated to the partitioning (or distribution) coefficient between the aquifer material and groundwater, K_D

mg/kg adsorbed



Slope = $K_D = C_{sorb}/C_{water}$

mg/L dissolved

Importance of Sorption

Substance	K_{ow}	R_f
acrolein	0.8	1
chloroform	93	6
benzene	135	8
tricloroethylene	195	13
chlorobenzene	692	24
DDT	8,000,000	19,609

- Which substance migrates further from contamination source?
- Which substance tends to remain near the source?
- Which substance can be removed easier using activated carbon adsorption?

Why is Groundwater Contamination Such a Big Challenge?

- The chemicals involved:
  - xenobiotic : foreign to natural biota
  - anthropogenic : of human origin
  - toxic (cause a variety of health effects)
  - resistant to environmental degradation (recalcitrance)
  - relatively mobile or relatively immobile (risk)

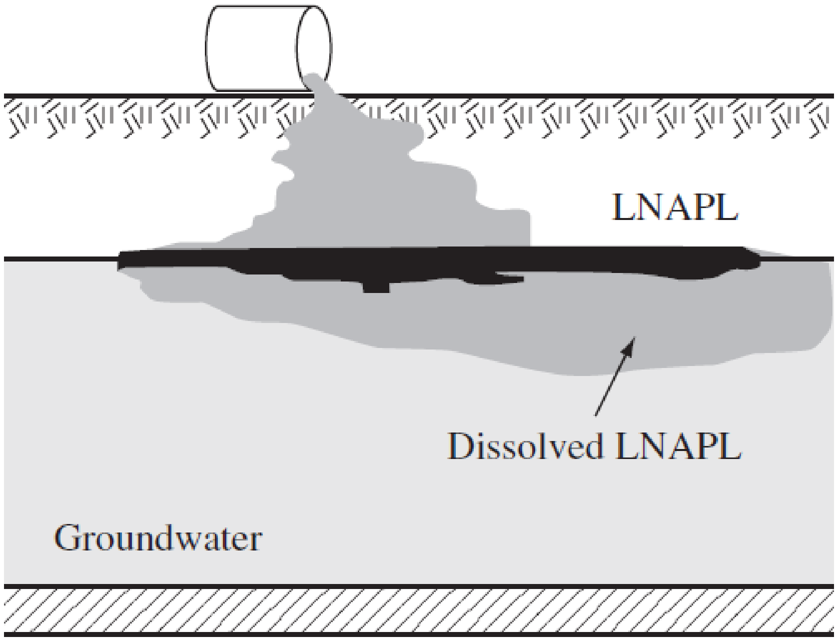
- The “treatment domain”
  - The contaminants are “out of site.” Thus, contamination is difficult to find, and once found, may still be difficult to remediate.

Different Treatment Domains
DNAPL vs. LNAPL

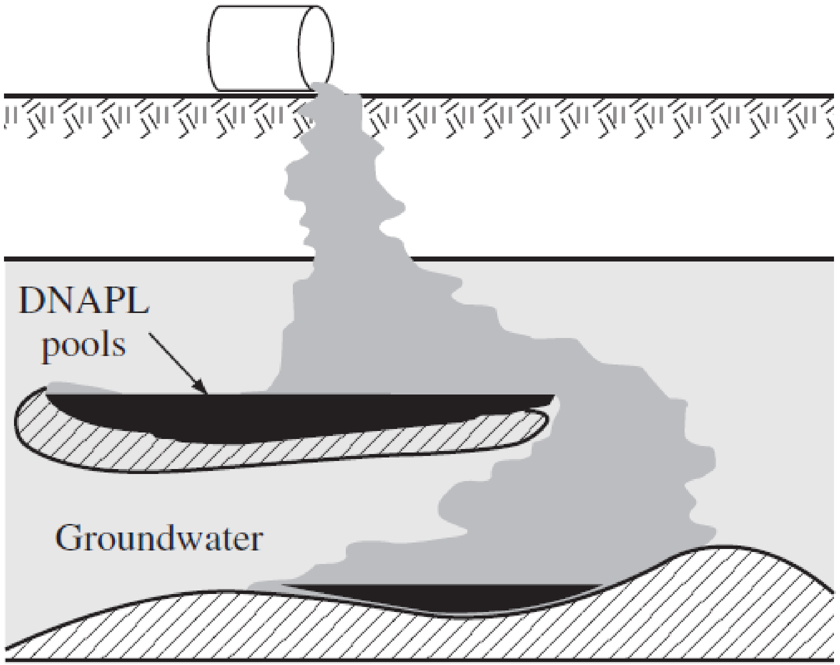
NAPL: nonaqueous-phase liquids

LNAPL: light nonaqueous-phase liquids

DNAPL: dense nonaqueous-phase liquids



(a) LNAPLs

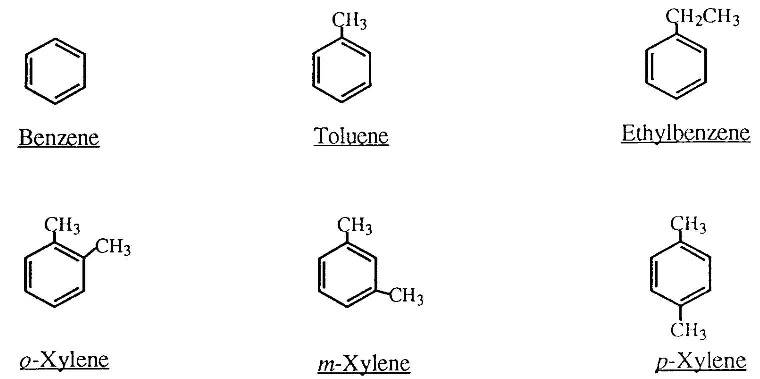


(b) DNAPLs

Common Pollutants

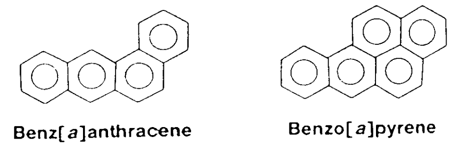
1. Hydrocarbons

a) BTEX COMPOUNDS



- Sources: Fuel production, transportation and storage
- Toxic to CNS, benzene can cause leukemia at 1 ppb
- Relatively high solubility in water = high migration potential
- Specific gravity < 1 = floaters
- Volatile, hydrophobic, biodegradable

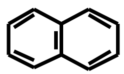
b) PAH COMPOUNDS



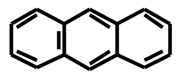
- Sources: Petroleum spills, and combustion of organics
- Many are carcinogens
- Low solubility in water, sorb strongly onto soil

Common Pollutants

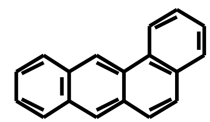
- Representative PAHs



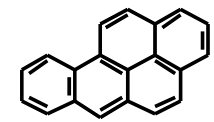
Naphthalene



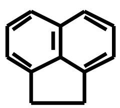
Anthracene



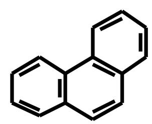
Benz(a)anthracene



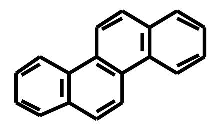
Benzo(a)pyrene



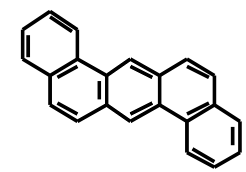
Acenaphthene



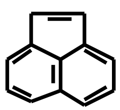
Phenanthrene



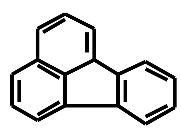
Chrysene



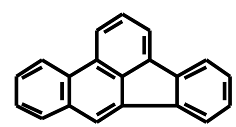
Dibenz(a,h)anthracene



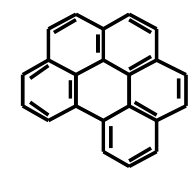
Acenaphthylene



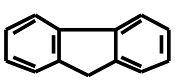
Fluoranthene



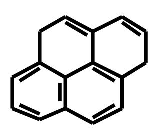
Benzo(b)fluoranthene



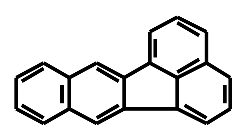
Benzo(g,h,i)perylene



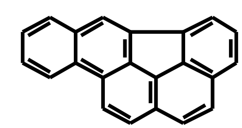
Fluorene



Pyrene



Benzo(k)fluoranthene

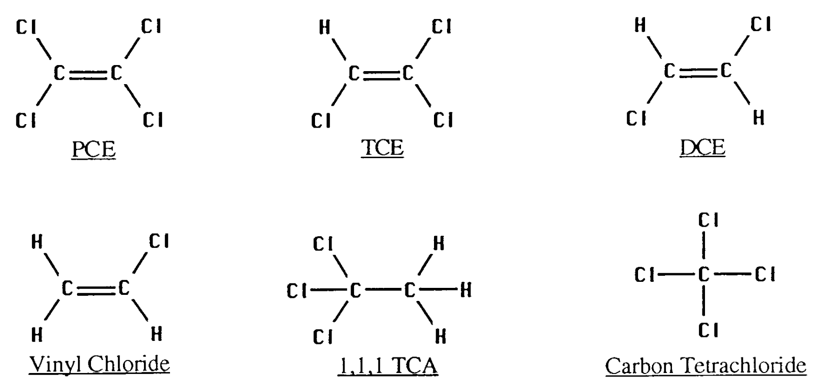


Indeno(1,2,3-cd)pyrene

Common Pollutants

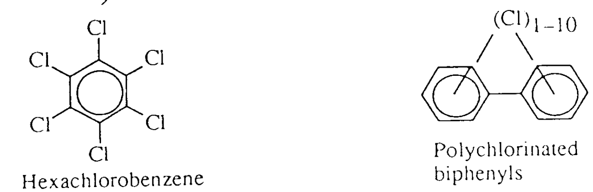
2. Chlorinated compounds

a) CHLORINATED ALIPHATICS



- Sources: Solvents, degreasers, propellants, polymers
- Carcinogenic (Vinyl chloride very potent)
- Relatively high solubility in water = high migration potential
- Specific gravity > 1 = sinkers
- Volatile, biotransformable, hydrophobic (except VC and CT)

b) CHLORINATED AROMATICS

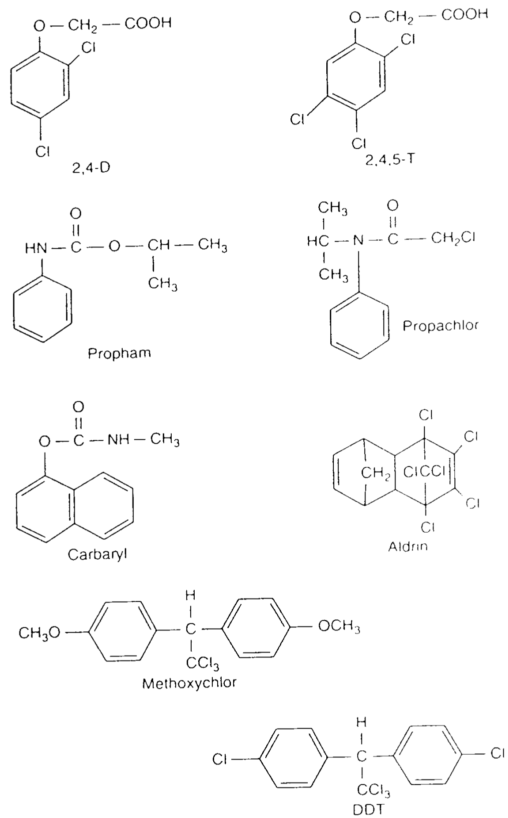


- Sources: Wood preservers, fungicides, dielectric fluids
- Diverse toxic effects, many are carcinogens
- Low solubility in water, sorb strongly onto soil

Common Pollutants

3. Pesticides

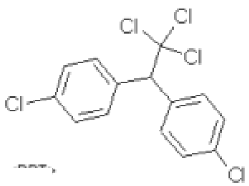
Biodegradable Recalcitrant



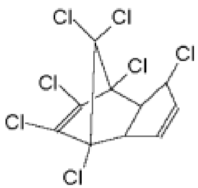
- Sources: Agricultural activities
- Persistent (biomagnification due to lipophillic nature)
- Generally sorb strongly onto soil
- Small changes in chemical structure affect biodegradation
- Degradable and recalcitrant are relative terms, and do not imply neither instant degradation nor indefinite resistance

Common Pollutants

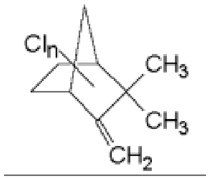
Organochlorides ***Organophosphates*** ***Carbamates***



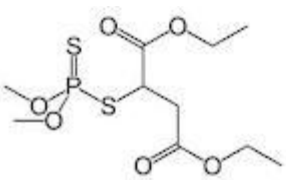
DDT



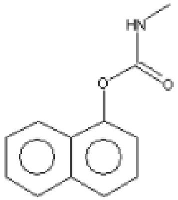
Heptachlor



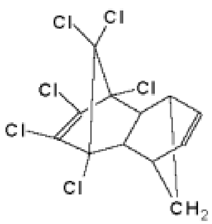
Toxaphene



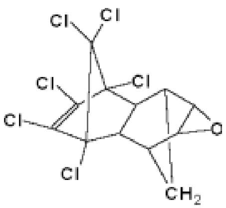
Malathion



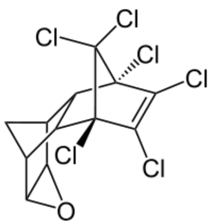
Carbaryl



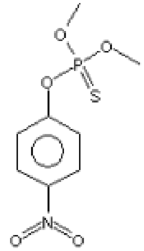
Aldrin



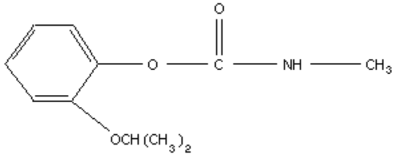
Dieldrin



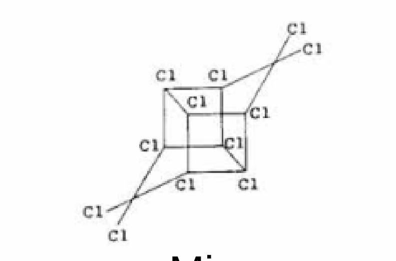
Endrin



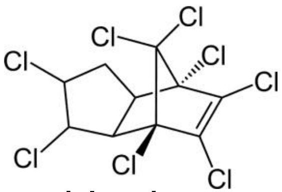
Methyl parathion



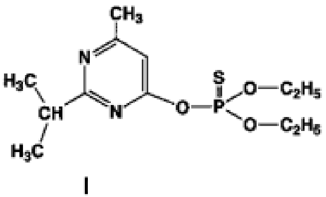
Baigon



Mirex



Chlordane



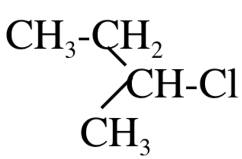
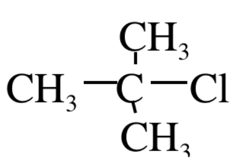
Diazinon

Structure vs. Properties

- Each substance has its own properties, reactivities, and effects. *Hazardous substances with similar chemical structures can have very different environmental fates and consequences:*

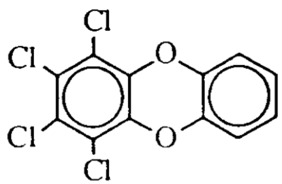
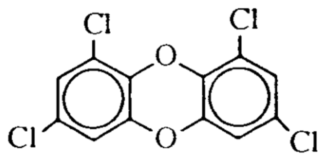
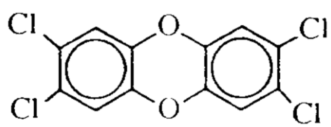
- Hydrolysis of chlorobutane:

  $C_4H_9Cl + H_2O \rightarrow C_4H_9OH + H^+ + Cl^-$

structure of isomer	half life ($t_{1/2}$)
$CH_3-CH_2-CH_2-CH_2-Cl$	1 year
	1 month
	30 sec

Structure vs. Toxicity

- Toxicity of tetrachlorodibenzo(1,4)dioxin (TCDD's)

structure of isomer	Lethal dose to kill rats (LD_{50})
	1 g/kg
	0.1 g/kg
	0.00004 g/kg (VERY TOXIC)

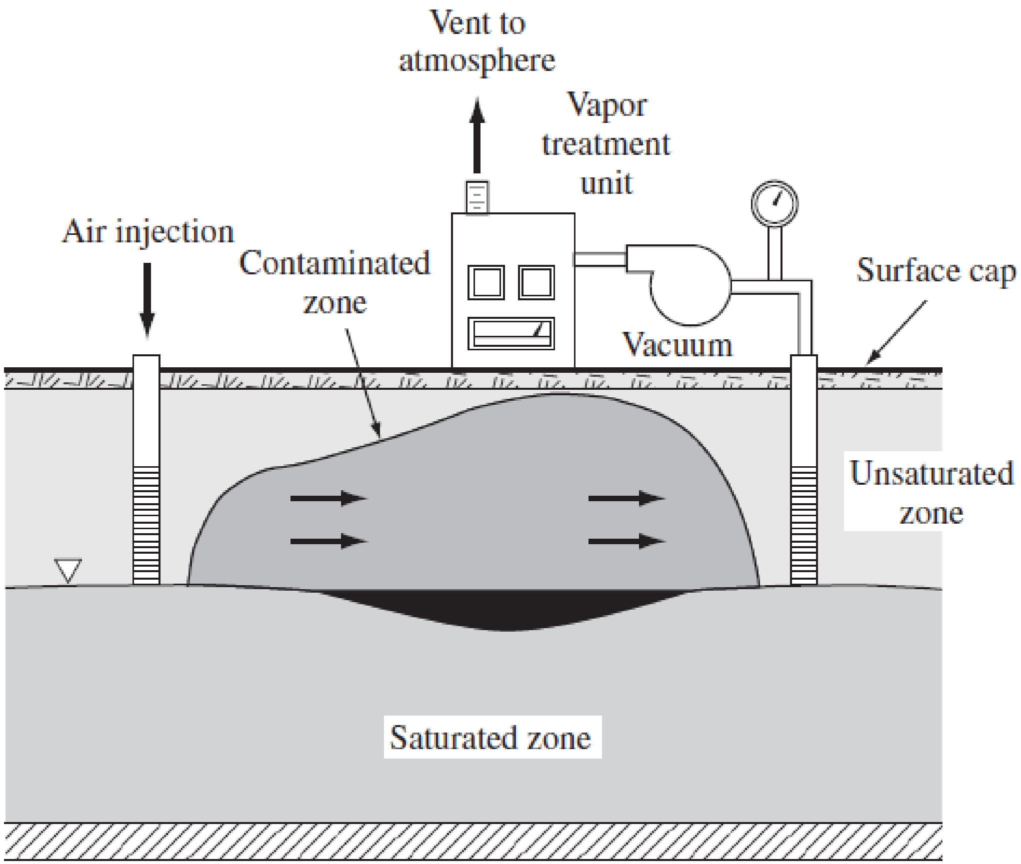
Groundwater Remediation Technologies

- **Characteristics**
  - Takes long time, hard to operate
  - Closely related to soil remediation
- **Classification**
  - In situ treatment
  - Ex situ Treatment

  - Bioremediation
  - Phytoremediation
  - Chemical treatment

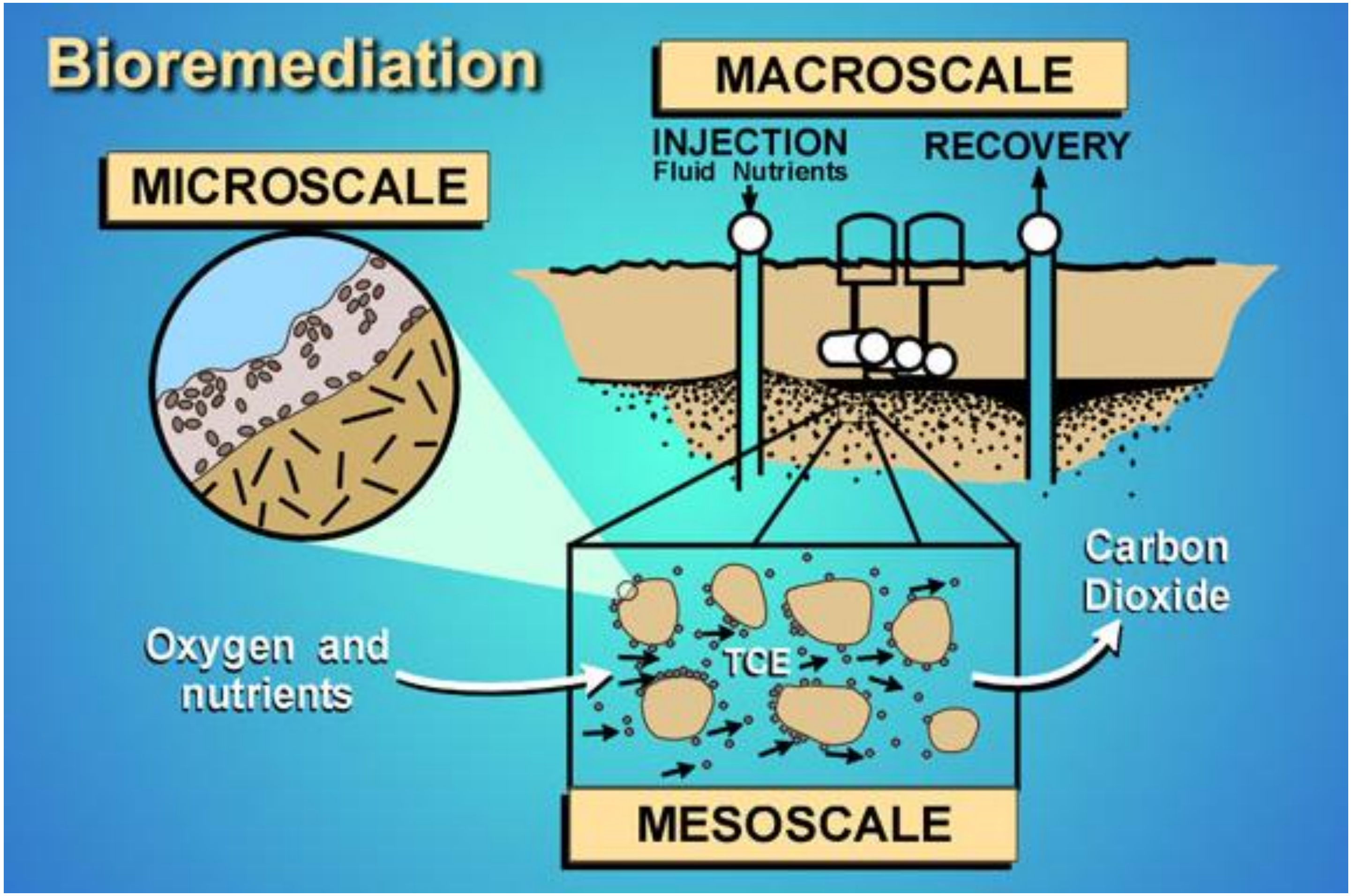
  & others

Groundwater Remediation Technologies



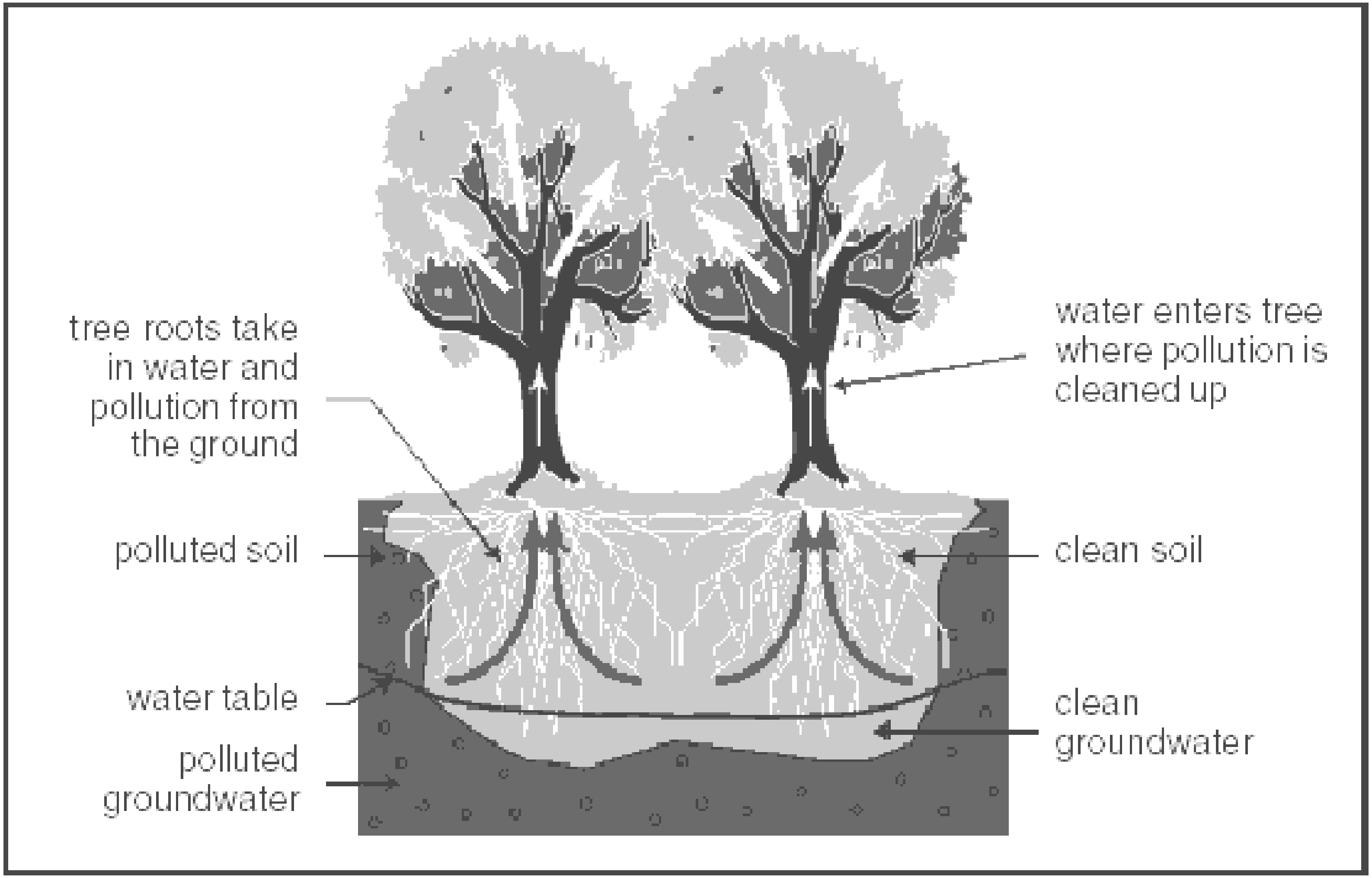
Soil Vapor Extraction

Groundwater Remediation Technologies



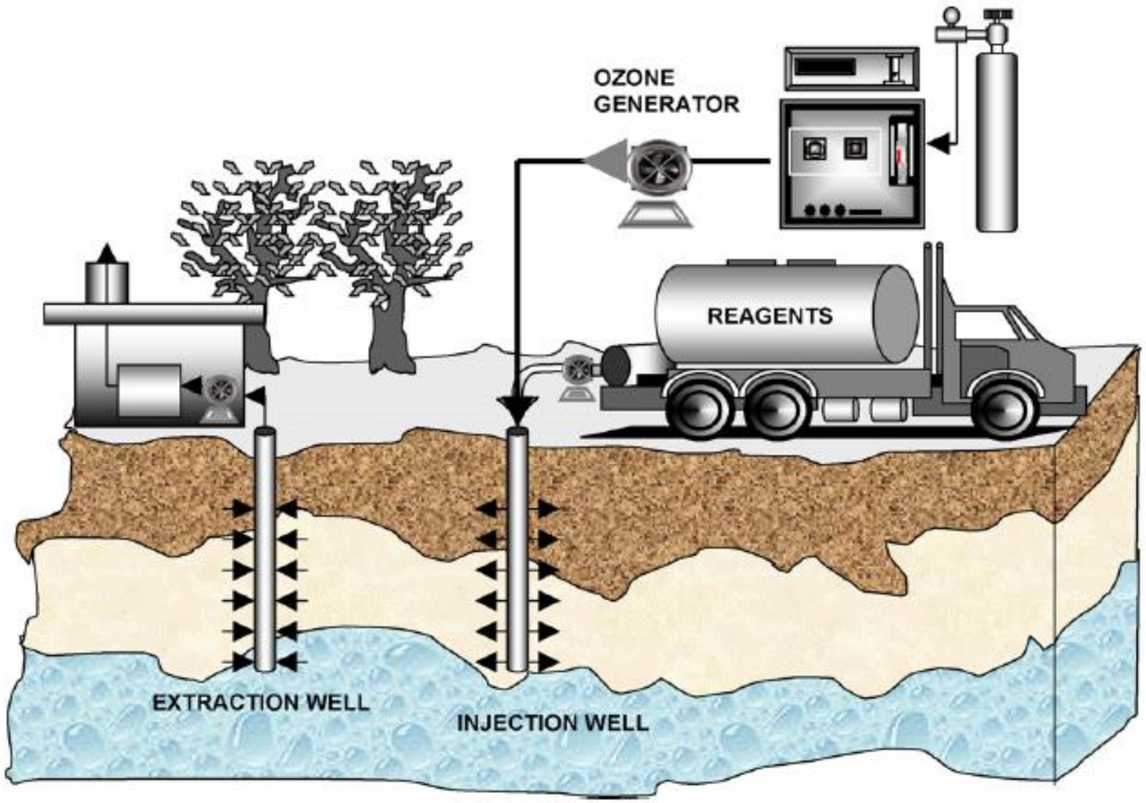
Bioremediation
(from the webpage of Center for Biofilm Engineering, MSU-Bozeman)

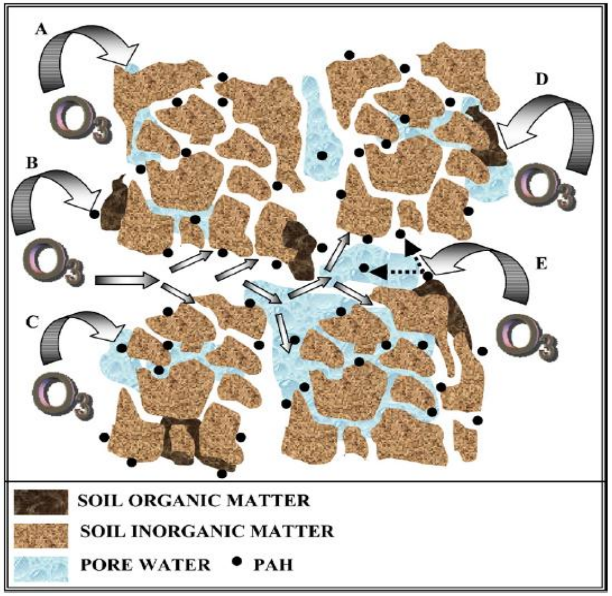
Groundwater Remediation Technologies



Phytoremediation (from the webpage of US EPA)

Groundwater Remediation Technologies

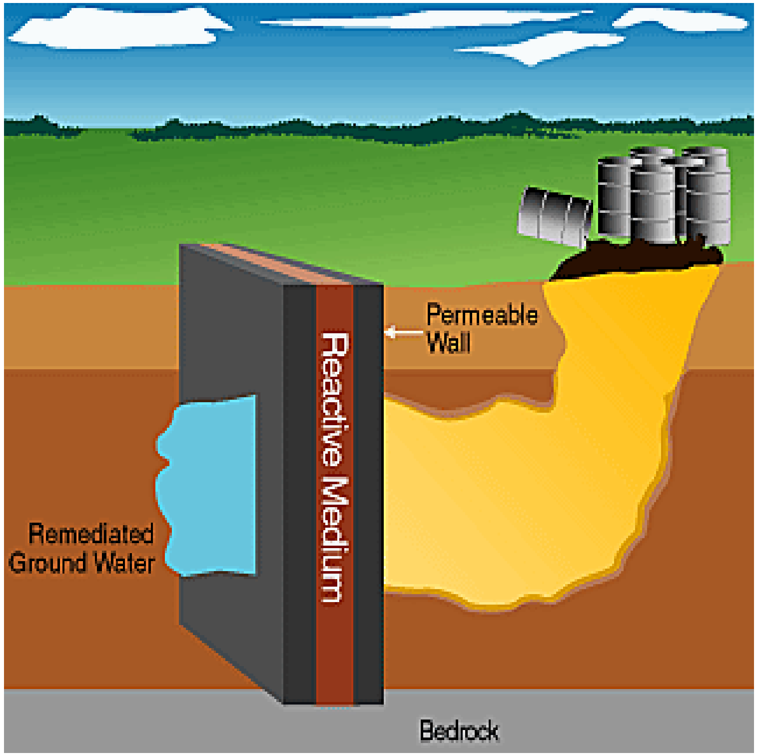


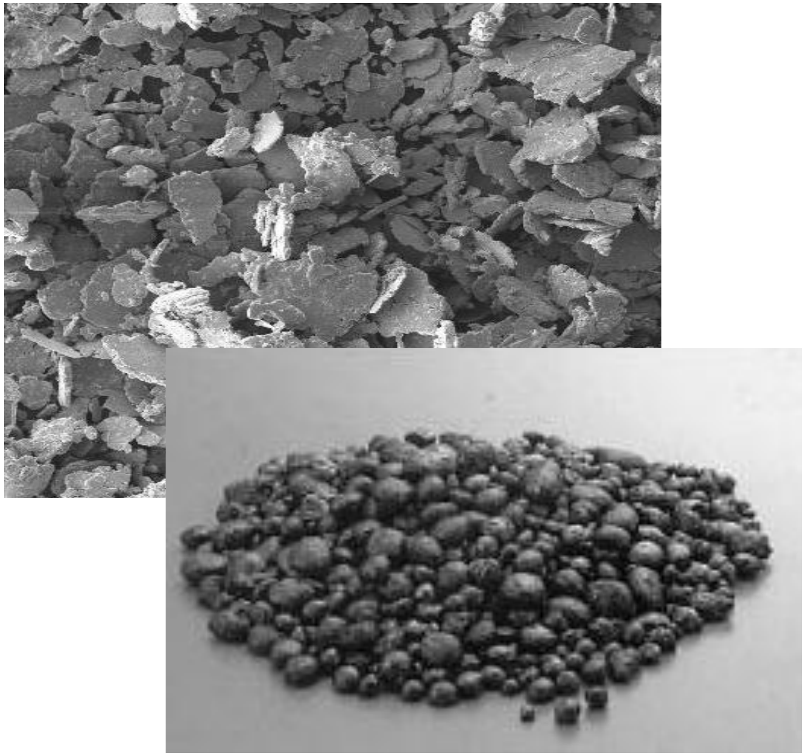


Chemical Oxidation

(ozone, Fenton's reagent, permanganate, persulfates, etc.)

Groundwater Remediation Technologies





Groundwater treatment using a ZVI permeable reactive barrier (PRB)

(ZVI: zero-valent iron)