

Contaminant properties

Lecture 1

Learning outcomes

- Concept of remediation
- Partitioning
- Dry/wet density
- Contaminant types and properties

Remediation

- What is remediation?

Process to remove contaminants or transform them into harmless compounds

- What is bioremediation?

Process relying on microbial activity to remove or transform contaminants

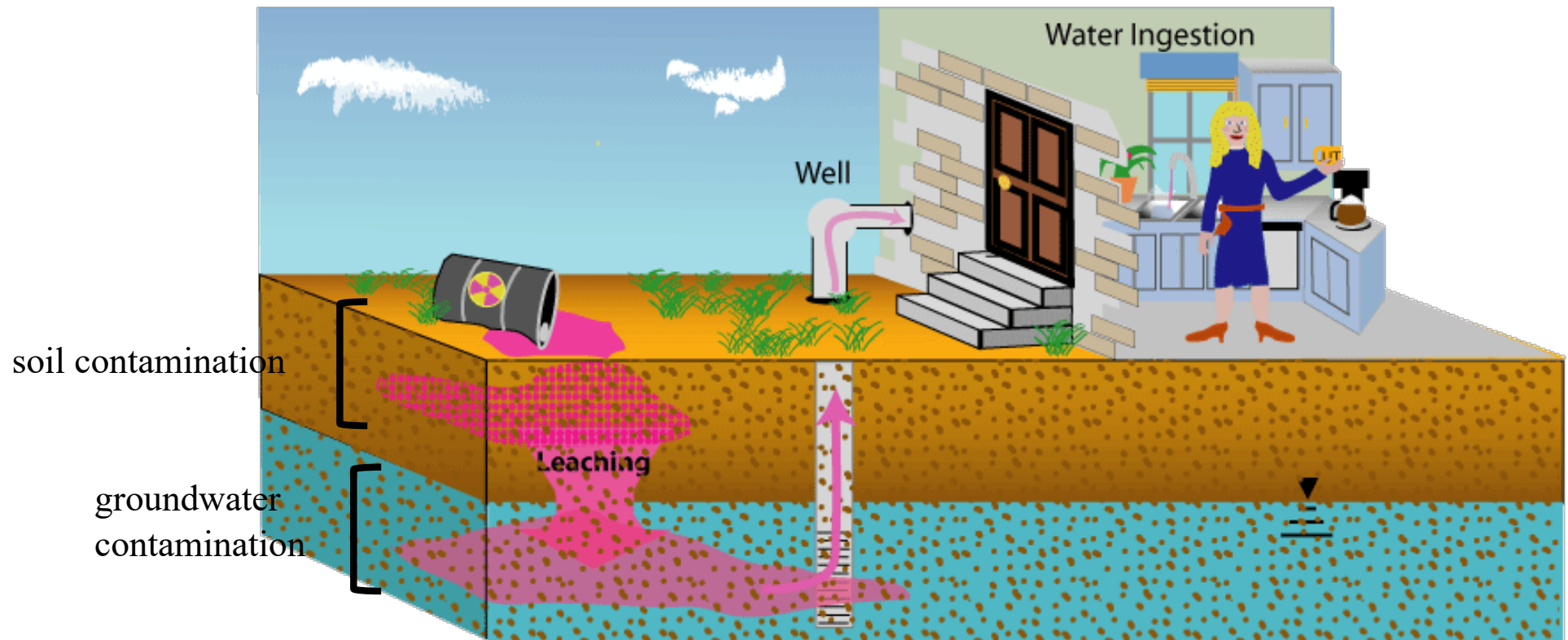
Major Concern:

Transport of contamination off site by ground and surface water flow

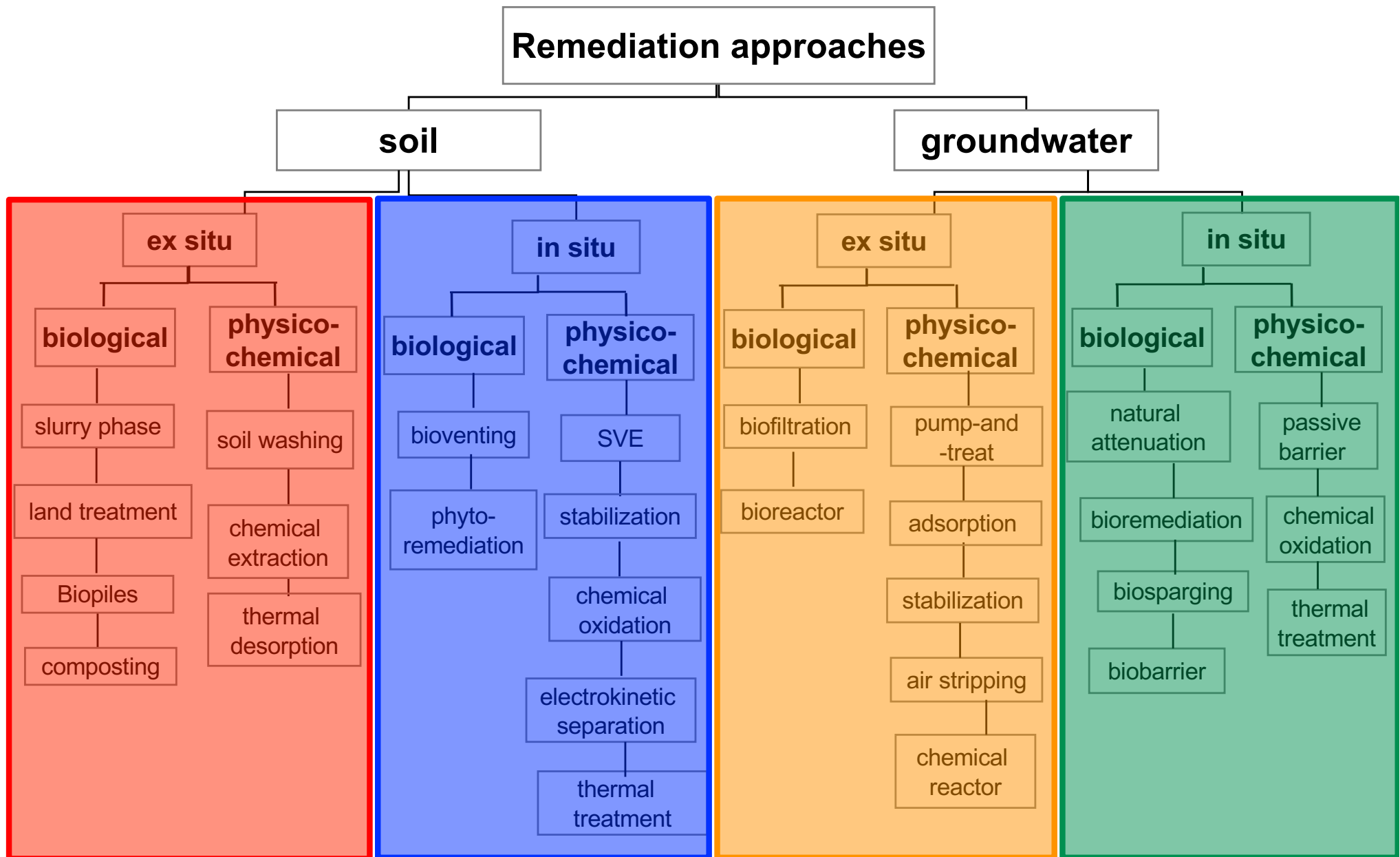
Challenges:

Unknowns in subsurface flow properties, contaminant behavior, response of microbial communities

Types of contaminated environments

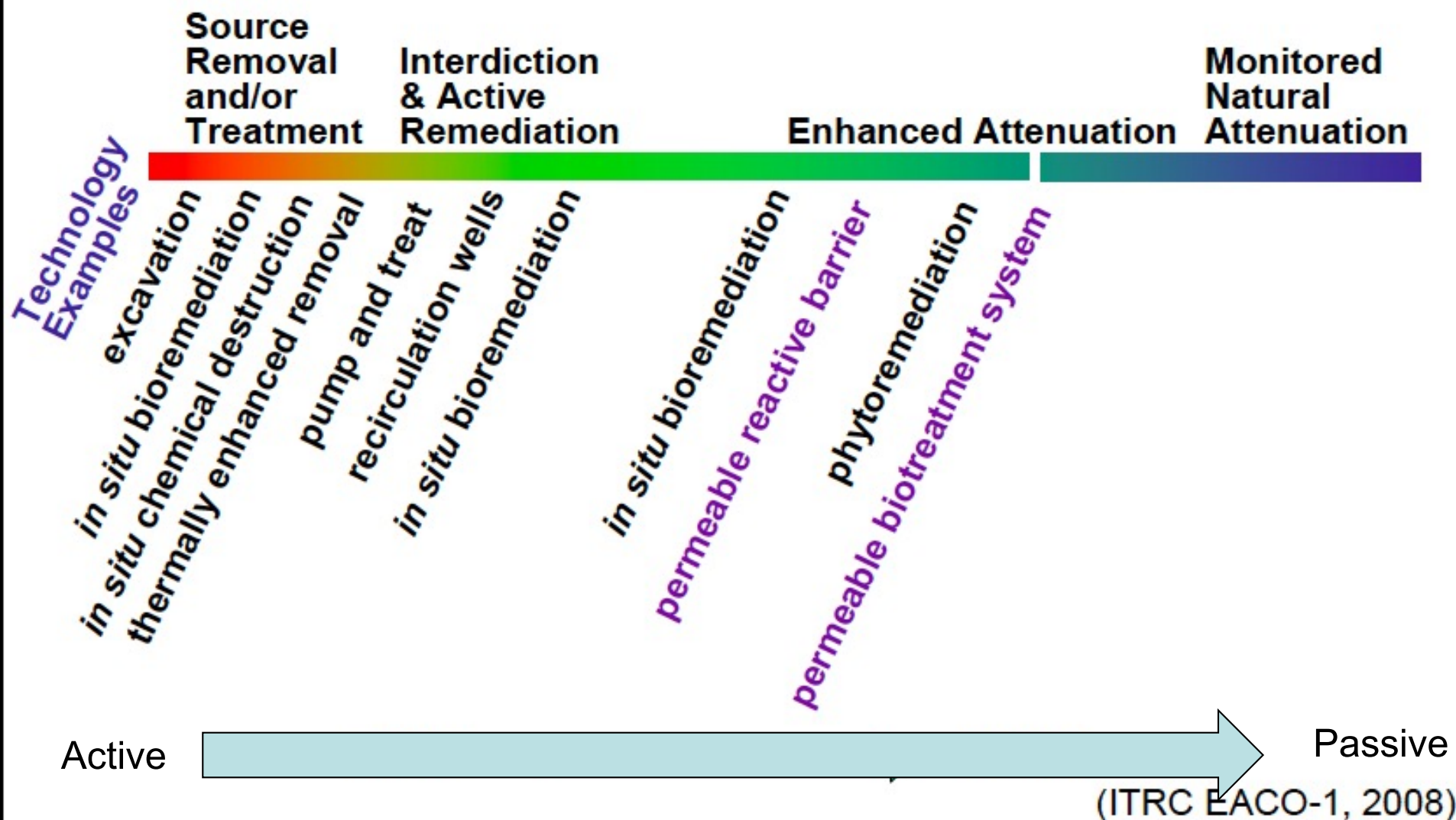


Remediation approaches



Continuum of Remediation Technologies: Active to Passive

Technology Class



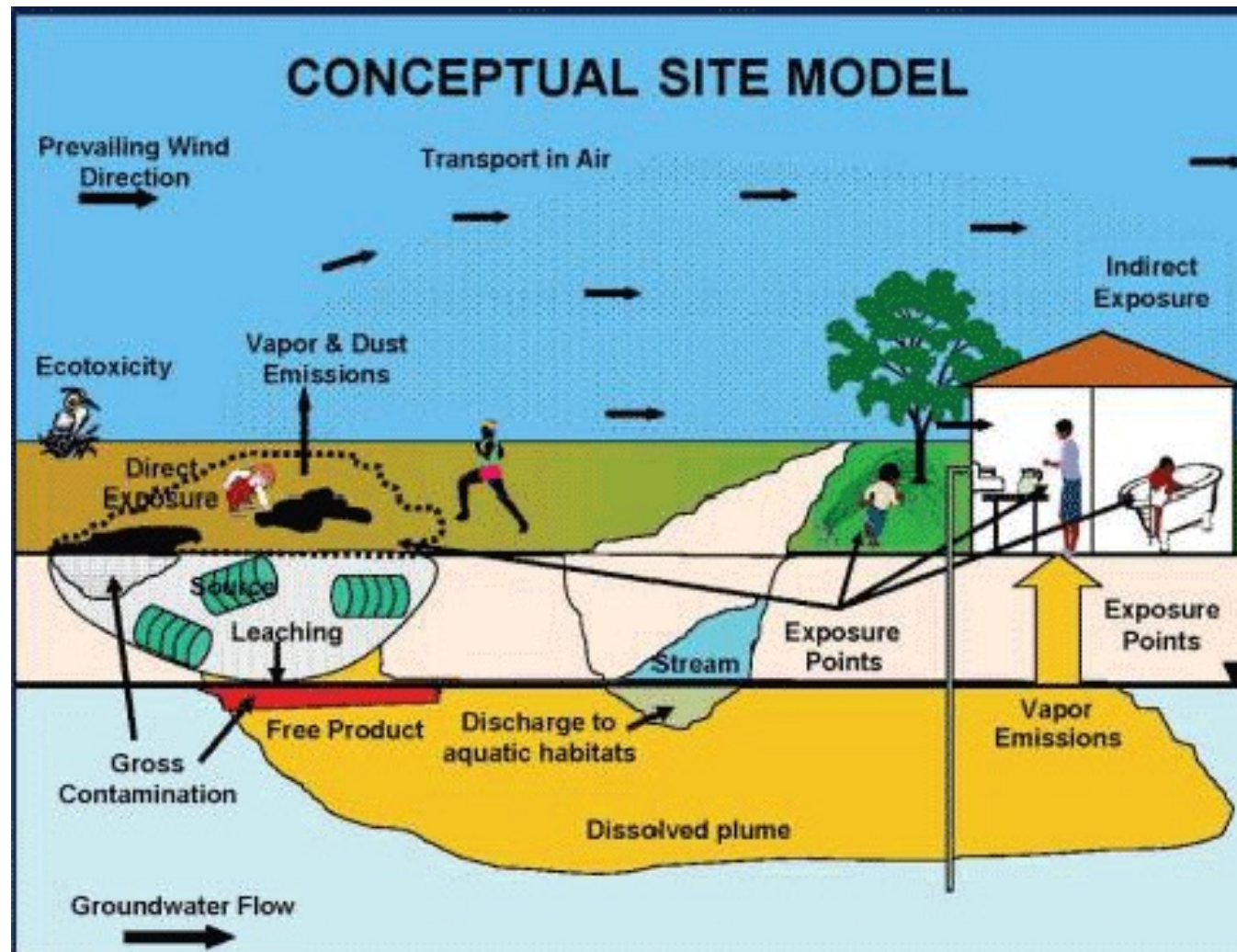
Cost of soil remediation approaches (in US)

	Type	Cost	comment
<i>In situ</i>	Bioventing	79-970 US\$/ m ³ soil	
	Enhanced biodegradation	30-100 US\$/ m ³ soil	
	phytoremediation	147-2,322 US\$/ m ³ soil	
	Chemical oxidation	No data	
	Electrokinetic separation	15-117 US\$/ m ³ soil	No full-scale implementation
	Soil flushing	18-49 US\$/ yard ³ soil	
	Soil vapor extraction	405-1,485 US\$/m ³ soil	
	Solidification/stabilization		depends on mixing technology and amendment
	In situ vitrification	\$375-425 per ton of soil	Few commercial applications
	In situ thermal treatment	29-62 US\$ /yard ³ soil	
<i>Ex situ</i>	Biopiles	130-260 US\$/ m ³ soil	
	Composting	481-578 US\$ /yard ³ soil	
	Land-farming	100 US\$/ m ³ soil	Add one-time laboratory and field test costs (125,000-150,000 US\$)
	Slurry-phase biological treatment	100-160 US\$/ m ³ soil	
	Soil washing	70-187 US\$/ m ³ soil	
	Chemical extraction	358-1717 US\$/ m ³ soil	
	Excavation and off-site disposal	300-510 US\$/ m ³ soil	Off-site disposal can vary in cost

Cost of groundwater remediation approaches (in US)

	Type	Cost	comment
<i>In situ</i>	biosparging/nitrate enhancement	10-60 US\$/ m ³ GW	
	biobarrier		
	Passive barrier	0.08-0.21 US\$/cubic yard GW	
	Chemical oxidation	\$31-175 US\$ /10,000 gal. GW	
	Thermal treatment	50-300 US\$/cubic yard GW 963-1,961 US\$/m ³ of barrier	
<i>Ex situ</i>	Biofiltration (gas phase)	5-10 US\$/kg contaminant	
	Bioreactor	21-167 US\$/1,000 gal. GW	
	Adsorption (gas phase)	\$1,000 for a 100-ft ³ /min unit to \$40,000 for a 7,000-ft ³ /min unit. Carbon costs 2 to 3 US\$ per pound.	
	Adsorption (liquid phase)	0.32-1.70 US\$ per 1,000 liters GW	
	Air stripping	4-21 US\$/10,000 gal. GW	

Source control vs. plume remediation



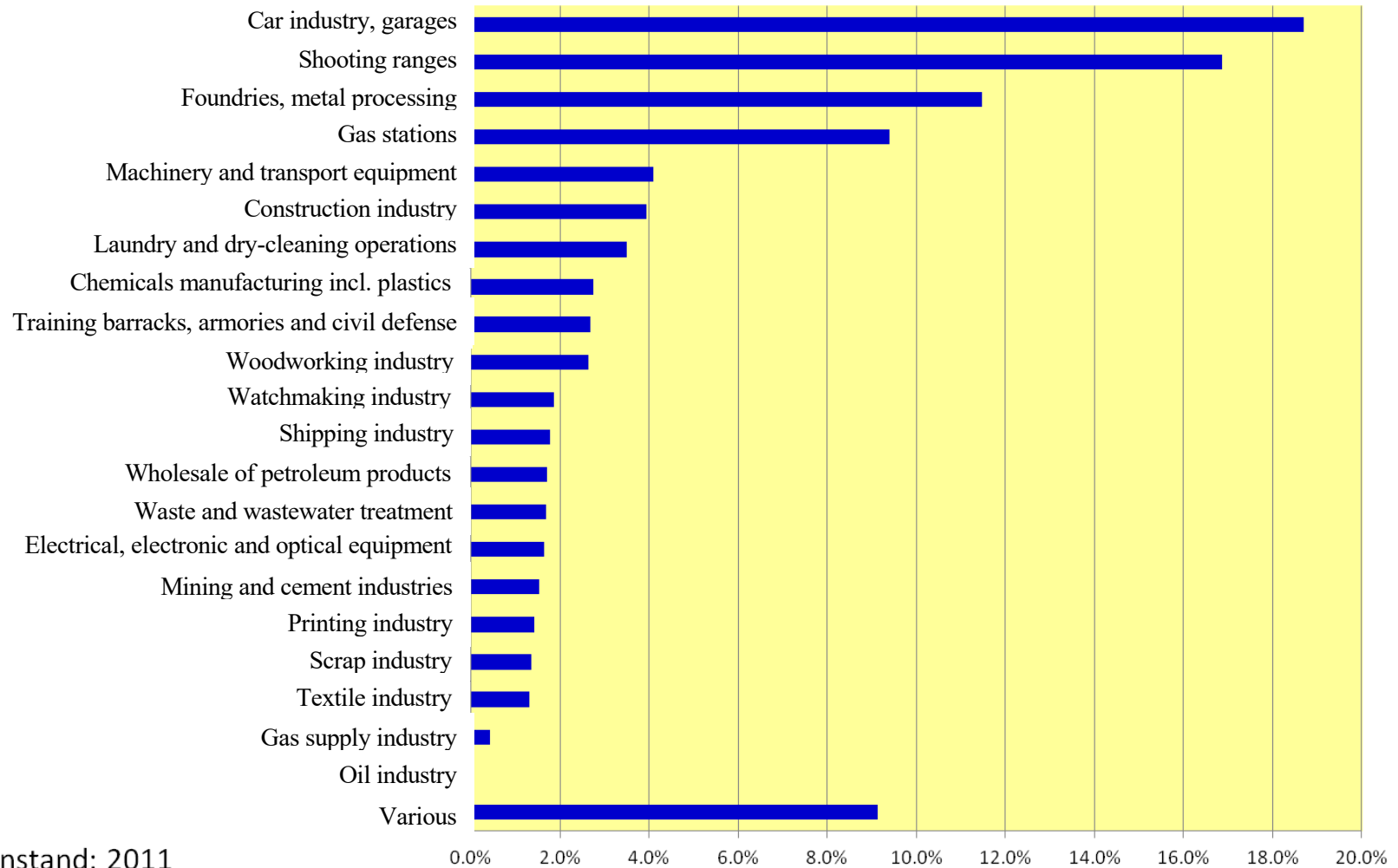
In Switzerland

- Of the approximately 700 soil remediation carried out to date- traditional methods are predominant
- Excavation of contaminated material and soil washing
- Securing of sites (barriers)
- *In situ* measures not fully accepted
- ‘The search for perfect solutions should be avoided’

In Switzerland

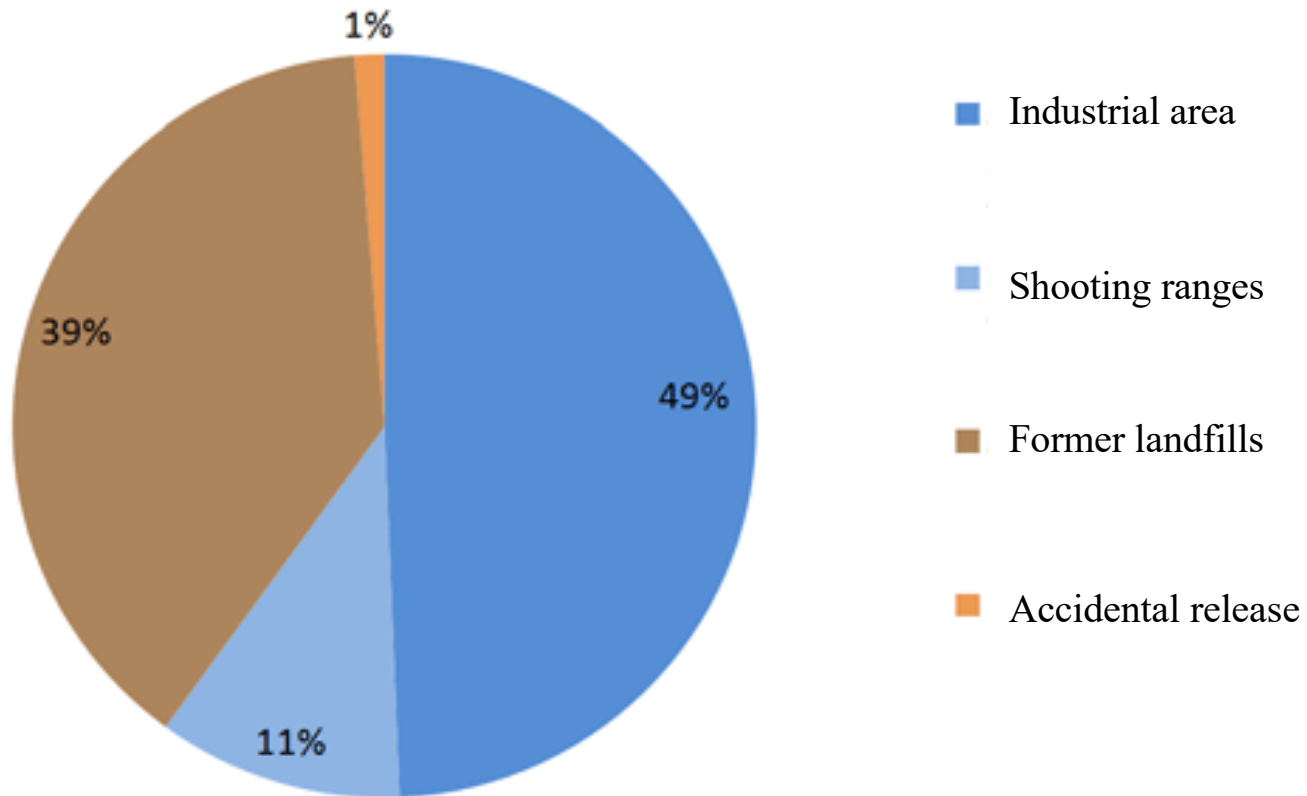
Contamination sources

Operating business: Types



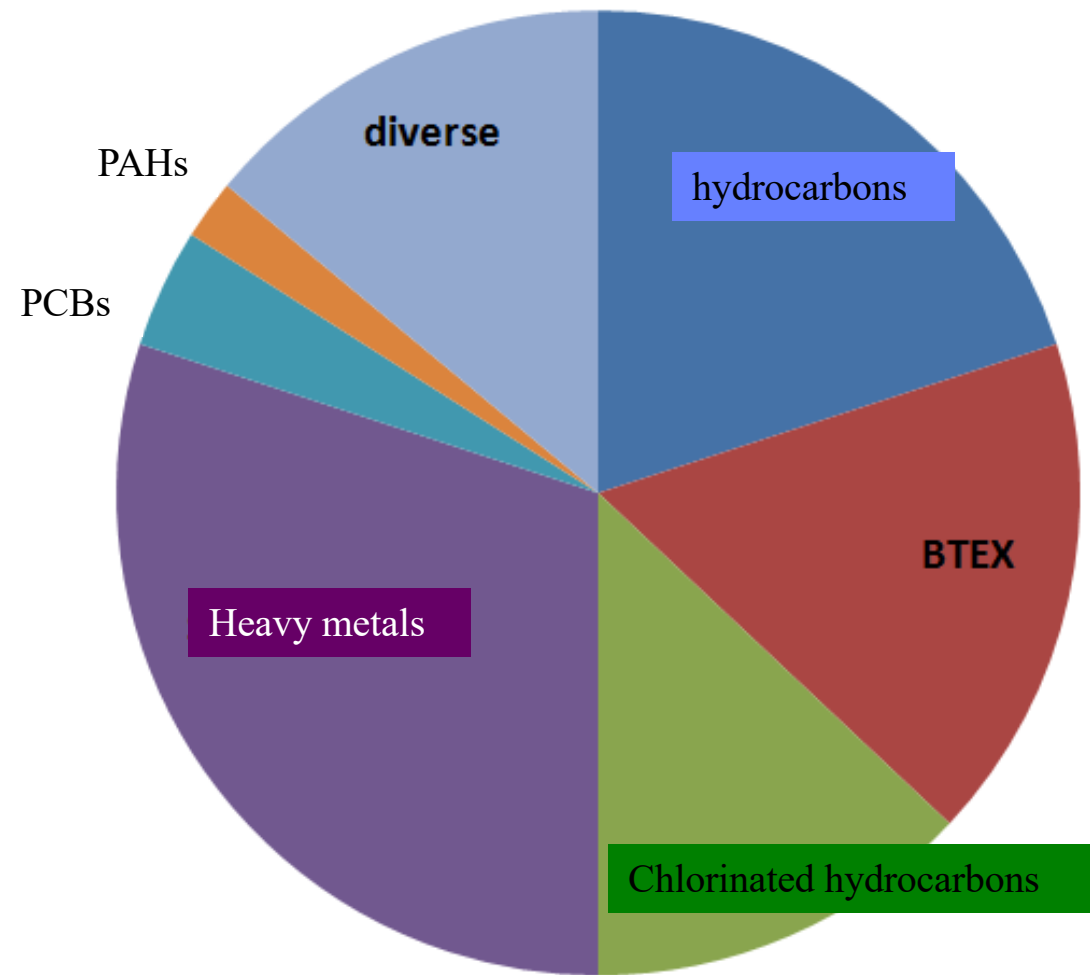
In Switzerland

Type of contamination area



In Switzerland

Contaminants



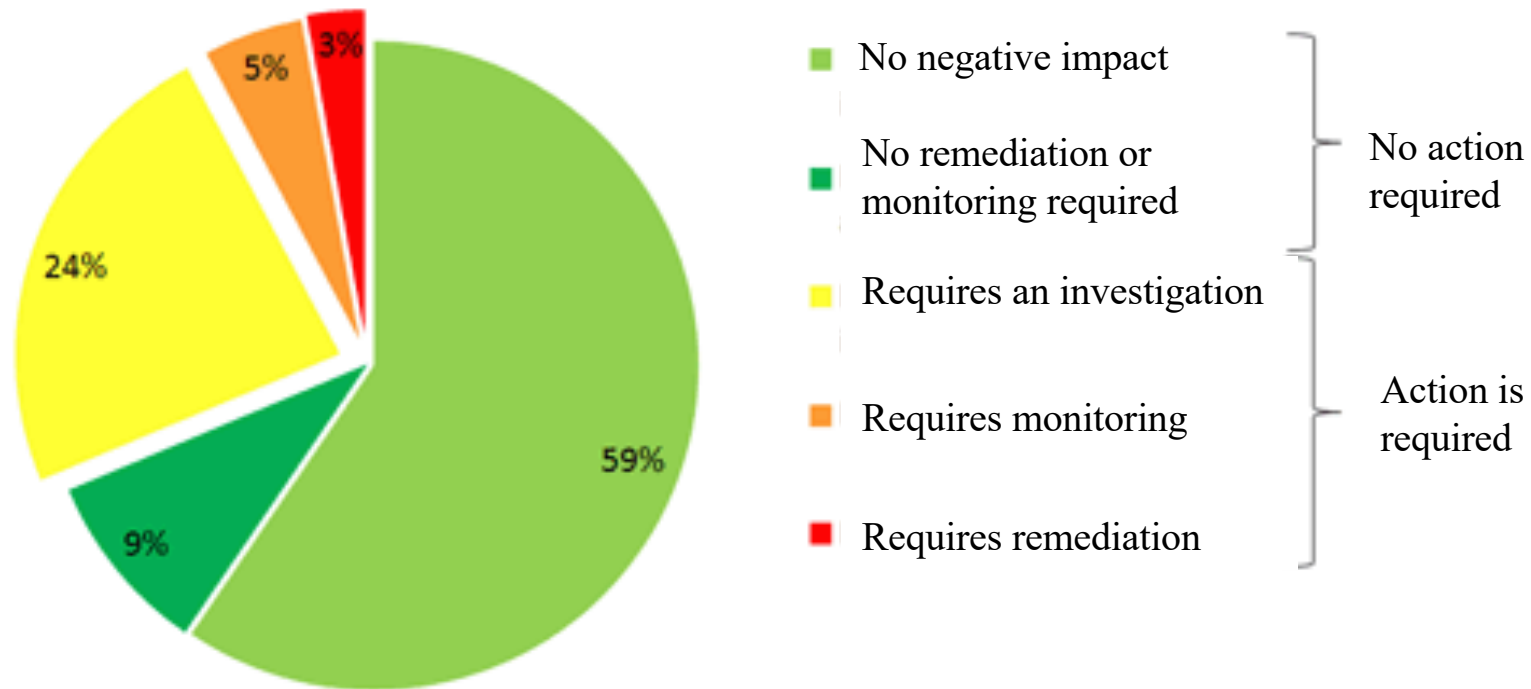
In Switzerland

Location of contaminated sites



In Switzerland

Sites to be remediated

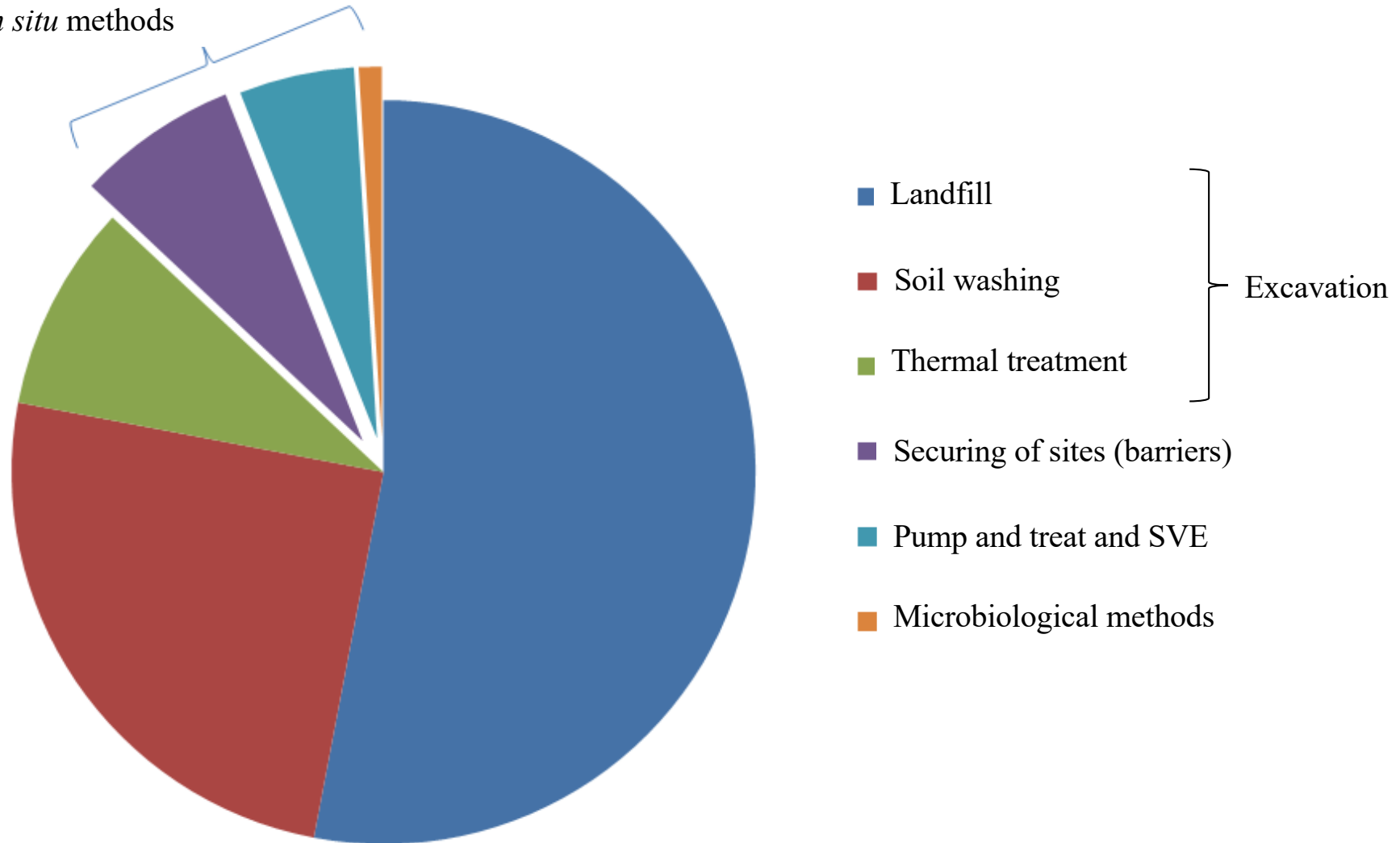


- 38,000 known contaminated sites
- About 4,000 need to be remediated (700 already cleaned up)

In Switzerland

Remediation methods

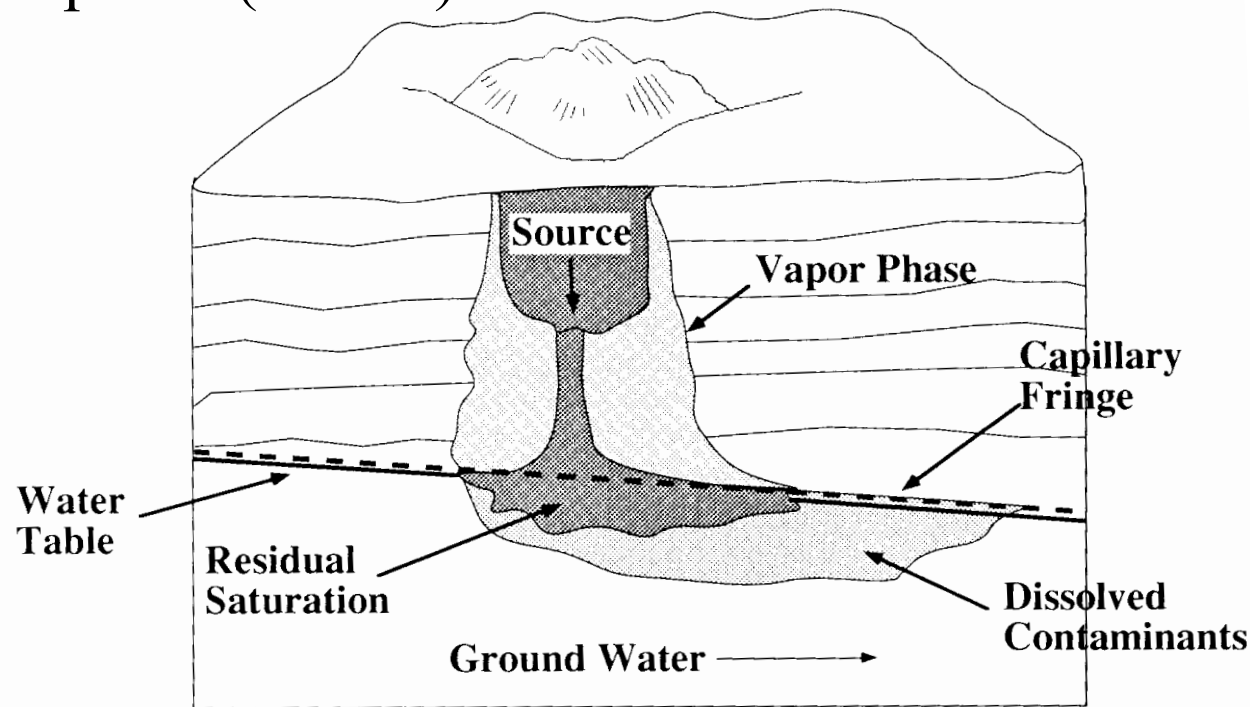
In situ methods



Contaminant properties

The contaminant is present in many different phases in the subsurface:

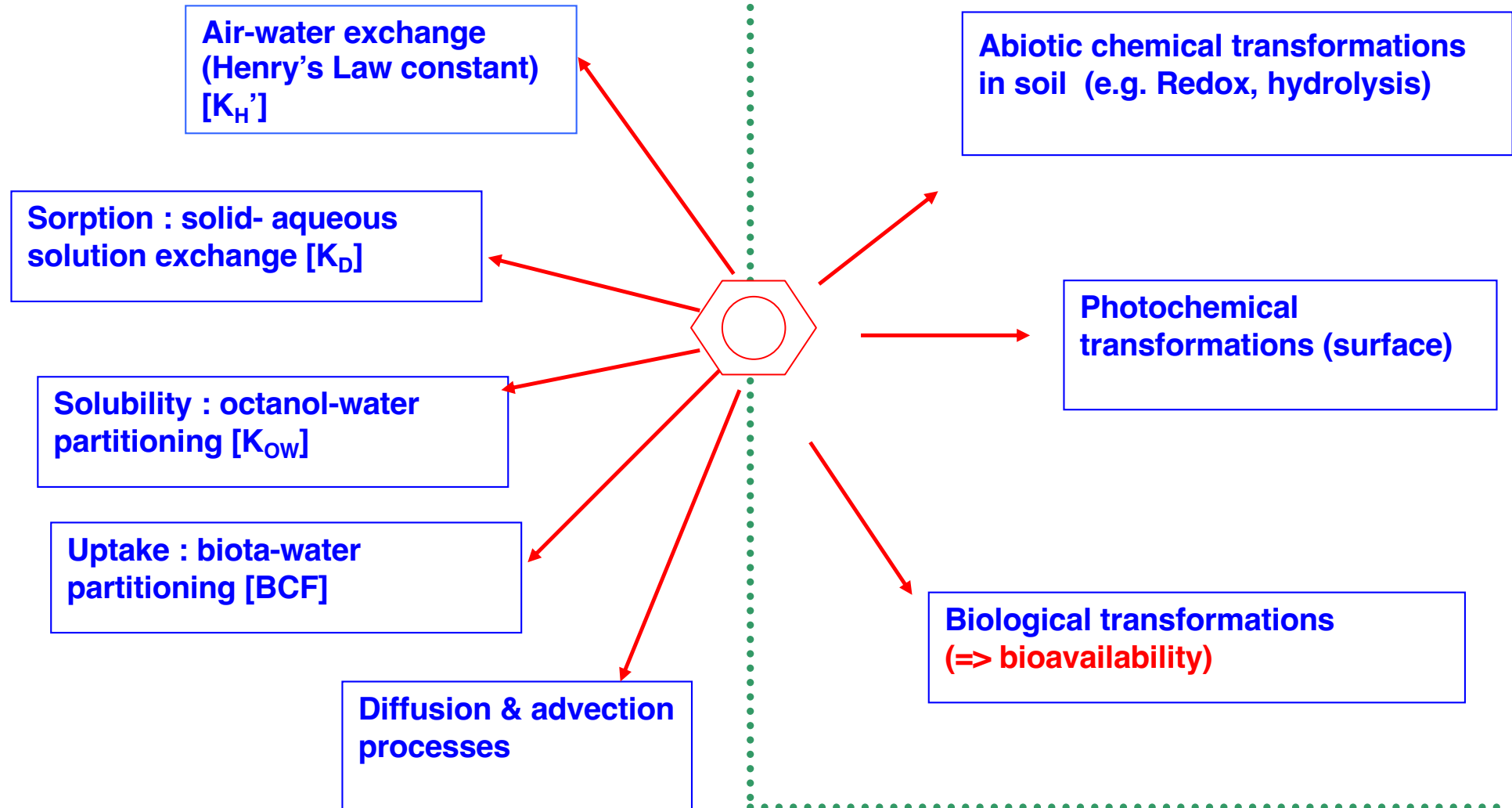
- vapor phase
- solid phase (sorbed)
- aqueous phase (dissolved)
- non-aqueous phase (NAPL)



The challenge is to target all these phases

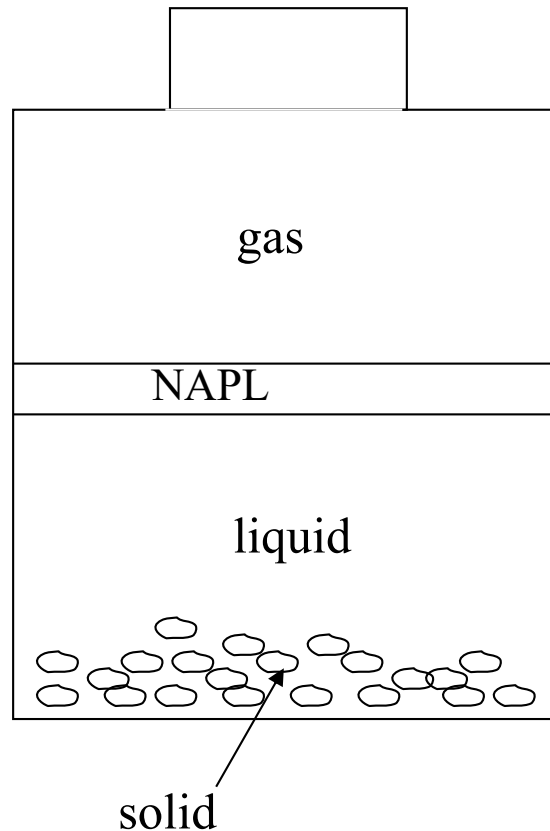
Environmental Fate of a Pollutant: Partitioning and transformations

Physical processes → **TRANSPORT**



Chemical / biological processes → **TRANSFORMATION**

Partitioning of a compound



V_L = volume of solution (L)

V_G = volume of gas (L)

M_S = mass of dry solid (g)

V_{NAPL} = volume of NAPL (L)

A compound (i) added to a closed bottle containing soil and water and a gas phase will partition into all three phases:

- $C_{i, aq}$ (mg/L water)
- $C_{i, g}$ (mg/L gas)
- $C_{i, s}$ (mg/g **dry solid**)
- $C_{i, NAPL}$ (mg/L NAPL)

The concentration of i in aqueous, gaseous, sorbed and non-aqueous phase will depend on:

- K_H' = gas-water partitioning
- K_D = sorbed- water partitioning
- K_{NW} = NAPL-water partitioning

• The amount of i in each phase (including the non-aqueous phase) is:

- $m_{i, aq} = C_{i, aq} * V_L$
- $m_{i, g} = C_{i, g} * V_G$
- $m_{i, s} = C_{i, s} * M_S$
- $m_{i, NAPL} = C_{i, NAPL} * V_{NAPL}$

Partitioning relationships

Air-water= Henry's Law constant

$$K_H' [-] = \frac{\text{molar conc. in gas}}{\text{molar conc. in aq. sol'n}} = \frac{C_{i,g} \text{ (mol in gas phase/L gas phase)}}{C_{i,aq} \text{ (mol in solution /L liquid)}} = \frac{P_i^{\text{sat}} / RT \text{ (mol/L)}}{C_{i,aq} \text{ (mol/L)}}$$

$$R = 82.06 \cdot 10^{-3} \text{ atm.L/mol.K; } T \text{ in K}$$

Soil-water= soil-water partitioning coefficient

$$K_D \text{ [m}^3\text{/g]} = \frac{\text{conc. sorbed (g/g)}}{\text{conc. in aq. sol'n (g/m}^3\text{)}} = \frac{C_{i,s} \text{ (g sorbed /g dry solid)}}{C_{i,aq} \text{ (g in solution /m}^3\text{ liquid)}}$$

NAPL-water= NAPL-water partitioning coefficient

$$K_{NW} [-] = \frac{C_{i,NAPL} \text{ (mol in NAPL phase/L NAPL phase)}}{C_{i,aq} \text{ (mol in solution /L liquid)}}$$

Note that all these partitioning coefficients include **the aqueous phase**

Henry's Law

Air-water partition= Henry's Law constant

$$K_H' [-] = \frac{\text{molar conc. in gas}}{\text{molar conc. in aq. sol'n}} = \frac{C_{i,g} \text{ (mol in gas phase/L gas phase)}}{C_{i,aq} \text{ (mol in solution /L liquid)}} = \frac{P_i^{\text{sat}} / RT \text{ (mol/L)}}{C_{i,aq} \text{ (mol/L)}}$$

$$R = 82.06 \cdot 10^{-3} \text{ atm.L/mol.K; } T \text{ in K}$$

$$K_H^v \frac{\text{L.atm}}{\text{mol}} = \frac{\text{partial pressure}}{\text{molar conc. in aq. sol'n}} = \frac{P \text{ (atm)}}{C_{i,aq} \text{ (mol in solution /L liquid)}} = \frac{P_i^{\text{sat}} \text{ (atm)}}{C_{i,aq} \text{ (mol/L)}}$$

Where does K_D (soil-water partitioning) come from?

K_D is derived from K_{OC}

K_{OC} = organic carbon/liquid partitioning coefficient (m^3/g)

$$K_D (m^3/g) = K_{OC} * f_{oc}$$

f_{oc} = organic carbon fraction in soil [g OC/g soil]

K_{OC} is derived from K_{ow} through an empirical relationship

$\log K_{OC} = a * \log K_{ow} + c$ where a and c are empirical constants

$$K_{ow} [-] = \frac{\text{conc. in octanol (mol/L)}}{\text{conc. in aq. sol'n (mol/L)}} = \frac{C_{i,oct} (\text{mol in octanol/L octanol})}{C_{i,aq} (\text{mol in solution/L water})}$$

K_{OW} can be directly measured (like K_H ' and K_{NW}) or computed

Mass and volume relationships in the soil matrix

- The soil (or sediment) is composed of solids, water and air.
- The solid portion is made of minerals, organic matter and microorganisms.
- The void volume in soil is filled with air and water. (mass of air is negligible)
- Due to density differences between air and water, dry and wet soil densities are different.

M_S = mass of dry solid (g)

V_S = volume of dry solid (m^3) V_L = volume of water in soil (m^3) V_G = volume of gas in soil (m^3)

V_T = total volume of soil (m^3) = $V_S + V_L + V_G$ M_L = mass of water (g) = $\rho_W * V_L$
with ρ_W water density (g/m^3)

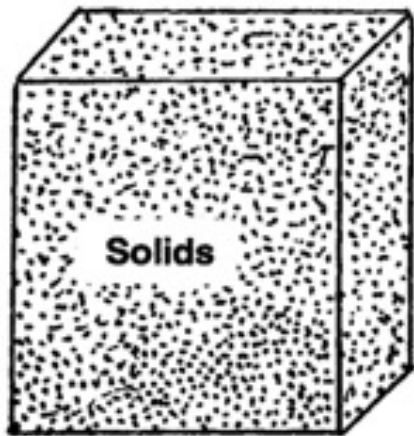
$$\rho_S = (\text{dry}) \text{ solids density } (g/m^3) = \frac{\text{mass of dry solid (g)}}{\text{volume of dry solid } (m^3)} = \frac{M_S (g)}{V_S (m^3)}$$

$$\rho_b = \text{dry bulk density } (g/m^3) = \frac{\text{mass of dry solid (g)}}{\text{Total soil volume } (m^3)} = \frac{M_S (g)}{V_T (m^3)}$$

$$\rho_{wb} = \text{wet bulk density } (g/m^3) = \frac{\text{mass of wet soil (g)}}{\text{Total soil volume } (m^3)} = \frac{M_S + M_L (g)}{V_T (m^3)}$$

$$\rho_b < \rho_S$$

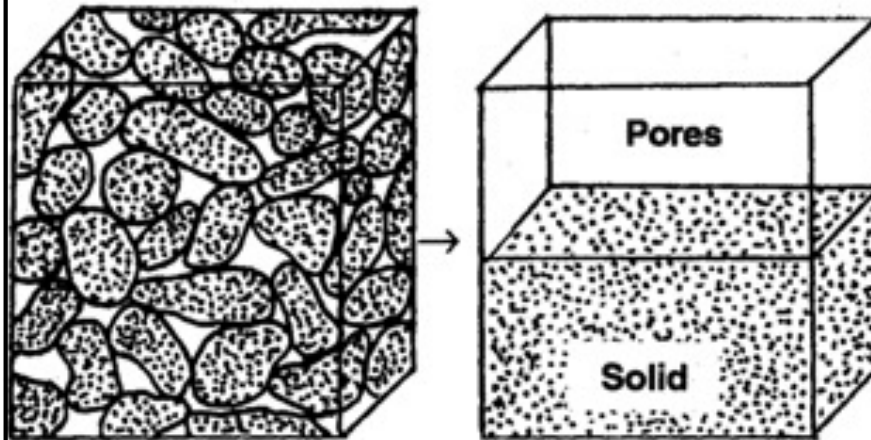
$$\rho_b < \rho_{wb}$$



solids density

100% solid
 $M_S = \text{Weight} = 2.66 \text{ g}$
 $V_S = \text{Volume} = 1 \text{ cm}^3$
 $\rho_s = 2.66 \text{ g/cm}^3$

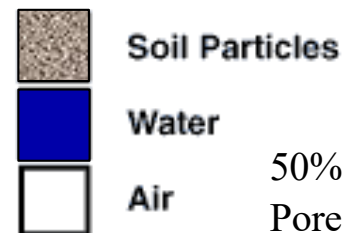
$$\rho_s = \frac{M_S (\text{g})}{V_S (\text{cm}^3)}$$



dry bulk density

50% solid, 50% pore space
 $M_S = \text{Weight} = 1.33 \text{ g}$
 $V_T = \text{Volume} = 1 \text{ cm}^3$
 $\rho_b = 1.33 \text{ g/cm}^3$

$$\rho_b = \frac{M_S (\text{g})}{V_T (\text{cm}^3)}$$



wet bulk density

50% solid, 50% pore space
 Pore space: 40% water, 60% air

$M_S = 1.33 \text{ g}$
 $M_L = 0.2 \text{ g}$
 $V_T = 1 \text{ cm}^3$

$$\rho_{wb} = 1.53 \text{ g/cm}^3$$

$$\rho_{wb} = \frac{M_T (\text{g})}{V_T (\text{cm}^3)} = \frac{M_L + M_S (\text{g})}{V_T (\text{cm}^3)}$$

Dimensionless sorption coefficient K_p

Convert K_D to a dimensionless ratio of mass concentration (K_p)

$$\begin{aligned}
 K_p \quad [-] &= \frac{\text{conc. sorbed (g/m}^3\text{)}}{\text{conc. in aq. sol'n (g/m}^3\text{)}} = \frac{C_{i,s, \text{ vol}} \text{ (g sorbed /m}^3\text{ solid)}}{C_{i, \text{ aq}} \text{ (g in solution/m}^3\text{ liquid)}} \\
 &= \frac{C_{i,s} \text{ (g sorbed /g dry solid)}}{C_{i, \text{ aq}} \text{ (g in solution /m}^3\text{ liquid)}} * \frac{\rho_s \text{ (g dry solid)}}{\text{(m}^3\text{ solid)}} = K_D \rho_s
 \end{aligned}$$

ρ_s solid density (g/m³) = $\frac{\text{g dry solid}}{\text{m}^3 \text{ dry solid}}$

$$K_p = \frac{C_{i,s, \text{ vol}}}{C_{i, \text{ aq}}} = K_D \rho_s$$

Where $C_{i,s, \text{ vol}}$ is the volume-based concentration of sorbed compound i on the solid phase

$$C_{i,s, \text{ vol}} \text{ (g sorbed/m}^3\text{ solid)} = C_{i,s} \text{ (g sorbed/g solid)} * \rho_s \text{ (g solid/m}^3\text{ solid)}$$

Mass distribution coefficient

If solids are suspended in water or an aquifer is being considered, the mass distribution of a substance i between solid and liquid is:

$$\frac{m_{i,s}}{m_{i,aq}} = \frac{\text{mass } i \text{ on dry solid}}{\text{mass } i \text{ in solution}} = \text{mass distribution coefficient}$$

$$\frac{m_{i,s}}{m_{i,aq}} = \frac{C_{i,s} * V_s * \rho_s}{C_{i,aq} * V_L} = K_p * \frac{V_s}{V_L} = K_D * \rho_s * \frac{V_s}{V_L} = K_D * \left(\frac{M_s}{V_L} \right) = K_D * C_{ss}$$

C_{ss} is concentration of suspended solids (g dry solids/m³ solution)= M_s/V_L

M_s is the total mass of dry solids (g solids)= ρ_s (g solid/m³ solid) * V_s (m³ solid)

$f_{i,s}$ is the fraction of total mass i in solids (assuming no gas phase)

$$f_{i,s} = \frac{\text{mass of } i \text{ on solids}}{\text{total mass of } i} = \frac{m_{i,s}}{m_{i,s} + m_{i,aq}} = \frac{\left(m_{i,s} / m_{i,aq} \right)}{\left(m_{i,s} + m_{i,aq} \right) / m_{i,aq}} = \frac{\left(m_{i,s} / m_{i,aq} \right)}{\left(m_{i,s} / m_{i,aq} \right) + 1}$$

$$f_{i,s} = \frac{K_D * C_{ss}}{K_D * C_{ss} + 1}$$

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$$\rho_b = \text{dry bulk density (g/m}^3\text{)} = \frac{\text{mass of dry solid (g)}}{\text{Total soil volume (m}^3\text{)}} = \frac{M_S \text{ (g)}}{V_T \text{ (m}^3\text{)}}$$

$$\rho_{wb} = \text{wet bulk density (g/m}^3\text{)} = \frac{\text{mass of wet soil (g)}}{\text{Total soil volume (m}^3\text{)}} = \frac{M_S + M_L \text{ (g)}}{V_T \text{ (m}^3\text{)}}$$

$$\varepsilon = \text{porosity [-]} = \frac{\text{volume of void (m}^3\text{)}}{\text{total volume of soil (m}^3\text{)}} = \frac{V_L + V_G \text{ (m}^3\text{)}}{V_T \text{ (m}^3\text{)}}$$

$$\omega = \text{soil moisture content (mass basis) [-]} = \frac{\text{mass of water (g)}}{\text{mass of dry solids (g)}} = \frac{M_L \text{ (g)}}{M_S \text{ (g)}}$$

$$\theta = \text{soil moisture content (volume basis) [-]} = \frac{\text{volume of water (m}^3\text{)}}{\text{Total volume of soil (m}^3\text{)}} = \frac{V_L \text{ (m}^3\text{)}}{V_T \text{ (m}^3\text{)}}$$

Dry bulk density of soils

Soil Bulk Density

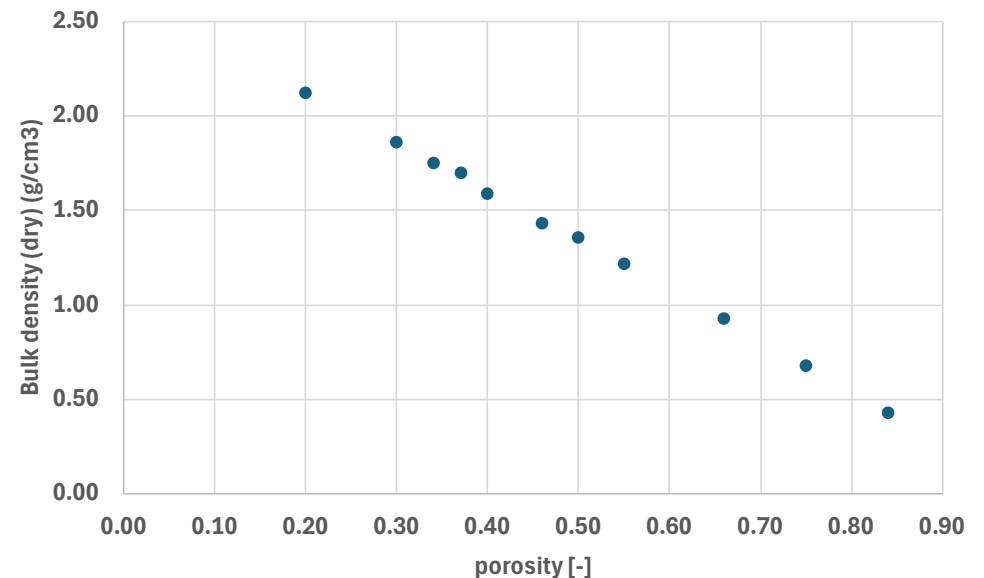
$$\rho_b = \frac{M_s \text{ (g)}}{V_T \text{ (m}^3\text{)}}$$

Soil Description	Porosity	ρ_k (dry g/cm ³)
Uniform sand, loose	0.46	1.43
Uniform sand, dense	0.34	1.75
Mixed-grain sand, loose	0.40	1.59
Mixed-grain sand, dense	0.30	1.86
Windblown silt (loess)	0.50	1.36
Glacial till, very mixed-grained	0.20	2.12
Soft glacial clay	0.55	1.22
Stiff glacial clay	0.37	1.70
Soft slightly organic clay	0.66	0.93
Soft very organic clay	0.75	0.68
Soft montmorillonitic clay (calcium bentonite)	0.84	0.43

^a From Peck et al. (1962).

High porosity typically results in **low ρ_b** .

This is because the solid phase takes up less volume (meaning less mass) than a low porosity material.



In-class problem 1:

Part 1. A groundwater is impacted by gasoline, and the average dissolved gasoline concentration is 20 mg/L. In situ bioremediation is being considered for the aquifer with the following characteristics:

Porosity= 0.35; Organic content= 0.02; **Dry bulk density** of aquifer materials= 1.6 g/cm³; Toluene (C₇H₈): K_{oc}= 182 L/kg

What is the concentration of toluene adsorbed to the solid? How much toluene is present in the solid phase of 1 m³ of aquifer sediment?

$$\varepsilon = 0.35; f_{oc} = 0.02; \rho_b = 1.6 \text{ g/cm}^3; K_{oc} = 182 \text{ L/kg}; C_{tol, aq} = 20 \text{ mg/L}$$

In-class problem 1:

Part 2. A groundwater is impacted by gasoline, and the average dissolved gasoline concentration is 20 mg/L. In situ bioremediation is being considered for the aquifer with the following characteristics:

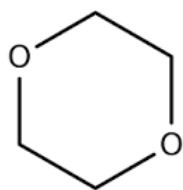
Porosity= 0.35; Organic content= 0.02; **Wet bulk density** of aquifer materials= 1.6 g/cm³; Toluene (C₇H₈): K_{oc}= 182 L/kg

What is the concentration of toluene adsorbed to the solid? How much toluene is present in the solid phase 1 m³ of aquifer sediment?

$$\varepsilon = 0.35; f_{oc} = 0.02; \rho_{wb} = 1.6 \text{ g/cm}^3; K_{oc} = 182 \text{ L/kg}; C_{tol, aq} = 20 \text{ mg/L}$$

Partitioning of compounds among phases

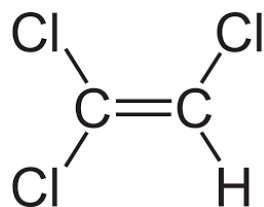
	unit	1,4-dioxane	benzene	TCE	1,1,1-TCA	1,1-DCE
Water solubility	g/L (25 °C)	1,000	1.79	1.28	0.91	2.42
Henry's Law	atm.L/mol at 25 °C	4.8×10^{-3}	5.55	9.85	16	26.1
LogK _{OC}	-	1.23	1.75	2.0	1.95	1.85
Log K _{ow}	-	-0.27	2.13	2.42	2.49	2.13



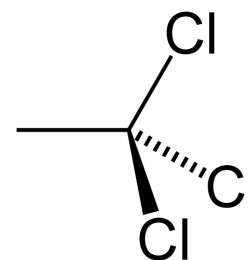
1,4-dioxane



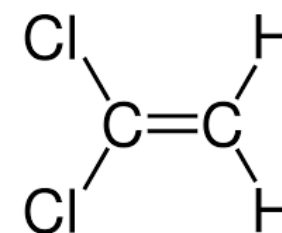
benzene



trichloroethylene
(TCE)



1,1,1-TCA
1,1,1-trichloroethane

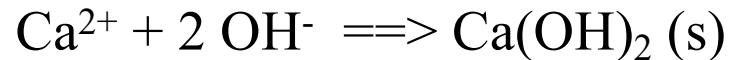


1,1-DCE
1,1-dichloroethylene

Other useful parameters

- Solubility product:

Solubility is the degree to which a solute will dissolve into a solvent. The solubility of chemicals in water is a function of the chemical species and temperature. Solubility is usually expressed in g/L.



$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = 6.5 \times 10^{-6}$$

- In-class problem 2:

Calculate the solubility of Ca(OH)_2 in g/L at pH 12

MW of Ca(OH)_2 is 74 g/mol

Other useful parameters

- Vapor pressure:
When a liquid is in contact with air, molecules leave the liquid as a vapor, via evaporation.
- Vapor pressure of a pure liquid is the pressure exerted by the vapor on the liquid at equilibrium

Raoult's law:

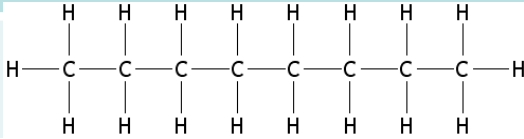
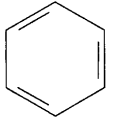
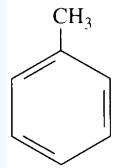
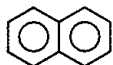
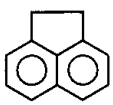
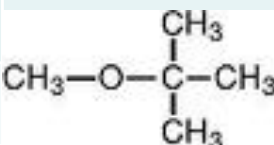
- $p_a = p_{vp, a}^* x_a$ and $p_b = p_{vp, b}^* x_b$
- p_a = partial vapor pressure of component a over the solution
- $p_{vp, a}^*$ = vapor pressure of pure component a
- x_a = mole fraction of component a in solution = $\text{mol a} / (\text{mol a} + \text{mol b})$
- $p_{\text{total}} = p_a + p_b$

Major classes of contaminants

- Petroleum hydrocarbons (including PAHs= polyaromatic hydrocarbons)
- Halogenated hydrocarbons (including PCBs= polychlorinated biphenyls)
- Pesticides
- Explosives
- PFAS
- Inorganic

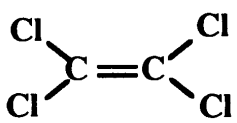
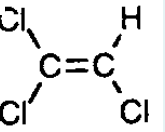
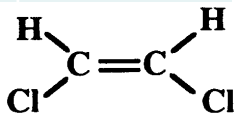
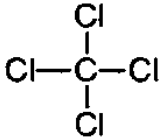
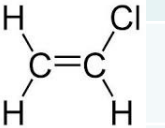
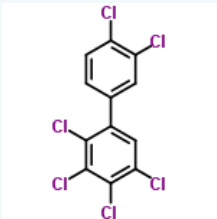
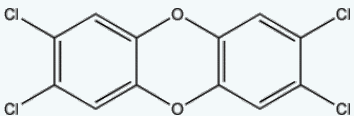
Petroleum hydrocarbons

- Aliphatic hydrocarbons
- Aromatic hydrocarbons (BTEX)
- Polycyclic aromatic hydrocarbons (PAHs)
- Oxygenates (added as fuel oxygenates for more efficient combustion)

	examples	structure	Water solubility (mg/L)	MW (g/mol)	source
aliphatic	octane hexane		0.78	114.23	fuel
aromatic	Benzene Toluene Ethylbenzene Xylene	 Benzene	1,800	78.1	fuel
		 Toluene	470	92.14	
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene Acenaphthalene	 Naphthalene	31.7	128.2	Burning byproduct, coal gas manufacturing
		 Acenaphthene	3.9	154.2	
			50,000	88.15	
oxygenates	MTBE				38 additives

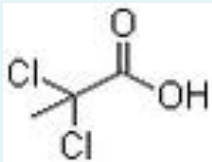
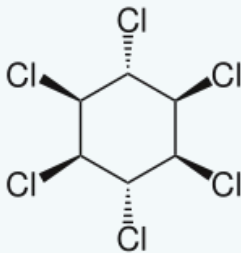
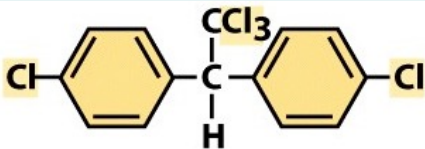
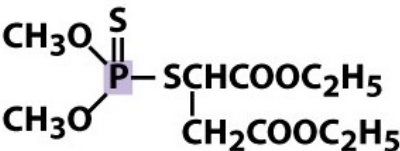
Halogenated hydrocarbons

- Halogenated aliphatics
- Halogenated aromatics

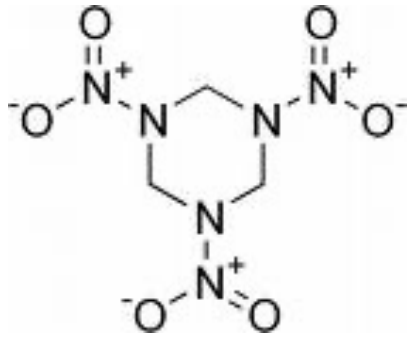
	examples	structure	Water solubility (mg/L)	MW (g/mol)	source
aliphatic	Tetrachloroethylene (PCE)		150	155.8	Dry cleaning, electronics, garages, military
	Trichloroethylene (TCE)		1,280	131.4	
	Dichloroethylene (DCE)		400	96.9	
	Carbon tetrachloride (CT)		785	153.8	
	Vinyl chloride (VC)				
Aromatic (dioxins and PCBs) often mixtures	2,3,3',4,4',5-Hexachlorobiphenyl		< 40 µg/L	360.8	Wood treatment, insulators
	2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8,-TCDD)		19.3 ng/L	321.9	Combustion, exhaust

Pesticides

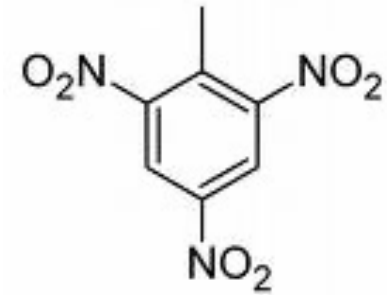
Large number of pesticides with many variations.

	examples	structure	Water solubility (mg/L)	MW (g/mol)	use
Halogenated aliphatic	2,2-dichloropropionic acid (Dalapon)		500 g/L	143	herbicide
Chlorinated cyclic aliphatics	Lindane		7.3	290.8	insecticide (not in use)
Halogenated aromatics	DDT		0.025	354.5	insecticide (not in use)
Organophosphates	Malathion		130	330.4	insecticide

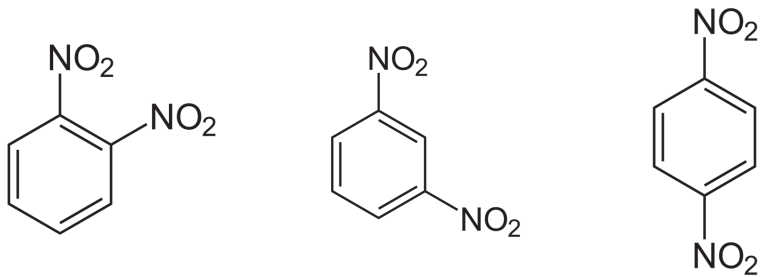
Explosives



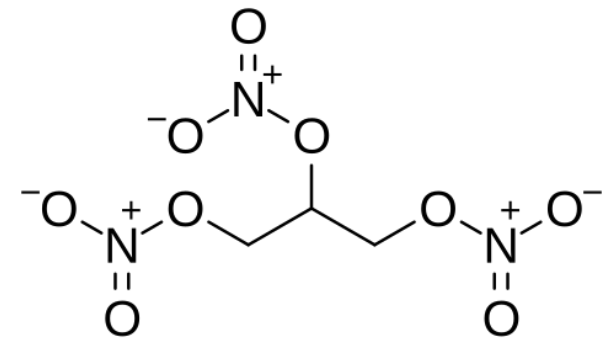
1,3,5-Trinitroperhydro-1,3,5-triazine
(RDX or T4)



Trinitrotoluene (TNT)



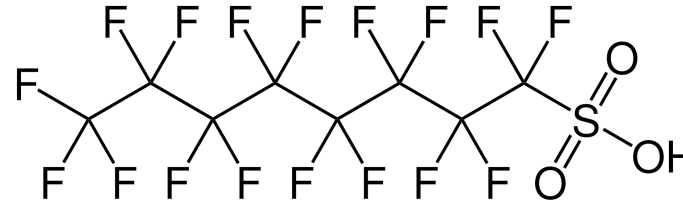
Dinitrobenzene (DNB)



Nitroglycerin

Emerging contaminants

Per and Poly-fluoroalkyl substances (PFAS)



- A large and complex family of compounds, all containing several F atoms
- Chemical designed to resist heat, oil, stains, and water
- Many are persistent due to the C-F bond (“forever chemicals”)
- Evidence for bio-accumulation
- Present everywhere at low concentrations (< European limit for drinking water- 0.5 µg/L)

- PFOA: perfluoro-octanoic acid
(8-carbon chain)



- PFOS: perfluoro-octanesulfonic acid
(8-carbon chain and sulfonate group)



Example:

In les Vernets (new development in Geneva on former military site), very high concentrations of PFAS in soil and GW (>1,000 ug/L). No legal basis in Switzerland for GW. Soil separation and washing was used to reduce the volume of contaminated material (by 75%). Gravel was recycled into cement, and the contaminated material was landfilled in type B (low-contamination) landfill in Geneva and in type E landfill (contaminated materials) in Bern.

Metals

1 H																	1 H	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		118	

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- $\text{Cr(VI)} = \text{CrO}_4^{2-}$
- $\text{U(VI)} = \text{UO}_2^{2+}$,
- $\text{Se(VI)} = \text{SeO}_4^{2-}$
- Zn^{2+} , Cd^{2+} , Pb^{2+}