Lecture 3: Characteristics and Partitioning of Contaminants

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Faculty of Engineering & Applied Science
3.1 Introduction

- The behavior and partitioning of subsurface contaminants determined by (a) properties of contaminants; and (b) the processes affecting subsurface materials and contaminants transport

1. General categories of processes affecting subsurface behavior and partitioning

- Hydrodynamic processes e.g. advection and dispersion
- Abiotic processes e.g. adsorption, volatilization and ion exchange
- Biotic processes e.g. aerobic, anoxic, and anaerobic biodegradation
(2) Classification of soil contaminants

- By definition, soil contaminants can be classified into

  ✓ Organic ➞ compounds that contain organic carbon ➞ e.g. petroleum products (gasoline, kerosene, diesel fuel...), polynuclear aromatic hydrocarbons (PAHs)

  ✓ Inorganic ➞ those that contain no organic carbon (mainly metal contaminants) ➞ e.g. Cr, Cd, Zn, Pb, Hg, As, Ni, Cu, Ag
- By activities, soil contaminants can be divided into

  ✓ Nonreactive (conservative contaminants) ➔ affected only by hydrodynamic processes

  ✓ Reactive ➔ contaminants that have the potential to be reactive during the abiotic and biotic processes

Note: reactive contaminants may not really reactive if the subsurface environment is not conducive to the reactions that affect their partitioning ➔ a need of soil remediation engineering to enhance the potential
By solubility and density, soil contaminants can be classified into

- soluble contaminants ➔ most inorganic and part of organic solute
- LNAPLs (light nonaqueous phase liquids) ➔ NAPLs with densities less than water (many petroleum products, especially gasoline and its derivatives)
- DNAPLs (dense nonaqueous phase liquids) ➔ NAPLs with densities greater than water (many chlorinated solvents, most pesticides, and many other liquid organic contaminants)
Soluble contaminants dissolve in water and form elongated plumes of contamination that arise at a point source and stretch out following groundwater flow direction.

Source: Zoller, 1994
Density effects how NAPLs move through the subsurface environment

LNAPLs float on water, but DNAPLs sink in
✓ NAPLs ➔ slight-solubility of these contaminants is sufficient to produce plumes of dissolved constituents ➔ move off into the surrounding environment

✓ Serious groundwater pollution over relatively large volumes of aquifer ➔ arise from very small spills or leaching rates

✓ As long as NAPLs remains in the ground ➔ aqueous-phase continuous to be released ➔ creating long-term pollution (tens to hundreds of years)

Presence of NAPLs in subsurface ➔

One of the major environmental concerns
3.2 Characteristics of soil contaminants

3.2.1 Lump parameters for contaminant quantification

(1) Total petroleum hydrocarbons (TPH)

- A remarkably wide array of compounds that originally come from crude oil ($C_1$ to $C_{40}$)
- So many different chemicals in crude oil and in other petroleum products $\Rightarrow$ it is not practical to measure each one separately $\Rightarrow$ measure the total amount of TPH at a site
- Chemicals that may be found in TPH $\Rightarrow$ hexane, jet fuels, mineral oils, BTEX, and naphthalene, as well as other petroleum products and gasoline components $\Rightarrow$ can be determined by GC analysis
(2) Total organic carbon (TOC)

- Amount of carbon bound in an organic compound
- Indicator of water quality or cleanliness of subsurface environment
- Measurement \( \Rightarrow \) \( \text{TOC} = \text{total carbon (TC)} - \text{inorganic carbon (IC)} \)
(3) Biological oxygen demand (BOD)

- A chemical procedure for determining the uptake rate of dissolved oxygen by the biological organisms in a sample
- Widely used parameter of organic pollution (e.g. investigation of remediation projects)
- Measurement $\Rightarrow \text{BOD}_5$ and $\text{BOD}_{\text{ultimate}}$

(4) Chemical oxygen demand (COD)

- The mass of oxygen consumed per liter of sample solution
- Used to estimate the total oxygen demand of contaminated sites
- Approximately 65% of COD $\Rightarrow \text{BOD}$
3.2.2 Contaminant properties

(1) Solubility

- The property of a solid, liquid, or gaseous chemical substance called solute to dissolve in a liquid solvent to form a homogeneous solution

- Measurement of the solubility of a pure substance in a specific solvent → the saturation concentration where adding more solute does not increase the concentration of the solution (the solution is equilibrium with the substance at a specified temperature and pressure, e.g. 25 °C, 1 atm)
Micro view of unsaturated zone

Contaminant concentrations:

- $C_w$, mg/L or mol/m$^3$
  concentration in water
- $C_g$, mg/L or ppmv
  concentration in gas
- $C_s$, g/kg
  concentration in solids

\[
C_g(\text{ppmv}) = \frac{C_g(\text{mg/l}) \times 24,000(\text{ml/mol})}{MW(\text{g/mol})}
\]
(2) Vapor pressure

- The pressure of a vapor in thermodynamic equilibrium with its condensed phases in a closed container

- A substance with a high vapor pressure at normal temperatures ➔ volatile

- The vapor pressure of a single component in a mixture ➔ partial pressure

Dalton's Law of partial pressures ➔

"In a mixture of gases, each gas exerts pressure independently of the other gases. The partial pressure of each gas is proportional to the amount (as measured by percent volume of mole number) of that gas in the mixture"
For a gas mixture containing $n_A$ mole of gas A, $n_B$ mole of gas B, and $n_C$ mole of gas C, with total volume = $V$ and temperature = $T$

The partial pressures ➔

$$P_A = \frac{n_A RT}{V} = \frac{n_A}{n_{total}} P_{total}$$

$$P_B = \frac{n_B RT}{V} = \frac{n_B}{n_{total}} P_{total}$$

$$P_C = \frac{n_C RT}{V} = \frac{n_C}{n_{total}} P_{total}$$

**Example 3-1:** A gas mixture contains 65% $\text{N}_2$, 30% $\text{O}_2$, and 5% $\text{CO}_2$. If 800 kg of the gas mixture is stored in a tank at a pressure of 200 kPa, calculate the partial pressure of each component present.
(3) Henry’s law constant

- Linkage of solubility and vapor pressure $\rightarrow$ gas-liquid transfer

**Henry's Law**

The amount of a gas that will dissolve in a solution is directly proportional to the partial pressure of that gas in contact with the solvent.

$$K_H = \frac{P_i}{C_w}$$

Where

- $P_i =$ partial pressure of a contaminant $i$ in the gas (atm)
- $C_w =$ concentration of the contaminant $i$ in the solution (mol/m$^3$)
- $K_H =$ Henry's law constant (atm-m$^3$/mol)
- $K_H \Rightarrow$ has dimensions (atm-m$^3$/mol)
- $K_{H}' \Rightarrow$ dimensionless

$$K_{H}' = \frac{K_H}{RT}$$

Where

$R = \text{gas constant} = 8.20575 \times 10^{-5}$ (atm-m$^3$/mol-K)

$T = \text{temperature} \ (K)$

### Henry's law and constants

<table>
<thead>
<tr>
<th>Gas</th>
<th>$O_2$</th>
<th>$H_2$</th>
<th>$CO_2$</th>
<th>$N_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_H$ (atm-m$^3$/mol)</td>
<td>0.769</td>
<td>1.282</td>
<td>0.029</td>
<td>1.639</td>
</tr>
<tr>
<td>Gas</td>
<td>He</td>
<td>Ne</td>
<td>Ar</td>
<td>CO</td>
</tr>
<tr>
<td>$K_H$ (atm-m$^3$/mol)</td>
<td>2.702</td>
<td>2.222</td>
<td>0.714</td>
<td>1.052</td>
</tr>
</tbody>
</table>
(4) Liquid viscosity

- A measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress ➔ in units of centipoise (cP)

- Means thickness in everyday terms ➔ describes a fluid's internal resistance to flow

- Relating to the pumpability of a contaminant (e.g. NAPL), the rate of spreading or flow into the extraction well
(5) Interfacial tension with water

- A measurement of the cohesive (excess) energy present at an interface arising from the imbalance of forces between molecules at an interface (gas/liquid, liquid/liquid, gas/solid, liquid/solid) → in units of dynes/cm

- Plays an important role in emulsification which is the process of preparing emulsions during some soil remediation treatments
3.3 Processes affecting subsurface materials and contaminants transport

3.3.1 Hydrodynamic Processes

(1) Advection

- Refers to the movement caused by the flow of groundwater rate of advective contaminant migration ➞ equal to the rate of ground water flow

- Advective flow velocities are calculated from Darcy's law

  ✓ Darcy’s velocity (v), or discharge velocity ➞ v = Ki

  ✓ Seepage velocity (v_S) ➞ since the actual flow is limited to the pore space only ➞ v_S = v /n_e = Ki/n_e
Advective flux ($F_A$)

- The contaminant mass flux due to groundwater advection ➔
  mass per unit cross area per unit time

- Under one-dimensional steady-state flow condition, the advective flux $F_A$ ➔

$$F_A = n_e v_s C$$

Where

$n_e =$ effective porosity
$v_s =$ seepage velocity
$C =$ contaminant concentration
Under uniform conditions, the advective transport is described by

\[ \frac{dC}{dt} = -V_s \frac{dC}{dx} \]

Example 3-2: At a landfill site, dissolved chloride in a concentration of 1000 mg/l is being transported along with the leachate through a 5-ft-thick natural silty sand layer into an underlying aquifer. The flow velocity is 0.03 m/day and the effective porosity of silty sand is 0.1. What is the mass flux of chloride into the aquifer per unit base area of the landfill due to advection alone?
(2) Dispersion

- Spreading of the contaminant as it moves in a porous medium
- Two underlying processes ➔ molecular diffusion and mechanical dispersion

Hydrodynamic dispersion = molecular diffusion + mechanical dispersion

**Molecular Diffusion** ➔ spread due to concentration gradients without flow of water

![Diagram of molecular diffusion](image)
Molecular diffusive flux \((F_D)\)

- Movement of contaminant mass in porous media by molecular diffusion (Brownian motion) – proportional to concentration gradient →

\[
F_D = -D^* n_e \frac{dC}{dx} = -\tau D_0 n_e \frac{dC}{dx}
\]

Where

\(F_D\) = diffusive mass flux per unit area per unit time
\(D^*\) = effective diffusion coefficient
\(\tau\) = tortuosity coefficient (<1)
\(D_0\) = self-diffusion coefficient
\(n_e\) = effective porosity
\(\frac{dC}{dx}\) = contaminant concentration gradient

- Based on the Fick’s first law, the contaminant diffuse rate in soil is given by →

\[
\frac{dC}{dt} = D^* \frac{d^2C}{dx^2}
\]
The contaminant concentration at a distance $x$ from the source at time $t$ (with an initial concentration of $C_0$) is given by

$$C(x, t) = C_0 \times \text{erfc}\left(\frac{x}{2\sqrt{D^* t}}\right)$$

The complementary error function ($\text{erfc}$) is given by

$$\text{erfc}(u) = 1 - \text{erf}(u)$$

$$\text{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-\eta^2} d\eta$$

**Example 3-3:** At a landfill site, leachate accumulated over a 0.3-m thick clay liner contains dissolved chloride in a concentration of 1000 mg/l. If the tortuosity is equal to 0.5, what would be the concentration of chloride at a depth of 3m after 100 years of diffusion/ Neglect the effects of advection.
- Molecular diffusion is not a big factor in saturated groundwater flow → mechanical dispersion dominates diffusion.

- Molecular diffusion can be important (even dominant) in vapor transport in unsaturated (Vadose) zone.

- **Mechanical Dispersion** ➔

  - Occurs due to velocity variations of the flow in a porous media.
Experiment ==> solutes tend to disperse as they travel along the pipe
Mechanical diffusive flux ($F_M$)

- Movement of contaminant mass in porous media by mechanical diffusion
- $F_M$ can be effectively approximated by the same relationship as diffusion—i.e., that flux is proportional to concentration gradient:

$$F_M = -D_M n_e \frac{dC}{dx}$$

Where

- $n_e$ = effective porosity
- $dC/dx$ = contaminant concentration gradient
- $D_M = \alpha_L \times \nu_S$ = dispersion coefficient
- $\alpha_L$ = longitudinal dispersivity
Traditional view of hydrodynamic processes

- Combined transport flux from advection, molecular diffusion and mechanical dispersion (in one dimension) \( \Rightarrow F = F_A + F_D + F_M \)

- Dispersion by the hydrodynamic processes \( \Rightarrow \)

\[
D_H = D^* + D_M = \tau D_O + \alpha_L u
\]
Application of the ADE (Advection-Dispersion Equation)

-- ADE is widely used in environmental problems dealing with transport of solutes in a mobile medium.

-- For example ➔ Oil tank leakage in a site: What is C in the well t years?
3.3.2 Abiotic Processes

» Adsorption

☐ a phenomenon by which chemicals become associated with solid phases

- Adsorption ➔ chemicals adhere to surface of solid
- Absorption ➔ chemicals penetrate into solid
- Sorption ➔ includes both
If the adsorptive process is rapid compared with the flow velocity, contaminant chemicals will reach an equilibrium condition adsorbed phase and the process can be described by an equilibrium adsorption isotherm.

Adsorption depends on properties of activated carbon, chemistry of adsorbate, pH and temperature of water, each application requires development of adsorption isotherm.

An adsorption isotherm relates $S$ (solid phase concentration = mass of absorbate (contaminants)/mass of adsorbent) to $C$ (liquid phase concentration of absorbate).

Adsorption process is quantified via an adsorption isotherm which can take multiple forms.
The linear adsorption isotherm can be described by the equation:

\[ S = K_d \ C \]

Where

- \( S \) = mass of contaminant adsorbed per dry unit weight of the solid adsorbent (mg/kg)
- \( C \) = concentration of contaminants in solution in equilibrium with the mass of contaminants adsorbed onto the solid adsorbent (mg/l)
- \( K_d \) = distribution coefficient (L/kg)

We can develop a differential equation to describe the slope of a linear isotherm:

\[ \frac{\partial C}{\partial C} = K_d \]

\( K_d \) = slope of the linear adsorption isotherm
- Relationship between $K_d$ and $K_{OC}$:

✓ Soil organic carbon-water partitioning coefficient ($K_{OC}$) ➞ the ratio of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium chemical concentration in solution

$K_{OC}$ values are useful in predicting the mobility of organic soil contaminants; higher $K_{OC}$ values correlate to less mobile organic chemicals while lower $K_{OC}$ values correlate to more mobile organic chemicals

✓ The "distribution coefficient" ($K_d$) ➞ the "soil-water" partitioning coefficient. $K_d$(L/kg) is the ratio of a chemical's sorbed concentration (mg/kg) to the dissolved concentration (mg/L) at equilibrium
✓ $K_{OC}$ is the $K_d$ normalized to total organic carbon content
✓ Both $K_{OC}$ and $K_d$ ➔ are used to calculate a soil concentration that is protective of ground water using the 3-phase and 4-phase equilibrium partitioning models
✓ $K_{OC}$ is chemical-specific ➔ more applied to characterizing organic contaminants
✓ $K_d$ is chemical- and site-specific ➔ more applied to characterizing heavy metals
✓ For organics, $K_d$ may be calculated by multiplying $K_{OC}$ by foc (the mass fraction of soil organic carbon content ➔

$$K_d = K_{OC} \times f_{OC}$$

Example:

If a Brown Chernozemic soil with an organic carbon content of 1% (foc = 0.01) has a $K_d$ value of 1000 (mL/g soil), then the $K_{OC}$ value will be $(1000 \text{ mL/g soil})/0.01 = 100,000 \text{ mL/g soil}$
- We can develop a term called the retardation factor, \( R \), to describe linear adsorption:

\[
R = 1 + \frac{B_d}{\theta} K_d
\]

where

- \( B_d \) = bulk density of the soil (g/cm\(^3\))
- \( \theta \) = volumetric moisture content (fraction)
- \( K_d \) = partition coefficient (L/kg)

- The governing equation is affected by this term as follows:

\[
R \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C}{\partial x_j} \right) \frac{\partial}{\partial x_i} (v_i C) + \frac{q_s}{\theta} C_s
\]

If \( v_x \) = average linear groundwater flow velocity, then \( v_C \) = velocity of the contaminant \( \rightarrow \)

\[
v_c = \frac{v_x}{R}
\]
Example 3-4: pesticide in aquifer (Springer, 1994)

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Initial C (mg/L)</th>
<th>Equilibrium C (mg/L)</th>
<th>Mass adsorbed (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.79</td>
<td>1.25</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.39</td>
<td>0.66</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.07</td>
<td>0.18</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>0.03</td>
<td>0.096</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>0.01</td>
<td>0.018</td>
</tr>
<tr>
<td>6</td>
<td>0.005</td>
<td>0.003</td>
<td>0.011</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

(1) Plot the data on a provided graph
(2) Determine Kd.
(3) Assume a bulk density of 1.78 g/cm³ and a volumetric moisture content of 0.45. Calculate the retardation factor.
(4) If the average groundwater velocity is 50 cm/day, what is the velocity of the pesticide transport?
The Freundlich adsorption isotherm mathematically expressed as

\[ S = \frac{x}{m} = KC^{1/n} \]

or

\[ S = \frac{x}{m} = KP^{1/n} \]

Where
- \( x \) = mass of contaminants
- \( m \) = mass of adsorbent
- \( p \) = Equilibrium pressure of contaminants
- \( c \) = Equilibrium concentration of contaminants in solution
- \( K \) and \( 1/n \) = constants for a given contaminant and adsorbent at a particular temperature
The Langmuir isotherm \( \Rightarrow \) the equation is stated as

\[
\Gamma = \Gamma_{\text{max}} \frac{KC}{1 + KC}
\]

Where

\( \Gamma \) (or \( S \)) \( \Rightarrow \) amount adsorbed (equilibrium absorbent-phase concentration of contaminants)

\( \Gamma_{\text{max}} \) \( \Rightarrow \) maximum amount adsorbed as \( C \) increases

\( K \) \( \Rightarrow \) Langmuir adsorption constant

\( C \) \( \Rightarrow \) Equilibrium concentration of contaminants in solution
Linear isotherm

Freundlich isotherm

Langmuir isotherm

\[ S \text{ (g/g)} \]

\[ C \text{ (g/mL)} \]

\[ S \text{ (g/g)} \]

\[ C \text{ (g/mL)} \]

\[ S \text{ (g/g)} \]

\[ C \text{ (g/mL)} \]

\[ \Gamma_{\text{max}} \]
3.3.3 Biotic processes

➢ Biochemical transformation (Biodegradation)

☐ Microbial process that converse organic contaminants into water, CO$_2$, inorganic materials and biomass

☐ The most important mechanism for removal of contaminant from the environment

☐ Organic molecules are transformed (degraded) by enzymes that reside within the cell walls of microorganisms
Biodegradation involves more biological components than just the microorganisms that directly attack contaminants (the primary degraders, green ones)

Primary degraders need to compete with (a) sources of energy (such as oxygen) + (b) nutrients (such as N and P) + (c) other microorganisms (shown in yellow) that have effect on metabolites and other compounds that are released by oil-degrading bacteria and vice versa.
3.4 Relationships of $C_W$, $C_g$, and $C_S$

Solid $\leftrightarrow$ water

$$\frac{C_s}{C_w} = K_d = \frac{\text{mg/kg solid}}{\text{mg/L water}}$$

$K_d$ = partition coefficient

Water $\leftrightarrow$ vapor

$$\frac{C_g}{C_w} = K_H = \frac{\text{mol/m}^3 \text{ air}}{\text{mg/m}^3 \text{ water}}$$

$K_H$ = Henry’s Law constant
Volume-related properties

- Bulk density \( \rho_b = \frac{\text{mass of solids}}{\text{total volume}} \)
- Porosity \( n = \theta = \frac{V_v}{V_T} \)
- Volumetric water content or water-filled porosity \( \theta_w = \frac{V_w}{V_T} \)
- Saturation \( S = \frac{V_w}{V_v} \)
- Gas-filled porosity \( \theta_g \) (or \( \theta_a \)) \( = \frac{V_g}{V_T} \)
- \( \theta_w + \theta_g = n \)
Where...

Contaminants concentration in soil ...

Total mass in unit volume of soil:
\[ C_T = \rho_b C_s + \theta_w C_W + \theta_g C_g \rightarrow \text{In the zone of aeration} \]

If soil is saturated, \( \theta_g = 0 \) and \( \theta_w = n \)
\[ C_T = \rho_b C_s + n C_W \rightarrow \text{In the zone of saturation} \]
Example 3-5: During site investigations of a former gas station, a soil sample was collected in unsaturated silt at 2 meters below ground surface. The water table is located at 4 meters below ground surface. A laboratory analysis of the soil sample for TCE found a concentration of 1 mg/kg in this sample. The owner states he never used TCE on the site and the soil must have been contaminated by the underlying ground water, which is contaminated by a neighboring business. If the measured TCE concentration in the ground water is 10,000 μg/L, show mathematically if it is a reasonable hypothesis that the soil was contaminated by the underlying ground water. You can assume steady-state conditions, that the soil has a porosity of 0.4, that the soil saturation is 0.25, that the bulk density of the soil is 1.65 g/mL, and that the soil fraction organic carbon ($f_{OC}$) is 0.001. The Henry’s Law constant for TCE is $9.1 \times 10^{-3}$ atm-m$^3$/mole You can also assume that there is only molecular diffusion within the vadose zone.