INTERPHASE MASS TRANSFER

[Note: My bias is toward relationships involving nonpolar organic compounds. Many Air Force pollutants fall in this category (i.e., fuels and solvents). Some of the comments below are not applicable to other compounds (i.e., ionizing compounds)].

Δ Storage term of the MBE accounts for solute mass in all phases (water, air, NAPL, soil, etc.)

To solve the MBE, need equation in terms of <u>ONE</u> variable (usually solute concentration in water, C_w)

Need to know:
- <u>Equilibrium</u> constants between solute in each phase
- <u>Kinetics</u>, or rates for the interphase mass transfer

EQUILIBRIUM RELATIONSHIPS:

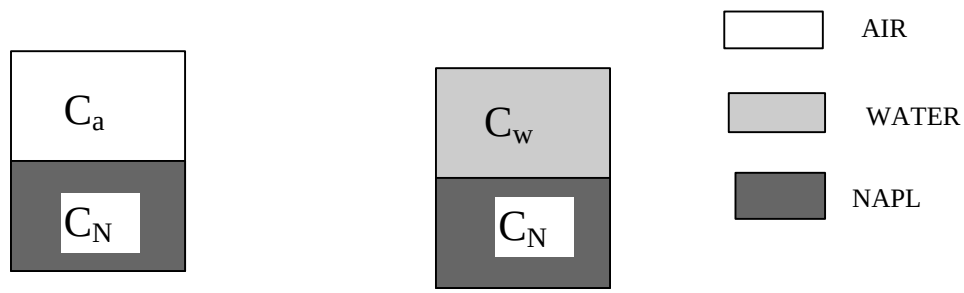
Generally, we are interested in the relationship between solute concentration in the water phase with solute in each of the other phases.

$C_a = f(C_w)$ $C_N = f(C_w)$ $S = f(C_w)$

- Water is usually the wetting phase; water surrounds all of the other phases (exception: NAPL can be in direct contact with air).
- Water is usually the phase we are interested in from at transport perspective (esp. advection).
- If solute is in equilibrium with all phases, the pathway for mass transfer is not important.

<u>Fluid-Fluid Equilibria = Partitioning</u> (Solute dissolves from one phase into the other).

[1] Single component (pure) NAPL / air or water:



For a single component NAPL, $C_N = \rho_N$, and the solute is <u>saturated</u> in the air and water phases:

- C_a derived from vapor pressure, P_v.
- C_w = Aqueous solubility, S_w.

[2] Single solute of a multiple-component NAPL (e.g., benzene as a component of gasoline) / air or water:

Raoult's Law (written for water/NAPL system):

$$X_{i(w)} = X_{i(N)} X^0_{i(w)}$$

Mole fraction of component i in water

Mole fraction of component i in NAPL

Mole fraction of component i in water in equilibrium with pure component i (i.e., solubility of pure compound)

Raoult's Law can be rewritten in terms of a partition coefficient:

$$K_{N/w} = \frac{C_N}{C_w} = \frac{1}{\overline{n}_N S_w}$$

NAPL/water partition coefficient

Average molecular volume of NAPL

Aqueous solubility of pure compound (mol/L)

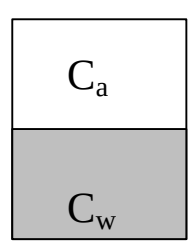
If the pure compound (i.e., the solute) is a crystalline solid at the temperature and pressure of interest, the aqueous solubility is replaced with the hypothetical super-cooled liquid solubility, S_{scl}.

- The NAPL/water partition coefficient is estimated from parameters that can be easily determined.
- A NAPL/air partition coefficient can be similarly derived if needed.
- If the properties of the bulk NAPL change with the dissolution process, the partition coefficient can change. However, this is unlikely in most environmental applications.
- This approach works well for many organic NAPLs (gasoline, diesel, coal tar) see: *Cline et al., ES&T, 25:914-920, 1991; Lee et al., ES&T, 26:2104-2110, 1992 and 26:2110-2115, 1992.*

[3] Air/water partitioning:

$$C_a = HC_w$$

Henry's Constant (watch units!)



Water-Solid Phase Equilibria = Many Processes:

- Adsorption: Reactions at solid interface
- Absorption: Dissolution into the solid

Combine the two into nonspecific process, "sorption"

Solid matter in soil is heterogeneous:
- Mineral surfaces (charged or neutral)
- Inorganic coatings (oxides)
- Humic material
- Microbes

Sorption process depends on the solute and sorbent chemistry.
- Cationic solutes (many metals) associate with negatively charged clay surfaces by ion exchange.
- Nonpolar organic compounds associate with hydrophobic functional groups in soil organic matter.

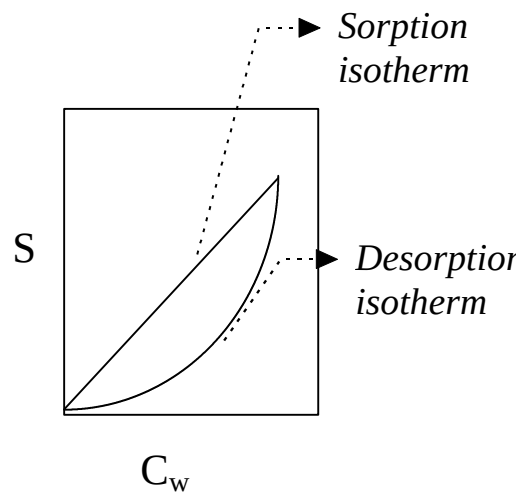
Sorption can be ideal or nonideal: (*Brusseau and Rao, Critical Reviews in Environmental Control, 19:33-99, 1989*)

IDEAL SORPTION	NONIDEAL SORPTION
Linear isotherm	Nonlinear isotherm
Instantaneous	Rate-limited
Singular	Hysteretic
Reversible	Nonreversible

If we can assume ideal conditions, sorption is easier to model.

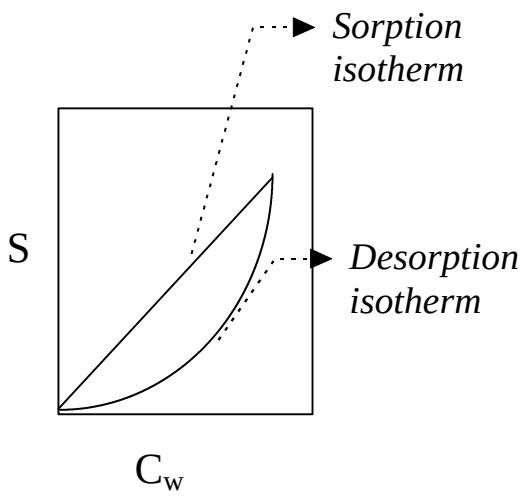
SINGULAR VS. HYSTERETIC SORPTION:

Singular isotherm: sorption and desorption isotherms are the same.
Hysteretic isotherm: sorption and desorption isotherms are not the same.

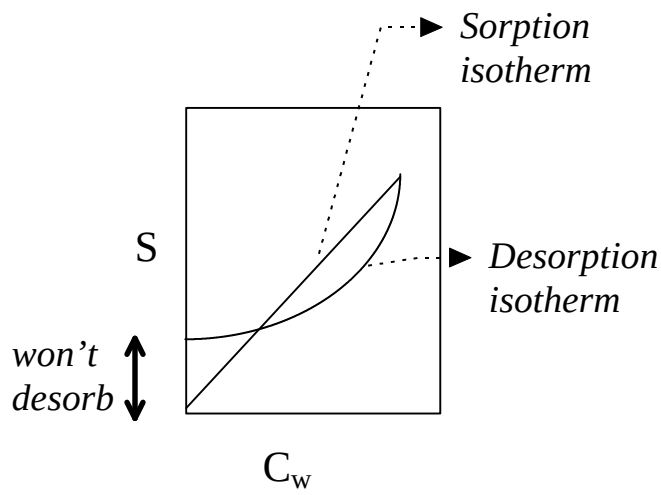


REVERSIBLE VS. NONREVERSIBLE SORPTION:

Reversible: All solute that sorbs will desorb.
Nonrevesible: Some solute becomes permanently bound to soil (usually the result of chemical reaction).



Hysteretic, Revesible Isotherm



Nonreversible Sorption

ISOTHERM LINEARITY:

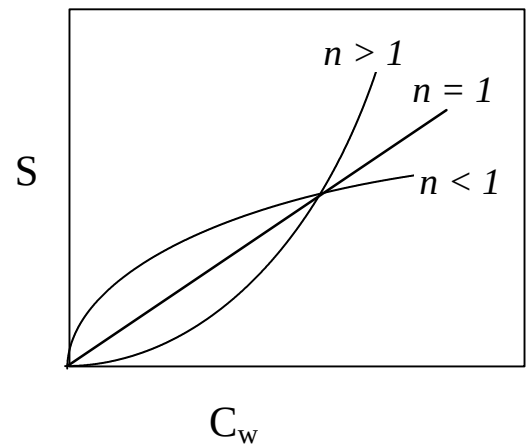
Isotherm: Relationship between solute concentrations in different phases at a constant temperature.

Isotherms can be linear or curved.

Freundlich Isotherm:

$$S = K_F C_w^{\,n}$$

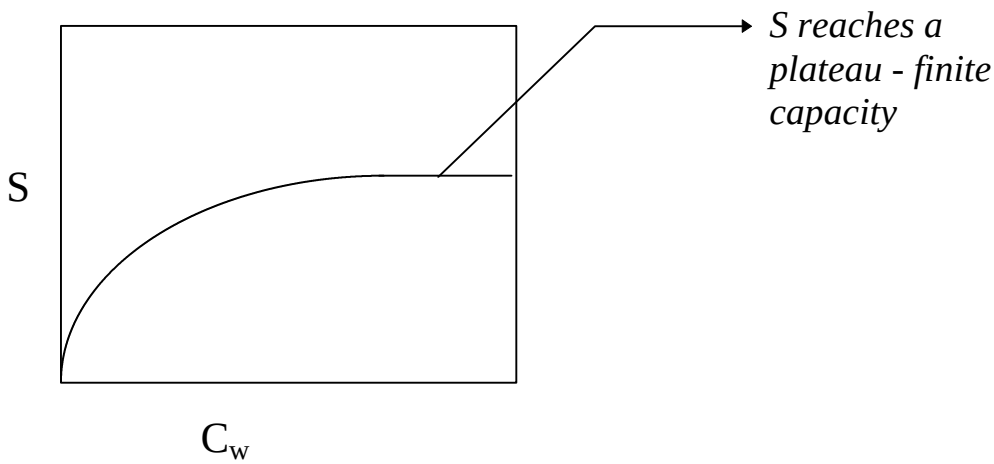
Sorption Coefficient



Causes of nonlinearity:

- n>1: multi-layer sorption; precipitation
- n=1: partitioning
- n<1: finite capacity for sorption

Limiting case for n<1: Langmuir Isotherm



<u>Linearity effects on kinetics</u>: In the MBE, we need the change in concentration with time.

$$\frac{\partial S}{\partial t} = K_F n C_w^{n-1} \frac{\partial C_w}{\partial t}$$

- If $n \neq 1$, the rate of sorption is dependent on the solute concentration!
- If $n > 1$: sorption rate increases with increases concentration.
- If $n < 1$: sorption rate decreases with increasing concentration.

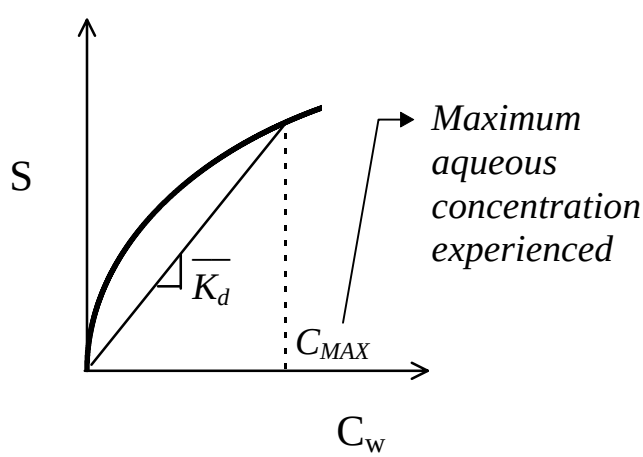
<u>Linearizing Isotherms</u>:

- Linear isotherms are mathematically simple--preferred for models.
- How can we get a linear isotherm?
  - "Linearize" a nonlinear isotherm.
  - All isotherms are linear at low concentrations.

Method 1: Predicts travel time
(Not concentration profile)

$$S = K_F C_w^n$$

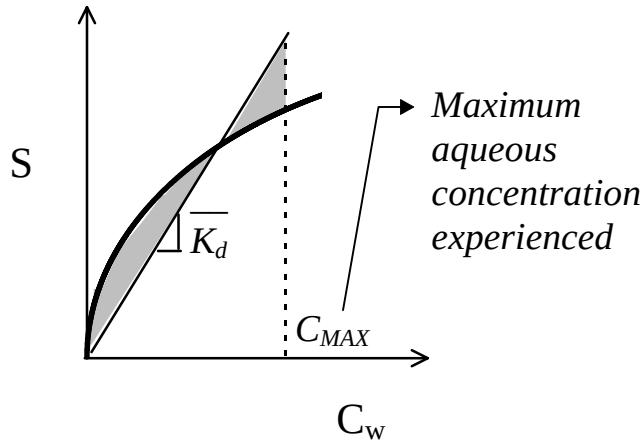
Freundlich Sorption Coefficient



$$\overline{K_d} = K_F C_{MAX}^{n-1}$$

Linearized Sorption Coefficient

Method 2: Predicts mass



$$\overline{K_d} = \frac{2K_F C_{MAX}^{n-1}}{n+1}$$

- All isotherms (Freundlich, Langmuir, Linear) are approximately linear at LOW concentrations.
- Water chemistry usually involves dilute solutions (LOW concentrations).
- How low is low? For nonpolar organic compounds, isotherms are generally linear if C_w < 1/2 Aqueous solubility.
- Linear assumption is often okay.

<u>ESTIMATING SORPTION COEFFICIENTS:</u>

Definitions:

K_d = <u>Distribution Coefficient</u>.

- K_d is constant for a given soil, solute, and solute concentration.
- If the isotherm is linear, K_d is a function of soil and solute only!
- Units: Vol/mass (mL/g).

$$K_d = \frac{S}{C_w} \quad \text{(at equilibrium)} = \frac{\text{Sorbed Concentration}}{\text{Aqueous Concentration}}$$

K_p = Partition Coefficient.

- Sorption process is assumed to be partitioning (usually nonpolar organic compounds associating with soil organic matter).
- Linear isotherm; K_p is independent of solute concentration.
- Units: Vol/mass (mL/g).

$$K_p = \frac{S}{C_w} \quad \text{(at equilibrium)}$$

Even if the isotherm is linear, K_d is different for every soil and every solute. How can we estimate its value?

[1] Estimating K_d for nonpolar organic compounds:

- If significant soil organic matter is present (f_{oc} > 0.1 percent), it is the largest sorption sink is nonpolar organic compounds.
- Normalize K_d to fraction of organic carbon (f_{oc}).
  - $K_d = f(f_{oc}, \text{solute})$
  - $K_{oc} = K_d/f_{oc} = f(\text{solute})$
- *Karrickhoff, Chemosphere, 10:833-846, 1981* found strong correlation between K_d and f_{oc} for a given solute. (see graph).

Estimate K_{oc}, Organic Carbon Partition Coefficient:

- Regressions with hypothetical super-cooled liquid aqueous solubility (*Karrickhoff, 1981*):

$$\log K_{oc} = -0.921 \log S_{scl}$$

- Regressions with octanol/water partition coefficient (*Karickhoff, et al., Water Research, 13:241-248, 1979; Means, et al., ES&T, 14:1524-1528, 1980; Karrickhoff, 1981*):

$$\log K_{oc} = \log K_{o/w} + b; \quad b = -0.21 \text{ to } -0.346$$

THEREFORE: We can estimate the K_p from: $K_p = K_{oc} f_{oc}$

- Available data on solute (octanol/water partition coefficient).
- Measure f_{oc} of soil (wet chemical methods, furnace, etc.).

WHY? May have lots of solutes/Isotherms are expensive, etc.

LIMITS: $f_{oc} \geq 0.001$; Nonpolar organic compounds only.

<u>[2] Estimating K_d for Cations</u>:

Metal contaminants are often present in water as cations (+ charge). Sorption process is predominantly ION EXCHANGE with clay minerals that have negatively charged surface.

A soil's capacity for sorbing cations is known as the CATION EXCHANGE CAPACITY (CEC). Units = meq/g or mol/m^2.

Typical ion exchange reaction:

$$M^+ + Na{:}Soil \Leftrightarrow Na^+ + M{:}Soil$$

Metal contaminant in solution

Dominant cation sorbed to soil

Dominant cation in solution

Metal contaminant adsorbed to soil

The chemical equilibrium for this reaction is:

$$K_{ie} = \frac{[M{:}Soil][Na^+]}{[M^+][Na{:}Soil]}$$

Also: $$(CEC)\frac{\rho_B}{\theta} = [M{:}Soil] + [Na{:}Soil]$$

Rearranging: $$[M{:}Soil] = \frac{K_{ie}[M^+](CEC)\frac{\rho_B}{\theta}}{[Na^+] + K_{ie}[M^+]}$$

Equation for Langmiur isotherm.

Remember: $$K_d = \frac{S}{C_W} = \frac{[M{:}Soil]\frac{\theta}{\rho_B}}{[M^+]}$$

So if $[Na^+] >> K_{ie}[M^+]$: $$K_d \approx \frac{K_{ie}(CEC)}{[Na^+]}$$

Cation exchange capacity (mol/g)

Ion exchange equilibrium coefficient

Competing ion concentration (mol/L)

And if $[Na^+] << K_{ie}[M^+]$: $$S = S_{max} \rightarrow (CEC)MW_M$$

- At low concentrations, cation sorption is linear.
- At very high concentrations, cation sorption is finite.

Summary for Ionic Sorption:

- K_d for cations can be related to chemical constants.
  - Constants are more difficult to determine than for nonpolar organics.
  - May have competitive effects from several ions.
- There is a similar process for anions.
  - For most soils, AEC << CEC; anions often considered "nonsorbing."

SUMMARY: INTERPHASE EQUILIBRIA

Water-Air Partition Coefficient = Henry's Constant

$$C_a = HC_w$$

Units of H = f(units of C_a and C_w)

Water-NAPL Partition Coefficient → Raoult's Law Approach

$$C_N = K_{N/w} C_w \qquad K_{N/w} = \frac{1}{\bar{\nu}_N S_{scl}}$$

$\bar{\nu}_N$ = Average molar volume of NAPL
S_{scl} = Hypothetical super-cooled liquid solubility of solute

Water-Solid Phase Distribution Coefficient

$$S = K_d C_w$$

for nonpolar organic solutes, $K_d = K_{oc} f_{oc}$