

Phase equilibrium

Chemical equilibria – pure phase & water

Let's define K:

$$Y_i \rightleftharpoons Y_{aq,sat} \quad K = \frac{\{Y\}_{aq,sat}}{\{Y\}_i}$$

- { }: activity, a unitless thermodynamic property
 - []: molarity; (): eq/L

- For pure phase Y_i , activity is defined as

$$\{Y\}_i = 1 \text{ (liquid, solid)}$$

$$\{Y\}_i = p_i \text{ (gas)} \quad p_i: \text{ pressure in atm}$$

- For a dilute aqueous solution

$$\{Y\}_{aq} \approx [Y]_{aq}$$

- So: $K \approx \frac{[Y]_{aq,sat}}{p_i}$ or $[Y]_{aq,sat}$

(gas as pure phase)

(liquid or solid as pure phase)

What is a “dilute aqueous solution”?

Rule of thumb: Solution can be considered dilute if water molecules make up 99.9% or more of the solution entities

What's ideal behavior?

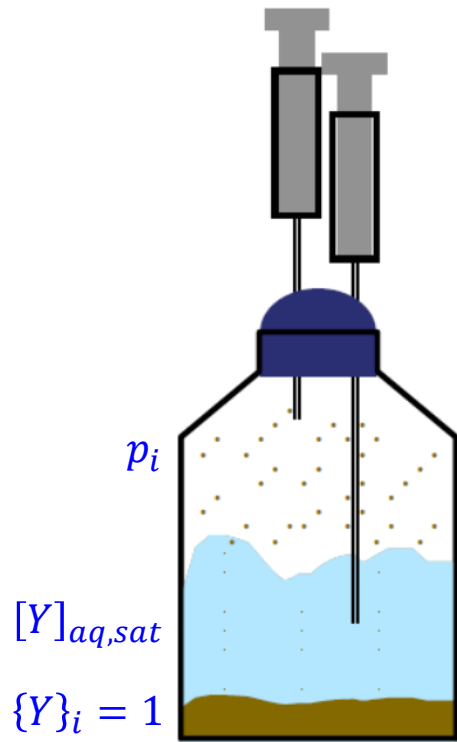
- An individual molecule's properties (energy distribution, tendency to react, dissolve, vaporize, etc.) are independent of the presence and/or concentration of any other molecules in the phase

Gas phase

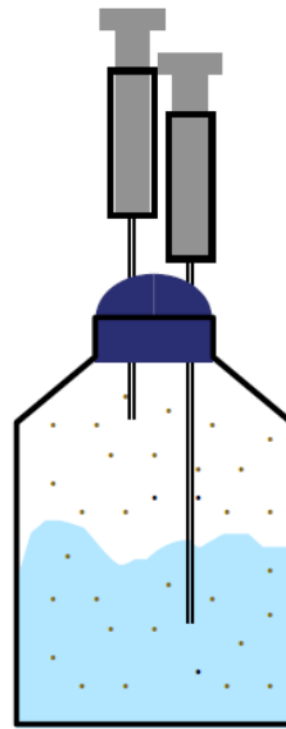
$$Energy = PV = n_t RT = RT \sum_i n_i$$
$$p_i = \frac{n_i RT}{V}; \quad P = \sum_i p_i$$

- **Dilute solution approximation: dissolved component “i” behaves (quasi-) ideally**
 - 1st unit of “i” added has the same effect as nth unit
 - Effect of adding a unit of “i” may not be the same as adding a unit of “j”

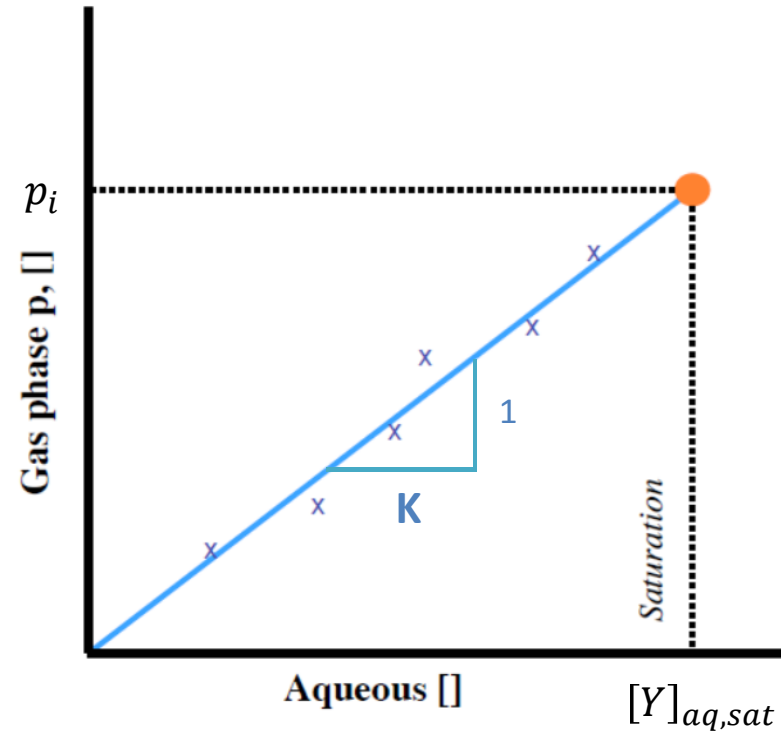
Air/water partitioning: Henry's constant



Saturation



Calibration curve



Air/water partitioning: Henry's constant

$$H_{-} = \frac{(-)_{air}}{(-)_{aqueous}}$$

- **Linear partitioning because:**
 - Gas phase behaves ideally
 - Dissolution of i in water does not affect water's properties (dilute solution, $x_i < \sim 10^{-3}$)

$$H_{xy} = \frac{x_g}{x_{aq}} = \frac{\text{mole fraction}_g}{\text{mole fraction}_{aq}}$$

$$H_{cc} = \frac{\text{moles/vol}_g}{\text{moles/vol}_{aq}} = \frac{p_i}{[C_i]_{aq} \times RT}$$

$$H_{pc} = \frac{p_i}{[C_i]_{aq}}, \quad \frac{l - atm}{mole}$$

- **Constant is defined using a variety of unit combinations**
 - Mole fraction, atmosphere, molar concentration, mg/L, ...
 - H's numerical value depends on units
 - Watch out for "1/H"

Henry's constants: the different forms

At 1 atm, 25°C,

$$H_{xy} = \frac{x_g}{x_{aq}} = \frac{55.3p_i}{[C_i]_{aq}}$$

p_i = mole fraction in gas phase

gas phase behaves ideally

$p_T = 1 \text{ atm}$

pure water [] is ~55.3 mole/L @ 25°C

assume $C_{i,aq} \ll 55.3 \text{ mole/L}$

$$H_{cc} = \frac{\text{moles/vol}_g}{\text{moles/vol}_{aq}} = \frac{p_i}{[C_i]_{aq} \times RT} = \frac{p_i}{[C_i]_{aq} \times 24.47}$$

@ $T = 298\text{K}$ & $p_T = 1 \text{ atm}$

1 mole of gas occupies 24.47 L

$$H_{pc} = \frac{p_i}{[C_i]_{aq}}, \quad \frac{l - atm}{mole}$$

$$H_{pc} = 0.01807 \times H_{xy} = 24.47 \times H_{cc} @ 25^\circ\text{C}, 1 \text{ atm}$$

Aqueous solubility and vapor pressure

Properties of some organic chemicals of environmental interest						
Name	Formula	Mol. Wt.	Melt, C	Boil, C	$-\log(p^{\text{sat}})^1$	$-\log(C^{\text{sat}})^2$
methane [@]	CH ₄	16.0	-182.5	-164.0	-2.44	2.82
n-butane [@]	C ₄ H ₁₀	58.1	-138.4	-0.4	-0.39	2.98
n-hexane	C ₆ H ₁₄	86.2	-95.0	69.0	0.69	3.83
cyclohexane	C ₆ H ₁₂	84.2	6.6	80.7	0.90	3.15
1-hexene	C ₆ H ₁₂	84.2	-139.8	63.4	0.60	3.15
benzene	C ₆ H ₆	78.1	5.5	80.1	0.90	1.64
1-hexanol	C ₆ H ₁₄ O	102.2	-46.7	158.0	2.85	0.88
1-octanol	C ₈ H ₁₈ O	130.2	-16.7	194.4		2.35
toluene	C ₇ H ₈	92.1	-95.0	110.6	1.42	2.25
chlorobenzene	C ₆ H ₅ Cl	112.6	-45.6	132.0	1.80	2.35
1,4dichlorobenzene	C ₆ H ₄ Cl ₂	147.0	53.1	174.0	3.04	3.39
bromobenzene	C ₆ H ₅ Br	157.0	-30.8	156.0	2.25	2.64
dioxin [#]	C ₁₂ H ₄ O ₂ Cl ₄	322.0	305	421	11.6	10.3
[@] gas at 25C--p ^{sat} refers to pressure needed to obtain pure liquid at 25C						
[#] 2,3,7,8-tetra-chlorodibenzo-p-dioxin						
¹ vapor pressure @ 25C, atmospheres						
² concentration in saturated aqueous solution, moles/l, 25C						

Mass partitioning between air & water

Henry's constant

$$H_{cc} = \frac{p_i}{C_{i,aq} \times RT} = \frac{C_{i,g}}{C_{i,aq}}$$

Phase volumes

$$V_g, V_{aq}$$

Masses (Moles)

$$M_{tot}, M_g, M_{aq}$$

$$R_{g/aq} = \frac{M_g}{M_{aq}} = \frac{H_{cc} \times V_g}{V_{aq}}$$

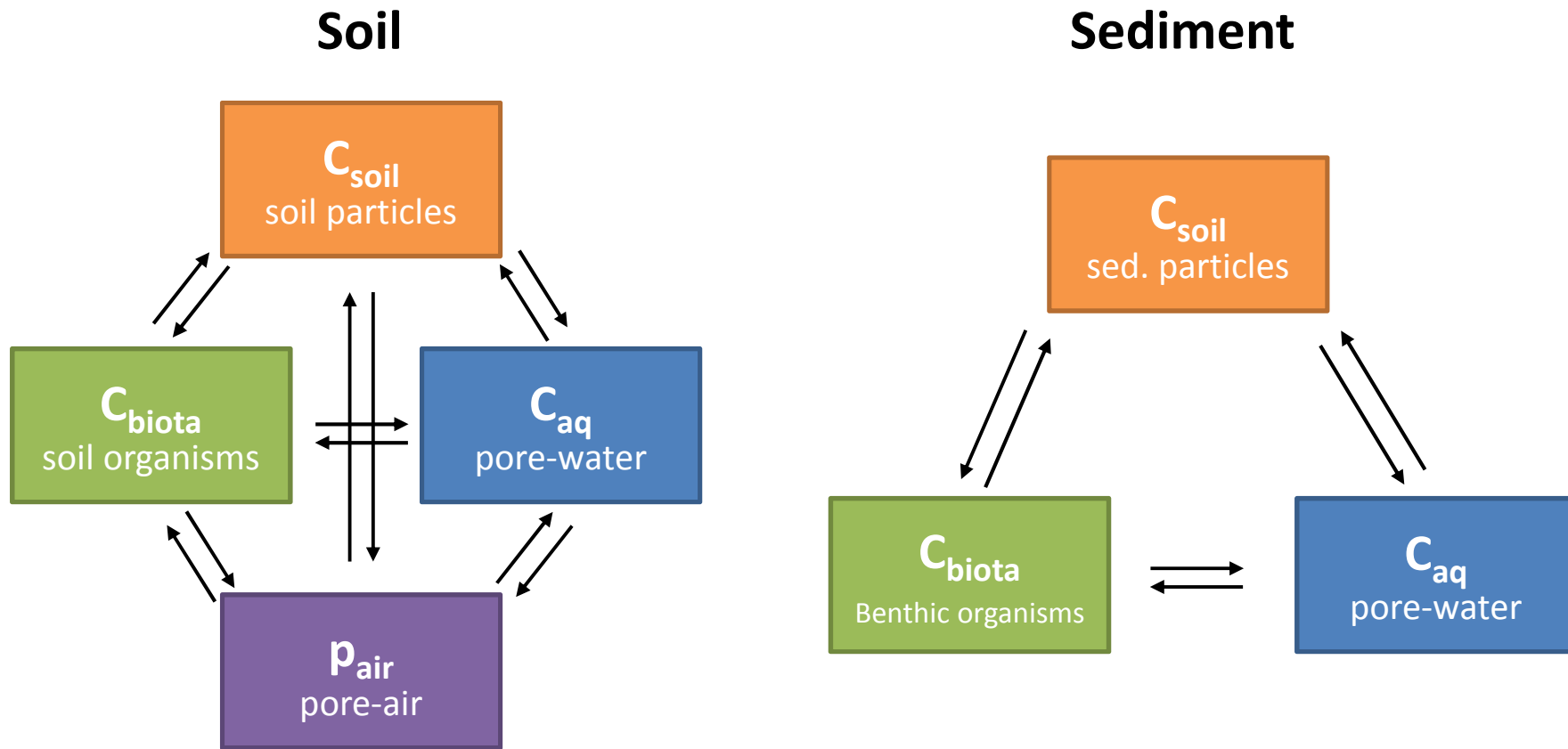
$$M_g = M_{tot} \times \frac{R_{g/aq}}{1 + R_{g/aq}} = M_{tot} \times \frac{H_{cc} \times V_g}{V_{aq} + H_{cc} \times V_g}$$

$$M_{aq} = M_{tot} \times \frac{1}{1 + R_{g/aq}} = M_{tot} \times \frac{V_{aq}}{V_{aq} + H_{cc} \times V_g}$$

Mass partitioning between air & water

Q: A 1.000 L bottle is filled with 500.0 mL water. Then, 42.1 mg 1-hexene (MW: 84.2) is added. After sealing the bottle, it is left at 25°C until equilibrium between air and water. How will the 1-hexene mass partition between air and water in the bottle?

Additional phase - solid

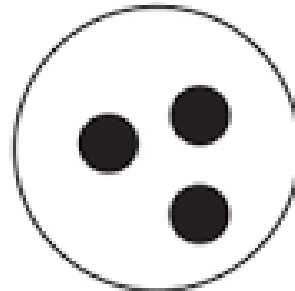


- Need equilibrium between
 - C_{aq} & C_{soil} (or C_{sed})
 - C_{aq} & C_{biota}

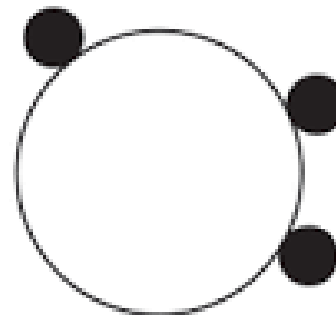
Mass exchange b/w solid particles & water

- **Sorption**

- Any accumulation of a substance on/below the surface of solids
- sorbate vs. sorbent – “sth that is sorbed” vs. “sth that sorbs”
- adsorption vs. absorption
 - on the surface vs. in the entire volume of the sorbent



absorption



adsorption

Sorption isotherms

- Isotherm – constant temp. & at thermodynamic equilibrium
- Various models to describe C_s vs. C_{air} , C_s vs. C_{aq} sorption isotherm
- Frequently used sorption isotherms for C_s vs. C_{aq}

- **Langmuir isotherm**

$$C_s = \frac{a \cdot b \cdot C_{aq}}{1 + b \cdot C_{aq}}$$

C_s = concentration in solid at equilibrium [g sorbate/kg solid]

C_{aq} = concentration in water at equilibrium [g sorbate/L water]

a, b = Langmuir constants

a – unit: [g sorbate/kg solid], represents sorption capacity

b – unit: [L water/g sorbate], $a \times b$ represents sorbate-sorbent affinity

(Assumptions)

- **Ad**sorption occurs on fixed number of surface sites
- Monolayer coverage, no interaction between adsorbates
- No lateral movement of molecules on the surface

Sorption isotherms

– Freundlich isotherm

$$C_S = K_F \cdot C_{aq}^{1/n}$$

K_F = Freundlich sorption coefficient

$[(g \text{ sorbate/kg solid}) \cdot (L \text{ water/g sorbate})^{-1/n}]$

n = Freundlich exponent (unitless)

- Empirical relationship
- Can fit to a case when both adsorption & absorption occur

– For the case of $n=1$ of Freundlich isotherm, we see linear relationship

$$C_S = K_p \cdot C_{aq}$$

K_p = solid-water partitioning coefficient

$[L \text{ sorbate/kg solid}]$

- Some refer the sorption mechanism as “partitioning” if linear isotherm is observed

Linear sorption isotherm (partitioning)

- Theoretically, linear isotherm is observed when
 - Absorption is the dominant process
 - So, linear isotherm is more likely to be observed for gel-like sorbents than rigid ones
 - Lipid fraction of organisms – gel-like
 - Organic matter in soils & sediments – some gel-like & some rigid fractions
- Can also be observed at low C_{aq} range even when adsorption is dominant
 - Review Langmuir isotherm!
- We will limit our discussion on linear sorption (partitioning)

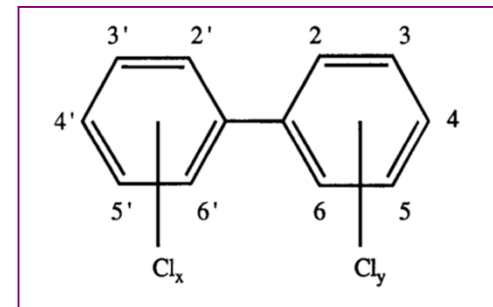
Contaminants in organisms - terms

- **Bioaccumulation**
 - Net contaminant accumulation (all sources) in & on an organism
- **Bioconcentration**
 - Net contaminant accumulation (from water) in & on an organism
- **Biomagnification**
 - Contaminant conc. increase from trophic level “n” to “n+1”
- **Bioaccumulation factor (BAF)**
 - C_{biota}/C_{source}
- **Bioconcentration factor (BCF)**
 - C_{biota}/C_{aq}
- **Biomagnification factor**
 - $C_{biota}^{n+1}/C_{biota}^n$

Transport against hydraulic gradient



- Salmons concentrate PCBs (biovectors)



PCB molecular structure

PCBs in Lake Ontario

PCB congener	microgram PCB per *		
	52	66	153
MW	291.97	291.97	360.71
dissolved	6.3E-0.5	3.1E-0.5	5.0E-0.5
bottom sediment	25	46	25
suspended sediment	15	27	23
plankton	2.4	1.6	2.2
mysids	3.5	15	30
amphipods	22	30	45
oligochaetes	6.3	8.3	7.5
small smelt	7.6	2.7	64
large smelt	18	72	130
trout/salmon	62	160	430

*L for dissolved; kg dry wt. for sediments; kg wet wt. for organisms

Oliver & Nilmi, 1988, ES&T, 22:388-397

Hydrophobic organic compounds (HOCs)

- **Partitioning to biota**
 - Tend to partition to lipids
 - Lipids are fat soluble, naturally occurring molecules
 - Fats, oils, waxes, some vitamins (A, D, E, K), glycerides
 - Have hydrocarbon chains - hydrophobic
- **Partitioning to soils & sediments**
 - HOCs partition much more strongly to the natural organic matter (NOM) fraction of soil than to mineral phases
 - Hydrophobic regions of NOM
 - Only surfaces of minerals are accessible to contaminants
 - NOM typically dominates partitioning down to $f_{oc} \sim 0.001$

*f_{oc} = organic carbon fraction in soil or sediment
[g organic carbon/g soil or sediment]*

Octanol water partition coefficient

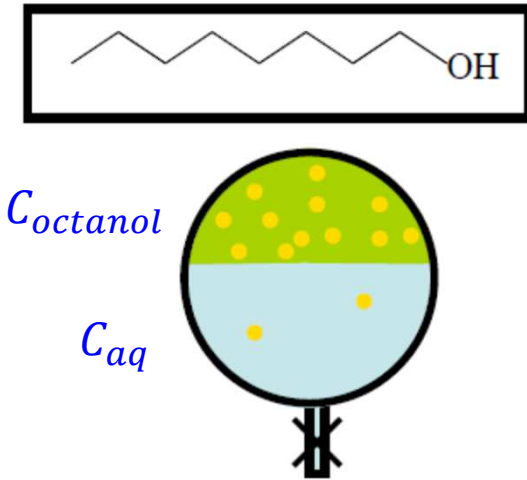
- ***n*-octanol, C₈H₁₇OH**
 - Surrogate for natural organic phases
 - Soil/sediment organic matter (SOM), dissolved organic matter (DOM), lipids
 - Octanol-water partition coefficient, K_{ow}

$$K_{ow} = \frac{C_{octanol}}{C_{aq}}$$

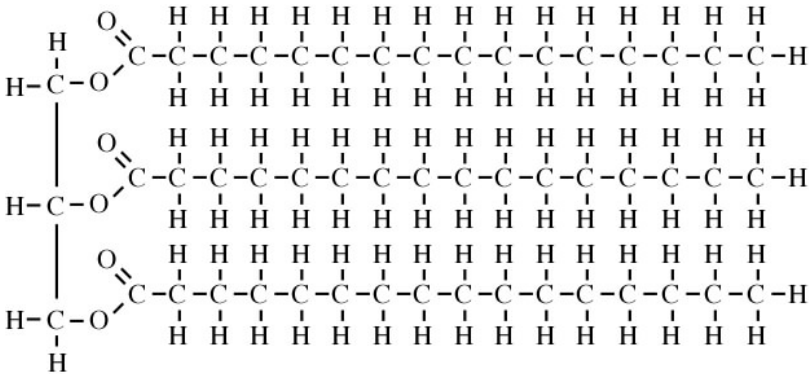
C_{octanol} = concentration in octanol at equilibrium [g sorbate/L octanol]

C_{aq} = concentration in water at equilibrium [g sorbate/L water]

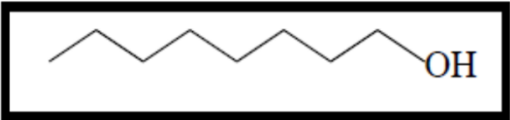
So, *K_{ow}* is unitless



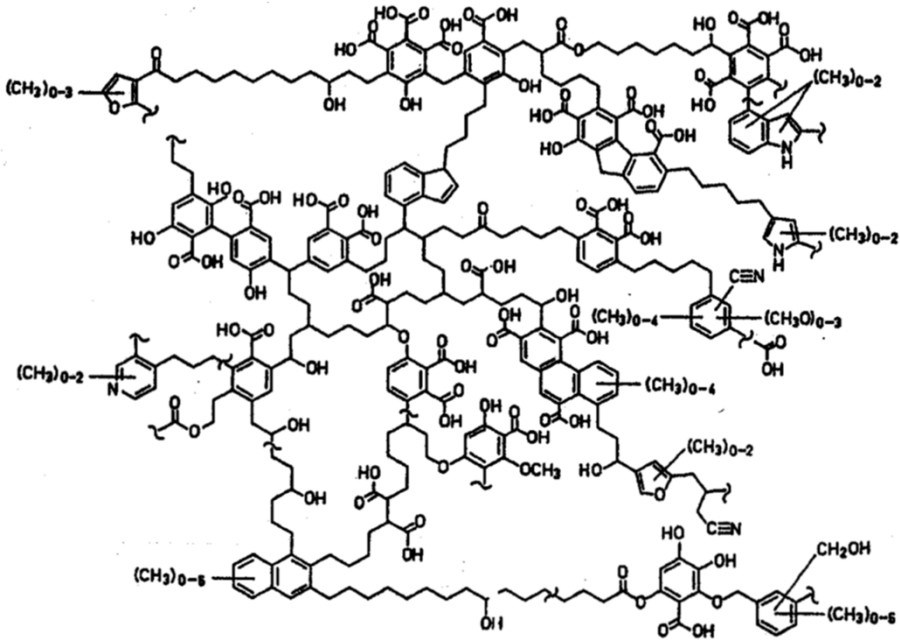
Lipid & humic substance examples



fat molecule – example



cf) octanol



humic substance – example

Aq. solubility, vapor pressure, K_{ow}

Compound	Formula	$\log K_{ow}$	$-\log(p^{sat})^1$	$-\log(C^{sat})^2$
methane	CH ₄	1.09	-2.44	2.82
n-butane [@]	C ₄ H ₁₀	2.89	-0.39	2.98
n-hexane	C ₆ H ₁₄	4.00	0.69	3.83
cyclohexane	C ₆ H ₁₂	3.44	0.90	3.15
1-hexene	C ₆ H ₁₂	3.40	0.60	3.15
benzene	C ₆ H ₆	2.17	0.90	1.64
1-hexanol	C ₆ H ₁₄ O	2.03	2.85	0.88
1-octanol	C ₈ H ₁₈ O	2.84		2.35
toluene	C ₇ H ₈	2.69	1.42	2.25
chlorobenzene	C ₆ H ₅ Cl	2.78	1.80	2.35
1,4 dichlorobenzene	C ₆ H ₄ Cl ₂	3.45	3.04	3.39
bromobenzene	C ₆ H ₅ Br	2.99	2.25	2.64
dioxin [#]	C ₁₂ H ₄ O ₂ Cl ₄	6.64	11.6	10.3

[@]gas at 25C-- p^{sat} refers to pressure needed to obtain pure liquid at 25C

[#]2,3,7,8-tetra-chlorodibenzo-p-dioxin

¹vapor pressure @ 25C, atmospheres

²concentration in saturated aqueous solution, moles/l, 25C

Using K_{ow} – HOC partitioning to biota

- Bioconcentration factor (BCF) = C_{biota}/C_{aq}
 - C_{biota} unit: [g sorbate/kg body weight]
 - BCF not necessarily representative of equilibrium state
- If equilibrium can be assumed, may use octanol as a surrogate for lipid
 - Lipid fraction by weight -- α ($\alpha=10-30\%$ for humans)
 - For a rough estimate, assume 1 kg lipid = 1 kg octanol

$$BCF \approx \frac{\alpha}{0.826} K_{ow}$$

0.826 = density of octanol [kg octanol/L octanol]

** Note K_{ow} [L water/L octanol]*

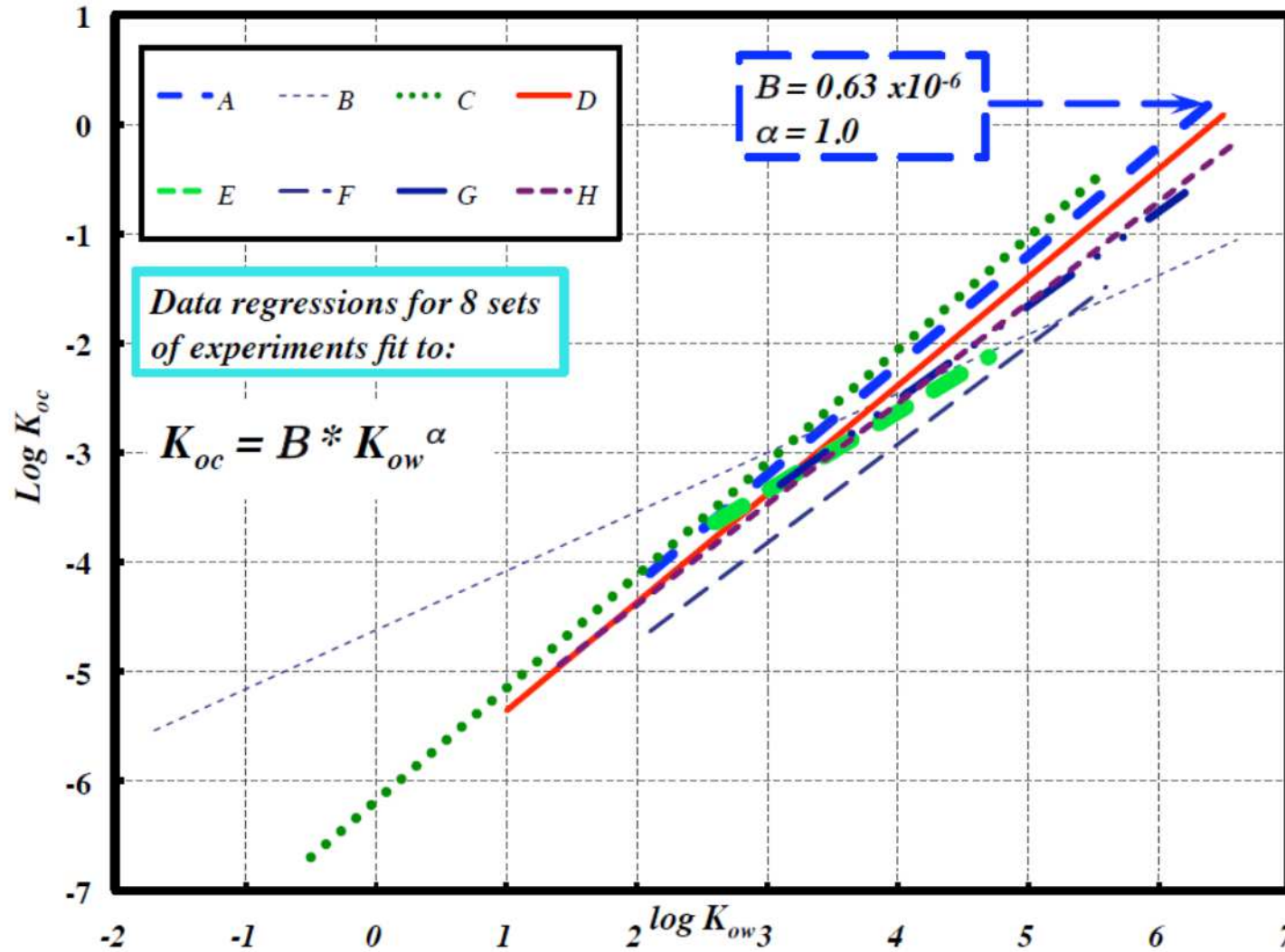
Using K_{ow} – HOC partitioning to soil/sediment

- As NOM dominates sorption for HOCs,

$$\frac{C_s}{C_{aq}} = K_p = f_{oc} \cdot K_{oc} \quad K_{oc} = \text{organic carbon-normalized partitioning coefficient}$$

- Various units of K_p & K_{oc} can be used:
 - volume of water / dry weight of solid
 - m^3/g , mL/mg , L/g , L/kg , L/mg , ...
 - Numerical value will depend on the units used
- Use K_{ow} to predict K_{oc}
 - K_{ow} - K_{oc} relationship needed!
 - Note K_{oc} range of ~2 orders of magnitude for a single compound has been reported
 - Use caution when using K_{oc} without experimental determination

Organic carbon/water partitioning, K_{oc}



Here, K_{oc} unit is $[m^3/g]$

Organic carbon/water partitioning, K_{oc}

$$K_{oc} = \beta \times K_{ow}^{\alpha}$$

Ref.	# of compounds	Range of log K_{ow}	$\beta \times 10^6$	α	r
A Karickhoff et al., 1979	10	2.1~6.6	0.63	1.0	1.0
B Kenaga & Goring, 1980	45	-1.7~6.6	24	0.54	0.93
C Rao & Davidson, 1980	15	-0.5~5.6	0.66	1.03	0.95
D Karickhoff, 1981	6	1.0~6.5	0.45	0.99	0.99
E Schwarzenbach & Westall, 1981	12	2.6~4.7	3.1	0.72	0.97
F Chio et al., 1983	12	2.1~5.6	0.3	0.90	0.99
G Mingelgrin & Gerstl, 1983	7	3.1~6.2	1.1	0.87	0.85
H Curtis et al., 1986	22	1.4~6.6	0.59	0.92	0.94

(K_{oc} in [m^3/g])

- Use "A" (Karickhoff et al., 1979) for this class

Phase equilibrium – chemical potential

At equilibrium

$$\mu_i^{pure} = \mu_i^{gas} = \mu_i^s = \mu_i^{aq}$$

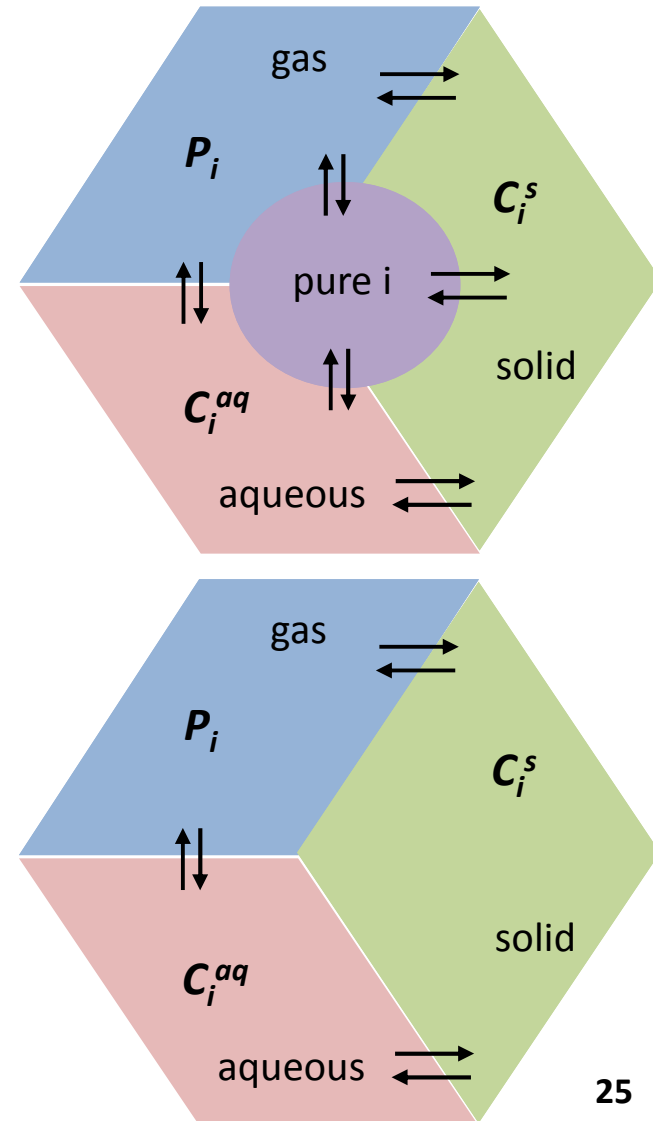
(If pure phase exists)

$$\mu_i^{eq} = \mu_i^{gas} = \mu_i^s = \mu_i^{aq}$$

(If pure phase does not exist)

- μ is the chemical potential; it has units of energy – difficult to measure
- Chemical potential is related to activity

$$\{i\}_{g,s,aq} \propto e^{\mu}$$
- For gas phase, activity equals partial pressure expressed in atm



Phase equilibrium - fugacity

Define the **fugacity** of a substance i in any phase to be equal to the **partial pressure of i** that is in equilibrium with the phase

At equilibrium

$$f_i^{pure} = f_i^s = f_i^{aq} = f_i^{gas} = p_i^{sat} \quad (\text{if pure phase exists})$$

$$f_i^s = f_i^{aq} = f_i^{gas} = p_i \quad (\text{if pure phase does not exist})$$

- **Why use p_i ?**
 - Pressure is comprehensible & measurable
 - Gas phase behaves ideally – a good reference
 - $p_i \propto \{i\} \propto [i]$

Phase equilibrium - fugacity

- Advantage of fugacity approach
 - **Predict multi-phase equilibrium partitioning** in a minimally complex fashion
- Fugacity approach is applicable
 - In dilute systems when partitioning is linear among different phases
 - Suited for volatile compounds

Equilibrium partitioning between phases

- Linear partitioning among phases: review our discussions
 - Henry's law for **gas/water partitioning**:

$$p_i = H_{pc} \times C_i^{aq} \quad \text{or} \quad C_i^{gas} = H_{cc} \times C_i^{aq}$$

- Linear partitioning among **water and any other phases**:

$$C_i^s = K_p \times C_i^{aq}$$

$$C_i^{biota} = BCF \times C_i^{aq}$$

$$C_i^{oct} = K_{ow} \times C_i^{aq}$$

:

Applying fugacity approach

- **So:** if a system is at equilibrium and partitioning is linear, we can relate the concentration of a compound in any phase to partial pressure, or **fugacity**
- **Now:** introduce “Z value”, the fugacity capacity factor (unit: mole/atm/m³), to relate fugacity to concentration.
- **Then:**

$$C_i^j = f_i Z_i^j$$

$$\text{Moles}_i^j = C_i^j V^j = f_i Z_i^j V^j$$

$$\sum_j \text{Moles}_i^j = \sum_j C_i^j V^j = f_i \sum_j Z_i^j V^j \quad (\text{when } C_i^j \text{ are all expressed as moles/volume})$$

Z values for different phases

- **Gas phase**

$$p_i V^{gas} = nRT$$

$$\frac{n_i}{V^{gas}} = C_i^{gas} = \frac{p_i}{RT} = \frac{f_i}{RT} \quad \Rightarrow \quad Z_i^{gas} = \frac{1}{RT}$$

- **Aqueous phase**

$$p_i = f_i = H_{pc} C_i^{aq}$$

$$C_i^{aq} = \frac{f_i}{H_{pc}} \quad \Rightarrow \quad Z_i^{aq} = \frac{1}{H_{pc}}$$

- **Octanol**

$$C_i^{oct} = K_{ow} C_i^{aq} = f_i \times \frac{K_{ow}}{H_{pc}} \quad \Rightarrow \quad Z_i^{oct} = \frac{K_{ow}}{H_{pc}}$$

Z values for different phases

- **Solid phase**

$$C_i^{s*} = K_p C_i^{aq}$$

Here, C_i^{s*} is per weight basis;

K_p has a dimension of (vol. water) / (weight solid)

$$C_i^s = \rho_s K_p C_i^{aq} = f_i \times \frac{\rho_s K_p}{H_{pc}} \quad \Rightarrow \quad Z_i^s = \frac{\rho_s K_p}{H_{pc}}$$

C_i^s should be per volume basis

- or, we may use:

$$Z_i^{s*} = \frac{C_i^{s*}}{f_i} = \frac{K_p C_i^{aq}}{f_i} = \frac{K_p}{H_{pc}}$$

Z_i^{s*} has a unit of moles/atm/kg
if C_i^{s*} is in moles/kg

- then,

$$\text{Moles}_i^s = C_i^{s*} M^s = f_i Z_i^{s*} M^s$$

Applying fugacity approach

- **Our potential interest: how mass will be distributed among phases.**
- **Need:**
 - Compartment volumes or masses
 - Equilibrium constants (Henry's constant, K_{ow} , K_p , etc.)

$$M_i^{total} = \sum_j C_i^j V^j = f_i \sum_j Z_i^j V^j = p_i \sum_j Z_i^j V^j$$

If Z_i^{j} is obtained for any solid phase, substitute $Z_i^j V^j$ with $Z_i^{j*} M^j$ for that phase*

- If we know M_i^{total} , we can calculate f_i and then determine C_i^j s and distributions among compartments
- If we know f_i , we can calculate M_i^{total} and then determine C_i^j s and distributions among compartments