

CVEN 4474/5474 Haz Waste Outline

- Contaminant characteristics and partitioning
 - Which compounds are important?
 - Solubility
 - Partitioning into air (vapor pressure, H')
 - Sorption onto soil
 - Example problem

Toxic Compounds of Interest

- ATSDR CERCLA Priority List
 - Most prevalent and toxic
- Most total chemicals in production waste
- Largest released chemical by TRI

Primary groups of priority chemicals (ATSDR)

- Metals (As, Pb, Hg, Cd, Cr; 5 of top 20)
- Chlorinated organics (VC, PCBs, CF, DDT TCE; 9 of top 20)
- Volatile organics (VOCs; 4 of top 20)
- Aromatic organics (benzene, PAHs; 9 of top 20)
- Pesticides (3 of top 20)

Fate of Chemicals in Environment based on Contaminant Characteristics

- Solubility
- Volatility
- Sorption onto Soil

Where to find chemical properties?

- LaGrega text Appendix B
 - Vapor pressure, solubility, log Kow
 - Be cautious of temperature!

Solubility

- Maximum concentration in water at equilibrium with the pure substance
- Generally increases with increasing temperature
- Effect of compound form
 - Example: solid naphthalene 31 mg/L @ 25°C
 - Liquid naphthalene 112 mg/L @ 25°C
- Other “environmental” effects
 - pH, cosolvents, ions *Joe Ryan’s Ochem class!*

Water Solubility at Equilibrium with Compound Mixture

- Due to co-solvent effects in the separate phase (such as oil), solubility in water not as high as for pure compound
- Raoult's Law [equilibrium]
 - $C_{w_i} = C_{s_i} * X_i$
 - $P_a = P_{v_p_a} * X_a$
 - X is the mole fraction of compd of interest in a mixture [usually NAPL]
- Example: gasoline

Gasoline Example

- If 1 L of water is added to 1 L of gasoline in a closed container and allowed to sit, what will be the benzene conc. in the water after 1 week?
- What is the concentration of benzene in water at equilibrium with gasoline?
- Look up solubility of benzene (App B)
 - 1780 mg/L at 25°C New txt error! Not 178 mg/L
- Determine the mole fraction of benzene in gasoline Convert from mass or volume composition to moles using MWs; 1%
 - 1780 mg/L * 0.01 = 17.80 mg/L

Volatility

- Vapor pressure: partial pressure of a compound at equilibrium with pure compound
- Varies based on temperature, "mixtures" by Raoult's Law
- Vapor density: if MW > 29 g/mol it is more dense than air and will sink to ground

Volatility example

- 1 L of pure benzene is added into an empty 2 L container and sealed shut. After 1 month what is the likely concentration of benzene in the air in ppm-v and mg/L?

Look up vapor pressure: 95.2 mm Hg @ 20C

Convert VP to concentration:

95.2 mmHg / 760 mmHg; equiv. to mol/mol AND vol/vol

0.125 L benz/L air * 1,000,000 = 125,000 ppm-v

$$\frac{0.125 \text{ mol B}}{\text{mol air}} * \frac{78 \text{ g B}}{\text{mol B}} * \frac{1 \text{ mol air}}{24 \text{ L air}} = 406 \text{ mg/L}$$

$pV = nRT$

Air:Water Partitioning

- Henry's Law "constants"
 - $H' = C_g / C_w$; H = Vapor Pressure/solubility
 - $\frac{\text{L}_w / \text{L}_a}{\text{atm} / \text{mol/m}^3}$
 - $H' = H/RT$
 - Vapor pressure and solubility must be at same temp.
- Environmental effects
 - Temperature, H, mixtures, dissolved salts, suspended solids, NOM, surfactants....
 - "Reference" value vs environmental value

Example use of H'

- If H' @ 25°C is 0.2 and Cw at equilibrium = 1 mg/L, what is Ca?
 - $H' = Ca/Cw$ $Ca = H' Cw = 0.2 * 1 \text{ mg/L} = 0.2 \text{ mg/L}$
 - If water and air at equilibrium have ? 0.2 ppm concentrations of 10 mg/L and 1 mg/L, respectively, what is H'?
 - $H' = Ca/Cw = 1 \text{ mg/L} / 10 \text{ mg/L} = 0.1$
 - If Cw = 10 mg/L and Ca = 1 ppm-v at equilibrium, what is H'?
 - $Ca = 1 \text{ ppm-v} = \frac{1 \text{ mol}}{10^6 \text{ mol air}} * \frac{1 \text{ mol air}}{24 \text{ L air}} * \frac{\text{MW compd g}}{\text{mol}}$
- Therefore, can't solve w/o temp & compd mol wt

Partitioning out of Water due to Hydrophobic Interactions

- Octanol : Water partition coefficient @ equil.
 - $K_{ow} = C_{oct} / C_w$ L_w/L_o
 - Easy measure; reported for many organics
- Soil : Water partition coefficient
 - $K_p = C_s / C_w$ units? $\frac{\text{mg/kg}}{\text{mg/L}} = \frac{\text{mass org C}}{\text{mass soil solids}} \frac{\text{L}}{\text{mL}}$
 - $K_p \sim f_{oc} K_{oc}$; $K_{oc} = C_{oc} / C_w$
 - K_{oc} can be estimated from K_{ow}

Partitioning out of Water for Inorganics

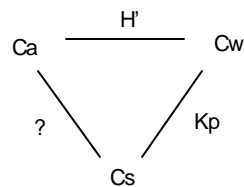
- Precipitate carbonates, phosphates, etc.
 - Highly pH dependant
 - See solubility product constants in water chemistry (grad class)
- Exchange ions with soil
 - Sand generally (-) charge, therefore cation exchange capacity (CEC) of soil

K_p values vs soil type summarized in Charbeneau GW txt: Cr 30-1500; Pb 270-16000

Mobile Soil Particles

- Colloids
- Mobile in groundwater
- May lead to error in fate assumption if ignored
 - Example: if ignore colloids, Pu at Rocky Flats o.k. (not mobile)
 - If Pu at Rocky Flats migrates in GW due to colloid association, as observed, not safe

Key: Equilibrium Assumptions!



$$C_a / C_w = H'$$

$$H' / K_p = C_a / C_s$$

$$C_s / C_w = K_p$$

Example Problem: TCE

- A 50-gal drum initially full of TCE is used to degrease machine parts.
- Over time, TCE volatilizes out of the drum... when it is half full it is placed outside... it rains...
- The drum is capped and contains:
 - 100 g "sediment" from parts, 40% TCE, 50% water, and 10% air by volume.
- After 10 years what will be the TCE distribution in the barrel?