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

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)

Toxic Compounds of Interest

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

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]
  – \( C_w = C_s \cdot X \)
  – \( P_a = P_{vp} \cdot X_a \)
  – \( X \) is the mole fraction of cmpd 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 \times 0.01 = 17.80 mg/L

Volutility

• 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

Volutility 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 @ 20°C
  Convert VP to concentration:
  \[ \frac{95.2 \text{ mmHg}}{760 \text{ mmHg}} \cdot \frac{0.125 \text{ mol B}}{1 \text{ mol air}} = 406 \text{ mg/L} \]

Air:Water Partitioning

• Henry’s Law “constants”
  – \( H’ = \frac{Q_a}{C_w} \cdot H = \text{Vapor Pressure/solubility} \)
  \( \frac{L_w}{L_a} \cdot \text{atm} / \text{mol/m}^3 \)
  \( H’ = \frac{H}{RT} \)
  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 \( C_w \) at equilibrium = 1 mg/L, what is \( C_a \)?
  \[ H’ = \frac{C_a}{C_w} \quad C_a = H’ \cdot C_w = 0.2 \cdot 1 \text{ mg/L} = 0.2 \text{ mg/L} \]
• If water and air at equilibrium have concentrations of 10 mg/L and 1 mg/L, respectively, what is \( H’ \)?
  \[ H’ = \frac{C_a}{C_w} = 1 \text{ mg/L} / 10 \text{ mg/L} = 0.1 \]
• If \( C_w = 10 \text{ mg/L} \) and \( C_a = 1 \text{ ppm-v} \) at equilibrium, what is \( H’ \)?
  \[ C_a = 1 \text{ ppm-v} = \frac{1 \text{ mol}}{10^6 \text{ mol air}} \cdot \frac{1 \text{ mol air} \cdot \text{MW cmpd g}}{24 \text{ L air}} \]
Therefore, can’t solve w/o temp & cmpd mol wt
Partitioning out of Water due to Hydrophobic Interactions

- Octanol : Water partition coefficient @ equil.
  \[ K_{ow} = \frac{C_{oct}}{C_w} \times \frac{L_w}{L_o} \]
  - Easy measure; reported for many organics

- Soil : Water partition coefficient
  \[ K_p = \frac{C_s}{C_w} \] units? \( \text{mg/kg} / \text{mg/L} = \text{L/kg} = \text{mL/g} \)
  \[ K_p \sim f_{oc} K_{oc}; \quad K_{oc} = \frac{C_{oc}}{C_w} \]
  \[ K_{oc} \text{ can be estimated from } K_{ow} \]

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

Kp 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!

\[ \frac{C_p}{C_w} = \frac{H'}{H'/K_p} = \frac{C_p}{C_s} \]
\[ \frac{C_s}{C_w} = K_p \]

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?