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 (benz, PAHs; 9 of top 20)
- Pesticides (3 of top 20)

Fate of Chemicals in Environment based on Contaminant Characteristics

- Solubility
- Volatility
- Sorption onto Soil

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

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
  - $C_{wi} = C_{si} \times X_{i}$
  - $P_{a} = P_{vp} \times X_{a}$
- Example: gasoline
Gasoline Example

- Look up solubility of benzene (App A)
  - 1780 mg/L at 25°C
- Assume the mole fraction of benzene in gasoline is 1%
- What is the concentration of benzene in water at equilibrium with gasoline?

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

Air: Water Partitioning

- Henry’s Law “constants”
  - $H’ = C_a/C_w$; $H = \text{Vapor Pressure/solubility}$
  - $H’ = H/RT$
  - 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 $C_w$ at equilibrium = 1 mg/L, what is $C_a$?
- If water and air at equilibrium have concentrations of 10 mg/L and 1 mg/L, respectively, what is $H’$?
- If $C_w = 10$ mg/L and $C_a = 1$ ppm-v at equilibrium, what is $H’$?

Partitioning out of Water due to Hydrophobic Interactions

- Octanol : Water partition coefficient
  - $K_{ow} = C_{oct}/C_w$ Lw/Lo
  - Easy measure; reported for many organics
- Soil : Water partition coefficient
  - $K_p = C_s/C_w$ units? mg/kg / mg/L = kg/L
  - $K_p \sim \text{loc} \ K_{oc}$; $K_{oc} = C_{oc}/C_w$
  - $K_{oc}$ can be estimated from $K_{ow}$
    - Example: 4-48 txt $K_{oc} = 0.63$ $K_{ow}$

Where to find chemical properties?

- LaGrega text Appendix A
  - Vapor pressure, solubility, log $K_{ow}$
  - Be cautious of temperature!
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

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!

\[
\begin{align*}
\text{Ca/Cw} &= H' \\
\text{H’/Kp} &= \text{Ca/Cs} \\
\text{Cs/Cw} &= Kp
\end{align*}
\]

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?