Partitioning of contaminants (fugacity)

fugacity (f) -

for an ideal gas:

$f = P$ (pressure in Pa)

For a volatile liquid like benzene, once equilibrium between a liquid and a vapor phase is reached:

$$f_{liquid} = f_{vapor}$$

The value for f is 12,700 Pa, the vapor pressure.

If a chemical is discharged into the environment, then:

$$f_{air} = f_{water} = f_{biota} = f_{sorbed} \quad \text{(at equilibrium)}$$

The concentration is typically the concern and it influences the fugacity:

$$C \propto f$$

After inserting a proportionality constant (Z):

$$C = Z f$$

Where Z has the units mol m^{-3} Pa^{-1}.

How do we get Z?

The ratio of a chemical's concentration in any two phases is equal to the ratio of the Z factors:

$$\frac{C_{air}}{C_{water}} = \frac{Z_{air}}{Z_{water}}$$

How can this information be used to predict the distribution of a chemical?

Benzene example.

Since Mass of a chemical = Conc * vol

$M = CV = fZV$

In class problem.

A model environment containing 6 compartments has 100 moles of benzene added.

Step 1. Determine important physical properties for benzene.

H	557 Pa m^3 $mole^{-1}$
K_{OW}	135
K_{sorb} (soil w/ 2% OC)	1.1
K_{sorb} (sediment, susp. solids w/ 4% OC)	2.2
K_{biota} (fish w/ 5% lipid)	6.7

Steps 2 & 3. Determine the volume of each phase and calculate Z values based on step 1 information (provided for you).

Compartments	V (m^3)	Z	VZ	M	C
Air	10^{10}	4.04×10^{-4}			
Water	7×10^{6}	1.8×10^{-3}			
Soil	9×10^{3}	2×10^{-3}			
Susp. solids	35	4×10^{-3}			
Sediment	2.1×10^{4}	4×10^{-3}			
Fish	3.5	1.2×10^{-2}			
Total ($\Sigma Z_i V_i$)			4.05×10^{6}		

Step 4. Calculate ZV for each and determine the fugacity (f) using:

$$f = M_{total} / \Sigma Z_i V_i$$

Step 5. Use the f value to calculate the benzene mass in each phase:

$$M_i = f Z_i V_i$$

Step 6. Calculate the benzene concentration in each phase:

$$C_i = M_i/V_i$$

So where is most of the benzene by mass?

Where is it most concentrated?

Take home problem 1.

What if you are dealing with 100 moles of DDT in the same system?

H	2.3 Pa m^3 $mole^{-1}$
K_{OW}	1,555,000
K_{sorb} (soil w/ 2% OC)	12,700
K_{sorb} (sediment, susp. solids 4% OC)	25,400
K_{biota} (fish w/ 5% lipid)	77,400

If f = 3.46 x 10^{-7} Pa, where is DDT distributed (mass and concentration)?

Compart.	V (m^3)	Z	VZ	M	C
Air	10^{10}	4.04 x 10^{-4}			
Water	7 x 10^6	0.435			
Soil	9 x 10^3	5522			
Susp. solids	35	11043			
Sediment	2.1 x 10^4	11043			
Fish	3.5	33652			

Total ($\Sigma Z_i V_i$) =

Take home problem 2.

What if you are dealing with 60 moles of naphthalene in the same system?

K_{sorb} (soil w/ 2% OC)	18
K_{sorb} (sediment, susp. solids w/ 4% OC)	36
K_{biota} (fish w/ 5% lipid)	112

What is the value for f?

Where is naphthalene distributed (mass and concentration)?

Compart.	V (m^3)	Z	VZ	M	C
Air	10^{10}	4.04×10^{-4}			
Water	7×10^{6}	0.0239			
Soil	9×10^{3}	0.43			
Susp. solids	35	0.86			
Sediment	2.1×10^{4}	0.86			
Fish	3.5	2.667			

Total $(\Sigma Z_i V_i)$