ESM 222 Fate and Transport of Pollutants in the Environment

Lab #3: Equilibrium Distribution

Due Date: 5/02/2008

Objective:

Understand the partitioning behavior of different organic compounds when released into different compartments:

- Air/Water (Henry's Law, K_H)
- Octanol/Water (K_{ow})
- Air/Water/Sediments

We will use a subset of the organic compounds we observed in Lab 2, namely:

- TCE
- MTBE
- Hexane (change from dodecane which has very low C_w^{sat})

Methods:

Preparation of Aqueous Solutions

Instead of adding direct NAPL, we will add the organics already dissolved in water. This will speed up the equilibration process. In the separation funnels in the fume hood you will find NAPL/water systems that have been in contact for weeks, so that the water is fully saturated with the organic of interest. We want to prepare aqueous solutions with approximately 20 mg/L (about 20 ppm) of organic, except for Hexane, which will be 10 mg/L (about 10 ppm).

- For Hexane, the equilibrium saturation is about 10 ppm, so you can take the amount of water you need directly from the separation funnel into a graduated cylinder.
- For MTBE, first fill a calibrated 100-mL flask with 100 mL of DI water up to the mark. Then take out about 2-3 mL from the separation funnel and pipette 50 µL into the 100-mL flask. Cap the 100-mL flask immediately and swirl it for about a minute to get good mixing. You now have a ~20 ppm solution of MTBE.
- For TCE, first fill a calibrated 100-mL flask with about 95 mL of DI water. Then take out about 2-3 mL from the separation

funnel and pipette 1.55 mL into the 100-mL flask. Add sufficient DI water to reach the 100 mL mark. Cap the 100-mL flask immediately and swirl it for about a minute to get good mixing.

K_H, Air / Water Partitioning

- We will do 3 different ratios of air to water volumes: 10/30, 20/20, 30/10, using the clear glass 40-mL EPA vials. Each group will be assigned a ratio as presented in Table 1 (below).
- Using a graduated cylinder, add exactly 10, 20 or 30 mL of contaminated water to a 40-mL EPA vial. You need to prepare 3 vials (one for each organic). Label them BEFORE you add the solution.
- To allow for full equilibrium, we will let the compounds equilibrate for one week.
- Next week, open the vial, extract 1.5 mL of water using a pipette and place in a 2-mL vial for the GC/MS. Make sure your vials are labeled correctly BEFORE you transfer materials, to avoid confusion.
- Provide your samples to the TA to run in the GC/MS.
- Collect your GC/MS output in the following days.

K_{ow}, Octanol / Water Partitioning

- We will do 3 different ratios of octanol to water volumes: 10/30, 20/20, 30/10, using the clear glass 40-mL EPA vials. Each group will be assigned a ratio as presented in Table 1 (below).
- Using a graduated cylinder, add exactly 10, 20 or 30 mL of contaminated water to a 40-mL EPA vial. You need to prepare 3 vials (one for each organic). Label them BEFORE you add the solution.
- Add the necessary octanol using a burette, measuring the amount of octanol you needed for each vial, and cap tightly immediately. Turn the bottle upside down and shake vigorously for about 1 min.
- To allow for full equilibrium, we will let the compounds equilibrate for one week.
- Next week, open the vial, decant some of the floating octanol into a organic waste beaker and then extract 1.5 mL of water using a pipette and place in a 2-mL vial for the GC/MS. Make sure your vials are labeled correctly BEFORE you transfer materials, to avoid confusion.
- Provide your samples to the TA to run in the GC/MS.
- Collect your GC/MS output in the following days.

Air / Water / Sediments Partitioning

- We will do 3 different ratios of air to water volumes: 10/30, 20/20, 30/10, using the clear glass 40-mL EPA vials. Each group will be assigned a ratio as presented in Table 1 (below).
- Using weighing paper as a "container", weigh three lots of about 5 g of fine, organic-rich sediments to add to each vial. Fold the weighing paper twice and unfold, to make a simple container.
- Add about 5 g of fine sediments to each vial. Weigh the vial before you add the sediment in the analytical balance to the nearest 0.001 g and then after you've added the sediments. Record the exact amount of sediment added.
- Using a graduated cylinder, add exactly 10, 20 or 30 mL of contaminated water to a 40-mL EPA vial. You need to prepare 3 vials (one for each organic). Label them BEFORE you add the solution. Cap tightly immediately. Shake for about 1 min.
- To allow for full equilibrium, we will let the compounds equilibrate for one week.
- Next week, open the vial, extract 1.5 mL of water using a pipette and place in a 2-mL vial for the GC/MS. Avoid collecting sediments with the pipette. Make sure your vials are labeled correctly BEFORE you transfer materials, to avoid confusion.
- Provide your samples to the TA to run in the GC/MS.
- Collect your GC/MS output in the following days.

Based on an analysis of the sediment materials, they have a high organic content of 27.5% ± 1.0%.

Table 1. Volume ratios for each experiment

Group	Air/Water	Octanol/Water	Air/Water/Sediment
1	10/30	10/30	10/30
2	10/30	10/30	10/30
3	20/20	20/20	20/20
4	20/20	20/20	20/20
5	30/10	30/10	30/10
6	30/10	30/10	30/10

Report and Analysis

In a short report prepared by the group, present the following:

1. Estimate of $\mathbf{K_H}$ for each organic, based on your experimental work. Compare to published values of $\mathbf{K_H}$.
2. Estimate of $\mathbf{K_{ow}}$ for each organic, based on your experimental work. Compare to published values of $\mathbf{K_{ow}}$.
3. Mass fraction of organic in each compartment for your air/water/sediment ratios. Do the calculation with your experimental and literature values of $\mathbf{K_H}$ for each organic. Comment on any significant differences.
4. If you had collected 5 g of sediments representative of conditions in 1000 kg of sediments, estimate the total mass of organic present in these sediments.

We will compare the results from the various groups in a later lab session.