Fate & Transport of Chemicals in the Environment

Homework #4
Due Monday, Feb. 14, 2022

University of South Florida
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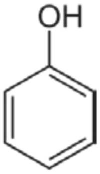
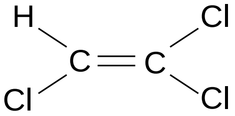
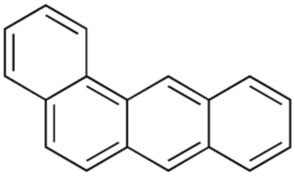
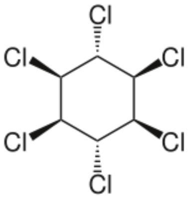
In this assignment, you will determine how four chemicals partition between different compartments or phases in the environment. The four contaminants are:

phenol, a chemical intermediate used in the synthesis of many other chemicals and products  	**trichloroethene** (also called trichloroethylene, or TCE), a chlorinated alkene used as a solvent and de-greasing agent; suspected carcinogen 
benz[a]anthracene (also called tetraphene), a polycyclic aromatic hydrocarbon (PAH); known carcinogen; formed as a product of incomplete combustion 	**lindane** (also called hexachlorocyclohexane), an agricultural insecticide, banned worldwide (with some exceptions) in 2009 because it is persistent, bioaccumulative, and toxic (PBT) 

These chemicals have different chemical structures and chemical properties, which, as you will investigate, leads them to behave differently in the environment.

To investigate how these chemicals behave in the environment, you will use the "ChemFate" Excel workbook that I created and will provide to you. The Excel workbook that I created is based on previous versions created by Professors Paul Roberts, Dick Luthy, and Greg Lowry; their versions were originally based on the research of Donald Mackay and his co-workers. You can find Prof Mackay's work in many highly cited journal papers, or in this book:

Mackay D (1991). *Multimedia Environmental Models: The Fugacity Approach*. Lewis Publishers: Chelsea, MI.

The ChemFate spreadsheet calculates the distribution of compounds among six compartments that are assumed to be in equilibrium: air, water, soil, sediment, suspended solids, and biota. In class, we talked about partitioning between soil and water – the sediment and the suspended solids are essentially the same thing as the soil, but possibly with a different fraction of organic carbon.

If I did a good job creating the spreadsheet, then it should be easy to use. You will enter *chemical properties* and *environmental characteristics* in the input page; then ChemFate uses the input data to perform calculations and to give you output. Each output page has a tab in the Excel workbook.

In this assignment, we will consider a fictional lake, based on an example from a paper of Mackay and Paterson (1981, *Environmental Science & Technology*, pp 1006–1014). Here is information about the lake (modified very slightly from the original 1981 article).

Water: 7×10^6 m^3, density ρ = 1000 kg/m^3
Air above the lake: 1×10^{10} m^3
Soil (lake shore): 9×10^3 m^3, density ρ = 1500 kg/m^3, organic carbon $f_{OC} = 0.02$
Sediment: 2.1×10^4 m^3, density ρ = 1500 kg/m^3, organic carbon $f_{OC} = 0.10$
Suspended solids: 35 m^3, density ρ = 1500 kg/m^3, organic carbon $f_{OC} = 0.04$
Biota (fish): 3.5 m^3, density ρ = 1000 kg/m^3

We will assume that 100 mol of each of the four contaminants have been spilled (or somehow introduced) into the lake. The ChemFate workbook will tell us where these contaminants reside, and their concentrations in each compartment, once the system reaches equilibrium.

1. (15 pts) Look up the necessary chemical properties for each of the four chemicals, and enter the data into the appropriate fields of the ChemFate input spreadsheet. Also enter the environmental characteristics and the names of your group members in the appropriate fields. Most of the chemical property data are provided in Table 2.3 of your text book.

   Assume the temperature of the system is 25 °C. Also assume that there are 100.0 mol of each chemical present.

   You will need to estimate good coefficients for the K_{OC}-K_{OW} relationship. Use Table 3.1 in the text. For phenol and benz[a]anthracene, use the correlation for “aromatic compounds”. For TCE and lindane, use the Karickhoff “all-purpose” correlation given in the text on p 83. Make sure your units are OK.

   Print out the page of input data and submit it with your write-up. Also print out the four output pages and submit those too. You will use these five pages to answer question 2 of this assignment.

   Hint: watch your units! Make sure you are using correct units throughout.

2. (40 pts) Now let's look at the results that you got. Use your outputs from problem 1 to answer the following.

    (a) (25-ish pts) Discuss the distribution of mass of the four compounds, and explain the differences in partitioning among the six compartments in terms of the compounds' physical-chemical properties. In which compartment(s) does each chemical "prefer" to reside? – why? Which compound(s) partition(s) most strongly into the air? Which one(s) into the water, and into the sediment? How does the observed behavior depend upon the *chemical properties* and the *environmental characteristics*?

    (b) (5-ish pts) Look at the graphs of concentration for the four chemicals. In particular, note the scale of the y-axis for each of the four chemicals. You should notice that one of the four chemicals is (overall) present at much lower concentrations than the other three chemicals. Which of the four chemicals is present at the lowest concentrations? Why? Which chemical is present at the *highest* concentrations? Why? Hint: think about your answer to part (a) – in which compartment do these chemicals "prefer" to reside, and how is that relevant?

    (c) (5-ish pts) For any given compound, you should see a pattern if you look at the compound's concentrations in the three solid compartments: soil, sediment, suspended solids. This pattern should look the same for each of the four compounds. Describe the pattern that you observe, and explain why it occurs.

    (d) (5-ish pts) Of the six compartments, which compartment or compartments generally exhibit the highest *concentrations* of the contaminants? Why? – what properties or coefficients are relevant? Does the compartment with the highest concentration always have the most contaminant mass? Why or why not?

3. (15 pts) For each chemical, we had to choose coefficients to use for the K_{OC}-K_{OW} relationship. There is some uncertainty in choosing the "right" K_{OC}-K_{OW} relationship. Let's see if our choice of coefficients makes a big difference to the overall predictions of the spreadsheet. Pick one of the four chemicals, and for that chemical, choose a different K_{OC}-K_{OW} relationship that seems like it might be reasonable. (Clearly state what relationship you are choosing, and why.) Re-run the model using the new K_{OC}-K_{OW} relationship, and print out the relevant output page to submit. Compare the "new" results to the "old" results: did the results change? By a little or by a lot? Why?

4. (25 pts) Let's find out how important the temperature is. We'll repeat the calculation for TCE, but this time at 5 °C. To do this, you will have to adjust the temperature field in the spreadsheet, and also the field for vapor pressure. We will assume that aqueous solubility, K_{OW}, and the K_{OC}-K_{OW} relationship do not change with temperature; but the vapor pressure does change. So we have to come up with a way of estimating the vapor pressure at 5 °C.

Vapor pressure depends on temperature according to the following:

$$\frac{dP^v}{dT} = \frac{P^v\,\Delta H}{R\,T^2}$$

which can be re-written equivalently as

$$\frac{d\,\ln(P^v)}{d(1/T)} = -\frac{\Delta H}{R}$$

where P^v is vapor pressure, T is temperature, R is the ideal gas constant, and ΔH is the molar heat of vaporization, i.e., the energy per mole required to convert TCE from the liquid phase to the gas phase at the temperature of interest. (Sometimes it is called the "latent" heat of vaporization.) The top equation is the *Clausius-Clapeyron equation*; the bottom one is a *van't Hoff relationship* (usually used for describing temperature dependence of equilibrium constants, but here used for vapor pressure).

According to the second equation, if we assume that ΔH is approximately constant over the temperature range of interest, we can graph $\ln(P^v)$ versus $1/T$, and we should get a straight line, with slope $-\Delta H/R$. Let's find out. I found the following data in my old CRC handbook.

Vapor pressure of TCE as a function of temperature

vapor pressure (mm Hg):	1	10	40	100	400	760
temperature (°C):	–43.8	–12.4	+11.9	+31.4	+67.0	+86.7

Reference: Handbook of Chemistry and Physics, CRC Press, 65th Ed., 1984, p. D-200.

(a) Graph the data. Do you get a straight line as the theory predicts? Hint: what units do you need to use for temperature? (You might want to convert the vapor pressure to units of atm or Pa, but that is optional.)

(b) Estimate the molar heat of vaporization of TCE based on the CRC data. Report your answer in units of kJ/mol. I found a published value of 8.31 kcal/mol, which is equivalent to 34.8 kJ/mol. Is your estimate close to this published value?

(c) Estimate the vapor pressure of TCE at 5 °C. Report your answer in units of both atm and Pa. Hint: use the best-fit line for the graph you made in part (a).

(d) Re-run the ChemFate model at 5 °C, using the vapor pressure that you determined in part (c). Attach your print-out for the new temperature. Discuss and explain the results for 5 °C as compared to the "base case" of 25 °C. What changed? Why? Did it change by a little or a lot? Pay attention to the *concentration* of TCE in the different compartments as well as the mass.

5. (5 pts) Please provide me with constructive feedback about the spreadsheet. Was it easy to use, or difficult? Was it easy to understand the outputs? If something was not easy, please describe the difficulty you had. If you have suggestions for changes or improvements, please let me know. I want to improve this tool over time, but I need your feedback to know what problems it has. Be honest but constructive.