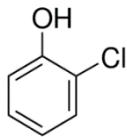
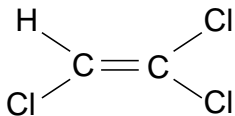
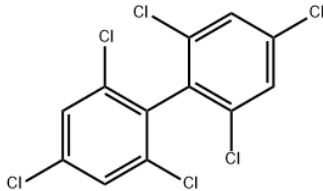
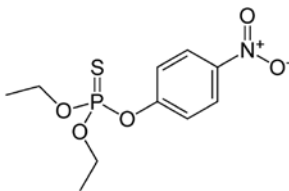


ENV 6002: Physical & Chemical Principles of Environmental Engineering

Fall 2021
Homework #4
Due Tuesday, Sept. 28, 2021

University of South Florida
Civil & Environmental Engineering
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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:

<p>2-chlorophenol, a disinfectant and a chemical intermediate used in the synthesis of pesticides, pharmaceuticals, and dyes</p> 	<p>trichloroethene (also called trichloroethylene, or TCE), a chlorinated alkene used commonly as a solvent and de-greasing agent</p> 
<p>2,2',4,4',6,6'-hexachlorobiphenyl, a polychlorinated biphenyl (PCB), no longer allowed to be manufactured in the USA, but formerly used in many industrial applications</p> 	<p>parathion, a potent organophosphate insecticide, which has been banned in many countries due to its toxicity to non-target organisms (such as humans)</p> 

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

We will assume that 100 mol of each of the four contaminants have been spilled 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 your text book, either in Table 6-1 or in Appendix A.6.1.

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

The coefficients for the $K_{\text{OC}}\text{-}K_{\text{OW}}$ relationship are not in your text book. You'll have to get those from somewhere else. For chlorophenol and hexachlorobiphenyl, use the table from Schwarzenbach et al. (2017) to locate appropriate coefficients. For parathion, use the table from Gerstl (1990) to locate appropriate coefficients. For TCE, use the Karickhoff "all-purpose" correlation.

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. (35 pts) Now let's look at the results that you got. Use your outputs from problem 1 to answer the following.
- (a) (20-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 generally exhibits the highest *concentrations* of the contaminants? Why? – what property or coefficient is relevant? Does the compartment with the highest concentrations also 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. 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. (30 pts) Let's find out how important the temperature is. For TCE, repeat the computations at 5 °C and 35 °C. To do this, you will have to adjust the temperature field 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.

(a) Estimate the vapor pressure of TCE at the new temperatures, as follows. Consult the tabular data summary (below). The data table does not give you the vapor pressure at 5 °C or 35 °C. We will have to interpolate. Use the vapor pressure data to determine the best-fit coefficients of the following equation:

$$\log(P^{sat}) = m/T + b$$

where m and b are the coefficients that you must determine. This equation comes from either the Clausius-Clapeyron relation or the van't Hoff relation.

Once you have the equation, you can easily determine P^{sat} at the desired temperatures.

Table 1: 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.

Note: You might want to convert pressure from mm Hg to Pa or atm

(b) Re-run the ChemFate model at the new temperatures, using the vapor pressures that you determined. Attach your print-outs for those two temperatures. Discuss and explain the results for 5 °C and 35 °C as compared to 25 °C. Pay attention to the *concentration* of TCE in the different compartments as well as the mass.

(c) BONUS QUESTION -- not required -- use your results from part (a) to estimate the heat of vaporization, ΔH , for TCE. Report your answer in units of kJ/mol. Compare your estimated value to a published literature value.

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. Probably, I did not get it perfect on the first try, and it needs improvement, but I need your feedback to know what problems it has. Over time, I will try to improve this spreadsheet tool.