<u>Fugacity Model Calculations: Computer Lab Assignment</u>

Introduction

The aim of the computer lab is to learn how to use fugacity models for calculations of the distribution of persistent organic pollutants in the environment. Furthermore, the lab will help you to familiarize with important concepts and physical/chemical properties commonly used in environmental chemistry.

Fugacity models can be used for calculations of distribution of compounds in a unit world. The unit world is a model world with well-defined compartments (e.g. water, soil, air, biota). The unit world is supposed to reflect the real world or a part of the real world. There are models of different levels: I-IV. In this computer lab, we will use level I and II, which are the simplest ones. In these models, there is chemical equilibrium and steady state. Level I is an equilibrium calculation for a closed unit world. At level II, emissions into the unit world and removal mechanisms are taken into account.

The fugacity approach is not necessary. The distribution can be calculated by ordinary mass balance equations. However, the use of a fugacity model has many advantages. The standardized form facilitates the clearness of the calculations. Moreover, additional information is achieved. Beside the concentration and fractional mass distribution of the compound in each compartment, also some useful fugacity-based parameters are achieved. These parameters are directly comparable between the compartments and will therefore make it easy to understand and get an overview of the interaction of the compound with the environment.

Such parameters are the **fugacity f** (Pa), the **fugacity capacity Z** (mol m^{-3} Pa^{-1}), and the parameter **D** (mol h^{-1} Pa^{-1}). **Fugacity** means fleeing or escaping tendency, and can be viewed as the partial pressure, which a chemical exerts as it attempts to escape from one phase and migrate to another. The **fugacity capacity** is a measurement of the compartment's capacity to hold a compound. **D** is a transport parameter, which is used to describe the rate of the inflow of the compound (advection) and the rate of different removal processes. On level II, there are two such removal processes: advection and degradation.

It is also possible to get the residence time of the compound (h); i.e. the average time, which the compound will spend in the unit world before it, will be degraded or removed by advection. The greatest advantage with the fugacity model is that it is possible to expand to higher levels depending on available information or which complexity is desired.

Usually, the models are built on at least four compartments: air, water, soil and sediment. Other commonly included compartments are aquatic biota, suspended sediment, aerosol and terrestrial biota. It is possible to build a variety of unit worlds for different purposes: lakes, landscapes, countries, lab experiments, houses etc.

For the calculations some input data are required:

For the unit world it is necessary to know:
- Compartments (which should be included?)
- ([*]Temperature)

and for each **compartment**
- Volume
- Organic carbon or lipid content
- Density

For the compound it is necessary to know:

- **Molecular Weight** ($g\,mol^{-1}$)

- **Vapor pressure P** (Pa): the vapor pressure for the subcooled liquid (**P_l) is commonly used, since the concentration in the environment is too low to allow formation of crystals.

- **Water solubility C** ($mol\ m^{-3}$): the water solubility for the subcooled liquid ([**]C_l) is commonly used, since the concentration in the environment is too low to allow formation of crystals.

- **Octanol-water partition coefficient K_{ow}** (no unit):

[*] Please note: The temperature is only used for the calculation of the air density and for the relation H/RT. The greatest temperature influence is on the partition coefficients, which are determined (or predicted) for a given temperature (often +25°C).
[**] P_S can be used, but only if C_S is used, since $H=P_S/C_S=P_l/C_l$ i.e. the energy needed to overcome the crystallization energy is eliminated.

Laboratory report

You work in groups of two. One laboratory report per group should be written and sent to sarah.josefsson@slu.se at the latest on October 10. The manual calculation sheets are handed in and checked during the computer lab.

1. Front page
Name, Date, Supervisor, Title

2. Theory
Aim

Answers to the following questions:

[1] Which three basic physico-chemical parameters of a compound (apart from the molecular weight) are used as input for distribution calculations in a fugacity model world at level I? Include units.

[2] In a handbook with environmental data there is information on Henry law's constants, H (m^3 Pa mol^{-1}). What does H express? How can low and high values be interpreted, respectively?

[3] For environmental chemists it is essential to determine partition coefficients. To distinguish between different partition coefficients they are expressed as K with an index. Which partition coefficients do the constants K_{OW} and K_{OC} represent? Include formulas and units.

[4] Fugacity models at level I could easily be replaced with simple mass balance calculations. The great advantages with fugacity models are actually from level III and above, i.e. at non-equilibrium situations. However, already at level I, a new parameter is introduced, which contributes with interesting knowledge. For each compartment a Z-value is calculated. What does Z express? Include units.

[5] If the fugacity (f) of a compound is equal in all compartments, what does that tell you? What happens if the fugacity differs between compartments?

[6] What does D express? Include units. Give some examples of some processes that can be expressed with D.

[7] Steady-state and equilibrium are central concepts in the fugacity model world. You have got a hardcopy of "Figure 2.1", which explains the concepts. There are five different situations A-E in the figure. Below are five different scenarios. Suggest a letter A-E and a model level (I-IV) for each scenario and assume that no degradation occurs:

1) A factory continuously releases a highly persistent pollutant to a lake and the emission does not fluctuate. The H of the compound is fairly high.
2) A factory continuously releases a highly persistent pollutant to a creek. The compound has fairly high H, and the emission fluctuates greatly over time.
3) A compound is diluted in a closed aquarium with fishes.

4) A chemical is introduced continuously into the air and water of an aquarium with in and out flows in such a way that no net flow is occurring between the compartments. There is no fluctuation in the flow rate.
5) Same as above, but with fluctuation in the flow rate.

3. Computer lab

In the assignment we will practice model calculations manually and by computers (Excel). Ask the teacher for the spreadsheets. Present results for each lab part (1-7, please observe that question 4 is removed). Include manual calculation, percentage distribution and other parameters when asked for. **Please note: Do not attach each Excel calculation, except for question 7**. In most cases it is enough to copy the percentage distribution and a few other numbers to a Word document. Don't forget to include units (also on D-values). Present results in tables or diagrams (preferable). Comment and discuss your results briefly.

1. Calculate manually the distribution of hexachlorobenzene (HCB) in a unit world at "Fugacity model level I", i.e. an equilibrium calculation. Use the standardized 'Fugacity forms' 1 and 2. All input data are listed in the tables below. Skip the calculations that follow after the percentage distribution.

Compartment	Volume (m^3)	Density (kg m^{-3})	Organic carbon or lipid fraction
Air	1.00E+14	calculated value	----
Water	2.00E+11	1000	----
Soil	9.00E+09	2400	0.02
Sediment	1.00E+08	2400	0.04
Susp. Sediment	1.00E+06	1500	0.20
"Fish"	2.00E+06	1000	0.05

Parameter	Value
Mass HCB (kg)	100000
Temperature (°C)	27.5
Molecular weight	284.8
Vapor pressure (Pa)	0.0023
Water solubility (g m^{-3})	0.005
Log K_{ow}	5.5

2. Check the percentage distribution of HCB, Z and ZV values from task 1 by using the **EXCEL spreadsheet = Level I**. Open the file as "read-only". The spreadsheet is made such as it reflects the standardized 'Fugacity forms' as much as possible. In the "spread-sheet" there are already data for "Hypotan".

Make the necessary changes of the in-data. Please note: in-data are in the squares with borders. Do not change other cells, since these contain the model functions.

Did the values agree with part 1? Comment.

Note the Z and ZV values + concentrations and amounts of HCB, compare the values between compartments and comment briefly. What do the Z and ZV values tell you? How do values correlate?

3. This question can be seen as a "sensitivity analysis". Use the same input data and Excel file as in task 2. Calculate what difference it will make to change the in-data according to A, B and C respectively. What happens? Note the percentage distribution and compare with the values from task 2. Present the data in a table and give explanatory comments. Which changes is the model most sensitive to?

A. The air volume is increased 10 times?
(This is more interesting than it might sound. Think about which height of an air column above the defined land is the most correct to use, i.e. how much of the air column will be able to interact with land.)

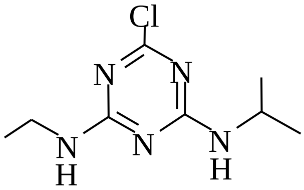
B. Case 1: The sediment volume is increased 5 times?
Case 2: The organic carbon content of the sediment is increased 5 times.
Do also compare case 1 and 2?

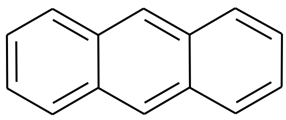
C. The organic carbon content of the soil is decreased from 0.02 to 0.002
Compare Z, ZV and %-distribution.

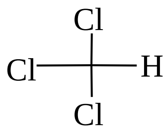
5. Here, the distribution of some organic compounds in a model world is studied. Use the values given in task 1 (and 2) as in-data for the compartments, except for the organic carbon content of the soil, which should be kept at 0.002. Calculate Henrys law's constants and relative distribution by using a level I model.

Present the distribution data (%) and Henrys law's constants in a table and comment the distribution on the basis of H and log K_{ow}.

	Anthracene	DDT	Chloroform	Atrazine
Molecular weight	178.2	354.5	119.4	215.7
Vapor pressure (Pa)	0.001	1.33E-05	23100	3.00E-06
Water solubility (g m^{-3})	0.045	0.0017	8200	33
log K_{ow}	4.54	5.98	2	2.33


Atrazine


Anthracene


Chloroform

6. Now, we move on to Fugacity level II. Calculate the distribution of HCB with **EXCEL-file level II = Level II**.

Use the same in-data as in task 1 (and 2), and complete with data from the table below. Remember to change the organic carbon content back to 0.02.

Parameter	
Emission of HCB (kg h^{-1})	1000
t(½) air (h)	17000
t(½) water (h)	55000
t(½) soil (h)	55000
t(½) sediment (h)	55000
Air residence time (h)	600
Water residence time (h)	7000
Air inflow concentration (mol m^{-3})	0.3 E-09
Water inflow concentration (mol m^{-3})	2.0 E-06

The degradation in fish and suspended sediment is negligible, and the half-life is thus infinite (enter as 1E+99 in the spreadsheet).

A) Compare the results with the Level I calculations (task 1 and 2). What difference did it make for the percentage distribution to include the emission, the advection and the degradation of HCB?

Do also note the D(reaction), D(advection) and D(total) values. Present the data in a table and comment. Which outflow pathways (losses) are the most important?

Note that the flux (N in mol/h) is given by

$N_{ADV} = D_{ADV} * f$
$N_{REA}=D_{REA} * f$

Since f is equal in all compartments (at Level I and II), D-values can be directly compared for information on importance of fluxes (mol/h) for systems that have reached equilibrium.

B) How does the degradation affect the HCB concentrations in the model? How much less HCB will exist in the system (i.e. how much lower will the concentration of HCB be) with the given half-lives in comparison to having infinite half-lives (1E+99) for sediment, water, soil and air? Present the data as relative decrease in % and give explanatory comments.

7. En grupp scouter har råkat slå läger på ett område som är förorenat med DDT och bensen. På området finns en sjö som scouterna använder som dricksvattenkälla och för att fånga fisk till middag. Scouterna kan få i sig föroreningar via fyra olika exponeringsvägar: 1) luften de andas, 2) vattnet de dricker, 3) fisken de äter och 4) jordpartiklar de råkar få i munnen, t.ex. via händerna. Vilken är den dominerande exponeringsvägen för DDT respektive bensen? Anta att ingen nedbrytning sker och att det inte finns någon transport in/ut ur modellvärlden, dvs använd en Nivå I-modell.

Det här är det förorenade områdets mått:

Compartment	Volume (m^3)	Density (kg m^{-3})	Organic carbon or lipid fraction
Air	1,00E+7	calculated value	----
Water	1,00E+4	1000	----
Soil	1,00E+06	2400	0,02
Sediment	10	2400	0,04
Susp. sediment	0,1	1500	0,20
"Fish"	0,2	1000	0,05

Detta är ämnenas egenskaper:

	DDT	Benzene
Molecular weight	354,5	78,11
Vapor pressure (Pa)	1,33E-05	13000
Water solubility (g m^{-3})	0,0017	0,00175
log K_{ow}	5,98	2,13

Det finns 2000 kg av varje ämne på området. Varje dag får scouterna i sig 1 g jordpartiklar. För de övriga exponeringsvägarna får ni uppskatta mängderna. Tips: för jord och fisk är det smidigt att arbeta med g (eller µg) förorening per gram, för luft och vatten g (eller µg) förorening per kubikmeter.

Ange hur många gram (eller µg) en scout får i sig varje dag från respektive exponeringsväg för de två ämnena. Bifoga Excelark och visa uträkningar.