

How to use a Level I Fugacity Model to Estimate Contaminant Partitioning in the Subsurface

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This document describes the use of the level I fugacity model to estimate contaminant fate in the subsurface. This simple model can be very useful for building a conceptual site model and understanding what phases of the subsurface are likely to contain contaminant mass. It is an excellent tool in the classroom that allows students the opportunity to artificially manipulate environmental or chemical parameters to see how these effect contaminant fate (for example, it is instructive to look at a system with and without a residual nonaqueous phase liquid (NAPL) phase to show students how a small residual phase can control partitioning). It is also a useful communication tool that allows non-technical parties involved in the remediation process to understand controlling factors of chemical behavior in the subsurface. Finally, we have used the model to successfully estimate chemical partitioning in simple laboratory microcosms when using radiolabeled compounds.

This model is not intended to provide information that a more complex fate and transport model will provide, nor is it representative of systems that are not in equilibrium (or close to equilibrium). Be sure to use it appropriately.

Included in the document are:

- A brief introduction to fugacity
- A link to download an EXCEL based fugacity calculator
- Some links to Fugacity model internet sites
- An example of a fugacity calculation
- Definitions for terms used in this document

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A brief introduction to fugacity

Simple environmental fate models can be useful for evaluating equilibrium chemical distribution between environmental phases (air, water, soil). Chemicals are usually introduced to a particular phase of the environment, but migrate into other phases as thermodynamic equilibrium is approached. Although environmental systems may never reach true equilibrium, simple equilibrium models can be used as tools for sample plan development, analysis of possible exposure pathways, feasibility assessment of possible remediation strategies, and for assessment of potential environmental fate of new chemicals.

The term "**fugacity**" was introduced in 1901 by G.N Lewis to describe the "**escaping**" tendency of a chemical species from a particular environmental compartment (e.g., air, water, soil, etc.). The term comes from the Latin root *fugere* which describes a "fleeing" or "escaping". Where chemical potential within a particular compartment is related logarithmically to concentration, the equilibrium criterion of *fugacity* is linearly related to concentration. **Fugacity (f) has units of pressure**, and environmental compartments in equilibrium with each other have equal fugacity values (i.e., the tendency to leave one compartment and enter a second is equal to the tendency of the chemical to leave the second and enter the first).

Each environmental medium has a certain **fugacity capacity (Z)** that describes the relationship between chemical concentration and fugacity in the same way that heat capacity describes the change in temperature of a given material for a particular input of heat. Thus, environmental media with high Z values can retain greater amounts of a given chemical while maintaining low fugacity values.

For more on Fugacity see:

Mackay, Donald (2001) **Multimedia Environmental Models: The Fugacity Approach, second edition**. Lewis Publishers, CRC Press, Boca Raton, FL. ISBN: 1566705428

[Mackay includes a "surface soil model" (p.194) that incorporates loss mechanisms of degradation, volatilization, and leaching. Various models based on the fugacity approach, including Level II and III fugacity models are available at:

<http://www.trentu.ca/cemc/models/models.html>]

Sawhney, B.L. and Brown, K., Eds. (1989). **Reactions and Movements of Organic Chemicals in soils**. SSSA Special Publication Number 22, Soil Science Society of America, Madison, WI. ISBN: 089118788X

[Chapter 7 offers an example of a subsurface fugacity model with calculations (p. 187). The authors use the soil "bulk density" in their calculation instead of the density of the soil solids, but this generally does not cause too much error in the final result.]

A simple fugacity "calculator" for subsurface environments

Download at <http://www.infoclearinghouse.com/files/FugacityEXCEL.xls>

The spreadsheet based model pictured below is a simple level I fugacity model for calculating equilibrium phase distributions between the subsurface phases of a contaminated soil system including soil, air, water and a residual non-aqueous phase liquid (NAPL) often present in contaminated soils. The model is in EXCEL spreadsheet format and includes a database of chemical values for common contaminants that can be copied and pasted into the appropriate fields for model calculations. To use the spreadsheet:

- 1-Go to the "chemical data" tab and select and copy the information for the chemical that you are interested in.
- 2-Return to the "Fugacity-level 1" tab and paste the information into the "compound name" cell to view the environmental distribution results
- 3-Modify site or chemical characteristics as needed

The screenshot displays the Microsoft Excel interface for the "FugacityEXCEL" spreadsheet. The main window shows the "LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)" spreadsheet. The spreadsheet is divided into several sections:

- CHEMICAL CHARACTERISTICS** (copy and paste from chemical data tab):
 - Enter the compound name: Benzene
 - Enter the molecular weight: 78.11
 - Enter water solubility (mg/L): 1.78E+03
 - Enter vapor Pressure (mmHg): 7.60E+01
 - Enter Henry's law constant (atm*m³/mol): 5.43E-03
 - Enter Log Kow: 2.13
 - Enter Log Koc: 1.81
- SITE CHARACTERISTICS** (Enter the following):
 - Volume of air (m³): 25
 - Volume of Water(m³): 25
 - Volume of Soil(m³): 50
 - Volume of NAPL(m³): 0
 - total volume (m³) is: 100**
 - Enter the % organic carbon in the soil phase: 0.5
 - Enter the Soil Phase Density (Kg/m³): 2400
 - Enter the total mass of the compound in the system (g): 1.00E+00
- RESULTS** table:

Compartment	Concentration (mg/L)	% distribution
Air	3.25E-03	8.14
Water	1.44E-02	36.03
Soil	1.12E-02	55.83
NAPL	0.00E+00	0.00
Sum=		100.0
- Environmental Distribution** charts:
 - A pie chart showing the distribution: Soil (56%), Water (36%), Air (8%), and NAPL (0%).
 - A bar chart showing the distribution: Air (8.14%), Water (36.03%), Soil (55.83%), and NAPL (0.00%).

Instructions for using the "Fugacity Calculator":

- 1-Find the chemical that you are interested in under the "Chemical Data" tab
- 2-Copy the selected data and return to the "Fugacity-level 1" tab
- 3-Paste the data into the "chemical characteristics" area and view your results
- 4-Modifications can be made to the "site characteristics" inputs to better represent a specific site
- 5-Mouse over cells with red corners to view notes about specific parameters

Fugacity (and other fate model) Internet Sites

<http://www.trentu.ca/cemc/welcome.html>

Environmental modeling center at Trent University-current Home of Dr. Don Mackay-many fugacity based models (including non-equilibrium models) are available.

<http://www.epa.gov/ceampubl/>

USEPA Center for Exposure Assessment Modeling (CEAM). Provides proven predictive exposure assessment techniques for aquatic, terrestrial, and multimedia pathways for organic chemicals and metals. Many models are available.

<http://www.engineering.usu.edu/uwrl/fugacity/fugacity.html>

Fugacity tutorial site at Utah State University. This site is still under construction, but provides useful examples (see "case studies") and a non-Excel based fugacity calculator program that comes as a .zip file.

<http://members.iquest.net/~jdwolt/model.earth.soils.html>

(Tools for environmental modeling page-fugacity models link to University of Trent)

An example of the level 1 fugacity calculation

The following shows a level I (steady state equilibrium) fugacity calculation for a subsurface environment along with the required environmental and chemical information (while working these problems by hand is not particularly difficult, I like to use the spreadsheet presented earlier):

Chemical: benzene
MW= 78.18 g/mol
Mass= 1.0 gram = 1.28E-2 moles
Henry's constant (H) =550 m³ Pa/mol
Soil/water partition coefficient* (K_d)=0.3228

*(the K_d is calculated by multiplying the fraction of organic carbon in the soil (f_{oc}, here assumed to be 0.005 or 0.5%) by the organic carbon normalized partition coefficient (K_{oc}, 64.5 for benzene). In this example, K_d = f_{oc} * K_{oc} = 0.005*64.56 = 0.3228)

First, define the environmental compartments and their volumes. This example uses three compartments, air, water, and soil in a subsurface environment (i.e., the three compartments are actually "soil" air, "soil" water, and "soil" solids). [A residual nonaqueous phase liquid (NAPL) could also be added.] Total volume (V_T) is 100 m³.

$$\begin{aligned}V_{\text{air}} &= 25\text{m}^3 \\V_{\text{water}} &= 25\text{m}^3 \\V_{\text{soil}} &= 50\text{m}^3\end{aligned}$$

Next, calculate the fugacity capacity (Z) for each phase. The fugacity capacity for air (Z_{air}) is always 1/RT and Z_{water} is defined by the inverse of the Henry's constant. Z values for other compartments can be calculated if the compartment density (ρ) and a partition coefficient with another phase are known (in this case, the soil/water partition coefficient or K_d is used along with the soil particle density, ρ_s, estimated at 2.4 kg/l). [If a NAPL phase is included in the model, Z_{NAPL} = Z_{water} * K_{ow} where K_{ow} is the octanol water partition coefficient for the contaminant being modeled.]

$$\begin{aligned}Z_{\text{air}} &= 1/RT = 1/(8.3145)(293\text{K}) = \mathbf{0.00041 \text{ mol/m}^3\text{-Pa}} \\Z_{\text{water}} &= 1/H=1/550 = \mathbf{0.00182 \text{ mol/m}^3\text{-Pa}} \\Z_{\text{soil}} &= K_d * \rho_s * Z_{\text{water}} = (0.3228)(2.4)(0.00182)= \mathbf{0.0014 \text{ mol/m}^3\text{-Pa}}\end{aligned}$$

The equilibrium fugacity (f), which is equal for all compartments, is then given by:

$$f = M / \sum Z_i V_i = 1.28\text{E-2 moles} / (0.00041*25 + 0.00182*25 + 0.0014*50) = \mathbf{0.102 \text{ Pa}}$$

Where M is the number of moles of chemical that are present.

Next, calculate the moles (m) of benzene in each compartment and the resultant concentrations (C):

$$m_{\text{air}} = f_{\text{air}} * Z_{\text{air}} * V_{\text{air}} = 0.102 * 0.00041 * 25 = \mathbf{0.0011 \text{ moles}}$$

$$C_{\text{air}} = f_{\text{air}} * Z_{\text{air}} = 0.102 * 0.00041 = 4.2\text{E-}5 \text{ moles/m}^3 * 78.18 = \mathbf{0.0033 \text{ mg/l}}$$

$$m_{\text{water}} = f_{\text{water}} * Z_{\text{water}} * V_{\text{water}} = 0.102 * 0.00182 * 25 = \mathbf{0.0046 \text{ moles}}$$

$$C_{\text{water}} = f_{\text{water}} * Z_{\text{water}} = 0.102 * 0.00182 = 1.86\text{E-}4 \text{ moles/m}^3 * 78.18 = \mathbf{0.15 \text{ mg/l}}$$

$$m_{\text{soil}} = f_{\text{soil}} * Z_{\text{soil}} * V_{\text{soil}} = 0.102 * 0.0014 * 50 = \mathbf{0.0071 \text{ moles}}$$

$$C_{\text{soil}} = f_{\text{soil}} * Z_{\text{soil}} = 0.102 * 0.0014 = 1.4\text{E-}4 \text{ moles/m}^3 * 78.18 = \mathbf{0.011 \text{ mg/l}}$$

Finally, calculate the equilibrium distribution of benzene among the different compartments:

$$\% \text{ in air} = 0.0011 \text{ moles} / 0.0128 \text{ moles} * 100 = \mathbf{8.6\%}$$

$$\% \text{ in water} = 0.0046 \text{ moles} / 0.0128 \text{ moles} * 100 = \mathbf{35.9\%}$$

$$\% \text{ on soil} = 0.0071 \text{ moles} / 0.0128 \text{ moles} * 100 = \mathbf{55.5\%}$$

Definitions

The following definitions are for parameters and terms used in the fugacity model. They are also available in the "Fugacity calculator" spreadsheet as annotations.

Molecular Weight- the sum of the masses of the atoms (atomic masses) in a molecule, expressed in atomic mass units. The molecular weight of various chemicals can be commonly found in chemical databases or catalogs provided by chemical supply companies.

Water Solubility (mg/l) - Water solubility governs the extent to which a contaminant will partition into the aqueous phase. More soluble contaminants would be expected to migrate further in the subsurface than less soluble compounds. The greater the water solubility of a compound, the greater will be the tendency for that compound to migrate with the aqueous advective flow component. Contaminants with higher water solubilities are more amenable to removal from the saturated zone by pump and treat technology. These same compounds, however, are more likely to migrate through the vadose zone to ground water.

Reference

Subsurface Contamination Reference Guide. Prepared by the EPA Office of Emergency and Remedial Response, October 1990. EPA/540/2-90/01. (a copy of this document can be downloaded at InfoClearinghouse.com)

Vapor Pressure (mm Hg) - The vapor pressure of a compound provides an indication of the extent to which the compound will volatilize. The tendency of a compound to volatilize will rise proportionately with its vapor pressure. Compounds with higher vapor pressures are more amenable to treatment with vacuum extraction technologies. For comparative purposes, the vapor pressure of water at 20 °C is 17.5 mm Hg.

Reference

Subsurface Contamination Reference Guide. Prepared by the EPA Office of Emergency and Remedial Response, October 1990. EPA/540/2-90/01.

Henry's Law Constant ($\text{atm}\cdot\text{m}^3/\text{mol}$) - Henry's Law Constant provides an indication of the extent to which a compound will volatilize from an aqueous solution. It is determined by measuring equilibrium concentrations of a given chemical in a two-phase air-water system and then calculating the ratio between the air phase concentration and water phase concentration. It can also be estimated by the ratio of vapor pressure to water solubility. The greater the Henry's Law Constant of a compound, the greater will be the tendency of the compound to volatilize from aqueous solution. Compounds with higher Henry's Law constants are more amenable to treatment with vacuum extraction technologies.

Reference

Subsurface Contamination Reference Guide. Prepared by the EPA Office of Emergency and Remedial Response, October 1990. EPA/540/2-90/01.

MacKay, D. 2001. Multiple Environmental Models, the Fugacity Approach. Lewis Publishers, Boca Raton, FL.

Octanol/Water Partition Coefficient (K_{OW}) - The octanol/water partition coefficient is a measure of the extent to which a contaminant partitions between octanol and water. It is the ratio of the concentration of the compound in octanol to the concentration of the compound in water. The K_{OW} provides an indication of the extent to which a compound will adsorb to a soil or an aquifer solid, particularly organic material. The greater the K_{OW} , value of a compound, the greater will be its tendency to be adsorbed in the subsurface. Because the K_{OW} ratio can be quite large, it is commonly reported as the \log_{10} of the K_{OW} or simply the $\log K_{OW}$.

Reference

Subsurface Contamination Reference Guide. Prepared by the EPA Office of Emergency and Remedial Response, October 1990. EPA/540/2-90/01.

Organic Carbon Partition Coefficient (K_{OC}) - The organic carbon partition coefficient is the ratio of the amount of chemical adsorbed per unit weight of organic carbon in the soil to the concentration of the chemical in aqueous solution at equilibrium. The K_{OC} is similar to the K_{OW} and is commonly reported as the $\log K_{OC}$ because it is often a large number.

Total Mass (g)- The estimated total mass (in grams) of the contaminant in the system can be entered here if the fugacity model is being used to estimate actual masses in the various phases of the evaluative site. Changing the total mass will not effect the contaminant distribution on a percentage basis, but will effect the concentrations in the different phases.

Volume (m^3) – This is the volume of each component in the evaluative system in cubic meters. Actual estimated volumes of a known system can be entered or the default values of a “normal” unsaturated soil system can be used.

Percent – This is the percentage of the total volume that the phase occupies based on the entered volume of that phase.

Air – “air” refers to the subsurface soil atmosphere. Normal volume ranges for the air phase are between 0 and 40% of the total volume.

Typical value in an unsaturated system: 25%

Typical value in a saturated (aquifer) system: 0%

Water – “water” refers to the subsurface water content. Normal volume ranges for the water phase are between 5 and 50% of the total volume.

Typical value in an unsaturated system: 25%

Typical value in a saturated (aquifer) system: 40%

Soil – “soil” refers to the solid soil volume in the subsurface. It is comprised of both mineral and organic components. Normal volume ranges for the soil phase are between 40 and 60% of the total volume.

Typical value in an unsaturated system: 50%

Typical value in a saturated (aquifer) system: 60%

NAPL – “NAPL” is an abbreviation for “nonaqueous phase liquid” and refers to the residual pure phase solvent or oily waste volume that is often present in the source area of a contaminated site. Normal volume ranges for the NAPL phase are between 0 and 50% of the total volume.

Typical value in an unsaturated system: 0%

Typical value in a saturated (aquifer) system: 0%

% organic carbon – This is the percentage of organic carbon in the soil solids. Soil “organic matter” is typically comprised of 50 to 60% organic carbon, so care should be taken to enter the percentage of organic carbon, not the percentage of organic matter. Typical ranges for soils are between 0.2 and 5.0%. “Organic soils” contain 20% or more organic carbon.

Typical value in an unsaturated system: 0.5%

Typical value in a saturated (aquifer) system: 0.2%

Soil density(kg/m³) – This is the soil solid phase particle density. Typical values for mineral soils range between 2300 kg/m³ and 2700 kg/m³.

Typical value in an unsaturated system: 2400 kg/m³

Typical value in a saturated (aquifer) system: 2600 kg/m³