

Tracking the Distribution of Organic Compounds using Fugacity Model

Jong-Man Baek and So-Jin Park[†]

Department of Chemical Engineering, Chungnam National University,
220, Kung-dong, Yusung-gu, Taejeon 305-764, Korea
(Received 9 April 1999 • accepted 23 November 1999)

Abstract—A fugacity model that can be used to evaluate the environmental fate of various organic compounds is described. The model employs the fugacity concept and treats the environment as four bulk compartments. By undertaking a calculation under steady state non-equilibrium conditions, one can obtain information about a chemical's partitioning, transformation and environmental process. In this work, the fugacity model applied to trichloroethylene in the specified region of lake of Daechung and the behavior of trichloroethylene is presented. The results give a picture of the chemical's fate in an evaluative environment.

Key words: Fugacity, Model, Partition Coefficient, Chemical Fate, Environment

INTRODUCTION

The widespread use and disposal of polluted chemicals contaminate the environment with the passing of time. Understanding how polluted chemicals migrate through our environmental multimedia has become increasingly concerned with predicting the fate and transport of chemicals which are subject to accumulation in environmental compartments where biota and human exposure are significant; it is also essential to predict the environmental effects of new chemicals. Chemicals used industrially, commercially and domestically are discharged into the environment. Among them, toxic chemicals are our concern because they move through the food chain and have toxic effects on animals and humans. Till now toxic effects have been neglected due to low concentration in the environment. It is necessary to understand and predict the sources, fates and effects of chemical substances in the environment for appropriate monitoring and assessment.

For this purpose there is an incentive to develop methods of calculating or modeling the multimedia environmental fate of organic compounds especially for toxic chemicals. Several multimedia models such as ChemCAN [Mackay and Paterson, 1996], CalTOX [Makone, 1993], HAZCHEM [ECETOC, 1994], simple BOX [van de Meent, 1993], SMCM [Cohen et al., 1990] have been developed internationally to produce a comprehensive picture of the environmental behavior of organic compounds. However, in Korea there have been no specific studies in this area as a thermodynamic approach except for studying the measurement of the octanol-water partition coefficient (K_{ow}) by Park et al. [1997]. The fugacity model, by using physical-chemical properties, environmental conditions and rate of emission, is one of the developing methods, which can be used to estimate prevailing concentration under steady state and unsteady state conditions. This fugacity concept is now applied to a variety of chemicals and environmental conditions.

We review a relatively simple four-compartment fugacity model which is reduced to four immiscible phases (air, water, soil and bottom sediment) from the number of environmental media. Equilibrium is assumed within each phase. Partitioning, reaction, and diffusive and nondiffusive transfer processes are generally considered. These transfer processes are expressed in terms of transfer coefficient (D) values. D values are defined to quantify transport rates. Each D contains two terms, a fugacity capacity (Z) value which characterizes the capacity of each phase for the chemical and is obtained from physical-chemical data, and kinetics or transport rate terms such as mass-transfer coefficient, diffusivity or advective flow rate.

In this paper the results of the fugacity model for assessing the fate of trichloroethylene (TCE) in a four-compartment system under steady state non-equilibrium conditions are presented and provide understanding about its fate and environmental concentration.

THEORY

Fugacity is a thermodynamic quantity related to chemical potential or activity that characterizes the escaping tendency from a phase. It has units of pressure and can be related to concentration. At equilibrium, fugacities of each phase are equal. Partitioning of a chemical between phases can be described by the equilibrium criteria of fugacity regarded as a partial pressure of the chemical in a phase and is related to concentration C (mol/m³) by the expression

$$C=fZ \quad (1)$$

where Z is the fugacity capacity. The determination of Z requires the knowledge of the other equilibrium relationship called partition coefficient. Partition coefficient (K_{12}) for a chemical between two immiscible phases is defined as the ratio of concentration and it can be related with fugacity capacity as

$$K_{12}=C_1/C_2=f_1Z_1/f_2Z_2=Z_1/Z_2 \quad (2)$$

[†]To whom correspondence should be addressed.
E-mail: sjpark@hanbat.chungnam.ac.kr

each phase.

Fugacity capacity for each evaluative compartment is calculated by a combination of the fugacity concept and partition coefficient as follows:

for air (Z_a)

$$Z_a = 1/RT \quad (3-1)$$

for water (Z_w)

$$Z_w = 1/H = Z_a RT/H = C_s/P_s \quad (3-2)$$

for soil, sediment

$$Z_s = Z_w K_{sw} = Z_w \phi_s \phi K_{oc} \quad (3-3)$$

where $K_{oc} = 0.41 K_{ow}$ [Mackay, 1991]

Chemicals move between phases by both diffusive and non-diffusive processes. The diffusive flux N (mol/h) between two phases 1 and 2 can be described by

$$N = D(f_1 - f_2) \quad (4)$$

where D (mol/hPa) is a transfer coefficient and f_1 and f_2 are the phase fugacities. The difference between f_1 and f_2 determines the direction of diffusive flux that take place from high to low fugacity. Nondiffusive or one-way transfer process between phases can also be described by a transport parameter as

$$N = GC = GFZ = Df \quad (5)$$

where G (m^3/h) is the volumetric flow rate. For reaction kinetics, first order reaction process in a phase is assumed because most organic compounds are present at low concentration, and it can be described as

$$N = k_R V Z f = D_R f \quad (6)$$

where k_R is the first order rate constant, V (m^3) is the phase volume.

Intermedia D values can be estimated from the nature of each contributing process and a variety of flow rate, areas mass transfer coefficients. Detailed D value equations are listed in Table 1. The mass balance equation for each compartment is then calcu-

lated as

for air

$$E_1 + G_{A1} C_{B1} + f_2 D_{21} + f_3 D_{31} = f_1 (D_{12} + D_{13} + D_{R1} + D_{A1}) = f_1 D_{T1} \quad (7)$$

for water

$$E_2 + G_{A2} C_{B2} + f_1 D_{12} + f_3 D_{32} + f_4 D_{42} = f_2 (D_{21} + D_{24} + D_{R2} + D_{A2}) = f_2 D_{T2} \quad (8)$$

for soil

$$E_3 + f_1 D_{13} = f_3 (D_{31} + D_{32} + D_{R3} + D_{A3}) = f_3 D_{T3} \quad (9)$$

for sediment

$$E_4 + f_2 D_{24} = f_4 (D_{42} + D_{R4} + D_{A4}) = f_4 D_{T4} \quad (10)$$

From Eqs. (7) through (10), the fugacities should be obtained.

An additional information includes the overall persistence or residence time calculated by

$$t_o = M/E \quad (11)$$

where M is amount of moles presented in the compartment and E is emitted amounts. The reaction and advection persistence are

$$t_R = M/\sum D_{Ri} \quad \text{and} \quad t_A = M/\sum D_{Ai} \quad (12)$$

where t_R and t_A are reaction and advection persistence (h), respectively. Clearly

$$1/t_o = 1/t_R + 1/t_A \quad (13)$$

where $1/t_o$ is the overall persistence.

RESULTS

Trichloroethylene (TCE), a major industrial solvent, which has been detected in ambient air, may be contained in drinking water. TCE in four compartments is introduced and concentrations are calculated by the fugacity model and compared with data reported by Mackay and Parterson [1991]. Table 2 shows the calculated and reported concentration and fugacities for the four bulk

Table 1. Intermedia transfer D value equations for each compartment

Compartment	Process	Individual D	Total D
Air(1)-water(2)	Diffusion	$D_v = 1/(1/k_{VA} A_{12} Z_{11} + 1/k_{VW} A_{12} Z_{22})$	$D_{12} = D_v + D_{QW} + D_{DW} + D_{FW}$
	Rain	$D_{QW} = A_{12} U_Q Z_{22}$	$D_{21} = D_v$
	Wet deposition	$D_{DW} = A_{12} U_Q Q \Phi_{13} Z_{13}$	
	Dry deposition	$D_F = A_{12} U_F \Phi_{13} Z_{13}$	
Air(1)-soil(3)	Diffusion	$D_s = 1/(1/k_{SA} A_{13} Z_{11} + Y_3/(A_{13} B_{A3} Z_{11} + B_{W3} Z_{22}))$	$D_{13} = D_s + D_{DS} + D_{QS} + D_{FS}$
	Rain	$D_{QS} = A_{13} U_Q Z_{22}$	$D_{31} = D_s$
	Wet deposition	$D_{DS} = A_{13} U_Q Q \Phi_{13} Z_{13}$	
	Dry deposition	$D_{FS} = A_{13} U_F \Phi_{13} Z_{13}$	
Soil(3)-water(2)	Soil runoff	$D_{sw} = A_{13} U_s W Z_{33}$	$D_{32} = D_{sw} + D_{ww}$
	Water runoff	$D_{ww} = A_{12} U_{ww} Z_{22}$	$D_{23} = 0$
Sediment(4)-water(2)	Diffusion	$D_s = 1/(1/k_{SW} A_{24} Z_{22} + Y_4/B_{W4} A_{24} Z_{22})$	$D_{24} = D_Y + D_{DX}$
	Deposition	$D_{DX} = G_{DX} Z_{23}$	$D_{42} = D_Y + D_{RX}$
	Resuspension	$D_{RX} = G_{RX} Z_{43}$	
Reaction	Bulk phase	$D_R = k_R V_i Z_i$	$D_R = k_R V_i Z_i$
	Pure phase	$D_{Rij} = k_{Rij} V_{ij} Z_{ij}$	$D_R = \sum k_{Rij} V_{ij} Z_{ij}$
Advection	Bulk phase	$D_{Ai} = G_i Z_i$	$D_{Ai} = G_i Z_i$

Table 2. Calculated and reported concentration and phase fugacities for the four bulk phases

	Air	Water	Soil	Sediment	Fugacities			
	ng/m ³	ng/l	mg/kg	ng/g	Air	Water	Soil	Sediment
This work	5610	184	2.8e-5	0.52	0.00010	0.0016	0.00010	0.0014
Mackay [1991]	11000	270	3.7e-5	0.6	0.00021	0.0025	0.00021	0.0025
Cohen [1985]	6400	<6000		0.07				

Table 3. Physical-chemical properties used in the fugacity model. Data are from Mackay et al. [1993]

Temperature (°C)	20
Molecular weight (g/mol)	131
Aqueous solubility (g/cm ³)	1100
Vapor pressure (Pa)	9900
Octanol water partition coefficient (K_{ow})	2.53

Table 4. Characteristics of the environment conditions of specified region of lake Daechung used in the model

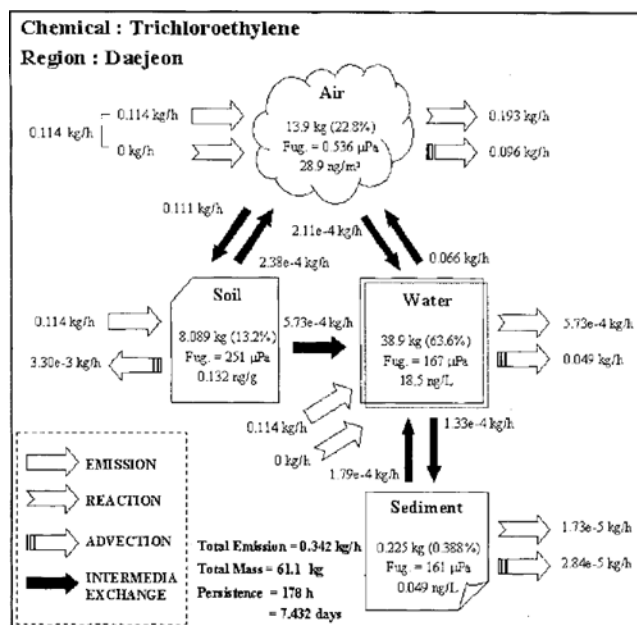
Total surface area (Km ²)	482
Surface covered by water (%total)	15
Average air height (Km)	1
Average water depth (m)	29
Average soil depth (cm)	10
Average sediment depth (cm)	5
Environmental temperature (°C)	20

Table 5. Order of magnitude values of transport parameters used in the model. Data are generic values from Mackay et al. [1993]

U	m/h
Air side, air-water MTC	5
Water side, air-water MTC	0.05
Rain rate	1.0e-4
Aerosol deposition	6.0e-10
Soil-air phase diffusion MTC	0.02
Soil-water phase diffusion MTC	1.0e-5
Soil-air boundary layer MTC	5
Sediment-water MTC	1.0e-4
Sediment deposition	5.0e-7
Sediment resuspension	2.0e-7
Soil-water runoff	5.0e-5
Soil-solid runoff	1.0e-8
Sediment burial	1.0e-6

Note: MTC is mass transfer coefficient.

phases. The reported magnitudes of concentration in air, water, soil and sediment by Mackay and Paterson [1991] are in good agreement with those predicted by Cohen et al. [1985]. The calculated magnitudes of concentration in this work show the reasonable agreement with both data. Utilizing this fugacity model, specific calculation was performed for predicting behavior of TCE in the specified region of the lake of Daechung located at the central part of South Korea. The utilized physical-chemical

**Fig. 1. Distribution of TCE. Emissions into air, water, and soil (respectively 1,000 kg/yr).****Table 6. Calculated results of phase properties and compositions**

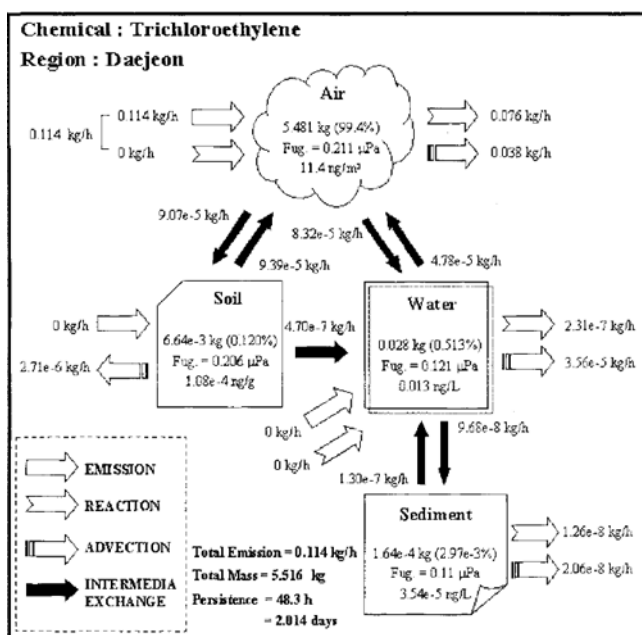
Phase	Air	Water	Soil	Sediment
Bulk m ³	4.8e-14	2.1e+9	4.1e+7	3.6e+8
Density Kg/m ³	1.206	1000	1500	1280
Bulk Z value	4.1e-4	8.46e-4	5.99e-3	2.94e-3
Emission Kg/y	1000	1000	1000	0
Fugacity	5.36e-7	1.67e-4	2.51e-4	1.61e-4
Concentration g/m ³	0.029	18.5	197	62.3
Amount Kg	13.9	38.9	8.08	0.225

properties and environmental conditions are given in Tables 3 and 4. The transport parameters used are generic values without modifications suggested by Mackay et al. [1993] as shown in Table 5.

Calculation results by fugacity model are shown in Fig. 1 for the distribution of TCE emitted by 1,000 Kg/yr to air, water and soil, respectively, which were based on the partition and transport coefficient shown in Tables 6 and 7. The overall persistence is 178 hrs. Most of TCE is found in water. The net transfers of TCE are deposition from air to soil and volatilization from water to air, whereas the transfer from soil to water is negligible. Net water-sediment transfer is small. Reaction in air is the main removal mechanism. The steady state buildup of TCE is 61.1 Kg.

Table 7. Calculated values of intermedia transport

	Half time (h)	Equv. flow (m ³ /h)	D value (mol/pah)	Rates (mol/h)
Air to water	407	7.31e+6	3001	1.61e-3
Air to soil	50.7	8.25e+6	3387	1.81e-3
Water to air	407	3.54e+6	295	0.499
Water to sediment	7016	9645	8.157	1.36e-3
Soil to air	50.7	5.6e+5	3352	0.841
Soil to water	9789	2900	17.4	4.36e-3
Sediment to water	1163	2137	6.277	1.01e-3

**Fig. 2. Distribution of TCE. Emissions into air (1,000 kg/yr).**

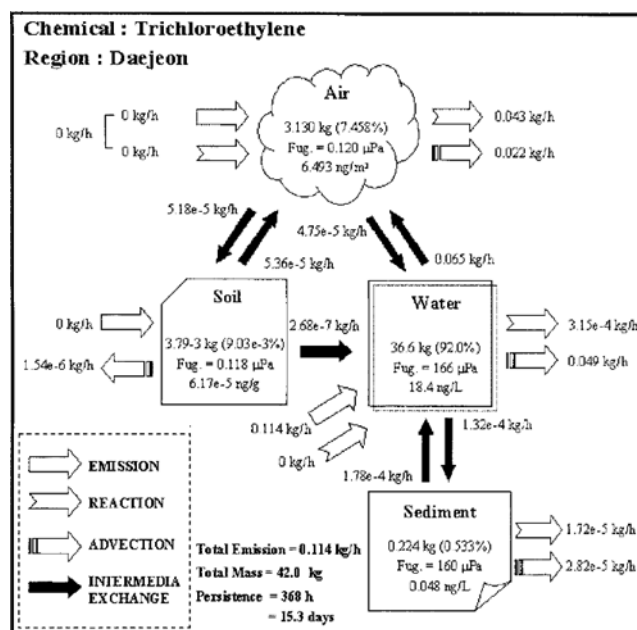
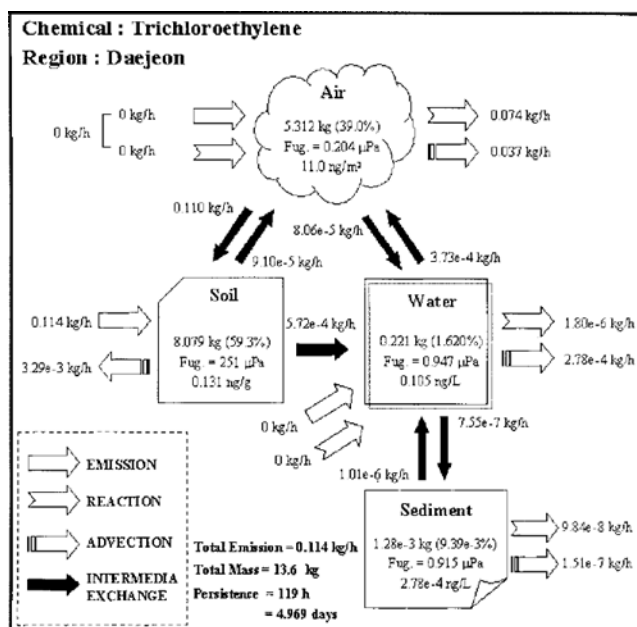
From this result, actual relative emission to air, water and soil can be estimated. Environmental conditions vary in time and space and the reaction rate and constant vary seasonally. Only a few reliable data are usually available.

Fig. 2 shows that for 1,000 Kg/yr of TCE emitted into the air, the amount in air is 5.48 kg, and minimum persistence is 48.3 hrs. Additional amounts expected are 6.64e-3 kg in soil, 0.028 kg in water and 1.64e-4 kg in sediment, giving a total amount of 5.516 kg. The net transfer between compartments has a similar order of magnitude.

Fig. 3 gives similar data for emission to water; the overall persistence is 368 hrs. The principal intermedia process is reaction in water and volatilization from water to air.

For soil in Fig. 4, the overall persistence is 119 hrs. Important conclusions can be drawn from these depictions of a chemical's fate. When emissions to all three media occur simultaneously, the fate is the sum of the individual emissions because of the linear equation used in the fugacity model. Overall, the environmental persistence depends on how the chemical is discharged into the environment.

DISCUSSION

**Fig. 3. Distribution of TCE. Emissions into water (1,000 kg/yr).****Fig. 4. Distribution of TCE. Emissions into soil (1,000 kg/yr).**

In the fugacity model, the following parameters are required for the calculation of fate of organic compounds in the environment: water solubility, saturated vapor pressure and octanol water partition coefficient (K_{ow}). The model also requires other environmental parameters such as mass transfer coefficient (MTC), emission rate and density of various compounds. To validate these results, an analysis requiring a various input parameters is necessary. A few of the input parameters may control the fate of organic compounds. If a parameter is identified to be very influential to determining the fate of organic compounds, the parameter should be measured with great accuracy for better results.

Table 8. Results of sensitivity for each input parameter

Parameter	Sensitivity (S)
Vapor pressure	0.357
Solubility	3.929
K_{ow}	0.12
Air side MTC	0.0016
Rain rate	0
Half-life in air	23.57e-5

For this reason, a sensitivity analysis for the air compartment was performed for the few selected input parameters that were considered to be the most influential factors for the results. Sensitivity (S) is determined from the change (about 10%) in each input parameter I and the change in C_A as $S = (\Delta C_A / C_A) / (\Delta I / I)$ where C_A is air concentration, I is input parameter. The results in Table 8 show that the key parameters are the water solubility, the vapor pressure and K_{ow} . As shown in the result, most TCE is found in water and air and solubility is considered the most dominant factor for the exact prediction of TCE's fate. Other environmental factors could be negligible. Each sensitivity factor is determined independently. Actually, all of these input parameters should be considered. However, if the most influential factor is identified, the result can be assured to some extent.

The fugacity model can be therefore applied to determine general features of organic compounds in the environment. It is possible to predict the behavior of new chemicals and to estimate the order of magnitude concentration, the dominant reaction, role of advective loss and the intermedia transport characteristics.

CONCLUSIONS

The fugacity model is a relatively simple, rapid method for predicting the environmental fate process for specific organic compounds. The primary advantage of this model is that it provides the general behavior profile of specified chemicals. This simple fugacity model serves to illustrate and reinforce the concept of a multimedia approach. Future work should be concentrated on the extension of the fugacity model to more specific situations and other chemical compounds. In addition, the better physical-chemical properties and more information gathering on the magnitude of emissions will improve the applicability of this model. Also, the validation of the fugacity model is required in various environmental media.

ACKNOWLEDGEMENTS

This work was supported by grant No. 98-2-10-03-01-2 from the Basic Research Program of the KOSEF. The authors thank the KOSEF and Green Environment Co. Ltd. for financial support.

NOMENCLATURE

A : interface area

C : concentration
D : transfer coefficient
E : emission
f : fugacity
G : volumetric flow rate
K : partition coefficient
 k_R : reaction constant
M : amount of mole
N : flux
R : gas constant
S : sensitivity
T : temperature
 t_w : advection persistence time
 t_b : residence time
 t_R : reaction persistence time
V : phase volume
Z : fugacity capacity
 ϕ_i : ratio of organic carbon
 ϕ : density

REFERENCES

- Cohen, Y. and Patrick A. R., "Multimedia Modeling of Environmental Transport: Trichloroethylene Test Case," *Environ. Sci. Tech.*, **19**, 412 (1985).
- Cohen, Y., Tsai, W., Chetty, S. L. and Mayer, G. J., "Dynamic Partitioning of Organic Chemicals in Regional Environments: A Multimedia Screening-Level Modeling Approach," *Environ. Sci. Tech.*, **24**, 1549 (1990).
- ECETOC, "HAZCHEM: A Mathematical Model for Use in Risk Assessment of Substance," Brussels, Belgium (1994).
- Mackay, D., "Multimedia Environmental Model; the Fugacity Approach," Lewis Pub. Inc. (1991).
- Mackay, D. and Paterson, E., "ChemCAN: A Regional Level III Fugacity Model for Assessing Chemical Fate in Canada," Trent University, Canada (1996).
- Mackay, D. and Paterson, S., "Evaluating the Multimedia Fate of Organic Chemicals: A Level III Fugacity Model," *Environ. Sci. Tech.*, **25**, 427 (1991).
- Mackay, D., Shiu, W. Y. and Ma, K. C., "Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals," USA (1993).
- MaKone, T. E., "CalTOX, A Multimedia Total-Exposure Model for Hazardous Waste Sites Part 2: The Dynamic Multimedia Transport and Transformation Model; Lawrence Livermore National Laboratory," Livermore, CA (1993).
- Park, S. J., Ryu, S. A. and Han, S. D., "Measurement of 1 Octanol/Water Partition Coefficient by Using Generator Column Method and Relationship between 1 Octanol/Water Partition Coefficient and Water Solubility," *HWAHAK KONGHAK*, **35**, 3 (1997).
- van de Meent, D., "SimpleBOX: A Generic Multimedia Fate Evaluation Model; RIVM," Biltoeben, Netherlands (1993).