

Distribution of Synthetic Organic Pollutants Between Water and Air*

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Abstract: *Production and application of large quantities of synthetic organic compounds have resulted in a widespread contamination of the water environment. Many synthetic organic compounds are found toxic. Some are mutagenic and carcinogenic even at trace level concentration. The impact of these pollutants has become one of the major issues of environmental concern in recent years.*

The exchange of organic chemicals across the air-water interface is a significant process affecting the fate of organic compounds released into rivers and lakes. Benzene, toluene, trichloroethylene and tetrachloroethylene were selected as the model chemicals in this study. These four chemicals have been classified as priority pollutants by the U.S. Environmental Protection Agency and designated as hazardous waste chemicals by the Ontario Ministry of Environment, Canada. The equilibrium distribution of the selected volatile organic compounds between air and water was simulated in the laboratory at the University of Saskatchewan. A gas chromatograph headspace auto sampler system was used to analyze the chemical concentrations. Partition coefficients were determined from the experimental results.

The effect of ionic strength on the equilibrium partitioning of selected organic compounds was also investigated in this study. Concentrations of sodium chloride from 100 mol·m⁻³ to 1 000 mol·m⁻³ were used to simulate various ionic strengths in water at temperature of 20°C. Typical sea-water was simulated with 3.5% sodium chloride and tested at temperatures from 15°C to 45°C. The salting-out coefficients for the selected organic compounds were determined.

Keywords: *Equilibrium partitioning, hazardous waste organics, water pollution*

1. Introduction

Over the years, various synthetic organic compounds have been produced and widely used in domestic and industrial applications both in quantity and in variety. It was estimated that more than 50 000 compounds were used in commerce in 1978 and an additional 500 to 1 000 new compounds are formulated and introduced into our societies every year (MUNZ,1985). While we enjoy using these synthetic organic compounds, the release of many of these chemicals during the production, distribution and application has severely contaminated the air, water and soil environments. Once

* Received 1997-02-25; accepted 1998-03-27.

released into water environment, these chemicals may undergo several different transport and transformation processes as shown in Figure 1 (COHEN, 1986; PENG *et al.*, 1990; PENG *et al.*, 1993; PENG *et al.*, 1994; PENG *et al.*, 1995).

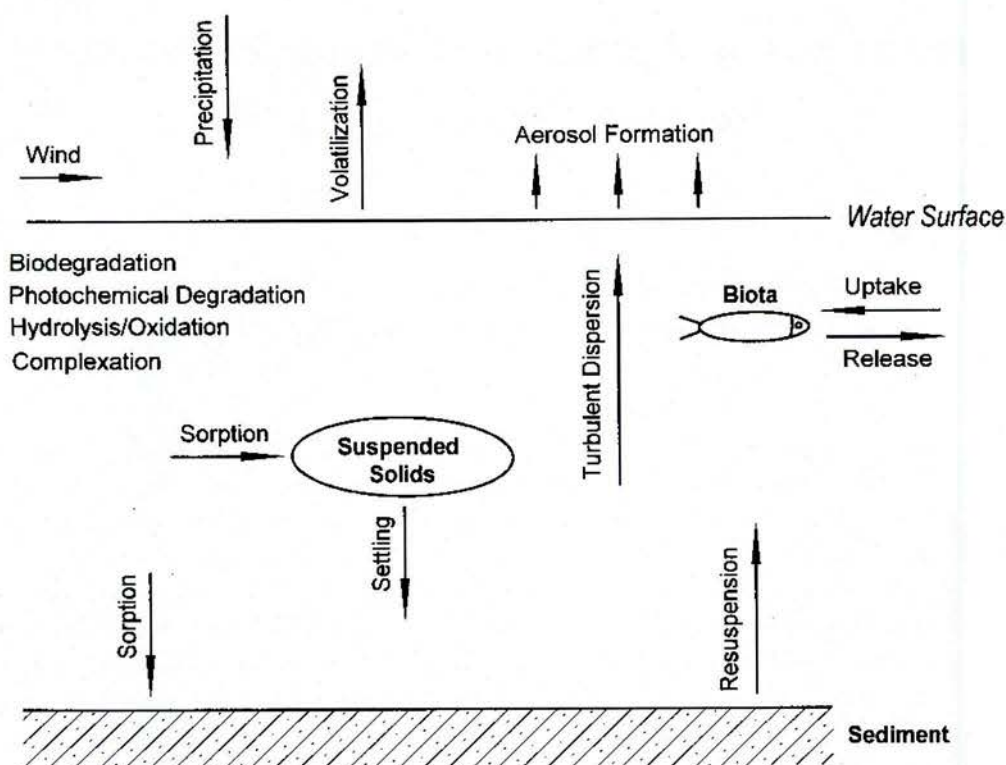


Fig. 1 Fate of discharged chemicals in the environment

Mass transfer processes from the water compartment into atmosphere, sediment and organisms include volatilization, sorption by sediment and suspended solids, sedimentation and resuspension of solids, aerosol formation at air-water interface and uptake and release by biota. Mass transport within the water bodies includes turbulent dispersion and convection due to currents, surface wind shear and waves in the upper mixed layer, turbulent mixing and dispersion in confined flows such as rivers and diffusion between the upper mixed layer and the bottom layer. Transformation of the chemicals includes biodegradation, photochemical degradation and degradation by chemical processes such as hydrolysis and free-radical oxidation (COHEN, 1986).

Concerns over the effects of the synthetic organic wastes in the environment have been increasing for years, especially of the volatile organic compounds (VOCs), because of their severe toxic effects (THOMAS, 1990). Volatile organic compounds represent a large group of chemicals, which have a tendency to evaporate into air phase under normal environmental conditions. Generally, they are characterized by their low solubility in water and high vapor pressure. Volatile organic compounds have been widely used in many domestic and industrial applications. Examples are gasoline, organic solvent and pesticides. Many volatile organic compounds are severe toxic. On

the EPA 129 priority pollutant list, 34 are volatile organic compounds (CALLAHAN *et al.*, 1979). Some of them are suspected carcinogens, mutagens and teratogens (KURZEL and CETRULO, 1981). Public awareness of volatile organic compounds has focused much media attention on their presence in drinking water and potential health risks. In the United States Environmental Protection Agency (EPA) primary drinking water standards for 83 specific drinking water contaminants, established under the amended US Safe Drinking Water Act (SDWA) in 1986, twenty two volatile organic compounds have been included. For example, the maximum contaminant level (MCL) was 0.005 mg·L⁻¹ for benzene, trichloroethylene (TCE) and tetrachloroethylene (PCE), and 2.0 mg·L⁻¹ for toluene (COTRUVO and REGELSKI, 1989). The US National Organics Monitoring Survey (NOMS) on 21 ground water and 92 surface water supply systems conducted from March 1976 to January 1977 revealed that 28 water systems (6 ground water and 22 surface water) were contaminated by trichloroethylene and 7 systems (2 ground water and 5 surface water) were contaminated by benzene (WESTRICK, 1990). The minimum reporting levels of concentration were 0.03 µg·L⁻¹ and 0.1 to 0.2 µg·L⁻¹ for trichloroethylene and benzene respectively. The maximum concentrations detected for trichloroethylene and benzene were 49 µg·L⁻¹ and 1.8 µg·L⁻¹ respectively.

Equilibrium partitioning of volatile organic compounds between water and air is governed by Henry's law as:

$$H_c = \frac{C_G}{C_L} \quad (1)$$

where H_c is the partition coefficient, C_G is the gas phase chemical concentration (mol·m⁻³), and C_L is the liquid phase chemical concentration (mol·m⁻³). At normal environmental conditions and dilute chemical concentration, the partition coefficient, H_c , can be converted to Henry's law constant as

$$H = RTH_c \quad (2)$$

where R is the ideal gas constant, T is the absolute temperature (K), and H is Henry's law constant defined as a proportionality constant between gas partial pressure and liquid concentration of a given chemical at equilibrium under a constant temperature as:

$$H = \frac{P_i}{C_L} \quad (3)$$

where H is Henry's constant (atm·m³·mol⁻¹), P_i is the partial pressure of the chemical in air (atm). Information on equilibrium partitioning of volatile organic compounds between water and air phase is very important. It is used to characterize the volatility of organic wastes, required by many mass transport models to determine the fate of organic wastes released into water environment (MACKAY and YEUN, 1983; SMITH *et al.*, 1980; THOMANN *et al.*, 1991), and required by design and performance models of air stripping process for the remediation of contaminated waters (BALL *et al.*, 1982; HAND *et al.*, 1986; LAMARCHE and DROSTE, 1989; NIRMALAKHANDAN *et al.*, 1987; ROBERTS *et al.*, 1985; ROBERTS and LEVY, 1985; SPEECE *et al.*, 1987; STAUDINGER *et al.*, 1990).

THOMAS (1982) described Henry's constant to be one of the most important characteristics in determining the volatility of a specific chemical and classified the volatility of chemicals by the level of Henry's constant, H . A compound with H less than about 10^{-7} atm-m³-mol⁻¹ is considered less volatile than water and in a solution its concentration will increase as the water evaporates. A compound with H greater than 10^{-7} but less than 10^{-5} atm-m³-mol is considered of low volatility. In this case, gas-phase resistance dominates the liquid-phase resistance by a factor of at least ten and the transfer is gas-phase controlled. For compounds of medium volatility, with H greater than 10^{-5} but less than 10^{-3} atm-m³-mol⁻¹, liquid-phase and gas-phase resistances are both significant and should be considered. High-volatility compounds are those having Henry's constant larger than 10^{-3} atm-m³-mol⁻¹. For these compounds, the water-phase resistance dominates by a factor of at least ten and therefore controls the rate of mass transfer.

Volatilization as a mass transport process from surface waters such as lakes and rivers into air is a major pathway to determine the distribution of the discharged organic chemicals in the different environmental compartments. Field studies by THOMANN *et al.* (1991) on the fate of polychlorinated biphenyls (PCBs) in Hudson River estuary at New York showed that about 66% of the total of 270 tonnes discharged to the estuary from 1947 to 1987 had volatilized into the air environment. In this study, equilibrium partitioning of volatile organic compounds between air and water was simulated using a static headspace technique.

2. Materials and Methods

Four chemicals, benzene, toluene, trichloroethylene (TCE), and tetrachloroethylene (PCE) were chosen in this study. These chemicals are produced world-wide and used both in domestic and industrial applications, which has led to widespread environmental contaminations. For example, US EPA reported in a document titled "the 1994 Toxics Release Inventory" that a total of 168 million pounds toluene was released into the US environment in that year. All the selected chemicals are high volatility organic compounds. They have been found to be toxic to human beings, animals and aquatic organisms and plants (MOORE *et al.*, 1991) and have been designated as hazardous waste chemicals by the Ontario Ministry of Environment (1985) and classified as priority pollutants by the U.S. Environmental Protection Agency (CALLAHAN *et al.*, 1979).

Aqueous solutions of the selected volatile organic compounds in concentrations of 0.0056 mol-m⁻³, 0.0047 mol-m⁻³, 0.0056 mol-m⁻³ and 0.0049 mol-m⁻³ were prepared and added into the glass containers. The glass containers were then tightly sealed. The containers were loaded into a temperature controlled headspace auto-sampler for a period of one hour in order for the chemicals to partition between water and air phases until equilibrium. According to mass balance principle, the total chemical mass added to each container equals the summation of the chemical solute in gas phase and liquid phase at equilibrium:

$$C_{Lo} V_L = C_L V_L + C_G V_G \quad (4)$$

where C_{Lo} is the initial chemical concentration of the prepared aqueous solution, V_L is the liquid

sample volume added into the container, and V_G is the gas volume in the container. Substitution of Equation 1 into Equation 4 gives:

$$\frac{1}{C_G} = \frac{1}{C_{Lo}} \left(\frac{1}{H_c} + \frac{V_G}{V_L} \right) \quad (5)$$

Chemical concentration in the gas phase was analyzed by a gas chromatograph (GC) and was proportional to the integrated area counts of GC peak, y :

$$y = kC_G \quad (6)$$

Substitution of the gas-liquid volume ratio, $x = V_G/V_L$, and Equations. 2 and 6 into Equation 5 yields:

$$\frac{1}{y} = \frac{k}{C_{Lo}} \left(\frac{1}{RTH} + x \right) \quad (7)$$

Eight different gas-liquid volume ratios were used in the equilibrium partitioning experiment. They were 1.2, 2.1, 3.4, 4.5, 6.3, 7.8, 10.0 and 13.7. Henry's law constant was determined by curve-fitting of Equation 7 with the measured $1/y$ values versus eight gas-liquid volume ratios, x . Equilibrium partitioning experiments were conducted for benzene, toluene, trichloroethylene and tetrachloroethylene in fresh water under seven different temperatures, 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, 40 °C and 45 °C. To simulate the effect of ionic strength on the equilibrium partitioning of benzene, toluene, trichloroethylene and tetrachloroethylene, six concentrations of sodium chloride solutions, 0 mol·m⁻³, 100 mol·m⁻³, 300 mol·m⁻³, 500 mol·m⁻³, 700 mol·m⁻³ and 1 000 mol·m⁻³, were tested at a temperature of 20 °C and a typical sea-water of 36‰ salinity simulated by a concentration of 639 mol·m⁻³ sodium chloride was tested under seven different temperatures, 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, 40 °C and 45 °C.

3. Results and Discussion

The experimental data obtained from the equilibrium partitioning tests under various conditions were used to determine the partition coefficient, Henry's constants, by curve-fitting Equation 7 with reciprocal of GC readings of the gas phase chemical concentrations against the gas-liquid volume ratios used in the tests. The curve-fitting was carried out by using a technical graphics and data analysis computer program, Axum for Windows, version 4.0 released by TriMetrix, Inc., USA. Figure 2 shows a typical correlation for benzene in 500 mol·m⁻³ sodium chloride aqueous solution at 20 °C. In Figure 2, empty circles represent three replicates used for each gas-liquid volume ratio, solid line represents the best fit of Equation 7 and dotted lines quantify the 95% confidence interval. The correlation coefficients from curve-fitting Equation 7 were better than 0.998 for all the tests.

The partition coefficient or Henry constant for volatile organic compounds in fresh water is much dependent on temperature, and can be correlated by van't Hoff expression as:

$$\log H_F = A - \frac{B}{T} \quad (8)$$

where H_F is Henry's constant of volatile organic compounds in fresh water, A and B are constants for a given chemical, T is the absolute temperature.

Dissolved ions in water affect the equilibrium partitioning of volatile organic compounds between water and air. Partition coefficient

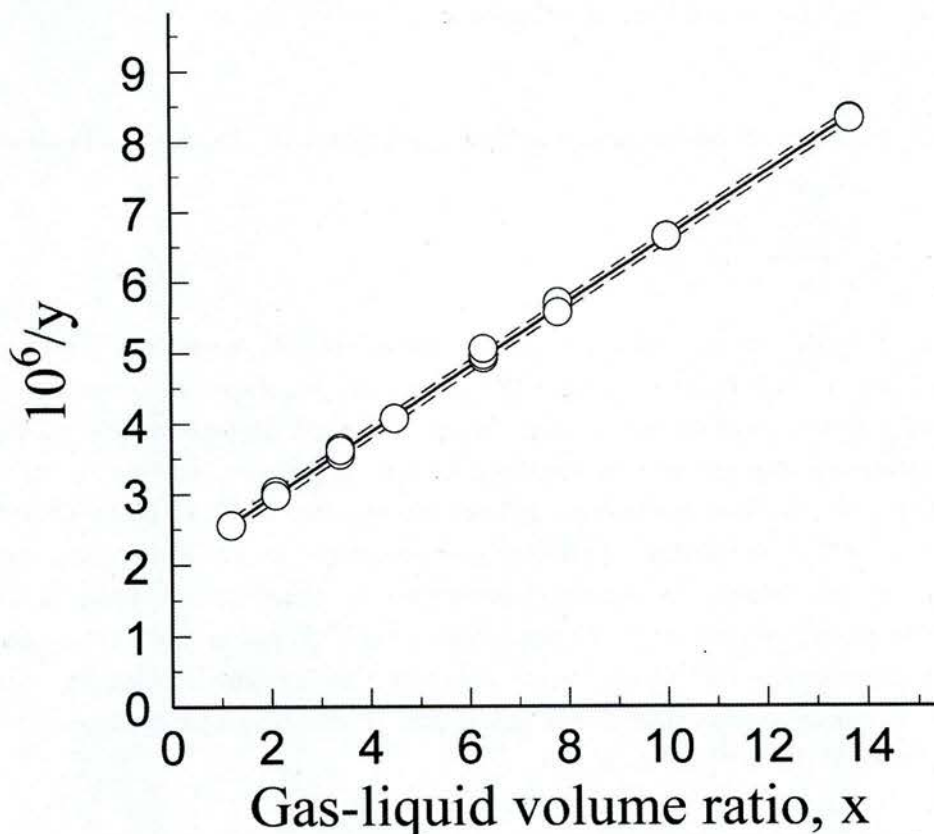


Fig. 2 Curve-fitting of Eq. 7 for benzene in 500 mol·m⁻³ NaCl aqueous solution at 20 °C, dotted lines represent 95 % confidence interval

or Henry's constant in salted water can be correlated to the partition coefficient in fresh water for a given volatile organic compound as (SNOEYINK and JENKINS. 1980):

$$\log\left(\frac{H}{H_F}\right) = \frac{1}{2} k_s \sum (C_i \cdot Z_i^2) \quad (9)$$

where k_s is salting-out coefficient, m³·mol⁻¹, C_i is concentration of ionic species i in the solution, mol·m⁻³, and Z_i is electrical charge of species i . Substitution of Equation 8 into Equation 9 gives:

$$\log H = A - \frac{B}{T} + \frac{1}{2} k_s \sum (C_i \cdot Z_i^2) \quad (10)$$

The partition coefficients determined from the experimental results under various conditions were used to calculate parameters A , B and k_s for benzene, toluene, trichloroethylene and tetrachloroethylene by curve-fitting Equation 10. Table 1 shows the estimated parameters and correlation coefficients. The correlation coefficients were all better than 0.997, indicating good fitness of Equation 10 to the measured partition coefficients.

Figure 3 shows a comparison of predicted values of partition coefficients with the measured values.

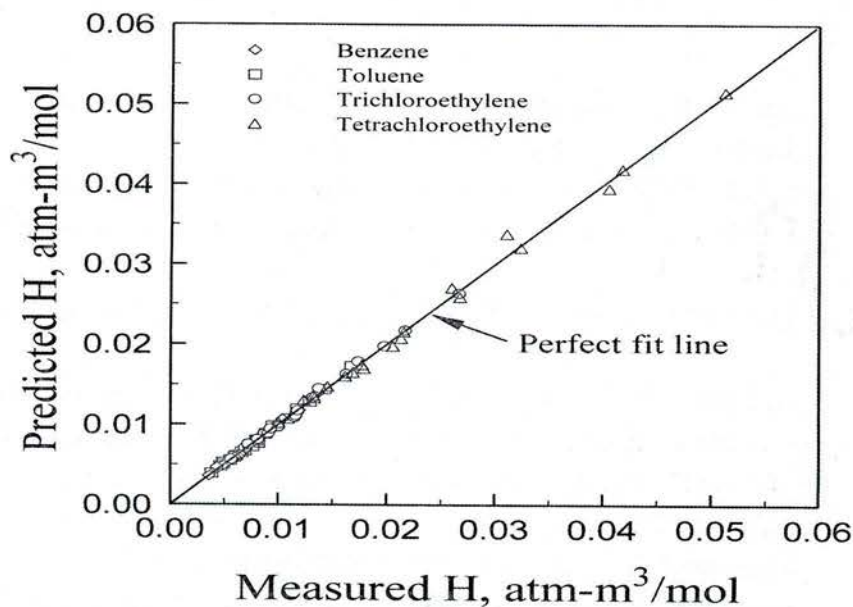


Fig. 3 Comparison of predicted partition coefficient with the measured values

Tab.1 Estimated parameters and correlation coefficients of Equation 10 for benzene, toluene, trichloroethylene and tetrachloroethylene

| | A | B | k_s | Correlation Coef. |
|---------------------|-------|-------|----------|-------------------|
| Benzene | 2.565 | 1 444 | 0.000181 | 0.997 |
| Toluene | 3.089 | 1 585 | 0.000204 | 0.997 |
| Trichloroethylene | 3.524 | 1 664 | 0.000196 | 0.998 |
| Tetrachloroethylene | 4.249 | 1 798 | 0.000181 | 0.997 |

4. Conclusions

Equilibrium partition coefficient is an important parameter in determining the fate of volatile organic compounds released to rivers and lakes. A mathematical model incorporating van't Hoff expression and salting-out coefficient was developed to predict the partition coefficient under dif-

ferent temperatures in presence of dissolved ions in water. The model was verified and the model parameters were determined with experimental data for benzene, toluene, trichloroethylene and tetrachloroethylene.

Acknowledgements

This research was supported through an NSERC research grant and an NSERC equipment grant from the Natural Science and Engineering Research Council of Canada. I thank my graduate student, Ms. Aroma Wan, for her assistance in conducting the laboratory tests.

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