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MASS TRANSPORT OF SELECTED VOLATILE ORGANIC COMPOUNDS FROM LIQUID PHASE INTO AIR PHASE

by

Jian Peng

A Dissertation submitted to the Faculty of Graduate Studies and Research through the Department of Civil and Environmental Engineering in Partial Fulfilment of the Requirements for the degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario, Canada 1993
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ABSTRACT

Production and application of many synthetic organic chemicals have led to widespread contamination of the air, water and soil environments. The mass transport of volatile organic compounds from liquid phase into air phase is an important pathway in determining the fate of such chemicals released into the environment. A comprehensive investigation on the mass transfer rate of four selected high volatile chemicals, benzene, toluene, trichloroethylene (TCE) and tetrachloroethylene (PCE) under various environmental condition has been conducted in this research.

For volatilization of chemicals from water into air under different turbulent intensities in bulk water, four conditions were identified as ideal stagnant condition, near stagnant condition, completely mixed condition without breaking surface film and completely mixed condition with broken film. A mathematical model was developed by solving a partial differential equation with appropriate boundary condition (Fick’s diffusion law) to predict volatilization from stagnant water. This model was further simplified to approximate solution with a relative error of less than 9.5%. The laboratory experiments were conducted and the results were used to calibrate the developed model. It was found that the volatilization rate constant was inversely proportional to 1.81th power of water depth.

For water bulk turbulent condition, a mathematical model incorporating an idealized surface film renewal concept was used to predict volatilization rate. The
experiments were conducted under nine different turbulent intensities, expressed in terms of velocity gradient (G), equal to 0, 25, 50, 75, 100, 125, 150, 175 and 200 \( \text{m/s}^4 \) and four different water depths of 0.6, 1.2, 1.5 and 1.8 m. The developed model was verified and calibrated with the observed experimental data.

The effect of surface shear caused by wind on the volatilization rate was studied by simulating 5 different wind velocities, 0, 0.5, 1.0, 2.0, 3.5 and 5.0 m/s. It was found that increasing the wind velocities from 0 to 5 m/s had increased the volatilization rate constant by 5 to 6 times.

Evaporation of pure chemicals from point sources under stagnant air condition and strong wind condition were theoretically modelled and experimentally simulated. It was found that the vapour pressure, molecular mass and temperature were important parameters in determining the evaporation rates for both conditions. The diameter of point source was found to be important for stagnant air condition, but irrelevant for strong wind condition.

The models developed in this study and further verified and calibrated by the experimental results, should provide a useful tool to predict the fate of high volatile organic chemicals when released into the environment.
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Acknowledgments are also due to the Civil and Environmental Engineering Department for the use of their facilities, and the Natural Sciences and Engineering Research Council of Canada for the financial assistance provided for this research.

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CHAPTER ONE

INTRODUCTION

1.1 Background

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 1000 new compounds are formulated and introduced into our societies every year (Münz 1985). While human beings 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. Concerns over the effects of these chemicals in the environment have been increasing for years, especially of the volatile organic compounds (VOCs), because of their severe toxic effects (Thomas 1990). Many of these VOCs are suspected carcinogens, mutagens and teratogens (Kurzel and Cetrulo 1981). Public awareness of VOCs has focused much media attention on their presence in drinking water and potential health risks. In the US 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 MCL (maximum contaminant level) was 0.005 mg/L for benzene, TCE and PCE, and 2.0 mg/L 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 and 0.1 to 0.2 µg/L for TCE and benzene respectively. The maximum concentrations detected for TCE and benzene were 49 µg/L and 1.8 µg/L respectively.

Mass transport of chemicals from the liquid phase into the air phase is an important pathway to control the distribution of these chemicals in the different environmental compartments, once they are released into the environment. Field studies by Thomann (1991) on the fate of PCBs in Hudson River estuary showed that about 66% of the total of 270 tonnes discharged to the estuary from 1947 to 1987 had volatilized into the air environment. Therefore, thorough understanding the phenomena of the mass transport process is of fundamental importance in determining the fate of the released chemicals in the environment.

The models developed in this study, and further verified and calibrated by the experimental data, should provide a useful tool to predict the fate of volatile organic compounds released into the environment.
1.2 Objective

The objective of this study was to investigate the mass transfer rate of four selected high volatility organic compounds, benzene, toluene, trichloroethylene (TCE) and tetrachloroethylene (PCE), from liquid phase into air phase under different environmental conditions.

1.3 Scope of Study

The study included theoretical analysis of the mass transport process and experimental tests in the laboratory under different environmental conditions. Theoretical analyses were carried out and mathematical models were developed and verified for following conditions:

- Volatilization of high volatility organic compounds from stagnant water
- Volatilization of high volatility organic compounds from agitated water
- Evaporation of pure chemicals from point sources into quiescent air
- Evaporation of pure chemicals from point sources in presence of strong wind.

Laboratory experiments on the mass transport of the selected chemicals under those conditions were conducted and experimental data collected were used to verify and calibrate the theoretically developed models. In addition, the volatilization of all selected chemicals under different wind velocity conditions was studied in the laboratory.
CHAPTER TWO
LITERATURE REVIEW

2.1 Selection of Chemicals

Four chemicals, benzene, toluene, trichloroethylene (TCE), and tetrachloroethylene (PCE) are chosen in this study. These chemicals are produced worldwide and used both in domestic and industrial applications, which has led to widespread environmental contaminations. All selected chemicals are high volatility organic compounds. They have been found to be toxic to human beings, animals and aquatic organisms and plants 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 1979).

2.1.1 Production and Uses of the Selected Chemicals

The chemicals selected in this research are produced and used heavily in both domestic and industrial applications.

Benzene is a common solvent used in industry because it can dissolve most
organic compounds. It has many other names such as benzole, benzol, phene, benzin, benzine, benzolene, bicarburet of hydrogen, carbon oil, coal naphtha, cyclohexatriene, mineral naphtha, motor benzol, nitration benzene, phenyl hydride and pyrobenzol (EnviroTIPS 1984). The chemical formula of benzene is C₆H₆, and its CAS (chemical abstract service) registry number is 71-43-2. It is a clear, colourless liquid, which is highly flammable with a low boiling point and high vapour pressure, and has a gasoline-like odour. In Canada, benzene is mainly manufactured in Ontario and Quebec (EnviroTIPS 1984). The largest production facilities of benzene are located in Sarnia, Ontario, and in Montreal, Quebec. The market area is also in these two provinces (EnviroTIPS 1984). It is produced from petroleum feedstock reformation and hydrodealkylation of substituted aromatics. The platinum catalyst technique is used for the conversion from petroleum naphtha to benzene. The major uses of benzene are as a solvent and an intermediate in the production of many chemicals such as ethylbenzene/styrene, cumene, cyclohexane and maleic anhydride. Domestic production was 566.5 kilotons in 1980 (EnviroTIPS 1984), and 688 kilotons in 1985 (Jaques 1990).

Toluene is the common name for methylbenzene with the chemical formula C₅H₈CH₃. It is a clear, colourless, watery liquid with an aromatic smell (EnviroTIPS 1984a). The CAS registry number of toluene is 108-88-3 (CCOHS 1988). Toluene is a commercially-important intermediate chemical produced throughout the world in enormous quantities (5 - 10x10⁴ tonnes) (WHO 1985). Canadian production of toluene in 1982 was 470,000 tonnes along with an import of 1,100 tonnes. In Canada, toluene is mainly used as a solvent in production of cleaners, inks, paints, lacquers, resins,
pesticides, and adhesives, as well as a gasoline component. It is also used to make explosives, dyes and many other chemicals (EnviroTIPS 1984a; CCOHS 1988). In 1982, 39 percent was used as solvents, 25 percent for benzene production and 22 percent for benzoic acid/phenol production (EnviroTIPS 1984a). Toluene is manufactured by catalytic reformation of naphthene-rich petroleum feedstock fractions, generally in conjunction with the production of benzene and xylene (EnviroTIPS 1984a).

Trichloroethylene (TCE) is an unsaturated, low molecular mass C₂ compound with the formula Cl₂C=CHCl. It is a colourless, non-flammable liquid with a slightly sweet smell similar to chloroform (CCOHS 1986). The CAS registry number of TCE is 79-01-6. Other common names for TCE are acetylene trichloride, chlorelen, chloooethlen, narcogen, petzinol, triasol, and trichlorothene (Moore et al. 1991). A major use of TCE is in metal degreasing; other significant uses are in textile cleaning, as a solvent in preparing certain adhesives, varnishes, paints and printing inks. It is also used in solvent extraction processes (CCOHS 1986; Moore et al. 1991; WHO 1985a). It is no longer used as a grain fumigant and as an anaesthetic vapour (CCOHS 1986; WHO 1985a).

Commercial production of TCE is carried out by the chlorination of ethylene and dichloroethane. In 1976, Canadian production of TCE was 12,500 tonnes (Moore et al. 1991), whereas imports were 200 tonnes. Total demand for TCE in that year was 12,700 tonnes, of which 10,000 tonnes were used in the metal cleaning industry, 2,500 tonnes in the production of tetrachloroethylene and the remainder for miscellaneous uses, export sales and inventory adjustment. Since 1976, the consumption of TCE has continuously declined due to stringent environmental restrictions. The closure of C-I-L’s
Quebec perchlor/trichlor (TCE) plant, one of two domestic factories in Canada, has led to the import as a main supply source in 1985. In 1988, TCE import was 3,000 tonnes, of which 2,900 tonnes were used by the metal cleaning industry. The forecast of domestic consumption of TCE in 1992 was 2,200 tonnes (Moore et al. 1991).

Tetrachloroethylene (PCE) is a nonflammable, clear and colourless liquid under normal conditions with the chemical formula of C₂Cl₄. Common trade names include alkilostin, antisal 1, antisol 1, blancosolv no. 2, dee slove, didakene, dowper, ent 1860, fedal un, mid solv, nema, per, perawin, perc, perchlor, perclene, per-ex, perk, perklone, perm-a-kleen, persec, phillsolv, tetlen, tetracap, tetrager, tetraleno, tetrealx, tetravec, tetropil and wacker-per (WHO 1987). The CAS registry number is 127-18-4. The major use of PCE is in dry cleaning and metal degreasing as a solvent. Other applications are in processing and finishing in the textile industry, in the manufacturing of fluorocarbons, as an extraction solvent, veterinary anthelmintic and heat exchange fluid. World production of tetrachloroethylene was 680,000 tonnes in 1972 and 1000,000 tonnes in 1974 (WHO 1984). In 1980, the USA produced about 350,000 tonnes (USITC 1981). Tetrachloroethylene is manufactured by oxyhydrochlorination, perchlorination and dehydrochlorination of hydrocarbons or chlorinated hydrocarbons.

2.1.2 Environmental Concerns of the Selected Chemicals

Applications of the volatile organic compounds have caused widespread contamination of soil, air and water environments (both surface and subsurface water
compartment). Many volatile organic compounds are hazardous and some of them are found to be carcinogenic. Public concern over the environmental pollution of these chemicals has been increasing for years.

Benzene is toxic to human beings. It irritates upon skin contact and eye contact. Acute effects on humans include drowsiness, dizziness, headache, light-headedness, nausea and decreased coordination through action on the nervous system. Prolonged low level exposure may impair the formation of red and white blood cells and platelets and damage the nervous system. Benzene is reported to be carcinogenic. The values of TLV-TWA (threshold limit value-time weighted average) and TLV-STEL (threshold limit value-short term exposure limit) in air are 30 and 75 mg/m³, respectively (BDH 1991). Benzene is reported to be toxic to aquatic life (EnviroTIPS 1984). It is bioaccumulative in living organisms, and is hazardous to waterfowl and animals. The main sources of man-made environmental pollution from benzene arise from the use of gasoline, the production of chemicals using benzene as a feedstock and refinery operations (EnviroTIPS 1984). Other significant sources include transportation and storage leaks, stationary fuel combustion and coke production. When spilled on the ground, benzene is gradually adsorbed onto the soil and the excess can penetrate down to the groundwater table causing underground water contamination. When spilled on the water, benzene will float on the surface because its density is less than that of water. A very small amount of benzene will be dissolved into the water due to its low solubility and part of the dissolved benzene may be adsorbed by the suspended solids in the water body. Benzene is a high volatility chemical. In 1985, about 34,150 tonnes of benzene was estimated to
enter the atmosphere in Canada (Jaques 1990). Benzene has been found to be present in fish, dairy products and eggs. Concentrations of 300 μg/L in water and 2100 μg/kg in eggs have been reported (Jaques 1990).

Toluene is a derivative of benzene. It is also toxic to human beings. The mode of entry is through inhalation, ingestion and skin contact. It primarily affects the central nervous system. Acute exposure may cause tiredness, muscle weakness, headache, dizziness, confusion, poor coordination, nausea and vomiting. Chronic exposure may affect the memory and thinking ability, emotions and coordination. The exposure limits of toluene in air are 375 and 560 mg/m³ as TLV-TWA and TLV-STEEL respectively (BDH 1990). Toluene is toxic to aquatic life. Toxicity range for short term exposure for fish is 10 to 65 mg/L. The 96-h LC₅₀ is 10 mg/L or less for fish. A concentration of less than 0.25 mg/L of toluene in water is sufficient to taint the flavour of fish flesh (EnviroTIPS 1984a). Similar to benzene, toluene is less dense than water and slightly soluble in water. When spilled on water or ground, toluene will enter the environment in a similar way as benzene does. It is estimated that 86% of the toluene produced is eventually released into the biosphere. As high as 65% of the release is caused by the emission from motor vehicles and aircraft exhaust and losses during gasoline marketing activities, spills, and cigarette smoke; about 33% is from the industrial application and 2% is lost during its production. Toluene has been detected in drinking water at concentration up to 0.027 mg/L, well water at 0.005 to 0.1 mg/L and raw surface water at 0.001 to 0.015 mg/L (WHO 1985).

TCE is considered a moderately toxic substance. The main toxic effect is also
related to the depression of the central nervous system, which may lead to dizziness, headache, vertigo, nausea and excessive fatigue and even tremors, coma and death depending upon the exposure level (WHO 1985a). It may irritate skin or eyes on contact. The exposure limits of TCE in air are 50 and 200 ppm for TLV-TWA and TLV-STEL respectively (BDH 1989). TCE can enter the aquatic environment through a number of routes, including industrial discharges, landfill leaching, accidental spills, leaky storage tanks and disposal from individual households. TCE has been detected in both fresh surface water and marine water from a number of sites worldwide, particularly near industrial and urban areas. The presence of trace levels of TCE in non-industrial areas may be due to atmospheric transport. The TCE concentration of up to 90.0 µg/L has been detected in Canadian surface water (Moore et al. 1991).

PCE is another chlorinated organic compound that is increasingly causing public concern over its impact on the environment. Many studies show that PCE is toxic to human beings, animals, aquatic organisms and plants. PCE exposure of 560 mg/m³ of air can cause eye irritation, 1400 mg/m³ and higher concentrations can cause central nervous system depression related symptoms such as light-headedness, dizziness, drowsiness, headache, nausea, fatigue and impaired coordination (WHO 1985). The 6-hour LD₅₀ and LC₅₀ for rats were found to be 13,000 mg/kg of body mass and 27,800 mg/m³ respectively. The PCE concentrations of 3.5 to 21 mg/L in water were found to be lethal for half the number of the aquatic organisms exposed for 2 to 4 days (WHO 1987). It is estimated that 85% of the PCE used annually in the USA is lost to the atmosphere. Worldwide contaminations of water environment with PCE have also been
reported (WHO 1987). Concentrations of 0.01 to 46 μg/L were found in West European surface water. The concentrations in North East Atlantic Ocean ranged between 0.2 and 0.8 ng/L (WHO 1987).

2.1.3 Physical and Chemical Properties of the Selected Chemicals

Physical and chemical properties of the volatile organic compounds are important in determining the fate of these chemicals in the environment. These properties influence how they are detected and analyzed, how they migrate in and out of the aquatic environment and how they can be removed (Mackay and Shiu 1990). Table 2.1 provides a number of major properties of the four selected organic compounds.
Table 2.1 Physical and Chemical Properties of Selected Organic Compounds

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Toluene</th>
<th>TCE</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₆H₆</td>
<td>C₆H₅CH₃</td>
<td>C₂HCl₃</td>
<td>C₂Cl₄</td>
</tr>
<tr>
<td>Molecular Mass</td>
<td>78.12</td>
<td>92.15</td>
<td>131.40</td>
<td>165.82</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colourless liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LeBas Molar Volume (mL/mol)</td>
<td>96.0</td>
<td>118.2</td>
<td>107.1</td>
<td>128</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>5.53</td>
<td>-95</td>
<td>-87</td>
<td>-22</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>80.1</td>
<td>110.6</td>
<td>87</td>
<td>121.2</td>
</tr>
<tr>
<td>Flammable</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Vapour Pressure (kPa)</td>
<td>10.1 @20°C</td>
<td>3.7 @25°C</td>
<td>8.0 @20°C</td>
<td>1.9 @20°C</td>
</tr>
<tr>
<td>Specific Gravity @20°C</td>
<td>0.879</td>
<td>0.8623</td>
<td>1.47</td>
<td>1.62</td>
</tr>
<tr>
<td>Diffusivity in Water @25°C (m²/d)</td>
<td>9.42*10⁻⁵</td>
<td>8.21*10⁻⁵</td>
<td>8.29*10⁻⁵</td>
<td>7.52*10⁻⁵</td>
</tr>
<tr>
<td>Viscosity @20°C (g/m-s)</td>
<td>0.6468</td>
<td>0.590</td>
<td>0.58</td>
<td>0.880</td>
</tr>
<tr>
<td>Water Solubility (mg/L)</td>
<td>1800 @25°C</td>
<td>535 @25°C</td>
<td>1100 @25°C</td>
<td>150 @20°C</td>
</tr>
<tr>
<td>Octanol/H₂O Partition Coefficient</td>
<td>2.14</td>
<td>2.69</td>
<td>2.29</td>
<td>2.86</td>
</tr>
<tr>
<td>Dimensionless Henry Const @20°C</td>
<td>0.306</td>
<td>0.244</td>
<td>0.430</td>
<td>0.535</td>
</tr>
</tbody>
</table>
2.2 Mass Transport of Chemicals from Liquid Phase into Air Phase

Mass transport of chemicals from the liquid phase into air includes volatilization and evaporation processes. Volatilization is defined as a mass transfer process of chemicals from water or soil into air compartment. It is one of the most important routes in determining the distribution of organic chemicals between water, air and soil environments. Field studies by Thomann (1991) on the fate of PCBs in the Hudson River estuary showed that about 66% of the total of 270 tonnes discharged to the estuary from 1947 to 1987 had volatilized into the air environment. Evaporation is defined as a mass transfer process of the chemical from its pure liquid state into air. Knowledge of the mass transfer processes is important in predicting the fate of these chemicals once they enter the environment.

2.2.1 Distribution of Chemicals in Multimedia Compartment

When released into water environment, the chemical may undergo several different transport and transformation processes as shown in Figure 2.1 (Cohen 1986, Peng et al. 1990, Peng et al. 1993, Peng et al. 1993a and Peng et al. 1993b). 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
Figure 2.1 Representation of fate of chemical in the environment
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).

2.2.2 Mathematical Models

Mass transport between air-water interface has been approached mathematically by previous investigators in a variety of ways. Major models are summarized below.

2.2.2.1 Lewis and Whitman Two-Film Theory

Lewis and Whitman (1924) proposed a well known concept in describing mass transfer process between gas and liquid phases. They assumed that there are two layers, either in stagnant or laminar state, at gas-liquid interface as shown in Figure 2.2.

The resistance of the two films, the gas-film and liquid-film, controls the total mass transfer process in the system. The mass transfer of chemicals from liquid bulk to gas phase can be divided into several steps. The chemical in the liquid bulk phase is first transported to the liquid-film by turbulence, then it crosses through the liquid film by molecular diffusion, then it crosses over the gas-film by gas molecular diffusion and then it is diluted into bulk gas by turbulence. The driving forces of the mass transfer process
Figure 2.2 Schematic representation of two-film concept
are turbulent diffusion while in both liquid bulk and gas bulk phases and molecular diffusion in either liquid film or gas film. The turbulent diffusion is known to be several hundred times stronger than molecular diffusion (Bird et al. 1960). Therefore, the resistance in both the bulk liquid and the gas phases is considered negligible as compared to that in the gas/liquid films. The concentration profiles can be assumed to be reasonably uniform in the bulk phases. At gas-liquid interface, an instant dynamic equilibrium of chemical distribution between gas and liquid films is assumed to be established at any moment. This equilibrium is described by the Henry's law as (Levenspiel 1962):

\[ C_{i,g} = H \cdot C_{i,l} \]  

(2.1)

where

\[ C_{i,g} = \text{chemical concentration at interface on gas-film side, } M/L^3; \]

\[ H = \text{dimensionless Henry's law constant;} \]

\[ C_{i,l} = \text{chemical concentration at interface on liquid-film side, } M/L^3. \]

By applying the Fick's molecular diffusion law, the mass transfer rate across the liquid film can be formulated as:

\[ -\frac{dm}{dt} = D_l A \frac{C_l - C_{i,l}}{\delta_l} \]  

(2.2)

and across the gas-film:

\[ -\frac{dm}{dt} = D_g A \frac{C_{i,g} - C_g}{\delta_g} \]  

(2.3)
where

\( m \) = mass of the chemical in concern, \( M \);

\( t \) = time, \( T \);

\( A \) = area of the interface, \( T \);

\( D_i \) = molecular diffusion of the chemical in liquid phase, \( L^2/T \);

\( D_g \) = molecular diffusion of the chemical in gas phase, \( L^2/T \);

\( C_i \) = chemical concentration in liquid bulk, \( M/L^3 \);

\( C_g \) = chemical concentration in liquid gas, \( M/L^3 \);

\( \delta_i \) = thickness of the liquid film, \( L \);

\( \delta_g \) = thickness of the gas film, \( L \).

Since the accurate measurement of the film thickness is not possible in practice, the liquid-phase exchange coefficient, \( k_i \), and the gas-phase exchange coefficient, \( k_g \), are commonly defined and used as:

\[
k_i = \frac{D_i}{\delta_i}
\]

\[
k_g = \frac{D_g}{\delta_g}
\]  

(2.4)

Substituting \( k_i \) and \( k_g \) into Equations 2.2 and 2.3 respectively, equating them and solving with Equation 2.1 simultaneously for \( C_{i,l} \) and \( C_{i,g} \) give:

\[
C_{i,l} = \frac{k_i C_i + k_g C_g}{k_i + k_g H^T}
\]  

(2.5)

and
\[ C_{i,x} = \frac{k_i C_i + k_g C_g}{k_i/H + k_g} \quad (2.6) \]

By substituting values for \( C_{i,l} \) and \( C_{i,x} \) from Equations 2.5 and 2.6 into Equations 2.2 and 2.3, one gets:

\[ -\frac{dm}{dt} = A \frac{C_s/H - C_i}{1/k_i + 1/H k_g} \quad (2.7) \]

and:

\[ -\frac{dm}{dt} = A \frac{C_g - H C_i}{1/k_g + H/k_i} \quad (2.8) \]

The overall mass transfer coefficients for the liquid phase, \( K_l \), and gas phase, \( K_g \), can be defined as:

\[ \frac{1}{K_l} = \frac{1}{k_i} + \frac{1}{H k_g} \quad (2.9) \]

and:

\[ \frac{1}{K_g} = \frac{1}{k_g} + \frac{H}{k_l} \quad (2.10) \]

Substitution of \( K_l \) and \( K_g \) into the Equations 2.7 and 2.8 yields:

\[ -\frac{dm}{dt} = A K_i \left( \frac{C_s}{H} - C_i \right) \quad (2.11) \]

and:
\[-\frac{dm}{dt} = A K_\varepsilon (C_\varepsilon - H C_p) \] (2.12)

2.2.2.2 Higbie Penetration Theory

Lewis and Whitman's assumption of steady-state films is not appropriate for short life surface films. Higbie (1935) proposed a so called "penetration theory" to explain the gas transfer process occurring in bubbler absorbers, spray absorbers and packed towers. It is believed that the liquid film is continuously replaced by bulk liquid and the age of each surface element is so short that unsteady-state film can be assumed. Higbie's investigations were concerned with the liquid-film resistance only and the resistance of the gas-film was considered to be negligible. By solving the Fick's diffusion equation with appropriate boundary condition, it was shown that:

\[-\frac{dm}{dt} = 2 A (C_i - \frac{C_\varepsilon}{H}) \sqrt{\frac{D_i}{\pi t_e}} \] (2.13)

\[= k_i A (C_i - \frac{C_\varepsilon}{H}) \]

where the liquid-phase exchange coefficient, \( k_i \), was defined as:

\[k_i = 2 \sqrt{\frac{D_i}{\pi t_e}} \] (2.14)

where \( t_e \) = time of exposure, T.
2.2.2.3 Danckwerts Surface Renewal Theory

Danckwerts (1951) extended Higbie's penetration theory by assuming a nonuniform age distribution of surface elements. By assuming that each surface element was replaced by bulk liquid at an equal chance, which was independent of its age on the surface, the surface age distribution function was derived as:

\[ \phi(\theta) = s \exp(-s \theta) \]  

(2.15)

where

\[ \phi = \text{surface age distribution function, } T^{-1}; \]

\[ \theta = \text{exposure time of the surface elements, } T; \]

\[ s = \text{mean fractional rate of production of fresh surface, } T^{-1}. \]

Incorporating this surface age distribution function into film diffusion equation and the related boundary conditions yields:

\[ -\frac{dm}{dt} = A \sqrt{D_1 s} (C_{i-} - C_i) \]  

(2.16)

It was further proposed there existed a liquid sublayer right underneath the liquid-film, where the chemical was transported through by eddy diffusion. Therefore, the liquid-phase exchange coefficient was expressed as:

\[ \frac{1}{k_i} = \frac{1}{k_e} + \frac{1}{\sqrt{D_1 s}} \]  

(2.17)

where \( k_e = \text{mass-transfer coefficient for eddy diffusion, } T^{-1}. \)
2.2.2.4 Toor and Marchello's Film-Penetration Theory

In solving Fick's diffusion equation, both the penetration theory and the surface renewal theory assumed infinite thickness of a liquid film as one of the boundary conditions, which is somewhat unrealistic. Toor and Marchello (1958) improved this by assuming a definite liquid film thickness, \( \delta \), as shown in Figure 2.3 and described as:

\[
\frac{\partial C}{\partial t} = D_I \frac{\partial^2 C}{\partial y^2} \\
\text{sub to: } C = C_i \quad \text{for } t = 0, \ h \geq y \geq 0; \\
\text{and } C = C_{i,1} \quad \text{for } t > 0, \ y = 0; \\
C = C_i \quad \text{for } t > 0, \ y = \delta_i
\]  

(2.18)

The above equation was solved under both rapid surface replacement (short life surface elements) and slow surface replacement (long life) conditions, respectively. Applying Danckwerts' surface distribution function, the solution converged to Lewis and Whitman's film model under slow surface replacement conditions and approached Danckwert's surface renewal model under rapid surface replacement conditions. Under slow surface replacement conditions, the life time of each surface element is considered to be long enough so that the film is completely penetrated; therefore, the assumption of a steady-state film made by Lewis and Whitman is valid. Under rapid surface replacement conditions, the life time of each surface element is so short that the film is not penetrated at all and it is considered that the steady state chemical concentration profile is never established before being replaced by fresh bulk liquid.
Figure 2.3 Mass transport across definite thickness liquid film
Tsvogliou (1967) found that inert gases could be used as tracers for oxygen reaeration measurement. Solubilities of oxygen and the inert gases in water are both fairly low and the mass transfer rates of these gases are liquid-phase controlled. Therefore, the rate constant varies only with the diffusivity of different gases for a given water system. Smith and Bomberger (1979) and Smith, Bomberger and Haynes (1980) extended this concept to approach the volatilization of high-volatility chemicals. Since the reaeration of many natural water systems such as lakes and rivers has been measured, and if the ratio of the diffusivity of oxygen to that of a chemical can be estimated or the ratio of the mass transfer rate can be measured in the laboratory, the volatilization rate can be predicted simply by multiplying the ratio (correction factor) by field value of oxygen mass transfer rate. The fundamental relation proposed is:

\[
\frac{k_{\text{field}}^c}{k_{\text{lab}}^c} = \frac{k_{\text{field}}^o}{k_{\text{lab}}^o} = \left( \frac{D_i^c}{D_i^o} \right)^n \quad 1 \geq n \geq 0.5
\]  

(2.19)

where

\[ k_{\text{field}}^c = \text{field volatilization rate constant of chemical, T}^{-1}; \]
\[ k_{\text{field}}^o = \text{field reaeration rate constant, T}^{-1}; \]
\[ k_{\text{lab}}^c = \text{volatilization rate constant of chemical measured in the laboratory, T}^{-1}; \]
\[ k_{\text{lab}}^o = \text{reaeration rate constant measured in the laboratory, T}^{-1}; \]
\[ D_i^c = \text{molecular diffusivity of chemical in water, L}^2/\text{T}; \]
\[ D_i^o = \text{molecular diffusivity of oxygen in water, L}^2/\text{T}; \]
\( n = \text{constant.} \)

The value of \( n \) in the above equation is determined by turbulent intensity. As discussed by Toor and Marchello, \( n \) is equal to unity for slow surface replacement conditions (low turbulent intensity), and 0.5 for rapid surface replacement conditions (strong turbulent intensity). The diffusivities of the chemicals in water, if not available from the literature source, may be estimated by several mathematical models. The Othmer-Thakar relation is the most convenient (Reid and Sherwood 1966), and is recommended by Smith, Bomberger and Haynes (1980):

\[
D_f^c = \frac{0.443 \times 10^{-3}}{\mu_w^{1.1} V_b^{0.5}}
\]  

(2.20)

where

\( D_f^c = \text{molecular diffusivity in water, mm}^2/\text{s;} \)

\( \mu_w = \text{water viscosity, g/mm-s;} \)

\( V_b = \text{molar volume of the chemical at its normal boiling point, mm}^3/\text{mol.} \)

This method can be applied easily in practice. However, the turbulent conditions in the natural water compartments (streams, ponds, and lakes) will probably be different from conditions in the laboratory where the ratio of the mass transfer rate of a chemical to that of oxygen is measured. This may cause errors since the value of \( n \) is different from laboratory condition to field conditions and the uncertainty of such error is difficult to quantify.

In summary, large production and application of synthetic organic compounds has led to widespread contamination of the environment. Many of the synthetic organic
compounds are toxic. Volatilization is an important pathway in determining the fate of these chemicals in the environment. This study was initiated to investigate the mass transport processes of high volatility organic compounds from the liquid phase into the air phase under various environmental conditions and to provide useful information to the environment regulation agencies and practicing engineers in the event these compounds are implicated in an accident or spill.
CHAPTER THREE
THEORETICAL DEVELOPMENTS

3.1 Characterization of the Mass Transfer Process

Mass transport of a chemical solute from the water compartment into the atmosphere undergoes several steps, which are dependent on the physical and chemical properties of the chemical and the environmental conditions encountered. As shown in Figure 3.1, it includes (i) transport of the pollutant molecules through the bulk water to the liquid film where the driving forces may be molecular diffusion, turbulent diffusion, and/or dispersion due to the thermal and density currents; (ii) transport across the two-film interface with the molecular diffusion as the only driving force; and (iii) transport from the interface to bulk atmosphere when the driving force is a combination of turbulent diffusion, molecular diffusion and dispersion.

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-m$^3$/mol is considered less volatile than water and in a solution its
Figure 3.1 Mass transport of chemical solutes from water into air
concentration will increase as the water evaporates. A compound with $H$ greater than $10^7$ but less than $10^{-5}$ atm-m$^3$/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 $10^{-3}$ but less than $10^{-3}$ atm-m$^3$/mol, 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-m$^3$/mol. For these compounds, the water-phase resistance dominates by a factor of at least ten and therefore controls the rate of mass transfer. This research is focused on the mass transport of high-volatility organic compounds.

Turbulence intensity in the bulk water is another factor which can have a significant effect on the rate of mass transfer process, especially in deep water bodies. The following four different conditions can be identified.

3.1.1 Ideal Stagnant Condition

Under ideal stagnant conditions, the bulk liquid phase is assumed to be completely stagnant and turbulent diffusion and dispersion do not occur. The molecular diffusion is the only force to drive the chemicals through the entire depth of the water column to air phase above.

This ideal stagnant condition does not exist in real situations.
3.1.2 Near-Stagnant Condition

Under this condition, it is assumed that two different flow regimes occur in the water column. A lower degree of turbulence introduced into the bulk liquid phase results in a certain amount of dispersion and turbulent diffusion in the bulk liquid. A surface layer known as a liquid-film is formed at the water-air interface due to surface restriction. Although turbulent diffusion and dispersion can be several hundred times stronger than molecular diffusion (Bird et al. 1960), the total resistance of the entire water column can be significantly large for situations where the bulk water is several meters deep and turbulence is not strong. In the liquid film, the water is either in stagnant or in laminar regime and the driving force is the molecular diffusion. Even when the thickness of the liquid film is usually less than one millimetre (Bird et al. 1960), the total resistance exerted by this film is significant because of the small driving force produced by molecular diffusion. The resistance of both liquid-film and bulk water phases has to be specified in determining the volatilization rate of a chemical. The presence of both liquid film resistance and bulk liquid-phase resistance makes direct mathematical modelling more difficult.

This condition may represent the situations where industrial wastes from accidental spills are held in on-site holding tanks for final treatment and disposal.
3.1.3 Completely Mixed Condition

As the turbulence increases to a higher level, but without breaking the integrity of the surface film, the resistance to transport of chemicals in bulk water becomes negligible as compared to the resistance of the liquid-film. A uniform concentration of chemicals in the bulk water is established. Thus, for high volatility organic compounds, under completely mixed conditions, the liquid film controls the volatilization process and the molecular diffusion in this film is the driving force. Several mathematical models have been developed based on the film concept. One of these models was presented by Mackay and Leinonen (1975), Cohen et al. (1978), and Mackay and Yeun (1983) as:

\[ C_i = C_0 e^{-kt} \]  \hspace{1cm} (3.1)

where:

\[ k = \left( \frac{A}{V} \right) \left( \frac{D_i}{\delta_i} \right) \]  \hspace{1cm} (3.2)

where

- \( C_0 \) = initial concentration of chemical in water, \( M/L^3 \);
- \( V \) = volume of the water body, \( L^3 \).

This condition may represent the volatilization of chemicals from rivers and water ponds where turbulence is relatively high.
3.1.4 Completely Mixed Condition with Broken Film

A further increase in the turbulence breaks up the surface film. The bulk water is then in a completely mixed condition without exerting any resistance to the transport of the chemicals. The strong turbulence breaks up the surface film into small pieces and the broken film is continuously replaced by the liquid from the bulk water under the surface film. This surface renewal concept was originally proposed by Higbie (1935) and further advanced by Danckwerts (1953) and Toor and Marchello (1958) to describe gas absorption into a turbulent liquid. The rate constant was found to be:

\[ k_L = \sqrt{D_i \cdot r} \]  

(3.3)

where

\[ k_i = \text{liquid-phase exchange coefficient, T}^{-1}; \]
\[ r = \text{surface renewal rate constant, T}^{-1}; \]
\[ D_i = \text{molecular diffusivity of chemical in liquid phase, L}^2/\text{T}. \]

However, the quantitative correlation to link the surface renewal rate constant to bulk liquid turbulence intensity has not been reported.

This condition may represent fast rivers, certain water and wastewater treatment units where turbulence is high enough to break up the surface film.

The surface turbulence effect on volatilization due to wind velocity through shear friction is another important parameter. Wind shear friction can significantly increase the surface renewal rate constant and therefore increase the volatilization rate.
3.2 Mathematical Modelling

3.2.1 Volatilization of a Chemical Solute from Water into the Air Compartment

3.2.1.1 Volatilization under an Ideal Stagnant Condition

For high-volatility chemicals with $H > 10^{-3}$ atm·m$^3$/mol, the resistance of the gas phase is negligible as compared to the liquid phase (Thomas 1982). The liquid phase resistance controls the mass transfer rate of such chemicals from water to air environment and has been investigated in this study.

Under a completely stagnant condition, the transport of a chemical in the liquid occurs by diffusion due to the chemical concentration gradient. Fick's diffusion equation, which is a parabolic partial differential equation (Hines and Maddox 1985; and Fogler 1986), is applied for these conditions. If the initial and boundary conditions are simple, this equation can be solved analytically. For completely stagnant water, the physical characteristics of the liquid can be assumed to be homogeneous with a constant diffusivity throughout the entire water column. It is further assumed that there are no sinks and sources at the bottom and the wall; the air-liquid interface is the only place where the exchange of chemicals can take place. According to Fick's diffusion equation (Hines and Maddox 1985; and Fogler 1986):

$$\frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial y^2} \quad (t > 0, \ h \geq y \geq 0) \quad (3.4)$$
For initial condition:

\[ C(y, 0) = C_o \]  \hspace{2cm} (3.5)

and boundary condition:

\[
\begin{align*}
C(h, t) &= 0 \\
\left[ \frac{\partial C}{\partial y} \right]_{y=0} &= 0
\end{align*}
\]  \hspace{2cm} (3.6)

where

- \( C \) = chemical concentration in stagnant water phase, \( M/L^3 \);
- \( y \) = distance from the bottom, \( L \);
- \( t \) = time elapsed, \( T \);
- \( h \) = depth of water column, \( L \);
- \( C_o \) = initial chemical concentration in water phase, \( M/L^3 \).

The above boundary conditions indicate that, at the bottom of the water column, the Neumann boundary condition (no source or sink) exists and on top of the column, the Dirichlet boundary condition is assumed, i.e., the existing air current in the atmosphere carries away any volatilized solute. Even without air current, the chemical solute can be diluted into the atmosphere by molecular diffusion quickly and the resistance in the air is negligible as compared to one in the water phase because the diffusivity of the chemical in air phase is usually 10^5 to 10^6 times higher than its diffusivity in water. For all these situations, the background atmospheric level is assumed to be negligible (Cohen 1978; Thomas 1982). Under ideal stagnant water condition, the local chemical concentration in the water phase is a function of
volatilization time elapsed and the location of that point (water depth), as shown in Figure 3.2.

By reflection through horizontal axis and transformation of the coordinates to \(-h\) distance in \(y\) direction, the equation becomes:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2} \quad (t > 0, \ 2h \geq y \geq 0)
\]  

(3.7)

With the initial condition:

\[
C(y, 0) = C_o
\]  

(3.8)

and the boundary condition:

\[
C(0, t) = 0 \quad \quad C(2h, t) = 0
\]  

(3.9)

The above mass transport equation can be solved by the separation-of-variables method (Young 1972 and Tyn 1980). The solution obtained for the above equation is:

\[
C(y, t) = \sum_{n=1}^{\infty} C_n \exp[-D\left(\frac{n\pi}{2h}\right)^2 t] \sin\left(\frac{n\pi}{2h} y\right)
\]  

(3.10)

where:

\[
C_n = \frac{1}{h} \int_0^{2h} C_0 \sin\left(\frac{n\pi}{2h} \xi\right) \, d\xi = \frac{2}{n\pi} C_0 [1 - \cos(n\pi)]
\]  

(3.11)

or:
Figure 3.2 Volatilization of high VOCs from a stagnant water
\[ C_n = \begin{cases} \frac{4C_0}{n\pi}, & n = 1, 3, 5, \ldots \\ 0, & n = 2, 4, 6, \ldots \end{cases} \]  \hspace{1cm} (3.12)

Therefore,

\[ C(y, t) = \sum_{n=1}^{\infty} \frac{4C_0}{(2n-1)\pi} \exp\left(-D_i \left[ \frac{(2n-1)\pi}{2h} \right]^2 t \right) \sin \left( \frac{(2n-1)\pi}{2h} y \right) \]  \hspace{1cm} (3.13)

By transforming the coordinates back to the initial C-t system, the concentration distribution profile is represented by a series solution:

\[ C(y, t) = \sum_{n=1}^{\infty} \frac{4C_0}{(2n-1)\pi} \exp\left(-D_i \left[ \frac{(2n-1)\pi}{2h} \right]^2 t \right) \sin \left( \frac{(2n-1)\pi}{2h} (y+h) \right) \]  \hspace{1cm} (3.14)

subject to \( t > 0 \) and \( h > y > 0 \)

The average concentration with regard to the elapsed volatilization time can be obtained by integrating the local concentration with respect to depth:

\[ C_{L, \text{avg}} = \frac{1}{h} \sum_{n=1}^{\infty} \frac{4C_0}{(2n-1)\pi} \exp\left(-D_i \left[ \frac{(2n-1)\pi}{2h} \right]^2 t \right) \int_0^h \sin \left( \frac{(2n-1)\pi}{2h} (y+h) \right) dy \]  \hspace{1cm} (3.15)

or

\[ C_{L, \text{avg}} = \frac{8C_0}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp\left(-D_i \left[ \frac{(2n-1)\pi}{2h} \right]^2 t \right) \]  \hspace{1cm} (3.16)

where \( C_{L, \text{avg}} = \) water-depth-weighted average concentration in the water column, \( \text{M/L}^3 \).

The above solution for the average concentration is a series which is difficult to apply in practice. This solution can be expanded as:
\[ C_{L,\text{avg}} = \frac{8}{\pi^2} C_o \exp \left[ -D_l \left( \frac{\pi}{2h} \right)^2 t \right] + \epsilon(t) \]  

(3.17)

where \( \epsilon(t) \) is infinitely smaller than the first term in the equation. By neglecting \( \epsilon(t) \) and making the term \( 8/\pi^2 \) equal to unity to satisfy the initial condition, the solution can be approximated as:

\[ C_{L,\text{avg}} = C_o \exp \left( -\frac{\pi^2}{4h^2} D_l t \right) \]  

(3.18)

or

\[ C_{L,\text{avg}} = C_o \exp(-k t) \]  

(3.19)

where \( k \) is the volatilization rate constant and is represented as:

\[ k = \frac{\pi^2}{4h^2} D_l \]  

(3.20)

Therefore, the mass transfer coefficient, \( k_m \), becomes:

\[ k_m = \frac{\pi^2}{4h} D_l \]  

(3.21)

The error introduced by this mathematical approximation is analyzed and quantified as below.

Set

\[ \alpha = \exp \left[ -\left( \frac{\pi}{2h} D_l \right) \right] \]  

(3.22)

with \( 0 \leq \alpha \leq 1 \)

and since

38
\[
\frac{\pi^2}{8} = 1 + \frac{1}{3^2} + \frac{1}{5^2} + \frac{1}{7^2} + \cdots 
\]  
(3.23)

The simplified model, Equation 3.18, can be expanded as:

\[
(C_{L,\text{avg}})_{\text{simplified}} = C_o \frac{8}{\pi^2} (1 + \frac{1}{3^2} + \frac{1}{5^2} + \cdots) 
\]

\[
= \frac{8C_o}{\pi^2} \sum_{n=1}^{\infty} \left[ \frac{1}{(2n-1)^2} \alpha \right] 
\]

and the theoretical model, Equation 3.16, can be written as:

\[
(C_{L,\text{avg}})_{\text{theoretical}} = \frac{8C_o}{\pi^2} \sum_{n=1}^{\infty} \left[ \frac{1}{(2n-1)^2} \alpha^{2n-1} \right] 
\]

Therefore, the relative error

\[
\Delta = \frac{(C_{L,\text{avg}})_{\text{simplified}} - (C_{L,\text{avg}})_{\text{theoretical}}}{(C_{L,\text{avg}})_{\text{simplified}}} 
\]

\[
= \frac{8}{\pi^2} \left[ \frac{1}{3^2} (1-\alpha) + \frac{1}{5^2} (1-\alpha^2) + \cdots \right] 
\]

since \(0 \leq \alpha \leq 1\) and with substitution of Equation 3.23,

\[
0 \leq \Delta \leq \frac{8}{\pi^2} \left( \frac{1}{3^2} + \frac{1}{5^2} + \frac{1}{7^2} + \cdots \right) 
\]

\[
\text{or} \quad 0 \leq \Delta \leq \frac{8}{\pi^2} 
\]

(3.27)

Since the parameters of the simplified model are obtained by the best fit method, the actual relative error introduced by the approximation is:

\[
-\frac{1}{2} \left( 1 - \frac{8}{\pi^2} \right) \leq \Delta \leq \frac{1}{2} \left( 1 - \frac{8}{\pi^2} \right) 
\]

\[
\text{or} \quad -0.095 \leq \Delta \leq 0.095 
\]

(3.28)
The simplified model for the ideal stagnant condition is similar to Equation 3.1, the model for complete water bulk mixing condition, developed by other researchers (Mackay and Yeun 1983) from two-film theory. However, under completely mixed conditions, the volatilization rate constant, \( k \), is expressed as:

\[
k = \frac{D_l}{\delta_i h}
\]

which are different from Equations 3.20 and 3.21 for ideal stagnant condition.

3.2.1.2 Completely Mixed Condition with Broken Film

For a strong turbulent bulk water, the concept of surface renewal has been considered to be more realistic than the two-film theory for describing the mass transfer process across the air-water interface (Danckwert 1951). The surface film is broken up to small pieces and renewed continuously due to the turbulence near the interface. In order to derive a mathematical model, each piece of the broken film is idealized with proper coordinates and is shown in Figure 3.3. It is assumed that the size of the broken film is of the order of eddies size and that the fresh fluid from the bulk water with the recoverable fraction of turbulent kinetic energy enters the film with a rate of \( U_h \) at the edge of the small film and large turbulent eddies scratch the film at the rate of \( U_r \) from
Figure 3.3 Schematic diagram of idealized surface renewal
the bottom side. Mass balance around the film of a volume of \(2x\cdot2x\cdot\delta_l\) yields:

\[
u_x \cdot 4 \cdot 2x \cdot \delta_l = U_v \cdot 2x \cdot 2x
\]

or

\[
u_x = \frac{U_v x}{2\delta_l}
\]

(3.31)

where

\[
\delta_l = \text{thickness of the liquid film, L;}
\]

\[
x = \text{the distance of an element from centre and velocity across the element, L;}
\]

\[
u_x = \frac{-dx}{dt}, \text{ L/T.}
\]

At \(x = a\), Equation 3.31 becomes:

\[
U_h = \frac{U_v a}{2\delta_l}
\]

(3.32)

Substituting the value of \(U_v\) from Equation 3.32 into Equation 3.31 gives:

\[
u_x = -\frac{dx}{dt} = \frac{U_h x}{a}
\]

(3.33)

Integration of the above equation yields:

\[
\int \frac{dx}{x} = \int \frac{-U_h dt}{a}
\]

(3.34)

\[
i.e. \quad x = a e^{-\frac{u_x t}{a}}
\]

Percentage of cumulative film area with age less than \(t\) can be calculated as:

\[
F(t) = \frac{1}{(2a)^2}[(2a)^2-(2x)^2] = 1 - e^{-\frac{2u_x t}{a}}
\]

(3.35)
And film age distribution function can be written as:

\[
f(t) = \frac{dF(t)}{dt} = \frac{2U_h e^{-\frac{2U_i t}{a}}}{a}
\]  

(3.36)

By assuming that the friction loss inside the film is negligible, the mechanical energy balance around the film of a volume of \(2a \cdot 2a \cdot \delta_i\) gives:

\[
(4 \cdot 2a \cdot \delta_i) U_h \beta E = \frac{\rho U_i^2}{2} - 2a \cdot 2a \cdot U_i
\]  

(3.37)

where

\[E = \text{kinetic energy of the turbulence, } J/L^3;\]

\[\beta = \text{fraction of recoverable turbulent energy.}\]

Substitution of \(U_i = 2\delta_i U_i/a\) obtained from Equation 3.32 into Equation 3.37 yields:

\[
\frac{U_h}{a} = \frac{1}{2\delta_i} \sqrt{\frac{2\beta E}{\rho}}
\]  

(3.38)

Therefore, by substituting Equation 3.38 into Equation 3.36, the film age distribution function can be written as:

\[
f(t) = \frac{1}{\delta_i} \sqrt{\frac{2\beta E}{\rho}} \exp\left(-\frac{1}{\delta_i} \sqrt{\frac{2\beta E}{\rho}} t\right)
\]

(3.39)

Although the broken film was assumed to be square, any other shape would have resulted in the similar general equation. The mass transfer process through the film can be formulated by using Fick's diffusion equation (Hines and Maddox 1985; Fogler 1986) as:
\[
\frac{\partial C}{\partial \tau} = D_t \frac{\partial^2 C}{\partial y^2}
\]

subject to:
\[
\begin{align*}
C &= C_L \quad \text{at} \quad \tau = 0 \\
C &= C_i \quad \text{at} \quad y = 0 \\
C &= C_L \quad \text{at} \quad y = \delta_t
\end{align*}
\]

where
\[
C = \text{local chemical concentration in the film, M/L}^3;
\]
\[
y = \text{vertical coordinate, L};
\]
\[
\tau = \text{time, T}.
\]

The mass transfer rate across the surface area \(dA\), having the age of \(t\), is given by:
\[
dm = -D_t \left[ \frac{\partial C}{\partial y} \right]_{y=0, \tau=t} \ dA
\]

where \(\dot{m}\) = mass transfer rate of the chemical across the surface, M/T.

The \(d\dot{m}\) can be obtained by solving Equations 3.40 and 3.41 (Young 1972; Tyn 1980) as:
\[
d\dot{m} = (C_L - C) \left[ \frac{D_t}{\pi t} \left[ 1 + 2 \sum_{n=1}^{\infty} \exp\left(-\frac{n^2 \delta_t^2}{D t}\right) \right] \right] \ dA
\]

The mass transfer rate across the total surface area \(A\) can be computed by substituting \(dA = A \cdot f(t) \ dt\) and film age distribution function, the \(f(t)\) from Equation 3.39, into Equation 3.42, and then integrating with respect to the film age from zero to infinity to obtain:
\[ \dot{m} = (C_L - C_i) A \left[ \frac{D_i}{\delta_i} \left( \frac{2 \beta E_i}{\rho} \right) \frac{1}{2} \left[ 1 + 2 \sum_{n=1}^\infty \exp(-2n) \left( \frac{\delta_i}{D_i} \left( \frac{2 \beta E_i}{\rho} \right) \right) \right] \right] \]  

(3.43)

The summation term in the Equation 3.43 is a geometrical progression and it converges to:

\[ \sum = \frac{\exp(-2) \left( \frac{\delta_i}{D_i} \left( \frac{2 \beta E_i}{\rho} \right) \right)}{1 - \exp(-2) \left( \frac{\delta_i}{D_i} \left( \frac{2 \beta E_i}{\rho} \right) \right)} \]  

(3.44)

Therefore, mass transfer flux can be written as:

\[ N = (C_L - C_i) \left[ \frac{D_i}{\delta_i} \left( \frac{2 \beta E_i}{\rho} \right) \frac{1+\exp(-2)}{2} \left( \frac{\delta_i}{D_i} \left( \frac{2 \beta E_i}{\rho} \right) \right) \right] \left( \frac{1}{1 - \exp(-2) \left( \frac{\delta_i}{D_i} \left( \frac{2 \beta E_i}{\rho} \right) \right)} \right) \]  

(3.45)

\[ = K_L (C_L - C_i) \]

where

\[ N = \dot{m}/A = \text{mass transfer flux, } M/T/L^2; \]

\[ K_L = \text{liquid film mass transfer coefficient, } L/T. \]

Since the turbulent kinetic energy can be expressed as (Hinze 1959):

\[ E = \rho \frac{u'^2}{2} \]  

(3.46)

where

\[ u' = \text{turbulent intensity, } L/T; \]
\[ \rho = \text{water density, } M/L^3. \]

Therefore, \( K_L \), can be written as:

\[
K_L = \frac{D_l \beta^{0.5} u'}{\delta_i} \left( \frac{1 + \exp(-2 \frac{\delta_i \beta^{0.5} u'}{D_l})}{1 - \exp(-2 \frac{\delta_i \beta^{0.5} u'}{D_l})} \right)
\]  

(3.47)

Equation 3.47 is not mathematically definite at \( u' = 0 \). The value of the \( K_L \) approaches \( D_l/\delta_i \) when \( u' \) approaches zero.

The volatilization process of chemicals from a turbulent water to air environment can be predicted by substituting Equation 3.47 into the chemical mass balance equation around the water compartment as:

\[
V \frac{dC_L}{dt} = -K_L A (C_L - C_i)
\]  

(3.48)

where \( V = \text{volume of water, } L^3. \)

Integration of Equation 3.48 yields:

\[
C_L = (C_0 - C_i) \exp(-\frac{K_L A}{V} t) + C_i
\]

\[
= (C_0 - C_i) \exp(-k t) + C_i
\]  

(3.49)

where \( C_0 = \text{initial chemical concentration in water bulk phase, } M/L^3. \)

For high-volatility organic compounds with Henry's law constant larger than \( 10^3 \) atm\(\cdot\)m\(^3\)/mol, the resistance of the gas phase is negligible compared to the liquid phase (Thomas 1982) and the chemical concentration at interface can be approximated to be
the bulk air phase concentration. The concentration of the most organics in bulk air phase (background concentration) is generally assumed to be negligible. Therefore, \( C_i \) is approximated to zero, and Equation 3.49 is reduced to:

\[
C_L = C_0 \exp\left( -\frac{K_{te} A}{V} t \right)
\]  

(3.50)

or

\[
C_L = C_0 \exp(-kt)
\]  

(3.51)

where \( k = \) volatilization rate constant = \( K_{te} A/V, \text{T}^{-1} \).

The turbulent intensity, \( u' \), is difficult to measure in practice, but it can be related to energy dissipation, \( \varepsilon \), (Hinze 1959) as:

\[
\varepsilon = B \frac{u'^3}{l_e}
\]  

(3.52)

where

\[ B = \text{constant}; \]

\[ l_e = \text{average size of the energy-containing eddies, L}. \]

The energy dissipation can be written in terms of velocity gradient \( G \) (Fair et al. 1968) as:

\[
G = \sqrt{\frac{\varepsilon}{\mu}}
\]  

(3.53)

Therefore
\[ u' = \left( \frac{\mu l}{B} G^2 \right)^{1/3} \]  \hfill (3.54)

and

\[ \left( \beta^2 u' \right)^{1/2} = \left( \beta^2 \frac{\mu l}{B} \right)^{1/2} G^{1/3} = \alpha G^{1/3} \]  \hfill (3.55)

And \( K_L \) becomes

\[ K_L = \alpha \left[ \frac{D}{\delta_l} \right]^{1/3} \frac{1 + \exp(-2 \alpha \sqrt{\frac{\delta_i}{D} G^{1/3}})}{1 - \exp(-2 \alpha \sqrt{\frac{\delta_i}{D} G^{1/3}})} \]  \hfill (3.56)

For the volatilization experiments conducted in this study, the surface area to volume ratio was equal to the inverse of the total water depth. Therefore, the volatilization rate constant can be written as:

\[ k = \alpha \left[ \frac{D_i}{\delta_i} \right]^{1/3} \frac{1 + \exp(-2 \alpha \sqrt{\frac{\delta_i}{D_i} G^{1/3}})}{1 - \exp(-2 \alpha \sqrt{\frac{\delta_i}{D_i} G^{1/3}})} \]  \hfill (3.57)

where \( h = \) total water depth, L.

For a turbulent water column agitated by mechanical mixing blades, the velocity gradient, \( G \), is determined by the following equation (Fair et al. 1968):
\[ G = \sqrt{\frac{1.44 \times 10^{-4} C_D \rho [(1-k_t) N_{rev}]^3 b r_b^4 n_b}{\mu V}} \]  

(3.58)

where

- \( C_D \) = drag coefficient = 1.8;
- \( k_t \) = slip factor = 0.25;
- \( N_{rev} \) = revolution speed of the shaft, \( \text{T}^{-1} \);
- \( b \) = vertical depth of the blades, \( \text{L} \);
- \( r_b \) = effective radius of the blades, \( \text{L} \);
- \( n_b \) = number of the blades installed in each column;
- \( \mu \) = viscosity of the water, \( \text{M/L/T} \).

3.2.2 Evaporation of Pure Chemicals from Point Sources into Air

3.2.2.1 Evaporation into Quiescent Air Environment

Several assumptions are made in order to develop a mathematical model for the above condition. These include:

- Steady-state condition is valid throughout the entire evaporation process. The chemicals concerned in this study are high volatility organics. Therefore, a steady-state is established in a very short period. The transition period is negligible and is not considered in this study.

- At gas-liquid interface, the liquid chemical is vaporized into the gas phase
without exerting any resistance to the whole mass transfer process. The heat transfer is sufficient to provide the latent heat required for the vaporization. Therefore, the chemical concentration in gas phase at the interface is considered to be equal to the saturation concentration and the partial pressure of the chemical is equal to its vapour pressure, $P_v$.

- There exists a thin gas layer on top of the liquid chemical, called gas-film, which is in either stagnant or laminar condition because of the restriction effect of the liquid surface. The driving force for the transport of the chemical through this film is molecular diffusion.

- In the bulk air phase, the chemical is transported outwards in a radial direction to a hemisphere because of the symmetry. The driving force for the chemical transport is turbulent diffusion and dispersion (molecular diffusion is negligible as compared to the turbulent diffusion).

Figure 3.4 shows the mass transfer of a chemical across the gas-film. According to Fick's diffusion law, the mass flux per unit area of the film can be written as:

$$N_f = \frac{D_\delta (C_{i,\delta} - C_f)}{\delta_\delta}$$  \hspace{1cm} (3.59)

where

- $D_\delta = \text{molecular diffusion of the chemical in the air, } L^2/T$;
- $C_{i,\delta} = \text{chemical concentration in the gas phase at gas-liquid interface, } M/L^3$;
- $C_f = \text{chemical concentration at boundary between gas-film and bulk air, } M/L^3$;
- $\delta_\delta = \text{thickness of the gas film, } L$. 

50
Figure 3.4 Evaporation of chemical from point source into quiescent air
In hydrology, the evaporation flux of water from water compartment is called evaporation rate. The same terminology has been used for evaporation flux of chemicals in this study.

According to the ideal gas law:

\[ P \cdot V = n \cdot R \cdot T = \frac{W}{M_w} \cdot R \cdot T \]  \hspace{1cm} (3.60)

where

\( P \) = partial pressure of the chemical in the gas phase, \( M/L/T^2 \);
\( V \) = volume, \( L^3 \);
\( n \) = number of moles of the chemical in the volume \( V \);
\( R \) = ideal gas constant;
\( T \) = temperature in K;
\( W \) = mass of the chemical in the volume \( V \), \( M \);
\( M_w \) = molecular mass of the chemical, \( M/mole \).

At the gas-liquid interface, the partial pressure of the chemical in gas phase is equal to the vapour pressure according to the previous assumption. Therefore, the value of \( C_{is} \) can be calculated from the following equation:

\[ C_{is} = \frac{W}{V} = \frac{P \cdot M_w}{R \cdot T} \]  \hspace{1cm} (3.61)

where \( P_v \) = vapour pressure of the chemical, \( M/L/T^2 \).

From Figure 3.4, where a spherical coordinate system is used because of
symmetry, mass balance around a control volume of the hemisphere of radius \( R \) yields:

\[
\text{Rate of Accumulation} = N_f \frac{\pi}{4} d^2 - N_R 2\pi R^2 \tag{3.62}
\]

where

\( d = \) surface diameter of the container, L;

\( N_R = \) mass flux at radius \( R \) in the radial direction, M/L^2/T.

For steady-state condition, rate of accumulation in the control volume is equal to zero. Therefore, Equation 3.62 becomes:

\[
N_R R^2 = \frac{1}{8} N_f d^2 \tag{3.63}
\]

According to Fick's diffusion law, the mass flux at radius \( R \) can be expressed as:

\[
N_R = -D_t \frac{dC}{dR} \tag{3.64}
\]

where \( D_t = \) summation of the turbulent diffusivity and dispersion, L^2/T.

Substitution of Equation 3.64 and \( r = d/2 \) into Equation 3.63 yields:

\[
dC = -\frac{N_f r^2}{2 D_t} \frac{dR}{R^2} \tag{3.65}
\]

Integration of the above equation yields:

\[
\left[ dC = -\frac{N_f r^2}{2 D_t} \int_r^c \frac{dR}{R^2} \right] \tag{3.66}
\]

or

53
\[ C - C_j = \frac{N_j r^2}{2D_t} \left( \frac{1}{R} - \frac{1}{r} \right) \]  

(3.67)

Since \( C \) approaches zero as \( R \) approaches infinity (boundary condition), \( C_j \) can be found from Equation 3.67 as:

\[ C_j = \frac{N_j r}{2D_t} \]  

(3.68)

Substitution of Equations 3.61 and 3.68 into Equation 3.59 yields:

\[ N_j = \frac{P_v M_w}{R_e T} \frac{1}{\delta_e} \frac{r}{D_e + \frac{r}{2D_t}} \]  

(3.69)

This equation predicts the evaporation rate of a pure chemical from point sources into quiescent air environment.

### 3.2.2.2 Evaporation in the Presence of a Strong Wind

Strong wind is expected to blow away any vaporized chemical molecules on top of the gas-film. Therefore, the chemical concentration in the bulk air phase is assumed to be zero in this case (Figure 3.5). According to Fick's diffusion law, the mass flux per unit film area can be written as:

\[ N_j = D_e \frac{C_{1,e}}{\delta_e} \]  

(3.70)

Substitution of Equation 3.61 into Equation 3.70 yields:

\[ N_j = \frac{P_v M_w D_e}{R_e T \delta_e} \]  

(3.71)
Figure 3.5 Evaporation of chemical from point source in presence of strong wind
CHAPTER FOUR
EXPERIMENTAL PROCEDURES

4.1 Experimental Setup

4.1.1 Volatilization of Chemical Solute from Water into Air

The bench scale experiments were conducted in the university laboratory to investigate the volatilization rate of selected organic compounds from water into the air compartment under various environmental conditions, i.e., different levels of surface turbulence and water bulk mixing. Four chemicals, benzene, toluene, trichloroethylene, and tetrachloroethylene were tested in these experiments. These chemicals were purchased from Fisher Scientific Company and BDH Chemicals Ltd. and were of analytical reagent quality. The solubilities of benzene, toluene, TCE and PCE in water are 1800, 515, 1070 and 150 mg/L or 2.052, 0.597, 0.731 and 0.092 mL/L (Yurteri et al. 1987), respectively. All of these chemicals are high-volatility organic compounds with Henry’s constant five to thirteen times larger than 10^3 atm-m^3/mol (Yurteri et al. 1987). Chemical solutions were prepared by dissolving these organic compounds in distilled-
deionized water to 50% of their solubilities. Complete dissolution was achieved by stirring the contents in the flask with a magnetic mixer for about 24 hours.

4.1.1.1 Volatilization from Water without Agitation

Volatilization of selected chemicals from a water compartment without agitation was conducted under a fume hood. Four chemical solutions, benzene, toluene, TCE and PCE, were prepared using 1000-mL volumetric flasks. Ten glass containers with internal diameter of 20 mm and a depth of 75 mm were placed in a fume hood. These test containers were filled quickly, but without agitation, to the brim with one of the four prepared solutions each time. Air velocities, measured with a velometer at a distance of 100 mm above the test vials, were less than 0.1 m/s. The air temperature during the test periods was 25 ± 1 °C. At different time intervals during the volatilization test, two liquid samples were collected from each vial. Before sampling, the test container was sealed with a teflon coated cap and shaken in order to achieve a uniform concentration inside. Soon after the test container was reopened, a sample of one mL was taken from the vial at a depth of 50 mm below the water surface. This one mL sample then was transferred into a 20 mL headspace vial purchased from the Hewlett Packard Company. The second sample was immediately taken from the same test vial using the same procedure. Once the two samples were collected, the content of the container was then discarded. The headspace vials were sealed immediately with appropriate teflon septa and aluminium caps using a crimper. These were refrigerated at 4 °C until the final
chemical analyses were carried out using a Gas Chromatograph. In addition, volatilization of benzene with different water depths in the vials were tested with similar procedures. Glass containers with 15 mm diameter, 150 mm depth and 17 mm diameter, 300 mm depth were used for these tests.

4.1.1.2 Volatilization of Selected Chemicals in the Presence of Wind

The effect of surface turbulence on volatilization rate was studied by blowing wind at different velocities over the water surface. The air temperature during the test periods was 25 ± 1 °C. Glass containers with internal diameter of 20 mm and a depth of 75 mm were used in these experiments. These test containers were filled quickly, but without agitation, with one of the four prepared solutions each time. Wind velocities of 0, 0.5, 1.0, 2.0, 3.5, 5.0 m/s were simulated by adjusting the window opening of the fume hood. Wind velocity was measured with a velometer at 100 mm height above the liquid surface of the test containers. The wind velocity profile was observed to be uniform. The similar sampling procedure used previously for the experiment of volatilization from quiescent water was followed. Each container was sampled to provide the chemical concentration at different volatilization time and then was discarded.

4.1.1.3 Volatilization of Selected Chemicals from Agitated Water Columns

The experiments on the effect of water bulk turbulence on the rate of volatilization
of the selected four organic compounds from water into air environment were conducted in a walk-in fume hood. Four glass columns, with inner-diameter of 100 mm and four different heights, were set up in the walk-in fume hood. All columns were equipped with sampling ports as shown in Figure 4.1. Water bulk turbulence was simulated by installing a shaft provided with several flat blades of 60 mm in horizontal length and 30 mm in vertical length and provided with a variable speed motor. Each column was filled with the appropriate chemical solution. Air temperature in the fume hood was 24 ± 2 °C during the test period. Water samples were taken at different depths and at different time intervals during the volatilization test. For representative top surface samples, a one mL sample was taken directly from each column at a depth of 50 mm below the surface. This sample was then transferred into a 20 mL headspace vial. For other samples from different sampling ports, a glass tube from the sampling port was inserted in a 20 mL vial to the bottom. After discarding sample equal to two volumes of the vial, a one mL sample was taken from the glass container at 50 mm below the surface and transferred into a 20 mL headspace vial. All headspace vials were sealed immediately with appropriate teflon septa and aluminum caps. These were kept in a refrigerator at 4°C until the chemical analyses were carried out.

4.1.2 Evaporation of Pure Chemicals from Point Sources

These experiments were conducted in the laboratory to investigate the evaporation of the selected chemicals from point sources. Benzene and toluene were purchased from
Figure 4.1 Details of the columns used for bulk turbulence studies
the Aldrich Chemical Company, Inc., USA. The purities of the chemicals were 97% and 99% for benzene and toluene, respectively. TCE and PCE were purchased from BDH Chemicals Ltd., and were of analytical reagent quality. Four circular glass vessels with different sizes, as shown in Table 4.1, were used as the chemical container for the evaporation study.

Table 4.1. Specification of the Glass Vessels Used in the Experiments.

<table>
<thead>
<tr>
<th>Container Label</th>
<th>Diameter (mm)</th>
<th>Surface Area (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>39</td>
<td>0.001194</td>
</tr>
<tr>
<td>B</td>
<td>46</td>
<td>0.001661</td>
</tr>
<tr>
<td>C</td>
<td>64</td>
<td>0.003215</td>
</tr>
<tr>
<td>D</td>
<td>83.5</td>
<td>0.005473</td>
</tr>
</tbody>
</table>

The experiments were carried out under two different environmental conditions. One was done under stagnant bulk air condition and the other one was done under strong wind, 5 m/s, condition.

4.1.2.1 Evaporation of Selected Chemicals under Stagnant Condition

The selected pure chemicals were transferred into designated glass vessels as mentioned earlier and the containers were placed on a top-loading electronic balance. This balance, Mettler PC 2000, had a weighing range of 2000 grams with the readability of 0.01 gram. The evaporation time, the air temperature and the reading of the mass of chemicals were recorded at different time intervals.
4.1.2.2 Evaporation of Selected Chemicals in the Presence of Strong Wind

The experiments on evaporation in the presence of strong wind were conducted in the fume hood. A wind velocity of about 5 m/s was simulated by adjusting the fume hood window to an appropriate opening. The same experimental procedure, as used for the previous evaporation tests, was followed.

4.2 Analysis of the Chemical Concentrations in Water

The headspace technique (Dietz and Singley 1979), where the samples reach an equilibrium between the liquid and vapour phases under a controlled constant temperature, was used to analyze the sample concentration. A Hewlett Packard 19395A head-space sampler coupled to a Hewlett Packard 5890A Gas Chromatograph with a HP-1 (Methyl-Silicone Gum), 5m×0.53mm×2.65μm capillary column and a FID detector was used. The headspace vials were kept in an oil bath inside of the headspace sampler at 45°C for 90 min for the chemical to reach the equilibrium between the liquid and vapour phases. After an equilibrium had been reached, a one mL gas sample was drawn from the vial by the sampling loop of the headspace sampler and injected into the following HP Gas Chromatograph for analysis. The gas chromatograph was calibrated with standard samples prepared by the same procedure as for the test samples to minimize the systematic errors. The temperature used for the oven, where the column was located, was 50°C. The temperature for the FID detector was set up at 250°C, and the temperature for
the injection port was 225°C.

4.2.1 Calibration of Headspace Gas Chromatograph System

Chemical concentrations in all the water samples collected in the study were analyzed by the Gas Chromatograph headspace method described above. It was necessary to set up the GC analysis in a manner that a linear calibration relationship existed over the entire range of concentrations being analyzed, as the samples were compared to the calibration curve established with the standards (Zytnier 1988). The headspace vial designed for the automatic headspace sampler had about 20 mL capacity. By using different liquid to air volume ratio in the vial, the chemical concentration in the headspace air was adjusted. This can be demonstrated by development of an operation function as below.

The background chemical concentration in air was assumed to be negligible. A volume of $V_w$ water sample with chemical concentration of $C_{w,r}$ was placed into a headspace vial with volume $V_h$. Therefore, the volume of vapour phase in headspace vial was $V_v = V_h - V_w$. After an equilibrium between vapour phase and water phase had reached, the chemical concentration in vapour phase and water phase could be related by Henry's law as:

$$\gamma_v C_v = H \gamma_w C_w$$  \hspace{1cm} (4.1)
where

\( \gamma_v = \) activity coefficient in vapour;

\( \gamma_w = \) activity coefficient in water;

\( C_v = \) chemical concentration in vapour phase after equilibrium, M/L^3;

\( C_w = \) chemical concentration in water phase after equilibrium, M/L^3;

\( H = \) dimensionless Henry's law constant.

Since the concentration of the selected chemicals in water was very low (less than 1000 mg/L), the solutions were considered to be dilute and the activity coefficients approach unity. Therefore, Equation 4.1 is reduced to:

\[
C_v = H C_w
\]  
(4.2)

Assuming no chemical leak from headspace vial to outside environment (perfect seal), the mass conservation of chemical before and after the equilibrium yields:

\[
C_{w,0} V_w = C_v V_v + C_w V_w
\]  
(4.3)

After substituting Equation 4.2 into Equation 4.3, \( C_v \) can be solved to be:

\[
C_v = \frac{1}{\frac{V_v}{V_w} + \frac{1}{H}} C_w
\]  
(4.4)

and the \( C_w \) is expressed as:

\[
C_w = \left( \frac{V_v}{V_w + \frac{1}{H}} \right) C_v
\]  
(4.5)

Equations 4.4 and 4.5 show that the operation function for the headspace analysis
method is a linear line passing through the origin. Equation 4.4 also indicates that bigger the water sample volume used (low vapour volume to water volume ratio), the higher will be the chemical concentration in vapour phase and consequently provide higher sensitivity to the system. However, there is a maximum vapour concentration that will saturate the FID detector installed in GC. Equation 4.5 indicates that lower concentration in water sample will cause the saturation of the detector if the water sample volume is larger. For the concentration range used in the study, it was found that one mL water sample volume was appropriate because it provided the required detection limits and linear calibration curves for all selected organic chemicals, as shown in Figures 4.2 to 4.5. The quality control of the chemical analysis was conducted by measuring six samples with the known concentration for each chemical, respectively. It was found that the relative deviation was less than 4%.
Figure 4.2 Calibration of gas chromatograph with benzene by headspace method
Figure 4.3 Calibration of gas chromatograph with toluene by headspace method
Figure 4.4 Calibration of gas chromatograph with TCE by headspace method
Figure 4.5 Calibration of gas chromatograph with PCE by headspace method
CHAPTER FIVE
RESULTS AND ANALYSIS

5.1 Volatilization of Selected Chemicals from Stagnant Water

All organic compounds selected in this study were tested for their volatilization from stagnant water. The data collected at different time intervals in each experiment were plotted in Figures 5.1 to 5.6, for benzene under three different water depths, 75 mm, 150 mm and 300 mm, and toluene, TCE and PCE under 75 mm water depth. \( C_t \) in these figures represents the chemical concentration in water at time \( t \). These data were fitted to the first-order kinetic volatilization equation. The volatilization rate constant was calculated by performing linear regression analysis with \( \ln(C) \) against \( t \) for each run. The correlation coefficient for each analysis was also determined. Table 5.1 shows the results of the regression analysis for these experiments.
Figure 5.1 Volatilization of benzene from stagnant water
water depth = 75 mm
Figure 5.2 Volatilization of benzene from stagnant water
water depth = 150 mm
Figure 5.3 Volatilization of benzene from stagnant water
water depth = 300 mm
Figure 5.4 Volatilization of toluene from stagnant water
water depth = 75 mm
Figure 5.5 Volatilization of TCE from stagnant water
water depth = 75 mm
Figure 5.6 Volatilization of PCE from stagnant water
water depth = 75 mm
Table 5.1 Volatilization rate constant under stagnant condition.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Water Depth (mm)</th>
<th>Measured k (d^4)</th>
<th>Correlation Coeff. R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>75</td>
<td>0.945</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.2698</td>
<td>0.983</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.0765</td>
<td>0.968</td>
</tr>
<tr>
<td>Toluene</td>
<td>75</td>
<td>0.996</td>
<td>0.983</td>
</tr>
<tr>
<td>TCE</td>
<td>75</td>
<td>1.114</td>
<td>0.961</td>
</tr>
<tr>
<td>PCE</td>
<td>75</td>
<td>0.664</td>
<td>0.966</td>
</tr>
</tbody>
</table>

5.2 Volatilization of Selected Chemicals in Presence of Wind

The effect of surface shear, one of the most important environmental parameters, on the volatilization rate was investigated in these experiments. The volatilization of selected chemicals from water into air under different wind velocity conditions was observed to follow the first order kinetics as well. The calculated volatilization rate constant for each wind velocity is tabulated in Table 5.2.
Table 5.2 Volatilization rate constant, $d^{-1}$, under various wind velocities.

<table>
<thead>
<tr>
<th>Wind Velocity (m/s)</th>
<th>Benzene</th>
<th>Toluene</th>
<th>TCE</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.945</td>
<td>0.996</td>
<td>1.114</td>
<td>0.664</td>
</tr>
<tr>
<td>0.5</td>
<td>1.83</td>
<td>1.12</td>
<td>2.18</td>
<td>1.21</td>
</tr>
<tr>
<td>1.0</td>
<td>2.64</td>
<td>1.98</td>
<td>2.74</td>
<td>1.69</td>
</tr>
<tr>
<td>2.0</td>
<td>3.22</td>
<td>2.98</td>
<td>4.06</td>
<td>3.18</td>
</tr>
<tr>
<td>3.5</td>
<td>4.21</td>
<td>4.14</td>
<td>4.45</td>
<td>4.41</td>
</tr>
<tr>
<td>5.0</td>
<td>5.23</td>
<td>6.87</td>
<td>6.40</td>
<td>5.67</td>
</tr>
</tbody>
</table>

5.3 Volatilization of Selected Chemicals from Turbulent Water

The effect of mechanical agitation in bulk water, another important parameter, on the volatilization rate was tested in this set of experiments. During all these experiments, the chemical concentration profile in water phase was observed to be nearly uniform throughout the water column. Figure 5.7 shows a typical distribution of chemical in the water column at two different times. Therefore, the average value of the concentrations taken at different depths in each column was used to represent the water
Figure 5.7 Concentration distribution of benzene in Column-D, mixing intensity = 50 s⁻¹
bulk phase concentration and was used to determine the volatilization rate constant under different water depths and various turbulent conditions. All these experiments were observed to follow the first order kinetic equation with respect to the water bulk phase concentration. Figure 5.8 shows a typical plot of the experiments conducted in this set. Nine different water bulk turbulence intensities (expressed in terms of velocity gradient, \( G \)) equal to 0, 25, 50, 75, 100, 125, 150, 175 and 200 s\(^{-1}\) were tested. In addition, four different water depths, 0.6, 1.2, 1.5 and 1.8 m, were used. Water depth is the inverse of the surface area to volume ratio, which is one of important physical parameters to specify the conditions in the water compartment. Table 5.3 shows the calculated volatilization rate constant values under different bulk turbulence intensities and different surface area to volume ratios for the selected four chemicals.
Figure 5.8 Volatilization of toluene from 1.2 m water column, mixing intensity = 75 s$^{-1}$
Table 5.3 Computed Volatilization Rate Constant, $k$ in d$^{-1}$, for Bulk Mixing Experiments.

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>G 1/s</th>
<th>A/V 1.667 m$^{-1}$</th>
<th>A/V 0.833 m$^{-1}$</th>
<th>A/V 0.667 m$^{-1}$</th>
<th>A/V 0.556 m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BENZENE</td>
<td>25</td>
<td>0.657</td>
<td></td>
<td></td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.802</td>
<td></td>
<td></td>
<td>0.535</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.96</td>
<td></td>
<td></td>
<td>0.664</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.249</td>
<td></td>
<td></td>
<td>0.833</td>
</tr>
<tr>
<td>TOLUENE</td>
<td>25</td>
<td>0.606</td>
<td></td>
<td></td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.744</td>
<td></td>
<td></td>
<td>0.496</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td></td>
<td></td>
<td>0.846</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.86</td>
<td>0.92</td>
<td>0.76</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td></td>
<td>0.998</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>1.115</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2.3</td>
<td>1.18</td>
<td>0.93</td>
<td>0.74</td>
</tr>
<tr>
<td>TCE</td>
<td>25</td>
<td>0.62</td>
<td></td>
<td></td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.748</td>
<td></td>
<td></td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.92</td>
<td></td>
<td></td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.171</td>
<td></td>
<td></td>
<td>0.781</td>
</tr>
<tr>
<td>PCE</td>
<td>25</td>
<td>0.576</td>
<td></td>
<td></td>
<td>0.384</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.71</td>
<td></td>
<td></td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.7</td>
<td>0.89</td>
<td>0.71</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2.23</td>
<td>1.12</td>
<td>0.89</td>
<td>0.77</td>
</tr>
</tbody>
</table>
5.4 Evaporation of Selected Chemicals from Point Sources

Evaporation of the four selected chemicals from four glass vessels with different sizes was tested under both quiescent and windy air conditions. All the evaporated mass data were observed to follow a linear correlation with respect to the time elapsed. Figures 5.9 to 5.12 show the experimental results for evaporation of benzene, toluene, TCE and PCE from one of the four vessels under quiescent air condition. Similar behaviour was observed in other vessel sizes. The evaporation rate was calculated by performing a linear regression analysis with vaporized mass of chemical against time elapsed. Table 5.4 shows the result of the regression analysis for all the experiments conducted under quiescent air condition. The air temperature reported in Table 5.4 is the average value of the temperature read at each time when the mass of the liquid chemical was measured. The statistical deviations in the evaporation rate for each chemical for four tests is due to the variations in temperature, diameter of the point sources and the experimental bias. It was observed that the regression lines did not pass through the origin in Figures 5.9 to 5.12. The reason is that in the beginning of each test, the chemical concentration in air was zero and the driving force was larger. After several minutes, the chemical had built up in the air phase to the steady state concentration and the evaporation rate had slowed down to a constant level.

Figures 5.13 to 5.16 show the experimental results for evaporation of benzene, toluene, TCE and PCE from one of four vessels under 5 m/s wind condition. The evaporation rate for each experiment was calculated by performing a linear regression
Figure 5.9 Evaporation of benzene from Container-A under stagnant condition
Figure 5.10 Evaporation of toluene from Container-A under stagnant condition
Figure 5.11 Evaporation of TCE from Container-A under stagnant condition
Figure 5.12 Evaporation of PCE from Container-A under stagnant condition
analysis with vaporized mass of chemical against time elapsed. Table 5.5 shows the results of the regression analysis for all the experiments conducted under 5 m/s wind condition.

Table 5.4 Evaporation of Pure Chemicals from Point Source into Quiescent Air.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Diameter of vessel (mm)</th>
<th>Evaporation rate (g/m²/h)</th>
<th>Correlation Coeff. R</th>
<th>Air Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>39</td>
<td>2734</td>
<td>0.995</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>2934</td>
<td>0.996</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>2499</td>
<td>0.997</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>83.5</td>
<td>2613</td>
<td>0.998</td>
<td>26.1</td>
</tr>
<tr>
<td>Average</td>
<td>39</td>
<td>2695</td>
<td></td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>1016</td>
<td>0.995</td>
<td>26.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>46</td>
<td>969</td>
<td>0.996</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>856</td>
<td>0.997</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>83.5</td>
<td>839</td>
<td>0.998</td>
<td>26.0</td>
</tr>
<tr>
<td>Average</td>
<td>39</td>
<td>920</td>
<td></td>
<td>26.0</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>3730</td>
<td>0.996</td>
<td>24.8</td>
</tr>
<tr>
<td>TCE</td>
<td>64</td>
<td>3494</td>
<td>0.994</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>83.5</td>
<td>3521</td>
<td>0.998</td>
<td>27.5</td>
</tr>
<tr>
<td>Average</td>
<td>39</td>
<td>3420</td>
<td></td>
<td>24.7</td>
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<td></td>
<td>46</td>
<td>1178</td>
<td>1.000</td>
<td>25.3</td>
</tr>
<tr>
<td>PCE</td>
<td>64</td>
<td>1181</td>
<td>1.000</td>
<td>25.7</td>
</tr>
<tr>
<td></td>
<td>83.5</td>
<td>1014</td>
<td>0.999</td>
<td>25.0</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>1108</td>
<td>0.999</td>
<td>25.5</td>
</tr>
</tbody>
</table>

88
Figure 5.13 Evaporation of benzene from Container-A under 5 m/s wind condition
Figure 5.14 Evaporation of toluene from Container-A under 5 m/s wind condition
Figure 5.15 Evaporation of TCE from Container-A under 5 m/s wind condition
Figure 5.16 Evaporation of PCE from Container-A under 5 m/s wind condition
Table 5.5 Evaporation of Pure Chemicals from Point Source
under 5 m/s Wind Condition.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Diameter of vessel (mm)</th>
<th>Evaporation rate (g/m²/h)</th>
<th>Correlation Coeff. R</th>
<th>Air Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>39</td>
<td>13603</td>
<td>0.999</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>12638</td>
<td>0.998</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>11560</td>
<td>0.999</td>
<td>23.2</td>
</tr>
<tr>
<td></td>
<td>83.5</td>
<td>12372</td>
<td>0.999</td>
<td>23.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>39</td>
<td>4019</td>
<td>0.993</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>4026</td>
<td>0.998</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>4019</td>
<td>1.000</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>83.5</td>
<td>3801</td>
<td>0.999</td>
<td>23.0</td>
</tr>
<tr>
<td>TCE</td>
<td>39</td>
<td>15754</td>
<td>0.999</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>15308</td>
<td>0.999</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>15529</td>
<td>1.000</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>83.5</td>
<td>15708</td>
<td>0.998</td>
<td>24.0</td>
</tr>
<tr>
<td>PCE</td>
<td>39</td>
<td>5214</td>
<td>1.000</td>
<td>23.3</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>5307</td>
<td>1.000</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>4884</td>
<td>1.000</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td>83.5</td>
<td>4531</td>
<td>0.999</td>
<td>24.9</td>
</tr>
</tbody>
</table>
CHAPTER SIX

DISCUSSION

6.1 Volatilization of Selected Chemicals from Stagnant Water

Under stagnant water condition, the resistance in the bulk water to the mass transport of chemicals from water into air can not be neglected. A mathematical model, Equation 3.16, developed previously for such a condition was used to predict the experimental results. The diffusion coefficient, $D_i$, in the theoretical model, Equation 3.16 was estimated by minimizing the objective function, $z$, as shown below:

$$z = \sum_{i=1}^{n} [C(t) - C_i]^2 \Rightarrow \text{Min} \tag{6.1}$$

where

$C_i = \text{average concentration obtained experimentally, } M/L^3$;

$C(t) = \text{average concentration obtained from the model, } M/L^3$.

The golden-section algorithm (Wismer and Chattergy 1978) was used and an appropriate computer programme was written to carry out the above objective analysis. Calculated optimum values of diffusion coefficient, $D_i$, were used to plot the best-fitting
curves of the theoretical solution in Figures 6.1, 6.2, and 6.3 for three typical sets of data for benzene under different water depths.

The simplified model, Equation 3.19, which is a first order kinetics equation, can be transformed to the following linear function by taking natural logarithms on both sides of the equation:

\[
\ln C_t = -k t + \ln C_o
\]  

(6.2)

The method of least squares was used for the regression equation, Equation 6.2, to calculate the volatilization rate constants. The least square lines are also plotted in Figures 6.1, 6.2 and 6.3 for comparison.

Figures 6.1, 6.2, and 6.3 for volatilization of benzene show that both the theoretical and approximate model plots fit the experimental data well, although the theoretical solution shows a better fit to the experimental data. The linear correlation analysis of data by the simplified model indicates that the volatilization rate constants, \( k \), for benzene under the experimental condition were 0.945, 0.270 and 0.0765 d\(^{-1}\) with correlation coefficients of 0.990, 0.983 and 0.968 for water depths of 75, 150 and 300 mm respectively.

In order to quantify the model simulation errors and experimental errors, statistical analyses were carried out on the observed data. 95% confidence intervals for both population means and individual measurements were calculated (Kennedy and Neville 1986) and are plotted in Figures 6.1, 6.2, and 6.3.

Similar analyses of data were carried out by the simplified model for toluene, trichloroethylene, and tetrachloroethylene. The values obtained for the volatilization rate
Figure 6.1 Modelling of volatilization of benzene from stagnant water, water depth = 75 mm
Figure 6.2 Modelling of volatilization of benzene from stagnant water, water depth = 150 mm
Figure 6.3 Modelling of volatilization of benzene from stagnant water, water depth = 300 mm
constants, \( k \), with 75 mm depth were 0.996, 1.114 and 0.644 d\(^{-1}\) respectively. The correlation coefficients in all cases were better than 0.95 as shown in Table 5.1.

According to the simplified model, Equation 3.20, the volatilization rate constant under stagnant condition is inversely proportional to the square of the water depth, while for completely mixed condition, Equation 3.2, it is inversely proportional to the water depth. These two equations, Equation 3.2 and Equation 3.20, become similar if the liquid-film thickness, \( \delta_n \), is taken to be equal to \( h \) (assumption made for stagnant condition). In order to determine the dependence of the volatilization rate constant on water depth, the experimental data were analyzed using the following generalized equation:

\[
k = \frac{\text{Const}}{h^n}
\]  

(6.3)

By taking logarithms, this equation becomes:

\[
\ln(k) = -n \ln(h) + \ln(\text{Const})
\]  

(6.4)

The volatilization rate constants obtained for benzene with water depths of 75, 150, and 300 mm are plotted against water depth on log-log scale in Figure 6.4. Regression analysis of the above linearized equation provided the values for \( n \) and \( \text{Const} \) as 1.81 and 2378, respectively with a correlation coefficient of 1.00. Therefore, the volatilization rate constant for benzene under experimental conditions can be represented as:

\[
k = \frac{2378}{h^{1.81}}
\]  

(6.5)
Figure 6.4 Volatilization rate constant of benzene versus water depth under stagnant condition

\[ r = 1.00 \]
\[ n = 1.81 \]
where $h$ is water depth in mm. The value of $n$ falls between 2.0 (stagnant condition) and 1.0 (turbulent condition).

The comparison of volatilization rate constants, $k$, for different organic compounds is shown in Table 6.1. It includes the values calculated from the experimental data as well as the values calculated from the diffusion coefficient according to Equation 3.20. The diffusion coefficient values were obtained from literature. The measured values of $k$ from this study under stagnant condition are 19.5 to 30.6 times higher than those calculated from Equation 3.20. This, along with the deviation of the measured $n$ from 2 to 1.81 in Equation 6.5, indicate that the experiments conducted in this study were not under completely stagnant conditions. Variation of temperature and surface disturbance due to air currents may have caused a certain amount of dispersion in bulk water phase. However, this increase in $k$ caused by temperature variation and air currents is considerably less as compared to the increase due to bulk water turbulence. Table 6.1 shows that the values of $k$ obtained by Cohen et al. (1978) for benzene and toluene under turbulent conditions are 1226 and 1332 times higher than those calculated from Equation 3.20. Therefore, the experimental conditions used in this study can be considered as a near-stagnant condition where active mixing was not present in bulk water phase. Under a near-stagnant condition, a change of a few degrees in temperature, which is not important to high mass transfer process under completely mixed conditions as indicated by Thomas (1982) and Cohen (1978), may have a significant effect on the volatilization process.
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Diffusivity\textsuperscript{ab} at 25 °C (mm(^2)/s)</th>
<th>Water Depth (mm)</th>
<th>Measured k (d(^{-1}))</th>
<th>Computed k from Eq. 3.20 (d(^{-1}))</th>
<th>Measured k/Computed k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.09×10(^{-3})</td>
<td>75</td>
<td>0.945\textsuperscript{e}</td>
<td>0.0414</td>
<td>22.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>0.2698\textsuperscript{c}</td>
<td>0.0103</td>
<td>26.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>0.0765\textsuperscript{e}</td>
<td>0.00258</td>
<td>29.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>620</td>
<td>0.806\textsuperscript{d}</td>
<td>0.000605</td>
<td>1332</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.95×10(^{-3})</td>
<td>75</td>
<td>0.996\textsuperscript{e}</td>
<td>0.0360</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>620</td>
<td>0.646\textsuperscript{d}</td>
<td>0.000527</td>
<td>1226</td>
</tr>
<tr>
<td>TCE</td>
<td>0.96×10(^{-3})</td>
<td>75</td>
<td>1.114\textsuperscript{e}</td>
<td>0.0364</td>
<td>30.6</td>
</tr>
<tr>
<td>PCE</td>
<td>0.87×10(^{-3})</td>
<td>75</td>
<td>0.664\textsuperscript{d}</td>
<td>0.0330</td>
<td>19.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ratcliff and Reid (1961)
\textsuperscript{b}Tucker and Nelken (1982)
\textsuperscript{c}measured in this work
\textsuperscript{d}measured by Cohen et al. (1978) under bulk water turbulent condition
6.2 Volatilization of Selected Chemicals in Presence of Wind

Wind blowing over the air-water interface has significant effect on the mass transport of high volatility organic compounds from water into air. The surface shear caused by wind will break up the liquid film to increase the surface renewal rate, where the resistance dominates for the mass transport of high volatile organics. Also it will transfer kinetic energy of the wind into the main water body to create turbulent mixing inside the water body. Therefore an increase in surface shear due to wind will increase the volatilization rate. Figures 6.5 to 6.8 show the effect of wind velocity on the volatilization rate constant for benzene, toluene, TCE and PCE respectively. It is observed that the volatilization rate constant increases as the wind velocity increases. These experimental results also show that increase of wind velocity from near stagnant to 5 m/s has increased the volatilization rate constants by 4 to 6 times for all four selected chemicals under the condition where the bulk water agitation is only due to wind velocity.

Mathematical modelling of the volatilization rate constant versus wind velocity was carried out by using a linear equation. Regression analysis with volatilization rate constant against wind velocity yields the following correlations:

for benzene,

\[ k = 0.7859 \nu_w + 1.456 \]  \hspace{1cm} (6.6)

for toluene,
Figure 6.5 Wind effect on volatilization rate of benzene
Figure 6.6 Wind effect on volatilization rate of toluene
Figure 6.7 Wind effect on volatilization rate of TCE
Figure 6.8 Wind effect on volatilization rate of PCE
\[ k = 1.1416 v_w - 0.735 \]  
(6.7)

for TCE.

\[ k = 0.9527 v_w + 1.586 \]  
(6.8)

for PCE.

\[ k = 0.9978 v_w + 0.811 \]  
(6.9)

where \( v_w \) = wind velocity, L/T.

Equations 6.6 to 6.9 were then used to plot the best-fit lines in Figures 6.5 to 6.8.

The correlation coefficients for the above equations were 0.9832, 0.9866, 0.9765 and 0.9942 respectively. These equations are similar to the model used to calculate evaporation rate of water from water surface into air under different wind velocities (Rohwer 1931). Equations 6.6 to 6.9 are empirical models which have been calibrated by the experimental results under wind velocity from 0 to 5 m/s. Therefore, they are only applicable in the tested wind velocity range.

6.3 Volatilization of Selected Chemicals from Turbulent Water

The effect of bulk water agitation on the volatilization of chemicals from water into air is discussed in this section. The mechanical agitation in bulk water can increase the turbulent diffusion and dispersion in main water body and, therefore, reduce the
resistance to mass transport processes in that region. It was found that slight disturbance from outside caused a significant increase in diffusion and dispersion so that the total resistance in the main water could be neglected. This was confirmed by the uniform concentration profile throughout water column observed during the experiments, as shown in Figure 5.7.

Bulk turbulence can apply shear force to liquid film through viscosity. This shear force, if strong enough, will break up the liquid film, causing surface refreshment by the water element from the bulk. This process transports not only water molecules but also chemicals from main water into liquid film to replace old film elements. Those old film elements contain less chemical concentration, because part of chemical solute has volatilized into air. The higher concentration gradient created by the surface refreshment will increase molecular diffusion rate in the film and, therefore, increase the total volatilization rate. A mathematical model was developed in this study by using an idealized conceptual surface renewal process. This model indicates that volatilization of high volatility chemicals from water into air follows a first order kinetic equation with respect to the chemical concentration in bulk water and was verified by the experimental results shown in Figure 5.8. The model, Equation 3.50, shows that the volatilization rate constant is in proportion to the surface area to volume ratio. Figures 6.9 and 6.10 show the volatilization rate constant of toluene and PCE under three different turbulent intensities, \( G = 0, 100 \) and \( 200 \) \( \text{s}^{-1} \), versus four different surface area to volume ratios tested in these experiments. These experimental results clearly verify the linear correlation.
Figure 6.9 Volatilization of toluene under different surface area to volume ratio
Figure 6.10 Volatilization of PCE under different surface area to volume ratio
The influence of turbulent intensity on the volatilization rate constant was also investigated in this section. Experiments on volatilization of toluene from a water column with 1.20 m depth were conducted under nine different turbulent intensities and the data were used to calibrate the model parameters of Equation 3.57. The criterion of least squares (Patkowsky 1990) was used to estimate the parameters of the model. The diffusivity, \( D_n \), for toluene at 25 °C was assumed to be \( 8.21 \times 10^{-4} \) m\(^2\)/d (Ratcliff and Reid 1961). The parameters \( \alpha \) and \( \delta \) were determined to be \( 0.381 \) (m/d\(^{1/2}\)s\(^{1/3}\)) and \( 2.97 \times 10^{-4} \) m respectively by performing a regression analysis on the volatilization rate constant \( k \) against the velocity gradient, \( G \), using Equation 3.57. In order to determine quantitatively the goodness of fit of the model, the standard error of estimate, \( S_e \), was calculated (McCuen 1985) as

\[
S_e = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (\hat{k}_i - k_i)^2} = 0.0567
\]

where

\( v = \) degrees of freedom, and equals the sample size minus the number of unknowns (equal to 9-2=7 in this case);

\( n = \) number of observations (equal to 9);

\( \hat{k}_i = \) model value, T\(^{-1}\);

\( k_i = \) observed value, T\(^{-1}\).

This value of \( S_e \) was compared with the calculated value of the standard deviation, \( S_k \), of \( k \) (McCuen, 1985) as

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\[ S_r = \frac{1}{n-1} \sum_{i=1}^{n} (k_i - \bar{k})^2 = 0.308 \]

where \( \bar{k} \) = the average observed value, T\(^{-1}\).

The computed value for \( S_r \) is close to zero and is small as compared to the computed \( S_k \) value. This indicates that the proposed model is statistically reliable. The correlation coefficient of regression was computed to be (McCuen 1985):

\[ R = \frac{\sum_{i=1}^{n} (\hat{k}_i - \bar{k})^2}{\sum_{i=1}^{n} (k_i - \bar{k})^2} = 0.971 \]

Equation 3.57, with the calculated values of \( \alpha \) and \( \delta \), was then used to compute the volatilization rate constant \( k \) for toluene at different \( G \) values. These \( k \) values are plotted in Figure 6.11, showing that a good agreement has been achieved.

With the diffusivity values of 9.42*10\(^{-5}\), 8.21*10\(^{-5}\), 8.29*10\(^{-5}\), and 7.52*10\(^{-5}\) m\(^2\)/d at 25\(^\circ\)C for benzene, toluene, TCE and PCE respectively (Ratcliff and Reid 1961; and Tucker and Nelken 1982), the calibrated model was used to predict the volatilization rate constants for each of these organic compounds under different turbulent intensities and different water depths. The predicted values are plotted against the observed values in Figure 6.12, showing good agreement. With the computed values of \( \alpha = 0.381 \) (m/d)\(^{1/2}\)s\(^{1/2}\) and \( \delta_i = 2.97\times10^{-4} \) m, Equation 3.56 becomes:
Figure 6.11 Volatilization of toluene from turbulent water
water depth = 1.20 m
Figure 6.12 Comparison of predicted values with measured values of volatilization rate constant
\[ K_t = 22.1 D_i^{\frac{1}{2}} G^{\frac{1}{3}} \frac{1 - \exp(-0.0131 D_i^{\frac{1}{2}} G^{\frac{1}{3}})}{1 - \exp(-0.0131 D_i^{\frac{1}{2}} G^{\frac{1}{3}})} \] (6.10)

where \( D_i \) is in m²/d and \( G \) is in s⁻¹. The volatilization rate constant can be calculated as:

\[ k = K_t \frac{A}{V} \] (6.11)

The mass transport model, Equations 6.10 and 6.11, can be used to predict the fate of volatile organic compounds in water and wastewater treatment units, such as channels, coagulation and flocculation tanks, aeration tanks, etc. where the velocity gradient, \( G \), can be computed. Knowing the volatilization rate constant and the water depth, the amount of chemical volatilized and the remaining concentration in water phase can be estimated.

Several researchers have investigated the mass transport process of air stripping of the volatile organic chemicals using counter-current aeration towers and mechanical surface agitation (Kavanaugh and Trussell 1980, Roberts et al. 1985, Roberts and Levy 1985, Nirmalakhandan et al. 1990, Little and Selleck 1991, Nirmalakhandan et al. 1992, Boyden et al. 1992 and Nirmalakhandan et al. 1993). The observed mass transport rate constants ranged from 30 to 520 d⁻¹ for TCE and PCE (Roberts et al. 1985), which are hundreds time higher than those observed in this study. It is believed that much larger gas-liquid interface area in their experiments caused the difference in the rate constant. Roberts and Levy (1985) observed that the mass transport rate constant was proportional to the power input of mechanical surface agitators, while in this study the mass transport
rate constant (volatilization rate constant) is proportional to the one-sixth power of the power input of the mixer in bulk water phase at high power input. For completely mixed condition, the resistance to the mass transport is mainly present in the liquid film. Therefore, the surface agitation is more energy efficient. In addition, it can provide larger gas-liquid interface by creating water droplets, which will increase the mass transport process.

When humic substances are present in water, the solubility of organic compounds can increase due to the effect of formation of micelles (Tanford 1973). However, when a certain amount of organic compound is added to water containing humic substances, the resulting concentration will be lower. As a result, the volatilization rate is expected to decrease. Further investigation is recommended in this area.

6.4 Evaporation of Selected Chemicals from Point Sources

The evaporation process of high volatility pure chemicals from a liquid pool is different from the volatilization process of such chemicals. The main resistance for the volatilization process is present in water phase and/or liquid film because of very slow molecular diffusion in water and the resistance in air and gas film is usually negligible. For the evaporation of pure chemicals, whenever the top layer of chemical molecules is vaporized into the air phase, the next layer of chemical molecules in the liquid pool becomes immediately available for subsequent evaporation. Therefore, the resistance in the liquid phase is zero, and the evaporation process becomes gas phase controlled. Since the diffusivity in air is usually $10^5$ to $10^6$ times higher than that in water phase for
the same chemical, the evaporation rate is expected to be much faster than the volatilization rate. This is confirmed by direct comparison of the time required for transport of the same amount of chemical per unit surface area from liquid phase into air by these two different processes.

The difference in the prevailing resistance results in the different type of relation for the mass transport rate to the environmental parameter. For example, the volatilization is closely related to the surface area to volume ratio (inverse of the depth of liquid phase), as indicated by Equations 3.18 and 3.50, while the evaporation rate is independent of it as indicated by Equations 3.69 and 3.71. Also, the evaporation process is a linear function of time, Figures 5.9 to 5.12, as compare to an exponential correlation for the volatilization, in Figures 5.1 to 5.6, and 5.8.

The evaporation of high volatility organics from point source is dependent of the properties of the chemical and the environmental conditions. These include molecular mass of the chemical, its vapour pressure and diffusivity in the air, as well as air temperature, wind velocity, and dimension of the air-liquid interface.

6.4.1 Evaporation of Pure Chemicals under Stagnant Air Condition

A mathematical model, Equation 3.69, was developed in this study to predict the evaporation rate under stagnant air condition. For regression analysis, this model can be transformed into following equation:
\[
\frac{P_v M_w}{N_f R_g T} = \frac{\delta g}{D_g} + \frac{r}{2D_r}
\]  \hspace{1cm} (6.12)

The vapour pressure, \( P_v \), of the four selected chemicals under different air temperatures, \( T \), can be calculated by the Clausius-Clapeyron equation (Grain 1982):

\[
\log_{10} P_v = -\frac{A}{T} + B
\]  \hspace{1cm} (6.13)

where \( A \) and \( B \) are constant for a given chemical. With the known vapour pressure of a chemical at two different air temperature, the constants, \( A \) and \( B \), can be determined for each selected chemical, as shown in Table 6.2. Table 6.2 also shows that the vapour pressure of four selected chemicals significantly varies with the air temperature. Therefore, this variation cannot be neglected in the modelling.

**Table 6.2 Calculation of Vapour Pressure of Four Selected Chemicals under Different Air Temperature.**

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Toluene</th>
<th>TCE</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp, ( T_1 ) (°K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>298.2</td>
<td>293.2</td>
<td>293.2</td>
<td></td>
</tr>
<tr>
<td>( P_v ) at ( T_1 ) (mm Hg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.75</td>
<td>60.00</td>
<td>14.25</td>
<td></td>
</tr>
<tr>
<td>Temp, ( T_2 ) (°K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313.2</td>
<td>303.2</td>
<td>313.2</td>
<td></td>
</tr>
<tr>
<td>( P_v ) at ( T_2 ) (mm Hg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>59.25</td>
<td>95.25</td>
<td>41.7</td>
<td></td>
</tr>
<tr>
<td>( A ) (°K)</td>
<td>1784.8</td>
<td>2051.14</td>
<td>1784.31</td>
<td>2141.12</td>
</tr>
<tr>
<td>( B (\log_{10} \text{mm Hg}) )</td>
<td>7.9622</td>
<td>8.3217</td>
<td>7.8638</td>
<td>8.4564</td>
</tr>
</tbody>
</table>

The temperature effect on the diffusivity of chemical in air can be modelled as (Tucker and Nelken 1982):
\[ D_s \propto T^{1.75} \]  

(6.14)

The percentage variation in diffusivity between 20 and 30 °C (293.2 to 303.2 °K) can be calculated as:

\[
\Delta D_s = \frac{303.2^{1.75} - 293.2^{1.75}}{293.2^{1.75}} = 0.060 = 6.0 \% 
\]  

(6.15)

All the evaporation experiments were conducted within this temperature range. Since the variation of diffusivity in the air is less than 6%, it is considered to be negligible in the mathematical modelling. Therefore, the diffusivity values of four selected chemicals at air temperature of 25 °C are used in the modelling. These are 0.03168, 0.03042, 0.03002 and 0.02882 m²/h for benzene, toluene, TCE and PCE respectively.

The regression analysis were performed on Equation 6.12 with experimental data and the known values of diffusivity and the calculated vapour pressure according to Equation 6.13. Table 6.3 shows the calculated thickness of gas film and the turbulent diffusion/ dispersion coefficient in air for benzene, toluene, TCE and PCE.

Figures 6.13 to 6.16 show the best fit lines and the experimental results transformed by Equation 6.12. It should be noted that the radius of the point source is considered to be equal to the radius of the container.

The average value of thickness of gas film for four different chemicals is computed to be 3.63 mm with the standard deviation of 0.114, and the average value of turbulent diffusion/ dispersion coefficient is 0.433 m²/h with the standard deviation of 0.0043. Substitution of these two average values into Equation 3.69 gives:
Figure 6.13 Evaporation of benzene from point source under stagnant air condition
Figure 6.14 Evaporation of toluene from point source under stagnant air condition
Figure 6.15 Evaporation of TCE from point source under stagnant air condition
Figure 6.16 Evaporation of PCE from point source under stagnant air condition
Table 6.3 Regression Results for Evaporation of Chemicals into Quiescent Air

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Toluene</th>
<th>TCE</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of gas film (mm)</td>
<td>3.57</td>
<td>3.78</td>
<td>3.66</td>
<td>3.52</td>
</tr>
<tr>
<td>Turbulent Diffusivity (m²/h)</td>
<td>0.437</td>
<td>0.435</td>
<td>0.427</td>
<td>0.433</td>
</tr>
<tr>
<td>Correlation Coefficient, R</td>
<td>0.9899</td>
<td>0.9910</td>
<td>0.9859</td>
<td>0.9988</td>
</tr>
</tbody>
</table>

\[
N_e = \frac{P_v M_w}{R_e T} \frac{0.866 D_g}{3.144 \times 10^{-3} + r D_g} \quad (6.16)
\]

Equation 6.16 was then used to calculate the evaporation rate of four selected chemicals from four glass containers of different diameters. Figure 6.17 shows the predicted values against the experimental results of evaporation rate under stagnant air condition.

6.4.2 Evaporation of Pure Chemicals under Strong Wind Condition

Strong wind can blow away any vaporized chemicals above the liquid pool and, therefore, the resistance of the mass transport in the bulk air is negligible. Chemical concentration in the bulk air (background level) is usually close to zero. The evaporation rate is controlled by the molecular diffusion of the chemical in gas film. Strong wind also reduces the thickness of the gas film and consequently increases the evaporation rate. A mathematical model was developed to predict the evaporation process under this
Figure 6.17 Predicted evaporation rate versus measured evaporation rate under stagnant air condition
condition. The experimental results of evaporation of four selected chemicals in presence of 5 m/s wind were used to verify and calibrate this model. Table 6.4 shows the calculation of thickness of gas film for each experiment, using Equation 3.71. The average values of gas-film thickness were computed to be 9.50*10^{-4}, 9.74*10^{-4}, 9.80*10^{-4} and 9.38*10^{-4} m with the standard deviations of 5.80*10^{-5}, 2.44*10^{-5}, 3.03*10^{-5} and 1.02*10^{-4} m for benzene, toluene, TCE and PCE respectively. These values are close to each other and their average value is computed to be 9.605*10^{-4} m (0.9605 mm) with the standard deviation of 1.98*10^{-3} m (0.0198 mm). Substitution of \( \delta_s \) equal to 9.605*10^{-4} m into Equation 3.71 gives:

\[
N_f = 1041 \frac{P_r M_w D_s}{R_s T} 
\]  \hspace{1cm} (6.17)

Equation 6.17 then was used to predict the experimental results conducted in this study. The calculated values of evaporation rate according to Equation 6.17 and the measured values in this study, plotted in Figure 6.18, show good agreement.

The evaporation equations developed above can be used with confidence to predict the evaporation rate of pure chemicals from point source. Knowing the evaporation rate, the amount of chemicals vaporized within a certain period can be calculated.

For the evaporation of a chemical mixture, the evaporation rate of each component is no longer equal to the rate when its pure state is used. The total evaporation rate of the chemical mixture can be estimated by considering the concentration weighted rate calculated for each component by using the above developed equations (Mackay and Shiu 1990).
Table 6.4 Computation of Gas-Film Thickness for Evaporation of Four Selected Chemicals at 5 m/s Wind Velocity

<table>
<thead>
<tr>
<th>Chemical</th>
<th>( N_r ), g/m²/h</th>
<th>Temp, °K</th>
<th>( M_w ), g/mol</th>
<th>( P_v ), mmHg</th>
<th>( D_g ), m²/h</th>
<th>( \delta_g ), m</th>
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CHAPTER SEVEN

CONCLUSIONS

The mass transport of high volatility organic compounds from liquid phase into air phase is an important pathway to determine the distribution of these chemicals in different environmental compartments when these chemicals are discharged into water bodies or when the spill occurs. The results presented in this dissertation are based on a comprehensive investigation of the mass transfer under various turbulent conditions. The following conclusions are drawn:

7.1 Volatilization Process

1. Bulk turbulence in water phase can significantly affect the transport of chemical solute from water into air (volatilization process). Prevailing resistances to the transport vary with the water bulk turbulence condition. Four conditions are identified as ideal stagnant condition, near stagnant condition, completely mixed condition and completely mixed condition with broken film.

2. Under ideal stagnant condition, a theoretical model to predict the volatilization has been developed by solving an appropriate Fick’s diffusion differential
equation. The model is further simplified to an approximate equation with a relative error of 9.5%. This simplified model is an exponential function in terms of the volatilization rate constant and time which is similar to the model for completely mixed condition (first order kinetic equation). However, the rate constant under ideal stagnant condition is inversely proportional to the square of water depth, instead of water depth multiplied by liquid-film thickness for completely mixed condition, since the entire stagnant water depth behaves like the liquid-film.

3. The experiments were conducted under a near stagnant condition. It was found that the mass transfer process followed first order kinetic equation with the volatilization rate constant being higher than the values predicted by the model for ideal stagnant condition. In addition, the dependence of rate constant on water depth for benzene under tested condition was found to be inversely proportional to the 1.81th power, against 2.0 for ideal stagnant condition and 1.0 for completely mixed condition.

4. A conceptual model for the volatilization of chemicals from water under completely mixed condition with broken film, based on a surface renewal concept, has been proposed. This mathematical model can predict the volatilization rate constant under different turbulent intensities (expressed as the velocity gradient, $G$) and different surface area to volume ratios. This model has been verified and calibrated by the experiments conducted in the laboratory on four different chemicals from four glass columns with different depths. The water bulk turbulence significantly accelerates the rate of the volatilization process, i.e., the higher the turbulent intensity, the faster the chemical will go into the air phase.
7.2 Evaporation

1. Evaporation of pure chemicals from a point source into quiescent air condition has been investigated. It was found from the laboratory experiments that the vaporized mass of chemical has a linear correlation to the time elapsed. A mathematical model incorporating the size of the point source, vapour pressure, diffusivity, molecular mass of the chemical and air temperature has been developed to predict the evaporation rate. This model has been verified and calibrated by the experimental results for all the selected chemicals. The thickness of gas film and the turbulent diffusion/dispersion coefficient under this condition were determined to be 3.63 mm and 0.433 m²/h with the standard deviation of 0.114 mm and 0.0043 m²/h, respectively. It was observed that the increase in size of the point source decreased the evaporation rate per unit surface area under this condition.

2. Evaporation of pure chemicals from a point source under windy conditions (5 m/s) has also been investigated. It was found that wind can dramatically increase the evaporation rate (4 or 5 times) by reducing thickness of gas film and eliminating the mass transport resistance in bulk air phase. A mathematical model has been developed to predict the evaporation rate and it has been verified and calibrated by the experimental results. The thickness of gas film was determined to be 0.9065 mm with the standard deviation of 0.0198 mm. It was found that the evaporation rate was independent of the size of point source under this condition.
REFERENCE


trihalomethanes," *Journal AWWA*, April, 138-146.


NOMENCLATURE

\( A \)  surface area, \( L^2 \)

\( a \)  half size of broken surface element, \( L \)

\( b \)  vertical depth of the blades, \( L \)

\( C \)  local chemical concentration, \( M/L^3 \)

\( C_D \)  drag coefficient = 1.8

\( C_f \)  chemical concentration at boundary between gas-film and bulk air, \( M/L^3 \)

\( C_g \)  chemical concentration in gas phase, \( M/L^3 \)

\( C_{i,g} \)  chemical concentration at interface on gas-film side, \( M/L^3 \)

\( C_{i,l} \)  Chemical concentration at interface on liquid-film side, \( M/L^3 \)

\( C_L \)  chemical concentration in water bulk, \( M/L^3 \)

\( C_{L,avg} \)  water-depth-weighted average concentration in the water column, \( M/L^3 \)

\( C_l \)  Chemical concentration in liquid phase, \( M/L^3 \)

\( C_o \)  initial concentration of chemical in water bulk, \( M/L^3 \)

\( C_t \)  average concentration obtained experimentally at time \( t \), \( M/L^3 \)

\( C_v \)  chemical concentration in vapour phase after equilibrium, \( M/L^3 \)

\( C_w \)  chemical concentration in water phase after equilibrium, \( M/L^3 \)
\(C(t)\)  average concentration obtained from the model, M/L^{3}
\(D'_{t}\)  molecular diffusivity of chemical in water, L^{2}/T
\(D_{t}\)  molecular diffusion of the chemical in gas phase, L^{2}/T
\(D_{l}\)  molecular diffusion of the chemical in liquid phase, L^{2}/T
\(D'_{l}\)  molecular diffusivity of oxygen in water, L^{2}/T
\(d\)  surface diameter of the container, L
\(E\)  kinetic energy of the turbulence, J/L^{3}
\(G\)  velocity gradient, T^{-1}
\(h\)  depth of water column, L
\(k'_{f,eld}\)  field volatilization rate constant of chemical, T^{-1}
\(k'_{l,ab}\)  volatilization rate constant of chemical measured in the laboratory, T^{-1}
\(k_{e}\)  mass transfer coefficient for eddy diffusion, L/T
\(K_{g}\)  overall mass transfer coefficient for the gas-phase, L/T
\(K_{l}\)  overall mass transfer coefficient for the liquid-phase, L/T
\(k_{g}\)  gas-phase exchange coefficient, L/T
\(k_{l}\)  observed k value, T^{-1}
\(k_{l}\)  liquid-phase exchange coefficient, L/T
\(k_{m}\)  mass transfer coefficient, L/T
\(k'_{f,ield}\)  field reaeration rate constant, T^{-1}
\(k'_{l,ab}\)  reaeration rate constant measured in laboratory, T^{-1}
\(k_{i}\)  slip factor = 0.25
\(\bar{k}\)  average observed value, T^{-1}
$\dot{k}_i$  model value of $k$, T\(^{-1}\)

$L_e$  average size of the energy-containing eddies, L

$M_w$  molecular mass of the chemical, M/mole

$\dot{m}$  mass transfer rate of the chemical across the surface, M/T

$N$  $\dot{m}/A = $ mass transfer flux, M/T/L\(^2\)

$N_R$  mass flux at radius $R$ in the radial direction, M/L\(^2\)/T

$N_{rev}$  revolution speed of the shaft, T\(^{-1}\)

$n$  number of moles of the chemical in the volume $V$

$n_b$  number of the blades installed in each column

$P$  partial pressure of the chemical in the gas phase, M/L/T\(^2\)

$P_v$  vapour pressure of the chemical, M/L/T\(^2\)

$R_g$  ideal gas constant

$r$  surface renewal rate constant, T\(^{-1}\)

$r_b$  effective radius of the blades, L

$S_e$  standard error of estimate

$S_k$  standard deviation

$s$  mean fractional rate of production of fresh surface, T\(^{-1}\)

$T$  temperature in K

$t_e$  time of exposure, T

$u'$  turbulent intensity, L/T

$u_x$  dx/dt, L/T

$V$  volume, L\(^3\)
\( V_b \)  
molar volume of the chemical at its normal boiling point, mm\(^3\)/mol

\( \nu \)  
degrees of freedom

\( \nu_w \)  
wind velocity, L/T

\( W \)  
mass of the chemical in the volume \( V \), M

\( x \)  
horizontal coordinate, L

\( y \)  
vertical coordinate, L

\( \beta \)  
fraction of recoverable turbulent energy

\( \gamma_r \)  
activity coefficient in vapour;

\( \gamma_w \)  
activity coefficient in water;

\( \delta_g \)  
thickness of the gas film, L

\( \delta_l \)  
thickness of the liquid film, L

\( \varepsilon \)  
energy dissipation

\( \theta \)  
exposure time of the surface elements, T

\( \mu \)  
viscosity of the water, M/L/T

\( \mu_w \)  
water viscosity, g/mm-s

\( \rho \)  
water density, M/L\(^3\)

\( \phi \)  
surface age distribution function, T\(^{-1}\)

Note: In dimensions for these notations, M indicates mass, L indicates length and T indicates time.
VITA AUCTORIS

Jian Peng was born on May 5, 1958 in Beijing, P.R. China. He obtained his B.Sc. in Civil Engineering from Beijing Civil Engineering and Architectural Institute in 1982 and his M.Sc. in Environmental Engineering from Tsinghua University, Beijing, in 1984.

He worked as a process engineer in the Engineering Design & Research Institute, Ministry of Machinery & Electronics, Beijing from 1984 to 1987 and served as a project engineer in Chinese Academy of Environmental Sciences, Beijing from 1987 to 1989.

In 1989, he enrolled in the Faculty of Graduate Studies at the University of Windsor in a program leading to the degree of Doctor of Philosophy in Environmental Engineering.