1988

Behaviour of five organic priority pollutants in aqueous environments.

Glenn R. Chodola

University of Windsor

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BEHAVIOUR OF FIVE ORGANIC PRIORITY
POLLUTANTS IN AQUEOUS ENVIRONMENTS

by

Glenn R. Chodola

A Thesis
submitted to the
Faculty of Graduate Studies and Research
through the Department of
Civil and Environmental Engineering in Partial
Fulfillment of the requirements for the Degree
of Master of Applied Science at
the University of Windsor

Windsor, Ontario, Canada

1988
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To my wife Sandra
ABSTRACT

Laboratory studies were undertaken to evaluate several processes that influence the behaviour and fate of synthetic organic chemicals in aqueous environments. Five toxic organic priority pollutants: benzene, methylene chloride, tetrachloroethylene, toluene and trichloroethylene, were investigated in order to determine their susceptibility to the transformation processes of direct photolysis and/or hydrolysis. In addition, benzene, methylene chloride and toluene were examined for volatilization from water and mass flux movement by diffusion into water.

The experimental findings for direct photolysis indicated that the susceptibility was negligible for all the selected organic compounds. Also, all the organics were found to be hydrolytically stable over the range of initial concentrations employed in both acidic and basic environments.

Benzene, methylene chloride and toluene exhibited relatively rapid rates of volatilization and these rates were significantly influenced by the area to volume ratio, A/V. The overall liquid film coefficients, $K_{OLW}$, at the water-air
interface for benzene, methylene chloride and toluene were observed to be 0.029, 0.003 and 0.027 m/h, respectively, under the specified conditions.

The mass flux experiments indicated that under quiescent conditions, the mass transfer occurring at the water-chemical interface of a submerged pool of methylene chloride was minimal. For benzene and toluene, the mass transfer into the water column occurred in the early stage of the study while these floating chemicals were volatilizing into the atmosphere.
ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude and appreciation to his advisor Dr. N. Biswas for his encouragement, guidance and advice in the development of this thesis. A special thanks is also extended to Dr. J.K. Bewtra for his invaluable advice and input during the author’s research investigation.

Many thanks go to my wife Sandra for her support and patience during the trying times encountered throughout this ordeal.

Finally, acknowledgment is also due to the Civil Engineering Department for the use of their facilities and the Natural Sciences and Engineering Research Council of Canada in their financial assistance provided for this project.
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CHAPTER ONE
INTRODUCTION

1.1 Background

In North America, a large quantity of synthetic organic chemicals is produced annually. During their manufacture, transportation, use and disposal, significant quantities are released into different environmental compartments. This has led to widespread contamination of certain vital natural resources with organic compounds. In the United States, organic chemical contamination of the groundwater has become a serious problem. Approximately 40% to 50% of the population in the United States relies on groundwater as a source of drinking water (Hutchins et al., 1985). Recent studies indicate that a number of these water supplies are contaminated with volatile organic chemicals (Barbash and Roberts, 1986). Many of these organic compounds can be toxic to humans when present in large quantities or concentrations. However, even exposure to only trace levels of organics can be hazardous to human health because many show evidence of being carcinogenic to animals or humans (Environment Canada, 1984-A, Federal Register, 1985, WHO, 1984-A and WHO, 1985-B).
It has been suggested that up to $18 \times 10^9$ kg of organic chemicals enter the environment annually worldwide (Iliff, 1972) and still the knowledge concerning the environmental fate and effects of many of these compounds is limited (Hutchins *et al.*, 1985). Therefore, it is important that a sufficient understanding is obtained on organic chemicals for their transformations and physical transport pathways in the environment.

1.2 Scope of the Study

A substantial amount of research has been conducted on the degradation and transport of synthetic organics in the last twenty years. However, much of this work has been limited to organic insecticides and herbicides in typical agricultural soil material. Little work had been done with industrial organics in sediment-water systems (Gambrell *et al.*, 1984). It is important to know the fate of these industrial organic chemicals in surface waters since many of these compounds can have a detrimental impact on the environment and pose serious threats to human health. Only in recent years has investigation begun to determine the persistence and degradation of industrial organic compounds in water systems (Gambrell *et al.*, 1984).

It is reported that the net degradation of chemicals in the environment depends both on the physical and chemical properties of the compound, on the reaction conditions and
transport patterns imposed by the environment itself (Wolfe et al., 1980). In aquatic environments, transformation and physical transport represent two key processes that influence the fate of organic chemicals. Transformation or degradation of a compound in the environment results from three main mechanisms: microbial degradation, photochemical degradation and chemical degradation (Howard et al., 1978). Microbial degradation is most important for compounds that are released into soil media. Photolysis is an important parameter that can influence the behaviour and fate of chemicals in the environment (Reimers and Anderson, 1983). Chemical transformation by hydrolysis can also be considered a significant parameter in degrading organic compounds in the environment. Two important physical transport processes of organic chemicals are volatilization from water and mass flux movement by diffusion into water.

The purpose of this research was to investigate the fate of five selected volatile industrial organics in aqueous solutions through a laboratory study using two transformation and two physical transport processes. The main objectives of the research are to:

(i) Determine if the selected volatile organics are susceptible to the transformation processes of direct photolysis and/or acid-base hydrolysis.

(ii) Determine their rate of volatilization from water under varying area to volume ratios.
(iii) Examine the flux movement of the selected chemicals into water under quiescent conditions.

1.3 Volatile Organics Selected for Study

The five volatile industrial organics selected for this investigation are: benzene, methylene chloride, tetrachloroethylene, toluene and trichloroethylene. These organic chemicals were chosen on the basis of their extensive use in domestic and industrial applications. As a direct result of this wide use, many groundwater aquifers have been found to be contaminated with one or more of these organic compounds not only in North America, but also worldwide (Barbash and Roberts, 1986, La Poe, 1985, Petura, 1981, Sorrell et al., 1985 and Westrick et al., 1984). It is likely that as water sampling programs become more encompassing, additional water supplies polluted by these organics will be discovered.

The selected volatile chemicals are all on the list of priority pollutants established by the U.S. Environmental Protection Agency, USEPA. All these chemicals have been placed in category Rank 4, which includes pollutants that are persistent but nonaccumulative in the environment and are toxic to humans in direct exposure (Chapman et al., 1982).
CHAPTER TWO

BACKGROUND AND LITERATURE REVIEW

Pertinent background information on the selected organic chemicals is reviewed in this chapter.

2.1 Organic Chemicals

Organic compounds are a class of chemicals that always contain carbon, C, and few other elements, such as: oxygen, O; hydrogen, H; nitrogen, N; and chlorine, Cl. An immense number of substances contain carbon, there are more than five million known organic compounds (Ouellette, 1984). The reasons why carbon forms so many compounds are: (i) carbon bonds are quite stable, (ii) they form strong covalent bonds with many other atoms and (iii) carbon atoms can concatenate, i.e. they have the ability to combine with one another to form chain like structures (Ouellette, 1984). Also, the molecular masses of organic compounds may be very high, often well over 1000 (Sawyer and McCarty, 1978).

Volatile organics can be described as organic compounds that have an inherently high Henry’s Law constant. Henry’s Law constant, H, is the ratio of a compound concentration in air to its concentration in water at equilibrium. It is known
that higher the pH value, the greater is the tendency for a chemical to volatilize (Namkung and Rittmann, 1987). In addition, most volatile organic chemicals have a molecular mass less than 1000. In this study, the selected volatile organic chemicals all have molecular masses less than 175.

2.2 Uses and Properties of the Selected Organics

In this section, a brief review of the major uses of the five selected chemicals, along with some of their important physical properties, are given.

2.2.1 Benzene

Benzene is a colourless, flammable liquid with a gasoline-like odour and is used as an additive in motor fuels, as a solvent and as a chemical intermediate (Keil, 1978). Benzene is an aromatic organic compound. In Canada, benzene is produced only in Ontario and Quebec where a total of 566,500 tonnes were manufactured in 1980 (Environment Canada, 1984-A). Table 2-1 displays some of the important physical properties of benzene.

2.2.2 Methylene Chloride

Methylene chloride, a nonflammable, colourless liquid with an ethereal odour, is widely used as a multipurpose solvent and paint remover (Keil, 1978). Methylene chloride is an unsaturated chlorinated aliphatic compound. World produc-
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<thead>
<tr>
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<th>Chemical Formula</th>
<th>Molecular Mass</th>
<th>Henry's Law Constant*</th>
<th>Vapour Pressure* mm Hg</th>
<th>Density* g/mL</th>
<th>Solubility* mg/L</th>
<th>Reference</th>
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<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>78.12</td>
<td>0.306</td>
<td>75.8</td>
<td>0.877</td>
<td>1800⁺</td>
<td>Environment Canada, 1984-A</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yurteri et al., 1987</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>CH₂Cl₂</td>
<td>84.93</td>
<td>0.077</td>
<td>349</td>
<td>1.324</td>
<td>20000⁺</td>
<td>WHO, 1984-A</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yurteri et al., 1987</td>
</tr>
<tr>
<td>Tetrachloro-</td>
<td>C₂Cl₄</td>
<td>165.82</td>
<td>0.535</td>
<td>14</td>
<td>1.622</td>
<td>150⁺</td>
<td>WHO, 1984-B</td>
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<tr>
<td>ethylene</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>92.13</td>
<td>0.244</td>
<td>28.7⁺</td>
<td>0.863</td>
<td>515⁺</td>
<td>WHO, 1985-A</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yurteri et al., 1987</td>
</tr>
<tr>
<td>Trichloro-</td>
<td>C₂HCl₃</td>
<td>131.40</td>
<td>0.430</td>
<td>57.8</td>
<td>1.464</td>
<td>1070⁺</td>
<td>WHO, 1985-B</td>
</tr>
<tr>
<td>ethylene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yurteri et al., 1987</td>
</tr>
</tbody>
</table>

* at 20°C
⁺ at 25°C
tion of methylene chloride in 1980 amounted to 570,000 tonnes (WHO, 1984-B). Table 2-1 presents pertinent data on its physical properties.

2.2.3 Tetrachloroethylene

Tetrachloroethylene is a nonflammable, colourless liquid compound that has an ethereal odour (Keil, 1978) and is an unsaturated chlorinated aliphatic compound. It is principally used as a solvent in the dry-cleaning and textile industries; another important use is in metal degreasing. World production in 1974 amounted to 1,000,000 tonnes (WHO, 1984-A). Table 2-1 lists some of the important physical properties.

2.2.4 Toluene

Toluene is a volatile liquid that is flammable and explosive (Keil, 1978) and is an aromatic compound. It has great importance as an intermediate chemical and as a solvent. Up to 95% of the toluene produced annually in the U.S. is blended directly into gasoline as a component to increase the octane rating (WHO, 1985-A). In Canada, toluene is produced in Ontario, British Columbia and Quebec. Domestic production in 1982 totaled 470,000 tonnes (Environment Canada, 1984-B). Some physical properties of toluene are presented in Table 2-1.
2.2.5 Trichloroethylene

In its pure state, trichloroethylene is a colourless liquid with a characteristic, slightly sweet odour (Keil, 1978) and is an unsaturated chlorinated aliphatic compound. A major use of trichloroethylene is in metal degreasing; other significant applications are found in textile cleaning and many household products such as spot removers and rug cleaners (Love Jr. and Eilers, 1982). World production in 1979 amounted to 450,000 tonnes (WHO, 1985-B). Some physical properties of trichloroethylene are listed in Table 2-1.

2.3 Toxicity of the Selected Organics

For completeness, only limited information is presented in this section on the toxicity effects of these organics on human health. For a more comprehensive understanding of their toxicity to animals or humans, the reader is referred to the references provided.

Toxicity is defined as the capacity of a specific chemical or physical agent to produce an adverse effect on living organisms (Wallace, 1978). A number of terms are used in various countries to express the level of contamination of pollutants in drinking water that are considered to be an acceptable risk for human consumption. The term used by the USEPA is maximum contaminant levels, MCLs, which are enforceable standards that are based on the treatment technology costs and some other feasibility factors. In Canada, the
equivalent terminology employed is maximum acceptable limit, MAL, which are not legally enforceable in the majority of Canadian provinces (Sayre, 1988). The USEPA was recently authorized to set national regulations concerning MCLs and to establish proposed MCLs for certain volatile organic compounds, VOCs, in drinking water. Table 2-2 displays a comparison of the USMCLs to CDNMALs regulations for certain VOCs in drinking water.

<table>
<thead>
<tr>
<th>Compound</th>
<th>USMCLs mg/L</th>
<th>CDNMALs mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.005*</td>
<td>NS+</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>0.005*</td>
<td>-</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>0.005</td>
<td>NS+</td>
</tr>
<tr>
<td>Toluene</td>
<td>2*</td>
<td>-</td>
</tr>
</tbody>
</table>

* proposed by EPA
+ no standard

The organic chemicals that have shown evidence of being carcinogenic to animals or human beings include benzene, tetrachloroethylene and trichloroethylene (Environment Canada, 1984-A, Federal Register, 1985, WHO, 1984-A and WHO, 1985-B).

Animal-experiment data are inadequate for assessing whether or not methylene chloride should be considered carcinogenic to human beings (WHO, 1984-B). At present, toluene
is not considered to be a carcinogenic chemical. However, long-term occupational exposure to toluene and abuse of it may be associated with permanent pathological changes and further investigations are justified (WHO, 1985-A).

2.4 Transformation Processes

The ensuing sections review the two transformation processes, photolysis and hydrolysis, that were used in conducting the investigations on the selected organics.

2.4.1 Photolysis

"Phototransformation" or "photolysis" is simply a light induced change in the structure of a molecule. In the natural environment, sunlight is the source that provides the incident light required to initiate a photochemical reaction in a compound. Photolysis of a contaminant in an aquatic environment appears to be an important process that may have a considerable effect on its persistence and degradation. Many organic chemicals introduced into the environment absorb sunlight and undergo transformation to new molecular species (Mill and Mabey, 1985). This is especially true of atmospheric contaminants and many organic pesticides (Howard et al., 1981).

There are two main photochemical processes that account for transformation of pollutants in aquatic environments. One of these is direct photolysis. This involves direct ab-
sorption of light by the pollutant followed by a chemical reaction. In deionized water, direct photolysis is the only mechanism for photochemical transformation (Zepp and Cline, 1977). The second process is indirect photolysis which involves absorption of light by a "sensitizer" molecule followed by energy transfer to a molecule of another species that does not absorb light in the same wavelength region (Zepp, 1980).

The environmental phototransformation behaviour of a chemical can be determined by conducting an aqueous photolysis test. This involves exposing aqueous solutions of the contaminant to either sunlight or an artificial light source for a specified length of time. In order to find the reaction rate, samples are withdrawn periodically and the reduction in chemical concentration is determined. Since photolysis reactions are assumed to be described by a first order rate expression (Zepp, 1980), the reduction in concentration follows a general equation of the form (ASTM, 1982):

$$\frac{P}{P_0} = e^{-kPt} \quad (2-1)$$

or

$$\ln P = -kPt + b' \quad (2-1a)$$

where,

- $P_0$ = initial concentration of parent chemical,
- $P$ = concentration of parent chemical,
- $k_p$ = photolysis first order rate constant,
- $t$ = time,
- $b'$ = natural log of the concentration of the parent chemical at time zero = $\ln P_0$
The rate data can be expressed in terms of half-lives, \( t_{1/2} \), which is the time required for the chemical concentration to decrease to half its initial value by using the following equation (ASTM, 1982):

\[
t_{1/2} = \ln \frac{2}{k_p} = \frac{0.693}{k_p}
\]  

(2-2)

The data obtained from this test can give an indication of the potential for or susceptibility to direct photolysis of a chemical in a relatively short time span. If a significant disappearance of the parent chemical, say greater than 10%, is observed over a short time span, then direct photolysis would represent a significant degradation pathway. Therefore, further testing through a more complex investigation procedure would be justified. This would involve calculating the reaction quantum yield and determining the light intensity. The light intensity can be determined by using an actinometer, which is a compound that photoreacts with a known quantum yield (Howard et al., 1981), that is irradiated at the same time as the samples. One widely recommended actinometer for use in laboratory photochemical studies is potassium ferrioxalate (Calvert and Pitts, 1966). The reaction quantum yield, which defines the efficiency of the photochemical process (Mill and Mabey, 1985), can then be readily calculated from these data using established equations.
A brief description of this process is presented in order to further discuss the role of photodegradation of organic pollutants. The wavelengths that produce most photochemical reactions fall into the ultraviolet, UV, range of 40-400 nm. However, essentially no light with wavelengths less than 290 ± 10 nm is received at the earth's surface because of atmospheric absorption and molecular scattering (Zepp and Cline, 1977). Thus, 300-400 nm is the most significant range of UV wavelengths since it would be principally responsible for the phototransformation of pollutants in the environment.

The following two basic laws govern photochemical reactions (Calvert and Pitts, 1966):

(i) only light absorbed by a molecule is responsible for a reaction,

(ii) one molecule is activated for each light photon or quantum absorbed in a system.

While the first law is self explanatory, a further development of the second law is required. When a molecule absorbs light at a certain wavelength, the resulting product is an excited molecule that possesses energy. This energy, E, kJ/mole, can be determined from the wavelength of the absorbed light, λ, nm, using the following equation (Mill and Mabey, 1985):
\[ E = N \ h \ c \ \lambda^{-1} = 1.20 \times 10^5 \ (\lambda^{-1}) \] 

(2-3)

where,

- \( N \) = Avogadro's number, molecules/mole
- \( h \) = Planck's constant, erg-s
- \( c \) = velocity of light, m/s.

Energies corresponding to some UV wavelengths were calculated using Eq. 2-3 and are presented in Table 2-3.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Energy (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>480</td>
</tr>
<tr>
<td>300</td>
<td>400</td>
</tr>
<tr>
<td>350</td>
<td>343</td>
</tr>
<tr>
<td>400</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 2-3 shows that as the wavelength increases, the available energy decreases for those molecules that absorb in the UV range. As mentioned previously, light with wavelength less than approximately 300 nm does not reach the earth's surface. Therefore, Table 2-3 indicates that for all practical purposes, the energy provided by natural sunlight will not exceed about 400 kJ/mole.
The energy requirements for certain chemical bond dissociations were taken from Neely (1980) and are tabulated in Table 2-4.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy for Cleavage (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-OH</td>
<td>495</td>
</tr>
<tr>
<td>C-H</td>
<td>436</td>
</tr>
<tr>
<td>C-Cl</td>
<td>335</td>
</tr>
<tr>
<td>HO-OH</td>
<td>201</td>
</tr>
</tbody>
</table>

Table 2-4 shows that the energy required to break a C-H bond is higher than the maximum energy provided by the sunlight. Therefore, chemicals such as benzene and toluene, which contain these bonds, would not be expected to experience direct photolysis in natural aqueous environments. However, chemicals such as methylene chloride, tetrachloroethylene and trichloroethylene that contain C-Cl bonds and which would be capable of absorbing light at the proper wavelength, could be broken down under the influence of UV light. Consequently, many chlorinated chemicals would be susceptible to transformation by direct photolysis in aquatic environments.
Wavelength distribution and incident light intensity are the most important factors affecting a material's rate of photolysis (ASTM, 1982). Other environmental variables that influence the photoprocess are temperature, pH, dissolved organics, suspended sediments and solvent. Since the conversion of a ground state molecule to its excited state has no temperature dependence, it is therefore desirable to have a temperature control of ± 2°C over the process in order to achieve an accurate rate constant for the chemical under study (Mill and Mabey, 1985). The effect of pH of the reaction solution on the phototransformation of a pollutant is not fully understood, some can be pH dependent while others are not. The humus component of the dissolved organic matter in natural water can affect the aquatic photoreactions of certain chemicals in two ways, by attenuating sunlight and by providing "sensitizer" molecules (Zepp et al., 1984). Suspended sediments can have a negative effect on the photoreaction because they can shield the pollutant from the available light and cause scattering (Miller and Zepp, 1979). The use of co-solvents should be avoided because they could donate sensitizer molecules and thus the reaction might not involve only direct photolysis. Also, it is quite possible that a compound that does not absorb in a solvent such as hexane, may absorb light in the natural environment (Howard
et al., 1981). Therefore, if possible, the only solvent that is employed in direct photolysis studies of a contaminant is water.

With the concern over the possible adverse affects of many pollutants that enter the environment, numerous studies have been carried out on sunlight-induced photoreactions of organic chemicals. Unlike the aquatic environment, degradation by photolysis in the earth's atmosphere is the dominant process (Zepp, 1980). Many industrial organics have been thoroughly investigated as to their rates of atmospheric photodecomposition and the by-products produced (Altshuller and Bufalini, 1971, Darnall et al., 1976 and Spence et al., 1976). Both benzene and toluene have been found to photooxidize at a rapid rate in the atmosphere (Davis et al., 1975). Dilling et al. (1976) observed that under simulated atmospheric conditions, the time required for 50% disappearance of tetrachloroethylene and trichloroethylene, i.e. half-life, was about 14 and 3.5 hours, respectively. The half-life of methylene chloride in the troposphere is estimated to be in the range of one to four months (Dilling and Goersch, 1980).

Efforts to understand the photolysis process that can influence the behaviour of organics in water has not kept pace with the corresponding efforts in the field of air pollution, since unlike smog, organic contamination of water cannot be readily detected by the human senses. The majority of
the early studies on direct photolysis of compounds in aqueous solutions have been concerned with organic herbicides and insecticides (Acher, 1982, Khan et al., 1980, Saunders and Mosier, 1980 and Wolfe et al., 1977). This work on agricultural chemicals has provided an insight into the photochemical degradation for this class of organic contaminants. However, the information on direct photolysis of industrial organics in surface waters has not been investigated as extensively.

For benzene and toluene, not much consideration has been given to transformation by direct photolysis as a possible pathway for their elimination from aqueous environments. This is primarily due to their strong C-H bonds, which in order to be dissociated, would require a substantial shift in the UV wavelengths. However, some work has been performed on these two aromatic compounds using indirect photolysis as the elimination process. Mansour (1985) found that in the presence of hydrogen peroxide and wavelengths greater than 290 nm, the substrate disappearance of benzene and toluene is about 25% and 18%, respectively, in a photoreaction time of not more than five hours. With wavelengths less than 290 nm and for the same time period, the disappearance of the two chemicals approximately doubled.

Studies are inconclusive as to whether direct photolysis can degrade trichloroethylene in aqueous solutions (Walker, 1984). A study by Jensen and Rosenberg (1975) in which they
exposed sealed flasks containing either tetrachloroethylene or trichloroethylene to daylight and then comparing against similar systems maintained in the dark, found that there was no significant difference between the two systems in terms of their concentrations. Dilling et al. (1975) performed reactivity studies on five chlorinated compounds in aerated water by exposing 1 mg/L solutions of the compounds to sunlight for a period of twelve months. Dilling et al. (1975) noted that exposure to the natural sunlight had the greatest effect on the reactivities of tetrachloroethylene and trichloroethylene. In these experiments, the solutions in the sealed tubes had a significant headspace. Thus, Dilling et al. (1975) concluded that since these chemicals were volatile from water, part of the reaction had occurred, probably due to oxidation, in the headspace of the vessels.

2.4.2 Hydrolysis

Hydrolysis is a process in which a chemical is transformed to a different compound as the result of a reaction with water, in the absence of light and microorganisms (ASTM, 1983). Hydrolysis can become a significant transformation route for organic chemicals in aquatic environments. The reaction equation that describes this process is:

\[ R - X + H_2O \rightarrow R - OH + X^- + H^+ \]  \hspace{1cm} (2-4)
In this reaction, a chemical transformation occurs in which an organic molecule, \( R - X \), reacts with water to cleave a carbon - X bond in the original molecule and form a new carbon - oxygen bond. The net effect is a direct displacement of \( X \) by \( \text{OH}^+ \), (Neely; 1985). The importance of this reaction is that the end product is usually less toxic and more susceptible to further decomposition by other processes in the environment as compared to the original chemical.

It is generally observed that the rate of hydrolysis of an organic chemical in water follows a first order reaction. A generalized expression for the rate of reaction is given as (ASTM, 1983):

\[
\frac{dC}{dt} = -k_H C \tag{2-5}
\]

where,

- \( k_H \) = hydrolysis pseudo first order rate constant at a specific pH and temperature,
- \( C \) = concentration of chemical,
- \( t \) = time.

Because natural systems are usually buffered, hydrolysis reactions in the environment are generally pseudo first order.

Experimental hydrolytic measurements usually involve maintaining a chemical in acidic and basic solutions at an elevated temperature that is held constant over the period of the study. The stability can be determined by finding the percent disappearance of the parent chemical over the study
period. If less than a 10% reduction of the compound is determined, then it can be considered hydrolytically stable (ASTM, 1983). However, if a significant reduction in the concentration is found, then a rate constant can be determined for the chemical. This can be accomplished by withdrawing samples and monitoring the extent of degradation per unit time over the length of the study. Then a plot of the logarithm of the concentration of the compound versus time results in the experimental data fitting the following form of equation:

\[ \ln C = -k_H t + \ln C_0 \]  
\[ \text{(2-6)} \]

where,

- \( C \) = concentration at time \( t \),
- \( C_0 \) = initial concentration.

Thus, the rate constant for the compound can be obtained from the slope of the line described in Eq. 2-6. The half-life, \( t_{1/2} \), may then be calculated from:

\[ t_{1/2} = \frac{0.693}{k_H} \]  
\[ \text{(2-7)} \]

Hydrolysis experiments are fairly easy to run and the data obtained can be interpreted and related to environmental situations with a high degree of reliability (Howard et al., 1981). The resulting data that are generated from a study
can then provide a sufficient base as to the assessment of the stability or susceptibility to hydrolysis of a chemical in aqueous environments.

The factors that have the most effect on the rate of hydrolysis include pH, temperature, metal-ion catalysis, reaction medium and sediments (Faust, 1977). The temperature and pH of the reaction medium play a significant role in the chemical's ability to experience hydrolysis. Some organic chemicals will only undergo hydrolysis in an extreme pH condition, i.e. only when the reaction medium is acidic or basic in nature. In general, base catalysis appears to be more important than acid catalysis in environmental studies (Mill et al., 1980). The effect of temperature on this process, in the range of 0° to 50°C, is that for every 1°C change there is a 10% change in the rate constant and for a 10°C change, the rate constant will change by a factor of two (Neely, 1985). Therefore, by conducting hydrolysis experiments at elevated temperatures, the susceptibility of the chemical to this process can be determined in a shorter time span than would be required under ambient conditions. It is believed that metal ions do not play a significant role in most hydrolysis reactions of chemicals that occur in the environment (Mabey and Mill, 1978). However, laboratory studies indicate that for certain types of compounds, solution phase metal ion catalysis may be important (Wolfe, 1980). Pearson and McConnell (1975) noted that the reactions of certain
chloroaliphatic compounds, namely tetrachloroethylene and trichloroethylene, were considerably accelerated in water in the presence of metals such as iron. Freshwater systems are characterized by low organic content and low ionic strength (Mabey and Mill, 1978). Thus, the use of distilled water buffers to perform hydrolysis studies is adequate because they closely model freshwater systems. Water with high ionic strength, such as ocean or brackish water, can affect the rate of hydrolysis. The rate can either be accelerated or retarded depending on the substrate, the specific salts and their concentrations (Neely, 1985). Mabey and Mill (1978) found that in most cases, when a massive amount of salt was used, the rate constant had changed by 30% to 40%. The influence of sediments on the hydrolysis rate is a subject that has not been extensively explored and its role on this process needs to be investigated further.

Dilling et al. (1975) carried out experimental reactivity studies on several chlorinated compounds at a 1 mg/L concentration level in aqueous solutions stored in the dark. Their findings indicated that in unbuffered water with pH≈7 and at 25°C, the major reaction for methylene chloride was due to ionic hydrolysis. Dilling et al. (1975) also found that a disappearance in both tetrachloroethylene and trichloroethylene had occurred but noted that no differentiation was made between the simultaneous reactions of oxidation and hydrolysis that transacted in the sealed ampules.
Specific information pertaining to the hydrolysis of benzene and toluene in aquatic environments is not available. However, the benzene group, which include toluene, is considered to be resistant to hydrolysis under ambient conditions since nucleophilic attack of the aromatic ring by water or hydroxide ions will be impeded by its negative charge-density (Neely, 1985).

2.5 Physical Transport Process

The following two sections review the two physical transport processes, volatilization and mass flux, employed in this study on the selected volatile organic chemicals. Also presented in these sections are some theoretical aspects of these two transport processes.

2.5.1 Volatilization from Water

The volatilization of organic chemicals from a water body can be an important mass transfer route from water to air. The volatilization process represents the physical transport of an organic compound through the water-air interface and into the surrounding atmosphere. The volatilization of an organic compound from the water phase to the air phase is dependent on the physical and chemical properties of the compound, the presence of other chemical compounds, the
hydrodynamic and other physical properties of the water body and the physical properties of the atmosphere above the water surface', (Gowda et al., 1985).

The physical and chemical properties of organic chemicals affecting volatilization include: Henry's Law constant, diffusion coefficient, molecular mass and molecular diameter. The volatilization rate is also influenced by the presence of some modifying materials such as: absorbents, electrolytes, emulsions and organic film (Thomas, 1982). The physical properties of a water body that influence the volatilization process are the turbulence, the volume and the exposed surface area. Also, atmospheric conditions, particularly wind speed and stability, affect this process. Temperature affects the vapour pressure and solubility, and thus, influences the volatility of a chemical (Gowda et al., 1985).

The two-film theory of Lewis and Whitman is generally utilized to describe the volatilization of organic compounds from water', (Gowda et al., 1985). The assumptions made in the two-film theory are that the bulk water and air phase are uniformly mixed and both phases are separated by thin film layers of liquid and gas, as represented in Figure 2-1. The movement in the bulk layers is by turbulent transfer and the movement through the film layers is by molecular diffusion (Neely, 1980). These thin film layers provide the major resistance to the mass transfer of a chemical.
Figure 2-1 Schematic of the Two-Film Theory (modified from Gowda et al., 1985)
The two-film theory can be depicted by Fick's first law of molecular diffusion which in differential form, can be expressed as (ASCE et al., 1969):

\[ \text{Total Flux} = \dot{A}j = -D_L \frac{\delta C}{\delta Y_L} \big|_1 = -D_G \frac{\delta C}{\delta Y_G} \big|_2 \quad (2-8) \]

where,

\[ \left( \frac{\delta C}{\delta Y_L} \right)_1 \text{ = concentration gradient through liquid film, kg/m}^2/\text{m}, \]
\[ \left( \frac{\delta C}{\delta Y_G} \right)_2 \text{ = concentration gradient through gas film, kg/m}^2/\text{m}, \]
\[ D_L \text{ = diffusion coefficient through liquid, m}^2/\text{h}, \]
\[ D_G \text{ = diffusion coefficient through gas, m}^2/\text{h}, \]
\[ A \text{ = cross-sectional area, m}^2, \]
\[ j \text{ = mass flux, kg/m}^2/\text{h}. \]

Based on the assumptions that convection is insignificant and the concentrations are in equilibrium on either side of the interface, the mass transfer across the two-layer system represented in Figure 2-2 can be expressed as (Zytner, 1988):

\[ \frac{\delta X}{\delta t} = -A j = D_{OL} A \left( \frac{\delta C}{\delta Y} \right) \quad (2-9) \]

where,

\[ \frac{\delta X}{\delta t} \text{ = mass flow rate, kg/h}, \]
\[ \frac{\delta C}{\delta Y} \text{ = overall concentration gradient, kg/m}^3/\text{m}, \]
\[ D_{OL} \text{ = overall diffusion coefficient, m}^2/\text{h}, \]
\[ t \text{ = time, h}. \]

If the overall liquid mass transfer coefficient, \( K_{OL} \), is defined as \( K_{OL} = D_{OL}/Y \), then Eq. 2-9 can be restated as:

\[ \frac{\delta X}{\delta t} = K_{OL} A (C_L - C_G) \quad (2-10) \]
$C_G \approx 0$

$-A_j = \delta X / \delta t$

Figure 2-2 Schematic of Volatilization Transport
(Zytner, 1988)
where,

\[ C_L = \text{concentration of compound in liquid, kg/m}^3, \]
\[ C_G = \text{concentration of compound in gas, kg/m}^3. \]

The turbulent transfer in the gas phase dissipates the compound's concentration in the air and it can be assumed that \( C_G \) approaches zero. Therefore, Eq. 2-10 can be simplified to:

\[
\frac{\delta X}{\delta t} = K_{OLAC_L} \tag{2-11}
\]

Since \( \delta X = -\delta C_L V \) \( \tag{2-12} \)

where, \( V = \text{bulk liquid volume, m}^3. \)

Therefore, by combining Eq. 2-12 with Eq. 2-11 and dividing through by \( V \) yields:

\[
\frac{\delta C_L}{\delta t} = -K_{OL}(A/V)C_L \tag{2-13}
\]

Rearranging and substituting \( k' = K_{OL}(A/V) \) into Eq. 2-13 gives:

\[
\frac{\delta C_L}{C_L} = -k' \delta t \tag{2-14}
\]

Integrating Eq. 2-14 with the boundary conditions of:

\( C_L = C_0 \) at \( t = 0 \) and \( C_L = C \) at \( t = t \), yields:

\[
\ln(C_L) \bigg|_0^t = -k' t \tag{2-15a}
\]
\[ \ln(C/C_0) = -k't \]  
\[ C/C_0 = e^{-k't} \]  
(2-15b)  
(2-15c)

Setting \( k' = 2.303k \) gives

\[ C/C_0 = e^{-2.303kt} \]  
(2-16)

or \[ C/C_0 = 10^{-kt} \]  
(2-17)

where,

\[ C = \text{final concentration in liquid after time } t, \text{ kg/m}^3; \]
\[ C_0 = \text{initial concentration in liquid, kg/m}^3; \]
\[ k = \text{volatilization rate constant, l/h}; \]
\[ t = \text{time, h}. \]

Equations 2-16 or 2-17 can be used to describe the decay in concentration of a chemical in water through the transport process of volatilization. In this study, the rate of volatilization from water for the chemicals were all developed using the first order reaction of base 10, as expressed by Eq. 2-17.

At atmospheric pressures, the gas phase approaches ideal behaviour and the Henry's law constant, \( H_i \), can be expressed as (Yurteri et al., 1987):

\[ H_i = C_{G,i}/C_{L,i} \]  
(2-18)
where,

\[ H_i = \text{dimensionless Henry's Law constant for component } i, \]
\[ C_{G,i} = \text{equilibrium gas-phase concentration of } i, \text{mole/m}^3, \]
\[ C_{L,i} = \text{equilibrium liquid-phase concentration of } i, \text{mole/m}^3. \]

Yurteri et al. (1987) have pointed out that the absolute value of \( H \) for a given compound varies not only with the equilibrium temperature but also with the chemical composition of the liquid medium. This variation can be as much as 35% in complex mixtures.

The value of \( H \) for a chemical can be used as an indicator of the pollutant's likelihood to volatilize. As mentioned earlier, the greater the \( H \) value, the greater is the tendency for a chemical to volatilize. This relationship is shown in Table 2-5, which was taken from a study by Namkung and Rittmann (1987) on estimating emissions of volatile organic chemicals, VOCs, from wastewater treatment plants, WWTPs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( H ) atm-m^3/mole</th>
<th>Volatilization Losses percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.0046</td>
<td>2.6</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>0.0025</td>
<td>1.5</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>0.0230</td>
<td>83.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.0057</td>
<td>3.2</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>0.0100</td>
<td>69.4</td>
</tr>
</tbody>
</table>
Dilling et al. (1975) conducted evaporation rate studies on several aliphatic chlorinated organic chemicals and showed that evaporation can be rapid for these compounds from water into the atmosphere. Table 2-6 displays the evaporation time required from water for 50% and 90% depletion of certain relevant chemicals as determined by Dilling et al. (1975).

| Compound           | Time for Evaporation from Water
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>minutes</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>21 ± 3</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>27 ± 3</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>21 ± 3</td>
</tr>
</tbody>
</table>

Similarly, both the aromatic organic compounds benzene and toluene also exhibited rapid evaporation from aqueous solutions (Mackay and Leinonen, 1975).

Dilling et al. (1975) noted that the stirring speed had a marked effect on the evaporation rate. With stirring, it took about 25 minutes for 50% depletion of methylene chloride, tetrachloroethylene and trichloroethylene, while without stirring, the time required to achieve a similar
depletion was more than 90 minutes. A study by Rathbun and Tai (1981) showed that by increasing the stirring rate of the water, the mass transfer rates also increased for benzene, methylene chloride and toluene.

Mackay and Yeun (1983) found that as the wind speed was intensified, the overall liquid mass transfer coefficients for both benzene and toluene increased. Dilling et al. (1975) also noted that the wind velocity across the water surface increased the rate of evaporation as compared to still air conditions and lowering the temperature decreased the evaporation of all the chlorinated compounds.

2.5.2 Mass Flux Movement into Water

The term mass flux is a relatively new concept which describes the movement of a chemical through a water body. The basis for this expression can be visualized from a chemical spill that occurs in an aquatic environment. The result would be a pool or blob of the pollutant either floating or sinking, depending on its density, in the water body and then over a period of time, the chemical mass would begin to flow or flux into the liquid phase by diffusion. If the flux movement of a chemical is recorded with time, then a rate of mass transfer for this chemical can be obtained. This value can be useful in choosing the proper remedial actions required for the removal of a contaminant spilled in aqueous environments.
In the literature, limited information is available on the mass flux movement through water for organic chemicals. The term "mass flux" was used by Chan et al. (1986) to define the "dissolved" fraction of certain contaminants from a spill of tetrachloroethylene, PCE, into the St. Clair River. From the research conducted at the University of Windsor, Zytner (1988) found that PCE does moderately diffuse into stagnant water. He developed an empirical equation to describe this flux movement from the resulting experimental data using the Thomas method for BOD coefficient determination. Also, a theoretical equation was developed by Zytner (1988) to describe the mass flow of a compound into water. The following expression which describes the mass flow of a substance into water, as depicted in Figure 2-3, was used in developing the final form of the equation (Zytner, 1988):

$$A_j = \frac{\delta X_j}{\delta t} = K_{OL1}A(C_{is}-C_L) \quad (2-19)$$

where,

- $\delta X_j/\delta t$ = mass flow rate at chemical-water interface, kg/h,
- $K_{OL1}$ = overall liquid film coefficient at chemical-water interface, m/h,
- $A$ = cross-sectional area of vessel, m$^2$,
- $C_{is}$ = saturation concentration of the chemical liquid at the interface, kg/m$^3$,
- $C_L$ = concentration of chemical in water, kg/m$^3$. 
Figure 2-3 Representation of Mass Flux into Water
(Zytner, 1988)
By applying the concept of two-film theory at the chemical-water interface, Zytner (1988) produced the following equation which represents the mass flux of a chemical submerged in a body of water:

\[ \frac{C_F}{C_{is}} = 1 - e^{-K_{OL1}(A/V)t} \]  

(2-20)

where,

\[ C_F = \text{chemical concentration in water at any time, } t, \text{ kg/m}^3, \]
\[ V = \text{volume of the vessel, m}^3, \]
\[ t = \text{time, h}. \]

For a submerged pool of chemical in water, the processes of diffusion into the water and volatilization from water are occurring simultaneously, as shown in Fig. 2-3. Zytner (1988) combined Eqs. 2-10 and 2-19 and wrote a mass balance equation to describe the effect of mass transfer from the submerged compound into the water and subsequent volatilization into the atmosphere. The equation that was ultimately produced to express the combination of these two processes:

\[ \frac{C_L}{C_{is}} = \frac{K_{OL1}}{(K_{OL1} + K_{OL2})} (1 - e^{-(K_{OL1}+K_{OL2})(A/V)t}) \]  

(2-21)

where,

\[ K_{OL1} = \text{overall liquid film coefficient at the chemical-water interface, m/h,} \]
\[ K_{OL2} = \text{overall liquid film coefficient at the water-air interface, m/h,} \]
\[ C_L = \text{concentration of the chemical in water, kg/m}^3, \]
\[ C_{is} = \text{saturation concentration of the chemical in liquid at the interface, kg/m}^3. \]
For PCE, a flux rate of 0.028 kg/m²/d was determined by Zytner (1988). This rate is considered to be a slow rate of transfer. Therefore, it was concluded that in case of a PCE spill into a stagnant water body, there would be sufficient time available to collect the spill of PCE before it diffused into the body of water.
CHAPTER THREE

EXPERIMENTAL PROCEDURE

This chapter describes the procedures, equipment and set-up used for the experiments conducted in this study.

3.1 General

The entire study was divided into four parts. In part one, studies were carried out to investigate the potential for phototransformation of the selected volatile organics in an aquatic environment under laboratory conditions. Part two was designed to see if hydrolysis was a significant transformation path for the organic chemicals in aqueous solutions. The rates of volatilization of the organic compounds across the air-water interface were studied in part three. Finally, part four examined the flux movement of an organic chemical through a column of deionized water under non-turbulent conditions.

3.2 Chemicals

The organic chemicals selected for this study were obtained from Fisher Scientific Co. and BDH Chemicals Ltd. All chemicals were of analytical reagent quality with the highest available purity (99% minimum).
3.3 Photolysis Experiment

Figure 3-1 shows the flowchart used in conducting the direct photolysis experiment. For this part, all five organic chemicals were tested to determine their susceptibility to direct photolysis.

Organic-free deionized water was used in all experiments and it was obtained by passing distilled water through an activated carbon filter and then through a Barnstead Ultrapure DI cartridge. Typical pH readings of the water were 5.5 ± 0.1 and were measured using a pH meter, Model 901, manufactured by Orion Research Inc. Since the presence or absence of oxygen can have an effect on the photochemical process (ASTM, 1982) and since most areas receiving sunlight are aerobic in nature therefore, prior to each photolysis experiment, the deionized water was saturated with air. The measured dissolved oxygen content was typically, 8.8 mg/L as determined by a YSI Model 57 dissolved oxygen meter. All the photolysis experiments were performed at room temperature, 22 ± 2°C.

From previously prepared stock solutions, the organic chemicals were diluted to concentration levels of 1 mg/L and 10 mg/L. The reaction vessels containing the irradiated solutions were fabricated from 23 mm I.D. quartz glass tubing into 35 mL test tubes. Quartz glass was chosen as the material to construct the containers because it allows more than 85% transmission of light of wavelengths greater than
Pure Chemical

Chemical Dose
relevant range
1 and 10 mg/L

Test Solutions
in saturated water
(pH=5.5, temp.=22°C).
Exposed to UV light
for five consecutive
days, with samples
taken at t = 1, 2
and 5 days.

Dark
Control Solutions
in saturated water
(pH=5.5, temp.=22°C).
Samples taken at t =
0, 1, 2 and 5 days.

Samples
analyzed on GC
by static head-
space technique.

Obtained
integrated areas
compared between
test and control
solutions.

If difference is
<10%, no real
potential exists
for phototransformation
of the organic chemical.

Figure 3-1 Flowchart of the Photolysis Experiment
260 nm (Hwang et al., 1987). The dark controls were placed in 15 mL borosilicate glass vials which were securely capped and contained zero headspace.

The laboratory irradiation apparatus consisted of four General Electric fluorescent lights (F15T8.BLB) and unit holders mounted horizontally over a black, rectangular base. This lighting source provided maximum emission at the 366 nm wavelength range (Sargent-Welch, 1985-86) of ultraviolet light. The tubes exposed to light were placed horizontally on the top of the base. Dark controls were placed beneath the base with all sources of light sealed off. A shield enclosed the apparatus to reduce any extraneous light from reaching the exposed solutions and to protect other laboratory personnel from the potentially harmful UV light.

Before placement in the apparatus, the quartz glass tubes containing the test solutions were securely sealed by the following procedure to prevent any losses. First, rubber stoppers were wrapped in aluminum foil before inserting into the filled tubes. Then a 10 mm wide layer of teflon tape was wrapped around the neck of each tube. Finally, adhesive tape was applied to hold the teflon in place. After sealing, a small headspace was always maintained in the vessels. In order to minimize possible losses through volatilization, the bottom end of the test tubes were elevated slightly from the base. The purpose of this was to create a trap in order to contain any chemical build-up in the headspace.
Once the irradiation apparatus was set-up, samples of each organic chemical, at the two specified concentration levels, were exposed to the ultraviolet light source for a period of five days. Exposed samples were withdrawn at time intervals of one, two and five days with the contents from their reaction vessels carefully transferred into 15 mL screw-cap vials to assure that no headspace was created. Parallel dark controls were run in each case with these samples also withdrawn at the above time intervals. Both the exposed and control solutions were stored in a refrigerator at 4 ± 1°C until the experiment was completed. The samples were analyzed following the procedure outlined in Chapter Four.

3.4 Hydrolysis Experiment

Figure 3-2 provides the flowchart for this experiment. All five selected organics were employed to ascertain whether the chemicals could be considered hydrolytically stable.

Buffer solutions at pH 4.00 and 9.20 ± 0.010 were prepared from potassium hydrogen phthalate, 0.05 M and sodium borate decahydrate, 0.01 M, respectively, according to the Standard Methods, (APHA et al., 1985). The pH of the buffer solutions were recorded both before and after a hydrolysis experiment. The difference between the pH readings were all found to be within ± 0.20 of each other. All the hydrolysis tests were run using organic-free deionized water.
Pure Chemical

Chemical Dose
three concentrations
50% & 25% of water sol.;
1 x 10^-4 M.

Acidic Deionized Solutions pH=4

Test solutions at 50°C for 7 days.

Basic Deionized Solutions pH=9

Test solutions at 50°C for 7 days.

Samples analyzed on GC by static head-space technique.

Control solutions at 4°C for 7 days.

Obtained integrated areas compared between their respective samples.

Control solutions at 4°C for 7 days.

If difference is <10%, chemical is hydrolytically stable.

Figure 3-2 Flowchart of the Hydrolysis Experiment
Three initial concentrations were examined at each pH level. Two of the concentration levels were 50% and 25% of the organic chemical's solubility in water. The third level corresponded to $1 \times 10^{-4}$ M, recommended by ASTM (1983). The latter concentration produced a range of 0.04% to 11% of the individual chemical's solubility in water.

In order to obtain the desired concentrations, the organic chemical was added directly to the prepared buffer solutions and thoroughly mixed for a minimum period of 12 hours using a magnetic stirrer. The fortified buffer solutions were then transferred into 15 mL vials with no headspace, and securely sealed by using rubber/teflon coated septums placed in the open-top caps. A minimum of three sample vials were prepared, both for the test and control solutions, for each hydrolysis experiment.

The test solutions in the sealed vials were maintained at a temperature of $50 \pm 1^\circ C$ in total darkness for a period of seven days. The control solutions with zero headspace were stored at $4 \pm 1^\circ C$, also in complete darkness, for the same time period. At the conclusion of the experiment, the test solutions and control samples were analyzed by the procedure described in Chapter Four.
3.5 Volatilization Experiment

Three of the five organic chemicals, namely benzene, methylene chloride and toluene were used to study their rate of volatilization from deionized water.

Five different area to volume ratios, \( A/V \), 6.841, 11.218, 23.941, 33.935 and 42.237 \( 1/m \) were selected. The ratio factor, \( A/V \), represents exposed water area per unit of volume of water. Also, three different concentration levels, 25%, 50% and 75% of the chemical's solubility in water expressed in mg/L, were used.

All the volatilization experiments were conducted in a laboratory fume hood. This was done both to carry away the dangerous organic fumes and to create a constant air velocity, thus causing turbulence over the exposed water area. The velocity was measured using an Alnor Velometer (Type 302) and was found to average about 10 km/h (2.8 m/s). The air velocity and room temperature, 22°C, were kept constant for all experimental runs.

Various area to volume ratios were achieved by using containers of different sizes and shapes. For each run, enough containers were utilized to permit duplicate samples to be taken at the desired time intervals, 30 or 60 minutes. The run periods ranged between 4 and 10 hours. Once a sample was taken, it was poured into 15 mL screw-cap vial with no
headspace. The vials were securely sealed and stored at 4 ± 1°C until analyzed. The analytical procedure is described in Chapter Four.

3.6 Flux Experiment

The same three organic chemicals, benzene, methylene chloride and toluene used in the volatilization experiment were also studied in the mass flux investigation. The flux movement of the pure organic chemical through a stagnant column of water was studied in two 3.5 L and one 8 L cylinders. The 3.5 L cylinders used for benzene and toluene were filled with 3 L of deionized water. For methylene chloride, 4 L of water were used in the 8 L cylinder.

Both benzene and toluene have densities less than water and therefore float when placed in water. A pool of the pure chemical was created by pipetting 300 mL of benzene and toluene into their respective cylinders. In order to minimize turbulence and mixing of the chemicals with the water, they were slowly released down the cylinder wall. The volume of benzene and toluene added represented theoretical concentrations of 42 and 144 times their respective water solubilities. Methylene chloride has a relatively high specific gravity and therefore sinks when placed in water. In order to create a pool of 600 mL, the chemical was pumped into the cylinder with the discharge tube submerged to the bottom of the cylinder. However, the methylene chloride
quickly dissolved the tubing on the pump head. Consequently, a different approach which worked satisfactorily was taken. A piece of tubing was connected to a glass funnel and the outlet end of the tubing was placed at the bottom of the cylinder. The chemical was poured into the funnel and, with the aid of clamps, was allowed to flow at a slow rate. This ensured that a minimum agitation was created at the bottom of the cylinder. The volume of methylene chloride introduced represented a theoretical concentration of 10 times its solubility. This experiment was conducted under the fume hood with quiescent conditions maintained in all the cylinders.

The flux experiments were conducted for a period of 24 days. Duplicate samples were taken at the same time every day. The samples for benzene and toluene were withdrawn by a port, located 0.10 m off the bottom of the cylinders. Samples of methylene chloride were drawn by means of a pipette. The sampling location for methylene chloride was at approximately the mid-point between the chemical-water interface and the water surface in the cylinder. The one sampling point employed to represent the concentration of the chemicals in their cylinders was based on the results from work performed by Zytner (1988) on the mass flux movement of tetrachloroethylene into water. He determined from the analysis of samples taken at several points in the water column that there was no significant difference in the con-
centration between the various levels. Once removed, the samples were stored with zero headspace in 15 mL vials at 4 ± 1°C. They were analyzed according to the procedure given in Chapter Four.
CHAPTER FOUR

ANALYTICAL PROCEDURE

The procedures used in the analysis of the five selected volatile organics are described in this chapter.

4.1 General

The selected volatile organic chemicals were analyzed with a gas chromatograph, GC. A GC consists of three main parts, an injector, a column, oven and a detector.

A liquid or gas sample is injected with a syringe through a port, into the carrier gas stream which flows through the column at a selected rate.

The column is a piece of tubing that can be made of metal or glass and ranges in diameter from 0.5 to 2 mm, with lengths up to 10 m. The time a molecule will spend in a column, known as the retention time, is a function of both its boiling point and its affinity for the coating in the column (Lesage, 1982).

The detector receives the compounds that elute off the column. For the analysis of priority pollutants, two types of detectors are mainly used: flame ionization and electron capture. Ultimately, the detector generates an electrical
current that is recorded as a triangular peak on chart paper. The area under this peak is proportional to the concentration contained in the specimen being examined.

4.2 Extraction Techniques

Before using a GC to analyze a sample, the specimens must first be prepared for the compounds under investigation. Two methods widely used for analyzing volatile organics in aqueous solutions are the "purge and trap" and the "headspace" techniques. These two procedures were examined for their suitability for application in this study.

4.2.1 Purge and Trap

The purge and trap method has been developed based on the work of Bellar and Lichtenberg (1974). This procedure is widely accepted and is recommended by the USEPA for GC analysis of volatile organic compounds.

In the purge and trap method, the volatile compounds are extracted from the water by bubbling an inert gas through the sample, thus causing the volatile organics to leave the sample. Then the effluent gas is passed over a trap where the volatiles are adsorbed. After a fixed period of time, the trap is quickly heated and the contents are transferred into the GC via the injector port. The trap has to be conditioned for 7 to 10 minutes before subsequent sampling can proceed.
4.2.2 Headspace Technique

The headspace technique, commonly referred to as the static headspace, is based on the fact that when a water sample that contains volatile organic compounds is sealed in a vial, organics will equilibrate between the water and vial headspace (Dietz and Singley, 1979). The partition of the organics between the two phases is a function of vapour pressure, temperature and ratio of headspace to volume of liquid. By keeping the temperature and volume ratio constant, the concentration in the gaseous phase becomes dependent on the concentration in the liquid phase. Therefore, analysis can be performed by simply injecting a sample of the headspace volume into a GC.

After comparing the advantages and disadvantages of the two techniques described above, the static headspace method was chosen over the purge and trap method for use in this study. This decision was based on the following considerations:

(i) The static headspace method can analyze a sample with only a fraction of the time required than that by the purge and trap method, without losing any significant accuracy (Castello et al., 1982, and Walker, 1984).

(ii) The purge and trap method produces chromatograms that are of poorer quality than those observed with the headspace technique with regard to peak tailing and detector noise (Kolb et al., 1983).
(iii) A form of sample cleanup occurs in static headspace because only relatively volatile water-insoluble compounds tend to partition in the headspace (Dietz and Singley, 1979).

(iv) The static headspace technique can be used for a wide range of concentrations, from μg/L to mg/L (Walker, 1984).

(v) Column and detector contamination are prevented and chromatographic interferences are minimized in the static headspace technique because only gaseous samples are injected into the GC (Dietz and Singley, 1979).

(vi) Gas extractions by the purge and trap method require more complicated instrumentation which was not available in this laboratory, compared to the static headspace technique.

4.3 GC Operating Conditions

The GC employed in this investigation was a Hewlett-Packard, HP, model 5890A, equipped with a flame ionization detector, FID. The following operating conditions were adopted based on the literature review, personal communications and numerous trial runs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column oven temperature</td>
<td>40°C</td>
</tr>
<tr>
<td>Injection temperature</td>
<td>225°C</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Carrier gas flowrate -(N)</td>
<td>25 mL/min</td>
</tr>
<tr>
<td>Detector gas flowrate -(H)</td>
<td>50 mL/min</td>
</tr>
<tr>
<td></td>
<td>400 mL/min</td>
</tr>
</tbody>
</table>
The particular column used in this study was a Megabore, 5 m x 530 μm x 2.65 μm film thickness. An HP 3393-A integrator was used for recording the electrical current and plotting the resulting chromatographs.

With the above conditions programmed into the GC, sharp triangular peaks were obtained for all the selected volatile organic chemicals. The approximate retention times were found to be:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.35 min.</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>0.10 min.</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>0.90 min.</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.75 min.</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>0.40 min.</td>
</tr>
</tbody>
</table>

Fouling of the column and detector is a common problem associated in GC work. It is mainly caused by a build-up of residue through continuous injections. This problem was remedied by conditioning the column and detector at high temperatures. In this study, after a set of samples had been completed, the column and detector were conditioned at 200°C and 300°C, respectively, which proved to be satisfactory.

4.4 Standard and Sample Preparation

All glassware used in the preparation of standards and analysis of samples were cleaned in the following steps: detergent wash, tap water rinse, methanol rinse and deionized
water rinse. Then the glassware was allowed to dry in a oven at 150° C for at least 12 hours (Dietz and Singley, 1979). This sequence was followed to ensure that the glassware used was organic-free.

Standards for all the organic chemicals used were prepared in 1 L or 2 L volumetric flasks. Initially, concentrations at 75% of the chemical's respective solubilities were prepared and subsequent lower concentrations were made through dilutions. The standards were prepared by adding the required volume of pure chemical to the respective flask with the aid of an Eppendorf micro-pipette. The solution was thoroughly mixed for a period of not less than eight hours using a magnetic stirrer, after which it was transferred into an amber bottle and stored at 4 ± 1°C. The comparison of fresh and old standards showed that all the chemicals could be stored for a period of up to one month under the specified conditions.

In static headspace technique, the standards and samples for analysis had to undergo pretreatment. A headspace of 5 mL was created by using constant volume pipettes. This ratio of headspace volume to liquid volume in the 15 mL vials was chosen based on the literature (Walker, 1984 and Zytner, 1988).

After creating the headspace, the vials were shaken for 60 seconds (Dietz and Singley, 1979) and then placed in a constant temperature water bath set at 30°C. The temperature
value itself was not critical but it was important to hold the temperature constant for all the vials being tested. All the samples remained in the bath for a minimum of 30 minutes before analysis (Dietz and Singley, 1979). This time period allowed the volatile organic chemical to attain equilibrium between the liquid and gas phases.

After the elapsed time, a vial was removed, shaken for 15 seconds and then allowed to stand for 30 seconds before a sample of the headspace gas was removed (Dietz and Singley, 1979). A volume of gas was withdrawn by using either a 250 µL or 500 µL capacity Hamilton gastight syringe, series 1000, and injected into the GC. Usually, the injection volumes ranged between 100 and 250 µL. Before the next sample was injected, the syringe barrel and needle were flushed with prepurified nitrogen gas for approximately 30 seconds to ensure removal of any organic residue.

4.5 Standard and Sample Calibration

In the photolysis and hydrolysis experiments, it was only important to know the percent difference between the test and control solutions integrated areas and not the actual amount of organics present. The variation between the two values was determined by subtracting the integrated areas obtained from the analysis. Therefore, in these two experiments, calibration curves were not developed. However, organic concentration values were required in the
volatilization and flux experiments. In order to obtain concentration levels in unknown samples, first standards containing known amounts of the chemical were analyzed. From this relationship, a graph was developed between the known concentration and their corresponding integrated areas. The unknown concentration values for that particular chemical were then determined from this calibration graph. Figures 4-1 and 4-2 are typical calibration graphs. As can be seen from the plots, a linear relationship exists between the integrated area and the corresponding concentration of the chemical. The following correlation coefficient, $r^2$, calculated for different chemicals show confidence in the results and the method:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.998</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>0.971</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.988</td>
</tr>
</tbody>
</table>

In order to account for possible losses in the GC signal, calibration curves were developed when a set of samples were to be analyzed from the volatilization and flux experiments.
Figure 4-1 Typical Calibration Curves for Benzene and Toluene
Figure 4-2 Typical Calibration Curve for Methylene Chloride
CHAPTER FIVE
RESULTS AND DISCUSSION

This chapter provides the results and discussion from the experiments conducted on the selected organic compounds.

5.1 General

In the two transformation processes, it was assumed when the samples were being analyzed on the GC there would be no masking of the signal output produced by any degradation products that were possibly formed as a result of a transformation of the parent chemical. This assumption was based in part on the reported dissimilarities of the degradation by-product compounds that have resulted by a transformation of the parent chemical from these two processes. For example, the degradation by hydrolysis of halogenated aliphatic compounds in water leads initially to the production of alcohols (Vogel et al., 1987) and it has been reported that the photochemical degradation products of trichloroethylene are phosgene and acetyl chlorides (Smith, 1987). It should be noted that from the analysis of the samples obtained in the direct photolysis and hydrolysis experiments, only one sharp peak, in all cases, were displayed on the chromatographs for
each chemical under study. Therefore, the corresponding integrated areas to these individual peaks were solely attributed and assigned to the original parent chemical and were used in the following calculations that involved the two transformation processes.

5.2 Photolysis

Table 5-1 shows the data collected from photochemical experiments conducted on the organic chemicals. It was necessary to determine the experimental error in order to ascertain whether a valid transformation of the parent chemical has taken place and, therefore, could be considered susceptible to direct photolysis. The errors in photolysis experiments were calculated as follows:

(i) "mean values" that represent the average integrated areas of at least three samples, recorded daily for dark control solutions, were calculated and assumed to be equal to the initial concentrations of the respective chemical.

(ii) then the maximum and minimum differences between the "mean values" and the average integrated areas observed daily for the control solutions were determined for each chemical and initial concentrations.

(iii) the range between the maximum positive and minimum negative differences, found for each chemical and concentration was considered as the respective experimental error.
Table 5-1 - Photolysis Data for the Organic Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration mg/L</th>
<th>Integrated Area Controlled*</th>
<th>Area Exposed+</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1</td>
<td>10731</td>
<td>10516</td>
<td>-2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>13282</td>
<td>13153</td>
<td>-1</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>1</td>
<td>4605</td>
<td>4620</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>8808</td>
<td>8456</td>
<td>-4</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>1</td>
<td>7670</td>
<td>7231</td>
<td>-6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16600</td>
<td>15770</td>
<td>-5</td>
</tr>
<tr>
<td>Toluene</td>
<td>1</td>
<td>15635</td>
<td>15479</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16829</td>
<td>16324</td>
<td>-3</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>1</td>
<td>6851</td>
<td>6509</td>
<td>-5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>8318</td>
<td>7985</td>
<td>-4</td>
</tr>
</tbody>
</table>

* these are the "mean values" for their respective initial concentrations which were calculated from at least three sample vials.

+ these are the lowest values of the average integrated areas obtained daily for a set of at least three samples and usually represents the day five value.
The largest error found for any chemical at one concentration level ranged between +5 to -10 percent. However, in the majority of the cases, the differences were found to be within ±5 percent. Therefore, the experimental error associated with the data from the photolysis investigation was assumed to be ±5 percent.

The initial concentrations of the chemicals since the dark controls represented the stability of the parent chemical. As mentioned, the experimental error for the controls was determined to be 5 percent. Therefore, if a decrease in the concentration of the exposed solutions was found to be greater than 5 percent in the five day period, then the chemical may be considered to be susceptible to direct photolysis under the appointed laboratory conditions.

From the data obtained in the photolysis study for the controls and UV exposed solutions, the percent difference between the control and UV exposed data were normally within ±5 percent of one another. Since the majority of these percent differences are within the range of no statistical differences between the control and UV exposed solutions for all the chemicals used in this study,
The results for benzene and toluene show that direct photolysis is an insignificant degradation process in deionized water. This outcome was expected because of the strong C-H bond, which can not be broken readily by UV wavelengths greater than 290 nm (Neely, 1980). In order for these chemicals to experience degradation by direct photolysis in surface waters, there would have to be a substantial shift in the UV wavelengths derived from sunlight. However, for this to happen in the natural environment can be considered remote. It is more probable that indirect photolysis could play an important part in degrading these two chemicals in natural aquatic environments. As shown by Mansour (1985), benzene and toluene are susceptible to indirect photolysis, even at wavelengths greater than 290 nm and as indicated by Zepp et al. (1984), the humus component of natural waters can provide the necessary "sensitizer" molecules for this reaction to proceed. Therefore, the possibility exists that through the process of indirect photolysis, these two compounds could be degraded in natural surface waters.

The data obtained for methylene chloride in this study also indicate resistance to degradation by direct photolysis in the deionized water. Also, Dilling and Goersch (1980), stated that significant decomposition of methylene chloride by direct photolysis was not expected in the troposphere,
Therefore, it appears that elimination of methylene chloride in the environment by direct photolysis would not be a significant process.

Likewise, both tetrachloroethylene and trichloroethylene demonstrated a high resistance to decomposition by direct photolysis in the deionized aqueous solutions. Jensen and Rosenberg (1975), using a closed system in which no volatilization could occur, also detected no significant difference in tetrachloroethylene or trichloroethylene concentrations for systems maintained in darkness compared to similar systems exposed to daylight. Walker (1984) mentioned that direct photolysis studies are not conclusive as to whether trichloroethylene can be considered susceptible to this process. It does seem from this study that in deionized water, both chemicals can be considered not susceptible to the transformation process of direct photolysis.

Therefore, the results obtained on all three chlorinated organics do indicate that under the prescribed laboratory conditions, the susceptibility to transformation by direct photolysis is minimal. If the laboratory data can be extrapolated with some certainty, the process of direct photolysis would not appear to be a significant transformation pathway for these organics in an aquatic environment that was free of either suspended sediments or natural organics. However, this imposed restriction is highly unlikely to exist in any natural water systems. No information was
found on these three chlorinated organics as to their susceptibility to the process of indirect photolysis. But, if the same reasoning is applied to these chemicals as was to benzene and toluene, the process of indirect photolysis might play an important role in transforming these chlorinated organics in surface waters.

5.3 Hydrolysis

Table 5-2 displays the data obtained from the hydrolysis experiments on the organic chemicals. Again, the experimental error must be determined before a valid decision can be made as to whether any of the organic chemicals appeared to be susceptible to hydrolysis.

In the hydrolysis experiment, the error was calculated as follows:

(i) "mean values" representing the average integrated areas of at least three samples at 4°C were determined and assumed to be equal to the initial concentrations for each chemical.

(ii) then the maximum and minimum differences between the "mean values" and the integrated areas used for their calculation were determined.

(iii) the range between the maximum positive and minimum negative differences, found for each chemical and concentration was taken to be the experimental error.
Table 5-2 - Hydrolysis Data for the Selected Organic Chemicals

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration mg/L</th>
<th>Acidic Solution (pH=4) Integrated Areas for Samples at 4°C</th>
<th>Percent Difference</th>
<th>Basic Solution (pH=9) Integrated Areas for Samples at 4°C</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4°C*</td>
<td>50°C*</td>
<td></td>
<td>4°C*</td>
</tr>
<tr>
<td>Benzene</td>
<td>900</td>
<td>11650</td>
<td>10925</td>
<td>-6</td>
<td>11316</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>11795</td>
<td>11391</td>
<td>-3</td>
<td>11634</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>15737</td>
<td>15439</td>
<td>-2</td>
<td>17428</td>
</tr>
<tr>
<td>Methylene</td>
<td>10000</td>
<td>10048</td>
<td>10322</td>
<td>+3</td>
<td>9364</td>
</tr>
<tr>
<td>Chloride</td>
<td>5000</td>
<td>10178</td>
<td>10076</td>
<td>-1</td>
<td>11033</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>10472</td>
<td>11481</td>
<td>+9</td>
<td>12286</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>75</td>
<td>47805</td>
<td>48260</td>
<td>+1</td>
<td>46900</td>
</tr>
<tr>
<td></td>
<td>37.5</td>
<td>20285</td>
<td>18992</td>
<td>-6</td>
<td>18990</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>41498</td>
<td>38910</td>
<td>-6</td>
<td>40853</td>
</tr>
<tr>
<td>Toluene</td>
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<td>42867</td>
<td>42807</td>
<td>&lt;1</td>
<td>43302</td>
</tr>
<tr>
<td></td>
<td>128.75</td>
<td>33475</td>
<td>32414</td>
<td>-3</td>
<td>31348</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>2469</td>
<td>2556</td>
<td>+4</td>
<td>2306</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>535</td>
<td>15784</td>
<td>16065</td>
<td>+2</td>
<td>17351</td>
</tr>
<tr>
<td></td>
<td>267.5</td>
<td>23189</td>
<td>23334</td>
<td>+1</td>
<td>8259</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>21473</td>
<td>22083</td>
<td>+3</td>
<td>6388</td>
</tr>
</tbody>
</table>

* these are the "mean values" for the respective initial concentration based on a minimum of three sample vials.

+ these represent the average integrated area values based on at least three specimens.
In the hydrolysis study, the largest and smallest range in differences were +4% to -10% and +1% to -1%, respectively. However, the majority of the calculated differences ranged between ± 5 percent. Therefore, the experimental error in the hydrolysis studies was assumed to be ± 5 percent.

In the hydrolysis experiments, the refrigerated solutions were used as controls to represent the initial concentration of the chemicals. The oven samples, which were at an elevated temperature in order to accelerate the hydrolysis reaction, were compared with their controls to test for any differences between the two. If less than a 10 percent difference is detected between the samples stored at 4°C and 50°C, after seven days, the chemical can be considered hydrolytically stable ASTM (1983).

The differences between the oven samples and their controls may not necessarily represent the actual change until the experimental errors are taken into consideration. A relative difference greater than 10 percent may exist between the two owing to this error. Thus, the influence of the experimental error on the data was taken into account in order to determine the absolute differences between the oven samples and their controls.

The raw data collected in the hydrolysis investigation on the selected organics are given in Table 5-2. As mentioned previously, the experimental error in this study was taken as ± 5 percent. An overall analysis of the results
presented in Table 5-2 indicates that there are almost no statistically significant changes that exist between the oven samples and controls since most of the calculated percent differences are reasonably within the range of the experimental error. This observation is especially true from the results obtained when the chemicals were in acidic conditions. In basic conditions, the data for methylene chloride, tetrachloroethylene and trichloroethylene reveal some significant differences at their lowest concentrations. However, these seem to be isolated occurrences since their other two concentrations do not display a similar pattern. Perhaps the initial concentration levels for these organic chemicals had some influence on the process but no definite pattern is produced based on these observations. Mabey and Mill (1978) have stated that the rate of hydrolysis of a chemical is independent of its concentration. Therefore, it is believed that another process, such as volatilization, was responsible for causing certain losses of these three chemicals.

The results for benzene and toluene indicate that their susceptibility to hydrolysis in both extremely acidic and basic environments was negligible. Their resistance to hydrolysis, under more environmentally relevant situations of pH and temperature is expected due to their strong C-H bond (Neely, 1985). Since deionized water has low organic content and low ionic strength, it closely mimics a freshwater system
(Mabey and Mill, 1978). Therefore, the laboratory results can be extrapolated with some confidence, that benzene and toluene are not expected to experience any significant transformation by a hydrolytic reaction under environmentally relevant conditions of pH and temperatures that are found in most freshwater systems.

Methylene chloride, tetrachloroethylene and trichloroethylene, in a highly acidic solution, display similar resistance to hydrolysis. In the basic solution, these chemicals do not display a clearly discernible direction as to their susceptibility to hydrolysis. However, if the total disappearance of these chemicals was assumed to be related to a hydrolysis reaction, an estimate of their half-lives would be around six months at 25°C (ASTM, 1983). This would be in general agreement with the findings of Djil ling et al. (1975) in which a half-life for a hydrolysis reaction of methylene chloride in unbuffered water was experimentally determined to be 18 months. The numerical values themselves are not as important as the time frame. As reported by Suffet et al. (1981), the longer it takes for a chemical to be hydrolyzed in water, the more significant becomes the other processes, such as volatilization and biodegradation. Therefore, for these three chlorinated organics with estimated half-lives from this study measured in months, sufficient time exists for other processes to exert their influence.
Therefore, all the selected organic chemicals under the prescribed laboratory conditions appear to be resistant to the transformation process of hydrolysis, even when the environments are acidic or basic. As stated, it was observed that under the acidic conditions, the selected organics were found to be the most stable. This is in general agreement with Mill et al. (1980) who stated that acid catalysis appeared not to be as important as base catalysis in environmental studies. Under basic conditions, the three chlorinated compounds, at their lowest concentration level, gave a possible indication of susceptibility to hydrolysis. However, this condition was not substantiated by the rest of their data. Overall, it appears that hydrolysis would not be a significant transformation process of any of these organics in environmentally relevant conditions found in most natural freshwater systems.

5.4 Volatilization from Water

The data collected from the volatilization experiments were found to produce a linear relationship between the decay in concentration and time when plotted on a semi-logarithmic scale. Figure 5-1 shows a typical plot of this relationship for toluene at A/V = 11.218 l/m. The coefficients of best fit lines, presented in Tables 5-3 to 5-5, were obtained by mean-square regression on the individual data sets for different concentrations of benzene, methylene chloride and
Figure 5-1 Volatilization of Toluene from Deionized Water (Area/Vol=11.218 1/m)
toluene. It is shown that, the slopes of these lines represents the volatilization rate constants, \( k \), under the specified conditions.

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Area/Volume (1/m)</th>
<th>Rate Constant (base 10) (1/h)</th>
<th>Intercept</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1350</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.841</td>
<td>-0.0132</td>
<td>-0.0023</td>
<td>0.868</td>
<td></td>
</tr>
<tr>
<td>11.218</td>
<td>-0.0414</td>
<td>+0.0036</td>
<td>0.888</td>
<td></td>
</tr>
<tr>
<td>23.941</td>
<td>-0.2390</td>
<td>+0.0299</td>
<td>0.858</td>
<td></td>
</tr>
<tr>
<td>33.935</td>
<td>-0.2554</td>
<td>+0.0071</td>
<td>0.930</td>
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</tr>
<tr>
<td>42.237</td>
<td>-0.5504</td>
<td>+0.0229</td>
<td>0.869</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.841</td>
<td>-0.0559</td>
<td>+0.0049</td>
<td>0.913</td>
<td></td>
</tr>
<tr>
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<td>-0.0590</td>
<td>+0.0066</td>
<td>0.905</td>
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</tr>
<tr>
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<td>+0.0361</td>
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</tr>
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<td>+0.0175</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>0.922</td>
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<tr>
<td>42.237</td>
<td>-0.5424</td>
<td>+0.0011</td>
<td>0.973</td>
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</table>
Table 5-4 - Regression Coefficients of Best Fit Lines for Volatilization of Methylene Chloride from Water

<table>
<thead>
<tr>
<th>Concentration mg/L</th>
<th>Area/Volume 1/m</th>
<th>Rate Constant (base 10) 1/h</th>
<th>Intercept 1/h</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>15000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.841</td>
<td>n/a*</td>
<td>-0.0059</td>
<td>-0.0012</td>
<td>0.873</td>
</tr>
<tr>
<td>11.218</td>
<td>-0.0206</td>
<td>-0.0007</td>
<td>0.978</td>
<td></td>
</tr>
<tr>
<td>23.941</td>
<td>-0.0244</td>
<td>-0.0049</td>
<td>0.850</td>
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<tr>
<td>33.935</td>
<td>-0.0561</td>
<td>-0.0016</td>
<td>0.951</td>
<td></td>
</tr>
<tr>
<td>42.237</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>10000</td>
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<td></td>
<td></td>
</tr>
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<td>0.902</td>
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<td>-0.0005</td>
<td>0.904</td>
<td></td>
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<td>-0.0319</td>
<td>-0.0037</td>
<td>0.873</td>
<td></td>
</tr>
<tr>
<td>33.935</td>
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<td>-0.0023</td>
<td>0.968</td>
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<td>42.237</td>
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<td>n/a*</td>
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<td>+0.0001</td>
<td>0.988</td>
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<td>+0.0009</td>
<td>0.950</td>
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<tr>
<td>33.935</td>
<td>-0.0558</td>
<td>+0.0001</td>
<td>0.954</td>
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</tr>
<tr>
<td>42.237</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* not applicable because, at this A/V value, a first order reaction was not strictly followed.
<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Area/Volume (1/m)</th>
<th>Rate Constant (base 10)</th>
<th>Intercept</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.841</td>
<td>-0.0360</td>
<td>+0.0036</td>
<td>0.955</td>
<td></td>
</tr>
<tr>
<td>11.218</td>
<td>-0.0387</td>
<td>-0.0018</td>
<td>0.984</td>
<td></td>
</tr>
<tr>
<td>386.25</td>
<td>-0.1853</td>
<td>+0.0040</td>
<td>0.952</td>
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<tr>
<td>33.935</td>
<td>-0.3359</td>
<td>+0.0169</td>
<td>0.873</td>
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<td>0.967</td>
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<tr>
<td>6.841</td>
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<td>-0.0008</td>
<td>0.987</td>
<td></td>
</tr>
<tr>
<td>11.218</td>
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<td>+0.0035</td>
<td>0.952</td>
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<tr>
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<td>+0.0143</td>
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<tr>
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<td>+0.0115</td>
<td>0.932</td>
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<td>0.975</td>
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</tr>
<tr>
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<td>-0.0034</td>
<td>0.943</td>
<td></td>
</tr>
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<td>+0.0019</td>
<td>0.986</td>
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</tr>
<tr>
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<td>+0.0110</td>
<td>0.986</td>
<td></td>
</tr>
<tr>
<td>33.935</td>
<td>-0.2637</td>
<td>+0.0012</td>
<td>0.975</td>
<td></td>
</tr>
<tr>
<td>42.237</td>
<td>-0.4182</td>
<td>+0.0089</td>
<td>0.987</td>
<td></td>
</tr>
</tbody>
</table>
Figures 5-2 to 5-4 show for each chemical the plot of the slope values i.e. volatilization rate constants, against the area to volume ratios on arithmetic scales. The coefficients at all concentrations in Tables 5-3 to 5-5 were then regressed separately for each chemical to observe if a correlation existed between the volatilization rate constant and area to volume ratio. The result was a single equation, dependent on A/V value but independent of the initial concentration, developed for each chemical and expressed as:

Benzène \[ k_W = 0.0126(A/V) - 0.0040 \quad r^2 = 0.903 \quad (5-1) \]

Methylene Chloride \[ k_W = 0.0012(A/V) - 0.0003 \quad r^2 = 0.813 \quad (5-2) \]

Toluene \[ k_W = 0.0119(A/V) - 0.0541 \quad r^2 = 0.901 \quad (5-3) \]

where, \( k_W \) = volatilization rate constant from water, 1/h
A = exposed surface area, m²
V = volume of container, m³.

Equations 5-1 to 5-3 are presented graphically in Figures 5-2 to 5-4. The predicted lines are forced through the origin to eliminate the intercept.

It must be noted that the volatilization rate equations 5-1 to 5-3 were developed for different A/V values, independent of concentration and based on a temperature of 22 ± 2°C and an average wind velocity across the exposed water surface of 2.8 m/s.
Figure 5-2 Volatilization Rate Constant of Benzene Versus Area to Volume Ratios
Figure 5-3 Volatilization Rate Constant of Methylene Chloride Versus Area to Volume Ratios
Figure 5-4 Volatilization Rate Constant of Toluene Versus Area to Volume Ratios
In the development of the theoretical relationship between the disappearance of a chemical with time due to volatilization, it was assumed that a first order reaction was followed and that the initial concentration of the chemical had no influence on this process. However, a problem was encountered in the case of methylene chloride for volatilization experiments. Figure 5-5 indicates that a first order reaction was not strictly followed for the smallest area to volume ratio of 6.841 l/m. But, as the A/V value was increased, a first order reaction was followed as shown in Figure 5-6. Therefore, it is suspected that the initial concentration had some influence over the volatilization rate of methylene chloride from water. This behaviour requires further in-depth investigation which was beyond the scope of this study. Therefore, it was decided to ignore the volatilization data obtained for methylene chloride with A/V = 6.841 l/m from further discussion.

The data in Tables 5-3 to 5-5 indicate that an increase in the area to volume ratio increases the rate of volatilization of a compound from the water surface. Based on the observed dependence, Eqs. 5-1 to 5-3 were developed to express the rate of volatilization as a function of area to volume ratio. The importance of the A/V parameter has also been recognized by other investigators (Abdel-Gawad, 1985, ASCE et al., 1969 and Zytner, 1988). In larger bodies of water, such as a river, the parameter A/V approaches the factor 1/d,
Figure 5-5 Volatilization of Methylene Chloride from Deionized Water (Area/Vol = 6.841 1/m)
Figure 5-6 Volatilization of Methylene Chloride from Deionized Water (Area/Vol= 42.237 1/m)
where \( d \) is depth in meters. Typically, most rivers would have shallow depths, say close to \( d=1 \) m, which corresponds to an A/V value of around 1 l/m. But, as a river's depth increases, the A/V values will progressively become much smaller. In this study, the A/V values ranged from about 6 to 42 l/m. These values are more representative of a situation where a chemical spill has occurred. Since in this case, the anticipated depths of any resulting chemical pools would be extremely shallow and will therefore, subsequently lead to large A/V values.

It should be emphasized again that Eqs. 5-1 to 5-3 were developed from the data in the volatilization studies based on a temperature of about 22°C and an average air velocity across the water surface of 2.8 m/s. These are two important factors to be recognized because, as reported in the literature (Dilling et al., 1975, Mackay and Yeun, 1983 and Spencer et al., 1982), they can have a great influence on the rate of volatilization of organic compounds.

In this study, benzene, methylene chloride and toluene exhibited, to varying degrees, rapid volatilization from aqueous solutions. This behaviour has also been shown in experiments performed by others (Cadena et al., 1984, Dilling et al., 1975 and Mackay and Leinonen, 1975). This suggests that volatilization is a very important physical transport process for these organic compounds from aqueous environments.
The results of the volatilization investigation for benzene and toluene show that their rates of volatilization from water are similar, although benzene's rate was found to be slightly higher. This behaviour was expected since benzene has a higher Henry's law constant, $H$, as compared to toluene (see Table 2-1). As shown in a study by Namkung and Rittmann (1987), the higher the $H$ values, the greater are the volatilization losses of these organic compounds. Therefore, under similar conditions, benzene would be anticipated to have a higher volatilization rate constant than toluene. Among the three chemicals studied, methylene chloride was observed to have the lowest rate of volatilization from water. Again, this can be explained with its $H$ value. Methylene chloride has a $H$ value that is much lower than that for either benzene or toluene (see Table 2-1). Therefore, by exposing these three chemicals to similar conditions, the rate of volatilization for methylene chloride would be expected to be the lowest.

By employing some of the equations developed earlier in Chapter Two on the theory of volatilization, certain useful relationships can be determined. The value of the overall liquid film coefficient at the liquid-gas interface, $K_{OLW}$, can be determined if the volatilization rate constant from water, $k_W$, is divided by the $A/V$ values. The linear plots of $k_W$ versus $A/V$ are shown in Figs. 5-2 to 5-4. By combining
the slope of the line that is forced through the origin with 
\[ k' = K_{OL}(A/V) \] and \[ k' = 2.303k \], the value for \( K_{OLW} \) can be ob-
tained from the following relationship:

\[ K_{OLW}(A/V) = 2.303k_w \]  \hspace{1cm} (5-6)

or \[ K_{OLW} = 2.303k_w(V/A) \]  \hspace{1cm} (5-6a)

From Eq. 5-6a and Eqs. 5-1 to 5-3, the values of \( K_{OLW} \) were
calculated to be 0.029, 0.003 and 0.027 m/hr respectively for
benzene, methylene chloride and toluene. The values of \( K_{OLW} \)
found in this study for benzene, methylene chloride and
toluene are at least an order of magnitude lower than other
\( K_{OLW} \) values reported in the literature (Mackay and Yeun, 1983
and Rathbun and Tai, 1981). This large discrepancy arose
possibly because of the employment of magnetic stirrers,
higher wind velocities and higher temperatures in their
studies which improves the rate of mass transfer and ul-
timately increases the value of \( K_{OLW} \). Therefore, an absolute
comparison between the values of \( K_{OLW} \) is not feasible due to
the differences that existed between the experimental condi-
tions. However, a relative comparison does indicate that the
\( K_{OLW} \) values found in this investigation would be expected to
be lower due to the cited differences. And in this study,
was found to be the case.

Another relationship can be developed by taking the
anti-log of Equation 2-17 which gives:
\[
\log(\frac{C}{C_0}) = -k_W t
\]  \hspace{1cm} (5-7)

The values of \(k_W\) for benzene, methylene chloride and toluene can be determined from Eqs 5-1 to 5-3 respectively, for any A/V value. Once \(k_W\) is known, Eq. 5-7 can then be used to determine the concentration of the chemical remaining in the water after time \(t\), in hours.

5.5 Mass Flux Movement into Water

Figure 5-7 indicates how the concentration of methylene chloride, which sinks due to its relatively high density varied with time in the mass flux experiment. The figure shows that the concentration decreased in the first few days and then increased slowly as the chemical diffused into the water to reach a maximum value of about 1250 mg/L. After this, the concentration kept fluctuating until the conclusion of the experiment.

An approach using the Thomas method for BOD coefficient determination employed by Zytner (1988) to express the concentration level as a function of time for the flux movement of tetrachloroethylene through water, was applied to the data obtained for methylene chloride. However, this approach failed to produce a meaningful empirical equation to describe the relationship between the concentration and time for methylene chloride.
Figure 5-7 The Flux Movement of Methylene Chloride Through a Column of Water
As mentioned, Figure 5-7 shows the variation in the concentration of methylene chloride with time. The initial decrease in concentration for the first few days was not expected and is not fully understood. It is believed that this condition arose because contamination of the organic-free water had occurred while adding methylene chloride to the cylinder. This is substantiated from the experimental data by the day-zero samples, withdrawn immediately after the addition of the chemical, which already had an initial concentration of about 1000 mg/L. There should have been a negligible amount, if any, of the chemical present in these samples.

After five days, the concentration of methylene chloride within the water column began to show a gradual increase as shown in Figure 5-7. This suggests that some mass transfer from the submerged pool of chemical had taken place. The highest concentration measured for methylene chloride in the flux study occurred on the fourteenth day and was determined to be about 1250 mg/L. This represents about 6 percent of its solubility in water. For the next seven days, the concentration level fluctuated and at the termination of this experiment it had leveled off at about 650 mg/L.

As stated, the development of an empirical equation failed to produce any rational relationship for the mass being diffused into the water with time for methylene chloride. However, certain comments can be made concerning
the flux movement of methylene chloride through water. The highest concentration achieved in the flux experiment for methylene chloride corresponded to about 6 percent of its water solubility. However, most of the time this concentration remained well below the 6 percent value. Visual observations made each day on the 600 mL pool of methylene chloride, added to the cylinder, revealed that very little of the chemical mass had disappeared during the total length of this study. Based on the maximum concentration obtained and the initial volume, it is estimated that a total flux of about 0.005 kg had left the submerged pool over the entire 24-day period of the experiment.

The inferences of these observations are that the flux movement of methylene chloride through water proceeds at a very slow rate and does not appear to be a significant physical transport process under quiescent conditions. Therefore, a spill of methylene chloride into an aqueous environment would remain intact for an extended period thus allowing sufficient time to collect a submerged pool of this chemical. It must be recognized that the above comments apply to situations where very low turbulence occurs, such as in a stagnant pond or deep lake, where as considerable variations in turbulence may be encountered in certain natural water bodies, such as in rapid-flowing rivers.
Figures 5-8 and 5-9 show how the concentrations of benzene and toluene, which float in water due to their relatively low densities, were found to vary with time in the mass flux experiments. Both Figs. 5-8 and 5-9 show that the concentrations of benzene and toluene had reached the maximum values of about 265 and 135 mg/L, respectively, on the first day. After that their concentrations decreased slowly for several weeks until their levels reached about 5 mg/L and stayed there until the termination of the experiments. Since the diffusion into the water occurred during the first few days, the sampling periods employed in this study failed to accurately monitor this transfer. However, the data collected from this investigation were used to determine the rate of volatilization of the two chemicals from their water columns and are displayed in Figures 5-10 and 5-11. For better interpretation, the data values that were less than one-half percent of the chemical's solubility are omitted. The graphs, Figs. 5-10 and 5-11, were plotted on a semi-logarithmic scale with the best fit lines being forced through the origin. The following regression equations were developed:

\[
\frac{C}{C_S} = -10 \times 0.1282(t) \quad r^2 = 0.978 \quad (5-4)
\]
\[
\frac{C}{C_S} = -10 \times 0.1069(t) \quad r^2 = 0.967 \quad (5-5)
\]
Figure 5-8 The Flux Movement of Benzene Through a Column of Water
Figure 5-9 The Flux Movement of Toluene Through a Column of Water
Figure 5-10 Volatilization of Benzene from a Column of Deionized Water (Area/Vol=2.28 1/m)
Figure 5-11 Volatilization of Toluene from a Column of Deionized Water (Area/Vol=2.28 1/m)
where,
\[
\begin{align*}
C &= \text{chemical concentration at time } t, \text{ mg/L} \\
C_s &= \text{solubility of the chemical, mg/L} \\
t &= \text{time, d.}
\end{align*}
\]

It is worth mentioning that the data used to produce Equations 5-4 and 5-5 were obtained under an ambient temperature of 22° ± 2° C and the air movement over the top of the cylinders was considered to be negligible.

For benzene and toluene, a special situation existed in the mass flux experiment due to their low specific gravities. The floating pool created by these two chemicals in their cylinders had evaporated in a period of less than two days. During this time, the chemical source was present, a certain fraction of these compounds had diffused into the water columns. The concentration in the water columns had reached a maximum level, in a period of less than two days, of about 15% and 25% of the respective solubilities of benzene and toluene in water. Once the source of the contaminant i.e. the floating pool had completely dissipated, the remaining dissolved fraction of the chemical in the water began to volatilize. This loss of the remaining dissolved benzene and toluene through the volatilization process is displayed in Figs. 5-8 and 5-9. The initial frequency of sampling employed in this experiment was insufficient to observe the diffusion into the water column. It was established then for chemicals with relatively low densities such as benzene and toluene, the first few days represent the most critical
period in order to determine the mass transfer into water. Therefore, it is suggested that the initial sampling frequency, in mass flux experiments involving low density compounds, be increased in order to observe and determine the kinetics for diffusion into the water.

No attempt was made to develop a theoretical derivation on the flux movement of benzene or toluene in water since not enough data points were collected in the first two days of the investigation. Instead, only the rate of volatilization of benzene and toluene from the water columns were determined under the quiescent conditions maintained in the flux experiments. In order to calculate the volatilization of benzene and toluene, the value of their solubility in water, $C_S$, was used to represent the initial concentration, $C_0$, since this is the maximum level that could be expected. Figures 5-10 and 5-11 were produced by dividing the daily concentrations determined in the water column by the respective water solubilities for benzene and toluene and plotting them against time on a semi-logarithmic scale. As previously mentioned, any data points that were found to be less than one-half percent of the chemicals solubility were omitted from further consideration for both chemicals. The data removed by this restriction represented the concentration level in the water that had reached a steady-state over a certain time period. For benzene and toluene, these periods were about 14
and 18 days, respectively (see Figs. 5-10 and 5-11). These points can be removed since they were found to have only a minimal influence on the calculated rate of volatilization.

The linear plots in Figs. 5-10 and 5-11 are represented by Eqs. 5-4 and 5-5. A comparison was made between the volatilization rate constants from water, $k_W$, determined in the flux experiments and the $k_W$ values predicted by using Equations 5-1 and 5-3, for both benzene and toluene respectively. The $k_W$ determined in the flux experiments were based on an area to volume ratio of 2.28 l/m. Substituting $A/V = 2.28$ l/m into Eqs. 5-1 and 5-3, derived experimentally from the volatilization study, gives predicted $k_W$ values for benzene and toluene as 0.025 and 0.023 l/h respectively. The rates of volatilization determined for benzene and toluene from the flux study were 0.005 and 0.004 l/h respectively. This large difference in the $k_W$ values between the flux and volatilization experiments was expected. Equations 5-1 and 5-3 were developed for an average air velocity across the water surface of 2.8 m/s where as the flux studies were conducted under stagnant conditions. It has been reported by others (Cohen et al., 1978, Dilling et al., 1975 and Spencer et al., 1982) that overall, an increase in the wind velocity at the water surface increases the rate of volatilization. Therefore, higher values of $k_W$ were calculated by using Eqs.
5-1 and 5-3 as compared to those actually observed in the flux investigation because of the significant difference that existed in the air velocities between these two experiments.
CHAPTER SIX
CONCLUSIONS

From the research undertaken to investigate the behaviour and fate of the organic chemicals, benzene, methylene chloride, tetrachloroethylene, toluene and trichloroethylene in aqueous environments, the following conclusions are drawn:

1. The susceptibility to direct photolysis was negligible for all five organics under the prescribed laboratory conditions.

2. In an acidic solution and over the range of concentrations used, the organics were all found to be hydrolytically stable. In a basic solution only the chlorinated compounds at their lowest concentration level indicated a possible susceptibility to hydrolysis. However, there was no clear direction that could be discerned from the data.

3. Volatilization of benzene, methylene chloride and toluene from water was relatively rapid. The rate of volatilization of these chemicals were found to be independ-
ent of their initial concentration. The area to volume ratio was observed to be the most significant factor that noticeably influenced the rate of volatilization.

4. The overall liquid film coefficients, $K_{OLW}$, at the water-air interface for benzene, methylene chloride and toluene were observed to be 0.029, 0.003 and 0.027 m/h, respectively, under the specified conditions.

5. Under quiescent conditions, the mass transfer rate of a submerged pool of methylene chloride in water was found to be minimal. It was estimated that about 0.005 kg of methylene chloride had fluxed into the water column over a period of 24 days. Both benzene and toluene exhibited a mass flux by diffusion into the water column from the floating pool while these chemicals were volatilizing into the atmosphere.
REFERENCES


VITA AUCTORIS

Glenn R. Chodola was born on January 9, 1960 in Windsor, Ontario, Canada. He graduated from Centennial Secondary School in June, 1979 and entered the University of Windsor in September, 1980. Graduating in June, 1984 he received a Bachelor of Applied Science Degree in Geological Engineering.

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