STUDY OF TEMPERATURE EFFECTS ON AIR STRIPPING OF VOLATILE ORGANICS FROM WATER

Ву

RAGHUPATHI REDDY PAKANATI Bachelor of Technology Osmania University

Hyderabad, India

1980

Submitted to the Faculty of the Graduate College of the Oklahoma State University in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE December, 1984 .



.

, ,

STUDY OF TEMPERATURE EFFECTS ON AIR STRIPPING OF VOLATILE ORGANICS FROM WATER

Thesis Approved:

Thesis Adviser - Ke $\overline{6}$

Dean the Graduate College of

ACKNOWL EDGMENTS

I wish to express my sincere appreciation and gratitude to the following persons: Dr. John N. Veenstra, my principal adviser, for his guidance, understanding, patience, and encouragement throughout this study; Dr. Don F. Kincannon, for his service as a member of my committee and also for his interest and invaluable help on the gas chromatograph, without which this work would not have been possible; Dr. Enos L. Stover, for his service as a member of my committee, and also for his encouragement and help in the experimental design in early stages of this project and willing assistance throughout this study; Mr. Gerald H. Stotts and Mr. Cecil K. Sharp for their help in setting up the experimental apparatus.

Special thanks are extended to my parents and my brother-in-law and sister, Mr. and Mrs. Srinivasa R. Pinnapureddy, for their love, encouragement, and support during this study.

iii

TABLE OF CONTENTS

Chapte	r																							Page
١.	INTRO	DUCTIO	Ν.	• •		• •	•••	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	1
		Scope	and (Obje	cti	ves	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	2
11.	LITER	ATURE	REVII	EW	•••		•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	4
		Previo Theore	us Wo tica	ork I Co	on nsi	Stri dera	ippi atic	i ng ons]	•	•	•	•	•	•	•	•	•	•	•	•	•	•	4 7
111.	EXPER	IMENTA	L ME	r ho d	s.		•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	17
		Equipme Procedu Analyt	ent ures ical	Tec	••• ••• hn i	ques	•••••••••••••••••••••••••••••••••••••••	• •	•	•	• •	•	•	•	•	•	•	• •	•	•	• •	• •	•	17 22 27
١٧.	RESUL	TS AND	DISC	cuss	ION	• •	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	32
		Tower (Effect Effect Effect Effect Mass Ti Predic	Chara of (of / of / of / ranst	acte Gas: \ir Vate Henr Fer Col	ris Liq Tem r T y's Coe umn	tics uid pera empe Law ffic Per	Rat Ratur erat v Co cier	tio re tur ons nts	e ta		• • • •	• • • •	• • • •	• • • • •	• • • •	• • • •	•	• • • •	• • • •	• • • • •	• • • •	• • • •	• • • •	32 34 41 46 52 65
۷.	CONCL	USIONS	•	•••	•••		•	•	•	•	•	•		•	•	•	•	•	•	•	•	•	•	72
BIBLIO	GRAPHY		•••	•••			•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	74
APPEND	IXA-	DETERI ∆H/R I HENRY	MINA FOR 'S L/	FION FHE AW C	OF TEM ONS	THE PERA TANT	E C(ATUR F H	DRR RE	REC DE	TI PE	ON ND	IF) Den	FAC NCE	СТС С •)R)F •	•	•	•	•	•	•	•	•	77
APPEND	IX B -	SOLUT EQUAT	ION - ION -	го т	ΉE • •	NUME	BER	0F •	т .	RA •	.NS •	FE •	ER •	UN •	IIT •	s •		•		•	•	•	•	83
APPEND	IX C -	TABLE	S OF	EXP	ERI	ΜΕΝΊ	ΓAL	RE	SU	ILT	S				•		•	•			•	•		87

~

LIST OF TABLES

Table		Page
۱.	Feed Solution Components and Their Properties	24
11.	Results of Hydraulic Loading Study	35
111.	Operating Flow Rates of Air and Water	37
١٧.	Percent Removal as a Function of Influent Air Temperature for 22°C Influent Water	42
۷.	Percent Removal as a Function of Influent Air Temperature for 15°C Influent Water	43
V1.	Henry's Law Constants as a Function of Temperature	50
VII.	Percent Reduction in Removal as a Function of Percent Drop in H From 22°C to 15°C	51
VIII.	Summary of Procedure Used to Calculate the Experimental Mass Transfer Coefficient	56
١Χ.	Experimental Overall Mass Transfer Coefficients	57
х.	Estimated Individual Phase Resistances and Overall Mass Transfer Rates	59
XI.	Estimated Overall Mass Transfer Coefficients	61
XII.	Summary of Procedure Used to Predict Column Performance	66
XIII.	Estimated Percentage Reduction of Influent Contaminant Concentrations	67
XIV.	Vapor Pressure and Solubility as a Function of Temperature	80
XV.	Correction Factor ΔH/R for the Temperature Dependence of Henry's Law Constant H	82
XVI.	Results of Organics Stripping Study for 22°C Influent Water	88

Table		Page
XVII.	Results of Organics Stripping Study for 15°C Influent Water	90
XVIII.	Results of Oxygen Stripping Study for 22°C Influent Water	92
XIX.	Results of Oxygen Stripping Study for 15°C Influent Water	93
хх.	Comparison of Dissolved Oxygen Measure- ments by D.O. Probe and Modified Winkler Technique	94
XXI.	Temperature Profiles in Stripping Study for 22°C Influent Water	95
XXII.	Temperature Profiles in Stripping Study for 15°C Influent Water	96

LIST OF FIGURES

Figu	re	Page
1.	Counter Current Packed Tower	14
2.	Packed Column Apparatus	18
3.	Pressure Drop Across Packing Versus Gas Loading Rate for a Constant Liquid Loading Rate of 5.05 M ³ /M ² Hr	33
4.	One-Half Gas Loading Rate at Flooding Versus Ln Gas:Liquid Ratio With Data Points From Hydrau- lic Loading Studies	36
5.	Percentage Removal of Influent Contaminant as a Function of Gas:Liquid Ratio for 15°C Air Tem- perature	38
6.	Percentage Removal of Nitrobenzene as a Function of Gas:Liquid Ratio	40
7.	Percentage Removal of Nitrobenzene as a Function of Influent Air Temperature	44
8.	Percentage Reduction in Removal, Due to Change in the Temperature of Feed Water, as a Func- tion of Gas:Liquid Ratio for 15°C Air Temper- ature	47
9.	Percentage Reduction in Removal of Nitrobenzene, Due to Change in the Temperature of Feed Water, as a Function of Gas:Liquid Ratio	48
10.	Percentage Reduction in Removal of Contaminant Versus Percentage Drop in Henry's Law Constant for G/L = 46	53
11.	Percentage Reduction in Removal of Contaminant Versus Percentage Drop in Henry's Law Constant for G/L = 108	54
12.	Percentage Reduction in Removal of Contaminant Versus Percentage Drop in Henry's Law Constant for G/L = 175	55

.

Figure

13.	Measured Versus Estimated Mass Transfer Coeffi- cients for Carbon Tetrachloride	62
14.	Measured Versus Estimated Mass Transfer Coeffi- cients for Trichloroethylene	63
15.	Measured Versus Estimated Mass Transfer Coeffi- cients for Toluene	64
16.	Estimated and Measured Percentage Removal of Carbon Tetrachloride as a Function of Gas: Liquid Ratio	68
17.	Estimated and Measured Percentage Removal of Trichloroethylene as a Function of Gas: Liquid Ratio	69
18.	Estimated and Measured Percentage Removal of Toluene as a Function of Gas:Liquid Ratio	70
19.	Estimated and Measured Percentage Removal of Nitrobenzene as a Function of Gas:Liquid Ratio	71
20.	Temperature Dependence of Henry's Law Constant	79

Page

CHAPTER I

INTRODUCTION

Contamination of drinking water supplies, primarily groundwater, has been of serious concern recently. More than 40 percent of the U.S. population use groundwater for drinking, often without any treatment other than disinfection. Several wells in New York, Pennsylvania, Florida, New Jersey, Massachusetts, New Hampshire, and Connecticut have been found to be contaminated with organic compounds (1, 6, 9, 13, 20, 28). It is believed that this problem is spread throughout the country and not confined to these states. Owing to the advancement in analytical techniques, over 700 different organic compounds have been identified in public water supplies in the United States (18). These compounds are not naturally occurring. They are the result of industrial discharges, land farming, or improper disposal of the industrial wastes in dump sites. Individual households through the use of solvent septic tank cleaners and similar products, as well as the groundwater recharge of the treated wastewater, have also contributed to the problem.

Several methods are available for treating contaminated groundwater. They include:

- 1. Synthetic resin adsorbents
- 2. Coagulation and clarification
- 3. Reverse osmosis

4. Activated carbon adsorption

5. Air stripping.

The first three are effective in treating specific organic compounds. Activated carbon adsorption has been found to be successful in removing a broad spectrum of complex organic contaminants. However, most of the contaminants present fall into a group of liquids considered to be volatile organic chemicals. Because of their high volatility, most of these organics can be removed by a relatively inexpensive process called air stripping.

Stripping, as defined by Treybal (21, p. 3), is a "mass transfer operation due to direct contact of two immiscible phases." The mass transfer is a result of concentration differences between phases. Aeration, or air stripping, in the case of removing volatile organic compounds from water, may be described as the transfer of volatile organic compounds from the water phase into the air phase due to intimate contact of water and air. Air stripping techniques include diffused aeration, surface aeration, spray aeration, and counter-current packed tower aeration. Of the available aeration processes, counter current packed tower aeration is one of the most efficient in achieving mass transfer. A counter current packed tower provides a continuous contact of water and air. It is a vertical column that has been filled with packing or devices of large surface area so that the water distributed over the top of the packing trickles down the packed bed, exposing a large surface to contact the air that is forced upward.

Scope and Objectives

The primary objective of this research was to study the effect of

air and water temperatures on stripping. Five different organic compounds all classified as priority pollutants by the EPA were used in this study. The compounds were chosen so that they covered a wide range of volatility. The temperatures used were those that would be encountered in an actual field operating tower.

Several other objectives were also pursued. These include estimating the mass transfer coefficient for the substances at the different temperatures under study, predicting the column performance using the available design equations and comparing this with the experimental data.

CHAPTER II

LITERATURE REVIEW

Previous Work on Stripping

The use of air stripping is one of the oldest processes to purify water. Although its use to remove specific organic contaminants is a recent innovation, air stripping has been effectively employed to remove ammonia, carbon dioxide, hydrogen sulfide, and other taste and odor causing compounds from drinking water. Air stripping is not only recognized as an effective treatment method but also as an inexpensive method to purify water. Hazen in 1907 (7, p. 92) indicated "... the simplest, cheapest, and most generally applicable method of removing tastes and odors is by aeration."

The USEPA is in the process of considering regulations for the control of organic chemicals in drinking water (22, 24, 25, 26). This has led to widespread research, on the removal of organics from water, over the past decade. As a result, additional applications of aeration have been developed. It has been established that air stripping has potential not only to treat groundwater, but also wastewater when volatile organic contaminants are present.

Weinstein (27), discussing the applicability of air stripping to treat groundwater contaminated with halogenated organic solvents, pointed out that air stripping is a potential method for decontamination of aquifers. In addition, he also suggested that air stripping can be

applied to other wastewaters with similar contaminants, either alone or in combination with some other process.

Engelbrech et al. (3) recognized the importance of air stripping as a simultaneous removal method in the activated sludge process for petrochemical waste treatment. They further state that in cases where the wastes consist primarily of volatile compounds, air stripping might totally suffice as a treatment method.

The ability of air stripping to remove most of the trace organic compounds is no longer subject to question. McCarty (12) evaluating the full-scale stripping tower at water factory 21, operated by the Orange County water district in southern California, concluded that removal of 80 percent could be achieved for more than a third of the organic compounds on the EPA's list of priority pollutants. However, it should be noted that air stripping is an effective method only when the contaminants are highly volatile ones (9).

When contaminants other than the volatile compounds also are present, it is advisable to use air stripping in combination with other treatment methods. McKinnon (14) reported a 30 to 50 percent reduction in the operating costs of a 2 MGD water treatment plant by installing a 9 foot diameter, 25 foot height packed air stripping tower ahead of the GAC contactors, at Rockaway Township, New Jersey.

The design of packed towers for stripping volatile organic compounds from water depends mainly on type of contaminants, desired removal, and temperature of air and water. Gaudy et al. (4) studied the factors affecting the stripping of the organic compounds. Batch-stripping experiments using diffused aeration were conducted to study the effect of temperature, airflow rate, and tank geometry. They concluded, from

their findings, that the temperature has a significant effect on the mass-transfer coefficient, k_L^a . The tank geometry also had an effect on stripping. An increase in the cross section:volume ratio increased the stripping, suggesting a great influence of surface area availability on mass transfer. Airflow rates also had similar effects.

Dyksen (2) presented data from a 1 foot diameter, 12 foot tall pilot scale packed tower. Air stripping tests were conducted at several locations in the northeast. The results showed a strong influence of the Henry's law constant (H) and the gas:liquid ratios on the removal efficiency. Experiments conducted at various water temperatures, ranging from 4°C to 24°C, showed a need for an increase in packing depth at lower temperatures to achieve equal removal efficiency. To illustrate the effect of air temperature, a heat balance between water and air for a gas:liquid of 20:1 was calculated. Since the water temperature changed by less than 1°C, he concluded that the temperature of the air has little or no effect on the removal efficiency. However, it should be noted that the temperature of the air could play a significant role when the gas:liquid ratios are high (200:1 or more), the difference in the temperatures of the influent air and water is large, and the contaminants have a low Henry's law constant.

Proper design of stripping towers, therefore, also requires the ability to predict the performance for the variation in temperatures of water and air. Since the gas/liquid partition coefficient (H) is an important factor in the design of the stripping towers, it is useful to predict the effects of temperatures on it. Very little work is reported in the literature concerning the temperature effects on H. Kavanaugh (8) gave a Vant Hoff-type equation to model the relationship of Henry's law

constant with temperature. Gossett (5) experimentally evaluated Henry's law constant, over a temperature range from 10°C to 30°C, for six compounds. By a linear regression of the data he obtained equations for "H" dependence upon temperature.

The strippability of a compound cannot be solely based on "H". For instance, Singley et al. (18) found that at 25°C, although trichloroethylene has a higher "H" value than dichloroethane, dichloroethane is more easily removed. So it is necessary to evaluate the mass transfer coefficients and their dependence upon temperature for a proper design of a stripping tower.

Theoretical Considerations

Gas-Liquid Equilibrium

When two insoluble phases (air and water) are brought into contact in order to permit transfer of constituent substances between them, the transfer of the substances present in excess takes place until equilibrium is reached. The equilibrium attained is dynamic with the molecules continuing to transfer back and forth from one phase to the other, resulting in a zero net transfer. The concentration within each phase does not change after the equilibrium is reached. In nonideal dilute solutions like water and wastewater, the equilibrium situation is defined by Henry's law, which can be mathematically stated as (21)

$$H = \frac{P_A}{c_A^*}$$
(2.1)

where

 P_A = partial pressure of the compound A (atm); C_A^* = equilibrium aqueous concentration of A (moles/m³); and H = Henry's law constant (atm x m³/mole).

Henry's law is best obeyed when the mole fraction of the solute is less than 0.02 (10), and is good only if the solute does not associate, dissociate, or undergo chemical reaction with the solvent. A knowledge of Henry's law constant (H) is necessary to calculate the direction of the mass transfer and also the distribution of resistance to mass transfer between the air and the water. The larger the Henry's law constant, the greater will be the concentration of the substance in air, at equilibrium, and hence the more easily it will be removed by air stripping from water.

Temperature is one of the factors affecting Henry's law constants. Kavanaugh and Trussell (8) suggested that the dependence of Henry's law constants upon temperature can be calculated using the enthalpy of solution data in conjunction with the estimated H value at 20°C. They gave a Vant Hoff-type equation to model the relationship of Henry's law constant to temperature:

$$Ln H = \frac{-\Delta H}{RT} + K$$
(2.2)

where

H = Henry's law constant (atm x m³/mole); R = gas constant (1.987•K•cal/K•mole °K); T = absolute temperature (°K); K = constant; and ΔH = change in enthalpy due to dissolution of component in water (K•cal/K•mole). The above equation assumes that the enthalpy change caused by the dissolution of the contaminant in water is independent of the temperature, which is justified because of the small temperature range of water that is usually encountered in the field.

If H and H₁ are Henry's law constants at any two temperatures T and T₁, respectively, then Equation (2.2) can be written as

$$Ln H - Ln H_{1} = \frac{-\Delta H}{R} \left[\frac{1}{T} - \frac{1}{T_{1}}\right]$$
(2.3)

Noting that Ln H - Ln H₁ = Ln H/H₁, the equation takes the form

$$Ln \frac{H}{H_{1}} = \frac{-\Delta H}{R} \left[\frac{1}{T} - \frac{1}{T_{1}}\right]$$
(2.4)

Equation (2.4) permits the calculation of Henry's law constant at any temperature if its value at one temperature is known. The value of ΔH can be determined from the solubility and vapor pressure data and the method is presented in Appendix A.

Mass Transfer Coefficients

Several mathematical expressions have been developed to describe the rate of transfer of a substance across a phase boundary. One of the convenient expressions is

$$N = \kappa_{L} (C_{\ell} - C_{\ell}^{*}) = \kappa_{G} (C_{g}^{*} - C_{g})$$
(2.5)

where

N = molar flux (moles/area-time);
K_L = overall liquid phase mass transfer coefficient (m/hr);
K_G = overall gas phase mass transfer coefficient (m/hr);

$$\begin{split} \text{C}_{\&} &= \text{bulk concentration in the liquid phase (moles/m^3);} \\ \text{C}_{\&}^{*} &= \text{equilibrium concentration of the liquid phase (moles/m^3);} \\ \text{C}_{g} &= \text{bulk concentration in the gas phase (moles/m^3); and} \\ \text{C}_{g}^{*} &= \text{equilibrium concentration of the gas phase (moles/m^3).} \end{split}$$
 The terms K_L and K_G incorporate the diffusional resistances in both the

gas and liquid phases and are defined by reference to the local gas and liquid phase mass transfer coefficients as (11, 21)

$$\frac{1}{K_{L}} = \frac{1}{k_{\ell}} + \frac{RT}{H k_{g}}$$
(2.6)

and

$$\frac{1}{K_{G}} = \frac{H}{k_{\ell}Rt} + \frac{1}{k_{g}}$$
(2.7)

where

 k_{l} = local liquid phase mass transfer coefficient (m/hr); k_{g} = local gas phase mass transfer coefficient (m/hr); T = absolute temperature (°K); and R = gas constant (8.2 x 10⁻⁵ m³·atm/mole·°K).

The left-hand side term in Equations (2.6) and (2.7) is the total resistance (R) to mass transfer, either considering a liquid phase or a gas phase, and is equal to the sum of the individual phase resistances

$$R = r_{l} + r_{g}$$
(2.8)

When the resistance to mass transfer lies entirely in the liquid phase film; then $r_{a} = 0$ and

$$R = r_{g}$$
(2.9)

In such a case, the transfer is said to be liquid phase controlled or

liquid phase limited. Similarly, for a gas phase controlled transfer, the total resistance is

$$R = r_{g}$$
 (2.10)

As shown in Equation (2.5), either K_L or K_G can be used to estimate the transfer rate N. The choice of which to use depends upon the convenience of working with gas or liquid phase concentrations.

Estimation of Mass Transfer Coefficients

Liss and Slater (11) proposed a method to estimate individual phase mass transfer coefficients. They suggested that individual phase coefficients can be computed by multiplying the measured coefficients of a reference substance by the ratio of the square roots of the molecular weights of the reference substance, for which the coefficient is known, to that of the other substance:

$$k_{c} = k_{r} \frac{m_{r}^{0.5}}{m_{c}}$$
 (2.11)

where the subscript r denotes a reference substance and c denotes a substance for which k is unknown. Equation (2.11) is derived basically from the Lewis-Whitman two-film theory, which states the mass transfer rate coefficient is proportional to the diffusivity (k \propto D) and certain approximations (like constant molecular size) of the kinetic theory of gases leading to a relation between diffusivity and molecular weight as $D \propto m^{-0.5}$.

Using field data measurements of total resistance for transfer from sea to air, a value of $k_g = 30$ m/hr for water and $k_\ell = 0.2$ m/hr for oxygen was established. These values were obtained by considering that the

entire resistance to the transfer of water across the interface occurs in the gas phase while for oxygen all the resistance is in the liquid phase. Knowing the individual phase mass transfer coefficients from Equation (2.11), the overall mass transfer coefficients can be calculated using Equation (2.6) or (2.7).

In packed columns, it is often necessary to estimate a quantity K_L^a , which is the product of the overall mass transfer coefficient $K_L^{(m/hr)}$ and the specific interfacial area a (m^2/m^3) of the packing material. The specific interfacial area a is the amount of surface area per unit volume of packed bed across which mass transfer takes place. The interfacial area depends on the type of packing material and is different from one mass transfer system to another. The method of packing in the same system also affects the interfacial area.

The K_L of any compound can be calculated, if the K_L of a reference compound is known, using the following expression:

$$\frac{(K_La)_c}{(K_La)_r} = \frac{(K_L)_c}{(K_L)_r}$$
(2.12)

where the subscript c denotes the compound for which K_L is unknown, and r denotes the reference compound. In this expression the interfacial area a is the same in both terms.

Equation (2.12) allows the estimation of K_L^a for any compound, provided all conditions affecting a are reproducible. The K_L^a of the reference compound can be determined experimentally.

Column Design Equations

Methods for designing packed towers for gas absorption and air

stripping have been extensively developed in the field of chemical engineering and are given in standard texts on mass transfer (e.g., Treybal [21], Perry & Chilton [16], Sherwood, Pigford, & Wilke [17]). Generally, these design expressions are more suitable for handling concentrated solutions. However, more recently, Kavanaugh and Trussell (8), Mumford and Schnoor (15), and Singley et al. (18) developed expressions for analyzing and designing packed columns for water treatment, in which the liquid solution is dilute. The equations developed below are a slight modification of those presented by Kavanaugh and Trussell, in order to handle the set of units used in this study. Figure 1 shows a countercurrent packed tower having a cross-sectional area S. If a is the specific interfacial surface area of the packing material, then the interfacial area available for mass transfer in a differential depth dZ of the packing is given by

$$dA = aS dZ$$
 (2.13)

The mass flux in this volume element is then

$$N = \frac{d(\theta_{\ell} C_{\ell})}{dA} = \frac{d(\theta_{\ell} C_{\ell})}{aS dZ}$$
(2.14)

where θ_{ℓ} is the volumetric flow rate of liquid (m³/hr) and C_{ℓ} is the bulk concentration in the liquid (moles/m³). Combining this equation with Equation (2.5)

$$N = \frac{d(\theta_{\ell} C_{\ell})}{aS dZ} = K_{L}(C_{\ell} - C_{\ell}^{*})$$
(2.15)

In water treatment the solutions are dilute. If the water lost in the off-gas due to entrainment is negligible, then θ_{ℓ} remains essentially constant and Equation (2.15) can be rearranged as



.

.

Figure 1. Counter Current Packed Tower

14

.

$$\frac{\theta_{\ell}}{S} (dC_{\ell}) = K_{L} a(C_{\ell} - C_{\ell}^{*}) dZ$$
(2.16)

Noting that θ_{ℓ}/S = L, the liquid loading rate (m $^3/m^2-hr)$, and rearranging

$$\frac{L}{K_{L}a} \frac{dC_{\ell}}{(C_{\ell} - C_{\ell}^{*})} = dZ$$
(2.17)

the integral form becomes

$$\frac{L}{K_{L}a} \int_{c_{\chi}}^{c_{\chi}^{2}} \frac{dc_{\chi}}{(c_{\chi} - c_{\chi}^{*})} = Z$$
(2.18)

where 2 refers to the top of the tower and 1 to the bottom. The integral term in Equation (2.18) is called the number of transfer units (NTU). It is a dimensionless quantity and is a measure of the difficulty of stripping. The L/K_L a term is the height providing one gas transfer unit (HTU) and it characterizes the efficiency of mass transfer. Hence, a general expression for the total height needed for the desired removal can be written as

$$Z = (HTU) (NTU)$$
 (2.19)

The expression for NTU in Equation (2.18) cannot be solved directly because it involves two variables, C_{l} and C_{l}^{*} . However, by a material balance around the bottom or top section of the column, NTU can be solved analtyically, and is presented in Appendix B.

The solution for NTU is given as

$$NTU = \frac{S}{S-1} \left[Ln \frac{(S-1) c_{\ell}^2 / c_{\ell}^1 + 1}{S} \right]$$
(2.20)

where S is the stripping factor equal to

$$S = \frac{HG}{RT L}$$
(2.21)

and

R = gas constant (8.2 x
$$10^{-5} \frac{m^3 \cdot atom}{mole \cdot \kappa}$$

T = temperature in °K.

CHAPTER III

EXPERIMENTAL METHODS

Equipment

Packed Column

The experimental apparatus is shown in Figure 2. The system consisted of a glass column with an inside diameter of 7.52 cm (3 in.) and a length of 1.83 m (6 ft). The column consisted of three different sections--a 1.4 m (4 ft) high center piece, open at both ends, and two 0.35 m (1 ft) long end pieces sealed at one end. The inlet and exit ports for the gas and liquid streams and the manometer ports were located in the end pieces. The three pieces were connected together with two 80 mm (3 in.) stainless steel clamps having teflon gaskets. A 6 mm (1/4 in.) hardware cloth having a diameter equal to the inside diameter of the column was fixed in place between the center column and the lower end piece to support the packing. The teflon gasket in the stainless steel clamp supported the hardware cloth. The entire column was insulated and mounted, with wooden clamps, on a 0.91 m by 1.22 m (3 ft by 4 ft) sheet of plywood. The plywood sheet was supported by vertical cross members to form a stand.

A water-filled manometer was connected to the column by two pieces of tygon tubing as shown in Figure 2. A three-way valve was located in the tubing connecting the lower section of the column. The pressure



Figure 2. Packed Column Apparatus

difference across the packing was measured as the difference between the water levels in the two manometer arms when the three-way valve connected the manometer with the lower section of the column. The column pressure, above ambient, at the top of the column was measured by opening the end of the manometer connected to the lower section of the column to the atmosphere, using the three-way valve. The manometer also was mounted on the plywood sheet.

Liquid Flow System

Twenty-five liter glass bottles were used as the liquid feed reservoirs. The bottles were placed at a height about 15 cm (6 in.) higher than the liquid feed pump to maintain a positive pressure on the pump. A variable speed Masterflex peristaltic pump, with a 7018 head, was used to pump the feed solution. Liquid was withdrawn through a glass tube extending to the bottom of the glass bottle, through a two-holed rubber stopper. Through the other hole a short glass tube packed with glasswool was inserted to serve as a vent. An 8 mm (5/16 in.) I.D. teflon tube was used to carry the liquid to the top of the column. A Dwyer "Rate-Master" flow meter, model RMB-84-SSV, with a stainless steel float and a control valve at the inlet, was located in the line after the pump to measure the water flow rate. The flowmeter was able to measure from 0.2 to 2.4 liters/min. The flowmeter was mounted on the plywood board. Ahead of the flowmeter a glass "T" was inserted in the line. A glass valve was connected to the free end of the "T" to facilitate feed sampling. Stainless steel clamps were used at all joints.

The influent was introduced into the column through a 6 mm (1/4 in.) steel pipe passing through a screwtype glass adaptor, located at the top

center of the upper end piece of the column. The adaptor provided an airtight seal. A Hudson garden sprayer nozzle was soldered to the end of the steel pipe. The steel pipe extended 0.45 m $(1\frac{1}{2}$ ft) down into the column. This allowed a 15 cm (6 in.) distance between the nozzle and the packing. To hold the steel pipe (and the nozzle) at the center, and away from the sides of the column, it was passed through a 6 mm (1/4 in.) hardware cloth fixed in the upper stainless steel clamp. An even distribution of the liquid over the top of the packing, for different liquid flow rates, was maintained by adjusting the orifice of the nozzle.

The effluent from the column exited through a glass port at the bottom of the lower end piece of the column. The effluent flow was regulated by raising the effluent tube to an appropriate height over the glass port. Liquid flow rate was measured at the column drain using a one liter graduated cylinder and a stopwatch to calibrate the flowmeter exactly at each flow rate.

Gas Flow System

Laboratory compressed air was used as the gas supply to the column. The gas was first passed through a Dwyer "Rate-Master"flowmeter, model RMB-57-SSU, mounted on the plywood board next to the water flowmeter. Teflon tubing, 8 mm (5/16 in.) in diameter, was used to carry the gas from the flowmeter to the column.

From the flowmeter the gas was first sent through a heat exchanging coil. The heat exchanger consisted of two 15 m (50 ft) long, 1 cm (3/8 in.) copper tubings wound side by side into a 0.3 m (1 ft) diameter ring. The two coils were brazed together for better heat conductivity. Hot or cold water from a 57 litre "Precision Lo/Temptrol" water bath was

circulated through one of the tubes, while the gas passed through the other tube in the opposite direction. The heat exchanger was placed in a corrugated box filled with styrofoam packing peanuts to serve as insulation. Once equilibrium was reached, the heat exchanging system was capable of maintaining the required constant gas temperature for an indefinite time, at all combinations of temperatures and gas flows.

The gas from the heat exchanger was dried and then purified by passing it through two 30 cm long 2 cm I.D. plastic columns connected in series, and mounted vertically on the plywood board. The lower column was loosely packed with "Drierite," indicating type, anhydrous calcium sulfate, while the second column was packed with granular activated carbon. A glass "T" with a brass fitting was arranged in the line after the purifying columns to provide sampling for the influent air. The gas then entered the column. A thermometer was inserted into the center of the glass bulb through an airtight thermometer adaptor to measure the gas temperature. The entire gas line system from the heat exchanger to the inlet port of the column was insulated with insulating pipe wrap.

The gas which was introduced above the liquid level, in the lower end piece of the column, passed through the packing and exited the column through a 2 cm (3/4 in.) exit port located in the upper end piece of the column. A 2 cm (3/4 in.) rubber hose connected to the exit port carried the off-gas out of the room, through a nearby window, and discharged it to the atmosphere.

Procedures

Packing the Column

The following procedure was used to pack the column. The upper end of the column was removed. The manometer port and the liquid exit port in the lower end piece of the column were clamped shut. The gas inlet line to the column was temporarily disconnected at the glass "T" near the gas sampling port and held at a height of about 15 cm below the top of the center piece of the column. The column was filled with water until it was overflowing through the disconnected end of the gas line. Ceramic intalox saddles, 0.95 cm (3/8 in.) in diameter, were used as packing material. The packing material was poured through the standing water in small batches until a 3 ft (0.91 m) depth of the packing was reached. A plastic funnel, cut at the bottom and having the diameter at the top equal to the inside diameter of the column, was introduced halfway through the packing to serve as a redistributor. The water from the overflow was collected and measured. This gave the volume displaced by the packing alone. The void volume was calculated from this and the total volume of the packed bed, and was found to average 61 percent of the total bed volume. The tower was then drained, the gas line reconnected, and the upper end piece of the column replaced.

Hydraulic Loading Studies

The liquid feed pump was turned on and set for a flow rate of 19 *l*/hr on the flowmeter. The pump was allowed to run for sufficient time to warm up and reach a constant pumping rate. The flow rate was measured at the column drain using a one liter graduated cylinder and a stopwatch. Keeping the liquid flow rate constant, the gas flow rate was raised in increments of $1.4 \text{ m}^3/\text{hr}$, starting from zero to a point at which column flooding was observed. At each gas flow, the pressure drop across the packing and the column pressure at the top of the packing were measured and recorded. The gas flow at the column flooding was noted and the gas:liquid ratio at the point of flooding was calculated. The liquid flow rate was increased in increments of 7.6 %/hr until it reached 83 ℓ/hr ; the entire process was repeated at each flow rate.

Preparation of Feed Solutions

The feed solution was made in a 25 liter glass bottle. The feed solution was made so that it had a 5 mg/L concentration of each of the compounds listed in Table I, except for toluene where a 2.5 mg/L concentration was used.

A 30 ml stock solution of the feed containing only the volatile organic compounds (trichloroethylene, carbontetrachloride, and toluene) was prepared in a 40 ml glass vial with a teflon lined septum cap. The stock solution was prepared so as to use only 3 ml of it in 25 liters of feed solution. The necessary volumes of each of the above compounds were added to about 20 ml of methanol in a glass vial, using a Hamilton 1001-LTN l ml syringe. The syringe was rinsed with methanol several times between the compounds to avoid contamination. The final volume of the stock solution was made up to 30 ml with methanol. A 5 ml glass syringe was used to add methanol. The vial was capped tightly, shaken vigorously, and stored at 4°C. When it was exhausted, the stock solution was made again in the same above manner.

TABLE I

FEED SOLUTION COMPONENTS AND THEIR PROPERTIES

Compound	Melting Point (°C)	Boiling Point (^O C)	Molecular Weight (gm/gm.mole)	Density at 20 ⁰ C (gm/ml)	Solubility at 20 ⁰ C (mg/l)	Vapor Pressure at 20 ⁰ C (m.m.Hg)	Henry's Law Constant 'H' at 20 ⁰ C (atm. m ³ /mole)
Carbon tetrachloride	-22.6	76.8	154.0	1.584	820 ^a	89 ^a	0.025 ^C
Trichloroethylene	-73.0	87.2	131.4	1.456	1250 ^a	60 ^a	0.01 ^C
Toluene	-95.0	111.0	92.14	0.867	516 ^a	21.34 ^a	0.0057 ^C
Nitrobenzene	5.7	210.0	123.0	1.205	1900 ^b	0.15 ^b	0.000011 ^c
Dimethylpthalate	0.0	282.0	194.2	1.19	5000 ^b	<0.01 ^b	0.00000042 ^C

^a"Chemical Engineers Handbook," 5th ed. Perry and Chilton.

^b, Water Related Environmental Fate of 129 Priority Pollutants, Volume II-EPA-440/4-9-029b, Dec. 1979.

^CInnovative and Alternative Technology Assessment Manual, EPA-430/9-78-009 (1978).

The following procedure was followed to obtain two different temperatures for the feed water. The water from the tap had an average temperature of 14°C. About 22 liters of cold tap water was collected in a 25 liter glass bottle. The water temperature remained constant at this temperature for a long time period and at most increased by 1°C over a period of 4 hours. This water was used to make the 15°C feed solution. To prepare the 22°C water, 5 liters of warm water was added to about 17 liters of tap water in a 25 liter glass bottle which was then placed on a "Sargent-Welch" heavy duty magnetic stirrer. A 2 in. long teflon coated magnetic stirring bar was then placed at the bottom of the bottle and the stirrer was turned on. The water was stirred at least for 15 hours. This allowed the water to come to room temperature (about 22°C). The 5 liters of warm water were added to bring the water rapidly to room temperature.

To prepare the feed solution, the necessary volumes of the base neutrals (nitrobenzene and dimethylphalate) needed for a 25 liter solution were first added to about 300 ml of tap water in a 500 ml glass flask having a glass stopper. The flask was shaken vigorously for 10 minutes. The glass bottle containing 22 liters of water at the required temperature was placed on the magnetic stirrer. The stirrer was turned on and the water was allowed to stir for a few minutes. The 300 ml of the previously prepared base neutrals solution was added directly to the stirring water. The flask was rinsed with tapwater, at least 5 times, and the rinse water was added to the bottle. The water was then increased to the 25 liter mark by adding additional tap water and allowed to stir. After about 5 minutes of stirring, 3 ml of the volatile organic compound's stock solution was added to the water using a 5 ml glass syringe.

The stirring was continued for one hour with the cap tightly closed. The feed solution was then allowed to sit in the covered bottle for another hour prior to treatment.

Column Operation

The stripping of the organic compounds was studied at several different conditions, which are a combination of three different gas:liquid ratios, two water temperatures, and three air temperatures. The gas and liquid flow rates used were obtained from the hydraulic loading studies and were one-half those that would cause flooding at each ratio.

To begin each run, the water bath was turned on and the thermostat was adjusted to the required temperature. When the water bath reached a temperature close to the desired air temperature, the gas flow was turned on and set at the needed flow rate. The gas was allowed to run through the system for sufficient time until the thermometer in the gas line displayed a steady temperature. At this stage, by a trial-and-error adjustment of the thermostat of the water bath, the temperature of the air entering the column was adjusted exactly to the desired temperature. Once a steady state was reached, the system was capable to delivering the gas to the column at the set temperature for an indefinite period of time. The gas flow system, thus adjusted, was not disturbed until the completion of the run. By adjusting the variable speed controller, the feed pump was set to pump the desired flow. Twenty-five liters of water having the same temperature as the feed solution under study was first pumped to bring the liquid feedline and the packed column to a thermal equilibrium. The suction tube was then moved to the feed solution bottle; the flow rate was checked and adjusted if necessary.

The sample collection was begun after 5 liters of feed solution was pumped. Forty ml glass vials with teflon lined septum caps were used to collect samples for the volatile organic compounds analysis, while one liter glass bottles with teflon lined caps were used for the base neutral samples. The influent and effluent samples were collected in pairs. The influent samples were collected immediately after the effluent samples. Three such pairs of samples were collected for each run. At least 5 liters of feed solution was allowed to run through the column between the sample collection to give sufficient time (5 to 10 minutes) for steady state to be reached again. During this period, the pressure drop across the packing, the column pr-ssure at the top, effluent temperatures of water and air were measured. After all samples were collected, the liquid flow rate was checked and found to be in all cases nearly identical to the flow rate set initially. The gas flow was turned off and the suction tube was moved to another 25 liter bottle, and about 10 liters of fresh water was pumped to the column to rinse the packing free of any organics. The samples collected were labeled and stored at 4° C until analysis.

Analytical Techniques

Glassware Cleaning

All glassware was first washed with "Alconox" detergent and rinsed with tap water. The glassware was then filled with cleaning acid and soaked for 12 hours. The cleaning acid was removed and the glassware was rinsed several times with distilled water and then dried in a 200°C oven for at least 6 hours.
All caps and teflon seals were washed with the detergent and rinsed with tapwater. They were then submerged in distilled water for 24 hours, rinsed again with distilled water, and dried in a 50°C oven. The cleaned glassware was then sealed with the appropriate caps or stoppers.

Preparation of Standard Solutions

Separate standard solutions were prepared for the volatile organic compounds and the base neutrals. The standards were made in 1 ml glass vials having rubber stoppers.

The necessary amount of each of the organic compounds was first injected into 500 µl of methanol in the l ml glass vial. The glass syringe was rinsed with methanol between the addition of the organics to avoid contamination. The balance of the methanol was then added with a l ml glass syringe to bring the final volume to l ml. The vial was shaken vigorously and allowed to settle. A l:l dilution of the standard solution with methanol produced a standard solution with a 50 percent lower concentration. A total of five standards covering the expected concentration range were made using the above dilution technique. The standards thus prepared were labeled and stored at 4°C. Fresh standards were prepared every two weeks to avoid errors due to loss of organics in storage.

Volatile Organic Compound Analysis

Samples for the volatile organic compounds (VOC) analysis were collected in 40 ml teflon lined cap vials leaving no headspace and were stored at 4°C. The samples were brought to room temperature before analysis. The analysis was carried out on an "F&M" gas chromatograph model 810 equipped with a flame ionization detector. The column was a 0.18 m $\times 3.2 \text{ mm}$ 0.D. stainless steel column packed with 1 percent SP 1000. A purge and trap apparatus, "Tekmar" model LSC 1, having a 25 cm $\times 3.2 \text{ mm}$ 0.D. stainless steel trap packed with equal portions of silica gel and Tenax GC was used to purge the water samples. The sample volumes used were 25 ml for the effluents and 5 ml for the feed. The operating parameters for the gas chromatograph and the purge trap apparatus are listed below:

Initial temperature of oven =
$$140^{\circ}$$
C
Oven temperature program = 8° C/min
Final temperature of oven = 200° C
Upper limit interval = 10 min
Injection port temperature = 200° C
Detector temperature = 300° C
Purge time = 10 min
Purge time = 10 min
Purge rate = $70 \text{ ml/min of } N_2$
Desorb temp. = 200° C

The standards were analyzed by directly injecting 0.5 μ l of the solution into the gas chromatograph. Standard curves with the peak areas calculated by the electronic integrator versus mass were established. Qualitative determination of the compounds in the sample were made by comparing the peak retention times with that of the standards, while quantitative determinations were based on the peak areas. The percent recovery with the purge trap apparatus was about 94 percent for carbon-tetrachloride, 92 percent for trichloroethylene, and 84 percent for toluene.

Base Neutrals Analysis

One liter glass bottles with teflon lined caps were used to collect samples for the base neutrals analysis. The samples were collected leaving no head space and stored at 4°C. The samples were brought to room temperature before analysis. The water sample, 900 ml, was base extracted with three 60 ml portions of methylene chloride. A 50 percent NaOH solution was used to raise the pH of the H_2^0 to over 10.5. The extracted solvent was passed through anhydrous sodium sulfate to remove moisture and then concentrated to 1 ml. Of this 0.5 µl was injected into the "F&M" gas chromatograph. The base neutral GC column was a 0.18 m x 3.2 mm 0.D. stainless steel column packed with 3 percent SP 2250. The standards also were analyzed similarly by injecting 0.5 µl of the solution. The operating parameters for the gas chromatograph are listed below:

Initial temperature of oven = 80°C
Oven temperature program = 10°C/min
Final temperature of oven = 200°C
Upper limit interval = 2 min
Injection port temperature = 200°C
Detector temperature = 300°C.

Standard curves were established and based on the peak area's quantitative determination of the compounds in the sample were made. The percent recovery for nitrobenzene was 78 percent.

Oxygen Study

Two different temperature feed solutions (15°C and 22°C) were prepared for the oxygen study. The two temperatures for the feed water were obtained in the same manner outlined in the methods for preparing the feed solution for the mixed organics. The water was aerated with the laboratory air for at least 3 hours to produce a saturated oxygen solution.

Nitrogen gas was used to strip the oxygen from the water. The temperature of the nitrogen entering the column was controlled similar to the air described in the section "Gas Flow System." To avoid wastage of nitrogen, the system was brought to thermal equilibrium using air and switched to nitrogen to study the oxygen stripping. At least six pairs of influent and effluent samples were collected in 300 ml BOD bottles.

Immediately after sampling, the dissolved oxygen was measured with a D.O. probe (Beckman expandomatic SS-2 pH meter with Orion research oxygen electrode). To verify the accuracy of the D.O. probe, duplicate samples were collected for two runs, and the dissolved oxygen measured according to the modified Winkler technique.

CHAPTER IV

RESULTS AND DISCUSSION

Tower Characteristics

Determination of the operating gas and liquid flow rates at various gas:liquid ratios is necessary for operating a packed tower. The operating flow rates are generally chosen so the pressure drop across the packing is well below the flooding point.

The operating flow rates for this research were determined from the hydraulic loading studies. Data from the hydraulic loading studies were plotted on log-log plot with the pre-sure drop as ordinate and the gas loading rate as the abscissa. Figure 3 is a plot for one of the eight water loading rates that were selected to cover the range of the liquid feed pump. The figure shows that at a fixed water flow, the pressure drop increases with increased gas loading rate. This is principally because of the reduced free cross section available for the flow of water. Three distinct regions can be identified in the curve. Initially, the increase in the pressure drop is gradual. Then there is a sharp increase characterizing the column loading. As the gas loading rate is further increased, a second sharp increase in the pressure drop occurs. At this point, called the "flooding point," liquid holdup at the top of the packing and/or at other places of intermediate restriction in the packing (such as at the redistributor) began to appear. At the same time there was an increase in the entrainment of liquid by the off-gas.



The "flooding point" was obtained from the point of intersection of the tangents drawn at the upper portion of the curve as shown in Figure 3. The air loading rates at flooding, obtained from the hydraulic loading studies, are presented in Table II. Gas and liquid loading rates for the treatment studies were selected to be one-half those which would cause flooding at each gas:liquid ratio. Figure 4 shows a plot of onehalf the gas loading at flooding ($G_f/2$) versus Ln $G_f/2/L$. The operating flow rates of air and water were obtained from this plot. Since it was convenient to set the air flow rates at points marked on the flow meter, the air flow rates were first fixed. The appropriate gas:liquid ratios were then read from Figure 4 and the necessary liquid flow rates were calculated. The operating flow rates thus obtained are presented in Table III.

Effect of Gas:Liquid Ratio

The results of the stripping study are presented in Tables XVI and XVII of Appendix C. More than 90 percent removal was obtained for the highly volatile compounds at all combinations of temperatures and gas: liquid ratios. For nitrobenzene, the results show a wide range (3.5% to 28.5%) in the removal efficiency. Dimethylpthalate was the most nonvolatile compound used in this study. The percent recovery from the extraction was the lowest of all the compounds and also the recoveries were very inconsistent. Its removals were very low and therefore a small error in analysis altered the results to a large extent, making it impossible to compare. For this reason its results are not presented.

The effect of the gas:liquid ratio on the removal efficiency is depicted in Figure 5 for carbon tetrachloride, trichloroethylene, and

Rate (L)	at Flooding		G _{f/2}
$m^3/m^2 - hr$	(G _f) m ³ /m ² - hr	G _{f/2}	L
5.05	1894.00	947.00	187.50
5.86	1769.80	884.90	151.00
6.33	1906.40	953.20	150.59
8.42	1862.95	931.48	110.63
8.59	2111.34	1055.67	122.81
11.79	1695.28	847.64	71.89
14.35	1614.56	807.28	56.26
18.26	1459.30	729.66	39.96

TABLE II

RESULTS OF HYDRAULIC LOADING STUDY



Figure 4. One-Half Gas Loading Rate at Flood Versus Ln Gas:Liquid Ratio With Data Points From Hydraulic Loading Studies

TABLE III	
-----------	--

Air flow ft ³ /hr	Air Loading (G) m ³ /m ² - hr	G/L	Liquid Load- ing (L) m ³ /m ² - hr	Liquid Flow (lit/min)
120	745.18	46.0	16.20	1.202
150	931.48	108.0	8.63	0.640
150	931.48	175.0	5.32	0.395

OPERATING FLOW RATES OF AIR AND WATER



Figure 5. Percentage Removal of Influent Contaminant as a Function of the Gas:Liquid Ratio for 15°C Air Temperature

toluene, and in Figure 6 for nitrobenzene. Unlike Figure 6, Figure 5 was plotted for only one air temperature, because the removal efficiencies of carbon tetrachloride, trichloroethylene, and toluene did not change with air temperature and their plots at the other two temperatures would be basically the same. At a constant gas:liquid ratio, water at a lower temperature had a lower removal of the contaminant. As the gas:liquid ratio was increased, higher removals were obtained. A further increase would have resulted in a closer approach to 100 percent removal. In the case of the more volatile compounds (carbon tetrachloride, trichloroethylene, and toluene), it can be observed that for an increase of more than three times in the gas:liquid ratio (from 46:1 to 175:1), not more than a 5 percent increase in the removal efficiency has occur-This suggests that there is an optimum gas:liquid ratio for these red. compounds beyond which the removal efficiency does not increase very It is therefore necessary to find this optimum gas: liquid ratio much. when designing stripping columns.

The effect of gas:liquid ratios on removal efficiency for different temperatures of water can also be seen in these figures. For the volatile compounds (Figure 5) the increase in the gas:liquid ratio, although, has caused an increase in the percent removal for both temperatures of water; the increase for the 22°C influent water is less than that of the 15°C influent water. Also, the difference in percent removal for the two temperatures of the water is higher at lower gas:liquid ratio than at the higher ratio. This indicates a very pronounced effect on the removal of the volatile compounds at the lower gas:liquid ratios due to variations in the temperature of the influent water. For nitrobenzene (Figure 6), unlike the volatile compounds, the increase in removal



Figure 6. Percentage Removal of Nitrobenzene as a Function of Gas:Liquid Ratio

efficiency with the gas:liquid ratio was alike for both temperatures of water. A possible explanation for this observation is that nitrobenzene has most of its resistance to transfer in the gas phase. An increase in the gas:liquid ratio would increase the air turbulence and would therefore result in greater removal regardless of the temperature of water. This increase would continue until approximately 100 percent removal is achieved.

Effect of Air Temperature

The percentage removal of each of the contaminants at different influent air temperatures is presented in Tables IV and V for the two influent temperatures of water.

The data show that at any constant gas:liquid ratio, the temperature of influent air has no effect on the removal of the highly volatile organics (carbon tetrachloride, trichloroethylene, and toluene). This is true for both temperatures of water. For nitrobenzene, however, an increase in percent removal with temperature of the air was observed. The effect is shown graphically in Figure 7. For both temperatures of water, there is a larger increase in the percent removal at lower gas:liquid ratios than at higher ratios. It is also observed from the graph that as the temperature of the influent air increases, the difference in the percent removal for the two temperatures of water also increases. The increase in the difference is larger at the lower gas:liquid ratio than at the higher gas:liquid ratio.

This behavior can be best explained by considering the temperature profiles presented in Tables XXI and XXII of Appendix C. The difference in the temperatures of influent and effluent water in any run was not

TABLE IV

PERCENT REMOVAL AS A FUNCTION OF INFLUENT AIR TEMPERATURE FOR 22°C INFLUENT WATER

	A	ir Temperature	
G/L	5°C	15°C	35°C
	Carbon Te	trachloride	
46	94.8	95.1	94.9
108	95.8	95.3	96.0
175	97.1	97.2	97.6
	Trichlor	oethylene	
46	94.6	94.8	94.6
108	95.9	95.5	96.8
175	97.9	97.4	97.1
	<u>To1</u>	uene	
46	94.6	94.7	94.3
108	95.3	95.4	95.8
175	97.5	97.3	97.3
	Nitrob	enzene	
46	5.0	7.0	10.4
108	10.1	11.4	16.3
175	24.1	25.5	28.5

TABLE V

PERCENT REMOVAL AS A FUNCTION OF INFLUENT AIR TEMPERATURE FOR 15°C INFLUENT WATER

`

		Air Temperature			
G/L	5°C	1500	35°C		
	Carbon T	etrachloride			
46	90.0	88.6	91.1		
108	90.2	92.2	92.9		
175	94.5	94.3	96.4		
	Trichle	proethylene			
46	90.4	91.2	90.7		
108	91.0	92.15	93.3		
175	96.0	95.0	95.0		
	To	oluene			
46	89.9	90.8	90.9		
108	92.5	92.1	92.3		
175	94.0	95.1	95.3		
Nitrobenzene					
46	3.5	4.6	6.4		
108	5.9	8.1	10.0		
175	16.8	17.5	19.0		



more than 3°C. Because the liquid phase resistance dominates in the transfer of the highly volatile compounds from water to air, no significant change in transfer is expected due to this small change in the temperature of water. Accordingly, no difference in the removal was observed for carbon tetrachloride, trichloroethylene, and toluene due to changes in the temperature of air. Nitrobenzene is mostly gas-phase controlled; its behavior can be explained by considering the gas phase temperatures. In all runs, it was found that the temperature of air leaving the tower was nearly equal to the temperature of the influent water. However, it should be noted that a temperature profile occurred along the length of the column and that air at lower gas:liquid ratios attained the exit temperature faster than those at higher gas:liquid ratios.

When 5°C air was used, there was a cold temperature zone beginning at the bottom of the column with a 5°C temperature and extending up to some point in the column until it reached the exit temperature. The length of the cold zone increased with the gas:liquid ratio. Since there was only about 3°C difference in the temperature of the influent and effluent water, the temperature zone observed in the column should be mostly due to the temperature of the air. A similar effect was observed for the 35°C air, with a warm temperature zone in the column. Because a large portion of the resistance to transfer of nitrobenzene lies in the gas phase, the temperature of air, due to creation of hot or cold air zones in the column, could result in the observed larger removals at higher air temperature than at the lower temperature. The increase in the removal was greater at the lower gas:liquid ratios than at the higher ratios. This could be due to that fact that at higher ratios the increase in air turbulence had suppressed the temperature effects of air.

Effect of Water Temperature

Figures 8 and 9 show the effect of the temperature of water on removal of the more volatile compounds and nitrobenzene, respectively. In Figure 8, the effect is shown at only one influent air temperature, because the plots for the other two temperatures would be basically the same. As expected, all of the compounds showed a reduction in removal due to lowering of water temperature from 22°C to 15°C. The effect of the water temperature became smaller and smaller as the gas:liquid ratio increased, suggesting that desired removal can be achieved for any temperature of water by changing the gas:liquid ratio. It is also interesting to note from the slopes of these lines that as the gas:liquid ratio increases, the loss in removal efficiency reduces faster for the highly volatile compounds than for the semivolatile ones. In the case of nitrobenzene (Figure 9), another interesting behavior was observed. A larger effect (reduction) on removal was obtained at higher air temperatures, mainly due to the differences in the temperature zones created in the column. Also, as the gas:liquid ratio increased, the effect reduced more rapidly for the hotter air temperatures. For the 5°C air temperature, there was practically no change in the effect. Thus, a combination of the results of the effects of water and air temperatures indicates that in extreme conditions, when the temperature of both water and air drops, the semivolatile compounds are the ones that are most affected, and it is possible to reduce this effect by increasing the air temperature.

Effect of Henry's Law Constants

Henry's law constants for the compounds are presented in Table VI



Figure 8. Percentage Reduction in Removal, Due to Change in Temperature of Feed Water, as a Function of Gas:Liquid Ratio for 15°C Air Temperature



Figure 9. Percentage Reduction in Removal of Nitrobenzene, Due to Change in the Temperature of Feed Water, as a Function of Gas:Liquid Ratio

as a function of temperature. The compounds are arranged in order of decreasing Henry's law constants. Henry's law constants (H) at 15°C and 22°C were computed using the reported (23) values at 20°C and the following equation, as suggested previously:

$$Ln \frac{H}{H_{20}} = \frac{-\Delta H}{R} \left[\frac{1}{T} - \frac{1}{T_{20}} \right]$$
(4.1)

The Δ H/R values for each of the compounds was obtained from the solubility and vapor pressure data as presented in Appendix A. Henry's law constants at the two temperatures, for carbon tetrachloride and trichloroethylene, obtained by using Kavanaugh and Trussell's (8) correction and the experimental values for trichloroethylene obtained by Gossett (5) are also presented in Table VI. A comparison shows that all three values are close to each other. When the reported Henry's law constant for nitrobenzene was used to calculate the mass transfer coefficients, logarithms of negative numbers occurred in the calculations. So a value as obtained experimentally by Mumford (15) was used.

Table VII shows the percent drop in Henry's law constants due to lowering of the temperature from 22°C to 15°C, and the corresponding percent reduction in the removal of the contaminants. Among all the temperatures of the influent air, the 15°C temperature is closer to the two temperatures of feed water and hence would represent the best conditions of equilibrium. For this reason, the values presented in Table VII are those at the influent air temperature of 15°C.

It is clear that water temperature has a strong effect on the equilibrium constant (H). For the highly volatile compounds such as carbon tetrachloride and trichloroethylene, a change of 7°C (from 22°C to 15°C) in the temperature has resulted in more than a 25 percent drop in Henry's

TABLE VI

HENRY'S LAW CONSTANTS AS A FUNCTION OF TEMPERATURE

	Reported (23) Henry's Law Constants at 20 ⁰ C	Temper Correct (atm. m	ature ed 'H' ³ /mole)	Kavana Trussell's ed H (atm	augh and (8) Correct- n. m ³ /mole)	Gossett's tal H (atm	Experimen- . m3/mole)
Compound	(atm. m ³ /mole)	2200	15°C	22 ⁰ C	15°C	22 ⁰ C	15 [°] C
Carbon Tetrachloride	0.02500	0.0272000	0.0202000	0.02786	0.01893		
Trichloroethylene	0.01000	0.0109700	0.0078900	0.01095	0.00790	0.011048	0.007747
Toluene	0.00570	0.0060400	0.0049300				
Nitrobenzene	0.00001	0.0000112	0.0000074				
	0.00006*	0.0000674	0.0000445				
0xygen	0.77200**						

*Experimental value as obtained by Mumford (15).

**Kavanaugh and Trussell (8).

TABLE VII

PERCENT REDUCTION IN REMOVAL * AS A FUNCTION OF PERCENT DROP IN H FROM 22°C TO 15°C

Compound	Percent Drop in H from 22°C to 15°C	Perc G/L = 46	cent Drop in Remov G/L = 108	val at G/L = 175
Carbon Tetrachloride	25.7	5.26	4.08	2.26
Trichloroethylene	28.1	4.12	4.11	2.26
Toluene	30.4	4.23	3.35	2.67
Nitrobenzene	34.0	34.3	29.0	31.4

*At 15⁰C air temperature.

law constants. This drop in the H values increases with decreased volatility, suggesting that the semivolatiles are the most affected by the temperature.

Figures 10, 11, and 12 are plots of percent reduction of the contaminants versus percent drop in H for different gas:liquid ratios. A strong relation between the effect on H and percent removal is seen. It is apparent that compounds having a large effect on their Henry's law constant (H), in general, also have a large effect on their removal. The effect is not linear. Although there is a significant difference in the "percent drop in H" at the bottom portion of the curves, which represents the more volatile compounds, the difference in "percent reduction in removal" is relatively small. This indicates that the effect is alike on the highly volatile compounds. The difference increases rapidly as the semivolatiles are approached.

Mass Transfer Coefficients

In Chapter II, equations were presented to design a packed column. Using these equations and the experimental data, the overall mass transfer coefficients (K_La) were calculated. The procedure is outlined in Table VIII. The K_La values thus calculated are presented in Table IX. It can be observed that compounds with higher Henry's law constants (H), in general, have higher mass transfer coefficients. The values are lower at lower temperatures. The results also show that as the gas:liquid ratio increases the mass transfer coefficients for all compounds except nitrobenzene become alike. This is because of the turbulent conditions at higher gas:liquid ratio. At low gas:liquid ratios, the flows in the column are nearer to the laminar conditions. Under these conditions,



Figure 10. Percentage Reduction in Removal of Contaminant Versus Percentage Drop in Henry's Law Constant for G/L = 46



Figure 11. Percentage Reduction in Removal of Contaminant Versus Percentage Drop in Henry's Law Constant for G/L = 108



Figure 12. Percentage Reduction in Removal of Contaminant Versus Percentage Drop in Henry's Law Constant for G/L = 175

TABLE VIII

SUMMARY OF PROCEDURE USED TO CALCULATE THE EXPERIMENTAL MASS TRANSFER COEFFICIENT ($\kappa_{\mbox{\scriptsize L}}a$)

Calculate S, the stripping factor, using G/L and the estimated H:

$$S = \frac{HG}{RTL}$$

Estimate NTU, using the above S and the fraction of the influent contaminant remaining:

NTU =
$$\frac{S}{S-1} \left[Ln \frac{(S-1) c_{\ell}^2 / c_{\ell}^1 + 1}{S} \right]$$

Calculate HTU as:

$$HTU = \frac{Z}{NTU}$$

Calculate the mass transfer coefficient:

$$K_{L}a = \frac{L}{HTU}$$

TABLE	۱	Х
-------	---	---

EXPERIMENTAL OVERALL MASS TRANSFER COEFFICIENTS (κ_{L}^{a})

Temper-		Gas:Liquid Ratio			
ature	Compound	46	108	175	
22°C	Oxygen	55.0	31.40	22.65	
	Carbon Tetrachloride	54.8	32.00	21.40	
	Trichloroethylene	53.7	31.10	21.50	
	Toluene	53.6	29.90	21.60	
	Nitrobenzene	2.0	1.50	2.72	
15°C	0xygen*	48.8	27.60	20.12	
	Carbon Tetrachloride	44.7	24.91	17.80	
	Trichloroethylene	44.2	23.90	18.00	
	Toluene	41.5	23.70	17.70	
	Nitrobenzene	1.2	1.07	1.60	

*Corrected according to $(K_{L}a)_{T} = (K_{L}a)_{20} 1.024^{(T-20)}$; $K_{L}a = 1/hr$.

the mass transfer that is occurring is mostly due to molecular diffusion and hence the mass transfer rate will differ from compound to compound to a maximum extent (although not a large value). When turbulent conditions exist in the column (such as flooding or high gas:liquid ratios), the mass transfer is mainly caused by eddy diffusion and the mass transfer coefficients become alike for all compounds (21).

The mass transfer coefficients for the compounds are also estimated using the equations presented in Chapter II. Individual phase mass transfer coefficients were calculated according to Liss and Slater (11), using the measured transfer rates of reference compounds and the following equation:

$$k_{c} = k_{r} - \frac{m_{r}}{m_{c}}^{0.5}$$
 (4.2)

where the subscript r denotes reference compound. Water with $k_g = 30$ m/hr and oxygen with $k_{\ell} = 0.2$ m/hr (both at 20°C) were chosen as reference compounds. Since the k values vary with temperature, it is appropriate that k_g and k_{ℓ} of the reference compounds be corrected. The k_{ℓ} of oxygen was corrected according to

$$k_{\ell} = k_{\ell} 1.024^{(T-20)}$$
(4.3)

The k_g of water at 20°C was used throughout, without any correction, because information on its variation with temperature was not available. The results are shown in Table X. It is clear that for the highly volatile compounds (carbon tetrachloride, trichloroethylene, and toluene), the gas phase resistance is insignificant. Therefore, any error in the calculation of total resistance to transfer of these compounds resulting

TABLE X

ESTIMATED INDIVIDUAL PHASE RESISTANCES AND OVERALL MASS TRANSFER RATES

Compound	Liquid Phase Resistance at 20°C (r _l)	Gas Phase Resistance (r _g)	Percentage of Gas Phase Resistance	Mass* Transfer Rate (K _L)m/hr
0xygen	4.76			0.21**
Carbon Tetra- chloride	10.45	0.065	0.53	0.095
Trichloro- ethylene	9.65	0.149	1.50	0.1021
Toluene	8.08	0.227	2.70	0.1204
Nitrobenzene	9.34	23.460	72.00	0.0305
Oxygen	5.56			0.18**
Carbon Tetra- chloride	12.20	0.065		0.0815
Trichloro- ethylene	11.25	0.149		0.0877
Toluene	9.43	0.227		0.1036
Nitrobenzene				
	Compound Oxygen Carbon Tetra- chloride Trichloro- ethylene Toluene Nitrobenzene Oxygen Carbon Tetra- chloride Trichloro- ethylene Toluene Nitrobenzene	Liquid Phase Resistance at 20°C (rg) Oxygen 4.76 Carbon Tetra- chloride 10.45 Trichloro- ethylene 9.65 Toluene 8.08 Nitrobenzene 9.34 Oxygen 5.56 Carbon Tetra- chloride 12.20 Trichloro- ethylene 11.25 Toluene 9.43 Nitrobenzene	Liquid Phase Resistance at 20°C (r_{ℓ})Gas Phase Resistance (r_{g})Oxygen4.76Carbon Tetra- chloride10.45Olice0.065Trichloro- ethylene9.650.149Toluene8.080.227Nitrobenzene9.3423.460Oxygen5.56Carbon Tetra- chloride12.200.065Trichloro- ethylene9.3423.460Oxygen5.56Carbon Tetra- chloride11.250.149Toluene9.430.227Nitrobenzene	Liquid Phase Resistance at 20°C CompoundGas Phase Phase (r_g)Percentage of Gas Phase Resistance (r_g)0xygen4.76Carbon Tetra- chloride10.450.0650.53Trichloro- ethylene9.650.1491.50Toluene8.080.2272.70Nitrobenzene9.3423.46072.000xygen5.56Carbon Tetra- chloride12.200.065Trichloro- ethylene11.250.1491.50Nitrobenzene9.430.227

 $\stackrel{*}{\overset{}{\overset{}}} \frac{1}{K_{L}} = \frac{1}{K_{l}} + \frac{RT}{H_{l}K_{g}} .$

**Value from Liss and Slator (11) corrected for temperature according to $K_L = K_L$ 1.024(T-20). (T) (20)

***Mass transfer coefficients calculated neglecting the change in the gas phase resistance.

from not accounting for the changes in gas phase resistance is also negligible. The gas phase resistance increases with decreasing Henry's law constant. This can be explained by the two-film theory which relates the gas phase resistance to Henry's law constant. Nitrobenzene with a very low H has more than 70 percent of its total resistance in the gas phase. If the changes due to variation of temperature are not considered in predicting its gas phase resistance, enormous errors can result. It is therefore essential to take into account the variation in the k g of water when using it to predict the gas phase resistance of the less volatile compounds. The mass transfer rate K_L (m/hr) calculated according to

$$\frac{1}{K_{L}} = \frac{1}{K_{\ell}} + \frac{RT}{H K_{g}}$$
(4.4)

is presented in the last column of Table X. The mass transfer coefficient of nitrobenzene at 15° C was not estimated because it would be improper for the above reasons to estimate without considering the temperature effects on its gas phase. Using the estimated mass transfer coefficients and the measured K_La of oxygen, the overall mass transfer coefficient of all the compounds were estimated according to the follow relationship and are presented in Table XI:

$$(K_{L}a)_{c} = (K_{L}a)_{r} \left[\frac{K_{L}}{K_{L}}\right]$$
(4.5)

where the subscript r denotes the reference compound oxygen.

A comparison of these values with the experimental ones indicates that the estimated values are about half the measured values for carbontetrachloride, trichloroethylene, and toluene. Figures 13 through 15

Temper-		Gas:Liquid Ratio		
ature	Compound	46	108	175
22°C	Carbon Tetrachloride	24.2	14.1	10.3
	Trichloroethylene	26.0	15.1	11.0
	Toluene	30.6	17.8	13.0
	Nitrobenzene	7.8	4.5	3.3
15°C	Carbon Tetrachloride	21.5	12.5	9.1
	Trichloroethylene	23.1	13.5	9.8
	Toluene	27.3	16.0	11.6
	Nitrobenzene			

TABLE XI

ESTIMATED OVERALL MASS TRANSFER COEFFICIENTS (${\rm K}_{\rm L}{\rm a}$)

^{*}K_La = l/hr.



Figure 13. Measured Versus Estimated Mass Transfer Coefficients for Carbon Tetrachloride



Figure 14. Measured Versus Estimated Mass Transfer Coefficients for Trichloroethylene


Figure 15. Measured Versus Estimated Mass Transfer Coefficients for Toluene

are plots of measured versus estimated mass transfer coefficients. The reason for this low prediction could be in the k_{g} and k_{g} values of the reference compounds used. It should be noted that these values have been obtained at sea surface and would be different from the stripping process used in this study due to variation in the hydrodynamic conditions. Also, Equation (4.2), used to calculate the individual phase mass transfer coefficients, was obtained from the two-film theory (K D), which assumes that the transfer is due to molecular diffusion. In packed columns some turbulence exists at all gas:liquid ratios and hence the total diffusion will be the sum of eddy diffusion and molecular diffusion. For this reason, the predicted mass transfer coefficients differ from compound to compound to a larger extent than in the experimental values.

Predicting Column Performance

The equations presented in the previous section to determine the experimental K_La can be worked backward using the estimated K_La values to predict the column performance. Table XII summarizes the procedure. The estimated percentage removals obtained from the above procedure are presented in Table XIII. Figures 16 through 19 show plots of estimated and measured removals as a function of gas:liquid ratios. At all gas: liquid ratios, the estimated removals are found to be low for all the compounds except nitrobenzene, suggesting conservative design of the column could occur.

65

TABLE XII

SUMMARY OF PROCEDURE USED TO PREDICT COLUMN PERFORMANCE

Calculate S, the stripping factor, using G/L and the estimated H:

$$S = \frac{HG}{RTL}$$

Estimate HTU, using estimated $K_{L}a$:

 $HTU = \frac{L}{K_{L}a}$

Calculate NTU as

$$NTU = \frac{Z}{HTU}$$

Calculate the expected fraction (F) of influent contaminant remaining:

$$F = \frac{c_{\ell}^{1}}{c_{\ell}^{2}} = \frac{S - 1}{S \cdot e^{NTU(S - 1)/S} - 1}$$

Calculate predicted percentage removed:

Percent removed =
$$(1 - F) \times 100$$

TABLE XIII

ESTIMATED PERCENTAGE REDUCTION OF INFLU-ENT CONTAMINANT CONCENTRATIONS

Influent Water				
lemper-	Compound	<u> </u>	Liquid Ra	175
22°C	Carbon Tetrachloride	74.0	77.0	82.5
	Trichloroethylene	76.0	79.5	84.3
	Toluene	81.0	84.0	88.5
	Nitrobenzene	12.0	22.3	30.7
15°C	Carbon Tetrachloride	69.0	73.0	79.0
	Trichloroethylene	77.0	74.7	81.0
	Toluene	76.6	80.6	85.8
	Nitrobenzene			



Figure 16. Estimated and Measured Percentage Removal of Carbon Tetrachloride as a Function of Gas: Liquid Ratio



Figure 17. Estimated and Measured Percentage Removal of Trichloroethylene as a Function of Gas: Liquid Ratio



Figure 12. Estimated and Measured Percentage Removal of Toluene as a Function of Gas:Liquid Ratio



Figure 19. Estimated and Measured Percentage Removal of Nitrobenzene as a Function of Gas:Liquid Ratio

CHAPTER V

CONCLUSIONS

Based on the experimental evidence presented, the following conclusions may be drawn:

1. An increase in the gas:liquid ratio, in general, will cause an increase in the removal efficiency of all the compounds. The effect is more pronounced on low volatile compounds than in the higher ones.

2. The temperature of influent air, if in a reasonable range, has no effect on the removal of highly volatile compounds. As the air temperature increases, the removal of the semivolatile compounds increases.

3. The temperature of influent water does affect the removal efficiency of all the compounds. Lower removals are obtained at lower water temperatures. The effect is greater at smaller G/L ratios than at the higher ratios.

4. Compounds with high Henry's law constant (H), in general, have higher removal efficiencies. A strong relation between the effects on H and removal efficiency due to variation in temperature occurs. Compounds with smaller H values are the most affected due to the temperature variations.

The results of these studies also indicate that it is possible to estimate the mass transfer coefficients of the compounds at different temperatures by estimating the effect of temperature on Henry's law constant (H). The effect of temperature on H, in turn, can be predicted

72

from the effects on the vapor pressure and solubility of the compound. A conservative prediction of column performance can be made by using the estimated mass transfer coefficients.

The following suggestions are offered for future work. In view of the different behavior shown by nitrobenzene, it is necessary that additional studies on compounds with lower volatility should be undertaken. Kinetics of mass transfer in packed columns should be investigated in order to predict the mass transfer coefficient more correctly.

73

BIBLIOGRAPHY

- (1) Althof, W. F. et al., "Aquifer Decontamination for Volatile Organics: A Case History," Groundwater, 19, 5, 495-504 (1981).
- (2) Dyksen, J. E., "The Use of Aeration to Remove Volatile Organics From Groundwater," Presented at the <u>Annual Conference of</u> <u>American Water Works Association</u>, Miami Beach, Florida, May 16-20, 1982.
- (3) Engelbrecht, R. S. et al., "Diffused Air Stripping of Volatile Waste Components of Petrochemical Wastes," Journal Water Pollution Control Federation, 33, 127-135 (1961).
- (4) Gaudy, A. F. et al., "Stripping Kinetics of Volatile Components of Petrochemical Wastes," Journal Water Pollution Control Federation, <u>33</u>, 382-392 (1961).
- (5) Gossett, J. M., "Solute Gas Equilibria in Multiorganic Aqueous Systems," final report to Air Force Office of Scientific Research, Bolling AFB, Washington, D.C., 19.
- (6) Guerrera, A. A., "Chemical Contamination of Aquifers on Long Island, New York," <u>Journal American Water Works Association</u>, <u>4</u>, 190-199 (1981).
- (7) Hazen, A., <u>Clean Water and How to Get It</u>, John Wiley and Sons, Inc., New York, New York (1907).
- (8) Kavanaugh, M. C., and Trussel, R. R., "Design of Aeration Towers to Strip Volatile Contaminants From Drinking Water," Journal American Water Works Association, 72, 684-692 (1980).
- (9) Kelleher, D. L., Stover, E. L., and Sullivan, M., "Investigation of Volatile Organics Removal," presented at <u>New England Water</u> <u>Works Association Meeting</u>, Randolph, Massachusetts, Jan. 17, 1980.
- (10) King, M. B., "Phase Equilibrium in Mixtures," Pergamon Press, New York (1969).
- (11) Liss, P. S., and Slater, P. G., "Flux of Gases Across the Air-Sea Interface," Nature, 247, 181-184 (1974).
- (12) McCarty, P. L., "volatile Organic Contaminants Removal by Air Stripping," presented at the <u>American Water Works Associa-</u> tion Conference, San Francisco, Calif., June 24, 1979.

- (13) McCarty, P. L., Reinhard, M., and Rittman, B. E., "Trace Organics in Groundwater," <u>Environmental Science and Technology</u>, <u>15</u>, 40-51 (1981).
- (14) McKinnor, R. J., "Aeration Plus Carbon Adsorption Remove Organics From Rockaway Township (N.J.) Groundwater Supply," presented at the Annual Convention of American Society of Civil Engineers, New Orleans, Louisiana, Oct. 25-27, 1982.
- (15) Mumfor, R. L., and Schnoor, J. L., "Air Stripping of Volatile Organics in Water," presented at the <u>Annual Conference of</u> American Water Works Association, Miami Beach, Florida, 1982.
- (16) Perry, R. H., and Chilton, C. H., <u>Chemical Engineer's Handbook</u>, 5th ed., McGraw Hill Co., New York, New York (1973).
- (17) Sherwood, T. T., and Wilke, C., <u>Mass Transfer</u>, McGraw Hill Co., New York, New York (1975).
- (18) Singley, J. E. et al., "Trace Organics Removal by Air Stripping," prepared for American Water Works Association Research Foundation, May, 1980.
- (19) Stover, E. L., "Removal of Volatile Organics From Contaminated Groundwater," presented at the <u>2nd National Symposium on</u> <u>Aquifer Restoration and Groundwater Monitoring</u>, Cincinnati, Ohio, May 26-28, 1982.
- (20) Symons, J. M. et al., <u>Removal of Organic Contaminants From Drink-ing Water Using Techniques Other Than GAC Alone</u>, progress report submitted to USEPA, Cincinnati, Ohio, May, 1979.
- (21) Treybal, R. E., <u>Mass Transfer Operations</u>, 3rd ed., McGraw Hill Book Co., New York, New York (1980).
- (22) USEPA, "Control of Organic Chemical Contaminants in Drinking Water," Federal Reg. 43(28)5756 (1978).
- (23) USEPA, "Innovative and Alternative Technology Assessment Manual," EPA-430/9-78-009 (Feb., 1980).
- (24) USEPA, "National Intern Primary Drinking Water Regulations: Control of THMs in Drinking Water," Final Rule, Fed. Reg. 44 (231)68624 (1979).
- (25) USEPA, "National Primary Drinking Water Regulations," Fed. Reg. 40(248)59566 (1975).
- (26) USEPA, "Organic Chemical Contaminants Control Options in Drinking Water," Fed. Reg. 41(136)28991 (1976).

- (27) Weinstein, N. J., "A Successful Underground Water Decontamination System: Its Meaning for Future Projects," presented at the 2nd National Symposium on Aquifer Restoration and Groundwater Monitoring, Columbus, Ohio, May 26-28, 1982.
- (28) Woodhull, R. S., "Groundwater Contamination in Connecticut," <u>Jour-</u> nal American Water Works Association, <u>4</u>, 188-189 (1981).

APPENDIX A

DETERMINATION OF THE CORRECTION FACTOR Δ H/R FOR THE TEMPERATURE DEPENDENCE OF HENRY'S LAW CONSTANT H In Chapter II, the dependence of Henry's law constant upon temperature was given by

$$Ln H = \frac{-\Delta H}{RT} + k$$
 (A.1)

The determination of ΔH , the change in enthalpy due to dissolution of the component, requires knowledge of enthalpies of the solution at the same reference state, before and after the dissolution. Since this information is not easily available, the ΔH can be determined by plotting Ln H versus 1/T in accordance with Equation (A.1), which would yield a curve like the one in Figure 20. The slope of such a plot would give Δ H/R. The H values at various temperatures can be calculated as the ratio of the vapor pressure to solubility at the same temperature. lt should be noted that due to the discrepancy in the vapor pressure and solubility data available in the literature, it is necessary that the data on variation of solubility or vapor pressure with temperature should be obtained from a single source (i.e., at the same experimental conditions). In such a case, the intercept K obtained will be different with each set of data and hence cannot be used with Equation (A.1). However, the slope $\Delta H/R$ will remain almost the same in all cases and can be used with the modified form of Equation (A.1) which is given below:

$$Ln \frac{H}{H_{1}} = \frac{-\Delta H}{R} \left[\frac{1}{T} - \frac{1}{T_{1}} \right]$$
(A.2)

The above equation can be used to calculate H at any temperature if its value at some temperature is known.

Table XIV shows data on vapor pressure and solubility as a function of temperature for the compounds used in this research. Henry's



1/T

Figure 20. Temperature Dependence of Henry's Law Constant

, **1**

TABLE XIV

VAPOR PRESSURE AND SOLUBILITY AS A FUNCTION OF TEMPERATURE

т°с	Solubility* (moles/m3)	Vapor** Pressure (VP) (atm)	Henry's Law Constant H = VP/Sol (atm m ³ /mole)	1/T °K	Ln H [,]
	Tatura da la vida	(
Larbon	letrachioride				
15 20 25 30	5.00 5.00 5.00 5.26	0.04540 0.05658 0.07013 0.08816	0.00908 0.01132 0.01403 0.01676	0.00347 0.00341 0.00336 0.00330	-4.7018 -4.4817 -4.2668 -4.0888
Trichl	oroethylene***				
25 30 35 40	8.37 8.54 8.71 8.87	0.09790 0.12368 0.15658 0.19316	0.01170 0.01448 0.01798 0.02178	0.00336 0.00330 0.00325 0.00320	-4.4485 -4.2349 -4.0187 -3.8269
Toluen	e				
10 15 20 25	3.80 4.30 4.88 5.43	0.01645 0.02237 0.02890 0.03620	0.00430 0.00522 0.00590 0.00670	0.00354 0.00347 0.00341 0.00336	-5.4491 -5.2591 -5.1328 -5.0056
Nitrob	enzene				
45 50 55 60	19.90 21.40 23.17 25.28	0.00130 0.00160 0.00230 0.00330	0.00007 0.00007 0.00010 0.00013	0.00315 0.00310 0.00305 0.00301	-9.6400 -9.5007 -9.2174 -8.9403

*<u>Solubilities of Inorganic and Organic Compounds</u>, Pergamon Press, New York, 1963.

** R. H. Perry and C. H. Chilton, <u>Chemical Engineer's Handbook</u>, McGraw Hill Co., New York, NY (1973).

*** Encyclopedia of Chemical Technology, 2nd ed., Vol. 5, John Wiley and Sons, New York, NY (1964).

law constants (H) calculated as vapor pressure/solubility and the calculated I/T and Ln H are also presented in this table. By a linear regression of this, the slope Δ H/R for each of the compounds is obtained. The results are presented in Table XV along with the correlation coefficient.

ΤA	ΒL	Ē	X۷

CORRECTION FACTOR $\Delta H/R$ for the temperature dependence of Henry's LAW constant H

Compound	Correction Factor ∆H/R	Correlation Coefficient
Carbon Tetrachloride	-3586	0.9994
Trichloroethylene	-3992	0.9999
Toluene	-2460	0.9958
Nitrobenzene	-5034	0.9879

APPENDIX B

.

SOLUTION TO THE NUMBER OF TRANSFER UNITS EQUATION

$$\theta_{\ell}(C_{\ell} - C_{\ell}) = \theta_{g}(C_{g} - C_{g})$$
(B.1)

For clean air, $C'_g = 0$. Dividing both sides by the cross section (S) of the column, Equation (B.1) becomes

$$L(C_{\ell} - C_{\ell}) = G(C_{g})$$
(B.2)

Rearranging

$$C_{g} = \frac{L}{G} \left(C_{\ell} - C_{\ell}^{\dagger} \right)$$
(B.3)

The equilibrium concentration $C_{\underline{\ell}}^{\star}$ is given by Henry's law as

$$H = \frac{P_A}{c_{\ell}^{\star}}$$
(B.4)

According to Dalton's law, the partial pressure (P_A) is equal to the product of the total pressure (P_T) and the mole-fraction (Y_A) of the substance in air. Hence, Equation (B.4) becomes

$$H = \frac{P_T Y_A}{c_{\ell}^*}$$
(B.5)

At one atmosphere total pressure ($P_T = 1$), the number of moles in one m³ of air is given by

$$n = \frac{PV}{RT} = \frac{1}{RT}$$
(B.6)

where

$$R = 8.2056 \times 10^{-5} \text{ atm-m}^3/\text{mole }^\circ\text{K}; \text{ and}$$
$$T = \text{absolute temperature } (^\circ\text{K}).$$

The concentration of the substance in air is C $_{\rm g}$ (moles/m³). Expressing this in terms of mole fraction will yield

$$Y_{A} = \frac{C_{g}}{n} = C_{g} RT$$
(B.7)

Substituting this in Equation (B.5) and rearranging will give

$$c_{g} - \frac{H}{RT} c_{\ell}^{*}$$
(B.8)

Equating Equations (B.3) and (B.8), we have

$$\frac{H}{RT} C_{\ell}^{*} = \frac{L}{G} (C_{\ell} - C_{\ell}^{\dagger})$$
(B.9)

or

۰.

$$C_{\ell}^{*} = \frac{LRT}{GH} (C_{\ell} - C_{\ell}^{'})$$
(B.10)

Defining the stripping factor S = HG/RTL, Equation (B.10) can be written as

$$C_{\ell}^{*} = \frac{C_{\ell} - C_{\ell}^{\dagger}}{S}$$
(B.11)

In Chapter II, the expression for the number of transfer units (NTU) was given as

$$NTU = \int_{C_{\ell}}^{C_{\ell}^{2}} \frac{dC_{\ell}}{(C_{\ell} - C_{\ell}^{*})}$$
(B.12)

Substituting for the value of C^{\star}_{ℓ} will give

$$NTU = \int_{C_{\ell}}^{C_{\ell}^{2}} \frac{dC_{\ell}}{c - \left(\frac{C_{\ell} - C_{\ell}}{S}\right)}$$
(B.13)

Regrouping will give

NTU =
$$\int_{C_{\ell}}^{C_{\ell}^{2}} \frac{dC_{\ell}}{(S-1)C_{\ell}+C_{\ell}^{1}}$$
(B.14)

Evaluating the integral and noting that Ln A - Ln B = Ln A/B, Equation (B.14) takes the form:

$$NTU = \frac{S}{S-1} \left[Ln \frac{(S-1) c_{\ell}^{2} + c_{\ell}}{(S-1) c_{\ell}^{1} + c_{\ell}'} \right]$$
(B.15)

A further simplification will yield

NTU =
$$\frac{S}{S-1} \left[Ln \frac{(S-1) c_{\ell}^2 / c_{\ell}^1 + 1}{S} \right]$$
 (B.16)

APPENDIX C

TABLES OF EXPERIMENTAL RESULTS

.

TABLE XVI

G/L	Influent Air Temperature (°C)	Influent* Water Concentration (moles/m ³)	Effluent* Water Concentration (moles/m ³)	Percent Removal
Carbon	Tetrachloride		<u></u>	
46	5	36.86	1.94	94.80
	15	36.56	1.79	95.10
	35	33.76	1.70	94.94
108	5	32.30	1.35	95.80
	15	34.90	1.60	95.30
	35	27.00	1.10	96.00
175	5	24.42	0.69	97.15
	15	32.30	0.90	97.20
	35	27.86	0.67	97.60
Trichle	proethylene			
46	5	34.82	1.88	94.60
	15	37.67	1.95	94.80
	35	36.21	1.96	94.60
108	5	34.40	1.40	95.90
	15	32.53	1.45	95.56
	35	33.87	1.08	96.80
175	5	33.33	0.70	97.90
	15	36.60	0.97	97.40
	35	39.95	1.16	97.10
Toluene	2			
46	5	29.00	1.57	94.60
	15	30.80	1.64	94.70
	35	28.15	1.60	94.30
108	5	24.34	1.22	95.30
	15	26.37	1.22	95.40
	35	23.66	0.98	95.80
175	5	25.50	0.63	97.52
	15	24.07	0.65	97.30
	35	29.19	0.80	97.30

RESULTS OF ORGANICS STRIPPING STUDY FOR 22°C INFLUENT WATER

.

G/L	Influent Air Temperature (°C)	Influent* Water Concentration (moles/m3)	Effluent* Water Concentration (moles/m3)	Percent Removal
Nitrobe	enzene			
47	5	41.26	39.19	5.00
	15	46.34	43.09	7.00
	35	38.30	34.30	10.40
108	5	44.47	39.96	10.10
	15	40.65	36.02	11.40
	35	39.35	32.93	16.30
175	5	40.00	30.37	24.08
	15	51.71	38.36	25.50
	35	42.85	30.65	28.50

TABLE XVI (Continued)

*All values are average of three pairs of samples.

TABLE XVII

G/L	Influent Air Temperature (°C)	Influent* Water Concentration (moles/m3)	Effluent* Water Concentration (moles/m3)	Percent Removal
Carbon	Tetrachloride			<u></u>
46	5	35.71	3.54	90.08
	15	25.89	2.94	88.60
	35	33.31	2.95	91.13
108	5	34.47	3.40	90.20
	15	34.22	2.67	92.20
	35	29.29	2.04	92.90
175	5	24.10	1.31	94.55
	15	27.56	1.55	94.39
	35	30.52	1.10	96.40
Trichle	proethylene			
46	5	33.16	3.16	90.46
	15	32.66	2.77	91.20
	35	36.34	3.36	90.76
108	5	36.05	3.25	91.00
	15	35.00	3.20	90.80
	35	33.79	2.25	93.30
175	5	32.57	1.29	96.00
	15	35.44	1.78	95.00
	35	38.57	1.94	95.00
Toluene	2			
46	5	27.40	2.77	89.90
	15	27.00	2.47	90.80
	35	28.59	2.60	90.90
108	5	25.60	1.90	92.50
	15	25.79	2.03	92.10
	35	23.12	1.78	92.30
175	5	19.97	1.20	94.00
	15	27.00	1.30	95.17
	35	28.86	1.35	95.30

RESULTS OF ORGANICS STRIPPING STUDY FOR 15°C INFLUENT WATER

G/L	Influent Air Temperature (°C)	Influent* Water Concentration (moles/m ³)	Effluent* Water Concentration (moles/m ³)	Percent Removal
Nitrobe	enzene			
46	5	43.33	41.81	3.50
	15	39.00	37.24	4.60
	35	41.95	39.27	6.40
108	5	43.66	41.06	5.90
	15	40.98	37.64	8.10
	35	35.77	32.20	10.00
175	5	42.72	35.50	16.84
	15	41.58	34.20	17.50
	35	39.50	32.03	19.00

TABLE	XVII	(Continued)

.

*All values are average of three pairs of samples.

.

TABLE XVIII

.

-

RESULTS OF OXYGEN STRIPPING STUDY FOR 22°C INFLUENT WATER

G/L	Influent Nitrogen Temperature (°C)	Influent* Water Concentration (moles/m ³)	Effluent** Water Concentration (moles/m ³)	Percent Removal
46	5	0.26970	0.01340	95.03
	15			
	35	0.25840	0.01290	95.00
108	5	0.27340	0.01010	96.31
	15			
	35	0.27810	0.01082	96.10
175	5	0.27190	0.00600	97.80
	15			
	35	0.27090	0.00538	98.00

*All values are average of three to four samples.

**All values are average of eight to ten samples.

TABLE XIX

RESULTS OF OXYGEN STRIPPING STUDY FOR 15°C INFLUENT WATER

G/L	Influent Nitrogen Temperature (°C)	Influent* Water Concentration (moles/m ³)	Effluent** Water Concentration (moles/m ³)	Percent Removal
46	5			
	15	0.30300	0.01360	95.5
	35			
108	5	0.30300	0.01000	96.7
	15	0.30380	0.01016	96.6
	35	0.30300	0.01020	96.6
175	5			
	15	0.31620	0.00563	98.2
	35			
175	35 5 15 35	0.30300	0.01020	96 - 98 -

*All values are average of three to four samples.

**All values are average of eight to ten samples.

TABLE XX

COMPARISON OF DISSOLVED OXYGEN MEASUREMENTS BY D.O. PROBE AND MODIFIED WINKLER TECHNIQUE

Influent	Water Concentration*	Effluent Water	Concentration*
Probe	Winkler Method	Probe	Winkler Method
	G/L = 1	08	
	Influent Water Temp Influent Nitrogen Tem	perature = 22°C nperature = 35°C	2
8.55	8.45	0.38 0.40	0.40 0.45
8.55	8.55	0.25 0.30 0.30 0.27	0.35 0.30 0.35 0.25
Average:			
8.55	8.50	0.32	0.35
	G/L = 1 Influent Water Temp Influent Nitrogen Tem	108 perature = 14°C nperature = 35°(2
10.15 10.10 10.10	10.20 10.10 10.15	0.35 0.35 0.38 0.40 0.38 0.40	0.35 0.35 0.40 0.45 0.40 0.40
Average:			
10.117	10.15	0.38	0.39

^{*}Mg∕ℓ.

TABLE XXI

_

		4			
G/L	Influent Air Temperature (°C)	Effluent Air Temperature (°C)	Influent Water Temperature (°C)	Effluent Water Temperature (°C)	Ambient Temperature (°C)
46	5	19	21	21	21
	15	21.5	21	21	21
	35	22	22	22	22
108	5	20	22	19	23
	15	20	21	19	21
	35	23	22	23	22
175	5	21	21	17	23
	15	21	21	18.5	21
	35	22	21	21	22

TEMPERATURE PROFILES* IN STRIPPING STUDY FOR 22°C INFLUENT WATER

 $\star \mbox{All}$ values are average of three to four readings taken over the entire run.

.

TABLE XXII

TEMPERATURE PROFILES* IN STRIPPING STUDY FOR 15°C INFLUENT WATER

G/L	Influent Air Temperature (°C)	Effluent Air Temperature (°C)	Influent Water Temperature (°C)	Effluent Water Temperature (°C)	Ambient Temperature (°C)
46	5	15	15	15	21
	15	15	15	15	21
	35	16	15	16	22
108	5	14	14	14	23
	15	15	14	14	21
	35	17	14	15	22
175	5	13	14	12.5	23
	15	15	15	14.5	21
	35	16	14	16	22

 $\ast \mbox{All}$ values are average of three to four readings taken over the entire run.

VITA

Raghupathi Reddy Pakanati

Candidate for the Degree of

Master of Science

Thesis: STUDY OF TEMPERATURE EFFECTS ON AIR STRIPPING OF VOLATILE ORGANICS FROM WATER

Major Field: Bioenvironmental Engineering

Biographical:

- Personal Data: Born in Hyderabad, India, on April 4, 1956, the son of Dr. and Mrs. Ananth R. Pakanati.
- Education: Graduated from Andhra Vidyalaya College, Hyderabad, India, in June, 1975; received the Bachelor of Technology degree in Chemical Engineering from Osmania University, Hyderabad, India, in March, 1980; completed requirements for the Master of Science degree at Oklahoma State University in December, 1984.
- Professional Experience: Production Engineer, Uniloids Ltd., March, 1980, to December, 1982; Research Assistant, Oklahoma State University, April, 1982, to June, 1984.
- Membership in Professional Societies: National Society of Professional Engineers; Chi Epsilon.