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ABSTRACT

The Use of Henry's Law Constants in the Determination of Factors the Influence VOC Concentration in Aqueous and Gaseous Phases in Wastewater Treatment Plant

by
Hui-Zhi Yu

This study focuses on the determination and comparison of Henry's law constant of eight selected volatile organic compounds in the wastewater of Linden Roselle Sewerage Authority (LRSA) wastewater treatment plant. The factors that influence the vapor-aqueous equilibrium were studied by calculating the Henry's law constants of the different species determined in the gas phase before and after the spiking of different aqueous media. Both centrifuged and uncentrifuged wastewater samples were studied, and compared to distilled water.

For wastewater sample with no suspended particles, the amount of organics in wastewater appears to influence the Henry's law constant for compounds with low and medium dipole moment. For high dipole moment compounds, both dissolved organics in wastewater and the solubility of the compound influence the Henry's law constant. For species that form hydrogen bonds, hydrogen bond effects also play an important role.

For wastewater containing suspended particles, the parameters that influence the Henry's law constant include dipole moment of, salinity, and dissolved organics. For the species which form hydrogen bonds in water, a hydrogen bond effect was noted.
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This thesis is dedicated to my parents
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INTRODUCTION

During the treatment of wastewater containing organic solvents, large quantities of volatile organic compounds (VOCs) are released into air. Many of these compounds are toxic and carcinogenic, as shown in Table 1.1.\(^1\) The emissions of these organic compounds into the atmosphere lead to a complex array of chemical and physical transformations resulting in such apparently diverse effects as photochemical reaction, long-range transport, depletion in the stratospheric ozone layer, and global weather modification, etc. Under the 1984 Resource Conservation and Recovery Act, the U.S. Environmental Protection Agency (U.S.EPA) is required to take necessary measures to protect public health and the environment from these pollutants.

According to the studies of Berglund, et al,\(^2\) wastewater treatment facilities are one of the sources of organic air pollution. Volatile compounds have a greater potential for transfer to the air phase, while semivolatiles tend to partition into the organic layer or adsorb onto the suspended solids. Chemicals, including volatile and semivolatile species can be removed from the wastewater through biochemical degradation.

To determine the fate of VOCs in a wastewater treatment plant, Linden Roselle Sewerage Authority Plant (LRSA) project was proposed and accomplished to study the changes in concentrations of VOCs as wastewater passes through the different parts of the plant. During experiments, it was found that the emission of certain volatiles from samples of wastewater was less than emission from comparable concentrations of the same substances in distilled water.\(^3\) This research focused on the relationship between the VOCs concentration in gas phase in equilibrium with the aqueous solution, comparing distilled water and wastewater
samples. Table 1.2 lists the physical properties of the eight substances that were selected for study,\[^4\] along with their dipole moments (Table 1.3).\[^5\]

### 1.1 Injection Methods for Aqueous Sample Analysis

Basically there are two injection procedures for the analysis of water samples by gas chromatography (GC): direct injection and isolation/preconcentration. The application of the direct injection method is limited by the problems associated with the presence of water in the chromatographic column. Also, the detection limit or sensitivity of this method (~ 1 mg/l) is lower than that which can be achieved by isolation/preconcentration.\[^6-10\] In isolation/preconcentration, the analytes are transferred to a more suitable matrix, organic solvent or gas phase, for GC analysis, and are concentrated as well. Thus the sensitivity of the analysis is increased.\[^11-13\]

### 1.2 Headspace Sampling of VOCs in Aqueous Sample Analysis

Headspace sampling is an indirect method for volatile organic compound analysis, in which the vapor phase above the sample is injected instead of sample matrix itself. It is used for analyzing water samples containing volatile (b.p. < 150 °C), compounds with low water solubility and also many compounds which are classified as semivolatile or semi water soluble. There are three kinds of headspace sampling, static, dynamic, and purge-and-trap.

Static headspace is a technique which uses the vapor phase in thermodynamic equilibrium with an aqueous sample in a closed vessel, as the gas sample to be injected into the GC. The information obtained from the static headspace method is an indirect measurement of the species of interest in the original sample. The relationship of the concentrations of volatile organic
compounds in the vapor and aqueous phases have been studied.\textsuperscript{[14-21]} According to the works of Mackay and Shiu, \textit{et al.},\textsuperscript{[22-23]} Henry's law can be applied to the volatiles in the gas-water equilibrium. The parameters affecting the Henry's law constant include temperature, solubility, and vapor pressure of the compound, and the composition of aqueous phase.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
No. & Compound Name & Carcinogen (EPA) & Hazardous Substance (EPA) & Hazardous Waste (EPA) & Priority Toxics (EPA) \\
\hline
1 & MeOH & - & - & - & - \\
2 & EtOH & - & - & - & - \\
3 & ACN & - & - & + & - \\
4 & Ace & - & - & + & - \\
5 & IPA & - & - & - & - \\
6 & Ether & - & - & - & - \\
7 & MeCl₂ & + & - & + & + \\
8 & CS₂ & - & + & + & - \\
9 & Clform & +/animal & + & + & + \\
10 & EtAcet & - & - & + & - \\
11 & EtCl₂ & + & - & + & + \\
12 & 111-TCE & - & - & + & + \\
13 & n-ButOH & - & - & + & - \\
14 & Bz & + & + & + & + \\
15 & CCl₄ & +/animal & + & + & + \\
16 & Tric & +/animal & + & + & + \\
17 & MIBK & - & - & + & - \\
18 & Pyr & - & - & + & - \\
19 & Tol & - & + & + & + \\
20 & CIBz & - & + & + & + \\
21 & EtBz & - & + & + & + \\
22 & m-X & - & + & + & - \\
23 & p-X & - & + & + & - \\
24 & o-X & - & + & + & - \\
25 & 1,2-DiClBz & - & + & + & + \\
26 & DMF & - & - & + & - \\
27 & ELG & - & - & - & - \\
28 & MEK & - & - & - & - \\
\hline
\end{tabular}
\caption{Toxicity Data of 28 Target VOCs}
\end{table}
When a carrier gas is passed over the aqueous sample to remove the headspace vapor for accumulation in a trap, the method is referred to as dynamic headspace sampling. It is used for samples of low concentration or for those analytes with an unfavorable gas-water partition coefficient.[24-28]

In the purge-and-trap method, the carrier gas is introduced underneath the aqueous surface, stripping the volatile organics with a stream of gas bubbles. The analytes are then trapped for analysis. To improve the efficiency of the method, the extraction and trapping steps maybe operated in a closed loop with a fixed volume of gas recirculated through the solution (closed loop gas stripping analysis [CLSA]).[29,30] The stripping efficiency depends on the specific partition coefficient of analyst and the flow rate, stripping time and total volume of stripping carrier gas.

The carrier gas containing volatile organics of interest is passed through a trap to collect and concentrate the VOCs before injecting into a gas chromatograph. A sorbent trap packed with Tenax is one which is commonly used.[31,32] Cryogenic trapping, which involves freezing either part or all of the GC column is also widely used. The advantages of the latter method include simplicity, high sensitivity, and excellent reproducibility of relative retention time. Thermally unstable and polar compounds are less likely to be lost during cryogenic trapping than using sorbent trapping method by thermal desorption.[33]

The advantages of headspace sampling over other methods of analysis include minimal sample preparation, injection of a larger sample amount into the system (in this experiment, 130 ml instead of 1 ul), and the shorter analysis times.

1.3 Limitation of Headspace Sampling

The first problem in headspace sampling is cross contamination of the system, especially when a high-and-low concentration sample sequence is performed. This
problem can be avoided by replicate rinses using zero nitrogen, and doing a blank
analysis between each sample injection. The other problem is with polar
compounds, because they are less easily volatilized due to their hydrophilicity. This
problem can be minimized by the addition of salt to lower the solubility of the
organics.

Table 1.2 Physical Properties of the Eight Selected Compounds

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Abbre. Name</th>
<th>M.W. (g)</th>
<th>B.P. °C</th>
<th>Density (g/ml)</th>
<th>Solubility (H2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>ACN</td>
<td>41.05</td>
<td>81.6</td>
<td>0.7857</td>
<td>+</td>
</tr>
<tr>
<td>Acetone</td>
<td>ACE</td>
<td>58.08</td>
<td>56.2</td>
<td>0.7899</td>
<td>+</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>IPA</td>
<td>60.11</td>
<td>82.4</td>
<td>0.7865</td>
<td>+</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>Ether</td>
<td>74.12</td>
<td>34.51</td>
<td>0.71378</td>
<td>(+)</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>MeCl2</td>
<td>84.93</td>
<td>40.0</td>
<td>1.3266</td>
<td>(+)</td>
</tr>
<tr>
<td>Benzene</td>
<td>Bz</td>
<td>78.12</td>
<td>80.1</td>
<td>0.87865</td>
<td>(+)</td>
</tr>
<tr>
<td>Toluene</td>
<td>Tol</td>
<td>92.15</td>
<td>110.6</td>
<td>0.8669</td>
<td>-</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>1,2-DiClBz</td>
<td>147.01</td>
<td>180.5</td>
<td>1.3048</td>
<td>-</td>
</tr>
</tbody>
</table>

+: Soluble

(+): Slightly soluble

-: Insoluble
Table 1.3 Dipole Moments of the Selected Compounds at 20 °C

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Abbrev.</th>
<th>Molecular Name</th>
<th>Formula</th>
<th>u (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>ACN</td>
<td>C₂H₃N</td>
<td>3.39</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>ACE</td>
<td>C₃H₆O</td>
<td>3.35</td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>IPA</td>
<td>2-C₃H₈O</td>
<td>1.692</td>
<td></td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>Ether</td>
<td>C₄H₁₀O</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>MeCl₂</td>
<td>CH₂Cl₂</td>
<td>1.90</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>Bz</td>
<td>C₆H₆</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>Tol</td>
<td>C₇H₉</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>1,2-DiclBz</td>
<td>o-C₆H₄Cl₂</td>
<td>1.59</td>
<td></td>
</tr>
</tbody>
</table>

1.4 Henry's Law

Henry's law lends itself to an assortment of applications where mass is transferred between the liquid and gas phases. In 1803, William Henry stated that, at constant temperature, the solubility of a gas dissolved in a given volume of a solvent is directly proportional to its partial pressure in the gas phase in equilibrium with the solution:[35]

\[ p_i = K_{H,i} \cdot C_{i,i} \]  \hspace{1cm} (1)

At atmospheric pressure, gas phase approaches ideal behavior:

\[ K_{H,i} = \frac{X_i \cdot P_T}{n_i} = \frac{R \cdot T_e}{C_{i,i} \cdot V_T} \]  \hspace{1cm} (2)

by rearranging Equation 2, the commonly used form of the law is obtained:
\[
\frac{K_{H,i}}{R \times T_e} = \frac{C_{g,i}}{C_{l,i}}
\]

Where:
\( p_i \) = partial pressure of compound \( i \),
\( K_{H,i} \) = Henry's law constant for \( i \),
\( C_{l,i} \) = equilibrium liquid-phase concentration of \( i \),
\( P_T \) = total pressure of the gas phase,
\( X_i \) = mole fraction of \( i \) in the gas phase,
\( n_i \) = number of moles of \( i \) in the gas phase,
\( n_T \) = total number of moles of the gas phase,
\( V_T \) = total volume of the gas phase,
\( C_{g,i} \) = equilibrium gas-phase concentration of \( i \),
\( T_e \) = equilibrium temperature,
\( H_i \) = dimensionless Henry's law constant for \( i \), and
\( R \) = universal gas constant.

The effect of equilibrium temperature and water composition on \( H \) can be evaluated by expressing Henry's law as a limiting case of the generalized criterion for vapor-liquid equilibria. The vapor pressure of the compound in the gas phase is a function of temperature, activity, and molar volume, temperature and pressure, as shown in Equation 4.

\[
H_i = r_i \times p_i^o \times \left( \frac{v_s}{R \times T_e} \right)
\]

Where:
\( r_i \) = dimensionless liquid-phase activity coefficient for \( i \)
\( p_i^o \) = vapor pressure of pure \( i \) at equilibrium temperature
1.5 Determination of Henry's Law Constant

According to the comprehensive review by Mackay and Shiu on measuring Henry's law constant, there are three basic methods: (1) use of vapor pressure and solubility data; (2) direct measurement of vapor and aqueous concentrations in a system at equilibrium; (3) measurement of relative changes in concentrations of air and aqueous solution during an equilibrium air-water-exchange process.

The first method suffers from lack of reliable solubility data as well as greater error for compounds which have the solubilities exceeding a mole fraction of a few percent. The second method is usually applied only to high concentrations because of the difficulty of sampling and analyzing the low absolute values of the concentrations in both phases. It is difficult for species at levels similar to those found in environmental samples to be determined by the second method. The third method requires only measurement of relative concentration changes in one phase. In principle the method involves passing a gas stream through a vessel containing the dissolved solute under conditions such that near equilibrium is reached. This method occasionally suffers from difficulties in achieving adequate approach to equilibrium.

A new method termed EPICS (Equilibrium Partitioning in Closed Systems), was recently developed for determination of the Henry's constant. The EPICS method is based on the closed system mass balances. If the same mass of an organic compound is injected into two sealed containers holding different liquid volumes, the equilibrium distribution of the organic between the liquid and gas phase in container 1 and 2 is described by the equation:

\[ C_{l,1} V_{l,1} + C_{g,1} V_{g,1} = C_{l,2} V_{l,2} + C_{g,2} V_{g,2} \]  

\[(5)\]

\[ v_s = \text{molar volume of the solution} \]
Where:

\[ C_{l,1} \quad C_{g,2} \quad (C_{l,2}/C_{l,1})V_{l,2} - V_{l,1} \]

\[ H = \frac{C_{g,1}}{C_{l,1}} = \frac{C_{g,2}}{V_{l,2} - (C_{l,2}/C_{l,1})V_{g,2}} \]

\[ C_{g,1} \quad C_{g,2} \quad V_{g,1} - (C_{l,2}/C_{l,1})V_{g,2} \]

Equation 6 relates Henry's constant to liquid phase concentration and known volumes. A similar equation can be obtained by measuring the gas phase. Only relative concentrations are needed for the method, and it is also not necessary to know the exact quantity of organic compound added into the container as long as the same mass is introduced into each of them. These considerations make the EPICS method retain the primary advantage of the third method. However, the equilibration problem still exists.

### 1.6 Objective

In this investigation, the Henry's law constants of eight selected target compounds were measured by adding stock standard solution of the target compounds to a closed system and measuring the concentrations of the species in the vapor phases.

\[ C_{g,i} = H \cdot C_{l,i} \]  \hspace{1cm} (7)

\[ C_{g,i}' = H' \cdot (C_{l,i} + C_{std,i}) \]  \hspace{1cm} (8)

Where

\[ C_{g,i} \quad = \text{the concentration of } i \text{ in gas phase} \]

\[ C_{l,i} \quad = \text{the concentration of } i \text{ in liquid phase} \]

\[ C_{g,i}' \quad = \text{the concentration of } i \text{ in the gas phase after} \]
standard stock solution was added

\[ C_{std,i} = \text{the concentration of standard stock solution that added in the sample} \]

\[ H = \text{Henry's law constant of } i \text{ before standard addition} \]

\[ H' = \text{Henry's law constant of } i \text{ after standard addition} \]

Since the sample condition did not change before and after the addition of standard stock solution, the values of \( H \) and \( H' \) should be same under the condition that the interactions both of the organics in the standard, and of the organics in standard with aqueous phase can be neglected. Thus, \( H \) can be calculated by subtracting Equation 7 from Equation 8 and rearranging.

\[
H = \frac{C_{g,i}' - C_{g,i}}{C_{std,i}} \tag{9}
\]

From the differences in the values between the aqueous samples, the parameters which affect the Henry's law constant can be obtained. The effects of these parameters that change the constant in the wastewater system are discussed in this study.

As Berglund, et al. stated in their study that suspended solids played an important role in organic contribution during the wastewater treatment, both centrifuged and uncentrifuged samples were analyzed in this study to determine the effect of suspended solids on Henry's law constant. Also, the salinity of the samples was studied as well. The effects of suspended solids and salinity of the samples on Henry's law constant are discussed in this paper.
EXPERIMENTAL

2.1 Sampling

The scheme of the wastewater flow in the LRSA Sewerage Treatment Plant is shown in Figure 2.1. Duplicate wastewater samples were collected by filling and sealing Teflon capped glass bottles at each selected site. The samples were refrigerated in ice and returned to the lab within two hours. All samples were kept in ice-water baths and purged with air for 48 hours. The purged samples then divided into two parts. One part was centrifuged at a temperature of 0 °C (International Portable Refrigerated Centrifuge, Model PR-2) for 30 minutes and then sealed and stored in refrigerator, as was the other part. A field blank was prepared and stored in the same way as wastewater samples to determine the background level.

Three parts of the plant were selected as sampling sites.

Screen House: Samples were collected from the inflow pit

Setting Tank: The samples were taken from the center portion of tank system.

Roughing Filter Outlet: Samples from roughing filter outlet well were collected.

The concentrations of the samples from screen house represent the inlet concentration. The concentrations of setting tank indicate the concentration of the species during the treatment, and the samples from roughing filter outlet represent the final concentrations after the wastewater has been stripped of the major part of the volatile compounds. From the concentration changes between these samples, losses of volatiles at each stage of the wastewater treatment system can be estimated. From the changes in the Henry's law constant of these samples, an
overview of the parameters that affect the organic vapor-aqueous phase partition of the whole wastewater facility can be obtained.

2.2 Apparatus

A 1 liter bottle, capped with a Teflon faced septum and a plastic crown cap with a 3/16-in hole, was used as sampling bottle. A 0.012-in i.d. stainless steel tube was used as a needle to take a gas sample from the sealed bottle. A valve which connected to a 1/8-in i.d. stainless tubing was used to control the flow of sample gas and connect the needle to the gas chromatograph gas sampling inlet. The bottle was kept in a 20.0 °C water bath to let the sample equilibrate. The sampling system is shown in Figure 2.2.

A Varian 3700 Gas Chromatograph with a crosslinked methyl silicone capillary column (0.2 mm i.d. x 50 m in length, Hewlett Packard), Flame Ionization Detector (FID), and Electron Capture Detector (ECD) was used in the analysis. The effluent split ration of FID to ECD was 10:1. The signal from the ECD was used to determine the halogenated compounds.

The GC injection system was composed of a gas sampling valve, and cryogenic focusing manifold which consists of valve A and a 2 ml volume loop, as shown in Figure 2.3. All exposed lines, along with valve A, were held at a temperature of 120 °C. The tubing through which gas samples passed were heated to 60 °C by flexible tape. Valve B was connected to a glass bead filled cryogenic trap made of 15 cm long 1/8-in i.d. stainless tubing. A second cold trap was made of the first coil of the capillary column, by immersing it into liquid nitrogen for sample focusing before final injection.
Figure 2.1 The Scheme of the Wastewater Flow in the LRSA Sewerage Treatment Plant
The GC injection system was composed of a gas sampling valve, and cryogenic focusing manifold which consists of valve A and a 2 ml volume loop, as shown in Figure 2.3. All exposed lines, along with valve A, were held at a temperature of 120 °C. The tubing through which gas samples passed were heated to 60 °C by flexible tape. Valve B was connected to a glass bead filled cryogenic trap made of 15 cm long 1/8-in i.d. stainless tubing. A second cold trap was made of the first coil of the capillary column, by immersing it into liquid nitrogen for sample focusing before final injection.

A high precision pressure gauge connected to a 1.2 liter ballast cylinder was used to measure the sample volume. Since the concentration of the species in the sample analyzed in this experiment were high, the valve connecting the 1.2 liter cylinder and pressure gauge was closed. The volume of the remaining sample measuring system is 130 ml. A vacuum pump was used to clean and evacuate the system prior to filling with the gas sample. Samples were run with helium carrier gas at a flow rate of 2.0 ml/min. The whole system is shown in Figure 2.3.

All sample signals were collected and integrated by Chromatochart-PC software (Interactive Microwave Inc.) and A/D convertor, feeding into a microcomputer.

The gas chromatography operating conditions are listed below.

\[
\begin{align*}
\text{H}_2 &: \quad 30 \text{ ml/min} & \quad \text{FID} \\
\text{He} &: \quad 2 \text{ ml/min} & \quad \text{Column} \\
\text{N}_2 &: \quad 28 \text{ ml/min} & \quad \text{Make up of the column effluent} \\
\text{N}_2 &: \quad 27 \text{ ml/min} & \quad \text{Make up of the splitter ECD effluent} \\
\text{Air} &: \quad 300 \text{ ml/min} & \quad \text{FID}
\end{align*}
\]
The gas sample analysis temperature program was

Initial Temp.: 30 °C
Program Rate: 6 °C/min
Final Time: 210 °C

Hold Time: 8 min
Hold Time: 20 min

LEGEND:
1. Sampling bottle
2. Water bath
3. Valves
4. Sampling-needle
5. Insulating cover
6. Thermometer
7. Injection port

Figure 2.2 The Sampling System for GC Analysis
2.3 Sample Preparation

2.3.1. Preparation of Stock Standard Solution

a. A dry, cleaned 50 ml vial was weighed to the nearest 0.1 mg. Eight ml of methanol was added and it was allowed to stand unstoppered until all alcohol-wetted faces had dried. The vial was then weighed to the nearest 0.1 mg.

b. Each analyte was then immediately added into the vial without contacting the top of the vial. The weight was read after each addition.

c. The Teflon cap of the vial was screwed on after all the analytes were added. The substances were mixed by inverting the vial several times.

d. The stock standard solution vial was stored at 4 °C in refrigerator with the cap covered with Parafilm.

2.3.2. Preparation of Calibration Standard Gases

a. Standards were prepared in low pressure Summa treated stainless steel canisters, 6 liter in volume.

b. The cleaned, evacuated stainless steel canister was connected to a tee-fitting with one arm connected to zero nitrogen and the other sealed by a septum. The septum was heated to 40 °C.

c. A measured amount of stock standard solution was injected into the septum using a 5 ul microsyringe, while the canister valve was closed.

d. The valve of canister was opened and zero nitrogen was allowed to flow slowly into the canister. The final pressure was read on a pressure gauge.

f. A series of calibration standard gases were prepared as above by injecting different amounts of stock standard solution.
Figure 2.3 Schematic Diagram of Analytical System
2.4 Sample Analysis Procedure

a. Valves A and B were turned to the loading position (solid lines, as shown in Figure 2.3). Helium flow into the column was adjusted to 2 ml/min.
b. The 1 liter sampling bottle was filled with 500 ml of aqueous solution, sealed and kept at constant temperature of 20.0 °C in a water bath for 120 minutes to equilibrate. The sample injection tubing was heated to 100 °C.
c. The cryogenic trap was adjusted between -110 °C to -120 °C. The target compounds were condensed at this temperature while most of carbon dioxide passed through.
d. V5, the valve connecting stainless tubing needle and gas sampling inlet was opened to let the sample pass through the first cryotrap into the 130 ml ballast volume. The pressure P was read from the pressure gauge.
e. V5 was closed after injection. The focusing cold trap is placed into a liquid nitrogen bath to form cryotrap 2. The Dewar flask was replaced with a hot water bath at a temperature of about 95 °C to allow the condensed volatile compound in cryotrap 1 to vaporize. Valve B was turned to the transfer position (dotted line, as shown in Figure 2.3) to allow the carrier gas to transfer the sample to cryotrap 2 which is held at -196 °C. The transfer process took approximately 8 to 10 minutes.
f. After the sample was transferred to the column, the liquid nitrogen bath on cryotrap 2 was replaced by a 95 °C hot water bath for 8 minutes.
g. When the hot water bath was replaced, the temperature program of the GC and the signal collection system were started.
h. Two duplicate analysis were made on each sample. The whole system was flushed with zero nitrogen before and after each run.
2.5 Procedure of Identification:

A purchased gravimetrically prepared standard gas was used as identification standard (Alphagaz, Morrisville, PA). The calibration procedure for determination of retention times was carried out in the following steps.

a. The sample bottle was replaced by a zero grade nitrogen gas cylinder. The standard gas cylinder was connected to the inlet of sampling valve A.

b. The 1.2 liter gas cylinder valve was opened and the standard gas passed through through the 2 ml loop at 1 atm, 165 °C.

c. The gas sample valve A is moved to the left (dotted line). V5 was opened, allowing zero nitrogen pass through the 2 ml loop to carry the standard gas through the glass bead filled trap to the 1.2 liter ballast volume.

d. The standard gas was condensed and transferred to the GC in the same steps as the analysis described in 2.3. The operating conditions for the GC were the same as well.

e. The retention time of each species was previously determined by Sun.[37]

2.6 Calibration Procedure

The sampling bottle was replaced by the canister containing the calibration standard gas at 40 °C. The standard gas was injected by opening the valve on the canister. The standard mixture was analyzed under the same conditions as described for the sample analysis.

2.7 Determination of Henry's Law Constant

0.5 ul of the stock standard solution was spiked into the 1 liter bottle containing 500
2 ml aqueous sample using a 5 μl microsyringe. The bottle cap was screwed on immediately after the spike. The bottle was kept in water bath at a temperature of 20.0 °C for 120 minutes to let it equilibrate. The sample was then analyzed as in 2.3 above.

2.8 Determination of Suspended Solid

a. A crucible and cover was cleaned using cleaning solution and distilled water. These were dried in an oven at 150 °C for 12 hours. The crucible and cover were placed in a desiccator and kept for 24 hours.

b. A sample of centrifuged wastewater (or distilled water) was placed in the crucible and the total weight of sample, crucible and cover was determined to the nearest 0.1 mg.

c. The sample containing crucible was covered and placed in a 95 °C oven for 12 hours. The crucible and cover was cooled in a desiccator and kept for 24 hours.

d. The crucible and cover were weighed to nearest 0.1 mg.

e. The suspended solid of the sample can be calculated using Equation 10:

\[ C = \frac{W_2 - W_0}{W_1 - W_0} \times 10^3 \text{ (ppt)} \]  

Where

- \( C \) = the suspended solid of the sample
- \( W_2 \) = the weight of crucible and cover after the sample was dried
- \( W_1 \) = the weight of sample, crucible and cover
- \( W_0 \) = the weight of crucible and cover before sample adding
RESULT AND DISCUSSION

3.1 Analysis Results

The chromatogram of the standard gas is shown in Figure 3.1. Also shown is the standard gas for calibration as Figure 3.2 and Figure 3.3 of wastewater sample. The retention times of the 8 compounds are listed in Table 3.1.

The calibration curves of the eight species are shown in Figure 3.4 to Figure 3.12, respectively. Both amounts of original and spiking concentrations of species in gas phase of aqueous samples are listed in Table 3.2 (centrifuged) and Table 3.3 (uncentrifuged). Figure 3.13 to 3.20 show the graphs of the concentrations of the eight species in different samples, respectively. The suspended solid of the samples, calculated using Equation 10 are listed in Table 3.4.

3.2 Henry's Law Constant

Henry's law constant was calculated using Equation 9. The results are listed in Table 3.5 (centrifuged) and Table 3.6 (uncentrifuged). The comparison of different samples are shown in Table 3.7. Also shown are the comparisons of the Henry's law constants determined in different samples.(Figure 3.20 to Figure 3.27).
Table 3.1 Retention Times of Eight Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>( R_T,1 ) (sec)</th>
<th>( R_T,2 ) (sec)</th>
<th>( R_T,3 ) (sec)</th>
<th>( R_T ) (sec)</th>
<th>R.S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN</td>
<td>170</td>
<td>165</td>
<td>169</td>
<td>168</td>
<td>1.57</td>
</tr>
<tr>
<td>ACE</td>
<td>212</td>
<td>200</td>
<td>216</td>
<td>209</td>
<td>3.98</td>
</tr>
<tr>
<td>IPA</td>
<td>225</td>
<td>221</td>
<td>229</td>
<td>225</td>
<td>1.78</td>
</tr>
<tr>
<td>Ether</td>
<td>255</td>
<td>234</td>
<td>258</td>
<td>249</td>
<td>5.25</td>
</tr>
<tr>
<td>MeCl₂</td>
<td>274</td>
<td>268</td>
<td>281</td>
<td>274</td>
<td>2.37</td>
</tr>
<tr>
<td>Bz</td>
<td>606</td>
<td>614</td>
<td>619</td>
<td>613</td>
<td>1.07</td>
</tr>
<tr>
<td>Tol</td>
<td>938</td>
<td>934</td>
<td>946</td>
<td>939</td>
<td>0.650</td>
</tr>
<tr>
<td>1,2-DiClBz</td>
<td>1514</td>
<td>1557</td>
<td>1563</td>
<td>1545</td>
<td>1.73</td>
</tr>
</tbody>
</table>

Table 3.2 Concentrations of Eight Compounds in Gas Phase Over Centrifuged Aqueous Sample

Sample 1: Screen House  Sample 3: Roughing Filter Outlet
Sample 2: Setting Tank  Sample 4: Distilled Water

<table>
<thead>
<tr>
<th>Compound</th>
<th>Original (ppbv)</th>
<th>Spiked (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 2 3 4</td>
<td>1 2 3 4</td>
</tr>
<tr>
<td>ACN</td>
<td>3.83 2.85 2.25 1.99</td>
<td>3.40 2.89 3.47 2.29</td>
</tr>
<tr>
<td>ACE</td>
<td>11.7 10.8 2.81 2.65</td>
<td>9.80 12.0 3.27 2.84</td>
</tr>
<tr>
<td>IPA</td>
<td>3.66 2.93 3.30 2.90</td>
<td>3.35 3.29 3.10 2.93</td>
</tr>
<tr>
<td>Ether</td>
<td>- - - -</td>
<td>17.3 *36.9 11.9</td>
</tr>
<tr>
<td>MeCl₂</td>
<td>3.84 3.62 3.88 3.22</td>
<td>5.34 26.2 *50.6 22.9</td>
</tr>
<tr>
<td>Bz</td>
<td>1.21 0.797 0.986 0.752</td>
<td>2.26 7.54 *10.9 7.25</td>
</tr>
<tr>
<td>Tol</td>
<td>3.26 5.05 1.22 6.61</td>
<td>4.55 10.8 *11.4 10.5</td>
</tr>
<tr>
<td>1,2-DiClBz</td>
<td>4.89 6.36 4.83 4.91</td>
<td>4.68 33.0 *56.4 29.4</td>
</tr>
</tbody>
</table>

* : error may be involved
- : not determined
Figure 3.1 The Chromatogram of the Purchased Standard Gas
Figure 3.2 The Chromatogram of Standard Gas for Calibration
Figure 3.3 The Chromatogram of Wastewater Sample in LRSA Sewerage Treatment Plant
Figure 3.4  Calibration Curve of Acetonitrile

Figure 3.5  Calibration Curve of Acetone
Figure 3.6 Calibration Curve of Isopropanol

Figure 3.7 Calibration Curve of Diethyl Ether
Figure 3.8 Calibration Curve of Methylene Chloride

Figure 3.9 Calibration Curve of Benzene
Figure 3.10 Calibration Curve of Toluene

Figure 3.11 Calibration Curve of 1,2-Dichlorobenzene
<table>
<thead>
<tr>
<th>Compound</th>
<th>Original (ppbv)</th>
<th>Spiked (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>ACN</td>
<td>3.69</td>
<td>2.25</td>
</tr>
<tr>
<td>ACE</td>
<td>10.9</td>
<td>10.1</td>
</tr>
<tr>
<td>IPA</td>
<td>3.41</td>
<td>3.06</td>
</tr>
<tr>
<td>Ether</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MeCl₂</td>
<td>6.01</td>
<td>4.12</td>
</tr>
<tr>
<td>Bz</td>
<td>8.50</td>
<td>4.40</td>
</tr>
<tr>
<td>Tol</td>
<td>7.38</td>
<td>7.31</td>
</tr>
<tr>
<td>1,2-DiClBz</td>
<td>4.78</td>
<td>5.95</td>
</tr>
</tbody>
</table>

*: error may be involved
-: not determined
For Figure 3.12 to Figure 3.19

Sample 1: Screen House (Centrifuged)  
Sample 1': Screen House (Uncentrifuged)  
Sample 2: Setting Tank (Centrifuged)  
Sample 3: Roughing Filter Outlet (Centrifuged)  
Sample 3': Roughing Filter Outlet (Uncentrifuged)  
Sample 4: Distilled Water  
Sample a: Aqueous Sample  
Sample b: Aqueous Sample + Std.

Figure 3.12  Comparison of Different Samples  
(Acetonitrile Concentration)
Figure 3.13  Comparison of Different Samples  
(*Acetone Concentration*)

![Bar graph showing concentration of Different Samples.]

Figure 3.14  Comparison of Different Samples  
(*Isopropanol Concentration*)

![Bar graph showing concentration of Different Samples.]
Figure 3.15  
Comparison of Different Samples  
(*Diethyl Ether Concentration*)

Figure 3.16  
Comparison of Different Samples  
(*Methylene Chloride Concentration*)
Figure 3.17  Comparison of Different Samples
(Benzene Concentration)

Figure 3.18  Comparison of Different Samples
(Toluene Concentration)
Figure 3.19  
Comparison of Different Samples  
(*1, 2-Dichlorobenzene Concentration*)

Table 3.4 Suspended Solid of Centrifuged Sample and Distilled Water

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Salinity (ppt)</th>
<th>R.S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.03</td>
<td>4.80</td>
</tr>
<tr>
<td>2</td>
<td>1.10</td>
<td>12.6</td>
</tr>
<tr>
<td>3</td>
<td>0.74</td>
<td>13.0</td>
</tr>
<tr>
<td>4</td>
<td>0.0234</td>
<td>41.5</td>
</tr>
</tbody>
</table>

Sample 1: Screen House  
Sample 3: Roughing Filter Outlet  
Sample 2: Setting Tank  
Sample 4: Distilled Water
Table 3.5 The Henry's Law Constants of Different Samples Over Centrifuged Aqueous Sample

Sample 1: Screen House          Sample 3: Roughing Filter Outlet
Sample 2: Setting Tank          Sample 4: Distilled Water

<table>
<thead>
<tr>
<th>Compound</th>
<th>Centrifuged</th>
<th>Distilled water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>ACN</td>
<td>-</td>
<td>5.57x10^{-4}</td>
</tr>
<tr>
<td>ACE</td>
<td>-</td>
<td>1.55x10^{-2}</td>
</tr>
<tr>
<td>IPA</td>
<td>-</td>
<td>4.80x10^{-3}</td>
</tr>
<tr>
<td>Ether</td>
<td>1.63x10^{-2}</td>
<td>1.54x10^{-1}</td>
</tr>
<tr>
<td>MeCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6.95x10^{-3}</td>
<td>1.05x10^{-1}</td>
</tr>
<tr>
<td>Bz</td>
<td>3.41x10^{-2}</td>
<td>2.19x10^{-1}</td>
</tr>
<tr>
<td>Tol</td>
<td>3.61x10^{-2}</td>
<td>1.63x10^{-1}</td>
</tr>
<tr>
<td>1,2-DiClBz</td>
<td>-</td>
<td>1.25x10^{-1}</td>
</tr>
</tbody>
</table>

* : error may be involved
-
: experimental error in determination was too large to calculate a reasonable value for Henry's law constant
Table 3.6 The Henry's Law Constants of Different Samples Over Uncentrifuged Aqueous Sample

Sample 1: Screen House  Sample 3: Roughing Filter Outlet
Sample 2: Setting Tank  Sample 4: Distilled Water

<table>
<thead>
<tr>
<th>Compound</th>
<th>Uncentrifuged</th>
<th>Distilled water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>ACN</td>
<td>1.08x10^-2</td>
<td>1.77x10^-3</td>
</tr>
<tr>
<td>ACE</td>
<td>2.82x10^-2</td>
<td>-</td>
</tr>
<tr>
<td>IPA</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ether</td>
<td>1.46x10^-2</td>
<td>1.60x10^-1</td>
</tr>
<tr>
<td>MeCl₂</td>
<td>9.41x10^-2</td>
<td>1.01x10^-1</td>
</tr>
<tr>
<td>Bz</td>
<td>*7.68x10^-2</td>
<td>1.02x10^-1</td>
</tr>
<tr>
<td>Tol</td>
<td>*1.14x10^-1</td>
<td>1.04x10^-1</td>
</tr>
<tr>
<td>1,2-DiClBz</td>
<td>9.97x10^-2</td>
<td>1.04x10^-1</td>
</tr>
</tbody>
</table>

* : error may be involved
- : experimental error in determination was too large to calculate a reasonable value for Henry's law constant
Table 3.7 Comparison of Henry's Law Constant of Different Samples

Sample 1: Screen House       Sample 3: Roughing Filter Outlet
Sample 2: Setting Tank       Sample 4: Distilled Water

<table>
<thead>
<tr>
<th>Compound</th>
<th>Centrifuged</th>
<th>Uncentrifuged</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN</td>
<td>1&lt;2&lt;4&lt;3</td>
<td>3&lt;2&lt;4&lt;1</td>
</tr>
<tr>
<td>ACE</td>
<td>1&lt;4&lt;3&lt;2</td>
<td>2&lt;3&lt;4&lt;1</td>
</tr>
<tr>
<td>IPA</td>
<td>1&lt;3&lt;4&lt;2</td>
<td>3&lt;2&lt;1&lt;4</td>
</tr>
<tr>
<td>Ether</td>
<td>1&lt;4&lt;2&lt;3*</td>
<td>4&lt;3&lt;1&lt;2</td>
</tr>
<tr>
<td>MeCl₂</td>
<td>1&lt;4&lt;2&lt;3*</td>
<td>3&lt;4&lt;1&lt;2</td>
</tr>
<tr>
<td>Bz</td>
<td>1&lt;4&lt;2&lt;3*</td>
<td>1&lt;2&lt;3&lt;4</td>
</tr>
<tr>
<td>Tol</td>
<td>1&lt;4&lt;2&lt;3*</td>
<td>2&lt;4&lt;1&lt;3</td>
</tr>
<tr>
<td>1,2-DiClBz</td>
<td>1&lt;4&lt;2&lt;3*</td>
<td>3&lt;1&lt;2&lt;4</td>
</tr>
</tbody>
</table>

*: error may involved
For Figure 3.20 to Figure 3.27

Sample 1: Screen House (Centrifuged)  
Sample 1': Screen House (Uncentrifuged)  
Sample 2: Setting Tank (Centrifuged)  
Sample 3: Roughing Filter Outlet (Centrifuged)  
Sample 3': Roughing Filter Outlet (Unentrifuged)  
Sample 4: Distilled Water  
Sample a: Aqueous Sample  
Sample b: Aqueous Sample + Std.

Figure 3.20  
Comparison of Different Samples  
(H of Acetonitrile)
Figure 3.21
Comparison of Different Samples
($H$ of Acetone)

Figure 3.22
Comparison of Different Samples
($H$ of Isopropanol)
Figure 3.23
Comparison of Different Samples
\( (H \) of Diethyl Ether \)

Figure 3.24
Comparison of Different Samples
\( (H \) of Methylene Chloride \)
Figure 3.25
Comparison of Different Samples
(H of Benzene)

Figure 3.26
Comparison of Different Samples
(H of Toluene)
3.3 Discussion

3.3.1 Effect of Dipole Moment

1. For compounds which have dipole moments $u < 2.00$ D, i.e. diethyl ether; isopropanol; methylene chloride; benzene; toluene and 1,2-dichlorobenzene.

   For centrifuged samples, as shown in Table 3.7, Henry’s law constant changes in the direction $1 < 4 < 2 < 3$ (except isopropanol, this will be discussed later), where sample 1 was the wastewater from screen house; sample 2 was from setting tank; sample 3 was from roughing filter, and sample 4 was distilled water. In the wastewater samples, a larger portion of the spiked material tended to vaporize into gas phase as the wastewater was more fully treated, i.e. as the concentrations of organics was lower. This tendency might be caused by hydrophobicity of the spiked species. Since the polarities and solubilities of these compounds in water were small, they tend to vaporize. The organics in aqueous
phase can lower the tendency to vaporize because they provide a matrix for non-polar compounds solvation. As the wastewater was treated, the organic level in the aqueous phase went down. This caused solubility of non-polar, hydrophobic species added to the wastewater to decrease, i.e. more evaporated into the gas phase. While the organic level in distilled water was very low, the spiked standards dissolved in the water phase as well as vaporizing into the gas phase. The polar compounds of the spiked standard dissolved in water make a matrix for non-polar compound solvation. This caused the value of the Henry’s law constant of the species in distilled water matrix to fall between the values of wastewater matrix samples.

2. For the compounds that have dipole moments \( u > 2.00 \) D, acetonitrile and acetone

   In the centrifuged sample, the Henry' law constant changes in the order of \( 1 < 2 < 4 < 3 \) for acetonitrile. As for acetone, the trends in the constant and parameters causing the change will be discussed later. Because acetonitrile dissolves in water as well as in organics, the Henry's law constant trend is \( 1 < 2 < 3 \). The difference in the trends between acetonitrile and the non-polar species is that the value of the constant in distilled water is bigger than that of the setting tank sample for acetonitrile, in contrast to non-polar compounds. The Henry's law constant of non-polar compounds depends on the amount of organics in water because of the low solubility of these compounds. However, because acetonitrile can dissolve in water easily, the Henry's law constant depends on not only the amount of organics in water but also the solubility of acetonitrile.

   The amount of dissolved organics in wastewater appears to influences the Henry's Law constant of low and medium dipole moment volatile organic compounds. However, for high dipole moment species, the solubility of the
compound in water was high. The compound solubility influences the Henry's Law constant as well as dissolved organics.

**3.3.2 Effect of Suspended Solid**

1. For compounds which have dipole moments $\mu < 2.00 \text{ D}$, i.e. diethyl ether; isopropanol; methylene chloride; benzene; toluene and 1,2-dichlorobenzene.

In uncentrifuged samples, the compounds that have dipole moments $\mu < 1.00 \text{ D}$ (benzene and toluene) showed the same trends of Henry's law constant changes as centrifuged samples. However, the others (1.00 D < $\mu < 2.00 \text{ D}$) showed a trend of $3 < 1 < 2$. The different tendency might be caused by differences in the suspended solids salinity of the samples. The compounds that have very low dipole moments, such as benzene and toluene, are very likely to absorb on suspended particles in the aqueous phase as well as dissolve in organics present in wastewater. Since the solubilities of these compounds in water were very low, the tendency of these species to absorb on suspended particles maybe the primary mechanism holding the species in aqueous phase, and there may be a tendency to saturate on particles. When the standard solution was added, the vaporizing of the compound depended on the concentrations of organics in the wastewater as described in 3.3.1. In contrast, for the compounds that have dipole moments between 1.00 and 2.00 D, absorption on suspended particles occurs as well as dissolution in both water and organic in the wastewater. The tendency of these compounds to vaporize into gas phase is related to the suspended solid of the aqueous phase when standard stock solution was added. The results of sample suspended solid determination, as shown in Table 3.4, the suspended solid of the samples changed in the direction of $3 < 1 < 2$. This tendency indicates that suspended solid of samples may have caused the differences found in Henry's law constants. For the species in distilled water matrix, the values of constant
depends also on the compound solubility in water, since the organic level in distilled water is very low. For the compounds that dissolve only slightly in water, such as diethyl ether and methylene chloride, the values of Henry’s constant were lower in distilled water in contrast to the values of the constant for the insoluble compound 1,2-dichlorobenzene, as shown in Table 3.7.

3.3.3 Other Effects

1. For the compounds that have dipole moments $u > 2.00\ \text{D}$, acetonitrile and acetone

   For uncentrifuged samples, the parameters that influence the Henry’s law constant are complex. The solubility of acetonitrile in water plays an important role as do other factors, such as suspended solids and dipole moment and the interaction between the species and the organics in water.

2. Henry’s Law Constant of Isopropanol and Acetone

   For isopropanol and acetone, the Henry’s law constant change trends were different from the other species of similar dipole moments. These compounds showed trends which are difficult to explain which may be due to hydrogen bond effects and may also be caused by experimental error. Since these compounds are easily adsorbed on the walls of transfer system, the analyses tend to be less accurate.

3.3.4 Adjustment of Hypothesis

In this study, Henry’s Law constants were calculated based on the hypothesis that the interaction between the organics both in vapor and aqueous phases can be neglected. This hypothesis can only be applied to a very simple matrix. However, the wastewater samples studied in this investigation were very complex. The dissolved organics, suspended particles in wastewater matrix as well as the sample inorganic salinity may influence the selected compound behavior, and lead such a large error
that the hypothesis can not be used in estimating Henry's Law constant trends if not be adjusted.
CONCLUSION

In this study, both centrifuged and uncentrifuged wastewater samples from LRSA wastewater treatment plant were analyzed for determining the parameters that influence the vapor-aqueous equilibrium (Henry's law constant) of eight selected volatile organic compounds.

For centrifuged wastewater samples (no suspended particles are considered), the amount of organic concentration in wastewater appears to influence the Henry's Law constant for low and medium dipole moment volatile compounds. As to high dipole moment species, the solubility of the compound was as important as the concentration level of dissolved organics in determining the Henry's law constant change trends. However, for the compounds that can form hydrogen bonds when dissolved in water, such as isopropanol and acetone in this study, the hydrogen bond effect plays an important role in Henry's law constant.

For uncentrifuged wastewater samples, the parameters that influence the Henry's law constant are very complex. These parameters include the dipole moment of the compound, sample salinity and dissolved organics. For those species that can form hydrogen bonds when dissolved in water, the effect of hydrogen bond may also play an important role.

In this study, Henry's law constants were calculated based on the hypothesis that the interaction between the organics both in vapor and aqueous phases can be neglected. This theory can only be applied to a very simple matrix sample. For the wastewater sample analyzed in this study, this theoretical hypothesis needs to be adjusted. The adjustment of the hypothesis and the parameters that interfere the Henry's law constant should be considered for further study.
BIBLIOGRAPHY


