

## ABSTRACT

INGHAM, RACHEL SCOGNAMIGLIO. Henry's Law and Freundlich Adsorption Constants for Carcinogenic Volatile Organic Contaminants. (Under the direction of Detlef R.U. Knappe).

Thirteen carcinogenic volatile organic compounds (cVOCs) are being considered for group regulation under the Drinking Water Strategy of the U.S. Environmental Protection Agency. Eight cVOCs are currently regulated (benzene; carbon tetrachloride; 1,2-dichloroethane; 1,2-dichloropropane; dichloromethane; tetrachloroethylene; trichloroethylene; vinyl chloride), and three compounds are on the third contaminant candidate list (1,3-butadiene; 1,1-dichloroethane; 1,2,3-trichloropropane). Stakeholders identified two additional cVOCs for consideration (1,1,1,2-tetrachloroethane; 1,1,2,2-tetrachloroethane). The best available technology for removal of the currently regulated cVOCs is packed tower aeration (PTA) and granular activated carbon (GAC) adsorption; however, these technologies may not prove to be suitable for all 13 compounds under consideration. Accurate knowledge of Henry's Law constants (HLCs) and Freundlich adsorption constants is necessary to assess the feasibility of using PTA or GAC to remove candidate cVOCs.

The principal objective of this research was to determine the effects of temperature and background water quality on the HLCs describing cVOC partitioning between air and water. A second objective was to provide a summary of Freundlich adsorption constants describing cVOC adsorption by GAC.

A comprehensive literature survey showed that HLCs for the currently regulated cVOCs have been measured in numerous studies; however, data are sparse for the unregulated compounds. A similar literature survey found a small number of Freundlich

adsorption constants, though data are limited to one temperature and to aqueous-phase concentrations higher than those being considered in the cVOC rule.

To fill information gaps, HLCs were determined in the laboratory following a variable headspace technique. Experiments were conducted in four waters at temperatures ranging from 5 - 35° C. The original variable headspace method was altered by increasing the tested phase ratios from three to five and by determining aqueous-phase cVOC concentrations via direct injection high performance liquid chromatography. These changes were expected to reduce uncertainty in HLC estimates because the number of data points that were collected was increased and because free surfaces were avoided during sample analysis, thus reducing volatile losses. Temperature dependence of HLCs was determined based on the van't Hoff equation.

For the eight currently regulated compounds, experimental results supported previously published van't Hoff relationships describing the temperature dependence of HLCs. However, laboratory studies revealed key information for the additional compounds under consideration. For the potent carcinogen and currently unregulated 1,2,3-trichloropropane, experimental results indicate that it is not as volatile at lower temperatures as expected based on prior studies. HLCs for 1,3-butadiene had been determined in one previous study, and results obtained here expanded the temperature range of that study. Similarly, the range of available data points for 1,1,1,2-tetrachloroethane was expanded to include HLCs at temperatures below 20° C. Using a 24-hour equilibration time, 1,1,2,2-tetrachloroethane was found to undergo hydrolysis and form trichloroethylene at higher temperatures, and an approach was developed to account for 1,1,2,2-tetrachloroethane hydrolysis when determining its HLC. Background matrix effects such as total organic

carbon and total dissolved solids concentrations had negligible effects on HLC values.

Experimental results obtained in this study and literature data were compared with three HLC estimation tools [EPI Suite (HENRYWIN), SPARC, and ASAP]. Findings indicate that predictions based purely on compound structure or compound properties tended to deviate from expected values while those based on experimental data exhibited closer agreement with HLC values determined from the van't Hoff relationship developed from the literature survey and the experiments conducted in this research. Overall, eleven of the thirteen cVOC candidates for the new group regulation can be removed by PTA and/or GAC. 1,2-dichloroethane may be difficult to remove using either treatment technology. 1,1,2,2-TeCA is not amenable to removal by PTA and insufficient data are available to assess the feasibility of 1,1,2,2-TeCA removal by GAC adsorption.

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Henry's Law and Freundlich Adsorption Constants for Carcinogenic Volatile Organic  
Contaminants

by  
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## **DEDICATION**

This work would not have been possible without the patience, encouragement, and support

from my husband and children:

Andy

Ben

Jake

Hannah

Thank you for your unwavering confidence in my abilities, decisions, and endeavors.

## **BIOGRAPHY**

Rachel Scognamiglio Ingham completed her undergraduate degree in Agricultural and Biological Engineering at Cornell University in May 1993. Following graduation, she was employed for six years by Orange Water and Sewer Authority in Carrboro, North Carolina, first as a Chemist at the Jones Ferry Road Water Treatment Plant and later as an Engineering Assistant.

Rachel married Andy Ingham in July 1997. After taking time off to raise three children, Rachel returned to academia in 2009 to pursue a graduate degree in Civil Engineering at North Carolina State University.

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## ABBREVIATIONS

1/n	Freundlich Exponent
1,1-DCA	1,1-dichloroethane
1,1,1,2-TeCA	1,1,1,2-tetrachloroethane
1,1,2,2-TeCA	1,1,2,2-tetrachloroethane
1,2-DCA	1,2-dichloroethane
1,2-DCP	1,2-dichloropropane
1,2,3-TCP	1,2,3-trichloropropane
<i>a</i>	Interfacial Area per Volume Packing Material (m <sup>2</sup> /m <sup>3</sup> )
A	Curve Fitting Parameter (van't Hoff Equation)
AdDesignS	Adsorption Design Software
ASAP	Aeration System Analysis Program
atm	Atmospheres
B	Curve Fitting Parameter (van't Hoff Equation)
BP	Boiling Point
BV <sub>50</sub>	Bed Volumes Treated at 50% Breakthrough
C	Celsius
Ca	Calcium
CaCO <sub>3</sub>	Calcium Carbonate
CCL3	Contaminant Candidate List 3
C <sub>e</sub>	Effluent Concentration
CI	Confidence Interval
C <sub><i>i,ge</i></sub>	Equilibrium Gas (Vapor) Phase Concentration of Component <i>i</i> (mass/volume or mol/volume)
C <sub><i>i,l</i></sub>	Liquid (Aqueous) Phase Concentration at any Point in the PTA Column
C <sub><i>i,le</i></sub>	Equilibrium Liquid (Aqueous) Phase Concentration of Component <i>i</i> (mass/volume or mol/volume)
C <sub><i>i,lo</i></sub>	Initial Liquid (Aqueous) Phase Concentration of Component <i>i</i> (mass/volume or mol/volume)
cm	Centimeter
C <sub>o</sub>	Influent Concentration
CT	Carbon Tetrachloride
C <sub>TCE(aq)</sub>	Equilibrium Aqueous-Phase Concentration of TCE (mol/L)
C <sub>TCE(g)</sub>	Equilibrium Gas-Phase Concentration of TCE (mol/L)
C <sub>TeCA,corr,o</sub>	Corrected Initial Concentration of 1,1,2,2-TeCA (mol/L)
C <sub>TeCA,o</sub>	Initially Added Concentration of 1,1,2,2-TeCA (mol/L)
CUR	Carbon Usage Rate (g/L)
cVOC	Carcinogenic Volatile Organic Compound
C <sub>w</sub>	Molar Density of Water (55.6 kmol/m <sup>3</sup> )

d	Days
DBCP	1,2-dibromo-3-chloropropane
DF	Degrees of Freedom
DCM	Dichloromethane
DOM	Dissolved Organic Matter
DWS	Drinking Water Strategy
EBCT	Empty Bed Contact Time (min)
EDB	Ethylene Dibromide (1,2-dibromoethane)
EFDB	Environmental Fate Data Base
EPA	Environmental Protection Agency
EPICS	Equilibrium Partitioning in Closed Systems
EPI Suite	Estimation Program Interface Suite of EPA
Fe	Iron
g	Gram
GAC	Granular Activated Carbon
gal	Gallons
GLC	Gas-Liquid Chromatography
GLC-LLC	Gas-Liquid Chromatography and Liquid-Liquid Chromatography
h	Hours
H <sup>+</sup>	Hydrogen Ion
H <sub>cc</sub>	Henry's Law Constant (dimensionless, concentration)
H <sub>cc, 10°C</sub>	Dimensionless Henry's Law Constant at 10° C
H <sub>cc, 25°C</sub>	Dimensionless Henry's Law Constant at 25° C
H <sub>cc, TCE</sub>	H <sub>cc</sub> for TCE
HENRYWIN	Estimation Program, Henry's Law Constants
HLC	Henry's Law Constant
H <sub>2</sub> O	Water
HPLC	High Performance Liquid Chromatography
H <sub>pc</sub>	Henry's Law Constant of Component <i>i</i> (atm·L/mol)
H <sub>px</sub>	Henry's Law Constant of Component <i>i</i> (atm)
H <sub>yx</sub>	Henry's Law Constant of Component <i>i</i> (dimensionless, mole fraction)
{ <i>i</i> <sub>aq</sub> }	Liquid (Aqueous) Phase Activity of Component <i>i</i>
[ <i>i</i> <sub>aq</sub> ]	Liquid (Aqueous) Phase Concentration of Component <i>i</i> (mol/L)
{ <i>i</i> <sub>g</sub> }	Gas (Vapor) Phase Activity of Component <i>i</i>
[ <i>i</i> <sub>g</sub> ]	Gas (Vapor) Phase Concentration of Component <i>i</i> (mol/L or atm)
ILL	Illinois Groundwater
J <sub><i>i</i></sub>	Rate of Mass Transfer of Component <i>i</i> (kmol/s)

K	Freundlich Adsorption Constant (mg/g)(L/μg) <sup>1/n</sup>
K*	Apparent Capacity Parameter
k <sub>g</sub>	Local Gas-Phase Mass Transfer Coefficient (m/s)
K <sub>g</sub>	Overall Gas Mass Transfer Coefficient (kmol/s·atm·m <sup>2</sup> )
K <sub>h</sub>	Equilibrium Constant, Inverse of Henry's Law Constant (dimensionless)
k <sub>L</sub>	Local Liquid (Aqueous) Phase Mass Transfer Coefficient (m/s)
K <sub>L</sub>	Overall Liquid Mass Transfer Coefficient (m/s)
kmol	Kilomoles
K <sub>ow</sub>	Octanol Water Partition Coefficient
kPa	Kilopascals
L	Liter
lb	Pounds
m	Meter
M	Molar
mg	Milligram
Mg	Magnesium
M <sub>GAC</sub>	Mass of GAC in the Adsorber
min	Minutes
mM	Millimoles
Mn	Manganese
mol	Mole
mL	Milliliter
MTZ	Mass Transfer Zone
MW <sub>g</sub>	Molecular Weight of the Gas (g/mol)
MW <sub>l</sub>	Molecular Weight of the Liquid (g/mol)
n	Number of Samples in a Group
Na	Sodium
NaCl	Sodium Chloride
N <sub>i</sub>	Total Moles of Component <i>i</i>
N <sub>i,ge</sub>	Equilibrium Gas (Vapor) Moles of Component <i>i</i>
N <sub>i,le</sub>	Equilibrium Liquid (Aqueous) Moles of Component <i>i</i>
nm	Nanometers
NOM	Natural Organic Matter
N <sub>TCE(aq)</sub>	Equilibrium Aqueous-phase Mass of TCE (mol)
N <sub>TCE(g)</sub>	Equilibrium Gas-phase Mass of TCE (mol)
N <sub>TeCA,corr,o</sub>	Corrected Initial 1,1,2,2-TeCA Mass (mol)
N <sub>TeCA,o</sub>	Actual Initial 1,1,2,2-TeCA Mass (mol)

PCE	Tetrachloroethylene
$P_i$	Partial Pressure of a Component $i$ Above a Liquid Mixture (atm)
$P_i^\circ$	Vapor Pressure of the Pure Liquid (atm)
PI	Prediction Interval
$P_i^{\text{sat}}$	Vapor Pressure of a Water Saturated Solution of Component $i$ (atm)
$\text{pK}_a$	Logarithmic Measure of the Acid Dissociation Constant
$P_T$	Total (Atmospheric) Pressure
PTA	Packed Tower Aeration
PTFE	Polytetrafluoroethylene (Teflon)
$q_e$	Adsorbed cVOC Concentration at Equilibrium (mg/g)
$Q$	Flow Rate ( $\text{m}^3/\text{h}$ )
QPPR	Quantitative Property-Property Relationship
QSPR	Quantitative Structure-Property Relationship
$R$	Universal Gas Constant [ $\text{atm}\cdot\text{m}^3/(\text{mol}\cdot\text{K})$ ]
RL	Regression Line
R-NH <sub>2</sub>	Aniline
R-NH <sub>3</sub> <sup>+</sup>	Protonated Aniline
RTI	Research Triangle Institute
$s$	Seconds
$S^2$	Unbiased Estimator of the Variance of the Slope of the Line
SCWA	Suffolk County Water Authority
SMILES	Simplified Molecular-Input Line-Entry System
SPARC	SPARC Performs Automated Reasoning in Chemistry
SPME	Solid Phase Microextraction
SSS	Standard Stock Solution
StEPP	Software to Estimate Physical Properties
$t$	t-Test result
$T$	Absolute Temperature (K)
$t_{\text{bk}}$	Time to Breakthrough (d)
TCE	Trichloroethylene
$t_{\text{crit}}$	t-Test Critical Value
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
$T_U$	Upper Temperature (K)
UNIFAC	UNIQUAC Functional-group Activity Coefficients
UNIQUAC	UNIversal QUAsiChemical
UPW	Ultra-Pure Water
UV	Ultraviolet

$V_{\text{bed}}$	Volume of the GAC Bed ( $\text{m}^3$ )
VC	Vinyl Chloride
$V_{\text{g}}$	Gas Volume (mL)
$V_{\text{g}}/V_{\text{l}}$	Phase Ratio (dimensionless)
$V_{\text{l}}$	Liquid Volume (mL)
VLE	Vapor-Liquid Equilibrium
VP/AS	Vapor Pressure/Aqueous Solubility Ratio Method
VP/WSOL	Vapor Pressure/Water Solubility Ratio Method (HENRYWIN)
$\bar{X}$	Slope of the line (equivalent to HLC when the y-intercept = 1).
$X_i$	Mole Fraction of Component $i$ in the Liquid (Aqueous) Phase (dimensionless)
WRF	Water Research Foundation
$Y_i$	Mole Fraction of Component $i$ in the Gas (Vapor) Phase (dimensionless)
$\gamma_i$	Activity Coefficient of Component $i$
$\Delta G_i$	Change in Gibbs Free Energy of Component $i$ (J/mol)
$\Delta G_r$	Change in Gibbs Energy of Reaction (J/mol)
$\Delta G_r^\circ$	Change in Gibbs Energy of Reaction Under Standard Conditions (J/mol)
$\Delta H_i$	Change in Enthalpy of Component $i$ (J/mol)
$\Delta H_r$	Change in Enthalpy of Reaction (J/mol)
$\Delta H_r^\circ$	Change in Enthalpy of Reaction Under Standard Conditions (J/mol)
$\Delta S_i$	Change in Entropy of Component $i$ (J/mol·K)
$\Delta S_r$	Change in Entropy of Reaction (J/mol·K)
$\Delta S_r^\circ$	Change in Entropy of Reaction Under Standard Conditions (J/mol·K)
$\lambda$	Wavelength
$\mu\text{mol}$	Micromole
$\mu\text{g}$	Microgram
$\mu\text{S/cm}$	Microsiemens per Centimeter
$\rho_{\text{bed}}$	Density of the GAC Bed
$\rho_{\text{g}}$	Density of the Gas ( $\text{g}/\text{m}^3$ )
$\rho_{\text{l}}$	Density of the Liquid ( $\text{g}/\text{m}^3$ )
$\phi_i$	Gas-Phase Fugacity Coefficient (dimensionless)

## CHAPTER 1 – INTRODUCTION AND OBJECTIVES

### MOTIVATION

In 2010, the United States Environmental Protection Agency (EPA) announced its new Drinking Water Strategy (DWS) to strengthen public health protection. The first of four goals under the DWS was to address contaminants as a group, rather than individually, to minimize costs associated with drinking water protection. Sixteen carcinogenic volatile organic compounds (cVOCs) were identified for the first new group regulation. Priority was given to these compounds because they are known or probable human carcinogens and thus have comparable public health goals (U.S. EPA 2011). Of the sixteen cVOCs that were initially identified, eight are currently regulated [benzene; carbon tetrachloride (CT); 1,2-dichloroethane (1,2-DCA); 1,2-dichloropropane (1,2-DCP); dichloromethane (DCM); tetrachloroethylene (PCE); trichloroethylene (TCE); vinyl chloride (VC)] and eight are on the third contaminant candidate list (CCL3) [aniline; benzyl chloride; 1,3-butadiene; 1,1-dichloroethane (1,1-DCA); nitrobenzene; methyl oxirane; 1,2,3-trichloropropane (1,2,3-TCP); urethane]. Stakeholders also identified four additional cVOCs for consideration [1,1,1,2-tetrachloroethane (1,1,1,2-TeCA); 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA); 1,2-dibromoethane (aka ethylene dibromide, EDB); 1,2-dibromo-3-chloropropane (DBCP)]. Of these twenty compounds, several will likely be eliminated from the final cVOC group regulation because of such factors as low volatility from water and inability to measure all compounds with one analytical procedure (EPA Method 524.3). Attention has turned to 13 of

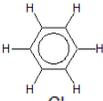
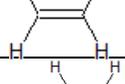
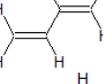
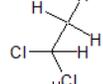
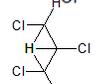
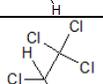
these compounds – the eight currently regulated cVOCs, three CCL3 compounds (1,3-butadiene; 1,1-DCA; 1,2,3-TCP) and two of the additional compounds (1,1,1,2-TeCA; 1,1,2,2-TeCA).

The chemical structures, octanol-water partition coefficients ( $K_{ow}$ ), aqueous solubilities, and oral cancer slope factors of the 13 candidate cVOCs are summarized in Table 1.1. The cVOCs are moderately hydrophobic, with  $\log K_{ow}$  values ranging from 1.25 (DCM) to 3.4 (PCE) and solubilities ranging from 206 mg/L (PCE) to 13,000 mg/L (DCM). The oral cancer slope factor, which is used to calculate cancer risk associated with exposure to drinking water contaminants, ranges from 0.002 [mg/(kg·day)]<sup>-1</sup> for DCM to 30 [mg/(kg·day)]<sup>-1</sup> for the potent carcinogen 1,2,3-TCP.

The best available technology for removal of the currently regulated cVOCs is packed tower aeration (PTA) and granular activated carbon (GAC) adsorption; however, these technologies may not prove to be suitable for the 13 cVOCs under consideration. Accurate knowledge of Henry's Law constants (HLCs) and Freundlich adsorption constants for these contaminants is necessary to assess the feasibility of using PTA or GAC treatment. HLC values and their temperature dependence are fairly well documented for the currently regulated cVOCs (Sander 1999; Staudinger & Roberts 1996, 2001; Warneck 2007). Also, Freundlich adsorption constants have been determined for several of the currently regulated cVOCs (Speth & Miltner 1990), though data are generally limited to one temperature and to concentrations higher than those being considered in the new cVOC rule. In contrast, few HLCs and Freundlich adsorption constants have been published for the CCL3 contaminants

and the additional cVOCs under consideration. Such information is needed to help utilities predict the capital and operating costs of meeting the new group cVOC regulation.

**Table 1.1**  
**cVOCs being considered for regulation under U.S. EPA's new group cVOC rule**

Compound	SMILES	Structure	log K <sub>ow</sub> <sup>a</sup> (25° C)	Aqueous Solubility <sup>a</sup> (mg/L)	Oral Cancer Slope Factor <sup>c</sup> [mg/(kg·day)] <sup>-1</sup>
benzene	c(ccc1)c1		2.13	1790	0.015
CT	C(Cl)(Cl)(Cl)Cl		2.83	793	0.07
1,2-DCA	ClCCCl		1.48	8600	0.047 <sup>d</sup>
1,2-DCP	ClCC(Cl)C		1.98	2800	0.036 <sup>d</sup>
DCM	ClCCl		1.25	13000	0.002
PCE	C(=C(Cl)Cl)(Cl)Cl		3.4	206	0.0021
TCE	C(=CCl)(Cl)Cl		2.42	1280	0.046
VC	C(=C)Cl		1.69 <sup>b</sup>	8800	0.72
1,3-butadiene	C(C=C)=C		1.99	735	3.4
CCL3 cVOCs					
1,1-DCA	C(Cl)(Cl)C		1.79	5040	0.0057
1,2,3-TCP	ClCC(Cl)CCl		2.27	1750	30
Additional cVOCs					
1,1,1,2-TeCA	C(CCl)(Cl)(Cl)Cl		2.647 <sup>b</sup>	1070	0.026
1,1,2,2-TeCA	C(C(Cl)Cl)(Cl)Cl		2.39	2830	0.2

<sup>a</sup>Estimation Program Interface (EPI) Suite of EPA

<sup>b</sup>SciFinder Scholar

<sup>c</sup>Integrated Risk Information System (IRIS)

<sup>d</sup>OEHAA Toxicity Criteria Database

## **RESEARCH OBJECTIVES**

The principal objective of this research was to determine the effects of temperature and background water quality on the HLCs describing cVOC partitioning between air and water. A second objective was to provide a summary of Freundlich adsorption constants describing cVOC adsorption by GAC. Specific objectives included:

1. Conducting extensive literature surveys to compile available HLCs and Freundlich adsorption constants for the target cVOCs,
2. Evaluating the accuracy of predictive tools in estimating HLCs, and
3. Conducting laboratory experiments to establish the dependence of HLC values on temperature and background water matrix [total organic carbon (TOC) and total dissolved solids (TDS) concentration].

Results from this research will aid water treatment professionals in (i) assessing the suitability of air stripping and GAC adsorption processes for the removal of currently unregulated cVOCs and (ii) optimizing the design and operation of air stripping and GAC adsorption processes for cVOC removal.

## CHAPTER 2 – BACKGROUND

### HENRY'S LAW

John J. Carroll's 1991 article entitled "What is Henry's Law?" seeks to explain what he claims is one of the most widely used, and often misused, principles of chemical thermodynamics. This principle dates back to 1803 and English chemist William Henry's "Experiments on the Quantity of Gases adsorbed by Water, at different Temperatures, and under different Pressures."

Although Raoult's Law was not established until 1882, it is mentioned here as a basis for understanding Henry's Law. Raoult's Law states that the ratio between the partial pressure of a component  $i$  above a liquid mixture ( $P_i$ , atm) and the vapor pressure of the pure liquid ( $P_i^o$ , atm) is proportional to the mole fraction of component  $i$  in the liquid phase ( $X_i$ , dimensionless) (Atkins & de Paula 2006).

$$P_i = X_i P_i^o \quad \text{or} \quad X_i = \frac{P_i}{P_i^o} \quad \text{Equation 2.1}$$

Ideal solutions obey Raoult's Law. Henry found that, for dilute, real solutions (such as those encountered in environmental applications), a linear relationship exists between the partial pressure of a solute and its mole fraction; however, the slope of the line is no longer the vapor pressure of the pure substance (Betterton 1992). This behavior, known as Henry's Law, is described by the equation

$$P_i = X_i H_{px} \quad \text{or} \quad H_{px} = \frac{P_i}{X_i} \quad \text{Equation 2.2}$$

where  $H_{px}$  is the HLC of component  $i$  (atm) (Atkins & de Paula 2006, Staudinger & Roberts 1996). The subscripts  $p$  and  $x$  indicate that the HLC value is based on partial pressure and mole fraction of the aqueous-phase component. Of note is the fact that this definition of Henry's Law has the gas-phase concentration in the numerator, meaning that a larger HLC value indicates greater volatility.

Henry's Law can also be written in terms of the component's activity or concentration:

$$P_i = H_{pc} \{i_{aq}\} = H_{pc} \gamma_i [i_{aq}] \quad \text{or} \quad H_{pc} = \frac{P_i}{\{i_{aq}\}} = \frac{P_i}{\gamma_i [i_{aq}]} \quad \text{Equation 2.3}$$

where  $\{i_{aq}\}$  describes the equilibrium aqueous-phase activity of component  $i$ ,  $\gamma_i$  represents the activity coefficient of component  $i$ ,  $[i_{aq}]$  is the equilibrium aqueous-phase concentration of component  $i$  (mol/L), and  $H_{pc}$  is the HLC of component  $i$  (atm·L/mol) (Atkins & de Paula 2006, Betterton 1992, Crittenden et al. 2005). The subscripts  $p$  and  $c$  indicate that the HLC value is based on partial pressure and aqueous-phase concentration. The activity coefficient is assumed to be 1 for most fresh waters with an ionic strength less than 0.01 M (Crittenden et al. 2005).

The various forms of Henry's Law give rise to a wide variety of reported units. Consistent with Staudinger and Roberts (1996), the dimensionless Henry's law constant,  $H_{cc}$ , is used in this research. The subscript  $c$  indicates that the HLC value is based on the concentrations of the gaseous and aqueous-phase components, respectively.

$$H_{cc} = \frac{[i_g]}{[i_{aq}]} = \frac{C_{i,ge}}{C_{i,le}} = \frac{\frac{\text{mol cVOC}}{L_{air}}}{\frac{\text{mol cVOC}}{L_{H_2O}}} \quad \text{Equation 2.4}$$

where  $[i_g]$  and  $C_{i,ge}$  represent the gas-phase concentration of compound  $i$  at equilibrium (mol/L) and  $C_{i,le}$  represents the equilibrium aqueous-phase concentration of compound  $i$  (mol/L). An alternate form of the dimensionless HLC, based on mole fractions of component  $i$  in the aqueous ( $X_i$ ) and gas-phase ( $Y_i$ ), is also reported in literature:

$$H_{yx} = \frac{Y_i}{X_i} \quad \text{Equation 2.5}$$

The subscripts x and y indicate that the HLC value is based on the mole fractions of the aqueous and gaseous phase components, respectively.

All data obtained through literature surveys were converted to  $H_{cc}$  using Equation 2.6 (see Table 2.1 for additional conversions)

$$H_{cc} = H_{yx} \left( \frac{MW_l}{\rho_l} \right) \left( \frac{\rho_g}{MW_g} \right) = \left( \frac{H_{px}}{RT} \right) \left( \frac{MW_l}{\rho_l} \right) = \frac{H_{pc}}{RT} \quad \text{Equation 2.6}$$

where  $MW_l$  and  $MW_g$  equal the molecular weight of the liquid (water) and gas (air) respectively (g/mol),  $\rho_l$  and  $\rho_g$  represent the density of the liquid (water) and gas (air) respectively (g/m<sup>3</sup>),  $R$  equals the universal gas constant [atm·m<sup>3</sup>/(mol·K)], and  $T$  is the absolute temperature (K) (Crittenden et al. 2005, Staudinger & Roberts 1996).

Another approach for expressing HLC is given by the equilibrium constant,  $K_h$  [mol/(L·atm)], describing the air to water partitioning of component  $i$  in the equation  $i_g \leftrightarrow i_{aq}$

$$K_h = \frac{\{i_{aq}\}}{\{i_g\}} \approx \frac{[i_{aq}]}{P_i} \quad \text{Equation 2.7}$$

where  $\{i_g\}$  equals the gas-phase activity of component  $i$  (Betterton 1992, Crittenden et al. 2005). Note that the aqueous-phase concentration is now in the numerator, meaning that a larger  $K_h$  value indicates greater solubility. Therefore, we define  $K_h$  as the inverse of  $H_{pc}$ .

**Table 2.1**  
Conversion equations for different HLCs

	$H_{px}$ (atm)	$H_{pc}$ (atm·L/mol)	$H_{yx}$	$H_{cc}$
$H_{px}$ (atm) =	1	$H_{pc} \left( \frac{\rho_l}{MW_l} \right)$	$H_{yx} RT \left( \frac{\rho_g}{MW_g} \right)$	$H_{cc} RT \left( \frac{\rho_l}{MW_l} \right)$
$H_{pc}$ (atm·L/mol) =	$H_{px} \left( \frac{MW_l}{\rho_l} \right)$	1	$H_{yx} RT \left( \frac{MW_l}{\rho_l} \right) \left( \frac{\rho_g}{MW_g} \right)$	$H_{cc} RT$
$H_{yx}$ =	$\left( \frac{H_{px}}{RT} \right) \left( \frac{\rho_g}{MW_g} \right)$	$\left( \frac{H_{pc}}{RT} \right) \left( \frac{\rho_l}{MW_l} \right) \left( \frac{MW_g}{\rho_g} \right)$	1	$H_{cc} \left( \frac{\rho_l}{MW_l} \right) \left( \frac{MW_g}{\rho_g} \right)$
$H_{cc}$ =	$\left( \frac{H_{px}}{RT} \right) \left( \frac{MW_l}{\rho_l} \right)$	$\frac{H_{pc}}{RT}$	$H_{yx} \left( \frac{MW_l}{\rho_l} \right) \left( \frac{\rho_g}{MW_g} \right)$	1

## FACTORS AFFECTING HENRY'S LAW CONSTANTS

### Temperature

To derive the temperature dependence of Henry's Law, one can start with the definition of Gibbs free energy

$$\Delta G_i = \Delta H_i - T\Delta S_i \quad \text{Equation 2.8}$$

where  $\Delta G_i$  is the change in Gibbs free energy of component  $i$  (J/mol),  $\Delta H_i$  represents the change in enthalpy of component  $i$  (J/mol), and  $\Delta S_i$  describes the change in entropy of component  $i$  (J/mol·K) (Benjamin 2002, Snoeyink & Jenkins 1980, ten Hulscher et al. 1992).

The change in Gibbs free energy of reaction, for any change in system conditions, is similarly written as

$$\Delta G_r = \Delta H_r - T\Delta S_r \quad \text{Equation 2.9}$$

Under standard conditions (25° C, 1000 kPa), this equation is written as

$$\Delta G_r^o = \Delta H_r^o - T\Delta S_r^o \quad \text{Equation 2.10}$$

The change in the Gibbs free energy for the reaction  $i_{aq} \leftrightarrow i_g$  can be determined by the expressions

$$\Delta G_r = \Delta G_r^o + RT \left[ \ln \left( \frac{\{i_g\}}{\{i_{aq}\}} \right) \right] \approx \Delta G_r^o + RT \left[ \ln \left( \frac{P_i}{[i_{aq}]} \right) \right] \quad \text{Equation 2.11}$$

$$\Delta G_r = \Delta G_r^o + RT [\ln(H_{pc})] \quad \text{Equation 2.12}$$

(Benjamin 2002). At equilibrium,  $\Delta G_r = 0$ ; therefore, Equation 2.12 becomes

$$0 = \Delta G_r^o + RT [\ln(H_{pc})] \quad \text{Equation 2.13}$$

$$\Delta G_r^o = -RT [\ln(H_{pc})] \quad \text{Equation 2.14}$$

$$\ln(H_{pc}) = -\frac{\Delta G_r^o}{RT} \quad \text{Equation 2.15}$$

Of note is the fact that Equation 2.15 applies at standard temperature and pressure.

Combining Equations 2.10 and 2.15 yields the linear van't Hoff equation

$$\ln(H_{pc}) = \frac{\Delta S_r^o}{R} - \frac{\Delta H_r^o}{R} \left( \frac{1}{T} \right) \quad \text{Equation 2.16}$$

(ten Hulscher et al. 1992). Assuming that  $\Delta S_r^o$  and  $\Delta H_r^o$  remain constant over the range of temperatures typical for drinking water treatment (0-40° C) (Benjamin 2002, Staudinger & Roberts 1996), the above equation can be rewritten in terms of the two adjustable parameters, A and B, as follows

$$\ln(H_{pc}) = A - \frac{B}{T} \quad \text{Equation 2.17}$$

where  $A = \Delta S_r^o / R$ ,  $B = \Delta H_r^o / R$ , and  $\Delta S_r^o$  and  $\Delta H_r^o$  can be estimated by corresponding values at 25° C.

Alternatively, Equation 2.15 can be rewritten as

$$\frac{d}{dT} \ln(H_{pc}) = -\frac{d}{dT} \left( \frac{\Delta H_{r,25C}^o}{RT} - \frac{\Delta S_{r,25C}^o}{R} \right) \quad \text{Equation 2.18}$$

from which an alternative van't Hoff relationship can be derived

$$\frac{d}{dT} \ln(H_{pc}) = -\left( \frac{\Delta H_{r,25C}^o}{R} \right) \cdot \frac{d}{dT} \left( \frac{1}{T} \right) \quad \text{Equation 2.19}$$

$$\frac{d}{dT} \ln(H_{pc}) = \frac{\Delta H_{r,25C}^o}{R} \cdot \left( \frac{1}{T^2} \right) \quad \text{Equation 2.20}$$

$$\int_{T_1}^{T_2} d \ln(H_{pc}) = \frac{\Delta H_{r,25C}^o}{R} \cdot \int_{T_1}^{T_2} \frac{dT}{T^2} \quad \text{Equation 2.21}$$

$$\ln(H_{pc,T_2}) - \ln(H_{pc,T_1}) = \frac{\Delta H_r^o}{R} \cdot \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Equation 2.22}$$

$$\ln\left(\frac{H_{pc,T_2}}{H_{pc,T_1}}\right) = \frac{\Delta H_r^o}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{Equation 2.23}$$

Equation 2.23 represents an alternative van't Hoff relationship that can be used to compute  $H_{pc}$  at any temperature, given one HLC value and  $\Delta H_r^o$  (Benjamin 2002, Staudinger & Roberts 1996).

## pH

Apart from aniline, the cVOCs under consideration for the group regulation are not ionizable and therefore unaffected by changes in pH. Aniline ( $R-NH_2$ ) is a weak base that becomes protonated at low pH values according to the reaction  $R-NH_3^+ \leftrightarrow R-NH_2 + H^+$ . The  $pK_a$  of  $R-NH_3^+$  is 4.6 (Bernauer et al. 2006). Therefore, the deprotonated neutral form is dominant in typical drinking water sources (pH≈6-8). Only the neutral form of aniline undergoes air-water partitioning.

## Compound Concentration

Munz & Roberts (1987) used both a predictive model (UNIFAC) and experimental results to quantify the effect of solute concentration on HLCs. By varying the solute concentration from infinite dilution (practically defined as just above their analytical detection limit of 1 µg/L) to the solubility limit, differences in HLCs were determined to be insignificant (<4%). The premise that HLCs are independent of compound concentration has been confirmed by several additional studies (Bissonette et al. 1990, Ervin et al. 1980).

It is important to note that some studies have reported an increase in HLC values with increasing concentration (e.g. Lincoff & Gossett 1981). Further analysis of the experimental method concluded that measurement errors associated with the batch air stripping technique may have caused an apparent concentration effect, and, therefore, the resulting HLC values should be considered with caution (Munz & Roberts 1987, Staudinger & Roberts 1996). HLC values from Lincoff & Gossett (1981) were not included in this study.

### **Co-Solute/Co-Solvent Effects**

Theoretically, the magnitude of HLCs may decrease in multi-contaminant mixtures due to an apparent increase in solubility (or “solubilizing effect”). For dilute solutions (<10,000 mg/L or 0.01 mole fraction) typical of drinking water sources, however, the presence of co-solutes and co-solvents is not expected to have a significant effect on HLCs (Staudinger & Roberts 1996). The results of Bissonette et al. (1990), Gossett (1987), and Munz & Roberts (1987) support the latter conclusion.

HLC depression may occur in co-solvent mixtures, especially in the presence of organic solvents such as methanol that can enhance the solubility of organic compounds with limited aqueous solubility. However, Gossett (1987) found no effect of up to 2% methanol addition on the HLC values for TCE. Munz and Roberts (1987) similarly found no significant difference in the HLC values of chloroform, CT, and hexachloroethane with <1% methanol addition.

## **Dissolved Salts**

In high ionic strength water, a compound's solubility may decrease due to the presence of dissolved salts (Fogg & Sangster 2003). This can lead to an increase in the solute's activity coefficient and a corresponding increase in HLC, a phenomenon known as the "salting out" effect (Staudinger & Roberts 1996). Gossett (1987) investigated the effect of ionic strength on HLC and found no significant (>10%) effect at salt concentrations <0.2 M. For most water supplies, the ionic strength is < 5mM (Crittenden et al. 2005).

## **Dissolved Organic Matter and Suspended Solids**

When a solute is associated with dissolved organic matter (DOM) and/or sorbed to suspended solids, it is not available to participate in air-water partitioning. The result is an increase in apparent solubility and thus an apparent decrease in HLC. The more hydrophobic a compound (i.e. larger  $K_{ow}$ ), the more susceptible it is to this effect.

Yurteri et al. (1987) evaluated the effect of DOM on the HLC of toluene by varying the humic acid concentration from 1-10 mg/L and found HLCs varied within 10% with no apparent trend. Further work by Anderson (1992) concluded that the HLC values for benzene and toluene were unchanged with humic acid additions up to 500 mg/L while the HLC of o-xylene decreased slightly. Staudinger & Roberts (1996) conclude that, for organic compounds of moderate hydrophobicity ( $\log K_{ow} \approx 1-3$ ), a significant decrease in HLC will not occur unless a substantial amount of humics is present (1 g/L). Among the cVOCs being considered for the group regulation, PCE is the most hydrophobic with a  $\log K_{ow}$  value of 3.4 (Table 1.1).

## **Natural Water Matrix Effects**

Determination of HLCs in natural waters may lead to deviations from HLCs measured in ultrapure water due to complex interactions from the effects already discussed in this section – pH, compound concentration, multi-contaminant mixtures, co-solvent and co-solute, dissolved salts, dissolved organic matter and suspended solids (Staudinger & Roberts 1996). Data that compare HLCs in groundwater and ultrapure water are scarce; however, studies by Bissonette et al. (1990) and Robbins et al. (1993) found no significant differences (at the 95% confidence level) in HLC values between contaminated groundwater and deionized/distilled water.

## **Implications on Current Study**

Based on the above review of factors that can affect the magnitude of HLCs, temperature is anticipated to have the strongest influence. Effects of other parameters are likely to have only minimal impact on HLC determinations because the experimental portion of this study utilized:

- cVOCs that
  - are not ionizable,
  - exhibit a log  $K_{ow}$  range of 1.25 to 3.4, and
- background water matrices that had
  - negligible suspended solids concentrations,
  - low TOC concentrations (<2 mg/L), and
  - ionic strength <0.05M.

## HLC ESTIMATION METHODS

### Quantitative Property-Property Relationships

The volatility of a compound, as expressed by the HLC, is a property that can be predicted from other compound properties through the use of quantitative property-property relationships (QPPRs). When a component exists in two phases, in this case air and water, equilibrium will be reached when the chemical potentials or fugacities in each of the two phases are equal (Mackay & Shiu 1981). Put mathematically

$$\gamma_i X_i P_i^{sat} = \phi_i Y_i P_T \quad \text{Equation 2.24}$$

where  $P_i^{sat}$  is the vapor pressure of a water saturated solution of component  $i$  (atm),  $\phi_i$  is the air-phase fugacity coefficient (dimensionless), and  $P_T$  represents the total (atmospheric) pressure (Staudinger & Roberts 1996). In the above equation, the fugacity coefficient describes the “non-ideality” of the component in the gas-phase, and the activity coefficient describes the “non-ideality” of the component in the aqueous-phase. For environmental applications,  $\phi_i$  is assumed to be 1, and the fugacity of the vapor phase can then be approximated by the partial pressure ( $P_i = Y_i P_T$ ) (Mackay & Shiu 1981). Combining Equations 2.5 and 2.24 yields the following equation

$$H_{yx} = \frac{Y_i}{X_i} = \frac{\gamma_i P_i^{sat}}{P_T} \quad \text{Equation 2.25}$$

HLCs can therefore be predicted from activity coefficients and vapor pressure. Activity coefficients can be established in three ways:

- Experimental determination of  $\gamma_i$  can be accomplished using a gas-liquid chromatography technique (GLC, Barr & Newsham 1987), a gas-liquid and liquid-

liquid chromatography technique (GLC-LLC), or a differential static cell equilibrium method (Wright et al. 1992).

- $\gamma_i$  can be estimated using aqueous solubility in a technique known as the vapor pressure/aqueous solubility ratio method (VP/AS) (Staudinger & Roberts 1996). This technique requires knowledge of the vapor pressure and aqueous solubility at the temperature and pressure of interest. While the VP/AS method yields reasonably accurate HLCs (Dearden & Schuurmann 2003), it relies on two key assumptions:
  - The vapor pressure of the water saturated solution of component  $i$  equals that of the pure component  $i$ .
  - The activity coefficient does not vary with concentration.

However, these assumptions fail when a component is exceedingly soluble in water (>0.05 mole fraction) (Staudinger & Roberts 1996). Additionally, the variance in HLCs estimated by the VP/AS method is determined by the sum of variances in vapor pressure and aqueous solubility measurements (Mackay & Shiu 1981), and vapor pressure measurements can differ by a factor of 2-3 for low vapor pressure, high molecular weight solutes (Nirmalakhandan & Speece 1988).

- $\gamma_i$  can be extrapolated from vapor-liquid equilibrium data (VLE) at higher concentrations (>0.01 mole fraction) using models such as the bond contribution or UNIFAC (UNIQUAC Functional-group Activity Coefficients) group contribution method (Staudinger & Roberts 1996). Since these models correlate  $\log(\text{HLC})$  with terms related to component structure, from which  $\gamma_i$  is calculated, they are termed

quantitative structure-property relationships, or QSPRs (discussed in the following section).

### **Quantitative Structure-Property Relationships**

UNIFAC accounts for the molecular structure (size and shape) of the component, as well as functional group interactions, to predict  $\gamma_i$ , which in turn is combined with vapor pressure data to predict HLC. This method is particularly attractive because it can be used to predict activity coefficients for components that have not been studied experimentally. The accuracy of UNIFAC-derived HLC values has been studied by Leighton & Calo (1981), Munz & Roberts (1987), and Ashworth et al. (1988), among others. Though Leighton & Calo (1981) concluded reasonable agreement between experimentally determined HLC values and those predicted by UNIFAC, the authors noted that discrepancies increased as compounds became more chlorinated. Munz & Roberts (1987) and Ashworth et al. (1988) found significant deviations between experimental and UNIFAC-predicted HLC values.

### **Predictive Models Used in this Study**

The following tools were used to estimate Henry's Law constants for the target cVOCs:

- *Estimation Program Interface (EPI) Suite of EPA* (<http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm>). EPI Suite references experimentally determined HLCs from the Syracuse Research Corporation's Physical Properties (SRC PHYS PROP) database. For a given cVOC, results are limited to one study and temperature (Figure 2.1 gives a

representative example for PCE). In addition, EPI Suite contains the predictive tool HENRYWIN. HENRYWIN utilizes multiple methods to estimate HLC values:

- i. The bond contribution method – This method, a QSPR updated by Meylan & Howard (1991), yields a single HLC at 25° C (Figures 2.2-2.3).
- ii. The group contribution method – Hine & Majorkee (1975) described this QSPR method for estimating a single HLC at 25° C (Figures 2.2-2.3)
- iii. HLC Temperature Variance - HENRYWIN also has the capability to provide the temperature dependence of HLCs. When possible, experimental results along with the van't Hoff relationship from one study (located through the Syracuse Research Corporation's Environmental Fate Data Base (EFDB) system) are used to show the temperature dependence. Data sources differ between compounds. Figure 2.2 gives a representative example for PCE. If experimental data are not available, HENRYWIN utilizes analogies based on

Experimental Data from PhysProp Database:	
CAS Number	000127-18-4
Chem Name	TETRACHLOROETHENE
MP (deg C)	-22.3
BP (deg C)	121.3
Log Kow	3.40
Kow ref	HANSCH,C ET AL. (1995)
Water Sol	206 mg/L
WS temp	25 deg C
WS ref	HORVATH,AL ET AL. (1999)
Vapor Pr	18.5 mm Hg
VP temp	25 deg C
VP ref	RIDDICK,JA ET AL. (1986)
Henry LC	1.77E-02 atm-m3/mole
HLC temp	24 deg C
HLC ref	GOSSETT,JM (1987)
..	

**Figure 2.1**  
**Screenshot of EPI Suite showing database value of HLC for PCE**

chemical structure and the Henry's Law constant at 25° C, estimated or retrieved from the database. Figure 2.3 shows a representative example for 1,3-butadiene with HLC temperature dependence based on the alkene slope analogy. Note also that the "Exp HLC" value shown in Figure 2.3 for 1,3-butadiene was actually derived from vapor pressure and water solubility as shown by the "Exp Ref.", which lists VP/WSOL.

Bond Est : 1.65E-002 atm-m3/mole (1.67E+003 Pa-m3/mole)			
Group Est: 1.77E-002 atm-m3/mole (1.80E+003 Pa-m3/mole)			
SMILES:	(=C(CL)CL)(CL)CL		
CHEM:	Ethene, tetrachloro-		
MOL FOR:	C2 CL4		
MOL WT:	165.83		
----- HENRYWIN v3.20 Results -----			
Experimental Database Structure Match:			
Name:	TETRACHLOROETHENE		
CAS Num:	000127-18-4		
Exp HLC:	1.77E-02 atm-m3/mole (1.79E+003 Pa-m3/mole)		
Temper:	24 deg C		
Exp Ref:	GOSSETT,JM (1987)		
Henry LC Temperature Variation:			
Source:	GOSSETT,JM (1987)		
HLC (atm-m3/mole) = exp(12.4500 - (4918/T)) {T in deg K}			
Temp (C)	atm-m3/mole	unitless	Pa-m3/mole
-----	-----	-----	-----
0	0.00387	0.173	392
5	0.00535	0.234	542
10	0.00731	0.315	741
15	0.00988	0.418	1E+003
20	0.0132	0.55	1.34E+003
25	0.0175	0.716	1.78E+003
30	0.023	0.924	2.33E+003
35	0.0299	1.18	3.03E+003
40	0.0386	1.5	3.91E+003
45	0.0494	1.89	5.01E+003
50	0.0628	2.37	6.36E+003
-----			
CLASS	BOND CONTRIBUTION DESCRIPTION	COMMENT	VALUE
FRAGMENT	4 Cd-CL		0.1704
FRAGMENT	1 Cd=Cd		0.0000
RESULT	BOND ESTIMATION METHOD for LWAPC VALUE	TOTAL	0.170
-----			
HENRYs LAW CONSTANT at 25 deg C = 1.65E-002 atm-m3/mole			
= 6.76E-001 unitless			
= 1.67E+003 Pa-m3/mole			
-----			
	GROUP CONTRIBUTION DESCRIPTION	COMMENT	VALUE
	2 Cd (CL)(CL)	ESTIMATE	0.14
RESULT	GROUP ESTIMATION METHOD for LOG GAMMA VALUE	TOTAL	0.14
-----			
HENRYs LAW CONSTANT at 25 deg C = 1.77E-002 atm-m3/mole			
= 7.24E-001 unitless			
= 1.80E+003 Pa-m3/mole			

**Figure 2.2**  
**HENRYWIN results for PCE**

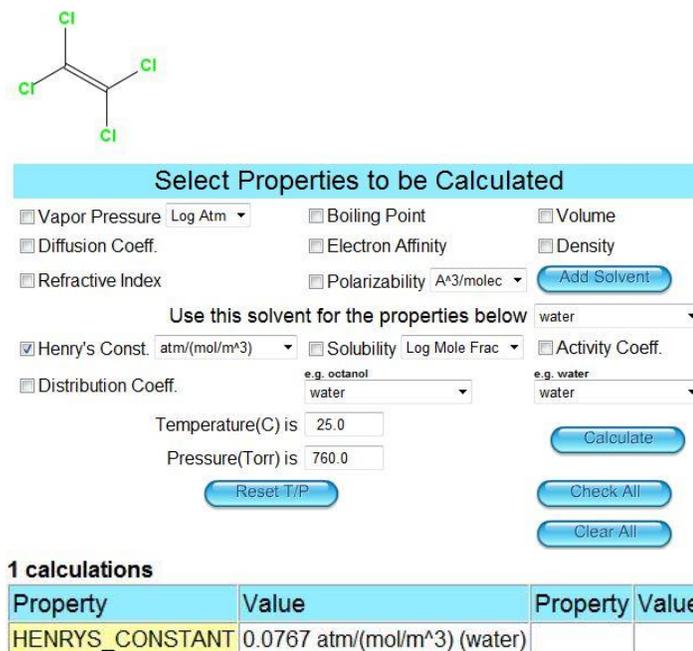
Bond Est : 7.79E-002 atm-m3/mole (7.90E+003 Pa-m3/mole)			
Group Est: 7.05E-002 atm-m3/mole (7.15E+003 Pa-m3/mole)			
SMILES :	C(C=C)=C		
CHEM :	1,3-butadiene		
MOL FOR:	C4 H6		
MOL WT:	54.09		
----- HENRYWIN v3.20 Results -----			
Experimental Database Structure Match:			
Name:	1,3-BUTADIENE		
CAS Num:	000106-99-0		
Exp HLC:	7.36E-02 atm-m3/mole (7.46E+003 Pa-m3/mole)		
Temper:	25 deg C		
Exp Ref:	VP/WSOL		
Henry LC Temperature Variation:			
Source:	Alkene slope analogy		
HLC (atm-m3/mole) = exp(9.4649 - (3600/T)) {T in deg K}			
Temp (C)	atm-m3/mole	unitless	Pa-m3/mole
0	0.0244	1.09	2.47E+003
5	0.0309	1.35	3.13E+003
10	0.0388	1.67	3.93E+003
15	0.0484	2.05	4.9E+003
20	0.0599	2.49	6.07E+003
25	0.0736	3.01	7.46E+003
30	0.0898	3.61	9.1E+003
35	0.109	4.31	1.1E+004
40	0.131	5.11	1.33E+004
45	0.157	6.02	1.59E+004
50	0.187	7.06	1.9E+004
-----			
CLASS	BOND CONTRIBUTION DESCRIPTION	COMMENT	VALUE
HYDROGEN	6 Hydrogen to Carbon (olefinic) Bonds		-0.6029
FRAGMENT	1 Cd-Cd		0.0997
FRAGMENT	2 Cd=Cd		0.0000
RESULT	BOND ESTIMATION METHOD for LWAPC VALUE	TOTAL	-0.503
-----			
HENRYs LAW CONSTANT at 25 deg C = 7.79E-002 atm-m3/mole			
= 3.19E+000 unitless			
= 7.90E+003 Pa-m3/mole			
-----			
	GROUP CONTRIBUTION DESCRIPTION	COMMENT	VALUE
	2 Cd-H2		-0.82
	2 CdH (Cd)		0.36
RESULT	GROUP ESTIMATION METHOD for LOG GAMMA VALUE	TOTAL	-0.46
-----			
HENRYs LAW CONSTANT at 25 deg C = 7.05E-002 atm-m3/mole			
= 2.88E+000 unitless			
= 7.15E+003 Pa-m3/mole			

**Figure 2.3**  
**HENRYWIN results for 1,3-butadiene**

- *SPARC* (SPARC Performs Automated Reasoning in Chemistry) on-line calculator (<http://archemcalc.com/sparc>). *SPARC* uses mathematical algorithms to estimate physical properties for a wide range of organic compounds and is another example of a QSPR. Henry's Law constants are found by adding the log of the vapor pressure of the pure solute and the log of the activity coefficient of the solute in the solvent at infinite dilution (Equation 2.26).

$$\log(HLC) = \log(P_i^o) + \log(\gamma_i) \quad \text{Equation 2.26}$$

Vapor pressure is estimated by calculating the temperature dependence of the molecular interactions that contribute to vapor pressure, such as dispersion, dipole-dipole, induction (dipole-dispersion) and hydrogen bonding interactions. The temperature dependence of most of the interactions is log-linear. However, dipole-dipole and hydrogen bonding also have a second order dependence as they have a dependence on orientation. As temperature increases, hydrogen bonding becomes weaker. Therefore, a plot of log vapor pressure as a function of temperature will yield a fairly straight line for alkanes that do not undergo hydrogen-bonding, while that for molecules, for which hydrogen bonding interactions are important, will exhibit curvature. The same applies for activity coefficients; however, the temperature dependence is more complex as dispersion, dipole-dipole, induction (dipole-dispersion) and hydrogen bonding components between the molecule and solvent need to be considered (Carreira 2013). A representative example of the *SPARC* interface for PCE at a temperature of 25° C is shown in Figure 2.4.



**Select Properties to be Calculated**

Vapor Pressure Log Atm     Boiling Point     Volume  
 Diffusion Coeff.     Electron Affinity     Density  
 Refractive Index     Polarizability A^3/molec   

Use this solvent for the properties below: water

Henry's Const. atm/(mol/m^3)     Solubility Log Mole Frac     Activity Coeff.  
 Distribution Coeff.    e.g. octanol water    e.g. water water

Temperature(C) is 25.0      
 Pressure(Torr) is 760.0      
   

**1 calculations**

Property	Value	Property	Value
HENRYS_CONSTANT	0.0767 atm/(mol/m^3) (water)		

**Figure 2.4**  
**Screenshot showing SPARC interface and estimated HLC for PCE**

- *Aeration System Analysis Program (ASAP)* (Hand et al.1999). ASAP is an estimation tool designed to calculate design parameters and expected performance for PTA. Properties for target compounds can be manually entered into ASAP or imported from the Software to Estimate Physical Properties (StEPP) database. StEPP provides several estimation methods to supplement experimental data for many physical compound properties. Estimates for Henry's Law constants are arranged in preferential order according to the following hierarchy:
  - Regression of data points - StEPP uses a regression of data points [plotting the van't Hoff relationship,  $\ln(H_{px}) = A - B/T$ ] to predict Henry's Law constants

at temperatures of interest (Figure 2.5). The van't Hoff relationship is based on the data of Howe et al. (1987)/Ashworth et al. (1988) (RTI Database), when available. These studies list experimental data for several compounds at multiple temperatures (typically between 10-30° C). For compounds not studied by Howe et al. (1987)/Ashworth et al (1988), estimated HLCs at single discrete temperatures are cited from Yaws et al. (1992) or the U.S. EPA Superfund Public Health Evaluation Manual (1986).

- ii. UNIFAC fit with data point – UNIFAC calculations are based on the activity coefficient at infinite dilution and the pure component vapor pressure. Staudinger and Roberts (1996) note that a major limitation of UNIFAC is errors associated with the extrapolation of VLE data. ASAP attempts to overcome these errors by adjusting the UNIFAC value to available experimental data, using an offset between the natural log of the UNIFAC HLC value and the experimental HLC value at the closest database temperature. The offset is then applied to the UNIFAC value at the temperature of interest. The resulting HLC value is reported as UNIFAC Fit with Data Pt. (Figure 2.5). In some cases, the offset is quite large, indicating the magnitude of difference between the mathematically predicted and experimental values (Figure 2.6). Because this method utilizes data points, not values derived from a van't Hoff equation, HLC values obtained via the UNIFAC Fit with Data Pt. approach do not follow a log-linear trend.

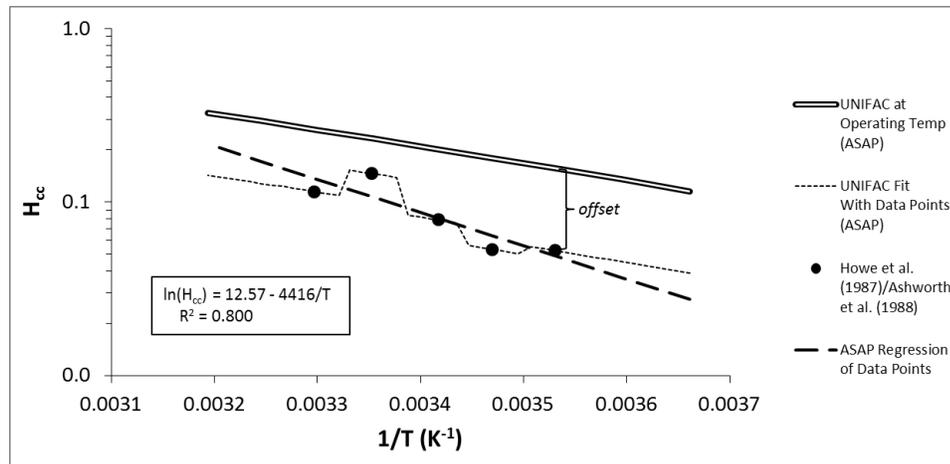
- iii. UNIFAC at operating temperature - HLC value predicted by UNIFAC at the temperature of interest without adjustment (Figure 2.5).
- iv. Database – Individual data points are listed in the database dropdown box. The HLC determined at the temperature closest to the temperature of interest is highlighted (Figure 2.5)
- v. UNIFAC at database temperatures – This method is the same as (iii); however, UNIFAC estimated HLCs, at the same temperatures used by Howe et al. (1987)/Ashworth et al. (1988), are listed in the dropdown box.

The screenshot shows a dialog box titled "Henry's Constant". At the top left, there is a section for "Current Henry's Constant Information" with a "Value [-]" of 0.744 and a "Source" of "Regression of Data Points". To the right are buttons for "Accept Selected Henry's Constant" and "Cancel". Below this is a table with columns: "Source", "Henry's Constant (-)", "Temp. (C)", "T min (C)", and "T max (C)".

Source	Henry's Constant (-)	Temp. (C)	T min (C)	T max (C)
<input checked="" type="radio"/> Regression of Data Points	0.744	25.0	N/A	N/A
<input type="radio"/> UNIFAC Fit with Data Pt.	0.696	25.0		
<input type="radio"/> UNIFAC at Operating T	0.544	25.0		
<input type="radio"/> Database	0.696	25.0		
RTI	0.696	25.0		
<input type="radio"/> UNIFAC @ Database T's	0.544	25.0		
UNIFAC	0.544	25.0		
<input type="radio"/> User Input				

At the bottom, there is a dropdown menu for "UNIFAC Group Interaction Database:" set to "Environmental VLE".

**Figure 2.5**  
HLCs predicted by StEPP for PCE at 25°C



**Figure 2.6**  
**ASAP regression of data points and UNIFAC estimated HLCs for 1,2-DCP**  
**(note the offset)**

## EXPERIMENTAL METHODS FOR THE DETERMINATION OF HLC

There are two general experimental approaches that have been used to determine HLCs, static and dynamic techniques.

### Dynamic Techniques

Dynamic approaches measure HLCs by determining the change in concentration of a component in the liquid phase while effecting a near equilibrium exchange with the gas-phase (Gossett 1987). Two such techniques are often used:

- *Batch air stripping* is carried out in a bubble column apparatus, and HLCs are calculated based on measurement of the loss of compound from the liquid phase into the gas bubble stream (Mackay et al. 1979, Warner et al. 1987, Gossett et al. 1985). Seven assumptions were made for the governing equations to hold true; however,

Lincoff (1983) states that two of these assumptions (equilibrium between gas/liquid phases and complete mixing) are difficult to ensure and could raise potential problems with HLC determination by this method.

- *Concurrent flow* is carried out in a wetted wall apparatus, and HLCs are calculated based on aqueous-phase concentration measurements as an organic contaminant equilibrates between a thin film and a concurrent flow of gas in a vertical column (Staudinger & Roberts 1996). As is the case with batch air stripping, the concurrent flow technique must also ensure that equilibrium is achieved.

### **Static Techniques**

Static approaches utilize a closed system to achieve equilibration, and HLCs are determined by direct measurement of a compound's aqueous and/or gas concentration. Four such techniques are often used:

- *Single equilibration* is the simplest of the four methods presented. A specific mass of compound is placed into a gas-tight container with known volumes of water and air, and HLCs are calculated based on measurement of the equilibrium compound concentration in one or both phases (Bissonette 1990, Lamarch & Droste 1989, Sato & Nakajima 1979b, Staudinger & Roberts 1996). If analysis is carried out in only one phase, a mass balance is used to calculate the concentration in the other phase.
- In the *multiple equilibration* technique, an aqueous concentration of compound is added to a variable headspace vessel (e.g. gas-tight syringe), and a specific amount of headspace is then introduced into the vessel. After equilibration, the solute

- concentration is determined in one phase, the air is expelled, and the same amount of solute-free air is pulled back into the system. HLCs are calculated based on compound concentrations measurements after two or more subsequent equilibrations (Munz 1985, Munz & Roberts 1987, Staudinger & Roberts 1996).
- The *Equilibrium Partitioning in Closed Systems (EPICS)* technique utilizes a mass balance between two similar systems, at the same temperature but containing differing volumes of air and water (Lincoff 1983). A specific mass of compound is placed into two sets of triplicate reactors, and HLCs are calculated based on measurement of the equilibrium compound concentration in the gas-phase (Dewulf et al. 1995, Gossett et al. 1985, Kondoh & Nakajima 1997, Staudinger & Roberts 1996) or the aqueous-phase (Lau et al. 2010). The original method was suitable for compounds with  $H_{cc}$  values between 0.1 and 1 and relied on the assumption that equal masses of compound would be added to the two systems. A modified technique eliminated this assumption by accounting for gravimetric differences in compound addition and broadened the range of applicability (Gossett 1987). Further modifications, including the measurement of gas-phase concentrations via solid-phase microextraction (SPME) allowed this method to accurately determine HLCs for compounds with  $H_{cc}$  values down to 0.003 (Dewulf et al. 1999).
  - *Variable headspace method* is the most recent of the four methods presented. A solution containing a given aqueous concentration of compound is added to three reactors with differing air:water ratios (or phase ratios). After equilibration, the gas-phase solute concentration is determined in each reactor. HLCs are calculated from

the slope of a linear regression describing the dependence of the inverse of the chromatographic peak area as a function of the air:water ratio (Robbins et al. 1993, Staudinger & Roberts 1996).

## **TREATMENT TECHNOLOGIES FOR cVOC REMOVAL**

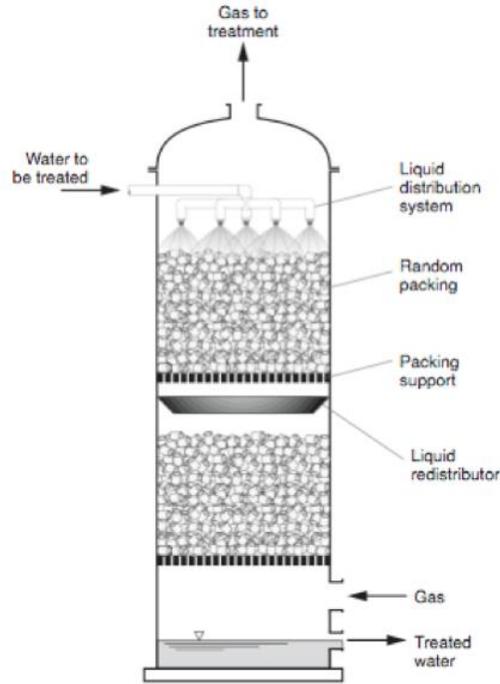
### **Packed Tower Aeration**

Packed towers are either cylindrical columns or rectangular towers, filled with an irregular shaped inert packing material. Contaminated water is pumped to the top of the tower where it is dispersed evenly and flows down through the packing material. A blower introduces air into the system, commonly countercurrent to the flow of water. The packing material provides high void volumes, disrupts the flow of water, and increases the air:water interfacial area, allowing for the transfer of cVOCs from the aqueous to the gas-phase (Crittenden et al. 2005).

In PTA, the difference between equilibrium and actual solute concentration determines the mass transfer rate between phases, which is mathematically represented by

$$J_i = K_L a (C_{i,e} - C_{i,l}) \quad \text{Equation 2.27}$$

where  $J_i$  represents the rate of mass transfer of component  $i$  (kmol/s),  $K_L$  is the overall liquid mass transfer coefficient (m/s),  $a$  equals the interfacial area per volume of packing material ( $\text{m}^2/\text{m}^3$ ), and  $C_{i,l}$  represents the aqueous-phase concentration at any point in the column.  $K_L$  is related to the local liquid and gas-phase mass transfer coefficients ( $k_L$  and  $k_g$  respectively) by



**Figure 2.7**  
**Schematic of a Packed Tower Air Stripper** (source: Crittenden et al. 2005)

the expression

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{C_w}{k_g H_{px}} \quad \text{Equation 2.28}$$

where  $C_w$  is the molar density of water ( $55.6 \text{ kmol/m}^3$ ). Similarly,  $K_g$ , the overall gas mass transfer coefficient ( $\text{kmol/s}\cdot\text{atm}\cdot\text{m}^2$ ) is related to  $k_L$  and  $k_g$  by the equation

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{H_{px}}{k_L C_w} \quad \text{Equation 2.29}$$

For solutes that exhibit very low volatility ( $H_{cc} < 0.002$ ),  $K_g$  and  $K_L$  are controlled by the mass transfer resistance in the gas-phase.

$$K_L \approx k_g \left( \frac{H_{px}}{C_w} \right) \quad \text{Equation 2.30}$$

$$K_g \approx k_g \quad \text{Equation 2.31}$$

For compounds with low volatility ( $0.002 < H_{cc} < 0.05$ ),  $K_g$  and  $K_L$  are controlled by both gas and liquid mass resistances (Hand et al. 2011). Increasing the air flow rate can increase  $k_g$  which in turn can lead to increased removal of compounds with  $H_{cc}$  values  $< 0.05$ . Increasing the interfacial area  $a$  will increase  $k_L$  which in turn will lead to increased removal of compounds with  $H_{cc}$  values  $> 0.002$  (Kavenaugh & Trussell 1980).

Tower height, or more exactly the height of the packing material, is a critical design criterion, especially when high removals of compounds with low volatility are required. As HLC decreases, tall towers or towers in series are needed to meet the target removal (Cornwell et al. 2011).

The goal of the design engineer is to maximize the rate of cVOC mass transfer and minimize costs. Based on examination of the energy requirement curve, a maximum air:water ratio of 100:1 was chosen as the feasibility limit. This air:water ratio translates into a recommended minimum  $H_{cc}$  of 0.05 for a contaminant to be effectively removed via PTA (Cornwell et al. 2011). U.S. EPA has suggested PTA may be a feasible option for compounds with  $H_{cc}$  values as low as 0.01; however, no theoretical basis for this cut off has been provided.

## Activated Carbon Adsorption

### *Freundlich Adsorption Constants*

The Freundlich isotherm equation is a common model used to describe the equilibrium adsorption capacity of activated carbon:

$$q_e = KC_{i,le}^{1/n} \quad \text{Equation 2.32}$$

In this model,  $q_e$ , the adsorbed cVOC concentration (mg/g) at equilibrium, is related to  $C_{i,le}$  ( $\mu\text{g/L}$ ) through the use of  $K$ , the Freundlich adsorption constant  $(\text{mg/g})(\text{L}/\mu\text{g})^{1/n}$ , and  $1/n$ , the Freundlich exponent. For the units shown here, the Freundlich adsorption constant reflects the adsorption capacity of the adsorbent (activated carbon) for the adsorbate (cVOC) at a  $C_{i,le}$  value of  $1 \mu\text{g/L}$ .

### *Design of Granular Activated Carbon Adsorbers*

While  $K$  values from batch adsorption isotherms help quantify the adsorbability of a contaminant on a specific activated carbon, they cannot accurately predict the performance of GAC columns. Concentration profiles and breakthrough curves for a single adsorbate in a GAC bed are shown in Figure 2.8. The mass transfer zone (MTZ) is the length of GAC bed necessary for the aqueous solute to be adsorbed by the GAC. Solute will begin to appear in the effluent as the adsorption capacity of the bed becomes exhausted, and the adsorption equilibrium is reached when the effluent concentration matches the influent concentration. Breakthrough is defined as the time when the effluent concentration of the GAC adsorber exceeds treatment objectives ( $t_{bk}$ , d). A mass balance at  $t_{bk}$  is given by

$$t_{bk}QC_o = q_eM_{GAC} \quad \text{Equation 2.33}$$

where,  $Q$  represents the flow rate (m<sup>3</sup>/h),  $C_o$  is the influent solute concentration, and  $M_{GAC}$  equals the mass of GAC (g) (Crittenden et al. 2005). Rearranging Equation 2.33 yields the carbon usage rate (CUR, g/L) which describes the rate of GAC exhaustion and indicates how frequently carbon must be replaced.

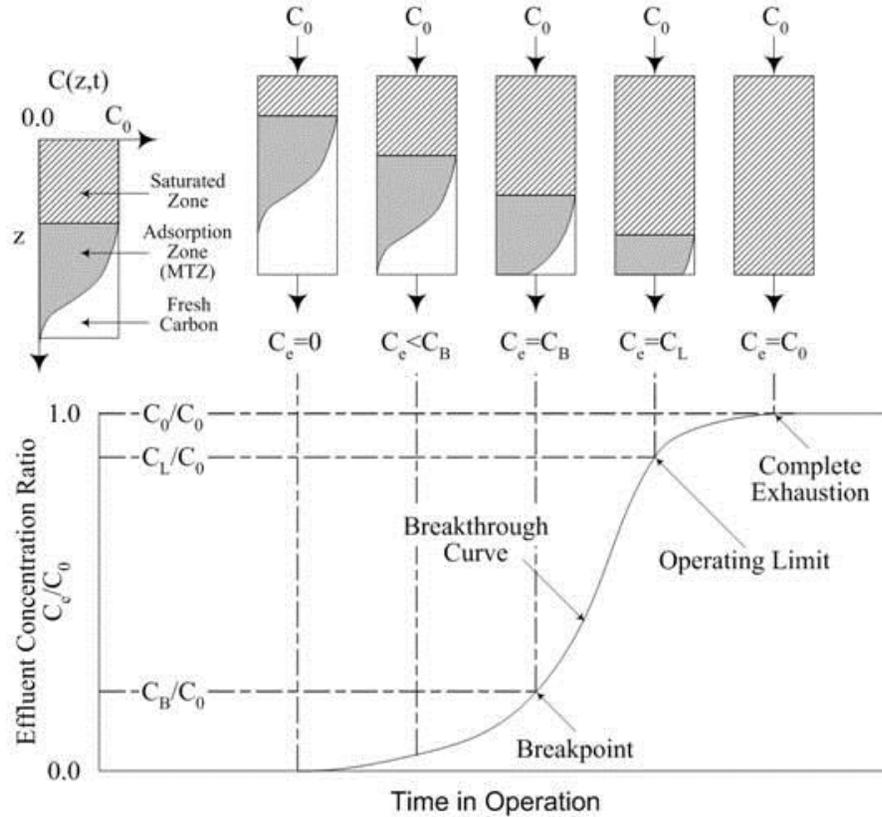
$$CUR = \frac{M_{GAC}}{t_{bk}Q} = \frac{C_o}{q_e} \quad \text{Equation 2.34}$$

The empty bed contact time (*EBCT*, h) is also an important parameter in the design of GAC adsorbers, and is calculated as the volume of the GAC bed ( $V_{bed}$ , m<sup>3</sup>) divided by  $Q$ .

$$EBCT = \frac{V_{bed}}{Q} \quad \text{Equation 2.35}$$

*EBCT* for fixed-bed adsorbers used in water treatment generally ranges between 5 and 30 minutes and varies for different contaminants (Crittenden et al. 2005). For an adsorber with an *EBCT* of 15 minutes, one bed volume of water is treated every 15 minutes and 96 bed volumes of water are treated per day.

Batch and packed bed reactors differ when trace pollutants, such as cVOCs, compete with natural organic matter (NOM) for adsorption sites. NOM adsorbs to GAC ahead of the mass transfer zone of the contaminant, a phenomenon known as preloading, which is not captured in batch tests. An apparent capacity parameter,  $K^*$ , has been suggested to describe the adsorption capacity of trace contaminants in packed bed GAC adsorbers,  $K^*$  can be calculated by assuming that the quantity of water treated to 50% breakthrough in a non-ideal adsorber approaches that treated to exhaustion of an ideal plug flow reactor, a good



**Figure 2.8**

**Concentration profiles and breakthrough curves for a GAC adsorber**

(source: [http://purewaterlab.org/pwl\\_net/labs/D2\\_Process\\_Units/D2L4\\_Activated\\_Carbon/Mass\\_Transfer\\_Zone.html](http://purewaterlab.org/pwl_net/labs/D2_Process_Units/D2L4_Activated_Carbon/Mass_Transfer_Zone.html))

assumption if the MTZ is symmetrical. A mass balance around the ideal adsorber yields

$$\frac{(C_o - C_e)Qt}{M_{GAC}} = q_e - K^* C_o^{1/n} \quad \text{Equation 2.36}$$

where  $C_e$  is the effluent solute concentration. In order to simplify this equation,  $C_e$  is

assumed to be zero.  $Qt$  can be replaced by the number of bed volumes treated at 50%

breakthrough ( $BV_{50}$ ) times  $V_{bed}$ , and the equation can be rearranged to form

$$K^* = \frac{(BV_{50} \cdot V_{bed})}{M_{GAC}} = \frac{C_o}{C_o^{1/n}} \quad \text{Equation 2.37}$$

(Corwin and Summers 2010). When NOM is present in the fixed-bed system and the trace pollutant concentration is low,  $1/n$  approaches 1 (Knappe et al. 1998), and Equation 2.37 reduces to

$$K^* = \frac{BV_{50}}{\rho_{bed}} = \frac{1}{CUR} \quad \text{Equation 2.38}$$

where  $\rho_{bed} = M_{GAC}/V_{bed}$ .

In the case of GAC adsorbers, the goal of the design engineer is to maximize the number of bed volumes treated to breakthrough while minimizing the carbon change out frequency. CUR values between 0.35-0.6 lb GAC/1000 gal, corresponding to bed volumes ranging from 11,500 to 6,700 have been suggested as possible practical limits for removal of cVOCs by GAC adsorption.

## CHAPTER 3 – HENRY’S LAW CONSTANTS FOR CARCINOGENIC VOLATILE ORGANIC COMPOUNDS

### ABSTRACT

Thirteen carcinogenic volatile organic compounds (cVOCs) are being considered for a new group regulation under the U.S. EPA’s Drinking Water Strategy. The 13 cVOCs include eight currently regulated compounds [benzene; carbon tetrachloride (CT); 1,2-dichloroethane (1,2-DCA); 1,2-dichloropropane (1,2-DCP); dichloromethane (DCM); tetrachloroethylene (PCE); trichloroethylene (TCE); vinyl chloride (VC)], three compounds on the third contaminant candidate list (CCL3) [1,3-butadiene; 1,1-dichloroethane (1,1-DCA); 1,2,3-trichloropropane (1,2,3-TCP)], and two additional cVOCs [1,1,1,2-tetrachloroethane (1,1,1,2-TeCA); 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA)]. In this study, the effects of temperature and background water quality on Henry’s Law constants (HLCs) were evaluated for the 13 target cVOCs. Numerous studies containing measured HLCs for the currently regulated cVOCs were identified in a comprehensive literature survey. Literature data were sparse for the unregulated compounds, however. To fill information gaps, HLCs were determined in the laboratory following a modified version of the variable headspace technique. Experiments were conducted in ultrapure water, two groundwaters [Illinois and Suffolk County Water Authority (SCWA) groundwater], and a salt amended groundwater [SCWA groundwater + 1500 mg/L NaCl] at temperatures ranging from 5 - 35° C. Total organic carbon (TOC) and total dissolved solids (TDS) concentrations had

negligible effects on HLCs. For the potent and currently unregulated 1,2,3-TCP, experimental results indicate that it is not as volatile at lower temperatures as expected based on prior studies.

## INTRODUCTION

### Henry's Law

For air stripping applications in drinking water treatment, Henry's Law describes the equilibrium partitioning between water and air and is described by the equation  $i_{aq} \leftrightarrow i_g$

$$H_{pc} = \frac{\{i_g\}}{\{i_{aq}\}} = \frac{\phi_i P_i}{\gamma_i [i_{aq}]} \approx \frac{P_i}{[i_{aq}]} \quad \text{Equation 3.1}$$

where  $H_{pc}$  is the HLC of component  $i$  (atm·L/mol),  $\{i_g\}$  equals the gas-phase activity of component  $i$ ,  $\{i_{aq}\}$  describes the aqueous-phase activity of component  $i$ ,  $\phi_i$  is the fugacity coefficient of component  $i$ ,  $P_i$  is the equilibrium partial pressure of component  $i$  (atm),  $\gamma_i$  represents the activity coefficient of component  $i$ , and  $[i_{aq}]$  equals the aqueous-phase concentration of component  $i$  (mol/L) (Atkins & de Paula 2006). The activity coefficient is assumed to be 1 for most fresh waters with an ionic strength less than 0.01 M (Crittenden et al. 2005). Similarly,  $\phi_i$  is typically assumed to be 1, suggesting ideal gas behavior. Of note is the fact that this definition of Henry's Law has the gas-phase concentration in the numerator, meaning that a larger HLC value indicates greater volatility.

Alternative forms of Henry's Law utilize different units to express aqueous-phase and gas-phase concentrations and give rise to a wide variety of HLC units. Consistent with

Staudinger and Roberts (1996), the dimensionless Henry's law constant,  $H_{cc}$ , is used in this research

$$H_{cc} = \frac{C_{i,ge}}{C_{i,le}} \quad \text{Equation 3.2}$$

where  $C_{i,ge}$  is the equilibrium gas-phase concentration of compound  $i$  (mol/L) and  $C_{i,le}$  represents the equilibrium aqueous-phase concentration of compound  $i$  on a per volume basis. An additional form of Henry's Law yields an alternative dimensionless HLC,  $H_{yx}$ , which is based on mole fractions of component  $i$  in the aqueous-phase ( $X_i$ ) and in the gas-phase ( $Y_i$ )

$$H_{yx} = \frac{Y_i}{X_i} \quad \text{Equation 3.3}$$

Yet another alternative is to base the HLC on partial pressure and the aqueous-phase mole fraction as shown in Equation 3.4, where  $H_{px}$  has units of atm.

$$H_{px} = \frac{P_i}{X_i} \quad \text{Equation 3.4}$$

All data obtained through literature surveys were converted to the dimensionless HLC using Equation 3.5

$$H_{cc} = H_{yx} \left( \frac{MW_l}{\rho_l} \right) \left( \frac{\rho_g}{MW_g} \right) = \left( \frac{H_{px}}{RT} \right) \left( \frac{MW_l}{\rho_l} \right) = \frac{H_{pc}}{RT} \quad \text{Equation 3.5}$$

where  $MW_l$  and  $MW_g$  equal the molecular weight of the liquid (water) and gas (air), respectively (g/mol),  $\rho_l$  and  $\rho_g$  represent the density of the water and air, respectively (g/m<sup>3</sup>),

$R$  equals the universal gas constant [ $\text{atm}\cdot\text{m}^3/(\text{mol}\cdot\text{K})$ ], and  $T$  is the absolute temperature (K) (Crittenden et al. 2005, Staudinger & Roberts 1996).

Another approach for expressing HLC is given by the equilibrium constant,  $K_h$  (dimensionless), describing the air to water partitioning of component  $i$  in the equation



$$K_h = \frac{\{i_{aq}\}}{\{i_g\}} \approx \frac{[i_{aq}]}{P_i} \quad \text{Equation 3.6}$$

(Betterton 1992, Crittenden et al. 2005). Note that the aqueous-phase concentration is now in the numerator, meaning that a larger  $K_h$  value indicates greater solubility. Therefore,  $K_h$  is the inverse of  $H_{pc}$ .

### Temperature Dependence of Henry's Law Constants

The temperature dependence of Henry's Law is described by a van't Hoff relationship

$$\ln(H_{cc}) = A - \frac{B}{T} \quad \text{Equation 3.7}$$

where  $A$  and  $B$  are adjustable parameters.

An interesting point, made by Heron et al. (1998) states that many authors use both Equation 3.7 (with  $H_{cc}$ ) and Equation 3.8 (with  $H_{pc}$ )

$$\ln(H_{pc}) = A - \frac{B}{T} \quad \text{Equation 3.8}$$

Knowing that  $H_{pc}$  and  $H_{cc}$  are related by Equation 3.5, Heron et. al (1998) surmise that the temperature dependence of  $H_{cc}$  and  $H_{pc}$  cannot be the same. Through mathematical derivation

and with the assumption that the heat of dissolution remains constant, the authors conclude that the proper equation for the dimensionless HLC should take the form

$$\ln(H_{cc}) = A - \frac{B}{T} - \ln T \quad \text{Equation 3.9}$$

However, over narrow temperature ranges, for example 10-30° C, the change in absolute temperature is limited (<7%), and ignoring the  $\ln T$  term yields minimal errors. Therefore, the application of Equation 3.7 will effectively describe the temperature dependence of  $H_{cc}$  over temperature ranges of interest from a drinking water treatment perspective.

The value calculated for  $A$  will vary depending on the form of the HLC used in the van't Hoff equation. However, the value determined for  $B$  will remain constant for all HLCs presented in this section, with the exception of  $H_{cc}$ . If  $H_{cc}$  is used in the van't Hoff equation,  $\Delta H_r^o$  can be found using the following relationship

$$\Delta H_r^o = \left( B + \frac{T_U + T_L}{2} \right) \cdot R \quad \text{Equation 3.10}$$

where  $T_U$  and  $T_L$  are the upper and lower temperatures, respectively (K) (Staudinger & Roberts 2001). For all other forms of the HLC,  $\Delta H_r^o$  can be calculated as follows:

$$\Delta H_r^o = R \cdot B \quad \text{Equation 3.11}$$

where  $R$  is the ideal gas constant ( $8.314 \times 10^{-3}$  kJ/mol).

## Background Water Matrix effects on Henry’s Law Constants

Temperature was anticipated to have the greatest influence on HLCs. The effects of other water quality parameters, summarized in Table 3.1, were expected to have minimal on HLC values.

**Table 3.1**  
**Background water matrix effects on Henry’s Law Constants**

<b>Water Quality Parameter</b>	<b>Effect on Henry’s Law Constant</b>
<b>pH</b>	Important for compounds that dissociate in water (Staudinger & Roberts 1996). The cVOCs under consideration for the group regulation are not ionizable and are therefore unaffected by changes in pH.
<b>Compound Concentration</b>	Model predictions and experimental results indicate that compound concentration from infinite dilution to the limits of aqueous solubility have negligible impacts on HLCs (Munz & Roberts 1987).
<b>Co-Solute/ Co-Solvent</b>	Previous studies (Gossett 1987, Munz & Roberts 1987) found no effect of up to 2% methanol addition on HLC values, and multi-component mixtures are not expected to have an effect on HLC values at drinking water relevant conditions.
<b>Dissolved Salts</b>	A compound’s aqueous solubility may decrease due to the presence of dissolved salts, leading to an increase in the solute’s activity coefficient and a corresponding increase in HLC (Fogg & Sangster 2003). This “salting out” effect is potentially important at salt concentrations of >0.2 M.
<b>Dissolved Organic Matter/ Suspended Solids</b>	When a solute is associated with dissolved organic matter (DOM) and/or adsorbed to suspended solids, it is not available to participate in air-water partitioning, resulting in an increase in apparent solubility and an apparent decrease in HLC (Staudinger & Roberts 1996). The more hydrophobic a compound (e.g. exhibiting a higher octanol-water partition coefficient, $K_{ow}$ ), the more susceptible is it to this effect. For organic compounds of moderate hydrophobicity ( $\log K_{ow} \approx 1-3$ ), a significant decrease in HLC will not occur unless a substantial amount of humics are present (1 g/L).
<b>Natural Water</b>	Determination of HLCs in natural waters may lead to deviations from HLCs expected in ultrapure water due to complex interactions from pH, compound concentration, multi-contaminant mixtures, co-solvent and co-solute, dissolved salts, dissolved organic matter and suspended solids. Data are scarce; however, previous studies (Bissonette et al. 1990, Robbins et al. 1993) found no significant differences (at the 95% confidence level) in HLC values between contaminated groundwater and deionized/distilled water.

## **Methods for the Determination of Henry's Law Constants**

Two general experimental approaches have been used to determine HLC values. In static experiments, a compound's aqueous and/or gas-phase concentrations is measured after equilibration of both phases in a closed system (Staudinger & Roberts 1996). In dynamic experiments, the change in concentration of a component in the liquid phase is measured while effecting a near equilibrium exchange with the gas-phase (Gossett 1987). HLC experimental methods are summarized in Table 3.2.

Additionally, activity coefficients can be measured experimentally using gas-liquid chromatography [GLC, Barr & Newsham (1987), Tse et al. (1992)], gas-liquid and liquid-liquid chromatography (GLC-LLC), or differential static cell (Wright et al. 1992) methods. Activity coefficient data must be used in conjunction with vapor pressures to calculate HLCs.

**Table 3.2**  
**Methods for the determination of Henry's Law constants**

Type	Technique	Experimental Approach
<b>Dynamic</b>	<b>Batch Air Stripping</b>	Carried out in a bubble column apparatus. HLCs are calculated based on measurement of the loss of compound from the liquid phase into the gas bubble stream (Gossett 1987)
	<b>Wetted Wall Column</b>	HLCs are calculated based on concentration measurements as an organic contaminant equilibrates between a thin film and a concurrent flow of gas in a vertical column (Staudinger & Roberts 1996).
<b>Static</b>	<b>Single Equilibration</b>	A specific mass of compound is placed into a gas-tight container with known volumes of water and air. HLCs are calculated based on measurement of the equilibrium compound concentration in one or both phases. If analysis is carried out in one phase, a mass balance is used to calculate concentration in the other phase.
	<b>Multiple Equilibration</b>	An aqueous concentration of compound is added to a variable headspace vessel, and a specific amount of headspace is introduced. After equilibration, the solute concentration is determined in one phase, the air is expelled, and the same amount of solute-free air is pulled back into the system. HLCs are calculated based on compound concentrations measurements after two or more subsequent equilibrations (Munz & Roberts 1987).
	<b>Equilibrium Partitioning in Closed Systems (EPICS)</b>	Utilizes a mass balance between two similar systems containing differing volumes of air and water. A mass of compound is placed into two sets of triplicate reactors, and HLCs are calculated based on measurement of the equilibrium compound concentration in the gas-phase (Dewulf et al. 1995). The original method relied on the assumption that equal masses of compound would be added to the two systems. A modified technique eliminated this assumption by accounting for gravimetric differences in mass addition and improved precision (Gossett 1987). Further modifications included the measurement of gas-phase concentrations via solid-phase microextraction (SPME) (Dewulf et al. 1999).
	<b>Variable Headspace Method</b>	An aqueous concentration of compound is added to three reactors with differing air:water ratios (phase ratios). After equilibration, the gas-phase solute concentration is determined in each reactor. HLCs are calculated from the slope of a linear regression describing the dependence of the inverse of the chromatographic peak area as a function of the phase ratio (Robbins et al. 1993).

## MATERIALS

### Water

Experiments were conducted in ultrapure water (UPW), Illinois (ILL) groundwater, Suffolk County Water Authority (SCWA) groundwater, and SCWA amended with 1500 mg/L NaCl (Table 3.3).

**Table 3.3**  
**Water quality parameters for background water matrices**

	UPW	SCWA	ILL	SCWA + NaCl
<b>TOC (mg/L)</b>	<0.1	0.81	1.3	N/M
<b>UV-254 (absorbance/cm)</b>	N/M	0.0024	0.031	N/M
<b>Conductivity (<math>\mu</math>S/cm)</b>	~17	244	562	2988
<b>TDS<sup>a</sup> (mg/L)</b>	N/M	156	360	1912
<b>Ionic Strength<sup>a</sup></b>	N/M	3.9E-03	9.0E-03	4.8E-02
<b>Total Alkalinity (mg/L as CaCO<sub>3</sub>)</b>	N/M	29	288	N/M
<b>Na (mg/L)</b>	N/M	17	24	608 <sup>b</sup>
<b>Ca (mg/L)</b>	N/M	15.5	53.7	N/M
<b>Fe (mg/L)</b>	N/M	<0.05	<0.05	N/M
<b>Mn (mg/L)</b>	N/M	<0.005	<0.005	N/M
<b>Mg (mg/L)</b>	N/M	6.48	23.3	N/M

<sup>a</sup>based on specific conductivity measurements - ionic strength =  $2.5E-05 \cdot \text{TDS (mg/L)}$ ,

ionic strength =  $1.6E-05 \cdot \text{specific conductance } (\mu\text{S/cm})$  (Snoeyink & Jenkins 1980)

<sup>b</sup>calculated based on 1500 mg/L addition of NaCl to SCWA groundwater

N/M – not measured

### Target Compounds and Stock Solutions

Target compounds were grouped into mixtures based on anticipated aqueous-phase concentrations after equilibration and the ability of the employed HPLC method to separate the compounds (Appendix A - representative HPLC chromatograms). Effects of background water matrix and temperature were evaluated as shown in Table 3.4.

**Table 3.4**  
**Experimental design for the determination of H<sub>cc</sub>**

<b>Factor</b>	<b>Levels</b>	<b>Compound Mixtures</b>
Background water matrix (10° C)	(1) UPW (2) SCWA (3) ILL (4) SCWA+NaCl	<b>Mix 1</b> – DCM; 1,2-DCP; 1,1,1,2-TeCA; 1,1,2,2-TeCA; PCE <b>Mix 2</b> – 1,2-DCA; EDB; 1,2,3-TCP; TCE
Temperature (SCWA)	5, 10, 15, 25, 35° C	<b>Mix 1</b> <b>Mix 2</b>
Temperature (SCWA)	25, 35° C	<b>Single solute studies</b> – 1,1,1,2-TeCA; 1,1,2,2-TeCA
Temperature (SCWA)	5, 15, 23, 30° C	<b>Mix 3</b> – benzene, 1,1-DCA <b>Mix 4</b> – VC; 1,3-butadiene; CT

Concentrated standard stock solutions (SSS) for mixtures 1-3 were prepared by placing 40 mL of purge and trap grade methanol (Fisher Scientific A453-1) into a pre-weighed 40-mL clear borosilicate glass vial. The vial was capped with a PTFE-lined septum and polypropylene open top screw cap and weighed to the nearest 0.1 mg using a Mettler AE200 balance. Neat compounds were added through the septum and below the methanol level in the vial using Hamilton gas-tight syringes of appropriate sizes [#1005 (5 mL), #1001 (1 mL), #1710 (0.1 mL), Table 3.5]. Compound concentrations were determined by weighing the syringe before and after cVOC addition. To add redundancy, vial weights were taken after each cVOC addition; however, these weights were used to cross-check accuracy of syringe weights. After addition of the final cVOC of a given mixture, the septum was replaced, and the stock solution was stored at -10° C.

**Table 3.5**  
**Compounds for standard stock solutions**

Compound	Supplier	Boiling Point <sup>a</sup> (° C)	Density <sup>a</sup> (g/mol)	Volume added to VOA vial (mL)	SSS initial concentration (mg/L)	SSS initial molarity (µmol/L)
benzene	Sigma-Aldrich	78.8	0.873	0.046	1,000	12,802
CT	Sigma-Aldrich	76	1.697	0.12	5,000	32,506
1,2-DCA	Sigma-Aldrich	83.5	1.173	0.17	5,000	50,525
1,2-DCP	Sigma-Aldrich	95.5	1.116	0.18	5,000	44,252
DCM	Riedel-de Haen	40	1.252	0.16	5,000	58,872
PCE	Sigma-Aldrich	119.1	1.653	0.048	2,000	12,061
TCE	Aldrich	87.2	1.474	0.054	2,000	15,222
VC	U.S. EPA	-10.5	0.918	--	8,600	137,600
1,3-butadiene	U.S. EPA	-4.4	0.638	--	7,200	133,111
1,1-DCA	Fluka	57.3	1.168	0.17	5,000	50,525
1,2,3-TCP	Aldrich	157	1.309	0.15	5,000	33,914
1,1,1,2-TeCA	Sigma-Aldrich	130.2	1.566	0.064	2,500	14,894
1,1,2,2-TeCA	Sigma-Aldrich	146.5	1.556	0.064	2,500	14,894

<sup>a</sup>SciFinder Scholar

Due to the low boiling points of VC and 1,3-butadiene (-10.5 and -4.4° C), individual SSSs were prepared by the U.S. EPA (Cincinnati, OH) by bubbling the pure gas-phase component through methanol. The SSS for mix 4 was then prepared by placing 30 mL of purge and trap grade methanol into a pre-weighed 40-mL clear borosilicate glass vial. The vial was capped with a PTFE-lined septum and polypropylene open top screw cap and weighed to the nearest 0.1 mg. Pure, reagent grade CT was added through the septum and below the methanol level in the vial. A 22-gauge needle was placed through the septa, 4-5 mLs of VC SSS prepared by the U.S. EPA and 1,3-butadiene SSS prepared by the U.S. EPA were added through the septum (below the methanol level in the vial) by appropriate syringes. After addition of each cVOCs, the vial was weighed. Based on the large volume of VC and 1,3-butadiene added, concentrations were determined based on vial weights for the

compounds in mix 4. After the 3<sup>rd</sup> cVOC was added, the septum was replaced, and the stock solution was stored at -10° C.

### **Glassware**

Glassware was rinsed with HPLC grade methanol (Fisher Scientific A-452-4) and allowed to dry in the fume hood. Subsequently, glassware was rinsed three times with tap water and three times with deionized water, covered with aluminum foil, and placed in a 105° C drying oven.

## **METHODS**

### **Literature Survey**

One hundred sixty articles were reviewed to obtain HLC data for the target cVOCs. Ninety articles that contained experimentally determined HLCs in non-saline, dilute, aqueous solutions between temperatures of 0-40° C were included in the literature survey as summarized in Table 3.6. If studies were cited in review articles, the original sources were consulted. Individual HLC values from the literature were plotted as a function of  $1/T$ , and the combined literature data for each compound were analyzed by linear regression to determine the temperature dependence of  $\ln(H_{cc})$  using Equation 3.7.

**Table 3.6**  
**Literature sources for Henry's Law constants**

Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	
benzene		X	X	X	X		X	X	X	X		X		X	X		X										X		X	X	X
CT	X			X	X						X	X	X		X							X		X		X	X		X	X	X
1,2-DCA	X	X		X	X						X		X												X					X	X
1,2-DCP											X		X																	X	X
DCM	X			X	X						X		X							X						X	X		X	X	X
PCE					X						X		X		X					X						X	X	X	X	X	X
TCE					X						X		X		X			X	X	X		X	X			X	X	X	X	X	X
VC					Z																					X					X
1,3-butadiene																															
1,1-DCA	X										X														X	X			X		X
1,2,3-TCP														X																	
1,1,1,2-TeCA											X																				
1,1,1,2,2-TeCA											X		X												X						X

X - paper cited in literature regression

Y - paper not cited in literature regression - data collected at T>40° C

Z - paper not cited in literature regression - data varied from published values by several orders of magnitude

*1 – Rex (1906), 2 – Saylor et al. (1938), 3 – Wasik & Tsang (1970), 4 – Hartkopf & Karger (1973), 5 – Brown & Wasik (1974), 6 – Pearson & McConnell (1975), 7 – Vitenberg et al. (1975), 8 – Green & Frank (1979), 9 – Mackay et al. (1979), 10 – Sato & Nakajima (1979a), 11 – Sato & Nakajima (1979b), 12 – Tsibul'skii et al. (1979), 13 – Balls (1980), 14 – Leighton & Calo (1981), 15 – Sanemasa et al. (1981), 16 – Munz & Roberts (1982), 17 – Sanemasa et al. (1982), 18 – Gossett (1983), 19 – Garbarini & Lion (1985), 20 – Gossett et al. (1985), 21 – Munz (1985), 22 – Schoene & Steinhanses (1985), 23 – Munz & Roberts (1986), 24 – Barr & Newsham (1987), 25 – Gossett (1987), 26 – Hellmann (1987), 27 – Munz & Roberts (1987), 28 – Warner et al. (1987), 29 – Yurteri et al. (1987), 30 – Howe et al. (1987)/Ashworth et al. (1988)*

**Table 3.6 Continued**

Compound	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	
benzene	X	X				X	X					Y	X	X	X	X	X	X	X	X		X	X		X		X		X	X	
CT					X					X	X		X	X	X								X							X	X
1,2-DCA		X	X							X	X			X		X							X						X	X	
1,2-DCP										X	X					X													X	X	
DCM		X								X	X			X		X		X											X	X	X
PCE				X	X				X					X		X		X		X			X						X	X	X
TCE	X	X	X	X			X			X	X			X								X	X			X	X	X	X	X	X
VC																															
1,3-butadiene																															
1,1-DCA			X							X	X												X						X	X	
1,2,3-TCP					X																									X	
1,1,1,2-TeCA										X	X																			X	
1,1,1,2-TeCA										X	X			X															X	X	

X - paper cited in literature regression

Y - paper not cited in literature regression - data collected at T>40° C

Z - paper not cited in literature regression - data varied from published values by several orders of magnitude

**31** – Keeley et al. (1988), **32** – Guitart et al. (1989), **33** – Lamarche & Droste (1989), **34** – Bissonette et al. (1990), **35** - Tancrede & Yanagisawa (1990), **36** – Anderson (1992), **37** – Cooling et al. (1992), **38** – Jayasinghe et al. (1992), **39** – Kolb et al. (1992), **40** – Tse et al. (1992), **41** – Wright et al. (1992), **42** – Etre et al. (1993), **43** – Hansen et al. (1993), **44** – Hoff et al. (1993), **45** – Li & Carr (1993), **46** – Li et al. (1993), **47** – Perlinger et al. (1993), **48** – Robbins et al. (1993), **49** – Zhang & Pawliszyn (1993), **50** – Khalfaoui & Newsham (1994a), **51** – Khalfaoui & Newsham (1994b), **52** – Nielsen et al. (1994), **53** – Dewulf et al. (1995), **54** – Heal et al. (1995), **55** – Alaei et al. (1996), **56** – Ramachandran et al. (1996), **57** – Turner et al. (1996), **58** – Hovorka & Dohnal (1997), **59** – Kondoh & Nakajima (1997), **60** – Park et al. (1997)

**Table 3.6 Continued**

Compound	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	Total # papers cited
benzene	X	X		X	X	X		X	X		X			X	X	X		X	X		X		X	X	Y	X		X	X		53
CT			X							X																	X	X			27
1,2-DCA													X															X	X		21
1,2-DCP								X	X						X		X												X		13
DCM			X							X	X										X							X	X		25
PCE	X	X		X				X	X			X																X	X		30
TCE	X	X		X			X		X	X		X		X	X						X		X					X	X	X	47
VC																											X	X			4
1,3-butadiene																														X	1
1,1-DCA														X														X	X		15
1,2,3-TCP																												X			4
1,1,1,2-TeCA																												X			5
1,1,2,2-TeCA																												X			10

X - paper cited in literature regression

Y - paper not cited in literature regression - data collected at T>40° C

Z - paper not cited in literature regression - data varied from published values by several orders of magnitude

**61** – Peng & Wan (1997), **62** – Allen et al. (1998), **63** – Chiang et al. (1998), **64** – de Wolf & Lieder (1998), **65** – Peng & Wan (1998), **66** – Altschuh et al. (1999), **67** – Dewulf et al. (1999), **68** – Dohnal & Hovorka (1999), **69** – Ryu & Park (1999), **70** – David et al. (2000), **71** – Miller & Stuart (2000), **72** – Vane & Giroux (2000), **73** – Ayuttaya et al. (2001), **74** – Bierwagen & Keller (2001), **75** – Gorgenyi et al. (2002), **76** – Bakierowska & Trzeszczynski (2003), **77** – Bobadilla et al. (2003), **78** – Cheng et al. (2003), **79** – Karl et al. (2003), **80** - Shimotori & Arnold (2003), **81** – Lodge & Danso (2007), **82** – Helburn et al. (2008), **83** – Li et al. (2008), **84** – Sieg et al. (2009), **85** – Lau et al. (2010), **86** – Starokozhev et al. (2011), **87** – Chen et al. (2012), **88** – Hiatt (2013), **89** – Zhang et al. (2013), **90** – Rogers (2014)

### Experimental Method for Determination of $H_{cc}$ Values

Dimensionless  $H_{cc}$  values were determined using an experimental method similar to the variable headspace technique developed by Robbins et al. (1993). The original method, which relied on the measurement of gas-phase concentrations in three batch reactors with different air:water ratios (phase ratios), was changed as follows: (1) the number of tested phase ratios was increased from three to five, and (2) aqueous-phase cVOC concentrations

were analyzed via direct injection HPLC. These changes were expected to reduce uncertainty in  $H_{cc}$  estimates because (1) additional phase ratios decrease uncertainty in the parameter estimates from the linear regression analysis performed on the experimental data (see details below) and (2) sampling the aqueous-phase with a gas-tight syringe followed by direct injection into the HPLC minimized free surfaces, thus reducing volatile losses during sample handling. Results from the variable headspace method were

- Compared to published data by adding the experimentally determined  $H_{cc}$  values from this study to the van't Hoff plots developed from the literature review, and
- Combined with the literature data for each compound to calculate recommended curve fitting parameters,  $A$  and  $B$ , determined from the literature survey and experimental results of study.

## Theory

Following the theoretical development by Robbins et al. (1993), a mole balance of component  $i$  at chemical equilibrium is expressed as:

$$N_i = N_{i,le} + N_{i,ge} \quad \text{Equation 3.12}$$

where  $N_i$  represents the total moles of component  $i$  in the closed container,  $N_{i,le}$  equals the moles of component  $i$  in the liquid phase at equilibrium, and  $N_{i,ge}$  represents the moles of component  $i$  in the gas-phase at equilibrium.

If both sides of Equation 3.12 are divided by the volume of the liquid phase ( $V_l$ ), the expression shown in Equation 3.13 results:

$$C_{i,lo} = C_{i,le} + \frac{N_{i,ge}}{V_l} \quad \text{Equation 3.13}$$

where  $C_{i,lo}$  represents the initial concentration of component  $i$  in the liquid phase,  $C_{i,le}$  equals the equilibrium concentration of component  $i$  in the liquid phase, and  $V_l$  is the volume of the liquid phase.

Multiplying the second term on the right of Equation 3.13 by  $(V_g/V_l)$  yields:

$$C_{i,lo} = C_{i,le} + C_{i,ge} \frac{V_g}{V_l} \quad \text{Equation 3.14}$$

where  $V_g$  is the volume of the gas-phase,  $C_{i,le}$  equals the equilibrium concentration of component  $i$  in the gas-phase, and  $V_g/V_l$  represents the phase ratio. Substituting Henry's Law (Equation 3.2) into Equation 3.14 and rearranging gives:

$$\frac{C_{i,lo}}{C_{i,le}} = H_{cc} \left( \frac{V_g}{V_l} \right) + 1 \quad \text{Equation 3.15}$$

Equation 3.15 suggests that a plot of the initial aqueous-phase concentration divided by the equilibrium aqueous-phase concentration ( $C_{i,lo}/C_{i,le}$ ) as a function of the phase ratio ( $V_g/V_l$ ) will give a straight line with slope =  $H_{cc}$  and y-intercept = 1. Correlation coefficients for the variable headspace method plots demonstrated a high degree of linearity with values ranging from 0.9529-0.9995 (Appendix B – representative variable headspace plots).

## Reactor Preparation

Five 250-mL clear glass bottles (exact volume of each bottle was measured) were filled with varying amounts of water and capped with Mininert valves. The volume of water

in each reactor was determined by weighing the bottles both before and after water addition. Volumes of stock solution were drawn into appropriate syringes, the reactors were inverted, and stock solution was added below the surface of the water to achieve initial liquid concentrations of ~50 mg/L, 25 mg/L, 20 mg/L or 10 mg/L, depending on the volatility and the HPLC detector response for each cVOC. Exact volumes of SSS addition were calculated by obtaining the difference in weight between the full and empty syringes and dividing by the density of methanol (Appendix C – representative SSS concentration and phase ratio calculations). The bottles were then placed in zippered neoprene bottle sleeve insulators, inverted, and clamped to a ring stand. The ring stand was placed in an incubator/shaker (New Brunswick Scientific C25KC) set at the desired temperature [exact experimental temperature was measured with a Traceable Calibration Control Co. thermometer (#77776-720) set in a water-filled bottle in the incubator], and samples were allowed to equilibrate overnight. Prior studies by Gossett (1987) observed the effect of equilibration time on HLCs and found no significant difference when measured at 1, 18, and 48 hours.

### **HPLC Analysis**

Immediately before analysis, clamps with bottle and sleeve attached, were individually taken out of the incubator and were reattached, with bottles inverted, to a ring stand in a fume hood. Approximately 3.5 mL of liquid was removed from the reactors by inserting a 5-mL gas-tight luer lock syringe with disposable 22-gauge needle through the septum of the Mininert valve. After sample withdrawal, the disposable needle was replaced with a 2-way valve. A Hamilton 22-gauge blunt tip needle was placed on the end of the

valve, the needle was inserted into the manual injection port of the HPLC, and 0.5 mL of the sample was injected.

Separation and quantitation of cVOCs was conducted by reverse-phase HPLC analysis (Waters Breeze 1525 Binary HPLC Pump). A manual sample injection valve (Rheodyne 7725i), 250- $\mu$ L sample loop, and XSelect HSS T3 (5 $\mu$ m, 250 mm x 4.6 mm) column were used. The mobile phase (acetonitrile:water at 55%:45% v/v) was pumped through the column at a flow rate of 1.5 mL/min. Concentrations of cVOCs were quantified by UV detection (Waters 2487 Dual  $\lambda$  Absorbance Detector) at 190 and 195 nm. Control of instrumentation, acquisition of data, and processing of data were performed through Waters Breeze 2 Software.

Calibration curves were prepared for every HPLC sample set. The peak area (x-axis) was plotted against the known concentration in mg/L (y-axis). Calibration curves for the target cVOCs were highly linear with  $r^2$  values between 0.996 and 1 (Appendix D – representative calibration curves).

## **RESULTS AND DISCUSSION**

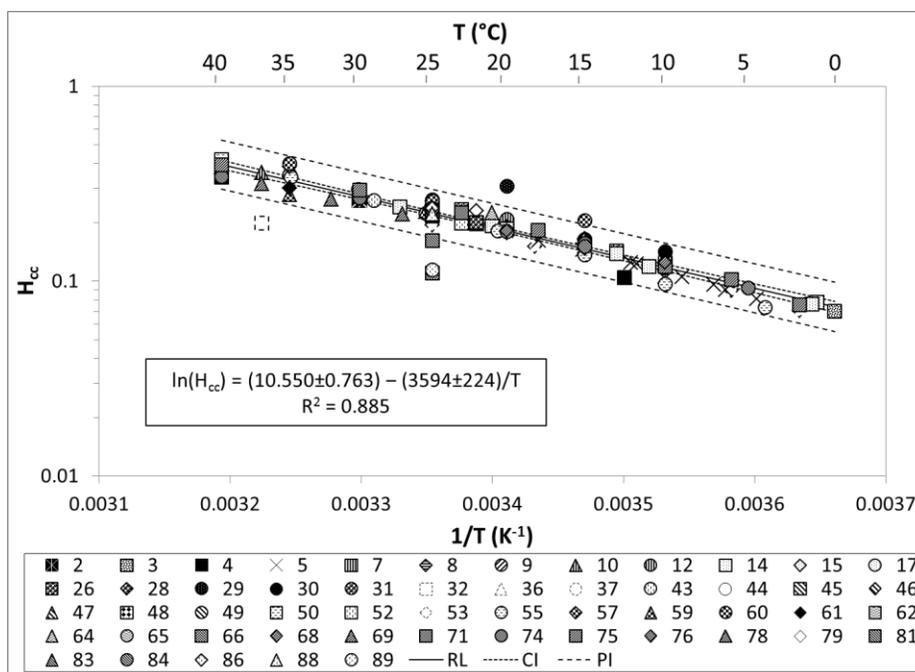
### **Benzene**

Of the target cVOCs, HLC data for benzene were found in 53 literature sources, making it the most frequently studied compound among the cVOCs evaluated here. Earliest HLC measurements for benzene date back to the solubility studies of Saylor et al. (1938). HLC values cited in the literature survey were determined using both dynamic (batch air stripping) and static (single/multiple equilibration, EPICS, variable headspace) methods as

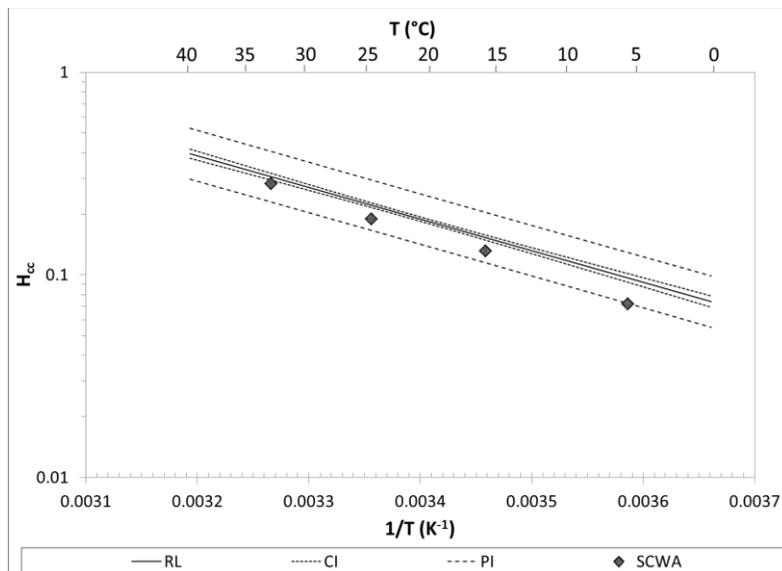
well as measurement of activity coefficients (GLC). To establish the temperature dependence of the HLC for benzene, the literature data were summarized in a van't Hoff plot (Figure 3.1, Table 3.6 – legend key). There was relatively good agreement between literature values ( $r^2=0.885$ ) for the van't Hoff temperature dependence.

Experimental data obtained in this study for benzene in SCWA groundwater fell within the 95% prediction bands of the van't Hoff relationship (Figure 3.2); however, the slope is steeper such that HLC values began to deviate from the trend established in the literature as temperature decreased. At 10° C, the  $H_{cc}$  value predicted from the literature survey relationship was 0.117 with upper and lower bounds (95% prediction bands) of 0.157 and 0.0882, respectively. Using the van't Hoff relationship derived from the experimental data from this study, the  $H_{cc}$  value for benzene is predicted to be 0.0919 (Table 3.7).

The van't Hoff relationship developed from the literature survey and the experimental data as well as all models consulted [EPI Suite (HENRYWIN), SPARC, ASAP] predicted  $H_{cc}$  values  $>0.05$  at 10° C (Table 3.7), indicating that benzene is amenable to removal by PTA. However, the HLC value (0.364) predicted by SPARC at 10° C was higher than that from other model predictions by a factor of 3. SPARC predictions for benzene did not follow a log-linear van't Hoff relationship and veered away from other model predictions at temperatures below 25° C (Figure 3.3).



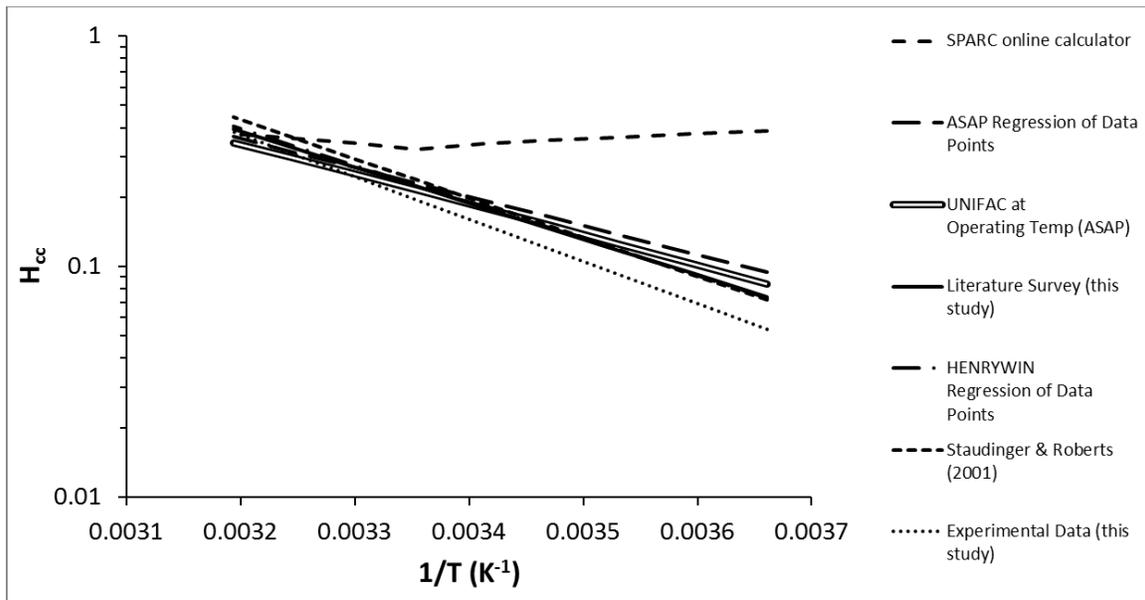
**Figure 3.1**  
**Temperature dependence of  $H_{cc}$  for benzene based on results reported in 53 studies**  
 (Note: consult Table 3.6 for legend key)



**Figure 3.2**  
**Comparison of experimental results for benzene obtained in this study and van't Hoff relationship obtained from literature survey**  
 (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)

**Table 3.7**  
**Summary of HLCs for benzene at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.117	10.550	3594	0.885	53
Experimental data obtained in this study	0.0919	12.517	4220	0.997	1
Literature survey + experimental data (this study)	0.116	10.645	3623	0.885	54
Staudinger & Roberts (2001)	0.118	11.637	3899	-	9
HENRYWIN regression of data points (based on Leighton & Calo 1981)	0.117	-	-	-	-
SPARC on-line calculator	0.364	-	-	-	-
ASAP regression of data points	0.137	-	-	-	-
UNIFAC fit with data points (ASAP)	0.142	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.125	-	-	-	-



**Figure 3.3**  
**Comparison of HLC estimation methods for benzene**  
**[Note: Results for HENRYWIN overlap with those for Literature Survey (this study)]**

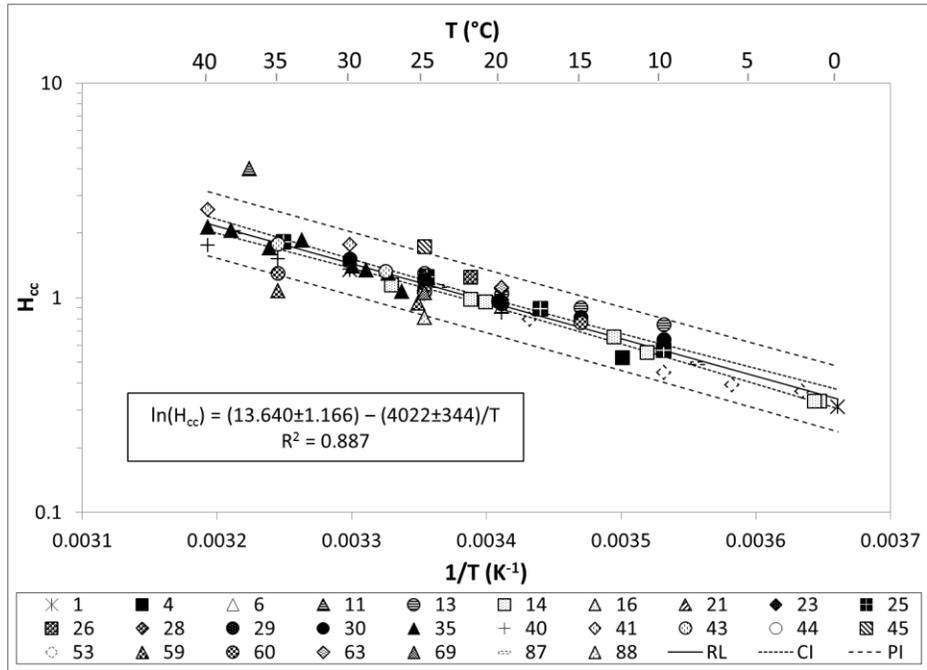
## Carbon tetrachloride

The van't Hoff relationship for CT shown in Figure 3.4 was developed from 27 published studies that used dynamic (batch air stripping) and static (single/multiple equilibration, EPICS, variable headspace) methods as well as solubility studies and measurements of activity coefficients (GLC) for the determination of HLCs. Cited studies cover over a century of research, from 1908 to 2013. For the more recent papers, six out of seven studies published after 1995 used the EPICS or modified EPICS techniques. The  $r^2$  value for the temperature dependence of literature  $H_{cc}$  values was 0.887 (Figure 3.4), indicating relatively close agreement among the published studies. Based on the regression equation for CT shown in Figure 3.4, the best estimate of  $H_{cc}$  at 10°C is 0.568 with upper and lower bounds of 0.800 and 0.404 (95% PI). In other words, uncertainty in the  $H_{cc}$  value for CT was within 41% of the mean.

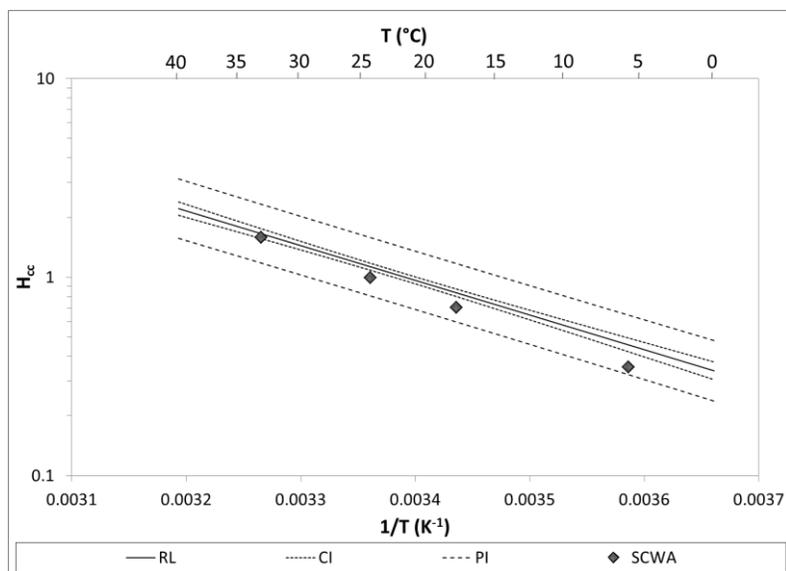
Experimental values for CT fell within the 95% PI (Figure 3.5). However, the slope of the van't Hoff relationship developed from the experimental data was steeper, such that HLC values began to deviate from the trend established in the literature as temperature decreased.

For CT, the  $H_{cc}$  values predicted by all models were greater than 0.5 (Table 3.8), indicating that its high volatility makes it an excellent candidate for removal by PTA. There was close agreement between the  $H_{cc}$  values obtained from van't Hoff relationship developed from the literature survey and experimental data as well as the temperature variation in EPI Suite's HENRYWIN. However, the HLC values predicted by SPARC predictions did not

follow a log-linear van't Hoff relationship and deviated from other model predictions by a factor of ~2 at 10° C (Figure 3.6, Table 3.8).



**Figure 3.4**  
**Temperature dependence of  $H_{cc}$  for CT based on results reported in 27 studies**  
**(Note: consult Table 3.6 for legend key)**

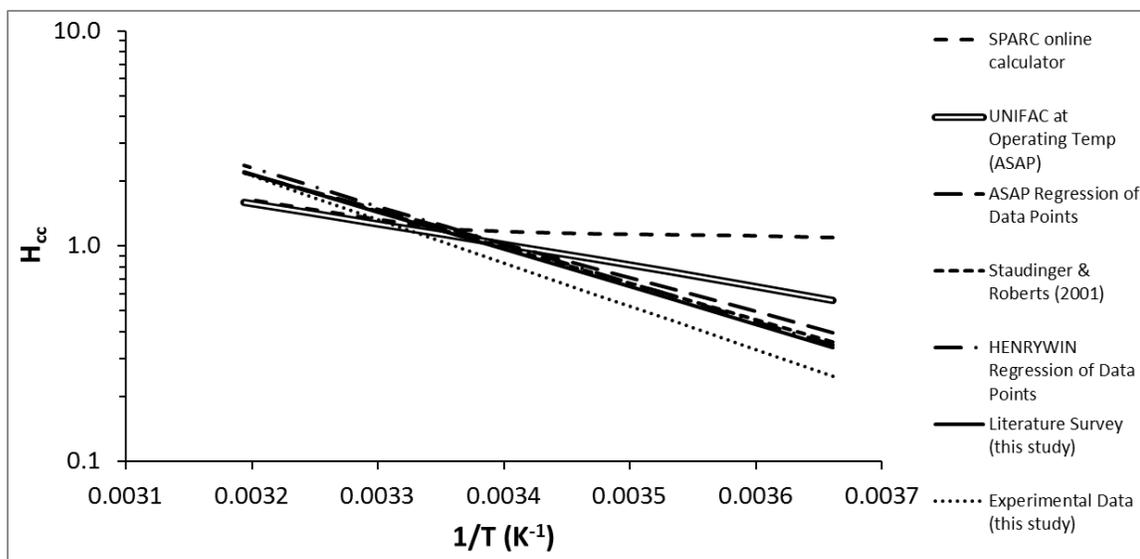


**Figure 3.5**

**Comparison of experimental results for CT obtained in this study and van't Hoff relationship obtained from literature survey (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)**

**Table 3.8**  
**Summary of HLCs for CT at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.568	13.640	4022	0.887	27
Experimental data obtained in this study	0.452	15.656	4658	1.00	1
Literature survey + experimental data (this study)	0.560	13.800	4072	0.890	28
Staudinger & Roberts (2001)	0.590	13.210	3890	-	9
HENRYWIN regression of data points (based on Gossett 1987)	0.591	-	-	-	-
SPARC on-line calculator	1.123	-	-	-	-
ASAP regression of data points	0.634	-	-	-	-
UNIFAC fit with data points (ASAP)	0.637	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.756	-	-	-	-



**Figure 3.6**  
**Comparison of HLC estimation methods for CT**

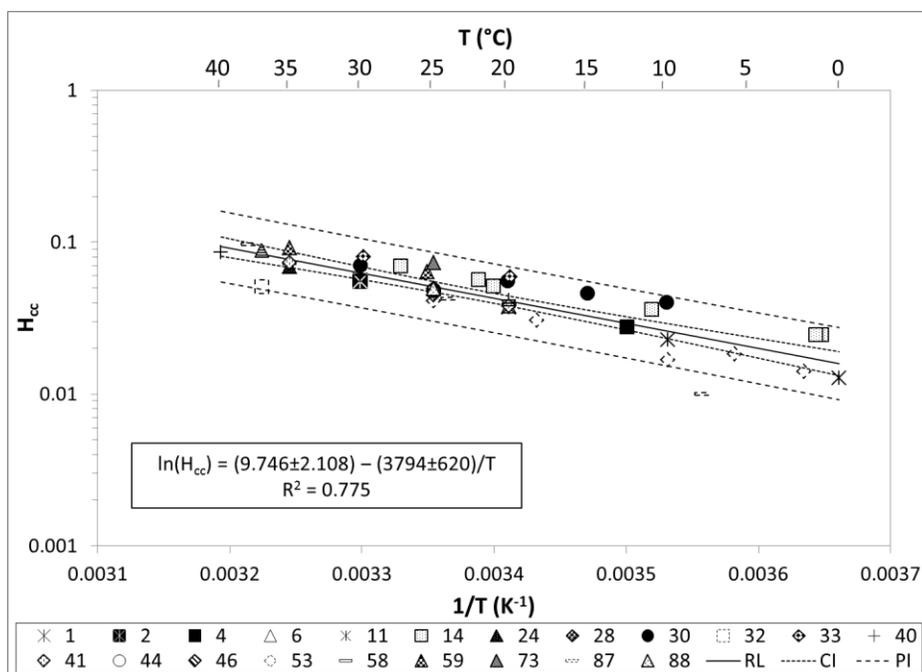
### 1,2-dichloroethane

Twenty-one published studies were used to develop the van't Hoff relationship for 1,2-DCA shown in Figure 3.7. HLC values cited in the literature survey were determined by dynamic (batch air stripping) and static (single equilibration, EPICS) methods as well as solubility studies and measurements of activity coefficients (GLC, differential static cell). 1,2-DCA was one of two currently regulated compounds that exhibited a larger uncertainty in  $H_{cc}$  estimates ( $r^2 = 0.775$ ). Based on the regression equation for 1,2-DCA shown in Figure 3.7, the best estimate of  $H_{cc}$  at 10°C is 0.0259 with upper and lower bounds of 0.0440 and 0.0153 (95% PI), respectively. For 1,2-DCA, uncertainty in the  $H_{cc}$  value was within 70% of the mean.

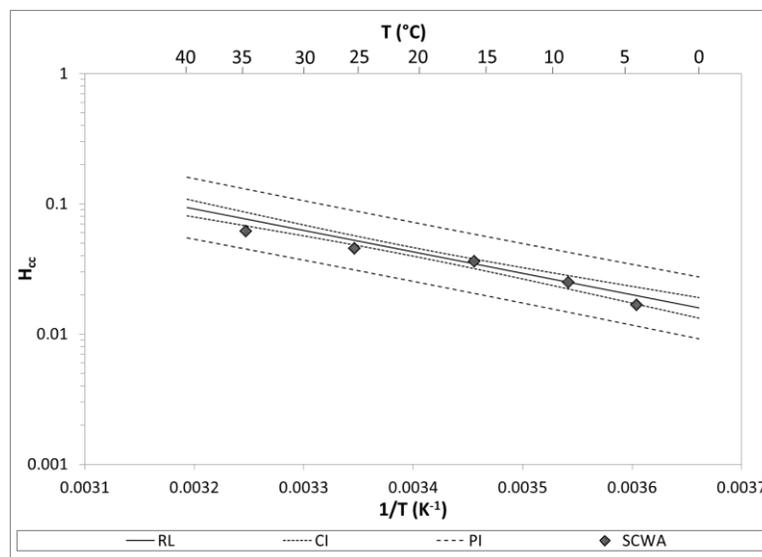
Experimental data obtained in this study for 1,2-DCA in SCWA groundwater closely followed the trendline established by the van't Hoff relationship developed from the

literature survey (Figure 3.8), with all five data points falling within the 95% PI. Using the van't Hoff relationship derived from experimental data from this study, the  $H_{cc}$  value for 1,2-DCA is predicted to be 0.0242 at 10° C (Table 3.9), a difference of 7% from that predicted by the van't Hoff relationship developed from the literature survey and within the 95% CI (0.0231-0.0291). With an HLC value <0.05, 1,2-DCA is the one currently regulated cVOC that is poorly strippable.

At 10° C, there was very good agreement between the van't Hoff relationships developed from the literature survey and experimental results in this study and that of Staudinger & Roberts (2001) as well as the predictive tools HENRYWIN and SPARC (Table 3.9). However, the HLC value (0.0348) predicted by UNIFAC at 10° C was 27% higher than the HLC values predicted by other models (Figure 3.9, Table 3.9).



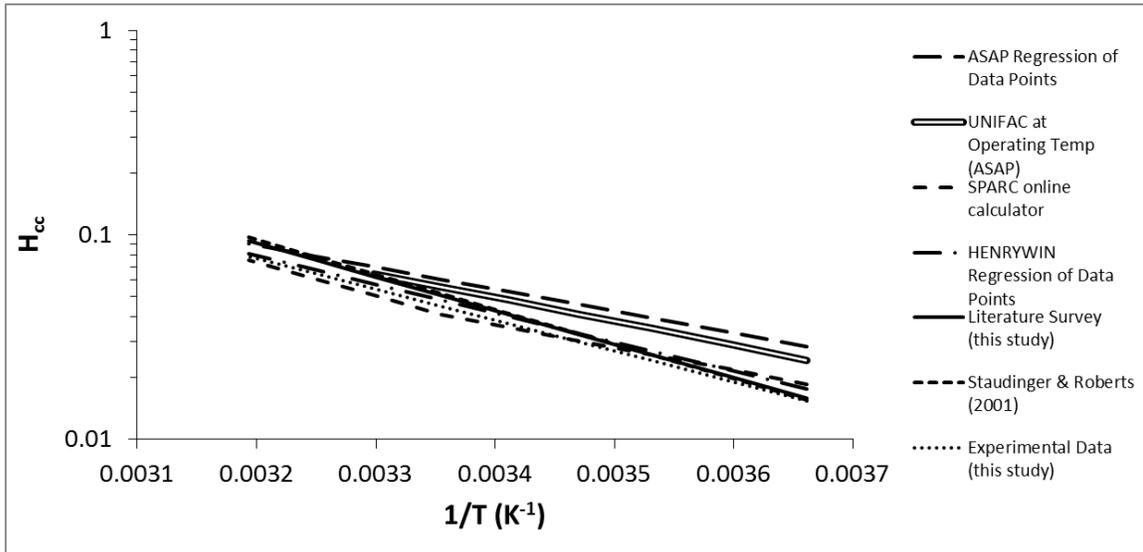
**Figure 3.7**  
**Temperature dependence of  $H_{cc}$  for 1,2-DCA based on results reported in 21 studies**  
**(Note: consult Table 3.6 for legend key)**



**Figure 3.8**  
**Comparison of experimental results for 1,2-DCA obtained in this study and van't Hoff**  
**relationship obtained from literature survey**  
**(RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)**

**Table 3.9**  
**Summary of HLCs for 1,2-DCA at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.0259	9.746	3794	0.775	21
Experimental data obtained in this study	0.0242	8.553	3475	0.964	1
Literature survey + experimental data (this study)	0.0257	9.705	3784	0.791	22
Staudinger & Roberts (2001)	0.0258	10.212	3927	-	4
HENRYWIN regression of data points (based on Leighton & Calo 1981)	0.027	-	-	-	-
SPARC on-line calculator	0.026	-	-	-	-
ASAP regression of data points	0.0388	-	-	-	-
UNIFAC fit with data points (ASAP)	0.0497	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.0348	-	-	-	-



**Figure 3.9**  
**Comparison of HLC estimation methods for 1,2-DCA**  
 [Note: results for Staudinger & Roberts (2001) overlap with those for Literature Survey (this study)]

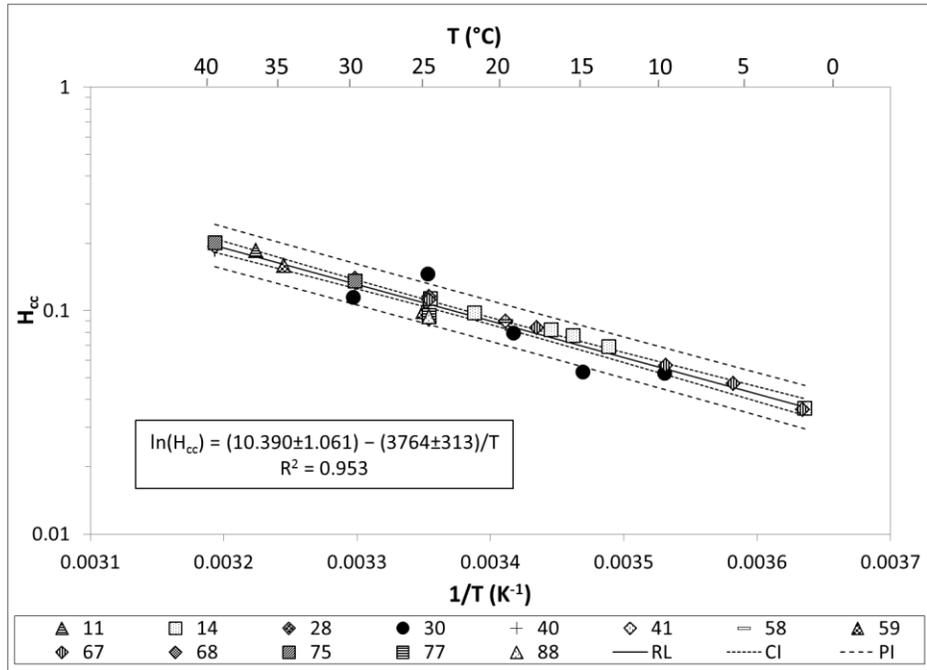
## 1,2-dichloropropane

HLC data for 1,2-DCP were found in 13 literature sources that used dynamic (batch air stripping) and static (single equilibration, EPICS) methods as well as measurement of activity coefficients (GLC, differential static cell) for the determination of HLCs. To establish the temperature dependence of the HLC for 1,2-DCP, the literature data were summarized in a van't Hoff plot (Figure 3.10). Among the eight currently regulated compounds, 1,2-DCP had the closest agreement between studies ( $r^2=0.953$ ) for the van't Hoff temperature dependence.

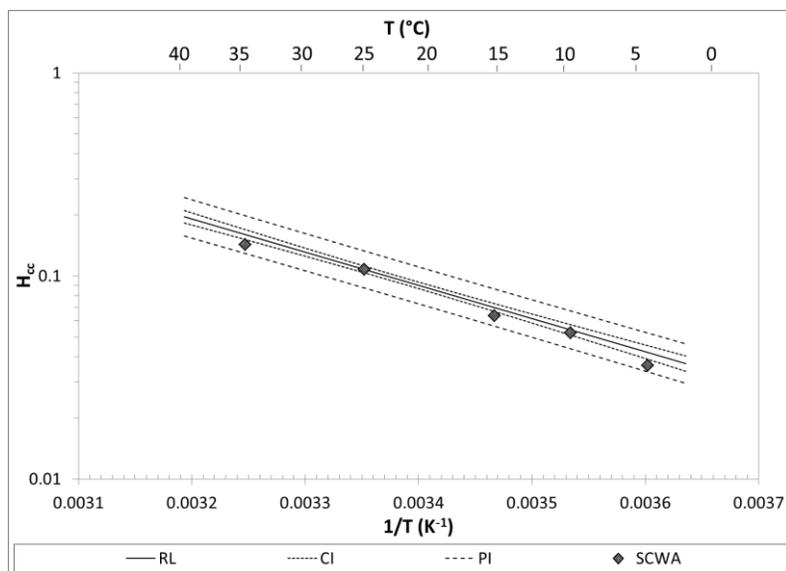
Experimental data obtained in this study for 1,2-DCP in SCWA groundwater closely followed the trendline established by the literature survey data, with all five data points falling within the 95% PI (Figure 3.11). The van Hoff relationship derived from experimental data predicted an  $H_{cc}$  of 0.0503 for 1,2-DCP at 10° C (Table 3.10), well within the literature survey upper and lower bounds of 0.0679 and 0.0442, respectively, based on the 95% PI.

Between 0-40° C, there was close agreement between the  $H_{cc}$  values obtained from van't Hoff relationships developed from the literature survey in this study and the temperature variation from HENRYWIN. The HLC values predicted by SPARC did not follow a log-linear van't Hoff relationship; however, the predicted temperature dependence from SPARC converged with the van't Hoff relationships derived from the literature survey and HENRYWIN at 10° (Figure 3.12, Table 3.10). At 10° C, seven out of eight models consulted estimated an  $H_{cc}$  value  $>0.05$  for 1,2-DCP, putting it just over the minimum recommended  $H_{cc}$  for removal by PTA (Table 3.10). ASAP Regression of Data Points

predicted an  $H_{cc}$  of 0.0478 for 1,2-DCP at 10° C while the HLC value predicted by UNIFAC at 10° C was higher than that from other model predictions by a factor of 2.8 (Table 3.10).



**Figure 3.10**  
**Temperature dependence of  $H_{cc}$  for 1,2-DCP based on results reported in 13 studies**  
**(Note: consult Table 3.6 for legend key)**

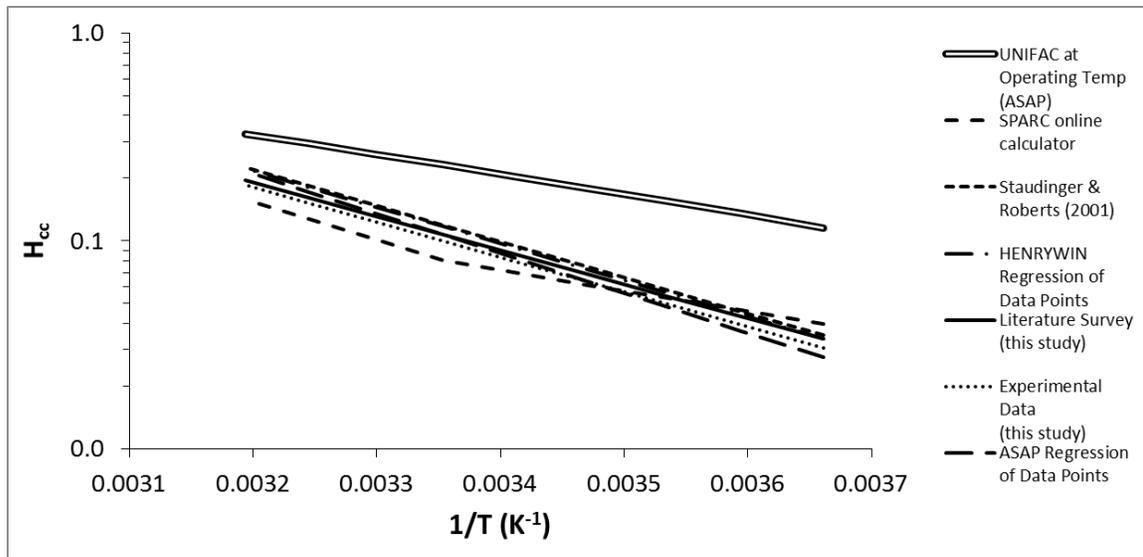


**Figure 3.11**

**Comparison of experimental results for 1,2-DCP obtained in this study and van't Hoff relationship obtained from literature survey (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)**

**Table 3.10**  
**Summary of HLCs for 1,2-DCP at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.0548	10.39	3764	0.953	13
Experimental data obtained in this study	0.0503	10.601	3848	0.988	1
Literature survey + experimental data (this study)	0.0538	10.543	3813	0.957	14
Staudinger & Roberts (2001)	0.0586	11.234	3984	-	3
HENRYWIN regression of data points (based on Leighton & Calo 1981)	0.057	-	-	-	-
SPARC on-line calculator	0.053	-	-	-	-
ASAP regression of data points	0.0478	-	-	-	-
UNIFAC fit with data points (ASAP)	0.0519	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.154	-	-	-	-



**Figure 3.12**

**Comparison of HLC estimation methods for 1,2-DCP**

**[Note: results for Staudinger & Roberts (2001) overlap with those for HENRYWIN]**

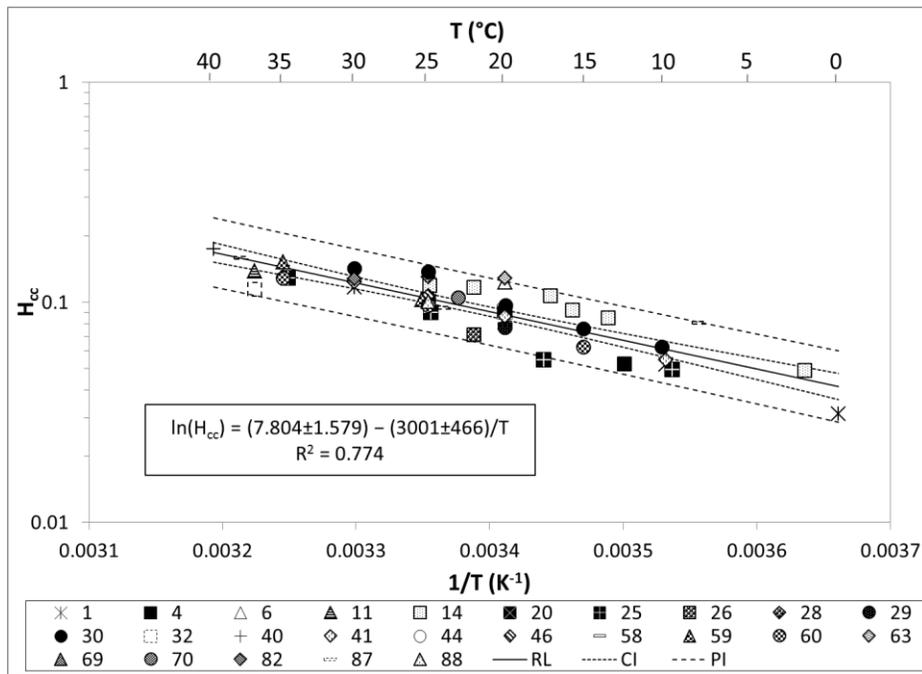
**Dichloromethane**

The van't Hoff relationship for DCM shown in Figure 3.13 was developed from 25 published studies that utilized measurement of activity coefficients (GLC, differential static cell) as well as dynamic methods (batch air stripping) and static methods (single equilibration, EPICS) for the determination of HLCs. Among the currently regulated compounds, uncertainty in  $H_{cc}$  estimates was largest for DCM ( $r^2 = 0.774$ ). Based on the regression equation for DCM shown in Figure 3.13, the best estimate of  $H_{cc}$  at 10°C is 0.0612 with upper and lower bounds of 0.0875 and 0.0428 (95% PI), respectively. For DCM, uncertainty in the  $H_{cc}$  value was within 43% of the mean.

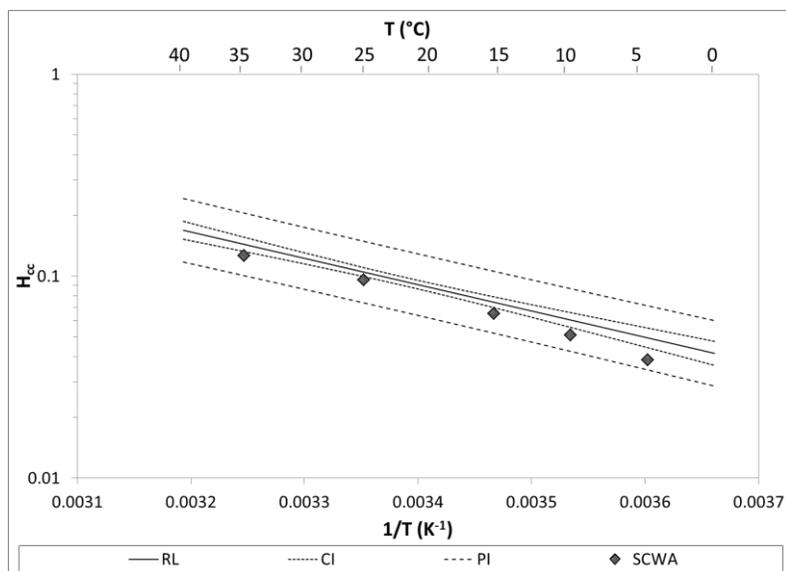
As with the other regulated compounds, experimental data obtained in this study for DCM in SCWA groundwater fell within the 95% PI (Figure 3.14). At 10° C, the van't Hoff

relationship developed from the literature survey (0.0612) differed from that derived from the van't Hoff relationship developed from experimental data (0.0509) by 17% (Table 3.11).

In the temperature range 0-40° C, consistency in HLC values was shown between the van't Hoff relationships developed from the literature survey in this study, experimental data, Staudinger & Roberts (2001), and ASAP as well as the predictive models UNIFAC and HENRYWIN (Figure 3.15 Table 3.11). The predicted  $H_{cc}$  values at 10° C were above 0.05, making DCM amenable to removal by PTA. However, SPARC under-predicted  $H_{cc}$  at 10° C by a factor of ~2, erroneously indicating an  $H_{cc}$  value that falls below the minimum recommended  $H_{cc}$  for effective removal by PTA (Figure 3.15, Table 3.11).



**Figure 3.13**  
**Temperature dependence of  $H_{cc}$  for DCM based on results reported in 25 studies**  
**(Note: consult Table 3.6 for legend key)**

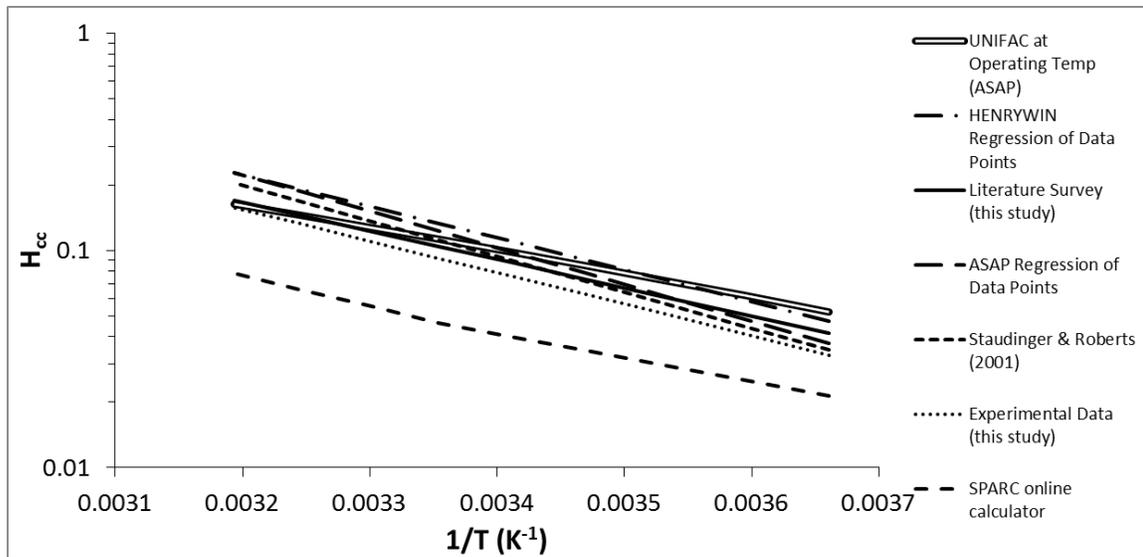


**Figure 3.14**

**Comparison of experimental results for DCM obtained in this study and van't Hoff relationship obtained from literature survey (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)**

**Table 3.11**  
**Summary of HLCs for DCM at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.0612	7.804	3001	0.774	25
Experimental data obtained in this study	0.0509	8.807	3337	0.994	1
Literature survey + experimental data (this study)	0.0595	8.130	3101	0.798	26
Staudinger & Roberts (2001)	0.0568	10.504	3786	-	5
HENRYWIN regression of data points (based on Leighton & Calo 1981)	0.0731	-	-	-	-
SPARC on-line calculator	0.03	-	-	-	-
ASAP regression of data points	0.0607	-	-	-	-
UNIFAC fit with data points (ASAP)	0.0643	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.0719	-	-	-	-



**Figure 3.15**  
**Comparison of HLC estimation methods for DCM**

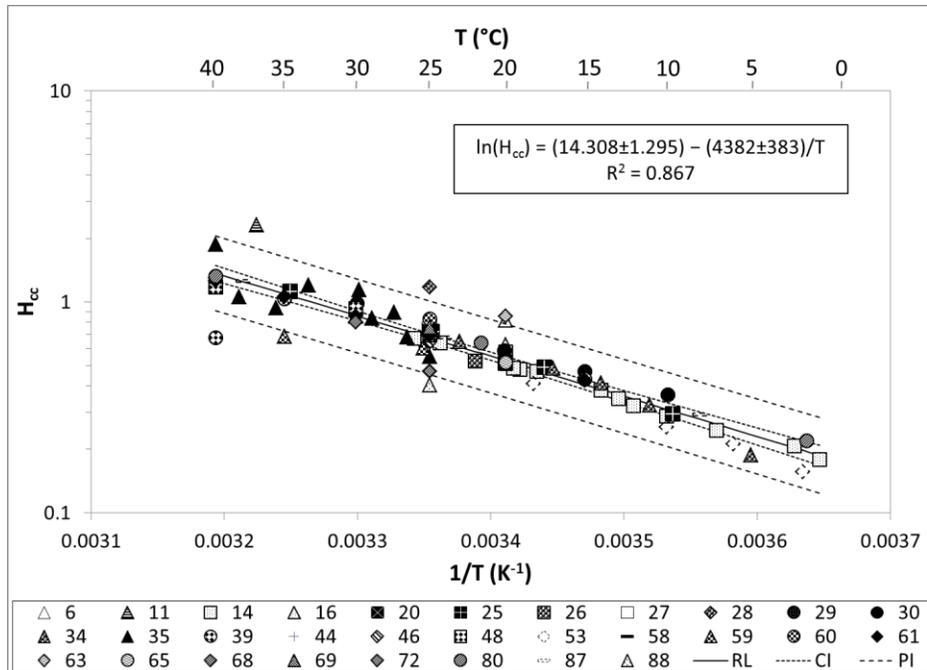
### **Tetrachloroethylene**

To establish the temperature dependence of HLC for PCE, data from 30 literature sources were summarized in a van't Hoff plot (Figure 3.16). HLC measurements were obtained through static (single/multiple equilibration, EPICS, variable headspace) and dynamic methods (batch air stripping), two of which used an automatic sampler (studies 61 and 65 - Peng & Wan 1997, 1998). The  $r^2$  value for the temperature dependence of literature  $H_{cc}$  values was 0.867, indicating relatively close agreement among published studies.

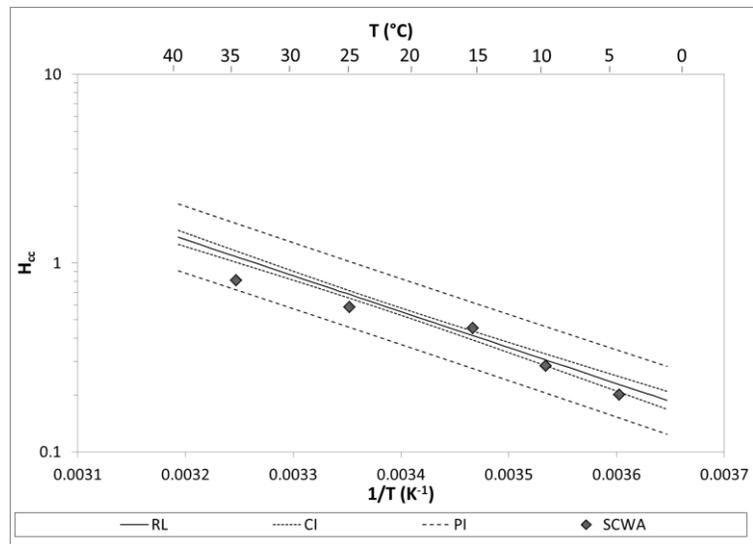
Experimental data obtained in this study for PCE in SCWA groundwater fell within the 95% PI of the van't Hoff relationship derived from the literature survey (Figure 3.17). At 10° C, the  $H_{cc}$  estimate from the literature survey relationship was 0.311, with upper and lower bounds of 0.466 and 0.207, respectively (95% PI). Using the van't Hoff relationship

developed from the experimental data from this study, the  $H_{cc}$  value for PCE is predicted to be 0.292 (Table 3.12).

Data from the HENRYWIN predictive model and van't Hoff relationship developed from the literature survey were in close agreement, with  $H_{cc}$  values at 10° C of 0.315 and 0.311, respectively (Table 3.12). The slope of the temperature dependence obtained from UNIFAC was flatter and crossed the van't Hoff relationships derived from HENRYWIN and the literature survey data in this study at 15° C. As a result, UNIFAC under-predicting  $H_{cc}$  at temperatures exceeding 15° C and over-predicted  $H_{cc}$  below 15° C (Figure 3.18). SPARC predictions for PCE did not follow a log-linear van't Hoff relationship and switched from a negative to a positive slope below 25 ° C. At 10° C, SPARC predicted an  $H_{cc}$  value of 3.512 for PCE (Table 3.12), an over-prediction by a factor of 11.3 relative to the literature survey value.



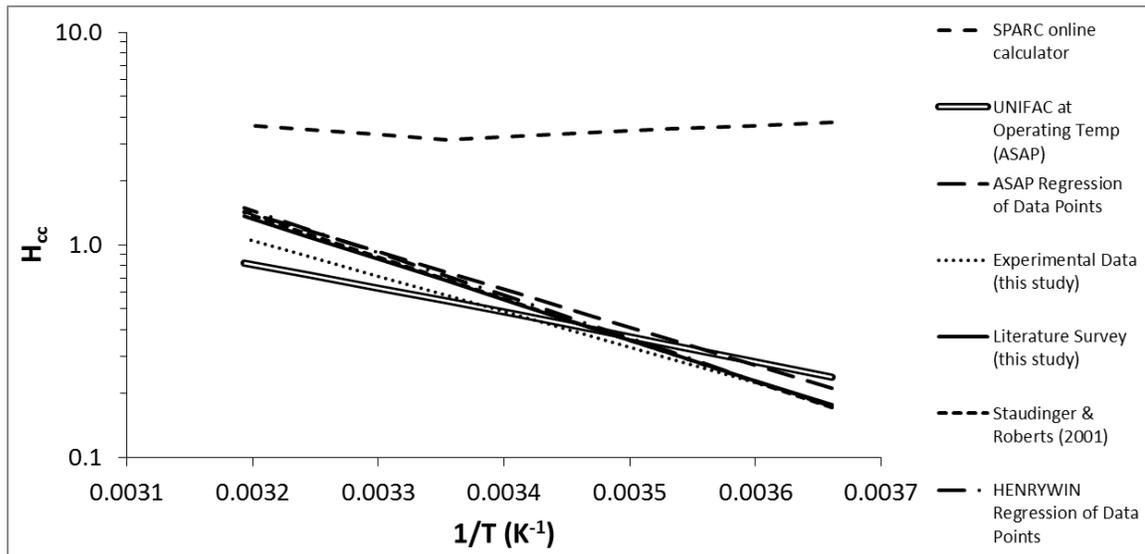
**Figure 3.16**  
**Temperature dependence of  $H_{cc}$  for PCE based on results reported in 30 studies**  
 (Note: consult Table 3.6 for legend key)



**Figure 3.17**  
**Comparison of experimental results for PCE obtained in this study and van't Hoff relationship obtained from literature survey**  
 (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)

**Table 3.12**  
**Summary of HLCs for PCE at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.311	14.308	4382	0.867	30
Experimental data obtained in this study	0.292	12.325	3838	0.958	1
Literature survey + experimental data (this study)	0.309	14.259	4370	0.871	31
Staudinger & Roberts (2001)	0.309	14.725	4502	-	12
HENRYWIN regression of data points (based on Gossett 1987)	0.315	-	-	-	-
SPARC on-line calculator	3.512	-	-	-	-
ASAP regression of data points	0.355	-	-	-	-
UNIFAC fit with data points (ASAP)	0.361	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.337	-	-	-	-



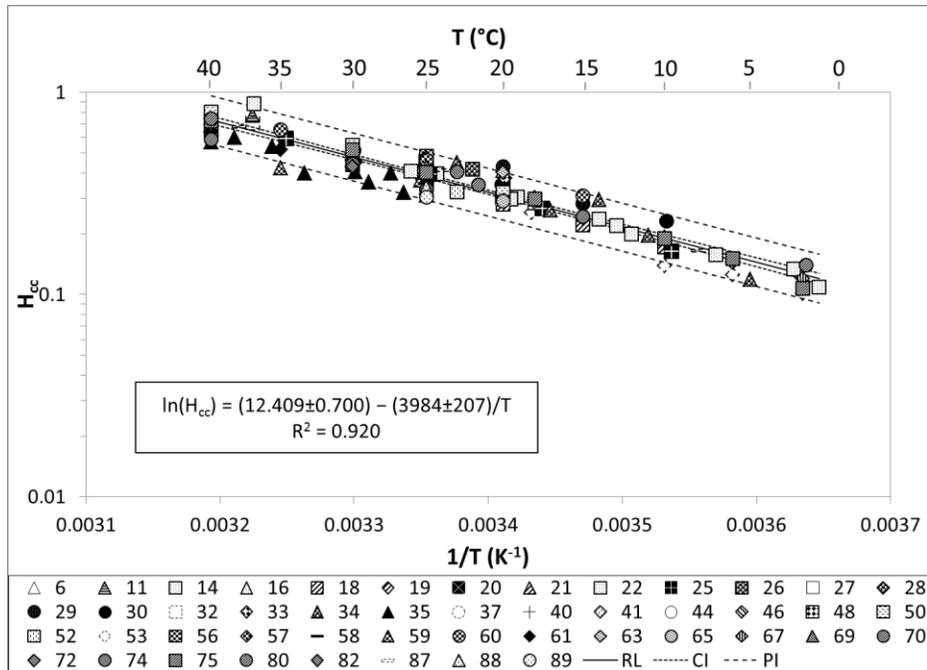
**Figure 3.18**  
**Comparison of HLC estimation methods for PCE**  
 [Note: results for Staudinger & Roberts (2001) and HENRYWIN overlap with those for Literature Survey (this study)]

## Trichloroethylene

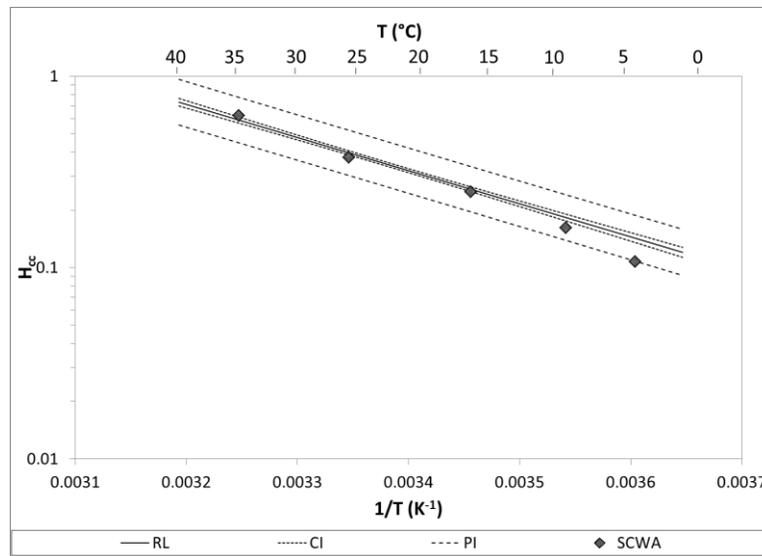
Of the target cVOCs, HLC data for TCE were found in 47 literature sources, making it the second most frequently studied compound among the cVOCs evaluated here. HLC values cited in the literature survey were determined from measurements of activity coefficients (GLC), static methods (single/multiple equilibration, EPICS, variable headspace), and dynamic methods (batch air stripping). Literature data for TCE were among the most consistent for the compounds evaluated in this study, and an  $r^2$  value of 0.920 was associated with the van't Hoff regression (Figure 3.19).

Experimental data obtained in SCWA groundwater for TCE in this study followed the trendline predicted by the literature survey values (Figure 3.20). The van't Hoff relationship describing the experimental data yielded an  $H_{cc}$  estimate of 0.162, a value that falls within the upper and lower bounds of the 95% PI (0.250 and 0.144, respectively).

$H_{cc}$  model predictions at 10° C were consistent between the van't Hoff relationships developed from the literature survey, experimental data, Staudinger & Roberts (2001), the ASAP regression of data points, and from HENRYWIN (Figure 3.21, Table 3.13). However, the HLC value predicted by UNIFAC at 10° C was higher than that from other model predictions by a factor of ~1.5. Similarly, the HLC value predicted by SPARC for TCE at 10° C was higher than other models by a factor of 10 (Figure 3.21, Table 3.13). Of the target cVOCs, errors in SPARC calculations were highest for PCE and TCE.



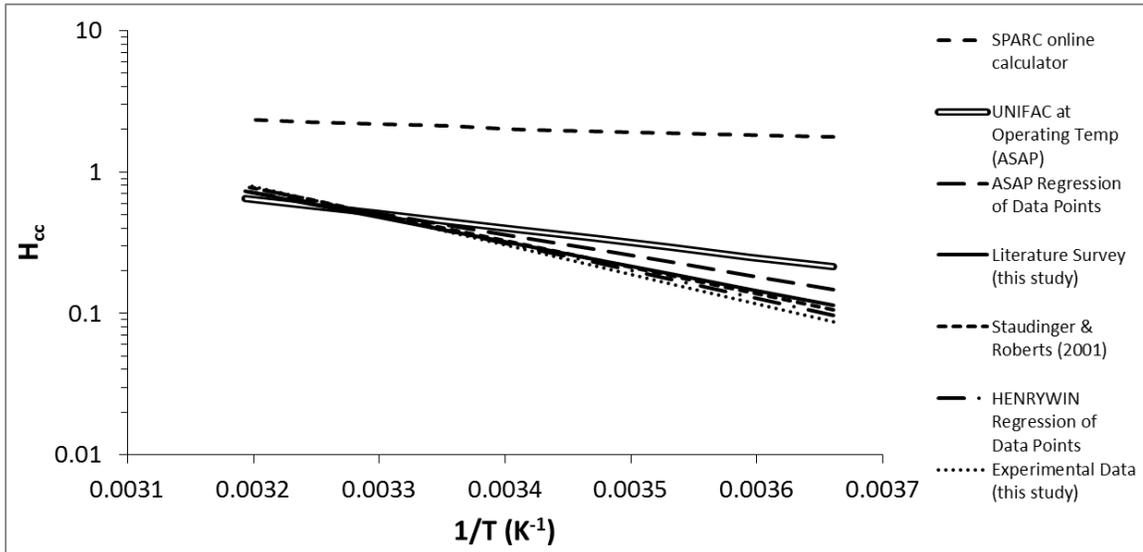
**Figure 3.19**  
**Temperature dependence of  $H_{cc}$  for TCE based on results reported in 47 studies**  
**(Note: consult Table 3.6 for legend key)**



**Figure 3.20**  
**Comparison of experimental results for TCE obtained in this study and van't Hoff**  
**relationship obtained from literature survey**  
**(RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)**

**Table 3.13**  
**Summary of HLCs for TCE at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.190	12.409	3984	0.920	47
Experimental data obtained in this study	0.162	15.021	4769	0.990	1
Literature survey + experimental data (this study)	0.188	12.574	4034	0.923	48
Staudinger & Roberts (2001)	0.185	13.528	4309	-	12
HENRYWIN regression of data points (based on Gossett 1987)	0.174	-	-	-	-
SPARC on-line calculator	1.864	-	-	-	-
ASAP regression of data points	0.227	-	-	-	-
UNIFAC fit with data points (ASAP)	0.23	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.289	-	-	-	-



**Figure 3.21**  
**Comparison of HLC estimation methods for TCE**

A sensitivity analysis was conducted with the TCE data to investigate different forms of the van't Hoff equations presented by Heron et al. (1988) (Equations 3.7-3.11). As shown in Table 3.14, the  $B$  value remains constant when HLCs other than  $H_{cc}$  are used in the van't

Hoff equation ( $A-B/T$ ). The correction to include a third term ( $\ln T$ ) to the van't Hoff equation for  $H_{cc}$  corrects the  $B$  value such that it matches those for  $H_{pc}$  and  $H_{yx}$ .

Of the 90 articles reviewed, authors used  $H_{yx}$  (Leighton & Calo 1981),  $H_{cc}$  (Dewulf et al. 1999),  $H_{pc}$  (Gossett 1983, 1985, 1987), and  $H_{px}$  (Peng & Wan 1997, 1998) in the van't Hoff relationships of the form  $A-B/T$  to describe the temperature dependence of HLCs, and it is stated in many studies that  $B$  is related to  $\Delta H_r^o$ . As shown in Table 3.14, application of Equations 3.10 and 3.11 yield consistent  $\Delta H_r^o$  values representing the enthalpy of TCE dissolution from air into water.

**Table 3.14**  
**Sensitivity analysis of regression equations for TCE**

Form of van't Hoff equation	A	B (K)	$\Delta H_r^o$ kJ/(mol)
$\ln(H_{cc}) = A - B/T$	12.409	3984	35.56
$\ln(H_{pc}) = A - B/T$	9.687	4278	35.57
$\ln(H_{yx}) = A - B/T$	20.61	4278	35.57
$\ln(H_{cc}) = A - B/T - \ln T$	19.094	4278	35.57

Ten Hulscher et al. (1992) note that the van't Hoff equation shown in Equation 3.8, can be rewritten as

$$\ln(H_{pc}) = \frac{\Delta S_r^o}{R} - \frac{\Delta H_r^o}{R} \left( \frac{1}{T} \right) \quad \text{Equation 3.16}$$

In other words, when  $H_{pc}$  is used in the van't Hoff equation [ $\ln(H_{pc}) = A-B/T$ ], the adjustable parameter  $A$  is shown to be related to entropy change associated with air:water partitioning of

the cVOC. Alternatively, van't Hoff equations utilizing  $H_{cc}$  (Equations 3.7 and 3.9) and  $H_{yx}$  give other values for  $A$  due to additional terms associated with the unit conversion.

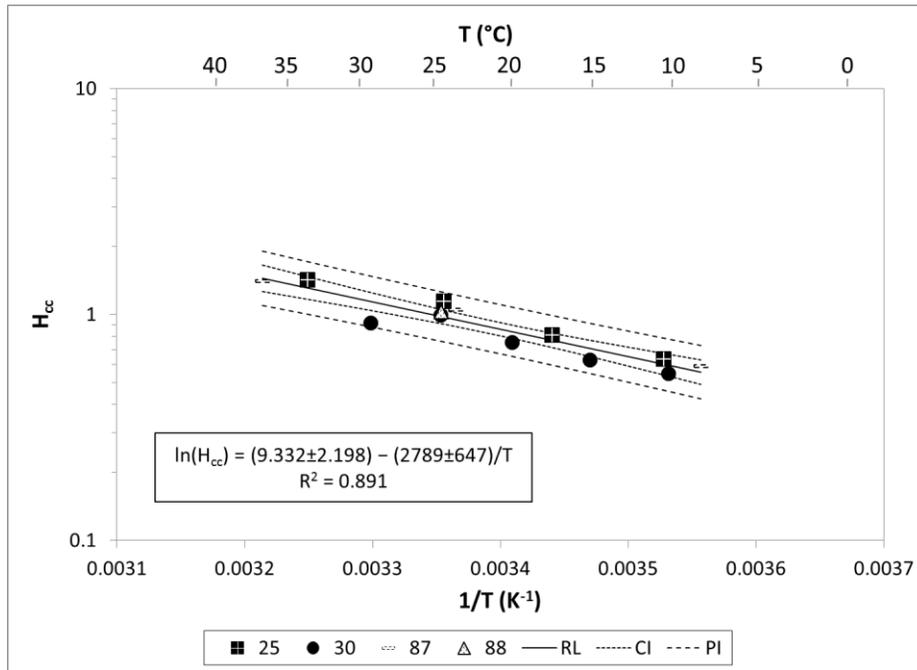
### **Vinyl chloride**

Of the eight currently regulated cVOCs, HLC data for VC were found in only five literature sources, making it the least frequently studied compound among the currently regulated cVOCs. Moreover, the HLC for VC reported by Pearson & McConnell (1975) (study 6) was found to lie outside the range of confidence for the data set (Warneck 2007) and thus was not included in the development of the van't Hoff relationship. There was good agreement found in the remaining four literature data sets ( $r^2=0.891$ , Figure 3.22).

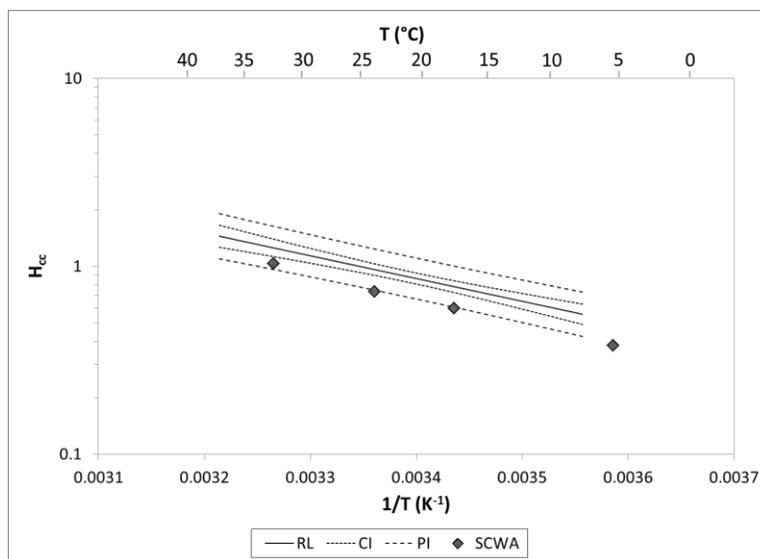
Experimental values obtained in this study for VC helped to expand the knowledge base for this compound. While all of the data collected in this study fell below the regression line established by the literature data, it closely followed the lower bound of the 95% PI (Figure 3.23). At 10° C, the van't Hoff relationship describing the experimental data yielded an  $H_{cc}$  estimate of 0.446 (Table 3.15), within upper and lower bounds of the 95% PI for the literature survey data (0.778 and 0.457, respectively).

Of the models consulted, there was close agreement in  $H_{cc}$  values estimated from the van't Hoff relationship developed from the literature survey in this study, ASAP regression of data points, and the HENRYWIN temperature variation (Figure 3.24). The temperature dependences of UNIFAC and SPARC exhibited flatter slopes. UNIFAC tended to under-predict  $H_{cc}$  for VC above 25° C and over-predict  $H_{cc}$  below 25° C. SPARC over-predicted  $H_{cc}$

for VC over the entire temperature range 0-40° C. At 10° C, the HLC predicted by SPARC exceeded that predicted by the literature survey by a factor of 2.8 (Table 3.15).



**Figure 3.22**  
**Temperature dependence of  $H_{cc}$  for VC based on results reported in 4 studies**  
**(Note: consult Table 3.6 for legend key)**

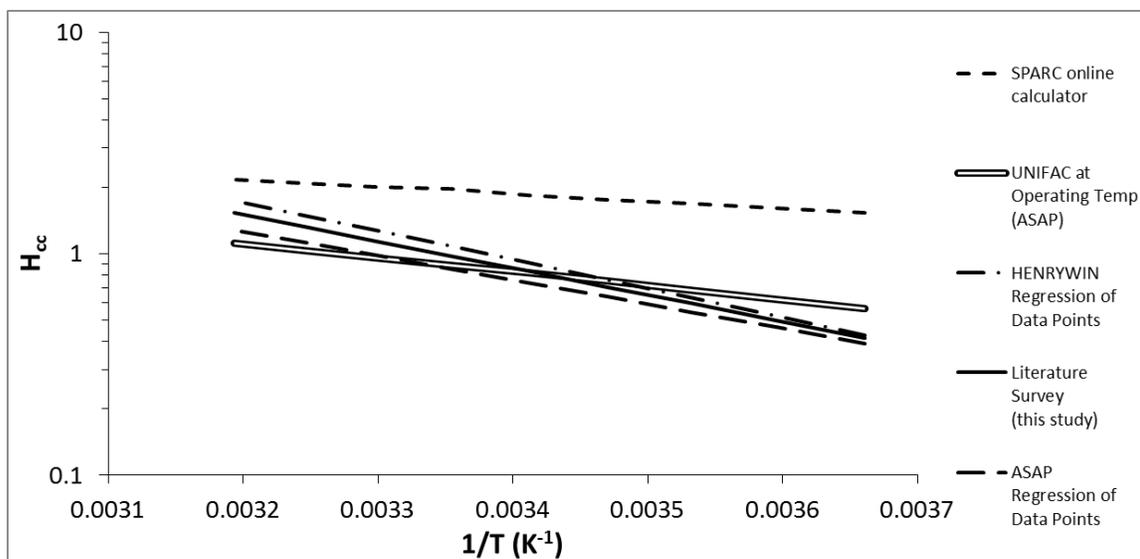


**Figure 3.23**

**Comparison of experimental results for VC obtained in this study and van't Hoff relationship obtained from literature survey (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)**

**Table 3.15**  
**Summary of HLCs for VC at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.596	9.332	2789	0.891	4
Experimental data obtained in this study	0.446	10.052	3075	0.998	1
Literature survey + experimental data (this study)	0.550	9.785	2940	0.834	5
Staudinger & Roberts (2001)	-	-	-	-	-
HENRYWIN regression of data points (based on Gossett 1987)	0.633	-	-	-	-
SPARC on-line calculator	1.679	-	-	-	-
ASAP regression of data points	0.546	-	-	-	-
UNIFAC fit with data points (ASAP)	0.450	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.686	-	-	-	-



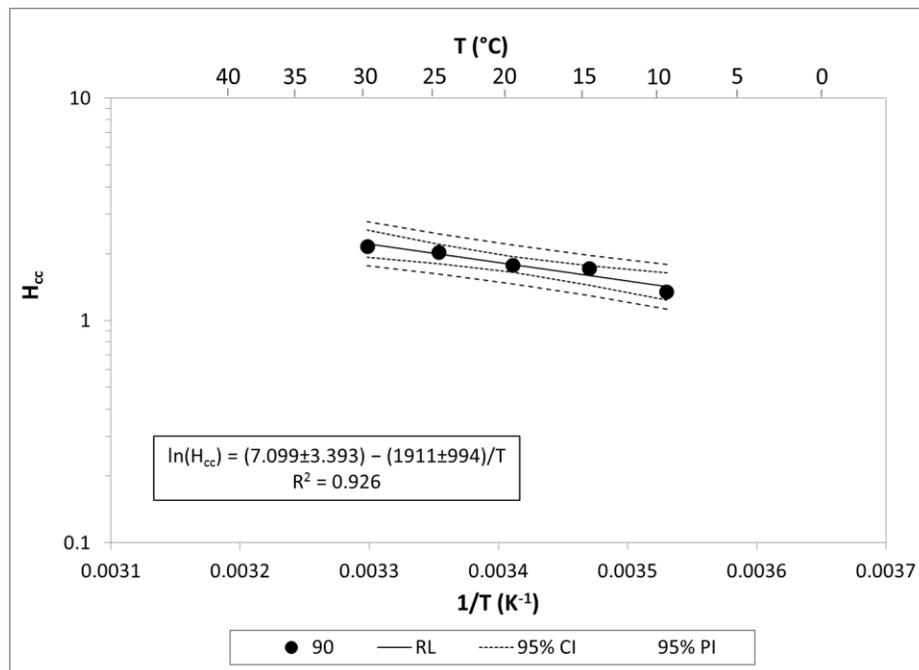
**Figure 3.24**  
**Comparison of HLC estimation methods for VC**  
**[Note – VC was not studied by Staudinger & Roberts (2001)]**

### 1,3-butadiene

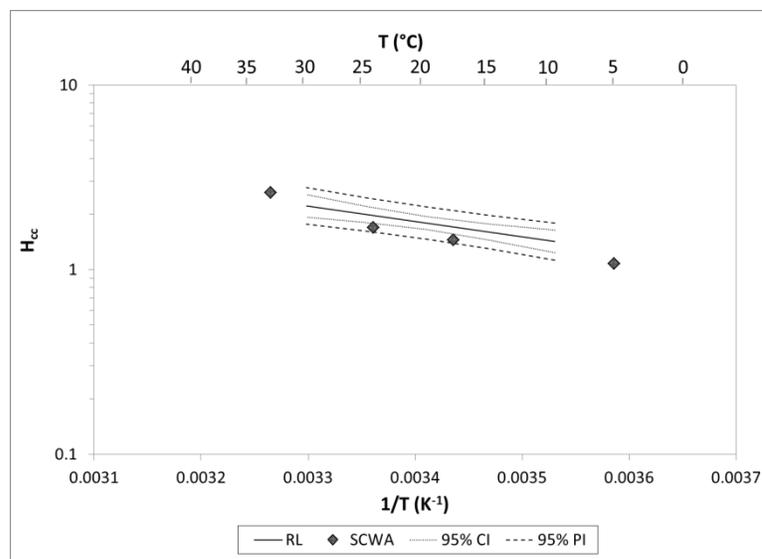
Data for 1,3-butadiene were absent in the literature. While ASAP includes experimental values from the RTI database for 1,3-butadiene, a copy of the original Air Force Report ESL-TR-86-66 by Howe et al. (1987) did not list 1,3-butadiene as one of the compounds studied. Data were obtained through personal communication with one of the authors (Rogers 2014). The resulting van't Hoff relationship had an  $r^2$  value of 0.926 (Figure 3.25) and yielded an  $H_{cc}$  value of 1.42 at 10° C.

Experimental values obtained for 1,3-butadiene in this study corroborated the findings of Rogers (2014) and expanded the temperature range for which experimental data are available (Figure 3.26).  $H_{cc}$  values predicted by the van't Hoff relationship developed from the literature survey and UNIFAC at 10° C were in close agreement (Table 3.16).

Again, SPARC did not follow a log-linear van't Hoff relationship and crossed the regression line derived from the data of Roger (2014) at 15° C (Figure 3.27). HENRYWIN did not have experimental results for 1,3-butadiene in its database and instead used an alkene slope analogy to derive HLC values. The HLC values predicted by HENRYWIN closely matched literature survey estimates at low temperatures (0-5° C) but over-predicted  $H_{cc}$  at higher temperatures (Figure 3.27).



**Figure 3.25**  
**Temperature dependence of  $H_{cc}$  for 1,3-butadiene based on results reported in 1 study**  
**(Note: consult Table 3.6 for legend key)**



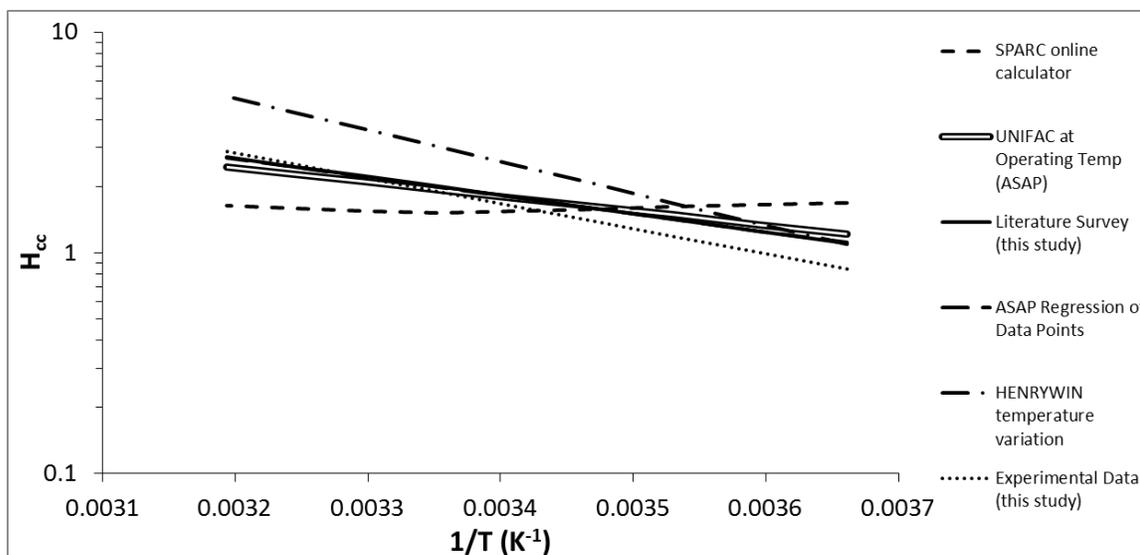
**Figure 3.26**

**Comparison of experimental results for 1,3-butadiene obtained in this study and van't Hoff relationship obtained from literature survey (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)**

**Table 3.16**

**Summary of HLCs for 1,3-butadiene at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	1.42	7.099	1911	0.926	1
Experimental data obtained in this study	1.18	9.496	2641	0.946	1
Literature survey + experimental data (this study)	1.29	8.596	2362	0.887	2
Staudinger & Roberts (2001)	-	-	-	-	-
HENRYWIN regression of data points (based on alkene slope analogy)	1.67	-	-	-	-
SPARC on-line calculator	1.61	-	-	-	-
ASAP regression of data points	1.42	-	-	-	-
UNIFAC fit with data points (ASAP)	1.34	-	-	-	-
UNIFAC at operating temperature (ASAP)	1.48	-	-	-	-



**Figure 3.27**

**Comparison of HLC estimation methods for 1,3-butadiene**

**[Note: results for ASAP Regression of Data Points overlap with those for Literature Survey (this study). 1,3-butadiene was not studied by Staudinger & Roberts (2001)]**

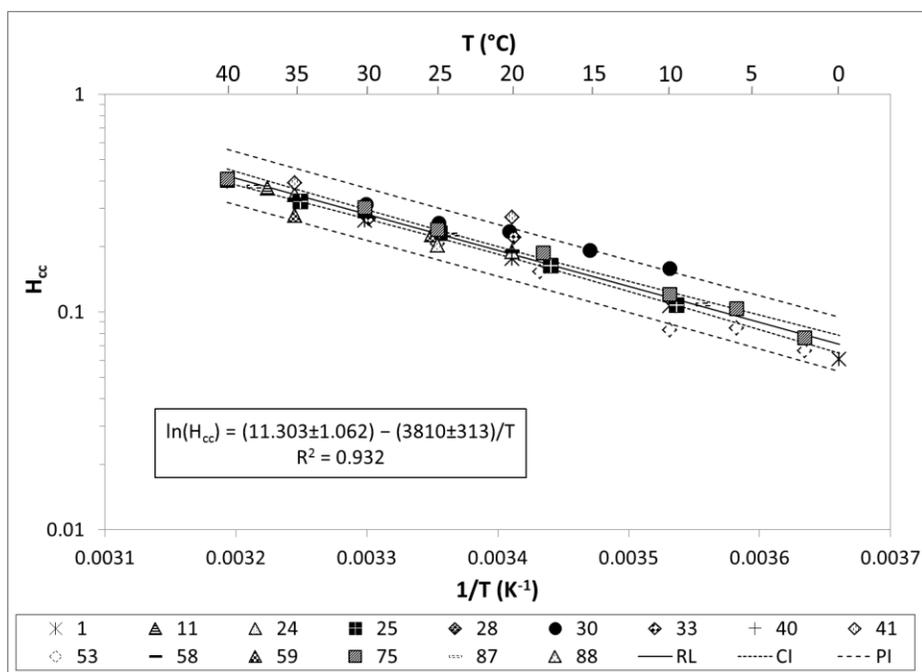
**1,1-dichloroethane**

HLC data for 1,1-DCA were found in 15 literature sources, making it the most frequently studied compound among the CCL3 cVOCs. Studies utilized dynamic (batch air stripping) and static (single equilibration, EPICS) approaches as well as measurement of activity coefficients (GLC, differential static cell) to measure HLCs. To establish the temperature dependence of the HLC for 1,1-DCA, the literature data were summarized in a van't Hoff plot (Figure 3.28). The  $r^2$  value for the van't Hoff relationship derived from the literature data was 0.932, making 1,1-DCA the CCL3 cVOC, for which  $H_{cc}$  estimates have the lowest uncertainty. Based on the regression equation for 1,1-DCA shown in Figure 3.28, the best estimate of  $H_{cc}$  at 10° C is 0.116 with upper and lower bounds of 0.151 and 0.0865,

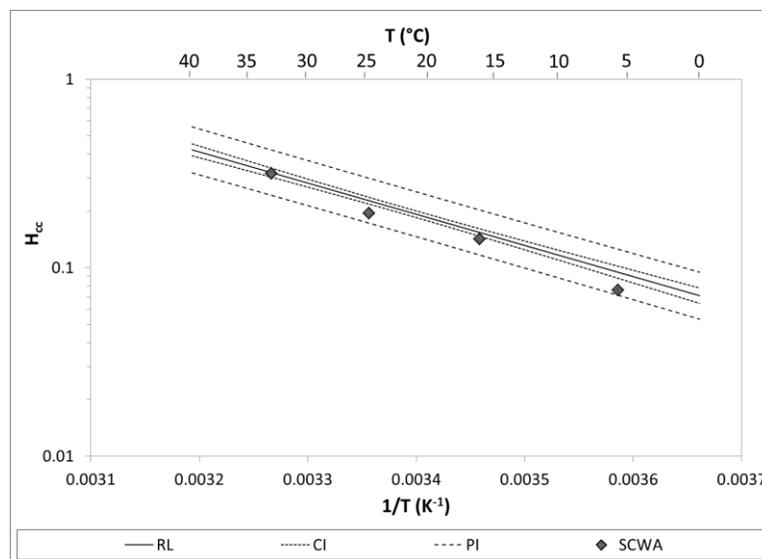
respectively (95% PI). In other words, uncertainty in the  $H_{cc}$  value for 1,1-DCA is within 30% of the mean.

As was the case for the currently regulated cVOCs, experimental results for 1,1-DCA obtained in this study in SCWA groundwater followed the trendline established by the literature survey regression equation (Figure 3.29), with all four data points falling within the 95% PI. At 10° C, the  $H_{cc}$  estimate from the van't Hoff relationship derived from experimental values was 0.0976 (Table 3.17), a difference of 16% from the value estimated from the literature survey.

At 10° C, there was close agreement between  $H_{cc}$  estimates obtained with the van't Hoff relationship developed from the literature survey and that obtained by the HENRYWIN temperature variation (Table 3.17). The  $H_{cc}$  values predicted by SPARC did not follow a log-linear van't Hoff relationship and tended to under-predict HLCs while UNIFAC over-predicted HLC values (Figure 3.30, Table 3.17).



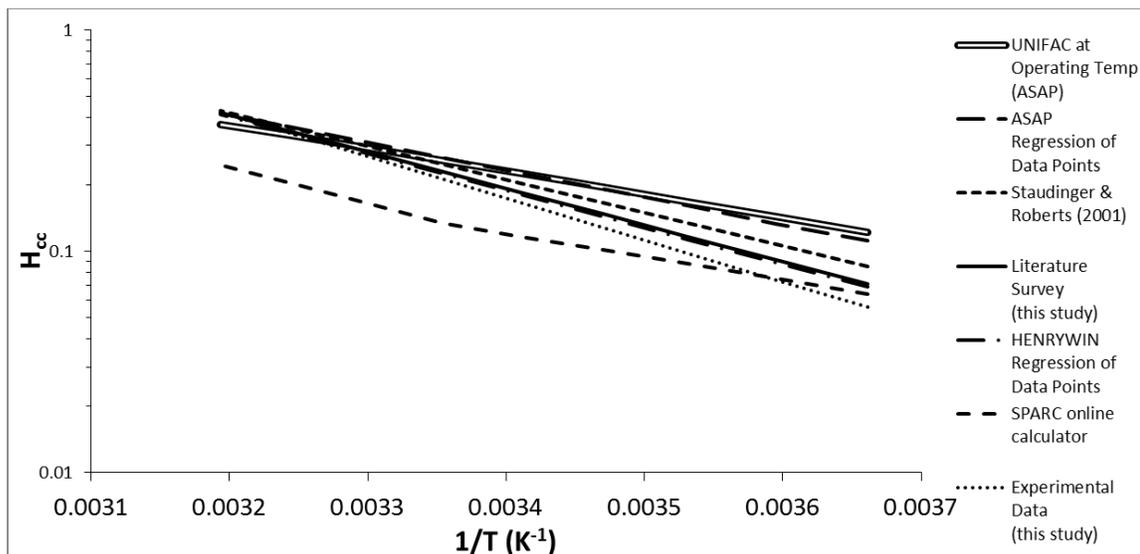
**Figure 3.28**  
**Temperature dependence of  $H_{cc}$  for 1,1-DCA based on results reported in 15 studies**  
 (Note: consult Table 3.6 for legend key)



**Figure 3.29**  
**Comparison of experimental results for 1,1-DCA obtained in this study and van't Hoff relationship obtained from literature survey**  
 (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)

**Table 3.17**  
**Summary of HLCs for 1,1-DCA at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.116	11.303	3810	0.932	15
Experimental data obtained in this study	0.0976	12.987	4336	0.992	1
Literature survey + experimental data (this study)	0.115	11.470	3861	0.933	16
Staudinger & Roberts (2001)	0.133	10.170	3450	-	5
HENRYWIN regression of data points (based on Gossett 1987)	0.113	-	-	-	-
SPARC on-line calculator	0.087	-	-	-	-
ASAP regression of data points	0.16	-	-	-	-
UNIFAC fit with data points (ASAP)	0.158	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.167	-	-	-	-



**Figure 3.30**

**Comparison of HLC estimation methods for 1,1-DCA**

[Note: results for HENRYWIN overlap with those for Literature Survey (this study)]

**1,2,3-trichloropropane**

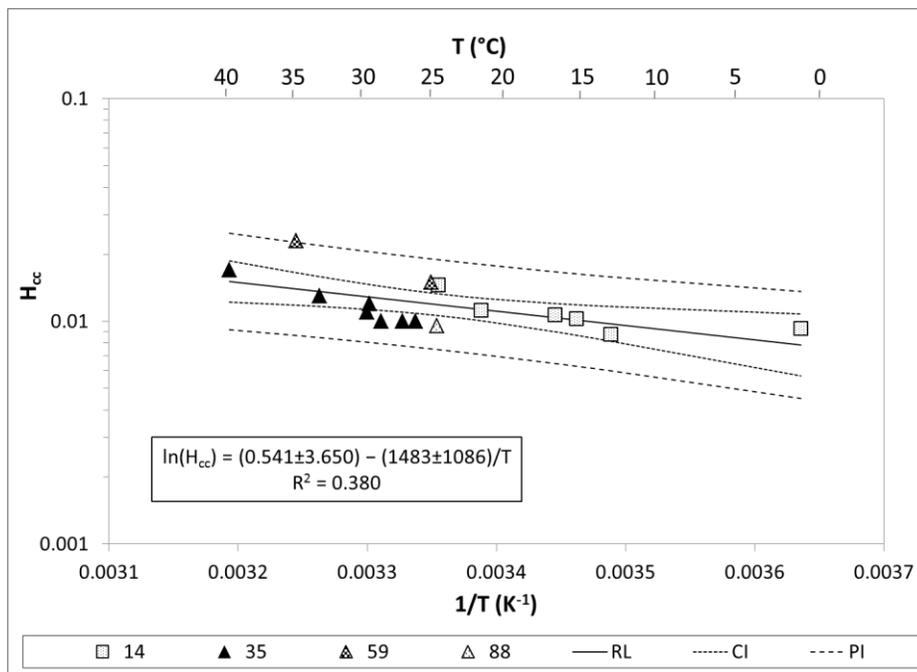
Of the CCL3 contaminants, consistency among published HLC values could only be evaluated for 1,1-DCA and 1,2,3-TCP. While consistency was observed for 1,1-DCA the

same was not the case for 1,2,3-TCP ( $r^2 = 0.380$ , Figure 3.31). Four literature sources were cited, each utilizing a different method to determine HLC values (EPICS, single/multiple equilibrium, and batch air stripping).

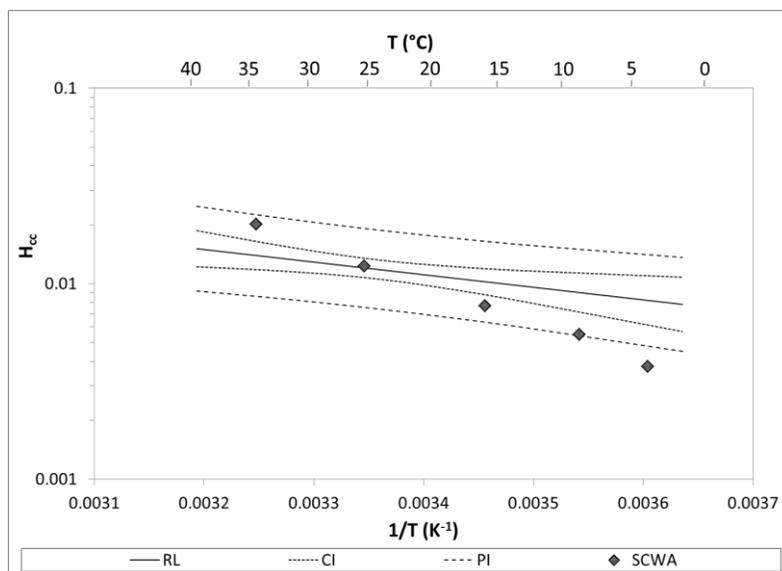
Experimental results obtained in this study for 1,2,3-TCP in SCWA groundwater deviated from the regression line developed from the literature survey (Figure 3.32). The van't Hoff relationship developed from the literature survey yielded an  $H_{cc}$  estimate of 0.00913 at 10° C. In contrast, an  $H_{cc}$  value of 0.00545 was estimated from the experimental data obtained in this study.

Also, there was poor agreement among predictive tools (Table 3.18). At a temperature of 10° C, predictions of  $H_{cc}$  values ranged from 0.00555 for SPARC to 0.0142 for UNIFAC (Table 3.18). An interesting observation is that the temperature-dependent HLC values predicted by HENRYWIN for 1,2,3-TCP are based on the adjustable van't Hoff parameters,  $A$  and  $B$  in Equation 3.8, published by Leighton & Calo (1981). The difference between the smaller slope of the regression equation developed from the literature data, which was heavily influenced by Leighton and Calo (1981, study 14), and the larger slope of the HENRYWIN line can be explained by the fact that Leighton and Calo (1981) appear to have omitted the data point obtained at the lowest tested temperature in their determination of  $A$  and  $B$  while it was included in the data set from which the literature survey regression line was developed (Figure 3.33). A second van't Hoff relationship was developed for 1,2,3-TCP that omitted the Leighton & Calo (1981) data set (Figure 3.34) and yielded an  $r^2$  value of 0.469. The experimental data obtained in this study effectively extend the trend established by the modified literature regression line as illustrated in Figure 3.35. The modified

regression line yields a predicted  $H_{cc}$  value of 0.00509 at 10° C (Figure 3.36, Table 3.18) while the relationship established by the experimental data obtained in this study led to an  $H_{cc}$  estimate of 0.00545 at 10° C. While both regressions indicate that 1,2,3-TCP is poorly strippable, experimental results obtained in this study imply that it may be more difficult to remove 1,2,3-TCP by PTA at lower temperatures than previously predicted. The temperature dependence of the HLC for 1,2,3-TCP that was developed from the experimental data obtained in this study is in close agreement with that of Staudinger & Roberts (2001) as well as with predictions from SPARC (Figure 3.36).



**Figure 3.31**  
**Temperature dependence of  $H_{cc}$  for 1,2,3-TCP based on results reported in 4 studies**  
 (Note: consult Table 3.6 for legend key)

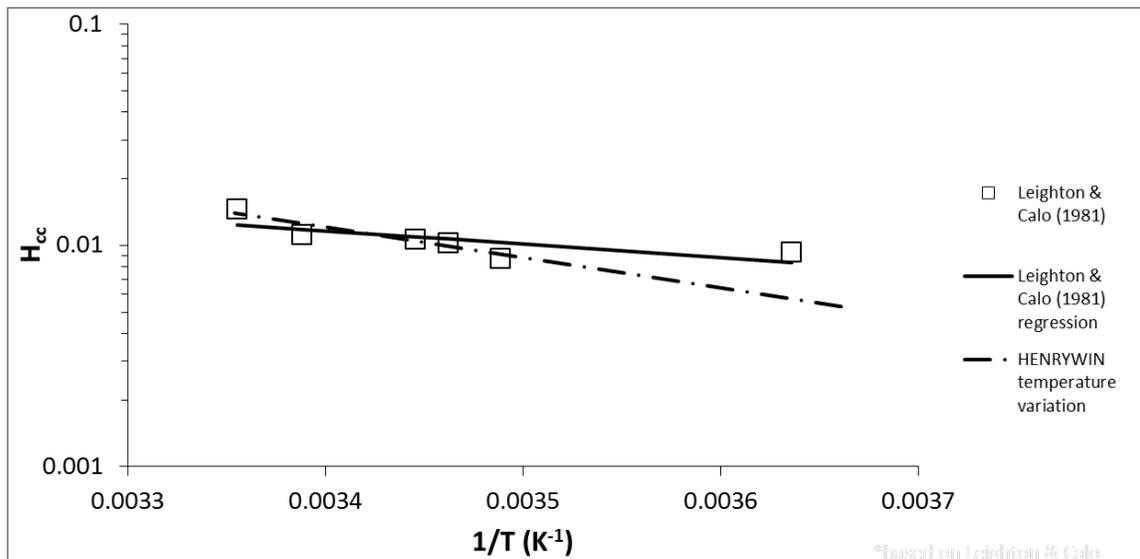


**Figure 3.32**

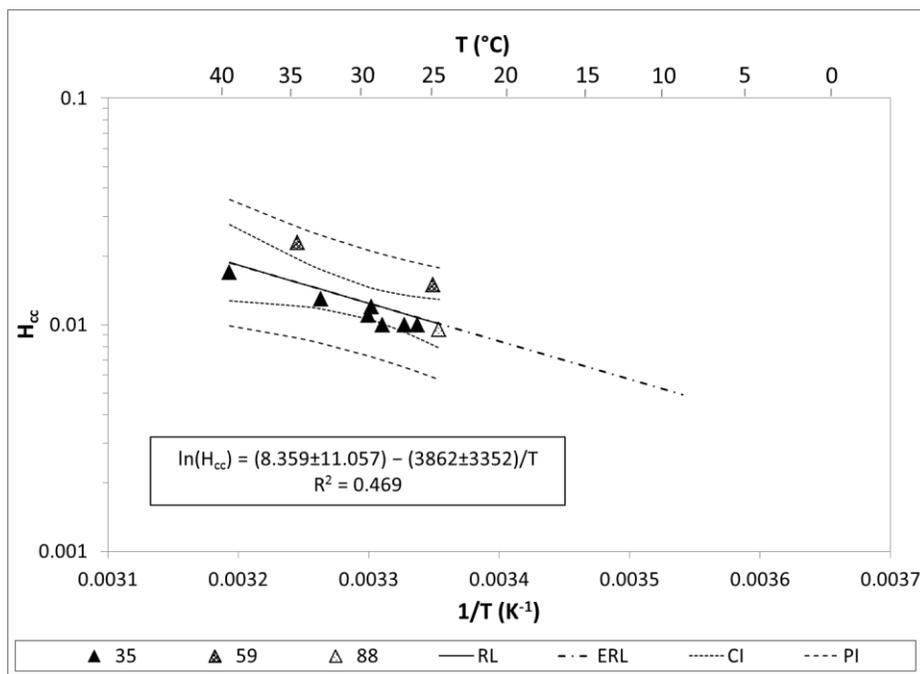
**Comparison of experimental results for 1,2,3-TCP obtained in this study and van't Hoff relationship obtained from literature survey (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)**

**Table 3.18**  
**Summary of HLCs for 1,2,3-TCP at 10°C and van't Hoff coefficients**

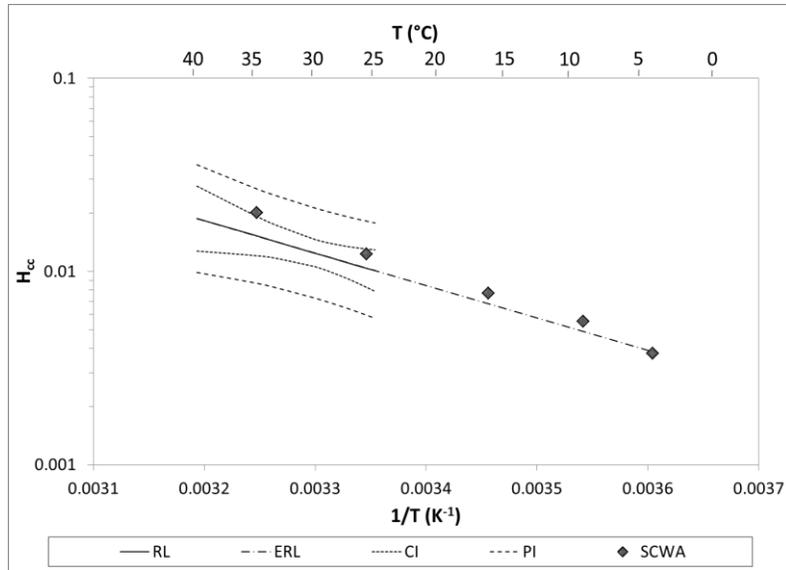
Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.00913	0.541	1483	0.380	4
Literature survey (omitting Leighton & Calo 1981)	0.00509	8.359	3862	0.469	3
Experimental data obtained in this study	0.00545	10.875	4555	0.997	1
Literature survey (omitting Leighton & Calo 1981) + experimental data (this study)	0.00534	8.329	3840	0.837	4
Staudinger & Roberts (2001)	0.00615	7.077	3445	-	2
HENRYWIN regression of data points (based on Leighton & Calo 1981)	0.0082	-	-	-	-
SPARC on-line calculator	0.00555	-	-	-	-
ASAP regression of data points	-	-	-	-	-
UNIFAC fit with data points (ASAP)*	0.0075	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.0142	-	-	-	-



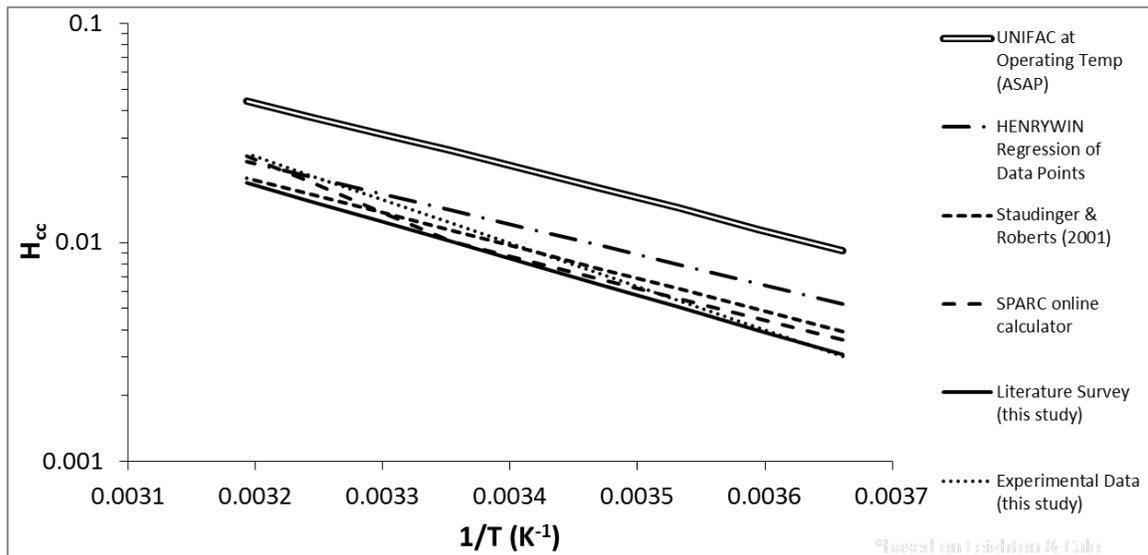
**Figure 3.33**  
**Comparison of van't Hoff relationships developed from Leighton & Calo (1981) data. Solid line based on entire data set, dashed line omits data point at  $1.9^\circ C$  and reflects relationship used by HENRYWIN.**



**Figure 3.34**  
**Temperature dependence of  $H_{cc}$  for 1,2,3-TCP [omitting Leighton & Calo (1981)]**



**Figure 3.35**  
**Comparison of experimental results for 1,2,3-TCP obtained in this study and van't Hoff relationship obtained from literature survey [omitting Leighton & Calo (1981)]**



**Figure 3.36**  
**Comparison of HLC estimation methods for 1,2,3-TCP**  
 [Note - 1,2,3-TCP was not studied by Howe et al. (1987)/Ashworth et al. (1988); therefore, HLC values could not be obtained with the ASAP Regression of Data Points tool.]

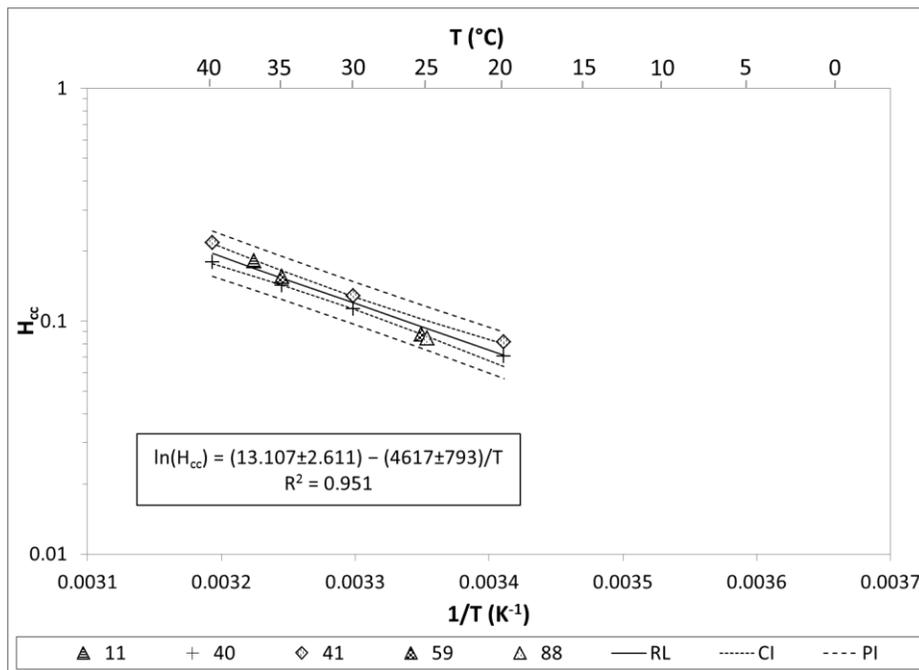
### **1,1,1,2-tetrachloroethane**

Five published studies were used to develop the van't Hoff relationship for 1,1,1,2-TeCA shown in Figure 3.37. HLCs were determined using static (single equilibration, EPICS) approaches as well as measurement of activity coefficients (GLC, differential static cell). Literature data were limited to a temperature range  $>20^{\circ}\text{C}$ , and showed good agreement for the van't Hoff temperature dependence ( $r^2=0.951$ ).

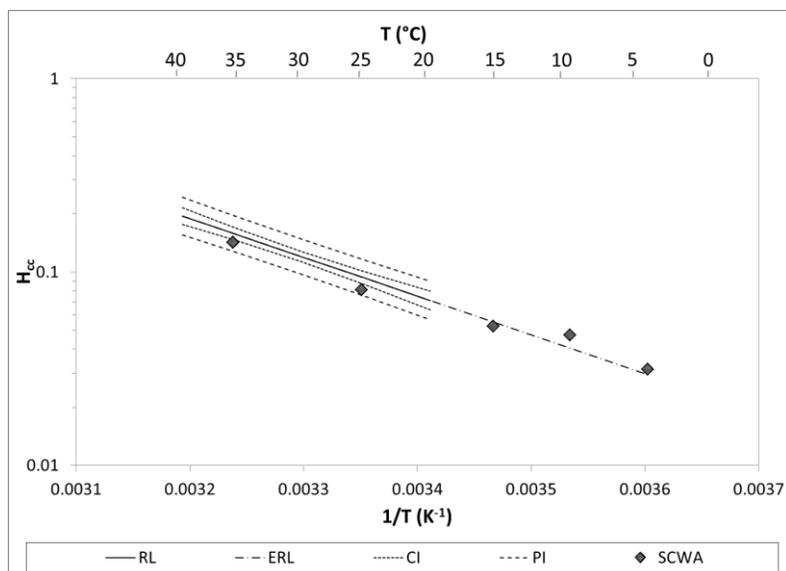
Experimental results for 1,1,1,2-TeCA obtained in this study in SCWA groundwater at 25 and 35°C deviated from the literature survey trendline when run in the multi-solute mixture 1. Results from single solute experiments revealed that 1,1,2,2-TeCA undergoes hydrolysis at elevated temperatures, and TCE is formed as a hydrolysis product, consistent with previous findings (Washington 1995). TCE co-eluted with 1,1,1,2-TeCA during HPLC analysis. Thus results for both 1,1,2,2-TeCA and 1,1,1,2-TeCA could not be obtained in mixture, especially when long equilibration times were used at elevated temperatures. Experiments for 1,1,1,2-TeCA were consequently run in same-day (2-hour equilibration time) single-solute experiments. The resulting experimental data followed the trendline established by the literature survey above  $20^{\circ}\text{C}$ , and data at lower temperatures followed the extrapolated regression line (Figure 3.38).

With the exception of SPARC, predictive tools yielded  $H_{cc}$  values at  $10^{\circ}\text{C}$  that were in fairly close agreement (Table 3.19), and the same holds true for the temperature dependence (Figure 3.39). The literature survey regression equation and predictive model UNIFAC yielded  $H_{cc}$  values  $<0.05$  (0.0408, 0.0466, respectively) while the HENRYWIN temperature variation and the predictive tool SPARC estimated  $H_{cc}$  values  $>0.05$  (0.0548,

0.0878, respectively). Based on the van't Hoff relationship developed from experimental data, an  $H_{cc}$  value of 0.0429 was estimated at 10° C, a value that is in close agreement with those obtained from the literature survey and UNIFAC model. Results for 1,1,1,2-TeCA indicate that PTA may not be an effective technology for 1,1,1,2-TeCA removal, especially at lower water temperatures.



**Figure 3.37**  
**Temperature dependence of  $H_{cc}$  for 1,1,1,2-TeCA based on results reported in 5 studies**  
**(Note: consult Table 3.6 for legend key)**

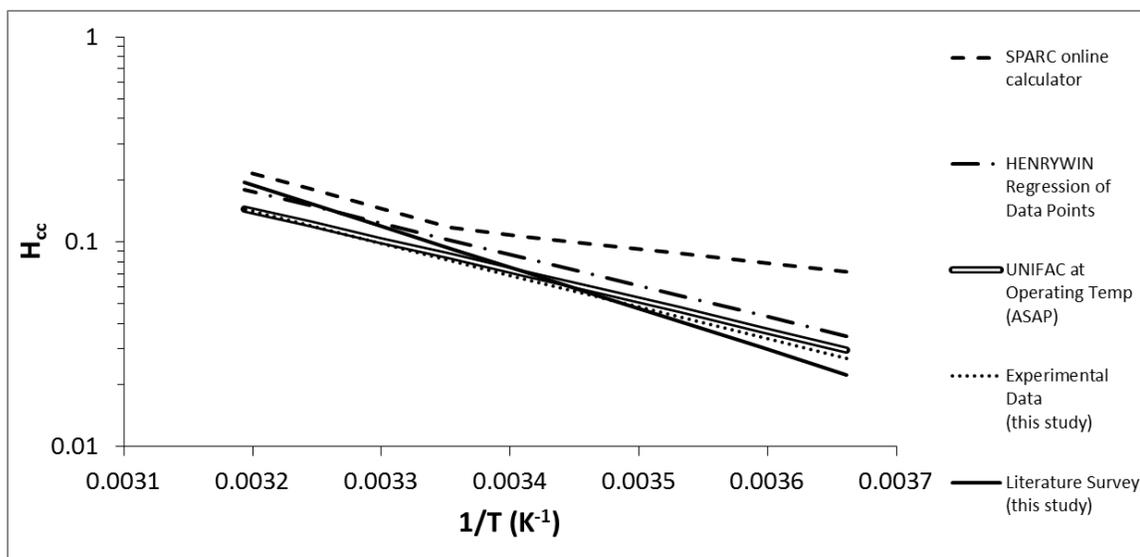


**Figure 3.38**

**Comparison of experimental results for 1,1,1,2-TeCA obtained in this study and van't Hoff relationship obtained from literature survey (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)**

**Table 3.19**  
**Summary of HLCs for 1,1,1,2-TeCA at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.0408	13.107	4617	0.951	5
Experimental data obtained in this study	0.0429	9.477	3575	0.965	1
Literature survey + experimental data (this study)	0.0424	12.367	4397	0.972	6
Staudinger & Roberts (2001)	-	-	-	-	-
HENRYWIN regression of data points (based on haloalkane slope analogy)	0.0548	-	-	-	-
SPARC on-line calculator	0.0878	-	-	-	-
ASAP regression of data points	-	-	-	-	-
UNIFAC fit with data points (ASAP)	-	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.0466	-	-	-	-



**Figure 3.39**

**Comparison of HLC estimation methods for 1,1,1,2-TeCA**

[Note - 1,1,1,2-TeCA HLC was not studied by Staudinger & Roberts (2001) or Howe et al. (1987)/Ashworth et al. (1988); therefore, HLC values could not be obtained with the ASAP regression of data points and UNIFAC fit with data points tools.]

**1,1,2,2-tetrachloroethane**

Among the two additional cVOCs, 1,1,2,2-TeCA was more frequently studied. HLC data were found in ten literature sources that utilized dynamic (batch air stripping), static (single equilibration, EPICS), and measured activity coefficients (GLC, differential static cell) approaches for the determination of the HLC. As seen in Figure 3.40, there was considerable scatter in the data ( $r^2=0.641$ ). Based on the regression equation for 1,1,2,2-TeCA shown in Figure 3.40, the best estimate of  $H_{cc}$  at 10°C is 0.00840 with upper and lower bounds of 0.0167 and 0.00427 (95% PI). In other words, uncertainty in the  $H_{cc}$  value for 1,1,2,2-TeCA was within 99% of the mean.

Experimental results for 1,1,2,2-TeCA at 25 and 35° C also deviated from the literature survey trendline when tested together in multi-solute mixture 1 (Table 3.4). 1,1,2,2-TeCA undergoes hydrolysis at elevated temperatures, and TCE is formed as a product of hydrolysis (Washington 1995). 1,1,2,2-TeCA was consequently run in same-day (2-hour equilibration time) single-solute experiments. Utilizing a 2-hour equilibration limited the molar conversion of 1,1,2,2-TeCA by hydrolysis to 12% at 35° C. In order to account for 1,1,2,2-TeCA losses, equilibrium aqueous-phase TCE concentrations were measured by HPLC. Assuming a 1:1 mole conversion, the following modifications were made to the variable headspace method

$$N_{TeCA,corr,o} = N_{TeCA,o} - (N_{TCE(aq)} + N_{TCE(g)}) \quad \text{Equation 3.17}$$

where  $N_{TeCA,corr,o}$  is the corrected initial 1,1,2,2-TeCA mass (mol),  $N_{TeCA,o}$  is the actual initial 1,1,2,2-TeCA mass (mol),  $N_{TCE(aq)}$  is the equilibrium aqueous TCE mass (mol), and  $N_{TCE(g)}$  is the equilibrium gas-phase mass of TCE (mol). Following the derivation of the variable headspace method (*Materials and Methods, Theory*), Equation 3.17 can be rewritten as

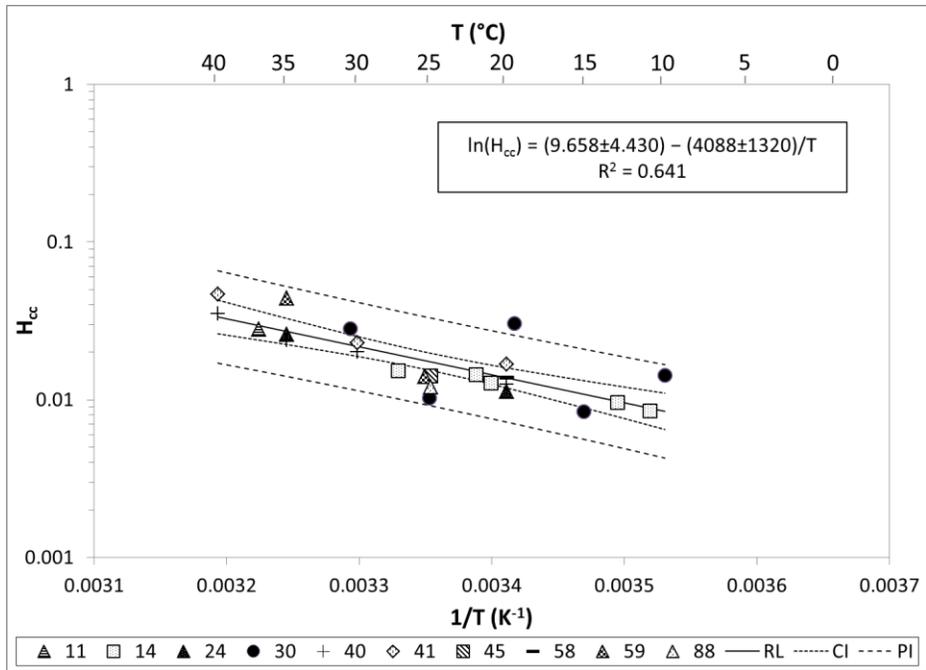
$$C_{TeCA,corr,o} = C_{TeCA,o} - (C_{TCE(aq)} + C_{TCE(g)} \cdot \frac{V_g}{V_l}) \quad \text{Equation 3.18}$$

where  $C_{TeCA,corr,o}$  equals the corrected initial concentration of 1,1,2,2-TeCA (mol/L),  $C_{TeCA,o}$  represents the initially added concentration of 1,1,2,2-TeCA (mol/L),  $C_{TCE(aq)}$  is the equilibrium aqueous-phase concentration of 1,1,2,2-TeCA (mol/L), and  $C_{TCE(g)}$  equals the equilibrium gas-phase concentration of 1,1,2,2-TeCA (mol/L). Substituting Equation 3.2 for Henry's Law yields

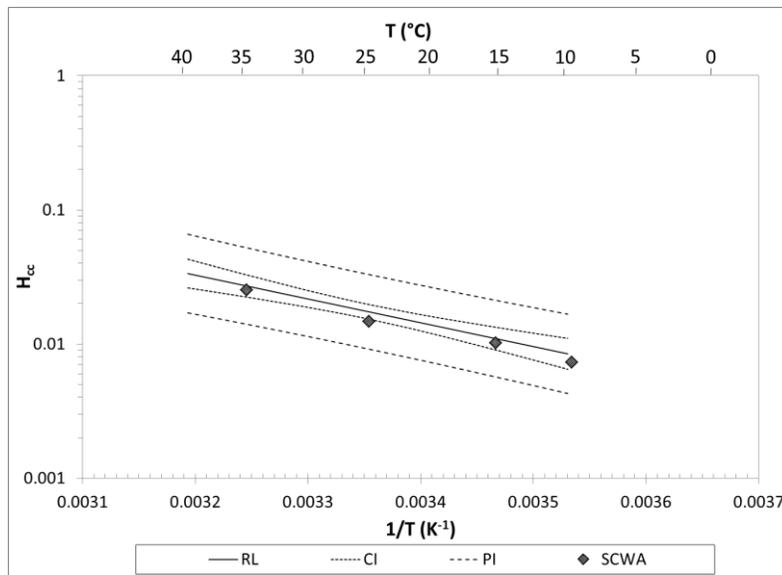
$$C_{TeCA,corr,o} = C_{TeCA,o} - (C_{TCE(aq)} + H_{cc,TCE} \cdot C_{TCE(aq)} \cdot \frac{V_g}{V_l}) \quad \text{Equation 3.19}$$

where  $H_{cc,TCE}$  is the  $H_{cc}$  of TCE at 35° C, taken from the van't Hoff relationship developed from the literature survey in this study. After calculating  $C_{TeCA,corr,o}$ , the equilibrium aqueous-phase concentration of 1,1,2,2-TeCA was measured by HPLC, and the modified variable headspace method was used to calculate the HLC of 1,1,2,2-TeCA, resulting in a decrease from 0.0261 to 0.0238 (corrected). With this approach, the experimental results for 1,1,2,2-TeCA followed the trendline established from the literature survey data (Figure 3.41), with all four data points falling well within the 95% PI.

$H_{cc}$  predicted by the van't Hoff relationship developed from the literature survey in this study (0.00840) was in direct agreement with that obtained by HENRYWIN at 10° C (Table 3.20). At 10° C, the HLC value predicted by SPARC was higher by a factor of 1.6 while that predicted by UNIFAC was higher by a factor of 4.3 (Figure 3.42, Table 3.20).



**Figure 3.40**  
**Temperature dependence of  $H_{cc}$  for 1,1,2,2-TeCA based on results reported in 10 studies (Note: consult Table 3.6 for legend key)**



**Figure 3.41**  
**Comparison of experimental results for 1,1,2,2-TeCA obtained in this study and van't Hoff relationship obtained from literature survey**

(RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)

Table 3.20

Summary of HLCs for 1,1,2,2-TeCA at 10°C and van't Hoff coefficients

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.00840	9.658	4088	0.641	10
Experimental data obtained in this study	0.00745	9.796	4161	0.950	1
Literature survey + experimental data (this study)	0.00766	10.865	4456	0.742	11
Staudinger & Roberts (2001)	0.00992	5.594	2890	-	2
HENRYWIN regression of data points (based on Leighton & Calo 1981)	0.00840	-	-	-	-
SPARC on-line calculator	0.0133	-	-	-	-
ASAP regression of data points	0.0117	-	-	-	-
UNIFAC fit with data points (ASAP)	0.014	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.0355	-	-	-	-

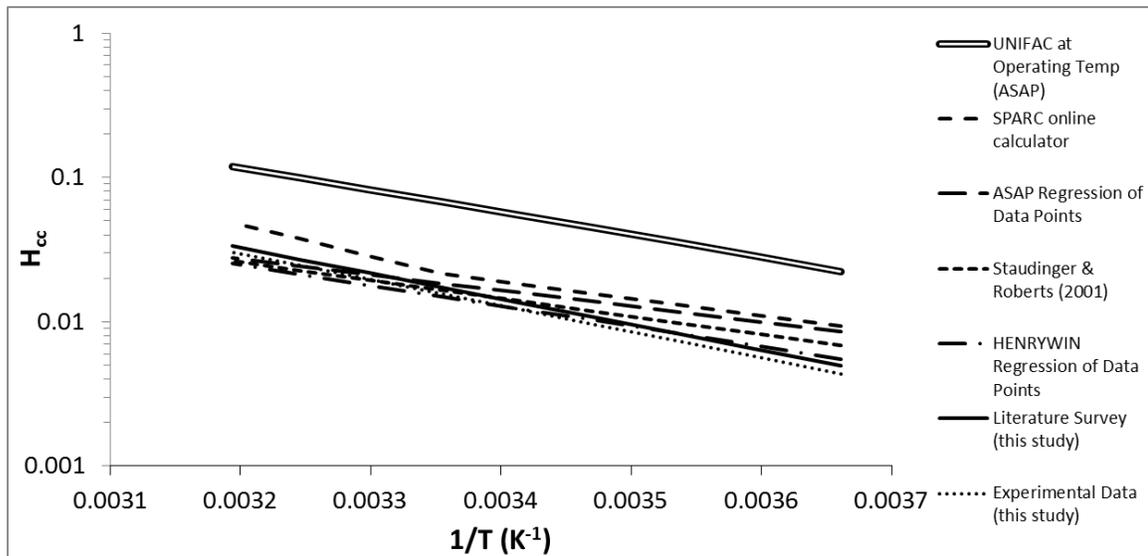


Figure 3.42  
Comparison of HLC estimation methods for 1,1,2,2-TeCA

### Background Water Matrix

HLCs evaluated in the four background water matrices at 10° C were compared using pairwise two-tailed t-tests (Equation 3.22), assuming normal distributions with unequal

sample sizes (some experiments were conducted in duplicate) and unequal variances. The null hypothesis, i.e. the difference between slopes of the phase ratio plots is zero (HLCs are the same), was rejected at  $t > t_{crit}$  at 95% with varying degrees of freedom ( $DF$ , Equation 3.20).

$$DF = \frac{\left(\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}\right)^2}{\frac{\left(\frac{S_1^2}{n_1}\right)^2}{n_1 - 1} + \frac{\left(\frac{S_2^2}{n_2}\right)^2}{n_2 - 1}} \quad \text{Equation 3.20}$$

$$S_{\bar{X}_1 - \bar{X}_2} = \sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}} \quad \text{Equation 3.21}$$

$$t = \frac{\bar{X}_1 - \bar{X}_2}{S_{\bar{X}_1 - \bar{X}_2}} \quad \text{Equation 3.22}$$

where  $S^2$  equals the unbiased estimator of the variance of the slope of the line,  $n$  represents the number of samples in a group, and  $\bar{X}$  equals the slope of the line (equivalent to HLC when the y-intercept = 1). The  $t_{crit}$  values ranged from 2.36-3.18, and  $t$  values were smaller than  $t_{crit}$  for all studied cVOC compounds (Table 3.21). The null hypothesis cannot be rejected, suggesting that HLC values were consistent among different background water matrices.

To confirm the findings of the t-test,  $H_{cc}$  values for mixtures 1 and 2 were compared across background water matrices (Table 3.22). There were no trends found among the tested compounds, supporting the conclusion that HLCs were consistent across water matrices.

**Table 3.21**  
**t-test values for mixtures 1 and 2 in different background water matrices**

Mix	Compound	UP/ILL	UP/SCWA	UP/SCWA+NaCl	ILL/SCWA	ILL/SCWA+NaCl	SCWA/SCWA+NaCl
1	DCM	0.10	0.01	0.08	0.10	0.01	0.07
	1,2-DCP	0.17	0.02	0.03	0.16	0.14	0.01
	1,1,2,2-TeCA	0.06	0.17	0.06	0.12	0.00	0.13
	1,1,1,2-TeCA	0.35	0.30	0.39	0.75	0.15	0.72
	PCE	0.61	0.30	0.43	0.09	0.02	0.06
2	1,2-DCA	0.16	0.02	0.24	0.14	0.31	0.16
	EDB	0.08	0.06	0.12	0.11	0.16	0.03
	1,2,3-TCP	0.02	0.20	0.40	0.22	0.44	0.18
	TCE	0.13	0.19	0.13	0.04	0.21	0.25

**Table 3.22**  
**Experimental HLC results for cVOC mixtures 1 and 2 in background water matrices**

Mix	compound	UPW			ILL			SCWA			SCWA+NaCl		
		temp (° C)	H <sub>cc</sub>	95% CI	temp (° C)	H <sub>cc</sub>	95% CI	temp (° C)	H <sub>cc</sub>	95% CI	temp (° C)	H <sub>cc</sub>	95% CI
1	DCM		0.0511	± 0.00408		0.0525	± 0.00270		0.0512	± 0.00301		0.0524	± 0.00234
	1,2-DCP		0.0527	± 0.00223		0.0505	± 0.00370		0.0525	± 0.00471		0.0522	± 0.00378
	1,1,2,2-TeCA	9.7	0.00686	± 0.00863	9.8	0.00700	± 0.00114	9.8	0.00726	± 0.00606	9.7	0.00699	± 0.00101
	1,1,1,2-TeCA		0.0430	± 0.00284		0.0393	± 0.00377		0.0472	± 0.00314		0.0379	± 0.000937
	PCE		0.255	± 0.0276		0.292	± 0.0214		0.284	± 0.0296		0.291	± 0.0281
2	1,2-DCA		0.0249	± 0.00129		0.0260	± 0.000975		0.0248	± 0.00298		0.0236	± 0.00170
	EDB		0.0141	± 0.00116		0.0144	± 0.00112		0.0139	± 0.00185		0.0137	± 0.00112
	1,2,3-TCP	9.5	0.00517	± 0.000534	9.7	0.00514	± 0.000512	9.2	0.00552	± 0.000602	9.6	0.00584	± 0.000722
	TCE		0.169	± 0.00937		0.163	± 0.0105		0.161	± 0.0179		0.174	± 0.00449

## **ACKNOWLEDGEMENTS**

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## CHAPTER 4 – HENRY’S LAW CONSTANTS FOR ADDITIONAL CVOCS AND FREUNDLICH ADSORPTION CONSTANTS

### HENRY’S LAW CONSTANTS

Among the 90 articles that were reviewed for HLC data, only 14 contained data for the other seven compounds that were proposed for consideration in the new cVOC group regulation (summarized in Table 4.1). All HLCs were determined experimentally in non-saline, dilute, aqueous solutions between the temperatures 0-40° C. Individual data points from the literature were plotted in a van’t Hoff plot format, and the combined literature data for each compound were analyzed by linear regression to determine the temperature dependence of  $H_{cc}$  using Equation 3.7.

**Table 4.1**  
**Literature review for Henry’s Law constants**

Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	
aniline																															
benzyl chloride																															
nitrobenzene																											X		X		
methyl oxirane																															
urethane																															
EDB																															X
DBCP																															

*1 – Rex (1906), 2 – Saylor et al. (1938), 3 – Wasik & Tsang (1970), 4 – Hartkopf & Karger (1973), 5 – Brown & Wasik (1974), 6 – Pearson & McConnell (1975), 7 – Vitenberg et al. (1975), 8 – Green & Frank (1979), 9 – Mackay et al. (1979), 10 – Sato & Nakajima (1979a), 11 – Sato & Nakajima (1979b), 12 – Tsibul'skii et al. (1979), 13 – Balls (1980), 14 – Leighton & Calo (1981), 15 – Sanemasa et al. (1981), 16 – Munz & Roberts (1982), 17 – Sanemasa et al. (1982), 18 – Gossett (1983), 19 – Garbarini & Lion (1985), 20 – Gossett et al. (1985), 21 – Munz (1985), 22 – Schoene & Steinhanses (1985), 23 – Munz & Roberts (1986), 24 – Barr & Newsham (1987), 25 – Gossett (1987), 26 – Hellmann (1987), 27 – Munz & Roberts (1987), 28 – Warner et al. (1987), 29 – Yurteri et al. (1987), 30 – Howe et al. (1987)/Ashworth et al. (1988)*

**Table 4.1 Continued**

Compound	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
aniline							X															X							
benzyl chloride														X														X	
nitrobenzene																													
methyl oxirane																													
urethane																													
EDB																				X								X	X
DBCP																													X

31 – Keeley et al. (1988), 32 – Guitart et al. (1989), 33 – Lamarche & Droste (1989), 34 – Bissonette et al. (1990), 35 – Tancrede & Yanagisawa (1990), 36 – Anderson (1992), 37 – Cooling et al. (1992), 38 – Jayasinghe et al. (1992), 39 – Kolb et al. (1992), 40 – Tse et al. (1992), 41 – Wright et al. (1992), 42 – Ettore et al. (1993), 43 – Hansen et al. (1993), 44 – Hoff et al. (1993), 45 – Li & Carr (1993), 46 – Li et al. (1993), 47 – Perlinger et al. (1993), 48 – Robbins et al. (1993), 49 – Zhang & Pawliszyn (1993), 50 – Khalfaoui & Newsham (1994a), 51 – Khalfaoui & Newsham (1994b), 52 – Nielsen et al. (1994), 53 – Dewulf et al. (1995), 54 – Heal et al. (1995), 55 – Alaei et al. (1996), 56 – Ramachandran et al. (1996), 57 – Turner et al. (1996), 58 – Hovorka & Dohnal (1997), 59 – Kondoh & Nakajima (1997), 60 – Park et al. (1997),

**Table 4.1 Continued**

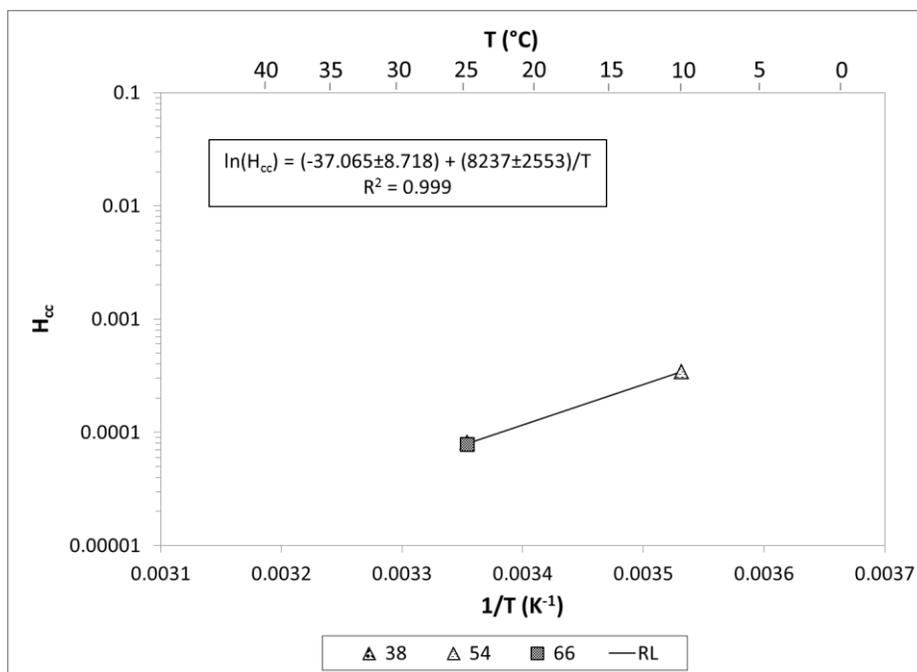
Compound	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	Total # papers cited
aniline						X																									3
benzyl chloride																												X			3
nitrobenzene						X	X																					X	X		6
methyl oxirane																															0
urethane																															0
EDB								X																				X			6
DBCP																												X			2

61 – Peng & Wan (1997), 62 – Allen et al. (1998), 63 – Chiang et al. (1998), 64 – de Wolf & Lieder (1998), 65 – Peng & Wan (1998), 66 – Altschuh et al. (1999), 67 – Dewulf et al. (1999), 68 – Dohmal & Hovorka (1999), 69 – Ryu & Park (1999), 70 – David et al. (2000), 71 – Miller & Stuart (2000), 72 – Vane & Giroux (2000), 73 – Ayuttaya et al. (2001), 74 – Bierwagen & Keller (2001), 75 – Gorgenyi et al. (2002), 76 – Bakierowska & Trzeszczynski (2003), 77 – Bobadilla et al. (2003), 78 – Cheng et al. (2003), 79 – Karl et al. (2003), 80 – Shimotori & Arnold (2003), 81 – Lodge & Danso (2007), 82 – Helburn et al. (2008), 83 – Li et al. (2008), 84 – Sieg et al. (2009), 85 – Lau et al. (2010), 86 – Starokozhev et al. (2011), 87 – Chen et al. (2012), 88 – Hiatt (2013), 89 – Zhang et al. (2013), 90 – Rogers (2014)

## Aniline

With three data points at two temperatures, it was not possible to evaluate consistency of HLC values based on the literature survey for aniline. However, based on the limited data, aniline was found to be the only one of the compounds under consideration that exhibited a positive slope in the van't Hoff relationship (Figure 4.1). This observation likely indicates that at least a subset of the available data is not reliable.

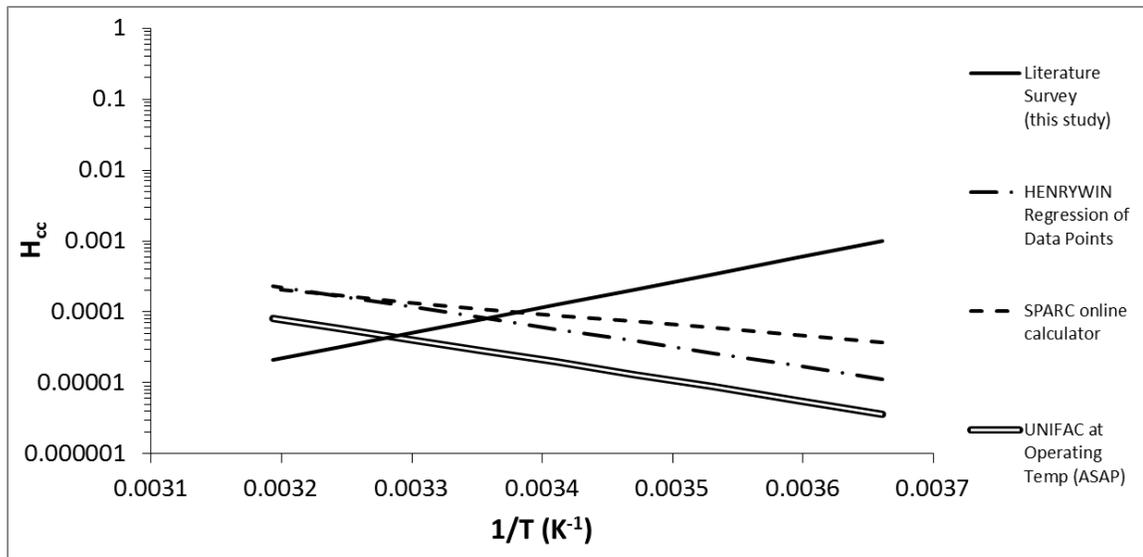
There was little agreement among  $H_{cc}$  predictions from the models (Figure 4.2). The literature survey regression line suggested an  $H_{cc}$  at 10° C of 0.000344 while the temperature dependence of HENRYWIN yielded an  $H_{cc}$  of 0.0000263 (Table 4.2). SPARC and UNIFAC predicted  $H_{cc}$  values of 0.0000594 and 0.00000874, respectively. Regardless, based on the low volatility from water, all models imply that aniline is not amenable to removal by PTA (Figure 4.2).



**Figure 4.1**  
**Temperature dependence of  $H_{cc}$  for aniline based on results reported in 3 studies.**  
**Note: Consult Table 4.1 for legend key.**

**Table 4.2**  
**Summary of HLCs for aniline at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.000344	-37.065	8237	0.999	3
Experimental data obtained in this study	-	-	-	-	-
Staudinger & Roberts (2001)	-	-	-	-	-
HENRYWIN regression of data points (based on VP/AS data)	0.0000263	-	-	-	-
SPARC on-line calculator	0.0000594	-	-	-	-
ASAP regression of data points	-	-	-	-	-
UNIFAC fit with data points (ASAP)	-	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.00000874	-	-	-	-



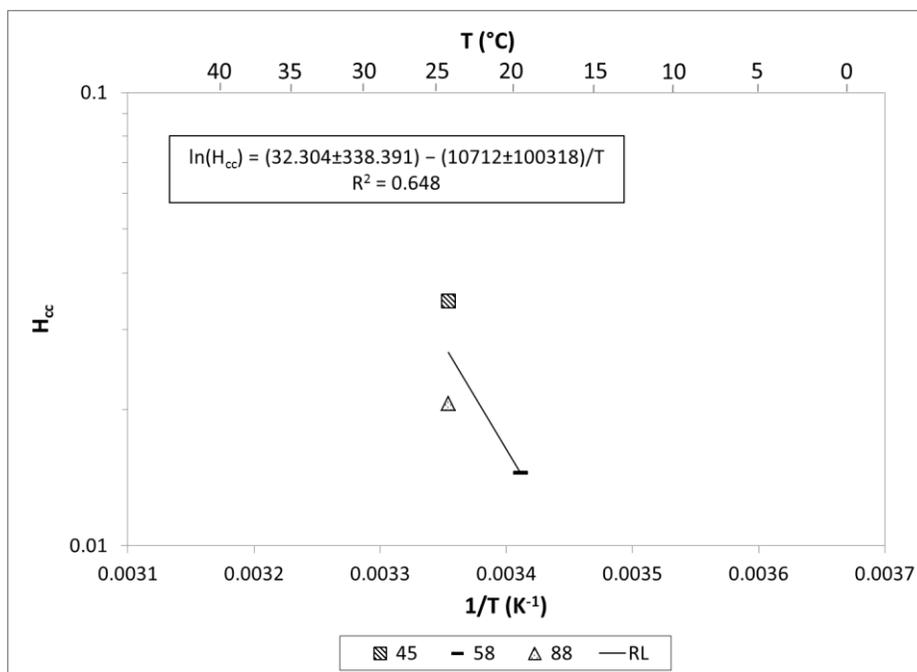
**Figure 4.2**

**Comparison of HLC estimation methods for aniline**

**[Note - Aniline was not studied by Staudinger & Roberts (2001) or Howe et al. (1987)/Ashworth et al. (1988); therefore, HLC values could not be obtained with the ASAP regression of data points or UNIFAC fit with data points tools.]**

**Benzyl chloride**

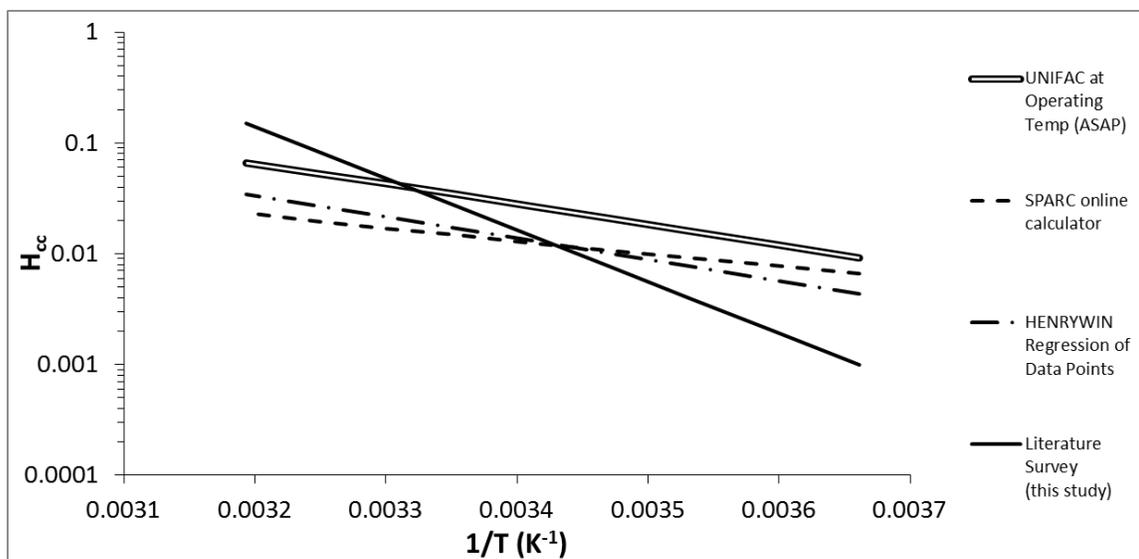
With three data points at two temperatures, it was not possible to evaluate consistency among HLC values based on the literature survey for benzyl chloride (Figure 4.3). The literature survey regression equation produced an  $H_{cc}$  at 10° C of 0.0040 while HENRYWIN yielded an  $H_{cc}$  of 0.00769 (Table 4.3). SPARC and UNIFAC predicted  $H_{cc}$  values of 0.00921 and 0.0161, respectively. Models predictions and experimental data from the literature imply that benzyl chloride is not readily removed by PTA at typical groundwater temperatures (Figure 4.4).



**Figure 4.3**  
**Temperature dependence of  $H_{cc}$  for benzyl chloride based on results reported in 3 studies. Note: Consult Table 4.1 for legend key.**

**Table 4.3**  
**Summary of HLCs for benzyl chloride at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.0040	32.304	10712	0.648	3
Experimental data obtained in this study	-	-	-	-	-
Staudinger & Roberts (2001)	-	-	-	-	-
HENRYWIN regression of data points (based on similar compound slope analogy)	0.00769	-	-	-	-
SPARC on-line calculator	0.00921	-	-	-	-
ASAP regression of data points	-	-	-	-	-
UNIFAC fit with data points (ASAP)	-	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.0161	-	-	-	-



**Figure 4.4**

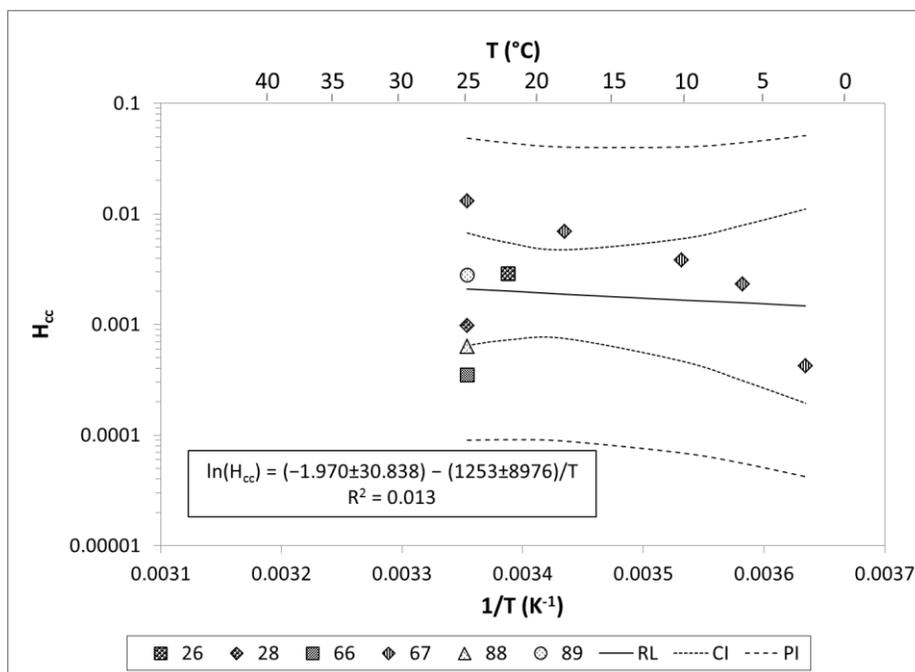
**Comparison of HLC estimation methods for benzyl chloride**

**[Note – Benzyl chloride was not studied by Staudinger & Roberts (2001) or Howe et al. (1987)/Ashworth et al. (1988); therefore, HLC values could not be obtained with the ASAP regression of data points or UNIFAC fit with data points tools.]**

**Nitrobenzene**

While HLC data for nitrobenzene were found in six of the 90 studies evaluated, four of those studies evaluated the HLC at a single temperature (25° C) and very poor agreement was found among the published values ( $r^2=0.013$ , Figure 4.5).

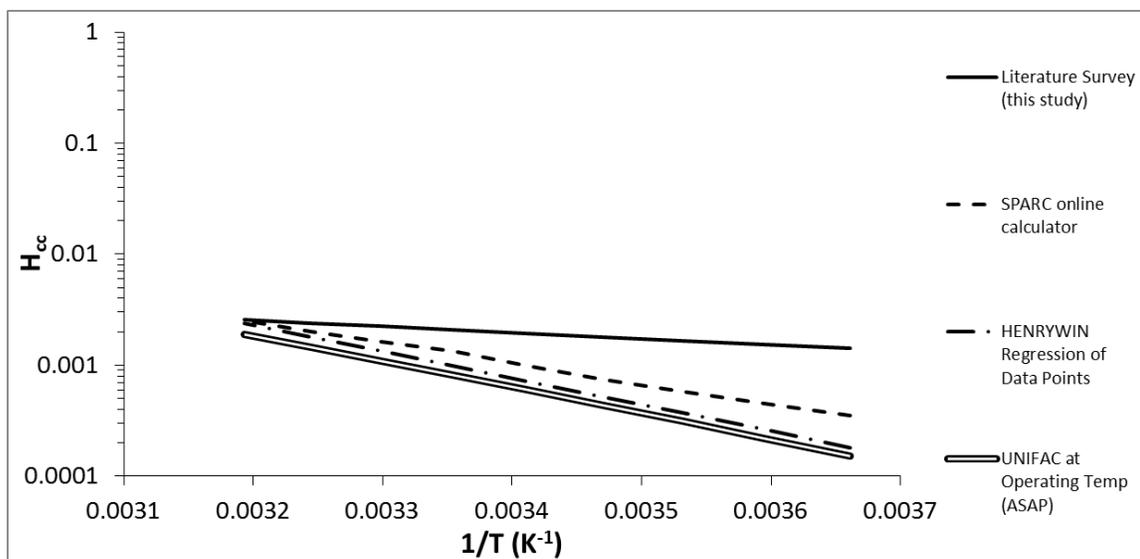
The van't Hoff regression from the literature data returned the highest  $H_{cc}$  estimate at 10° C (0.00167, Table 4.4). UNIFAC and HENRYWIN yielded similar  $H_{cc,10^{\circ}C}$  values (0.000312 and 0.000371, respectively) while SPARC returned a value of 0.000581 (Table 4.4). Based on the low volatility from water, all models suggest that nitrobenzene is not amenable to removal by PTA (Figure 4.6).



**Figure 4.5**  
**Temperature dependence of  $H_{cc}$  for nitrobenzene based on results reported in 6 studies.**  
**Note: Consult Table 4.1 for legend key.**

**Table 4.4**  
**Summary of HLCs for nitrobenzene at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}(10^{\circ}\text{C})$	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.00167	-1.970	1253	0.013	6
Experimental data obtained in this study	-	-	-	-	-
Staudinger & Roberts (2001)	-	-	-	-	-
HENRYWIN regression of data points (based on VP/AS data)	0.000371	-	-	-	-
SPARC on-line calculator	0.000581	-	-	-	-
ASAP regression of data points	-	-	-	-	-
UNIFAC fit with data points (ASAP)	-	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.000312	-	-	-	-



**Figure 4.6**

**Comparison of HLC estimation methods for nitrobenzene**

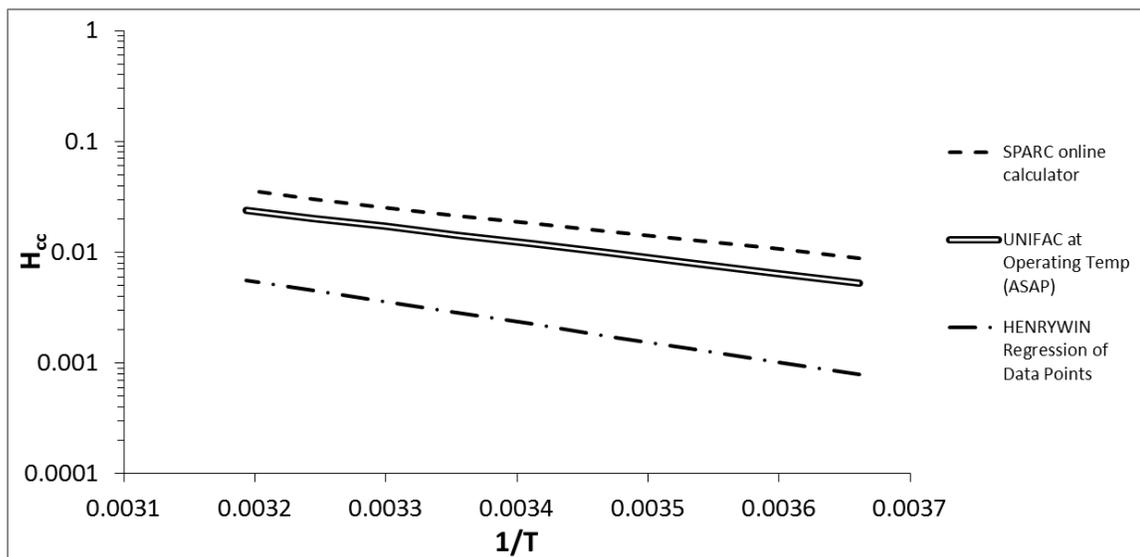
**[Note - nitrobenzene was not studied by Staudinger & Roberts (2001) or Howe et al. (1987)/Ashworth et al. (1988); therefore, HLC values could not be obtained with the ASAP regression of data points or UNIFAC fit with data points tools.]**

**Methyl oxirane**

No experimental data were found for methyl oxirane; therefore, no literature survey van't Hoff relationship could be developed. Again, poor agreement was found among HLC values predicted by the three models (Figure 4.7). HENRYWIN did not have experimental data on which to base the temperature dependence; therefore, temperature dependence was predicted using an ether slope analogy, and  $H_{cc}$  at 10° C was determined to be 0.00135 (Table 4.5). UNIFAC predicted an  $H_{cc}$  that was 6 times higher (0.0081) than that predicted by HENRYWIN while SPARC estimated an  $H_{cc,10^{\circ}C}$  that was 9.6 times higher than the HENRYWIN predicted value. Based on the predicted low volatility from water, it appears that methyl oxirane is not amenable to removal by PTA.

**Table 4.5**  
**Summary of HLCs for methyl oxirane at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	-	-	-	-	-
Experimental data obtained in this study	-	-	-	-	-
Staudinger & Roberts (2001)	-	-	-	-	-
HENRYWIN regression of data points (based on ether slope analogy)	0.00135	-	-	-	-
SPARC on-line calculator	0.0129	-	-	-	-
ASAP regression of data points	-	-	-	-	-
UNIFAC fit with data points (ASAP)	-	-	-	-	-
UNIFAC at operating temperature (ASAP)	0.0081	-	-	-	-



**Figure 4.7**

**Comparison of HLC estimation methods for methyl oxirane**

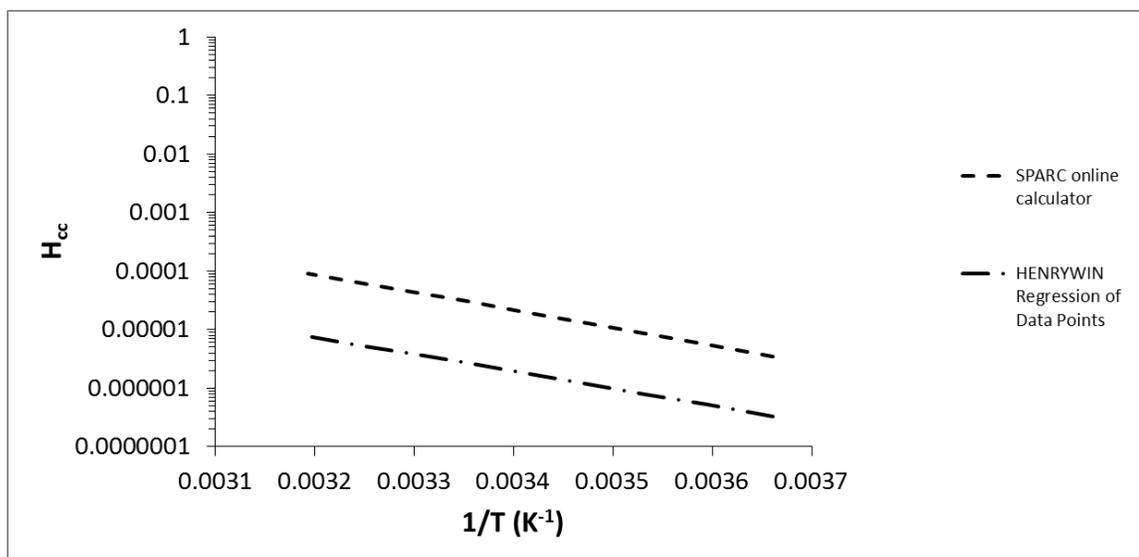
**[Note – Experimental data was not found for methyl oxirane. Furthermore, it was not studied by Staudinger & Roberts (2001) or Howe et al. (1987)/Ashworth et al. (1988); therefore, HLC values could not be obtained with the Literature survey (this study), ASAP regression of data points or UNIFAC fit with data points tools.]**

## Urethane

No experimental data was found for urethane; therefore, no literature based van't Hoff relationship could be developed. Urethane was also not found in the ASAP database, and therefore no UNIFAC predictions were obtained. HENRYWIN did not contain experimental data on which to base the temperature dependence either; therefore, temperature dependence was predicted using VP/AS data (Figure 4.8).  $H_{cc}$  at 10° C was determined to be 7.98E-07 while SPARC estimated an  $H_{cc,10^{\circ}C}$  of 8.61E-06 (Table 4.6). Urethane was not included in studies by Staudinger & Roberts (2001) and Howe et al. (1987)/Ashworth et al. (1988). Therefore, no HLC data was available for ASAP regression of data points or UNIFAC fit with data points. Based on the predicted low volatility from water, it appears that urethane is not amenable to removal by PTA.

**Table 4.6**  
**Summary of HLCs for urethane at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	-	-	-	-	-
Experimental data obtained in this study	-	-	-	-	-
Staudinger & Roberts (2001)	-	-	-	-	-
HENRYWIN regression of data points (based on VP/AS data)	0.000000798	-	-	-	-
SPARC on-line calculator	0.00000861	-	-	-	-
ASAP regression of data points	-	-	-	-	-
UNIFAC fit with data points (ASAP)	-	-	-	-	-
UNIFAC at operating temperature (ASAP)	-	-	-	-	-



**Figure 4.8**

**Comparison of HLC estimation methods for urethane**

**[Note – Experimental data was not found for urethane. Furthermore, it was not studied by Staudinger & Roberts (2001) or Howe et al. (1987)/Ashworth et al. (1988) and did not have UNIFAC data available; therefore, HLC values could not be obtained with the Literature survey (this study), ASAP regression of data points, UNIFAC fit with data points and UNIFAC at operating temperature tools.]**

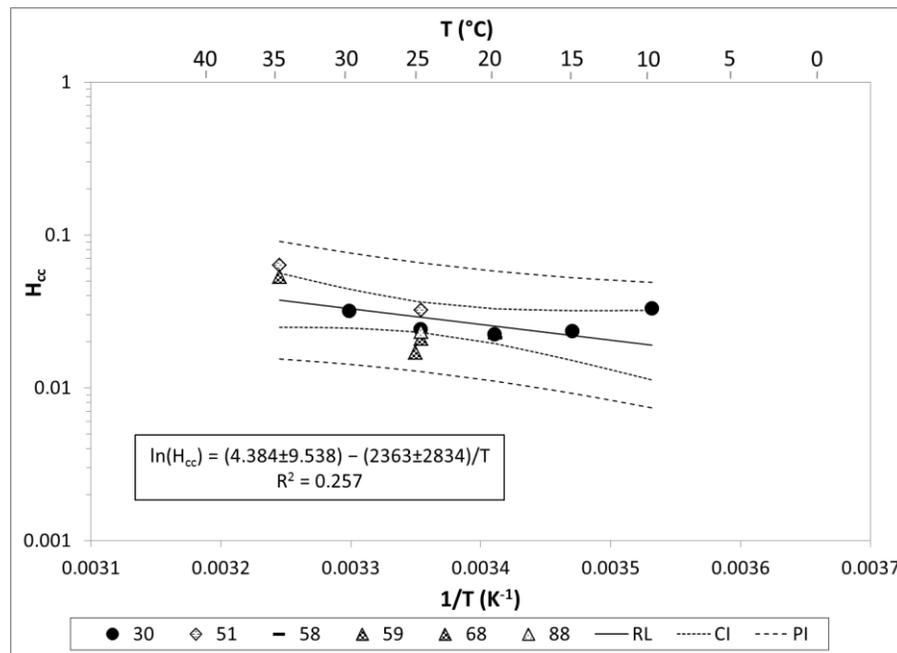
**1,2-dibromoethane**

Data from six studies were used to develop the van't Hoff relationship describing the temperature dependence of the HLC for EDB (Figure 4.9). Of note is the observation that the results of Howe et al. (1987) do not follow a log-linear trend, effecting a poor correlation ( $r^2 = 0.257$ ). Experimental results obtained in this study for EDB in SCWA groundwater deviated from the regression line developed from the literature survey (Figure 4.10).

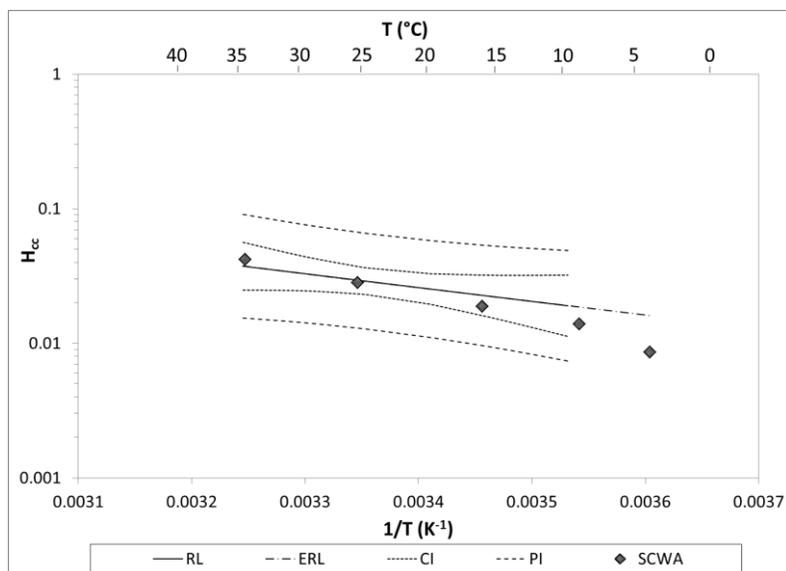
Further investigation revealed that Howe et al. (1987) reported duplicate values for EDB (components 36 and 136) while Ashworth et al. (1988) (based on Howe et al. 1987) did not report the duplicate values. Omitting Howe et al. (1987) component 36 [as was done in

Ashworth (1988)] results in an improved  $r^2$  (0.726), tighter confidence and prediction band intervals, and a steeper slope (Figure 4.11). By omitting Howe et al. component 36, the data obtained in this study followed the trend established by the modified literature survey, as illustrated in Figure 4.12.

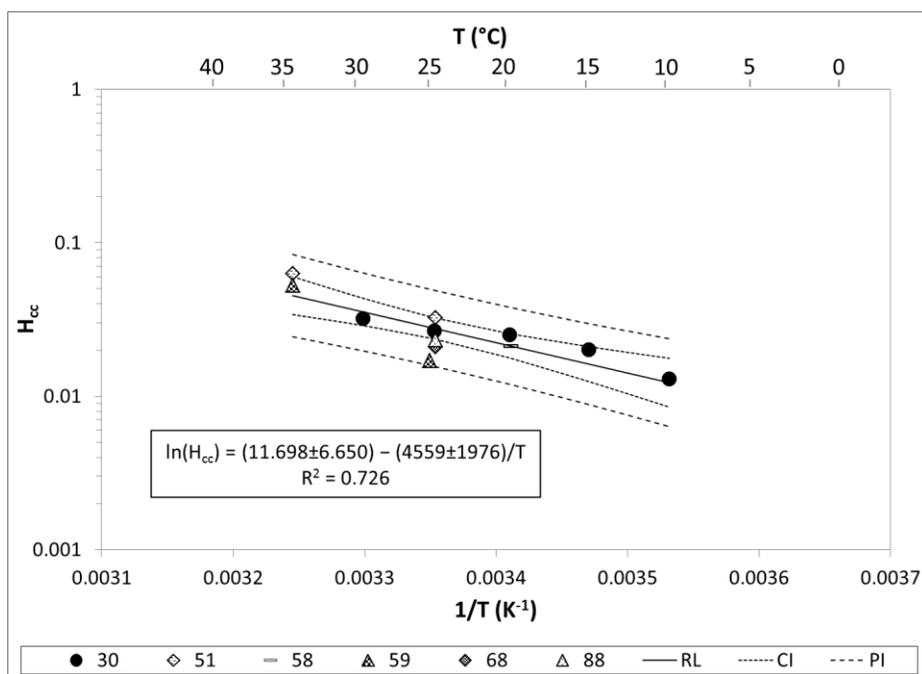
Omitting component 36 from Howe et al. (1987), there was excellent agreement between the  $H_{cc}$  value at 10° C obtained from the literature survey regression (0.0123), the experimental data obtained in this study (0.0130), Staudinger & Roberts (2001) (0.0146), and the HENRYWIN  $H_{cc}$  value (0.0130, Figure 4.13, Table 4.7). SPARC predicted the lowest  $H_{cc,10^\circ C}$  of 0.00689 (Table 4.7). There were no HLC data for EDB available through UNIFAC. The low  $H_{cc}$  values for EDB indicate that it is poorly strippable.



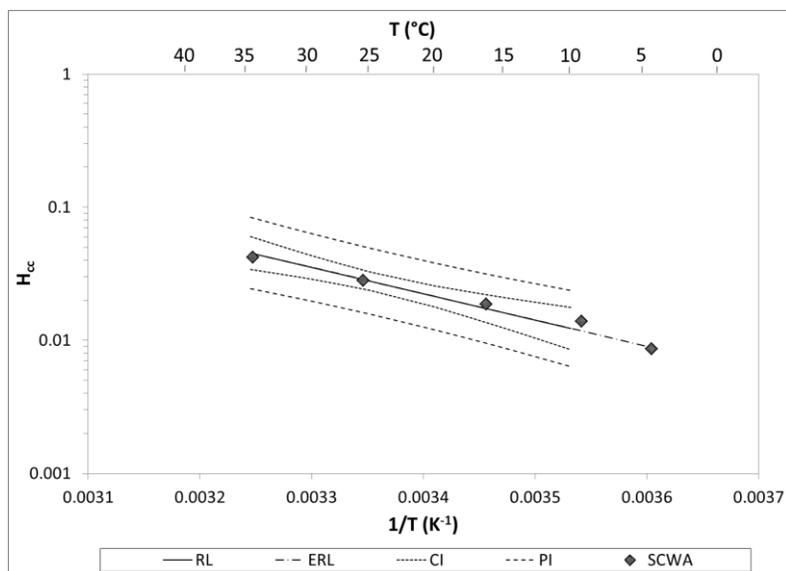
**Figure 4.9**  
**Temperature dependence of  $H_{cc}$  for EDB based on results reported in 6 studies.**  
**Note: Consult Table 4.1 for legend key.**



**Figure 4.10**  
**Comparison of experimental results for EDB obtained in this study and van't Hoff relationship obtained from literature survey**  
 (RL: regression line, CI: 95% confidence interval, PI: 95% prediction interval)



**Figure 4.11**  
**Temperature dependence of  $H_{cc}$  for EDB [omitting Howe et al. (1987) component 36]**

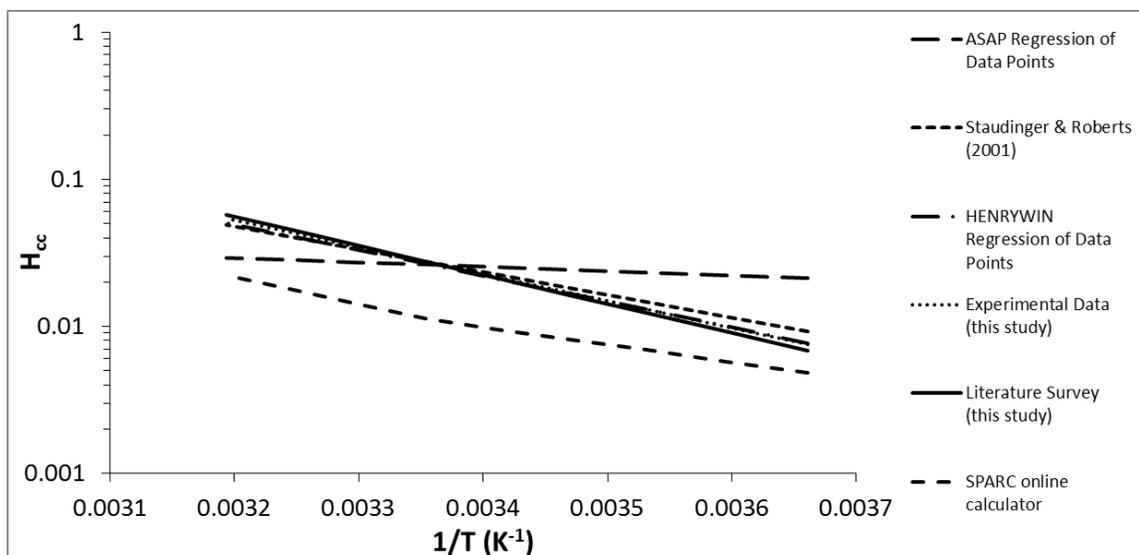


**Figure 4.12**

**Comparison of experimental results for EDB obtained in this study and van't Hoff relationship obtained from literature survey [omitting Howe et al. (1987) component 36]**

**Table 4.7**  
**Summary of HLCs for EDB at 10°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.0190	4.384	2363	0.257	6
Literature survey (omitting Howe et al. 1987 component 36)	0.0123	11.698	4559	0.726	6
Experimental data obtained in this study	0.0130	10.530	4211	0.982	1
Literature survey (omitting Howe et al. 1987) + experimental data (this study)	0.0127	11.024	4357	0.842	7
Staudinger & Roberts (2001)	0.0146	8.431	3583	0.928	1
HENRYWIN regression of data points (based on VP/AS data)	0.0130	-	-	-	-
SPARC on-line calculator	0.00689	-	-	-	-
ASAP regression of data points	0.0233	-	-	-	-
UNIFAC fit with data points (ASAP)	-	-	-	-	-
UNIFAC at operating temperature (ASAP)	-	-	-	-	-



**Figure 4.13**

**Comparison of HLC estimation methods for EDB**

[Note – EDB did not have UNIFAC data available; therefore, HLC values could not be obtained with the UNIFAC fit with data points and UNIFAC at operating temperature tools.]

HLCs for EDB at 10° C were evaluated in four background water matrices (Table 4.8) and compared using pairwise two-tailed *t*-tests. Calculated *t* values were smaller than *t<sub>crit</sub>*, suggesting that HLC values were consistent across different background water matrices.

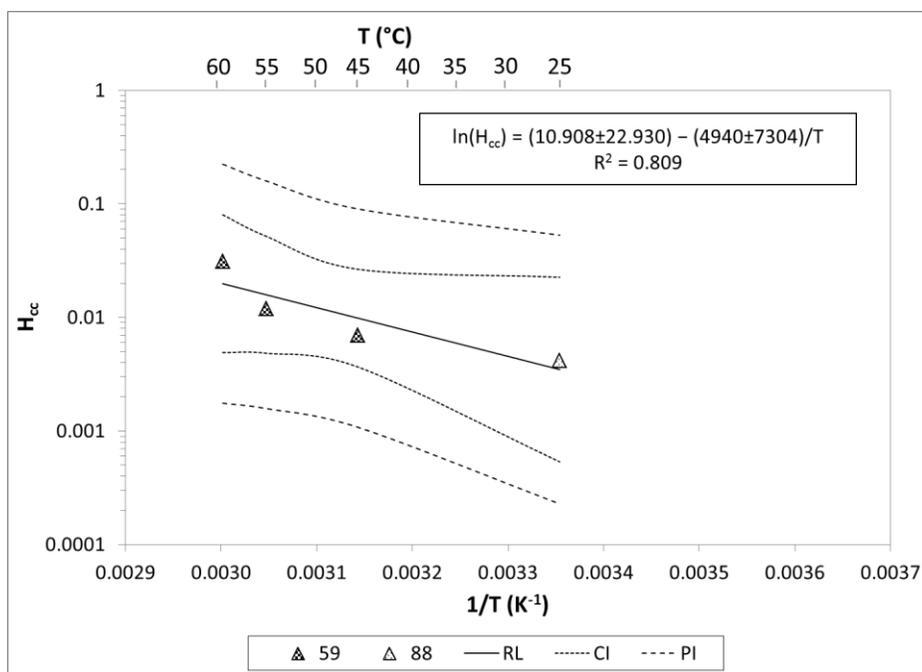
**Table 4.8**  
**Experimental HLC results for EDB in background water matrices**

	Temperature (° C)	H <sub>cc</sub>	95% CI
UPW	9.5	0.0141	±0.00116
ILL	9.7	0.0144	±0.00112
SCWA	9.2	0.0139	±0.00185
SCWA+NaCl	9.6	0.0137	±0.00112

## 1,2-dibromo-3-chloropropane

HLC data for DBCP were found in only two studies at temperatures between 25-60° C (Figure 4.14). Because no data were found for lower temperatures,  $H_{cc}$  values for DBCP will be discussed for a temperature of 25° C. While agreement in data was fairly good ( $r^2=0.809$ ), confidence and prediction intervals were large due to the lack of data. Based on the regression analysis of DBCP, the best estimate of  $H_{cc}$  at 25°C is 0.00348 with upper and lower bounds of 0.0531 and 0.000228 (95% PI), respectively.

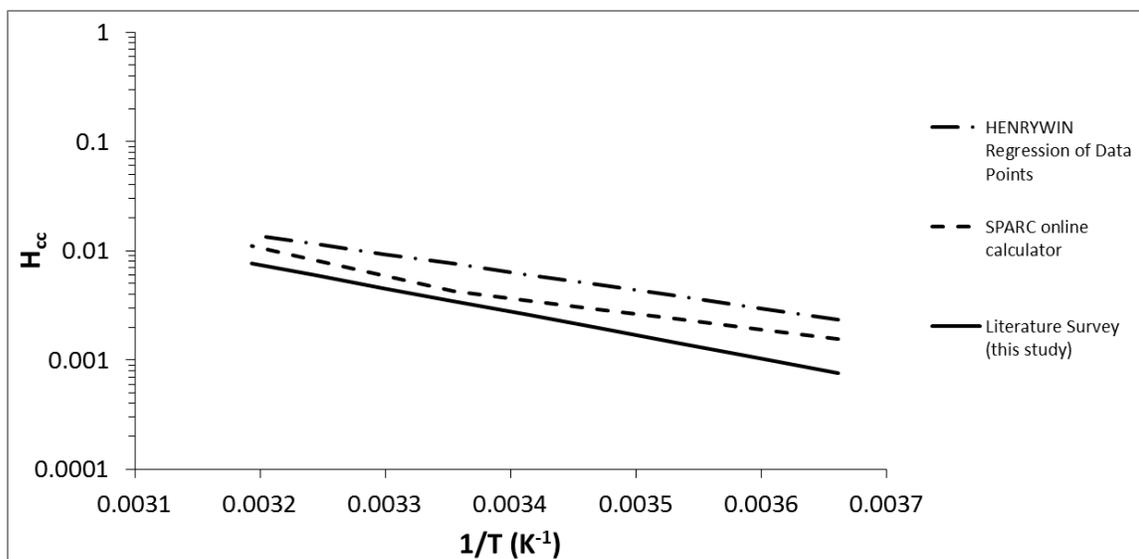
DBCP is not included in the ASAP database, and therefore no UNIFAC predictions were obtained. HENRYWIN did not contain experimental data on which to base a temperature dependence and therefore used a halopropane slope analogy to predict an  $H_{cc}$  value of 0.00760 at 25° C, a factor of 2 higher than the mean suggested by the literature survey (Table 4.9). SPARC estimated  $H_{cc,25^\circ C}$  at 0.00429 (Table 4.8). In other words, based on the van't Hoff relationship developed from the literature survey, both prediction models (HENRYWIN and SPARC) overestimated  $H_{cc}$  at 25°C (Figure 4.15). It is important to note that both models were based on chemical properties and not experimental data. DBCP was not included in studies by Staudinger & Roberts (2001) and Howe et al.(1987)/Ashworth et al. (1988). Additionally, there were no HLC data for DBCP available through UNIFAC. Therefore, no HLC predictions were available for ASAP regression of data points or UNIFAC fit with data points. Based on the low volatility from water, all models suggest that DBCP is poorly strippable.



**Figure 4.14**  
**Temperature dependence of  $H_{cc}$  for DBCP based on results reported in 2 studies.**  
**Note: Consult Table 4.1 for legend key.**

**Table 4.9**  
**Summary of HLCs for DBCP at 25°C and van't Hoff coefficients**

Approach for Estimating $H_{cc}$	$H_{cc}$ (10°C)	A	B	$r^2$	Number of data sets
Literature survey conducted in this study	0.00348	10.908	4940	0.809	2
Experimental data obtained in this study	-	-	-	-	-
Literature survey + experimental data (this study)	-	-	-	-	-
Staudinger & Roberts (2001)	-	-	-	-	-
HENRYWIN regression of data points (based on halopropane slope analogy)	0.00760	-	-	-	-
SPARC on-line calculator	0.00429	-	-	-	-
ASAP regression of data points	-	-	-	-	-
UNIFAC fit with data points (ASAP)	-	-	-	-	-
UNIFAC at operating temperature (ASAP)	-	-	-	-	-



**Figure 4.15**

**Comparison of HLC estimation methods for DBCP**

**[Note – DBCP was not studied by Staudinger & Roberts (2001) or Howe et al. (1987)/Ashworth et al. (1988) and did not have UNIFAC data available; therefore, HLC values could not be obtained with the ASAP regression of data points, UNIFAC fit with data points, and UNIFAC at operating temperature tools.]**

**FREUNDLICH ADSORPTION CONSTANTS**

Freundlich adsorption constants were found in 17 articles and are summarized in Table 4.10. Most Freundlich adsorption constants were determined via batch isotherm experiments in distilled/deionized water in the temperature range of 20-30° C; Speth & Miltner (1990) provided the most extensive database of Freundlich adsorption constants (Table 4.11). Overall, data were found for seven of the eight currently regulated cVOCs, two of the eight CCL3 cVOCs, and the four additional cVOCs. No data were found for the CCL3 compounds aniline; benzyl chloride; 1,3-butadiene; nitrobenzene; methyl oxirane; and urethane.

**Table 4.10**  
**Literature review for Freundlich adsorption constants**

Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Total # papers cited
benzene					X													1
CT					X	X		X					X					4
1,2-DCA					X								X				X	3
1,2-DCP	X				X							X						2
DCM					X											X		2
PCE			X		X	X		X	X				X					6
TCE		X	X	X	X	X	X	X	X	X	X		X	X	X			12
VC																		0
aniline																		0
benzyl chloride																		0
1,3-butadiene																		0
1,1-DCA					X	X											X	3
nitrobenzene																		0
methyl oxirane																		0
1,2,3-TCP					X													1
urethane																		0
1,1,1,2-TeCA					X													1
1,1,2,2-TeCA												X	X					2
EDB					X													1
DBCP					X													1

*1* – Clark et al. (1989), *3* – Notthakun et al. (1989), *3* – Snoeyink et al. (1989), *4* – Summers & Crittenden (1989), *5* - Speth & Miltner (1990), *6* – Urano et al. (1991), *7* – Kilduff et al. (1998), *8* – Giaya et al. (2000), *9* – Yu & Chou (2000), *10* – Kilduff & Karanfil (2002), *11* – Li et al. (20002), *12* – Bemnowska et al. (2003), *13* – Pelech et al. (2003), *14* – Karanfil & Dastgheib (2004), *15* – Erto et al. (2010), *16* – Khan et al. (2010), *17* – Fotta (2012)

**Table 4.11**  
**Freundlich adsorption constants (Speth & Miltner 1990)**

<b>Compound</b>	<b>K (mg/g)(L/μg)<sup>1/n</sup></b>	<b>Equilibration times</b>	<b>C<sub>e</sub> (μg/L)</b>	<b>Temp (° C)</b>
benzene	1.26	3 weeks	462-3.2	24
CT	0.387	varied	429-9.1	24
1,2-DCA	0.129	varied	717-42.8	24
1,2-DCP	0.313	3 weeks	196-4.1	24
DCM	0.00625	3 weeks	715-18.1	24
PCE	4.05	3 weeks	421-3.6	24
TCE	2	3 weeks	442-7.7	24
VC	-	-	-	-
aniline	-	-	-	-
benzyl chloride	-	-	-	-
1,3-butadiene	-	-	-	-
1,1-DCA	0.0646	3 weeks	559-13.4	24
nitrobenzene	-	-	-	-
methyl oxirane	-	-	-	-
1,2,3-TCP	1.08	3 weeks	791-3.4	24
urethane	-	-	-	-
1,1,1,2-TeCA	1.07	3 weeks	738-1.2	24
1,1,2,2-TeCA	-	-	-	-
EDB	0.888	3 weeks	111-0.2	24
DBCP	6.91	3 weeks	69.2-0.2	24

## CHAPTER 5 – SUMMARY AND CONCLUSIONS

### LITERATURE SURVEY

An extensive literature review was performed to compile published HLC data for the cVOCs that were identified for regulation under the new DWS. In 90 articles, data were found for the eight currently regulated cVOCs, six of the eight CCL3 cVOCs, and the four additional cVOCs. Experimental HLC data were not found for the CCL3 compounds methyl oxirane and urethane.

The literature data for each compound were combined and analyzed to determine the temperature dependence of  $H_{cc}$  using a van't Hoff relationship [ $\ln(H_{cc}) = A - B/T$ ]. The combined data, RL, 95% CI, and 95% PI were plotted. Among the currently regulated compounds, uncertainty in  $H_{cc}$  estimates was largest for DCM ( $r^2 = 0.774$ , Figure 3.13). Of the three CCL3 contaminants most likely considered for the new group regulation, consistency among published Henry's Law constant values could only be evaluated for 1,1-DCA and 1,2,3-TCP. Good agreement among published literature values was observed for 1,1-DCA ( $r^2 = 0.932$ , Figure 3.28) while poor agreement was seen for 1,2,3-TCP ( $r^2 = 0.380$ , Figure 3.31). Among the two additional compounds most likely considered for the new group regulation, uncertainty in  $H_{cc}$  estimates was larger for 1,1,2,2-TeCA ( $r^2 = 0.641$ , Figure 3.40) and smaller for 1,1,1,2-TeCA ( $r^2 = 0.951$ , Figure 3.37).

For many of the additional CCL3 compounds, reliable van't Hoff relationships could not be developed from the literature survey due to the limited number of published data sets (e.g. aniline, Figure 4.1). Additionally, single studies can skew van't Hoff relationships, especially when the HLC data do not follow a log-linear temperature dependence, as

illustrated with the data of Leighton & Calo (1981) (study 14) for 1,2,3-TCP (Figure 3.31) and with the data of Howe et al. (1987)/Ashworth (1988) (study 30) for EDB (Figure 4.9).

A similar literature review was performed to compile existing Freundlich adsorption constant data. Experimental results were found for seven of the eight currently regulated cVOCs, two of the eight CCL3 cVOCs, and the four additional cVOCs. TCE and PCE were the most widely studied of the 20 compounds, while data were scarce for several CCL3 and additional compounds. No data were found for the CCL3 compounds aniline; benzyl chloride; 1,3-butadiene; nitrobenzene; methyl oxirane; and urethane.

## **ESTIMATION TOOLS**

$H_{cc}$  values resulting from the van't Hoff relationships developed from the literature survey and the experimental data collected in this study were compared with values resulting from three predictive tools (HENRYWIN through EPI Suite, SPARC, and UNIFAC through ASAP) and the most comprehensive literature survey to date (Staudinger & Roberts 2001, Table 5.1). For the 14 compounds for which reliable van't Hoff relationships could be developed, the HLCs estimated from estimation tools deviated from those obtained with the literature survey and experimental data from this study as follows (Tables 5.1-5.2):

1.  $\pm 30\%$  when compared to the literature survey of Staudinger and Roberts (2001).

Furthermore, HLC data were not included for the cVOCs VC; 1,3-butadiene; and 1,1,1,2-TeCA.

2.  $\pm 83\%$  when compared to the ASAP Regression of Data Points, developed from Howe et al. (1987)/Ashworth et al. (1988). Additionally, HLC data were not included for the cVOCs 1,2,3-TCP and 1,1,1,2-TeCA.
3.  $\pm 54\%$ ; when compared to the regression of data points for HENRYWIN based on experimental data. Note that a 54% difference was associated with the  $H_{cc,10^{\circ}C}$  for 1,2,3-TCP utilizing the regression of Leighton & Calo (1981) data, which were excluded from this study. The data of Leighton and Calo (1981) deviated substantially from data collected in this and other studies as discussed in Chapter 3.
4.  $\pm 29\%$  when compared to the regression of data points for HERYWIN based on VP/AS data and/or slope analogies.
5.  $\pm 363\%$  when compared to the UNIFAC at Operating Temperature. Furthermore, HLC data were not included for the cVOC EDB.
6.  $\pm 1037\%$  when compared to SPARC.

The above analysis illustrates that HLC predictions based on QSPRs (UNIFAC at Operating Temperature, SPARC) exhibited some of the largest deviations from data-based HLC estimates.

**Table 5.1.**  
**Comparison of predicted  $H_{cc}$  at 10° C**

<b>compound</b>	<b>Literature Survey + Experimental Data (this study)</b>	<b>HENRYWIN</b>	<b>SPARC on-line calculator</b>	<b>ASAP Regression of Data Points</b>	<b>UNIFAC Fit with Data Points</b>	<b>UNIFAC at Operating Temperature</b>	<b>Staudinger &amp; Roberts (2001)</b>
<b>benzene</b>	0.116	0.117*	0.364	0.137	0.142	0.125	0.118
<b>CT</b>	0.560	0.591*	1.123	0.634	0.637	0.756	0.590
<b>1,2-DCA</b>	0.0257	0.027*	0.026	0.0388	0.0497	0.0344	0.0258
<b>1,2-DCP</b>	0.0538	0.057*	0.053	0.0478	0.0519	0.154	0.0586
<b>DCM</b>	0.0595	0.0731*	0.03	0.0607	0.0643	0.0719	0.0568
<b>PCE</b>	0.309	0.315*	3.512	0.355	0.361	0.337	0.309
<b>TCE</b>	0.188	0.174*	1.864	0.227	0.23	0.289	0.185
<b>VC</b>	0.550	0.633*	1.679	0.546	0.450	0.686	-
<b>1,3-butadiene</b>	1.29	1.67**	1.61	1.42	1.34	1.48	-
<b>1,1-DCA</b>	0.115	0.113*	0.087	0.16	0.158	0.167	0.133
<b>1,2,3-TCP</b>	0.00534	0.0082*	0.006	-	0.0075	0.0142	0.00615
<b>1,1,1,2-TeCA</b>	0.0424	0.0548**	0.0878	-	-	0.046	-
<b>1,1,2,2-TeCA</b>	0.00766	0.0084*	0.0133	0.0117	0.014	0.0355	0.00992
<b>EDB</b>	0.0127	0.013**	0.0069	0.02324	-	-	0.0146

\*based on regression of data points

\*\*based on slope analogy and/or VP/AS data

**Table 5.2.**  
**Comparison of H<sub>cc</sub> obtained from a given predictive tool and recommended H<sub>cc</sub> at 10° C**

Compound	Percent Difference Between Literature Survey + Experimental Results and...					
	HENRYWIN	SPARC on-line calculator	ASAP Regression of Data Points	UNIFAC Fit with Data Points	UNIFAC at Operating Temperature	Staudinger & Roberts (2001)
benzene	1	214	18	22	8	2
CT	6	101	13	14	35	5
1,2-DCA	5	1	51	93	34	0
1,2-DCP	6	-1	-11	-4	186	9
DCM	23	-50	2	8	21	-5
PCE	2	1037	15	17	9	0
TCE	-7	891	21	22	54	-2
VC	15	205	-1	-18	25	N/P
1,3-butadiene	29	25	10	4	15	N/P
1,1-DCA	-2	-24	39	37	45	16
1,2,3-TCP	54	12	N/P	40	166	15
1,1,1,2-TeCA	29	107	N/P	N/P	8	N/P
1,1,2,2-TeCA	10	74	53	83	363	30
EDB	2	-46	83	N/P	N/P	15

N/P: not possible because predictive tool did not contain information for stated cVOC

## BACKGROUND WATER MATRIX

HLCs for cVOC mixtures 1 (DCM; 1,2-DCP; 1,1,2,2-TeCA; 1,1,1,2-TeCA; and PCE, Table 3.4) and 2 (1,2-DCA; 1,2-DBA; 1,2,3-TCP, and TCE, Table 3.4) were determined at 10°C in four different background water matrices (UPW, ILL, SCWA, and SCWA amended with 1500 mg/L NaCl). Henry's Law constants in the four background water matrices were compared using pairwise two-tailed t-tests with a null hypothesis indicating that there is no difference between slopes (HLCs were the same). Normal distributions with unequal sample sizes (due to repeated experiments) and unequal variances were assumed. The associated  $t_{crit}$  values ranged from 2.36-3.18; for all of the compounds,  $t$  was less than  $t_{crit}$  (largest  $t$  value was 0.75). Therefore, the null hypothesis cannot be rejected, suggesting that background water matrix effects that may be attributable to the presence of TOC (<2 mg/L) and TDS (<1950 mg/L) were negligible, supporting the findings of Bissonette et al. (1990) and Robbins et al. (1993).

## TEMPERATURE EFFECTS

HLCs for fourteen cVOCs were determined experimentally in SCWA groundwater at temperatures ranging from 4-36° C (Appendix E). Using van't Hoff plots, experimental results obtained with the variable headspace method in this study were compared to literature data. For the eight currently regulated cVOCs, the experimental data followed the trendline established by the literature survey data (i.e. experimental data points fell within the 95% prediction bands and often within the 95% confidence intervals). The same was true for the CCL3 compounds 1,1,DCA and 1,3-butadiene.

The comparison between experimental data and literature data also revealed important information for 1,2,3-TCP and EDB. Experimental results obtained in this study followed the literature data once numbers from Leighton & Calo (1981) for 1,2,3-TCP and Howe et al. (1987) component 36 for EDB were removed. HLCs in both data sets did not follow a log-linear temperature dependence.

Furthermore, experimental results obtained here expanded the temperature range of HLC data available for both 1,3-butadiene and 1,1,1,2-TeCA. For 1,1,1,2-TeCA and 1,1,2,2-TeCA, single solute experiments were conducted such that corrections could be made to account for hydrolysis of 1,1,2,2-TeCA, which leads to the formation of TCE.

## **RECOMMENDATIONS**

If water treatment professionals follow the rule of thumb to predict HLCs [HLCs double every ten degrees (Staudinger & Roberts 2001)], errors could occur, resulting in suboptimal PTA design, operation, and/or contaminant removal. Instead, compound specific *A* and *B* values should be used to estimate HLCs.

Experimental results and literature survey data were combined to determine suggested *A* and *B* values (Table 5.3). Compared to the  $r^2$  values obtained from the literature data analysis, addition of the experimental data obtained here yielded the same or higher  $r^2$  values for 12 out of 14 cVOCs. Correlation coefficients for the van't Hoff relationships range from 0.742 (1,1,2,2-TeCA) to 0.972 (1,1,1,2-TeCA).  $r^2$  for 1,2,3-TCP exhibited the greatest increase, from 0.469 to 0.837. Conversely, addition of the experimental data developed in this study to the limited literature data sets for VC and 1,3-butadiene decreased the

**Table 5.3**  
**Suggested A and B values based on literature survey plus experimental data (this study)**

compound	Intercept* (A)	Slope* (B)	Number of data sets	r <sup>2</sup>	H <sub>cc</sub> (10° C)
benzene	10.645±0.757	3623±223	54	0.885	0.116
CT	13.800±1.13	4072±333	28	0.890	0.560
1,2-DCA	9.705±1.90	3784±559	22	0.791	0.0257
1,2-DCP	10.543±0.943	3813±278	14	0.957	0.0538
DCM	8.130±1.44	3101±425	26	0.798	0.0595
PCE	14.259±1.23	4370±363	31	0.871	0.309
TCE	12.574±0.682	4034±201	48	0.923	0.188
VC	9.785±2.45	2940±722	5	0.834	0.550
1,3-butadiene	8.596±2.57	2362±754	2	0.887	1.29
1,1-DCA	11.470±1.02	3861±301	16	0.933	0.115
1,2,3-TCP	8.329±3.40	3840±1016	4	0.837	0.00534
1,1,1,2-TeCA	12.367±1.44	4397±430	6	0.972	0.0424
1,1,2,2-TeCA	10.865±3.43	4456±1018	11	0.742	0.00766
EDB	11.024±3.51	4357±1036	7	0.842	0.0127

\*Mean±95%CI

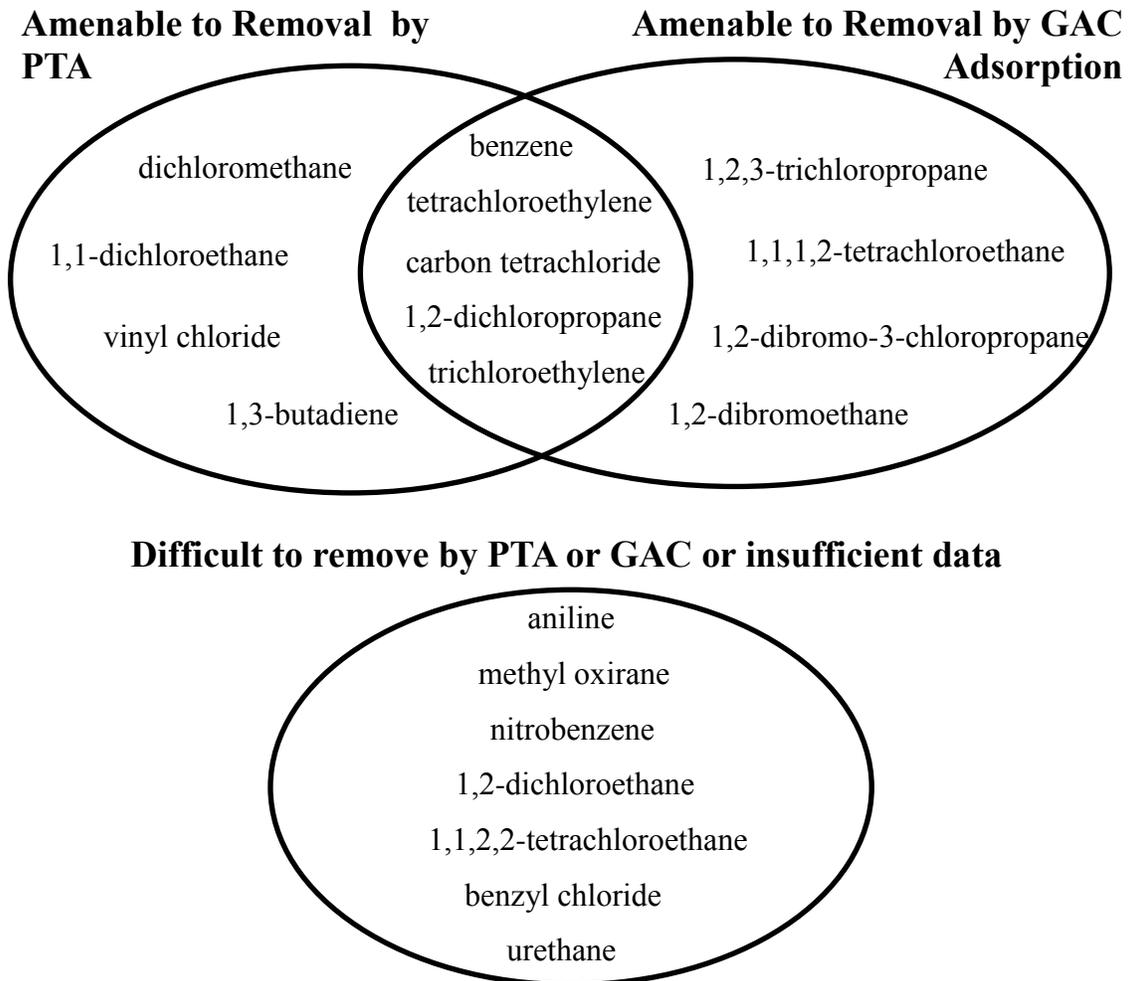
correlation coefficients of the van't Hoff relationships by approximately 5%.

Based on HLC values estimated by the van't Hoff relationships developed from the literature survey and experimental results in this study, seven of the eight currently regulated cVOCs and the CCL3 compounds 1,3-butadiene and 1,1-DCA exhibit HLCs that make them moderate to good candidates for removal by PTA ( $H_{cc,10^{\circ}C} > 0.05$ , Figure 5.1, Table 5.3).

One of the currently regulated compounds (1,2-DCA), six of the CCL3 cVOCs (nitrobenzene; benzyl chloride; 1,2,3-TCP; aniline; urethane, methyl oxirane) and all four additional compounds are considered to be poorly strippable based on available HLC data or predicted HLC values. Furthermore, for the potent and currently unregulated 1,2,3-TCP,

experimental results indicate that it may be more difficult to remove 1,2,3-TCP by PTA at lower temperatures than previously predicted.

For those compounds that are not amenable to removal by PTA, Freundlich adsorption constants, based on  $K$  values obtained through the literature survey, suggest that 1,2,3-TCP is a CCL3 cVOC that can be effectively removed by GAC as can three of the four additional cVOCs (1,1,1,2-TeCA; EDB; and DBCP)[ $K > 0.2 \text{ (mg/g)(L/}\mu\text{g)}^{1/n}$ , Figure 5.1). 1,2-DCA is difficult to remove by both PTA and GAC. Insufficient data are available to assess the effectiveness of either PTA or GAC for the removal of aniline; benzyl chloride; nitrobenzene; methyl oxirane; urethane; and 1,1,2,2-TeCA.



**Figure 5.1**  
**Treatment Options Based on Predicted HLCs and Freundlich Adsorption Constants**  
 (Amenable:  $H_{cc,10^{\circ}C} > 0.05, K < 0.2 \text{ (mg/g)(L/\mu g)}^{1/n}$ )

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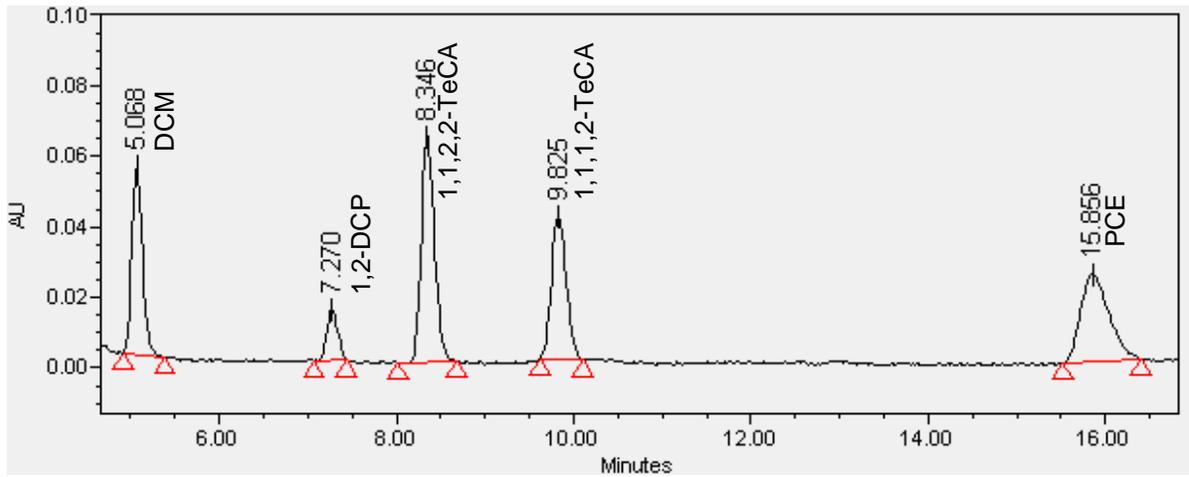
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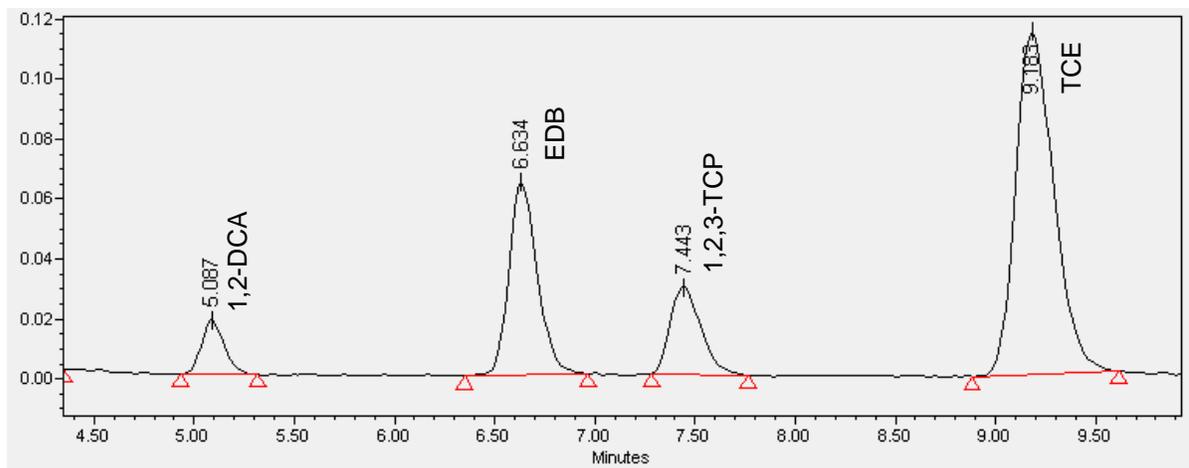
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## **APPENDICES**

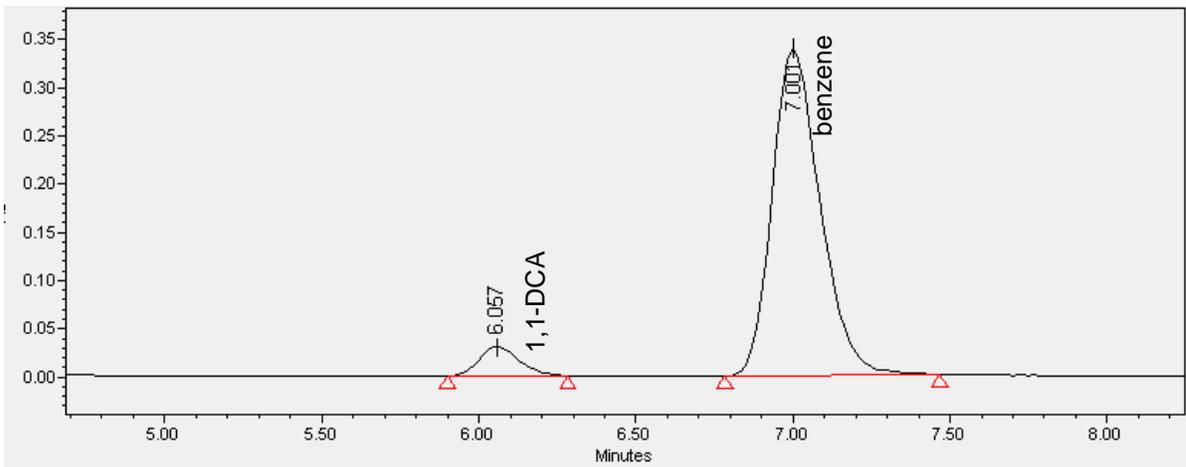
## APPENDIX A – REPRESENTATIVE HPLC CHROMATOGRAMS



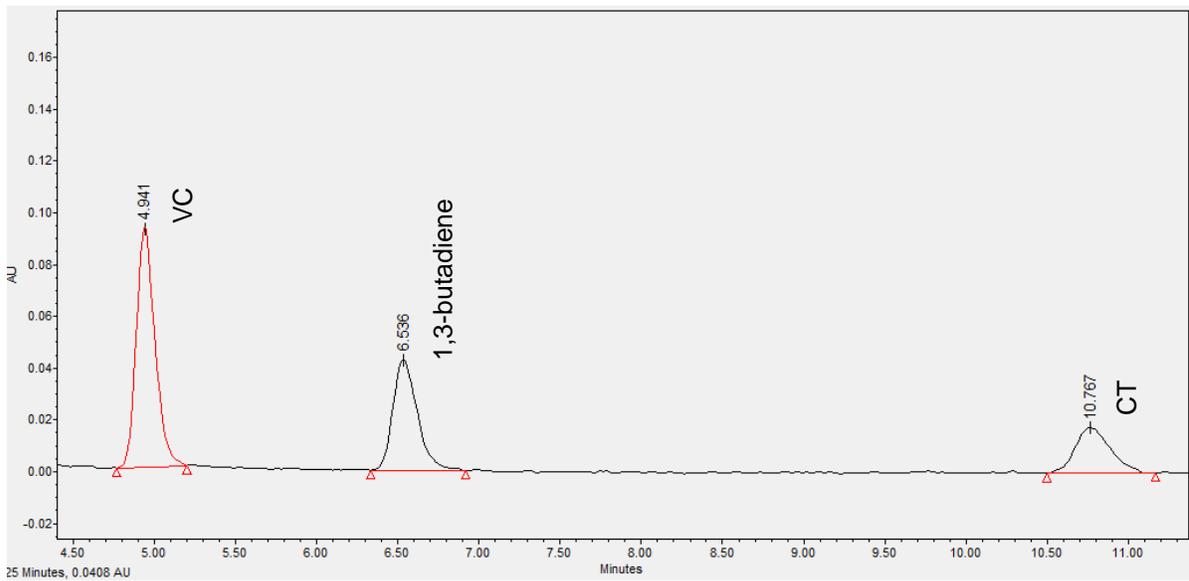
**Figure A.1**  
**(08/15/13) HPLC chromatogram for mix 1 in SCWA**



**Figure A.2**  
**(10/08/13) HPLC chromatogram for mix 2 in SCWA**

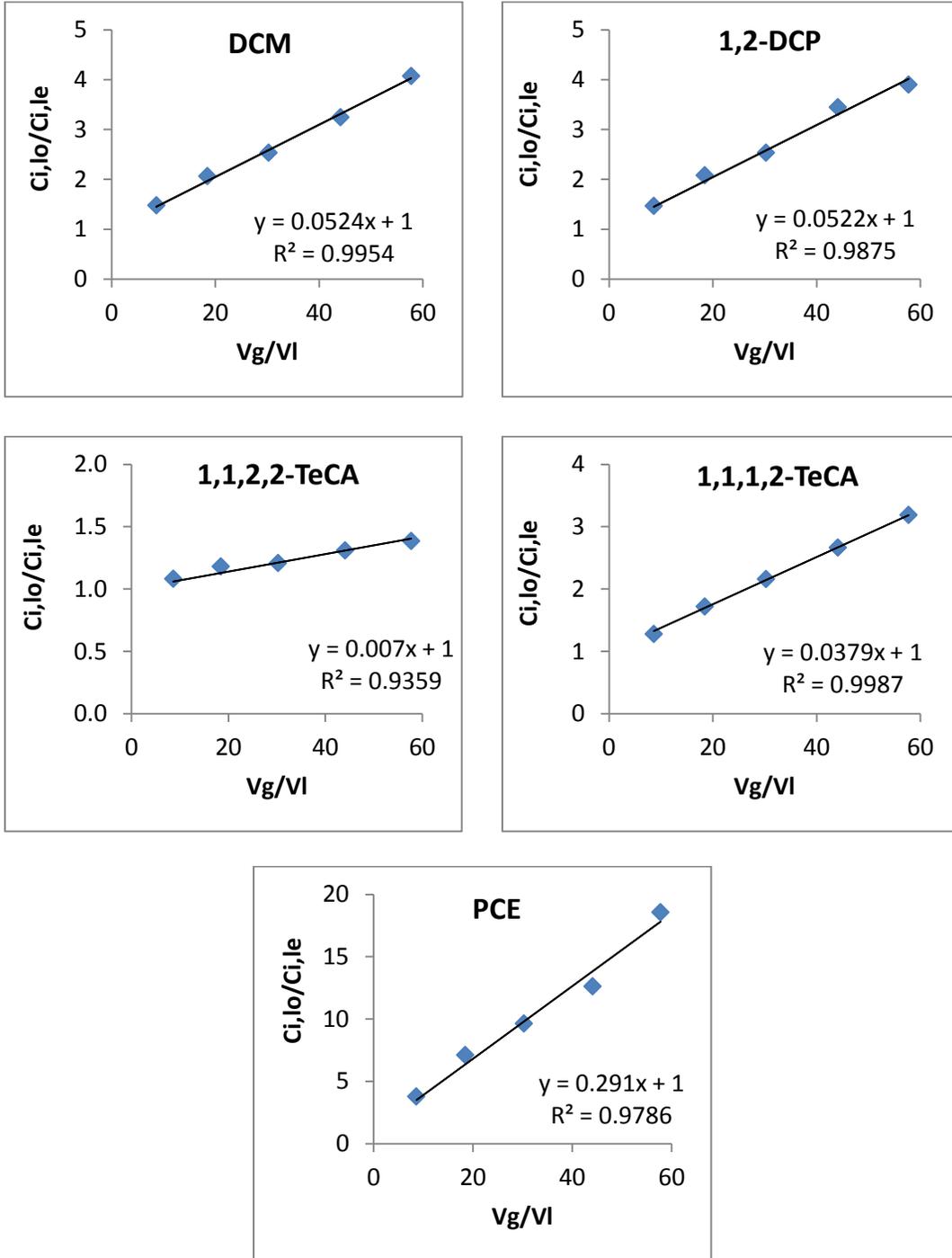


**Figure A.3**  
**(04/11/14) HPLC chromatogram for mix 3 in SCWA**

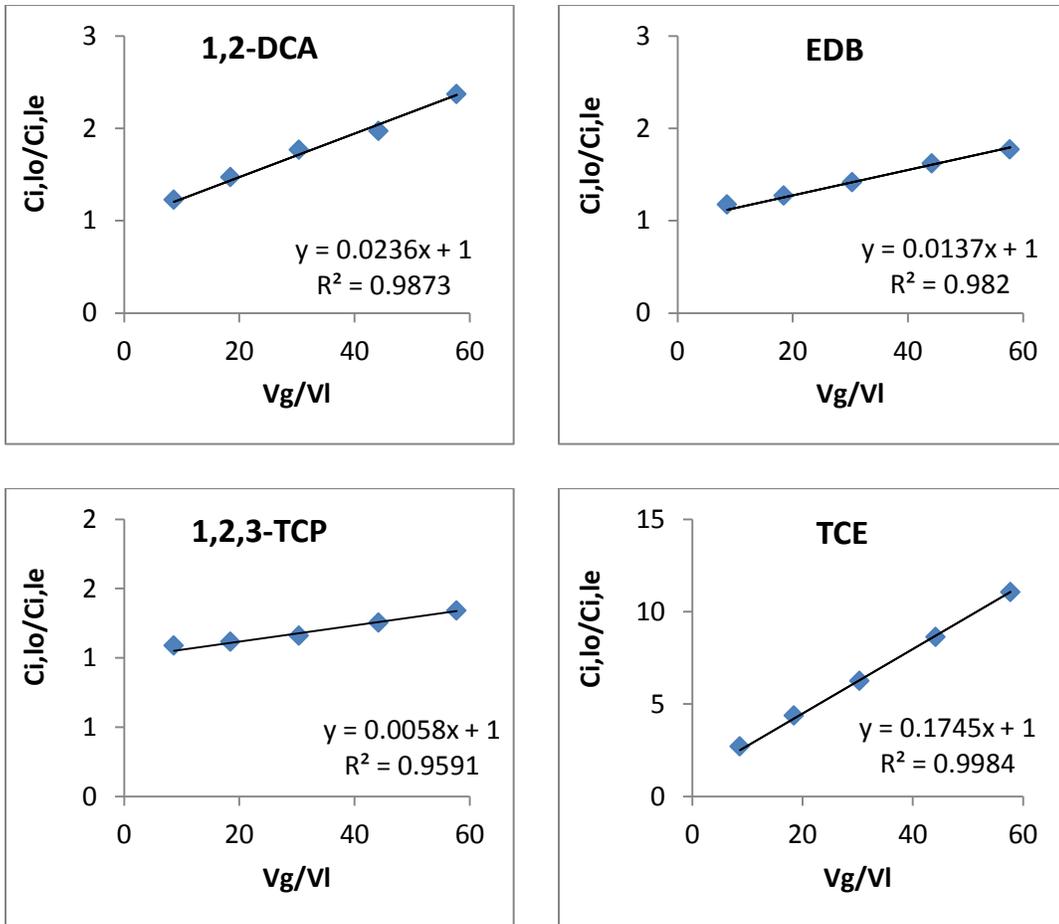


**Figure A.4**  
**(04/17/14) HPLC chromatogram for mix 4 in SCWA**

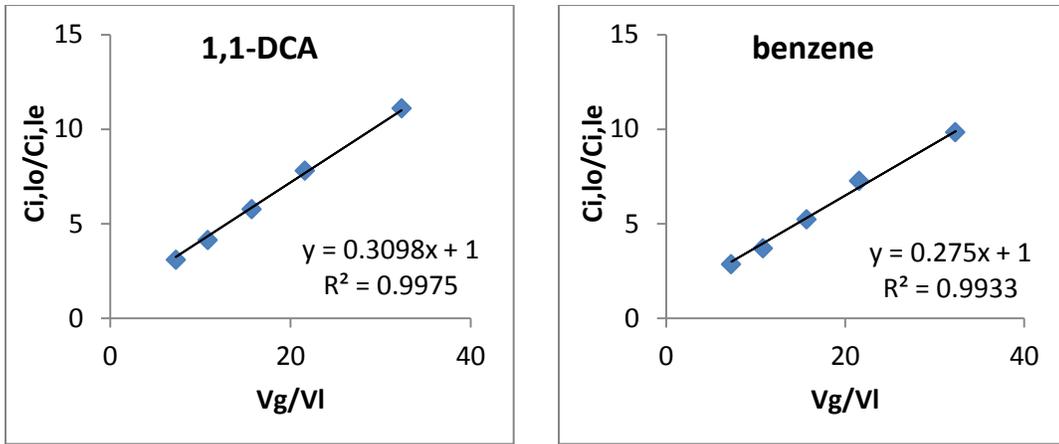
**APPENDIX B – REPRESENTATIVE VARIABLE HEADSPACE RESULTS**



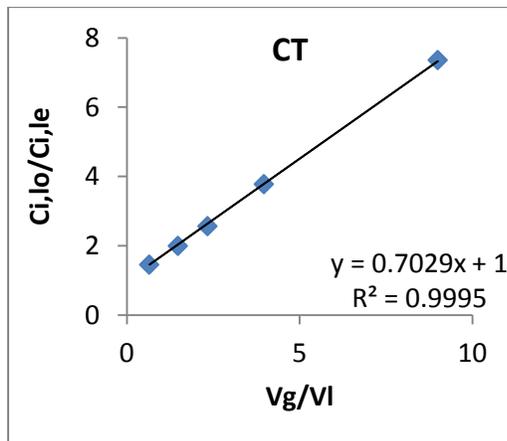
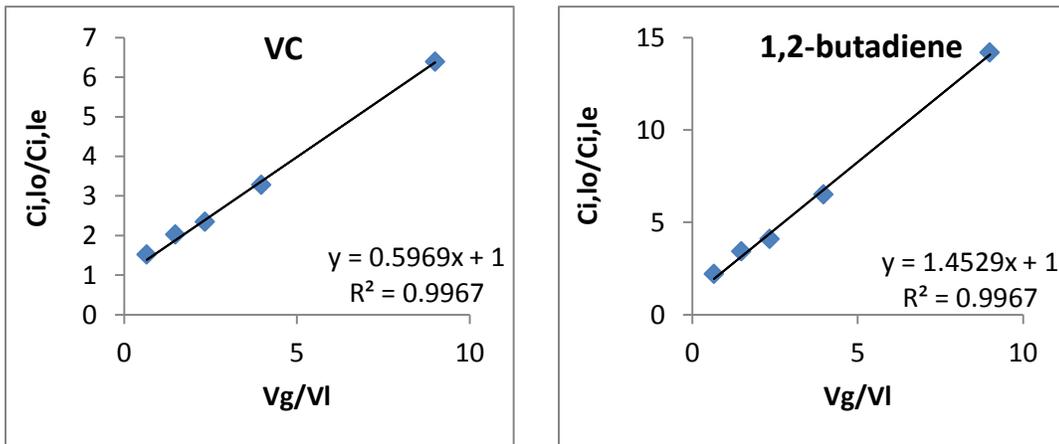
**Figure B.1**  
**(10/01/13) Variable headspace results for mix 1 in SCWA+NaCl**



**Figure B.2**  
**(09/26/13) Variable headspace results for mix 2 in SCWA+NaCl**



**Figure B.3**  
**(04/08/14) Variable headspace results for mix 3 in SCWA**



**Figure B.4**  
**(04/22/14) Variable headspace results for mix 4 in SCWA**

**APPENDIX C – REPRESENTATIVE STANDARD STOCK SOLUTION CONCENTRATION AND PHASE RATIO  
CALCULATIONS**

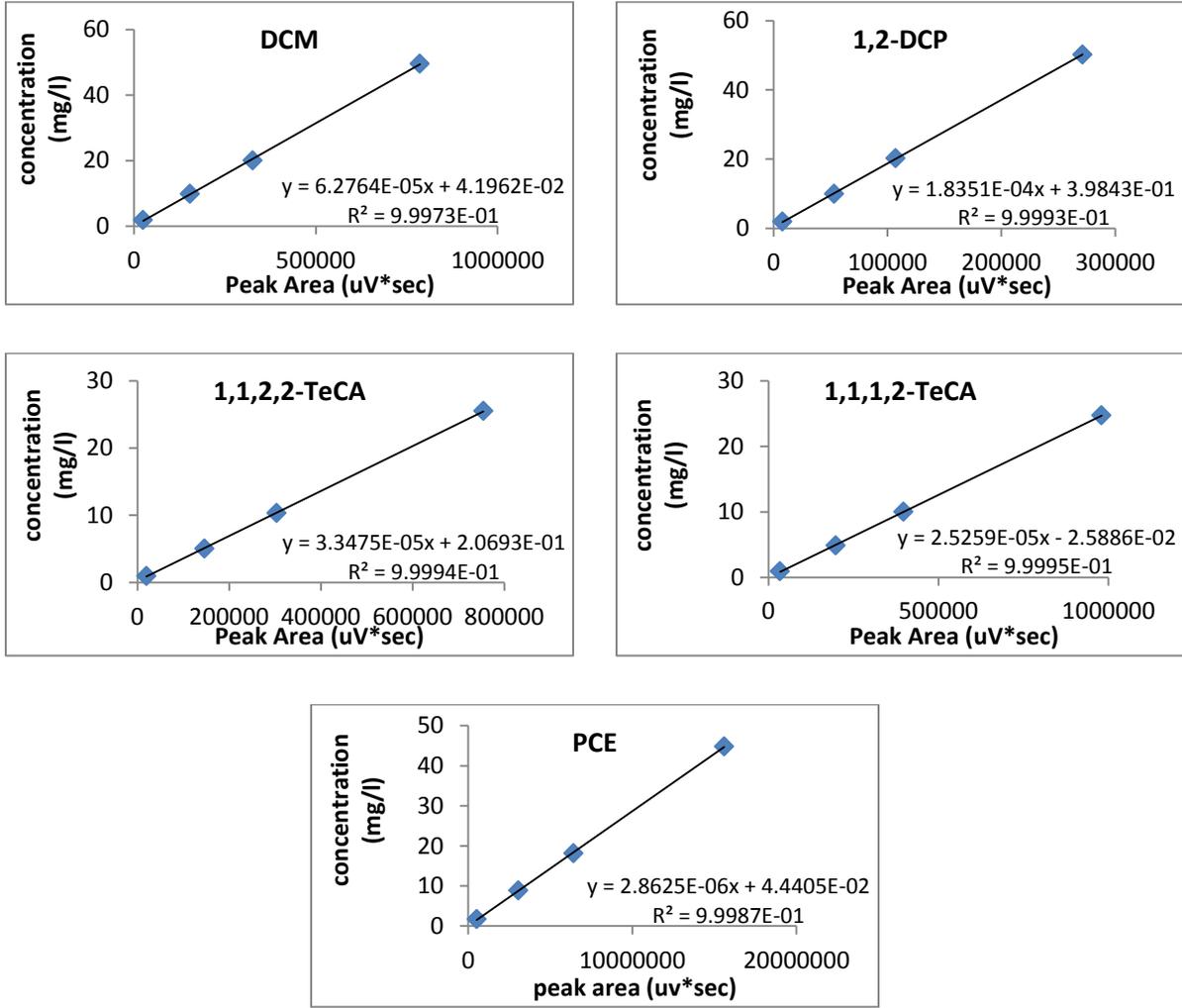
**Table C.1  
SSS calculations (mix 1, 9/30/2013)**

	syringe weight (g)		weight added (g)	volume added (mL)	concentration (mg/l)
	before	after			
methanol	55.7583	24.4132	31.3451	39.587	-
DCM	27.3376	27.1344	0.2032	0.162	5,067
1,2-DCP	27.3114	27.1126	0.1988	0.178	4,957
1,1,2,2-TeCA	14.3053	14.2023	0.103	0.066	2,568
1,1,1,2-TeCA	14.3017	14.2021	0.0996	0.064	2,484
PCE	14.2795	14.2025	0.077	0.047	1,920

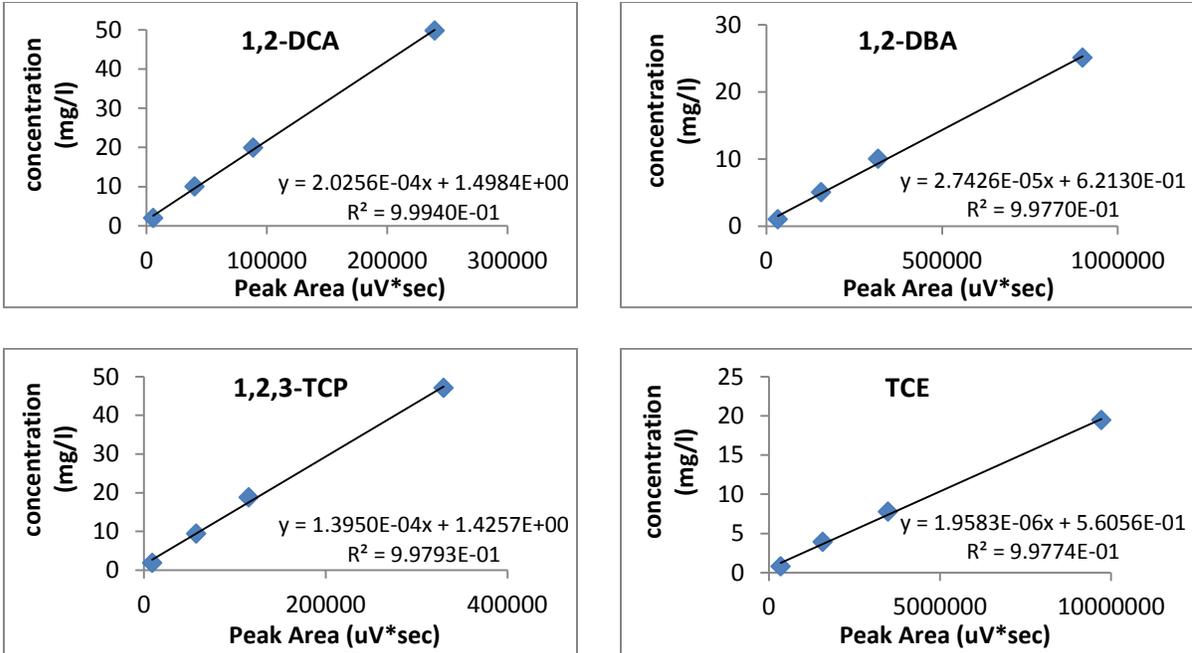
**Table C.2**  
**Phase ratio calculations (mix 1, SCWA+NaCl, 9/30/2013)**

		syringe weight (g)			volume added (mL)	volume bottle (mL)	bottle weight (g)		volume liquid (mL)	V <sub>g</sub> /V <sub>l</sub>	concentration (mg/L)
		before	after	weight added			before	after			
bottle 4-1	DCM										50.26
	1,2-DCP										49.18
	1,1,2,2-TeCA	27.3182	27.1139	0.2043	0.258	250.7	176.3022	202.0537	26.01	8.64	25.48
	1,1,1,2-TeCA										24.64
	PCE										19.05
bottle 4-2	DCM										49.45
	1,2-DCP										48.38
	1,1,2,2-TeCA	27.2135	27.114	0.0995	0.126	250.7	176.2540	189.0047	12.88	18.47	25.06
	1,1,1,2-TeCA										24.24
	PCE										18.74
bottle 18	DCM										50.30
	1,2-DCP										49.21
	1,1,2,2-TeCA	14.2649	14.2013	0.0636	0.080	253.2	172.8995	180.9108	8.09	30.29	25.50
	1,1,1,2-TeCA										24.65
	PCE										19.06
bottle 4-4	DCM										50.64
	1,2-DCP										49.54
	1,1,2,2-TeCA	14.2454	14.2014	0.044	0.056	250.8	176.2337	181.7382	5.56	44.11	25.67
	1,1,1,2-TeCA										24.82
	PCE										19.19
bottle 21	DCM										51.23
	1,2-DCP										50.12
	1,1,2,2-TeCA	14.2357	14.2013	0.0344	0.043	252.4	175.3906	179.6439	4.30	57.74	25.97
	1,1,1,2-TeCA										25.11
	PCE										19.41

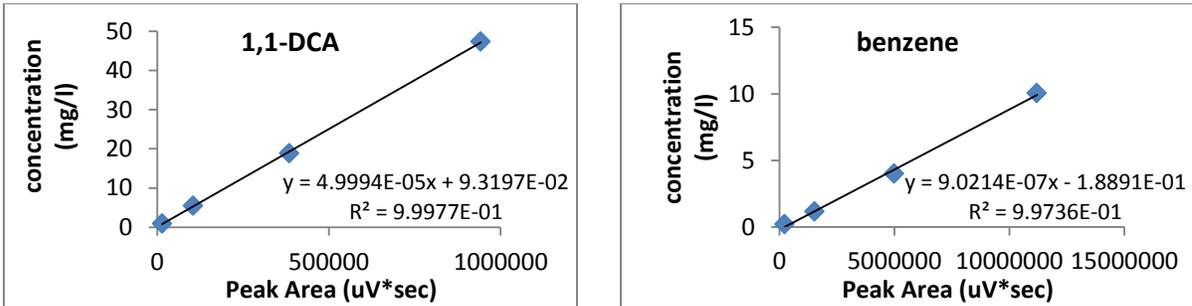
**APPENDIX D - REPRESENTATIVE CALIBRATION CURVES FROM HPLC ANALYSIS**



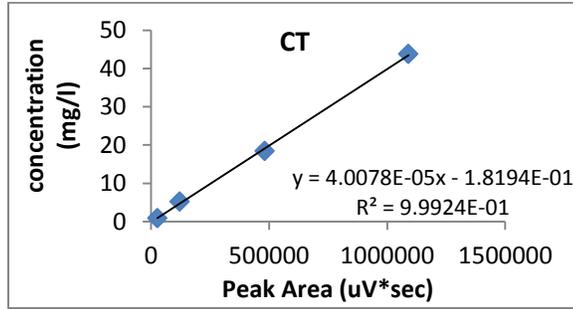
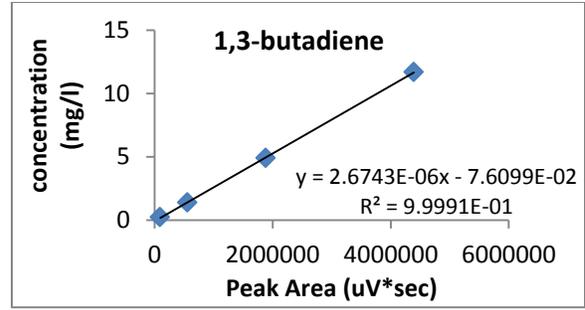
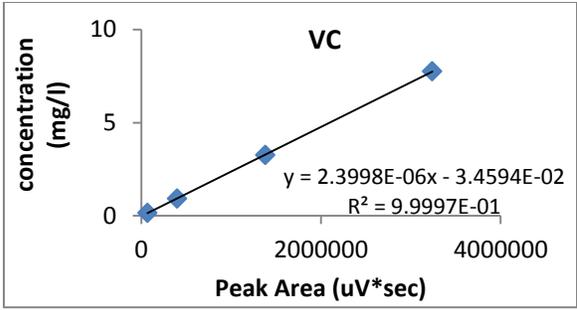
**Figure D.1**  
**(01/16/14) HPLC calibration curves for mix 1 in SCWA**



**Figure D.2**  
**(01/10/14) HPLC calibration curves for mix 2 in SCWA**



**Figure D.3**  
**(04/11/14) HPLC calibration curves for mix 3 in SCWA**



**Figure D.4**  
**(04/17/14) HPLC calibration curves for mix 4 in SCWA**

**APPENDIX E – EXPERIMENTAL RESULTS**

**Table E.1  
H<sub>cc</sub> values for mixtures 1-4 in SCWA groundwater**

<b>compound</b>	<b>Temperature (° C)</b>	<b>H<sub>cc</sub></b>								
<b>benzene</b>	5.7	0.0716	--	--	16.0	0.131	24.8	0.189	33.0	0.281
<b>CT</b>	5.7	0.353	--	--	17.9	0.703	24.4	0.991	33.1	1.58
<b>1,2-DCA</b>	4.3	0.0167	9.2	0.0248	16.2	0.0359	25.7	0.0455	34.8	0.0617
<b>1,2-DCP</b>	4.5	0.0363	9.8	0.0525	15.3	0.0635	25.2	0.108	34.8	0.142
<b>DCM</b>	4.5	0.0386	9.8	0.0512	15.3	0.0651	25.2	0.0961	34.8	0.127
<b>PCE</b>	4.5	0.201	9.8	0.285	15.3	0.453	25.2	0.586	34.8	0.811
<b>TCE</b>	4.3	0.107	9.2	0.161	16.2	0.248	25.7	0.376	34.8	0.624
<b>VC</b>	5.7	0.380	--	--	17.9	0.597	24.4	0.734	33.1	1.03
<b>1,3-butadiene</b>	5.7	1.08	--	--	17.9	1.45	24.4	1.69	33.1	2.61
<b>1,1-DCA</b>	5.7	0.0760	--	--	16.0	0.142	24.8	0.195	33.0	0.317
<b>1,2,3-TCP</b>	4.3	0.00376	9.2	0.00552	16.2	0.00767	25.7	0.0123	34.8	0.0201
<b>1,1,1,2-TeCA</b>	4.5	0.0313	9.8	0.0472	15.3	0.0525	25.3	0.0808	35.7	0.143
<b>1,1,2,2-TeCA</b>	--	--	9.8	0.00726	15.3	0.0102	25.0	0.0147	35.0	0.0252
<b>EDB</b>	4.3	0.00858	9.2	0.0139	16.2	0.0187	25.7	0.0281	34.8	0.0419