TREATMENT OF CARCINOGENIC VOLATILE ORGANIC CONTAMINANTS USING UV AND the UV/H_2O_2 ADVANCED OXIDATION PROCESS

by

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B.Sc. Chemical Engineering, Miami University, 2013

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirement for the degree of
Master of Science
Department of Civil, Environmental and Architectural Engineering
2015

This thesis entitled:
Treatment of Carcinogenic Volatile Organic Contaminants Using UV and the UV/H_2O_2
Advanced Oxidation Process
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Abstract

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Treatment of Carcinogenic Volatile Organic Contaminants Using UV and the UV/H_2O_2 Advanced Oxidation Process

Thesis directed by Professor Karl G. Linden

Volatile organic compounds (VOCs) are chemicals that are potentially hazardous to human health and the environment. Some VOCs have been shown to cause cancer in animals and are classified as potential human carcinogens. The United States Environmental Protection Agency (USEPA) is considering regulating as many as 16 VOCs as a group instead of individually. This approach of regulating chemicals implies that these grouped chemicals could be remediated by a single technology or perhaps a group of technologies. Advanced oxidation processes (AOPs) such as ultra-violet (UV) light in combination with hydrogen peroxide (UV/H_2O_2) are potential treatment processes for VOC removal. Given the applicability of AOP as a VOC treatment technology, there are fundamental gaps to understand and predict the transformation of VOCs. There is a need to understand the removal efficiencies of individual VOCs with AOP and how the treatment process is affected by changes in the water matrix. Eleven VOCs were studied for their reactivity with UV and OH radicals using a low pressure mercury vapor UV radiation source emitting principally at 253.7nm. These VOCs include one aromatic organic, benzene; two chlorinated alkenes, trichloroethylene and tetrachloroethylene; four chlorinated ethanes, 1,1,2,2-tetrachloroethane, 1,1,1,2-tetrachloroethane, 1,1-dichloroethane, 1,2-dichloroethane;two chlorinated methanes, dichloromethane and carbon tetrachloride and two chlorinated propanes, 1,2-dichloropropane and 1,2,3-trichloropropane. The aromatic organic and chlorinated alkenes showed the highest reactivity during both direct photolysis and UV induced OH radical oxidation.

There was little or no removal of the chlorinated alkanes when exposed to UV only. Degradation using UV/H_2O_2 AOP was evident among all 11 VOCs. Experimentally, 1,1, 2,2-terachloroethane showed the lowest reactivity along with carbon tetrachloride. A common feature among the two chemicals is that they have the highest number of chlorine atoms in the group which fundamentally affect their reaction with OH radicals. To ensure the effective degradation of all VOCs in a single UV AOP system, optimization and design of UV-based hydroxyl radical oxidation systems should be based on the most chlorinated VOCs if the new regulation is enforced. UV-based AOP should be used for those compounds most amenable to oxidation while other technologies fill in for the slower reacting compounds.

Dedication

This thesis is firstly dedicated to my family for the unwavering love and support throughout the start of my life. Secondly, I dedicate it to all my academic and career mentors that noticed my passion and drive to not just learn but to also succeed! Finally, I dedicate this thesis to three amazing women that inspire me every day to be a better person: **Stella Masiwa Mandona**, **Wendy Bongjoh** and **Samiah Ghounaim**. Their quest and persistence to live a whole hearted life, grace and love for others is beyond measure. I am forever inspired.

Acknowledgements

It is with great honor for me to express my deepest gratitude and thanks to my advisor and mentor **Prof. Karl G Linden** for his guidance and wisdom throughout my research journey. I am forever enamored of his dedication and hard work towards his research. His sound advice, meticulous scrutiny of the work and ingenious scientific approach have helped me to stretch my thinking and be better than what I thought I could be. One of my favorite authors, Shiv Khera once said, “Winners don’t do different things but do things differently.” Prof Karl is exemplary of this quote and I am deeply honored to have been part of his research.

I would also like to extend my gratitude to **Dr. James Rosenblum** for his support, encouragement and ideas throughout my experimental work. This thesis would not have been possible without your daily guidance. I appreciate your efforts and forever indebted.

Being surrounded by the passionate and hardworking students of the Linden Lab motivated me to do my best every time. I would like to extend a special thanks to **Jeanette Neethling, Kurby Sitterly, Sydney Ulliman, Tesfa Yacob, Robyn Hallowell, Erin Printy, Ian Morissey, Simon Mostafa, Sarah Beck** and **Natalie Hull** who assisted me with my research work.

I am grateful for the support I received from the faculty and staff in the Environmental Sustainability Group and I have a deep sense of gratitude towards **Prof. Scott Summers**, **Prof. Jason Ren** and **Prof. Rita Klees** for their mentorship, scholarly and career advice.

Undoubtedly, I would like to thank my friends and family who have been pillars of strength and encouragement throughout this research journey. I would like to specially thank my host family, **Carol and Mike Baum** for sharing their home, family and life during my time in Boulder.

Contents

List of Abbreviations

AOP	Advanced Oxidation Process
cVOC	carcinogenic volatile organic compound
DBCP	1,2-Dibromo-3-chloropropane
DWS	Drinking Water Strategy
EDB	1,2-Dibromoethane
EMP	Environmental Management Plan
IARC	International Agency Research Center for Cancer
GAC	Granular Activated Carbon
KCM	Konkola Copper Mines
LP	Low Pressure
MCL	Maximum Contaminant Limit
MP	Medium Pressure
MW	Molecular Weight
NWDR	National Water Drinking Regulation
ORD	Office of Research and Development
PCE	Tetrachloroethylene
PTA	Packed Tower Aeration
PTFE	Polytetrafluorethylene
QY	Quantum Yield
SITE	Superfund Innovative Technology Evaluation
TCE	Trichloroethylene
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency

UV	Ultra-violet light
VOC	Volatile Organic Compound
WHO	World Health Organization
ZEMA	Zambia Environment Management Agency

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1. Introduction

Volatile organic compounds (VOCs) are carbon-containing chemicals, (except carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate) that have potential to be gaseous under room temperature and pressure. These chemicals tend to partake in photochemical reactions and are potentially hazardous to human health and the environment. Many have been shown to cause cancer in animals and are classified as potential human carcinogens. With that, they are uniquely referred to as carcinogenic volatile compounds, cVOCs (US EPA, 2015).

VOCs range from aromatic organics to chlorinated alkanes and alkenes. Aromatic organics such as benzene are fuel components that help to increase the combustion efficiency of gasoline. The chlorinated chemicals are frequently used during dry cleaning, decaffeinating coffee, cleaning metallic machinery and dissolving grease build up in septic tanks. Chlorinated chemicals can also be found in household products from ink removers, correction fluids, adhesives, plastic wrap, water pipes, automotive and wood furniture cleaners. In addition to household exposure, VOCs enter the water system by contaminated groundwater sources. This contamination of groundwater originates from septic tanks, hazardous waste dumps, landfills and waste from industrial processing. Contamination also results from malpractices particularly industrial spills or leaks of waste that contaminate the ground water (New Jersey Dept. of Health, 1997).

Due to their toxic nature, the United States Environmental Protection Agency (US EPA) is currently regulating 8 VOCs having a maximum contaminant limit of 0.005mg/L (US EPA, 2009). These VOCs include benzene, carbon tetrachloride, 1,2-dichloroethane, 1,2-dichloropropane, dichloromethane, tetrachloroethylene (PCE), trichloroethylene (TCE) and vinyl chloride. However there are still 12 VOCs that are unregulated. Eight of these VOCs come from the third

Contaminant Candidate List particularly aniline, benzyl chloride, 1,3-butadiene, 1,1-dichloroethane, nitrobenzene, oxirane methyl, 1,2,3-trichloropropane and urethane. 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, 1,2-Dibromo-3-chloropropane (DBCP) and 1,2-Dibromoethane (EDB) are additional contaminants that the US EPA might add or substitute to the VOC group (American Water Works Association, 2014).

To resolve this issue of regulation, the US EPA revised its Drinking Water Strategy (DWS) in 2010 and one of the four goals of the DWS is to address contaminants as a group instead of individually. This group regulation would be more cost effective in addressing contaminants. Historically, the US EPA has performed a group regulation on total haloacetic acids, total trihalomethane, gross alpha radionuclides and beta radionuclides. For contaminants to be regulated as a group, the contaminants should ideally have similar health endpoints, be measured by the same analytical method and can be treated using the same technology. It does not matter if the chemicals occur individually or occur together (US EPA, 2012).

There are several technologies that have been shown to remove VOCs and these include air stripping in a packed tower aeration (PTA), advanced oxidation processing, biological treatment and granular activated carbon (GAC). According to the US EPA, PTA and GAC are recognized as the best available technology for the removal of VOCs (US EPA, 1989).

While the USEPA is considering to regulate VOCs as a group, it is simultaneously about to review the regulation of TCE and PCE with anticipation that they would provide stricter regulation of these chemicals due to scientific advancements. If both strategies of VOC regulation and stricter regulation for TCE and PCE are enforced, then design and operational parameters of the treatment processes would have to change to comply with new regulation. These parameter changes would not be possible without accurately understanding these processes.

OH radical based oxidation is a potential treatment process for VOC removal. OH radicals can be formed with or without a coupled UV light process. These OH radicals react with organics through OH radical addition or hydrogen atom abstraction. These species have been used in the past (US EPA, 1990) to remove various VOCs such as TCE, PCE, Vinyl chloride, 1,2-dichloroethane and benzene. Despite the proven success of OH radical based oxidation as a VOC treatment technology, there is still a need to know if this treatment method can degrade other VOCs, at which point a comprehensive model can be developed to predict their transformation. Therefore, there is a need to understand the removal efficiencies of all VOCs with OH radical based oxidation and whether the treatment process is affected by changes in the water matrix.

In this research study, it is hypothesized that UV alone and a UV/H_2O_2 advanced oxidation process can remove VOCs by effectively transforming the parent compounds. This report presents the results of UV and UV/H_2O_2 degradation trends of 11 VOCs using UV light at 253.7nm. This study involved the determination of the fundamental quantum yields (the number of moles of compound degraded per mole of photons absorbed) of removal and assessment of hydrogen peroxide's enhancement in the removal process through modeling. The results are then evaluated against existing data and through modeling to provide an overall determination and prediction of the process efficiency.

2. Background

2.1 Physical and Chemical Properties of VOCs

Most VOCs are colorless liquids that tend to vaporize easily at room temperature and pressure. If not liquid, they are gaseous or solid in nature (Huang et al, 2014). Expectedly, VOCs have very low melting points but a varying range of boiling points. Most VOCs are denser than water while having low aqueous solubility and low molecular weights (MWs). The chemical structure of these VOCs ranges from aromatic organics to halogenated alkanes and alkenes. A summary of the physiochemical properties of the liquid VOCs investigated in this study can be seen in Table 1.

Table 1: Physiochemical properties of select VOCs

Chemical Formula	MW (g/mol)	Density (g/ml)	Melting Point (°C)	Boiling Point (° C)	Henry's law Constant (mol/m^3-Pa)	Solubility (g/L)
Benzene	78.11	0.874	5.5	80	1.70E-03	1.88
Trichloroethylene	131.4	1.463	-84.8	86.7	1.00E-03	1.10
Tetrachloroethylene	165.8	1.623	-22	121	6.20E-04	0.15
1,1,2,2-Tetrachloro ethane	167.9	1.586	-43	147	2.40E-02	2.96
1,1,1,2-Tetrachloro ethane	168	1.598	-70.2	138	4.20E-03	1.55
1,1-dichloroethane	99	1.174	-97	57.2	1.70E-03	5.06
1,2-dichloroethane	98.96	1.256	-35	83	8.90E-03	8.65
Dichloromethane	84.93	1.325	-97	39.9	3.60E-03	20.0
Carbon Tetrachloride	153.8	1.594	-23	76.5	3.40E-04	0.77
1,2-dichloropropane	113.0	1.156	-100	95.5	3.40E-03	2.80
1,2,3-trichloropropane	147.5	1.387	-14	156	3.60E-02	1.75

2.2 Mode of Exposure, Health Impacts and Regulation of VOCs

2.2.1 Mode of Exposure

VOCs enter the environment through different routes. They enter the water systems particularly via ground water through leaks and discharge from industrial factories. They are released into the atmosphere through volatilization after which VOCs enter surface waters through the hydrological cycle when rainfall occurs. Human beings get exposed to these chemicals in three ways that is through dermal absorption, ingestion when drinking contaminated water and inhalation of VOC-laden air (Huang et al, 2014). A pictorial illustration can be seen in Figure 1.

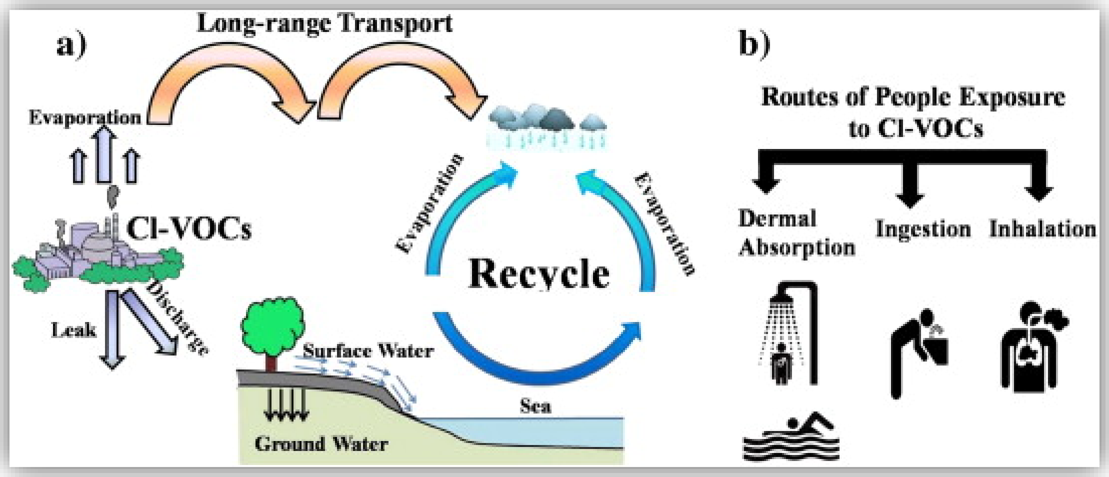


Figure 1: Fate and Transport of VOCs [Source: Huang et al, 2014]

2.2.2 Health Impacts

Several factors are to be considered when looking at the health impact of VOCs on human health. These factors include the type of VOC, amount of VOC one is exposed to and the length of exposure. Acute health effects include dizziness, respiratory tract irritation while chronic health effects include damage to major organs such as lungs, liver, kidneys and brain leading to cancer (Minnesota Dept. of Health, 2015). However, there is still no conclusive evidence that indicates that *all* VOCs are carcinogenic to human beings. Scientific studies, conducted with rats (Nagano et al, 2006), have shown detrimental health effects by these chemicals but more epidemiological studies are needed to validate deleterious effects in human beings.

Due to the varying evidence of the toxicity of VOCs, VOCs have been categorized in the likelihood that they can cause cancer. The maximum occupational exposure limits of VOCs in the US (level of VOC that leads to toxicity) and the likelihood that they can cause cancer as categorized by the international agency for research on cancer (IARC) is shown in Table 2. Group 1 represents the chemicals that are carcinogenic to humans; Group 2A is *probably* carcinogenic to humans; Group 2B stands for *possibly* carcinogenic to humans; while Group 3 and Group 4 are not classifiable as to its carcinogenicity to humans, and probably not carcinogenic to humans, respectively. The occupational exposure limit is a time weighted average of about 8 hours a day (Huang et al, 2014).

Table 2: Carcinogenic categorization of VOCs and occupational exposure limits in the US [Source: * Occupational Safety and Health Administration, 2015; **IARC, 2015)

VOC	Occupational exposure limits in the US*	Carcinogenicity**
Benzene	1 ppm	Group 1
trichloroethylene	100 ppm	Group 1
tetrachloroethylene	25 ppm	Group 2A
1,1,2,2-tetrachloroethane	100 ppm	Group 3
1,1,1,2-tetrachloroethane	NOT ESTABLISHED	Group 2B
1,1-dichloroethane	100 ppm	Not available
1,2-dichloroethane	NOT AVAILABLE	Group 2B
dichloromethane	25 ppm	Group 2A
carbon tetrachloride	10ppm	Group 2B
1,2-dichloropropane	10 ppm	Group 1
1,2, 3-trichloropropane	50ppm	Group 2A

2.2.3 Monitoring and Regulation

In attempts to protect the environment and human health from VOCs, measures have been put in place to regulate some of the VOCs. Maximum contaminant limits (MCLs) for these regulated VOCs have been established. These MCLs are representative of concentrations of VOCs below which no expected or anticipated adverse health effects would occur. In the United States, states are allowed to set different MCLs. However, the USEPA has set an MCL of 5 µg/L for the currently regulated VOCs which include benzene, carbon tetrachloride, 1,2- dichloroethane; 1,2-dichloropropane, dichloromethane, PCE, TCE and vinyl chloride (NDWR, 2009).

In February 2011, it was determined that VOCs would be the first group considered for a new group regulation and as many as 16 VOCs would be grouped. Besides the currently regulated VOCs, the following chemicals would potentially be regulated: aniline, benzyl chloride, 1,3-butadiene, 1,1-dichloroethane, nitrobenzene, oxirane methyl, 1,2,3-trichloropropane, urethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, 1,2-Dibromo-3-chloropropane (DBCP) and 1,2-Dibromoethane (EDB).

While the US EPA is considering to regulate VOCs as a group, it is simultaneously about to review the regulation of TCE and PCE with anticipation that they would provide stricter regulation on these chemicals due to scientific advances. This would imply that the MCL would be much lower than 5µg/L, possibly in the sub-microgram to nano-gram per liter level.

2.3 VOC Remediation Technologies

In light of their detrimental nature to the environment and public health, several removal technologies have been developed to alleviate VOC pollution. The technologies can be divided up into two categories: non-destructive or destructive (transformative) technologies (Huang et al, 2014). Non-destructive technologies do not chemically change the VOC but rather transfer the VOC from one phase to another. These removal processes take advantage of the physical properties particularly the high volatility and hydrophobic nature of VOCs. These technologies include adsorption and air stripping which are also regarded by the US EPA as the best available technology (BAT). The transformative technologies involve bond breakage and results in the formation of new products. These transformative technologies can be divided into three categories thermal incineration and natural degradation, advanced oxidation processes and reduction methods.

2.3.1 Adsorption

This process involves the use of adsorptive media such as granular activated carbon where VOCs are transferred from the liquid phase to the solid phase. This remediation technology is highly regarded because it is robust (Huang et al, 2014) and effective for removal of gaseous VOCs at low concentrations and works equally well with high aqueous concentrations. However, this technology requires the costly process of regenerating the used carbon or the spent carbon has to be disposed of safely. In addition, adsorption on GAC could be inefficient when handling low aqueous VOC concentrations (US EPA, 1990).

2.3.2 Packed Tower Aeration

This technology leverages the low aqueous solubility of VOCs in that air is purged through the solution and the VOCs are released into the air (Huang et al, 2014). Like adsorption, its effective at relatively high aqueous concentrations and the VOC-laden air has to be dealt with safely (US EPA, 1990).

2.3.3 Thermal Incineration and Natural Degradation

Thermal incineration involves the use of high heat to destroy VOCs. However, VOCs are not highly flammable and thus a large amount of heat energy is required (temperatures up to 1000°C) for complete destruction. This adds tremendously to the cost of the process including the capital cost required to build thick-walled incinerators (Huang et al, 2014). Highly toxic products such as polychlorinated dibenzodioxins and chlorinated dibenzofurans can be produced, limiting the use of combustion (Munter, 2011).

There are also microorganisms that can degrade VOCs to less harmful products but VOCs due to their toxic nature are not the sole carbon source of these microorganisms. There is need for these micro-organisms to first acclimate to their VOC laden environment before they can adapt to consuming VOCs. Even then, the likelihood of inhibition of these microorganisms can slow down or halt degradation (Huang et al, 2014).

2.3.4 Advanced Oxidation Processes (AOPs)

AOPs can proceed via two reaction pathways-the first involves using oxygen at high temperature (200 to 300°C) and pressure (1 to 20 MPA). The second pathway involves high energy oxidants such as hydrogen peroxide and ozone with or without photons with a purpose of producing highly reactive OH radicals. The latter pathway takes different forms which could be either photochemical or non-photochemical. These processes include ozonation at a high pH, ozone/H_2O_2, Ozone/Catalyst, Fenton process (H_2O_2/Fe^{2+}), Photo Fenton, Ozone/ UV, UV/H_2O_2 and photocatalytic oxidation (Munter, 2011). The OH radicals formed react with organic contaminants, breaking them down to form new products. The reaction mechanism is explained in detail in Section 2.4.

Numerous laboratory and pilot studies have been performed on the applicability of VOC removal in the United States and Europe. In the United States, a thorough investigation of VOC remediation was undertaken by Ultrox International in conjunction with the US EPA. The study looked at the effectiveness of an onsite UV/Ozone/H_2O_2 system in removing VOCs from groundwater located at identified superfund sites (US EPA, 1990). In Finland, feasibility studies on the removal of PCE and TCE from an aquifer using Ozone/H_2O_2 and UV/H_2O_2 were performed (Hirvonen et al, 1996). AOPs are gaining popularity due to the diversity of water contaminants they can remove. They have the ability to not only remove recalcitrant organics but also various types of pathogenic microorganisms.

2.3.5 Reduction Methods

There are also innovative methods that have recently been developed to remediate VOCs. These methods use the electronegativity nature of chlorine. They make use of electron donors that can provide electrons to form non-chlorinated products and chloride ions which can be removed in aqueous solutions. These reduction technologies include zero valent metal and bimetal reduction, catalytic hydrodechlorination and electrochemical reduction (Huang et al, 2014).

2.4 Advanced Oxidation Process: UV/H_2O_2

2.4.1 Concept

Hydrogen peroxide-assisted oxidation has shown to degrade a broad suite of organic contaminants. UV light in the UVC region (wavelengths between 200nm-280nm) is used to break apart hydrogen peroxide to leverage the oxidative power of hydroxyl radicals that subsequently react with the targeted compounds (Crittenden and Hu, 1997). These OH radicals then react with organics either by OH radical addition or H abstraction (Von Sontaag, 1997 cited by Chen et al, 2006). These reactions can be seen below:

$H_2O_2 + h\upsilon \rightarrow \bullet OH + \bullet OH$ (Primary photolysis of H_2O_2)

$\bullet OH + R_2C{=}CR_2 \rightarrow R_2(HO)C\text{-}CR_2$ (OH radical addition)

$\bullet OH + RH \rightarrow H_2O + \bullet R$ (H abstraction)

There are two common UV sources that can be used to degrade these chemicals namely low and medium pressure mercury arc lamps. The low pressure (LP) lamp emits monochromatic light at 254nm while a medium pressure (MP) lamp emits polychromatic light from approximately 200 to 400nm. This research uses low pressure lamps.

2.4.2 Modeling

2.4.2.1 Modeling OH radical based Oxidation

To describe the degradation of a VOC by OH radicals, the indirect photolysis rate constant (k’$_i$) for the reaction between the VOC and OH radicals is determined. The mathematical definition of OH radical based degradation can be seen in Equation 1 (Sharpless and Linden, 2003).

$$-\frac{d[VOC]}{dt}=k'_i[VOC]=k_{OH}[\bullet OH]_{SS}[VOC] \quad \text{(Equation 1)}$$

As can be seen from Equation 1, k’$_i$ is the product of the OH radical steady state concentration ($[\bullet OH]_{ss}$) and the second order rate constant of the VOC and OH radicals (k_{OH}). The OH steady state concentration is the ratio of the rate of formation of OH radicals by the UV/H_2O_2 mechanism to the rate of consumption of OH radicals by scavenger species in the water. The mathematical definition of this concentration can be seen in Equation 2 (Sharpless and Linden, 2003).

$$[OH]_{ss}=\frac{\sum K_{a,H202}(\lambda)^{*}\phi_{OH}*[H_2O_2]}{\sum_i k_{s,i}\,[S]} \qquad \text{(Equation 2)}$$

From equation 2, $ka_{,H2O2}$, is a term representative of the UV light absorbed by hydrogen peroxide, $\Phi_{\bullet OH}$ is the quantum yield for photolysis of H_2O_2 into 2•OH radicals (taken as 1 for the region below 300 nm) and $k_{s,i}$ are pseudo-first-order rates of reaction of •OH with scavengers ([S]). In this research study, where ultra-pure water was used, the scavengers included hydrogen peroxide and the VOC itself due to its high concentration of 5000µg/L. The $ka_{,H2O2}$ is further mathematically defined in equation 3 (Sharpless and Linden, 2003) .

$$k_{a,H202}(\lambda)=\frac{\sum_\lambda E_p^0(\lambda)*\varepsilon_{H202}(\lambda)[1-10^{-(a(\lambda)+\varepsilon_{H202}(\lambda)[H202])z}}{(a(\lambda)+\varepsilon_{H202}(\lambda)[H202])z} \quad \text{(Equation 3)}$$

In equation 3, E^0p is the incident photon irradiance (10^{-3} Einstein cm^{-2} s^{-1}), ε (λ) is the decadic molar absorption coefficient of VOC (M^{-1} cm^{-1}), a (λ) is the solution absorbance (cm^{-1}) and z is the depth of the sample (cm). The molar absorption coefficient is a parameter that describes the amount of light absorbed per unit concentration per path length. This parameter is vital in calculating the quantum yield of the chemical and is further explained in section 2.4.2.2.

Equation 1 can be integrated to establish equation 4 below. With this equation, the natural logarithm of the ratio of the concentration at an exposure time, t to the concentration at t=0 was determined and plotted against time. The experimental slope of k'i, can be compared to the predicted k'i which is a product of the second order reaction rate constant (k_{OH}) and the OH radical steady state concentration.

$$\mathbf{Ln\left(\frac{[VOC]}{[VOC_0]}\right) = -k'_i * t = -k_{OH} * OH_{SS} * t} \qquad \text{(Equation 4)}$$

2.4.2.2 Modeling Degradation by UV only

During a UV-based advanced oxidation process, there is a possibility that UV light at 254nm can be absorbed by the targeted VOC. Like OH radical based oxidation, the degradation of the VOC using UV light only can be described by determining the pseudo first order rate constant for direct photolysis (k'_d). The degradation trend is defined mathematically in Equation 5 (Sharpless and Linden, 2003).

$$-\frac{d[VOC]}{dt} = k'_d[VOC] = \left(\sum\nolimits_\lambda k_s(\lambda)\right) * \phi * [VOC] \; \text{(Equation 5)}$$

In these equations, k'_d is the pseudo first order rate constant for direct photolysis (s^{-1}), $k_s(\lambda)$ is the specific rate of light absorption by the VOC (Einstein mol^{-1} s^{-1}) and Φ is the quantum yield for removal (mol $Einstein^{-1}$). The k_s (λ) is further defined in Equation 6 (Sharpless and Linden, 2003).

$$\boldsymbol{k_S\,(\lambda) = \frac{E_P^0(\lambda)*\varepsilon(\lambda)*[1-10^{-a(\lambda)z}]}{a(\lambda)*z}} \quad \text{(Equation 6)}$$

In equation 6, the E^0p is the incident photon irradiance (10^{-3} Einstein cm^{-2} s^{-1}), ε (λ) is the decadic molar absorption coefficient of VOC (M^{-1} cm^{-1}), a (λ) is the solution absorbance (cm^{-1}) and z is the depth of the sample (cm).

Equation 5 can also be integrated to establish Equation 7. With this equation, a plot of Ln ([VOC]/ [VOC_0]) against time can be plotted with slope k'_d.

$$\boldsymbol{Ln\left(\frac{[VOC]}{[VOC_0]}\right) = -k'_d * t} \quad \text{(Equation 7)}$$

The quantum yield in equation 5 is an inherent property of a chemical and is defined as the moles of chemical transformed divided by the moles of photons *absorbed* and can be calculated using equation 8. For direct photolysis to occur, a chemical must absorb photons and these photons would need to be bring about transformational change. The efficiency of this process is described by the quantum yield (Rosenfeldt and Linden, 2004). Also, it is important to note that the quantum yield of decay is less than or equal to 1 as photons cannot be shared and the photon-molecular interaction is a 1: 1 ratio. From equation 8, it can be seen that the quantum yield is a function of the degradation rate constant and molar absorption coefficient.

$$\boldsymbol{\Phi(\lambda) = \frac{k'_d}{\sum_\lambda \frac{E_P^0(\lambda)*\varepsilon(\lambda)*[1-10^{-a(\lambda)z}]}{a(\lambda)*z}}} \quad \text{(Equation 8)}$$

2.4.2.3 Assessing Volatilization

As previously stated, VOCs can easily vaporize and thus there is a possibility that during UV exposure and solution transfers, there could be an inherent loss of VOC that can lead to pseudo degradation trends. Research studies such as the study done by Dilling et al (1975) investigating the evaporation rates of 1000 mg/L methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene show that the aqueous solutions, stirred at 200 rpm in an open container at 25 C reduce by 50% in 30 minutes and by 90% in 90 min. Therefore, it was necessary to investigate the extent of volatilization of these chemicals during UV exposure experiments despite the solutions being stored with no headspace.

Quantifying volatilization requires the use of a mass transfer model such as the two film theory which is based on the idea that there are two films around the boundary (or interface) of two phases, in this case gaseous and liquid. Depending on the resistance of each film in each phase, there will be a dominating direction of flow. In the case of highly volatile chemicals, the resistance is in the liquid, resulting in the transfer of chemicals to the gaseous phase (Roberts and Daendllker, 1983). In this research, however, characterization of volatilization was not the main objective but rather assessing the extent of volatility and deciding if this factor had a substantial impact on the results collected during direct and indirect photolysis experiments. The investigation was done by establishing the exact experimental set up as with the UV exposure experiments except no UV was present. The concentration of VOC was monitored at different times equivalent to the exposure times if UV was present. The results were also modeled similarly as shown in Equation 9 where k'_v is *simplistically* regarded as the VOC removal constant.

$$\boldsymbol{Ln\left(\frac{[VOC]}{[VOC_0]}\right) = -k'_V * t} \text{ (Equation 9)}$$

2.4.2.4 Determination of the direct and indirect photolysis rate constants from experimental data

During UV/H_2O_2 experimentation, a conservative assumption of three different processes is made and therefore, the aggregated removal of a VOC is mathematically defined as in Equation 10 (Sharpless and Linden, 2003).

$$\frac{-d[VOC]}{dt} = (k'_i + k'_d + k'_v)[VOC] \text{ (Equation 10)}$$

To determine the value of k'_i, k'_d and k'_v should be subtracted from the overall rate of degradation for the UV/ H_2O_2 advanced oxidation process. The result can then be compared to the product of the established k_{OH} and the OH radical steady state concentration. In addition, during a UV only experiments, two processes are taking place and the aggregated removal of the VOC is mathematically defined as in Equation 11 (Sharpless and Linden, 2003). The true value of k'_d is determined by subtracting k'_v from the overall rate of degradation.

$$\frac{-d[VOC]}{dt} = (k'_d + k'_v)[VOC] \text{ (Equation 11)}$$

3. Methods and Materials

3.1 Materials

Benzene, trichloroethylene, tetrachloroethylene, 1,1,2,2-tetrachloroethane, 1,1,1,2-tetrachloroethane, 1,1-dichloroethane, 1,2-dichloroethane, dichloromethane, carbon tetrachloride, 1,2-dichloropropane and 1,2,3-trichloropropane were purchased from Sigma Aldrich. The chemicals were purchased as neat solvents and used as received.

3.2 Photolysis Experiments

Stock solutions of each VOC were prepared using ultrapure water (with a resistivity of 18 MΩ cm). The concentrations of the stock solutions were no greater than half the solubility limit to ensure complete dissolution. For each VOC, an aliquot of the stock solution was added to a one gallon bottle to make a standard solution of 5000µg/L with no headspace. The volumes used to prepare the 5000 µg/L can be seen in Appendix A3. The solution was then decanted into twelve sealed 300 ml bottles with no headspace. Each bottle represented a sample to be exposed at a predetermined UV dose. 1mL of 5000 ppm hydrogen peroxide was added to half a dozen of the bottles before each UV exposure for OH radical oxidation. The concentration of 15 mg/L hydrogen peroxide was achieved and verified (Klassen et al, 1994).

The UV exposure experiments were carried out in a bench scale UV "collimated beam" apparatus as shown in Figure 2. Four LP UV lamps (15 watt, #G15T8) are enclosed in a shutter box and the sample is placed a specified distance (12.5 cm) below the shutter. The incident UV irradiance in W/cm^2 was measured using a radiometer (International Light Inc., Model 1700/SED 240/W).

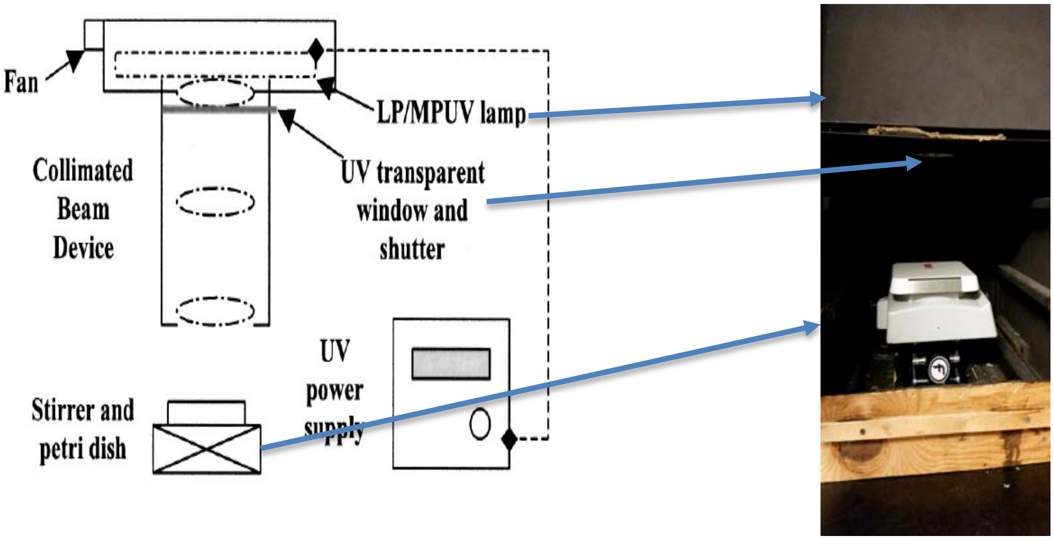


Figure 2: Schematic and picture of UV reactor [Source of Schematic: Bolton and Linden, 2003]

For each exposure, a sample from the 300 mL bottle was transferred into a 285 ml-quartz vessel with no headspace. This fused quartz vessel has two nipples providing access to add and remove samples following UV exposure. The vessel can be seen in Figure 3.

Figure 3: Quartz vessel customized for VOC samples

The sample was irradiated with gentle stirring by a magnetic stirring bar. The sample was then exposed to UV fluences of up to 1600 mJ/cm^2 by varying the exposure times. The exposure times were determined by a spreadsheet program that accounted for the type of lamp, solution absorbance, incident irradiance as well as the fundamental factors that affect the irradiance on the sample namely the divergence, reflection and petri factors. The calculation of these factors can be seen in Appendix A1. All the values were logged into the spreadsheet program to determine the average irradiance; amount of UV irradiance delivered throughout the sample. The desired fluence is divided by the average irradiance to determine the exposure time needed. The addition of hydrogen peroxide in one half of the sample set was accounted for in the spreadsheet program by adjusting the solution absorbance at 254nm which is higher than the sample without hydrogen peroxide. In this way, the same UV dose could be delivered to the samples with the addition of hydrogen peroxide.

3.3 Analytical Methods

For each irradiated sample, two 42 ml samples were removed from the quartz vessel and directly placed in 40-mL vials up to the brim and capped with screw caps with a polytetrafluorethylene (PTFE) septum. For the hydrogen peroxide based oxidation, 15 mg/L of bovine catalase was added (achieving a 1: 1 ratio with hydrogen peroxide) for quenching. Bovine catalase was chosen as the quenching agent based on a research study by Keen et al (2013). In this study, it was concluded that bovine catalase was the ideal quencher for samples that would be used for any subsequent toxicity assays-an element that was taken into account in a side study.

The vials were then placed in an auto-sampler (SOLATek 72). The auto sampler then transferred a 5mL liquid sample to a purge-and-trap concentrator (Stratum PTC). Samples were purged by bubbling helium (inert gas) to initiate volatilization, and concentrated in a cooled sorbent tube that condenses the VOCs. When purging was complete, the sorbent tube was heated and back flushed with helium to desorb trapped sample components onto the capillary gas chromatography column. The column was temperature controlled to separate the method’s analytes which are subsequently detected with a flame ionization detector (Agilent 7890a, GC-FID) for identification and measurement of the VOCs. Calibrations were made by analyzing aqueous dilutions of the VOC that were 10 to 500 times greater in concentration than the detection limit range of 5 to 10 μg/L. The corresponding peak areas at a particular retention time were produced after which a plot of the peak area against the concentration was made to establish a mathematical relationship. This standard curve was then used to determine the concentration of the UV exposed samples and compare the concentrations to the starting concentration of 5000 µg/L. Further details of the operating parameters of the analytical instrumentation can be found in Appendix A2.

The degradation trends of the VOCs were evaluated by plotting the natural logarithm of the ratio of the concentration at an exposure time, t to the concentration at t=0 against fluence. The degradation rate constant was determined from the slope.

The peak areas of the duplicate samples were further analyzed by assessing the linearity of the averaged data using the coefficient of determination (r^2) as well as determining any statistical differences between the two sets of data from the "p-value" of the t-test. If the p-value is less than 0.05 the data is statistically different and if the p-value is greater than 0.05, the results are not statistically different. Both values were calculated using an excel spreadsheet program. For the t-test, a *two tailed distribution* and a *two-sample of unequal variance* were selected as the pre-set conditions in Excel.

The solution absorbance at 254nm was determined using a UV 100 Cary Spectrophotometer and 1 cm quartz vial. This parameter is vital for determining the exposure time in photolysis experiments as well as the molar absorption coefficient-a parameter needed for the calculation of the quantum yield. This paramter was accounted for in this study by taking a full wavelength scan of the sample and logging the absorbance data into the spreadsheet model.

The molar absorption coefficients of the VOCs were determined by making different concentrations of the VOC and measuring the absorbance at 254nm after which a plot of absorbance against concentration was created. The slope of the graph was representative of the molar absorption coefficient. The data collected for these experiments can be seen in Appendix B1.

3.4 Volatilization Control Experiments

These experiments were set up exactly the same way as that of the UV exposure experiments except no UV was present. Varying times equivalent to exposure times if UV was present were used. The same analytical procedure was also applied and an experimental removal constant (k_v) was determined.

4. Results and Discussion

4.1 Molar Absorption Spectra

Table 3 shows the molar absorption coefficients of the 11 VOCs investigated at 254nm. The aromatic organic, benzene and the chlorinated alkenes, tetrachloroethylene and trichloroethylene have the highest molar absorption coefficients. The chloroethanes are in between the double bonded organics and the chloropropanes, which seem to absorb UV light the least. The chloromethanes are scattered in their molar absorptivity with carbon tetrachloride having a significantly higher molar absorptivity than dichloromethane. This order of extinction coefficients indicates that benzene, trichloroethylene and tetrachloroethylene can likely be degraded by UV alone followed by carbon tetrachloride, chloroethanes and chloropropanes.

Table 3: Molar absorption coefficient of VOC at 254nm

VOC	Molar Absorption Coefficient (M^{-1} cm^{-1})
tetrachloroethylene	204.98
benzene	130.61
trichloroethylene	7.39
carbon tetrachloride	5.77
1,1,2,2-tetrachloroethane	4.87
1,1,1,2- tetrachloroethane	1.83
1,2-dichloroethane	1.32
dichloromethane	0.84
1,1-dichloroethane	0.48
1,2,3-trichloropropane	0.36
1,2-dichloropropane	0.18

The VOC plots of the molar absorption coefficient across the wavelength range from 200 to 300nm in Figure 4 shows an increase in the molar absorptivity of carbon tetrachloride, 1,1,2,2-tetrachloroethane, 1,1,1,2-tetrachloroethane along with trichloroethylene and tetrachloroethylene. Benzene shows a decreasing trend below 254nm and then starts to increase below wavelengths of

220nm. This increase in the molar absorptivity of several of the chlorinated organics is indicative that the use of a medium pressure lamp can potentially improve the degradation of the VOCs as it has emission peaks across the 200-300nm range (Sharpless et al, 2003). However, before the use of a medium pressure lamp, attention should be paid to the species in the groundwater particularly nitrate ions. Nitrate strongly absorbs UV below 240nm resulting in the formation of nitrite and OH radicals (Sharpless et al, 2003). Initially the OH radical formation could help in the degradation but over time, accumulating nitrite will scavenge the OH radicals possibly leading to lower degradation rates. The use of either low or medium pressure lamps to remediate specific compounds should be coupled with knowledge of native groundwater constituents to determine the most efficient UV source.

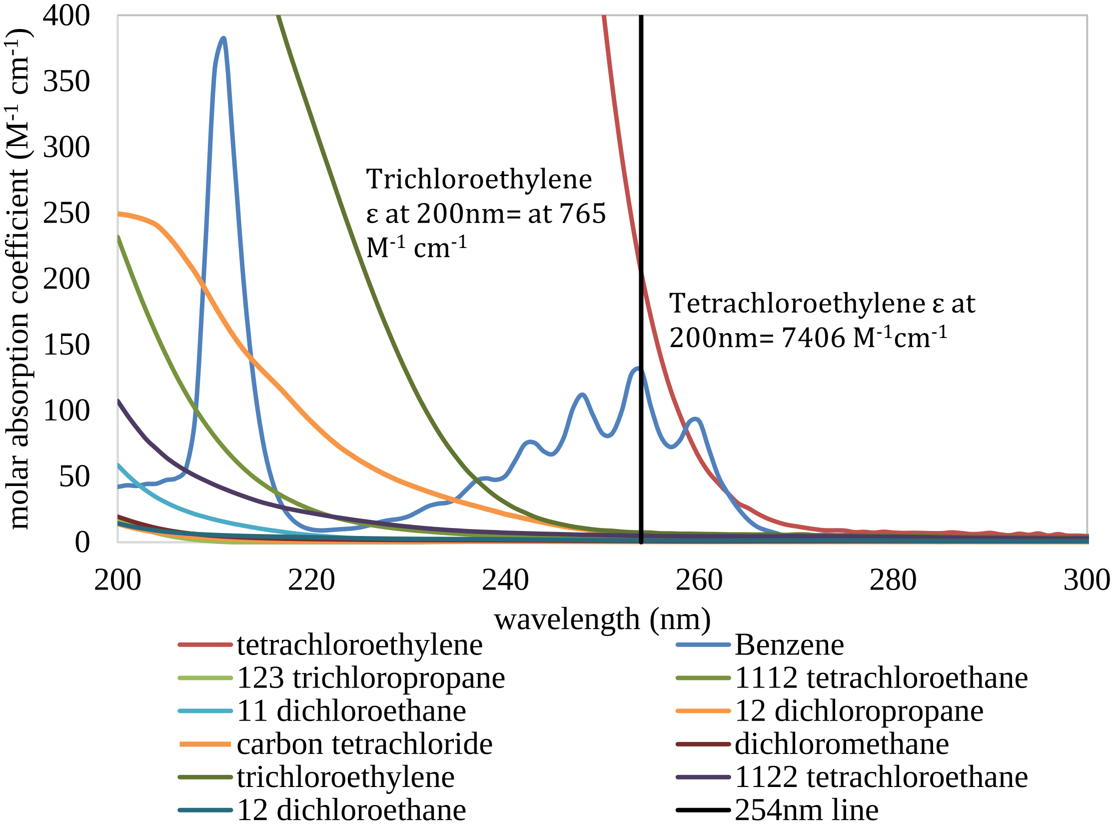


Figure 4: The molar absorption spectra of the VOCs between 200 and 400 nm

4.2 Degradation of VOCs by UV Photolysis

All the 11 VOCs were first evaluated for degradation by UV alone. Degradation trends were determined by calculating the natural logarithm of the ratio of the concentration at an exposure time, t to the concentration at t=0. This value was then plotted against the fluence measured in units of m J/cm^2. The quantum yields were also calculated to evaluate the potential degradation efficiency of the VOCs.

4.2.1 General Trend

Figure 5 shows the degradation trends of the VOCs when exposed only to UV light at 254nm up to a fluence of approximately 1200 mJ/cm^2 which is in the range used by municipal water treatment facilities to remediate organic contaminants. Four out of the 11 VOCs show no degradation with their trend lines slightly above or around the zero axis. These VOCs include 1,1-dichloroethane, 1,1,1,2-tetrachloroethane, 1,2,3-trichloropropane and dichloromethane. The rest of the 7 VOCs show some degradation. Tetrachloroethylene degrades the fastest while benzene, trichloroethylene, 1,1,2,2 tetrachloroethane, 1,2-dichloroethane, 1,2-dichloropropane and carbon tetrachloride have similar degradation rates. With the exception of 1,2-dichloropropane, these degrading VOCs also have the highest molar absorption coefficients in the group. The overall decay of a compound is a function of the quantum yield (parameter that describes the degradation efficiency) and molar absorption coefficient. Therefore, the molar absorption coefficient may be indicative of UV photolysis of a VOC.

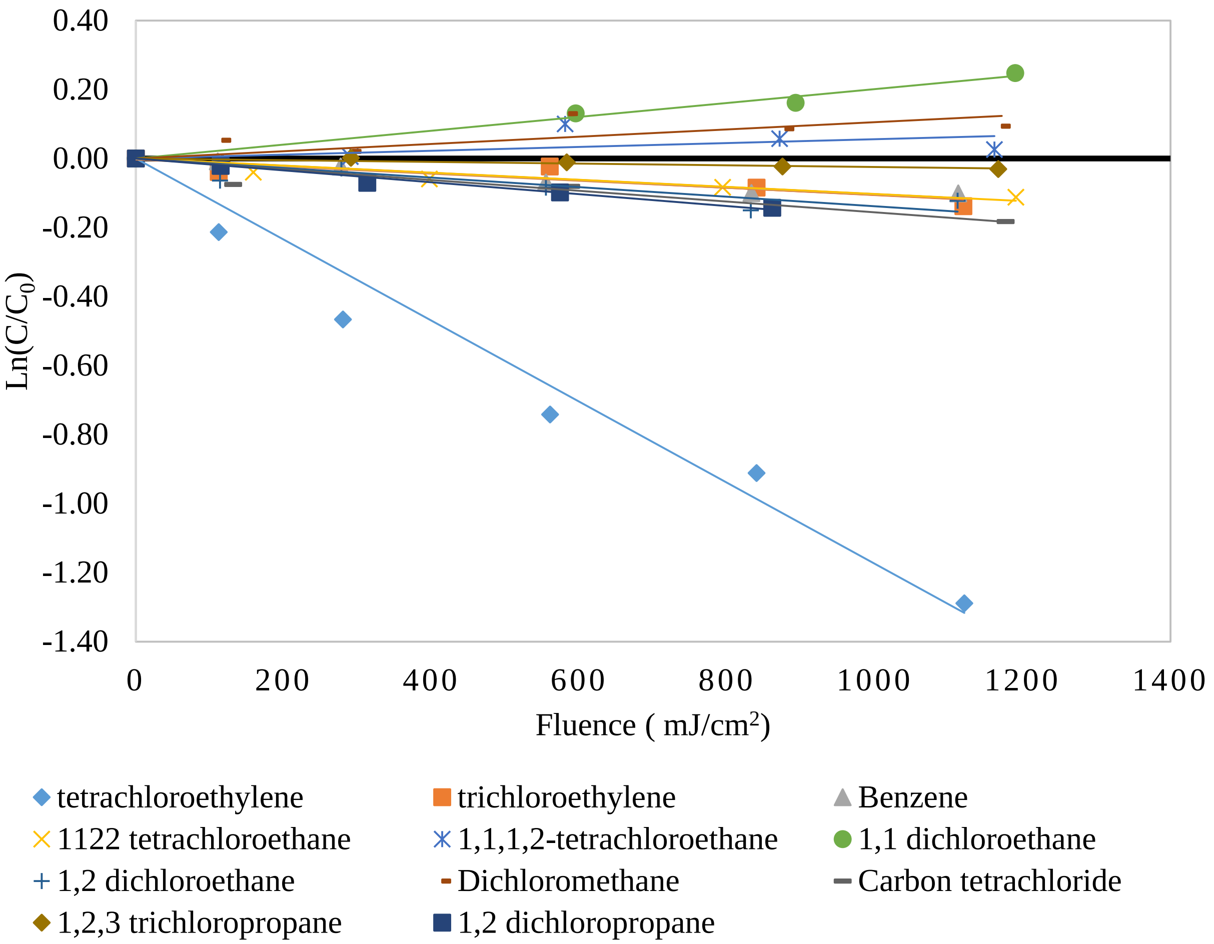


Figure 5: VOC removal during UV photolysis

The validity of the degradation trends was statistically analyzed by evaluating how well the data fit a trend line and whether the duplicate set of peak area data was statistically different. Therefore, the coefficient of determination (r^2) and the p-value of the t-test were calculated. These values are presented in Table 4 along with the corresponding degradation rate constants of the VOCs.

Table 4: The UV direct photolysis degradation constants, coefficient of determination and p-value of VOCs

VOC	k'$_d$ (cm^2/mJ)	R^2	p-value
Benzene	-1.023E-04	0.9438	0.4564
tetrachloroethylene	-1.073E-03	0.9653	0.9472
trichloroethylene	-1.028E-04	0.7946	0.9840
1,1,2,2-tetrachloroethane	-8.500E-05	0.8651	0.9442
1,1,1,2-tetrachloroethane	3.625E-05	0.0883	0.2662
1,1 dichloroethane	2.007E-04	0.9833	0.9186
1,2 dichloroethane	-1.135E-04	0.7047	0.4482
Dichloromethane	7.632E-05	0.3826	0.3606
Carbon tetrachloride	-1.318E-04	0.8202	0.3987
123-trichloropropane	-2.416E-05	0.7532	-
1,2-dichloropropane	-1.634E-04	0.9767	0.7119

As can be seen from Table 4, 1,1,1,2-tetrachloroethane and dichloromethane have relatively low r^2 values. From figure 5, these VOCs showed no degradation having positive slopes. This degradation trend is as a result of the fluctuating concentrations at different exposure times (See Appendix B2). These factors could be indicative of the instability of these VOCs particularly their natural tendency to quickly volatilize. Dichloromethane is known to diffuse through PTFE tubing even with no headspace (US EPA, 2003).

Table 4 also shows the p-values derived from the statistical analysis of the peak areas of the duplicate samples of each VOC. The p-values observed were greater than 0.05 and thus accepting the null hypothesis that the duplicate set of samples for each VOC were not different in concentration. There is no p-value available for 1, 2, 3-trichloropropane because the two sets of peak area data collected were statistically different with a p-value of 0.013; a value less than the threshold value of 0.05 (See Appendix B2). Therefore one set of peak area data was used to determine the degradation trend of the VOC.

4.2.2 Determination of Quantum Yield

The degradation of the 7 VOCs was further investigated by determining the quantum yield of decay. This was done by using equation 8 explained in Section 2.4.2.2. All the parameters in the equation were determined at 254nm and are presented in Table 5.

Table 5: Quantum Yield Determination at 254nm

	1	**2**	**3**	**4**	**5**	**6**	**7**
k'_d (x 10^{-5} s^{-1})	9.32	84.8	3.34	8.62	11.6	10.3	8.21
incident irradiance (x 10^{-4} W/cm^2)	8.74	8.48	8.92	9.03	9.05	8.28	8.62
Wavelength (x10^{-7} m)	2.54	2.54	2.54	2.54	2.54	2.54	2.54
incident photon irradiance (x 10^{-9} Es cm^{-2} s^{-1})	1.85	1.80	1.89	1.92	1.92	1.76	1.83
molar absorptivity (M^{-1} cm^{-1})	131	205	7.39	4.87	1.32	5.37	0.18
Solution absorbance (cm^{-1})	4.56E-03	4.45E-03	2.29E-04	4.47E-04	1.00E-12	1.00E-12	3.26E-03
Depth of Solution (cm)	7.3	7.3	7.3	7.3	7.3	7.3	7.3
QUANTUM YIELD	**0.174**	**1.04**	**1.04**	**4.03**	**19.79**	**4.7**	**111**

1=Benzene; 2=tetrachloroethylene; 3=trichloroethylene; 4=1, 1, 2, 2 tetrachloroethane; 5=1,2-dichloroethane; 6=carbon tetrachloride; 7=1,2-dichloropropane

As can be seen from Table 5, tetrachloroethylene, benzene, trichloroethylene have relatively lower experimental quantum yields compared to 1,1,2,2-tetrachloroethane, 1,2-dichloroethane, 1,2-dichloropropane and carbon tetrachloride. The higher quantum yields are an anomaly as the quantum yield of decay should be less than or equal to 1. This notion is based on the Stark-Einstein second law of photochemistry that states that photons cannot be shared and the photon-molecular interaction is a 1: 1 ratio. The observed large values could be a mathematical result of the low molar absorption coefficients indicating again the unlikelihood of degradation of these VOCs by UV light at 254 nm. The abnormality of these quantum yields can also be attested by the lack of data in the literature for the quantum yields and the molar absorption coefficients for these VOCs at 254nm.

On the other hand, the quantum yields of benzene, tetrachloroethylene, and trichloroethylene are compared to quantum yields determined by researchers Kang and Lee (1997). These values are 0.075, 0.31 and 0.12 respectively as shown in Table 6. The table also shows the corresponding molar absorption coefficients of benzene, tetrachloroethylene and trichloroethylene as 160, 181 and 8 M^{-1} cm^{-1} respectively. Seeing that the experimental molar absorption coefficients of the VOCs match well with the values found in the literature, the difference in the quantum yield calculations between the literature and experimental values could be as a result of the k'_d variation.

Table 6: Literature and experimental values of quantum yield and molar absorption coefficient (ε) of VOCs susceptible to degradation by UV at 254nm

Chemical	**Experimental Quantum Yield**	**Literature Quantum Yield**	**Experimental ϵ (M^{-1} cm^{-1})**	**Literature ϵ (M^{-1} cm^{-1})**
tetrachloroethylene	1.04	0.31	205	181
Benzene	0.19	0.075	131	160
trichloroethylene	1.04	0.12	7.39	8

4.3 Degradation of VOCs by UV Induced Advanced Oxidation

The VOCs were also evaluated for degradation by OH radicals produced by UV photolysis of hydrogen peroxide. The experimental indirect photolysis rate constant was compared to the predicted rate constant which is the product of the k_{OH} and the OH radical steady state concentration as seen from equation 1 below. This equation was described in section 2.4.2.1.

$$-\frac{d[VOC]}{dt} = k'_i[VOC] = k_{OH}[OH]_{SS}[VOC]$$

4.3.1 General Trend

Figure 8 shows the degradation of the VOCs when exposed to UV light at 254nm in the presence of hydrogen peroxide. Unlike degradation by UV only, it is evident that all the 11 VOCs are degraded by the UV-based AOP with varying degrees of removal. Expectedly, benzene, tetrachloroethylene and trichloroethylene which also showed degradation by UV alone had the highest overall decay rates. The remaining chlorinated alkanes showed similar decay rates with the chloropropanes having the highest decay rate among the group followed by the chloroethanes and chloromethanes. This hierarchy in degradation can be easily explained by the tendency in which OH radicals react. OH radicals react with organics by either adding to a double bond or by abstracting a hydrogen atom bound to a carbon atom. Benzene, trichloroethylene and tetrachloroethylene all have unsaturated bonds and it’s much faster for OH radicals to add to a double bond than to remove a hydrogen atom (Chen et al, 2006).

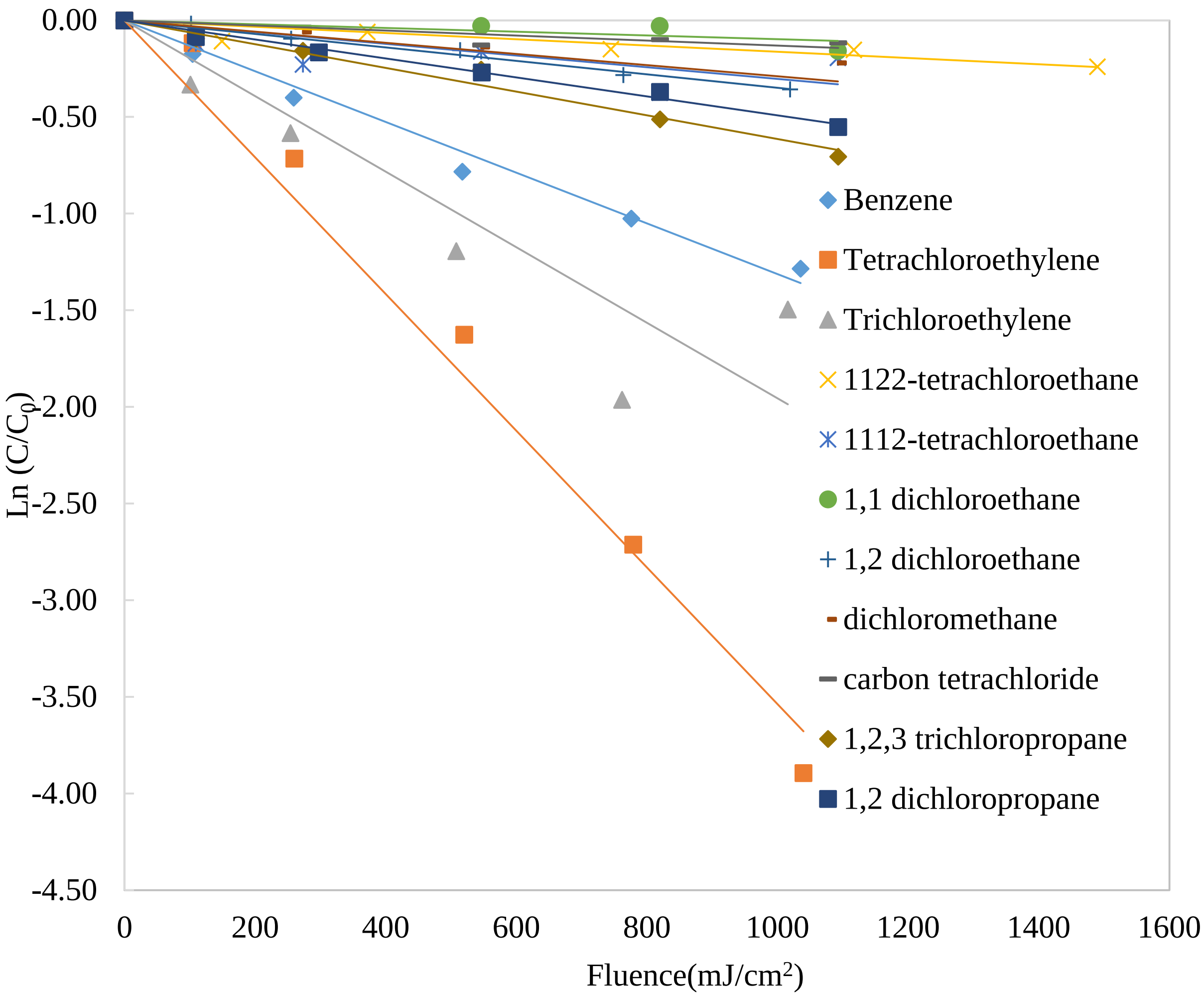


Figure 6: VOC degradation with UV and Hydrogen peroxide

Like direct photolysis experiments, the validity of the degradation trends were statistically analyzed by evaluating the coefficient of determination (r^2) and the p-value of the t-test. These values are presented in Table 7 along with the corresponding degradation rate constants of the VOCs.

Table 7: UV/H_2O_2 degradation rate constants, r^2 and p-values of VOCs

VOC	$k'_{UV+H2O2}$ (cm^2/mJ)	R^2	p-value
Benzene	-1.241E-03	0.9833	0.9216
tetrachloroethylene	-3.811E-03	0.9835	0.9659
trichloroethylene	-1.727E-03	0.8107	0.9661
1,1,2,2-tetrachloroethane	-1.301E-04	0.7439	0.8276
1,1,1,2-tetrachloroethane	-1.896E-04	0.1711	0.3558
1,1 dichloroethane	-1.214E-04	0.605	0.8684
1,2 dichloroethane	-3.612E-04	0.9879	0.9314
Dichloromethane	-2.469E-04	0.5988	0.5891
Carbon tetrachloride	-9.888E-05	0.5658	0.6998
123-trichloropropane	-4.867E-04	0.9767	0.9886
1,2-dichloropropane	-4.717E-04	0.9865	0.9161

As can be seen from Table 7, 1,1,1,2-tetrachloroethane,dichloromethane and carbon tetrachloride have relatively low r^2 values. Dichloromethane and 1,1,1,2-tetrachloroethane also showed a similar trend with UV photolysis indicating again that these VOCs are highly volatile and may not be effectively removed by a UV-based advanced oxidation process. Seeing that the p-values are all greater than 0.05, the duplicate set of peak area data for each VOC was not statistically different and therefore the average peak area was used to establish the degradation trends.

4.3.2 OH radical based Oxidation Modeling

The degradation of VOC using UV/H_2O_2 as seen in Figure 6 is a combination of degradation by UV, OH radicals, and removal possibly due to volatilization. To evaluate the degradation of the VOCs by OH radicals alone, the pseudo first order rate constant for indirect photolysis (k'_i) could be calculated. For each VOC, this rate constant can be found by subtracting the pseudo first order rate constants for direct photolysis and volatilization from the overall rate constant of UV AOP. This value can then be compared to the predicted indirect photolysis rate constant which is the product of the OH radical steady state concentration (calculated using equation 2) and the second order rate constant for the reaction of OH radicals with the targeted compound. Figure 7 shows the comparison of the predicted and experimental indirect photolysis rate constants.

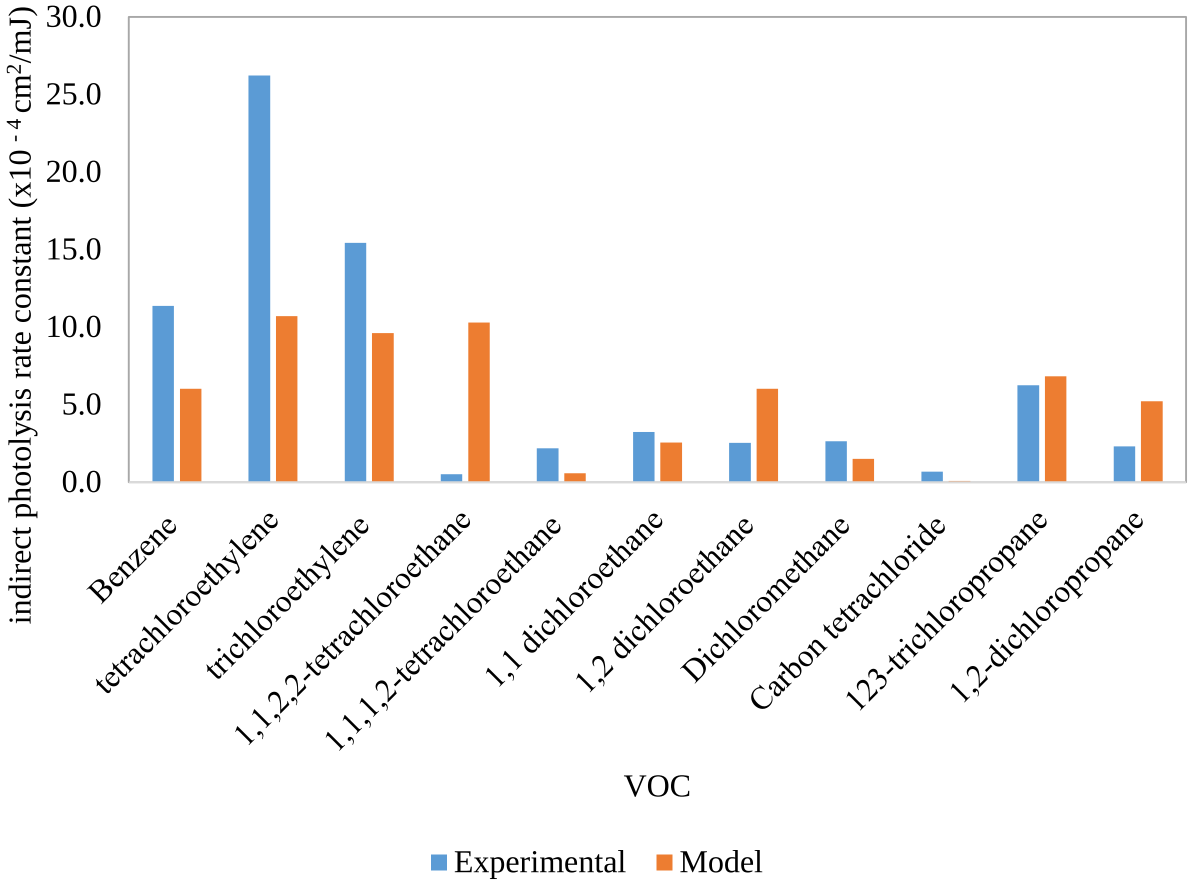


Figure 7: Comparison of experimental and predicted indirect photolysis rate constants

As illustrated in Figure 7, the steady state OH radical model is an accurate predictor of the destruction of VOCs with OH radicals. The chemicals with unsaturated bonds have the highest removal rate compared to those with saturated bonds owing to the fact that OH radicals react faster with double bonded contaminants than saturated organics (Chen et al, 2006). There is a considerable overestimation of the VOC,1,1,2,2-tetrachloroethane as the experimental rate constant is 20 times lower than the predicted rate constant and thus appearing to be an outlier. However, the predicted rate constant for carbon tetrachloride is lower than that of the experimental rate constant for 1,1,2,2 tetrachloroethane followed by 1,1,1,2-tetrachloroethane. The lower level of reactivity of these chemicals can be attributed to their high degree of chlorination. All three VOCs have a number of chlorine atoms. Carbon tetrachloride has four chlorine atoms on one carbon atom, 1,1,1,2 tetrachloroethane has three chlorine atoms on one carbon and 1,1,2,2 tetrachloroethane has two chlorine atoms on one carbon atom. This decreasing trend in the number of chlorine atoms on one carbon atom shows increasing reactivity as suggested in a study by Chen et al (2006).

In addition to their high degree of chlorination, these three VOCs also have the lowest second order rate constants (k_{OH}) and therefore it would be expected that they are the slowest reacting with OH radicals.

4.4 Volatilization Control

Volatilization control experiments were conducted to assess the extent of volatility and determine if this factor had a substantial impact on the results collected during direct and indirect photolysis experiments. The investigation was conducted by establishing the exact experimental set up as with the UV exposure experiments except no UV was present. Figure 8 shows the change in concentration of each VOC at times that are equivalent to exposure times if UV was present.

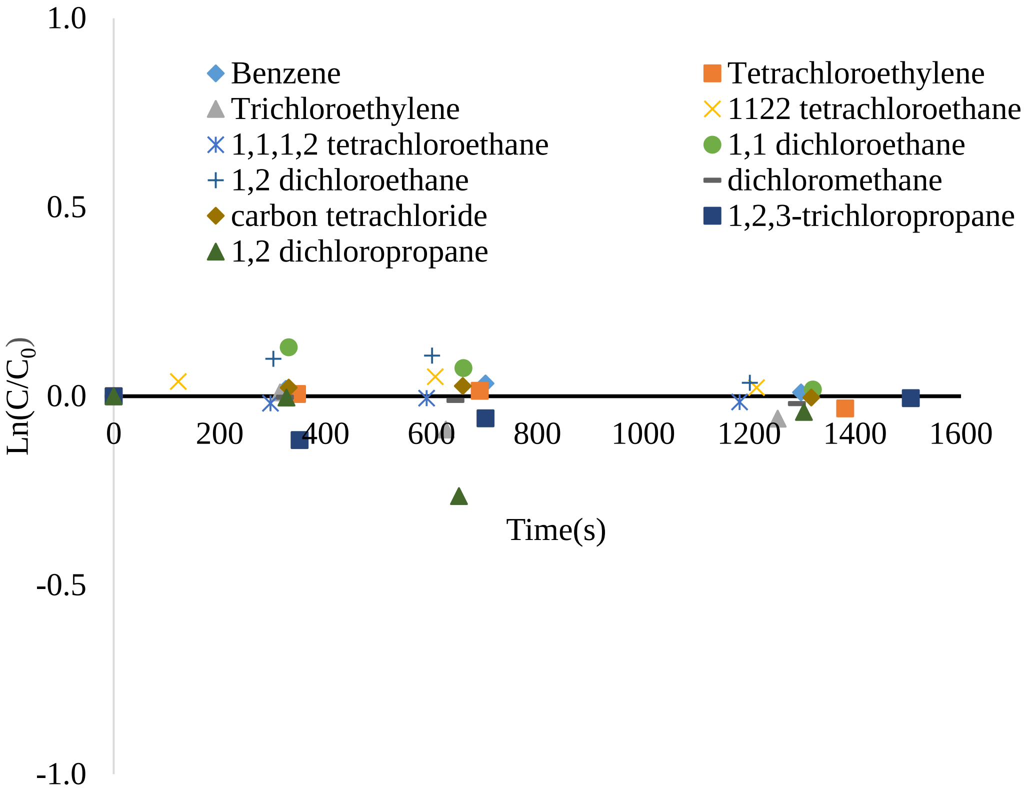


Figure 8: Concentration variation due to volatilization

From Figure 8, it can be seen that there is little or no variation in the concentration as the data points lie around the zero y- axis. This signifies that volatilization was not a substantial factor contributing to the removal of VOCs. However, the same analytical procedure was also applied and an experimental removal constant (k_v) was determined by using the SLOPE function in the excel spreadsheet program. All the VOC removal or degradation constants were then compared and the results of the analysis are presented in Figure 9.

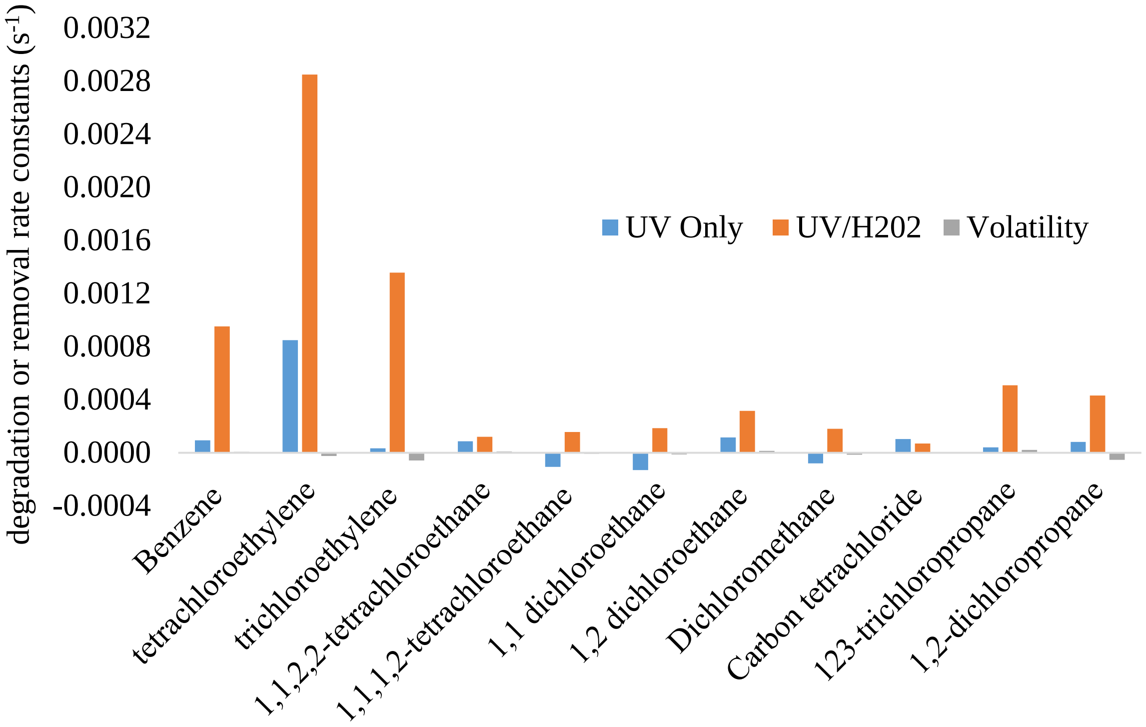
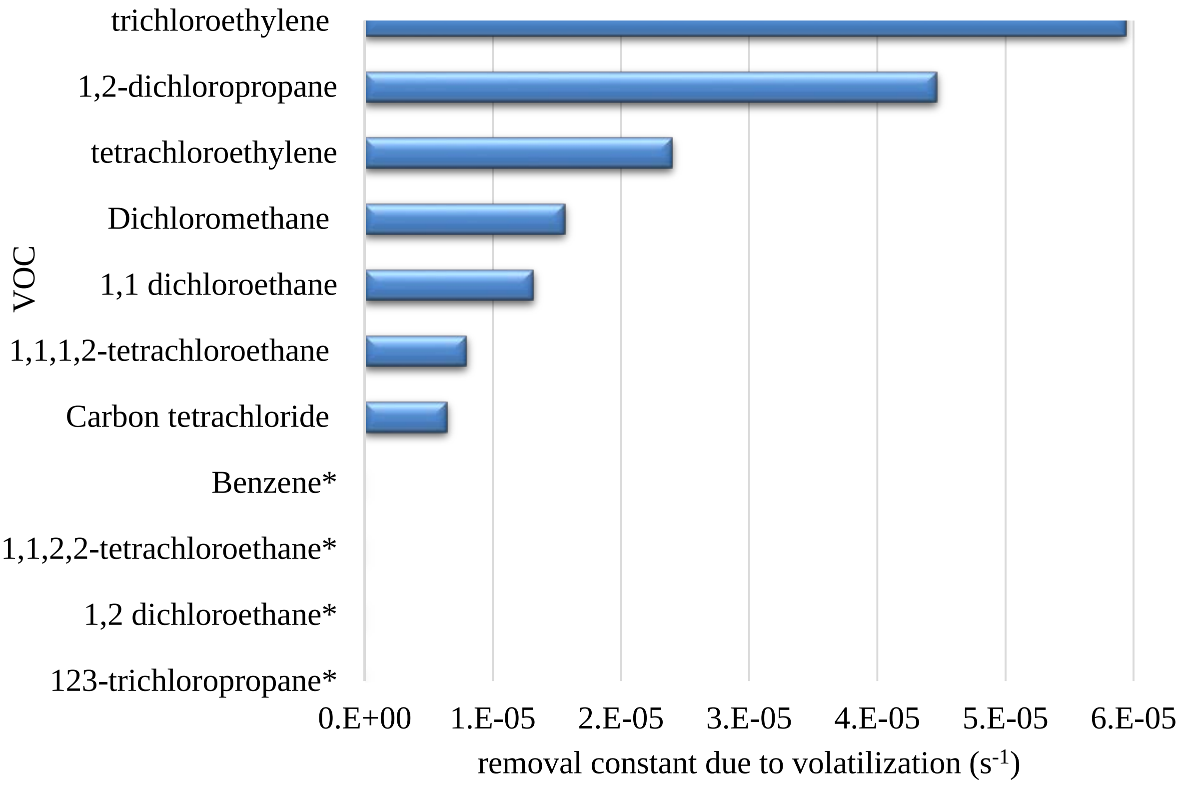


Figure 9: Comparison of removal constants for VOC removal by UV only, UV/H_2O_2 and volatilization

The data presented in Figure 9 confirms that the loss of the VOC due to volatilization during UV exposure runs is rather negligible and thus has very little influence on the degradation by UV and UVAOP.

The removal rate constants due to volatilization were further justified by comparing the increasing magnitude of the values, shown in Figure 10, with the Henry's law constants tabulated in Table 8.



**Removal rate constants are less than zero indicating no loss due to volatilization*

Figure 10: Volatility trend of VOCs based on the removal rate constants, k'$_v$ value

The Henry's law constants were based on equation 12 (Sander, 2014). In this study, the Henry's law constant is the ratio of the molar concentration of chemical (in mol/m^3) in the aqueous phase to the partial pressure (Pa) of the chemical in the gaseous phase at equilibrium.

$$\boldsymbol{H = \frac{C_a}{P}} \quad \text{(Equation 12)}$$

This ratio helps to provide an indication of the volatility of the VOC by comparing how much VOC is in water for a partial pressure of 1 Pascal. This means that the larger the henry's law constant, the more VOC is in the aqueous phase and therefore, the VOC is less volatile.

Table 8: Henry's Law Constants for VOCs

VOC Name	Henry's law Constant (mol/m^3-Pa)
1,2,3 trichloropropane	3.60E-02
1,1,2,2-tetrachloroethane	2.40E-02
1,2-dichloroethane	8.90E-03
1,1,1,2-tetrachloroethane	4.20E-03
dichloromethane	3.60E-03
1,2-Dichloropropane	3.40E-03
Benzene	1.70E-03
1,1 dichloroethane	1.70E-03
trichloroethylene	1.00E-03
tetrachloroethylene	6.20E-04
Carbon tetrachloride	3.40E-04

Comparing the data in Figure 10 and Table 8, both sets of data match fairly well with 1,2,3-trichloropropane, 1,1,2,2-tetrachloroetehane and 1,2-dichloroethane being the least volatile while trichloroethylene and tetrachloroethylene are among the highly volatile VOCs.

5. Degradation in Natural Groundwater

Another objective of this research was to evaluate the degradation of the VOCs in a different water matrix, natural groundwater. With this investigation, three indicator VOCs that is tetrachloroethylene, benzene and 1,2,3-trichloropropane were selected. These VOCs were chosen for their unique degradation trends in ultra-pure water.

The groundwater was first analyzed for total organic carbon (TOC), alkalinity, pH, turbidity, total nitrogen, nitrate, nitrite and phosphate concentrations. These water quality parameters helped to identify OH radical scavengers and their quantity. The groundwater was also analyzed for any VOC in the water by analyzing the GC peaks of the data at the established retention times for the VOCs.

After the groundwater analysis, the strategy outlined in Table 9 was followed to conduct successful UV exposure trials.

Table 9: Experimental Procedure for VOCs in groundwater

Task	Task Description
1	Formulate a stock solution of VOC taking into account the VOC's maximum solubility
2	Create a VOC standard solution of 5000 μg/L in ground water
3	Conduct UV Exposure of 5000 μg/L at different UV doses with and without hydrogen peroxide
4	Place UV exposed and Non-UV exposed samples into two "42ml" vials
5	Develop a standard curve on the GC for the VOC to be analyzed
6	Analyze duplicate samples using Purge Trap/GC set up
7	Based on standard curve developed, determine concentration of sample and compare to original concentration of 5000 μg/L

5.1 Groundwater Quality

The results from the water quality tests for the natural groundwater are presented in Table 10.

Table 10: Groundwater quality

Description	Value
pH	7.94
Alkalinity (mg/L CaCO3)	249
Nitrate (mg/L)	6.70
Nitrite (mg/L)	0.00
TOC (mg/L)	0.517
Phosphate (mg/L)	below the detectable range (<2 mg/L)
Total Nitrogen (mg/L)	7.20
Turbidity (NTU)	0.108

The data presented in Table 10 shows that the groundwater is neutral in PH and the water is clear (very low turbidity). The nitrogen in the water is mainly in the form of nitrate ions with the remaining quantity coming from organic matter.

5.2 Degradation of VOCs by UV Photolysis

Benzene, tetrachloroethylene and 1,2,3-trichloropropane were evaluated for degradation by UV alone. Degradation trends (Ln(C/C_0) against time) were plotted and the degradation rate constants were analyzed.

The data presented in Figure 11 shows the degradation trends of the VOCs when exposed only to UV light at 254nm up to a fluence of 1200 mJ/cm^2. All three compounds show degradation with 1,2,3 trichloropropane having the lowest degradation rate and tetrachloroethylene having the highest degradation rate.

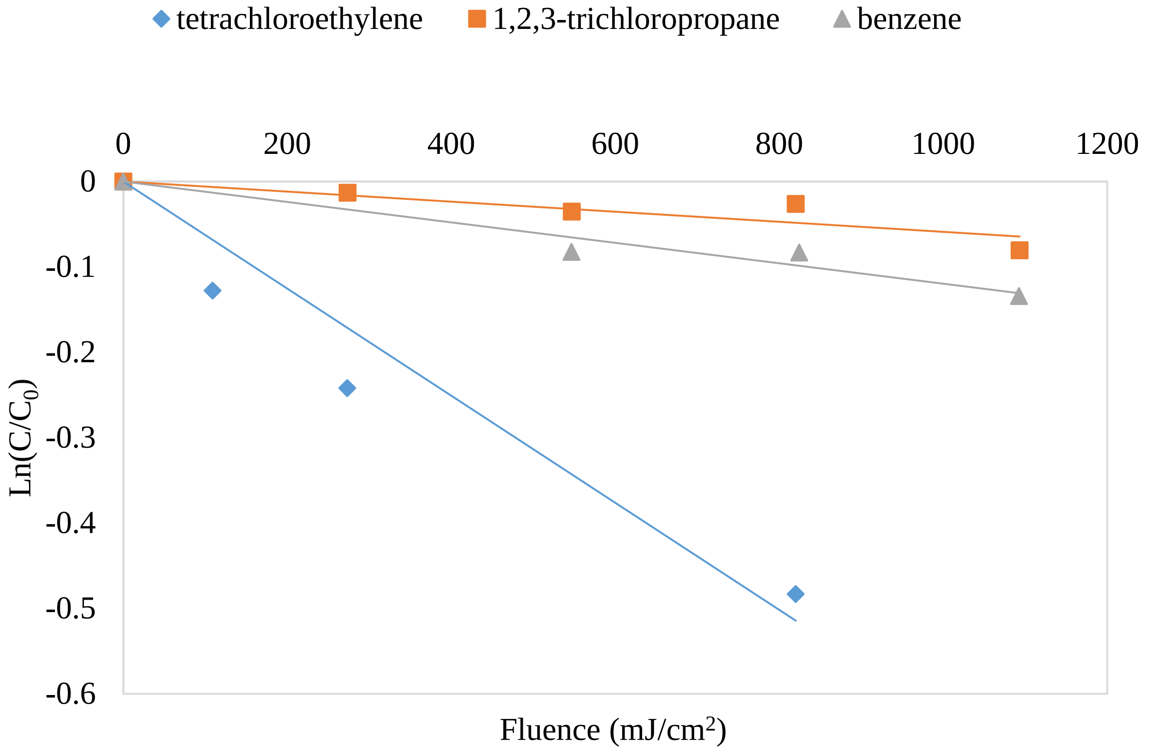


Figure 11: Degradation of VOC induced groundwater using UV only

The degradation rate constants were compared to the degradation rate constants determined for the VOCs in ultra-pure water. These removal rates can be seen in Table 11.

Table 11: Comparison of degradation rate constants of UV photolysis in ultra-pure water and groundwater

	GROUNDWATER		**ULTRA-PURE WATER**	
	Degradation rate constant (cm^2/mJ)	**R^2**	**Degradation rate constant(cm^2/mJ)**	**R^2**
Benzene	-1.15E-04	0.9403	-1.02E-04	0.9833
Tetrachloroethylene	-5.53E-04	0.9250	-1.07E-03	0.9835
1,2,3-trichloropropane	-6.35E-05	0.7966	-2.42E-05	0.9767

From Table 11, it can be seen that the three VOCs have similar rates of degradation in both ultra-pure water and groundwater. The differences in degradation rates could be due to light screening by the chemical species in the water (Sharpless et al, 2003). The preciseness of the degradation rate constants of these VOCs in both waters helps to validate the degradation trends established with ultra-pure water.

5.3 Degradation of VOCs by the UV/Hydrogen Peroxide AOP

The VOCs were also evaluated for degradation using UV and OH radicals produced from the breakdown of hydrogen peroxide. The experimental indirect photolysis rate constant was compared to the predicted rate constant which is the product of the k_{OH} and the OH radical steady state concentration as seen from equation 1 explained in section 2.4.2.2.

5.3.1 General Trend

Figure 12 shows the degradation of the VOCs when exposed to both UV light at 254nm and hydrogen peroxide. Like degradation by UV only, tetrachloroethylene degrades the fastest followed by benzene and lastly, 1,2.3-trichloropropane. This hierarchy in degradation can be explained by OH radicals' reaction mechanism with organics as mentioned earlier. Tetrachloroethylene and benzene have unsaturated bonds and it's much faster for OH radicals to add to a double bond than to remove a hydrogen atom as with 1,2,3-trichloropropane (Chen et al, 2006).

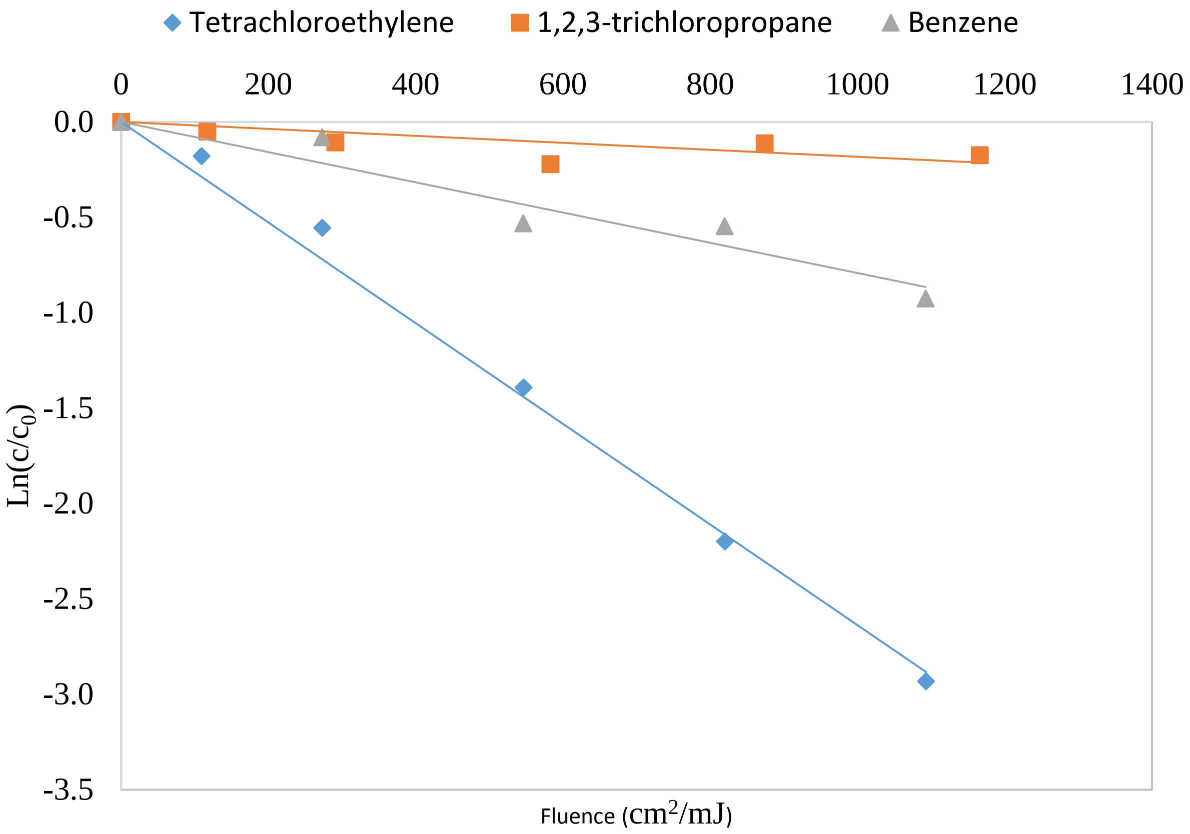


Figure 12: Degradation of VOC induced groundwater using UV and hydrogen peroxide

The degradation rate constants were compared to the degradation rate constants determined for the VOCs in ultra-pure water. These removal rates can be seen in Table 12.

Table 12: Comparison of degradation rate constants by UV and hydrogen peroxide in ultra-pure water and groundwater

UV and HYDROGEN PEROXIDE: DEGRADATION RATE CONSTANTS (cm^2/ mJ)				
	Groundwater	**R^2**	**Ultra-pure water**	**R^2**
Benzene	-8.76E-04	0.9267	-1.13E-03	0.9833
Tetrachloroethylene	-1.15E-03	0.9934	-2.62E-03	0.9835
1,2,3-trichloropropane	-3.51E-05	0.3633	-6.26E-04	0.9767

All three VOCs have lower degradation rate constants in groundwater than in ultra-pure water. The degradation rate constants for benzene and tetrachloroethylene in groundwater match fairly well for benzene and tetrachloroethylene in ultra-pure water. However,1, 2, 3-trichloropropane has a significantly lower degradation rate constant. This significant difference could be due to experimental error as there is also a lower r^2 value for that rate constant. The differences in degradation rates could also be due to light screening by the chemical species in the water and an increase in the OH radical scavengers in the water. As can be seen in Table 10, the groundwater has a high alkalinity of 249 mg/L as $CaCO_3$ which is a significant OH radical scavenger.

5.3.2 OH radical based Oxidation Modeling

The degradation of the three VOCs by OH radicals was evaluated by determining their experimental and predicted pseudo first order rate constants for indirect photolysis. These values were also compared to the degradation constants obtained in ultra-pure water as shown in Figure 13.

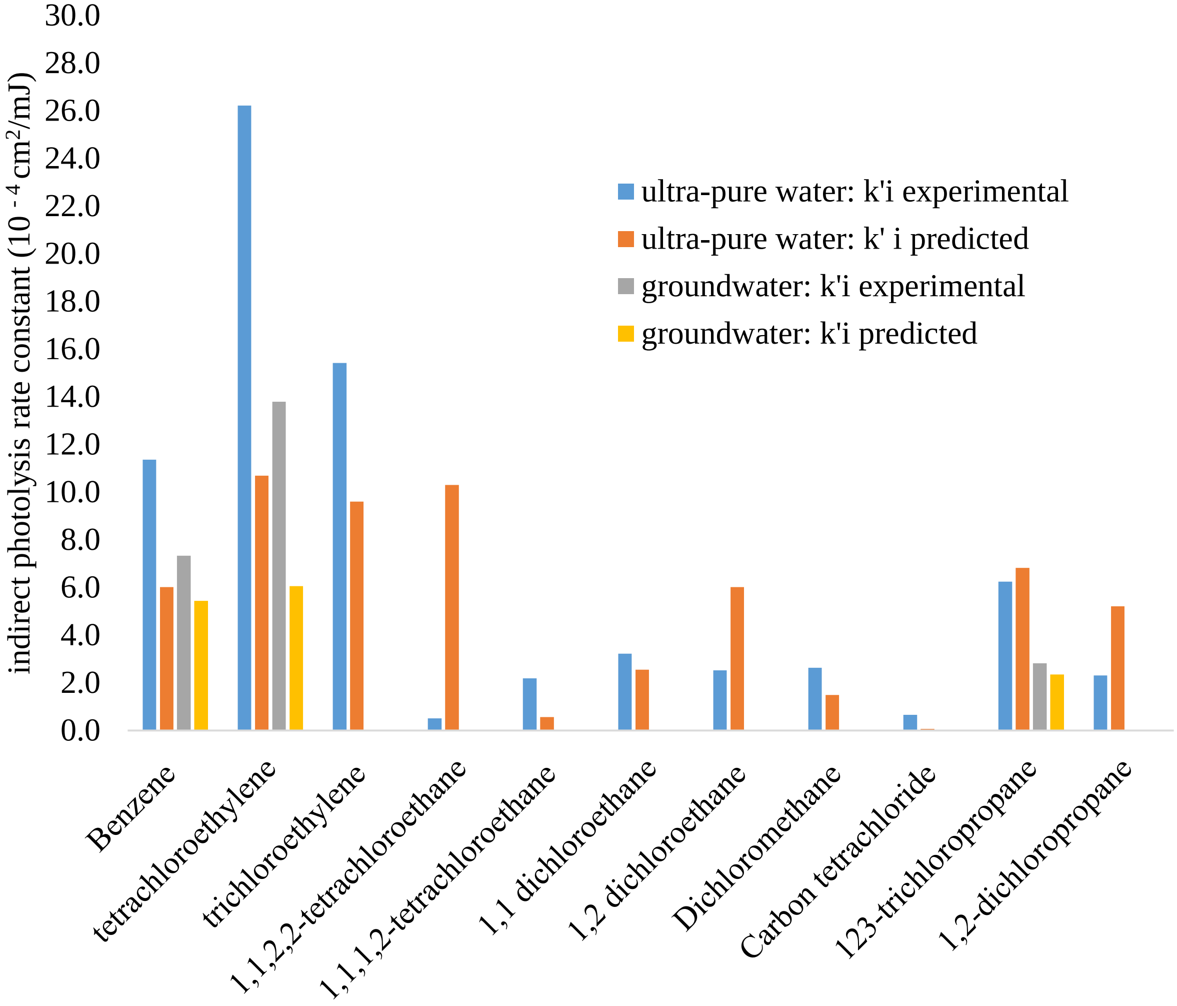


Figure 13: Indirect photolysis rate constants between experimental and predicted values of VOCs in ultra-pure water and groundwater

The data in Figure 13 shows both the experimental and predicted indirect photolysis rate constants are lower in groundwater than in ultra-pure water. Benzene and tetrachloroethylene have experimental degradation rate constants larger than what was predicted while 1,2,3 trichloropropane has a similar degradation rate constant. Again, the differences in the rate constants in both matrices could be attributed to several factors such as the presence of other chemical species in water that can slow down degradation due to scavenging.

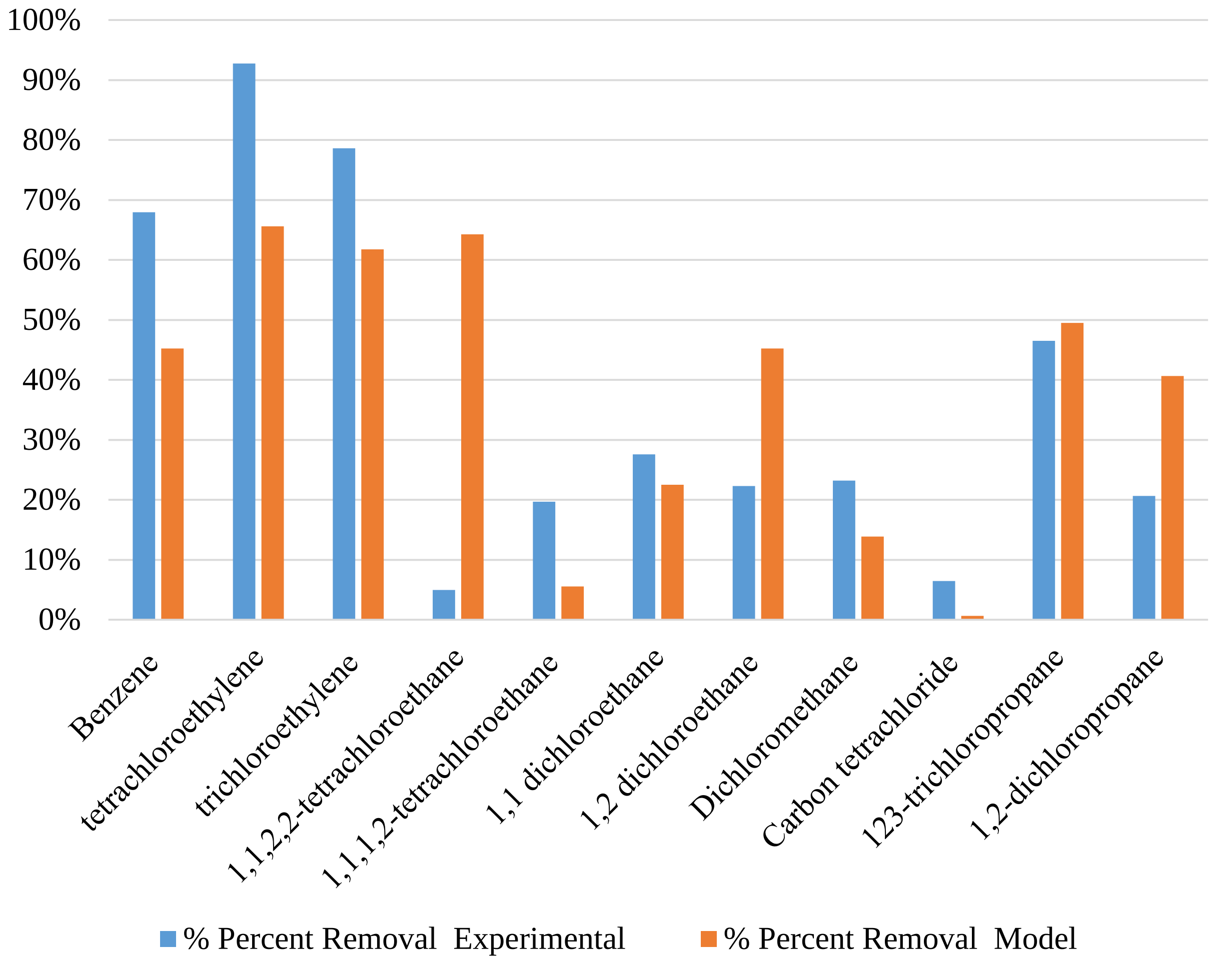
6. Conclusion

The aromatic organic and chlorinated alkenes showed the highest reactivity during both direct photolysis and UV induced OH radical oxidation. There was little or no removal of the chlorinated alkanes when exposed to UV light only. Degradation using UV/H_2O_2 AOP was evident among all 11 VOCs. Experimentally, 1,1,2,2-terachloroethane showed the lowest reactivity with OH radicals while carbon tetrachloride had the lowest predicted degradation rate constant followed by 1,1,1,2-tetrachloroethane. A common feature among the three chemicals is that they have the highest number of chlorine atoms in the group making it difficult for OH radicals to react with the VOCs. It has been established that the reaction of OH radicals with organics through H abstraction (reaction mechanism for chloroalkanes) is more difficult than OH radical addition (reaction mechanism for unsaturated organics).

7. Impact and Implications of the Research

From this research, it is evident that the UV/H_2O_2 advanced oxidation process is a more effective method of VOC removal from impacted drinking water than UV alone at 254nm. Therefore, a greater emphasis should be placed on optimizing OH radical based oxidation. To thoroughly understand the potential impact of this study, the percentage removal efficiencies and the amount of fluence needed to remove VOC equal or greater than 90% was determined using the bench-scale testing results. The analysis was then compared to the results of a full scale UV AOP technology performance. This study was conducted by Ultrox International in conjunction with the US EPA after which several implications were inferred.

Figure 14 shows the percent removal of 5000 µg/L VOC from ultra-pure water laden with 15 mg/L hydrogen peroxide. A UV fluence of 1000 mJ/cm^2 along with the experimental and predicted indirect photolysis rate constants are used to determine the fraction of VOC that can be removed.



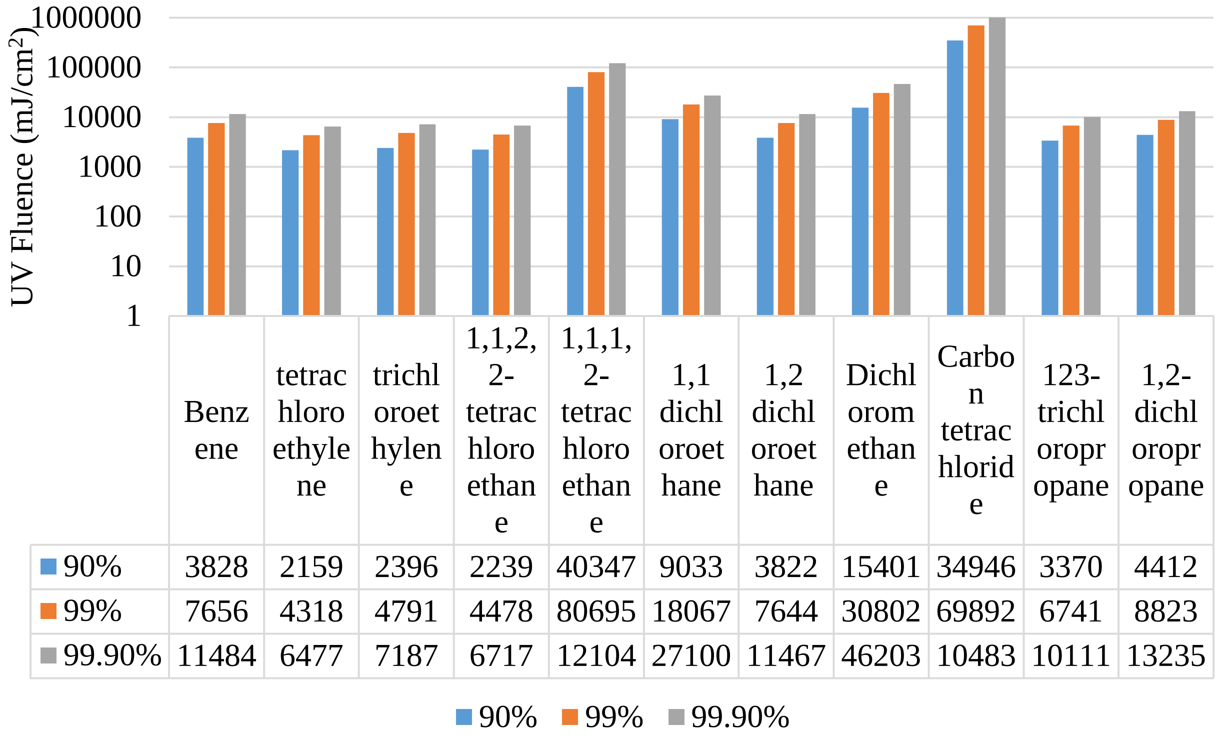
*This data is represented differently from the data in Figure 7

Figure 14: Percentage Removal of VOCs based on the indirect photolysis rate constants

As can be seen from the plot, nine out of the eleven compounds show similar percentage removal between predicted and experimental with an exception of 1,1,2,2 tetrachloroethane and carbon tetrachloride with large differences of 59% and 5% respectively. Experimentally, tetrachloroethylene has a percentage removal greater than 90%. It is followed by trichloroethylene and benzene with 79% and 68% removal respectively. On the other hand, the chloroalkanes have experimental percentage removals less than 50%.

From the data, it can be noted that for the same fluence, the removal efficiencies for each VOC are different. However, there seems to be a trend in the order of removal in that unsaturated organics have higher removal efficiencies followed by chloropropanes and lastly chloroethanes and chloromethanes. This implies that a longer residence time would be needed to achieve the same percentage of VOC removal among the 11 VOCs.

When the UV fluence required to achieve varying levels of removal for each VOC was plotted, it showed that differences not only lie among different chemical structure groups but also generally among the 11 VOCs. There is a substantial variation in fluence needed for varying levels of removal for one compound. This analysis is displayed in Figure 15.



	Benzene	tetrachloroethylene	trichloroethylene	1,1,2,2-tetrachloroethane	1,1,1,2-tetrachloroethane	1,1 dichloroethane	1,2 dichloroethane	Dichloromethane	Carbon tetrachloride	123-trichloropropane	1,2-dichloropropane
■ 90%	3828	2159	2396	2239	40347	9033	3822	15401	34946	3370	4412
■ 99%	7656	4318	4791	4478	80695	18067	7644	30802	69892	6741	8823
■ 99.90%	11484	6477	7187	6717	12104	27100	11467	46203	10483	10111	13235

Figure 15: UV fluence needed for 90%, 99% and 99.9% VOC degradation

As can be seen from Figure 15, among all VOCs, increasing the percentage removal from 90% to 99% requires twice the UV fluence. 1.5 times this fluence is then required to achieve a 99.9% removal. To achieve the same percentage removal among the different chemical structure leads to extremely large differences in UV fluence. For example, if a 90% removal of carbon tetrachloride and tetrachloroethylene was needed, this would require a fluence 160 times greater than the fluence needed to remove tetrachloroethylene.

The above results from the bench scale testing were compared to the results obtained in a 1989 study that was conducted by Ultrox International in conjunction with the USEPA under the Superfund Innovation Technology Evaluation (SITE) Program (USEPA, 1990). Ultrox International planned to conduct full scale testing of their UV oxidation technology so as to obtain valuable information on the effectiveness and costs of using this viable method of disinfection. The technology was tested at several sites but with a focus particularly on the Lorentz Barrel and Drum site located in San Jose, California. At this site various VOCs including trichloroethylene, vinyl chloride, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,2 dichloroethane, benzene, chloroform and tetrachloroethylene were detected. The first two chemicals on the list were at levels of a 100 and 40 µg/L while the rest of the chemicals had concentrations between 5 and 15 µg/L. The UV AOP technology is a 65 W 24-UV lamp system with hydrogen peroxide and ozone doses of about 13 mg/L and 110 mg/L respectively.

The results from this study showed a 90% removal of total VOCs. The three indicator VOCs that is TCE, 1,1 dichloroethane and 1,1,1 trichloroethane showed a 98%, 65% and 85% removal. Air stripping was considered as another mode of removal for 1,1 dichloroethane and 1,1,1 dichloroethane. A summary of their iterative experimental runs can be seen in Table 13.

Table 13: Ultrox UV technology performance for reproducible runs [Source: US EPA, 1990]

	Mean Influent (µg/L)	**Mean Effluent (µg/L)**	**Percent removal %**
Run A			
Trichloroethylene	65	1.2	98
1,1 Dichloroethane	11	5.3	54
1,1,1,-trichloroethane	4.3	0.75	83
Total VOCs	170	16	91
Run B			
Trichloroethylene	52	0.55	99
1,1 Dichloroethane	11	3.8	65
1,1,1,-trichloroethane	3.3	0.43	87
Total VOCs	150	12	92
Run C			
Trichloroethylene	49	0.63	99
1,1 Dichloroethane	10	4.2	60
1,1,1,-trichloroethane	3.2	0.49	85
Total VOCs	120	20	83

Based on these findings, it can be inferred that UVAOP is a viable option of remediation of VOC-laden water. Its efficiency is highly dependent on the type of chemical being removed, the starting concentration and what level of removal is required. Expectedly, trichloroethylene was removed successfully in the pilot study as well. The removal of 1,1 dichloroethane and 1,1,1 trichloroethane had lower rates of removal as suggested by the bench scale results. Air stripping was considered a major factor in the removal of theses VOCs and thus additional evidence of the inefficiency of UV-based technology in removing chloroalkanes.

8. Hazardous Waste in the Developing Countries

8.1 Introduction

VOCs are also found in developing countries and they originate from similar sources as those found in the United States (Jackson, 2006). If hazardous waste is defined as substances with the potential to cause detrimental effects to human health and the environment then VOCs make a small portion of the hazardous waste found in the developing world. The developing world is plagued with various toxic chemicals in high concentrations from organic solvents, hydrocarbons to pesticides and heavy metals (Sorensen et al, 2015). Fortunately, like in developed countries, environment protection institutions have been put in place, through legislation, to safeguard the environment through monitoring and regulating contamination (Probst and Beierle, 1999). However, these institutions are lagging behind in implementing effective and compliant environmental programs. This leads to an uncontrolled contamination of water systems and the environment at large; a situation exacerbated by increased industrial and economic growth (Kahn et al, 2015). Therefore, this segment of the report looks at the challenges the developing countries face in handling hazardous waste, the reasons it’s unclear to see, the current impacts in society and the way forward in improving the environmental management status. Several examples are gathered from an independent research study conducted in the capital city of Zambia, Lusaka.

8.2 Hazardous Waste Sources

Like in the developed world, hazardous waste in developing countries comes from different aspects of the society that is factories, agriculture, mining, transporters, disposal facilities and informal economic sectors such as small labor intensive businesses (Kahn et al, 2015). This waste includes organic solvents, pesticides, herbicides, acids and heavy metals (lead, zinc, cadmium, and chromium). Other kinds of waste include plastics, waste oils and electronic waste.

8.3 Hazardous Waste Management Problems

Measures have been put in place to address this waste so as to prevent pollution of the environment but there are still several challenges that developing countries face.

8.3.1 Lack of Trained Expertise and Appropriate Technology

There are very few professionals who are trained or knowledgeable about how to handle (collect, transport, store, treat and dispose) hazardous waste despite the strategies formulated to manage it. In addition, the technology to handle this type of waste is unavailable. This lack of expertise and technology leads to uncontrolled discharge of waste with no separation of hazardous and municipal waste (Kahn et al, 2015). In Zambia, the city of Lusaka has two major wastewater treatment plants; *Machinchi* and *Chunga*. The purpose of the former (Machinchi) wastewater treatment plant is to treat domestic waste that comes from households while the purpose of the latter (Chunga) wastewater treatment plant is to treat industrial waste. However, both treatment plants have the same infrastructure and operating conditions. On the industrial side, only biodegradable organics are measured and there is no measure of recalcitrant organics and heavy metals that pass through the system untransformed.

8.3.2 Lack of Coordination, Compliance and Enforcement

Administration in developing countries may have different agencies overseeing the management of the environment (Kahn et al, 2015). Even within one agency the responsibilities of each department are not clearly defined. This disorganized web of management results in confusion of who is exactly responsible for a particular task. Even if there is one regulatory body, the regulation and enforcement tends to be inconsistent and biased. In city of Lusaka, the enforcement is unclear among government-owned and/or controlled utilities. For example, when treatment plants discharge waste that exceeds the environmental limits, it’s uncertain whether the plants should be fined for the discharge, which is caused by dysfunctional operating systems. Also environmental management plans (EMPs) are requested by the Zambia Environment Management Agency (ZEMA) to obtain licenses and permits but these strategies formulated are not adhered to.

8.3.3 Lack of Knowledge about Waste Generation

Hazardous waste management is exacerbated by the lack of information on waste generators, the type of waste produced, quantity, how and where it is disposed of. Also, regulating bodies may not have the resources to monitor and identify contamination.

8.4 Silent Nature of Hazardous Waste Management in Developing Countries

The problems mentioned above tend to go unnoticed even by citizenry because of several factors (Kahn et al, 2015):

1) Little awareness about the effects of hazardous waste exposure.
2) Poor data collection on waste generated and documentation showing exposure.
3) Lack of advanced medical diagnostic tools to detect exposure to hazardous waste.
4) Communities are already burdened by disease-Malaria, HIV/AIDS and water borne illnesses caused by pathogenic contamination. Government and other supporting investors tend to direct financial resources towards these pressing issues. For example, the World Health Organization (WHO) puts an emphasis on dealing with microbiological problems because microbial risk is greater than chemical risk (WHO, 2015).
5) Due to a lack of jobs, individuals set up informal businesses that utilize toxic chemicals. To avoid the costs associated with registering with the environmental management agency, they illegally dump their waste in the water systems or create their own illegal dumpsites. Aside from utilizing toxic chemicals, individuals gain income from recovering precious metals and parts that they resell for profit to manufacturing businesses. An infamous

dumpsite near the city of Accra, Ghana is known to be a hub for scavengers who are constantly exposed to toxic waste as they try to search for valuable metals and parts to be resold (Black Smith Institute, 2015).

8.5 Current Impacts on Society

The detrimental effects of a lack of hazardous waste management around the world are too many to mention. These effects have infiltrated all facets of society around the world. Low income families and individuals are usually the hardest hit. The examples selected are in three different global regions.

8.5.1 Mining Industry in Zambia

The Zambian economy is heavily dependent on the mining industry. Most mines have been privatized to allow for better management and operating conditions. However, many of these foreign-invested mines have failed to comply with environmental standards when it pertains to discharging their waste into the environment. Recently, an international lawsuit has been filed against a UK-based company, Vedanta, that manages the Konkola Copper Mines (KCM) located in the *Copperbelt* region of the country. It is claimed that the company allowed for the contamination of the water resources in the nearby communities with sulphuric acid, heavy metals and other toxic chemicals. The drinking water supply for residents has been tested and toxic chemicals such as sulphuric acid have been identified. Residents have submitted complaints that they are suffering from burns and grave illnesses (Vidal, 2015).

8.5.2 Citarum River in Indonesia

The Citarum River, located on the Java island of Indonesia, is regarded as one of the dirtiest rivers in the world. This river has been contaminated by household waste and toxic chemicals from textile factories. However, it still serves as a drinking water source for Java's water authority. 80% of the water used by the utility comes from this river (Ericsson and Stangberg, 2010).

8.5.3 Matanza-Riachuelo river basin in Argentina

The Matanza-Riachuelo River in Argentina is a dumping ground for more than 15,000 factories (Ericsson and Stangberg, 2010). It is contaminated with volatile organic chemicals, petrochemicals and heavy metals. About 20,000 people live near the basin and 60% of those residents live in homes regarded unfit for habiting (Pietri et al, 2011 cited by Black Smith Institute, 2014). Undoubtedly, residents are burdened with disease such as diarrhea, respiratory infections and cancer (Black Smith Institute, 2013).

8.6 Moving Forward

Hazardous waste management in the developing world is uncompliant and ineffective. It is logical that there is a need for stricter enforcement of environmental legislation. There needs to be strict monitoring of origin, type and quantities of waste produced. This should be accompanied with strictly defining the term "hazardous" waste (Probst and Beierle, 1999). However, most importantly, there is a need to create a compliant culture to which education and technology plays a huge role. Many developing nations do not have the knowledge of how to handle their hazardous waste. They are limited to landfill sites, incineration and water treatment plants which are substandard and not well maintained. The technical know-how of some countries does not extend beyond these treatment processes. Hazard waste treatment technologies such as bio-filtration (Perez et al, 2013) and UV technology (Gruber et al, 2013) are available in these developing nations on a small scale but there is a need for large scale systems to treat these massive polluted waters. If the implementation of such large-scale treatment technologies is currently far-fetched, then there might be a need to redesign and optimize small scale systems to not only treat pathogens but toxic chemicals that further degrade human health.

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APPENDIX A: METHODS

1. Calculating Incident Irradiance Factors

The excel spreadsheet program used to determine the average irradiance takes into account three factors that impact the irradiance received by the sample. These factors include the petri, reflection and divergence factors. The calculations of these factors for this research are presented below.

1.1 Petri-Factor

The petri factor accounts for the difference in irradiance over the surface area of the sample being irradiated. It is defined as the ratio of the irradiance over the petri dish surface area to the irradiance at the center (Bolton and Linden, 2003). The petri factor is specific to the vessel size and the distance the sample surface is from the aperture of the UV apparatus. For this study, the petri-factor for the specialized vessel was calculated to be 0.976 at a distance of 12.5cm.

The petri factor was determined by measuring the irradiance along the axes starting from 0 (See Figure 16) and finding the average of the ratios of the irradiance at each point to the irradiance at the center. The results are shown in Table 14.

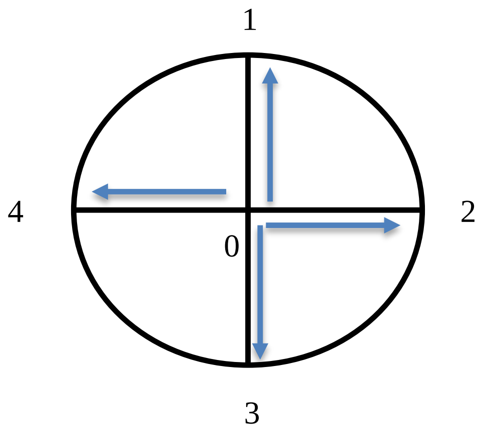


Figure 16: Diagrammatic illustration of determining the Petri Factor

Table 14: Petri factor Calculations

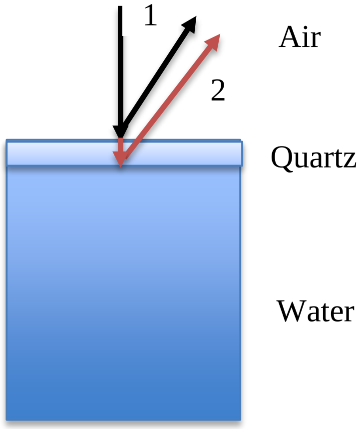
Axis Number	**1**	**2**	**3**	**4**
Measured Irradiance at the center (m W/cm2)	**0.911**	**0.927**	**0.911**	**0.894**
Decreasing irradiance measured along the axis	0.899	0.941	0.902	0.906
	0.872	0.955	0.883	0.905
	0.86	0.961	0.866	0.902
	0.845	0.959	0.846	0.898
	0.821	0.952	0.812	0.888
	0.791	0.938	0.779	0.878
Normalized data	1.000	1.000	1.000	1.000
	0.987	1.015	0.990	1.013
	0.957	1.030	0.969	1.012
	0.944	1.037	0.951	1.009
	0.928	1.035	0.929	1.004
	0.901	1.027	0.891	0.993
	0.868	1.012	0.855	0.982
Average of Normalized data	**0.976**			

1.2 Reflection Factor

The reflection factor accounts for UV light that is reflected off the interface between two media as the light travels from one medium to another. When light travels from one medium to another, the refractive index changes and the amount of UV light reflected from that change is determined. Having a quartz vessel as opposed to an open petri-dish (air→water), the UV light pathway is different, air→quartz → water and the reflection factor was calculated as 0.9547 (Bolton, 2001).

Determining the reflection factor can be seen in the calculations below where n_1 represents the refractive index of the medium the UV light is leaving while n_2 represents the refractive index of the medium in which UV light is entering. The reflection factor is determined by subtracting the amount of UV light reflected from the value of 1.

Calculating the reflection factor involves understanding the pathway of UV light during UV exposure:



Path 1: Air (n_1=1.00) → Quartz (n_2=1.52)

$$R = \frac{(n_1 - n_2)^\wedge 2}{(n_1 + n_2)^\wedge 2} = \frac{(1.00 - 1.52)^\wedge 2}{(1.00 + 1.52)^\wedge 2} = 0.0426$$

Path 2: Quartz (n_1=1.52) → Water (n_2=1.37)

$$R = \frac{(n_1 - n_2)^\wedge 2}{(n_1 + n_2)^\wedge 2} = \frac{(1.52 - 1.37)^\wedge 2}{(1.52 + 1.37)^\wedge 2} = 0.0027$$

$$Reflection\ Factor = 1 - 0.0426 - 0.0027 = 0.9547$$

1.3 Divergence factor

The divergence factor accounts for the UV light that diverges from the sample. The UV apparatus was set up to be quasi-collimated and thus a conservative assumption that little or no UV light rays diverged away from the quartz vessel was made. Therefore, a value of 1 was assumed for the divergence factor.

2. Analytical Determination using Purge-and-Trap/Gas Chromatography

The measurement and identification of VOCS was performed by using a purge and trap extraction followed by gas chromatography.

2.1 Purge-and-trap system

The purge-and-trap system comprises a unit that manually or automatically samples a predetermined volume (5 ml in this research) from the 42 ml-vial. This sample is transferred to a U-shaped purging device. The VOCs were purged for 11 minutes using helium gas at a flow rate of 40 mL/min at 36˚C.

When purging is complete, the analytes are collected on a VOCARB 3000 trap (Supelco, Bellefonte, PA) which is heated to 245˚C and back flushed for 2 minutes with helium to desorb trapped sample components at a flow of 100 mL/min.

After a successful transfer of the VOC to the capillary GC column, the sampler and purge-and-trap are baked (heated) at a temperature of 270˚C with a bake flow of 150 ml/min to eliminate residual VOC and thereby avoiding contamination due to carry-over. The bake temperature for the condenser is 175˚C and the bake time is 5 minutes.

2.2 Gas Chromatography with a Flame Ionization Detector

The purge-and–trap device was coupled to a gas chromatograph, Agilent 7890a, GC-FID. The device was equipped with a 30 m column (J &W Scientific DB-VRX, I.D. 0.45mm, liner thickness 2.55 µm, Folsom, CA) with helium as the gas carrier. The injector and the FID detector temperatures were set at 350˚C. Under these conditions, the retention times for the 11 VOCs are presented in Table 15.

Table 15: Retention time of VOCs

VOC	Retention time (min)
Benzene	5.450
Tetrachloroethylene	8.470
Trichloroethylene	5.951
1,1 dichloroethane	3.926
1,2 dichloroethane	5.085
1,1,2,2-tetrachloroethane	10.062
1,1,1,2-tetrachloroethane	9.085
Dichloromethane	3.135
Carbon tetrachloride	5.358
1,2,3 trichloropropane	10.178
1,2 dichloropropane	5.846

3. Preparation of Stock and Standard Solutions

For each VOC, a calculated volume of chemical was mixed with ultra-pure water to make a stock solution with a concentration not greater than 0.5 times that of the aqueous solubility of the chemicals. This was to help ascertain dissolution while using a significant volume to make the batch solution. The stock solution concentrations were calculated on the basis of no headspace in the containers. After adding the chemical to the water, the batch solutions were mechanically stirred for a minimum of 4 hours for complete mixing and dissolution. A volume of the VOC batch solution was then used to prepare a gallon of 5000µg/L of chemical which is then decanted into twelve 300ml bottles with no headspace for exposure. Table 16 shows the stock solution concentrations and the volumes used to make the standard solution of 5000µg/L

Table 16: Stock Concentrations and Volumes

VOC	**Max. Molar Solubility (mol/L)**	**0.5*Max. concentration (mol/L)**	**Actual Conc. Made (Mm)**	**Conc. in mass units (µg/L)**	**Vol.(ml) for GAL of 5000µg/L VOC**
Benzene	23.04	11.52	5.00	3.91E+05	49.80
tetrachloroethylene	0.90	0.45	0.45	7.46E+04	260.64
trichloroethylene	9.74	4.87	4.00	5.26E+05	37.01
1,1,2,2-tetrachloroethane	17.02	8.51	8.00	1.34E+06	14.48
1,1,1,2-tetrachloroethane	9.25	4.62	5.95*	1.00E+06	19.45
1,1 dichloroethane	51.11	25.56	5.05	5.00E+05	38.90
1,2-dichloroethane	87.91	43.96	40.00	3.96E+06	4.91
carbon tetrachloride	5.27	2.63	2.63	4.05E+05	48.08
dichloromethane	206.05	103.03	10.00	8.49E+05	22.90
1, 2 dichloropropane	23.01	11.51	11.38	1.29E+06	15.13
1,2,3 trichloropropane	11.86	5.93	6.78	1.00E+06	19.45

*Actual concentration made was higher because all the VOC was used as it was packaged in an ampule that could not be capped once opened.

APPENDIX B: RESULTS

1. Determination of Molar Absorption Coefficients

The molar absorption coefficient is a vital parameter needed to calculate the quantum yield of the VOC. With little or no data on the molar absorption coefficients of these VOCs at 254nm in the literature, there was a need to determine this inherent property. This parameter is equivalent to the slope of the plot of absorbance against concentration. Table 17 shows the VOC concentrations prepared and the corresponding absorbance at 254nm.

Table 17: VOC concentrations and corresponding absorbance for molar absorption coefficient determination

Benzene	Concentration (M)	1.00E-02	5.00E-03	1.00E-03	
	Absorbance	0.850861132	0.417958945	0.113088	
tetrachloroethylene	Concentration (M)	0.00045	0.0003375	0.000225	0.000113
	Absorbance	0.086984	0.060807	0.038035	0.017709
trichloroethylene	Concentration (M)	2.00E-03	1.00E-03	2.00E-04	
	Absorbance	0.014128442	0.010227969	0.00055	
1,1,2,2-tetrachloroethane	Concentration (M)	8.00E-03	6.00E-03	4.00E-03	2.00E-03
	Absorbance	0.039929695	0.030129081	0.018849	0.011231
1,1,1,2-tetrachloroethane	Concentration (M)	0.005952381	0.004464286	0.002976	0.001488
	Absorbance[*]	-0.00257	-0.0024	-0.00287	-0.00507
1,1-dichloroethane	Concentration (M)	0.005050505	0.003787879	0.002525	0.001263
	Absorbance*	-0.00262	-0.00394	-0.00389	-0.00467
1,2-dichloroethane	Concentration (M)	4.00E-02	2.00E-02	1.00E-02	4.00E-03
	Absorbance	0.062233575	0.039969116	0.022367	0.015058
dichloromethane	Concentration (M)	8.00E-02	5.00E-02	3.00E-02	1.00E-02
	Absorbance	0.076589979	0.045276634	0.031892	0.007578
carbon tetrachloride	Concentration (M)	2.50E-03	1.00E-03	5.00E-04	1.00E-04
	Absorbance	0.015212254	0.004549546	0.003263	0.001655
1,2,3- trichloropropane	Concentration (M)	0.006779661	0.005084746	0.00339	0.001695
	Absorbance*	-0.0038	-0.00324	-0.00508	-0.00525
1,2 -dichloropropane	Concentration (M)	0.011375759	0.008531819	0.005688	0.002844
	Absorbance*	-0.00405	-0.0048	-0.00548	-0.00553

---

[*] *The absorbance baseline of the spectrophotometer during these experiments was below zero and hence the negative absorbance measurements.*

2. Raw Data for Direct photolysis

The information below shows the experimental data and analytical results obtained from the GC for duplicated samples for each UV exposure in both ultra-pure water and groundwater. The two sets of peak area data for each VOC was tested for statistical difference after which the average was determined. The concentration was established by developing a mathematical relationship between known concentrations and their corresponding peak areas. The natural logarithm of the ratio of the concentration at an exposure time, t to the concentration at t=0 was calculated after which a degradation trend was established as presented in the report.

2.1 UV Photolysis Experiments Using Ultra-pure water

Table 18 is a summary of the analytical data obtained from the GC from UV exposure experiments using ultra-pure water.

Table 18: Experimental data for the UV exposure of VOCs in ultra-pure water

Benzene						
Av. Irradiance (mW/cm^2)	0.8419					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C$_0$)**
0	0	7573.7	7239.4	7406.55	5553.80	0
111	132	7289.9	7404	7346.95	5509.11	-0.0081
277	330	7350.1	7128.3	7239.2	5428.31	-0.0229
555	660	6984.5	6836.1	6910.3	5181.69	-0.0694
833	990	6739.4	6667.8	6703.6	5026.69	-0.0997
1113	1323	6809.9	6586.1	6698	5022.50	-0.1006
Tetrachloroethylene						
Av. Irradiance (mW/cm^2)	0.8484					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C$_0$)**
0	0	1882.1	1981.6	1931.85	5208.55	0
112	138	1538.3	1585.8	1562.05	4211.51	-0.2125
280	345	1203.7	1219.5	1211.6	3266.65	-0.4665
560.5	690	958.8	881.1	919.95	2480.32	-0.7419
840	1034	764.8	788	776.4	2093.29	-0.9116
1121	1379	525	539.6	532.3	1435.16	-1.2890
Trichloroethylene						
Av. Irradiance (mW/cm^2)	0.9039					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C$_0$)**
0	0	2839.2	2667.1	2753.15	4372.16	0
112	124	2697	2599.8	2648.4	4205.81	-0.0388
560	620	2848.9	2534.8	2691.85	4274.81	-0.0225
840	930	2432.6	2630.2	2531.4	4020.01	-0.0840
1120	1240	2161.6	2637.8	2399.7	3810.86	-0.1374
1,1,2,2-tetrachloroethane						
Av. Irradiance (mW/cm^2)	0.9005					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C$_0$)**
0	0	1786.2	1803.6	1794.9	5107.85	0
159	177	1760.8	1690.5	1725.65	4910.79	-0.0393
397	441	1685.1	1698.2	1691.65	4814.03	-0.0592
794	882	1617.7	1685.4	1651.55	4699.91	-0.0832

1191.0	1323	1616.4	1593	1604.7	4566.59	-0.1120
1,1,1,2-tetrachloroethane						
Av. Irradiance (mW/cm^2)	0.9252					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	2399.9	2024.3	2212.1	4911.41	0
290	314	2127.3	2324.4	2225.85	4941.94	0.0062
581	628	2439.2	2454.2	2446.7	5432.28	0.1008
871	942	2332.5	2355.3	2343.9	5204.04	0.0579
1162	1256	2327	2217.4	2272.2	5044.85	0.0268
1,1 dichloroethane						
Av. Irradiance (mW/cm^2)	0.828					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	2246.8	2547.1	2396.95	3521.82	0
595	719	2828.2	2636.5	2732.35	4014.62	0.1310
893	1079	2970	2664.3	2817.15	4139.22	0.1615
1190	1438	3072.2	3071.3	3071.75	4513.30	0.2481
1,2 dichloroethane						
Av. Irradiance (mW/cm^2)	0.9105					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	3677.3	3693.1	3685.2	4912.29	0
114	126	3480.4	3436.6	3458.5	4610.10	-0.0635
278	306	3512.5	3650.7	3581.6	4774.19	-0.0285
555	610	3266.9	3511.8	3389.35	4517.93	-0.0837
832	914	3092.3	3254.3	3173.3	4229.94	-0.1496
1112	1222	3248.6	3277.4	3263	4349.51	-0.1217
Dichloromethane						
Av. Irradiance (mW/cm^2)	0.8474					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	1354.9	1878.8	1616.85	4312.75	0
117	139	1795.2	1614	1704.6	4546.81	0.0529
293	346	1641.4	1659.2	1650.3	4401.97	0.0205
586	692	1834.9	1847.6	1841.25	4911.31	0.1300
879	1038	1742.9	1783.2	1763.05	4702.72	0.0866
1172	1384	1740.7	1810.9	1775.8	4736.73	0.0938

Carbon tetrachloride						
Av. Irradiance (mW/cm^2)	0.8298					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	335.7	371.8	353.75	5046.36	0
131.5	159	350	306.8	328.4	4684.74	-0.0744
589	710	319.7	333.1	326.4	4656.21	-0.0805
1177	1419	289.8	299.7	294.75	4204.71	-0.1825
1,2,3 trichloropropane						
Av. Irradiance (mW/cm^2)	0.8312					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Conc. (µg/L)**	**Ln(C/C_0)**		
0	0	3232.1	4998.61	0		
117	141	3193.1	4938.29	-0.012		
291	351	3240.6	5011.75	0.003		
583	702	3197.5	4945.10	-0.011		
875	1053	3158.3	4884.47	-0.023		
1167	1404	3137.1	4851.69	-0.030		
1,2-dichloropropane						
Av. Irradiance (mW/cm^2)	0.8392					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	7901.4	8177.6	8039.5	4951.35	0
114.5	137	7751.1	7989.7	7870.4	4847.20	-0.0213
313	373	7426.2	7557.8	7492	4614.15	-0.0705
574	685	7439.3	7144.3	7291.8	4490.85	-0.0976
861	1027	6931.8	7006.8	6969.3	4292.23	-0.1429

2.2 UV Photolysis Experiments Using Groundwater

Table 19 is a summary of the analytical data obtained from the GC from UV exposure experiments using groundwater.

Table 19: Experimental data for the UV exposure of VOCs in groundwater

<table>
<tr><th colspan="7">Tetrachloroethylene*</th></tr>
<tr><th>Av. Irradiance (mW/cm^2)</th><td colspan="6">0.7010</td></tr>
<tr><th>Fluence (mJ/cm^2)</th><th>time (s)</th><th>Peak area 1</th><th>Conc. (µg/L)</th><th colspan="3">Ln(C/C$_0$)</th></tr>
<tr><td>0</td><td>0</td><td>1873.2</td><td>3827.54</td><td colspan="3">0</td></tr>
<tr><td>109</td><td>156</td><td>1648.9</td><td>3369.23</td><td colspan="3">-0.1275</td></tr>
<tr><td>273</td><td>390</td><td>1470.8</td><td>3005.31</td><td colspan="3">-0.2418</td></tr>
<tr><td>820</td><td>1170</td><td>1155.7</td><td>2361.46</td><td colspan="3">-0.4829</td></tr>
<tr><th colspan="7">Benzene**</th></tr>
<tr><th>Av. Irradiance (mW/cm^2)</th><td colspan="6">0.7833</td></tr>
<tr><th>Fluence (mJ/cm^2)</th><th>time (s)</th><th>Peak area 2</th><th>Conc. (µg/L)</th><th colspan="3">Ln(C/C$_0$)</th></tr>
<tr><td>0</td><td>0</td><td>9247.8</td><td>5485.70</td><td colspan="3">0</td></tr>
<tr><td>546.5</td><td>698</td><td>8516.3</td><td>5051.79</td><td colspan="3">-0.08240</td></tr>
<tr><td>824.5</td><td>1053</td><td>8512.6</td><td>5049.59</td><td colspan="3">-0.08283</td></tr>
<tr><td>1092.5</td><td>1395</td><td>8089.6</td><td>4798.67</td><td colspan="3">-0.1338</td></tr>
<tr><th colspan="7">1,2,3 trichloropropane</th></tr>
<tr><th>Av. Irradiance (mW/cm^2)</th><td colspan="6">0.8203</td></tr>
<tr><th>Fluence (mJ/cm$^{2)}$</th><th>time (s)</th><th>Peak area 1</th><th>Peak area 2</th><th>Average</th><th>Conc. (µg/L)</th><th>Ln(C/C$_0$)</th></tr>
<tr><td>0</td><td>0</td><td>3547.2</td><td>3639.5</td><td>3593.35</td><td>6331.89</td><td>0</td></tr>
<tr><td>273.5</td><td>349</td><td>3495.7</td><td>3598</td><td>3546.85</td><td>6249.96</td><td>-0.01303</td></tr>
<tr><td>547</td><td>698</td><td>3485.1</td><td>3454.5</td><td>3469.8</td><td>6114.19</td><td>-0.03498</td></tr>
<tr><td>820</td><td>1047</td><td>3427.6</td><td>3574</td><td>3500.8</td><td>6168.81</td><td>-0.02609</td></tr>
<tr><td>1093</td><td>1395</td><td>3452.7</td><td>3179.5</td><td>3316.1</td><td>5843.35</td><td>-0.08030</td></tr>
</table>

* Only one set of data was consistent

** After a t-test, the sets of data were determined to be statistically different and one set of data was used.

3. Raw Data for UV/H_2O_2 Experiments

The information below shows the experimental data and analytical results from the GC for VOC degradation using UV and 15 mg/L of hydrogen peroxide in both ultra-pure water and groundwater. Like direct photolysis, the two sets of peak area data for each VOC was tested for statistical difference after which the average was determined. The concentration was established by developing a mathematical relationship between known concentrations and their corresponding peak areas. The natural logarithm of the ratio of the concentration at an exposure time, t to the concentration at t=0 was calculated after which a degradation trend was established as presented in the report.

3.1 UV/H_2O_2 Experiments Using Ultra-pure water

Table 20 is a summary of the analytical data obtained from the GC from UV exposure experiments using ultra-pure water.

Table 20: Experimental data for VOC degradation with UV and hydrogen peroxide in ultra-pure water

Benzene						
Av. Irradiance (mW/cm^2)	0.7605					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0.0	0	10963.2	10526.7	10744.95	4837.45	0
104.0	137	9336.6	8731	9033.8	4067.08	-0.1735
259.0	341	7231.2	7179	7205.1	3243.79	-0.3996
517.5	681	5063.8	4763	4913.4	2212.05	-0.7825
776.0	1021	3837.4	3872.1	3854.75	1735.44	-1.0251
1035.5	1362	2828.5	3115.9	2972.2	1338.11	-1.2851
Tetrachloroethylene						
Av. Irradiance (mW/cm^2)	0.754					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	1707.2	1745	1726.1	4653.82	0
104	138	1516.9	1551.2	1534.05	4136.02	-0.1180

260	345	825.9	862.1	844	2275.55	-0.7155
520	690	337.2	341.3	339.25	914.67	-1.6269
779	1034	117.2	112	114.6	308.98	-2.7122
1039.5	1379	33.4	36.9	35.15	94.77	-3.8940
Trichloroethylene						
Av. Irradiance (mW/cm^2)	0.8198					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0.0	0	3024.2	3186.9	3105.55	4931.79	0
101.0	124	2225.2	2228.2	2226.7	3536.13	-0.3327
254.0	310	1753.6	1709.7	1731.65	2749.96	-0.5841
508.0	620	947.8	934.2	941	1494.36	-1.1940
762.0	930	589.5	283.1	436.3	692.87	-1.9626
1016.0	1240	673.8	716.7	695.25	1104.10	-1.4967
1,1,2,2-tetrachloroethane						
Av. Irradiance (mW/cm^2)	0.8447					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0.0	0	1697.1	1834.3	1765.7	5024.76	0
149.0	177	1569.1	1598.2	1583.65	4506.69	-0.1088
372.0	441	1655.3	1667.4	1661.35	4727.80	-0.0609
745.0	882	1521.1	1521.5	1521.3	4329.25	-0.1490
1117.0	1323	1523.1	1510.9	1517	4317.02	-0.1518
1490.0	1764	1417.4	1358.4	1387.9	3949.63	-0.2408
1,1,1,2-tetrachloroethane						
Av. Irradiance (mW/cm^2)	0.8702					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	2480.2	2492.2	2486.2	5519.98	0
109	126	2206.9	2206.7	2206.8	4899.64	-0.1192
273	314	1973	1980.6	1976.8	4388.99	-0.2293
546	628	2217.8	2018.8	2118.3	4703.15	-0.1601
819.5	942	2148.3	1272.5	1710.4	3797.51	-0.3740
1092.5	1256	2054.8	2042.2	2048.5	4548.18	-0.1936
1,1 dichloroethane						
Av. Irradiance (mW/cm^2)	0.7599					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	2366.1	2083.2	2224.65	3268.66	0

546	719	2083.1	2242.7	2162.9	3177.93	-0.0281
819.5	1079	2177	2148.7	2162.85	3177.86	-0.0282
1092.5	1438	1756	2043.8	1899.9	2791.51	-0.1578
1,2 dichloroethane						
Av. Irradiance (mW/cm^2)	0.8365					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	3425.7	3366.2	3395.95	4526.73	0
102	122	3353	3324.3	3338.65	4450.35	-0.0170
255	305	3201.1	2980.3	3090.7	4119.83	-0.0942
514	615	2875.2	2941.9	2908.55	3877.03	-0.1549
764	914	2506.1	2608.7	2557.4	3408.96	-0.2836
1019	1219	2371.4	2383.6	2377.5	3169.15	-0.3565
Dichloromethane						
Av. Irradiance (mW/cm^2)	0.7896					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	1745.2	1869.9	1807.55	4821.42	0
109	139	1701.4	1538	1619.7	4320.35	-0.1097
273	346	1716.3	1686.8	1701.55	4538.68	-0.0604
546	692	1576.3	1575.6	1575.95	4203.65	-0.1371
819	1038	1427.7	1057.7	1242.7	3314.75	-0.3747
1092.5	1384	1443.5	1458.7	1451.1	3870.63	-0.2197
Carbon tetrachloride						
Av. Irradiance (mW/cm^2)	0.7701					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln (C/C_0)**
0	0	345.2	358.8	352	5021.40	0
109.5	142	332.9	334.1	333.5	4757.49	-0.0540
273	386	342.6	337.4	340	4850.21	-0.0347
546	710	327.4	291.6	309.5	4415.12	-0.1287
820	1065	330.2	307	318.6	4544.94	-0.0997
1093	1419	302.3	324.1	313.2	4467.90	-0.1168
1,2,3-trichloropropane						
Av. Irradiance (mW/cm^2)	0.7788					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	3160.4	3189.4	3174.9	4910.15	0
109.5	141	2896.4	2876.9	2886.65	4464.35	-0.0952

273	351	2719.9	2706.9	2713.4	4196.41	-0.1571
546	702	2428.5	2489.2	2458.85	3802.74	-0.2556
820	1053	1743.5	2060.9	1902.2	2941.85	-0.5123
1093	1404	1740.8	1397.6	1569.2	2426.85	-0.7047
1,2-dichloropropane						
Av. Irradiance (mW/cm^2)	0.7985					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C_0)**
0	0	7527.9	7347.1	7437.5	4580.59	0
109	137	7395.5	6234.9	6815.2	4197.33	-0.0874
297.5	373	6271.3	6340.2	6305.75	3883.57	-0.1651
547	685	5644.5	5720.4	5682.45	3499.69	-0.2692
820	1027	5059.7	5201.6	5130.65	3159.85	-0.3713
1093	1369	3979	4587.9	4283.45	2638.08	-0.5518

3.2 UV/H_2O_2 Experiments Using Groundwater

Table 21 is a summary of the analytical data obtained from the GC from UV exposure experiments using groundwater.

Table 21: Experimental data for VOC degradation with UV and hydrogen peroxide in groundwater

Tetrachloroethylene						
Av. Irradiance (mW/cm^2)	0.2969					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C$_0$)**
0	0	1608.2	1702.9	1655.55	3382.82	0
109.5	369	1446.7	1323.6	1385.15	2830.30	-0.1783
273	921	888.1	1011.7	949.9	1940.95	-0.5555
546.8	1841	345.6	477.1	411.35	840.52	-1.3924
820	2761	151.2	216	183.6	375.15	-2.1991
1093	3681	85.7	90.8	88.25	180.32	-2.9317
Benzene						
Av. Irradiance (mW/cm^2)	0.7269					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C$_0$)**
0	0	6110	6989	6549.5	3885.10	0
273	376	5780.2	6305.1	6042.65	3584.44	-0.0805
546	752	4333.2	3373.1	3853.15	2285.65	-0.5305
819.5	1128	3682.7	3901.6	3792.15	2249.47	-0.5465
1092.5	1504	2754.2	2435.6	2594.9	1539.27	-0.9258
1,2,3-trichloropropane						
Av. Irradiance (mW/cm^2)	0.7753					
Fluence (mJ/cm^2)	**time (s)**	**Peak Area 1**	**Peak Area 2**	**Average**	**Conc. (µg/L)**	**Ln(C/C$_0$)**
0	0	3483.8	3379.9	3431.85	6047.31	0
117	151	3438.1	3091.4	3264.75	5752.86	-0.04992
291	376	2895.5	3273.7	3084.6	5435.42	-0.10668
583	752	2376.4	3121.9	2749.15	4844.32	-0.22181
874	1128	3152.1	2985.9	3069	5407.93	-0.11175
1166	1504	2711	3051.7	2881.35	5077.27	-0.17484

4. OH Radical Based Oxidation Modeling

The information below shows a comparison of the experimental and predicted degradation trends of OH radical based oxidation in both ultra-pure water and groundwater. The data in blue represents the experimental degradation and while the data in orange represents the predicted degradation.

4.1 OH Radical Based Modeling Using Ultra-pure water

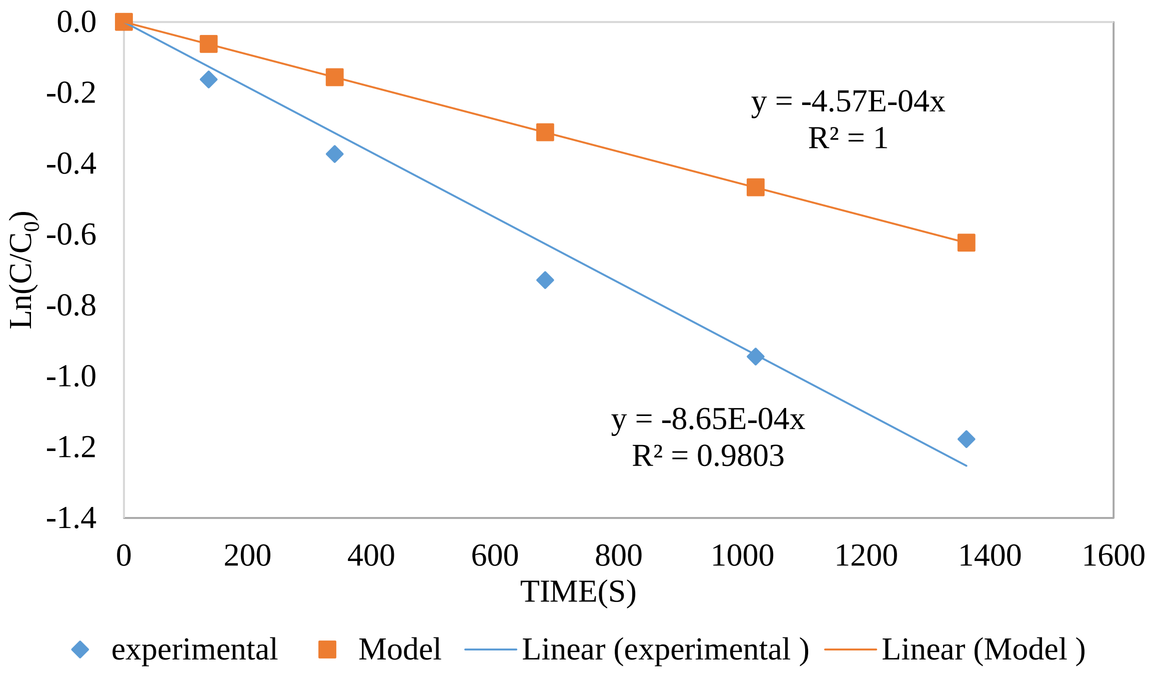


Figure 17: Benzene degradation with OH radicals

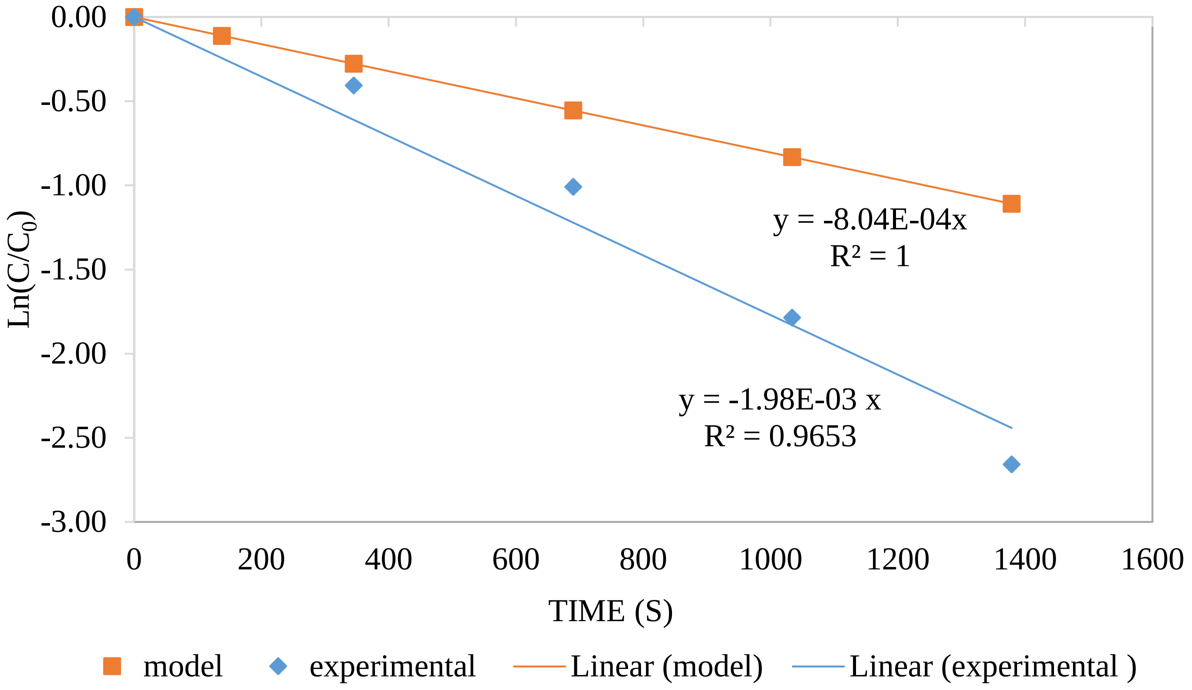


Figure 18: Tetrachloroethylene degradation with OH radicals

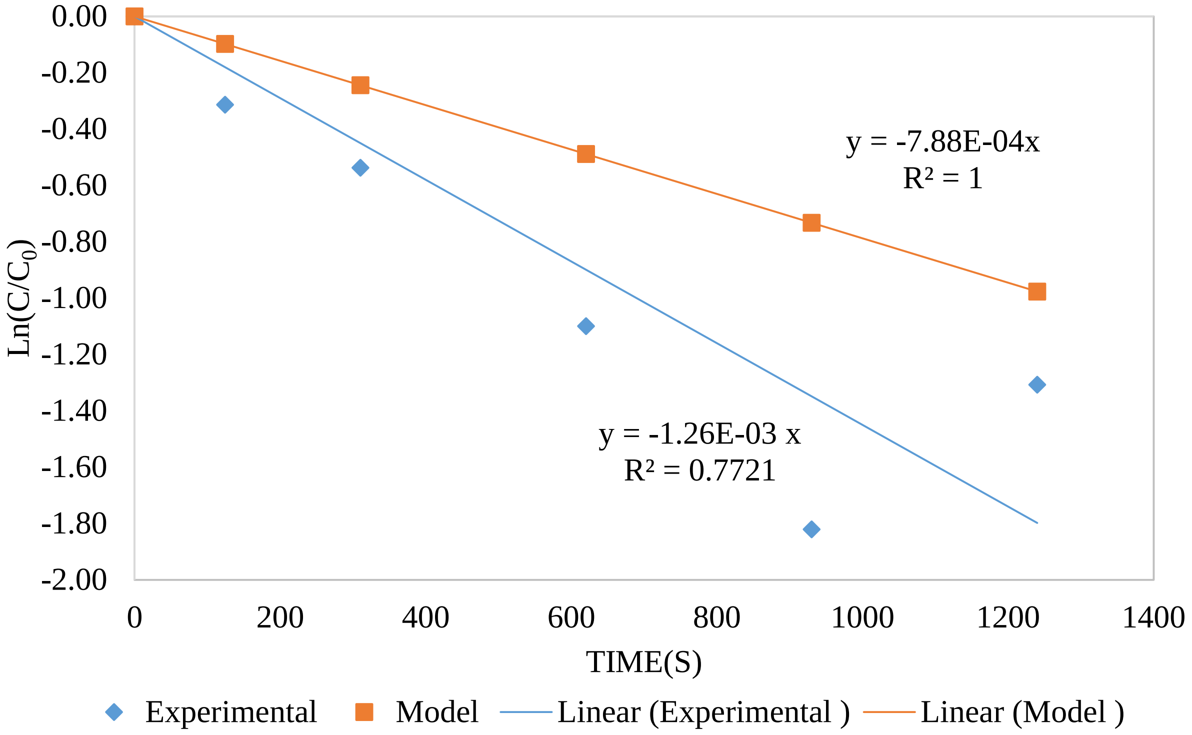


Figure 19: Trichloroethylene decay with OH radicals

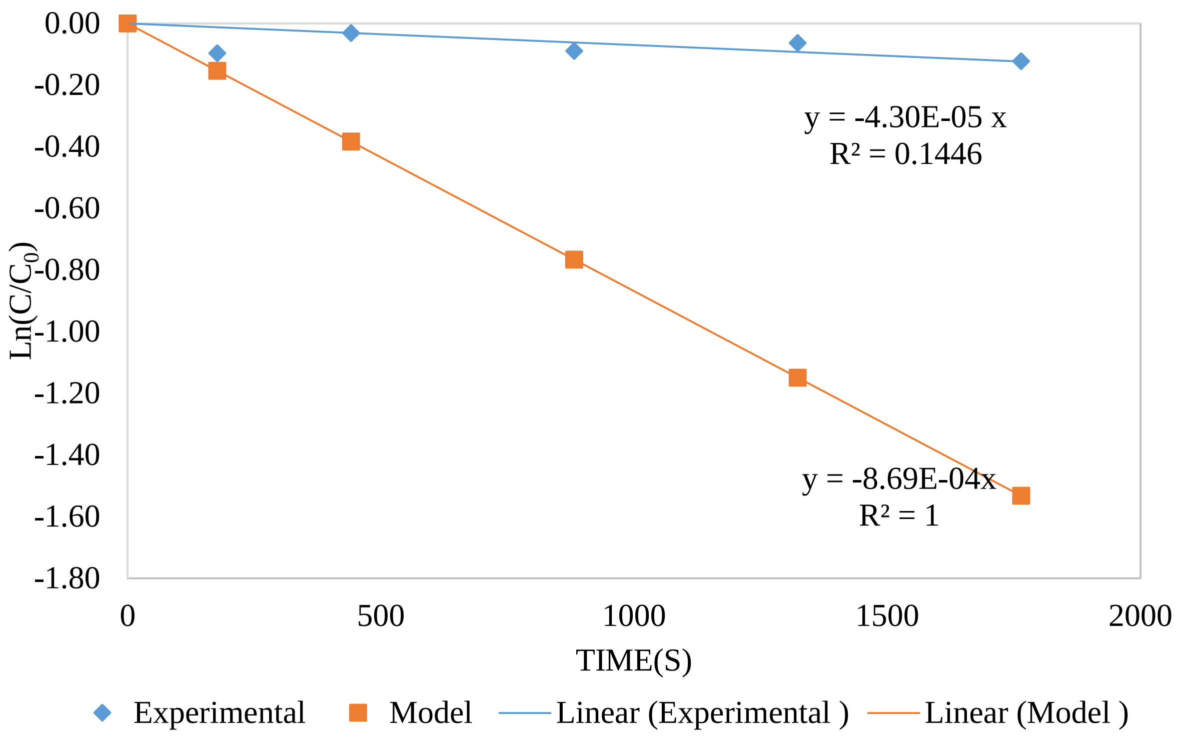


Figure 20:1, 1, 2, 2-tetrachloroethane degradation with OH radicals

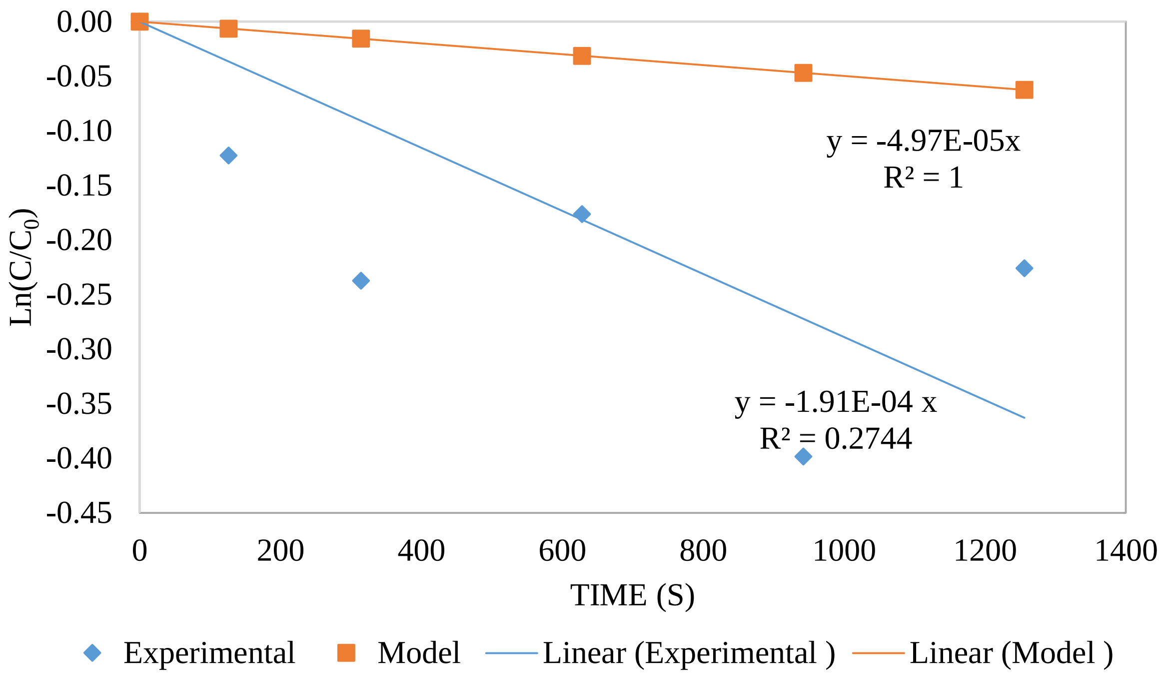


Figure 21: 1, 1, 1, 2-tetrachloroethane degradation with OH radicals

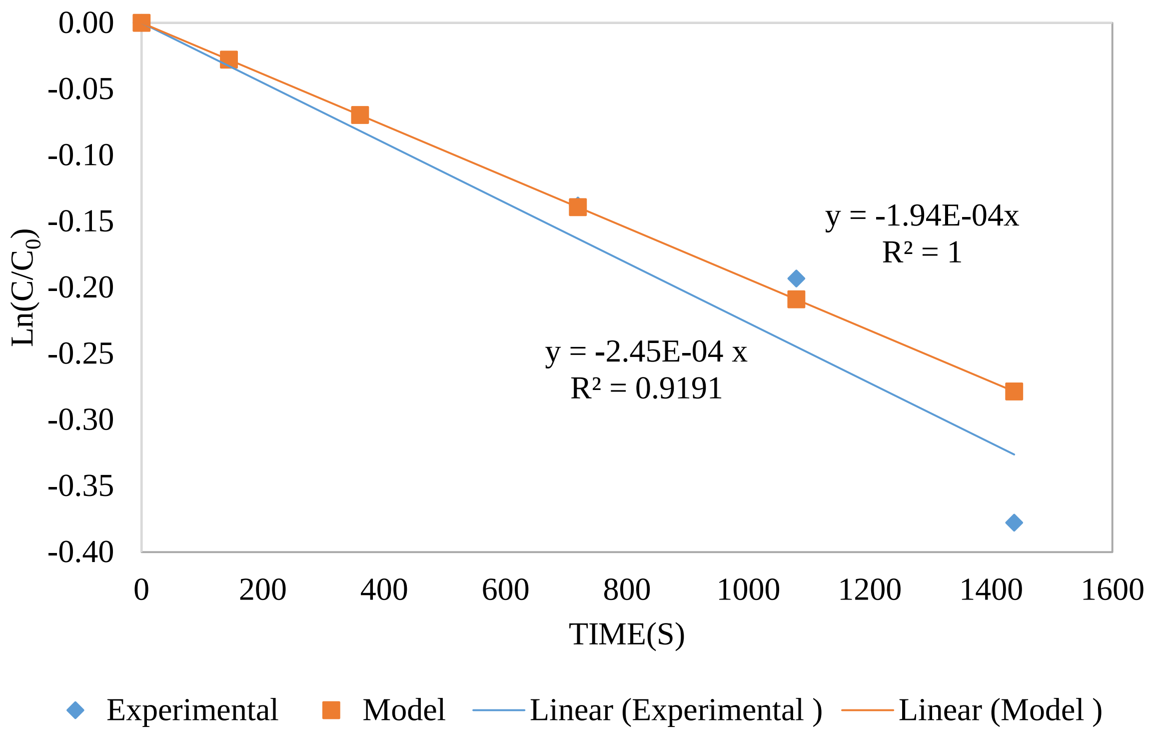


Figure 22: 1,1-dichloroethane degradation with OH radicals

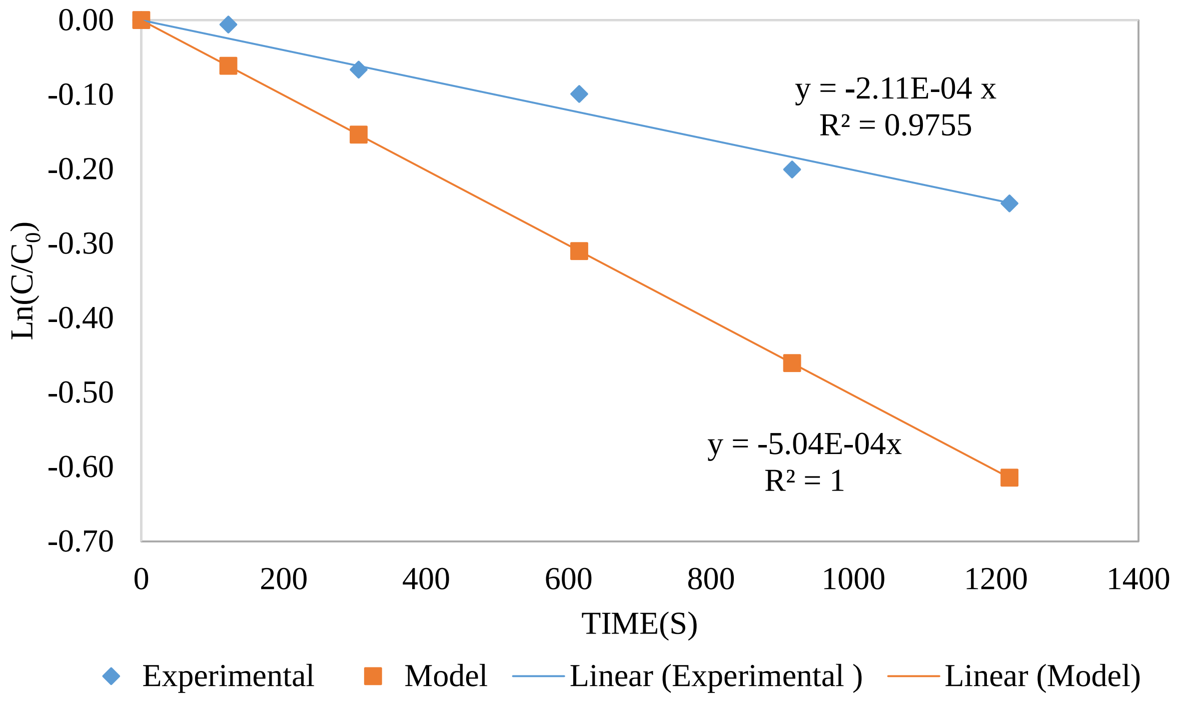


Figure 23: 1,2-dichloroethane degradation with OH radicals

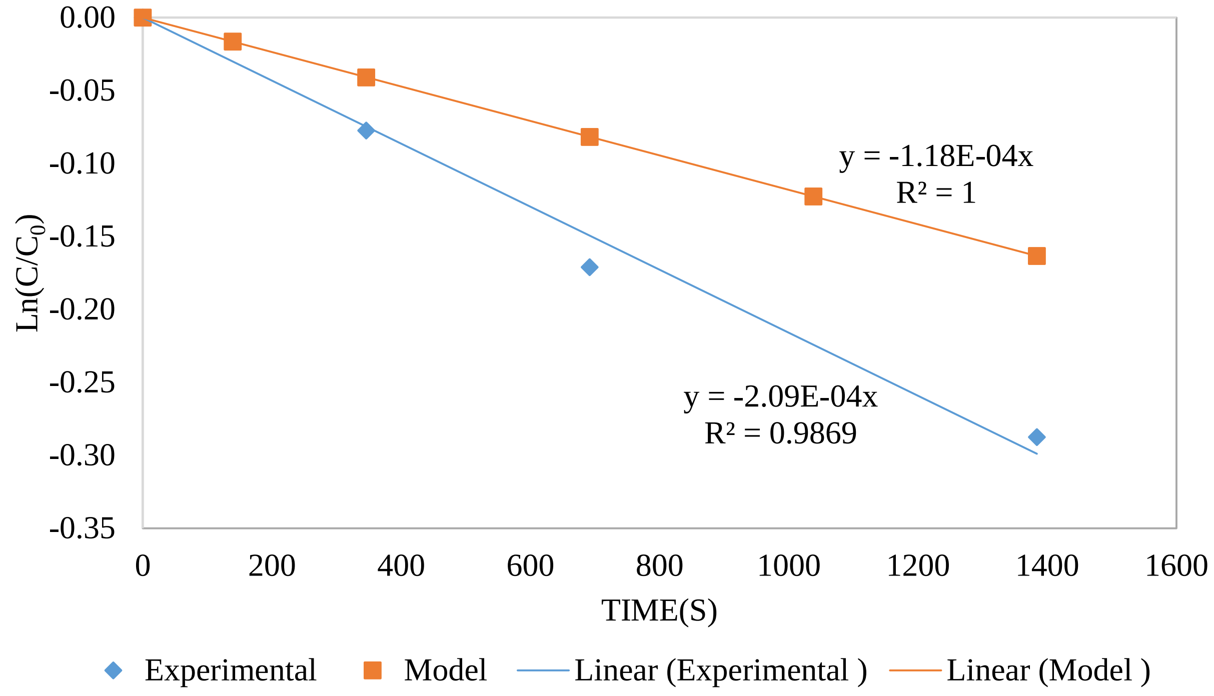


Figure 24: Dichloromethane degradation with OH radicals

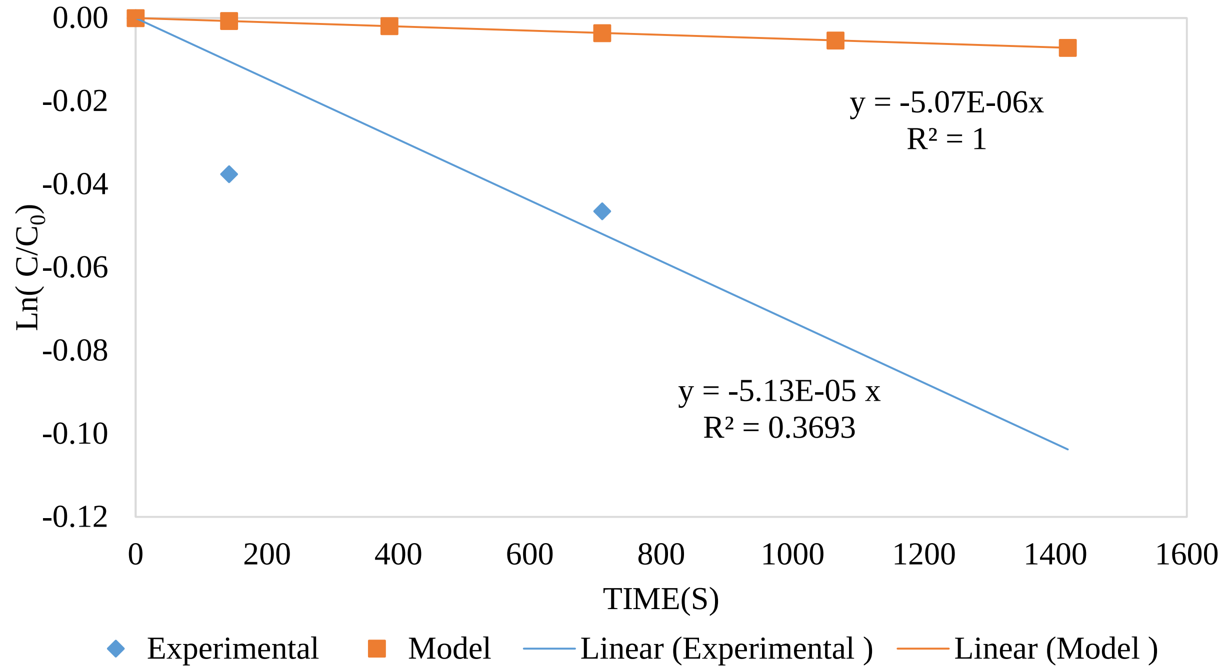


Figure 25: Carbon tetrachloride degradation with OH radicals

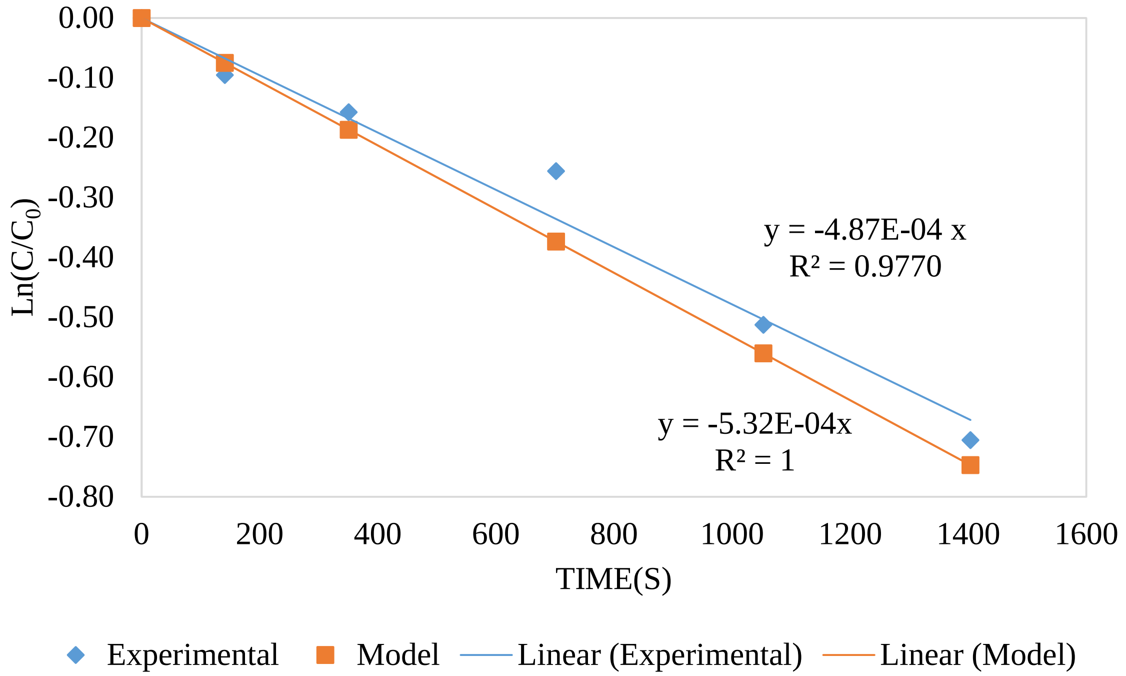


Figure 26: 1, 2, 3-trichloropropane degradation with OH radicals

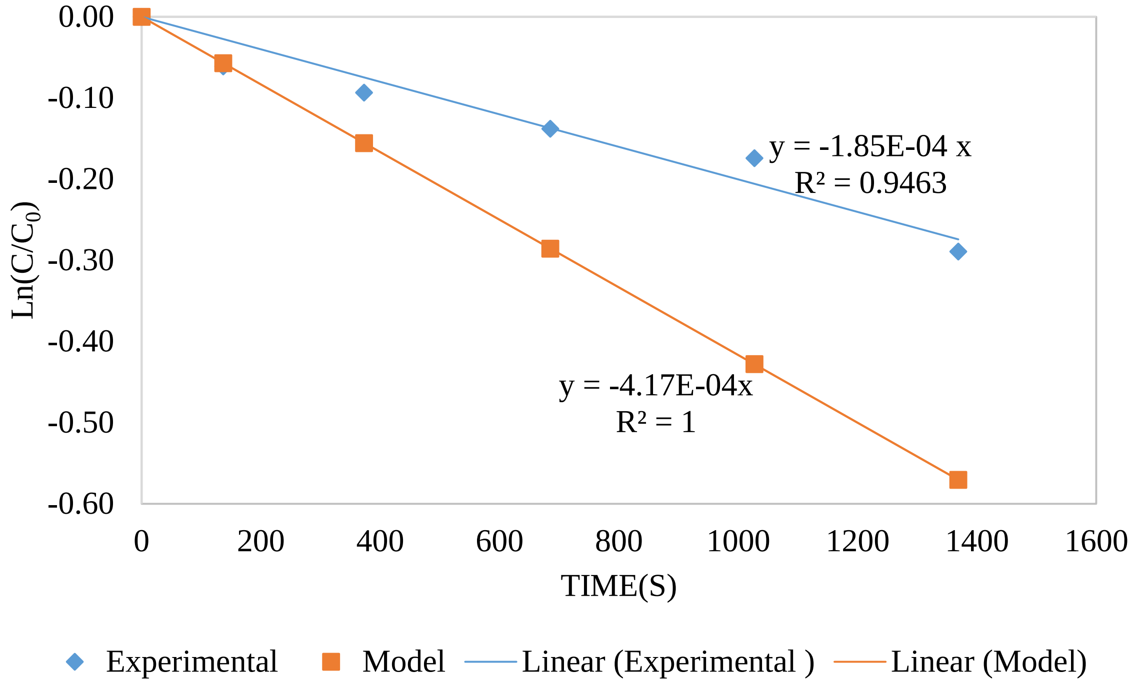


Figure 27: 1, 2-dichloropropane degradation with OH radicals

4.2 OH Radical Modeling Using Groundwater

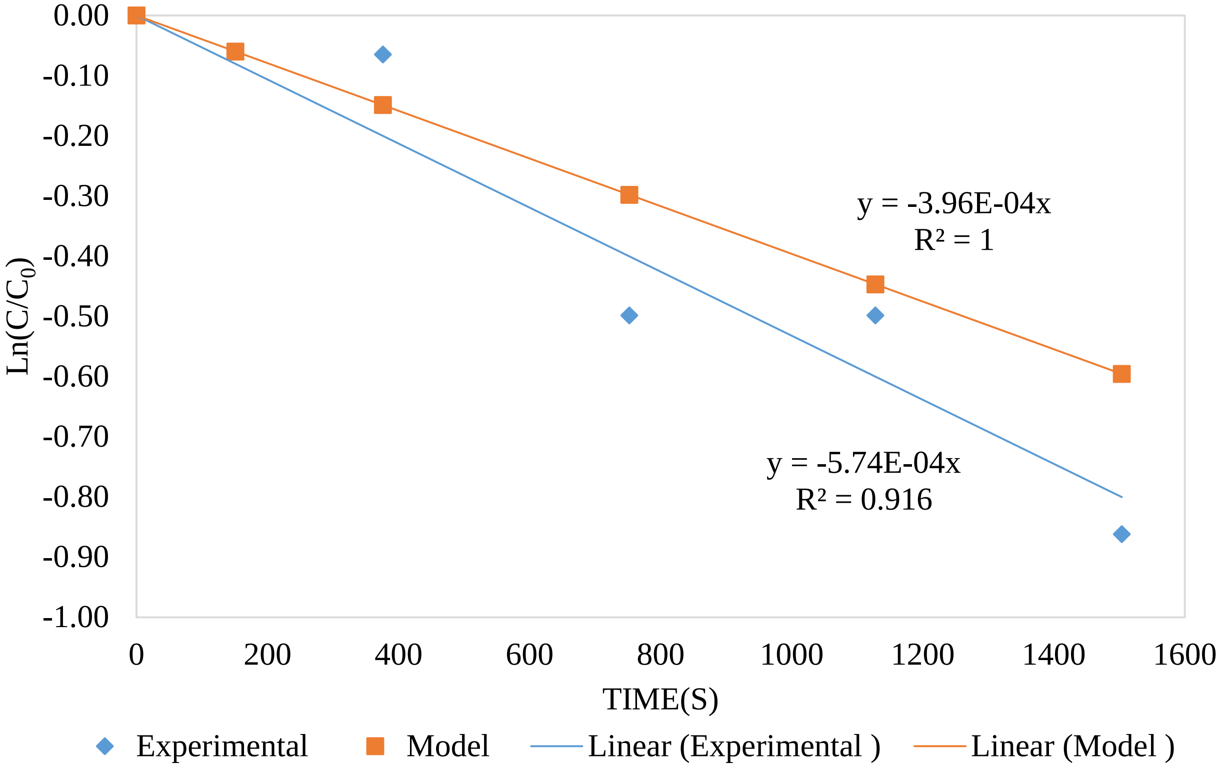


Figure 28: Benzene degradation with OH radicals

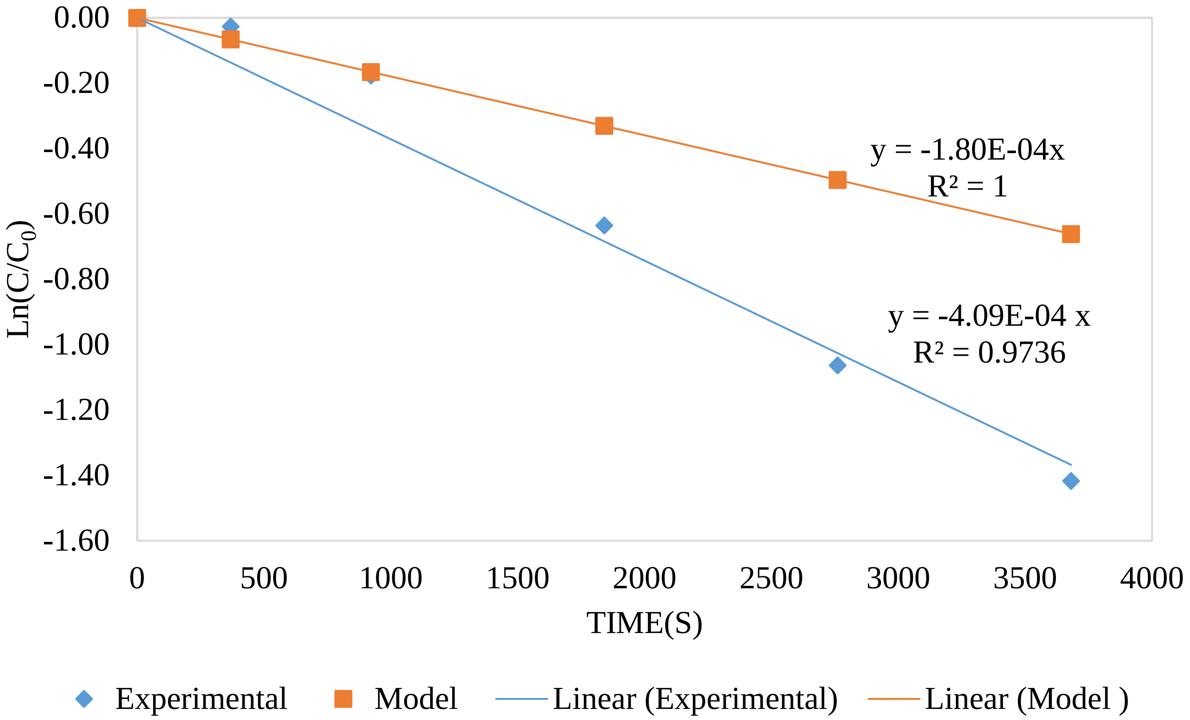


Figure 29: Tetrachloroethylene degradation with OH radicals

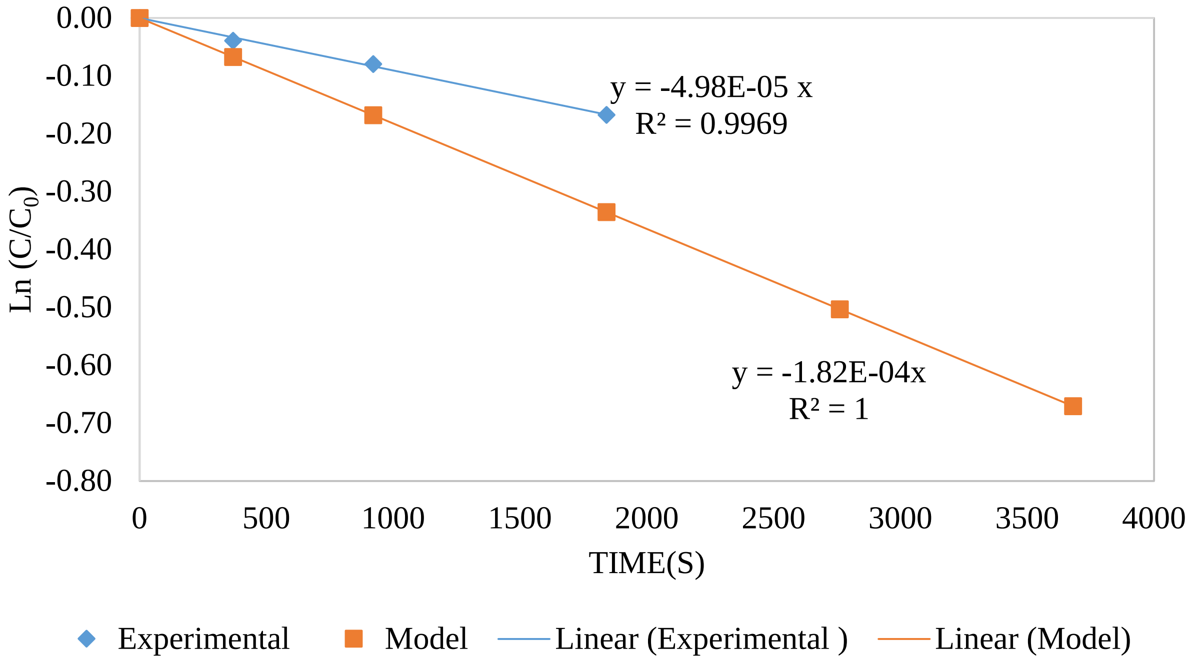


Figure 30:1, 2, 3 trichloropropane degradation with OH radicals