Predicting the Removal of Micropollutants in Lake Ontario and Grand River using Ozonation

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Micropollutants occur at low concentrations (µg/L to ng/L), can have a range of environmental and health effects, and can enter surface water through run-off from fields and wastewater discharge. Surface water is used for drinking water production and therefore, it is crucial to remove any micropollutants during drinking water treatment. Ozonation is an effective treatment process for degrading micropollutants involving the use of ozone (O_3) which also decomposes to produce the hydroxyl radical (●OH). The Rct value, a unitless parameter, represents the ratio of ●OH to O_3 exposure and is a water characteristic.

The Rct value is a crucial component of the micropollutant degradation model. However, implementation of this model has often been done under baseline or limited conditions. The primary objective of this thesis was to use this model to predict how effective the ozonation process was for three different drinking water treatment plants for a range of micropollutants and seasonal conditions. Seasonal Rct values were determined from measurements in water samples taken just prior to the ozone contactors of the 3 participating utilities using low and high applied ozone doses (1 and 4 mg/L). Water quality parameters as well as ●OH and O_3 decay curves and therefore Rct values were found to vary among the three treatment plants and the seasons. Rct values ranged from 10^{-8} to 10^{-9}, which were consistent with the literature. Rct values for the 1 mg/L applied ozone dose were more varied among the three treatment plants than Rct values obtained with the 4 mg/L applied ozone dose. Pearson correlation analysis was used to investigate correlations of all water quality parameters and applied ozone dose with the Rct values. Ozone dose had the strongest significant correlation, $p<0.05$, with the Rct value with a value of

-0.70 while temperature and pH both had moderate correlations. A step-wise linear regression indicated that ozone dose and temperature were important factors to model the Rct value with an R^2 value of 0.70.

The micropollutants microcystin-LR (MC-LR) and atrazine were then chosen to validate the micropollutant degradation model representing fast and slow reacting compounds respectively. The validation with

atrazine was successful with a better fit for the 1 mg/L applied ozone dose than for the 4 mg/L dose. Temperature modifications improved the fit for the 4 mg/L applied ozone dose, but did not make a difference for the 1 mg/L dose. Early deviations occurred between the simulated and experimental results and were hypothesized to be attributed to the inability to measure ozone degradation in the first phase.

The Rct value, rate constants, and ozone exposure were then input into the model to simulate micropollutant degradation. Temperature and pH modifications were employed to ensure that the model could be used under a variety of seasonal conditions. The rate constants of O_3 and ●OH with the cannabinoids Δ^9-Tetrahydrocannabinol (THC) and cannabidiol (CBD) were predicted with quantitative structure-property relationship (QSPR) models, since they were not available in the literature. Both compounds were found to be fast-reacting with both of the oxidants. Simulations showed that degradation of benzene, toluene, ethylbenzene and xylenes (BTEX) and atrazine was highest in Lake Ontario, which was likely due to its water quality e.g. lower dissolved organic carbon (DOC). Simulations for the cannabinoids THC and CBD and the cyanotoxins MC-LR, anatoxin-a (ANTX), and cylindrospermopsin (CYN) showed fast and complete removal in all three treatment plants under all seasonal conditions studied. Individual BTEX compounds were degraded according to their rate constants with ozone with benzene having the lowest percent removal and the xylenes having the highest. In an assumed spill scenario, benzene was rarely removed below its regulated level in Canadian drinking water while ethylbenzene was removed in all water sources below the regulated value except for one simulation. Overall, this thesis shows that the micropollutant degradation model can be used to predict how effective the ozonation process is in specific drinking water treatment plants. Seasonality was considered by sampling throughout the year and by employing temperature and pH modifications, which increased the applicability of this model to better simulate real world treatment situations. The use of previously developed QSPR models to predict reaction rate constants of micropollutants makes it possible to apply the micropollutant degradation model to basically any micropollutant of interest to a utility.

Acknowledgements

To start with, I would like to thank my supervisors Drs. Sigrid Peldszus and Peter M. Huck for their guidance, encouragement and support. They were always able to provide advice when challenges arose in and out of the lab and I am grateful for everything that they have taught me in the last couple of years.

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Thank you to Carol Moralejo from the Department of Chemical Engineering at the University of Waterloo for helping me troubleshoot problems with ozone generation and measurement; her patience, creativity, and positive outlook was much appreciated. I am also grateful of the support of Mark Merlau and Mark Sobon who helped with overall lab troubleshooting and were always willing to lend a helping hand.

I would like to thank Dr. Xiaohui Jin from the Walkerton Clean Water Center for the generating rate constants for the cannabis compounds, his help with the bench scale set-up and his overall guidance and advice.

This project was conducted in partnership with the City of Brantford, the Region of Waterloo and Halton Region. I would like to thank everyone at the plants who provided assistance during my sampling trips specifically Peter Clarke at the Region of Waterloo, Lindsay Chapin at the City of Brantford, and Bish Machcinski at Halton Region. This project was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC) in the form of an Industrial Research Chair in Water Treatment at the University of Waterloo.

Thank you to Diana Petrarca for being a supportive boss and an inspirational mentor. Working for you these past years has been an amazing experience.

Last but not least, I would like to thank my close friends and family who were there for me throughout the course of this thesis. They say it takes a village to raise a child but it also takes a village to raise a graduate student through their thesis. A special thank you to my mom, grandma, brother, Andrew, Erika, Ariel and Diana. You all are amazing human beings who provided me with encouragement and support when I needed it the most thank you for always being there for me.

Dedication

About half-way through this thesis I suffered an accident which resulted in a brain injury. Because of this I was unable to read, write, or process information for many months. I could not interact with those closest to me, and I feared that I would never be able to perform day to day activities as I had before the accident. It is with much amazement and gratitude that I sit here with a completed thesis, when only a year ago it was a struggle to read a few pages from a book. I would like to graciously thank all of the health professionals who helped me through my recovery and provided me with encouragement. Thank you also to my close family and friends who were a crucial support system.

In the spirit of recovery and surpassing what seem to be insurmountable obstacles, I would like to dedicate my thesis to those who similarly face major challenges. May you also find the light at the end of the tunnel.

"Things we lose have a way of coming back to us in the end, if not always in the way we expect."
-Luna Lovegood; Harry Potter and the Order of the Phoenix; J.K. Rowling.

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List of Acronyms

ADDA 3-amino-9-methyoxy-2,6,8-trimethyl-10-phenyl-4,6-decadienoic

ANTX anatoxin-a

BB building blocks

BP biopolymers

BTEX benzene, toluene, ethylbenzene and xylenes

CBD cannabidiol

CYN cylindrospermopsin

DBP disinfection by product

DOC dissolved organic carbon

E_a activation energy

HS humic substances

H_2O_2 hydrogen peroxide

LC-MS liquid chromatography tandem mass spectrometry

LC-OCD liquid chromatography organic carbon detection (LC-OCD)

LMW low-molecular weight

MAC maximum acceptable concentration

MC-LR microcystin-LR

Mdha methyl-dehydroalanine

MDL method detection limit

MRM multiple reaction monitoring

NOM natural organic matter

O_3 ozone

●**OH** hydroxyl radical

pCBA para-chlorobenzoic acid

SAC/OC Spectral Absorption Coefficient to organic carbon ratio

SUVA specific ultraviolet absorbance

THC Δ^9-Tetrahydrocannabinol

TOC total organic cabron

QSPR quantitative structure-property relationship

Chapter 1 Introduction

1.1 Problem Statement

Micropollutants are a major group of contaminants, named after their low concentrations (μg/l or ng/L) in aquatic systems (Schwarzenbach et al., 2006). They can enter surface water through run-off from agricultural sources and wastewater discharge, and they have been detected in groundwater, surface water and drinking water (Benotti et al., 2009; Jin & Peldszus, 2012; Snyder, 2008). Although micropollutants are present at low levels, they can still be harmful to human and environmental health (Luo et al., 2014). Due to this, for the safety of human health, it is crucial to remove these pollutants from our drinking water. Micropollutants can be difficult to regulate since there are many and they occur in a large range of household and industrial items (Luo et al., 2014). Some micropollutants such as benzene and the cyanotoxin MC-LR have known toxic effects on humans, and are therefore regulated in Canadian drinking water with enforceable maximum acceptable concentrations (MACs) which can be quite low (Health Canada 2016; Health Canada 2009). However, other compounds like ANTX and CYN are being assessed and will potentially be regulated in the future (Health Canada, 2016).

Ozonation is a water treatment process in which O_3 and ●OH act as oxidizers which can effectively degrade contaminants. One way to characterize these oxidants in a particular water source is through the Rct value. The Rct value is experimentally determined and represents the ratio of ●OH to O_3 exposure. It is crucial to characterize a water source with regards to its Rct value as micropollutants will react differently with both of these oxidizers.

However, the effectiveness of ozonation on micropollutant removal has not been as extensively studied at the drinking water plant level (von Gunten, 2003a). Drinking water treatment plants monitor regulated compounds but have less methods in place to assess how effective their plant is at removing unregulated micropollutants.

The micropollutant degradation model developed by Elovitz and von Gunten, (1999) can simulate the degradation of multiple micropollutants which is more time and cost effective than lab experiments (Jin, 2012). However, many applications of this model (e.g. Elovitz, and von Gunten, 1999; Jin, 2012) assume baseline conditions (pH=7, temperature=20^{o}C) and therefore do not consider the effect of seasonal water quality changes.

Seasonality is important as many water quality parameters such as pH, temperature, and organic content will change depending on the time of year. The change in these factors can then affect the degradation of micropollutants by ozone in the water source (Elovitz et al., 2000). Therefore, the model needs to be tailored for the conditions experienced at the drinking water treatment plant in order for it to be used to predict micropollutant degradation at the plant level. These predictions are valuable for utilities for assessing current performance of their ozonation process and for proactive planning.

There are a few inputs into the micropollutant degradation model, one being rate constants of the micropollutant with O_3 and ●OH. These rate constants can be obtained from the literature at baseline conditions (pH=7, temperature=20^{o}C). However, the rate constants need to be modified for seasonal temperatures and pH values which has not be done in numerous research articles (Elovitz, and von Gunten, 1999; Mcdowell et al., 2005; Vincent, et al., 2010) thereby limiting the applicability of the model.

In addition, if the rate constants are not available in the literature, they need to be experimentally measured in the lab which is time consuming and might not be feasible - especially if there are many contaminants of interest. These rate constants can now be predicted with recently created QSPR models (Jin et al., 2015; Jin et al., 2014). However, this method of using QSPR models to predict rate constants has not been employed in the literature.

Natural organic matter (NOM), which is always present in surface water and to a lesser degree in groundwater, reacts with oxidants thereby decreasing the amount of oxidants that are available to degrade micropollutants (Elovitz et al*.,* 2000). When examining the effect of NOM on the Rct value most literature looks at DOC as an overall parameter (Elovitz et al., 2000; Shin et al., 2015; Vincent et al., 2010; Zimmermann et al., 2011). However, liquid chromatography organic carbon detection (LC-OCD) can be used to separate NOM into its individual DOC fractions which can change seasonally. Looking at the individual DOC fractions can be useful because these can either decrease or increase during the ozonation process which can affect downstream water treatment processes (Croft, 2012; Pharand, 2014). Past research has used LC-OCD to investigate the effect of ozonation on various DOC fractions (Croft, 2012; Pharand, 2014), but to the author's knowledge this is the first study that looks at the effect of individual DOC fractions on the Rct value.

1.2 Objectives

Main Objective:

The objective of this research project is to predict the effectiveness of the ozonation process for a range of micropollutants in selected drinking water treatment plants thereby giving the water utilities a mechanism to gauge current performance and to plan proactively. This will be done in collaboration with 3 drinking water treatment plants in Ontario which use Grand River and Lake Ontario water as raw water. All plants employ ozone in their full-scale treatment train. Ozonation is characterized by the ratio of ozone to hydroxyl radical concentrations (Rct value) which will be determined for each of the participating utilities throughout the seasons. Contaminant degradation will then be modelled by using the micropollutant degradation model for a range of organic contaminants under various water quality conditions. The model will be validated prior to running simulations.

Sub-Objective 1:

Assess the use of Rct and micropollutant degradation models in the current literature.

Sub-Objective 2:

Determine the industry's expectations and research interests. The objective is to pick key contaminants, and water quality factors for treatment plant assessment which are of interest to the participating utilities.

Sub-Objective 3:

Measure the Rct values in pretreated waters in the 3 drinking water treatment plants to determine the seasonal changes in hydroxyl to ozone ratios. Use water samples taken just prior to the ozone contactors.

Sub-Objective 4:

Measure the NOM characteristics and other water quality parameters for all samplings of the 3 water treatment plants to assess similarities and differences.

Sub-Objective 5:

Measure the LC-OCD fractions before and after ozonation for the 3 water treatment plants to observe the effect of ozonation on the NOM characteristics.

Sub-Objective 6:

Validate the micropollutant degradation model by comparing modeled to experimental results for atrazine degradation by ozone. Atrazine is a pollutant of interest to the participating utilities.

Sub-Objective 7:

Investigate the effect of the first phase of ozone decay on the Rct value.

Sub-Objective 8:

Simulate the degradation of chosen contaminants throughout the year under various water quality conditions to provide the 3 treatment plants with an assessment of the effectiveness of their ozone process.

1.3 Thesis Approach and Structure

This thesis is made up of 5 chapters, with Chapters 3 and 4 having the structure of a paper format thesis each having their own methods, results and conclusions section. Chapter 2 consists of a literature review which provides a summary of published material that is relevant to this work. Chapter 3 describes the results of measuring seasonal ●OH and O_3 concentrations in the 3 treatment plants using the Indigo method and liquid chromatography mass spectrometry (LC-MS) and translating this into the Rct value. It also contrasts the water quality and NOM characteristics between the 3 treatment plants using LC-OCD while also considering the effect of ozone on NOM fractions. Chapter 4 describes the validation of the micropollutant degradation model using the developed atrazine LC-MS method to measure atrazine degradation and to compare these values to modelled atrazine degradation results. The influence of the first phase of the ozone decay on the Rct value is also investigated. It then presents seasonal simulations of a variety of micropollutants in the participating drinking water treatment plants by using the model and modifying input parameters for temperature and pH. Dr. Xiaohui Jin provided assistance to Chapter 4 by generating the rate constants for the cannabis compounds using QSPR models he had developed earlier in his research. These rate constants were no available from the literature. Chapter 5 concludes the thesis by providing a summary of results as well as recommendations for future research. References for all the chapters can be found at the end of the thesis in a single list. Supplementary information is located in the appendices.

Chapter 2 Literature Review

2.1 Introduction

Micropollutants, an emerging group of contaminants, are named after their small concentrations in aquatic systems (µg/L or ng/L). There has been growing concern around micropollutants due to their range in structures causing them to have different environmental and health effects. Difficulties can also arise when measuring their concentration in water sources, and during treatment (Jin, 2012). Micropollutants are difficult to regulate since they occur in a large range of household and industrial items (Schwarzenbach et al., 2006) and can include endocrine disrupting chemicals, personal care products, and pharmaceuticals to name a few (Westerhoff et al., 2005). They also originate from fertilizer and pesticide contamination through agricultural practices (Schwarzenbach et al., 2006). These can enter the water through various ways such as through run-off from agriculture, and wastewater discharge and have been found in groundwater, surface water and drinking water (Benotti et al., 2009; Jin & Peldszus, 2012; Snyder, 2008).

Thus far micropollutant regulation is limited with only a few of them having discharge guidelines. Further research is needed in this area so that their removal and toxicity can be understood and this can be used to guide further guide regulations (Luo et al., 2014). Even though they are present at low concentrations their toxicity is of great concern as they can have negative impacts on the environment and human health (Schwarzenbach et al., 2006). One of the main health concerns with micropollutants is that long term exposure could cause chronic conditions in humans (e.g. Snyder, 2008). Micropollutants can also cause toxicity and antibiotic resistance in bacteria (Luo et al., 2014). Therefore, drinking water treatment plants are crucial to remove these contaminants from our drinking water. This review and thesis will look specifically at benzene, toluene, ethylbenzene, xylenes, atrazine, ANTX, CYN, MC-LR, THC and CBD. These micropollutants were of interest to the three water treatment plants and were selected after a series of discussions with them.

2.2. Micropollutant Regulations and Toxicity

2.2.1 BTEX

BTEX refers to a group of volatile organic compounds: Benzene, toluene, ethylbenzene and o, m, p-xylenes (Fayemiwo et al., 2017; Mitra and Roy., 2011). BTEX is a constituent of petroleum items and can be found in water after oil or gasoline spills. Toluene and m-xylene make up over half of BTEX, with the rest of the compounds making up between 9-12%. BTEX is regulated in drinking water in Canada with MACs for each individual BTEX compound as can be seen from Table 2.1. Benzene is a human carcinogen and has the lowest MAC level of 5 µg/L (Health Canada, 2009). Toluene has the second lowest MAC level of 60 µg/L (Health Canada, 2014). Even though this compound has negative neurological effects on animals it cannot be classified as a carcinogen due to a lack of information (Health Canada, 2014). Ethylbenzene is possibly a carcinogen with long term studies on rats showing tumour development with a MAC level of 140 µg/L (Health Canada, 2014). Xylenes are not classified as carcinogenic but have negative neurological effects and a combined MAC level of 90 µg/L (Health Canada, 2014). In general, conventional treatment techniques such as coagulation and flocculation do not effectively remove BTEX from drinking water. Granular activated carbon adsorption is seen as an effective treatment, while oxidation processes such as ozonation may also be effective (Health Canada, 2009; Health Canada, 2014).

Table 2.1. BTEX percentage in gasoline, MAC levels, and molecular formulas. Molecular formula and percentage from (Mitra & Roy,2011). MAC levels from (Health Canada, 2009; Health Canada, 2014).

BTEX Fraction	Percentage in gasoline	MAC (μg/L)	Molecular Formula
Benzene	11	5	C_6H_6
Toluene	26	60	$C_6H_5CH_3$
Ethylbenzene	11	140	$C_6H_5CH_2CH_3$
p-Xylene	9	90 total	$C_6H_4(CH_3)_2$
m-Xylene	31	90 total	$C_6H_4(CH_3)_2$
o-Xylene	12	90 total	$C_6H_4(CH_3)_2$

2.2.2 Atrazine

Atrazine is a herbicide used to treat weeds on fields with corn and rapeseed in Canada and has a MAC of 5 μg/L in Canada (Health Canada, 2011). In comparison, the regulation is 3 μg/L in United States and has been banned for many years in Sweden due to atrazine's persistence in cool dry soils which are common in this country (Graymore et al*.,* 2001). This herbicide degrades slowly in water and can have a half-life of more than two years in neutral water. Depending on the soil conditions it can also stay in the soil for a full season (Health Canada, 2011). In addition, atrazine is usually applied to fields after rain events and therefore is more disposed to leaching and run-off (Graymore et al., 2001). In Canada, atrazine occurs frequently in surface and well water in areas where it is extensively used such as in Ontario, Quebec and British Columbia (Health Canada, 2011) at a concentration range of ng/L to μg/L (Hua et al*.*, 2006).

Atrazine is not effectively removed through conventional drinking water treatments such as coagulation, filtration and chlorination (Ternes et al., 2002; Verstraeten et al*.,* 2002). Therefore, other processes have been investigated to see which ones can effectively remove this contaminant. Ozone could be a potential approach to dealing with atrazine. Although, of note is that the rate constant of atrazine with O_3 is fairly low at 6 $M^{-1}S^{-1}$ (Acero et al., 2000). The structure of atrazine is shown below in Figure 2.1. The low

reactivity of atrazine could be partially explained by its ring of nitrogen which have an electron-withdrawing effect (Yao & Haag, 1991).

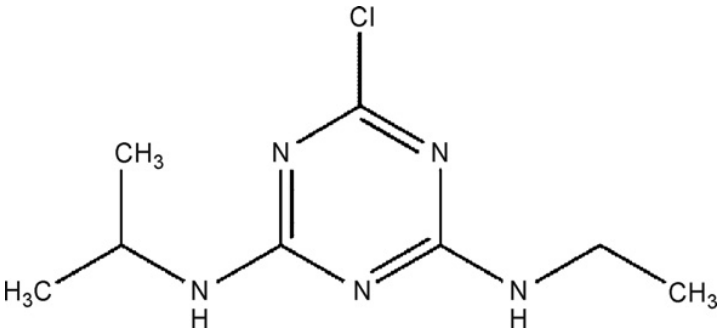
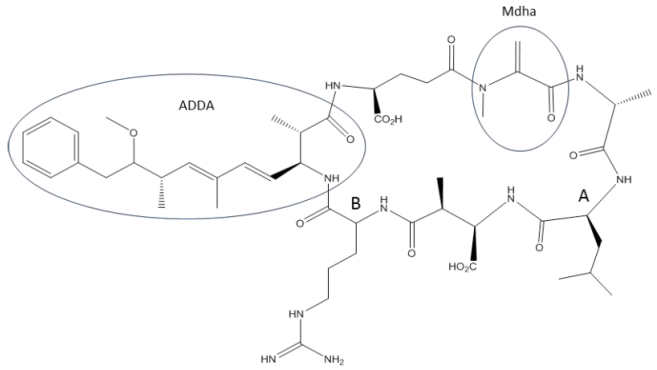


Figure 2.1 Structure of Atrazine (Vera et al., 2009)

2.2.3 Cyanotoxins

Cyanotoxins are made by cyanobacteria, formerly known as blue-green algae, which can be found in lakes in late summer and fall. Cyanobacterial blooms can occur under certain circumstances such as warm water temperature and high nutrient concentrations. Cyanobacteria produce cyanotoxins which are located within their cells (intracellular toxins). However, these cells can die and rupture during cyanobacterial blooms releasing the toxin from the cell (extracellular toxin) (Fromme et al., 2000). Cyanobacterial blooms can also contribute to taste and odour issues which lower the quality of the water (Westrick et al., 2010).

This study will focus on three cyanotoxins commonly detected in North America namely MC-LR, ANTX, and CYN. In freshwaters microcystins are one of the most common cyanotoxins and are produced by a variety of cyanobacterial species. They are the most varied and biggest group of cyanotoxins, but this study will only focus on one congener MC-LR (Zegura et al.,2011). MC-LR is one of the most studied microcystins and it is a hepatotoxin which can bioaccumulate in aquatic species. As can be seen from Figure 2.2 it contains ADDA (3-amino-9-methyoxy-2,6,8-trimethyl-10-phenyl-4,6-decadienoic) and Mdha (methyl-dehydroalanine) groups which can bind to and inhibit protein phosphatases in animals contributing to MC-LR's toxicity (Schmidt et al., 2014).



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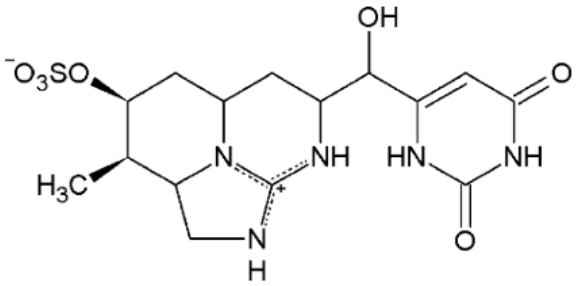

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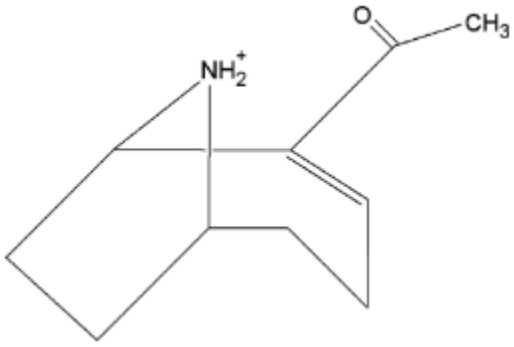


C

Figure 2.2 Structures of MC-LR, CYN and ANTX. A) MC-LR with its ADDA and Mdha groups circled (Schmidt et al., 2014) , B) CYN (Zegura et al.,2011), and C)ANTX (Zegura et al.,2011).

CYN is produced by various cyanobacteria species and is a hepatotoxin. As can be seen from Figure 2.2 it is an alkaloid and is zwitterionic (zero net charge) due to its positive guanidine and negative sulphate groups (Zegura et al.,2011). ANTX is an alkaloid and is a neurotoxin that produces acute effects and is produced by a couple of cyanobacterial species (Zegura et al.,2011). Its structure can be seen from Figure 2.2. The World Health Organization (WHO) has set guidelines of 1 µg/L for MC-LR and for CYN. However, ANTX does not have a guideline, since not enough is known on the toxic effects of ANTX on humans or animals (Rodríguez et al., 2007). In Canada the MAC for total microcystins in water is 1.5 µg/L while there are no Federal Guidelines for ANTX or CYN due to the fact that not enough information is known about their health impacts (Health Canada, 2016).

When looking at treatment options for cyanotoxins it is important to consider whether the toxin is intra or extracellular. During a cyanobacterial bloom most of the toxins are intracellular (Fromme et al., 2000; Hoeger et al., 2002). When conditions stop being optimal for cyanobacterial growth collapse will occur and intracellular toxins will be released as extracellular toxins (Westrick et al., 2010). Furthermore, extracellular toxins can be released during water treatment if cyanobacterial cells are ruptured. Researchers agree that cyanotoxin removal is optimal when unbroken cyanobacterial cells are removed which prevents contribution to extracellular toxin concentration (Chorus & Bartram, 1999; Westrick et al., 2010). Conventional treatment processes such as coagulation, sedimentation, and filtration are usually used to remove intracellular toxins. However, these processes are reported to not be effective for complete cyanotoxin removal (Hoeger et al., 2002; Jasim & Saththasivam, 2017; Rodríguez et al., 2007). Additional treatment processes such as ozonation and activated carbon are needed to treat extracellular toxins. However, care must be taken not to use high ozone doses as these can further lyse cyanobacterial cells producing more cyanotoxin (Miao & Tao, 2009).

2.2.4 Cannabis

An emerging area of micropollutants are recreational and illicit drugs which may not be removed by wastewater treatment plants and can enter surface water through their effluents. These drugs can then enter drinking water treatment plants since they use said surface water and these drugs may pose a risk for human consumption (Boleda et al., 2007., Boleda, et al., 2009). Cannabis contains cannabinoids, a group of compounds that act upon the cannabinoid receptors. THC contributes to the psychoactive effects of cannabis while CBD is an isomer of THC but does not have its psychoactive properties (Russo & Guy, 2006). See Figure 2.3 for structures of both of these compounds. Currently, neither CBD nor THC have guidelines for drinking water in Canada.

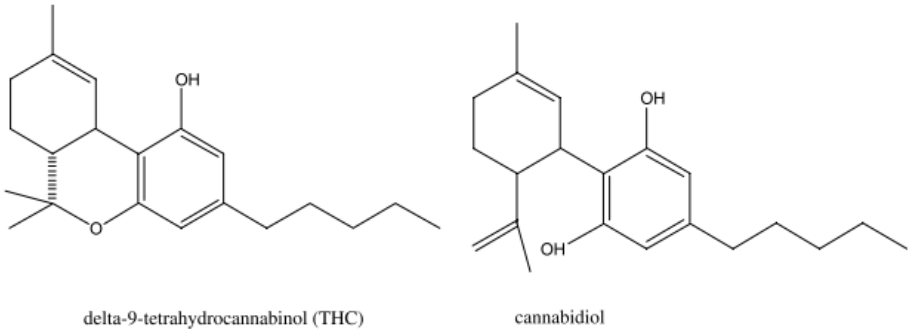


Figure 2.3 Structure of THC and CBD (Russo & Guy, 2006)

Previous studies have looked into monitoring the concentrations of certain drugs in surface water and wastewater (Bijlsma et al., 2009; Castiglioni et al., 2016; Boleda et al., 2007) using liquid chromatography tandem mass spectrometry (LCMS). Castiglioni et al., (2016) estimated drug use in different parts of a city using wastewater analysis and identified that some areas had higher use of THC which they hypothesized could be due to the nighttime establishments located in that area.

Boleda et al., (2007) were able to measure cannabinoids in the influent and effluent of wastewater treatment plants and found higher cannabinoids levels than previously reported which may suggest that the treatment processes used were not effective.

2.3 Ozonation Kinetics

2.3.1 ●OH and O_3 as Oxidants and the Rct Value

Ozonation, which involves the use of O_3, is an effective treatment for removing micropollutants in drinking water treatment plants. O_3 is an unstable oxidizing species and through a series of chain reactions decomposes to produce the ●OH (Figure 2.4) although ozone concentration is much higher than OH concentration in the water (von Gunten, 2003a).

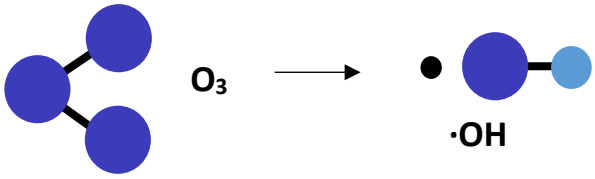


Figure 2.4: Decomposition of O_3 into ●OH

These two oxidizers, O_3 and ●OH, are important as they degrade contaminants in the water and need to be taken into consideration when assessing ozonation as a treatment (von Gunten, 2003a). O_3 is more selective than ●OH, reacting with compounds that have double bounds and other electron rich structures. If compounds are resistant to the oxidation of O_3 only then are they degraded by ●OH. ●OH is very reactive and non-specific and because of this is seen as the stronger oxidant out of the two (Elovitz & von Gunten, 1999). O_3 is effective at reacting with microbes and acts as a disinfectant, while ●OH does not due to its low concentration in the water. Drinking water treatment plants may choose to employ high applied ozone doses for disinfection, however, they have to be careful of disinfection by product (DBP) formation, which can be harmful to human health (von Gunten, 2003b).

DBPs can be formed through the reaction of oxidizing species with NOM micropollutants and bromide in the source water (Andrew et al., 2015). One of the main DBPs is bromate, which has been linked to cancer and can form when water containing bromide is ozonated (von Gunten, 2003b). It is generally thought that increasing the applied ozone dose will increase the amount of DBPs formed. Therefore, utilities need to optimize ozonation in order to have high enough oxidant doses for disinfection and micropollutant removal, but low enough so that not too many DBPs are formed (Elovitz & von Gunten, 1999).

O_3 concentration can either be measured directly by a spectrophotometer, or the Indigo method (Hoigné, 1994). However, ●OH has a high reactivity in water which makes it difficult to measure (Elovitz & von Gunten, 1999). Elovitz & von Gunten, (1999) were able to resolve this issue and used para-chlorobenzoic acid (pCBA) as a probe compound to indirectly measure ●OH concentration. pCBA makes a good probe compound because it reacts rapidly with ●OH and slowly with O_3 (Elovitz & von Gunten, 1999). Furthermore, Elovitz & von Gunten, (1999) also created a new parameter known as the Rct value which represents the ratio of ●OH to O_3 exposure as shown by equation 2.1.

$$R_{ct} = \frac{\bullet OH}{[O_3]}$$

Equation 2.1: The Rct value

Prior to the Rct value, researchers were unable to measure ●OH concentration. Their approach was to model ozone decomposition and the coinciding ●OH concentration that was based on a set of elementary reactions for a defined water system. However, large adjustments to the rate constants and data fitting needed to be employed for these models to be able to predict ozone degradation. Therefore, these were not effective methods to predict ozone and ●OH concentration (Elovitz & von Gunten, 1999). This problem was solved with the findings of Elovitz & von Gunten, (1999) who were able to measure both of these oxidants in water and further discovered that the Rct was constant and a water characteristic within the water samples that they studied.

2.3.2 Bi-Phasic Ozone Degradation

Ozone is unstable and reacts with other constituents in the water such as dissolved organic matter, making it highly dependent on the water quality, temperature and ozone dosage (Hoigné, 1994). When O_3 is added to the water it is initially decomposed rapidly as it reacts with water constituents. This is called the first phase and can range anywhere from 0-2 minutes and the end point of this phase is difficult to determine (Buffle et al., 2006a; Hoigne& Bader, 1994; Shin et al., 2015). The first phase is followed by a secondary phase that has a slower O_3 decomposition than the first (Buffle et al., 2006; Elovitz,& von Gunten, 1999). Together these two phases are referred to as the bi-phasic kinetics of ozone degradation (Buffle & von Gunten, 2006).

The ozone degradation in the second phase can be modelled using first order kinetics, and results in a constant Rct value (Elovitz & von Gunten, 1999). This constant Rct value is no longer dependent on the time of the reaction, and the Rct value becomes the ratio of ●OH to O_3 concentration for any point in the

reaction (Elovitz & von Gunten, 1999). In the first phase, it is more difficult to obtain data points and first order kinetics do not always hold. Therefore, most researchers generalize the Rct value to focus on the second phase and neglect the effect of the first phase (Elovitz & von Gunten, 1999). This review will do the same unless otherwise stated.

2.3.3 Rct Value & Water Quality Parameters

O_3 and ●OH, will react with water constituents other than micropollutants and therefore the Rct value will be affected by water quality (von Gunten, 2003b). The main factors that affect the Rct value are pH, alkalinity, temperature, and dissolved organic carbon (Elovitz et al., 2000).

The decomposition of ozone is dependent on the characteristics of the water source and can vary anywhere from seconds to hours. Higher pH, temperature, and NOM will all increase ozone decomposition resulting in more ●OH production which will increase the Rct value (Figure 2.5). On the other hand, alkalinity decreases O_3 decomposition and can scavenge ●OH both of which decrease the Rct value.

$$R_{ct} = \frac{[\bullet OH]}{[O_3]}$$

← pH ↑
← Temperature ↑
← DOM ↑
← Alkalinity ↓

Figure 2.5: Effects of water quality on the Rct value

NOM has a higher concentration (mg/L) than micropollutants (ng/L- µg/L) and will consume O_3 or ●OH thereby reducing the oxidation capacity of the ozone in the water (Peter & von Gunten, 2007). It has been shown in past experiments that water sources with low DOC levels will need smaller O_3 doses to remove micropollutants in comparison to samples with higher DOC levels (Peter & von Gunten, 2007). Due to difficulties in measuring NOM, substitute parameters are used instead such as DOC or TOC.

Another water quality factor which affects the Rct value is pH. Vincent et al., (2010) investigated the effect of water quality factors on the Rct value and found that pH was the most important variable. An increase in pH results in an increased number of hydroxide ions (OH^-) in the water source. These hydroxide ions will then react with O_3 to start a series of reactions which will result in ●OH production (von Gunten, 2003b). Therefore, an increase in pH will increase ozone decomposition, and result in a higher Rct value due to the increased production of ●OH (von Gunten, 2003b). Elovitz et al. (2000) observed a 40 fold increase in the Rct value with a pH increase from 6 to 9. Buffle et al. (2006) saw an increase in ozone decomposition with an increase in the pH value of 2 to about 7.9; where maximum ozone decomposition occurred at a pH=6.7. Rct values are also affected by temperature, with higher temperatures resulting in increased O_3 decay with no effect on ●OH exposure. This is significant as disinfection by O_3 is reduced by high temperatures, whereas ●OH oxidation remains unaffected (Elovitz et al., 2000). In Shin et al. (2015) an increase in temperature from 6 to 25^oC caused the Rct value to increase by a factor of 9.8. This is comparable to Elovitz et al. (2000) who observed a 14-fold increase in the Rct value with a temperature change from 5 to 35^oC. Shin et al.,(2015) concluded that temperature had the most significant effect on oxidation parameters in comparison to organic matter, alkalinity and pH.

Increasing alkalinity will result in a decreased Rct value, by decreasing the amount of ●OH. Carbonate species such as CO_3^{2-} and HCO^{3-} are inhibitors and react with ●OH to produce species that slow the rate of O_3 decomposition. In comparison to these inhibitors, promoters such as methanol react with ●OH and form species that increase the rate of O_3 breakdown(Elovitz et al., 2000).Overall, numerous articles have shown the significant effects that water quality has on the Rct values. Table 2.1 summarizes Rct values from various references that have a range in water quality, ozone doses and source water. As can be seen from this table Rct values vary from 10^{-6} to 10^{-10} ,however, the DOC range of these experiments were fairly low ranging from 0.7-2.7 mg C/L.

Table 2.1: The effect of ozone dose and water quality factors on the Rct value

Rct Value	Log Rct Value	$[O_3]$ (mg/L)	DOC (mg C/L)	Alkalinity	pH	Temperature (°C)	Source Water	Reference
$2.2*10^{-10}$	-9.66	2	0.8	5mM	7	12	Raw well water	(Acero et al., 2001)
$4*10^{-9}$	-8.40	2	2.7	3.8mM	7	12	Raw lake water	(Acero et al., 2001)
$5.0*10^{-9}$	-8.30	1	0.9	33 $mgCaCO_3$/ L	6.9	6	Sand-filtered lake water	(Shin et al., 2015)
$6*10^{-9}$	-8.22	1	-	2.5mM	8	5	Raw lake water	(Elovitz et al., 2000)
$7.9*10^{-9}$	-8.1	1	2.54	2 $mgCaCO_3$/ L	5.6	20	Partially treated lake water	(Vincent et al., 2010)
$1.1*10^{-8}$	-7.96	1	-	-	6.5	15	Raw lake water	(Elovitz & von Gunten, 1999)
$1.5*10^{-8}$	-7.82	2	2.5	3.9mM	7	11	Raw river water	(Acero et al., 2000)
$2.0*10^{-8}$	-7.70	1	0.7	34 $mgCaCO_3$/ L	6.7	20	Sand-filtered lake water	(Shin et al., 2015)
$5*10^{-8}$	-7.3	1	1.2	2.6mM	7.9	22	Raw lake water	(Peter & von Gunten, 2007)
$1.3*10^{-7}$	-6.89	1	1.7	40 $mgCaCO_3$/ L	6.6	26	Raw lake water	Shin, Hidayat, & Lee, 2015)
$2.5*10^{-7}$	-6.6	1	2.12	80 $mgCaCO_3$/ L	8.1	20	Partially treated river water	(Vincent et al., 2010)
$1.3*10^{-6}$	-5.9	2	2.12	80 $mgCaCO_3$/ L	8.1	20	Partially treated river water	(Vincent et al., 2010)

2.4 Modelling

2.4.1 Micropollutant Degradation Model

The micropollutant degradation model is an extension of the Rct value and was created by Elovitz & Gunten (1999) as can be seen from equation 2.2. This model can be used to predict the degradation of any micropollutant under a variety of seasonal conditions as well as varying ozone doses. The inputs into the model are as follows: second order rate constants of the micropollutant with ●OH and O_3 (k_{O3}, and $k_{\bullet OH}$), ozone exposure, and the Rct value.

$$\ln \frac{[P]}{[P]_0} = -\left(k_{\cdot OH,P} R_{ct} + k_{O_3,P}\right)\left(\int_0^t [O_3]dt\right)$$

Equation 2.2: Micropollutant Degradation Model

The Rct value is affected by water quality parameters and therefore this parameter represents water characteristics in the micropollutant degradation model (Elovitz & Gunten, 1999). The second order rate constants represent the reactivity of the selected micropollutant with the two oxidizing species. The ozone exposure shows the ozone concentration over a span of time (Elovitz & Gunten, 1999).

2.4.2 Seasonality and Model Modifications

As discussed previously, water quality variables will affect the Rct value. Therefore, seasonality will also have an impact on the Rct value as the water matrix will change in temperature, pH, alkalinity, and DOM at different points of the year (Elovitz et al., 2000). In order to incorporate seasonality into experiments, samples can be taken at various points throughout the year, Rct and water quality parameters are measured and the micropollutant degradation model can be modified for temperature and pH (Zimmermann et al., 2011).

The Arrhenius equation, as shown by equation 2.3 describes how reaction rate constants are affected by temperature.

$$k_{d,T2} = k_{d,T1} * \exp\left[\frac{E_a}{R} * \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

Equation 2.3: Arrhenius equation

From the equation, the k values ($k_{d,T1}$; $k_{d,T2}$; s^{-1}) give the decay constants at the two temperatures (T_1 and T_2; Kelvin). E_a represents the activation energy (kJ/mol), and R is the ideal gas constant. E_a is a representation of the reaction between ozone and the micropollutant.

The Arrhenius equation and E_a are often used to correct for temperatures in experiments that want to make their study more applicable (Zimmermann et al., 2011). However, changes in temperature have a greater effect on O_3 reactions than ●OH. Activation energies for ●OH have ranges of 5-10 kJ/mol in comparison to the large activation energy ranges of O_3 (Elliot & Simsons, 1984; Gardoni et al, 2012)

The micropollutant degradation model should also be modified for changes in pH. At different pH values, certain compounds can disassociate and their protonated and deprotonated forms will have individual rate constants with ●OH and O_3 (Jin, 2012). Overall, the rate constants with ●OH do not differ by much, while rate constants with O_3 will vary between protonated and deprotonated forms (Hoigné & Bader, 1983). The pH modification can be undertaken by determining the O_3 rate constant at a pH in which either the protonated or deprotonated form dominates (Jin, 2012). Therefore, at a given pH one would use the rate constant for the dominant form.

2.4.3 Rate Constants

Micropollutants have a diverse range of structural characteristics which affects their oxidation in water (Jin et al., 2014). Rate constants are used to measure the reactivity between these contaminants and ●OH and O_3. Overall, ●OH reacts non-specifically with micropollutants, while O_3 reactivity is dependent on micropollutant structure. Micropollutants which are susceptible to ozone are oxidized rapidly having high

rate constants. This is due to the reactivity of their electron rich structures with ozone. In contrast micropollutants which do not contain these structures are referred to as slow reactants with ozone. Therefore, rate constants will differ significantly between micropollutants (Mcdowell et al., 2005; von Gunten, 2003) .

The rate constants used in the micropollutant degradation model are measured under standard conditions ((T=20°C, pH=7) in ultrapure water. In order to extend the applicability of standard rate constants, modifications can be made for both pH and temperature. If modifications are not made, predictions are limited to the experimental conditions-pH, temperature- in which the rate constants were calculated. Currently, there are three main approaches to obtaining standard rate constants - published literature, experimental determination and model prediction (Figure 2.6).

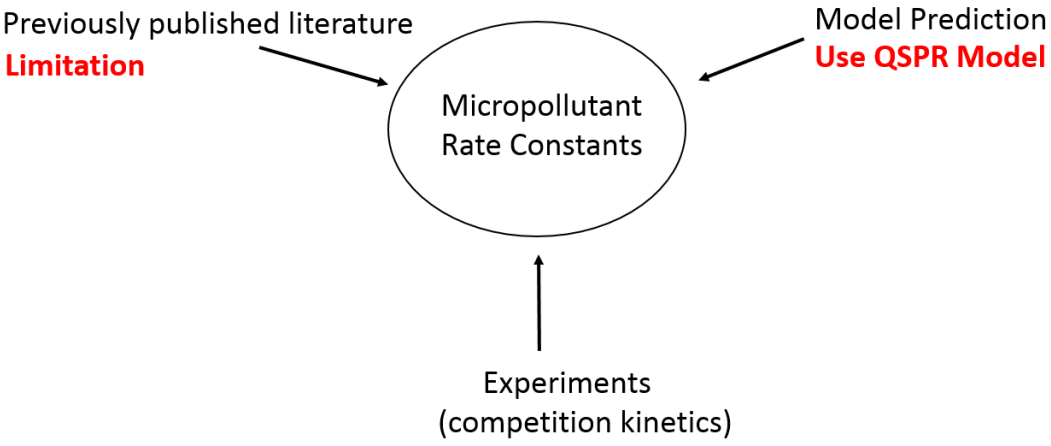


Figure 2.6: Different methods of obtaining micropollutant rate constants

The first approach obtaining standard k_{O3} and k_{OH} from literature is the easiest and often most preferred method. However, a major drawback is that some micropollutant rate constants have not been measured and therefore the researcher is limited in the range of compounds that they can explore (Jin, 2012). For example, Zimmermann et al., (2011) obtained k_{O3} and k_{OH} from published literature as they wanted to predict the degradation of 22 micropollutants, and the experimental approach would not be feasible in this case. However, these published rate constants were determined at experimental conditions that

differed from the conditions of Zimmermann et al., (2011). To solve this, rate constants were corrected for temperature by using the Arrhenius equation, and assuming an activation energy of 50 kJ/mol. Furthermore, acid-base speciation, and species-specific rate constants were taken into consideration to correct for pH.

The second approach involves the experimental determination of k_{O3}, and k_{OH}. Considering the vast amount of micropollutants in the environment this process can be both time and cost intensive when rate constants for several compounds are required. However, it is feasible if only few rate constants are needed. For example, Acero et al., (2000), only looked at one micropollutant atrazine and therefore experimental determination of k_{O3} and k_{OH} was a suitable choice. Mcdowell et al., (2005) also experimentally determined second order rate constants for two carbamazepine by products at a temperature of 20°C, and pHs of 6 and 8.

This leads directly into the third approach which are models that predict standard rate constants (Figure 2.6). Specifically, QSPR models are frequently employed for predicting the second order rate constants of micropollutants using their structural characteristics (Jin et al., 2014). The study of Jin et al., (2015) used QSPR models to accurately predict k_{O3} and k_{OH} values for an assortment of micropollutants. As with the other two rate constant approaches, these models have limitations. In this case, the QSPR is also set up at certain experimental conditions (pH, temperature) and modifications will need to be made to extend these second order rate constants to different pH and temperature conditions. Overall, k_{O3} and k_{OH} need to be obtained before predicting micropollutant degradation using the Elovitz and von Gunten model.

2.4.4 Application and Implementation in Drinking Water Treatment Plants

The use of the micropollutant degradation model has been seen in numerous research studies which focus on drinking water. These micropollutant simulations are important as they can be used as tools to assess the effectiveness of ozonation for micropollutant removal. This was seen in Vincent et al., (2010) , where

the degradation of multiple micropollutants (odour compounds, pesticides, and pharmaceuticals) were simulated for a specific water treatment plant.For validation purposes these predictions were then compared to the study of Snyder et al, (2006) resulting in similar micropollutant removal. The majority of micropollutants under investigation had low k_{o3} and high k_{OH} values, and overall researchers found that these micropollutants were not completely removed even at high applied ozone doses. For these pollutants due to their low reactivity with O_3, ●OH was more important for their removal. Therefore, in order to remove these pollutants from the water source, the ●OH concentration needed to be increased (Barry et al., 2014). In these, cases ozonation can be combined with hydrogen peroxide to promote ●OH formation and thereby help remove micropollutants as ozonation on its own may not be effective (Barry et al., 2014; Snyder et al., 2006).

The micropollutant degradation model can also be used to simulate the degradation of oxidation by-products of micropollutants. Mcdowell et al., (2005) used the micropollutant degradation model to simulate the degradation of carbamazepine and its by-products in lake water. Researchers then compared the model's predictions to validated lab results, which were found to be a good model fit. Although, this thesis will focus on modelling the degradation of micropollutants and will not model the removal of their by-products.

Acero et al., (2000) used the model to predict the removal of atrazine and its degradation products. Researchers found an upper bound on atrazine removal. If the level of atrazine in the intake water was greater than 0.1 µg/l then ozonation could not adequately remove enough of atrazine and its by-products to meet the European Union regulatory level of 0.1 µg/L. Therefore, this model can be used to assess what levels of micropollutant the treatment system can handle and whether or not ozone exposures should be increased.

In summary, the model allows for the prediction of the degradation of micropollutants and of their known, potentially harmful by-products. This can be predicted at a specific ozone dose allowing treatment plant operators to explore the trade-offs between increasing the ozone dose and removing more micropollutants, and contrast this with the potential increase in ozone disinfection by-products such as bromate.

2.5 Conclusions and Research Gaps

Micropollutants are difficult to regulate and can enter water sources through a variety of ways (Benotti et al., 2009). Furthermore, their structural range causes them to have different environmental and health effects and can make treatment removal difficult (Jin, 2012). The Rct value and micropollutant degradation model are very important tools that treatment plants can use to assess the effectiveness of their ozonation process on micropollutant removal. However, current research that employs the micropollutant degradation model assumes baseline conditions (pH=7, temperature=20^{o}C) (Elovitz, and von Gunten, 1999; Jin, 2012), and usually does not modify for temperature or pH (Elovitz, and von Gunten, 1999; Mcdowell et al., 2005; Vincent, et al., 2010). Furthermore, the use of QSPR models to predict rate constants is not heavily used in literature.

Chapter 3 Water Quality Characterization with Additional Effects of Ozone

3.1 Introduction

Ozone degrades rapidly in water in two phases forming ●OH. The first phase has rapid kinetics and is difficult to experimentally measure while the second phase is slower and can be modelled by first order kinetics (Elovitz, M., von Gunten, 1999). The Rct value is given by the ratio of ●OH to O_3 concentration and characterizes a water source with respect to their oxidation behaviour when ozone is applied. Both molecular ozone and ●OH can react with micropollutants and this Rct value can be further used to model micropollutant degradation therefore making it an important measurement.

Water quality parameters such as NOM, pH, temperature and alkalinity have all been shown to have an impact on the Rct value (Elovitz et al., 2000; Shin et al., 2015; Westerhoff et al., 1999). Temperature, pH and NOM increase O_3 decomposition and therefore increase the Rct value. In comparison, alkalinity decreases O_3 decomposition and decreases the Rct value (Elovitz et al., 2000).

NOM present in the water will react with the ozone and consume it providing less of it to react with the micropollutants (Elovitz et al., 2000). LC-OCD can be used to separate NOM into different fractions such as: humic substances, building blocks, biopolymers, low molecular weight (LMW) acids and LMW neutrals (Huber et al., 2010). Researchers have shown that NOM content changes before and after ozonation (Croft, 2012; Pharand, 2014). However, few researchers have looked at the effect of these various NOM fractions on the Rct value with most research focusing on DOC as a bulk measure representing NOM (Elovitz et al., 2000; Shin et al., 2015; Zimmermann et al., 2011).

Water quality can change significantly with the season and can affect ozonation kinetics (Shin et al., 2015). Many articles that look at oxidation kinetics (Elovitz, and von Gunten, 1999; Jin, 2012) often ignore the

effect of seasonality. These assume baseline conditions (pH=7, temperature=20^{o}C) producing results that are difficult to apply to real life problems in treatment plants.

Some researchers have incorporated seasonality into their experiments (Shin et al., 2015; Vincent et al., 2010) but often they look at smaller water quality ranges which could be due to the nature of the water source or they keep one of the variables constant. This study differs from these experiments as 3 different water sources were used, thus offering a wider range in temperature, pH, alkalinity, and NOM.

Therefore, the main objective of this chapter is to determine seasonal Rct values for three different waters obtained from full-scale water treatment plants and relate these results to seasonal water quality characteristics. This was accomplished by addressing sub-objectives 3 and 4. Sub-objective 3 was to measure seasonal ozone and the hydroxyl radical concentrations and to use these values to determine the Rct values in the three treatment plants. Sub-objective 4 was to measure and compare the NOM of the different water sources using LC-OCD and to determine the effect of ozonation and changing Rct values on the NOM fractions.

3.2 Materials & Methods

3.2.1 Selection of Treatment Plants and Sampling Procedure

Three drinking water treatment plants that used ozonation in their treatment trains and had different source waters were selected. Two of these treatment plants which will be referred to as Grand River A and B obtained their raw water from the Grand River. The third treatment plant which will be called Lake Ontario obtained its raw water from Lake Ontario.

Partially treated water samples were taken from the water treatment plants from the period of July 6 2016 to October 17 2017 with a variation in temperature of 3-26^{o}C, sampling dates and temperatures can be found in Appendix A.1. Experimental temperatures were chosen to simulate temperatures in the water

treatment plants. For example, if the water treatment temperature on September 28, 2016 was 20°C then experiments were completed at 20°C using a digital temperature controller (water bath) from PolyScience (IL, USA). There were two exceptions, sampling dates Lake Ontario March 2, 2017, and Grand River B March 13, 2017. For these waters, higher temperatures i.e. 10°C and 20°C were employed in the lab experiments compared to the actual water temperatures (3°C and 5°C) when sampling at the plant. This was done in order to simulate conditions in late spring/ early summer as sampling could not be done during this time.

Partially treated water samples were collected in 1L glass containers from the water treatment plant right before the water entered the ozone contact chamber. These partially treated water samples will be referred to as water samples throughout the thesis. The treatment process train in Grand River A was coagulation, sand ballasted flocculation (Actiflo™ process), sedimentation, ozonation, biological filtration, UV disinfection, chlorination and chloramination. Grand River B had coagulation, flocculation, sedimentation, ozonation, biofiltration, UV disinfection and chloramination. Lake Ontario has the following treatments: coagulation, sand ballasted flocculation (Actiflo™ process), ozonation, biofiltration, fluoridation, pH adjustment, and chlorine. Furthermore, Lake Ontario chlorinated the water at the intake to control for zebra mussels. The Actiflo™ process includes coagulation, flocculation and sedimentation and involves the use of microsand in addition to coagulant and polymers. Water samples were stored in coolers on ice after sampling and during transport. They were filtered in the lab using 0.45 pore size hydrophilic polythersulfone filters from Pall Life Sciences (WA,USA) and were stored at 4°C in a fridge until they were used (Elovitz, M., von Gunten, 1999).

3.2.2 Water Quality Characterization Methods

Temperature and pH were measured using a probe Benchtop pH/ISE model 420A (MA, USA) using Standard Methods 4500B. Alkalinity was determined using the alkalinity titration method that followed

Standard Methods 2320B. DOC was measured with LC-OCD instrumentation as described in the next section.

3.2.3 Liquid Chromatography Organic Carbon Detection (LC-OCD)

NOM analysis was performed for all of the water samples before ozonation and was implemented by Lin Shen through the use of LC-OCD (DOC Labor Huber, Germany) as described by Huber et al. , (2011). NOM analysis was also completed before and after ozonation for three samples (Lake Ontario March 2, 2017, Grand River A October 17, 2017, and Grand River B March 13, 2017) in order to determine the effect of O_3 on NOM fractions. A 0.45 µm pore size hydrophilic polyethersulfone membrane was used to filter the water samples before they were measured in the LC-OCD. In the LC-OCD, samples ran through a size exclusion column where NOM was separated into 5 fractions, followed by UV, organic carbon and organic nitrogen detection. The LC-OCD measured DOC, humic substances (HS), biopolymers (BP), building blocks (BB), LMW acids and LMW neutrals. ChromCALC software (DOC-Labor Huber, Germany) was used to integrate and evaluate the resulting chromatograms.

3.2.4 Measurement of O_3 and pCBA concentrations

The ozone stock solution was generated using a bench-scale system which will be described later. The ozone concentration of the stock solution was around 20 mg/L and its exact concentration was determined each time the solution was prepared using an UV-VIS spectrophotometer from Agilent Technologies (CA,USA) and measuring absorbance at 258 nm in a 1 cm cuvette (Elovitz, M., von Gunten, 1999). A portion of the stock solution was then added to the sample water to achieve applied ozone doses of 1 mg/L and 4 mg/L. Ozone concentrations were then measured in these solutions at preset time intervals using the Indigo method, as outlined in Standard Methods 4500-0_3B with a ratio of 1:1 Indigo solution to water. Experiments were completed previously to determine the optimal amount of Indigo

solution. The absorbance of the Indigo solution at a wavelength of 600nm was measured using an UV-Vis spectrophotometer.

●OH concentrations cannot be measure directly due to the high reactivity of the ●OH with components in the water leading to concentrations ≤ 10^{-12}M (Elovitz, M., von Gunten, 1999). Due to this, ●OH concentrations were measured indirectly through the use of pCBA. pCBA has a low reactivity with O_3 (kO_3 ≤ 0.15 $M^{-1}S^{-1}$) and a high reactivity with ●OH ($K_{\bullet OH}$ = $5*10^9$ $M^{-1}S^{-1}$) thereby making pCBA a good probe compound for ●OH (Elovitz, M., von Gunten, 1999). The pCBA spiking solution (0.1mM) which was used to spike the sample water at 0.25 µM, was prepared by dissolving pCBA in water instead of methanol. The spiking solution was prepared according to personal communications from Urs von Gunten (Elovitz, M., von Gunten, 1999): 0.0391g pCBA was added to 150 mL water with 400 µL of sodium hydroxide (1M). This was stirred overnight and filled to 250 mL then 50 µL hydrochloric acid (1M) was added to bring the pH level of the solution to 6.5-7.5.

3.2.5 pCBA Analysis by LC-MS

pCBA concentrations were measured using a LC-MS which was an 8030 model from Shimadzu (Japan) made up of a Shimadzu DGU-20A3R degassing unit and a Shimadzu LC-20 ADXR pump with a 100 µl injection loop system. The tandem quadrupole mass spectrometer was part of the LC-MS and used multiple reaction monitoring (MRM) to monitor precursor ions and product ions for each analyte. A Zorbax extended-C18 column (3mm internal diameter, 50mm length) with 1.8 micron packing was used for pCBA analysis (Agilent, USA). A Millipore Milli-Q ® UV PLUS water system (MA, USA) was used to produce high purity water. pCBA (99% purity), ammonium acetate (LC-MS grade), and methanol (LC-MS grade) were obtained from Sigma-Aldrich (WI,USA).

In order to warm up the instrument, samples were injected seven times into the LC-MS and calibration standards were measured at the beginning of each run. Every ten samples, one mid-level calibration control standard was measured, see Appendix A.2 for more details. Samples after the warmup injections performed consistently throughout the run.

The pCBA gradient method is outlined in Table 3.1.Mobile phase A, aqueous phase, was 5 mM of ammonium acetate in Milli-Q ® water, while mobile phase B, organic phase, was methanol. This method was based off of Vanderford et al., (2007) with some modifications. The injection volume was 50 µl with a column temperature of 35^{o}C and an eluent flow of 0.8 mL/min. Using Standard Methods 1020B the pCBA method detection limit (MDL) was determined to be 1.07 µg/L, using seven injections of the lowest calibration point of 1 µg/L. The standard LC-MS optimization was used to pick the MRM conditions and electrospray ionization was employed. A negative MRM monitored 155.00>111.00 and 155.00>35.00 transitions for pCBA. The stock solutions of pCBA for LC-MS analysis were dissolved in methanol to produce 1 g/L solutions, which was then diluted to the working solution of 0.01 g/L in Milli-Q ® water. This was used to make a nine-point calibration from 1-100 µg/L.

Table 3.1 LC-MS Mobile Phase Gradient for pCBA

Time (min)	**Methanol Percent Concentration**
0-1.70	Increase concentration 35%->50%
1.70-1.85	Increase concentration to 100%
1.85-3.85	Hold concentration at 100%
3.85-4.85	Decrease concentration 100%->35%
4.85-7.50	Hold concentration at 35%

3.2.6 Bench Scale Set-up for Generating Ozone

A bench scale system attached to a Pacific Ozone generator (model ICS005-C11, CA, USA) was used to generate ozone stock solution, see Figure 3.1. Operating parameters of the ozone generator were optimized to get the highest transferred ozone dose possible. This resulted in the following conditions: air flow= 5 scfm, pressure=8 psi, voltage= 5V at 100%, volume in gas wash bottles=950ml, water temperature=0°C (put in freezer for an hour beforehand). The bench scale set-up consisted of three 1-L glass wash bottles connected via Teflon tubing which is ozone resistant. The first bottle contained a bubble diffuser (30-60 microns) and Milli-Q ® water and was put into an ice bath in order to increase ozone diffusion (Figure 3.2). This bottle was attached directly to the ozone gas outflow pipe and allowed ozone gas to pass through the diffuser creating a concentrated ozone solution (~20 mg/L). The excess ozone gas was then quenched by the two bottles connected in series containing solutions of sodium thiosulfate (0.08M). Clamps attached to stands held the wash bottles in place while twist ties secured the tubes to the wash bottles.

Figure 3.1 Pacific Ozone Generator

Figure 3.2 Bench Scale Set-Up Generating an Ozone Stock Solution. The first wash bottle contains a bubble diffuser and was used to create the ozone stock solution. The next two bottles are filled with quenching solutions. The second bottle was the only bottle that did not contain a bubble diffuser.

The stock solution concentration was measured immediately after it was prepared as described in 3.2.4 and concentrations ranged from 18 to 25 mg/L depending on the batch

3.2.6 Ozonating Water Samples

An applied dose of ozone at 1 mg/L and 4 mg/L was added to the sample water by adding around 25 mL and 80 mL respectively of the ozone stock solution to the treated water to a final volume of 500 mL. The exact volume of ozone stock solution to be added was based on the ozone concentration in the stock solution which was measured just immediately after generating the solution and just prior to adding a portion of it to the sample water. The stock solution was added into an Erlenmeyer flask containing the sample water that was spiked to yield a pCBA concentration of 0.25µM (Elovitz and von Gunten, 1999). Validation and water quality characterization experiments accounted for this dilution by using a dilution factor for both the 1 mg/L and 4 mg/L applied ozone dose. The Erlenmeyer flask was then inverted three times and the stopwatch was started. Samples were taken at the following time points 20 seconds, 2, 4, 6, 8 and 10 minutes. Samples for determining pCBA and ozone concentrations were taken at each of these

time points (Elovitz and von Gunten, 1999). For pCBA concentrations, 1 mL of the water was pipetted into a vial for further analysis via the LC-MS. Ozone concentrations were measured using the Indigo method as outlined in 3.2.4.

3.3 Results and Discussion

3.3.1 Water Quality

Partially treated water samples were taken from the three treatment plants right before ozonation and after coagulation and flocculation. Grand River A and B had similar water quality characteristics in comparison to Lake Ontario as was expected due to their source water. Grand River water is impacted by agricultural run-off and treated municipal wastewater discharge. Grand River A and B had higher levels of DOC than Lake Ontario (Table 3.2).

It is important to note that partially treated water was analyzed in this thesis and will therefore have a lower NOM content than if raw water was studied. This partially treated water had already gone through treatment processes (i.e. coagulation and flocculation) that would have removed some of its NOM. For example Pharand, (2014) studied that same treatment plant in this study, Grand River A, and found that sand ballasted flocculation could result in a 30% removal of total organic carbon.

Ozone to DOC ratios varied from 0.24-0.63 mg/mg for the 1 mg/L applied ozone dose and 0.96-2.52 mg/mg for the 4 mg/L applied ozone dose. Alkalinity levels in Grand River samples reached a maximum of 180 mg $CaCO_3$/L in comparison to the 90 mg $CaCO_3$/L found in Lake Ontario. In all of the waters pH remained fairly neutral and fluctuated from 7.0-8.2.

Table 3.2: Water Quality parameters of partially treated full-scale water samples

Treatment Plant	Sampling Date	Sampling Temperature (^oC)	Alkalinity (mg $CaCO_3$/L)	pH	DOC (mg/L as Carbon)	Ozone/DOC ratio (mg/mg) 1 mg/L O_3 Applied Dose	Ozone/ DOC ratio (mg/mg) 4 mg/L O_3 Applied Dose
Grand River A	November 21 2016	7	100	7.8	3.87	0.26	1.03
	February 17 2017	3	180	8.1	3.29	0.30	1.22
	October 17 2017	14	46	7.6	3.52	0.28	1.14
Grand River B	July 6 2016	23	156	8.0	1.59	0.63	2.52
	August 8 2016	26	174	8.00	2.48	0.40	1.61
	November 7 2016	13	120	7.9	4.18	0.24	0.96
	January 6 2017	4	180	7.8	3.51	0.28	1.14
	March 13 2017	5	160	7.0	3.42	0.29	1.17
Lake Ontario	September 28 2016	20	90	8.2	1.99	0.50	2.01
	December 5 2016	5	90	7.7	2.03	0.49	1.97
	March 2 2017	3	80	8.1	1.80	0.56	2.22

As can been seen from Table 3.2, DOC levels varied depending on the source water for the treatment plant. In order to investigate the characteristics of the natural organic matter in these waters, LC-OCD analysis was applied to look at the different organic fractions. These fractions as detailed by Huber et al. (2011) are HS, BB, which are a result of the breakdown of humic substances, BP which are defined as having a molecular weight above 10kDa, LMW acids and LMW neutrals. Figure 3.3. shows the LC-OCD analysis for all three treatment plants.

HS made up the highest fraction of organic matter having an average of 60% in the Grand River water and 54% in the Lake Ontario source water (Figure 3.4). In both the Grand River and Lake Ontario HS values ranged from 1037 µg C/L to 2226 µg C/L. This coincides with literature findings that found that humic substances make up the majority of total DOC in pretreated waters with percentages of around 50-65% (Marhaba et al., 2008; Thurman, 1985).

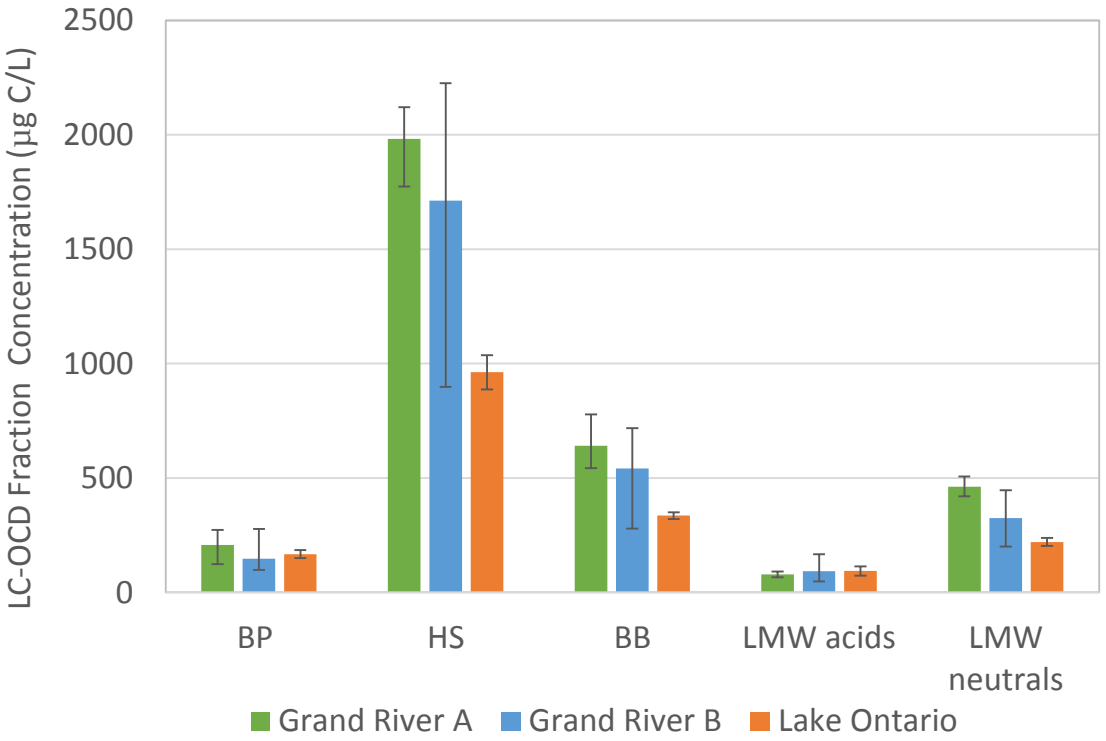


Figure 3.3: LC-OCD Fractions for 3 treatment plants from September-March (Grand River A Mean DOC= 3.56 µg C/L n= 3, Grand River B Mean DOC=3.04 µg C/L n= 5, Lake Ontario Mean DOC= 1.91 µg C/L n=2). Error bars are given by the maximum and minimum values. BP-bipolymers, HS-humic substances, BB-building blocks, LMW acids- low molecular weight acids, LMW neutrals- low molecular weight neutrals.

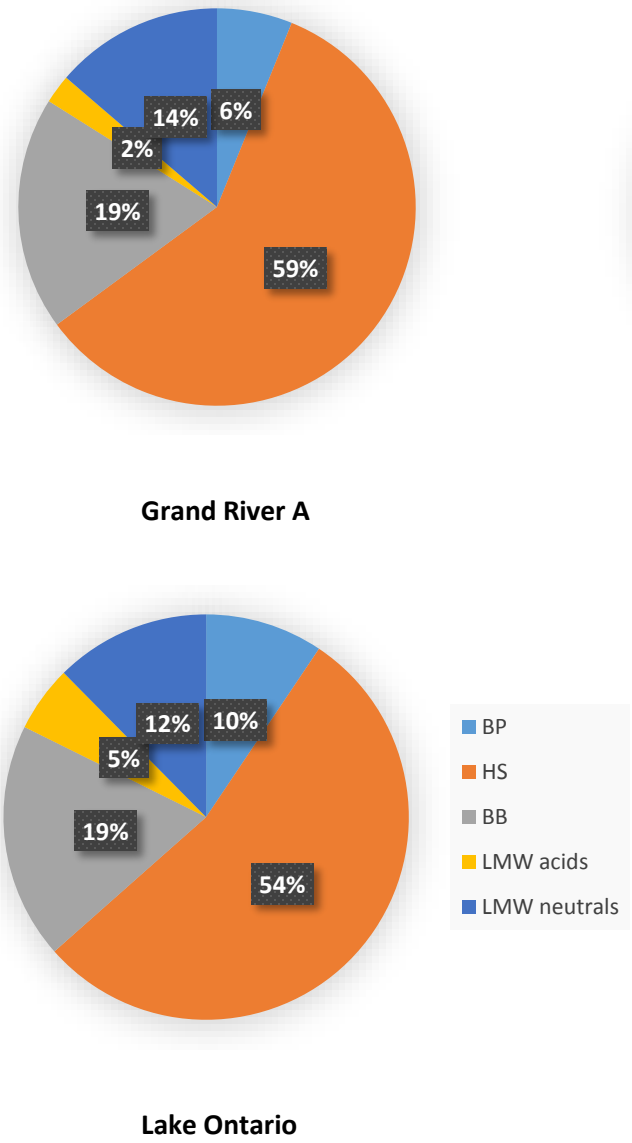


Figure 3.4: Composition of DOC expressed in average percent of organic matter fractions for Grand River A (n=3), Grand River B (n=5) and Lake Ontario (n=2) as determined by LC-OCD.

Building blocks, LMW neutrals, biopolymers, and LMW acids made up 19%, 12-14%, 5-10%, 2-5% of the DOC respectively in both Lake Ontario and Grand River source waters (Figure 3.4). These values are similar to other studies who have analyzed LC-OCD content in the Grand River and/or in Lake Ontario (Croft, 2012; Pharand, 2014; Stylianou et al., 2017).

Overall, the LC-OCD fractions were similar between Grand River and Lake Ontario treatment plants(Figure 3.4). The main differences were with humic substances with a difference of about 6% between the two water sources, and biopolymers with around a 5% difference.

Higher concentrations of biopolymer concentration were associated with warmer temperature as can be seen from Grand River A and B data in Figure 3.5, which was also observed by others (Croft, 2012; Siembida-Lösch et al., 2015). Lake Ontario LC-OCD data was not correlated with temperature because there were only two data points which could not be used to confirm a trend.

It is hypothesized that the trend between biopolymers and temperature may be a result of higher microbial activity occurring at high temperatures (Siembida-Lösch et al., 2015). The opposite relationship was seen with humic substances with higher concentrations associated with lower temperatures (Figure 3.6). The relationship between temperature and the other LC-OCD fractions can be seen in Appendix A.3, Figures A.1 and A.2.

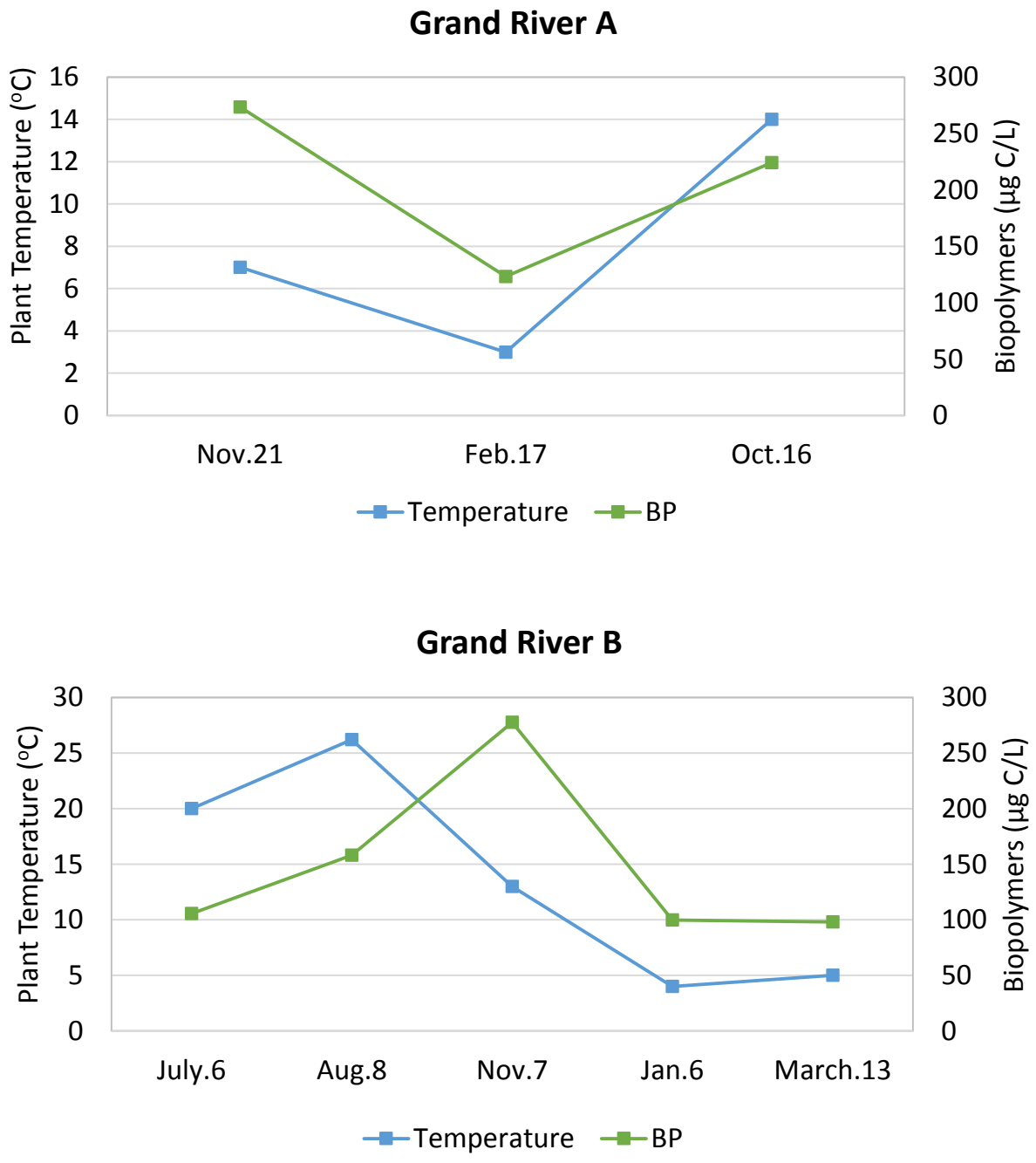


Figure 3.5: Biopolymers versus temperature trends over time for Grand River A and Grand River B

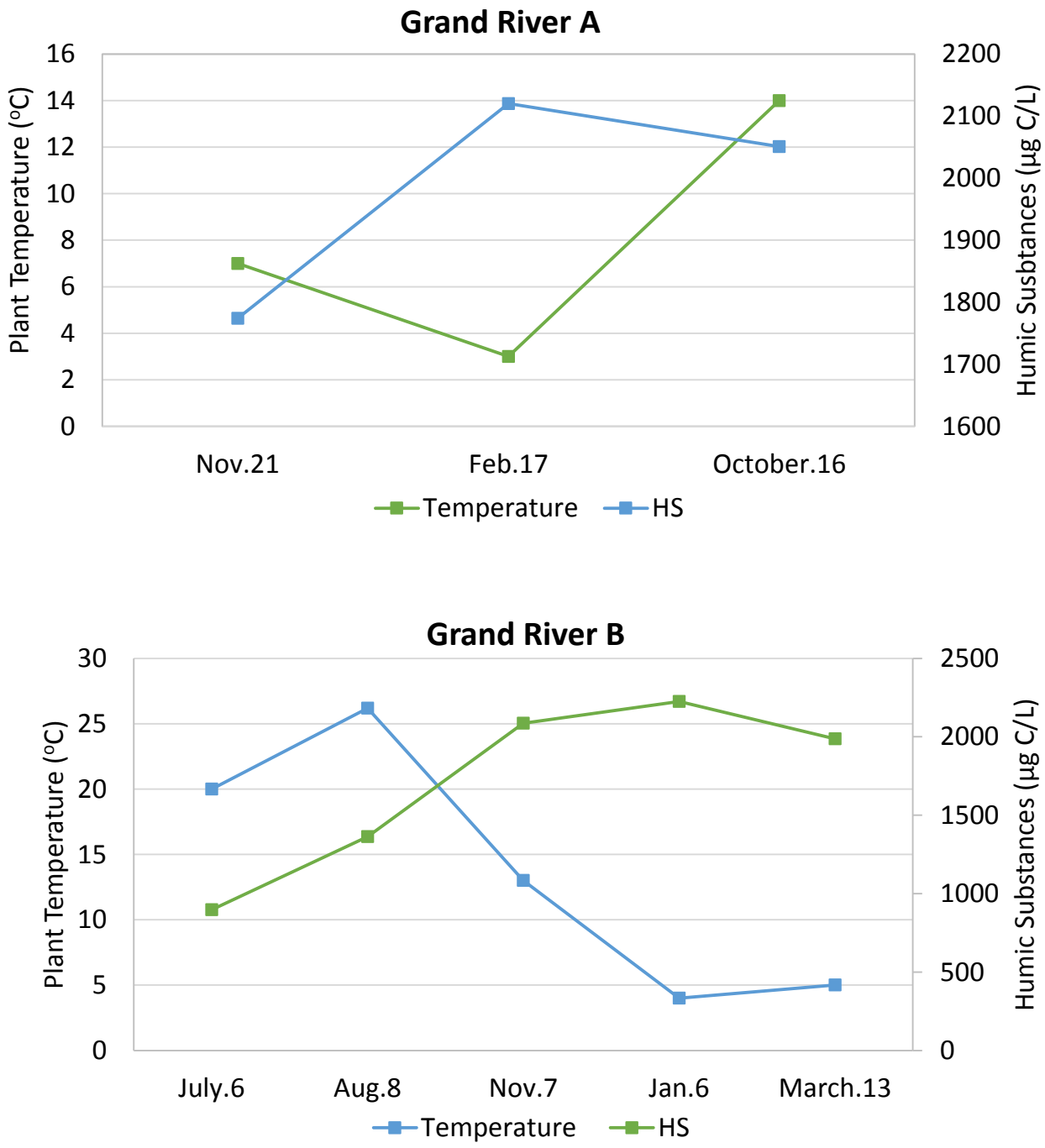


Figure 3.6: Humic substances versus temperature trends over time for Grand River A and Grand River B

The humic substances can be further described by the humic substances diagram shown in Figure 3.7 which was developed by Huber *et al*., (2010). This diagram shows the averages for samples taken at each water treatment plant and all the data points can be found in Figures A.2, A.3 and A.4 of Appendix A. In Figure 3.7 the Spectral Absorption Coefficient to organic carbon ratio (SAC/OC) of the humics fraction is on the y-axis which is the same as a specific ultraviolet absorbance (SUVA) value for the humics peak. This SAC/OC is a measure of the aromaticity of the humic substances fraction, while the x-axis displays the average nominal molecular weight in g/mol. This diagram shows both humic acids and fulvic acids which comprise humic substances. Humic acids are insoluble at a pH ≤ 1, while fulvic acids are soluble at this pH. As can be seen from Figure 3.7 all river and lake waters were in the fulvic acid region.

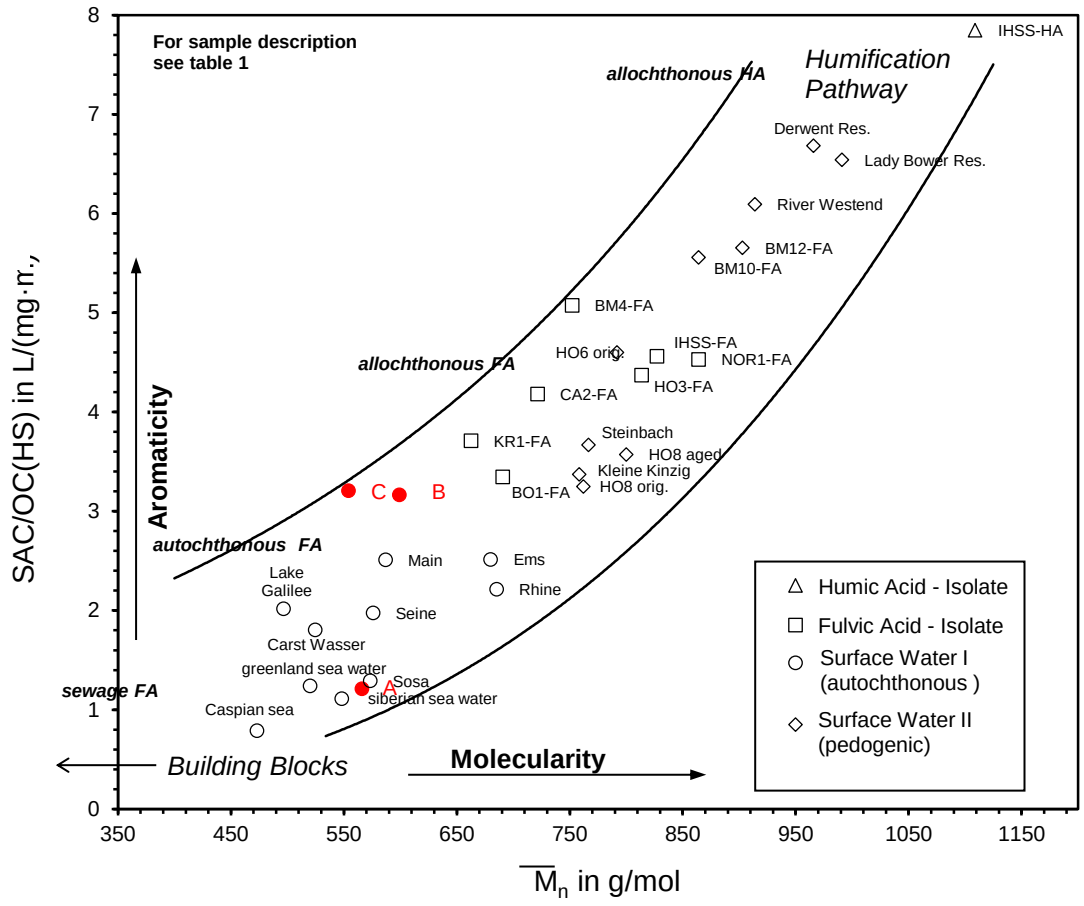


Figure 3.7 Humic Substances Diagram [Huber et al., 2011) for averages of A) Lake Ontario (n=2), B) Grand River A (n=3) and C) Grand River B (n=5)

In Figure 3.7 Lake Ontario (point A) is positioned on the left side near other lakes and seawater on the diagram such as Lake Sosa, and the Caspian Sea. Fulvic acids in these lakes are autochthonous (produced within the system). They are derived from the water column in contrast to being soil derived (Wilkinson *et al,* 1997) and are produced through microbial activity (Her *et al,* 2002). These fulvic acids have a low molecular weight and aromaticity (Her *et al,* 2002) as is shown by the position of Lake Ontario in Figure 3.7 .

Grand River A and B (points B and C) are positioned in between autochthonous and allochthonous fulvic acids as rivers contain NOM from both water and soil sources. Rivers receive output from sewage plants

which usually contains allochthonous fulvic acids, but they also contain microbes which produce autochthonous fulvic acids (Huber et al., 2010).

3.3.2 Effect of Ozonation on NOM Fractions

The effect of ozonation on the various NOM fractions were investigated using 1 mg/L and 4 mg/L of applied ozone doses in the time span of twenty-five minutes as shown in Figure 3.8. It can be seen that after ozonation the amount of biopolymers and humic substances decreased. The building blocks decreased in Grand River A and B but not in Lake Ontario. The LMW acids increased for all three treatments plants, and LMW neutrals decreased after treatment.

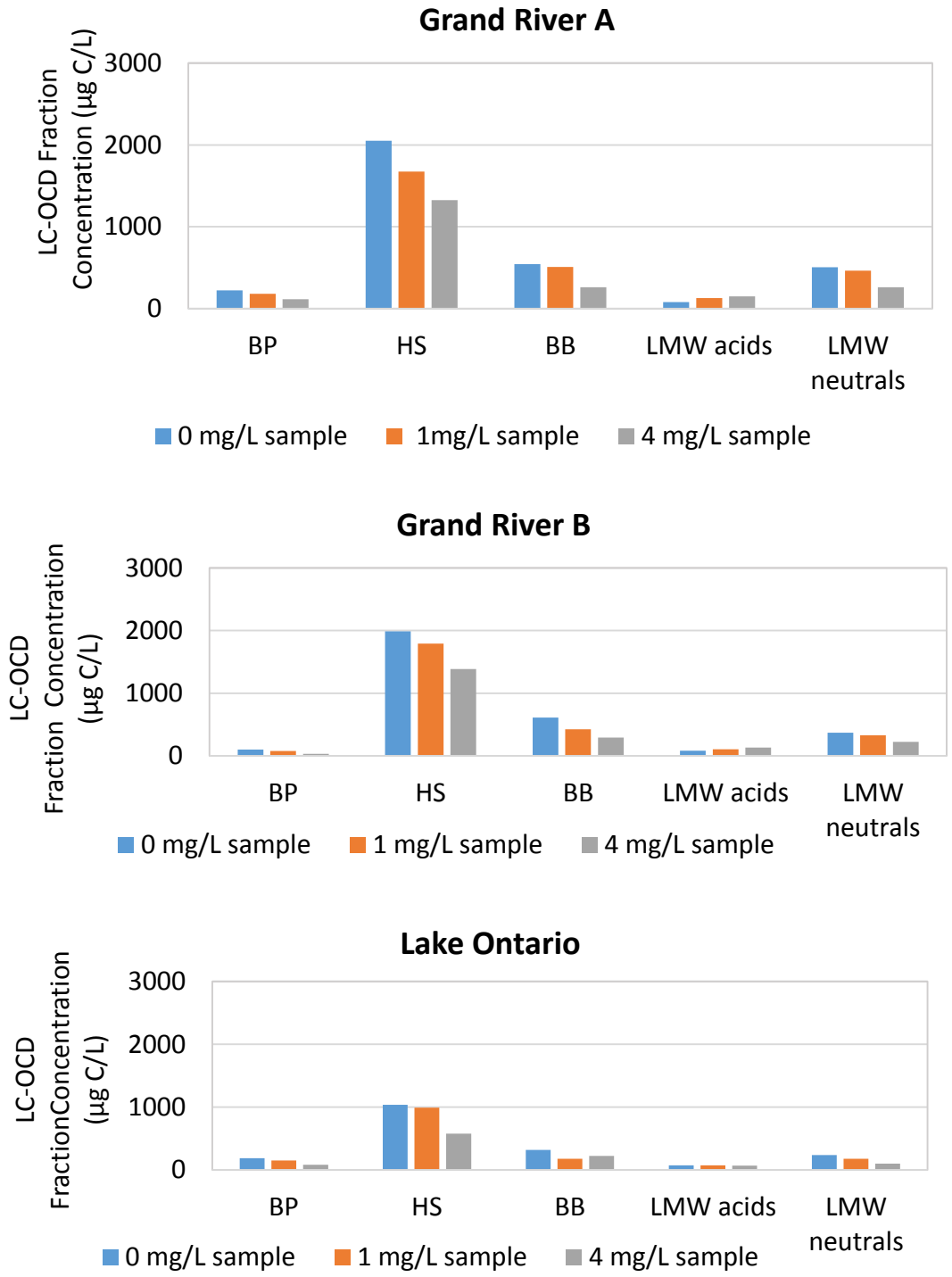


Figure 3.8: Effect of ozonation on Grand River A (October 17, 2017), Grand River B (March 13, 2017), and Lake Ontario (March 2, 2017) treated with 1 mg/L and 4 mg/L applied ozone doses.

In general, NOM fractions have a high molecular weight (humic substances and biopolymers) and are targeted in the initial stages of ozonation. These fractions are oxidized, thus generating by-products such as LMW acids that are hydrophilic and of lower molecular weight (Croft, 2012; González et al., 2013; Pharand, 2014).

Croft, (2012) and Pharand, (2014) both investigated the effect of ozonation on NOM fractions on the same full-scale treatment plants that were used in this thesis, Grand River B and A respectively. However, they completed full-scale treatment experiments while this thesis looked at bench-scale experiments. Both Croft, (2012) and Pharand, (2014) found similar results in that biopolymers and humic substances decreased after ozonation, while LMW acids increased. Pharand, (2014) further found that building blocks and LMW neutrals had poor removal through ozonation.

Siembida-Lösch et al., (2015) examined the effect of ozone on NOM fractions in a full-scale water treatment plant using Lake Ontario as its source water and applied ozone doses of 1 mg/L. They found that their low applied ozone dose resulted in low humic substances removal, a small increase in building blocks formation and almost no change in biopolymers and LMW-acids fractions. These low doses had low biopolymer removal (10% reduction), and were somewhat effective at reducing humic substances (33% reduction). In this thesis in the Lake Ontario plant a 1 mg/L ozone dose caused a 14% in biopolymer reduction, and no change in humic substances concentration.

Stylianou et al., (2017) ozonated their river water sample with ozone doses of 1 mg O_3/mg DOC and found that the addition of hydrogen peroxide (H_2O_2) caused a 4-6% increase in reduction for the humic and biopolymer fractions. This provides evidence that adding H_2O_2 to ozonation treatment may provide slight benefits for removing large DOC fractions. González et al., (2013) found that increasing their applied ozone dosage caused the amount of humic substances and biopolymers to decrease and the remaining NOM fractions were made up primarily of LMW acids, building blocks and LMW neutrals. This shows that

increasing ozone doses can decrease the amount of humic substances and biopolymer as also shown in this study (Figure 3.8). However, increasing the ozone dose has to be balanced with the concurrent production of harmful disinfection by-products such as bromate which is produced when waters containing bromide are ozonated (von Gunten, 2003a).

3.3.3 Challenges Encountered When Implementing Quantification of ●OH Radicals

●OH concentrations are hard to measure in water due to the high reactivity of ●OH (Elovitz, M., von Gunten, 1999). Therefore, pCBA can be used to indirectly measure ●OH concentrations. pCBA has a low reactivity with O_3 ($kO_3 \leq 0.15\ M^{-1}S^{-1}$) and a high reactivity with ●OH ($k_{\bullet OH} = 5*10^9\ M^{-1}S^{-1}$) thereby making pCBA a good probe compound for ●OH. pCBA is not expected to influence ozone degradation due to its low reactivity with ozone (Elovitz, M., von Gunten, 1999). Therefore, it was unusual, that the first few initial experiments showed that pCBA accelerated ozone degradation. The next few paragraphs will detail these experiments and will explain why pCBA appeared to degrade ozone rapidly.

After running numerous experiments during the months of May and June, a streamlined method was created as described in the materials and methods section (3.2). In this method partially treated water samples were spiked with ozone stock solution giving applied ozone dosages of 1 and 4 mg/L. The experiment was first run using Grand River B water, and only ozone decay was measured with no addition of pCBA (as LC-MS methods were not ready at this point). Figure 3.9 shows the degradation of ozone without the addition of pCBA (blue dots) with an ozone residual of 2.2 mg/L at 20 seconds.

This experiment was completed again at similar conditions with the addition of 0.5 µM of pCBA (grey and orange dots). The ozone residual was 0.14 mg/L at 20 seconds and degraded rapidly reaching a value of about 0.09 mg/L within 6 minutes. (Figure 3.9).

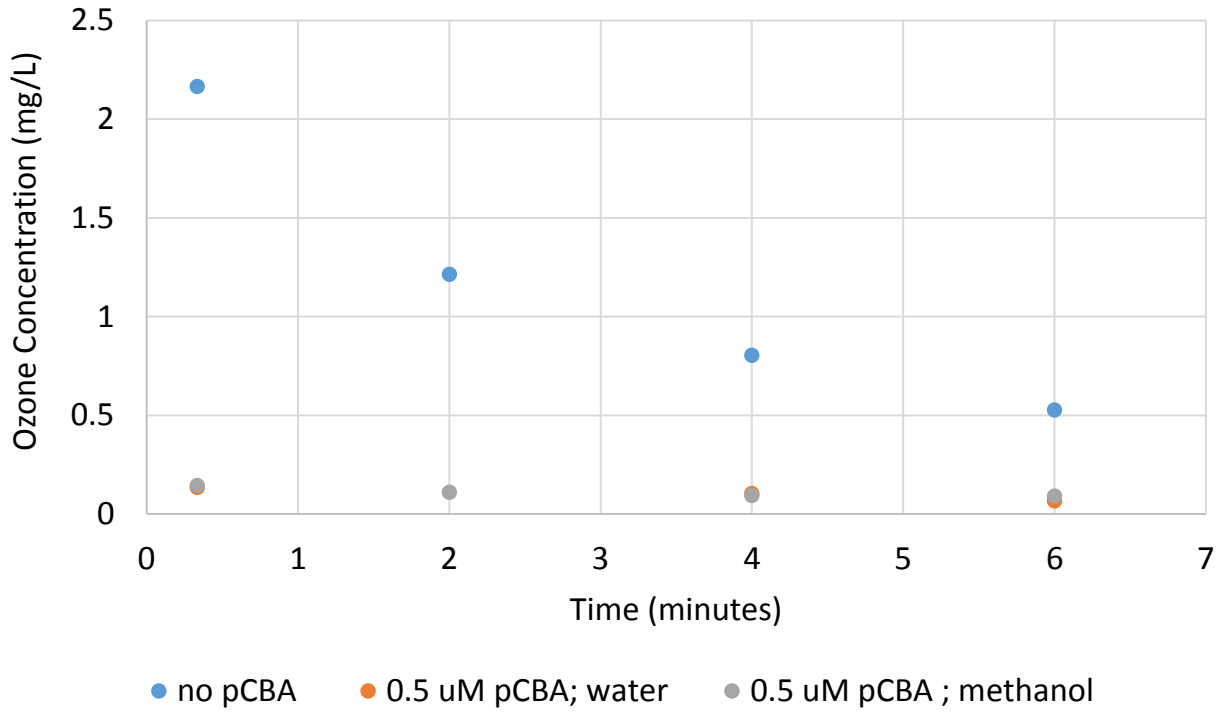


Figure 3.9: Ozone decay curve, applied ozone dose of 4 mg/L in Grand River B (August 8, 2016). 0.5 µM pCBA; water denotes that the spiking solution was made in water. 0.5 µM pCBA; methanol denotes that the spiking solution was made in methanol. Experimental conditions:, temperature=20°C, pH=7.8.

Methanol, which is an O_3 promoter, was found to be accelerating ozone degradation in those tests. To produce the stock solution, pCBA was first dissolved in methanol, due to its low solubility in water. This stock solution was then used to prepare the spiking solution which was also dissolved in methanol. The results of this can be seen by the grey dots from Figure 3.9 (0.5 µM pCBA in methanol). The next set of experiments were done with the same stock solution but the spiking solution was prepared in water instead of methanol. Results can be seen in Figure 3.9 (0.5 µM pCBA in water). In both of these experiments, the ozone degraded rapidly showing that even in the case of the spiking solution made in water the small amounts of methanol from the stock solution, 1:100 dilution, still lead to ozone scavenging.

As a result, a new method was put into place to prepare the pCBA stock and spiking solutions which did not use any methanol; see methods section 3.2.4 for more details.

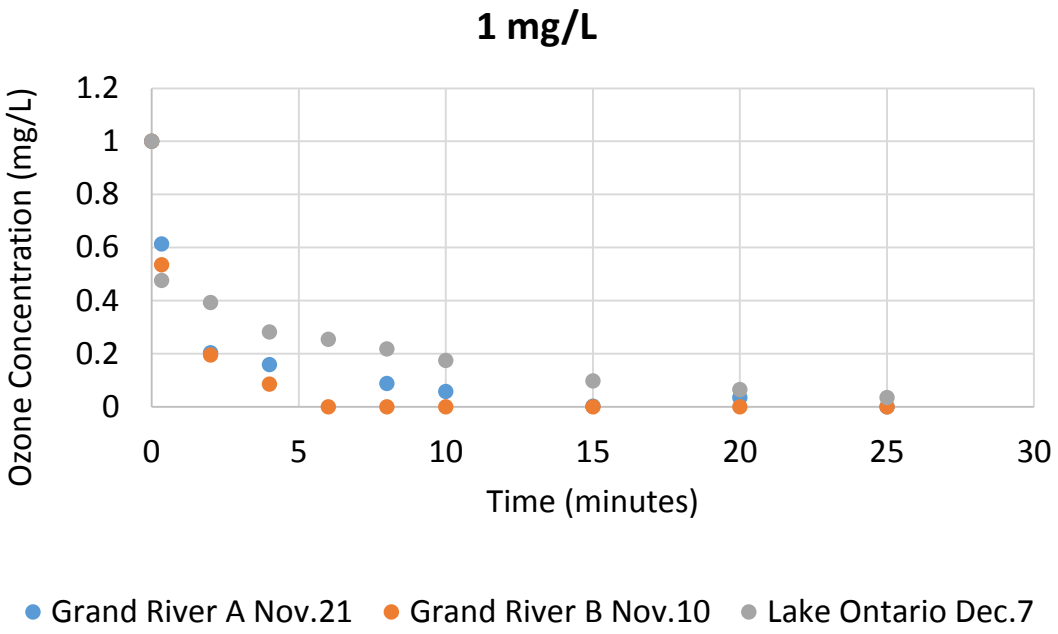
Yong & Lin, (2012) completed ozonation experiments and looked at the effect of methanol on ibuprofen degradation in aqueous solutions. The experimenters investigated a range of 0-0.2mM methanol and added the methanol separately as a model compound. They found that 87% of ibuprofen was degraded in the absence of methanol but the addition of 0.2mM of methanol decreased degradation to 62%. Yong & Lin, (2012) showed that methanol can lower O_3 and ●OH exposure by increasing ozone degradation which hinders contaminant degradation. This is important to note as other ozonation studies have used methanol has a stock solution for contaminants that have a low solubility in water such as Westerhoff et al., (2006). In this study the authors knew about the effect of methanol on ozone decay and attempted to minimize it by using small amounts of methanol in their spiking solutions. However, as seen in this thesis, even small amounts of methanol can affect ozone degradation and subsequently can hinder contaminant degradation and thus methanol should not be used as a solvent in ozonation studies.

3.3.4 Degradation of Ozone and ●OH in Surface Water

This section will focus on the pCBA and O_3 degradation curves generated in the 3 different surface waters (Figure 3.10 and Figure 3.11). These curves are used to calculate the Rct value created by Elovitz & von Gunten, (1999) which gives the ratio of ●OH concentration to O_3 concentration for a particular water. As can be seen from Figure 3.10 the Lake Ontario water had the highest ozone residual for both the 1 mg/L and 4 mg/L applied ozone doses at the 25 minute time point. This could be due to the fact that Lake Ontario has a lower DOC value in comparison to Grand River A and B which have similar DOC values. Lake Ontario on average had higher ozone to DOC ratios for both the applied ozone doses (Table 3.2) while Grand River A had the lowest ozone to DOC ratio. A larger amount of DOC content will cause more ozone to be consumed as it reacts with NOM in the water (Ling, 2012) and therefore a high ozone to DOC ratio will result in greater ozone residuals in the water. For the Grand River A and B at the 1 mg/L ozone dose often there was no ozone left after 4 minutes due to it being consumed by NOM while this did not occur

in Lake Ontario samples. This can be seen for Grand River B in Figure 3.10 where at 6 minutes the ozone residual is zero.

The ozone decay curves generated in this experiment show two phases with a rapid phase occurring under 20 seconds and a slower phase occurring after 20 seconds (showed in detail Figure 3.12). These two phases have also been observed in other experiments (Buffle et al., 2006a; Elovitz, & von Gunten, 1999; Hoigné, 1994; Shin et al , 2015). The slower secondary phase can be fitted with first order kinetics as shown by Elovitz & von Gunten, (1999). In this phase there is linearity in the Rct plot, which will be discussed in subsection 3.3.6, and consequently the Rct value is constant and can be used for modelling purposes (Elovitz & von Gunten, 1999). The rapid first phase of ozonation, <20 seconds, cannot be fitted with first order kinetics however, new methods such as the continuous quench-flow system can be used to measure ozone decay in the first phase (Buffle et al., 2006a).



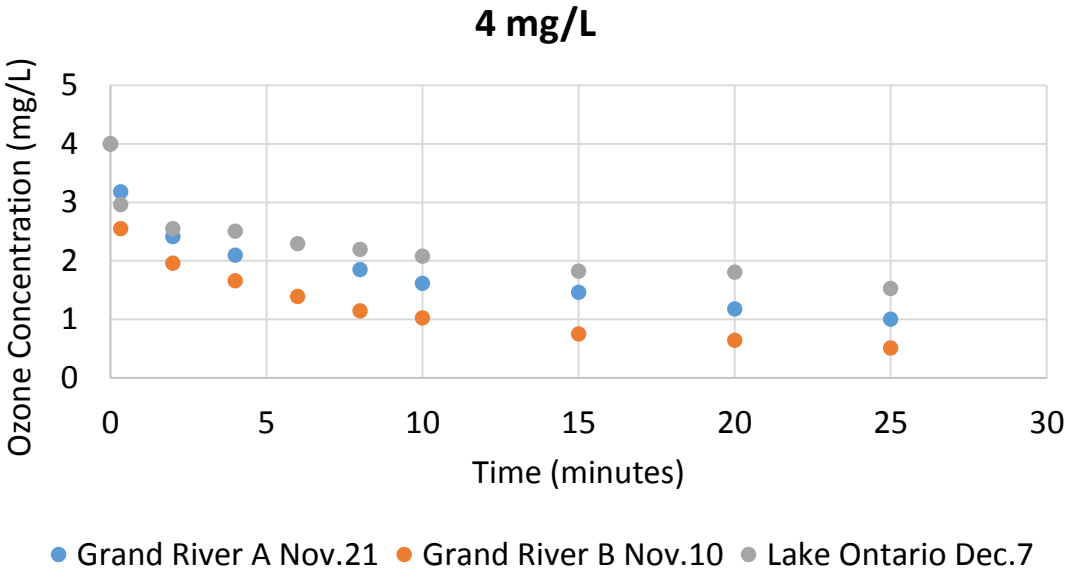
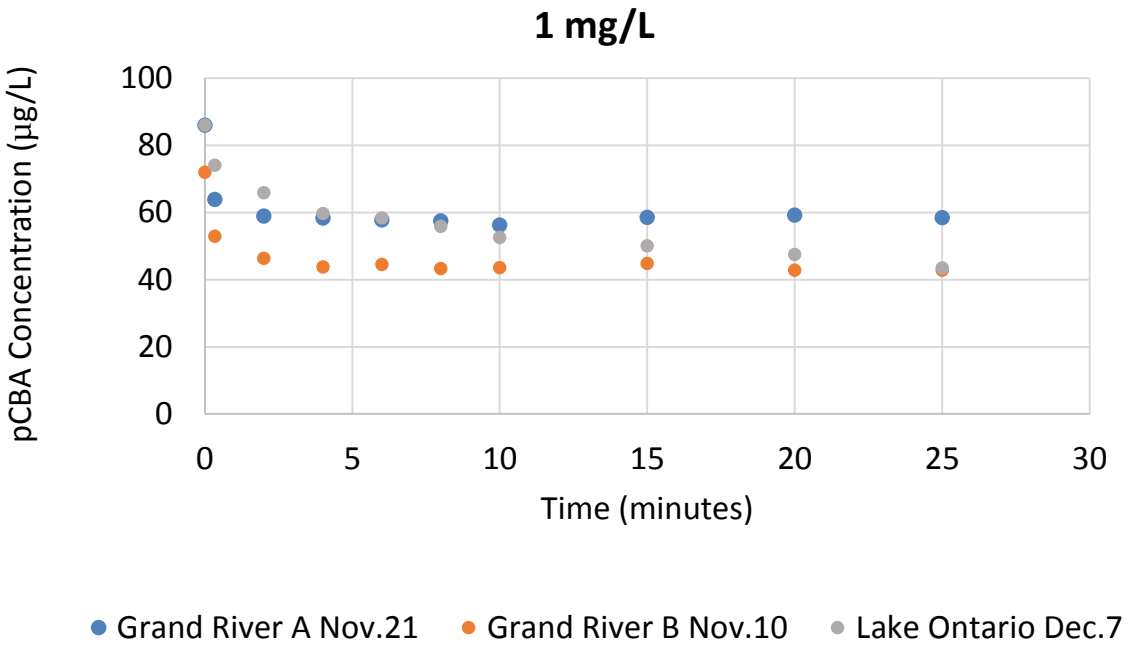


Figure 3.10: O_3 decay curves for a 25 minute reaction time, Grand River A (November 21, 2016, temperature=7°C), Grand River B (November 10, 2016, temperature=13°C), Lake Ontario (December 7, 2016, temperature 5°C).



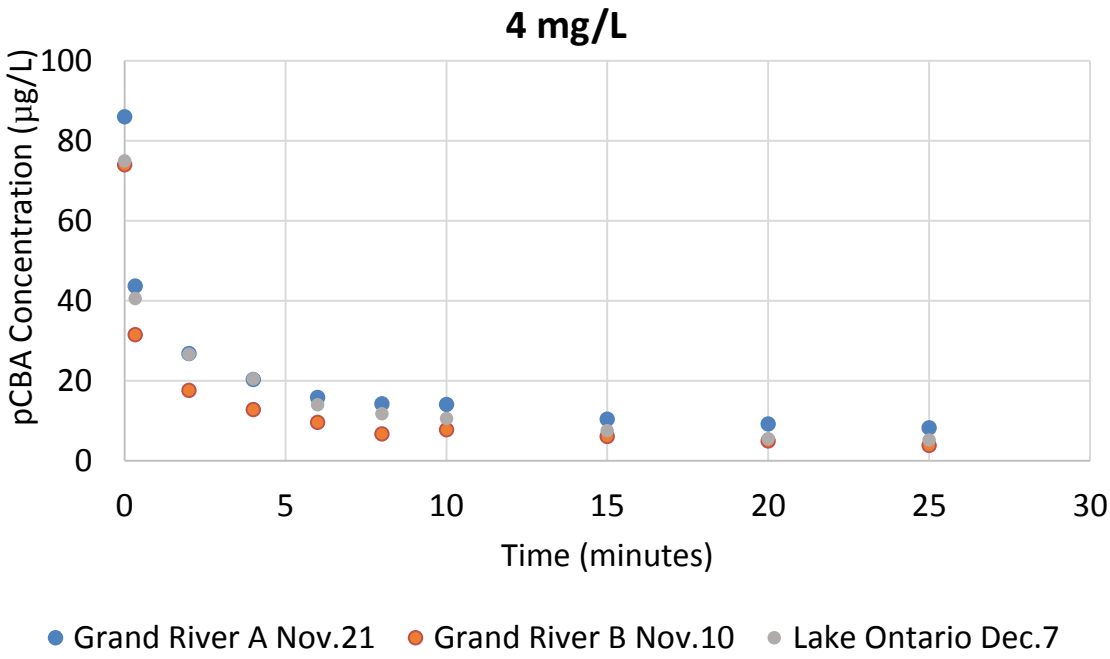


Figure 3.11: pCBA Decay curves for a 25 minute reaction time, Grand River A (November 21, 2016, temperature=7°C), Grand River B (November 10, 2016, temperature=13°C), Lake Ontario (December 7 2016, temperature 5°C).

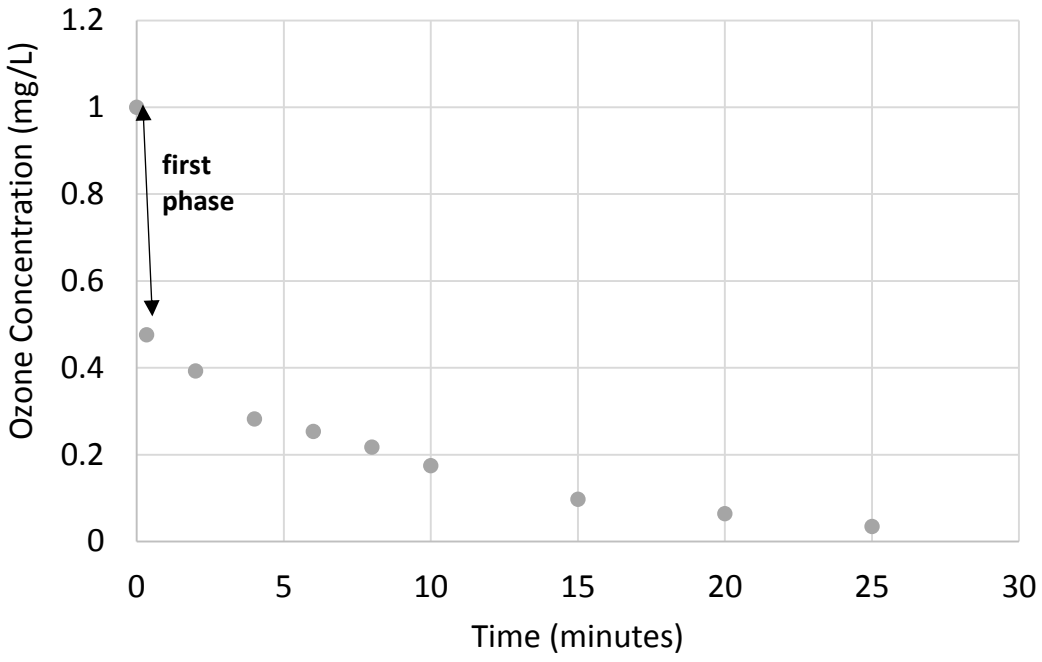


Figure 3.12: O_3 decay curves for a 1 mg/L dose and a 25 minute reaction time in Lake Ontario (December 7, 2016, temperature 5°C).

The first phase of ozonation starts at zero seconds when the ozone is added to the solution and is reported to range from 20 seconds to 2 minutes. Determining the extent and end point of this phase is often constrained by how fast the first sample can be taken (Buffle et al., 2006a; Elovitz & von Gunten, 1999; Hoigne & Bader, 1994; Shin et al., 2015).

This is important to note as different articles define the end of their first phase at different time points. Elovitz & von Gunten, (1999) methods did not allow them to measure ozonation from 0-30 seconds and they defined their first phase as 30-120 seconds and their secondary phase occurring after 120 seconds. Even though they were not able to measure this initial 30 seconds they still observed two phases of ozone degradation with fast degradation occurring up to 2 minutes and slow degradation afterwards.

On the other hand Liu et al., (2015) defined their first phase at 0-30 seconds and used time points >30 seconds for the Rct calculation. Shin et al., (2015) defined their first phase as 0-1 minute.

In this study, the first phase was defined as time points ≤19 seconds which follows other literature (Buffle, et al., 2006, II; Hoigne & Bader, 1994; Yong & Lin, 2013). The secondary slower phase was defined from 20 seconds-25 minutes and the Rct value was calculated from these time points. It was not possible to measure ozone degradation in the time period from 0 to 19 seconds as the methods did not allow for this. However, it was evident from the plots that ozone decay was a lot faster in the initial 20 seconds compared to the decay observed after 20 seconds.

In Figure 3.10 it can be seen that for the 1 mg/L dose the amount of ozone consumed in the first phase ranged from 0.47-0.61 mg/L. This is comparable to Shin et al., (2015) who defined their first phase as 0-1 minute and observed an initial consumption of 0.64 mg/L for their lake water source. Shin et al., (2015) also found that water that had been sand-filtered consumed less ozone in the first phase due to the decrease in DOC during sand-filtration which caused less ozone to be consumed.

As it can be seen from Figure 3.10 and 3.11, pCBA and O_3 decay varied between the three plants and between the two ozone dosages. These plants have different source waters and were sampled at different times of the year which would cause seasonal variation. These effects will be further discussed at the end of the chapter.

3.3.5 Reproducibility of Rct Value

As in any experiment, reproducibility is of the utmost importance to make sure that the results are sound. This section focuses on the reproducibility of the overall method to determine the Rct value which includes spiking the water samples with ozone, adding pCBA, measuring O_3 using the Indigo method, and measuring pCBA with LC-MS instrumentation. The reproducibility experiments were done at the 4 mg/L applied ozone dose with Lake Ontario source water. As it can be seen from Figure 3.13, replicate 1 and 2 had similar pCBA and O_3 decay curves. With an R^2 value of 0.97 for the O_3 decay curve and a value of 0.99

for the pCBA decay curve. The Rct values for the replicates were close with replicate 1 having an Rct value of $5.5*10^{-9}$ and replicate 2 had a value of $6.4*10^{-9}$ as shown by the slopes of the lines Figure 3.14.

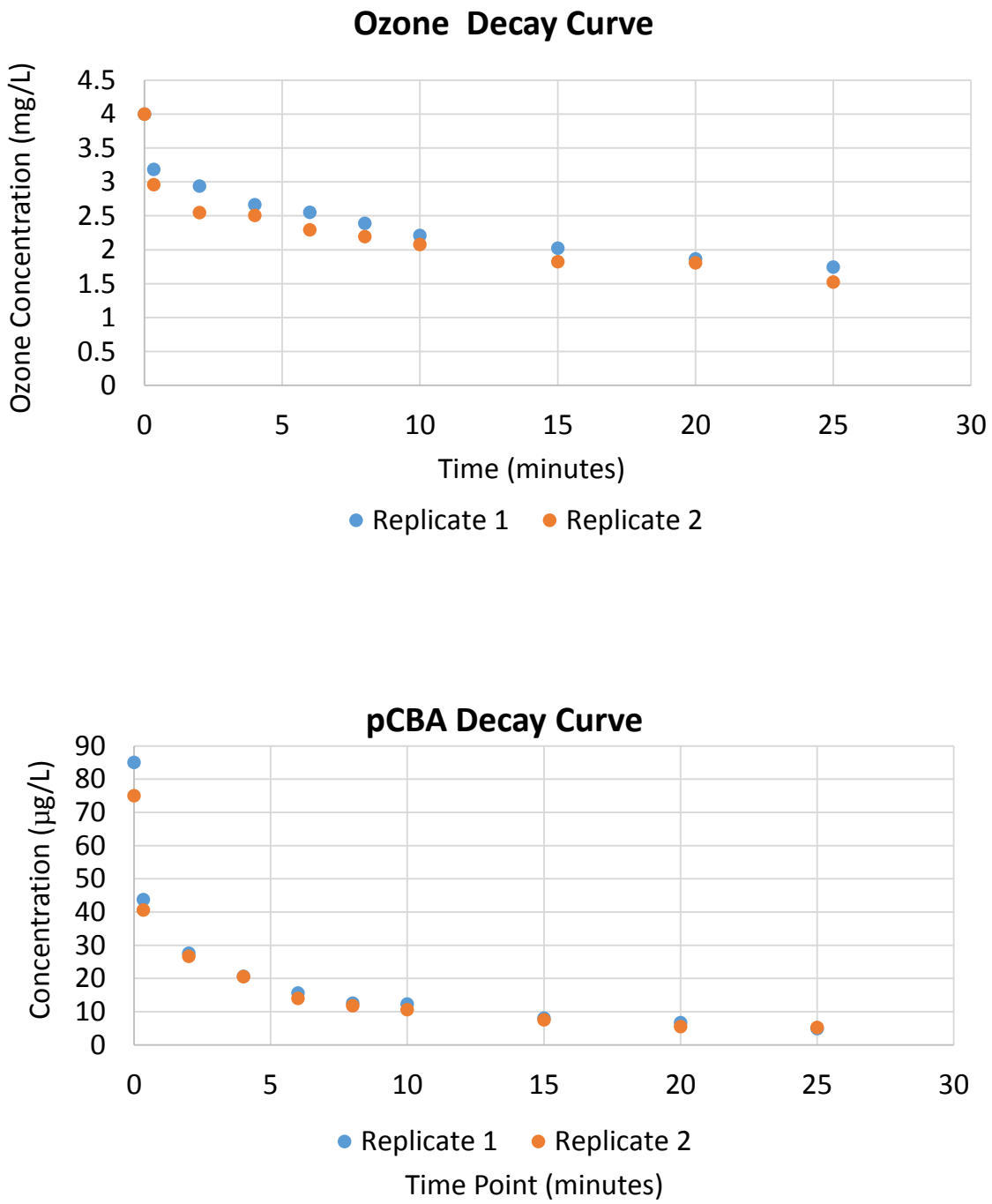


Figure 3.13: Ozone and pCBA decay curves at a 4 mg/L applied ozone dose in Lake Ontario (December 7, 2016, temperature=5°C) for Replicate 1 and 2. Top figure shows ozone decay curves and bottom figure shows pCBA decay curves with a spiking pCBA dose of 85 µg/L for replicate 1 and 75 µg/L for replicate 2.

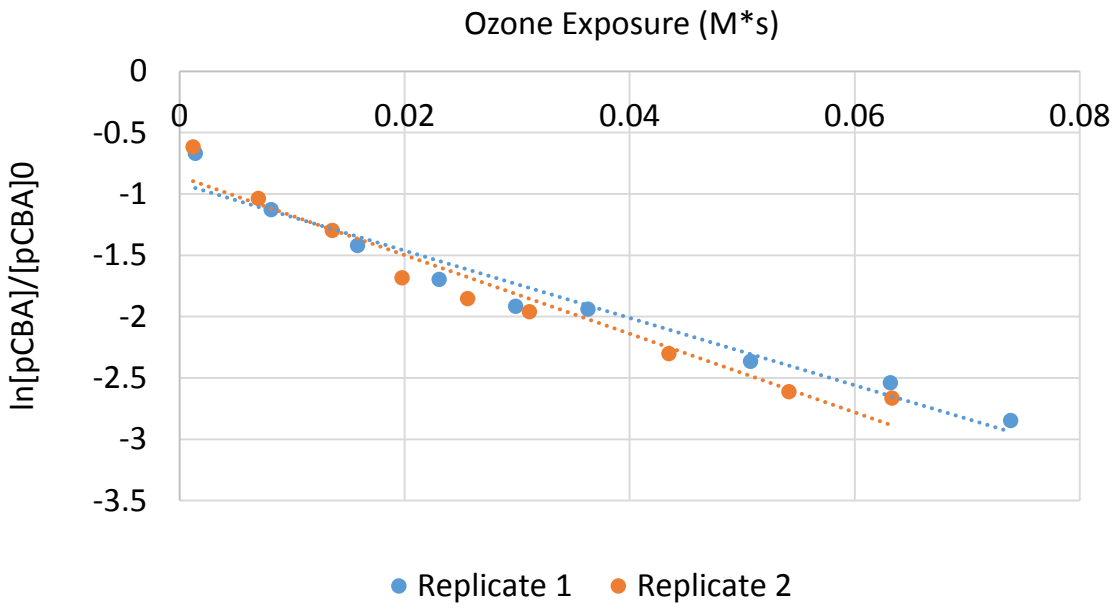


Figure 3.14: Rct Plots at a 4 mg/L applied ozone dose in Lake Ontario (December, 7 2016, temperature=5°C) for Replicate 1 and 2. Top figure shows ozone decay curves at a 4 mg/L applied ozone dose and bottom figure shows pCBA decay curves with a spiking pCBA dose of 85 µg/L for replicate 1 and 75 µg/L for replicate 2.

3.3.6 Rct values and Linearity Plots

The Rct value was developed by Elovitz & von Gunten, (1999) and is shown in equation 3.1. It is defined as the ratio of ●OH exposure to O_3 exposure and therefore the pCBA and O3 degradation data from earlier in this chapter were used to generate Rct values for each of the water samples taken at 1 and 4 mg/L applied ozone doses.

$$Rct = \frac{\int [\bullet OH] dt}{\int O_3 \, dt}$$

Equation 3.1 Rct concept (Elovitz & von Gunten, 1999)

In order to calculate the Rct value, equation 3.2 is used and the natural logarithm of pCBA degradation (ln ([pCBA]/$[pCBA]_0$)) is plotted versus the ozone exposure ($\int O_3 \, dt$) . The Rct value can be obtained from the slope of this plot divided by the rate constant of ●OH with pCBA ($k_{*OH/pCBA}$). An example is shown in Figure 3.15 which gives an R^2 value of 0.94 and results in an Rct value of $5.7*10^{-9}$. An alternative approach which was not used here would be to fit the non-transformed data using nonlinear least squares.

$$ln\left(\frac{[pCBA]}{[pCBA]_0}\right) = -k_{*OH/pCBA} \mathrm{Rct} \int [O_3] \, \mathrm{dt}$$

Equation 3.2 Rct equation (Elovitz & von Gunten, 1999)

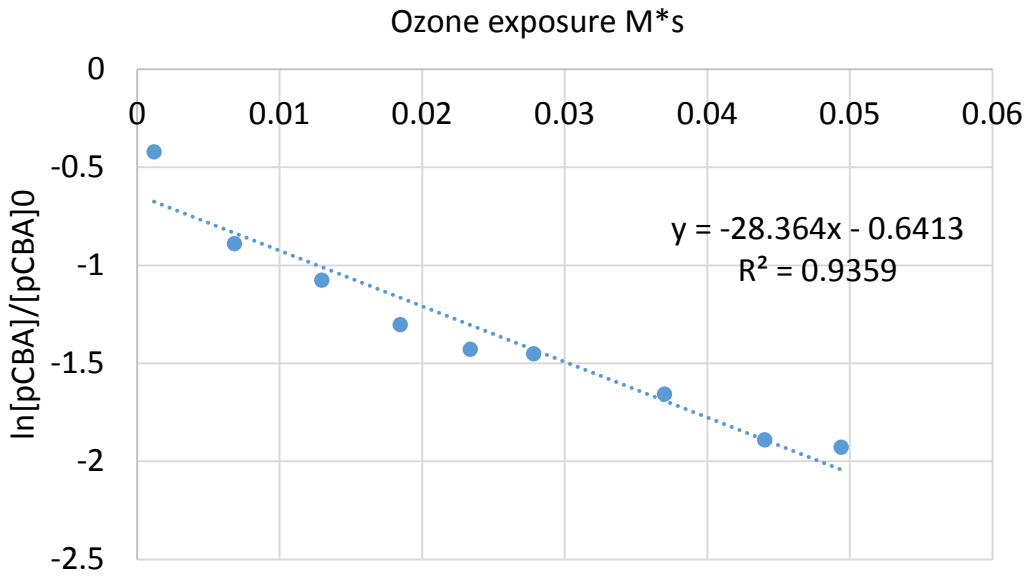


Figure 3.15 Rct plot for a 4 mg/L applied ozone dose for Grand River B (February 17, 2017, temperature= 3°C)

The Rct values calculated in this thesis as shown in Table 3.3 have a range of 10^{-8} to 10^{-9}. This range is similar to those found in literature for drinking water. Elovitz & von Gunten, (1999) found that in Swiss waters the Rct value ranged from 10^{-7} to 10^{-9}. Vincent et al., (2010) looked at five drinking water treatment plants in Montreal which had river source water and their Rct value was in the range of $10^{-6.4}$ to $10^{-8.4}$. Shin et al., (2015) found an Rct value range of 10^{-7} to 10^{-8} when they looked at lake water in Korea.

Table 3.3 Rct values for the three treatment plants at a 1 and 4 mg/L applied ozone dose

Plant	Sampling Dates	Ozone Dose (mg/L)	Rct value
Lake Ontario	September 28, 2016	1	$9.3*10^{-8}$
		4	$1.9*10^{-8}$
Grand River B	November 7, 2016	1	$2.58*10^{-8}$
		4	$9.69*10^{-9}$
Grand River A	November 21, 2016	1	$6.88*10^{-9}$
		4	$8.67*10^{-9}$
Lake Ontario	December 5, 2016	1	$2.06*10^{-8}$
		4	$5.49*10^{-9}$
	Replicate	4	$6.41*10^{-9}$
Grand River B	January 6, 2017	1	$1.76*10^{-8}$
		4	$6.43*10^{-9}$
Grand River A	February 17, 2017	1	$1.72*10^{-8}$
		4	$5.67*10^{-9}$
Lake Ontario	March 8, 2017	1	$9.19*10^{-9}$
		4	$7.07*10^{-9}$
Grand River B	March 13, 2017	1	$2.79*10^{-8}$
		4	$1.47*10^{-8}$
Grand River A	October 17, 2017	1	$2.97*10^{-8}$
		4	$8.95*10^{-9}$

The average Rct values for each of the treatment plants can be seen from Figure 3.16. One data point September 28 2016 for Lake Ontario at the 1 mg/L applied ozone dose had an unusually high Rct value. The effect of this can be seen by contrasting Figure 3.16 A (included high data point) which has a higher average for the Lake Ontario 1 mg/L applied ozone dose and longer error bars than Figure 3.16 B (did not include the high data point). The Rct values from the 4 mg/L applied ozone dose are similar between the plants. A higher Rct value means that either ozone depletion rates have increased and/or the amount of ●OH in the water has increased. This can depend on a variety of factors. For example Elovitz & von Gunten, (1999) found that increasing the temperature from 5-35^{o}C ●OH exposure stayed the same while O_3 exposure decreased.

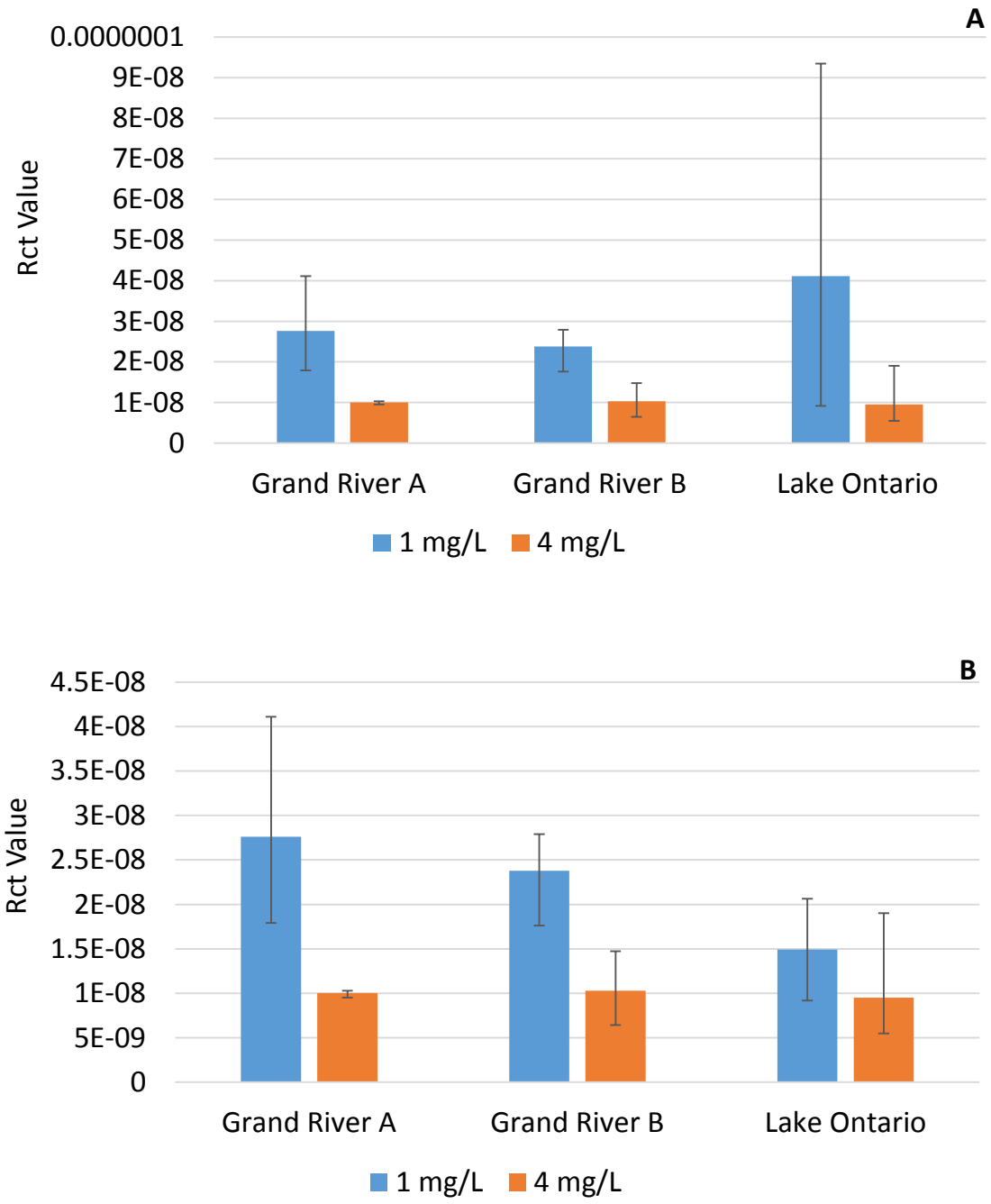


Figure 3.16 Average Rct values for the treatment plants from September to March (Grand River A (n=3), Grand River B (n=3), Lake Ontario 1 mg/L dose (n=3), 4 mg/L dose (n=4)). A) Includes September 28, 2016 data point from Lake Ontario for the 1 mg/L dose. B) Does not include September 28, 2016 data point from Lake Ontario for the 1 mg/L dose. Error bars represent the maximum and minimum values.

3.3.7 Effect of Seasonality and Applied Ozone Dose on the Rct Value

In this thesis the objective was to model the removal of micropollutants in three water treatment plants for different seasonal conditions. These treatment plants had different source waters with Grand River A and B on two different locations on the Grand River and the Lake Ontario plant getting its source water from Lake Ontario.

The goal was not to determine whether certain water quality parameters and ozone dose significantly affected the Rct value. Subsequently, experiments in this thesis were not designed to make these conclusions. Keeping this in mind this subsection will investigate the relationships between water quality parameters and the Rct value for the purpose of providing more information for future modeling simulations.

Oxidation kinetics are greatly affected by water quality parameters such as pH, temperature, alkalinity, and dissolved organic matter (Elovitz, et al., 2000; Shin *et al*., 2015; Westerhoff et al., 1999). Seasonality will affect water quality parameters such as increasing the NOM content in the water and will affect how key contaminants are ozonated. The effect of ozone dose on Rct value will also be investigated.

Firstly, a Pearson correlation matrix was employed in order to assess if there were any linear relationships between the –log Rct value (Vincent et al., 2010) and the water quality parameters and the ozone dose. This correlation was done on the data from both Grand River treatment plants and the Lake Ontario treatment plant. However, this was a relatively small data set and any results should be interpreted with caution. The results are shown in Table 3.4 which only includes parameters that had a correlation ≥ 0.30 with –logRct value. One of the sampling dates, Lake Ontario September 28, 2016, had to be removed from the Pearson correlation matrix as there were missing values for LC-OCD.

Table 3.4: Pearson Correlation Matrix with Grand River and Lake Ontario water sources

	-logRct value	Temperature	pH	Alkalinity	DOC
Temperature	-0.47	1.00			
pH	0.40	-0.68	1.00		
DOC	-0.30	0.27	-0.20	0.33	1.00
HS	-0.33	0.22	-0.14	0.53	0.89
Ozone Dose	0.71	-0.05	-0.01	-0.04	-0.08

DOC (Dissolved Organic Carbon), and HS (Humic Substances)

Temperature had a moderate positive correlation with the Rct value while pH had a moderate negative correlation with the Rct value. Shin *et al*., (2015) looked at temperatures in the range of 6-26^{o}C and found that their Rct value was positively correlated to temperature in their lake source water and that temperature had the most significant effect on the Rct value. This also fits with the findings of Elovitz et al*.,* (2000) who showed that there was a strong relationship between Rct value and temperature, as the temperature increased from 5 to 35^{o}C, a 14-fold increase in the Rct value was observed in lake water. These authors stated that ●OH exposure was not affected by the temperature while ozone exposure decreased.

From Table 3.4 it can be seen that applied ozone dose has the highest correlation with a value of 0.70 indicating a negative linear relationship between applied ozone dose and the Rct value, furthermore this correlation was significant ($p< 0.05$). Shin et al., (2015) saw a slight decrease in Rct value when increasing the applied ozone dose from 1 to 1.5 mg/L. It could be hypothesized that Shin et al., (2015) only found a slight decrease in Rct value because they only had a slight increase to their applied ozone dose.

On the other hand, Vincent et al. (2010)**,** who used lake and river water, had a higher applied ozone dose range from 1 mg/L to 3 mg/L and also stated that the Rct value decreased slightly with an increase in applied ozone dose. However, in Vincent et al., (2010) some of their waters, specifically river water were more impacted by an increase in applied ozone dose then others. In these waters, they observed Rct value

decrease from $10^{-6.6}$ to $10^{-5.6}$ when increasing from 1 to 3 mg/L which is similar to the results found in this study.

In order to better understand the effect of multiple variables on the Rct value, a forward step-wise multi-linear regression was employed using SPSS supplied from IBM (NY, USA). This analysis did not include 2 factor interactions. The dependent variable was identified as the –logRct, while the independent variables included all the water quality variables, ozone dose and LC-OCD data shown in Table 3.5. Correlations between independent variables were calculated to make sure that there were no strong correlations in the model to avoid multicollinearity (Table 3.4).

Table 3.5: Input Data for Multi-Linear Regression

Plant	Sampling Dates	Ozone Dose (mg/L)	Rct value	Temperature (^{o}C)	pH	Alkalinity (mg/L)	DOC (mg C/L)	Biopolymers (µg C/L)	Humic substances (µg C/L)	LMW acids (µg C/L)	LMW neutrals (µg C/L)
Grand River B	November 10, 2016	1	$2.58*10^{-8}$	13	7.9	120	4.18	278	2086	446	167
		4	$9.69*10^{-9}$	13	7.9	120	4.18	278	2086	446	167
Grand River A	November 21, 2016	1	$6.88*10^{-9}$	7	7.8	100	3.87	273	1774	461	91
		4	$8.67*10^{-9}$	7	7.8	100	3.87	273	1774	461	91
Lake Ontario	December 7, 2016	1	$2.06*10^{-8}$	5	7.7	90	2.03	150	887	203	114
		4	$5.49*10^{-9}$	5	7.7	90	2.03	150	887	203	114
		4	$6.41*10^{-9}$	5	7.7	90	2.03	150	887	203	114
Grand River B	February 9, 2017	1	$1.76*10^{-8}$	4	7.8	180	3.51	100	2226	358	48
		4	$6.43*10^{-9}$	4	7.8	180	3.51	100	2226	358	48
Grand River A	February 17, 2017	1	$1.72*10^{-8}$	3	8.1	180	3.29	123	2120	420	66
		4	$5.67*10^{-9}$	3	8.1	180	3.29	123	2120	420	66
Lake Ontario	March 8, 2017	1	$9.19*10^{-9}$	10	8.1	80	1.80	185	1037	238	74
		4	$7.07*10^{-9}$	10	8.1	80	1.80	185	1037	238	74
Grand River B	March 20, 2017	1	$2.79*10^{-8}$	20	7.0	160	3.42	98	1986	367	81
		4	$1.47*10^{-8}$	20	7.0	160	3.42	98	1986	367	81
Grand River A	October 17, 2017	1	$2.97*10^{-8}$	14	7.6	46	3.53	224	2051	506	81
		4	$8.95*10^{-9}$	14	7.6	46	3.53	224	2051	506	81

The model started off blank and independent variables were added to the model until there were no more improvements to significance (p=0.05). In the end, it identified two factors in the model applied ozone dose and temperature which were both significant ($p < 0.05$) with a coefficient of determination (R^2) of 0.70, while the coefficient of correlation (R) was 0.84 (Equation 3.3).

-logRctvalue =7.8-0.02x +0.11y

Equation 3.3 Multi-linear regression model where x=temperature and y=dose.

This multi-linear regression is in agreement with the literature stating that the temperature has a significant impact on the Rct value (Elovitz, et al., 2000; Shin et al., 2015). More specifically this has been reported for lake water, because there is more research using this source water, but as found in this thesis it also applies to river water. Seasonal change in a water source might not result in large ranges in pH and NOM, though a large change in water temperature is often reported. Therefore, this may result in temperature being the most significant factor as it has the most range in comparison to other variables (Shin *et al*., 2015).

Vincent *et al*., (2010) kept temperature constant in their experiments at 20^{o}C and had a range in their water quality parameters. These researchers found that pH, which ranged from 6-8.1, was the most significant variable for predicting the Rct value. Elovitz, et al. (2000) kept all parameters constant except for pH and found that increasing the pH from 6 to 9 caused a 40 fold increase in the Rct value. This was even greater than the effect of temperature in which an increase from 5 to 35^{o}C caused only a 14 fold increase in the Rct value. It can be hypothesized that in this thesis the large range in temperature (3-20) masked the effect of other parameters such as pH which had a much smaller range (7.0-8.2) than Elovitz et al. (2000). However, if this hypothesis is to be further investigated a larger sample size must be studied which was beyond the scope of this thesis.

3.4 Conclusions

In this chapter the seasonal Rct values for partially treated waters from three different full-scale drinking water treatment plants were determined by measuring the change in ozone and the hydroxyl radical concentrations over time. Water quality was characterized as well including NOM characterization by LC-OCD. The key findings are as follows:

Rct Value

- Pearson correlation analysis was employed and showed that ozone dose had the highest correlation with the Rct value with value of -0.70. While temperature and pH both had moderate correlations. A step-wise multi-linear regression determined that temperature and ozone dose were important factors affecting the Rct value and this gave an R^2 value of 0.70.
- Experiments were found to be reproducible when conducting replicate experiments. The Rct values for the replicates were close with replicate 1 having an Rct value of $5.5*10^9$ and replicate 2 having a value of $6.4*10^9$.
- ●OH radicals and O_3 decay varied between the waters from the three plants and between the two ozone dosages with Lake Ontario having the lowest ozone consumption due to its lower DOC.
- Rct values had a range of 10^{-8} to 10^{-9} which is similar to those found in literature for drinking water.
- Rct values from the 4 mg/L ozone dose was similar between the three treatment plants while Rct values from the 1 mg/L ozone dose varied.
- Two phases of ozone decay were observed with the second phase starting at 20 s. Amount of ozone consumed in the first phase ranged from 0.47-0.61 mg/L.
- Methanol should not be used as a solvent for pCBA as even a small amount of methanol can effect ozone degradation and therefore compromises experimental results.

Water Quality

- Grand River A and B had a similar NOM composition as shown through LC-OCD analysis. The humic substances diagram showed that the humic substances in these waters bordered between autochthonous and allochthonous fulvic acids while Lake Ontario was comprised of autochthonous fulvic acids. Overall, the humic substances in Grand River A and B had a higher aromaticity than Lake Ontario.
- Ozonation treatment caused a decrease in the amount of biopolymers, humic substances and LMW neutrals but increased the LMW acids. A higher applied ozone dose was found to reduce more humic substances and biopolymers.

Chapter 4 Validation of the Model and Simulation of Micropollutant Degradation

4.1 Introduction

Micropollutants have been detected in groundwater, surface water, and drinking water (Benotti et al., 2009; Jin & Peldszus, 2012; Snyder, 2008). These can include endocrine disrupting chemicals, personal care products, and pesticides (Westerhoff et al., 2005) , which can enter aquatic systems through many sources such as wastewater discharge and agricultural run-off (Schwarzenbach et al., 2006).

The micropollutants investigated in this chapter are benzene, toluene, ethylbenzene, and xylenes, atrazine, ANTX, CYN, MC-LR, THC and CBD. These micropollutants are of interest to the participating utilities and were selected after a series of discussions with them, which was one of the objectives of this thesis.

BTEX are a component of petroleum and can have adverse effects to human health (Mitra and Roy, 2011). BTEX is regulated in drinking water in Canada with an overall MAC level of 295 µg/L (Health Canada, 2009; Health Canada, 2014; Health Canada, 2017). Atrazine is one of the most frequently used herbicides in the world and its MAC in drinking water in Canada is 5 µg/L (Health Canada, 2011; Health Canada, 2017). Cyanotoxins ANTX, CYN and MC-LR are made by cyanobacteria (Westrick et al., 2010) . In Ontario, the MAC for total microcystins in water is 1.5 µg/L while ANTX and CYN do not have regulations (Health Canada, 2016; Health Canada, 2017*).* THC and CBD are compounds in cannabis that act on the cannabinoid receptors (Russo & Guy, 2006). THC and CBD are not currently regulated in drinking water in Canada, however, more interest has been directed to them due to the recent legalization of cannabis(Tasker, 2018).

There are a variety of conventional treatment processes that are able to degrade or transform these micropollutants into less harmful products (Schwarzenbach et al., 2006). However, ozonation is seen as

an effective treatment process for a range of micropollutants such as pharmaceuticals and endocrine disrupting compounds (Benotti et al., 2009). Due to the wide variety of micropollutants in drinking water the micropollutant degradation model developed by Elovitz and von Gunten (1999) has been referenced by numerous researchers (e.g. Shin et al., 2015; Zimmermann et al., 2011). This model is time and cost effective in comparison to lab experimentation and allows for the evaluation of multiple compounds.

Inputs to the model are the Rct value and ozone exposure, which are experimentally determined, whereas micropollutant rate constants with the oxidizing species can be obtained through literature (Elovitz, and von Gunten, 1999). Rate constants from literature are usually established at baseline conditions (pH=7, temperature=20^{o}C) and need to be modified in order to apply the model to typical drinking water treatment plant conditions.

However, some research articles employ standard conditions which can limit the applicability of their model (Elovitz and von Gunten, 1999; Jin, 2012; Mcdowell, et al., 2005). Other studies look at non-standard conditions but keep one water quality parameters constant or have a small range in their water quality variables (Shin et al., 2015; Vincent et al., 2010; Zimmermann et al., 2011). In the literature, there is a need to sample water quality parameters at real life conditions and to adjust the model so that it is applicable to drinking water treatment plant conditions.

Furthermore, if micropollutant rate constants are not available in the literature, they need to be experimentally determined in the lab. This may not be feasible if there are many compounds of interest. However, with the recent development of QSPR models the rate constants can be predicted using the compound's structural characteristics (Jin et al., 2015). This thesis incorporates the research of Jin, (2012) and predicts the rate constants for two active cannabis compounds, THC and CBD, for input into the micropollutant degradation model and subsequent modeling

of THC and CBD degradation. To the best of the author's knowledge this has never been done before in drinking water treatment.

The initial objective of this chapter was to test the validity of the micropollutant degradation model at applied ozone doses of 1 mg/L and 4 mg/L through bench scale experimentation with atrazine and microcystin-LR. Rct values for the waters used in these experiments were incorporated into the model to simulate atrazine and microcystin-LR removals and these were compared to experimental degradation results. After this the final and most important objective could be undertaken which was simulating the degradation of BTEX compounds, atrazine, ANTX, CYN, MC-LR, THC and CBD at a range of drinking water treatment plant conditions. This is a crucial step as it will give the drinking water treatment plants a predictive tool to assess how effective their ozonation process will be at degrading a variety of micropollutants.

4.2 Materials & Methods

4.2.1 Validation Experiments with MC-LR and Atrazine

The degradation of atrazine was experimentally determined in all three plants in February-March 2017 [Grand River A February 17, 2017 (3^{o}C), Grand River B March 13, 2017 (20^{o}C) and Lake Ontario March 2, 2017 (10^{o}C)]. These experiments were done at applied ozone doses of 1 mg/L and 4 mg/L where atrazine concentrations were measured from 20 s to 25 min in addition to ozone and OH radicals (pCBA) concentrations. The procedure outlined in section 3.2.6 was used. Before adding ozone, the sample water was spiked with atrazine to yield a concentration of 54 µg/L. Atrazine was 99% purity and obtained from SupelCo (PA, USA). The atrazine stock solution (10 mg/L) was made by weighing in 10 mg of neat compound into 1 L of Milli-Q ® water and stirring the solution for one hour. Atrazine had to be dissolved

in water to avoid the promoter effects of methanol. This solution was used to make the atrazine spiking solution of 5 mg/L by diluting it in Milli-Q water.

One MC-LR validation experiment was completed in Grand River A water using water sampled on November 21, 2016 and a 4 mg/L applied ozone dose. MC-LR concentration were measured from 20 s to 25 min in addition to ozone and OH radicals via pCBA. A 125 mL Erlenmeyer flask had to be used instead of a 500 mL flask to keep the amounts of MC-LR used as low as possible since this was an expensive product. The sample water was spiked with MC-LR to yield 100 µg/L. Besides these differences the same procedure was used as in 3.2.6. A 100 mg/L stock solution of MC-LR was made by dissolving 1 mg of MC-LR into 10 mL of Milli-Q ® water. This stock solution was then used to prepare a working solution of 1 mg/L.

4.2.2 Atrazine, and MC-LR Analysis by LC-MS

Two different methods were created one for atrazine and one for MC-LR. MC-LR and atrazine concentrations were all measured using an 8030 LC-MS model from Shimadzu (Japan) the same instrument that was used to measure pCBA in section 3.2.5.

A Zorbax extended-C18 column (3*50mm) with 1.8 micron packing was used for the analysis of both of the compounds (Agilent, USA). A Millipore Milli-Q ® UV PLUS water system (MA, USA) was used to produce high purity water. MC-LR was bought from EMD Millipore (ON, CA). Formic acid was obtained from Sigma-Aldrich (WI, USA) and was 99% purity. Acetonitrile and methanol were LC-MS grade from Sigma-Aldrich.

For atrazine an isocratic method was employed using a mobile phase A of 30% Milli-Q ® water and a mobile phase B of 70% acetonitrile. This was done with a total flow of 0.4 mL/min, run time of 4 minutes, and temperature of 40^{o}C with an injection volume of 50 µL. Using Standard Methods 1020B the atrazine method detection limit was determined to be 0.83 µg/L. For both MC-LR and atrazine the standard LC-MS

optimization was used to pick the MRM conditions and electrospray ionization was employed. A negative MRM mode monitored 216.10>174.10 and 216.10>96.10 transitions for atrazine.

For calibration curve standards and quality control standards, the stock solution of atrazine was prepared in methanol to produce 1000 mg/L solution which was then diluted to a working solution of 10 mg/L. This solution was used to make a nine-point calibration of 1- 100 µg/L.

MC-LR had a gradient method as used by Liu, (2017) and is shown Table 4.1. Mobile phase A consisted of 0.1% formic acid in Milli-Q ® water while mobile phase B was made up of 0.1% formic acid in acetonitrile. Stock solutions (100 mg/L) were made by dissolving 1 mg of MC-LR into 10 mL of Milli-Q ® water. This stock solution was then used to prepare a working solution of 1 mg/L. All MC-LR solutions were stored at -20^{o}C in amber glassware. A positive MRM mode monitored 498.30>135.00 and 995.20>134.95 transitions for MC-LR. The injection volume was 10 µL and the flow rate was 0.3 mL/min. The MDL, 0.1 µg/L, was determined by Liu, (2017) whose experiments were running at the same time. A nine-point calibration was run from 1-100 µg/L.

For both of the LC-MS methods one mid-level calibration control standard was measured every ten samples. Samples were injected seven times into the LC-MS to warm up the instrument then calibration standards were measured at the beginning of each run.

Table 4.1 LCMS mobile phase gradient for MC-LR

Time (min)	Acidified Acetonitrile Percent Concentration
0-1	20%
1-2	Increase concentration to 80%
2-5	Hold concentration at 80%
5-6	Increase concentration to 100%
6-10	Hold concentration at 100%
10-11	Decrease concentration to 20%
11-15	Hold concentration at 20%

4.2.3 Atrazine and MC-LR simulations

After bench-scale experiments were completed the micropollutant degradation model was used to compare simulated degradation results to experimentally determined results. Simulations in this chapter were completed by entering the measured Rct values and measured O_3 exposures and the individual micropollutant rate constants k_{O_3} and $k_{\bullet OH}$ into the micropollutant degradation model created by Elovitz & von Gunten, (1999) as can be seen from Equation 4.1

$$\ln \frac{[P]}{[P]_0} = -\left(k_{\bullet OH,P} R_{ct} + k_{O_3,P}\right)\left(\int_0^t [O_3]dt\right)$$

Equation 4.1 Micropollutant Degradation model (Elovitz & von Gunten, 1999)

The Rct value represents the ratio of ●OH to O_3 concentration and it was calculated using ●OH and O_3 concentration measured from 20 seconds-25 minutes. The O_3 exposure was calculated from 0 to 25 min by plotting the ozone concentration versus time with the area under the curve being O_3 exposure. This was done by fitting the data points to an exponential function and determining the area under the line by using integration. An exponential function was used since the ozone decay follows first-order kinetics.

Rate constants k_{O_3} and $k_{\bullet OH}$ were obtained through literature and modified for temperature and pH when needed as described in sections 4.2.4 and 4.2.5.

Initially, it was proposed that the degradation of two compounds, MC-LR and atrazine, would be measured and used for validation. Both of these compounds have a fast degradation with the ●OH radical with MC-LR having a rate constant of $1.1*10^{10}$ $M^{-1}S^{-1}$ while atrazine had a rate constant of $3*10^{9}$ $M^{-1}S^{-1}$. However, MC-LR reacts more readily with O_3 with a rate constant of $4.1*10^{5}$ $M^{-1}S^{-1}$ while atrazine reacts slower with O_3 with a rate constant of 6 $M^{-1}S^{-1}$ (Acero et al., 2000; Rodríguez et al., 2007). This approach ensured that the model could be adequately validated with two compounds from both ends of the reactivity spectrum with ozone. Atrazine was also chosen because it has been used as a validating compound by others (Acero et al., 2000; Elovitz & von Gunten, 1999). Atrazine and MC-LR were both of interest to the three treatment plants participating in this study as both compounds are regulated in Ontario and atrazine has been detected seasonally in the Grand River (Hallé, 2009).

4.2.4 Incorporating pH Modifications in the Micropollutant Degradation Model

Rate constants were obtained from literature as can been seen from Table 4.2 and were then modified as described below for temperature and pH. Some compounds can deprotonate, and depending on the pH value, they are either present in their protonated and deprotonated forms. These can have different rate constants with oxidants. In general, the rate constants with O_3 can differ substantially between protonated and deprotonated forms, while the rate constants with ●OH are usually close for both forms. Therefore, k_{O_3} values are pH dependent and this needs to be considered in the modelling (Hoigné & Bader, 1983).

The pH correction can be done by finding the rate constants for all the acid-base species and using these in the modelling (Jin, 2012; Zimmermann et al., 2011a). A second method is to determine the dominant

form (i.e. protonated or deprotonated) at the chosen pH value and use the corresponding rate constant (Jin, 2012). For compounds that disassociate (CYN, ANTX, atrazine) the second method was used.

Table 4.2 Rate constants from literature before temperature modifications; Atrazine (J.L. Acero et al., 2000) and (David Yao & Haag, 1991); BTEX (Hoigné & Bader, 1983); Cyanotoxins (Rodríguez et al., 2007); THC, CBD modelled in this study.

Compound	k_{O_3} ($M^{-1}S^{-1}$)	pH	$k_{.OH}$ ($M^{-1}S^{-1}$)
Benzene	2	2	$6.7*10^9$
Toluene	14	2	$6.8*10^9$
Ethylbenzene	14	2	$7.5*10^9$
o-Xylene	90	2	$6.7*10^9$
p-Xylene	140	2	$7.0*10^9$
m-Xylene	94	2	$7.5*10^9$
MC-LR	$4.1*10^5$	8	$1.1*10^{10}$
CYN	$3.4*10^5$	8	$5.5*10^9$
ANTX	$6.4*10^5$	8	$3.0*10^9$
THC	$10^{6.9}$	7	$10^{10.5}$
CBD	$10^{9.3}$	7	$10^{10.6}$
Atrazine	6.0	2-4.1	$3*10^9$

The reactions of O_3 with CYN and ANTX are pH dependent but not for MC-LR. MC-LR has three ionizable forms with three different pKas but ozone's point of attack are MC-LR's double bonds which are not effected by ionization. For CYN and ANTX the pH dependence follows the pKa values of the amine groups. For CYN the pKa value is 8.8. and for ANTX is 9.4 (Rodríguez et al., 2007). For ANTX in the pH range 6-9 the stable protonated form is dominant (Apeldoorn et al., 2007; Vlad et al., 2014), while in the pH range of 6-8.5 CYN is zwitterionic (He et al, 2013). pH dependence for CYN and ANTX had to be taken into account as different acid-base species would be dominate in the pH range of 4-12 (Rodríguez et al., 2007). Since the average pH for the water samples in this study were around 8, the rate constants for all three

cyanotoxins were chosen from a cyanotoxin studies which used a pH of 8 when determining rate constants.

The BTEX compounds are polyaromatic hydrocarbons. When pH values ranged from 1-7, pH has little to no effect on BTEX ko_3 values and therefore ko_3 values at different pH values are comparable (Butkovic et al., 1983; Jin, 2012). For this study ko_3 values were taken from the literature at acidic pH values (Hoigné & Bader, 1983).

Atrazine has a pKa value of 1.6 (Yao & Haag, 1991) and exists in its protonated form for pH values less than 2. Therefore, the deprotonated form would be dominate for pH>2 and the value at a pH of 4 was used in this study as was similarly done in Elovitz & von Gunten, (1999).

The ko_3 and $k_{\bullet OH}$ rate constants for the two active cannabis compounds, THC and CBD, to the best of the author's knowledge were not available in the literature. Therefore, QSPR models, developed by Jin et al., (2014), were used to model these rate constants at a neutral pH and room temperature conditions. Xiaohui Jin is a previous student of the NSERC Chair group and kindly offered to use his models, as described below, to determine the cannaboid rate constants which are provided in Table 4.2.

As Jin et al., (2014) have stated it would be very time intensive to experimentally determine the ko_3 for all micropollutants of interest. Although, there are rate constants for a lot of micropollutants (Hoigné & Bader, 1983) others are not available such as for some endocrine disrupting compounds and cannabinoids. Jin et al., (2014) developed a QSPR model using piece-wise linear regressions where the rate constants with O_3 were correlated to the structural characteristics of the compound.

Jin, (2012) proposed that various mechanisms may dominate depending on whether compounds reacted fast or slow with O_3. Therefore, using a piecewise linear regression model compounds were split up into these two groups and a linear sub-model was employed to fit the data.

In order to decide which sub-model to use, THC and CBD had to first be classified as either high or low-reactive compounds. This was done using a canonical discriminant function equation 5.10 from (Jin, 2012); both THC and CBD had a value of Class ≥0 and were determined to be high-reactive ($\log K_{O3} \geq 2.00$). The modelled rate constants of O_3 with THC and CBD respectively were $10^{6.9}$ and $10^{9.29}$ $M^{-1}S^{-1}$. Another QSPR model was used to predit the the $k_{\bullet OH}$ values for THC and CBD which were $10^{10.45}$ and $10^{10.61}$ $M^{-1}S^{-1}$ (Jin et al., 2015).

4.2.5 Incorporating Temperature Modifications in the Micropollutant Degradation Model

For temperature modifications the Arrhenius equation was used with the inputs of activation energy (E_A) in $Jmol^{-1}$, collision frequency parameter (A) in $mg^{-1}min^{-1}$, the ideal gas constant(R) (R = 8.314 $Jmol^{-1}$) and temperature in Kelvin as shown by Equation 4.2 (Driedger et al, 2001).

$$k = Aexp\left(-\frac{E_A}{RT}\right)$$

Equation 4.2 The Arrhenius Equation (Driedger et al, 2001)

This temperature modification method is similar to the one used by Zimmermann et al. (2011) in which the authors assumed an activation energy of 50 kJ/mol. This is within the E_a range of 35-50 kJ/mol for typical reactions with ozone when looking at aliphatic alcohols, ethylenes, benzenes and carbohydrates (Hoigné & Bader, 1983). For BTEX an E_a value of 40 kJ/mol was assumed in this study. This value was also used by Elovitz et al. (2000), who stated that this was reasonable due to 35-50 kJ/mol range in E_a found by Hoigné & Bader (1983). For atrazine an E_a of 36.5 kJ/mol was used as this value was available in literature and did not need to be assumed (J.L. Acero et al., 2000).

It should be noted that of the compounds modelled, only MC-LR with an E_A of 12.3kJ/mol (Rodríguez et al., 2007) did not fit in the range of 35-50 kJ/mol as proposed by Hoigné & Bader, (1983). However, this did not affect the modelling, since all cyanotoxins including MC-LR and all active cannabis compounds were modelled at room temperature and therefore temperature modifications did not need to be made.

Furthermore, micropollutants were simulated at experimental temperatures, see Chapter 3 Appendix A.2 for a complete list of sampling and experimental temperatures. For example for Grand River A October 17, 2017 and February 17, 2017 the high and low experimental temperatures were respectively 14ºC and 3ºC. Therefore, modelling simulations were also done at these temperatures. The three treatment plants had different high and low temperatures on the different sampling dates.

4.3 Results and Discussion

The micropollutant degradation model was used to simulate the degradation of atrazine in 1 mg/L (Figure 4.1) and in 4 mg/L applied ozone doses (Figure 4.2). Inputs to this model were the Rct value, O_3 exposure and the O_3 (6 $M^{-1}S^{-1}$) and ●OH ($3*10^9$ $M^{-1}S^{-1}$) rate constants for atrazine. Degradation of atrazine was also measured in these samples and these experimental results are compared to the simulated results.

In order to evaluate the model the first fast phase and the second slow phase of ozonation needed to be defined. The challenges with determining Rct values were discussed in Chapter 3 and the first phase was defined as being ≤19 seconds. The secondary phase of ozonation was measured from 20 seconds-25 minutes from which the Rct value was calculated. Note in this thesis ozone degradation was not measured for 0-19 seconds but was still defined as the first phase. Time points were able to be measured from 20 seconds-25 minutes. This fits the methods of Hoigné et al., (1994) who were also not able to measure ozone concentration from 0-19 seconds.

Due to atrazine's slow reaction with ozone its degradation could be monitored by measuring a residual concentration of atrazine up to 25 min. However, the reaction of MC-LR with O_3 was so fast that the MC-LR concentrations were below the MDL at the first sampling point of 19 seconds and therefore this could not be used for validation purposes.

4.3.1 Validation - Experimental versus Simulated Atrazine Results

For the 1 mg/L applied ozone dose in this study, the modelled results appeared to be quite close to the experimental results (Figure 4.1) for all three water sources. There were no differences seen between the three water sources at different temperatures. The residual plots also showed some systematic deviation in the early data points which will be discussed further below. Elovitz & von Gunten, (1999) also validated their model using atrazine at an applied ozone dosage of 1 mg/L and found that their modelled results matched the experimental results.

However, looking at the 4 mg/L dose the modelled results underestimated micropollutant degradation in all waters with Lake Ontario having the best match between modelled and experimental results (Figure 4.2). It is interesting to note that the author of this thesis did not find any other articles which validated their model at high applied ozone doses such as 4 mg/L. Similar to the 1 mg/L applied ozone, the temperature modified model for the 4 mg/L dose did not deviate from the room temperature model except for Grand River A (Figure 4.2 A).

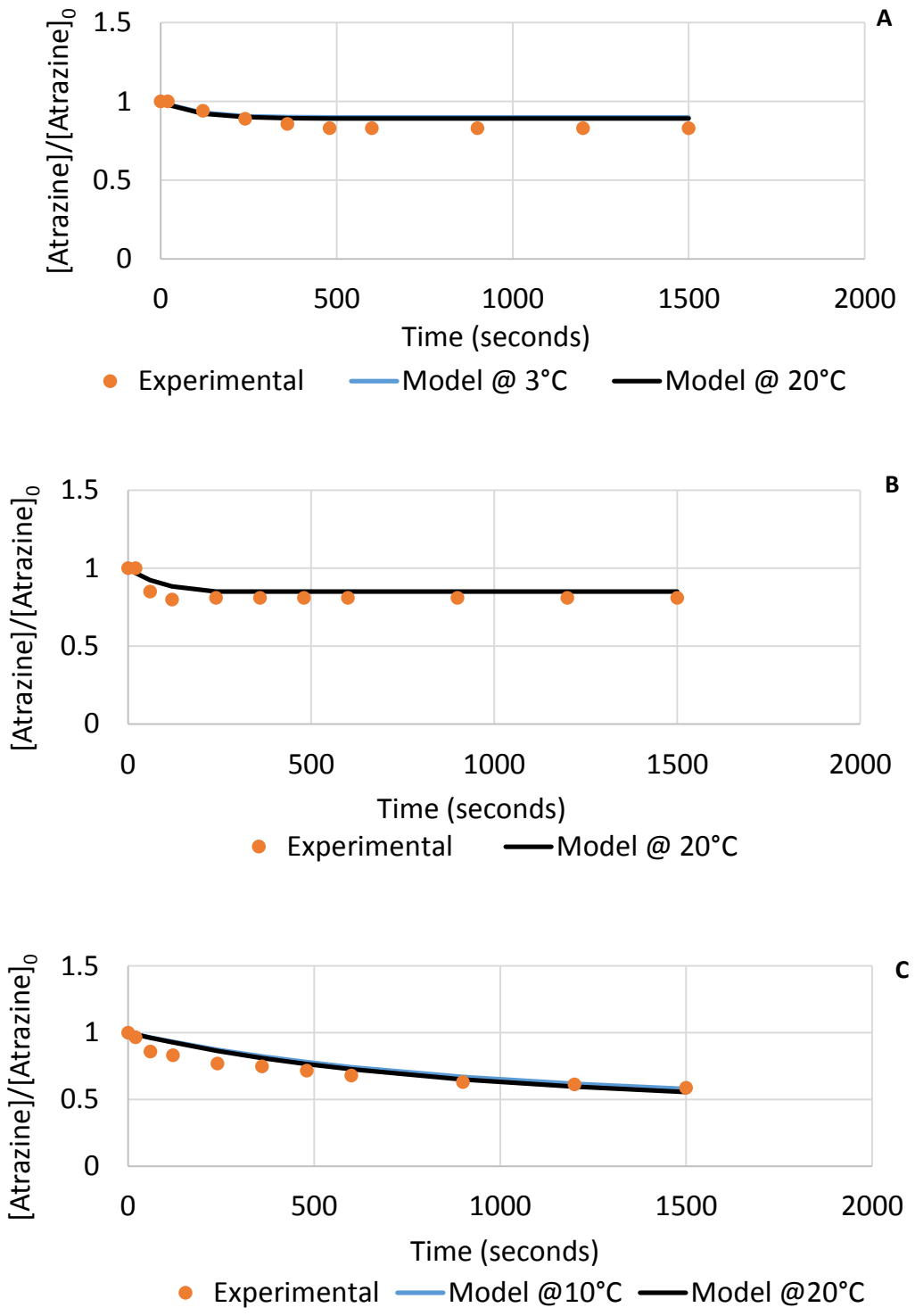


Figure 4.1: Atrazine validation graphs for an applied ozone dose of 1 mg/L modelled at 20°C and the sampling temperature A) Grand River A, B) Grand River B, C) Lake Ontario. Experiments were performed at different dates and temperatures: Grand River A (February 17, 2017, 3°C), Lake Ontario (March 2, 2017; 10°C), and Grand River B (March 13, 2017; 20°C). Atrazine spiking doses were as follows 46 µg/L (Grand River A), 55 µg/L (Grand River B) and 60 µg/L (Lake Ontario).

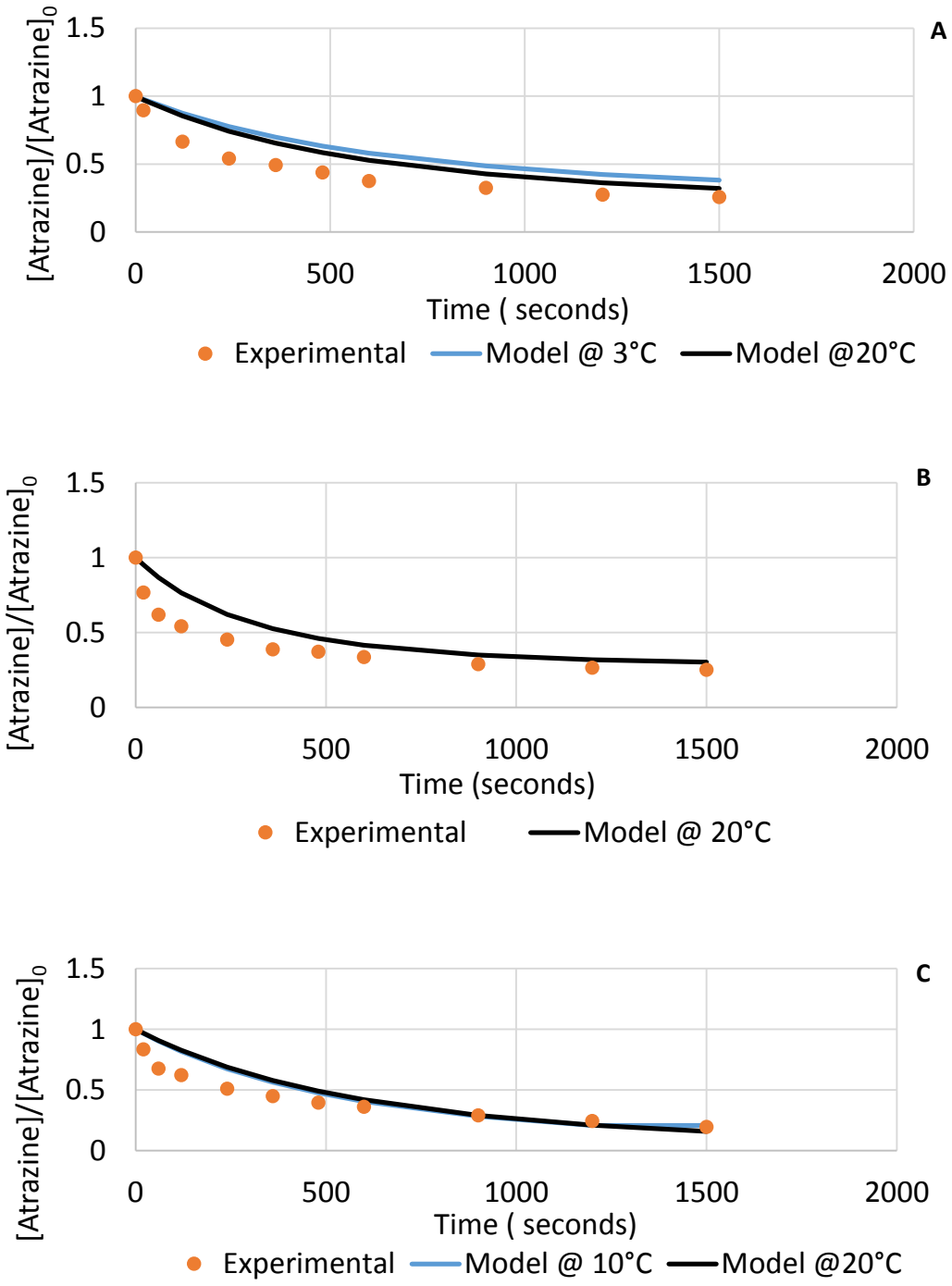


Figure 4.2 Atrazine validation graphs for an applied ozone dose of 4 mg/L modelled at 20°C and the sampling temperature. A) Grand River A, B) Grand River B, C) Lake Ontario. Experiments were performed at different dates and temperatures: Grand River A (February 17, 2017; 3°C), Lake Ontario (March 2, 2017; 10°C), and Grand River B (March 13, 2017; 20°C). Atrazine spiking doses were as follows 46 µg/L (Grand River A), 55 µg/L (Grand River B) and 60 µg/L (Lake Ontario).

It is hypothesized that the deviations in the earlier data points (Figures 4.1& 4.2) of the modelled results are due to difficulties in measuring ozone and OH radical concentrations in the 1st phase of ozonation from 0-19 seconds. The Rct value for the first phase, which can be 2-3 orders of magnitude larger than the second phase Rct value (Yong & Lin, 2012), could not be measured and was therefore not incorporated into the modelling results. This could likely be the reason for the underestimation of the simulated results.

Furthermore, ozone demand in the first phase was quite high with almost 50% of the applied ozone dose being used up for Grand River A and B at the 1 mg/L dose with values around 0.4 mg/L being consumed (Figure 4.3). Lake Ontario on the other hand had a lower ozone demand with only 0.1 mg/L being consumed in the first phase. This may be attributed to its lower DOC, Lake Ontario 1.8 mg/L C versus Grand River values between 3.3-3.4 mg/L C. For example, Shin et al., (2015) also found that a lot of ozone can be consumed in the first phase (which they defined as under 1 minute). These authors observed values of 0.31 mg/L of ozone demand for water that had been sand filtered, and 0.64 mg/L for raw lake water at applied ozone doses of 1 mg/L. Shin et al. (2015) showed that a water source with a higher NOM content has a higher ozone demand in the first phase similar to the results found within.

Elovitz & von Gunten, (1999) found that as much as 50% of ozone could be degraded in their first phase (defined as 30-120 seconds) at a 1 mg/L applied ozone dose. Although, the authors state that this first phase only contributed about fifteen percent to the overall O_3 exposure due to rapid kinetics. In comparison for ●OH thirty five percent of the first phase was attributed to the overall ●OH exposure. Due to the difficulties in collecting data for this first phase the authors suggest that these percentages should be viewed as preliminary.

Recent articles used the quench-flow technique in which the first phase Rct value (they define as less than 20 seconds) is measured. These studies have shown that the first phase Rct value can be 2-3 orders of magnitude larger than the second phase Rct value (Buffle et al., 2006a; Yong & Lin, 2012). Researchers

have suggested that the standard setup used for ozonation studies, is only suitable for obtaining the second phase Rct value (they define as greater than 20 seconds) (Yong & Lin, 2012). This was also shown by Elovitz & von Gunten, (1999) who used this standard setup and were not able to measure ozone degradation from 0-30 seconds. It is therefore suggested that future ozonation studies should use quench-flow techniques to measure the first phase Rct value and incorporate it into the modelling results. Measuring this first Rct phase would incorporate the large amount of O_3 degraded in this first phase and should improve simulation results. Overall, validation of the modelling was successful and one could proceed with the simulations.

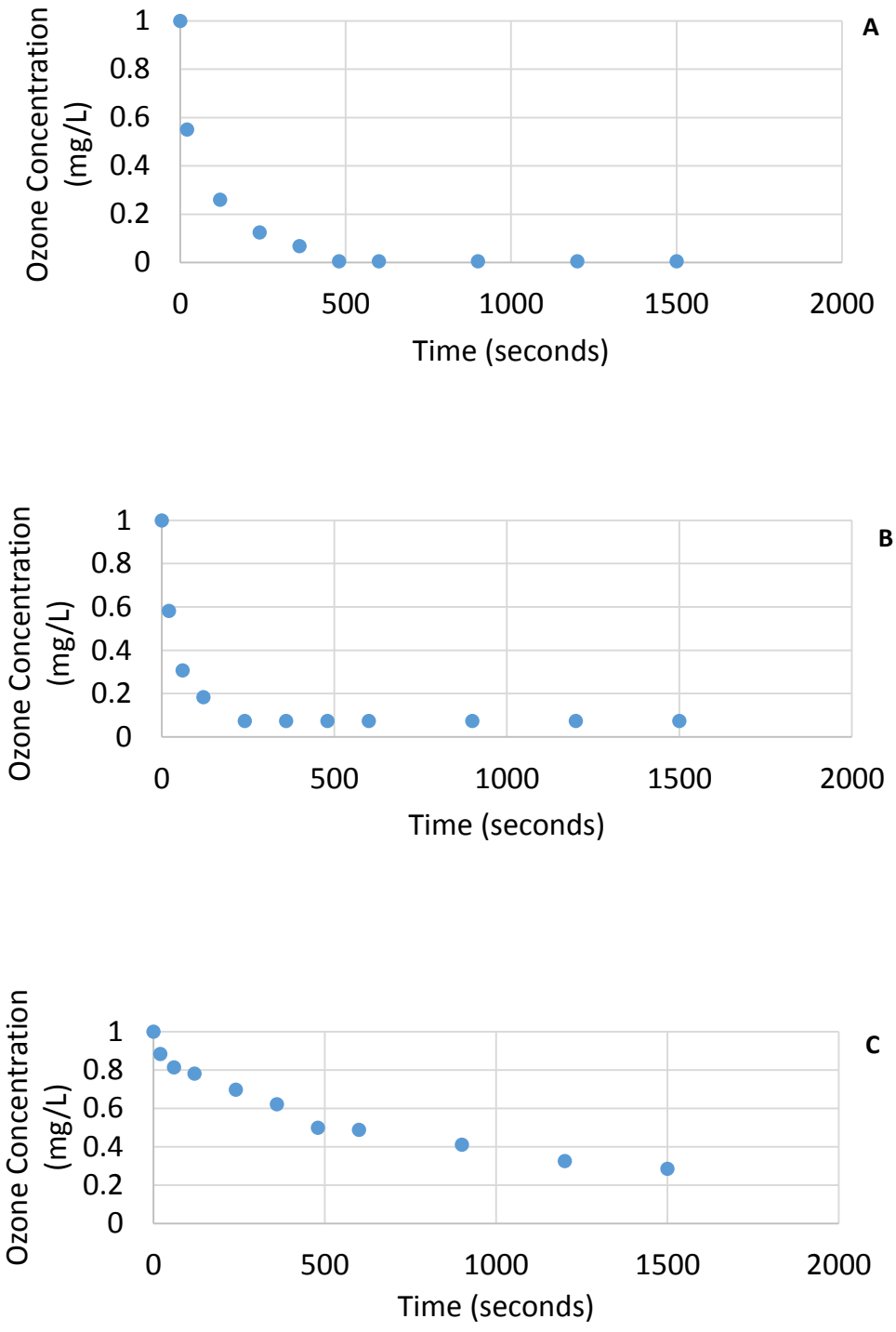


Figure 4.3 Ozone degradation (mg/L) at the 1 mg/L applied ozone dose. Concentrations determined by the Indigo method. A) Grand River A, B) Grand River B, C) Lake Ontario. Experimental dates and temperatures were Grand River A (February 17, 2017; 3°C; DOC: 3.3 mg/L C), Lake Ontario (March 2, 2017; 10°C; DOC: 1.8 mg/L C), and Grand River B (March 13, 2017; 20°C; DOC: 3.4 mg/L C).

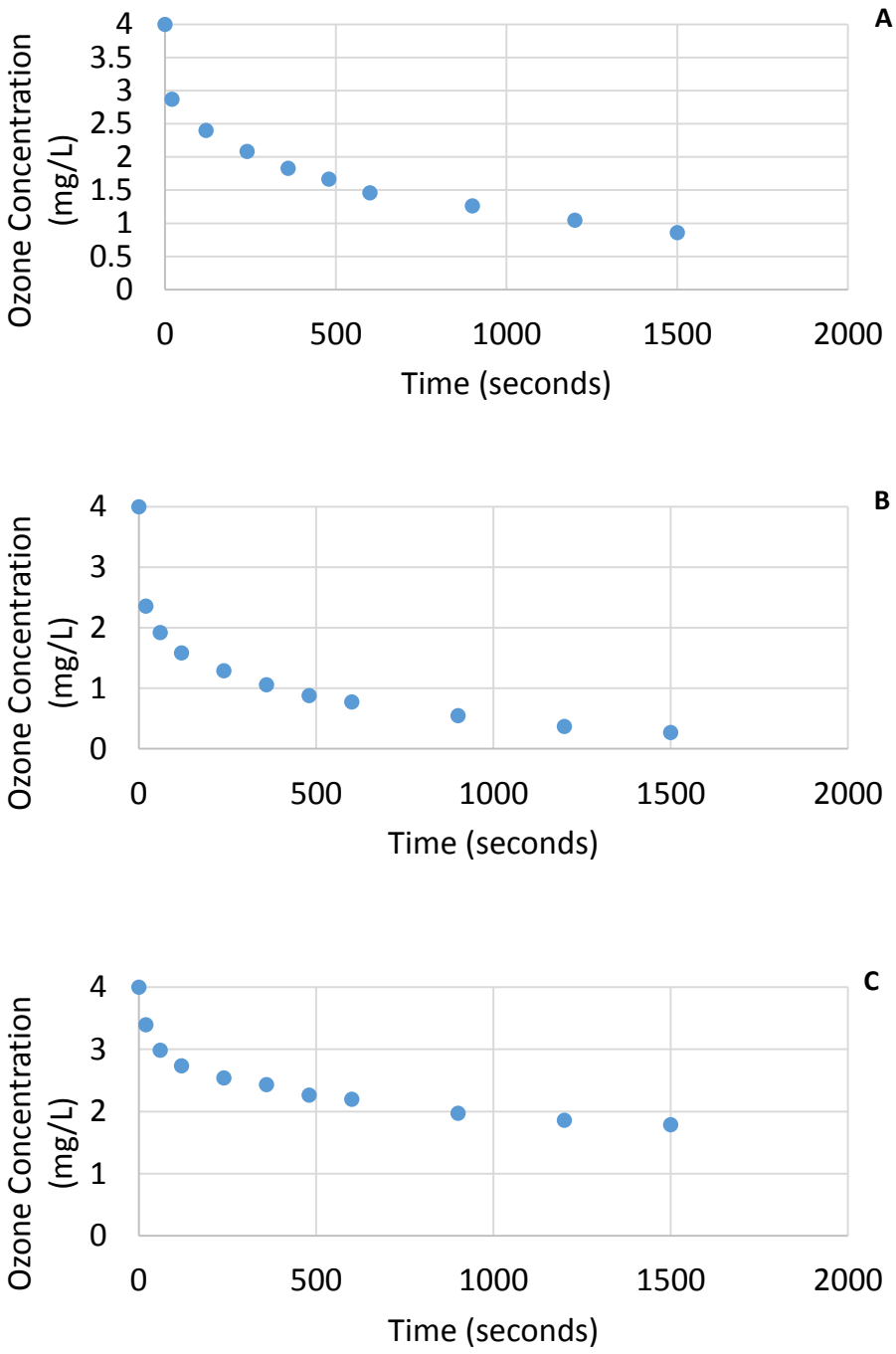


Figure 4.4 Ozone degradation (mg/L) at the 4 mg/L applied ozone dose. Concentrations determined by the Indigo method. A) Grand River A, B) Grand River B, C) Lake Ontario. Experimental dates and temperatures were Grand River A (February 17, 2017; 3°C; DOC: 3.3 mg/L C), Lake Ontario (March 2, 2017; 10°C; DOC: 1.8 mg/L C), and Grand River B (March 13, 2017; 20°C; DOC: 3.4 mg/L C).

4.3.2 Influence of the First phase on the Rct Value

As was described in Chapter 3 there are two phases of ozone decay; a rapid first phase and a slower secondary phase. However, there is currently a lot of variation in describing the extent of the first phase. For example Hoigne & Bader, (1994) described their first phase as less than 20 seconds. While Elovitz & von Gunten, (1999) used data from 30-120 seconds to calculate the Rct value for the first phase as they could not measure earlier data points. Overall, for modelling micropollutant degradation Elovitz & von Gunten, (1999) only use the Rct value from the second phase of ozonation (120 s onwards) and not the first phase. They state that this was valid because only a small percentage of the first phase contributed to the overall O_3 exposure.

Due to the fact that quench-flow techniques were not used in this thesis, there were not enough data points to describe the first phase of ozonation. The approach used in this thesis was based on the time intervals reported for the first phase in the literature and estimated the end of the first phase to be at twenty seconds, for further information see Chapter 3. However, Elovitz and von Gunten, (1999) defined the end of their first phase at two minutes.

Therefore this section contrasts two Rct values, Rct.V and Rct.O, which differed in the extent of the second phase of ozonation. This was done to determine which Rct value had a better fit for the Lake Ontario data. The Rct.V was calculated from time points greater than 2 minutes as defined by Elovitz & von Gunten, (1999). Rct.O was defined as the Rct value used in this study, and was calculated from time points 20 seconds-25 minutes.

The effect of the different Rct values can be seen in Figure 4.5 in the Lake Ontario water. For both applied ozone doses the simulation with the Rct.V input tends to underestimate atrazine degradation throughout the time period. However, it does come up with a good estimation at the 1500 second mark. This behavior

is more pronounced at the higher applied ozone dose of 4 mg/L. This underestimation is likely because the points from their first phase of the ozone degradation, 30-120 seconds, are not considered. Overall, as shown in Figure 4.5, Rct.O resulted in a better modelling simulation when comparing modelling results to the experimental data. The comparison of Rct.O versus Rct.V was not done for Grand River A and B water sources. Grand River sources were expected to have similar results as these samples have even more rapid degradation of ozone in the first phase which would be underestimated with the Rct.V calculation.

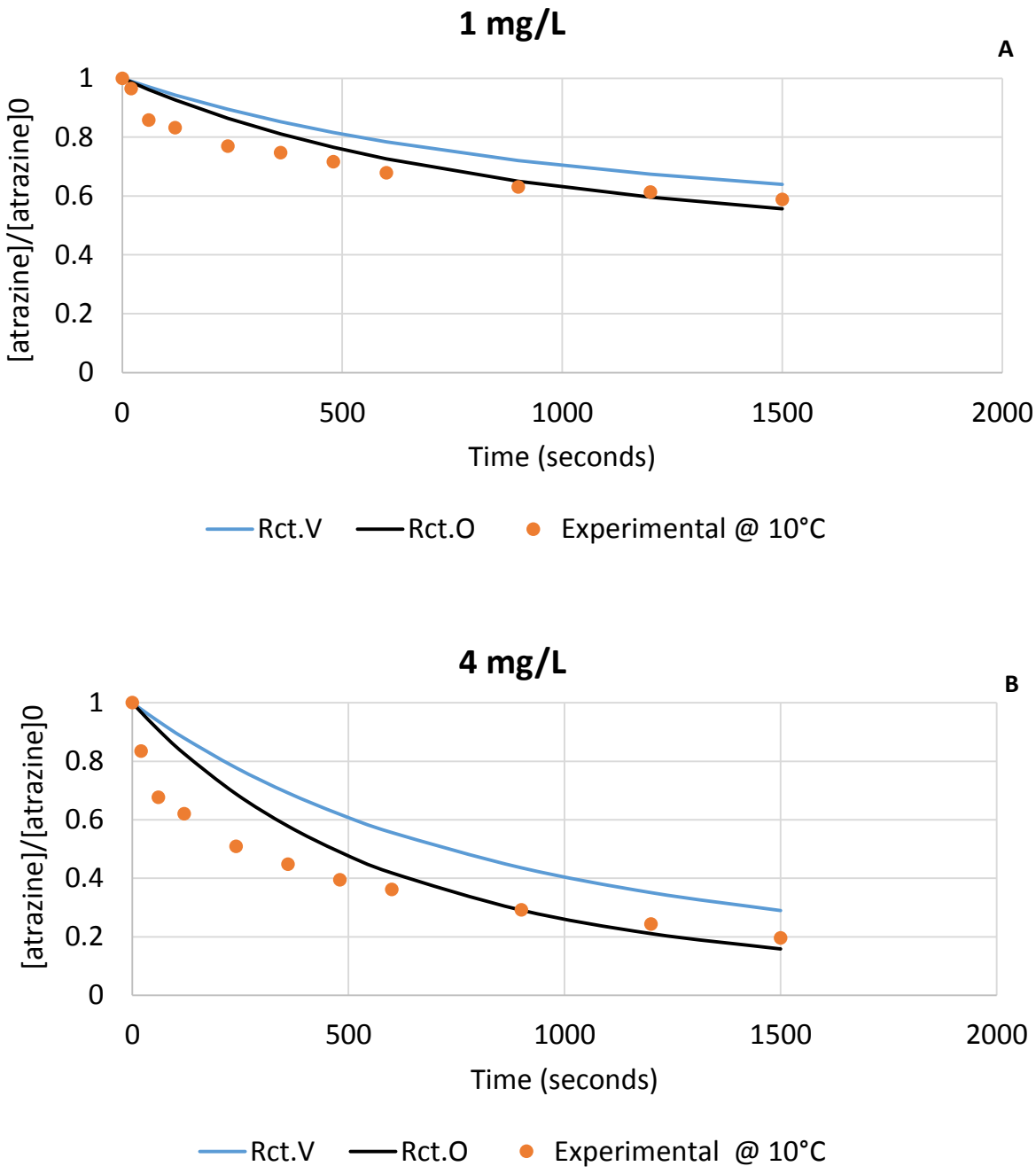


Figure 4.5 Comparison of Rct.V and Rct.O atrazine simulations with Lake Ontario experimental data at 1 mg/L and 4 mg/L applied ozone dose. A) 1 mg/l applied ozone dose, B) 4 mg/l applied ozone dose. Rct.V is calculated using all time points including and greater than 2 minutes and Rct.O is calculated using all time points including and greater than 19 seconds. Simulations are modelled at 20°C at a spiking dose of 60 µg/L of atrazine. Experimental temperature was 10°C on March 13, 2017. No temperature modifications were made.

In this thesis it was decided to consider points from 20 seconds-25 minutes (Rct.O) for Rct calculations for the following reasons. Firstly, in some of the water sources mainly in the Grand River the ozone got consumed quite rapidly, potentially due to high NOM. Due to this, at low applied ozone doses of 1 mg/L, there was often no ozone left in the water after 5 minutes, and sometimes even at the 2 minute mark. In this case it would not be possible to use Rct.V as there would be no data to calculate the Rct from. Therefore, the author thought that it would be best to define the first phase of ozonation as less than 19 seconds in order to capture some of the atrazine degradation occurring in those first few minutes. Second, multiple studies have defined the initial ozonation phase as less than 20 seconds (e.g. Buffle et al., 2006b; Hoigne & Bader, 1994). Lastly, Rct.O had a better fit between experimental and simulation results in comparison to Rct.V (Figure 4.5).

Section 4.4 Modelling of Micropollutant Degradation by Ozone

This section will focus on the simulation of a variety of micropollutants- BTEX compounds, atrazine, ANTX, CYN, MC-LR, THC and CBD. These micropollutants were chosen after discussion with the 3 treatment plants about which contaminants were of interest to them. The modelling approach as described in materials and methods 4.2.3 involved inputting the Rct value, O_3 exposure, and rate constants into the micropollutant degradation model (Equation 4.1). Modelling scenarios were chosen based on seasonal water samples and corresponding Rct values and ozone exposures. An overview of all water samples is provided in Table 3.2.

Section 4.4.1 Overall BTEX Degradation

After the micropollutant degradation model was validated, various compounds were simulated. A select number of micropollutants were chosen and their degradation in ozone was simulated under different conditions varying the following: seasons, source water, applied ozone dose and micropollutant concentrations. The author's intention was to simulate micropollutant degradation for these different conditions and the intention was not to show which variable affected degradation the most as the experiments were not set up in this manner.

BTEX is a component of petroleum products such as oil and gasoline and makes up 90% of gasoline fractions that originate in the water-soluble portion. BTEX refers to a group of naturally occurring compounds: Benzene, Toluene, Ethylbenzene and o, m and p-xylene. These can be found in water sources after oil or gasoline spills, or leakages from oil pipelines (Fayemiwo et al., 2017; Mitra and Roy., 2011).

These compounds are composed of hydrogen and carbon, and are polyaromatic hydrocarbons with various substituents. The rate constants for the individual compounds are shown in Table 4.3 with all of them having a relatively high reactivity with ●OH. The individual BTEX compounds have similar rate constants with $k_{\bullet OH}$ ranging from $6.7*10^9$ to $7.5*10^9$ ($M^{-1}S^{-1}$). This is due to the nonspecific nature of ●OH radical which will have a fairly high reactivity with most compounds and will attack carbon-hydrogen bonds. On the other hand, O_3 is more specific and reacts faster with compounds containing structural features such as double bonds, neutral amines and activated aromatic rings (Rodríguez et al., 2005; von Gunten, 2003).

In terms of ko_3 there is a large spread in reactivity of individual BTEX compounds with values in the range of 2-140 ($M^{-1}S^{-1}$). Fast reacting compounds with O_3 are in the range of 10^4-10^7 $M^{-1}S^{-1}$, medium reacting ones are in the range of 10^3-10^5 $M^{-1}S^{-1}$and slow reacting ones are in the range of 10^{-2} to 1.4 $M^{-1}S^{-1}$ (Jin,

2012). Benzene (2 $M^{-1}S^{-1}$) has the lowest reactivity of the BTEX compounds with ozone and therefore will be the hardest to degrade as seen in other studies (Derco et al., 2017), and p-xylene (140 $M^{-1}S^{-1}$) has the highest reactivity with ozone. The reactivity with ozone increases with the amount of substitution with methyl groups which explains why benzene (C_6H_6) which has no substituent, is the least reactive. Xylene isomer reactivity will depend on the position of the methyl groups relative to each other (von Gunten, 2003a).

BTEX can have adverse effects to human health such as irritating the sensory system (Mitra and Roy, 2011), however due to the fact that they are not often found in water systems their treatment can be overlooked (Fayemiwo et al., 2017). The different fractions of BTEX compounds typically found in gasoline are outlined in Table 4.3 which also show their MAC levels in Canada.

Table 4.3: BTEX fraction percentage of gasoline, initial concentrations assumed for modelling and rate constants. Molecular formula and percentage from (Mitra&Roy,2011). Rate constants for BTEX $k_{\bullet OH}$ (Sehested et al., 1974) expect Benzene $k_{\bullet OH}$ (Wols & Hofman-caris, 2012). BTEX ko_3 from (Hoigné & Bader, 1983). MAC levels from (Health Canada, 2009; Health Canada, 2014).

BTEX Fraction	Percentage in gasoline	Assumed Initial Concentration (µg/L)	MAC (µg/L)	Molecular Formula	ko_3 ($M^{-1}S^{-1}$)	$k_{\bullet OH}$ ($M^{-1}S^{-1}$)
Benzene	11	165	5	C_6H_6	2	$6.7*10^9$
Toluene	26	390	60	$C_6H_5CH_3$	14	$6.8*10^9$
Ethylbenzene	11	165	140	$C_6H_5CH_2CH_3$	14	$7.5*10^9$
p-Xylene	9	135	90 total	$C_6H_4(CH_3)_2$	140	$7.0*10^9$
m-Xylene	31	465	90 total	$C_6H_4(CH_3)_2$	94	$7.5*10^9$
o-Xylene	12	180	90 total	$C_6H_4(CH_3)_2$	90	$6.7*10^9$

This subsection will focus on the simulation of the ozonation of gasoline into Grand River and Lake Ontario. This is quite relevant as in 2016 motor oil leaked from an 800 L storage tank and it was thought that about half of this oil went into the Grand River (CTV Kitchener, 2016).

For the simulation the assumed initial concentrations of BTEX were based on information from oil spills (Trans Mountain Pipeline, 2013) , BTEX percent composition and the rate constants of BTEX with ●OH and O_3 were taken from the literature (see Table 4.3).

Figure 4.6 shows the remaining BTEX concentration left after a reaction time of 1500 seconds at high and low temperatures at applied ozone doses of 1 mg/L and 4 mg/L while Figure 4.7 shows the BTEX percent removal for the same scenario. The 4 mg/L applied ozone dose was able to degrade BTEX to levels below its MAC in all three treatment plants (Figure 4.6). In comparison, the 1 mg/L applied ozone dose was not as effective and only removed BTEX below its MAC level in Lake Ontario at the high temperature sampling point. Overall, Lake Ontario has the highest BTEX percent removal with removals ranging from 55-82% for the 1 mg/L applied ozone dose and 98-99% for the 4 mg/L dose (Figure 4.7). This could be because Lake Ontario has the highest ozone to DOC ratios out of all three of the water sources (Table 3.2).

Grand River B has the second highest BTEX removal with removals ranging from 23-37% for the 1 mg/L applied ozone dose and 94-96% for the 4 mg/L applied ozone dose (Figure 4.7); refer to Appendix B for more detail. Grand River has the lowest BTEX percent removal with ranges of 16-25% for the 1 mg/L dose and 93-97% for the 4 mg/L dose. Differences in degradation between water sources could also be because of differences in alkalinity, pH, and temperature.

A 4 mg/L applied ozone dose degraded BTEX more efficiently than the 1 mg/L applied ozone dose (Figure 4.7). It is well known that increasing applied ozone dose will increase contaminant degradation and was also observed by Westerhoff et al., (2006) when measuring 2-methylisoborneol oxidation. All 4 mg/L applied ozone dose removals were similar with no clear distinctions between the three water sources and influence of temperature.

For Grand River B and Lake Ontario higher temperatures resulted in more BTEX percent removal at the 1 mg/L applied ozone dose. For Grand River A BTEX degradation at 1 mg/L is greater at the lower temperature however this could be due to the higher DOC found at the 14^{o}C sampling point versus the 3^{o}C sampling point.

Temperature differences between the water sources could cause differences in BTEX percent removal. In Figures 4.6 and 4.7, it can be seen that lower temperatures have a small range (3-5ºC) while higher temperatures have a larger range (14-20ºC). This was because micropollutants were simulated at their experimental temperatures, see Table A.2 in Chapter 3 for more information on experimental temperatures. Modelling had to be completed at these specific temperatures, because they corresponded to experimentally measured Rct values and ozone exposures. Furthermore, Grand River A could not be sampled during the summer and therefore its high temperature was 14ºC in comparison to the other two plants which had a high temperature of 20ºC. Future experiments should model these compounds at the same high and low temperature in order to get consistent results.

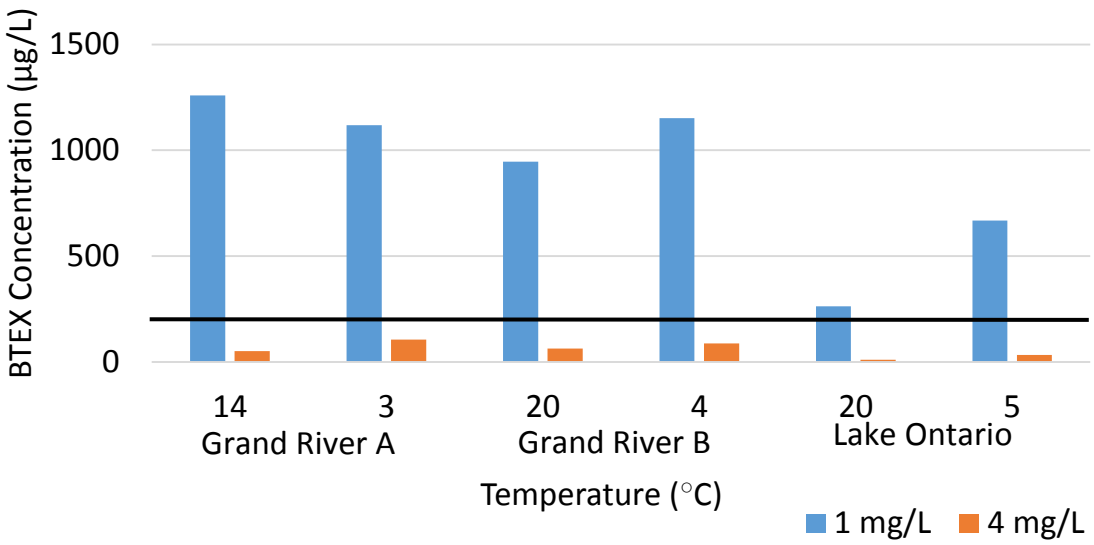


Figure 4.6 Overall BTEX degradation showing remaining BTEX concentration at the 1500 second mark for the three treatment plants at 1 mg/L and 4 mg/L applied ozone doses, and at high and low temperatures (°C). Grand River A (October 17, 2017; 14°C) and (February 17, 2017; 3°C). Grand River B (March 13, 2017; 20°C) and (January 6, 2017; 4°C). Lake Ontario (September 28, 2016; 20°C) and (December 5, 2016; 5°C). Assumed initial overall BTEX concentration was 1500 µg/L . The BTEX MAC is shown by the black line on the figure.

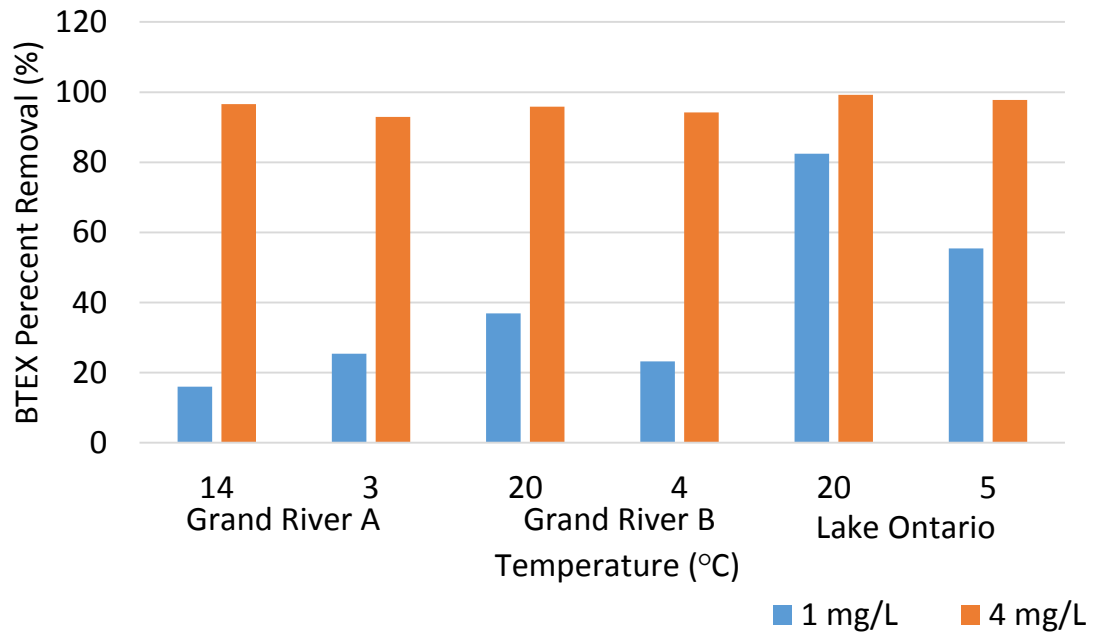


Figure 4.7 Overall BTEX Percent Removal at the 1500 second mark for the three treatment plants at 1 mg/L and 4 mg/L applied ozone doses, and at high and low temperatures (°C). Grand River A (October 17, 2017; 14°C) and (February 17,2017; 3°C). Grand River B (March 13,2017 ; 20°C) and (January 6,2017; 4°C). Lake Ontario (September 28, 2016; 20°C) and (December 5, 2016; 5°C). Assumed initial overall BTEX concentration was 1500 µg/L.

Section 4.4.2 BTEX Individual Components Degradation

From the last subsection it could be seen that BTEX percent removal differed due to a range of different factors not limited to source water quality, applied ozone dose, and temperature. In this section the degradation of individual BTEX components will be investigated.

The rate constant of the BTEX compounds with ko_3will affect how fast they are degraded with benzene having the lowest reactivity with O_3 and p-xylene having the highest (Table 4.3)

Another factor to take into consideration is the different initial concentrations of the individual BTEX compounds assumed for modelling (Table 4.3). The simulations in this subsection were modelled at an initial BTEX concentration of 1500 µg/L which were then further split up into the corresponding individual initial concentrations based on the component fraction in gasoline. Toluene and m-xylene make up over half of the BTEX with percentages of 26% and 13% respectively while the rest of components make up between 9-12% of the mixture each (Table 4.3). Note ethylbenzene and benzene overlap on many of the simulations (Figures 4.8-4.10) due to them having the same assumed initial concentration and similar reactivity with ozone (Table 4.3).

For all of the water sources the 4 mg/L applied ozone dose resulted in more BTEX component percent removal then the 1 mg/L dose see Figures 4.8-4.10. Furthermore, with a 4 mg/L applied ozone dose the composition of BTEX changed and toluene and m-xylene no longer made up over half the amount of BTEX, and benzene made up a larger percent fraction. In comparison, with the 1 mg/L dose the BTEX composition stayed more or less the same in the 3 treatment plants (Figures 4.8-4.10).

For the 1 mg/L applied ozone dose Grand River A and B had similar patterns of BTEX degradation whereas Lake Ontario had higher BTEX component degradations which could be due to its higher ozone to DOC ratio (Table 3.2). In comparison, for the 4 mg/L applied ozone dose the three treatment plants all had

comparable BTEX component degradations with Lake Ontario being slightly higher than the other two plants (Figures 4.8-4.10).

As stated in in section 4.4.1 an increase in temperature increased BTEX percent removal for Grand River B and Lake Ontario. In this section the effect of temperature on the individual BTEX components was investigated as can be seen from Figures 4.8-4.10. This was done by comparing a high and low temperature and calculating the difference in percent removal between these two. The tabulated results can be found in the Appendix B.

For Grand River B at an applied ozone dose of 1 mg/L and comparing temperatures of 4^{o}C to 20^{o}C it was found that BTEX removal increased with temperature in the range of 10-18% (Figure 4.9). These results are similar to Lake Ontario which at an applied ozone dose of 1 mg/L and a temperature change of 5 ^{o}C to 20^{o}C has an increase in percent removal in the range of 23-30% (Figure 4.10). For Grand River A this relationship between temperature and BTEX percent removal is not the same as it is in the other two water sources. At an applied ozone dose of 1 mg/L removals increase with an increase in temperature ranging from 8-10% (Figure 4.8). For the 4 mg/L applied ozone dose for all three treatment plants the percent differences were small and therefore a conclusion cannot be made on the effect of temperature on BTEX component degradation at this dose.

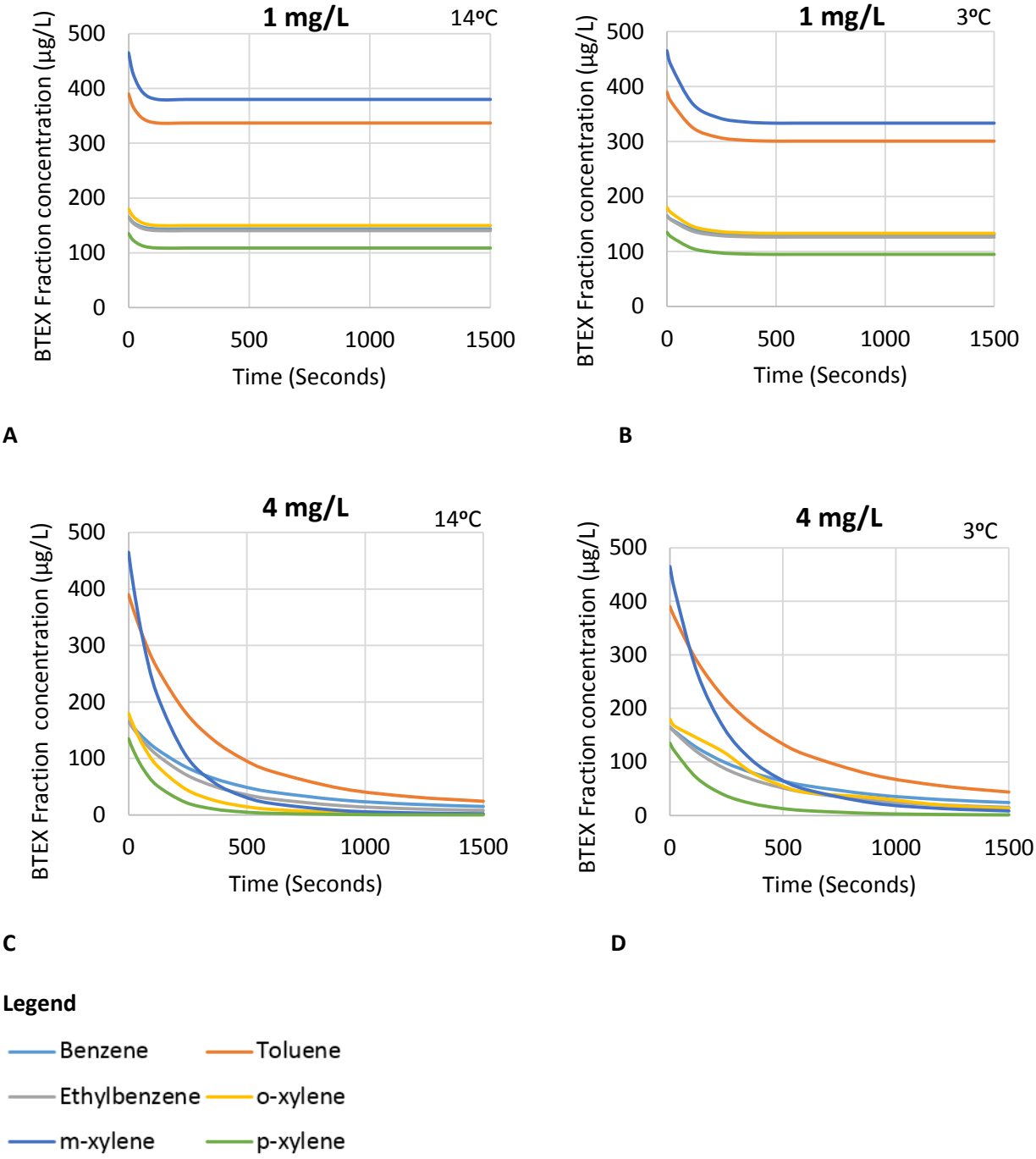


Figure 4.8 BTEX Simulation of individual compounds for Grand River A at applied ozone doses of 1 mg/L and 4 mg/L. A), C) High temperatures (October 17, 2017; 14°C) and B), D) Low temperatures (February 17, 2017; 3°C). Assumed initial overall BTEX concentration was 1500 µg/L, assumed initial individual BTEX compound concentrations are given in Table 4.3.

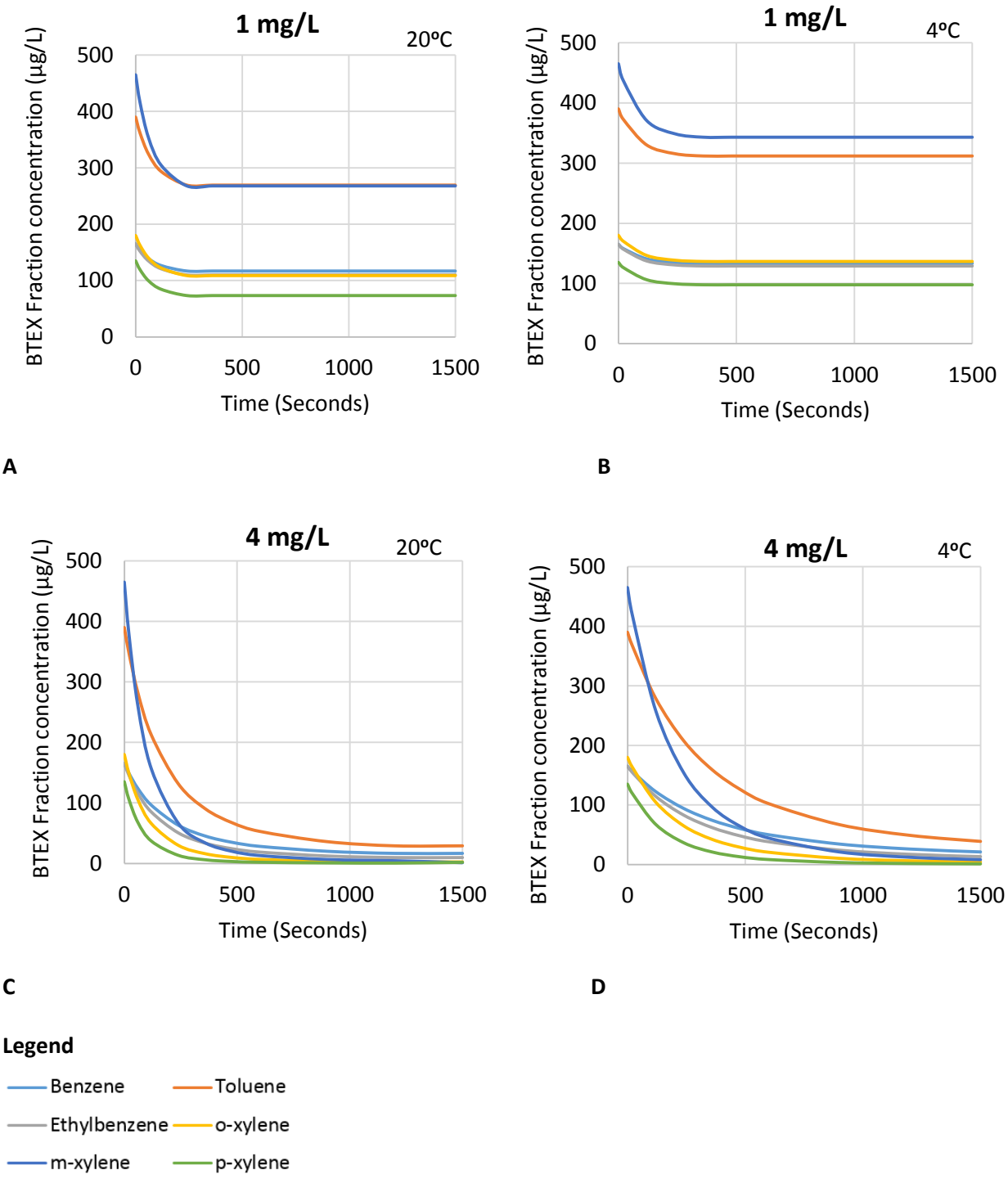


Figure 4.9 BTEX Simulation of individual compounds for Grand River B at applied ozone doses of 1 mg/L and 4 mg/L. A), C) High temperatures (March 13, 2017; 20ºC) and B), D) Low temperatures (January 6, 2017; 4ºC) Assumed initial overall BTEX concentration was 1500 µg/L, assumed initial individual BTEX compound concentrations are given in Table 4.3.

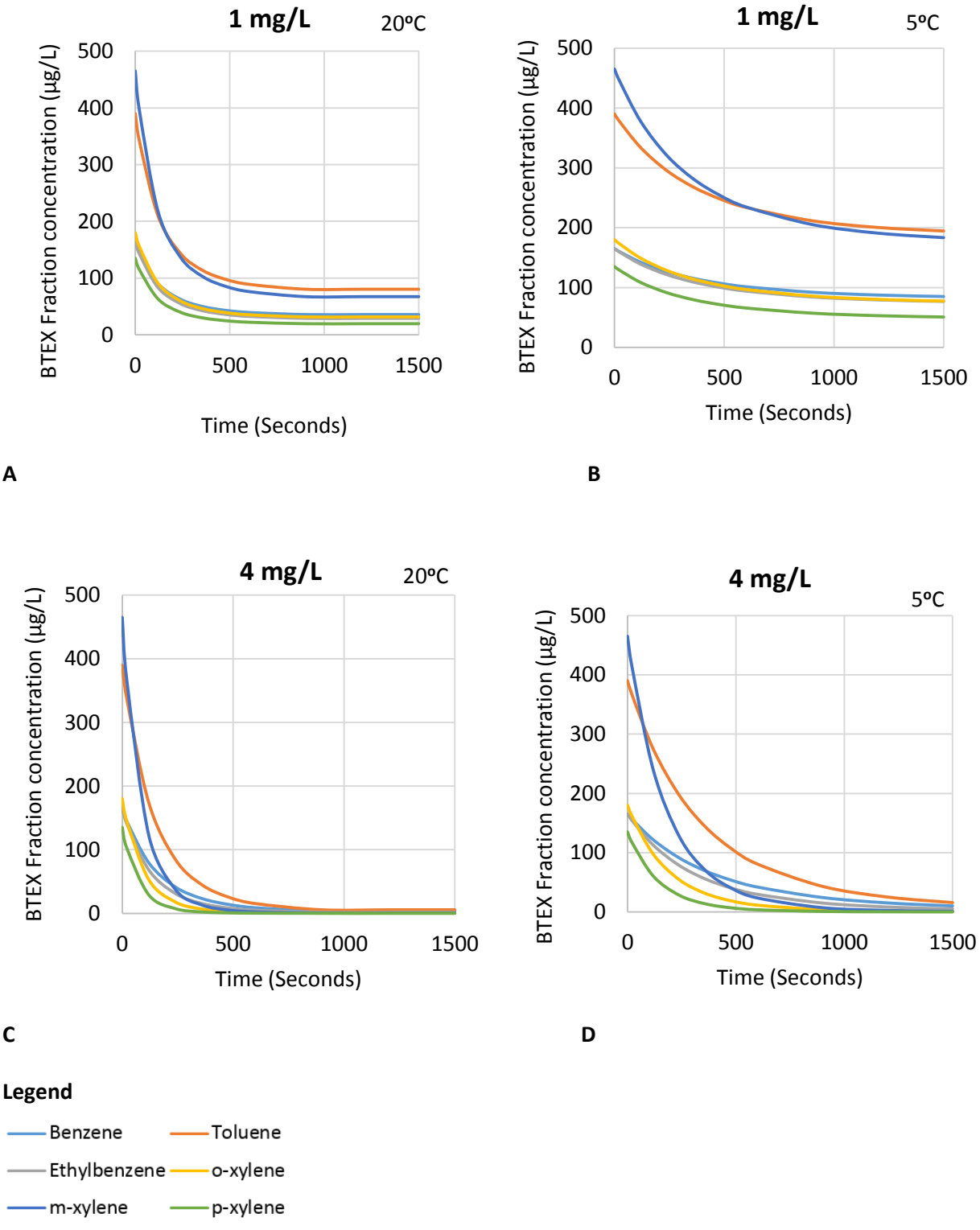


Figure 4.10 BTEX Simulation of individual compounds for Lake Ontario at applied ozone doses of 1 mg/L and 4 mg/L. A), C) High temperatures (September 28, 2016; 20°C) and B), D) Low temperatures (December 5, 2016; 5°C) .Assumed initial overall BTEX concentration was 1500 µg/L, assumed initial individual BTEX compound concentrations are given in Table 4.3.

As mentioned in the previous subsection Lake Ontario has the highest overall BTEX removal followed by Grand River B then Grand River A (Figure 4.7). When looking at the individual BTEX percent removal at both applied ozone doses and at high and low temperatures the trend emerges that the BTEX compounds are degraded according to their reactivity with ozone. For example, benzene has the lowest percent removal and xylenes have the highest percent removal (Figures 4.11-4.13), see Appendix B Table B.2 for more detail. This is due to the differences in rate constants as benzene has the lowest rate constant (2 $M^{-1}S^{-1}$) and will react very slowly with ozone and the xylenes have high rate constants which will allow them to be removed from the water more quickly (90-140 $M^{-1}S^{-1}$). This follows the results of Derco et al., (2017) who ozonated wastewater containing BTX compounds and found that p-xylene had 60% removal while benzene only had 20% removal. These researchers also found that compounds had the highest removal within the first five minutes of ozonation. This trend can also be seen in this study where the degradation curves level out around the ~5 minute mark (Figures 4.8-4.10). For 1 mg/L doses in the Grand River this could be a result of no ozone left after the 5 minutes, which occurs in a lot of the samples. Derco et al., (2017) also found that increased ozonation length increased the percent removal of the compounds. This was seen in this thesis where increasing the applied ozone dose from 1 mg/L to 4 mg/L resulted in increased BTEX degradation.

MACs are shown for each compound in Table 4.3 and the aim for every water treatment plant is to treat containments so that they are below these levels. These MAC levels are outlined in the Federal Guidelines. For example benzene is a carcinogen for humans and has the lowest MAC level of 5 µg/L (Health Canada, 2009).

Therefore, there are some things to consider when comparing the percent removal of the various individual BTEX compounds (Figures 4.11-4.13). For one, they are simulated at different initial

concentrations to represent their percentage in gasoline. Secondly, they all react differently with O_3 due to their rate constants, and have to be removed to specific levels in drinking water (MACs).

Overall, in the simulations it was found that benzene was rarely removed from the water below its MAC even at doses of 4 mg/L. It only reached the criteria of <5 µg/L in one simulation in Lake Ontario water at a temperature of 20°C and an applied ozone dose of 4 mg/L. This simulation provided optimal conditions for benzene to be degraded. It contained the source water which has the highest BTEX percent removal. This could possibly due to its lower DOC: Lake Ontario ~2 mg/L; Grand River ~3.4 mg/L. This simulation also had a high temperature of 20°C (which in Lake Ontario provides more BTEX removal), and was at the highest applied ozone dose.

Benzene's low percent removal from the water could be attributed to its low rate constant with O_3 (2 $M^{-1}S^{-1}$), and its relatively high assumed initial concentration (165 µg/L) in comparison to its relatively low MAC (5 µg/L). In fact benzene has the highest ratio of assumed initial concentration to MAC out of all the compounds which might explain in part why it is hard to remove this contaminant at levels below its MAC.

On the other hand ethylbenzene is more easily degraded at levels below its MAC (<140 µg/L).The only simulation where it did not do this was Grand River A at a temperature of 14°C and a 1 mg/L applied ozone dose. Grand River A has the worst BTEX removal out of all the water sources (possibly due to its high DOC of 3.3-3.5mg/L C), and this simulation was performed at the lowest applied ozone dose which might explain why the ethylbenzene concentration was higher than the MAC. Ethylbenzene has a fair reactivity with O_3 (14 $M^{-1}S^{-1}$), and has the lowest ratio of assumed initial concentration (165 µg/L) to MAC (140 µg/L). This might explain why this compound is easily removed from most water sources below its MAC.

Toluene is degraded below its MAC in all water sources and temperatures in simulations that have a 4 mg/L applied ozone dose, however, toluene is not degraded at levels below its MAC at applied ozone

doses of 1 mg/L in this study. Toluene has the same reactivity with O_3 as ethylbenzene (14 $M^{-1}S^{-1}$), however it has a higher assumed initial concentration (390 µg/L) and a lower MAC (60 µg/L) and therefore is not easy to get below its MAC as ethylbenzene.

Total xylene concentrations were degraded below its MAC level of 90µg/L in all water sources and temperatures for the 4 mg/L applied ozone dose. Although, for all of the water sources and temperatures the 1 mg/L applied ozone dose was not sufficient to remove total xylene concentrations below its MAC.

Overall, BTEX compounds were degraded more effectively at the 4 mg/L applied ozone dose. However, another method for increasing BTEX degradation would be to use O_3/UV processes as shown by the experimental results of Garoma et al., (2008). In this paper authors found that 99% removal was observed with the O_3/UV process in comparison to ozonation which could have removals as low as 27%. Authors used O_3 concentrations ranging from 29-53 mg/L and spiked at much higher concentrations than this study (Benzene levels of 3,191 µg/L).

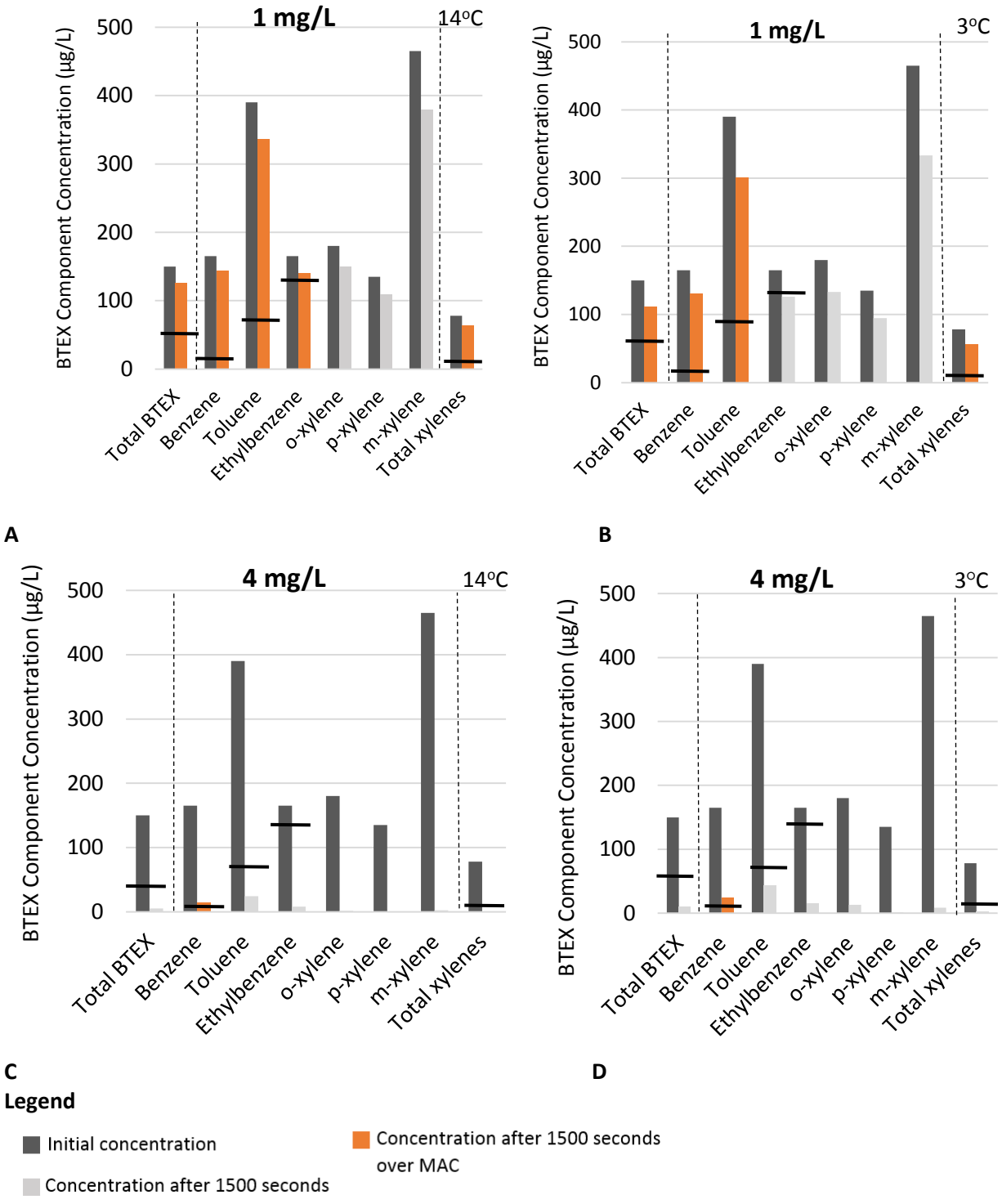


Figure 4.11 Simulated BTEX compound degradation for Grand River A at 1 mg/L and 4 mg/L applied ozone doses after 1500 second reaction time. A), C) High temperatures (October 17, 2017; 14°C; 3.5 mg C/L DOC) and B), D) Low temperatures (February 17, 2017; 3°C; DOC: 3.3 mg C/L). Black lines represent the MAC for each BTEX compound. Black dotted lines separate the total values (BTEX and Xylenes). Actual concentrations of total BTEX and total xylenes are higher by a factor of 10. Bars that are orange exceed the MAC for that compound. O, p , m-xylenes are regulated by a total MAC.

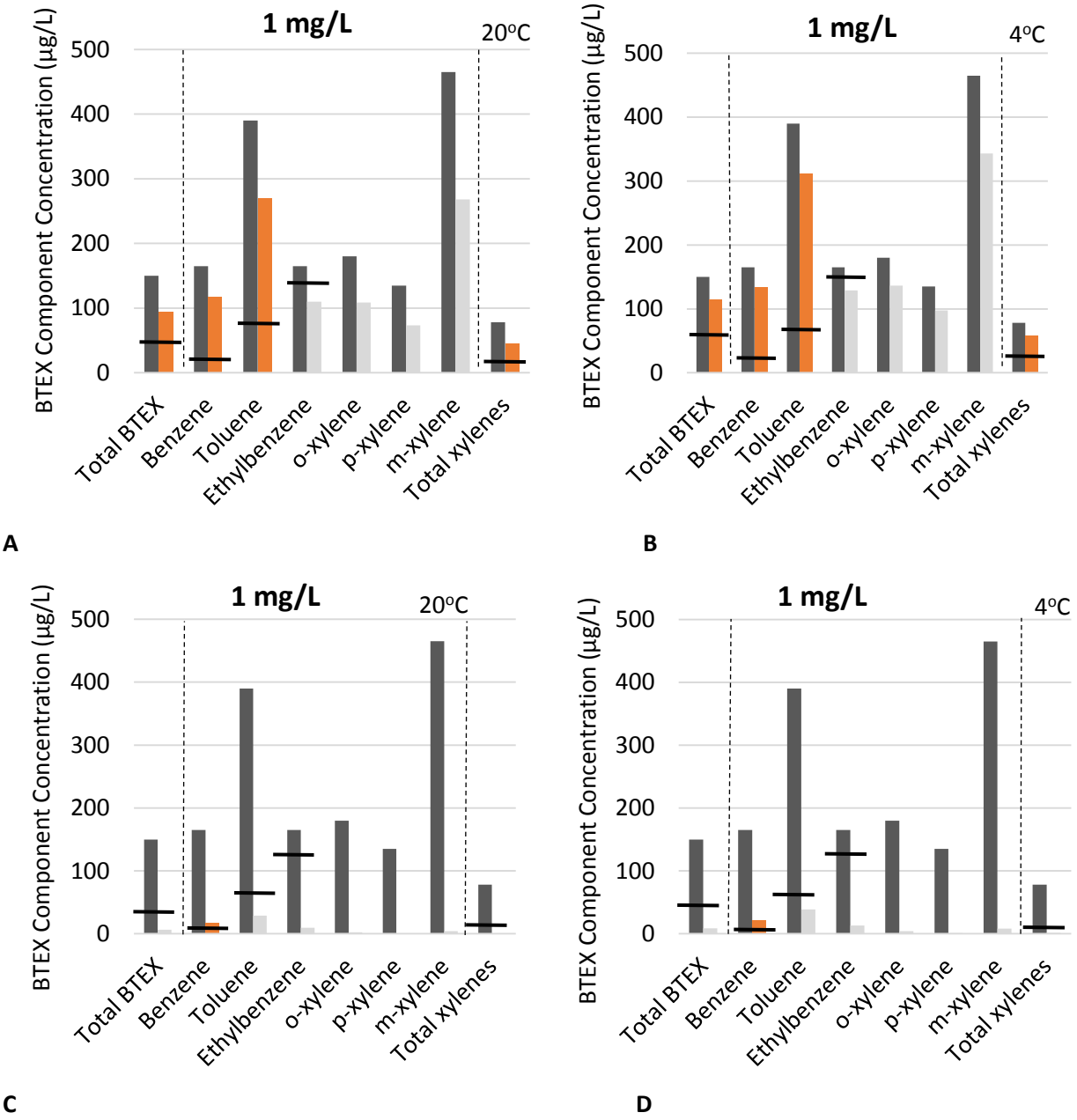


Figure 4.12 Simulated BTEX compound degradation for Grand River B at 1 mg/L and 4 mg/L applied ozone doses after 1500 second reaction. A), C) High temperatures (March 13,2017; 20°C; 3.4 mg C/L DOC C) and B), D) Low temperatures (January 6, 2017; 4°C; 3.5 mg C/L DOC). Black lines represent the MAC for each BTEX compound. Black dotted lines separate the total values (BTEX and Xylenes). Actual concentrations of total BTEX and total xylenes are higher by a factor of 10. Bars that are orange exceed the MAC for that compound. O, p , m-xylenes are regulated by a total MAC.

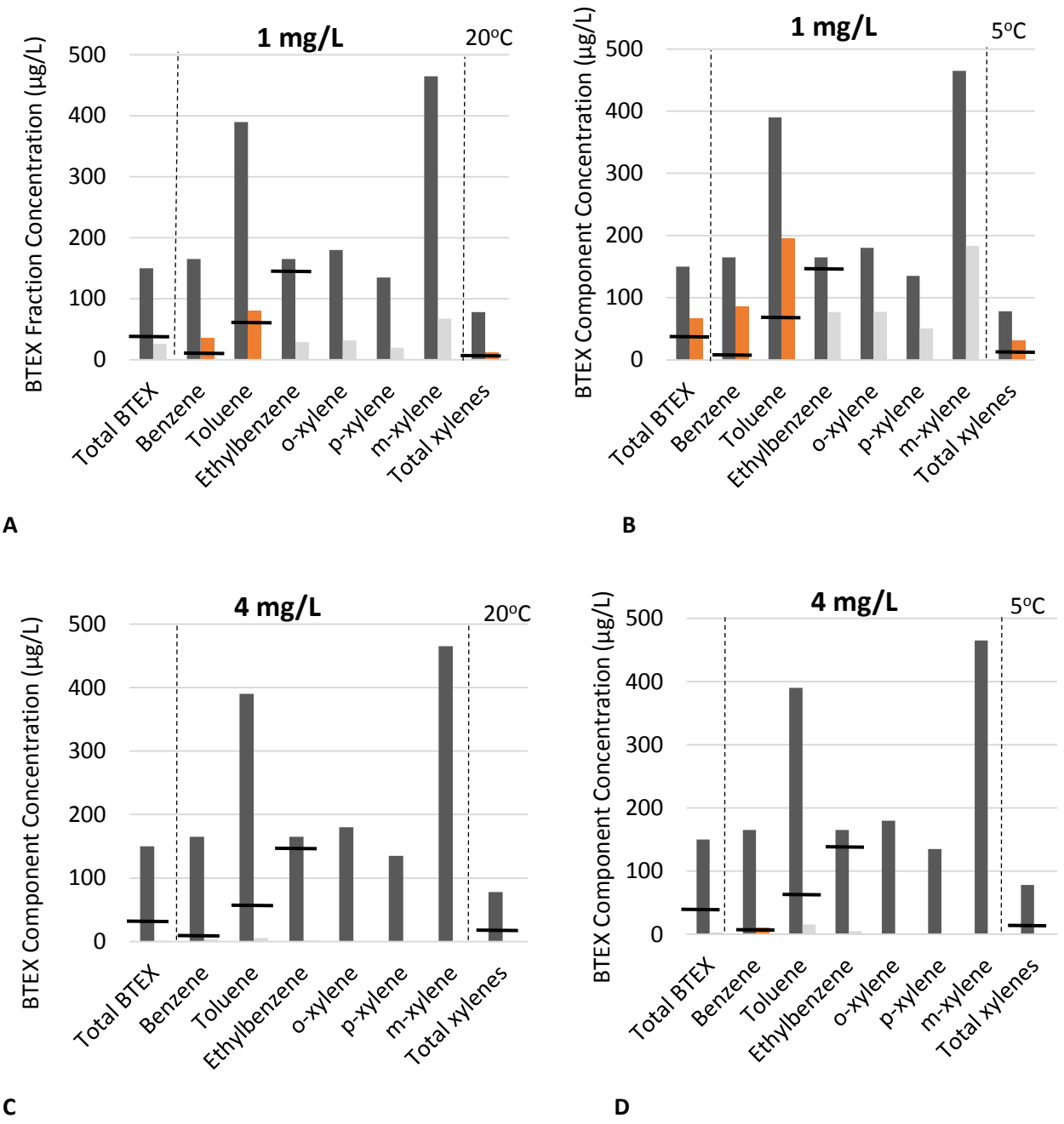


Figure 4.13 Total Simulated BTEX compound degradation for Lake Ontario at 1 mg/L and 4 mg/L applied ozone doses after 1500 second reaction time. A), C) High temperatures (September 28, 2016; 20°C: DOC: 2 mg/L C) and B), D) Low temperature (December 5, 2016; 5°C: DOC: 2 mg/L C). Black lines represent the MAC for each BTEX compound. Black dotted lines separate the total values (BTEX and Xylenes). Actual concentrations of total BTEX and total xylenes are higher by a factor of 10. Bars that are orange exceed the MAC for that compound. O, p , m-xylenes are regulated by a total MAC.

Section 4.4.3 Modelling Atrazine

Atrazine is one of the most frequently used herbicides globally and has a MAC of 5 µg/L in Canada (Health Canada, 2011). When used on land atrazine is one of the most commonly occurring herbicides in surface and well water (Health Canada, 2011) and is often found in a concentration range of ng/L to µg/L (Hua et al., 2006).

Conventional drinking water treatments such as coagulation, and filtration do not effectively remove atrazine (Ternes et al., 2002; Verstraeten et al., 2002). Therefore, ozone could be a potential approach to dealing with atrazine, although its rate constant with ozone is low at 6 $M^{-1}S^{-1}$ (Acero et al., 2000).

Due to the frequent occurrence of atrazine in Ontario waterways and its general persistence in the water simulating the degradation of this compound is of great interest to the three water treatment plants. Therefore, this subsection looks at the simulation of atrazine in spring and summer temperatures, the time frame when atrazine is applied on fields. As can be seen from Figure 4.14 and Figure 4.15 the Lake Ontario plant is the most effective at removing atrazine at both applied ozone doses of 1 mg/L and 4 mg/L. This could be because Lake Ontario has the lowest DOC values of all three plants and subsequently has the lowest ozone to DOC ratio (Table 3.2). Grand River A and B have similar atrazine degradation in the temperature range of 13-14^{o}C which could be due to similarities in water quality between the two as they both come from the Grand River. Lake

It was found that percent removal increased up to 64% as the applied ozone dose was increased from 1 mg/L to 4 mg/L (Figure 4.15). This is consistent with Snyder, et al., (2006) who completed bench-top pilot plant experiments with applied ozone doses of 1.25 mg/L and found that after 24 minutes the percent removal was 26%. When the applied ozone dose was increased to 2.5 mg/L the percent removal increased to 57%.

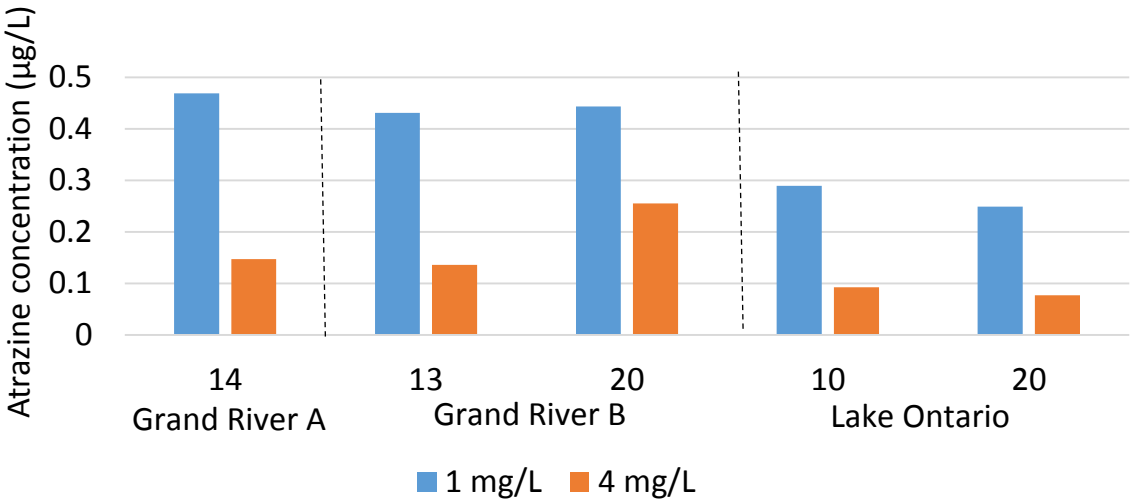


Figure 4.14 Simulated Atrazine concentration at the reaction time of 1500 seconds showing degradation for Grand River A, Grand River B and Lake Ontario. At spring and summer temperatures ranging from 10°C-20°C. Grand River A spring temperature (November 21, 2016; 14°C; DOC: 3.9 mg/L C). Grand River B summer temperature (March 13 2017; 20°C; DOC: 3.4 mg/L C) and spring temperature (November 7, 2016; 13°C ; DOC:4.2 mg/L). Lake Ontario summer temperature (September 28 2016; 20°C; DOC: 2 mg/L C), and spring temperature (March 2 2017; 10°C; DOC: 1.8 mg/L C). Assumed an initial concentration of 0.5 µg/L.

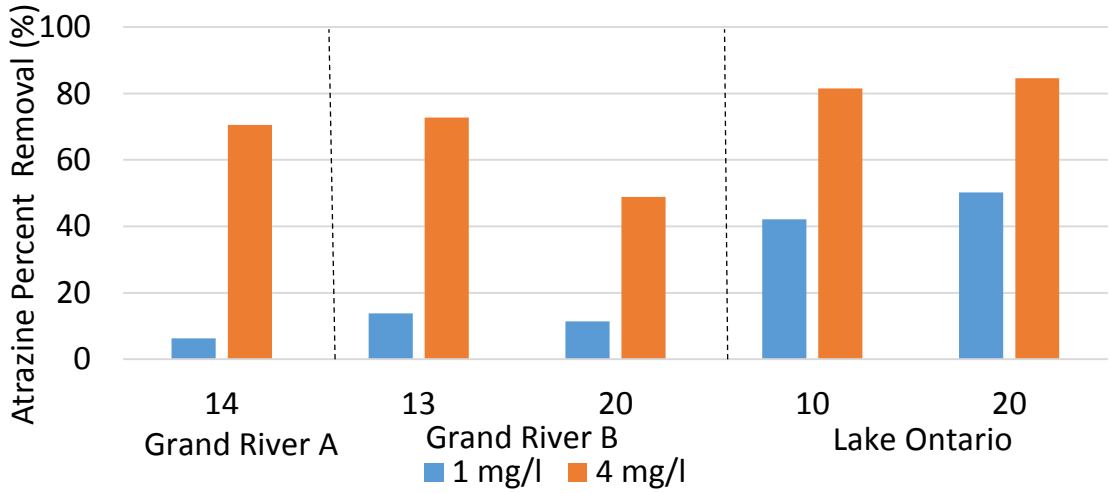


Figure 4.15 Simulated Atrazine percent removal at the reaction time of 1500 seconds showing degradation for Grand River A, Grand River B and Lake Ontario. At spring and summer temperatures ranging from 10°C-20°C. Grand River A spring temperature (November 21, 2016; 14°C; DOC: 3.9 mg/L C). Grand River B summer temperature (March 13 2017; 20°C; DOC: 3.4 mg/L C) and spring temperature (November 7, 2016; 13°C ; DOC:4.2 mg/L). Lake Ontario summer temperature (September 28 2016; 20°C; DOC: 2 mg/L C), and spring temperature (March 2 2017; 10°C; DOC: 1.8 mg/L C). Assumed an initial concentration of 0.5 µg/L.

When looking at temperature Grand River A only has one spring temperature data point as the researchers were not able to sample this plant during the summer. For the Grand River B plant an increase in temperature from 13 to 20^{o}C appears to cause a decrease in atrazine percent removal for the 1 mg/L applied ozone dose (Figure 4.15). While in Lake Ontario an increase in temperature appears to cause an increase in percent removal at both doses.

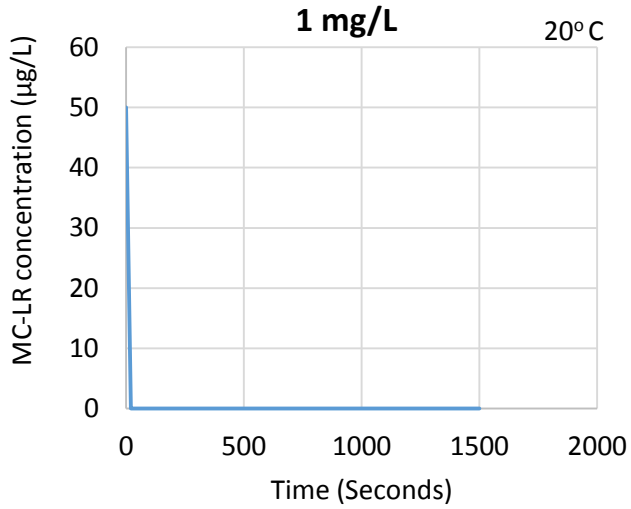
Overall, for the three plants percent removals ranged from 6-50% for the 1 mg/L applied ozone dose and 49-85% range for the 4 mg/L dose. Snyder, et al., (2006) completed bench-scale experiments with drinking water using applied ozone doses of 2.5 mg/L and found that atrazine was resistant to O_3 and had less than 50% removal. In Acero et al., (2000) atrazine percent removals of 60% were observed in bench-top experiments with applied ozone doses of 2 mg/L at 11^{o}C.

In this study, the water source seemed to impact atrazine degradation with Lake Ontario having the highest percent removal which could be due to its lower DOC. There could also be a relationship between temperature and atrazine percent removal overall, in Lake Ontario temperature appears to increase percent removal where the opposite hold for Grand River B. However not enough samples were taken in this study to make any conclusions. Other literature which looks at atrazine removal does not investigate the effect of temperature on degradation (Acero et al., 2000; Snyder et al., 2006; Broséus et al., 2009) and this should be taken into consideration for future studies.

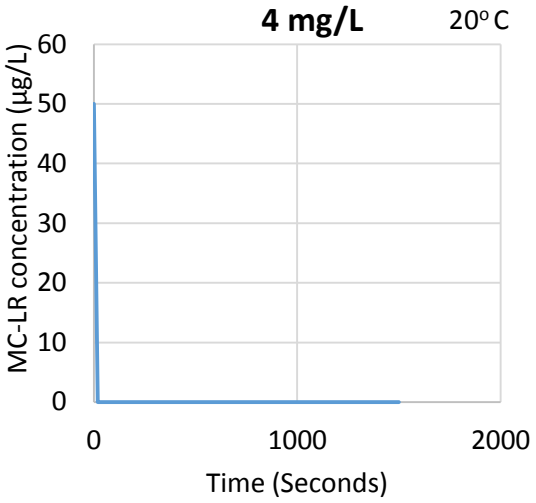
Section 4.4.4 Modelling Cyanotoxins

Cyanotoxins-MC-LR, ANTX, and CYN- are common in North America and are produced by cyanobacteria blooms which can be found in lakes (Fromme et al., 2000). In Canada the MAC for total microcystins in water is 1.5 µg/L, however, there are no MAC values in the Federal Drinking Water Guidelines for ANTX or CYN (Health Canada, 2016*).*

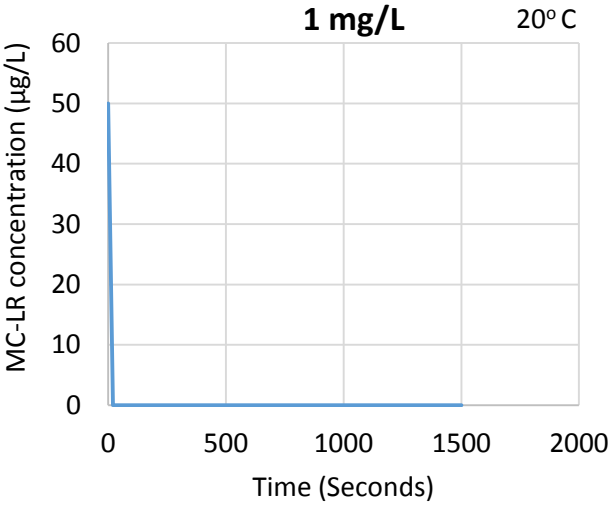
This study simulated the removal of extracellular MC-LR, CYN, and ANTX each at an assumed initial concentration of 50 µg/L as can be seen by Figure 4.16. These simulations were done at higher temperatures, because cyanobacteria blooms occur seasonally during the summer and fall. Therefore, the simulations could only be done on Lake Ontario and Grand River B water as these were both sampled during warmer temperatures while Grand River A was not. Figure 4.16 only shows the degradation of MC-LR but both CYN and ANTX had the same rapid removals. The degradation of these three cyanotoxins was very fast and at twenty seconds the concentration of these three toxins went to zero. This also fits with the experimental validation results in section 4.3 in which MC-LR was completely degraded in the first twenty seconds of the reaction with an initial MC-LR spiking dose of 100 µg/L.



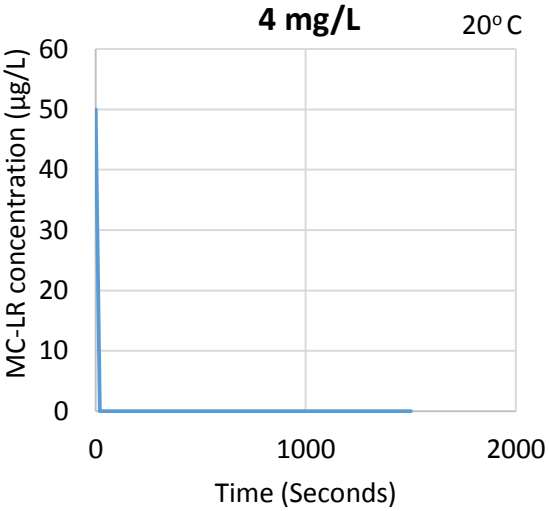
A –Lake Ontario



B-Lake Ontario



C –Grand River B



D- Grand River B

Figure 4.16 Simulated Cyanotoxin Removal in Lake Ontario and Grand River B at 1 mg/L and 4 mg/L applied ozone doses. A), B) Lake Ontario warm temperatures (September 28, 2016; 20 °C) and B), D) Grand River B warm temperatures (March 13, 2017; 20°C). Assumed an initial concentration of 50 µg/L.

Due to their chemical structure, double bonds and amino groups, ozone reacts quite fast with a lot of cyanotoxins (von Gunten, 2003a). At a pH of 8 the rate constants for MC-LR, CYN, and ANTX respectively are $4.1*10^5$, $3.4*10^5$ and $6.4*10^5$ $M^{-1}S^{-1}$ (Rodríguez et al., 2007). The half-life of MC-LR, CYN and ANTX with an applied ozone dose of 1 mg/L, and a pH of 8 are 0.08 sec (MC-LR), 0.10 sec (CYN) and 0.52 seconds (ANTX) (Rodríguez et al., 2007). Shawwa & Smith, (2001) investigated the degradation of free or extracellular MC-LR in appplied ozone doses of 0.1-2 mg/L and through experimentation found that the half-life of MC-LR was also < 1 second. This fits with the simulation results of this study in which zero cyanotoxin concentration at was found at 20 seconds (Figure 4.16).

As has been stated before less than 10% of the cyanotoxins are extracellular (Fromme et al., 2000; Hoeger et al., 2002) and extracellular cyanotoxins react rapidly with ozone and have a very short half-life. Most researchers agree that the focus should be on removing intact cyanobacterial cells (Chorus & Bartram, 1999; Westrick et al., 2010). Hoeger et al., (2002) propose that the focus should be on optimizing ozonation when there are high amounts of cyanobacterial cells. In their study they found that most of the microcystis cells ruptured at ozone concentrations of 1 mg/L which lead to the release of extracellular toxins. The authors mention that high enough ozone concentrations need to be used to degrade the cells and the cyanotoxins. They also found that when cells numbers were > 10^5 cells/mL an applied ozone dose of 1.5 mg/L was not enough to completely degrade the cyanotoxins. Overall, the cyanotoxins discussed in this subsection react very fast with ozone when they are in their extracellular form and are degraded at doses of 1 mg/L. Future studies should incorporate intracellular cyanotoxins concentration and the mechanisms in which they become extracellular and the ozone to DOC ratios of the water sources.

Section 4.4.5 Modelling Cannabinoids

In October 2018 cannabis will become legal in Canada and stores will be opening to sell it to the public (Tasker, 2018). Due to this, there might be more cannabinoids entering our water systems and therefore interest in removing cannabinoids from our waterways has increased (Environmental Science and Engineering, 2018).

Cannabis has rarely been detected in treated drinking water (Boleda et al., 2009) and to the best of the author's knowledge no literature could be found investigating the effects of ozonation on cannabis in drinking water. It is important to understand these interactions because studies have shown that conventional wastewater treatment plants cannot completely eliminate illicit drugs, which can lead to them ending up in drinking water treatment plant's source water(Petrovic et al., 2009; Yadav et al., 2017). THC and its metabolite THC-OH have had removals of under fifty percent in wastewater treatment plants while its other metabolite THC-COOH has eliminations around eighteen percent (Petrovic et al., 2009).

Some research has investigated the effect of conventional drinking water treatment processes specifically chlorine on THC-COOH and THC-OH. These articles have found that THC metabolites are completely removed after chlorination (Boleda et al., 2009; Castiglioni et al., 2011). This could be attributed to the high reactivity of chlorine with the THC metabolities as THC-COOH has a half-life of a few seconds with chlorine (Park et al., 2017). Therefore, due to the lack of information in this area the aim of this subsection was to provide ozone simulations for THC and CBD at drinking water treatment plant conditions.

However, due to the limited amount of research on cannabinoids in drinking water, to the best of the author's knowledge, the rate constants for O_3 with THC and CBD could not be found in the literature. Therefore, the rate constants of these compounds were modelled using QSPR relationship models developed by Jin et al., (2014) as is described further in detail in the methods Section 4.2.4. The rate

constants of O_3 with THC and CBD respectively were $10^{6.9}$ and $10^{9.29}$ $M^{-1}S^{-1}$. For $k_{\bullet OH}$ with THC and CBD were $10^{10.45}$ and $10^{10.61}$ $M^{-1}S^{-1}$ (Jin et al., 2015). Overall, the rate constants for THC and CBD were the only two compounds that were not obtained from literature.

These rate constants were then inputted into the micropollutant degradation model using the Rct values, and O_3 exposure data calculated in this study which gave the THC and CBD simulations as seen in Figure 4.17. The simulations for CBD were the same as THC with degradation values reaching zero at the twenty-second mark. The predicted degradation of CBD and THC lined up with their predicted rate constants which were quite fast. These results are similar to other research that has looked at oxidation experiments with cannabis compounds which found that the oxidant, specifically chlorine, has a high rate constant with the compounds and reacts rapidly with them (Park et al., 2017; Boleda et al., 2009, Castiglioni et al., 2011). Due to the fast reactivity of THC and CBD with ozone, low applied doses of 1 mg/L may be sufficient for their removal.

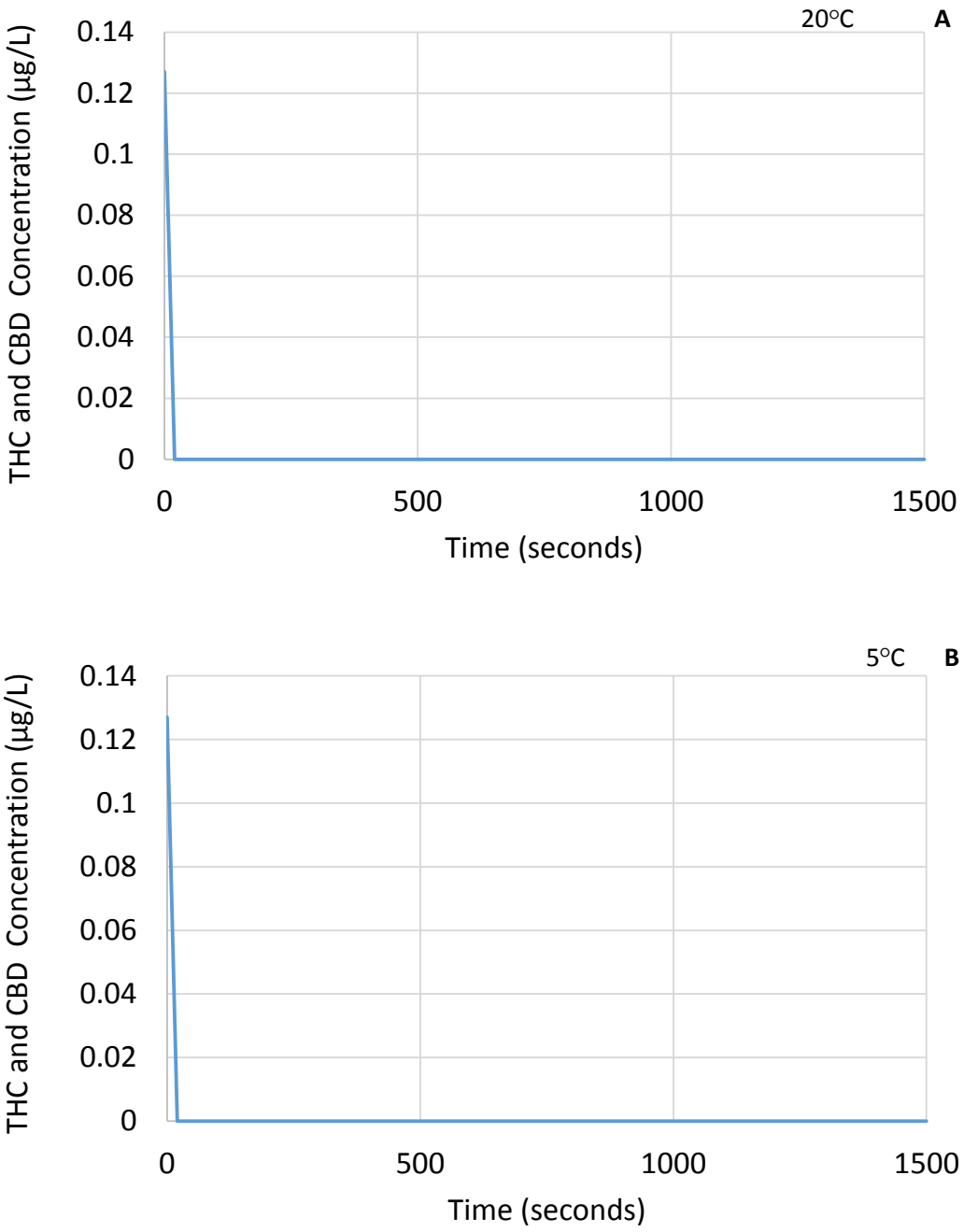


Figure 4.17 THC and CBD Simulated Degradation in Grand River B at a 1 mg/L applied ozone dose. A) High temperature (March 13, 2017; 20 °C) and B) Low temperature (January 6, 2017; 4°C). Initial assumed dose of THC was 0.125 µg/L.

Conclusion

In this chapter the micropollutant degradation model was validated through bench scale experiments with atrazine. Experimentally determined Rct values and O_3 exposures from Chapter 3 along with rate constants were inputted into this model to simulate the degradation of BTEX, atrazine, cyanotoxins and cannabis compounds. Furthermore, temperature and pH modifications were made to simulate micropollutant degradation at seasonal treatment plant conditions.

The key findings are the following:

Validation

- The micropollutant model was successfully validated using the relatively slow reacting atrazine.
- Comparison of experimental atrazine results appeared to be quite close to simulated results but there was a better fit for the 1 mg/L dose in comparison to the 4 mg/L dose.
- Deviations between experimental and simulated results were higher for the 4 mg/L applied ozone dose in comparison to the 1 mg/L dose. These deviations occurred at earlier time points and may be due to the inability to measure ozone decay from 0-19 seconds.
- The temperature modified model for the 1 mg/L and 4 mg/L applied ozone dose did not deviate from the room temperature model except for one case at the 4 mg/L ozone dose for Grand River A.
- Rct.O was used in this thesis using data from 20 s onwards for Rct calculation while Rct.V was based on the work of Elovitz and von Gunten, (1999) using data from 120 seconds onwards. Rct.O was found to result in a better fit with experimental data then Rct.V.

Simulations

- Lake Ontario had the highest BTEX simulated removal with results ranging from 55-82% for the 1 mg/L dose and 98-99% for the 4 mg/L dose. This was then followed by Grand River B and Grand River A. For Grand River B and Lake Ontario higher temperatures resulted in more BTEX percent removal but this was not seen in Grand River A.
- The simulations showed that BTEX compounds were degraded according to their rate constants with ozone. Benzene had the lowest percent removal and xylenes had the highest percent removal.
- The overall composition of BTEX changed at the 4 mg/L applied ozone dose and toluene and m-xylene no longer made up over half the amount of BTEX with benzene making up a larger fraction. The BTEX composition at the 1 mg/L applied ozone dose stayed the same in all 3 treatment plant simulations.
- Benzene was rarely removed from any of the waters studied below its MAC regardless of the conditions (temperature, DOC, applied ozone dose) due to its low MAC, high assumed initial concentrations, and low rate constant with ozone. Except for one condition ethylbenzene was removed under all of the investigated conditions below its MAC, due to its high MAC, low assumed initial concentration and fair reactivity with ozone.
- Lake Ontario had the highest simulated atrazine removal while Grand River A and B have similar atrazine degradation in the temperature range of 13-14^{o}C. Overall, for the three plants percent removals ranged from 6-50% for the 1 mg/L applied ozone dose and from 49-85% for the 4 mg/L applied ozone dose.
- QSPR models were used to predict the rate constants of ozone with THC ($10^{6.9}$ $M^{-1}S^{-1}$) and CBD ($10^{9.29}$ $M^{-1}S^{-1}$). They were also used to predict the rate constants of ●OH with THC ($10^{10.45}$ $M^{-1}S^{-1}$) and CBD ($10^{10.61}$ $M^{-1}S^{-1}$).

- Cannabis active compounds simulation showed rapid degradation of THC and CBD with concentrations approaching zero at the 20 second mark.
- The MC-LR simulation results lined up with experimental results obtained with MC-LR with rapid micropollutant degradation which was not detected at the first sampling point of 20 s.
- ANTX and CYN had rapid removals and at twenty seconds the concentration of these toxins went to zero.
- Future cyanotoxins simulation studies should consider intracellular cyanotoxins concentration and the mechanisms in which they become extracellular.

Simulations under seasonal drinking plant conditions showed that Lake Ontario had the highest removals for atrazine and BTEX which is likely because of its water quality and high ozone to DOC ratio. On the other hand, simulations for cannabis and cyanotoxin compounds showed fast removal regardless of the treatment plant or seasonal conditions.

Chapter 5 Conclusions and Recommendations

5.1 Summary and Conclusions

The overarching goal of this thesis was to predict the effectiveness of ozonation treatment for a variety of micropollutants throughout the year in Grand River and Lake Ontario water. This was done by modelling micropollutant degradation in a specific drinking water treatment plant in collaboration with three plants in Ontario. The three plants were sampled throughout the seasons to capture seasonal changes in various water quality parameters. Samples were brought back to the laboratory and bench-scale ozonation experiments were completed.

Applied ozone doses of 1 mg/L and 4 mg/L were used in this study which are representative of high and low doses used by the participating drinking water treatment plants. ●OH and O_3 concentrations were measured in order to determine the Rct value (Chapter 3). A variety of water quality parameters were measured- pH, temperature, alkalinity, DOC- which were later correlated to the Rct value. Furthermore, DOC fractions were further analyzed to investigate the effect of ozonation on them, as well as how these fractions differed between treatment plants (Chapter 3).

Rate constants with ●OH and O_3 were taken from the literature and modified for temperature and pH as required. CBD and THC rate constants were not available in the literature and were modelled using the QSPR model developed by Jin, (2012) (Chapter 4). Validation experiments were performed with atrazine in which LC-MS methods had to be developed (Chapter 4). The micropollutant degradation model was used to simulate the degradation of BTEX compounds, atrazine, ANTX, CYN, MC-LR, THC, and CBD under conditions encountered at the participating plants.

The findings and conclusions drawn from this work are outlined below:

5.1.1 Characterization of Water Quality and Rct Values

- Ozone dose was found to have the strongest correlation with the Rct value shown through Pearson correlation analysis, while temperature and pH had moderate correlations. A step-wise linear regression showed that ozone dose and temperature were important factors to predict the Rct value and gave an R^2 value of 0.70.
- ●OH and O_3 decay curves varied between the three treatment plants and Lake Ontario had the lowest amount of ozone consumed which was attributed to its lower DOC concentration. Thus, Lake Ontario had the highest ozone to DOC ratio out of all three plants.
- Rct values from the 4 mg/L ozone dose was similar between the three treatment plants while Rct values from the 1 mg/L ozone dose varied.
- LC-OCD analysis showed that Grand River A and B had similar NOM composition and that ozonation caused a decrease in all DOC fractions expect for LMW acids which increased.
- Methanol acted as a promoter and even small amounts of it affected ozone degradation. Therefore, it should not be used as a solvent for any of the oxidation experiments.

5.1.3 Implementation and Validation of the Micropollutant Model

Validation

- Initially, both atrazine and MC-LR were chosen to validate the model for both slow and fast reacting compounds. However, MC-LR reacted rapidly with ozone and was not detected at the first sampling point of 20 s. Due to this, MC-LR could not be used to validate the model.
- Atrazine was used to validate the micropollutant degradation model and a comparison between experimental and modelled results showed a better fit for the 1 mg/L applied ozone dose than for the 4 mg/L applied ozone dose. At both of the applied ozone doses the temperature modified model did not deviate from the room temperature model expect for one case for Grand River A at the 4 mg/L ozone dose.
- Early deviations between the simulated and experimental results were hypothesized to be a result of the inability to measure ozone concentration in the first phase of 0-19 seconds. In some samples as much as 50% of ozone was consumed in this first phase.
- Rct.O which was calculated from 20 s onwards and was employed in this thesis, was found to have a better fit with the experimental data than Rct.V, which was calculated from 120 s onwards. This showed that the duration of the first phase had an impact on the Rct value.

Simulations

- Lake Ontario had the highest simulated BTEX removal for both applied ozone doses followed by Grand River B and Grand River A.
- Individual BTEX compounds were degraded according to their ozone rate constants with the xylenes having the highest percent removal and benzene having the lowest. Due to its low MAC, low ozone rate constant, and high assumed initial concentration benzene was rarely removed from the water source below its MAC. Ethylbenzene having a high MAC, a fair reactivity with

ozone, and a low assumed initial concentration was removed in all the water sources below its MAC except for one condition.

- Atrazine simulations showed that Lake Ontario had the highest removal while Grand River A and B had similar removals.
- Simulations showed that the cyanotoxins MC-LR, ANTX and CYN and cannabinoids THC and CBD reacted rapidly with ozone and their concentrations approached zero within 20 s. The MC-LR simulation is consistent with the experimental MC-LR results.
- Lake Ontario had the highest removals for atrazine and BTEX which was likely due to its high ozone to DOC ratio and water quality. Simulations for cannabis and cyanotoxin compounds showed rapid removal regardless of the seasonal conditions or treatment plant.

5.1.3 Relevance to the Drinking Water Industry

This thesis demonstrated that modelling can be used as a tool to predict the effectiveness of the ozonation treatment process in drinking water treatment plants. Using bench-scale experiments, pre-treated drinking water samples from three treatment plants from Grand River and Lake Ontario were ozonated simulating treatment plant conditions. These experiments provided inputs to the model, most importantly the Rct value, and temperature and pH modifications were made to extend the model's applicability to many seasonal scenarios. Furthermore, a QSPR model was used to predict rate constants for CBD and THC, which could also be used in the future to predict degradation of micropollutants that do not have measured rate constants available.

Simulations showed that certain compounds (cyanotoxins ANTX, CYN and MC-LR, and cannabinoids THC and CBD) were effectively removed by low applied ozone doses, while other micropollutants (atrazine and BTEX) required higher ozone doses in order to increase their percent removal. Water quality factors such

as temperature and NOM were found to affect micropollutant degradation with certain conditions being optimal for contaminant removal.

5.2 Recommendations for Future Research

Over the course of this thesis several areas were highlighted for further investigation and future research should consider the following:

- The three treatment plants were sampled at least three times in different seasons. However, the researcher was unable to sample during the summer for some of the treatment plants. Future experiments, should aim to get more sampling points during this time in order to have a wider spread in temperature data.
- High and low applied ozone dosages of 1 mg/L and 4 mg/L were used in this study. Medium applied ozone dosages of 2-3 mg/L should be considered in the future so that treatment plants can have simulations for these exposures.
- The first phase of ozonation was defined to be under 19 seconds, with the secondary phase occurring after 20 seconds. Due to methodology, limitations ozonation could not be measured in this first phase. In order to incorporate this rapid degradation experiments should use quench-flow techniques**.**
- Experiments were set up to model micropollutants for seasonal conditions and were not designed to make conclusions about which water quality parameters significantly affected the Rct value. This would be a good objective to explore for future research in addition to attempting to accurately model the seasonal Rct value for different water sources with a larger dataset.
- The micropollutant degradation model was validated for one compound atrazine at 1 mg/L and 4 mg/l applied ozone doses. MC-LR could not be used to validate the model due to its fast reactivity

with ozone. Researchers in the future should perform validation with two or more compounds that have various reactivities with ozone.

- The QSPR model was used to predict rate constants for both CBD and THC. To the best of the author's knowledge these models do not seem to be heavily used in literature. Future research should use these models to predict rate constants for micropollutants that have not been experimentally determined.
- Due to time limitations BTEX and other compounds were usually simulated at only one initial assumed concentration. Therefore, in the future it would be beneficial to perform simulations at various initial assumed concentrations to investigate this as a factor.
- Cyanotoxin toxin simulations focused on extracellular concentration and future studies should consider intracellular cyanotoxins concentrations and the mechanisms through which they become extracellular.

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Appendix A
Supporting Information for Chapter 3

Appendix A.1. Sampling Information

Table A.1 Seasonal Sampling Dates, and sampling and lab temperatures for Grand River A, B and Lake Ontario. Two sampling dates in asterisks were not used for pCBA and O_3 experiments only LC-OCD data was taken for these sampling points

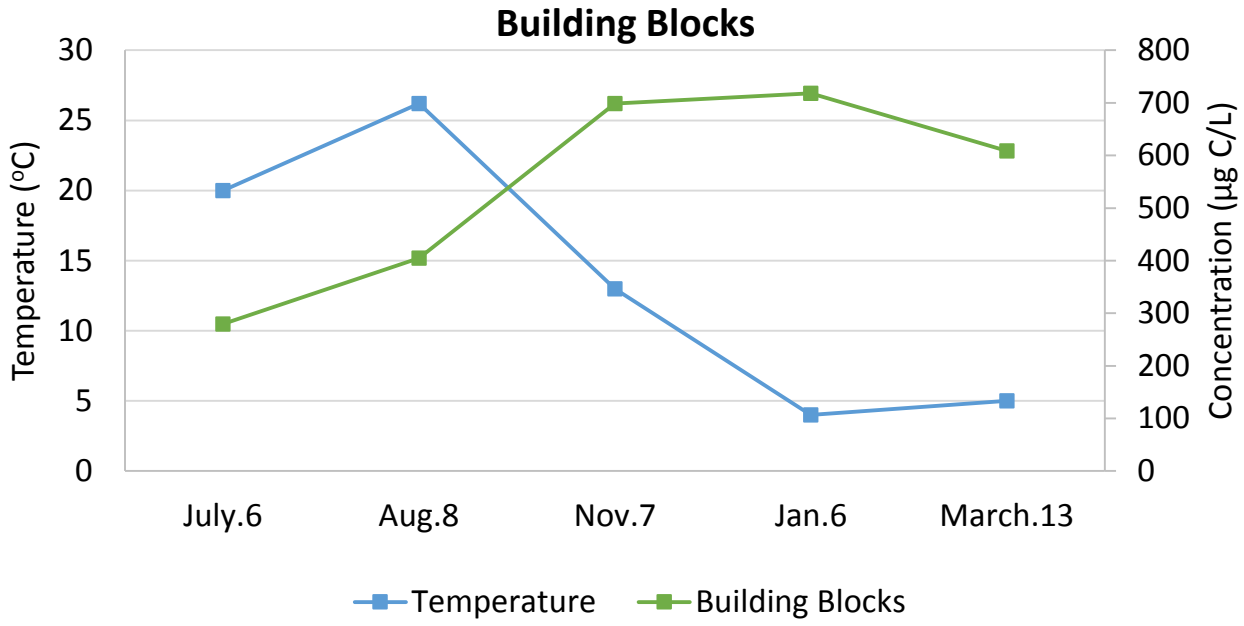
Plant	Sampling Date	Sampling Temperature (^oC)	Lab Temperature (^oC)
Grand River A	November 21, 2016	7	7
	February 17, 2017	3	3
	October 17, 2017	14	14
Grand River B	July 6 2016 *	23	20
	August 8, 2016*	26	20
	November ,7 2016	13	13
	January 6, 2017	4	4
	March 13, 2017	5	20
Lake Ontario	September 28, 2016	20	20
	December 5, 2016	5	5
	March 2, 2017	3	10

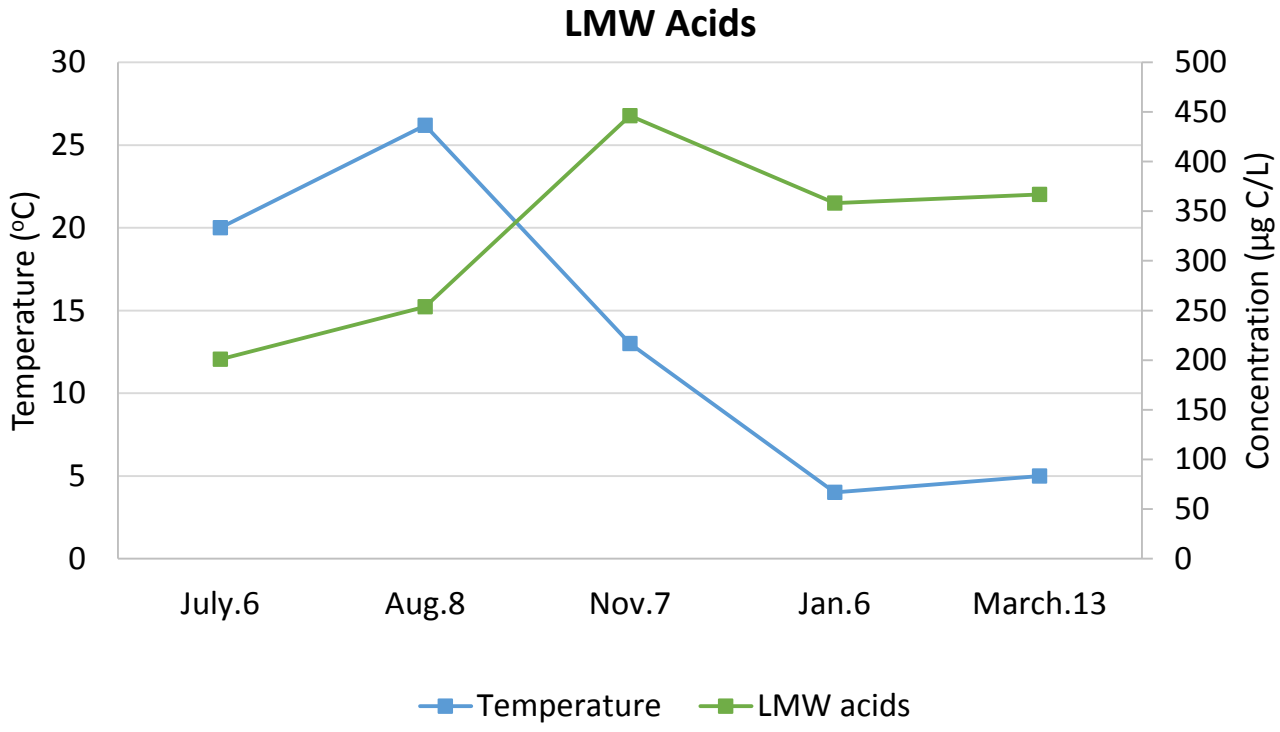
Appendix A.2. LC-MS Method

Table A.2 Examples of pCBA mid-level calibration control standards which were consistent throughout the run

Micropollutant	Treatment Plant	Sampling Date	Reported Concentration (µg/L)
pCBA	Lake Ontario	March.2 2017	49
			49
			50
pCBA	Grand River A	November 21 2017	50
			50
			52
pCBA	Grand River B	January 6 2017	48
			49
			51

Appendix A.3 LC-OCD Fraction Diagrams





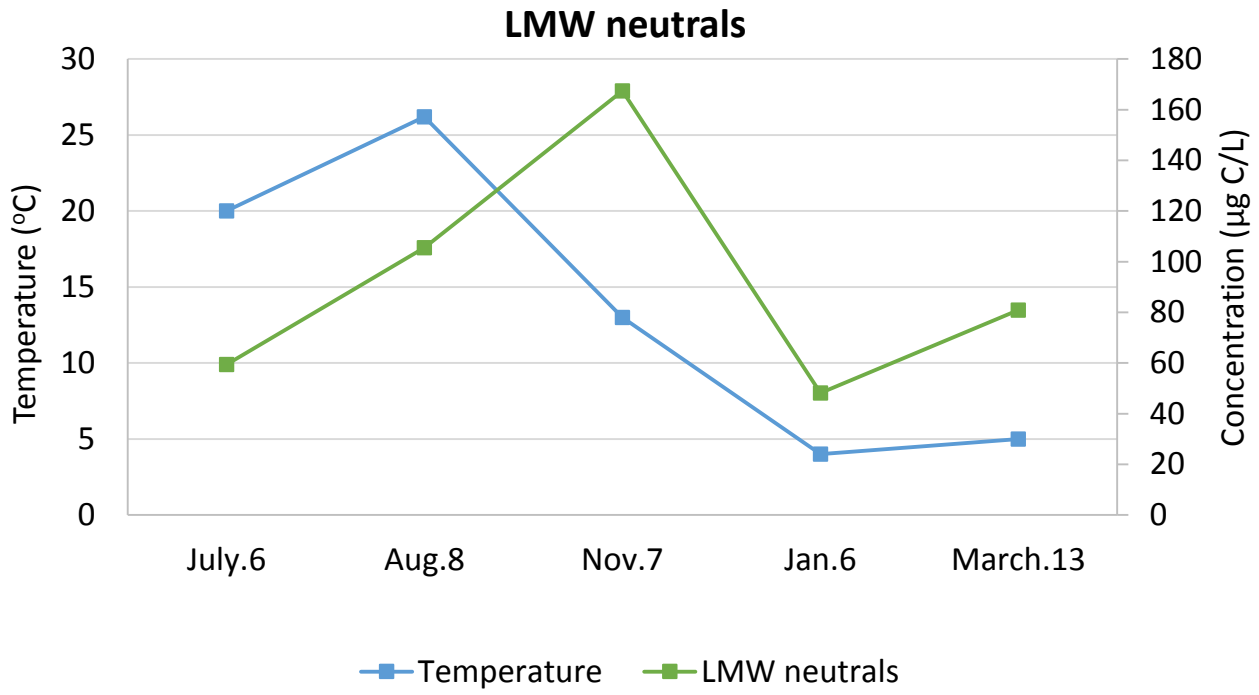
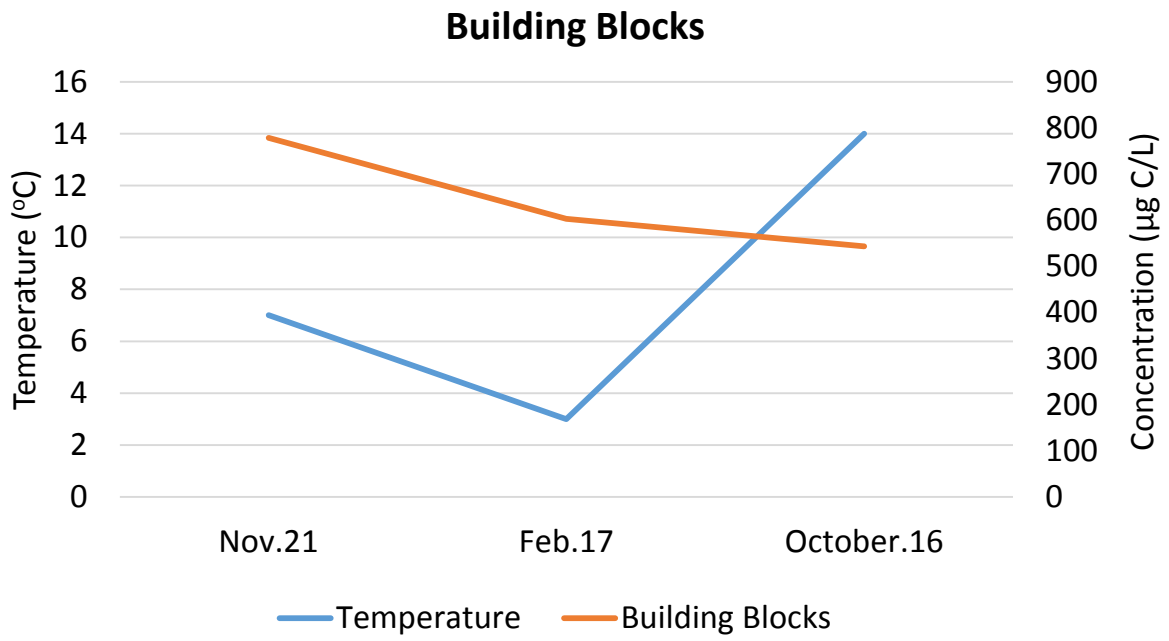
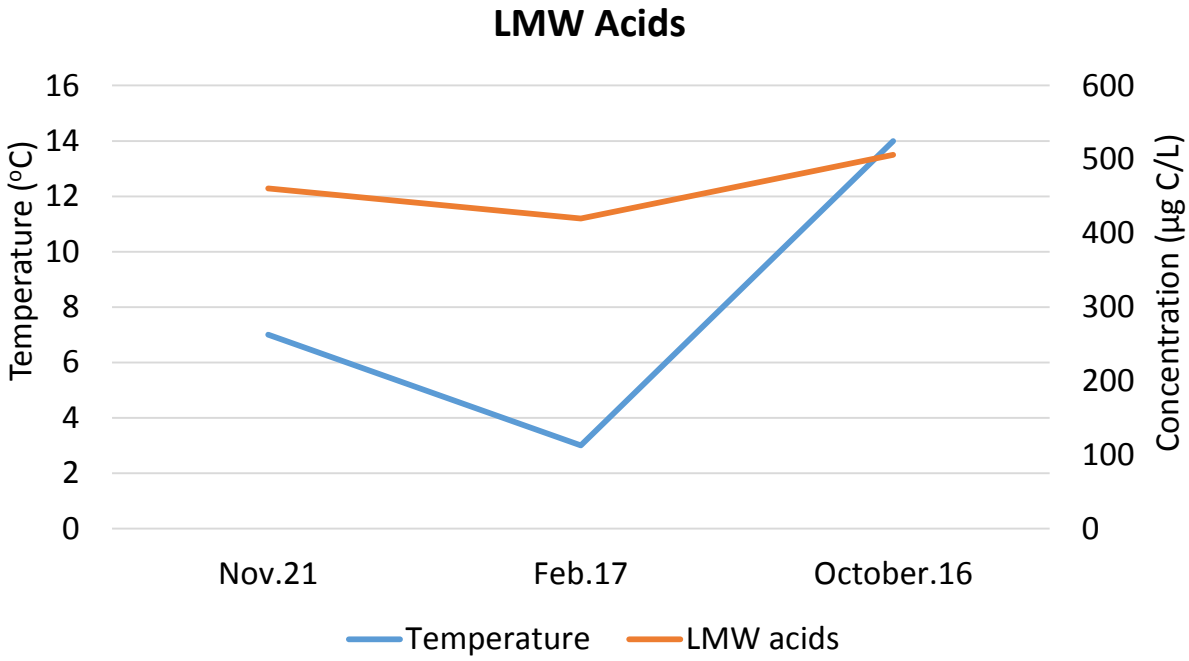


Figure A.1 Building blocks, LMW neutrals, and LMW acids versus temperature trends over time for Grand River B


Building Blocks
16
14
12
10
8
6
4
2
0
Temperature (°C)
900
800
700
600
500
400
300
200
100
0
Concentration (µg C/L)
Nov.21
Feb.17
October.16
Temperature
Building Blocks


LMW Acids
16
14
12
10
8
6
4
2
0
Temperature (°C)
600
500
400
300
200
100
0
Concentration (µg C/L)
Nov.21
Feb.17
October.16
Temperature
LMW acids

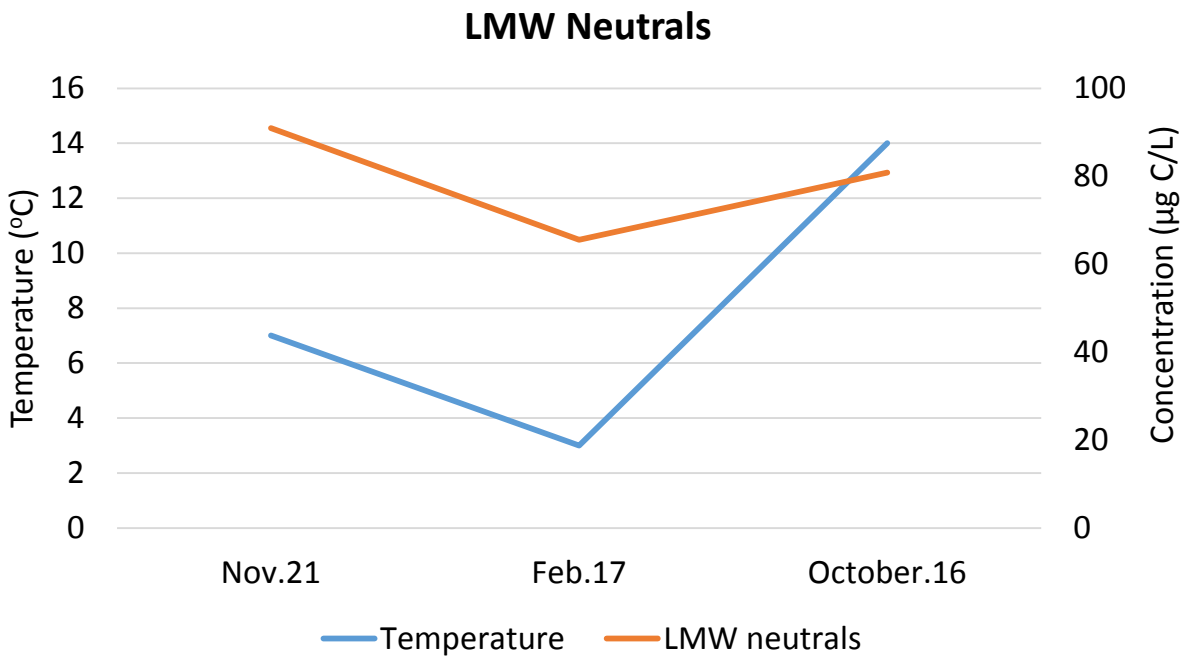


Figure A.2 Building blocks, LMW neutrals, and LMW acids versus temperature trends over time for Grand River A

Appendix A.4 Huber Diagrams

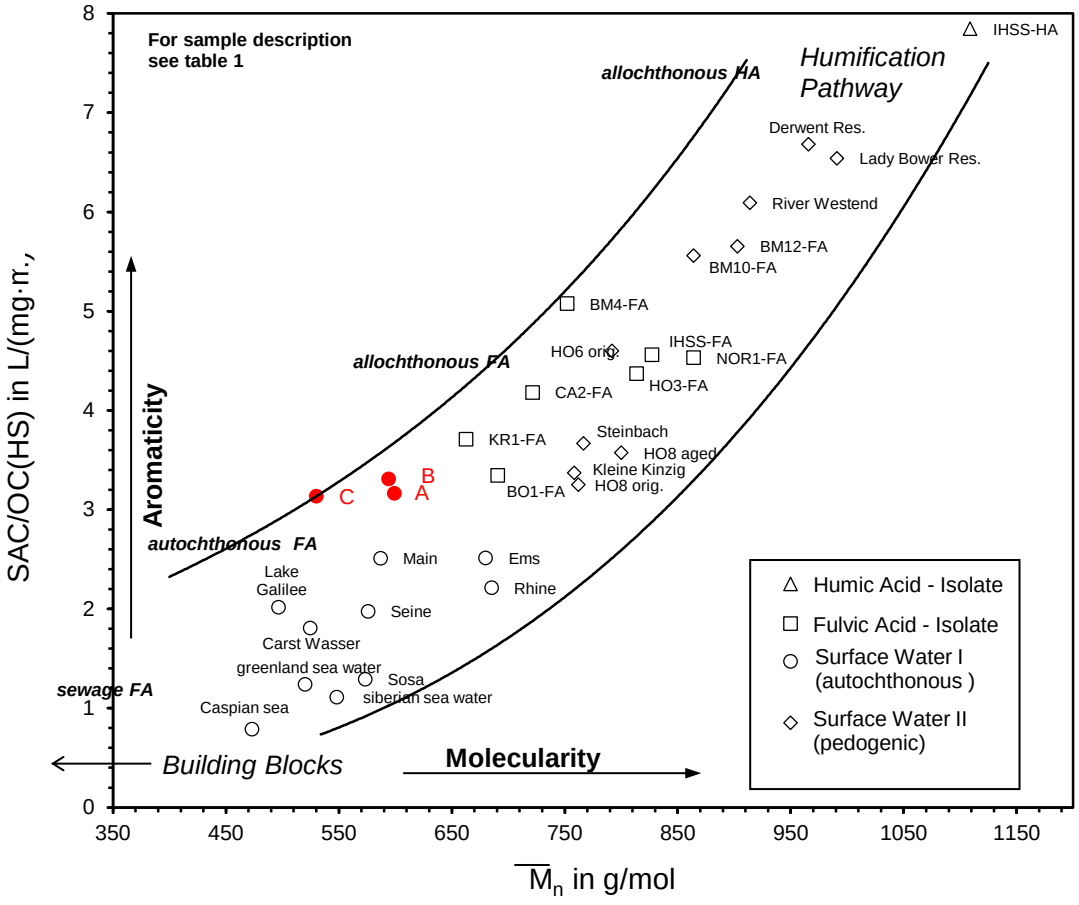


Figure A.2 Humic Substances Diagram for Grand River A. A) November 2016 ,B) February 2017 and C) October 2017.

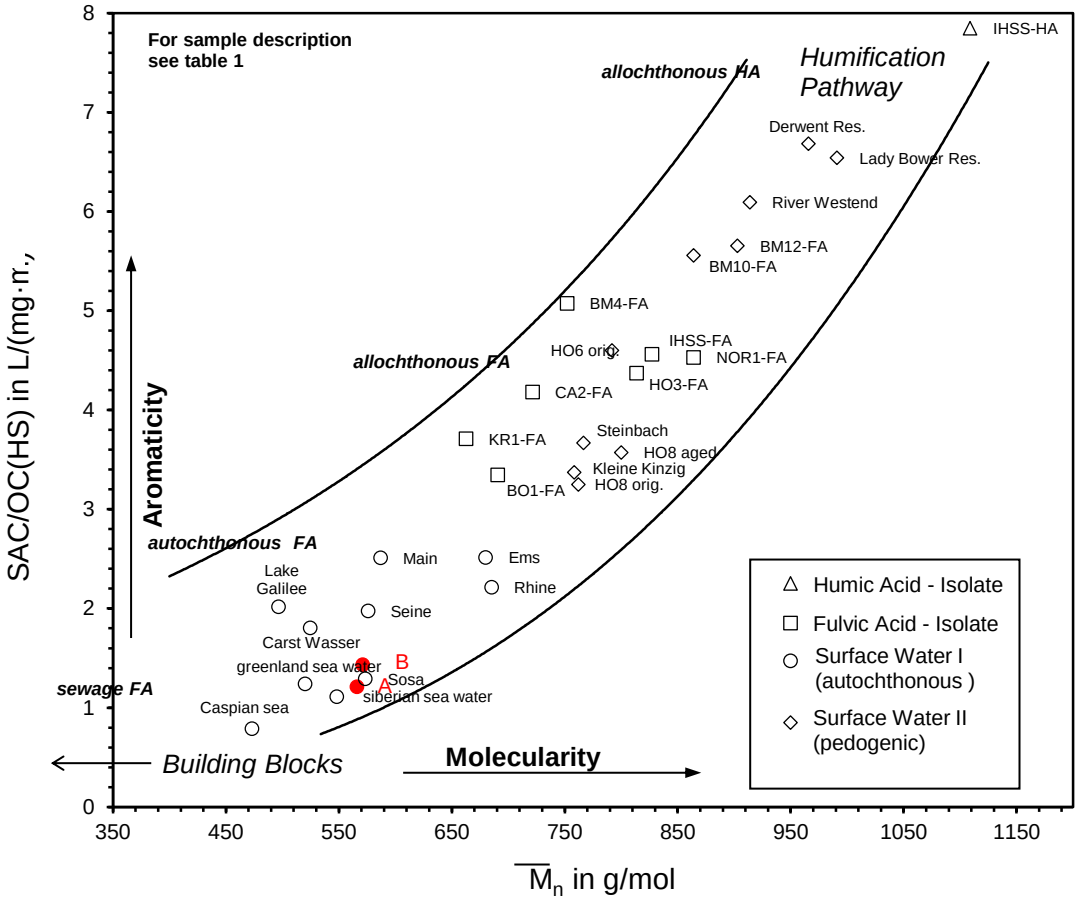


Figure A.3 Humic Substances Diagram for Lake Ontario. A) December 2016 ,B) March 2017

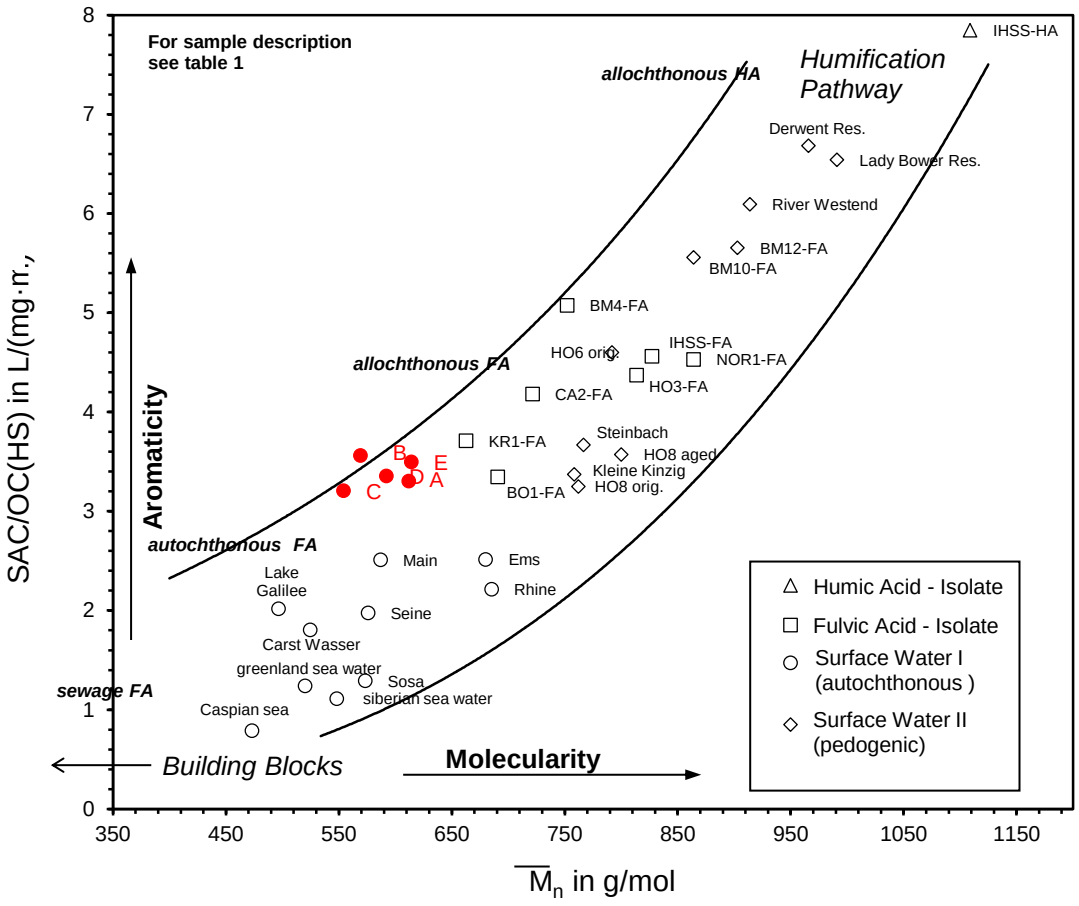


Figure A.4 Humic Substances Diagram for Grand River B. A) July 2016 , B) August 2016, C) November 2016 , D) January 2017,E) March 2017

Appendix B
Supporting Information for Chapter 4

Appendix B.1 Comparison of Rct.O and Rct.V plots

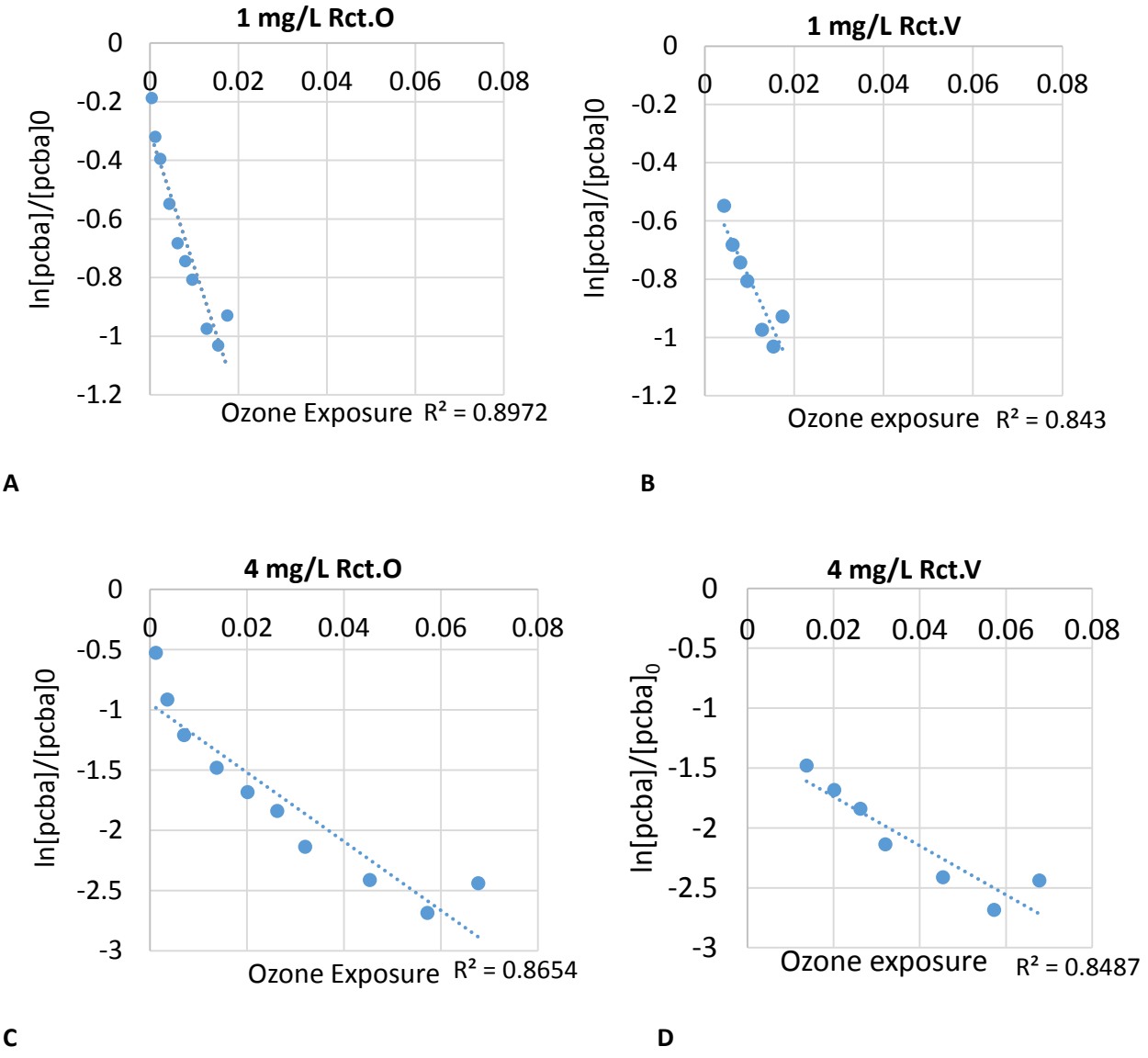


Figure B.1 Rct Plots ozone exposure versus ln[pcba]/[pcba]0 at 1 mg/L and 4 mg/L applied ozone doses for Lake Ontario. A), C) Rct.O and B), D) Rct.V. Experimental temperature was 10°C on March 13, 2017. Rct was calculated from the slopes of these plots.

Appendix B.2 BTEX Fraction Removal

Table B.2: Simulated BTEX fraction concentrations at the 1500 second mark at 1 mg/L and 4 mg/L applied ozone doses at warm and cool water temperatures

	Assumed Initial concentration (µg/L)	**O_3 1mg/L T1-µg/L**	**O_3 4 mg/L T1- µg/L**	**O_3 1 mg/L T2-µg/L**	**O_3 4 mg/L T2- µg/L**	**MAC (µg/L)**
Lake Ontario September 28, 2016; T1-20°C, December 5, 2016; T2-5°C						
BTEX after 1500 seconds	1500	263	11	668	33	295
Benzene	165	36	4	85	10	5
Toluene	390	80	6	195	16	60
Ethylbenzene	165	29	2	77	5	140
o-xylene	180	32	0	77	1	90 Total
p-xylene	135	20	0	51	0	90 Total
m-xylene	465	67	0	183	1	90 Total
Grand River A October 17, 2017; T1-14°C, February 17, 2017; T2-3°C						
BTEX after 1500 seconds	1500	1260	51	1119	106	295
Benzene	165	144	15	131	24	5
Toluene	390	337	24	301	44	60
Ethylbenzene	165	141	8	126	15	140
o-xylene	180	150	1	133	13	90 Total
p-xylene	135	109	0	95	1	90 Total
m-xylene	465	380	2	333	8	90 Total
Grand River B March 13, 2017; T1-20°C, January 6, 2017, T2-4°C						
BTEX after 1500 seconds	1500	946	63	1152	87	295
Benzene	165	117	17	133	21	5
Toluene	390	269	29	312	39	60
Ethylbenzene	165	110	10	129	13	140
o-xylene	180	109	2	137	4	90 Total
p-xylene	135	73	1	98	1	90 Total
m-xylene	465	268	4	343	8	90 Total

Table B.3: Simulated BTEX fraction percent removal at the 1500 second mark at 1 mg/L and 4 mg/L applied ozone doses at warm and cool water temperatures

	Assumed Initial concentration (µg/L)	**O_3 1mg/L T1-%**	**O_3 4 mg/L T1- %**	**O_3 1 mg/L T2-%**	**O_3 4 mg/L T2- %**	**MAC (µg/L)**
Lake Ontario September 28th 2016 T1-20°C, December 5th T2-5°C						
BTEX after 1500 seconds	1500	82	99	55	98	295
Benzene	165	78	98	48	94	5
Toluene	390	79	99	50	96	60
Ethylbenzene	165	82	99	53	97	140
o-xylene	180	82	100	57	100	90 Total
p-xylene	135	86	100	62	100	90 Total
m-xylene	465	86	100	61	100	90 Total
Grand River A October 17 2017 T1-14°C, February 17 2017 T2-3°C						
BTEX after 1500 seconds	1500	16	97	25	93	295
Benzene	165	13	91	21	85	5
Toluene	390	14	94	23	89	60
Ethylbenzene	165	15	95	23	91	140
o-xylene	180	17	99	26	93	90 Total
p-xylene	135	19	100	30	99	90 Total
m-xylene	465	18	100	28	98	90 Total
Grand River B March 13 2017 T1-20°C, January 6 2017, T2-4°C						
BTEX after 1500 seconds	1500	37	96	23	94	295
Benzene	165	29	90	19	87	5
Toluene	390	31	93	20	90	60
Ethylbenzene	165	33	94	22	92	140
o-xylene	180	40	99	24	98	90 Total
p-xylene	135	46	100	28	99	90 Total
m-xylene	465	42	99	26	98	90 Total

Table B.4: Simulated BTEX fraction percent removal with percent differences (T1-T2) at the 1500 second mark at 1 mg/L and 4 mg/L applied ozone doses at warm and cool temperatures

	O_3 1mg/L T1-%	**O_3 1mg/L T2-%**	**O_3 1 mg/L T1-T2- %**	**O_3 4 mg/L T1-%**	**O_3 4 mg/L T2- %**	**O_3 4 mg/L T1-T2- %**
Lake Ontario September 28th 2016 T1-20°C, December 5th T2-5°C						
BTEX after 1500 seconds	82	55	27	99	98	1
Benzene	78	48	30	98	94	4
Toluene	79	50	29	99	96	3
Ethylbenzene	82	53	29	99	97	2
o-xylene	82	57	26	100	100	0
p-xylene	86	62	23	100	100	0
m-xylene	86	61	25	100	100	0
Grand River A October 17 2017 T1-14°C, February 17 2017 T2-3°C						
BTEX after 1500 seconds	16	25	-9	97	93	4
Benzene	13	21	-8	91	85	6
Toluene	14	23	-9	94	89	5
Ethylbenzene	15	23	-9	95	91	4
o-xylene	17	26	-9	99	93	7
p-xylene	19	30	-10	100	99	1
m-xylene	18	28	-10	100	98	1
Grand River B March 13 2017 T1-20°C, January 6 2017, T2-4°C						
BTEX after 1500 seconds	37	23	14	96	94	2
Benzene	29	19	10	90	87	3
Toluene	31	20	11	93	90	3
Ethylbenzene	33	22	12	94	92	2
o-xylene	40	24	15	99	98	1
p-xylene	46	28	18	100	99	0
m-xylene	42	26	16	99	98	1