EFFECTS OF UV/H₂O₂ ADVANCED OXIDATION ON PHYSICAL AND CHEMICAL CHARACTERISTICS OF NATURAL ORGANIC MATTER IN RAW DRINKING WATER SOURCES

by

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Abstract

This thesis focused on the physical and chemical transformations undergone by natural organic matter (NOM) in two natural waters (from British Columbia, Canada) during ultraviolet plus hydrogen peroxide (UV/H$_2$O$_2$) advanced oxidation treatment as a function of UV fluence (up to 2000 mJ cm$^{-2}$) and initial H$_2$O$_2$ concentration (up to 20 mg L$^{-1}$). Under these conditions NOM was not mineralized but the hydroxyl radical (•OH) partially oxidized NOM leading to reductions in the chromophoric natural organic matter (CNOM) (i.e., NOM absorbing at 254 nm). NOM was degraded into more readily biodegradable compounds, such as aldehydes. An appreciable reduction in the very hydrophobic acid (VHA) fraction of NOM was observed. Considerable reductions in the formation potentials of trihalomethanes (THMs) or haloacetic acids (HAAs) were not observed. An increase in alkalinity slowed down the rate of degradation of CNOM during UV/H$_2$O$_2$.

A dynamic kinetic model was developed to predict the degradation of CNOM. Model parameters were developed using isolated aquatic NOM from Suwannee River. For the two natural waters, the model adequately predicted the degradation of CNOM as a function of initial H$_2$O$_2$ concentration, irradiation time (i.e., UV fluence). Including the reduction in CNOM improved the modeling of H$_2$O$_2$ degradation, but H$_2$O$_2$ degradation was still slightly under predicted.

For water that had undergone ultrafiltration (UF), NOM was readily mineralized during UV/H$_2$O$_2$ treatment due to the absence of high molecular size NOM. For water from which the VHA fraction of NOM was removed, UV/H$_2$O$_2$ treatment led to mineralisation of NOM suggesting that, when coupled with a pre-treatment capable of removing a large portion of the VHA fraction, UV/H$_2$O$_2$ can achieve reductions in TOC.

Combining UV/H$_2$O$_2$ with downstream biological activated carbon (BAC) filtration led to reductions in NOM and formation potentials of THMs and HAAs. Formaldehyde and H$_2$O$_2$ were effectively removed by BAC.

Development of a method for the determination of assimilable organic carbon (AOC) in UV/H$_2$O$_2$ treated water concluded that manganese dioxide was a suitable agent for the removal of H$_2$O$_2$ prior to AOC analysis. The method was applied to observe an increase in AOC as fluence increased during UV/H$_2$O$_2$ treatment of raw water.
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Nomenclature

$\varepsilon_{CNOM}$ – decadic molar absorption coefficient of chromophoric natural organic matter

$\varepsilon_{H_2O_2,254}$ – decadic molar absorption coefficient of $H_2O_2$ at 254 nm

$\varepsilon_{O_3,254}$ – decadic molar absorption coefficient of $O_3$ at 254 nm

$\Phi_{H_2O_2,OH}$ – primary quantum yield of $H_2O_2$ at 254 nm

<10 kg mol$^{-1}$ or <10 kDa – water that has undergone ultrafiltration

$A_{254}$ – absorbance at 254 nm

$A_{203}$ – absorbance at 203 nm

$A_{CNOM}$ – absorption coefficient for chromophoric natural organic matter

$A_{total,254}$ – total water absorption coefficient at 254 nm

AA – acetaldehyde

AMW – apparent molecular weight

AO – advanced oxidation

AOC – assimilable organic carbon

AOP – advanced oxidation process

BAC – biological activated carbon

BDOC – biodegradable dissolved organic carbon

CHA – charged hydrophilics fraction of natural organic matter

CNOM – chromophoric natural organic matter; fraction of natural organic matter that absorbs at 254 nm

CW – water collected from Capilano Reservoir, North Vancouver, British Columbia, Canada

DBP – disinfection by-product; disinfection formation potential

DBP-FP – disinfection formation potential

DCAA – dichloroacetic acid

DF – divergence factor

DOC – dissolved organic carbon

EBCT – empty bed contact time

$E_{avg}$ – average fluence rate through the water volume

$E_p^*$ – incident photon fluence rate

FA – formaldehyde

GAC – granular activated carbon

HAA – haloacetic acids

HAA-FP – haloacetic formation potential

HPB – hydrophobic fraction of natural organic matter
HPL – hydrophilic fraction of natural organic matter
HPSEC – high performance size exclusion chromatography
HS – humic substances
IXR – ion exchange resin
\( k'_{A_{CNOM}} \) – experimentally observed reaction rate constant for the reduction in absorption coefficient for chromophoric natural organic matter
\( k'_{C_{CNOM}} \) – experimentally observed reaction rate constant for the reduction of chromophoric natural organic matter
\( k'_{p_{CBA}} \) – experimentally observed reaction rate constant for the reduction of 4-chloro-benzoic acid
\( k_{a,H_2O_2,254} \) – specific rate of light absorption by \( H_2O_2 \) at 254 nm
\( k_{OH,TOC} \) – reaction rate constant for the reaction between total organic carbon and hydroxyl radical
\( k_{OH,CNOM} \) – reaction rate constant for the reaction between chromophoric natural organic matter and hydroxyl radical
LP – low pressure technology for ultraviolet lamps
MIEX® – magnetic ion exchange resin
MP – medium pressure technology for ultraviolet lamps
MW – molecular weight
MWCO – molecular weight cut off
NEU – neutral hydrophilics fraction of natural organic matter
NOM – natural organic matter
NRNOM – isolated natural organic matter from Nordic Reservoir
’OH – hydroxyl radical
OCD – organic carbon detection
pCBA – 4-chloro-benzoic acid
Post-DAX – water that has been exposed to DAX-8 resin and had the very hydrophobic fraction of natural organic matter remove
PRAM - polarity rapid assessment method
RF – reflection factor
SHA – slightly hydrophobic acids fraction of natural organic matter
SHAA-FP_{CNOM} – haloacetic acid formation potential divided by the amount of chromophoric natural organic matter
SHAA-FP_{TOC} – haloacetic acid formation potential divided by the concentration of total organic carbon
SRNOM – isolated natural organic matter from Suwannee River
STHM-FP_{CNOM} – trihalomethane formation potential divided by the amount of chromophoric natural organic matter
STHM-FP_{TOC} – trihalomethane formation potential divided by the concentration of total organic carbon
SUVA – specific ultraviolet absorbance
TCAA – trichloroacetic acid
TW – water collected from Trepanier Creek, Peachland, British Columbia, Canada
THM – trihalomethanes; trihalomethanes formation potential
THM-FP – trihalomethanes formation potential
TiO₂ – titanium dioxide
TOC – total organic carbon
UF – ultrafiltration
UV – ultraviolet
UV/H₂O₂ – advanced oxidation process utilizing ultraviolet and hydrogen peroxide
UV/O₃ – advanced oxidation process utilizing ultraviolet and ozone
VHA – very hydrophobic acids fraction of natural organic matter
VUV – vacuum ultraviolet
WF – water factor
z – water pathlength
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Co-Authorship Statement

All manuscript based chapters of this thesis were co-authored with the research supervisor Madjid Mohseni. My contribution was the collection and the analyses of data and the writing of the manuscripts. Dr. Mohseni contributed largely to the development of experimental plans, the analyses and the discussion of results, and the revision of drafts. Two of the chapters in this thesis were manuscripts co-authored with authors in addition to Dr. Mohseni.

**Chapter 5** was co-authored with Mohammed Mehdi Bazri. My contribution to this work was the development of the model, the collection and the analysis of data, and the writing of the manuscript. Mr. Bazri contributed significantly by writing the programming algorithm presented in Appendix C, debugging the programming code, and providing the model predicted results.

**Chapter 6** was co-authored with Mihaela Stefan, Alan Royce, and Ted Mao. For this manuscript my contribution was the collection and analysis of data, and the writing of the manuscript. Dr. Stefan, Mr. Royce, and Dr. Mao all contributed largely to the development of the experimental plan, the discussion of findings, and the revision of drafts.
Chapter 1
Introduction

The practice of ultraviolet (UV) disinfection of water dates back to the early twentieth century. In the last quarter century, UV has begun to replace chlorine as the primary disinfectant in drinking water treatment. This is largely due to the fact that UV has been demonstrated to be highly effective at inactivating Cryptosporidium parvum and Giardia lamblia (Bukhari et al. 1999; Craik et al. 2000, 2001). With the increased use of UV in drinking water treatment plants, much attention has been placed on developing UV-based advanced oxidation processes (AOP) for the removal of taste and odour compounds, micropollutants, and natural organic matter (NOM) from raw drinking water (Parsons 2004).

An AOP involves the formation of the hydroxyl radical (’OH) that carries out the oxidation and degradation of target species. Leading the way in commercial applications of UV-based AOPs is the process combining UV and hydrogen peroxide (UV/H₂O₂) (Parsons 2004). In UV/H₂O₂, UV photolyzes H₂O₂ leading to the formation of ’OH. UV/H₂O₂ AOP has been extensively researched for the removal of organic contaminants from drinking water, such as N-nitrosodimethylamine (Stefan & Bolton 2002; Sharpless & Linden 2003), methyl tert-butyl ether (Cater et al. 2000; Chang & Young 2000; Stefan et al. 2000; Kavanaugh et al. 2004), herbicides and pesticides (Kruithof et al. 2002), and taste and odour compounds, such as 2-methylisoborneol and geosmin (Rosenfeldt et al. 2005). Furthermore, there are currently a number of commercial UV/H₂O₂ applications for the treatment of drinking water originating from ground and surface reservoirs (Leach et al. 2006; Sarathy & Mohseni 2006). While the key objective of ’OH generation is to oxidize and degrade undesirable organic contaminants, ’OH also reacts with other species present in the water matrix, including NOM. While much research has focused on finding target contaminants susceptible to UV/H₂O₂, the fate of NOM during typical UV/H₂O₂ treatment conditions has received little attention.

NOM, a complex mixture of humic and fulvic acids, is ubiquitously present in surface waters and poses several challenges to drinking water treatment operations. With respect to water quality, NOM acts as a precursor for chlorination disinfection by-products (DBPs) and has potential to increase the biological regrowth potential of water in distribution systems. During UV/H₂O₂ AOP, NOM screens photons needed for the photolysis of H₂O₂ thus reducing the production of ’OH needed for contaminant removal.

Some research has focused on employing UV/H₂O₂ AO for the removal of NOM in an attempt to reduce the formation potential of DBPs (DBP-FPs). Under strong AO conditions (i.e., long irradiation
time and/or high initial H₂O₂ concentration), studies found that NOM was mineralized leading to a reduction in DBP formation (Kleiser & Frimmel 2000; Speitel et al. 2000; Liu et al. 2002; Thomson et al. 2002, 2004; Wang et al. 2006). These studies employed high UV fluences and/or H₂O₂ concentrations, well above the range of conditions typically applied for the oxidation of organic pollutants in drinking water (up to 1500 mJ cm⁻² and 20 mg L⁻¹ H₂O₂). Since very strong AO conditions are not economically feasible, due to high energy demand, UV/H₂O₂ AO is not been deemed a viable technology for the removal of NOM and/or DBP precursors.

It has been observed that under milder AO conditions (i.e., shorter irradiation times and/or lower initial H₂O₂ concentrations) and within the range of accepted conditions for commercial applications for organic pollutant removal, NOM underwent partial oxidation. This partial oxidation led to a reduction in aromaticity of NOM (Thomson et al. 2002, 2004a, 2004b), a reduction in high molecular size chromophoric (i.e. 254 nm UV absorbing) species with concomitant formation of lower molecular size chromophores (Thomson et al. 2004b), and an increase in biodegradable organics such as biodegradable organic carbon (BDOC) and/or low molecular weight compounds (Speitel et al. 2000; Liu et al. 2002; Thomson et al. 2004a; Toor & Mohseni 2007). But, given the primary focus of these studies was on UV/H₂O₂ as a treatment for the removal of NOM (i.e., under strong AO conditions), limited efforts went towards gathering and analyzing data on how NOM is affected and the implications on water quality related parameters when NOM is partially oxidized (i.e., under mild AO conditions). In short, NOM plays a critical role during commercial UV/H₂O₂ applications since it not only impacts the effectiveness of UV/H₂O₂, but also undergoes transformations that may impact water quality related parameters.

Proper understanding of how NOM is transformed under the conditions used in commercial applications and what products are formed are issues of key importance in the development of solutions to address potential problems. That is, how the physical and chemical characteristics of NOM are altered as a result of reaction with ’OH requires further attention. In order to better understand the extent of NOM transformation and its potential impacts on water characteristics, this research took a detailed look at the impact of UV/H₂O₂ AO on surface water’s NOM concentration, spectral characteristics, hydrophobicity, apparent molecular weight distribution (AMW), DBP-FPs, and biodegradability. Special attention was given to employing fluences and H₂O₂ concentrations within the acceptable range for commercial applications. As NOM is highly variable amongst sources, attention was also given to characterizing the NOM in this study and discussing the results with consideration of the unique characteristics of NOM. Furthermore, surface water was treated by membrane ultrafiltration (UF), to remove a portion of NOM, and subsequently treated by UV/H₂O₂. This allowed observation of how UV/H₂O₂ AO may impact NOM when NOM has been altered such that the concentration of NOM has been reduced and high molecular
size species have been removed. Also, a select fraction of the NOM, the very hydrophobic acids (VHA), was removed from the raw surface water and the impact of UV/H₂O₂ on NOM aromaticity, concentration, and DBP-FPs was observed. Finally, a dynamic kinetic model to estimate the extent of transformation of NOM after UV/H₂O₂ was developed. Overall, the results provided in depth and valuable insight into the implications of NOM oxidation during commercial drinking water UV/H₂O₂ applications.

1.1 Natural Organic Matter

1.1.1 Sources and Characteristics

Natural organic matter (NOM) is a complex mixture of organics that originate from the decomposition of detrital matter (Macalady 1997). The structure and chemical composition of NOM is not well understood due to its complexity and variability with respect to season and location. Chemically, NOM is grouped into non-humic substances and humic substances (HS). HS are non-polar organic acids derived from soil humus and terrestrial and aquatic plants. HS are further subdivided into humic acids, HS that precipitate out of solution at pH < 2, and fulvic acids, those that do not precipitate (Thurman 1985). The components of HS are grouped in accordance with an operational definition and do not represent a single pure compound due to their complex nature (Hayes et al. 1989).

The distinctions between fulvic and humic acid are based on their solubility characteristics. However, these represent only a general understanding of the chemical characteristics of HS and there is considerable overlap in the chemical properties of HS. Nevertheless, the general characteristics presented in Table 1.1 can be helpful in determining the best treatment process for a specific water quality. In general, humic acid is hydrophobic in nature, aromatic, and less soluble in water (Table 1.1). Fulvic acid, on the other hand, is more soluble, less aromatic and contains more acidic functional groups, such as carboxylic acids, that increase the overall charge density (Collins et al. 1986).
Table 1.1 Composition of NOM fractions based on literature data (Swietlik et al. 2004)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Organic compound class</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humic acid</td>
<td>Portion of humic substances precipitated at pH 1</td>
<td>(Peuravuori &amp; Pihlaja 1997)</td>
</tr>
<tr>
<td>Hydrophobic acid</td>
<td>Soil fulvic acids, C5–C9 aliphatic carboxylic acids, 1- and 2-ring aromatic carboxylic acids, 1- and 2-ring phenols</td>
<td>(Leenheer 1981; Aiken et al. 1992; Marhaba et al. 2000; Barber et al. 2001)</td>
</tr>
<tr>
<td>Hydrophobic base</td>
<td>1- and 2-ring aromatic amines except pyridine, proteinaceous substances</td>
<td>(Leenheer 1981; Aiken et al. 1992; Marhaba et al. 2000; Barber et al. 2001)</td>
</tr>
<tr>
<td>Hydrophobic neutral</td>
<td>A mix of hydrocarbons; &gt;C5 aliphatic alcohols, amides, esters, ketones, aldehydes; long chain (&gt;C9) aliphatic carboxylic acids and amines; &gt;3-ring aromatic carboxylic acids and amines</td>
<td>(Leenheer 1981; Aiken et al. 1992; Marhaba et al. 2000; Barber et al. 2001)</td>
</tr>
<tr>
<td>Hydrophilic acid</td>
<td>&lt;C5 aliphatic carboxylic acids, polyfunctional carboxylic acids, mixture of various hydroxy acids</td>
<td>(Leenheer 1981; Aiken et al. 1992; Marhaba et al. 2000; Barber et al. 2001)</td>
</tr>
<tr>
<td>Hydrophilic base</td>
<td>Amphoteric proteinaceous materials containing aliphatic amino acids, amino sugars, peptides and proteins; &gt;C9 aliphatic amines; pyridine</td>
<td>(Leenheer 1981; Aiken et al. 1992; Marhaba et al. 2000; Barber et al. 2001)</td>
</tr>
<tr>
<td>Hydrophilic neutral</td>
<td>Short chain aliphatic amines, alcohols, aldehydes, esters, ketones; &lt;C5 aliphatic amines; polyfunctional alcohols; carbohydrates; cyclic amides; polysaccharides</td>
<td>(Leenheer 1981; Aiken et al. 1992; Marhaba et al. 2000; Barber et al. 2001)</td>
</tr>
</tbody>
</table>

The physical characteristics of NOM in surface water changes with every source so it is important to characterize NOM with respect to size and molecular weight (MW) in each individual source. NOM in water can be separated into particulate and dissolved fractions. Dissolved fractions are defined as those that are able to pass through a 0.45 μm membrane filter. The remaining particles are part of the particulate fraction. The dissolved fraction is measured as dissolved organic carbon (DOC) while the total organic carbon (TOC) represents both the dissolved and particulate fractions. In drinking water, most NOM is in the dissolved fraction since the source is often not very turbid (Singer 1999a). The diameter of NOM in the dissolved fraction is difficult to measure but the MW can be determined using membrane fractionation or size exclusion chromatography. The MW of DOC can range from less than 500 g mol⁻¹ to greater than 10000 g mol⁻¹ and the distribution of MW varies depending on the source of NOM. Additionally, for a particular source, the MW distribution varies depending on the time of year (Klevens et al. 1996). In North American regions during the winter months NOM has a greater fraction in the greater than 10000 g mol⁻¹ range than in the less than 500 g mol⁻¹ range. Conversely, in the summer months the lower MW fraction dominates (Klevens et al. 1996). This effect is due to the biological activity in surface water, which is dependent on temperature and nutrient availability (Thurman 1985). Increased biological activity
leads to the degradation of high MW NOM as microorganisms use it as substrate and break it down to smaller fractions.

1.1.2 Characterization of Natural Organic Matter

1.1.2.1 Ultraviolet and Fluorescence Spectroscopy

The absorbance of UV by organic matter at 254 nm (A$_{254}$) is indicative of the aromatic nature of NOM (Nikolaou & Lekkas 2001). Therefore, it is a good parameter to monitor the impact of a specific treatment on the conjugated double bonds and the structure of NOM. Specific UV absorbance (SUVA) is defined as the ratio of A$_{254}$ to DOC and can give an indication of the relative amount of aromatic carbon in NOM (Singer 1999b).

Korshin et al. (1997) proposed that the composite electron-transfer (ET) and benzenoid (Bz) bands of the NOM could be extracted from the NOM’s absorbance of UV at 254 nm and 203 nm, respectively. Based on the ratio of absorbance of the ET band to the absorbance of the Bz band (A$_{254}$/A$_{203}$), the degree of activation of the aromatic rings can be interpreted. A low A$_{254}$/A$_{203}$ value was said to be representative of compounds in which the aromatic rings were substituted predominantly with aliphatic functional groups. Increasing A$_{254}$/A$_{203}$ was said to be an indication of higher substitution of aromatic rings in NOM with hydroxyl, carbonyl, ester, and carboxyl groups (Korshin et al. 1997).

Fluorescence excitation and emission spectroscopy also provides information for characterization of aquatic NOM. For NOM, the characteristic wavelengths are 345 nm for excitation and 415 nm emission (Nikolaou & Lekkas 2001). However, different fractions of NOM have different fluorescence wavelength maxima such as 470 nm for humic acids and 436 for fulvic acids (Krasner et al. 1996). In general, fulvic acids fluoresce the most while humic acids absorb the most (Nikolaou & Lekkas 2001). Therefore, combining fluorescence and UV spectroscopy can provide complementary information for the characterization of NOM in water.

1.1.2.2 Chemical Fractionation

NOM can be fractionated based on its acidic/basic and hydrophobic/hydrophilic properties. Hydrophilic and hydrophobic fractionations are performed using DAX-8 and XAD-4 resins in series and have been widely applied to characterize NOM (Leenheer 1981; Thurman 1985; Aiken et al. 1992). Chow et al. (2004) developed a rapid fractionation procedure to fractionate NOM into four fractions: very hydrophobic acid (VHA), slightly hydrophobic acid (SHA), hydrophilic charged (CHA), and hydrophilic neutral (NEU). Water is acidified to pH 2 and then passed through DAX-8 resin in order to remove the VHA fraction. The effluent of the DAX-8 resin is passed through XAD-4 resin onto which
the SHA fraction is adsorbed. The effluent from the XAD-4 is then adjusted to pH 8 and the CHA fraction is adsorbed onto IRA-958 resin. The effluent from all three resins represents the NEU fraction. This rapid fractionation method has been applied to observe the impact of conventional and enhanced coagulation with alum (Chow et al. 2004), vacuum UV irradiation (Buchanan et al. 2005), combined photooxidation and microfiltration (Malek et al. 2006), and photocatalysis (Liu et al. 2008a, 2008b) on the hydrophilic/hydrophobic speciation of NOM.

Recently the polarity rapid assessment method (PRAM) was presented as an alternative method for chemical characterization of NOM (Rosario-Ortiz et al. 2007). This method employed eight solid phase extraction sorbents including non-polar, polar, and anion exchange sorbents to fractionate NOM in terms of polarity. Advances in the PRAM have reduced the number of sorbents to three and demonstrated that similar information to DAX/XAD fractionation can be obtained (Philibert et al. 2008). A key advantage that the PRAM has over conventional DAX/XAD fractionation is that it is done under environmentally relevant conditions of pH and ionic strength (i.e., no pH adjustment required) (Rosario-Ortiz et al. 2007). As DAX/XAD fractionation has been demonstrated to assist with optimization of water treatment processes, the PRAM has been demonstrated to have potential to optimize processes such as coagulation (Philibert et al. 2008).

1.1.2.3 Molecular Weight Distribution

MW distribution of NOM is an important property in drinking water treatment since certain treatments are preferential to particular MW fractions. Separation using membranes with different molecular size/weight cutoffs is a method for obtaining different fractions of NOM based on their molecular size. The obtained fractions can then be exposed to treatment and the impact on specific MW fractions can be deduced. Also, some treatments may alter the MW distribution of NOM leading to changes in water quality.

High performance size exclusion chromatography (HPSEC) is a technique for determining the apparent molecular weight (AMW) distribution of NOM (Pelekani et al. 1999). In HPSEC, NOM is separated chromatographically using HPLC fitted with a SEC column. Lower MW compounds elute later since smaller molecules can penetrate the pores of the column. Combined with numerical data analysis by way of peak-fitting, HPSEC analysis can provide in depth qualitative and quantitative information on the response of different MW fractions of NOM to various drinking water treatment processes. HPSEC is typically done with UV absorbance detection at around 260 nm. However, this approach is limited to characterization of only the UV absorbing species while other organic compounds are neglected. A more powerful approach is to employ organic carbon detection (OCD) allowing for direct quantification of the
molecular weight distribution of organic carbon species. Chow et al. (2008) combined HPSEC with UV detection and peak fitting to assess NOM removal by coagulation. Thomson et al. (2004) also combined HPSEC with UV detection and peak fitting to investigate the impact of chlorine, ozone, white rot fungus, and UV/H₂O₂ on the depolymerisation of chromophoric NOM. Vuorio et al. (1998) applied HPSEC with UV detection to evaluate the changes in NOM MW distribution at each step of a full scale drinking water treatment process consisting of coagulation, flocculation, sedimentation, sand filtration, and ozonation. Allpike et al. (2005) used HPSEC with UV detection and OCD to compare the removal of different MW fractions of NOM in a full scale treatment plant where conventional enhanced coagulation was compared to combined magnetic ion exchange resin and coagulation.

HPSEC and membrane fractionation are simple and effective ways to obtain information regarding the molecular weight distribution of NOM. However, neither is able to precisely separate all molecular weight fractions and thus they only provide information with respect to the AMW. Membrane are assigned nominal molecular weight cut offs but in practice the AMW fractionation can depend on the volume of water used as well as the flow rate (Chow et al. 2005). Further, molecular weight cut offs are determined using specific molecules with known AMW, while NOM may behave quite differently during membrane separation (Chow et al. 2005). The separation of different AMW fractions by HPSEC is poor and chromatograms are quite convoluted since AMW fractions co-elute. Calibration is required to correlate retention time with AMW fractions which is done using polysulfonate standards with known molecular weights. However, as this material is not identical to NOM, the correlation between AMW and retention time is an approximation and NOM from different sources may behave differently during chromatography.

After calibration, HPSEC chromatograms generally yield an AMW distribution ranging from less than 300 g mol⁻¹ to greater than 2000 g mol⁻¹. By peak fitting, a method by which HPSEC chromatogram is deconvoluted, the AMW distribution can be split into specific fractions and each fraction can be associated with a class of compounds within the entire NOM. For example, the fitted peak centred at 1900 g mol⁻¹ represents high molecular weight humic substances (non-polar), the fitted peaks centred at 1200 g mol⁻¹ and 800 g mol⁻¹ are associated with low molecular weight humics, the fitted peak centred at 500 g mol⁻¹ represents building blocks, and the fitted peak centred at 300 g mol⁻¹ represent low molecular weight acids and nitrogen containing aromatics (Chow et al. 2008).
1.1.3 Problems Posed to Drinking Water Treatment

1.1.3.1 Disinfection By-products

Halogenated DBPs are formed when chlorine chemically reacts with NOM in source drinking water. This presence of potentially toxic and carcinogenic compounds or DBPs may have adverse health effects (Komulainen 2004). Trihalomethanes (THMs) and haloacetic acids (HAAs) are two common DBPs that are subject to increasingly stringent environmental and health regulations because of the concern over their health impacts (e.g., on human reproductive system). As a result, health authorities in Canada and elsewhere have introduced new guidelines for the control of DBPs in drinking water. An important aspect of drinking water treatment and quality is preventing and/or reducing the formation of DBPs. Thus, considerable research efforts have been and are being devoted towards examining various treatment processes and their impact on DBP reduction.

Decreasing or eliminating the addition of chlorine is one potential strategy for reducing DBPs. However, a disinfectant is required in distribution systems to mitigate microbial re-growth, which is also crucial in maintaining good drinking water quality. Therefore, completely eliminating the use of chlorine, or chlorinated compounds (e.g. chlorine dioxide, chloramines), is not a viable option for most treatment systems. Thus, most treatment strategies focus on eliminating/reducing the components of NOM that are DBP precursors as a starting point for DBP reduction. This usually involves decreasing the amount of NOM available for reaction with chlorine or converting NOM to the point where it no longer reacts with chlorine to form DBPs. Many treatment processes employ one or a combination of the preceding ideas in an attempt to reduce the formation of DBPs.

Two common methods applied for the evaluation of DBP precursors in water, are the formation potential test and the simulated distribution systems (SDS) test. DBP formation potentials (DBP-FPs), or specifically THMs formation potentials (THM-FPs) and HAAs formation potentials (HAA-FPs), are determined by adding an excess of chlorine to assure the maximum formation of DBPs (Xie 2004). The test conditions are generally standardized with respect to the concentration of chlorine added, incubation duration, incubation temperature, and pH (Xie 2004). DBP-FP tests are useful for evaluating the effects of water treatment processes on DBP precursor removal (Xie 2004). However, a drawback is that it does not give an indication of the formation of DBPs under actual chlorination and distribution system conditions (Xie 2004). On the other hand, the SDS test aims to simulate DBP formation under actual distribution system conditions (Xie 2004; Koch et al. 1991). It does so by conducting the test under the pH, temperature, and residual chlorine conditions found in the distribution system of choice (Xie 2004). The SDS test generally uses a lower chlorine dose than the DBP-FP tests so the measured DBPs after SDS
tests are usually lower than those measured after DBP-FP tests (Xie 2004). Once formed, DBPs can be measured by the approved methods, USEPA Method 551.1 (USEPA 1995a) for THMs and USEPA Method 552.2 (USEPA 1995b) for HAAs.

The physical and chemical characteristics of NOM and, more specifically, DBP precursors are important considerations in the selection of an optimal treatment technology. Efforts to correlate NOM properties with the formation of DBPs have been reviewed by Nikolaou & Lekkas (2001) and Chow et al. (Chow et al. 2005). For example, SUVA has been considered as a good indicator for the potential of NOM to form THMs (Chow et al. 2005; Chow et al. 2008) and HAAs (Croué et al. 2000; Kitis et al. 2002). In general, it has been shown that as the degree of aromaticity for source water increased the DBP-FP increased.

1.1.3.2 Biological Stability

The biological stability of water refers to the ability of the water to maintain a microbial population. For drinking water it is undesirable if the water is capable of maintaining a microbial population since this increases the potential for regrowth of pathogenic organisms and the consumers’ chance of contracting an infection. Organic carbon found in NOM is a primary substrate for microorganisms but the majority of NOM is recalcitrant to microorganisms so indicator measures have been introduced to assess the biological stability of water. The two most commonly applied indicators are biodegradable organic carbon (BDOC) and assimilable organic carbon (AOC). Further, determination of the concentration of low molecular weight carbonyls, such as aldehydes, ketones, and carboxylic acids, can provide insight into the biological stability of water since these compounds are readily biodegradable by microorganisms.

BDOC refers to the amount of DOC that is not recalcitrant and can be degraded by heterotrophic bacteria over a set duration (Escobar & Randall 2001). It consists of biodegradable compounds such as alcohols, organic acids, starches, fats, proteins, esters, and aldehydes (Spellman & Drinan 1999). Therefore, an observed increase in the concentration of any of these compounds would indicate an increase in BDOC and a decrease in biostability. During drinking water treatment it is desirable to reduce the BDOC of the water to ensure the potential for re-growth of pathogens in the distribution system is minimized. An increase in BDOC would negatively impact biological stability and general water quality (Charnock & Kjonnø 2000). BDOC is determined by measuring the reduction in DOC after a given period of time after the sample has been inoculated by microorganisms (Frias et al. 1995). The two most commonly applied methods for BDOC determination were developed by Servais et al. (1989) and Joret and Lévi (1986).
AOC describes the fraction of DOC that is readily assimilated by microorganisms resulting in an increase in biomass (Frias et al. 1995; Hammes & Egli 2005). AOC represents a small fraction (0.1-9%) of the TOC in water, but it is regarded as one of the main factors governing heterotrophic growth, and thus biological water stability (van der Kooij 2002; Hammes & Egli 2005). The determination of AOC has been standardized and is presented as Standard Method 9217 (Clescerl et al. 1999) but this method is not widely applied in practice. The primary reason for this is because SM 9217 is slow, tedious, and requires considerable technician labour (Hammes & Egli 2005). These obstacles are largely due to the fact that SM 9217 uses a pure culture, Pseudomonas fluorescens strain P-17 or Spirillum strain NOX, combined with plate counting for enumeration. Further, there are inherent disadvantages of using pure strains for detection of natural AOC since pure strains are not capable of assimilating all forms of organic carbon (Hammes & Egli 2005; van der Kooij 2002). Hammes & Egli (2005) developed a rapid, reliable, and reproducible method for AOC determination. This novel method combines a natural microbial consortium for the assimilation of AOC with fluorescent staining and flow cytometric enumeration of cells (Hammes & Egli 2005). This method has been successfully applied for evaluating the formation of AOC during ozonation of drinking water (Hammes et al. 2006) and phytoplankton (Hammes et al. 2007), determining the filterability of bacteria by micropore membrane filters (Wang et al. 2008), assessing the impact of microfiltration on the concentration of microbial communities in bottled water (Wang, et al. 2008), and assessing general microbial quality of drinking water (Berney et al. 2008).

Aldehydes constitute only 25-30% of BDOC (Nawrocki et al. 2003) so an increase in aldehydes would contribute to observed increases in BDOC and AOC. While determining the concentration of specific biodegradable chemicals, such as aldehydes, does not provide a direct measurement of the biological stability of water, it has both inductive and complementary value to BDOC and AOC data. Low concentrations (µg L⁻¹ level) of aldehydes can be determined relatively easily and at low cost by the approved USEPA Method 556.1 (USEPA 1999).

1.1.4 Technologies for Removal of Natural Organic Matter

A wide range of technologies is available for the removal of NOM. Certain technologies target the physical characteristics of NOM while physicochemical treatment processes take advantage of the chemical characteristics as well. Treatment technologies applied for NOM removal include coagulation, membrane processes, adsorption processes, ozonation, and advanced oxidation processes (AOPs).

Coagulation removes NOM by destabilizing its suspension in water allowing it to be removed by settling or filtration. Coagulation treatment processes are capable of removing nearly the entire particulate fraction of NOM and a portion of the dissolved fraction. If a particular source has a very large fraction of
NOM in the dissolved fraction, then conventional coagulation will not be highly effective. In the dissolved fraction, larger, hydrophobic constituents are more likely to be destabilized. The effectiveness of coagulation to remove NOM depends mainly on the numerous variables of coagulation processes including the coagulant, pH, coagulant dose, flocculation time, and NOM characteristics. Conventional and enhanced coagulation with alum preferentially removes the hydrophobic fraction of NOM, including the VHA and SHA fractions (Chow et al. 2005; Archer & Singer 2006). Sinha et al. (2004) provided a comprehensive study that characterized various metal coagulants and comparatively evaluated them on a natural source water (Sinha et al. 2004). Kuo et al. (1988) investigated the impact of coagulant dose, pH, pre-ozonation, and flocculation on particle formation and growth during coagulation using aluminum sulphate. Further, Kuo & Amy (1988) reported the impact of the same variables on DOC removal.

Membranes remove NOM based on molecular size. Therefore, selecting a MW cut off (MWCO) is dependent on the physical characteristics of NOM including the MW distribution of the NOM. A number of literature reports have investigated the ability of nanofiltration, ultrafiltration, and microfiltration to remove DBP precursors, primarily due to the rejection of the high molecular weight fraction of NOM (Taylor et al. 1987; Fu et al. 1994; Siddiqui et al. 2000; Ates et al. 2009). Studies have found that a MWCO of 500 kg mol\(^{-1}\) or less is needed to achieve greater than 90% DBP precursor removal (Singer 1999a). Typically, membranes are better at removing the hydrophobic fraction of NOM since it is less soluble in water and generally has a higher MW.

NOM can be removed from water by adsorption onto the surface of the granular activated carbon (GAC) or ion exchange resins (IXR). GAC and IXR have preference for highly charged, low MW compounds (Bolto et al. 2002). Adsorption processes are implemented prior to disinfection since the organic precursors of DBPs are generally more adsorbable than the DBPs themselves (Dickenson & Amy 2000). The decreased insolubility of humic acid is beneficial in adsorption applications on activated carbon (Dickenson & Amy 2000). The acidic nature of NOM is also important since a GAC media with surface acidity will repel acidic NOM. Summers et al. (1995), Symons et al. (1981), and Singer et al. (1994) all cited GAC as an effective method for removing NOM and reduction DBP-FPs but its performance depends on the empty bed contact time (EBCT), pH, and source water characteristics. A related technology is the use of biological activated carbon (BAC) for the removal of NOM. BAC performs similarly to GAC in terms of adsorption but differs in that the carbon is coated with a microbial film. This biofilm is capable of removing the fraction of NOM that is readily biodegradable, which generally consists of lower MW compounds. It has been demonstrated that biological activity within activated carbon systems increases the removal of DBP precursors (Wang et al. 1995; Warta et al. 1995).
Adsorption onto IXR has also been proposed for the removal of NOM. Resin characteristics play an important role with respect to what fraction of the NOM is removed. For example, hydrophobic resins are designed for the removal of the hydrophobic fraction of NOM. In addition, resin pore size is an important factor to consider when high MW fractions are to be adsorbed. The other mechanism by which IXR removes NOM is by ion exchange. This mechanism is dominant for the low MW fraction of NOM (Croué et al. 1999). Recently the magnetic ion exchange (MIEX®) resin has been developed and marketed by Orica Watercare. MIEX® is a strong-base anion exchange resin with a macroporous, polyacrylic structure (Boyer et al. 2008). In operation, MIEX® remains suspended in a completely mixed reactor consisting of a recycle stream in which a fraction of MIEX® is regenerated. MIEX® has been demonstrated to be highly effective at reducing DOC and DBP-FPs as well as reducing downstream coagulant demand so, thus, its application in commercial systems is on the rise (Fearing et al. 2004; Johnson & Singer 2004; Humbert et al. 2005, 2008; Boyer & Singer 2006; Tan & Kilduff 2007; Boyer et al. 2008; Mergen et al. 2008).

The use of ozone (O₃) in drinking water treatment applications including disinfection, oxidation and removal of micropollutants, NOM, taste and odour compounds, and colour has been extensively reviewed (Camel and Bermond 1998; Gottschalk et al. 2000). During ozonation, O₃ oxidizes NOM converting DOC to BDOC including compounds such as aldehydes and ketoacids (Schechter & Singer 1995; Siddiqui et al. 1997). As NOM is more biodegradable after ozonation, downstream biological treatment is very effective at removing residual NOM and reducing DBP-FPs (Miltner et al. 1992; Siddiqui et al. 1997). Tan & Amy (1991) compared ozonation with membrane treatment for the reduction of DBP precursors and reported that, although both treatments effectively reduced color, greater levels of DBPs were associated with ozonation after chlorination (Tan & Amy 1991).

1.1.5 Advanced Oxidation Processes for Natural Organic Removal

Advanced oxidation processes, such as the combination of ultraviolet and hydrogen peroxide (UV/H₂O₂), have recently received much attention for the reduction of NOM. These processes involve the production of the potent hydroxyl radical (•OH), which oxidize and degrade NOM. Complete oxidation reduces the total amount of NOM by a series of complex oxidation reactions that fragment carbon-carbon bonds until all carbon atoms are at the highest oxidation state in CO₂. Following is a review of literature on the removal of NOM by the photocatalysis, vacuum UV (VUV), and UV/ozone (UV/O₃) AOPs. The UV/H₂O₂ AOP will be discussed in detail after the following sections.
1.1.5.1 Photocatalysis

The process combining UV irradiation with titanium dioxide (TiO$_2$) is referred to as photocatalysis. TiO$_2$ has a band gap energy of 3.2-3.0 eV so UV of wavelengths less than 400 nm can excite pairs of electrons and holes. The photogenerated electrons react with dissolved oxygen to produce superoxide radical anions and the photogenerated holes react with water producing $^\cdot$OH. Most photocatalytic processes have low efficiency, typically <1%, due to reflection and scattering losses and electron-hole recombination at light intensities typically found in photoreactors (Hoffmann et al. 1995; Fujishima et al. 2000; Mills & Lee 2004). The key advantage of the photocatalysis over other AOPs is that no chemical addition (e.g., O$_3$, H$_2$O$_2$) is required to generate $^\cdot$OH.

Liu et al. (2008a) monitored the removal of Fluka humic acid in water during photocatalysis by observing changes in $A_{254}$, DOC, AMW distribution, THM-FPs, and the fractionation of NOM into VHA, SHA, CHA, and NEU fractions. Over 90% of $A_{254}$ and 80% of DOC was removed with subsequent reductions in THM-FPs down to 20 µg L$^{-1}$ (Liu et al. 2008a). As irradiation time increased, the VHA fraction decreased and the CHA fraction increased while the NEU fraction was the most persistent (Liu et al. 2008a). Following, Liu et al. (2008b) reported the impact of photocatalysis on the THM-FPs and HAA-FPs, AMW distribution, and hydrophobic/hydrophilic fractionation of NOM in water from Myoponga Reservoir. HPSEC showed that high AMW NOM was preferentially degraded (Liu et al. 2008b). Resin fractionation showed that the NOM was changed from predominantly hydrophobic to more hydrophilic constituents. THM-FPs were reduced while HAA-FPs were reduced less (Liu et al. 2008b).

Wiszniiowski et al. (2002) observed that during photocatalysis humic acid mineralization fell within two domains. First, TOC slightly decreased possibly due to the photodepolymerization of adsorbed humic acid on TiO$_2$ (Wiszniiowski et al. 2002). This was followed by pseudo-first-order degradation kinetics. It was also observed that photocatalysis improved the biodegradability of humic acid (Wiszniiowski et al. 2002).

Eggins et al. (1997) and Palmer et al. (2002) investigated the effects of concentration, temperature, oxygen, light intensity, and pH on the degradation of Aldrich humic acid in water during photocatalysis. In 12 minutes the humic acid concentration was reduced by half but to achieve 50% complete mineralisation 60 minutes were required (Eggins et al. 1997). In the absence of oxygen no degradation was observed (Eggins et al. 1997).

Li et al. (2002) aimed to improve the degradation of humic acid during photocatalysis by the addition of cationic ion calcium and magnesium. It was observed that the rate of degradation of humic acid during photocatalysis could be enhanced at neutral pH by increasing the cationic strength (Li et al. 2002).
Bekbölet & Balcioglu (1996) investigated the influence of hydrogen peroxide and bicarbonate on the degradation of humic acid and found that bicarbonate ions slowed down the degradation rate of humic acid. When hydrogen peroxide was present, natural pH yielded better removal of NOM while in the absence of hydrogen peroxide, low pH was optimal for NOM degradation (Bekbölet & Balcioglu 1996). Bekbölet & Özkösemen (1996) found that after photocatalysis of humic acid THM-FPs were reduced to below 100 µg L$^{-1}$ largely due to the mineralization of NOM. Selcuk & Bekbölet (2008) compared photocatalysis and photoelectrocatalysis (i.e., application of external electrical potential) as possible means of removing humic acid. It was found that photoelectrocatalysis outperformed photocatalysis since the application of an external potential increased the photoactivity of TiO$_2$. Bekbölet et al. (2002) compared the photocatalytic efficiency of two commercial titania brands, Degussa P-25 and Hombikat UV-100 for the degradation of humic acid in aqueous solutions. Although Hombikat UV-100 had a higher surface area, Degussa P-25 was found to be better for the degradation of humic acid. Bekbölet et al. (1996) investigated the impact of photocatalysis on the degradation and absorptivity on activated carbon of humic acid in water. In general, a slight decrease in absorptivity was observed after irradiation but under practical irradiation times no change in adsorption is expected (Bekbölet et al. 1996).

Huang et al. (2008) explored the potential of photocatalysis to control fouling of membranes by NOM. It was observed that increasing TiO$_2$ dosage increased decomposition kinetics while increasing TOC concentration decreased the degradation of NOM. Although TOC removal was relatively low, the photocatalysis process was very effective in controlling membrane fouling by NOM. This was attributed to reductions in aromatic of NOM and high molecular size species (Huang et al. 2008). This study, along with similar ones by Bai et al. (2009), Le-Clech et al. (2006), Fang et al. (2005), and Tay et al. (2001), concluded that there is strong potential for combined photocatalysis and membrane process as effective treatment scheme for the reduction of NOM. In light of these findings, recent research has focussed on developing novel TiO$_2$ based photocatalysts for use in combined photocatalytic and membrane processes for NOM removal (Fu et al. 2006; Xu et al. 2009; Zhang et al. 2009). In short, the researchers fabricated TiO$_2$ based photocatalysts that (i) had photocatalytic activity close to that of Degussa P-25, (ii) maintained a high level of activity after numerous reuses, (iii) had good mechanical strength, and (iv) were easily separated and recovered by membrane filtration while maintaining a high membrane flux (Fu et al. 2006; Xu et al. 2009; Zhang et al. 2009).

In general, the above studies demonstrated that NOM removal could be achieved by photocatalysis but required long irradiation times. Further research is required to improve process efficiency possibly through the development of novel photocatalysts and improvements on reactor design. Yet, it seems
promising that the partial oxidation of NOM under shorter irradiation times may have practical applications such as a pre-treatment to membrane filtration in order to reduce fouling due to NOM.

1.1.5.2 UV-Ozone

O₃ has a high oxidation potential but it is selective and may not completely oxidize some species. Therefore, AOPs that combine O₃ with UV or H₂O₂ to enhance 'OH production are often more effective than O₃ alone (Camel & Bermond 1998). The UV/O₃ AOP is initiated by the photolysis of O₃ by UV to form H₂O₂ and O₂. 'OH production is carried out by the reaction between O₃ and H₂O₂. With UV of 254 nm wavelength, the oxidation potential of the UV/O₃ AOP is high due to the high molar extinction coefficient of O₃ (εₒ₃,254 = 3300 M⁻¹ cm⁻¹) (Gottschalk et al. 2000). In addition, O₃ decays rapidly so the problem of residual concentrations in treated water is not of concern (Guittonneau et al. 1992).

Chin and Bérubé (2005) studied the efficacy of UV, O₃, and UV/O₃ at removing DBP precursors. At an O₃ dose of 0.62 mg O₃ mL⁻¹ and a fluence of 1600 mJ cm⁻², UV/O₃ was capable of mineralizing up to 50% of TOC and reducing DBP-FPs by roughly 70%. The reduction of TOC and DBP-FPs was attributed to the oxidation of NOM by both O₃ and 'OH. Amirsardari et al. (2001), Kusakabe et al. (1990), Sierka and Amy (1985), and Glaze et al. (1982) have all reported similar findings when treating water by UV/O₃.

As with all liquid phase O₃ processes, mass transfer limitations of O₃ into the liquid phase can severely decrease process efficiency and increase operating costs (Andreozzi et al. 1999). Another drawback of using O₃ arises when treating waters containing bromide, leading to the formation of bromate, a regulated carcinogenic byproduct (Xie 2004). For the stated reasons, the presence of UV/O₃ in commercial drinking water treatment is minimal (Sarathy & Mohseni 2006) and research has yet to convince industry that UV/O₃ is a feasible technology for the treatment of trace contaminants and/or NOM.

1.1.5.3 Vacuum UV

Low pressure mercury UV lamps have principle resonance lines at 185 nm and 254 nm. The lamps are typically constructed with a quartz envelope that permits transmission of only photons of 254 nm and above. By substituting the fused quartz envelope with a synthetic fused silica envelope, 90% of the 185 nm UV can be transmitted (Schalk et al. 2006). As 185 nm radiation lies within the vacuum UV range (i.e., less than 200 nm), the process involving the use of 185 nm radiation is referred to as VUV. During VUV irradiation of water 'OH are produced by the photolysis of water (Gonzalez & Braun 1995). Besides low pressure mercury UV lamps and their emission 185 nm radiation, excimer lamps have been designed
to emit at 172 nm. However, these lamps are currently very expensive so have limited practical applications.

Thomson et al. (2002) reported that VUV was five times more effective at reducing $A_{254}$ and DOC than UV irradiation with 254 nm alone. Parallel first-order kinetics were used to describe the reduction of $A_{254}$ for both lamps. Chromophores (i.e., species absorbing at 254 nm) were divided into three groups based on their reactivity (refractory, slow reacting, and quick reacting) and a kinetic model was applied to fit the experimental data. For the 254 nm UV process, most of the chromophores reacted slowly while only a small fraction was considered to be fast reacting since initially a fast drop in $A_{254}$ was observed. The VUV process differed in that the bulk of the chromophores reacted quickly. DOC removal was modeled using pseudo first order kinetics for the VUV process and zero order kinetics for the 254 nm UV process. Thomson et al. (2004b) reported that under similar conditions, VUV irradiation generated four times more $\text{H}_2\text{O}_2$, 25% less BDOC, and 30% less low MW carbonyl compounds than UV irradiation with 254 nm alone.

Buchanan et al. (2005) investigated the mechanisms by which NOM is transformed during VUV irradiation by studying the impact of the treatment on different chemical fractions (VHA, SHA, CHA, and NEU) of NOM. The VHA was found to be the most reactive during VUV treatment. The breakdown of the high MW hydrophobic acids led to the formation of biodegradable, low MW hydrophilics. The NEU fraction was reported to be the hardest to remove. Furthermore, Buchanan et al. (2006) went on to study the formation of hazardous by-products during VUV irradiation of NOM laden water. THM-FP was observed to slightly increase (insignificant when considering reported error bars) during VUV treatment at 254 nm fluences of about 20 000 and 40 000 mJ cm$^{-2}$, after which the THM-FP reduced with increasing the fluence. Although mineralisation of DOC led to a decrease in THM-FP, the amount of THM precursors in each of the fractions (VHA, SHA, CHA, and NEU) increased in the remaining DOC as indicated by increases in THM-FP per mg DOC. VUV treatment resulted in formation of $\text{H}_2\text{O}_2$. Buchanan et al. (2008) investigated the effectiveness of sequential VUV and BAC for the removal of NOM from natural water. VUV treatment resulted in rapid mineralisation of some fraction of NOM while the remaining NOM was increasingly biodegradable. The VUV+BAC process decreased the DOC concentration by 54%, THM-FPs by up to 70%, and HAA-FPs by 74%. (Buchanan et al. 2008). BAC was also demonstrated to remove the residual $\text{H}_2\text{O}_2$ produced during VUV irradiation (Buchanan et al. 2008).

Thus, VUV photooxidation has been shown to have major impacts on NOM but there is a need for further research to investigate the feasibility of VUV treatment for the removal of NOM in typical surface waters (low DOC, low $A_{254}$) and under fluences typically applied in UV-based AOPs (<2000 mJ cm$^{-2}$).
Also, the impacts of reactor pathlength and mixing need to be investigated in order to optimize treatment since 185 nm photons barely penetrate water.

1.2 Fundamentals of the UV/H$_2$O$_2$ Advanced Oxidation Process

In order to properly understand the impact of UV/H$_2$O$_2$ on NOM it is important to understand the mechanism by which 'OH is generated and the subsequent reactions that take place. In this section, basic photochemical theory, photochemical properties of H$_2$O$_2$, and chemical properties of 'OH are presented.

1.2.1 Photochemical Theory

Two laws of photochemistry are important with respect to UV/H$_2$O$_2$. The First Law of Photochemistry, the Grotthus-Draper Law, states that a photochemical reaction occurs only due to light absorbed by a molecule. In addition, the absorbed light must have enough energy to dissociate the weakest bond of the molecule. In the case of H$_2$O$_2$, photons with wavelengths less than or equal to 560 nm have enough energy to split the O-O bond (Bolton 2004). However, H$_2$O$_2$ absorbs negligibly at wavelengths above 300 nm and even at 254 nm the molar absorption coefficient of H$_2$O$_2$ is 19.6 L mol$^{-1}$ cm$^{-1}$ (Baxendale & Wilson 1957). This property of H$_2$O$_2$ has an impact on the performance of UV/H$_2$O$_2$ and will be discussed below.

The Second Law of Photochemistry, the Stark-Einstein Law, states that for each photon of light absorbed during a photochemical reaction, only one molecule can be activated. However, this does not mean that every photon absorbed by a molecule leads to a photochemical reaction.

Quantum yield is the term used to define the efficiency with which absorbed light produces some effect. It is defined as the number of times that a defined event occurs per photon absorbed by the system. In the case of UV/H$_2$O$_2$, the event is the photolysis of H$_2$O$_2$ yielding 'OH (Reaction 1). The overall quantum yield of this reaction has been found to be 1.0 for UV below 300 nm (Baxendale & Wilson 1957).

\[
\begin{align*}
(1) & \quad H_2O_2 + h\nu \rightarrow 2\cdotOH \\
(2) & \quad \cdotOH + H_2O_2 \rightarrow HO_2 + H_2O
\end{align*}
\]

At first glance this process looks highly efficient since one mole of H$_2$O$_2$ yields two moles of 'OH (Reaction 1). However, two key factors limit the efficiency of the process. First, since the molar extinction coefficient of H$_2$O$_2$ is very low, high concentrations of H$_2$O$_2$ are required to produce enough 'OH. However, this leads to the second problem, which is H$_2$O$_2$ itself scavenges the 'OH (Reaction 2). Therefore, high concentrations of H$_2$O$_2$ can reduce the effectiveness of the process (Wang et al. 1997; Ku
et al. 1998; Wang et al. 2000). Despite these limitations, with a high quantum yield, UV/H$_2$O$_2$ is regarded as being efficient for the generation of $\cdot$OH (Stefan & Williamson 2004).

### 1.2.2 Hydroxyl Radical Reactions

$\cdot$OH is highly reactive and short-lived. After fluorine, it is the most powerful oxidation agent with an oxidation potential of 2.8 V. On the downside, $\cdot$OH is non-specific so it will react with not only target contaminants, but also any species it comes in contact with.

In UV/H$_2$O$_2$ applications, $\cdot$OH can react with H$_2$O$_2$, other radicals (e.g., hydroperoxyl radical), target contaminants, and the water matrix (e.g., NOM, bicarbonate/carbonate). **Table 1.2** presents some of the species that $\cdot$OH can react with, the reaction pathways and the reaction rate constants. Since $\cdot$OH reacts rapidly with a large number of species and has a very short life, the concentration of $\cdot$OH is typically very low, 10$^{-13}$ to 10$^{-14}$ M, and it will not accumulate over time (Linden et al. 2007).

**Table 1.2** Hydroxyl radical reactions with various species found in water during UV/H$_2$O$_2$ advanced oxidation.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Reaction</th>
<th>Reaction Rate Constant (k)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen peroxide</td>
<td>$\cdot$OH + H$_2$O$_2$ → HO$_2$ + H$_2$O</td>
<td>2.7 x 10$^7$ M$^{-1}$ s$^{-1}$</td>
<td>(Buxton et al. 1988)</td>
</tr>
<tr>
<td>Hydroperoxyl radical</td>
<td>$\cdot$OH + HO$_2$ → O$_2$ + H$_2$O</td>
<td>6 x 10$^9$ M$^{-1}$ s$^{-1}$</td>
<td>(Buxton et al. 1988)</td>
</tr>
<tr>
<td>Carbonate</td>
<td>$\cdot$OH + CO$_3^{2-}$ → OH$^-$ + CO$_3^{-}$</td>
<td>3.9 x 10$^8$ M$^{-1}$ s$^{-1}$</td>
<td>(Buxton et al. 1988)</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>$\cdot$OH + HCO$_3^-$ → H$_2$O + CO$_3^{-}$</td>
<td>8.5 x 10$^6$ M$^{-1}$ s$^{-1}$</td>
<td>(Buxton et al. 1988)</td>
</tr>
<tr>
<td>Organic pollutants</td>
<td>P + $\cdot$OH → products</td>
<td>10$^6$ – 10$^{11}$ M$^{-1}$ s$^{-1}$</td>
<td>(Buxton et al. 1988)</td>
</tr>
<tr>
<td>Natural Organic matter</td>
<td>$\cdot$OH + TOC → products</td>
<td>2 x 10$^4$ L mgC$^{-1}$ s$^{-1}$</td>
<td>(von Sonntag 2007)</td>
</tr>
</tbody>
</table>

The mechanism by which $\cdot$OH attacks and breaks down organic carbon species, be it organic pollutants or NOM, is as follows. $\cdot$OH reacts with the organic compound either by OH addition to a carbon-carbon double bond or by abstraction of a carbon bound hydrogen (von Sonntag et al. 1997). Both mechanisms result in the formation of carbon-centred radicals (von Sonntag et al. 1997). These carbon-centred radicals quickly react with dissolved oxygen forming peroxyl radicals which, via numerous reactions, go on to form smaller carbonyl species which are eventually mineralized to carbon dioxide and water.

### 1.3 UV/H$_2$O$_2$ for Drinking Water Applications

The commercial application of UV/H$_2$O$_2$ in drinking water treatment processes dates back to the early 1990s. Sarathy & Mohseni (2006) overviewed UV/H$_2$O$_2$ applications in drinking water treatment, citing recent research and existing commercial installations. While earlier research (Baxendale & Wilson 1957;
Buxton et al. 1988) focused on the principles and theory behind UV/H\(_2\)O\(_2\) (i.e., quantum yields, reaction pathways, reaction rate constants, etc.), current research focuses mainly on the commercial application of UV/H\(_2\)O\(_2\). That is, much attention is paid to the effectiveness of UV/H\(_2\)O\(_2\) at treating specific drinking water contaminants including phenols (Esplugas et al. 2002; Fasnacht & Blough 2002), N-nitrosodimethylamine (Stefan & Bolton 2002; Sharpless & Linden 2003), methyl tert-butyl ether (Cater et al. 2000; Chang & Young 2000; Stefan et al. 2000; Kavanaugh et al. 2004), herbicides and pesticides (Kruithof et al. 2002), and taste and odour compounds such as 2-methylisoborneol and geosmin (Linden et al. 2005; Korategere et al. 2004; Rosenfeldt et al. 2005).

1.3.1 UV/H\(_2\)O\(_2\) Technology

The application of UV/H\(_2\)O\(_2\) for commercial drinking water treatment involves a continuous flow system including one or more UV reactors and a H\(_2\)O\(_2\) dosing component. The two key parameters that are of importance in the process are the UV fluence and the H\(_2\)O\(_2\) concentration.

UV fluence is the total radiant energy of all wavelengths received by an infinitesimally small sphere. It is the product of the fluence rate and the exposure time. The fluence rate is the total radiant power of all wavelengths received by an infinitesimally small sphere (Bolton 2004). The fluence rate of a UV source can be measured by using an actinometer, a chemical system or a physical device by which the number of photons in a beam absorbed into the defined space of a chemical reactor can be determined per unit time (Kuhn et al. 2004). A chemical actinometer is a substance, with a known quantum yield, which undergoes a photochemical conversion directly related to the number of photons absorbed. By measuring the rate of formation of product, the absorbed photon flux, or fluence rate, can be calculated (Kuhn et al. 2004). Kuhn et al. (2004) listed numerous chemical actinometers and standard procedures for use in the wavelength range from the UV to the red region of the spectrum. Physical devices, such as radiometers, are becoming more popular because of their ease of use and fast measurement of radiation output. However, they require frequent calibration and can deteriorate over time. Therefore, chemical actinometers are more accurate and reproducible than physical devices (Kuhn et al. 2004).

Once the fluence rate of a UV source is known, the fluence can be calculated by multiplying the fluence rate by the irradiation time. For flow-through reactors, the flowrate and reactor volume determine the irradiation time. Therefore, for a given reactor the fluence can be adjusted by manipulating the flowrate of the system. However, it should be noted that in annular reactors the relationship between fluence and flowrate is not linear due to hydraulic efficiency effects. Ideally, UV is delivered evenly to each fluid volume of water within the reactor (Stefan & Williamson 2004). However, hydrodynamic features such as internal baffles, upstream piping design, and entrance and exit configurations affect radial
and axial mixing of water within a reactor thus causing non-uniform flow (Stefan & Williamson 2004). In general, at high flowrates mixing efficiency is higher thanks to increased turbulence while at lower flowrates mixing efficiency drops thus reducing the fluence delivered to the entire water volume (Stefan & Williamson 2004). Fluence is also dependent on the number of lamps in the reactor, the placement and orientation of the lamps, and the amount of reflection off reactor walls (Bolton 2004; Stefan & Williamson 2004).

The H₂O₂ concentration inside the reactor is adjusted by dosing concentrated stock H₂O₂ into the feed water stream upstream of the UV reactor. Based on the desired concentration, the water flowrate, and the concentration of the stock, the dosing rate of H₂O₂ is set. Adequate mixing should take place prior to entering the UV reactor to ensure that H₂O₂ is uniformly distributed in the water.

1.3.2 Ultraviolet Lamps

There are currently two types of lamp technologies applied in drinking water UV/H₂O₂ applications: low-pressure (LP) amalgam lamps and medium-pressure mercury (Hg) lamps (MP). Key differences between these lamps are the emission spectrum and UV flux per unit arc length.

LP amalgam lamps are similar to LP Hg lamps but can have five times the UV flux per unit arc length (Schalk et al. 2006). This is achieved by substituting pure Hg with Hg amalgams with bismuth or indium (Heering 2004). LP amalgam lamps are particularly appealing for UV/H₂O₂ applications because they can achieve much higher fluence rates in the same footprint as LP Hg lamps. Both LP Hg and LP amalgam lamps have principle resonance lines at 185 nm and 254 nm and are about 35% efficient at converting electrical energy to UV at 254 nm. Typically LP lamps are constructed of a quartz envelope that permits transmission of only photons of 254 nm and above. By substituting the fused quartz envelope with a synthetic fused silica envelope 90% of 185 nm UV can be transmitted (Schalk et al. 2006). This technology can offer performance advantages to UV/H₂O₂ since 185 nm UV is easily absorbed by H₂O₂ and also 185 nm effectively photolyzes water yielding \(^{•}\text{OH}\).

MP lamps have a much higher UV flux per unit arc length than LP amalgam lamps, <35 W cm\(^{-2}\) versus <1 W cm\(^{-2}\) (Schalk et al. 2006). Therefore, MP lamp based reactors have much smaller footprints than LP amalgam based reactors designed for similar output. However, MP lamps also consume much more electrical energy and are less efficient at 5-15% UVC efficiency (Schalk et al. 2006). The key advantage offered by MP lamps is their ability to output a polychromatic spectrum. This is particularly useful in applications where direct photolysis of contaminants occurs at wavelengths other than 254 nm. MP lamps are typically constructed with a fused quartz envelope.
1.3.3 Operating Parameters of Commercial UV/H₂O₂ Installations

Kruithof et al. (2005) reported that when using a pilot-scale medium pressure mercury lamp reactor a fluence of 540 mJ cm⁻² and an initial H₂O₂ concentration of 6 mg L⁻¹ was needed to achieve at least 60% reduction in various organic contaminants in IJssel Lake water, Andijk, Netherlands (Kruithof et al. 2005). Martijn et al. (2005) subsequently reported on the ability of the full-scale UV/H₂O₂ installation in Andijk, Netherlands to achieve 80% atrazine degradation in IJssel Lake water using medium pressure reactors at a fluence of 540 mJ cm⁻² and an initial H₂O₂ concentration of 6 mg L⁻¹ (Martijn et al. 2005).

For a UV/H₂O₂ application in Aurora, Colorado, Swaim et al. (2007) reported that when using a low-pressure mercury lamp system a fluence of 857 mJ cm⁻² and an initial H₂O₂ concentration of 5 mg L⁻¹ was required to achieve a 1.2 log reduction of NDMA, reduction of taste and odour contaminants to below human odour threshold, and an 86% destruction of microcystin (Swaim et al. 2007).

These are just a few examples to provide a perspective of the range of operating parameters for commercial UV/H₂O₂ installations for the treatment of trace organic pollutants. In general, an initial H₂O₂ concentrations up to 15 mg L⁻¹ and fluence s up to 1500 mJ cm⁻² are deemed acceptable both from economical and energy requirement standpoints, using current technology (in communication with Trojan Technologies).

1.4 Modeling the UV/H₂O₂ Process

Designing a UV/H₂O₂ system for a practical application necessitates the prediction of H₂O₂ concentration and fluence requirements to achieve the desired levels of contaminant removal (Tühkanen 2004). There are a number of mathematical models, based on photochemical and chemical engineering principles, describing the UV/H₂O₂ AOP (Glaze et al. 1995; Liao & Gurol 1995; Stefan et al. 1996; Crittenden et al. 1999; Sharpless & Linden 2003; Song et al. 2008). Most of these models use a pseudo-steady-state assumption for the concentration of °OH. That is, it is assumed that the net formation rates of °OH is zero. Since °OH reacts rapidly with so many species, the concentration of °OH is very low and will not accumulate over time, so the pseudo-steady-state assumption is applicable (Linden et al. 2007).

Glaze et al. (1995) developed a kinetic model, applying the pseudo-steady-state assumption, for the oxidation of organics in water by UV/H₂O₂ using LP UV. The model involved a series of equations including the photolysis of H₂O₂ by UV, direct photolysis of the organic contaminant, and °OH reactions using rate constants obtained from the literature. The effect of UV intensity (and fluence), initial H₂O₂ concentration, and alkalinity were parameters that the model could incorporate to predict the destruction of an organic contaminant. While the model considered most of the important reactions in the system, it
Liao & Gurol (1995) also applied the pseudo-steady-state assumption to model the removal of organic pollutants from aqueous solution by UV/H\textsubscript{2}O\textsubscript{2} using LP UV. An approach similar to that of Glaze et al. (1995) was used for the kinetics of the reactions that take place in the system. In addition to alkalinity, UV intensity, and H\textsubscript{2}O\textsubscript{2} dosage, Liao & Gurol’s model included the effect of humic substance concentration. The authors considered both the effect of light screening by humic substances and \textsuperscript{'OH} scavenging. Yet, the model did not account for the reduction in light screening that occurs as humic substances are oxidized by \textsuperscript{'OH}. Liao & Gurol (1995) also compared model predictions of H\textsubscript{2}O\textsubscript{2} degradation to experimental results for UV/H\textsubscript{2}O\textsubscript{2} treatment with NOM present. Model predictions for H\textsubscript{2}O\textsubscript{2} degradation were slightly lower than experimental measurements (deviation not quantified) and were attributed to the model not including chain-promoting effect humic substances may have on H\textsubscript{2}O\textsubscript{2} degradation (Liao & Gurol 1995).

Stefan et al. (1996) derived a pseudo-steady-state approximation based model for the degradation of acetone using MP UV in a UV/H\textsubscript{2}O\textsubscript{2} system. A reaction mechanism for the mineralisation of acetone was proposed and a kinetic model was developed. The model was capable of generating a profile of the reactants and intermediates with good agreement to the experimental data. The model was very comprehensive with respect to the breakdown of acetone but it did not consider the effects of natural water constituents, such as bicarbonate and NOM.

Crittenden et al. (1999) developed the first dynamic model for the UV/H\textsubscript{2}O\textsubscript{2} destruction of organic contaminants. Also, outstandingly, the model considered the decrease in pH that occurs as a result of the formation of mineral acids and carbon dioxide. While the model gave better predictions than those based on the pseudo-steady-state assumption, it required proprietary software, commercialized as AdOx\textsuperscript{TM}, to carry out the solution of multiple differential equations. The model considered water quality parameters including alkalinity, phosphate ions, and humic substances. However, no attempt was made to see how the model fit experimental data gathered from tests done on natural waters. Also, the model did not account for the reduction in light screening that occurs as humic substances are oxidized by \textsuperscript{'OH}. The model’s ability to predict H\textsubscript{2}O\textsubscript{2} degradation was not reported.

Sharpless & Linden (2003) modeled the degradation of N-nitrosodimethylamine in synthetic “natural” water using LP and MP lamps with and without the addition of H\textsubscript{2}O\textsubscript{2}. The model used the
steady-state assumption (i.e., concentration of \( \cdot \)OH is constant over time) along with standard equations of photochemistry and was similar to the work done by Glaze et al. (1995) and Liao & Gurol (1995). This steady-state \( \cdot \)OH model incorporated terms for \( \cdot \)OH scavenging by NOM, alkalinity, and H\(_2\)O\(_2\). The model was successfully applied to experimental data gathered in the research and has also been successfully applied since (Rosenfeldt & Linden 2004; Rosenfeldt et al. 2005; Linden et al. 2007). Like previous models, it did not consider the change in water absorbance during treatment. Further, it did not have the ability to predict H\(_2\)O\(_2\) degradation since it assumed the degradation of H\(_2\)O\(_2\) was negligible, a valid assumption under short irradiation times.

Since the steady-state \( \cdot \)OH model relied on generic rate constants and surrogate NOM parameters to determine the \( \cdot \)OH scavenging factor of water, Rosenfeldt and Linden (2007) introduced the R\(_{\text{OH,UV}}\) concept into the steady-state \( \cdot \)OH model. R\(_{\text{OH,UV}}\) was defined as the experimentally determined \( \cdot \)OH radical exposure per UV fluence (Rosenfeldt & Linden 2007). It was reported that by replacing the generic water scavenging factor with the R\(_{\text{OH,UV}}\) term, improvements were made to model predictions of 17-\( \alpha \)-ethinyl estradiol and 17-\( \beta \)-estradiol in natural waters (Rosenfeldt & Linden 2007). The authors identified one drawback was that the tool was specific for a set of water conditions, so as water quality changes due to climatic and geographical conditions, scavenging and absorption characteristics would be affected, and thus R\(_{\text{OH,UV}}\) would need to be determined again (Rosenfeldt & Linden 2007).

Most recently, Song et al. (2008) presented a mechanistic, kinetic model for predicting the degradation of alachlor. The model considered all species dynamic and included the impacts of NOM and alkalinity, as well as the pH decrease that occurred during NOM mineralisation. The model attempted to predict H\(_2\)O\(_2\) degradation but it did not account for the reduction in screening of 254 nm UV that occurred as NOM was oxidized by \( \cdot \)OH. The model was very complete and, in general, an improvement on the AdOx\(^{\text{TM}}\) model in that it validated model predictions with experimental data gathered using natural waters. Overall, the model performed well but slightly overestimated reaction rates for water containing NOM at low pH (Song et al. 2008). It was utilised to provide insight into the complex free-radical reactions, mechanisms and kinetics for optimization of the UV/H\(_2\)O\(_2\) process (Song et al. 2008). Also, commendably, the model equations and solution were presented such that other researchers could reproduce it quite easily, unlike the AdOx\(^{\text{TM}}\) model. Yet, a few drawbacks to the model warrant improvement. First of all, the model under predicted the degradation of H\(_2\)O\(_2\) indicating that certain mechanisms were overlooked. While the model predicted the transformation of NOM, using absorbance at 310 nm as a surrogate, it did not incorporate this transformation into the rest of the model to observe how it would impact overall predictions including H\(_2\)O\(_2\) degradation. It seems unnecessary to use the absorbance at 310 nm to track changes in NOM especially considering that the characteristic wavelength
in such systems is 254 nm. Further, the model and experiments focussed on long irradiation times (i.e., high fluences) at which NOM was mineralized. Such conditions are excessive in industrial drinking water applications so the model was not demonstrated to be applicable, with respect to \( \text{H}_2\text{O}_2 \) and NOM degradation, under feasible advanced oxidation conditions.

### 1.5 Impacts of the UV/\( \text{H}_2\text{O}_2 \) Process on Natural Organic Matter

UV/\( \text{H}_2\text{O}_2 \) is applied for the treatment of trace contaminants in drinking water and yet its impact on NOM under the applied conditions has not gained much attention.

Kleiser & Frimmel (2000) exposed river water, with DOC of 2.3 mg L\(^{-1}\) and \( A_{254} \) of 0.042 cm\(^{-1}\), to a LP lamp in the presence of 4, 8, and 16 mg L\(^{-1}\) \( \text{H}_2\text{O}_2 \). An increase in THM-FP was observed after short irradiation times, less than 100 min. Under these irradiation times DOC removal was minimal. However, THM-FP dropped at an irradiation time of 1050 min and was attributed to the observed mineralisation of DOC. Fluences were not reported, but it is likely that the oxidation conditions at 100 min were similar to those typically found drinking water applications.

Liu et al. (2002) investigated the impact of LP, MP, and pulsed UV based UV/\( \text{H}_2\text{O}_2 \) technologies on DBP formation (THMs, HAAs, aldehydes and carboxylic acids) over a broad range of UV fluences (germicidal fluences up to 6500 mJ cm\(^{-2}\)) at a \( \text{H}_2\text{O}_2 \) dosage of 100 mg L\(^{-1}\). The results showed that at fluences up to 500 mJ cm\(^{-2}\), LP UV/\( \text{H}_2\text{O}_2 \) increased the THM-FPs and HAA-FPs by a maximum of 19% and 9%, respectively. Similarly, MP UV/\( \text{H}_2\text{O}_2 \) increased the THM-FPs and HAA-FPs by a maximum of 11% and 9%, respectively. These small increases in DPB-FPs were stated to be insignificant by the authors. At high UV fluences of 5000-6500 mJ cm\(^{-2}\), THMs and HAAs were reduced by approximately 50% by both LP and MP based processes. At such high UV fluences DBP-FPs are expected to drop since mineralisation of NOM occurs but such extensive treatment is not feasible for commercial applications due to the energy requirements. Also, the \( \text{H}_2\text{O}_2 \) concentration of 100 mg L\(^{-1}\) is much higher than those used for commercial applications, typically less than 20 mg L\(^{-1}\). UV/\( \text{H}_2\text{O}_2 \) also resulted in the formation of aldehydes and carboxylic acids at UV fluence above 140 mJ cm\(^{-2}\) (Liu et al. 2002). Although the work of Liu et al. (2002) provided valuable insight on how the oxidation of NOM during UV/\( \text{H}_2\text{O}_2 \) impacted water quality parameters, the results are not very informative for what occurs to NOM during the commercial UV/\( \text{H}_2\text{O}_2 \) treatment of drinking water. This is largely due to the lack of data for fluences between 500 and 2000 mJ cm\(^{-2}\) and the high \( \text{H}_2\text{O}_2 \) concentration.

Speitel et al. (2000) conducted experiments to assess the performance of LP UV/\( \text{H}_2\text{O}_2 \) with subsequent biodegradation for the removal of TOC and DBP precursors using two highly absorbing
natural waters. It was shown that increasing the LP UV irradiation during the LP UV/H$_2$O$_2$ process increased the BDOC and decreased TOC and A$_{254}$ of the water. Speitel et al. (2000) did not report the results in terms of fluence so it is difficult to compare these results to those of other studies. Also, H$_2$O$_2$ concentrations used were not clearly defined. Since the mineralisation of TOC was observed, it was likely that the oxidation conditions were strong (i.e., high fluences or high H$_2$O$_2$ dosage). This also justifies the observed 23% decrease in DBP-FP (Speitel et al. 2000). Furthermore, the study provided proof-of-concept on the effectiveness of LP UV/H$_2$O$_2$ combined with downstream biological treatment, but it did not give much information on the impact of LP UV/H$_2$O$_2$ specifically on NOM.

Wang et al. (2006) evaluated LP UV/H$_2$O$_2$ oxidation for the degradation of NOM in water. About 90% of humic acid was removed after 30 minutes of irradiation in the 10 L batch reactor using a 450 W high-pressure Hg vapour lamp in the presence of 0.01% H$_2$O$_2$. Specific UV fluences were not reported but due to the observation of TOC destruction it was likely fluences were very high (i.e., far greater than those in commercial applications). First-order kinetics were used to describe the kinetics of H$_2$O$_2$ and humic acid destruction. The molecular size distribution of humic substances was observed to shift towards smaller sizes as a result of the degradation of larger humic substances. THM-FP was also reduced, by up to 80%, largely due to the reduction of TOC. The research was quite unique in that Fourier transform infrared spectra was used to determine how LP UV/H$_2$O$_2$ affected the structure of NOM. Observed changes included destruction of functional groups of humic acid, including –OH (from –COOH and –COH), aromatic, -C=C, and –C=O conjugated aromatic rings. This study focused on the degradation of NOM during UV/H$_2$O$_2$ under strong treatment conditions and not the transformation of NOM under moderate treatment conditions.

Thomson et al. (2002) and Thomson et al. (2004b) focused on using LP UV/H$_2$O$_2$ and VUV for the decolourization of water laden with high amounts of NOM (>11 mg L$^{-1}$ TOC). Thomson et al. (2002) investigated the kinetics, mechanisms, and feasibility of treating highly coloured natural water by H$_2$O$_2$ with LP UV and VUV. Kinetic, but not mechanistic, models were applied to the data as a tool to understand the mechanisms that may take place and to give a basis for process scale-up. NOM degradation was described to occur in three parts: simultaneous rapid reduction of chromophores and H$_2$O$_2$ photolysis, followed by mineralisation of DOC. The reduction in chromophores was modeled using parallel first order kinetics. The model constants were calculated by minimizing the sum of square differences between the model and experimental data. The model suggested that chromophores were split into two different groups based on their reactivity: quick reacting chromophores reacted with OH while they were present (i.e., low fluences, H$_2$O$_2$ present) and slow reacting chromophores were removed through photooxidation (i.e., high fluences, H$_2$O$_2$ depleted). H$_2$O$_2$ concentration was accurately modeled
using a photochemical rate equation developed from the Beer-Lambert Law with the change in $A_{254}$ considered. DOC mineralisation followed pseudo first order kinetics and the rate of degradation was proportional to the initial $H_2O_2$ concentration. This was explained by assuming there was a pseudo-steady-state concentration of $\cdot OH$ in the reactor and the formation of $\cdot OH$ from $H_2O_2$ photolysis was equal to the loss of $\cdot OH$ due to reaction with DOC and $H_2O_2$. Loss of $\cdot OH$ due to reaction with carbonate scavengers was neglected. Therefore, there is a need to improve the model of Thomson et al. (2002) by incorporating the degradation of $H_2O_2$ and chromophoric NOM into the calculation of the steady-state $\cdot OH$ concentration, under LP UV/$H_2O_2$ conditions at which mineralisation of DOC does not take place. Thomson et al (2004b) also found that irradiation by VUV was more efficient than LP UV for $H_2O_2$ doses less than 15 mg L$^{-1}$ while at doses greater than 15 mg L$^{-1}$ the performance of the two systems became similar. Size exclusion chromatography revealed that treatment by VUV and 10.8 mg L$^{-1}$ of $H_2O_2$ preferentially removed larger molecules except in the initial stages.

Thomson et al. (2004a) studied the depolymerisation of chromophoric NOM by $\cdot OH$ generated by LP UV and VUV in the presence of $H_2O_2$. Both processes were found to preferentially oxidise higher MW materials. The simple depolymerisation model described above was successfully applied to the data. However, experimental results were insufficient and not in complete agreement to conclude confidently that the model accurately described degradation of chromophoric NOM by $\cdot OH$. Therefore, research is necessary to gather more experimental data to validate theoretical models and even to advance existing models.

Further to the above, Thomson et al. (2004b) used LP UV/$H_2O_2$ and VUV to investigate the removal of NOM from highly absorbing, high TOC, surface water. Since the water was high in TOC (15 mg L$^{-1}$) and high in $A_{254}$ (0.55 cm$^{-1}$), the fluence range studied was very high, 6000 to 450000 mJ cm$^{-2}$ but $H_2O_2$ dosage, at less than 15 mg L$^{-1}$, was within the feasible range for UV/$H_2O_2$ treatment of trace contaminants in drinking water. It was reported that the reduction of $A_{254}$ followed parallel first order kinetics. Increases in THM-FP, chlorine demand, BDOC, and low MW carbonyls were observed at lower fluences, likely prior to mineralisation of DOC.

Toor & Mohseni (2007) studied LP UV/$H_2O_2$ for the removal of DBP precursors and formation potentials from surface drinking water with a TOC less than 2.5 mg L$^{-1}$ and $A_{254}$ below 0.1 cm$^{-1}$. At an initial $H_2O_2$ concentration of 4 mg L$^{-1}$, THM-FP increased initially at fluences up to about 1000 mJ cm$^{-2}$ and then decreased as fluences increased to more than 2000 mJ cm$^{-2}$. Similarly, HAA-FP was reported above the initial levels for fluences up to about 2500 mJ cm$^{-2}$ after which decreases were observed. Also, mineralisation of TOC occurred at fluences greater than 2500 mJ cm$^{-2}$. At an initial $H_2O_2$ concentration of 23 mg L$^{-1}$, $H_2O_2$ concentration decreased linearly to 10 mg L$^{-1}$ and then seemed to plateau at fluences
equal to and greater than 1 500 mJ/cm^2. The work concluded the LP UV/H_2O_2, as a standalone treatment, is effective at reducing DBP-FPs but the energy requirements associated with the high UV fluence may make it economically unattractive. At lower fluences (500-1000 mJ cm^-2), however, substantial increases in BDOC were observed. Proof of concept studies showed that a combination of UV/H_2O_2 and downstream BAC treatment might be an effective and economically viable treatment for the removal of DBP precursors.

Parkinson et al. (2001) investigated the potential toxicity of 254 nm UV/H_2O_2-treated aquatic NOM. Toxicity measurements included *Vibrio fischeri* in the Microtox™ test, African green monkey kidney cells, and *Daphnia carinata* in an acute immobilization test. Toxicity was not apparent for the Microtox™ or kidney cells. However, UV/H_2O_2 treated water was acutely toxic to *D. carinata* after long irradiation times. This was attributed to the presence of copper ions that were released from NOM-metal binding sites (Parkinson et al. 2001). For human toxicity this would only be a problem if the concentration of copper in water was significantly high, in which case it would not be suitable for drinking. The fluences were not specifically reported but UV/H_2O_2 did not impact the toxicity of water at short irradiation times with the employed H_2O_2 concentration of 50 mg L^-1.

1.6 Thesis Scope

The scope of this work was to investigate the UV/H_2O_2 process and its impact on NOM at fluences and initial H_2O_2 concentrations typically found in commercial drinking water applications for the removal of trace pollutants and other undesirable compounds. This research aimed to contribute substantially to the understanding of NOM transformation as a result of reaction with •OH. By applying NOM characterization techniques to monitor the transformation of NOM during UV/H_2O_2 treatment, this research aimed to provide information supporting practical implications on water quality. Further, it was the objective to confirm whether or not characteristic changes in NOM led to changes in water quality by determining the impacts on DBP-FPs and biological stability. Thus, the research aimed to give the field a thorough assessment of how the application of UV/H_2O_2 to drinking water affects NOM and related water quality parameters (e.g., DBP-FPs, BDOC, and AOC).

Natural organic matter in two natural, raw, non pre-treated waters as well as NOM in one water pre-treated by two different processes was characterized before and during UV/H_2O_2 treatment.

Also, of emphasis, is that this research was conducted in close collaboration with Trojan Technologies, the industry leader in drinking water UV/H_2O_2 applications. In total, one year was spent at
1.7 Thesis Objectives

Within this scope, the specific objectives of this research were to:

1. Examine the effects of low pressure mercury amalgam lamps and
   - UV fluence: 0 to 2000 mJ cm\(^{-2}\)
   - H\(_2\)O\(_2\) concentration: 0 to 20 mg L\(^{-1}\)

   on the following metrics:
   - TOC concentration
   - spectroscopic properties of NOM
   - molecular weight distribution of NOM
   - hydrophobicity of NOM
   - THM-FPs and HAA-FPs
   - aldehydes concentration
   - BDOC
   - AOC
   - Residual H\(_2\)O\(_2\) concentration

   found in:
   - non-pretreated (raw) water obtained from Capilano Reservoir and Trepanier Creek
   - water from Capilano Reservoir pretreated by ultrafiltration
   - water from Capilano Reservoir with the very hydrophobic acid fraction of NOM removed

2. Develop a method utilizing a natural consortium of microorganisms, fluorescence staining, and flow cytometry for determination of AOC of UV/H\(_2\)O\(_2\) treated water.

3. Develop a dynamic and mechanistic kinetic model to predict
   - Degradation of H\(_2\)O\(_2\)
   - Reduction of chromophoric (i.e., 254 nm UV absorbing) natural organic matter

   during UV/H\(_2\)O\(_2\) treatment under varying UV irradiation time, initial H\(_2\)O\(_2\) concentrations, and levels of alkalinity.

4. At pilot scale, examine the effects of:
   - UV source: low pressure amalgam lamp
   - UV irradiation time
   - H\(_2\)O\(_2\) concentration

   on:
   - residual H\(_2\)O\(_2\)
   - BDOC
• aldehydes concentration
• THM-FPs and HAA-FPs
• spectroscopic properties of NOM
• TOC concentration

5. Compare the effectiveness of biological activated carbon and UV/H$_2$O$_2$ plus biological activated carbon as treatment strategies for NOM removal.

1.8 Thesis Layout

The above objectives were approached from various angles throughout the course of the research. This dissertation compiles the results and discusses them in the form of six unique manuscripts, each constituting one of the following six chapters. Not all the research results are included in the manuscripts so these data have been presented in the appendices. Following is a detailed description of how each of the above objectives has been met with respect to their presentation in the following chapters and/or appendices.

Chapter 2 contributes primarily to meeting Objective 1. It reports on the initial studies conducted using a commercially available low pressure Hg lamp UV reactor and one natural water and the same water treated by ultrafiltration. The impact of fluence and initial H$_2$O$_2$ concentration on TOC, spectroscopic properties of NOM, hydrophobicity of NOM, and BDOC are reported. Further, the impact of fluence and initial H$_2$O$_2$ concentration on the formation of aldehydes is reported for water from Capilano Reservoir treated by UV/H$_2$O$_2$ using a bench scale apparatus.

Chapter 3 presents an in depth look into the impact of fluence and initial H$_2$O$_2$ on the apparent molecular weight distribution of NOM. In this study, water from Capilano Reservoir and the same water treated by ultrafiltration were treated by UV/H$_2$O$_2$. Also noteworthy was the development and utilisation of a peak fitting procedure to convert qualitative HSPEC data to quantitative terms. Thus, Chapter 3 contributes to meetings objectives laid out under Objective 1.

Chapter 4 further contributes to Objective 1. In Chapter 4 the impact of fluence and initial H$_2$O$_2$ concentration on spectroscopic properties NOM, THM-FPs, HAA-FPs, and hydrophobicity of NOM is revisited. Water from Capilano Reservoir and the same water with the very hydrophobic acid fraction of NOM removed were treated by UV/H$_2$O$_2$ with a bench scale apparatus. The method of hydrophobic fractionation for this study was improvement over the one applied in Chapter 2, thus providing more accurate and reliable results. Further, DBP-FPs tests were done with numerous replicates and under tightly controlled conditions to ensure the most robust and reliable results.
Chapter 5 contributes primarily to meeting Objective 3. In Chapter 5 a mechanistic kinetic model that considers all species dynamic is developed to characterize the UV/H_2O_2 system. UV/H_2O_2 experiments were conducted using isolated NOM to create a “synthetic” water and results from the treatments were used to estimate model parameters. Subsequently, the model was applied to predict the degradation of H_2O_2 and chromophoric NOM during UV/H_2O_2 treatment of two natural waters along with these waters amended with additional alkalinity. Since spectroscopic properties of NOM and residual H_2O_2 are discussed for the both water from Capilano Reservoir and water from Trepanier Creek, Chapter 5 also contributes to Objective 1.

Chapter 6 contributes to meeting Objectives 1, 4, and 5. It reports on a concurrent study that used an industrial scale low pressure Hg lamp UV reactor and water from Fanshawe Lake to study the impact of fluence on the spectroscopic properties of NOM, THM-FPs, HAA-FPs, BDOC, and aldehydes concentration. Further, the performance of integrated UV/H_2O_2 and biological activated carbon is presented and discussed. Related results from this study are presented in Appendix D, which addresses Objectives 4 and 5 by presenting the results obtained using an industrial scale medium pressure Hg lamp UV reactor along with integration with downstream biological activated carbon.

The BDOC method applied to generate the data presented in Chapter 2, Chapter 6, and Appendix D provided far from ideal results. Therefore, attention was switched to the development of an AOC determination method and applying it to UV/H_2O_2 treated waters. AOC was preferred since it provides more valuable and relevant information for drinking water treatment systems. Chapter 7 presents research done towards developing in house capabilities of AOC determination and utilising this method for assessing the impact of fluence on the AOC of water from Capilano Reservoir treated by UV/H_2O_2. Thus, Chapter 7 addresses Objectives 1 and 2.

In Appendix A, additional data not contained within the manuscripts is presented. Presented first, contributing to Objective 1, is the influence of alkalinity on the concentration of aldehydes during UV/H_2O_2 treatment of water from Capilano Reservoir and water from Trepanier Creek. Next, the use of UV absorbance as an indicator parameter for the change in the hydrophilic fraction of natural organic matter and aldehydes concentration is presented. This work is considered to be closely tied to Objective 3 since, in combination with the kinetic model, the surrogate parameter could be used to predict changes in water quality. Presented third, contributing to Objective 1, is the influence of alkalinity on the molecular weight distribution of NOM during UV/H_2O_2 treatment of water from Capilano Reservoir and water from Trepanier Creek. Fourth is the impact of UV/H_2O_2 on Nordic Reservoir Natural Organic Matter synthetic water. This work was done with relation to Objective 3 but was not included in the manuscript. Finally,
characteristics of Nordic Reservoir Natural Organic Matter and Suwannee River Natural Organic Matter are compared.

Appendix B provides details about experimental protocols and analytical methods. Appendix C includes the programming code and sample calculations associated with Chapter 5 and Objective 3.

1.9 Reproducibility of Experiments and Statistical Analysis

In order to consider the reproducibility of the UV/H₂O₂ treatment experiments, experimental runs in Chapter 2, Chapter 3, and Chapter 4 were done in duplicate. In Chapter 2 and Chapter 3, the results are presented as the average of the two runs. In Chapter 4, results from each run are presented separately.

For the DBP-FP tests done in Chapter 4, chlorination of samples was done in triplicate and the reported values are the average DBP-FPs over the three chlorinated samples. Similarly, for the AOC measurements done in Chapter 7, triplicate samples were inoculated and incubated and the reported values are the average AOC values over the three incubated samples.

H₂O₂, TOC, spectroscopic, HPSEC, and aldehydes analysis were all done in duplicate. In other words, the respective analytical methods were carried out twice for each sample and the average reported.

In Chapter 2 and Chapter 3, error bars in figures are meant strictly for illustration as they represent the standard deviation for the results obtained over two UV/H₂O₂ runs. In Chapter 4, error bars on figures represent the standard deviation for the three triplicate DBP-FP tests. Thus, error bars in Chapter 4 are presented to indicate the statistical reproducibility of the DBP-FP tests. In Chapter 7 error bars in figures represent the standard deviation of the triplicate sample incubations.
Literature Cited


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USEPA. (1995b) Method 552.2: Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatization and gas chromatography with electron capture detection.


Chapter 2
The Fate of Natural Organic Matter during UV/H₂O₂ Advanced Oxidation of Drinking Water

2.1 Introduction

Under strong advanced oxidation (AO) conditions (i.e., long irradiation time and/or high initial H₂O₂ concentration), studies have found that natural organic matter (NOM) can be mineralized leading to a reduction in DBP formation (Kleiser & Frimmel 2000; Speitel et al. 2000; Liu et al. 2002; Thomson et al. 2002, 2004; Toor & Mohseni 2007; Wang et al. 2006). These studies employed high ultraviolet (UV) fluences and/or H₂O₂ concentrations, well above the range of conditions typically applied for the oxidation of organic pollutants in drinking water (up to 1500 mJ cm⁻² and 20 mg L⁻¹ H₂O₂). Since such strong AO conditions are not economically feasible, UV/H₂O₂ AO has not been deemed a viable technology for the removal of NOM and/or disinfection by-product (DBP) precursors.

Yet, it has been demonstrated that under milder AO conditions (i.e., shorter irradiation times and/or lower initial H₂O₂ concentrations), within the range of accepted conditions for commercial applications for organic pollutant removal, NOM undergoes partial oxidation. This partial oxidation leads to a reduction in aromaticity of NOM (Thomson et al. 2002, 2004a, 2004b; Section 3.3.1), a reduction in high molecular size chromophoric (i.e., 254 nm UV absorbing) species with concomitant formation of lower molecular size chromophores (Thomson et al. 2004a; Section 3.3.1), and an increase in biodegradable organics such as biodegradable organic carbon (BDOC) and low molecular weight compounds (Speitel et al. 2000; Liu et al. 2002; Thomson et al. 2004b). Yet, most previous studies have focussed on UV/H₂O₂ AO as a treatment for the removal of NOM. Few have investigated how NOM is transformed during milder AO conditions and what implications this has on overall water quality.

In order to better understand the extent of NOM transformation and its potential impacts on water characteristics, this research took a detailed look at the impact of UV/H₂O₂ AO on a surface water NOM concentration, spectral characteristics, hydrophobicity, and biodegradability under AO conditions typically applied in drinking water applications. Furthermore, this surface water was pre-treated by membrane ultrafiltration (UF) to remove the large molecular weight fraction of NOM and subsequently went through treatment by UV/H₂O₂. This allowed observation of how UV/H₂O₂ AO may impact NOM
when NOM has been altered such that the concentration of NOM has been reduced and high molecular size species have been removed.

2.2 Materials and Methods

These experiments comprised a preliminary study to understand NOM transformation under conditions near mineralization. The UV fluences applied were selected based on their relation to commercial drinking water applications (i.e., less than 2000 mJ cm\(^{-2}\)). The initial H\(_2\)O\(_2\) concentration of 20 mg L\(^{-1}\) was selected based on its applicability for commercial drinking water applications. However, it was later understood that this high level of H\(_2\)O\(_2\) would be excessive in applications where UV/H\(_2\)O\(_2\) would be used for micro pollutant removal (in communication with Trojan Technologies). The membrane filtration unit for this study was selected as previous research in this group employed it on the same water (Chowdhury et al. 2008). The molecular weight cut off was selected as the objective was to carry out ultrafiltration while not entirely removing NOM.

In order to consider the reproducibility of the UV/H\(_2\)O\(_2\) treatment experiments, duplicate runs were conducted. The data presented in this chapter are the average values of the two separate UV/H\(_2\)O\(_2\) runs. Error bars in figures are meant strictly for illustration as they represent the standard deviation for the results obtained over two UV/H\(_2\)O\(_2\) runs. For example, the error bars for SUVA values in Figure 2.3 represent the standard deviation between the SUVA values for the two individual runs.

2.2.1 Experimental Waters

Two different waters were used for the experimental work: (i) raw Capilano water (CW) which originated from Capilano Reservoir, providing drinking water for the Greater Vancouver region, British Columbia, Canada and (ii) the permeate of ultrafiltered CW (the <10 kg mol\(^{-1}\) fraction).

The Capilano Reservoir is formed by the damming of the Capilano River, which is fed by fall and winter rain runoff and the spring snowmelt. CW is a surface water of high quality since it has low total organic carbon (TOC) concentration (< 2.5 mg L\(^{-1}\)), turbidity (< 1 NTU), and alkalinity (< 10 mg CaCO\(_3\) L\(^{-1}\)) (Table 2.1). Currently, the drinking water supply from the Capilano Reservoir undergoes no coagulation/flocculation or filtration prior to chlorine disinfection. The water used for this particular study was obtained in May of 2005.
2.2.2 Ultrafiltration Treatment

UF was performed using a pilot scale membrane unit fitted with a tubular ceramic membrane (Clover \textit{INSIDE}, TAMILAB) with a nominal molecular weight of 10 kg mol$^{-1}$ and a total surface area of 0.04 m$^2$. The membrane reactor was operated in cross-flow mode. 25 L of CW was placed in a feed tank in stream of the membrane unit. The water was recirculated through the membrane back to the feed tank. The feed tank was filled occasionally with fresh CW to maintain a volume of at least 10 L. The membrane permeate was collected and designated as the $<10$ kg mol$^{-1}$ fraction.

2.2.3 UV/H$_2$O$_2$ Treatment

Two different reactor setups were employed for the bench scale UV/H$_2$O$_2$ studies. Setup #1 was employed for all results besides the aldehydes results. This setup consisted of a batch reactor in which the irradiation source was a TrojanUVMax™ (Trojan Technologies, London, Canada), containing a low-pressure high output mercury lamp with an output of 27.7 W at 254 nm. Water (40 L) in the feed tank was spiked with H$_2$O$_2$ solution (30% Fisher Scientific) to achieve a concentration of approximately 20 mg L$^{-1}$. The water was re-circulated through the reactor (Figure 2.1a) at a constant flowrate of 45 L min$^{-1}$. Sampling time were based on fluences calculated using Trojan’s proprietary fluence calculation model. Based on the flowrate and the absorbance of the water at 254 nm after the H$_2$O$_2$ spike and the reactor’s technical specifications, the model calculated the UV fluence delivered to the water after a single pass through the reactor. The recirculation time was adjusted accordingly to yield fluences 0 to 1500 mJ cm$^{-2}$.

Setup #2, used for the generating the aldehydes results, was a collimated beam apparatus (Figure 2.1b), consisting of low-pressure mercury lamp (Trojan Technologies, London, Canada) positioned 28 cm above a circular stirred reactor chamber. The reactor chamber was 8.75 cm in diameter and the water pathlength was 3.33 cm. The incident fluence rate for the given collimated beam and reactor was determined using iodide/iodate actinometry (described below). Samples were irradiated for calculated durations to achieve five different delivered fluences from 0 to 1400 mJ cm$^{-2}$. H$_2$O$_2$ was added initially to the reactor chamber to achieve concentrations of 0, 5, 10, 15, and 20 mg L$^{-1}$.

Prior to spectroscopic analysis, measurement of TOC concentration, resin fractionation, and analysis for aldehydes and BDOC, all H$_2$O$_2$ containing samples were quenched of H$_2$O$_2$ using bovine liver catalase (lyophilized powder, $\geq$10,000 units mg$^{-1}$ protein, Sigma Aldrich), at a concentration of 0.2 mg L$^{-1}$ in the sample. Catalase at this concentration has been demonstrated to be effective for removing H$_2$O$_2$ within 10 minutes (Liu et al. 2003). There was no observable increase in the TOC concentration measured after the addition of 0.2 mg L$^{-1}$ of catalase.
2.2.4 Analytical Methods

The following parameters were monitored in CW, the <10 kg mol\(^{-1}\) fraction, and the UV/H\(_2\)O\(_2\) AO treated waters: TOC concentration, absorbance at 254 nm (A\(_{254}\)), absorbance at 203 nm (A\(_{203}\)), percentage of BDOC, concentration of some aldehydes, and TOC concentration of hydrophilic and hydrophobic fractions.

TOC concentration was measured using a TOC analyzer (Shimadzu TOC-VCPH). A\(_{254}\) and A\(_{203}\) were determined using a spectrophotometer (Shimadzu UV-Mini 1240). Samples were analysed for 10 different aldehydes according to EPA Method 556.1 (USEPA 1999). Detection was performed according to Standard Method 6252 (Clescerl et al. 1999) using a gas chromatograph equipped with an ion trap mass spectrometer detector (GC-MS, Saturn 2200, Varian Inc.), a VF-5ms column (Varian Inc.), and a Combi-Pal (Pal System, CTC Analytics) autosampler. Concentrations of H\(_2\)O\(_2\) were measured by reaction with iodide catalyzed by molybdate (Klassen et al. 1994).

The percentage of BDOC was determined following the method given by Servais et al. (1989). First, 400 mL of water was vacuum evaporated down to 150 mL in order to increase the TOC concentration of the sample. This was necessary because the applied BDOC method is not highly accurate at low TOC concentrations (Servais et al. 1989). Concentration was performed using a Rotovap vacuum evaporator at a temperature of 50 °C, maintained using a water bath. The concentrated water was sterilized, by filtration through a 0.22 µm filter (Millex-GP, polyethersulfone, 33 mm, radio-sterilized, Millipore), and placed into four vials each containing 30 mL of sample. Two samples were seeded with 3 mL of raw CW and incubated in the dark at 25 °C for 5 days in a shaker (Lab Companion SI-600) at 10 rpm. TOC concentration was measured initially (TOC\(_0\)) in the two samples, without seed, and after 5 days (TOC\(_f\)) in the two samples, incubated seeded samples. The percentage of BDOC (%BDOC) was defined as \(\frac{\text{TOC}_{0}-\text{TOC}_{f}}{\text{TOC}_{0}}\times100\).

NOM fractionation was performed by exposing the waters to Supelite DAX-8 (Supelco) and Amberlite XAD-4 resins (Supelco) in series. Resins were cleaned and regenerated by submersion in methanol followed by successive rinsing with distilled water, 0.1 N NaOH, and 0.1 N HCl. The TOC concentration of the wash water was checked to ensure the resins were free of methanol. Following, 600 mL of water sample and 50 mL of DAX-8 were combined in an Erlenmeyer flask and stirred, with a magnetic stir bar and stir plate, for 3 hours. The water was decanted and the TOC concentration of DAX-8 treated water was measured. The remaining water was combined with 50 mL of XAD-4, stirred for 3 hours, and the final TOC concentration was measured. The hydrophobic fraction (HPB) was defined as the fraction of NOM that was adsorbed onto DAX-8. The fraction of NOM that was not adsorbed on
The incident fluence rate of 254 nm irradiation \( (E_p) \) was determined by iodide/iodate actinometry (Rahn 1997) in which potassium iodide (Reagent A.C.S., Fisher Scientific) was irradiated leading to the formation of triiodide. Potassium iodate (Certified A.C.S., Fisher Scientific) acted as an electron scavenger, while sodium borate (Laboratory grade, Fisher Scientific) buffered the reaction at a pH of 9.25 (Rahn 1997). A radiometer (IL1700, sensor SED240 for 254 nm, International Light Inc.) served as a reference. The average fluence rate through the water volume \( (E_{avg}) \) was used to calculate the delivered fluence. \( E_{avg} \) was defined as the product of \( E_p \), the water factor (WF), and the divergence factor (DF). The WF and DF are based on the water absorbance, path length, and the distance between the lamp and water surface (details provided elsewhere (Bolton & Linden 2003)).

2.3 Results and Discussion

This study investigated the impact of UF, UV/H\(_2\)O\(_2\), and combined UF plus UV/H\(_2\)O\(_2\) on the TOC concentration, spectral properties, hydrophobicity, biodegradability, and the formation of some aldehydes. UV/H\(_2\)O\(_2\) treatment was conducted on CW and the \(<10 \text{ kg mol}^{-1}\) fraction (i.e., CW treated by UF) with the characteristics summarized in Table 2.1. UF treatment was conducted using a pilot scale membrane unit, operated in cross-flow mode, fitted with a tubular ceramic membrane with a nominal molecular weight of 10 kg mol\(^{-1}\). Two different reactors were employed for UV/H\(_2\)O\(_2\) treatment. The first reactor was a commercially available annular reactor, a TrojanUVMax™ (Trojan Technologies, London, Canada), containing a low-pressure high output mercury lamp (Figure 2.1a). Water in the feed tank was spiked with H\(_2\)O\(_2\) solution to achieve a concentration of approximately 20 mg L\(^{-1}\) and the water was re-circulated through the reactor at a constant flowrate of 45 L min\(^{-1}\). The second reactor, used for the generating the aldehydes results, was a collimated beam apparatus, consisting of low-pressure mercury lamp positioned above a circular, stirred reactor chamber (Figure 2.1b).

2.3.1 Mineralisation of Total Organic Carbon upon Advanced Oxidation

UF of CW led to a 63% reduction in TOC concentration. CW had an initial TOC concentration of 2.18 mg L\(^{-1}\), while the TOC concentration of the \(<10 \text{ kg mol}^{-1}\) fraction was 0.92 mg L\(^{-1}\). Other work (Section 3.3.2) showed that UF of CW led to a removal of high molecular size species. It will therefore be of interest to compare the impact of UV/H\(_2\)O\(_2\) AO on CW and the \(<10 \text{ kg mol}^{-1}\) fraction, to understand
how UV/H₂O₂ may impact NOM when it has been altered such that the concentration of NOM has been reduced and high molecular size species have been removed.

As seen in Figure 2.2, for CW, the change in TOC concentration seemed to drop gradually as the fluence increased. Overall, a reduction in TOC concentration of 14.5% was observed after a fluence of 1500 mJ cm⁻². This suggests that, at an initial H₂O₂ concentration of 20 mg L⁻¹, some mineralisation of NOM in CW can be achieved but at higher fluences. These results are in agreement with the findings of Kleiser & Frimmel (2000), Speitel et al. (2000), Thomson et al. (2002), Thomson et al. (2004b), Wang et al. (2006), and Toor & Mohseni (2007), who all found that TOC concentration was effectively reduced by UV/H₂O₂ AO but this process required long irradiation times and/or high H₂O₂ concentrations.

For the <10 kg mol⁻¹ fraction, a TOC concentration reduction of about 27% was observed after a fluence of 1500 mJ cm⁻² (Figure 2.2). Figure 2.2 provides linear regression lines of the TOC data for both CW and the <10 kg mol⁻¹ fraction along with the upper and lower 95% confidence lines. Note that although the regression was forced through the origin, regression analysis showed that the y-intercept was not significantly different than zero at 95% confidence. Therefore, as the 95% confidence lines do not cross over, the reduction in TOC was significantly higher for the <10 kg mol⁻¹ fraction. This increased reduction could be due to either (i) a lower initial TOC concentration or (ii) the absence of high molecular weight species. A lower TOC concentration leads to less screening of the UV radiation by NOM, allowing more H₂O₂ to be photolyzed into hydroxyl radicals (•OH), thus increasing the rate of production of •OH. To test this hypothesis, Equation [2.1] below was used to compare the rate of production of •OH (R_{OH}) for the two waters. This equation has been presented to define the rate of formation of •OH from the photolysis of H₂O₂ with 254 nm UV (Glaze et al. 1995; Liao & Gurol 1995; Stefan et al. 1996; Crittenden et al. 1999; Sharpless & Linden 2003). The following variables were the same in both systems and cancelled out: N_o - incident photon irradiance or photon fluence rate (Es cm⁻² s⁻¹), εX - decadic molar absorption coefficient of H₂O₂ (L mol⁻¹ cm⁻¹), Φ_{OH} - hydroxyl radical quantum yield (1.0 in water), [H₂O₂] - concentration of H₂O₂ (mol L⁻¹). Thus, the remaining expression was calculated where a was equal to A_{254} and z was the path length of the reactor, 3.255 cm. In this way, it was calculated that the rate of production of •OH for the <10 kg mol⁻¹ fraction was about 25% times greater than that for CW. Based on this calculation, hypothesis (i) or the increased production of •OH was not the primary reason for a factor of two increase (from 15% TOC reduction to over 30%) in the mineralisation of TOC in the <10 kg mol⁻¹ fraction. Rather, it was likely due to a change in how •OH reacted with NOM caused by the removal of high molecular weight NOM due to UF treatment (i.e., hypothesis ii).
For the reaction between 'OH and NOM, Westerhoff et al. (1999) observed a slight dependency of the reaction rate constant on molecular weight. For 17 different NOM isolates, there was a positive correlation between the weight average molecular weights and the rate constant of the reaction between 'OH and NOM (Westerhoff et al. 1999). Section 3.3.1 observed that 'OH reacted more readily with higher apparent molecular weight NOM than lower apparent molecular weight NOM. This lead to the formation of lower apparent molecular weight NOM. Furthermore, when high molecular size species were absent, 'OH reacted more readily with lower apparent molecular weight species than before. UF is capable of removing high molecular size NOM (Pelekani et al. 1999; Section 3.3.2). Therefore, the increased reduction in TOC concentration for the <10 kg mol⁻¹ fraction was likely due to the absence of high molecular size NOM, thus increasing the reaction between 'OH and smaller molecular size NOM leading to more complete mineralisation.

2.3.2 Effects of Advanced Oxidation on the Spectroscopic Properties of Natural Organic Matter

Although UV/H₂O₂ AO was not highly effective at reducing the concentration of NOM in CW (maximum 14.5%), it had sizeable impacts on the structure of the NOM. As demonstrated in Figure 2.3, the specific UV absorbance (SUVA) of the two waters changed over the range of fluences. SUVA, defined as the ratio of A₂₅₄ to TOC concentration, gives an indication of the relative amount of aromatic and conjugated double bonded carbon structures in NOM (Singer 1999). For CW, a 55% reduction in aromatic and conjugated double bond carbon content was observed up to a fluence of 1000 mJ cm⁻² (Figure 2.3). As the TOC concentration change with fluence was less than 15%, most of the reduction in SUVA was due to the loss of aromatic and conjugated double bonded (i.e. 254 nm absorbing) species as was also observed by Speitel et al. (2000), Thomson et al. (2002), Thomson et al. (2004b), Toor & Mohseni (2007), and Section 3.3.1. Increasing the fluence above 1000 mJ cm⁻² did not yield any appreciable further reduction in SUVA. For ultrafiltered CW, the reduction in SUVA, 36%, was not as large as the reduction in SUVA observed for CW (Figure 2.3). This was primarily due to the lower initial SUVA of the <10 kg mol⁻¹ fraction since UF of CW led to a 34% reduction in SUVA (Figure 2.3). Furthermore, after a fluence of 125 mJ cm⁻² there was no further reduction in SUVA for this fraction. Interestingly, the SUVA for both CW and the <10 kg mol⁻¹ fraction appeared to reach a plateau at 1.7 L mg⁻¹ m⁻¹, after 1000 mJ cm⁻² for CW and 125 mJ cm⁻² for the <10 kg mol⁻¹ fraction. The initial reduction in SUVA to 1.7 L mg⁻¹ m⁻¹ was mostly due to a loss in aromatic and conjugated double bond species.
since the TOC concentration was only reduced slightly (Figure 2.2). The plateau reached by SUVA at 1.7 L mg⁻¹ m⁻¹ suggests that aromatic and conjugated double bond species and the TOC concentration were reduced proportionally after 1000 mJ cm⁻² for CW and 125 mJ cm⁻² for the <10 kg mol⁻¹ fraction. Thomson et al. (2004a) and Chapter 3 hypothesized that UV/H₂O₂ AO treatment led to preferential oxidation of higher molecular size NOM accompanied by the formation of lower molecular size NOM. Therefore, it is proposed that, at earlier stages of treatment, OH reacts more readily with aromatics and conjugated double bonds fragmenting them into smaller species that are less aromatic or not aromatic at all. After the concentration of aromatic and conjugated double bonds has been reduced sufficiently, reaction of OH with the smaller molecular sized NOM increased, leading to mineralisation and an observed reduction in both TOC concentration and A₂₅₄.

Figure 2.4 compares the degree of activation of aromatic rings in NOM in CW and the <10 kg mol⁻¹ fraction. This comparison is based on the relative absorbance at 254 nm and 203 nm, which represent the composite electron-transfer (ET) and benzenoid (Bz) bands, respectively (Korshin et al. 1997). Korshin et al. (1997) proposed that based on the ratio of absorbance of the ET band to the absorbance of the Bz band (A₂₅₄/A₂₀₃), the degree of activation of the aromatic rings in NOM could be interpreted. A low A₂₅₄/A₂₀₃ value was said to be representative of compounds in which the aromatic rings were substituted predominantly with aliphatic functional groups. Increasing A₂₅₄/A₂₀₃ was said to be an indication of higher substitution of aromatic rings in NOM with hydroxyl, carbonyl, ester, and carboxyl groups (Korshin et al. 1997). Based on this concept, the aromatic rings in CW are likely predominantly substituted with hydroxyl and carboxyl groups, while the aromatic rings in the <10 kg mol⁻¹ fraction are likely not highly substituted (Figure 2.4). Thus, UF of CW appeared to preferentially retain aromatic compounds with a higher degree of substitution. This was expected since more highly substituted aromatic compounds generally have higher molecular weight and thus can be removed more effectively by membrane pores.

For both CW and the <10 kg mol⁻¹ fraction, there was an observed change in the type of substitution of aromatic rings (Figure 2.4) during UV/H₂O₂ AO treatment. Therefore, oxidation of highly substituted aromatic rings appeared to occur. As with SUVA, a plateau was reached for A₂₅₄/A₂₀₃ and occurred at the same time at which the plateau for SUVA was observed.

2.3.3 Impact of UV/H₂O₂ on the Hydrophobicity of Natural Organic Matter

The effect of UV/H₂O₂ on the chemical characteristics of the NOM was assessed by quantifying the hydrophobic (HPB) and hydrophilic (HPL) fractions of CW NOM before and after AO treatment. Fractionation is not reported on the <10 kg mol⁻¹ fraction because the fractionation method employed was not sensitive to small changes in TOC. In general, the method had an error of 0.25 mg L⁻¹ when
measuring the TOC concentration before and after exposure to one of the resins. For CW, the changes observed exceeded this experimental error but for the < 10 kg mol\(^{-1}\) fraction, likely due to the low TOC concentration (0.92 mg L\(^{-1}\)) and composition of the NOM after UF, the experimental error in measurement masked any changes in chemical nature that may have occurred.

As illustrated in Figure 2.5, the ratio of HPL NOM to HPB NOM in CW increased upon AO treatment and increased as fluence increased. The observed change in the ratio of HPL NOM to HPB NOM indicated that the treatment preferentially reacted with the HPB fractions of NOM leading to the formation of more HPL products. For CW, at a fluence of 1500 mJ cm\(^{-2}\), about 25% of the HPB NOM had been converted to HPL NOM.

### 2.3.4 Biodegradability of Natural Organic Matter upon Advanced Oxidation

The impact of UF, UV/H\(_2\)O\(_2\), and combined UF and UV/H\(_2\)O\(_2\) on the biological stability of CW was assessed by observing the change in the %BDOC. For untreated CW the %BDOC was measured to be 5%. UF of CW appeared to increase the %BDOC by about three times. Considering the error bars, the increase in %BDOC could be mainly due to the removal of TOC by UF rather than a change in BDOC concentration. For UV/H\(_2\)O\(_2\) AO of CW and the < 10 kg mol\(^{-1}\) fraction, the %BDOC increased up to a fluence of 500 mJ cm\(^{-2}\), after which a plateau was observed (Figure 2.6). These results suggest that UV/H\(_2\)O\(_2\) oxidized recalcitrant NOM into more readily biodegradable compounds as was observed by Speitel et al. (2000), Thomson et al. (2004b), and Toor & Mohseni (2007). The plateau observed at higher fluences may be due to mineralisation of the BDOC. That is, at fluences greater than 500 mJ cm\(^{-2}\), biodegradable species may have been mineralized at the same rate that they were produced.

Noting the large error bars in Figure 2.6, it was not possible to make firm conclusions about the extent of impact of AO on the biological stability of the water. There were inherent deficiencies in the method of BDOC determination employed. Firstly, the concentration step applied resulted in up to about 13% loss in TOC based on mass balance. This indicated that there was a loss of organic carbon species during the concentration process. A possible mechanism for organic carbon loss was volatilization, during the vacuum evaporation process at 50 °C. Moreover, AO treatment would make more low molecular size compounds which would potentially be volatile and could be lost during the concentration process. Adsorption on the walls of the round bottom flask was unlikely since subsequent cleaning of the flask did not yield any TOC. Furthermore, the 0.22 µm polyethersulfone filters used for sterilization were not rinsed prior to use. It is possible that DOC was introduced into the water sample from the polyethersulfone filters. Moreover, this DOC may have been biodegradable thus increasing the %BDOC.
2.3.5 Formation of Aldehydes during Advanced Oxidation

As there was an apparent increase in %BDOC, as well as the hydrophilic fraction of NOM upon UV/H₂O₂ AO treatment, the formation of some low molecular weight compounds, namely aldehydes, was quantified (Figure 2.7). These UV/H₂O₂ AO treatments were conducted using a collimated beam apparatus (Setup #2), using CW collected more recently, in March 2006. The initial TOC concentration and SUVA of 2.2 mg L⁻¹ and 4.4 L mg⁻¹ m⁻¹, respectively, were similar to those for CW collected in May 2005 (Chapter 3). Samples were analysed for 10 different aldehydes but only the 4 smallest aldehydes, formaldehyde, acetaldehyde, propanal, and butanal were detected (detection limit of 3 µg L⁻¹). In CW, the total concentration of the four aldehydes was below 25 µg L⁻¹. Exposure to H₂O₂ alone did not noticeably change the concentration of the four aldehydes. With only UV irradiation, there was an observed increase in the total concentration of aldehydes at all fluences, up to about 45 µg L⁻¹ at a fluence of 1350 mJ cm⁻². Under advanced oxidation conditions, i.e. with the addition of H₂O₂, the concentration of aldehydes increased dramatically as was also observed by Liu et al. (2002) and Thomson et al. (2004b). At the strongest conditions (initial H₂O₂ concentration of 20 mg L⁻¹ and fluence of 1350 mJ cm⁻²) the concentration of aldehydes reached close to 175 µg L⁻¹. Additionally, it was clearly observed that an increase in either initial H₂O₂ concentration or fluence was accompanied by a greater formation of aldehydes. This is likely due to the increased exposure to •OH. An increase in •OH exposure leads to greater degradation of NOM and formation of low molecular carbonyls, such as these aldehydes. Interestingly, the increase in the concentration of aldehydes was primarily due to increases in the concentration of formaldehyde and acetaldehyde. Thomson et al. (2004b) investigated UV/H₂O₂ for the removal of NOM from a NOM laden surface water (TOC concentration of 15 mg L⁻¹) within a fluence range of, 6,000 to 450,000 mJ cm⁻² and an initial H₂O₂ concentration less than 15 mg L⁻¹. The investigators observed that butanal and propanal did not accumulate, while formaldehyde and acetaldehyde increased (Thomson et al. 2004b). Butanal reacts faster with •OH (k=3.9E9 M⁻¹ s⁻¹; Buxton et al. 1988) than formaldehyde (k=1.0E9 M⁻¹ s⁻¹; Buxton et al. 1988) and acetaldehyde (k=7.3E8 M⁻¹ s⁻¹; Buxton et al. 1988) so this could explain the lower accumulation of butanal (Thomson et al. 2004b). In addition to this, the rate of formation of butanal and propanal, due to reaction between •OH and NOM, may be slower than formation of formaldehyde and acetaldehyde.

It should be noted that for these experiments with Setup #2 the reduction in SUVA for CW after a fluence of 1000 mJ cm⁻² (about 55%; 3.3.1) was similar to that observed in the experiments using Setup #1 on CW at a fluence of 1000 mJ cm⁻² and an initial H₂O₂ concentration of 20 mg L⁻¹ (about 48%; Figure 4.3). As the changes in structure of NOM appear to have been similar between these experiments, the changes in %BDOC and aldehydes concentration were likely to be fairly similar. As aldehydes are readily
biodegradable, increase in the concentration of aldehydes supports the apparent increase in %BDOC of CW after UV/H₂O₂ AO treatment (Figure 2.6). Although the formation of more biodegradable products is undesirable in distributed water, the use of a downstream biological treatment, such as biological activated carbon, has been demonstrated to remove aldehydes (6.2.4) as well as BDOC (Toor & Mohseni 2007).

Thus, for waters in which AO is found to greatly reduce the biological stability of water, a downstream process may be necessary to improve water quality prior to distribution. This will depend on the concentration and characteristics of the NOM in the water as well as the strength of the AO conditions. For waters with low NOM (i.e. low TOC concentration), the formation of biodegradable species during AO will not be as great as for waters with greater concentration of NOM. Furthermore, other water quality parameters, such as alkalinity, may impact the extent to which biostability is impacted.

2.4 Acknowledgements

The authors acknowledge Sophie Pantin, Friedrick Po, Cedric Arnou, and Daniel Klein for assisting with experimental and analytical work, Ted Mao, Mihaela Stefan, Bill Cairns, Alan Royce, and Steve McDermid for valuable input and discussions, and Natural Science and Engineering Research Council of Canada and Trojan Technologies for financial support.
Table 2.1  Select characteristics of Capilano source water in 2005 and the waters used in this study (Capilano Water and the 10 kg mol⁻¹ fraction of Capilano Water).

<table>
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<th>Parameter</th>
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<th>CW used in experiments (May 2005)</th>
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<td>Range</td>
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<td>Alkalinity (mg CaCO₃ L⁻¹)</td>
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<td>N/A</td>
<td>0.409</td>
</tr>
</tbody>
</table>

† Source: The Greater Vancouver Water District Quality Control Annual Report 2005
N/A – not measured

Figure 2.1  Experimental UV/H₂O₂ AO reactors. (a) Setup #1: semi-batch reactor. (b) Setup #2: collimated beam apparatus.
Figure 2.2 $\ln \left(\frac{\text{TOC}}{\text{TOC}_0}\right)$ during UV/H$_2$O$_2$ AO of CW (□) and the $<10$ kg mol$^{-1}$ fraction (Δ) over a range of fluence and an initial H$_2$O$_2$ dose of 20 mg L$^{-1}$. Each point represents the average of two separate samples, each measured three times. Solid lines represent linear regression fits. Dashed lines represent the lower and upper 95% confidence intervals.

Figure 2.3 SUVA during UV/H$_2$O$_2$ AO of CW (□) and the $<10$ kg mol$^{-1}$ fraction (Δ) over a range of fluence with an initial H$_2$O$_2$ dose of 20 mg L$^{-1}$. Each point represents the average of two separate samples, each measured three times. Error bars represent the standard deviation between the average measurements of two separate samples.
Figure 2.4 Degree of substitution of aromatic rings in NOM during UV/H$_2$O$_2$ AO of CW (□) and the <10 kg mol$^{-1}$ fraction (Δ) over a range of fluence with an initial H$_2$O$_2$ dose of 20 mg L$^{-1}$. Each point represents the average of two separate samples, each measured three times. Error bars represent the standard deviation between the average measurements of two separate samples.

Figure 2.5 Ratio of HPL NOM to HPB NOM during UV/H$_2$O$_2$ AO of CW over a range of fluence with an initial H$_2$O$_2$ dose of 20 mg L$^{-1}$. 
**Figure 2.6** BDOC during UV/H$_2$O$_2$ AO of CW (□) and the <10 kg mol$^{-1}$ fraction (Δ) over a range of fluence with an initial H$_2$O$_2$ dose of 20 mg L$^{-1}$. Each point represents the average of two separate samples, each measured twice. Error bars represent the standard deviation between the average measurements of two separate samples.

**Figure 2.7** Concentration of aldehydes during UV/H$_2$O$_2$ AO treatment of CW over a range of fluence and initial H$_2$O$_2$ concentrations. Bars represent the average of two samples, each measured twice.
Literature Cited


Chapter 3
The Impact of UV/H₂O₂ Advanced Oxidation on Molecular Size Distribution of Chromophoric Natural Organic Matter²

3.1 Introduction

The aim of this study was to investigate how UV/H₂O₂ impacts natural organic matter (NOM) by observing the effects of UV/H₂O₂ on NOM’s molecular weight (MW) distribution. MW distribution of NOM is an important property in drinking water treatment since changes in MW distribution can lead to changes in DBP formation potential and biological regrowth potential (Vuorio et al. 1998; Thomson et al. 2002a, 2002b, 2004a, 2004b; Buchanan et al. 2004, 2005, 2006; Parkinson et al. 2003). In general, lower MW species are more biodegradable while higher MW species are more humic and aromatic in nature and may be more reactive with chlorine. Furthermore, the impact of membrane separation as well as combined membrane and UV/H₂O₂ treatment on NOM was studied. The latter was employed to investigate how hydroxyl radical (·OH) affects NOM’s MW distribution when the initial MW distribution of NOM is altered by pre-treatment.

High performance size exclusion chromatography (HPSEC) has been demonstrated to be an effective technique for determining the apparent MW (AMW) distribution of NOM (Pelekani et al. 1999). During HPSEC, NOM is detected by absorbance of 260 nm UV, thus yielding the AMW distribution of only chromophoric NOM (CNOM), NOM able to absorb at 260 nm (i.e. chromophores). In this study, HPSEC was employed to investigate the impact of ·OH, generated by UV/H₂O₂, on the AMW distribution of CNOM. While HPSEC yields valuable qualitative information regarding the AMW distribution of CNOM, the aggregate, convoluted peaks do not yield quantitative information regarding the impact of treatments on specific AMW fractions. Therefore, to better understand the impact of UV/H₂O₂ on CNOM and to be able to quantify the formation and reduction of specific AMW fractions, a peak fitting procedure was developed to convert qualitative HSPEC data to quantitative terms.

3.2 Materials and Methods

The UV fluences applied were selected based on their relation to commercial drinking water applications (i.e., less than 2000 mJ cm\(^{-2}\)). The range of initial H\(_2\)O\(_2\) concentrations of 5 to 20 mg L\(^{-1}\) was selected based on the typical range for commercial drinking water applications (in communication with Trojan Technologies). The membrane filtration unit for this study was selected as previous research in this group employed it on the same water (Chowdhury et al. 2008). The molecular weight cut off was selected as the objective was to carry out ultrafiltration while not entirely removing NOM.

In order to consider the reproducibility of the UV/H\(_2\)O\(_2\) treatment experiments, duplicate runs were conducted. The data presented in this chapter are the average values of the two separate UV/H\(_2\)O\(_2\) runs. Error bars in figures are meant strictly for illustration as they represent the standard deviation for the results obtained over two UV/H\(_2\)O\(_2\) runs.

3.2.1 Waters

The original source of water used in all experiments was the Capilano Reservoir, providing drinking water for the Greater Vancouver region, British Columbia, Canada. The damming of the Capilano River, which is fed by fall and winter rain runoff and the spring snowmelt, forms the reservoir. Given its low TOC, turbidity and alkalinity (Table 3.1) Capilano water (CW) was a surface water of very high quality and presently undergoes no coagulation/flocculation or filtration prior to chlorine disinfection. The water used for this particular study was obtained in March of 2006 and its characteristics are given in Table 3.1.

The water with <10 kDa was vacuum evaporated in order to increase the concentration of NOM in the sample. Concentration was done using a Rotovap vacuum evaporator at a temperature of 50 °C, maintained using a water bath. An initial volume of 450 mL was concentrated to 150 mL. The characteristics for concentrated <10 kDa CW are provided in Table 3.1.

3.2.2 Advanced Oxidation Treatment.

A collimated beam apparatus, consisting of low-pressure mercury lamp (Trojan Technologies, London, ON) positioned 28 cm above a circular stirred reactor chamber, was employed for the batch UV/H\(_2\)O\(_2\) studies. The reactor chamber was 8.75 cm in diameter and the water pathlength was 3.33 cm. Samples were irradiated for calculated durations to achieve five different delivered fluences from 0 to 1400 mJ/cm\(^2\). H\(_2\)O\(_2\) (30%, Fisher Scientific) was added initially to the reactor chamber at the concentrations of 0, 5, 10, 15, and 20 mg/L. Each treatment condition was carried out in duplicate. The entire water sample volume (200 mL) was used for the various analyses described below. H\(_2\)O\(_2\)
containing samples were quenched of \( \text{H}_2\text{O}_2 \) using 0.2 mg/L bovine liver catalase (lyophilized powder, \( \geq 10,000 \) units/mg protein, Sigma Aldrich) prior to absorbance at 254 nm (A\( _{254} \)), TOC, and HPSEC measurements and prior to chlorination.

### 3.2.3 Membrane Treatment (Ultrafiltration)

A tubular pilot scale membrane reactor fitted with a ceramic membrane (Clover \textit{INSIDE}, Tami Industries), with a molecular weight cutoff (MWCO) of 10 kDa and a surface area of 0.04 m\(^2\), was employed for ultrafiltration of CW. The membrane reactor was operated in cross-flow mode. The permeate was collected and analysed and used in UV/H\(_2\)O\(_2\) experiments.

### 3.2.4 Analytical Methods

Incident UV irradiance of 254 nm light (\( E^* \)) was determined by iodide/iodate actinometry (Rahn 1997) in which potassium iodide (Reagent A.C.S., Fisher Scientific) was irradiated leading to the formation of triiodide. Potassium iodate (Certified A.C.S., Fisher Scientific) acted as an electron scavenger while sodium borate (Laboratory grade, Fisher Scientific) buffered the reaction at a pH of 9.25 (Rahn 1997). A radiometer (IL1700, sensor SED240 for 254 nm, International Light Inc.) served as a reference. The fluence rate (\( E_{\text{avg}} \)) was used to calculate the delivered fluence. \( E_{\text{avg}} \) was defined as the product of \( E^* \), the reflection factor (RF) equal to 0.975 (Bolton & Linden 2003), the water factor (WF), and the divergence factor (DF). WF and DF are based on the water absorbance, path length, and the distance between the lamp and water surface (details are provided by Bolton & Linden (2003)).

\[ E_{\text{avg}} = E^* \times RF \times WF \times DF \]

\( \text{H}_2\text{O}_2 \) concentration was measured by reaction with iodide catalyzed by molybdate (Klassen et al. 1994). TOC was measured using a UV/persulfate oxidation TOC analyser (Shimadzu TOC-VCPH). Absorbance measurements were determined using a UV-Vis spectrophotometer (Shimadzu UV-Mini 1240) with a cell pathlength of 1 cm.

HPSEC was employed to determine the AMW distribution of NOM in untreated and treated waters. Following the method described by Pelekani et al. (1999), a Water 1535 Binary HPLC Pump fitted with a Waters Protein-Pak\textsuperscript{TM} 125 Å column and a Waters 2487 Dual\textsuperscript{a} Absorbance Detector, set to detection at 260 nm, served as the instrument for HPSEC analysis. The carrier solvent consisted of 0.02 M phosphate buffer (Laboratory grade, Fisher Scientific), at pH 6.8, adjusted with sodium chloride (Certified A.C.S,
Fisher Scientific) to 0.1 M ionic strength and the column flowrate was 0.7 mL/min. AMW was correlated to retention time by calibration with polysulfonate standards (7 kDa PSS7K, 4 kDa PSS4K, 2 kDa PSS2K, American Polymer Standards Corporation) and acetone (Certified A.C.S., Fisher Scientific) at a concentration of 1 g/L.

3.2.5 Resolution of High Performance Size Exclusion Chromatography Chromatograms

The typical HPSEC chromatogram of CNOM consists of an aggregate of peaks without clear resolution (Figure 3.1). In order to convert the distribution into quantifiable terms, the observed aggregate peak was resolved into a number of Gaussian peaks using Systat PeakFit v4.12 in a similar fashion presented by Thompson et al. (2004a). HPSEC data were imported into PeakFit and the “Autofit Peak III Deconvolution” function was applied using a peak type of extreme value 4 parameter tailed (area), a Gaussian response width of 20 seconds defined as a full width at half-maximum, a frequency domain filter of 60%, and an amplitude rejection threshold of 3%. These settings were selected based on the R² of the fit and yielded a R² > 0.97 for all peak fitted chromatograms. As illustrated in Figure 3.1, these settings established 14 peaks that summed up to form a “calculated” aggregate peak which represented the original aggregate peak. Thus, the above settings were used for deconvolution of all HPSEC data.

The resolved peaks were placed into AMW fractions based on their retention times using a calibration equation generated during each set of analyses. The largest AMW fraction, >1400 Da (F1), represented the leading edge of the chromatogram. The remaining AMW fractions represented observed peaks that were unresolved in the original chromatogram: 1100-1400 Da (F2), 850-1100 Da (F3), 650-850 Da (F4), 450-650 Da (F5), and <450 Da (F6). The areas of the individual peaks were quantified and the sums of areas of the peaks in any one fraction represented the quantity of CNOM in that size fraction. Each deconvolution presented is the average of deconvolutions performed on HPSEC chromatograms of duplicate samples. We have estimated the standard deviation to be maximum around 4% between deconvolutions of duplicate samples. Therefore, percent changes less than 4% should not be regarded as observable.

This approach allowed (i) the aggregate HPSEC chromatogram to be split up into smaller peaks, (ii) assignment of these resolved peaks into AMW fractions based on their retention times, and (iii) quantification of the CNOM in each AMW fraction.
3.3 Results and Discussion

3.3.1 Impact of UV/H₂O₂ on Molecular Size Distribution

The AO conditions applied in this study did not lead to mineralisation of NOM since there was no observed drop in TOC during UV/H₂O₂ (Figure 3.2). This suggests that under the fluence and H₂O₂ concentration typically applied in drinking water treatment applications, NOM is not removed. However, NOM underwent changes in the structural characteristics. Figure 3.3 illustrates that as fluence increased, in the presence of H₂O₂, NOM’s A₃₅₄ reduced. UV radiation of 254 nm is mainly absorbed by aromatic rings and conjugated double bonds so a reduction in A₃₅₄ indicates a loss of aromatic and conjugated double bond structures of NOM. Therefore, although NOM was not mineralized, partial oxidation led to ring opening and possible fragmentation of NOM structure. These observations suggest that under milder AO conditions larger NOM species may degrade leading to the formation of smaller species. Furthermore, lower H₂O₂ concentration resulted in less removal of aromatic and conjugated bonds (Figure 3.3). This can be attributed to the lower concentration of •OH since the concentration of •OH is dependent on the concentration of H₂O₂ in the reactor (Sharpless & Linden 2003). Meanwhile, in the absence of H₂O₂ there was no reduction in A₃₅₄ suggesting that, over the range of UV fluences applied, direct photolysis did not affect NOM and its structure (Figure 3.3).

It was observed that •OH, generated by UV/H₂O₂, preferentially reacted with larger molecular size CNOM resulting in an increase in lower molecular size CNOM (Figure 3.4). The total area under the HPSEC chromatograms decreased as treatment progressed. These areas have not been reported since their decrease is represented by the reduction in A₃₅₄ (Figure 3.3). Prior to irradiation, the HPSEC chromatogram of CW featured a large, early eluting peak followed by smaller, later eluting peaks. With an initial H₂O₂ concentration of 15 mg/L, as irradiation progressed (i.e., fluence increased), the leading edge and the first peak to elute reduced in size greatly while the second peak reduced to a lesser extent. The third peak seemed to slightly increase in size at fluences less than or equal 680 mJ/cm², followed by a decrease in size at fluences greater than or equal to 1000 mJ/cm². Finally, the last two peaks to elute increased in size after UV/H₂O₂ treatment at all fluences.

The PeakFit analysis was used to translate the observations into quantitative terms (Figure 3.5 and Figure 3.6). For CW, 33% of CNOM had an AMW greater than 1400Da while subsequent lower AMW CNOM made up lesser amounts of the CW CNOM, with CNOM of AMW less than 450Da making up only 5% of the total. As shown in Figure 3.5, with an initial H₂O₂ concentration of 15 mg/L, as UV exposure (i.e., fluence) increased up to 680 mJ/cm², a large reduction in higher AMW CNOM was observed: 56%, 49%, and 24% reductions in F1, F2, and F3, respectively. Meanwhile, smaller AMW
CNOM increased in concentration: 28% and 30% increases in F5 and F6, respectively. At fluences greater than or equal to 1000 mJ/cm², F1, F2, and F3 were further reduced, F4 began to reduce, and F5 and F6 remained relatively the same (Figure 3.5). This reduction in higher AMW CNOM and concomitant formation of smaller AMW CNOM led to a shift in molecular size distribution from one with a majority of large species to a more even molecular size distribution after UV/H₂O₂ treatment.

Thomson et al. (2004a) developed a “depolymerisation model” that described CNOM as a series of structural units joined by photolabile chemical bonds (Thomson et al. 2004a). For surface water highly laden with NOM (TOC > 10 mg/L), the model accurately described experimental observations of direct photolysis of CNOM, at high fluences (> 6000 mJ/cm²): UV irradiation preferentially removed larger AMW CNOM accompanied by a formation of smaller AMW CNOM (Thomson et al. 2004a). It is apparent that a similar depolymerisation mechanism existed for the reaction between \( \cdot \text{OH} \) and CNOM since Figure 3.5 suggests a correlation between AMW and the extent of reduction. Under conditions when TOC was not mineralized, \( \cdot \text{OH} \) reacted preferentially with, and fragmented, higher AMW CNOM, F1-F3, leading to the formation of smaller AMW CNOM, F4-F6. One explanation is, although \( \cdot \text{OH} \) is reactivity non-specific, the reaction rate constant between \( \cdot \text{OH} \) and CNOM is dependent on molecular weight (i.e. size). This hypothesis is supported by the work of Westerhoff et al. (1999) who observed a slight dependency of the reaction rate constant on molecular weight and aromaticity. For 17 different NOM isolates there was a positive correlation between the molecular weights and aromaticity of the NOM and the reaction rate constant between \( \cdot \text{OH} \) and the NOM. Higher molecular weight structures tend to be more aromatic in nature so may have a larger number of reaction sites (Westerhoff et al. 1999). Additionally, the observed correlation between percent reduction and AMW could be attributed to the higher concentration of F1, F2, and F3. F4, F5, and F6 were also susceptible to \( \cdot \text{OH} \) attack but reacted less rapidly due to their lower concentrations and lower rate constants. The slight increase followed by subsequent decrease in F4 suggests that: (i) initially, at fluences up to 680 mJ/cm², the large fragmentation of F1, F2, and F3 made the conditions such that the rate of formation of F4 exceeded its rate of degradation and (ii) once the concentrations of F1, F2, and F3 were for the most part reduced at fluences greater than 1000 mJ/cm², the rate of degradation of F4 exceeded its rate of formation. Meanwhile, over the range of fluences, the rates of formation of F5 and F6 were either faster than or the same as their rates of degradation so there was an overall increase in the concentrations of these species.

An increase in initial H₂O₂ concentration during the UV/H₂O₂ process resulted in greater reduction of higher AMW fractions and increase of smaller AMW fractions (Figure 3.5 and Figure 3.6). As shown in Figure 3.6, with an initial H₂O₂ concentration of 5 mg/L, F1, F2, and F3 were reduced by 65%, 53%, and 29%, respectively, after a fluence of 1350 mJ/cm². This is compared to the greater reductions of 74%,
60%, and 30% for F1, F2, and F3, respectively, under an initial H2O2 of 15 mg/L. The observed decreases in percent reduction of F1, F2, and F3 with 5 mg/L initial H2O2 can be attributed to the lower concentration of °OH in the reactor. Interestingly, even after a fluence of 1350 mJ/cm², there was no observed reduction in F4 (Figure 3.6). Therefore, it seems that the concentration of F1, F2, and F3 were not reduced sufficiently such that the rate of degradation of F4 exceeded its rate of formation.

Overall, the approach and analysis adopted in this research demonstrated that UV/H2O2 treatment under AO conditions typically applied in drinking water applications led to the partial oxidation and fragmentation of higher AMW CNOM. This fragmentation was accompanied by the formation of smaller AMW CNOM. This altered the molecular size distribution from one which was initially composed mainly of large species to a more even molecular size distribution after UV/H2O2 treatment. These observations suggested that the reaction rate between °OH and CNOM was dependent on molecular weight (i.e., size) as well as concentration of each AMW fraction. Furthermore, a decrease in concentration of °OH reduced the extent of partial oxidation and fragmentation of CNOM.

3.3.2 Impact of Ultrafiltration Followed by UV/H2O2 on Molecular Size Distribution

Ultrafiltration led to a large reduction in the concentration in TOC and A254 (Table 3.1). As a result ultrafiltration pre-treatment had a marked effect on the oxidation of NOM during UV/H2O2. While UV/H2O2 of CW did not result in complete oxidation at all fluences tested (Figure 3.2), UV/H2O2 treatment of <10 kDa CW resulted in mineralisation of up to 26% TOC at a fluence of 1500 mJ/cm² (data not shown). It was hypothesized that ultrafiltration removed the higher molecular weight NOM, leading to mineralisation of lower molecular weight NOM when exposed to °OH.

To determine how ultrafiltration impacted the MW distribution of CW, <10 kDa CW was subjected to HPSEC analysis. However, it was difficult to perform HPSEC analysis on <10 kDa CW due to low signal at 260 nm. Therefore, <10 kDa CW was vacuum evaporated to increase the concentration of CNOM followed by HPSEC. Concentration of <10 kDa CW yielded a TOC of 1.5 mg/L and A254 of 0.038 cm⁻¹ (Table 3.1). For A254, the mass balance was nearly closed with the final A254 being 15% greater than the theoretical level. However, mass balance on TOC left 38% of TOC unaccounted for. This indicates that there was a loss of non-chromophoric, organic carbon species during the concentration process. Possible mechanisms for organic carbon loss are volatilization or adsorption to the walls of the round bottom flask. The latter is not as likely since subsequent cleaning of the flask did not yield any TOC. It is more likely that the lost organics became volatile when the temperature was increased to 50 °C. Since there was no
observed loss in CNOM, HPSEC was applied to determine the AMW distribution of CNOM in concentrated <10 kDa CW.

Ultrafiltration altered the AMW distribution of CNOM such that the F1 was no longer present and F2 and F3 no longer made up the majority of CNOM (Figure 3.7). Pelekani et al. (1999) also observed that large pore size membranes (10 kDa and 30 kDa) removed NOM with AMWs well below the membrane MWCOs. These membranes are typically calibrated with proteins that may behave differently than NOM, so the nominal MWCOs of membranes should not be expected to reflect the actual molecular weight of NOM (Pelekani et al. 1999).

To observe the impacts of UV/H₂O₂ on CNOM when the AMW distribution is shifted, concentrated <10 kDa CW was exposed to UV/H₂O₂ and subsequently analysed by HPSEC. It should be taken into consideration that the impact of UV/H₂O₂ on CNOM may differ to some degree if the organic carbon species lost during concentration were present. As seen in Figure 3.7, although the concentrations of F2 and F3 were less than the concentrations of F4 and F5, •OH still had the greatest impact on the F2 and F3 with reductions of 76% and 71%, respectively, at the end of UV/H₂O₂ treatment. This supports the earlier hypothesis that the reaction rate constant for •OH with CNOM was dependent on AMW, increasing rapidly as AMW increased. Additionally, in contrast to their behaviours in CW not pre-treated by ultrafiltration, F4 and F5 underwent reductions, over the range of fluences (Figure 3.7). This observation is explained by the absence of F1 and reduced concentrations of F2 and F3, the apparent pools of CNOM whose fragmentation contribute to the formation of F4-F6. Thus, the conditions were such that the rates of degradation of F4 and F5 exceeded their rates of formation. Therefore, only when a large concentration of higher AMW CNOM was present, the rate of formation of smaller AMW CNOM exceeded their rate of degradation through reaction with •OH as seen in Figure 3.5 and Figure 3.6. This phenomenon was further observed in the behaviour of F6 in Figure 3.7. As fluence increased, F6 underwent an increase, up to 9% at 1100 mJ/cm², followed by reduction resulting in a final concentration close to the initial value (Figure 3.7). Therefore, it is apparent that the F2-F5 fractions, the pools of CNOM whose fragmentation contributed to the formation of F6, were such that the rate of their fragmentation exceeded the rate of removal of F6. Only after a fluence of 1350 mJ/cm², had the concentrations of F2-F5 reduced sufficiently to begin observing reductions in F6. Once again, these results may differ to some extent if <10 kDa CW had not been concentrated prior to UV/H₂O₂ treatment. It is unknown whether or not the lost organic species would affect the reaction between •OH and CNOM so this issue requires further investigation.

Overall, the results presented here demonstrated the impact of ultrafiltration on the AMW distribution of organic matter. Also, it was determined how the elimination of high AMW CNOM from raw water influenced the efficacy of UV/H₂O₂ process. That is, •OH reacted more effectively with all CNOM,
resulting in the reduction of all AMW fractions including smaller CNOM. The latter could be important because of the more biodegradable nature of smaller CNOM and their impact on the biological stability of water. UV/H₂O₂ oxidation of pre-treated raw water might be better suited for drinking water application since the partial oxidation of raw NOM could lead to an increase in smaller, biodegradable AMW fractions.

### 3.3.3 Importance of Water Characteristics

Much of the findings in this research are specific to CW and the observations and conclusions made in here could only be generalized upon consideration of this specific raw water. Although CW had a fairly low concentration of NOM, its A₂₅₄ (Table 3.1) was quite high for a low TOC water. This was because CW NOM had high aromatic character as indicated by the high SUVA, ratio of A₂₅₄ to TOC, of about 0.0405 L mg⁻¹ cm⁻¹. For typical UV/H₂O₂ treatments, one could expect CNOM in raw waters with higher SUVA to breakdown similarly to CW CNOM. This is because higher SUVA would indicate more aromatic and higher AMW CNOM whose fragmentation would lead to the formation of lower AMW species. On the other hand, the NOM in raw water with a low SUVA may breakdown similarly to the non-concentrated <10 kDa CW (SUVA = 0.0129 L mg⁻¹ cm⁻¹). That is, one could expect mineralization of NOM when the concentration of high AMW CNOM is low.

CW also had very low alkalinity (Table 3.1). Carbonate and bicarbonate are very strong scavengers of •OH and their presence often reduces the efficiency of AOPs. As alkalinity increases the rate of reaction between •OH and CNOM would decrease. Therefore, for raw water with alkalinity greater than CW, the impact of UV/H₂O₂ on CNOM may not be as marked as those observed for CW.

### 3.4 Acknowledgments

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Table 3.1  Select characteristics of Capilano source water during 2005 and the waters used in this study (Capilano Water, <10kDa Capilano Water, and concentrated <10 kDa Capilano Water).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CW reservoir (2005)†</th>
<th>CW used in experiments (March 2006)</th>
<th>&lt;10 kDa CW</th>
<th>Concentrated &lt;10 kDa CW</th>
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<tr>
<td></td>
<td>Avg</td>
<td>Range</td>
<td>Avg</td>
<td>Stdev</td>
</tr>
<tr>
<td>Alkalinity as (mg CaCO₃/L)</td>
<td>2.7</td>
<td>2.1-3.6</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Dissolved organic carbon (mg/L)</td>
<td>2.0</td>
<td>1.6-2.7</td>
<td>same as TOC</td>
<td>-</td>
</tr>
<tr>
<td>Total organic carbon (mg/L)</td>
<td>2.0</td>
<td>1.5-2.9</td>
<td>2.2</td>
<td>0.2</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td>6.2-6.9</td>
<td>6.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
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<td>0.32-5.9</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>A₂₅₄ (cm⁻¹)</td>
<td>0.081</td>
<td>0.055-0.108</td>
<td>0.098</td>
<td>0.008</td>
</tr>
</tbody>
</table>

† Source: The Greater Vancouver Water District Quality Control Annual Report 2005
N/A – not measured
Figure 3.1 HPSEC chromatogram of CW NOM and the results of the Peakfit deconvolution showing the calculated NOM and >1400 Da (F1), 1100-1400 Da (F2), 850-1100 (F3), 650-850 (F4), 450-650 (F5), and <450 Da (F6) molecular weight fractions.
Figure 3.2 The impact of fluence and initial \( \text{H}_2\text{O}_2 \) concentrations of 20 (○), 15 (□), 10 (△), and 5 (◇) mg/L on TOC of CW. Points represent the average of two samples, each measured three times. Error bars represent the standard deviation between the average measurements for two samples.
Figure 3.3  The impact of fluence and initial H$_2$O$_2$ concentrations of 20 (○), 15 (□), 10 (△), 5 (◊), and 0 (+) mg/L on $A_{254}$ of CW. Points represent the average of two samples, each measured twice. Error bars represent the standard deviation between the average measurement for two samples.
Figure 3.4 HPSEC chromatograms of CW treated by UV/H$_2$O$_2$ with fluences of 0 (+), 340 (◊), 680 (Δ), 1000 (□), and 1350 (O) mJ/cm$^2$ and an initial H$_2$O$_2$ concentration of 15 mg/L. Points represent the average of two samples, each sample analysed once.
Figure 3.5 Change in AMW fractions during the UV/H₂O₂ treatment of CW with fluences of 0, 340, 680, 1000, and 1350 mJ/cm² and an initial H₂O₂ concentration of 15 mg/L. Bars represent the average of two samples, each analysed once. Data labels indicate percent change.
Figure 3.6 Change in AMW fractions during the UV/H₂O₂ treatment of CW with fluences of 0, 340, 680, 1000, and 1350 mJ/cm² and an initial H₂O₂ concentration of 5 mg/L. Bars represent the average of two samples, each analysed once. Data labels indicate percent change.
Figure 3.7 Change in AMW fractions during the UV/H₂O₂ treatment of concentrated <10 kDa CW with fluences of 0, 340, 680, 1000, and 1350 mJ/cm² and an initial H₂O₂ concentration of 10 mg/L. Bars represent the average of two samples, each analysed once. Data labels indicate percent change.
Literature Cited


Chapter 4
Effects of UV/H$_2$O$_2$ Advanced Oxidation on Chemical Characteristics and Chlorine Reactivity of Surface Water Natural Organic Matter

4.1 Introduction

Natural organic matter (NOM) is a precursor to chlorination disinfection by-products (DBPs), including trihalomethanes (THMs) and haloacetic acids (HAAs). With the application of UV/H$_2$O$_2$ for the removal of organic contaminants, much of the chlorine demand is reduced since the UV irradiation simultaneously carries out disinfection. However, chlorine is still commonly applied as a secondary disinfectant in order to maintain a residual disinfectant in the distribution system to impede microbial regrowth. Thus, NOM can react with chlorine in the distribution system leading to the formation of DBPs. As UV/H$_2$O$_2$ treatment oxidizes NOM, the formation potential of THMs (THM-FPs) and HAAs (HAA-FPs) may be affected.

Within the acceptable range of fluence and H$_2$O$_2$ concentration, mineralization of NOM did not take place for raw surface water (Section 2.3.1; Section 3.3.1). However, NOM in surface water pre-treated by ultrafiltration was readily mineralized suggesting that UV/H$_2$O$_2$ can achieve NOM removal if higher molecular size NOM is removed by some form of pre-treatment (Section 2.3.1). With respect to DBP-FPs, it was demonstrated that substantial reduction could be achieved during UV/H$_2$O$_2$ but only under strong advanced oxidation conditions under which NOM was mineralized (Kleiser and Frimmel 2000; Thomson et al. 2004; Toor and Mohseni 2007). For low and intermediate fluences and initial H$_2$O$_2$ concentration less than 20 mg L$^{-1}$, it was reported that there was no reduction in THM-FP (Thomson et al. 2004; Kleiser and Frimmel 2000; Toor and Mohseni 2007; Section 6.3.1) or HAA-FP (Toor and Mohseni 2007; Section 6.3.1).

This research took a detailed look at how UV/H$_2$O$_2$ transformed NOM in raw surface water in terms of aromaticity and hydrophobicity and the impact of these changes on THM-FPs and HAA-FPs. Special attention was given to using fluences and H$_2$O$_2$ concentrations within the acceptable range for commercial applications. Further, a select fraction of the NOM, the very hydrophobic acids (VHA), was removed from the raw surface water and the impact of UV/H$_2$O$_2$ on NOM aromaticity, concentration, and THM-

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3 A version of this chapter has been submitted for publication. Sarathy, S.R. & Mohseni, M. Effects of UV/H$_2$O$_2$ advanced oxidation on chemical characteristics and chlorine reactivity of surface water natural organic matter.
FPs and HAA-FPs was observed. As NOM is highly variable amongst sources, special attention was given to characterizing the NOM in this study and discussing the results with consideration of its unique characteristics. The results provided insight into the implications of NOM oxidation during commercial drinking water applications and the potential for combining UV/H₂O₂ with pre-treatment to achieve NOM and DBP reduction.

4.2 Materials and Methods

The UV fluences applied were selected based on their relation to commercial drinking water applications (i.e., less than 2000 mJ cm⁻²). The initial H₂O₂ concentrations of 5 and 15 mg L⁻¹ were selected based on the typical range for commercial drinking water applications (in communication with Trojan Technologies).

In order to consider the reproducibility of the UV/H₂O₂ treatment experiments, duplicate runs were conducted. The data for each individual run are presented as the average values of multiple measurements. It was opted to present the data in this form as the analytical methods, namely DBP-FP tests and hydrophobicity tests, are prone to variation from one measurement to the next.

For the DBP-FP tests, chlorination of samples was done in triplicate and the reported values are the average DBP-FPs for the three chlorinated samples. Error bars in figures represent the standard deviation between the three chlorinated samples.

4.2.1 Source and Characteristics of Waters

Two different waters were experimented with in this study: (i) raw Capilano water (CW) originated from Capilano Reservoir which provides drinking water for the Greater Vancouver region, British Columbia, Canada and (ii) DAX-8 fractionated (see Section 4.2.3.3 for fractionation procedure) CW (Post-DAX water).

The Capilano Reservoir was formed by the damming of the Capilano River, which is fed by the fall and winter rain runoff and the spring snowmelt. CW is a surface water of high quality as it has low total organic carbon (TOC) concentration (<2.5 mg L⁻¹), turbidity (<1 NTU), and alkalinity (<5 mg CaCO₃ L⁻¹) (Table 4.1). Currently, the drinking water supply from the Capilano Reservoir undergoes no coagulation/flocculation or filtration prior to chlorine disinfection. The water used for this particular study was obtained in March of 2006.

Post-DAX water was prepared by passing 4 L of CW through the DAX-8 resin column (described below). This resulted in water for which the very hydrophobic acids had been removed. Prior to UV/H₂O₂
treatment, Post-DAX water was adjusted to a pH of approximately 6.8, the same pH as CW, using concentrated sodium hydroxide (Fisher Scientific).

4.2.2 UV/H₂O₂ Treatment of Water Samples

A collimated beam apparatus (Figure 4.1) was used as the UV irradiation instrument. It consisted of a low-pressure high-output mercury lamp (Trojan Technologies, London, ON) positioned 28 cm above a circular stirred reactor chamber. The reactor chamber was 6.4 cm in diameter and the water pathlength was 4.66 cm. The incident fluence rate for the given collimated beam and reactor was determined using iodide/iodate actinometry exactly as described in Section 3.2.4. A radiometer (IL1700, sensor SED240 for 254 nm, International Light Inc.) served as a reference. The average fluence rate through the water volume was determined as described in Section 3.2.4. Samples were irradiated for calculated durations to achieve five different delivered fluences from 0 to 2000 mJ cm⁻².

H₂O₂ (30%, Fisher Scientific) was added initially to the reactor chamber at concentrations of 5 or 15 mg L⁻¹. H₂O₂ concentration was measured by reaction with iodide catalyzed by molybdate (Klassen et al. 1994). All H₂O₂ containing samples were quenched of H₂O₂ using 0.2 mg L⁻¹ bovine liver catalase (lyophilized powder ≥10,000 units mg⁻¹ protein, Sigma Aldrich) prior to absorbance and TOC measurements, hydrophobic/hydrophilic fractionation, chlorine demand, THM-FP, and HAA-FP tests.

4.2.3 Analytical Methods

The following parameters were monitored in CW and the UV/H₂O₂ treated CW: TOC concentration, absorbance coefficient at 254 nm (A₂₅₄), hydrophobic/hydrophilic fractions, apparent molecular weight (AMW) distributions, chlorine demand, THM-FP, and HAA-FP. As Post-DAX water had already been fractionated, all of the above mentioned analyses, except hydrophobic/hydrophilic fractionation, were performed on Post-DAX water and UV/H₂O₂ treated Post-DAX water.

4.2.3.1 Total Organic Carbon Concentration and Spectroscopic Measurements

TOC concentration was measured using standard methods on a Shimadzu TOC-VCPH. All spectroscopic measurements (A₂₅₄, H₂O₂ measurement, and free chlorine measurement) were determined using a Shimadzu UV-Mini 1240.

4.2.3.2 High Performance Size exclusion Chromatography

High performance size exclusion chromatography (HPSEC) was employed to determine the AMW distribution of CNOM in untreated CW and Post-DAX water. The analytical method applied as well as the method for peak fitting were exactly as described in Section 3.2.5.
4.2.3.3 Hydrophobic/Hydrophilic Fractionation

The experimental method and apparatus applied for hydrophobic/hydrophilic fractionation were based on the rapid fractionation technique published by Chow et al. (2004). Two resins, Supelite DAX-8 (Supelco) and Amberlite XAD-4 (Supelco) were used in series to separate the NOM into three fractions:

- very hydrophobic acids (VHA): the percentage of the initial TOC adsorbed onto DAX-8, calculated by:

\[
\text{%VHA} = \frac{\text{TOC}_{\text{initial}} - \text{TOC}_{\text{after DAX-8}}}{\text{TOC}_{\text{initial}}} \times 100
\]

- slightly hydrophobic acids (SHA): the percentage of the initial TOC adsorbed onto XAD-4, calculated by:

\[
\text{%SHA} = \frac{\text{TOC}_{\text{after DAX-8}} - \text{TOC}_{\text{after XAD-4}}}{\text{TOC}_{\text{initial}}} \times 100
\]

- hydrophilic charged + hydrophilic NEU (CHA+NEU): the percentage of the initial TOC not adsorbed by either of the resins, calculated by:

\[
\text{%CH}(\text{A+NEU}) = \frac{\text{TOC}_{\text{after XAD-4}}}{\text{TOC}_{\text{initial}}} \times 100
\]

Each of the resins was pre-cleaned: Step 1 - Submersed in methanol (Reagent A.C.S., Fisher Scientific) and mixed overnight followed by decantation of methanol and resin fines; Step 2 - Submersed in acetonitrile (HPLC grade, Fisher Scientific) and mixed overnight followed by decantation of acetonitrile and resin fines; Step 3 - Submersed in deionised (DI) water and mixed, decanted and repeated until there was no TOC measured. Once cleaned, each resin was loaded onto a glass column (16 cm in length, 1.9 cm in diameter). Each column was connected to a peristaltic pump (7553-30, Cole-Parmer Instrument) and the pumps were set to run at a flowrate of 1 mL min\(^{-1}\) (0.1 bed volumes min\(^{-1}\)). Here the objective was not to perform a rapid fractionation, but rather to ensure all material was removed by the respective resins. Therefore, a very low flow rate was chosen to maximize the removal of fractions. The fractionation procedure involved adjusting the pH of 500 mL of sample to pH 2 using concentrated hydrochloric acid (Reagent A.C.S., Fisher Scientific) and then passing the sample through the column containing DAX-8 resin. Following exposure to the DAX-8 resin, 60 mL was removed for TOC analysis and the remaining sample was passed through the column containing XAD-4 resin. The final effluent was
measured for TOC. Between fractionation of samples, the resins were cleaned to prevent sample cross-
over due to leaching. The DAX-8 and XAD-4 resins were cleaned by passing 1 L of DI water through the
columns. Finally, DI water at pH 2 was passed through the columns until there was little trace of TOC (≤ 0.1 mg L⁻¹) in the effluent, upon which time the resins were deemed ready for the next sample.

4.2.3.4 Formation Potentials of Trihalomethanes and Haloacetic Acids and Chlorine Demand Determination

The water samples’ potentials to form THMs and HAAs were determined by spiking 30 mL of water sample with sodium hypochlorite (6% commercial bleach, Lavo Inc.) to achieve a free chlorine concentration of about 3 times the TOC concentration. Therefore, CW samples were spiked to 7.5 mg L⁻¹ (± 0.5 mg L⁻¹) and Post-DAX water was spiked to 3.5 mg L⁻¹ (± 0.5 mg L⁻¹). By doing so the ratio of free chlorine to TOC was maintained constant for the two different waters. Moreover, these initial concentrations of free chlorine yielded a 1 mg L⁻¹ free chlorine concentration after incubation. The samples were incubated at 22 °C for 7 days. After the chlorination period, according to the EPA Method 551.1 (USEPA 1995a), THMs were extracted and detected by gas chromatograph equipped with an ion trap mass spectrometer detector (GC-MS, Saturn 2200, Varian Inc.), a VF-5ms column (Varian Inc.), and a Combi-Pal (Pal System, CTC Analytics) autosampler. Due to the absence of bromide in the CW, chloroform was the primary THM generated. According to the EPA Method 552.2 (USEPA 1995b), HAAs were methylated, extracted, and detected by the GC-MS instrument described previously. Dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were the primary HAAs reported because of their relatively high concentrations and the absence of brominated HAAs.

Chlorine demand was taken as the difference between the initial measured free chlorine concentration and the free chlorine concentration measure after 7 days of incubation at 22°C. Free chlorine concentration was determined with free chlorine reagent powder pillows (DPD Method 8021, Hach).

4.3 Results and Discussion

4.3.1 Characteristics of Capilano Water and Post-DAX Water

In this study, two waters were exposed to UV/H₂O₂ treatment and changes in NOM characteristics and reactivity with chlorine were monitored. The purpose of using two waters was to compare and contrast the impacts of UV/H₂O₂ treatment on waters with different NOM composition and characteristics. Following are the results of the analyses done on the two waters as well as discussion on the implications of these characteristics on UV/H₂O₂ treatment.
4.3.1.1 Alkalinity, Total Organic Carbon Concentration, and Aromaticity of Capilano Water

CW was a raw surface water with TOC of 2.18 mg L\(^{-1}\), SUVA of 3.56 L mg\(^{-1}\) m\(^{-1}\), and alkalinity of less than 5 mg CaCO\(_3\) L\(^{-1}\) (Table 4.1). This combination of parameters made CW quite unique in character. Relative to the waters reported by Archer & Singer (2006), CW is very low in alkalinity. For the 343 non-blended surface waters with no oxidative pretreatment and alkalinity ranging from 0 to 60 mg CaCO\(_3\) L\(^{-1}\), the mean value was 38.2 mg CaCO\(_3\) L\(^{-1}\) (data collected and assimilated under the Information Collection Rule, USEPA) (Archer & Singer 2006).

Archer & Singer (2006) also reported TOC and SUVA for 152 non-blended surface waters with no oxidative pretreatment. For waters with TOC between 2 to 4 mg L\(^{-1}\), the mean SUVA was 2.87 L mg\(^{-1}\) m\(^{-1}\) with a standard deviation of 1.32 L mg\(^{-1}\) m\(^{-1}\). As SUVA is indicative of the aromatic character of NOM (Nikolaou & Lekkas 2001), in comparison to many North American surface waters, the NOM in CW had a high aromatic character (Table 4.1). A related parameter, \(A_{254}\) is an indicator of the amount of aromatic and conjugated double bond structures present in water, also termed chromophoric NOM (CNOM). Therefore, CW was high in CNOM concentration relative to many North American surface waters.

4.3.1.2 Fractionation of Capilano Water and Total Organic Carbon Concentration and Aromaticity of Post-DAX Water

The TOC fractionation profile of CW (Table 4.1) was 66% VHA, 17% SHA, and 18% CHA+NEU illustrating that the VHA fraction made up the majority of NOM present in CW. Post-DAX water was 76% lower in \(A_{254}\) than CW (Table 4.1). Thus, the fraction of NOM absent in Post-DAX water, the VHA fraction, represented 76% of the aromatic and conjugated double bond structure in CW. Additionally, the aromatic character (i.e., SUVA) for Post-DAX water was 1.89 L mg\(^{-1}\) m\(^{-1}\), 48% lower than that of CW. Therefore, the removal of VHA fraction resulted in modified water in which there was a lower concentration of NOM, less CNOM, and NOM of lower aromatic character. The reductions in aromaticity were expected since the VHA fraction generally includes soil fulvic acids, C\(_5\)-C\(_9\) carboxylic acids, 1- and 2-ring aromatic carboxylic acids, and 1- and 2-ring phenols (Leenheer 1981; Aiken et al. 1992; Marhaba et al. 2000; Barber et al. 2001; Swietlik et al. 2004; Buchanan et al. 2005).

4.3.1.3 Apparent Molecular Weight Distribution of Capilano Water and Post-DAX Water

The apparent molecular weight (AMW) distributions of CNOM in CW and Post-DAX water are illustrated in Figure 4.2 and Figure 4.3. CW consisted of predominantly high molecular weight CNOM with lower concentrations as AMW decreased. Removal of the VHA fraction led to reductions in all
AMW fractions, while high AMW fractions saw the largest reductions, up to 91% for the >1450 kg mol\(^{-1}\) fraction (Figure 4.3). Therefore, Post-DAX water contained NOM with much lower concentrations of high AMW CNOM than CW, and was predominantly composed of intermediate to low AMW CNOM.

### 4.3.1.4 Formation Potential of Disinfection By-products for Capilano Water and Post-DAX Water

The %VHA has been used as an indicator of NOM’s reactivity with chlorine to form THMs (Chow et al. 2005). For most waters, the VHA fraction has a higher potential to form THMs than other fractions and it is considered the major THM precursor (Chow et al. 2005). However, DAX-8 fractionation does not directly interact with the THM reactive carbon fraction and that the relation between %VHA and THM-FP can be different for different sources (Chow et al. 2005). The THM-FP of CW was 397 µg L\(^{-1}\) while that of Post-DAX water was 125 µg L\(^{-1}\). Thus, the VHA fraction of CW (i.e., the fraction absent from Post-DAX water), 66% of the TOC, was responsible for 69% of the THM-FP of CW (Table 4.1). However, this did not mean that the VHA fraction was the most reactive fraction with chlorine leading to the formation of THMs. Comparing the TOC specific THM-FP (STHM-FP\(_{TOC}\)), equal to the THM-FP divided by the TOC concentration, of CW and Post-DAX water revealed that the NOM in Post-DAX water was only 31% less reactive in forming THMs than the NOM in CW (Table 4.1). Had the VHA fraction represented the major precursors for THMs in CW, one would have expected Post-DAX water to have a much lower STHM-FP\(_{TOC}\). This demonstrated that most of the reduction in THM-FP observed after eliminating the VHA fraction was primarily due to the reduction in NOM concentration (i.e., TOC), rather than specific removal of a more reactive fraction of the NOM. Thus, one or more of the remaining SHA, CHA, and NEU fractions present in Post-DAX water was responsible for the NOM’s high reactivity with chlorine to form THMs.

Further, while SUVA and \(A_{254}\) are common surrogates for THM-FP, the lower aromaticity of Post-DAX water did not correlate with a reduction in reactivity with chlorine. Dividing the THM-FP by \(A_{254}\) yielded the CNOM specific THM-FP (STHM-FP\(_{CNOM}\)), a measure of the propensity of aromatic and conjugated double bond species of NOM (i.e., CNOM) to form THMs. Comparing the STHM-FP\(_{CNOM}\) for Post-DAX water and CW, it was observed that the CNOM in Post-DAX water was 27% more reactive with chlorine to form THMs than the CNOM in CW (Table 4.1). Therefore, for CW the CNOM may not represent the primary precursors for THMs.

While hydrophobic NOM is often considered the primary precursor for THMs, the hydrophilic fraction has been reported to be the major precursor of HAAs (Hwang et al. 2000). The HAA-FP of CW was 124 µg L\(^{-1}\) versus 64 µg L\(^{-1}\) for Post-DAX water (Table 4.1). Thus, the VHA fraction made up 48%
of the HAA-FP for CW. In terms of SHAA-FP$_{TOC}$, CW and Post-DAX water were almost identical (Table 4.1), supporting the hypothesis that hydrophilic NOM is highly reactive with chlorine to form HAAs. Finally, as with THMs, CNOM was not observed to be the primary precursor for HAAs as the SHAA-FP$_{CNOM}$ for Post-DAX water was 93% greater than that of CW (Table 4.1).

4.3.2 UV/H$_2$O$_2$ Advanced Oxidation Treatment on Capilano Water

4.3.2.1 Impact of UV/H$_2$O$_2$ on Ultraviolet Absorbance

Figure 4.4 illustrates the changes observed in $A_{254}$ and SUVA for CW treated with 15 mg L$^{-1}$ initial H$_2$O$_2$ concentration and fluences of 0, 500, 1000, 1500, and 2000 mJ cm$^{-2}$. A linear decrease was observed in both $A_{254}$ and SUVA. The fact the TOC was not mineralized during the process (data not shown) explained why reduction in SUVA was of the same degree as the reduction in $A_{254}$. These results agree very closely with that of previous studies on the impact of UV/H$_2$O$_2$ on CW (Section 2.3.2; Section 3.3.1) demonstrating that the observed phenomena (i.e., degradation of aromatic, conjugated double bond species by reaction with $'OH$) was consistent over numerous experimental treatments. Previously, it was demonstrated that this reduction in aromaticity was accompanied by a reduction in higher AMW CNOM leading to the formation of smaller AMW CNOM (Section 3.3.1). These reaction products included low molecular weight carbonyls such as aldehydes, ketones, and carboxylic acids (Thomson et al. 2004; Section 2.3.5). As these compounds tend to be less hydrophobic than their aromatic precursors, resin fractionation was applied in this study to observe if there was a reduction in NOM hydrophobicity.

4.3.2.2 Impact of UV/H$_2$O$_2$ on Hydrophobicity

As the low molecular weight carbonyls compounds tend to be less hydrophobic than their aromatic precursors, resin fractionation was applied in this study to observe if there was a reduction in NOM hydrophobicity. Figure 4.5 presents the changes observed in %VHA for CW treated with initial H$_2$O$_2$ concentrations of 5 and 15 mg L$^{-1}$ and fluences from 0 to 2000 mJ cm$^{-2}$. With 5 mg L$^{-1}$ initial H$_2$O$_2$, as fluence increased there was an apparent reduction in the fraction of VHA suggesting that NOM was converted to less hydrophobic characteristic as the duration of reaction with $'OH$ increased. An enhanced effect on %VHA of increasing the initial H$_2$O$_2$ concentration to 15 mg L$^{-1}$ was clear at fluences of 500 and 1000 mJ cm$^{-2}$ for Run 2 (Figure 4.5). However, at all other points the increased initial H$_2$O$_2$ concentration was not observed to greater reduce %VHA, contrary to expectations. This can partially be attributed to the fractionation method’s insensitivity in observing small changes in %VHA. The low TOC of CW decreased the fractionation method’s precision as the change in VHA in absolute terms was no more than 0.6 mg L$^{-1}$ TOC.
The observed reduction in %VHA supports other studies which reported reductions in %VHA during photocatalysis (Liu et al. 2008) and vacuum UV irradiation (Buchanan et al. 2008). Liu et al. (2008) observed a greater than 50% reduction in %VHA after irradiating, with titanium dioxide present, Myponga Reservoir water (around 10 mg L\(^{-1}\) TOC concentration) for 30 minutes. Buchanan et al. (2008) irradiated East Moorabol water (6.9 mg L\(^{-1}\) TOC concentration) with roughly 2.5 J cm\(^{-2}\) 185 nm vacuum UV (254 nm fluence of approximately 16 J cm\(^{-2}\)) and observed a greater than 50% reduction in %VHA. The lower reductions in %VHA observed in this study (less than 25%) can be attributed to the far milder advanced oxidation conditions applied in this study.

4.3.2.3 Impact of UV/H\(_2\)O\(_2\) on Disinfection By-product Formation Potentials

The impact of \(^{1}\)OH on NOM seemed to impact NOM characteristics (i.e., aromaticity and hydrophobicity) that typically signal reductions in DBP precursors. The effects of fluence, during UV/H\(_2\)O\(_2\) of CW, on THM-FP and HAA-FP are presented in Figure 4.6. In general, a decreasing trend was observed for THM-FP and HAA-FP as fluence increased. Although there were apparent reductions, it was noted that when considering the errors in formation potential tests (see error bars in Figure 4.6), these reductions were not always significant. Significant reductions were only observed during Run 1, for which THM-FP was decreased by 16% at a fluence of 2000 mJ cm\(^{-2}\) (t\(_{a,0.05}\) = 6.0) and HAA-FP was decreased by up to 42% at a fluence of 2000 mJ cm\(^{-2}\) (t\(_{a,0.05}\) = 6.4). At 95% confidence level (t-critical\(_{a,0.05}\), df:2, two tailed = 4.3), it was concluded that even at 2000 mJ cm\(^{-2}\), fluence did not have a very strong effect on reducing DBP-FPs. Lower fluences had even less or no significant effect on DBP-FPs. As TOC was not mineralized the apparent reductions in DBP-FPs, although not highly significant, were likely due to changes in the NOM character such as the reduction in aromaticity and hydrophobicity. Recall that, based on the results for STHM-FP\(_{CNOM}\) and SHAA-FP\(_{CNOM}\) for CW and Post-DAX (Table 4.1), CNOM was not observed to be the primary precursor for the DBPs. Therefore, although UV/H\(_2\)O\(_2\) led to large reductions in CNOM, the lack of highly significant reductions in DBP-FPs is not totally unexpected.

SUVA has been considered as a good indicator for the potential of NOM to form THMs (Chow et al. 2005; Chow et al. 2008) and HAAs (Croué et al. 2000; Kitis et al. 2002). During AOPs, including photocatalysis (Liu et al. 2008), UV-ozone (Chin & Bérubé 2005), and UV/H\(_2\)O\(_2\) (Kleiser & Frimmel 2000; Thomson et al. 2004; Toor & Mohseni 2007) observed reductions in SUVA were accompanied by reductions in appreciable DBP-FPs. However, this only occurred under conditions at which TOC reduction was also observed, so the reductions in DBP-FPs were likely due to the complete mineralisation of NOM more so than transformational changes causing reduced reactivity of NOM with chlorine. Although SUVA was an appropriate parameter for indicating DBP-FPs after the above mentioned treatments, for drinking water UV/H\(_2\)O\(_2\) processes there are conflicting reports on whether SUVA could
be a good indicator for DBP-FPs. At low and intermediate fluences and initial H₂O₂ concentration less than 20 mg L⁻¹, it has been reported that observed reductions in SUVA were not accompanied by reductions in THM-FPs (Kleiser & Frimmel 2000; Thomson et al. 2004; Section 6.2.2; Toor & Mohseni 2007) or HAA-FPs (Section 6.2.2; Toor & Mohseni 2007). The results in this study with CW did not agree with previous reports and, at 95% confidence level, showed positive correlation between SUVA and THM-FP and HAA-FP after UV/H₂O₂ treatment (Figure 4.7). This demonstrates that for this particular source water, SUVA may serve as an indicator parameter for DBP-FPs after UV/H₂O₂ treatment. Ozonation of CW, at ozone dosages at which TOC was either slightly or insignificantly reduced, also led to reductions in SUVA and DBP-FPs demonstrating the applicability of SUVA to serve as an indicator parameter for DBP-FPs after ozonation (Chin & Bérubé 2005; Chowdhury et al. 2008). Further, the correlation between THM-FP and SUVA was approximately 37 µg mg⁻¹ m⁻¹ and approximately 48 µg mg⁻¹ m⁻¹ for the relationship between HAA-FP and SUVA (calculated from data provided in Chin & Bérubé (2005). For UV/H₂O₂ treatment of CW, a slope of 32 µg mg⁻¹ m⁻¹ was obtained for THM-FP and 24 µg mg⁻¹ m⁻¹ for HAA-FP. These correlations for ozonation and UV/H₂O₂ treatment of CW agree remarkably well suggesting that similar transformations were undergone by DBP precursors in CW as a result of ozone or •OH attack.

Based on the observations herein, and those reported previously, under fluence and H₂O₂ concentrations typically applied in drinking water UV/H₂O₂ applications, large reductions in DBP-FPs are unlikely when treating raw surface water. As discussed earlier, for CW, CNOM and the VHA fraction were shown to not represent the primary DBP precursors. This could partially explain why the appreciable reductions in these portions of NOM during UV/H₂O₂ treatment did not lead to appreciable reductions in DBP-FPs of CW. But the fact that other studies, using NOM with distinctly different characteristics, observed no reduction in DBP-FPs (Kleiser & Frimmel 2000; Thomson et al. 2004; Section 6.2.2) suggests that this depends not only on the specific NOM’s characteristics, but also the mechanism by which •OH attacks NOM and the reactivity of products formed. Kleiser & Frimmel (2000) hypothesized that the •OH reaction with NOM can lead to an increase of alcohol- and keto-groups, which can be precursors for THMs. Further, the insertion of •OH in aromatic rings increases the reactivity with chlorine (Kleiser & Frimmel 2000).

4.3.3 UV/H₂O₂ Advanced Oxidation Treatment on Post-DAX Water

4.3.3.1 Impact of UV/H₂O₂ on Ultraviolet Absorbance

As for CW, UV/H₂O₂ treatment of Post-DAX water led to reduction in the aromaticity of NOM in Post-DAX water (Figure 4.8). However, while the reduction in A₂₅₄ for CW was 70% at a fluence of
2000 mJ cm$^{-2}$ and initial H$_2$O$_2$ concentration of 15 mg L$^{-1}$ (Figure 4.4), there was only a 44% reduction in $A_{254}$ for Post-DAX water under the same conditions. Noting that the initial $A_{254}$ of Post-DAX water is 76% lower than CW (Table 4.1), the rate of degradation of CNOM by $\cdot$OH was apparently dependent on the concentration of CNOM. This indicated that waters with lower initial $A_{254}$, or CNOM, would experience a slower reduction in $A_{254}$ during UV/H$_2$O$_2$ treatment, suggesting a second order rate of reduction (i.e., $d$[CNOM]$/dT = k[\cdot$OH][CNOM]).

Contrary to the observations for UV/H$_2$O$_2$ of CW NOM, treatment of Post-DAX water led to mineralisation of NOM, as indicated by a reduction in TOC (Figure 4.8). TOC reduction was 26% at a fluence of 500 mJ cm$^{-2}$ and increased up to 49% at a fluence of 2000 mJ cm$^{-2}$. Therefore, in the absence of high molecular size, very hydrophobic, aromatic species, $\cdot$OH reacted readily with the remaining NOM leading to mineralisation. Mineralisation of NOM was also observed when ultrafiltered CW was treated by UV/H$_2$O$_2$ and the mineralisation was attributed to the absence of high molecular size NOM in ultrafiltered CW (Section 2.3.1). These similar observations support the hypothesis that for NOM low in molecular size, hydrophobic, and aromatic character, mineralisation can occur at fluences and H$_2$O$_2$ concentrations typically applied in drinking water treatment applications.

SUVA for Post-DAX water fluctuated between about 1.5 and 2.5 L mg$^{-1}$ m$^{-1}$. This type of behaviour shows that the extent of removal for both CNOM and TOC was similar, as shown in Figure 4.8. Therefore, the NOM that was mineralized was apparently aromatic in character.

**4.3.3.2 Impact of UV/H$_2$O$_2$ on Disinfection By-product Formation Potentials**

Generally, for Post-DAX water THM-FP and HAA-FP decreased as fluence increased, up to 55% ($t_{\alpha=0.05} = 10.6$) and 44% ($t_{\alpha=0.05} = 6.8$), respectively, at a fluence of 2000 mJ cm$^{-2}$ for Run 1 of the UV/H$_2$O$_2$ oxidation (Figure 4.9). These reductions were greater than those observed for CW and could be attributed to the mineralisation of NOM. It has been previously reported that when UV/H$_2$O$_2$ led to mineralisation of NOM, there were appreciable reductions in DBP-FPs (Kleiser & Frimmel 2000; Thomson et al. 2004; Toor & Mohseni 2007). Therefore, although UV/H$_2$O$_2$ alone was not capable of largely reducing DBP-FPs, when coupled with an upstream process such as coagulation or membrane filtration that removes a large portion of VHA, high molecular weight, and aromatic NOM, synergistic reductions in DBP-FPs may be achievable.

**4.3.4 Implications of Water Characteristics**

The results presented in this chapter provided valuable insight into the impact of UV/H$_2$O$_2$ treatment on NOM. Yet, a number of the observations and conclusions were specific to the unique characteristics of
CW and the NOM in it. Further, the impacts of UV/H\textsubscript{2}O\textsubscript{2} on Post-DAX water provided indications of the effect of UV/H\textsubscript{2}O\textsubscript{2} on NOM of different character than CW NOM.

The low alkalinity of CW indicated a lack of inorganic carbon \textsuperscript{1}OH scavengers. This made the NOM in CW more prone to \textsuperscript{1}OH radical attack. For a low alkalinity water, one could expect NOM to be impacted more readily by \textsuperscript{1}OH than in higher alkalinity water. So, the observed changes in NOM would be of lower magnitude for waters with higher alkalinity. Also, recall that CW was higher in SUVA and CNOM than many surface waters. One could expect NOM in raw waters with high SUVA to transform similarly to CW NOM. On the other hand, the NOM in raw water with a low SUVA may transform similarly to the NOM in Post-DAX water and one could expect mineralisation of NOM, if alkalinity were also low.

It should be considered that in drinking water UV/H\textsubscript{2}O\textsubscript{2} applications, water is most often treated by some upstream treatment process such as coagulation, sand filtration, and/or membranes. This is done in order to improve the AOP by increasing UV transmittance and removing \textsuperscript{1}OH scavengers including NOM and inorganic carbon. The removal of the VHA fraction can be likened to the impact of conventional alum coagulation upstream of UV/H\textsubscript{2}O\textsubscript{2}. Conventional and enhanced coagulation with alum preferentially removes the hydrophobic fraction of NOM, including the VHA and SHA fractions (Chow et al. 2004; Archer & Singer 2006). Therefore, by studying the impact of UV/H\textsubscript{2}O\textsubscript{2} on Post-DAX water, clues were provided as to how UV/H\textsubscript{2}O\textsubscript{2} may impact source waters that have undergone conventional alum coagulation.

### 4.4 Acknowledgements

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Table 4.1  Select characteristics of Capilano Water and Post-DAX Water.

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<tr>
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<th>Alkalinity</th>
<th>TOC$^\dagger$</th>
<th>pH</th>
<th>$A_{254}$</th>
<th>SUVA</th>
<th>%VHA</th>
<th>%SHA</th>
<th>% (CHA+NEU)</th>
<th>THM-FP$^\ddagger$</th>
<th>STHM-FP$_{TOC}$</th>
<th>STHM-FP$_{CNOM}$</th>
<th>HAA-FP$^\ddagger$</th>
<th>SHAA-FP$_{TOC}$</th>
<th>SHAA-FP$_{CNOM}$</th>
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<tbody>
<tr>
<td>Capilano Water</td>
<td>&lt;5</td>
<td>2.53 ± 0.2</td>
<td>6.8</td>
<td>0.090</td>
<td>3.56</td>
<td>66</td>
<td>17</td>
<td>18</td>
<td>397</td>
<td>157</td>
<td>44</td>
<td>124</td>
<td>53</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>± 0.1</td>
<td>± 0.1</td>
<td>± 0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-DAX Water</td>
<td>&lt;5</td>
<td>1.16 ± 0.2</td>
<td>6.8</td>
<td>0.022</td>
<td>1.92</td>
<td>0</td>
<td>53</td>
<td>47</td>
<td>125</td>
<td>108</td>
<td>56</td>
<td>64</td>
<td>55</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>± 0.1</td>
<td>± 0.1</td>
<td>± 0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^\dagger$: Value presented is the average of greater than 5 measurements. ± is the typical range of fluctuation observed for the instrument.

$^\ddagger$: Value presented is the average of the initial values (i.e. 0 mJ cm$^{-2}$) presented in Figure 4.6 and Figure 4.9 for Runs 1 and 2.
Figure 4.1 Collimated beam apparatus employed for UV/H₂O₂ treatments.

Figure 4.2 HPSEC chromatogram of CW and Post-DAX water. Lines represent the average data of two samples, each sample analysed once.
Figure 4.3  Apparent molecular weight distribution of CNOM for CW and Post-DAX water. Bars represent the average of two samples, each analyzed once. Data labels indicate the percent difference in each fraction with respect to CW.

Figure 4.4  Impact of fluence on $A_{254}$ and SUVA of CW for two UV/H$_2$O$_2$ runs with initial H$_2$O$_2$ concentration of 15 mg L$^{-1}$. Points represent the average of two samples, each measured three times.
Figure 4.5 Change in %VHA of CW for two UV/H₂O₂ runs with initial H₂O₂ concentrations of 5 and 15 mg L⁻¹. Points represent the average of two samples, each measured three times. Solid and dashed lines are to guide viewer along points.

Figure 4.6 Impact of fluence on THM-FP and HAA-FP of CW for two UV/H₂O₂ runs with initial H₂O₂ concentration of 15 mg L⁻¹. Points represent the average of three samples, each chlorinated, incubated, and analyzed for THMs two times. Error bars represent the standard deviation among the measured THMs concentrations of the three samples. Solid and dashed lines are to guide viewer along points.
Figure 4.7 THM-FP and HAA-FP of CW as a function of SUVA. Solid lines represent linear regression lines. Slopes of regression lines are given with 95% confidence intervals.

Figure 4.8 Impact of fluence on $A_{254}$ for two UV/H$_2$O$_2$ runs and TOC for one UV/H$_2$O$_2$ run of Post-DAX water with initial H$_2$O$_2$ concentration of 15 mg L$^{-1}$. Points represent the average of two samples, each measured three times. Solid and dashed lines are to guide viewer along points.
Figure 4.9 Impact of fluence on THM-FP and HAA-FP of Post-DAX water for two UV/H₂O₂ runs with initial H₂O₂ concentration of 15 mg L⁻¹. Points represent the average of three samples, each chlorinated, incubated, and analyzed for THMs two times. Error bars represent the standard deviation among the measured THMs concentrations of the three samples. Solid and dashed lines are to guide viewer along points.
Literature Cited


USEPA. (1995a) Method 551.1: Determination of chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron capture detection.

USEPA. (1995b) Method 552.2: Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatization and gas chromatography with electron capture detection.
Chapter 5
Modeling the Transformation of Chromophoric Natural Organic Matter during UV/H$_2$O$_2$ Advanced Oxidation

5.1 Introduction

Designing a UV/H$_2$O$_2$ system for a practical application necessitates the prediction of H$_2$O$_2$ concentration and fluence requirements to achieve the desired levels of contaminant removal (Tühkanen 2004). There are a number of mathematical models, based on photochemical and chemical engineering principles, describing the UV/H$_2$O$_2$ advanced oxidation process (Glaze et al. 1995; Liao & Gurol 1995; Stefan et al. 1996; Crittenden et al. 1999; Sharpless & Linden 2003; Song et al. 2008). Some of these models use a pseudo-steady-state assumption for the concentration of hydroxyl radicals (•OH), assuming that the net formation of •OH is zero (Glaze et al. 1995; Liao & Gurol 1995; Stefan et al. 1996;) while others assume all species, including radicals, to be dynamic (Crittenden et al. 1999; Song et al. 2008). While the pseudo-steady-state assumption is a safe simplification, since •OH reacts rapidly with so many species and the concentration of •OH is very low and will not accumulate over time (Linden et al. 2007), a dynamic model is always a better descriptor of actual system behaviour.

Some of the existing models incorporate the •OH scavenging potential of natural organic matter (NOM) (Liao & Gurol 1995; Crittenden et al. 1999; Sharpless & Linden 2003) while only one models the degradation of NOM (Song et al. 2008). However, Song et al. (2008) primarily targeted the mineralization of NOM and so, did not address the partial degradation of NOM under practical operating conditions. In commercial drinking water UV/H$_2$O$_2$ applications, the oxidation conditions (i.e., fluences and/or H$_2$O$_2$ concentrations) are not strong enough to mineralize NOM. Instead, partial oxidation of NOM takes place, leading to constantly changing water characteristics that in turn affect process efficacy and water quality (Chapter 2; Chapter 3; Chapter 4; Chapter 6). For example, reduction in the absorbance of water at 254 nm UV would lead to an increase in the photolysis of H$_2$O$_2$, thereby increasing the rate of •OH production.

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A version of this chapter will be submitted for publication. Sarathy, S.R., Bazri, M., & Mohseni, M. Modeling the transformation of chromophoric natural organic matter during UV/H$_2$O$_2$ advanced oxidation.
The focus of this research has been the development of a dynamic kinetic model that predicted partial degradation of NOM by incorporating a surrogate parameter, the absorbance of 254 nm UV, representing structural transformation of NOM attributable to •OH attack. The portion of NOM that absorbed at 254 nm has been defined as chromophoric natural organic matter (CNOM). The model was developed using literature obtained reaction schemes and kinetic rate constants. To obtain reaction rate constants that were not available in the literature (i.e., for reactions between •OH and NOM), experiments were conducted with “synthetic” water using isolated Suwannee River Natural Organic Matter and model parameter estimation was applied to obtain the unknown model parameters. Subsequently, the model, using the literature and estimated rate constants, was evaluated and applied to two natural waters to predict the degradation of CNOM and H$_2$O$_2$ during UV/H$_2$O$_2$ treatment. Further, the natural waters were amended with additional alkalinity and treated in order to elucidate the impact of alkalinity on CNOM and H$_2$O$_2$ degradation.

5.2 Materials and Methods

5.2.1 Waters

“Synthetic” water was created to empirically estimate model parameters. Suwannee River Aquatic NOM (SRNOM-aquatic) (International Humic Substance Society) was added to ultrapure water (Millipore) at varying concentrations. A detailed description of the source of SRNOM-aquatic isolate as well as its chemical properties and the isolation method are available elsewhere (“International Humic Substances Society”). Total organic carbon (TOC) was used as a surrogate to quantify NOM. Table 5.1 summarizes the properties of the synthetic waters prepared.

The source of the first surface water, Capilano Water (CW) collected March of 2006, was the Capilano Reservoir which serves the Greater Vancouver Region, British Columbia, Canada. The second surface water originated from Trepanier Creek, providing drinking water for the town of Peachland, British Columbia, Canada. Trepanier Water (TW) was collected on May 25, 2008. At this time the water shed was experiencing elevated levels of colour and TOC due to the spring snow melt. The alkalinity of both CW and TW was modified by the addition of sodium bicarbonate (ACS Grade, Fisher Scientific). The characteristics of raw CW and TW are provided in Table 5.1.

5.2.2 Advanced Oxidation Treatment

A collimated beam apparatus, consisting of low pressure high output UV lamp (Trojan Technologies, London, ON) positioned 28 cm above a circular stirred reactor chamber was employed for the batch
UV/H$_2$O$_2$ studies. The reactor chamber was either a glass petri dish 5.5 cm in diameter and depth of 2.95 cm or a glass petri dish 8.75 cm in diameter and depth of 3.33 cm. The petri dish was covered with a thin quartz disc to prevent contamination from the air and evaporation. The reactor content was irradiated and samples were taken at various intervals from 0 to 150 minutes. This time frame was selected as it corresponded to a fluence range up to 2000 mJ cm$^{-2}$. H$_2$O$_2$ (30%, Fisher Scientific) was added initially to the reactor chamber at the desired concentrations. H$_2$O$_2$ containing samples were quenched of H$_2$O$_2$ using 0.2 mg L$^{-1}$ bovine liver catalase (lyophilized powder, ≥10,000 units mg$^{-1}$ protein, Sigma Aldrich) prior to absorbance and TOC.

5.2.3 Analytical Methods

The incident fluence rate ($E_\phi$) for the given collimated beam and reactor was determined using iodide/iodate actinometry exactly as described in Section 3.2.4. In some cases, a calibrated radiometer (IL1700, sensor SED240 for 254 nm, International Light Inc.) was used to determine $E_\phi$ following the standardized method for fluence determination (Bolton & Linden 2003).

H$_2$O$_2$ concentration was measured by reaction with iodide catalyzed by molybdate (Klassen et al. 1994). TOC was measured using a combustion catalytic oxidation/nondispersive infrared sensor TOC analyzer (Shimadzu TOC-VCPH) or a UV/persulfate oxidation method TOC analyzer (Sievers 900). Absorbance measurements were determined using a UV-Vis spectrophotometer (Shimadzu UV-Mini 1240 or Cary 100) with 1cm quartz cuvette (Hellma). Alkalinity was measured by Standard Method 2320 (Clescerl et al. 1998).

4-chloro-benzoic acid (pCBA) was detected using a Waters 600-MS HPLC equipped with a Waters 996 photodiode array detector, a Waters 717 plus autosampler, and Supelcosil LC-18 column. The eluent consisted of 0.5% H$_2$PO$_4$ and acetonitrile, at a ratio of 52%:48%, and was run at a column flowrate of 1.5 mL min$^{-1}$. The quantification wavelength for pCBA was at 238 nm.

The technique for hydrophobic/hydrophilic fractionation was based on the rapid fractionation technique published by Chow et al. (2004). Two resins, Supelite DAX-8 (Supelco) and Amberlite XAD-4 (Supelco) were used in series to separate the NOM into three fractions: (i) very hydrophobic acids (VHA), (ii) slightly hydrophobic acids (SHA), and (iii) charged plus neutral hydrophilics (CHA+NEU). The exact method and procedure is given in Section 4.2.3.3.
5.2.4 Kinetic Modeling Approach, Reaction Scheme, and Governing Rate Expressions

A kinetic model for the UV/H₂O₂ process was developed for predicting changes over time in the amounts of CNOM (i.e., 254 nm absorbing NOM), H₂O₂/HO₂⁻, carbonate species (HCO₃⁻/CO₃²⁻), and radical species (·OH, O₂⁻/HO₂⁻, CO₃⁻). The approach taken closely followed that of UV/H₂O₂ models developed previously by other researchers (Glaze et al. 1995; Liao & Gurol 1995; Crittenden et al. 1999; Stefan et al. 2000; Sharpless & Linden 2003; Song et al. 2008). Table 5.2 provides a summary of the reactions defined for the system along with the literature reaction rate constants used. Based on the reactions in Table 5.2, the overall kinetic rate expressions were defined by the ordinary differential equations given in Table 5.3.

The first term in Equation [5.1] represents the rate of photolysis of H₂O₂ which is dependent on the primary quantum yield of H₂O₂, Φ_H₂O₂, in Reaction 1 equal to 0.5, and the specific rate of light absorption by H₂O₂ at 254 nm, k_a,H₂O₂,254 (Es mol⁻¹ s⁻¹). As given by Sharpless & Linden (2003), the specific rate of light adsorption of H₂O₂ is defined as:

\[ [5.11] \]
\[ k_a,H₂O₂,254 = \frac{E_p^p \epsilon_{H₂O₂,254}[1 - 10^{-A_{total,254}z}] \times 1000}{A_{total,254}^z} \]

\[ [5.12] \]
\[ A_{total,254} = [H₂O₂] \epsilon_{H₂O₂,254} + [CNOM] \epsilon_{CNOM} \]

In Equation [5.11], E_p^p is the incident photon fluence rate (Es cm⁻² s⁻¹), z is the pathlength, and A_{total,254} is the total water absorption coefficient at 254 nm (cm⁻¹). A_{total,254} is defined by Equation [5.12] where \epsilon_{H₂O₂,254} is the decadic molar absorption coefficient of H₂O₂ at 254 nm (19.6 M⁻¹ cm⁻¹), and \epsilon_{CNOM} is the decadic molar absorption coefficient of CNOM. Recall that, by definition, CNOM only absorbs at 254 nm and that the absorption coefficient for CNOM, A_{CNOM} (cm⁻¹), is defined as:

\[ [5.13] \]
\[ A_{CNOM} = [CNOM] \epsilon_{CNOM} \]

As with the models developed by Crittenden et al. (1999) and Song et al. (2008), the model developed in this study employed non-steady-state for all radical species as defined by Equations [5.3-5.6]. In Equation [5.3], the first ten terms represent the scavenging of ·OH in the system. All the major scavengers
such as NOM (represented as TOC), carbonates, H$_2$O$_2$, and pCBA have been included. Note that although the model included the reaction between CNOM and $'OH$ (Reaction 26), CNOM need not be included in Equation [5.3] as one of the scavenging terms since CNOM is a subset of NOM. The last three terms in Equation [5.3] represent the generation of $'OH$, primarily due to the photolysis of H$_2$O$_2$.

Species contributing to alkalinity, namely bicarbonate and carbonate, are present in most natural waters and are major scavengers of $'OH$ (Reaction 4, Reaction 5), thus these reactions have been included in the model by Equations [5.7, 5.8].

In Equation [5.9] pCBA, the $'OH$ probe, could be substituted with any organic contaminant. Further, additional organic contaminants could be added to this model easily. pCBA is predominantly degraded by $'OH$ so its reaction with other species is neglected. Also, the direct photolysis of pCBA at 254 nm is negligible so is not included in this model. Of course, if pCBA was substituted with another compound that either is photolyzed at 254 nm or reacts with other free radicals, the kinetic rate expressions would require modification to include the necessary terms.

As defined by Reaction 26 and Equation [5.10], CNOM was assumed to be degraded by $'OH$ only. Direct photolysis of CNOM was neglected since prior experimental results demonstrated that when treatment was conducted in the absence of H$_2$O$_2$ (i.e., only UV irradiation), there was no reduction in CNOM (Section 3.3.1). This implied that under the irradiation conditions (i.e., incident photon fluence rate and irradiation time) implemented in this study CNOM is predominantly degraded by reaction with $'OH$.

As mineralisation of raw water TOC had previously not been observed that under the irradiation conditions implemented in this study (Section 2.3.1; Section 3.3.1), this model assumed TOC was constant over the duration of the treatment.

5.2.5 Empirical Approach for Parameter Estimation

Controlled experiments were conducted to gather data for estimating the two unknown reaction rate constants, $k_{OH,CNOM}$ (L mg$^{-1}$ s$^{-1}$) and $k_{OH,TOC}$ (L mol$^{-1}$ s$^{-1}$). Experiments were conducted with SRNOM-aquatic synthetic water in a factorial format with TOC levels of 1.33, 2.21, and 3.08 mg L$^{-1}$ and initial H$_2$O$_2$ concentration levels of approximately 5 and 15 mg L$^{-1}$. For each experiment, $E_p^c$ was 6.42E-10 Es cm$^{-2}$ s$^{-1}$ and pCBA was added initially at a concentration of approximately 200 µg L$^{-1}$. The water was then irradiated for 150 minutes with measurements of pCBA taken every 15 minutes and measurements of H$_2$O$_2$ and CNOM taken every 30 minutes.
In these experiments, pCBA served as an \( \cdot \text{OH} \) probe as its degradation rate is directly dependent on the \( \cdot \text{OH} \) concentration in the system. By monitoring the reduction of pCBA, competition kinetics was used to estimate the reaction rate constant for the reaction between \( \cdot \text{OH} \) and TOC, \( k_{\cdot \text{OH}, \text{TOC}} \). So, experimentally the following relationship was monitored:

\[
\frac{d[p\text{CBA}]}{dt} = -k'_{p\text{CBA}}[p\text{CBA}]
\]

where \( k'_{p\text{CBA}} \) is the apparent reaction rate constant for the reduction of pCBA (s\(^{-1}\)). Recall that pCBA only reacted with \( \cdot \text{OH} \) so Equation [5.14] can be written as Equation [5.9]. As \( k_{\cdot \text{OH},p\text{CBA}} \) is known, 5E9 L mol\(^{-1}\) s\(^{-1}\) (Neta & Dorfman 1968), the \( \cdot \text{OH} \) concentration is responsible for the measured \( k'_{p\text{CBA}} \). The only unknown component in Equation [5.3], i.e., \( k_{\cdot \text{OH}, \text{TOC}} \), can be estimated based on the experimental measurement of pCBA.

Since it was not possible to measure the molar concentration of CNOM and \( \varepsilon_{\text{CNOM}} \) is unknown, \( A_{\text{CNOM}} \) was measured. \( A_{\text{CNOM}} \) could be measured as it was the absorbance coefficient of the water at 254 nm after \( \text{H}_2\text{O}_2 \) was quenched. \( A_{\text{CNOM}} \) was used for the estimation of \( k_{\cdot \text{OH}, \text{CNOM}} \). So, experimentally the following relationship was monitored:

\[
\frac{dA_{\text{CNOM}}}{dt} = -k'_{A\text{CNOM}}A_{\text{CNOM}}
\]

where \( k'_{A\text{CNOM}} \) is the apparent reaction rate constant for the reduction in \( A_{\text{CNOM}} \) (s\(^{-1}\)). However, recall that, by definition, in Equation [5.13], \( A_{\text{CNOM}} \) is directly proportional to the molar concentration of CNOM and an unknown factor of \( \varepsilon_{\text{CNOM}} \). Therefore, Equation [5.15] can be written as:

\[
\varepsilon_{\text{CNOM}} \frac{d[\text{CNOM}]}{dt} = -k'_{C\text{CNOM}}[\text{CNOM}]\varepsilon_{\text{CNOM}}
\]

\[
[5.16]
\]
which simplifies to:

\[
\frac{d[CNOM]}{dt} = -k'_{CNOM}[CNOM]
\]

where \( k'_{CNOM} \) is the apparent reaction rate constant for the reduction of CNOM \((s^{-1})\). Finally, given the assumption that CNOM is only degraded by •OH, Equation [5.17] can be written as Equation [5.10]. Thus, the experimental data for \( A_{CNOM} \) could be used to determine \( k_{OH,CNOM} \).

5.2.6 Numerical Solution of Governing Rate Expressions and Parameter Estimation

The MATLAB function ode15s was used to solve the system of differential (stiff) equations (MATLAB code provided in Appendix C). \( k_{OH,CNOM} \) and \( k_{OH,TOC} \) were estimated by maximum likelihood estimation with a weighted least squares objective function (OF) given by:

\[
OF = \sum_{i=1}^{N} \left\{ \frac{(CNOM_{expt} - CNOM_{model})^2}{\sigma_{CNOM}^2} + \frac{(pCBA_{expt} - pCBA_{model})^2}{\sigma_{pCBA}^2} \right\}
\]

where \( i \) represents a measurement made at some point in time, \( CNOM_{expt} \) is the experimental measurement at \( i \), \( CNOM_{model} \) is the model prediction at \( i \), \( pCBA_{expt} \) is the experimental measurement at \( i \), and \( pCBA_{model} \) is the model prediction at \( i \). \( \sigma_{CNOM} \) and \( \sigma_{pCBA} \) are weighting parameters to compensate for error due to measurement. \( \sigma_{CNOM} \) was set equal to 0.002 cm\(^{-1}\) in order to represent the typical standard deviation observed when making absorbance measurement and \( \sigma_{pCBA} \) was set equal to 5 µg L\(^{-1}\) in order to represent the typical standard deviation observed when making pCBA measurements.

MATLAB’s fminsearch function was used to find values of \( k_{OH,CNOM} \) and \( k_{OH,TOC} \) that minimized the OF, in effect estimating the parameters that best fit model predictions to experimental data. The standard error for the parameters was determined by calculating the Fisher Information Matrix followed by determination of the covariance/sensitivity matrix (according to calculation procedure described by Englezos & Kalogerakis (2001)). From the calculated standard errors, the 95% confidence intervals of
each parameter was calculated and reported with the parameters. Appendix C provides the spreadsheet for calculation of the parameter standard errors.

5.2.7 UV/H2O2 Treatment of Natural Waters

The model was evaluated by comparing the model predicted concentrations for H2O2 and CNOM to experimental data collected during UV/H2O2 treatment of the two raw waters, CW and TW, as well as these waters with additional alkalinity. CW was treated by UV/H2O2 for up to 260 minutes with initial H2O2 concentrations ranging from 5 to 20 mg L\(^{-1}\) and an \(E_p^e\) between 2.54E-10 and 2.84E-10 Es cm\(^{-2}\) s\(^{-1}\). Further, CW was adjusted to alkalinities of approximately 50, 100, and 150 mg CaCO\(_3\) L\(^{-1}\) and was treated by UV/H2O2 for up to 120 minutes with initial H2O2 concentrations ranging from 5 to 15 mg L\(^{-1}\) and an \(E_p^e\) between 8.59E-10 and 9.72E-10 Es cm\(^{-2}\) s\(^{-1}\). TW and TW adjusted to alkalinities of 100 and 150 mg CaCO\(_3\) L\(^{-1}\) were treated by UV/H2O2 for up to 120 minutes with initial H2O2 concentrations ranging from 5 to 20 mg L\(^{-1}\) and an \(E_p^e\) between 9.03E-10 and 9.52E-10 Es cm\(^{-2}\) s\(^{-1}\).

5.3 Results and Discussion

The model proposed here was unique in that it considered the change in the absorption coefficient of water at 254 nm, \(A_{total,254}\), that occurred during UV/H2O2 treatment as a result of H2O2 and CNOM degradation. It was deemed necessary to consider the change in \(A_{total,254}\) since the kinetics of UV/H2O2 system inherently depend on \(A_{total,254}\) (Equations [5.1, 5.3]). Thus, it was clear that including the change in \(A_{total,254}\) provided a more complete characterization of the UV/H2O2 system.

5.3.1 Synthetic Water Observations and Model Parameter Estimation

Results from UV/H2O2 treatment of SRNOM-aquatic synthetic water are presented in Figure 5.1, Figure 5.2, and Figure 5.3. Using this experimental data and the set of kinetic rate expressions given above, the two unknown rate parameters, \(k_{OH,CNOM}\), and \(k_{OH,TOC}\), were estimated simultaneously by minimizing the weighted least squares between model predictions and experimental data. Figure 5.1, Figure 5.2, and Figure 5.3 also include the model predictions using the estimated rate parameters along with the root mean square error (RMSE), an indicator of model accuracy.

5.3.1.1 Hydroxyl Radical Scavenging by Natural Organic Matter

It was apparent that as the initial H2O2 concentration was increased, the observed rate of degradation of pCBA increased (Figure 5.1). This was expected since an increase in H2O2 yielded a greater concentration of \(^{\cdot}\)OH, thus increasing the degradation rate of the \(^{\cdot}\)OH probe. On the other hand, with
increasing concentration of TOC, the observed rate of degradation of pCBA was reduced (Figure 5.1). This also was expected since an increased TOC led to increased scavenging of 'OH by TOC, thus yielding less 'OH to react with pCBA.

The optimal reaction rate constant for the reaction between 'OH and TOC, \( k_{OH,TOC} \), was estimated at 1.14±0.10 E4 L mg\(^{-1}\) s\(^{-1}\). There were no previous studies reporting \( k_{OH,TOC} \) for the SRNOM-aquatic used in this study; however, past literature reports are available for \( k_{OH,TOC} \) for Suwannee River NOM fulvic acid (SRNOM-fulvic), Suwannee River NOM humic acid (SRNOM-humic) and NOM from other sources (Table 5.4). SRNOM-aquatic was preferred in this study since it was considered to be more representative of NOM found in natural waters, rather than fulvic or humic fraction isolates. Nonetheless, the \( k_{OH,TOC} \) estimated in this study for SRNOM-aquatic agreed reasonably well with the literature reports for \( k_{OH,TOC} \) for SRNOM-fulvic, SRNOM-humic, and NOM from other sources. The estimated value, 1.14±0.10 E4 L mg\(^{-1}\) s\(^{-1}\), was within error of the value reported by Westerhoff et al. (2007) for SRNOM-fulvic using pulse radiolysis with competition kinetics and direct transient growth (1.33±0.20 E4 L mg\(^{-1}\) s\(^{-1}\)). Slightly higher were the values for SRNOM-humic and Fluka Humic Acid reported by Goldstone et al. (2002) using \( \gamma \)-radiolysis with competition kinetics (1.90±0.05 E4 L mg\(^{-1}\) s\(^{-1}\)) and Liao & Gurol (1995) using UV/H\(_2\)O\(_2\) with numerical parameter estimation (1.60E4 L mg\(^{-1}\) s\(^{-1}\)), respectively. About three-fold the value estimated in this study were the values for SRNOM-fulvic reported by Goldstone et al. (2002) (2.70±0.05 E4 L mg\(^{-1}\) s\(^{-1}\)) and by Westerhoff et al. (2007) (3.08E4 L mg\(^{-1}\) s\(^{-1}\)) using ozonation with competition kinetics. Finally, the \( k_{OH,TOC} \) estimated in this study for SRNOM-aquatic was approximately two to three times lower than the average values for NOM isolates reported by Westerhoff et al. (1999) (2.54E4 L mg\(^{-1}\) s\(^{-1}\)) and Westerhoff et al. (2007) (3.00±0.45 E4 L mg\(^{-1}\) s\(^{-1}\)) and almost within error of the average value reported by Brezonik & Fulkerson-Brekken (1998) for five surface waters using nitrate-induced solar driven photolysis (2.30±0.77 E4 L mg\(^{-1}\) s\(^{-1}\)).

This variation between reported \( k_{OH,TOC} \) values demonstrates that estimation of the parameter is subject to the method used for 'OH production (i.e., ozonation, UV/H\(_2\)O\(_2\), pulse radiolysis, \( \gamma \)-radiolysis, or nitrate-induced solar driven photolysis), as well as the type of NOM employed (i.e., aquatic isolate, fulvic or humic isolates, or non-isolated/whole water). Yet, regardless of the 'OH production method or the type of NOM employed, \( k_{OH,TOC} \) has been reported to be around 2E4 L mg\(^{-1}\) s\(^{-1}\) (Reisz et al. 2003). As the \( k_{OH,TOC} \) estimated in this work agreed well with other literature values, it was deemed acceptable.

5.3.1.2 Degradation of Chromophoric Natural Organic Matter

Figure 5.2 illustrates the experimental data for \( A_{CNOM} \) for UV/H\(_2\)O\(_2\) treatment of SRNOM-aquatic synthetic water. Recall that \( A_{CNOM} \) is indicative of the concentration of CNOM (Equation [5.13]). As
expected, there was a marked reduction in CNOM as irradiation time increased (Figure 5.2) as was observed in Section 2.3.2 and Section 3.3.1. Further, it was apparent that as the initial H\textsubscript{2}O\textsubscript{2} concentration was increased, the observed rate of degradation of CNOM increased, also observed previously in Section 3.3.1. This observation was expected since an increase in H\textsubscript{2}O\textsubscript{2} yielded a greater concentration of •OH, thus increasing the degradation rate of CNOM. For $k_{\text{OH,CNOM}}$ the optimum value was estimated at 3.04±0.33 E\textsuperscript{8} L mol\textsuperscript{-1} s\textsuperscript{-1}. Literature estimates of $k_{\text{OH,CNOM}}$ were non-existent at the time of publication so it could not be compared.

Prediction of the change in CNOM was deemed valuable since in the UV/H\textsubscript{2}O\textsubscript{2} system CNOM would often be the major absorber of photons. Any change in $A_{\text{CNOM}}$ would have an impact on $A_{\text{total,254}}$ (Equation [5.12]), the photolysis of H\textsubscript{2}O\textsubscript{2} (Equation [5.1]), and subsequently the concentration of •OH (Equation [5.3]). A reduction in $A_{\text{CNOM}}$ would lead to greater absorption of photons by H\textsubscript{2}O\textsubscript{2}, thus improving photolysis and •OH production. Therefore, it was clear that by considering the change in CNOM, prediction of H\textsubscript{2}O\textsubscript{2} degradation would be more accurate.

5.3.1.3 Degradation of Hydrogen Peroxide

Similar to the UV/H\textsubscript{2}O\textsubscript{2} models presented in the literature, the model presented here considered photolysis to be the main pathway for H\textsubscript{2}O\textsubscript{2} degradation. As an improvement to past models, the present model also included the change in CNOM, thereby improving the modeling of H\textsubscript{2}O\textsubscript{2} degradation. Despite improving model predictions to some extent, the model developed here, as have past models, under predicted the measured H\textsubscript{2}O\textsubscript{2} concentrations (Figure 5.3).

Interestingly, the observed maximum extent of degradation of H\textsubscript{2}O\textsubscript{2} increased as TOC increased, from about 15% to 20% at a TOC of 1.33 mg L\textsuperscript{-1} to about 20% to 25% at a TOC of 3.08 mg L\textsuperscript{-1} (Figure 5.3). One would expect that if photolysis were the main pathway for H\textsubscript{2}O\textsubscript{2} degradation, an increased TOC would lead to slower degradation of H\textsubscript{2}O\textsubscript{2} since TOC increase would lead to higher CNOM and greater water absorbance. This would subsequently result in additional screening of UV and a reduction in the number of photons absorbed by H\textsubscript{2}O\textsubscript{2} thereby impeding the H\textsubscript{2}O\textsubscript{2} degradation. In fact, this phenomena was predicted by the model but was not confirmed by the experimental measurements (Figure 5.3). The model predicted best when the conditions were closest to pure water (RMSE < 0.035 for 1.33 mg L\textsuperscript{-1} TOC) and worst when TOC concentration was the highest (Figure 5.3). This demonstrated that the assumption of photolysis being the predominant mechanism for H\textsubscript{2}O\textsubscript{2} degradation may be true for water with very low amounts of NOM, but when NOM is present at even moderately low levels, other mechanisms, besides photolysis and reaction with radical species, contribute to H\textsubscript{2}O\textsubscript{2} degradation.
Song et al. (2008) and Liao & Gurol (1995) also compared model predictions of H$_2$O$_2$ degradation to experimental results for UV/H$_2$O$_2$ treatment with NOM present. Both studies reported that model predictions for H$_2$O$_2$ degradation deviated from the experimental data, with the model under predicting experimental measurements. Song et al. (2008) speculated that this under prediction could be due to H$_2$O$_2$ reacting with NOM. Our experimental results showed that when NOM was in water with H$_2$O$_2$ and no irradiation (i.e., dark reaction), there was no measurable reduction in H$_2$O$_2$ over several hours (data not shown). Thus, it is unlikely that the raw NOM reacts with H$_2$O$_2$ at a very high rate.

It is more plausible that H$_2$O$_2$ reacts readily with the products of the NOM and 'OH reaction. 'OH reacts with NOM either by 'OH addition to a carbon-carbon double bond or by abstraction of a carbon bound hydrogen (von Sonntag et al. 1997). Both mechanisms result in the formation of carbon-centred radicals (von Sonntag et al. 1997). These carbon-centred radicals quickly react with dissolved oxygen forming peroxyl radicals which, via various reactions, go on to form low molecular weight carbonyls such as aldehydes, ketones, carboxylic acids and eventually carbon dioxide. An alternate reaction for the carbon-centred radicals could be with H$_2$O$_2$. Neta et al. (1996) reported the reaction rate constants for oxygen and H$_2$O$_2$ with numerous aliphatic carbon-centred radicals. Reaction rate constants for reactions between carbon-centred radicals with oxygen were generally in the range of $10^8$ to $10^{10}$ L mol$^{-1}$ s$^{-1}$ versus $10^4$ to $10^6$ L mol$^{-1}$ s$^{-1}$ for reactions between carbon-centred radicals and H$_2$O$_2$ (Neta et al. 1996). Clearly the dominant reaction for carbon-centred radicals is with oxygen but their reaction with H$_2$O$_2$ cannot be ignored and this could explain the additional degradation, beyond photolysis, of H$_2$O$_2$. Further research is required to define expressions to more accurately model H$_2$O$_2$ degradation during UV/H$_2$O$_2$ advanced oxidation of water in which NOM is present.

5.3.2 Surface Water Observations and Model Evaluation

Results from UV/H$_2$O$_2$ treatment of CW and TW are presented in Figure 5.4, Figure 5.5, and Figure 5.6 as points, along with model predictions given as lines.

5.3.2.1 Degradation of Chromophoric Natural Organic Matter in Capilano Water and Trepanier Water

CW was treated by UV/H$_2$O$_2$ with initial H$_2$O$_2$ concentrations of approximately 5, 10, 15, and 20 mg L$^{-1}$ while TW was treated with initial H$_2$O$_2$ concentrations of approximately 5 and 15 mg L$^{-1}$. As expected, for both CW and TW, CNOM degraded as irradiation time increased (Figure 5.4). Note that for TW experiments, $E_P$ was over three times greater than the $E_P$ for the CW experiments. Therefore, the extent of degradation of CNOM at a specific time should not be directly compared. Nevertheless, a slower degradation over time was observed for TW but this was expected since TW had greater TOC and $A_{CNOM}$
than CW (Table 5.1). The higher $A_{CNOM}$ would result in lower photolysis of $\text{H}_2\text{O}_2$ and thus less $'$OH generation, thereby reducing the rate of degradation for CNOM. Further, TW also had alkalinity at 47 mg CaCO$_3$ L$^{-1}$ so, as bicarbonate and carbonate are scavengers of $'$OH, their presence would impede the rate of CNOM degradation (further results and discussion on the impact of alkalinity are provided below). As was observed for SRNOM-aquatic synthetic water (Figure 5.2), for CW and TW, there was a clear link between the extent of degradation of CNOM and the initial $\text{H}_2\text{O}_2$ concentration (Figure 5.4).

In general, the model predictions of CNOM degradation agreed well with the experimental results for UV/$\text{H}_2\text{O}_2$ to treat CW and TW. For CW, the model predicted very well the degradation of CNOM both as a function of irradiation time and initial $\text{H}_2\text{O}_2$ concentration. The RMSE, an indicator of model accuracy, ranged from 0.004 to 0.058 with an average of 0.040 indicating a percentage error of about 6% on average. Since both irradiation time and initial $\text{H}_2\text{O}_2$ concentration impact the level of $'$OH exposure, this agreement between model predictions and experimental observations reinforces the model’s assumption that CNOM is only degraded by $'$OH. For TW, model predictions were also fairly accurate for initial $\text{H}_2\text{O}_2$ concentrations of approximately 15 mg L$^{-1}$ (RMSE = 0.028) and 5 mg L$^{-1}$ (RMSE = 0.052) (Figure 5.4).

5.3.2.2 Impact of Alkalinity on Degradation of Chromophoric Natural Organic Matter

An increase in alkalinity resulted in lower degradation of CNOM for CW with approximately 10 or 15 mg L$^{-1}$ initial $\text{H}_2\text{O}_2$ concentration (Figure 5.5). In agreement with this observed behaviour, the model also predicted that an increase in alkalinity led to less degradation of CNOM. This was explained by the scavenging of $'$OH by bicarbonate (Reaction 4) and carbonate (Reaction 5) which resulted in less $'$OH available for reaction with NOM (Equation [5.3]). For TW, increasing alkalinity also resulted in lower degradation of CNOM with approximately 15 mg L$^{-1}$ initial $\text{H}_2\text{O}_2$ concentration (Figure 5.6). However, the experimental results did not show a clear trend, attributed to inherent errors encountered when doing absorbance measurements with grab samples and the slow degradation of TW CNOM. Recall that TW alone had a low degradation of CNOM (Figure 5.4) due to alkalinity and high $A_{CNOM}$. Therefore, large reductions in the rate of CNOM degradation were not observed experimentally using the alkalinity levels applied. That being said, model predications agreed quite well with the experimental results (Figure 5.6).

5.3.2.3 Degradation of Hydrogen Peroxide

As was observed with SRNOM-aquatic synthetic water, there was an apparent degradation of $\text{H}_2\text{O}_2$ during UV/$\text{H}_2\text{O}_2$ of CW and TW. The maximum extent of degradation ranged from 19% to 24% for CW with initial $\text{H}_2\text{O}_2$ concentrations of 5 and 15 mg L$^{-1}$ (Table 5.5). When alkalinity was added to CW at concentrations of about 50, 100, and 150 mg CaCO$_3$ L$^{-1}$, the maximum extent of degradation of $\text{H}_2\text{O}_2$
remained constant at around 19%, irrespective of the initial H_2O_2 or alkalinity (Table 5.5). Similarly for TW, additional alkalinity at concentrations of about 100 and 150 mg CaCO_3 L^{-1} did not considerably impact the maximum extent of degradation of H_2O_2, which was between 15% and 23% (Table 5.5). Therefore, experimental results did not demonstrate that a change in alkalinity considerably increased or decreased the observed degradation of H_2O_2. On the contrary, the model predicted that additional alkalinity resulted in greater degradation of H_2O_2, bringing the model predictions closer to the experimental results. This increased H_2O_2 degradation predicted by the model can be explained by the presence of the carbonate radical, formed as a result of •OH reaction with bicarbonate (Reaction 4) and carbonate (Reaction 5). The formed carbonate radical can go on to react with H_2O_2 (Reaction 15) thus contributing to H_2O_2 degradation. The RMSE between model predictions and experimental observations ranged from 0.012 to 0.041 for CW with alkalinity present compared to RMSE of 0.036 and 0.082 for raw CW (Table 5.5). Similarly for TW, model predictions were noticeably better as alkalinity increased as indicated by the lower RMSE values (Table 5.5). It is apparent that despite the improved performance of the model in predicting the degradation of H_2O_2 as alkalinity increased, the model still under predicted the experimentally observed degradation of H_2O_2 during UV/H_2O_2 treatment of CW and TW. This again can be explained by the hypothesis that reactions between H_2O_2 and carbon-centred radicals are important and contribute to the overall H_2O_2 degradation.

5.3.3 Implications of Natural Organic Matter Characteristics

NOM varies widely and its composition is largely dependent upon the autochthonous and allochthonous influences of a particular source. Subsequently, the characteristics of NOM can be very different from one source to the next. In this study, model parameters were generated using an isolated NOM dissolved in pure water to create synthetic water and these model parameters were applied to predict the degradation of CNOM during UV/H_2O_2 of natural waters. Although this approach has inherent disadvantages, largely due to differences in NOM characteristics, it yielded satisfactory results as discussed above. This satisfactory agreement could be partly due to the characteristics of three NOMs used in this study. As shown in Table 5.1, the specific ultraviolet absorbance (SUVA), a measure of the aromatic character of NOM (Nikolaou & Lekkas 2001), were quite similar. The SUVA for SRNOM-aquatic and CW were almost identical while SUVA for TW was about 17% greater than that of SRNOM-aquatic and CW. In terms of hydrophobic/hydrophilic fractionation, all three NOMs were composed of predominantly hydrophobic acids, from 80 to 86 percent VHA and SHA combined. These similarities in characteristics may have contributed to the observed similarities in the way these three NOMs reacted with •OH. The results may not have been as satisfactory had the characteristics of the NOM been very
different so future research should broaden the study to a range of NOMs that cover more diverse characteristics.

5.3.4 Potential Applications of the Model

While the model is not entirely unique, it incorporates unique features such as a term to account for the change in water absorbance as well as the reduction in H$_2$O$_2$ concentration. By including these features and considering all species dynamic, it comes closer to ideal characterization of the UV/H$_2$O$_2$ system. As residual H$_2$O$_2$ is present in all UV/H$_2$O$_2$ applications, and requires costly removal, accurate prediction is of high value for system design and cost reduction. The model can also be applied to predict the degradation of micropollutants.

The model tracks the transformation of NOM by the surrogate parameter CNOM. Changes in CNOM have been correlated with other changes in NOM such as reduction in VHA and formation of aldehydes (see Appendix A). Further, changes in CNOM have been correlated with the assimilable organic carbon (AOC) concentration during various stages of treatment including ozonation, carbon filtration, and slow sand filtration (van den Broeke et al. 2008). Thus, this model could also be applied to predict changes in water quality by using empirical correlations linking degradation of CNOM to changes in water quality.

The surrogate parameter CNOM could also be used in actual process operation to track the transformation of NOM as well as to approximate the 'OH concentration. In practice, this would involve simple monitoring of CNOM upstream and downstream of the UV/H$_2$O$_2$ process. Since the change in CNOM may correlate with changes in AOC, monitoring of CNOM would provide an indication of possible changes in biological stability of water after treatment. Further, since the reduction in CNOM is dependent on 'OH concentration, variation in its reduction would indicate a change in 'OH concentration. This could be due to a change in the concentration of water constituents, such as species contributing alkalinity, affecting the concentration of 'OH scavengers or a variation in a process parameter such as fluence or initial H$_2$O$_2$ concentration. As 'OH concentration impacts the removal of target contaminants, this simple method has the potential to improve process performance.

5.4 Acknowledgments

The authors acknowledge Anaig Rosmorduc and Steve McDermid for assisting with experimental and analytical work. We thank Ted Mao, Mihaela Stefan, Bill Cairns, Alan Royce, Gustavo Imoberdorf, Esteban Duran, and Bhushan Gopalini for all the valuable discussions. Natural Science and Engineering Research Council of Canada and Trojan Technologies are acknowledged for financial support. The authors would also like to thank the reviewers for their excellent feedback which strengthened this paper.
Table 5.1 Select characteristics of waters used in UV/H₂O₂ experiments. Table values are averages of numerous measurements.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Suwannee River Natural Organic Matter Synthetic Water</th>
<th>Capilano Water</th>
<th>Trepanier Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity (mg CaCO₃ L⁻¹)</td>
<td>none added</td>
<td>none detected</td>
<td>47</td>
</tr>
<tr>
<td>Total organic carbon (mg L⁻¹)</td>
<td>1.33/2.21/3.08</td>
<td>2.45</td>
<td>5.12</td>
</tr>
<tr>
<td>pH</td>
<td>5.5-5.8</td>
<td>6.5-6.8</td>
<td>7.5-7.7</td>
</tr>
<tr>
<td>A⁵ CNOM (cm⁻¹)</td>
<td>0.049/0.065/0.108</td>
<td>0.089</td>
<td>0.214</td>
</tr>
<tr>
<td>SUVA (L mg⁻¹ m⁻¹)</td>
<td>3.4</td>
<td>3.6</td>
<td>4.2</td>
</tr>
<tr>
<td>VHA (%)</td>
<td>80</td>
<td>66</td>
<td>76</td>
</tr>
<tr>
<td>SHA (%)</td>
<td>4</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>CHA+NEU (%)</td>
<td>16</td>
<td>14</td>
<td>19</td>
</tr>
</tbody>
</table>

Table 5.2 The series of reactions used in the kinetic model of the UV/H₂O₂ system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O₂ + hv → 2-OH</td>
<td>( \Phi_{H_2O_2,OH} = 0.5 ) (Baxendale &amp; Wilson 1957)</td>
</tr>
<tr>
<td>2</td>
<td>( \cdot OH + H₂O₂ → O₂⁻ + H₂O + H⁺ )</td>
<td>( k₂ = 2.7E7 ) L mol⁻¹ s⁻¹ (Buxton et al. 1988)</td>
</tr>
<tr>
<td>3</td>
<td>( \cdot OH + HO₂ → O₂⁻ + H₂O )</td>
<td>( k₃ = 7.5E9 ) L mol⁻¹ s⁻¹ (Buxton et al. 1988)</td>
</tr>
<tr>
<td>4</td>
<td>( \cdot OH + HCO₃⁻ → H₂O + CO₃⁻ )</td>
<td>( k₄ = 8.5E6 ) L mol⁻¹ s⁻¹ (Buxton et al. 1988)</td>
</tr>
<tr>
<td>5</td>
<td>( \cdot OH + CO₃⁻ → OH⁻ + CO₃²⁻ )</td>
<td>( k₅ = 3.9E8 ) L mol⁻¹ s⁻¹ (Buxton et al. 1988)</td>
</tr>
<tr>
<td>6</td>
<td>( \cdot OH + HO₂ → H₂O + O₂ )</td>
<td>( k₆ = 6.6E9 ) L mol⁻¹ s⁻¹ (Buxton et al. 1988)</td>
</tr>
<tr>
<td>7</td>
<td>( \cdot OH + O₂⁻ → OH⁻ + O₂ )</td>
<td>( k₇ = 8.0E9 ) L mol⁻¹ s⁻¹ (Buxton et al. 1988)</td>
</tr>
<tr>
<td>8</td>
<td>( \cdot OH + OH → H₂O₂ )</td>
<td>( k₈ = 5.5E9 ) L mol⁻¹ s⁻¹ (Buxton et al. 1988)</td>
</tr>
<tr>
<td>9</td>
<td>( \cdot OH + CO₃⁻ → OH⁻ + CO₃²⁻ )</td>
<td>( k₉ = 3.0E9 ) L mol⁻¹ s⁻¹ (Holeman et al. 1987)</td>
</tr>
<tr>
<td>10</td>
<td>( O₂⁻ + H₂O₂ → \cdot OH + OH⁻ + O₂ )</td>
<td>( k₁₀ = 0.13 ) L mol⁻¹ s⁻¹ (Bielski et al. 1985)</td>
</tr>
<tr>
<td>11</td>
<td>( O₂⁻ + CO₃⁻ → O₂ + CO₃²⁻ )</td>
<td>( k₁₁ = 6.5E8 ) L mol⁻¹ s⁻¹ (Eriksen et al. 1985)</td>
</tr>
<tr>
<td>12</td>
<td>( O₂⁻ + HO₂ + H₂O → H₂O₂ + OH⁻ + O₂ )</td>
<td>( k₁₂ = 9.7E7 ) L mol⁻¹ s⁻¹ (Buxton et al. 1988)</td>
</tr>
<tr>
<td>13</td>
<td>( HO₂ + HO₂ → H₂O₂ + O₂ )</td>
<td>( k₁₃ = 8.6E5 ) L mol⁻¹ s⁻¹ (Weinstein &amp; Bielski 1979)</td>
</tr>
<tr>
<td>14</td>
<td>( HO₂ + H₂O₂ → \cdot OH + H₂O + O₂ )</td>
<td>( k₁₄ = 3.7 ) L mol⁻¹ s⁻¹ (Buxton et al. 1988)</td>
</tr>
<tr>
<td>15</td>
<td>( CO₃⁻ + H₂O₂ → HCO₃⁻ + O₂⁻ + H⁺ )</td>
<td>( k₁₅ = 8.0E5 ) L mol⁻¹ s⁻¹ (Neta et al. 1988)</td>
</tr>
<tr>
<td>16</td>
<td>( CO₃⁻ + HO₂ → HCO₃⁻ + O₂ )</td>
<td>( k₁₆ = 3.0E7 ) L mol⁻¹ s⁻¹ (Neta et al. 1988)</td>
</tr>
<tr>
<td>17</td>
<td>( CO₃⁻ + O₂⁻ → 2CO₂⁻ )</td>
<td>( k₁₇ = 2.0E7 ) L mol⁻¹ s⁻¹ (Neta et al. 1988)</td>
</tr>
<tr>
<td>18</td>
<td>( H₂O₂ → H⁺ + HO₂⁻ )</td>
<td>( k₁₈ = 0.0356 ) s⁻¹ (Ershov &amp; Gordeev 2008)</td>
</tr>
<tr>
<td>19</td>
<td>( H⁺ + HO₂⁻ → H₂O₂ )</td>
<td>( k₁₉ = 2.0E10 ) L mol⁻¹ s⁻¹ (Ershov &amp; Gordeev 2008)</td>
</tr>
<tr>
<td>20</td>
<td>( HO₂ → H⁺ + O₂⁻ )</td>
<td>( k₂₀ = 7.0E5 ) s⁻¹ (Ershov &amp; Gordeev 2008)</td>
</tr>
<tr>
<td>21</td>
<td>( H⁺ + O₂⁻ → HO₂⁻ )</td>
<td>( k₂₁ = 4.5E10 ) L mol⁻¹ s⁻¹ (Ershov &amp; Gordeev 2008)</td>
</tr>
<tr>
<td>22</td>
<td>( HCO₃⁻ → H⁺ + CO₂⁻ )</td>
<td>( k₂₂ = 0.2 ) s⁻¹ (Brezonik 1994)</td>
</tr>
<tr>
<td>23</td>
<td>( H⁺ + CO₂⁻ → HCO₃⁻ )</td>
<td>( k₂₃ = 3.99E9 ) L mol⁻¹ s⁻¹ (Brezonik 1994)</td>
</tr>
<tr>
<td>24</td>
<td>( \cdot OH + pCBA → products )</td>
<td>( k_{OHpCBA} = 5E9 ) L mol⁻¹ s⁻¹ (Neta &amp; Dorfman 1968)</td>
</tr>
<tr>
<td>25</td>
<td>( \cdot OH + TOC → products )</td>
<td>( k_{OHTOC} = ? ) L mg⁻¹ s⁻¹ (Present work)</td>
</tr>
<tr>
<td>26</td>
<td>( \cdot OH + CNOM → products )</td>
<td>( k_{OHCNOM} = ? ) L mol⁻¹ s⁻¹ (Present work)</td>
</tr>
</tbody>
</table>
Table 5.3 The mathematical model’s system of ordinary differential equations.

| Equation | \[
\frac{d[H_2O_2]}{dt} = -k_{a,H_2O_2,OH}[H_2O_2] - k_2[\cdot OH][H_2O_2] - k_{10}[O_2^{-}][H_2O_2] - k_{14}[HO_2][H_2O_2]
- k_{15}[CO_3^{-}][H_2O_2] - k_{18}[H_2O_2] + k_6[\cdot OH]^2 + k_{12}[O_2^{-}][HO_2] + k_{13}[HO_2]^2
+ k_{19}[H^+][HO_2] \]
| | \[
\frac{d[HO_2]}{dt} = -k_3[\cdot OH][HO_2] - k_{16}[CO_3^{-}][HO_2] - k_{19}[H^+][HO_2] + k_{18}[H_2O_2] \]
| | \[
\frac{d[O_2^•]}{dt} = -k_7[\cdot OH][O_2^•] - k_{10}[O_2^•][H_2O_2] - k_{11}[O_2^•][CO_3^{-}] - k_{12}[O_2^•][HO_2] - k_{21}[H^+][O_2^•]
+ k_{2}[\cdot OH][H_2O_2] + k_3[\cdot OH][HO_2] + k_{15}[CO_3^{-}][H_2O_2] + k_{16}[CO_3^{-}][HO_2]
+ k_{20}[H_2O_2] \]
| | \[
\frac{d[HO_2]}{dt} = -k_6[\cdot OH][HO_2] - k_{12}[O_2^•][HO_2] - k_{13}[HO_2]^2 - k_{14}[HO_2][H_2O_2] - k_{20}[H_2O_2]
+ k_{21}[H^+][O_2^•] \]
| | \[
\frac{d[CO_3^•]}{dt} = -k_9[\cdot OH][CO_3^•] - k_{11}[O_2^•][CO_3^•] - k_{15}[CO_3^•][H_2O_2] - k_{16}[CO_3^•][HO_2] - k_{17}[CO_3^•]^2
+ k_4[\cdot OH][HCO_3^-] + k_5[\cdot OH][CO_3^2^-] \]
| | \[
\frac{d[HCO_3^-]}{dt} = -k_4[\cdot OH][HCO_3^-] - k_{22}[HCO_3^-] + k_{15}[CO_3^-][H_2O_2] + k_{16}[CO_3^-][HO_2]
+ k_{23}[H^+][CO_3^2^-] \]
| | \[
\frac{d[CO_3^2^-]}{dt} = -k_5[\cdot OH][CO_3^2^-] - k_{23}[H^+][CO_3^2^-] + k_9[\cdot OH][CO_3^2^-] + k_{11}[O_2^•][CO_3^-] + 2k_{17}[CO_3^-]^2
+ k_{22}[HCO_3^-] \]
| | \[
\frac{d[pCBA]}{dt} = -k_{O,pCBA}[\cdot OH][pCBA] \]
| | \[
\frac{d[CNOM]}{dt} = -k_{O,CNOM}[\cdot OH][CNOM] \]

Table 5.4 Empirically determined reaction rate constants for the reaction between hydroxyl radical and natural organic matter.

<table>
<thead>
<tr>
<th>NOM Source</th>
<th>(k_{O,TOC}) (L mg⁻¹ s⁻¹)</th>
<th>Determination Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suwannee River Aquatic NOM</td>
<td>1.14±0.10 E4</td>
<td>UV/H₂O₂ - competition kinetics</td>
<td>Present work (Westerhoff et al. 2007)</td>
</tr>
<tr>
<td>Suwannee River Fulvic Acid</td>
<td>1.33±0.20 E4</td>
<td>Pulse radiolysis - competition kinetics and direct transient growth</td>
<td></td>
</tr>
<tr>
<td>Suwannee River Fulvic Acid</td>
<td>3.08E4</td>
<td>Ozoneation - competition kinetics</td>
<td>(Westerhoff et al. 1999)</td>
</tr>
<tr>
<td>Suwannee River Fulvic Acid</td>
<td>2.70±0.05 E4</td>
<td>γ-radiolysis - competition kinetics</td>
<td>(Goldstone et al. 2002)</td>
</tr>
<tr>
<td>Suwannee River Humic Acid</td>
<td>1.90±0.05 E4</td>
<td>Υ-radiolysis - competition kinetics</td>
<td>(Goldstone et al. 2002)</td>
</tr>
<tr>
<td>Fluka Humic Acid</td>
<td>1.60E4</td>
<td>UV/H₂O₂ - numerical parameter estimation</td>
<td>(Liao &amp; Gurol 1995)</td>
</tr>
<tr>
<td>Average of six NOM isolates</td>
<td>2.54E4</td>
<td>Pulse radiolysis - competition kinetics and direct transient growth</td>
<td>(Westerhoff et al. 2007)</td>
</tr>
<tr>
<td>Average of sixteen NOM isolates</td>
<td>3.00±0.45 E4</td>
<td>Ozoneation - competition kinetics</td>
<td>(Westerhoff et al. 1999)</td>
</tr>
<tr>
<td>Average of five surface waters</td>
<td>2.30±0.77 E4</td>
<td>Nitrate-induced solar driven photolysis</td>
<td>(Brezonik &amp; Fulkerson-Brekken 1998)</td>
</tr>
</tbody>
</table>
Table 5.5 Experimentally observed and model predicted extent of hydrogen peroxide degradation (\([H_2O_2]_{\text{final}}/[H_2O_2]_0\)) for CW and TW over a range of alkalinity and H\(_2\)O\(_2\) concentrations.

<table>
<thead>
<tr>
<th>Approximate Alkalinity (mg CaCO(_3) L(^{-1}))</th>
<th>Approximate ([H_2O_2]_0) (mg L(^{-1}))</th>
<th>CW Observed</th>
<th>CW Predicted</th>
<th>CW RMSE</th>
<th>TW Observed</th>
<th>TW Predicted</th>
<th>TW RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>24</td>
<td>13</td>
<td>0.082</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>19</td>
<td>14</td>
<td>0.036</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>5</td>
<td>19</td>
<td>13</td>
<td>0.041</td>
<td>23</td>
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<td>15</td>
<td>19</td>
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<td>0.031</td>
<td>19</td>
<td>10</td>
<td>0.075</td>
</tr>
<tr>
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<td>5</td>
<td>18</td>
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<td>0.012</td>
<td>16</td>
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<td>16</td>
<td>-</td>
<td>21</td>
<td>10</td>
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<tr>
<td></td>
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<td>-</td>
<td>17</td>
<td>-</td>
<td>15</td>
<td>10</td>
<td>0.037</td>
</tr>
</tbody>
</table>
Figure 5.1 Degradation of pCBA during the UV/H₂O₂ treatment of SRNOM-aquatic synthetic water at an $E_p$ of 6.42E-10 Es cm⁻² s⁻¹ and varying levels of TOC and initial H₂O₂ concentration. Points represent experimental measurements and lines represent model predictions.

Figure 5.2 Degradation of CNOM during the UV/H₂O₂ treatment of SRNOM-aquatic synthetic water at an $E_p$ of 6.42E-10 Es cm⁻² s⁻¹ and varying levels of TOC and initial H₂O₂ concentration. Points represent experimental measurements and lines represent model predictions.
Figure 5.3 Degradation of H₂O₂ during the UV/H₂O₂ treatment of SRNOM-aquatic synthetic water at an $E_p$ of 6.42E-10 Es cm⁻² s⁻¹ and varying levels of TOC and initial H₂O₂ concentration. Points represent experimental measurements and lines represent model predictions.

Figure 5.4 Degradation of CNOM during the UV/H₂O₂ treatment of CW and TW at varying levels of initial H₂O₂ concentration. Points represent experimental measurements and lines represent model predictions.
Figure 5.5 Degradation of CNOM during the UV/H₂O₂ treatment of CW at an initial H₂O₂ concentration of 10 or 15 mg L⁻¹ and varying levels of alkalinity. Points represent experimental measurements and lines represent model predictions.

Figure 5.6 Degradation of CNOM during the UV/H₂O₂ treatment of TW at an initial H₂O₂ concentration of 15 mg L⁻¹ and varying levels of alkalinity. Points represent experimental measurements and lines represent model predictions.
Literature Cited


Chapter 6
Downstream Biological Treatment of UV/H₂O₂ Treated Water

6.1 Introduction

Previous chapters discussed the impact of the ultraviolet plus hydrogen peroxide (UV/H₂O₂) advanced oxidation process on natural organic matter (NOM) under lab-scale conditions. This allowed for in depth investigations into the transformation of NOM since experiments could be repeated and conditions were tightly controlled. Prior to these in depth lab-scale investigations, the pilot-scale study presented in this chapter was conducted to understand how UV/H₂O₂ treatment would impact NOM at conditions similar to large scale applications. In fact, this study laid the foundation and structure for the work presented in the previous chapters.

Also of interest in this study was the potential for the reduction of NOM, and subsequently DBP-FPs, by pilot-scale UV/H₂O₂ coupled with downstream biological activated carbon (BAC) filtration. Numerous studies have demonstrated the enhanced reduction of NOM with ozonation followed by BAC (Kim et al. 1997; Liang et al. 2003; Nishijima and Speitel 2004). The primary cause of the enhanced NOM removal by the combined ozone plus BAC process is the increase in NOM biodegradability during ozonation, thus enhancing removal of NOM by BAC. Similarly, past research investigated the ability of a lab-scale treatment process combining UV/H₂O₂ with BAC to remove total organic carbon (TOC) and reduce disinfection by-product formation potentials (DBP-FPs) (Toor & Mohseni 2007). Toor & Mohseni (2007) observed that a combination of UV/H₂O₂+BAC outperformed BAC alone with respect to the removal of TOC and DBP-FPs. This was due to an increase in biodegradable organic carbon (BDOC) generated by UV/H₂O₂, thus increasing the overall amount of NOM that BAC was capable of removing through biodegradation (Toor & Mohseni, 2007). Speitel et al. (2000) also observed reductions in TOC and dissolved organic halogen formation potential with a combined UV/H₂O₂+BAC system. Buchanan et al. (2008) reported that the combination of vacuum UV irradiation and BAC led to significant reductions in DOC as well as formation potentials of THMs and HAAs.

In summary, this research involved carrying out preliminary pilot-scale UV/H$_2$O$_2$ experiments for the purpose of investigating the impact of UV/H$_2$O$_2$ oxidation on DBP-FPs and the structure and biodegradability of NOM. Also, investigated was the ability of combined UV/H$_2$O$_2$ with downstream BAC to reduce NOM, DBP-FPs, aldehydes, and residual H$_2$O$_2$.

6.2 Materials and Methods

6.2.1 Source Water

Raw surface water (RSW) was transported from Fanshawe Lake, London, Ontario, Canada on September 12, 2005. Since the quality of RSW was poor (Table 6.1), it was decided to dilute RSW with high quality, dechlorinated city water (absorbance of 254 nm UV (A$_{254}$) < 0.04 cm$^{-1}$, TOC < 0.9 mg L$^{-1}$). Therefore, prior to treatment, approximately 3000 gallons (11,400 L) of transported RSW was diluted with 7,000 gallons (26,500 L) dechlorinated city water to a final volume of 10,000 gallons (37,900 L) of diluted surface water (DSW).

6.2.2 UV/H$_2$O$_2$ Treatment

Pilot-scale UV/H$_2$O$_2$ treatment was carried out at Trojan Technologies’ Environmental Contaminant Treatment (ECT) Research Facility in London, Ontario, Canada. Figure 6.1 presents a diagram of the setup. DSW was fed from an 11,000 gallon (41,600 L) holding tank into the reactor. The flowrate was adjusted using a butterfly valve upstream of the UV reactor. Before entering the UV reactor, DSW was spiked with H$_2$O$_2$ (30% Fisher Scientific) to a concentration of approximately 10 mg L$^{-1}$ of H$_2$O$_2$ using a peristaltic pump (Cole-Parmer). This concentration of H$_2$O$_2$ was selected since it is within the range of concentrations typically applied in commercial drinking water UV/H$_2$O$_2$ applications. Sample ports upstream and downstream of the reactor were used to collect untreated and treated DSW samples. Treated water was sent to the drain after sample collection. The following parameters were monitored in the raw and treated waters: TOC, A$_{254}$ and absorbance of 203 nm UV (A$_{203}$), trihalomethanes formation potentials (THM-FPs), haloacetic acids formation potentials (HAA-FPs), biodegradable dissolved organic carbon (BDOC), formaldehyde (FA) concentration, acetaldehyde (AA) concentration, and residual H$_2$O$_2$.

The UV reactor employed in the study was equipped with eight low-pressure amalgam lamps, fitted with quartz sleeves, and a 2 kW power input at 100% power. Irradiations were carried out at three different UV fluences (440, 630, and 880 mJ cm$^{-2}$), achieved by adjusting the flowrate through the reactor. This fluence range was selected since it is within the range of fluences typically applied in commercial drinking water UV/H$_2$O$_2$ applications. Fluence was calculated using Trojan Technologies’
proprietary computational fluid dynamics model, which utilizes numerical methods to determine fluence based on the reactor configuration, lamp properties and radiation field, the operating flowrate, and the $A_{254}$ of water after H$_2$O$_2$ addition.

6.2.3 Biological Activated Carbon Treatment

For BAC experiments, two identical BAC columns were designed, constructed, and acclimated at Trojan Technologies’ ECT Research Facility. Each column was made of PVC, had a height of 88 cm and diameter of 7.6 cm, and was capped from both ends. Two sample ports located 16 cm and 40 cm from the base of the column, allowed for sampling along the length of the columns. The packing material was a coconut shell based activated carbon (AC) with 12x30 mesh size and 0.6-0.85 mm effective size (USFilter Westates AC-1230-C). The AC bed height was 70 cm and was supported by a 10 cm high bed of glass beads (Potters Industries A-100-06/89). Each BAC column had its own feed water tank with a volume of 1000 gallons (3800 L). Water was fed into each column by peristaltic pumps (Cole-Palmer) at a flowrate of 150 mL/min. At this flowrate and with the above specified column dimensions, the empty bed contact time (EBCT) was 20 minutes. Prior to the actual experiments, the columns underwent acclimation in order to saturate the adsorption sites and develop a biofilm on the AC. RSW was collected from Waubuno Creek, London, ON and recirculated through the columns for up to 3 weeks and then drained and replaced with fresh RSW. Waubuno Creek water had an average TOC of 5 mg L$^{-1}$ and $A_{254}$ of 0.125 over the duration of acclimation. Acclimation was carried out for 4 months to ensure biological conditions were well developed.

Two experiments were conducted with BAC only. The first was carried out to study the ability of BAC to remove FA from water. Here, RSW was collected from Fanshawe Lake and spiked to 30-35 $\mu$g L$^{-1}$ FA. Over the course of one week, the influent and effluent waters were analyzed for FA concentration. The second experiment was carried out to study the ability of BAC to remove H$_2$O$_2$ from water. RSW from Fanshawe Lake was spiked to 10-12 mg L$^{-1}$ H$_2$O$_2$. Over the course of ten days, the influent and effluent waters were analyzed for H$_2$O$_2$ concentration.

6.2.4 Combined UV/H$_2$O$_2$ plus Biological Activated Carbon Treatment

Figure 6.2 presents a diagram of the UV/H$_2$O$_2$+BAC setup at Trojan Technologies’ ECT Research Facility. After DSW was treated by UV/H$_2$O$_2$, as described previously, it was stored in a tank with a volume of 1,000 gallons (3800 L). Meanwhile, untreated DSW was placed in a separate tank. Each of the storage tanks was connected to a BAC column and fed at a flowrate of 150 mL min$^{-1}$, 20 min EBCT, with a peristaltic pump (Cole-Parmer). AO BAC column received UV/H$_2$O$_2$ treated DSW and BAC Control
column served as a control, receiving DSW that was not pre-treated by UV/H₂O₂. Each run consisted of a 7 day acclimation period to the feed water and 7 days of sampling. During the sampling period, samples were collected every 2 days upstream and downstream of the BAC columns and the effluent was sent to the drain. The following parameters were monitored in the pre-BAC and post-BAC samples: H₂O₂ concentration, TOC, A₂₅₄μ and A₂₀₃μ, THM-FP, HAA-FP, BDOC, FA concentration, and AA concentration.

### 6.2.5 Analytical Methods

Sample analysis was performed at Trojan’s ECT Research Laboratory, London, Ontario, Canada. H₂O₂ concentration was measured by reaction with iodide catalysed by molybdate (Klassen et al. 1994). After measuring the H₂O₂ concentration, samples were quenched of H₂O₂ using 0.2 mg/L bovine liver catalase (Aldrich Canada) as recommended by Liu et al. (2003). TOC was measured using a UV/persulfate oxidation TOC analyzer (Sievers 800). UV absorbance was determined using a spectrophotometer with a 1 cm pathlength cell (Cary 50/100).

THM-FP and HAA-FP were maximum formation potential tests carried out by spiking an 80 mL water sample to a concentration of 10 mg free chlorine (sodium hypochlorite, Sigma Aldrich) per litre and incubating at 22 °C for 7 days. After the chlorination period, according to the EPA Method 551.1 (USEPA 1995a), THMs were extracted and detected by GC/ECD (HP 6890) equipped with an HP-5 column (30 m x 0.32 mm x 0.25 μm) and an HP 6890 autosampler. Chloroform was the primary THM detected and analysed due to the absence of bromide in the DSW. According to the EPA Method 552.2 (USEPA 1995b), HAAs were methylated, extracted, and detected by GC/MS (Varian Saturn 2000R) equipped with a CP-Sil 8 column (30 m x 0.25 mm x 0.25 μm) and a CTC Analytics Combi PAL autosampler. Dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were the primary HAAs reported because of their relatively high concentrations and the absence of brominated HAAs.

FA and AA were derivatized and extracted, according to the EPA Method 556.1 (USEPA 1999). Detection was performed according to Standard Methods 6252 (1998) using the GC/ECD system described above.

BDOC was determined following the method given be Servais et al. (1989). A 30 mL sample was seeded with 2 mL of RSW and incubated at 22 °C for 7 days. The TOC before and after incubation was measured and the percent difference was recorded as BDOC.
6.3 Results and Discussion

6.3.1 UV/H₂O₂ Treatment

The results obtained from the pilot-scale UV/H₂O₂ experiments are summarized in Table 6.2. Although there was no reduction in the quantity of NOM (i.e., TOC concentration), major changes in the structure of NOM occurred. As shown by the reduction of A₂₅₄ and A₂₅₄/A₂₀₃, there were reductions in chromophoric NOM and degree of substitution of aromatic rings (Table 6.2). 254 nm UV is mainly absorbed by aromatic structures and conjugated double bonds so a reduction in A₂₅₄ indicates a reduction in the aromaticity of NOM. Additionally, the degree of activation of aromatic rings can be interpreted by the ratio of A₂₅₄ to A₂₀₃ (A₂₅₄/A₂₀₃) (Korshin et al. 1997). Therefore, although NOM was not mineralised, partial oxidation led to fragmentation of its aromatic rings. These results are consistent with those obtained during the lab-scale experiments, which indicated major changes in size, hydrophobicity, structure, and composition of NOM despite little or no reduction in the concentration of TOC over the range of UV fluences tested (Chapter 2; Chapter 3; Chapter 4).

While reductions in A₂₅₄ and A₂₅₄/A₂₀₃ showed changes in NOM’s aromatic structure, NOM’s potential to form DBPs upon chlorination did not decrease, but rather increased with increasing UV fluence (Table 6.2). Similar observations have been reported in other studies where UV/H₂O₂ was investigated for the removal of NOM and/or DBP precursors (Kleiser & Frimmel 2000; Liu et al. 2002; Thomson et al. 2004; Toor & Mohseni 2007). In general, all those studies concluded that UV/H₂O₂ only effectively reduced DBP-FPs at very high fluences and/or H₂O₂ concentrations, conditions at which mineralisation of NOM took place. At weaker oxidation conditions, NOM was not mineralised and DBP-FPs either increased or remained the same. Kleiser & Frimmel (2000) hypothesized that this was due to an increase in the concentration of alcohol- and/or keto-groups, both of which can be precursors for THMs. Additionally, insertion of OH-group into aromatic structures increases reactivity with chlorine (Kleiser & Frimmel 2000). The results of this study also indicate that the formation of DBPs cannot be correlated with simple NOM characteristics such as A₂₅₄. While studies for untreated NOM, have positively correlated both aromaticity and degree of substitution of aromatic rings with DBP-FPs (Nikolaou & Lekkas 2001), these correlations do not seem to hold true once NOM has undergone oxidation by UV/H₂O₂.

In Chapter 4 it was also observed that a reduction in aromaticity did not directly correlate with changes in DBP-FPs. In Chapter 4 no reduction in THM-FPs occurred at fluences less than 1000 mJ cm⁻² which is consistent with the findings herein. However, while HAA-FPs were reduced even at the lowest fluence using the collimated beam apparatus with water from Capilano Reservoir (Chapter 4), HAA-FP
increased using the pilot-scale reactor with water from Fanshawe Lake. As the characteristics of NOM in Capilano Water and Fanshawe Lake Water are unique and very different from one another, one cannot expect them to behave identically during UV/H₂O₂ treatment. Further, the pilot-scale reactor employed a very high fluence rate and a short irradiation time to achieve the target fluence. On the other hand, the collimated beam apparatus employed a very low fluence rate and a long irradiation time to achieve similar fluence levels. It was out of the scope of this research to investigate the impact of fluence rate on NOM characteristics during UV/H₂O₂, but this variable could be responsible for some of the differences observed between the two experimental setups.

The UV/H₂O₂ process changed the biological stability of the water in that it led to the formation of aldehydes (i.e., FA and AA) and an increase in BDOC, with increasing UV fluence. Liu et al. (2002), Thomson et al. (2004), and Chapter 4 also observed increases in the concentration of aldehydes and other low molecular weight carbonyls during UV/H₂O₂. Since FA and AA are readily biodegradable, their increase would suggest an increase in BDOC. As shown in Table 6.2, BDOC increased by more than three folds from 5.3% in DSW to more than 18% in the UV/H₂O₂ treated water. Aldehydes constitute only 25-30% of BDOC (Nawrocki et al. 2003) so an increase in aldehydes only partially explains the observed three folds increase in BDOC. Hence, it is evident the formation of biodegradable aldehydes was accompanied by formation of other biodegradable species (Table 6.2). Similar increases in BDOC have been reported in other studies where surface water was treated by UV/H₂O₂ AOP (Speitel et al. 2000; Thomson et al. 2004; Toor & Mohseni 2007; Chapter 4). The observed increase in BDOC suggests that combining UV/H₂O₂ with a downstream treatment process capable of removing biodegradable species may lead to synergistic results with respect to removing NOM, thus reducing DBP-FPs, while improving biological stability.

At an initial H₂O₂ concentration of 10 mg L⁻¹, after the longest fluence of 880 mJ cm⁻², over 80% of the H₂O₂ remained in the water. This residual H₂O₂ is undesirable since it must be removed prior to distribution. Removal using a quenching agent adds additional operational costs thus a low-cost process capable of H₂O₂ removal would be advantageous.

6.3.2 Combined UV/H₂O₂ plus Biological Activated Carbon Treatment

Utilizing BAC downstream of the water treated by 880 mJ cm⁻² UV and 10 mg L⁻¹ initial H₂O₂ concentration provided effective degradation of NOM, i.e., up to 58% reduction of TOC (Table 6.3), which in turn, resulted in a drop in the formation of DBPs. With the combined treatment strategy, reductions of up to 75% and 60% were achieved for HAA-FP and THM-FP, respectively (Table 6.3). Toor & Mohseni (2007) reported that for surface water treated with 500 mJ cm⁻² of UV and 20 mg L⁻¹
initial H₂O₂ concentration, downstream BAC, at an EBCT of 8.2 min, removed 52% TOC, 42% THM-FP, and 45% HAA-FP. Additionally, Speitel et al. (2000) observed reductions in TOC and dissolved organic halogen formation potential for a combined UV/H₂O₂+BAC system. Toor & Mohseni (2007) also observed that a combination of UV/H₂O₂+BAC outperformed BAC alone with respect to the removal of TOC and DBP-FPs. This was due to an increase in BDOC generated by UV/H₂O₂, thus increasing the overall amount of NOM that BAC was capable of removing through biodegradation (Toor & Mohseni, 2007). Buchanan et al. (2008) combined vacuum UV irradiation with BAC and observed a 60% reduction in THM-FPs along with a 74% reduction in HAA-FPs.

In addition to facilitating the removal of NOM, the downstream BAC process was able to effectively remove residual H₂O₂ and FA, thereby improving the quality of the final treated water. FA was removed by up to about 85%, to a concentration similar to that detected in DSW (Figure 6.4). Also, BAC removed H₂O₂ by over 93% in the first section of the column, that is, at an EBCT of 4.2 min (Figure 6.3). By the time the water exited the column, at an EBCT of 20 min, no H₂O₂ was detected. Thus, BAC demonstrated to be a low-cost, highly effective method for removing the residual H₂O₂ after UV/H₂O₂, as well as improving the biological stability of the water, and reducing NOM concentration and DBP-FPs.

6.4 Acknowledgments

The authors thank Henry Wang, Stewart Hayes, Steve McDermid, and Wayne Lem for their assistance with experimental and analytical work. Natural Science and Engineering Research Council of Canada and Trojan Technologies are acknowledged for financial support.
Table 6.1  Characteristics of water used in experimentation originating from Fanshawe Lake, London, Ontario, Canada.

<table>
<thead>
<tr>
<th></th>
<th>$A_{254}$ (cm$^{-1}$)</th>
<th>TOC (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSW</td>
<td>0.165</td>
<td>6.8</td>
</tr>
<tr>
<td>DSW</td>
<td>0.051</td>
<td>2.24</td>
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</table>

Table 6.2  Change in water parameters during the pilot-scale UV/H$_2$O$_2$ oxidation process. Initial H$_2$O$_2$ concentration of 10 mg L$^{-1}$.

<table>
<thead>
<tr>
<th>Fluence (mJ cm$^{-2}$)</th>
<th>TOC (mg L$^{-1}$)</th>
<th>$A_{254}$ (cm$^{-1}$)</th>
<th>$A_{254}/A_{303}$ (cm$^{-1}$)</th>
<th>THM-FP (ppb)</th>
<th>HAA-FP (ppb)</th>
<th>FA (ppb)</th>
<th>AA (ppb)</th>
<th>BDOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.1 ± 0.0</td>
<td>0.046</td>
<td>0.110</td>
<td>30 ± 1</td>
<td>242 ± 13</td>
<td>7 ± 1</td>
<td>6 ± 1</td>
<td>5 ± 2</td>
</tr>
<tr>
<td></td>
<td>± 0.001</td>
<td>± 0.003</td>
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<tr>
<td>440</td>
<td>2.1 ± 0.1</td>
<td>0.035</td>
<td>0.085</td>
<td>52 ± 2</td>
<td>313 ± 46</td>
<td>16 ± 1</td>
<td>14 ± 1</td>
<td>19 ± 2</td>
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</tr>
<tr>
<td>630</td>
<td>2.1 ± 0.0</td>
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<td>0.082</td>
<td>58 ± 1</td>
<td>412 ± 12</td>
<td>17 ± 1</td>
<td>15 ± 1</td>
<td>15 ± 1</td>
</tr>
<tr>
<td></td>
<td>± 0.001</td>
<td>± 0.001</td>
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<tr>
<td>880</td>
<td>2.1 ± 0.1</td>
<td>0.031</td>
<td>0.078</td>
<td>56 ± 5</td>
<td>349 ± 20</td>
<td>19 ± 1</td>
<td>16 ± 1</td>
<td>18 ± 1</td>
</tr>
<tr>
<td></td>
<td>± 0.001</td>
<td>± 0.002</td>
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</tbody>
</table>

Table 6.3  Reduction in water parameters by pilot-scale BAC receiving UV/H$_2$O$_2$ treated DSW. Fluence of 880 mJ cm$^{-2}$ and initial H$_2$O$_2$ concentration of 10 mg L$^{-1}$. EBCT of 20 min.

<table>
<thead>
<tr>
<th>BAC Run Duration (day)</th>
<th>TOC Removal (%)</th>
<th>$A_{254}$ Removal (%)</th>
<th>THM-FP Removal (%)</th>
<th>HAA-FP Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>58</td>
<td>72</td>
<td>57</td>
<td>75</td>
</tr>
<tr>
<td>10</td>
<td>55</td>
<td>50</td>
<td>60</td>
<td>51</td>
</tr>
<tr>
<td>14</td>
<td>56</td>
<td>63</td>
<td>35</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 6.1 UV/H$_2$O$_2$ experimental setup located at Trojan Technologies’ ECT Pilot Facility.

Figure 6.2 UV/H$_2$O$_2$+BAC experimental setup located at Trojan Technologies’ ECT Pilot Facility.
Figure 6.3 H$_2$O$_2$ concentration of influent (■) and effluent, at 4.2 min EBCT, (□) waters of pilot-scale BAC column.

Figure 6.4 FA concentration of influent (■) and effluent (□), at 20 min EBCT, waters of pilot-scale BAC column.
Literature Cited


USEPA. (1995a) Method 551.1: Determination of chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron capture detection.

USEPA. (1995b) Method 552.2: Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatization and gas chromatography with electron capture detection.

Chapter 7
Method Development for Assimilable Organic Carbon Determination of UV/H$_2$O$_2$ Treated Water$^6$

7.1 Introduction

Literature reports on the impact of UV/H$_2$O$_2$ advanced oxidation on the level of assimilable organic carbon (AOC) are few in number. This is primarily because the standard method (SM) 9217 for AOC determination (Clescerl et al. 1999) is slow, tedious, and requires considerable technician labour (Hammes & Egli 2005). These obstacles are largely due to the fact that SM 9217 uses a pure culture, *Pseudomonas fluorescens* strain P-17 or *Spirillum* strain NOX, combined with plate counting for enumeration. Further, there are inherent disadvantages of using pure strains for detection of natural AOC since pure strains are not capable of assimilating all forms of biodegradable organic carbon (Hammes & Egli 2005; van der Kooij 2002).

Hammes & Egli (2005) developed a rapid, reliable, and reproducible method for AOC determination. This novel method combined a natural microbial consortium for the assimilation of AOC with fluorescent staining and flow cytometric enumeration of cells (Hammes & Egli 2005). In short, a sample of water was inoculated with a natural microbial consortium followed by incubation at 30 °C until the community reached stationary growth phase. At this point the sample was amended with a nucleic acid gel stain followed by enumeration with a flow cytometer with fluorescent emission and detection. This method has been successfully applied for evaluating the formation of AOC during ozonation of drinking water (Hammes et al. 2006) and phytoplankton (Hammes et al. 2007), determining the filterability of bacteria by micropore membrane filters (Wang et al. 2008), assessing the impact of microfiltration on the concentration of microbial communities in bottled water (Wang et al. 2008), and assessing general microbial quality of drinking water (Berney et al. 2008).

This study focussed on implementing the Hammes & Egli (2005) AOC method for determining the impact of UV/H$_2$O$_2$ advanced oxidation treatment on measured AOC. The first objective was to develop the ability to enumerate microbial cells via fluorescent staining and enumeration by flow cytometry. The next objective was to cultivate a natural microbial consortium to use for inoculating samples, determine

$^6$ A version of this chapter will be submitted for publication. Sarathy, S.R. & Mohseni, M. A method for determining assimilable organic carbon of water treated by UV/H$_2$O$_2$ advanced oxidation.
the time required to achieve stationary phase, and to determine the consortium’s yield coefficient on a
simple carbon source, sodium acetate (acetate-C). Also, as no literature was available reporting the impact
of H₂O₂ quenching agents on AOC determination, investigation was conducted to determine the optimal
H₂O₂ quenching agent to use prior to sample inoculation. Finally, the method developed in-house was
used to gather initial data observing the impact of UV/H₂O₂ irradiation time on the AOC detected in
natural water.

7.2 Materials and Methods

7.2.1 Preparation of Assimilable Organic Carbon Free Equipment

Glassware was prepared according to SM 9217 (Clescerl et al. 1999). First, 40 mL borosilicate vials
were washed with detergent and warm water and rinsed at least three times with ultrapure water.
Following, the vials were submerged in 0.1 N hydrochloric acid (Fisher Scientific) for a minimum of 10
hours. Next, the vials were rinsed with ultrapure water at least three times and left to air dry. Each vial
was then capped with aluminum foil and heated in a muffle furnace at 500 °C for 5 hours.

Plastic vial caps with Teflon-lined silicone septa were prepared according to SM 9217 (Clescerl et al.
1999). They were first washed with common detergent and warm water and rinsed with ultrapure water at
least three times. The caps and septa were then soaked in 10% sodium persulphate (Sigma Aldrich)
solution at 60 °C for at least 1 hour. Finally, they were rinsed at least three times with ultrapure water and
air dried. The cleaned and dried caps were fitted with cleaned and dried septa and screwed tightly onto the
cleaned and cooled glass vials.

Plastic syringes (Becton, Dickinson and Company) were rinsed by flushing with ultrapure water at
least 5 times before use. To remove AOC from syringe filters (0.22 μm, polyethersulfone, 33 mm filter
diameter, sterilized by γ-irradiation, Millex-GP, Millipore), they were rinsed by flushing with at least 250
mL of ultrapure water. Autoclaved pipette tips (Fisher Scientific) were rinsed at least three times with
ultrapure water prior to use.

7.2.2 Preparation of Natural Microbial Consortium Inoculum

An inoculum composed of a natural consortium of microbes was cultured following the method
developed by Hammes & Egli (2005). First, 30 mL of Capilano Water (CW) was sterilized by filtration
through 0.22 μm syringe filter and placed into a 40 mL vial. The sterilized CW sample was inoculated
with 10 μL mL⁻¹ of unfiltered/untreated CW, capped and vortexed, and incubated at 35 °C until stationary
growth phase was maintained. Stationary phase was confirmed by observing a constant cell concentration
over days. When the inoculum reached stationary phase it was deemed to be AOC free since all utilizable carbon had been consumed.

7.2.3 Growth of Natural Microbial Consortium

The incubation procedure was as follows. First 30 mL of water sample was sterilized into 40 mL glass vial by filtration through 0.22 μm filter. Next, 2.5 μL mL⁻¹ of mineral buffer was added as recommended by SM 9217 (Clescerl et al. 1999). The purpose of the mineral buffer was to ensure carbon was the only limiting nutrient. The recipe of the mineral buffer was 171 mg L⁻¹ K₂HPO₄ (99.99%, Sigma Aldrich), 767 mg L⁻¹ NH₄Cl (99.998%, Sigma Aldrich), and 1.44 g L⁻¹ KNO₃ (99.999%, Sigma Aldrich) in ultrapure water. For yield coefficient determination tests, the desired concentration of sodium acetate (99.995%, Sigma Aldrich) was added to ultrapure water along with 2.5 μL mL⁻¹ of mineral buffer. Finally, 3.33 μL mL⁻¹ of inoculum was added and the sample was capped, vortexed, and incubated at 35 °C for 3-4 days. Cells were enumerated over days and incubation was stopped when stationary phase was reached. The stationary phase concentration of cells indicated the amount of assimilable carbon (see Section 7.3.2).

7.2.4 Cell Staining and Enumeration by Flow Cytometry

In order to enumerate cells by flow cytometry, a fluorescent dye was added to water samples to stain the DNA of the cells as indicated by Hammes & Egli (2005). First, the water sample was vortexed to ensure a thoroughly mixed sample. 1 mL of the sample was pipetted into a flow cytometer tube (Polystyrene Round-Bottom Test Tube, 5 mL, snap cap, Becton, Dickinson and Company). This sample was stained with 10 μL of SYBR Green I nucleic acid gel stain (10,000X concentrate, Invitrogen) diluted 1:100 times in dimethyl sulfoxide (Sigma Aldrich). The stained sample was left in the dark for at least 20 minutes prior to analysis by flow cytometry.

Absolute cell counting was performed since a flow cytometer with volumetric control was not available. Flow cytometer counting beads were added to the stained sample at a known concentration. The beads solution was prepared as follows. The stock beads solution (Cyto-Cal 633 Alignment Beads, 3 μm, Duke Scientific) had an approximate concentration of 5E6 beads mL⁻¹. This stock was diluted by half to bring the approximate concentration to 2.5E6 beads mL⁻¹. To determine the exact concentration of beads in the dilution, manual counting of beads was performed as follows. 10 μL of diluted beads was pipetted onto a Neubauer counting chamber (Petroff-Hausser Counter, Hausser Scientific).
The beads were counted under microscope and the concentration of the diluted beads solutions was calculated based on Equation [7.1] given by the manufacturer of the Neubauer counting chamber.

\[ \text{(beads mL}^{-1}) = 50000 \times \text{Number of beads counted} \]

Prior to injection to the flow cytometer, 10 μL of the beads solution was added to the 1 mL stained sample. During the flow cytometry analysis, the beads and cells were enumerated simultaneously (see Section 7.3.1). The flow cytometer was configured to stop after counting 500 beads. Since the beads concentration was known, the cell concentration was determined according to Equation [7.2].

\[ \text{(cells mL}^{-1}) = \frac{(\text{beads mL}^{-1}) \times \text{Number of beads counted}}{\text{Number of cells counted}} \]

Flow cytometry analysis was performed with a BD FACS Calibur System (Becton, Dickinson and Company) with detector settings at forward scatter channel: voltage - E01, amp gain - 2.23, mode - Log; side scatter channel: voltage - 412, amp gain - 1.00, mode - Log; fluorescence channel 1: voltage - 597, amp gain - 1.00, mode - Log; fluorescence channel 2: voltage - 674, amp gain - 1.00, mode - Log; fluorescence channel 3: voltage - 520, amp gain - 1.00, mode - Log. The primary threshold parameter was the side scatter channel at a value of 0 and there was no compensation.

### 7.2.5 Hydrogen Peroxide Quenching Agents

H₂O₂ containing samples were quenched with different agents to observe the impact of quenching agents on AOC determination. The quenching agents included bovine liver catalase (lyophilized powder, ≥10,000 units mg⁻¹ protein, Sigma Aldrich), sodium thiosulfate (ACS Grade, Fisher Scientific), and manganese dioxide based granules (Clack Corporation). H₂O₂ concentration was measured by reaction with iodide catalyzed by molybdate (Klassen et al. 1994). H₂O₂ (30%, Fisher Scientific) was added to CW at a concentration of 8 mg L⁻¹ followed by addition of the quenching agents. Catalase was added to achieve a concentration of 0.02 mg L⁻¹. Experiments demonstrated that this was the minimal concentration of catalase required to quench 10 mg L⁻¹ H₂O₂ within 1 hour. It was desirable to minimize the amount of catalase added since experiments showed that catalase at 0.2 mg L⁻¹ contributed to cell growth, likely due to the organic carbon content in catalase. Sodium thiosulfate was added at a
concentration of 83.8 mg L$^{-1}$, according to the stoichiometric requirement for reaction with H$_2$O$_2$. 100 mg of manganese dioxide was added to 70 mL of water and mixed continuously for 1 hour. For all three H$_2$O$_2$ quenching procedures it was confirmed that there was no residual H$_2$O$_2$ detected. Once H$_2$O$_2$ was quenched, the samples went through the AOC method described above (i.e., inoculation, incubation, staining, and cell enumeration).

### 7.2.6 UV/H$_2$O$_2$ Treatment

A collimated beam apparatus, consisting of low pressure high output UV lamp (Trojan Technologies, London, ON) positioned 28 cm above a circular stirred reactor chamber was employed for the batch UV/H$_2$O$_2$ treatment of CW. The reactor chamber was a glass petri dish 5.5 cm in diameter and depth of 2.95 cm yielding a volume of 70 mL. The petri dish was covered with a thin quartz disc to prevent contamination from the air and evaporation. Samples were irradiated and samples were taken at various intervals from 0 to 90 minutes. H$_2$O$_2$ (30%, Fisher Scientific) was added initially to the reactor chamber at a concentration of about 5 mg L$^{-1}$.

### 7.3 Results and Discussion

#### 7.3.1 Cell Staining and Enumeration by Flow Cytometry

The first objective in the implementation of this AOC method was to develop the ability to enumerate microbial cells by flow cytometry. The staining method described above was applied to two different samples. The first was sterilized CW, by filtration through 0.22 μm filter, with stain and beads and the second was CW with stain and beads. These two samples were analyzed by the flow cytometer and the instrument settings were adjusted in order to enumerate the stained cells and beads. Figure 7.1 and Figure 7.2 provide a dot plot of the events seen by the flow cytometer detector. The x-axis represents the fluorescence intensity and the y-axis is the side scatter channel. Figure 7.1 presents the results for the sterilized CW sample with beads and stain. Since this sample was sterilized, no cells were present so all events observed were considered either background noise (i.e., small particulate matter in the water, not stained cells) or beads. The events at $<10^1$ on the fluorescence channel were designated background material and the cluster of beads were gated off accordingly (Figure 7.1). Positive stained cells would be enumerated with the respective gate (Figure 7.1 and Figure 7.2). As shown in Figure 7.2, stained CW with beads had many events within the positive gate. This demonstrated that the staining procedure and flow cytometer settings were optimized for enumeration of the types of microbial cells found in CW.
7.3.2 Growth of Natural Microbial Consortium on Acetate-C

With the enumeration method established, the next objective was to observe the growth curve of the natural microbial consortium over days and the stationary phase concentration of the cells on different concentrations of acetate-C. As illustrated in Figure 7.3, the concentration of cells increased both as a function of incubation time and acetate-C concentration. It was apparent that stationary growth phase was achieved after about 70 hours (Figure 7.3). Therefore, for all subsequent experiments the incubation time was between 3 and 4 days to ensure stationary growth phase had been achieved.

Figure 7.3 and Figure 7.4 present the stationary phase cell concentration versus the initial acetate-C concentration from two different experiments. There was a positive correlation between the initial acetate-C concentration and stationary phase cell concentration, demonstrating that the stationary phase cell concentration was indicative of the concentration of AOC (Figure 7.3, Figure 7.4). With this information, a yield coefficient, with units of cells μg⁻¹ acetate-C, was calculated based on Equation [7.3].

\[
[7.3] \qquad \text{Yield} = \frac{[\text{Cells}] \times \text{Volume of sample}}{[\text{acetateC}] \times \text{Volume of sample}} = \frac{\text{Number of cells in sample}}{\mu\text{g acetateC in sample}}
\]

Using the data presented in Figure 7.4, a slope of the plot of the number of cells at stationary phases versus the initial mass of acetate-C provided a yield coefficient of 1.76E7 cells μg⁻¹ acetate-C. With the data in Figure 7.3, a yield coefficient of 1.45E7 cells μg⁻¹ acetate-C was calculated. These yield coefficients were over two to three times greater than the value reported by Hammes and Egli (2005), 6.08E6 cells μg⁻¹ acetate-C, for a natural microbial consortium on acetate-C with incubation at 30°C. Hammes and Egli (2005) discussed the discrepancies between yield coefficients reported in the literature and concluded that use of a theoretical yield coefficient of 1E7 cells μg⁻¹ acetate-C, as suggested by van der Kooij (2002), was acceptable. Since the yield coefficients calculated from experiments in this study were in the same order as the recommended theoretical yield coefficient, it was decided, for simplification and conformity, that a yield coefficient of 1E7 cells μg⁻¹ C be used to convert the cell concentration to apparent AOC concentration as suggested by Hammes & Egli (2005) and subsequently adopted by Hammes et al. (2006, 2007) and Vital et al. (2007).

That being said, the question still arises as to why there was an 18% difference between yield coefficients calculated using data from different experiments (i.e., 1.76E7 versus 1.45E7 cells μg⁻¹ acetate-C). One would expect that since the carbon source (i.e., acetate-C) and the source of natural microbial consortium remained the same across experiments, the yield coefficient would be the same.
This discrepancy is attributed to inherent errors encountered during AOC determination. According to SM 9217, one can expect 5 to 10 µg L\(^{-1}\) of additional AOC due to organic carbon contamination during glassware preparation and sample handling (Clescerl et al. 1999). Based on this research, this seems to be a best case scenario and often greater contamination was observed primarily due to operator error during sample handling. The fact of the matter is that AOC determination is a highly sensitive metric and any source of organic carbon contamination can contribute to erroneous results. Therefore, operators require strong diligence and experience to self identify points of error and to self improve performance. One of the key advantages of this AOC method is that since it is faster, easier, and not as labour intensive as SM 9217, sample replication is encouraged leading to minimization of error due to operator carelessness. In practice, it has been observed that operators improve with experience. Nonetheless, for any given set of experiments, results were always compared to a control so as to discount any error due to organic carbon contamination.

7.3.3 Effects of Hydrogen Peroxide Quenching Agents on AOC Determination

A large amount of H\(_2\)O\(_2\) remains in solution after UV/H\(_2\)O\(_2\) advanced oxidation treatment (Section 5.3.1.3). Residual H\(_2\)O\(_2\) inhibits the growth of microorganisms and this has been confirmed by experiments (data not shown). Hence, AOC analyses are sensitive to H\(_2\)O\(_2\). Other analyses sensitive to H\(_2\)O\(_2\) are disinfection by-product formation potential tests and absorbance measurements, so residual H\(_2\)O\(_2\) must be quenched prior to these analyses. Liu et al. (2003) concluded that bovine liver catalase at a concentration of 0.2 mg L\(^{-1}\), was the optimal H\(_2\)O\(_2\) quencher since it was fast, convenient, and did not interfere with the investigated analyses. For these reasons bovine liver catalase is the most commonly applied H\(_2\)O\(_2\) quencher in laboratory scale UV/H\(_2\)O\(_2\) studies. However, no single H\(_2\)O\(_2\) quencher has been suggested in the literature for AOC analysis. Bovine liver catalase, due to its organic nature, may interfere with AOC quantification. SM 9217 suggests sodium thiosulfate be used for quenching residual chlorine prior to AOC determination as residual chlorine will inhibit growth of microorganisms (Clescerl et al. 1999). While sodium thiosulfate is suitable for the removal of residual chlorine, the suitability of sodium thiosulfate for H\(_2\)O\(_2\) prior to AOC measurement has not been reported. Manganese dioxide is also known to catalyze the degradation of H\(_2\)O\(_2\) so could possibly be appropriate for removing H\(_2\)O\(_2\) prior to AOC determination.

Figure 7.5 presents the results from one of the experiments conducted to determine the impact of bovine liver catalase, sodium thiosulfate, and manganese dioxide on AOC tests. As shown in Figure 7.5, catalase at a concentration of 0.02 mg L\(^{-1}\) increased the measured AOC concentration suggesting that even at very low concentrations (i.e., one order of magnitude less than the amount recommended by Liu
et al. (2003)), quenching \( \text{H}_2\text{O}_2 \) with catalase can interfere with subsequent AOC analysis (Figure 7.5). Meanwhile, sodium thiosulfate had the opposite effect on AOC determination in that quenching \( \text{H}_2\text{O}_2 \) with sodium thiosulfate severely inhibited cell growth resulting in a large underestimation of the AOC (Figure 7.5). The cause of this observation has not been concluded. One possible explanation is that the product of reaction between \( \text{H}_2\text{O}_2 \) and sodium thiosulfate, tetrathionate inhibits microbial growth. This hypothesis could be tested relatively easily by adding tetrathionate to water and performing the AOC analysis. Of the three quenching agents, manganese dioxide showed the least impact on AOC estimation, neither greatly increasing nor reducing the estimated AOC (Figure 7.5).

These observations were repeated but for further method development, it is recommended that quenching tests be repeated and AOC analysis be conducted both with this method as well as SM 9217. That being said, manganese dioxide was selected as the quenching agent for the following experiments investigating the impact of UV/H\( \text{O}_2 \) on AOC of CW.

### 7.3.4 Impact of UV/H\( \text{O}_2 \) Advanced Oxidation on Measured Assimilable Organic Carbon

The impact of UV/H\( \text{O}_2 \) treatment on the assimilability by microbes of NOM was determined by applying the above described AOC method to CW treated by UV/H\( \text{O}_2 \) at an initial \( \text{H}_2\text{O}_2 \) concentration of about 5 mg L\(^{-1} \). Figure 7.6 presents the average determined AOC concentrations for three separate experiments along with the standard deviation across the three experiments. Untreated CW had an average measured AOC concentration of 51 µg L\(^{-1} \) while CW with 5 mg L\(^{-1} \) \( \text{H}_2\text{O}_2 \) added and quenched with manganese dioxide had an average measured AOC concentration of 32 µg L\(^{-1} \) (Figure 7.6). The similarity between these values, along with the overlapping error bars, supports the observations in Figure 7.5 that manganese dioxide was suitable for quenching \( \text{H}_2\text{O}_2 \) prior to AOC determination by this method. However, note that the AOC for CW in Figure 7.5 was about twice the value reported in Figure 7.6. Data collected for Figure 7.5 was slightly elevated compared to those reported in Figure 7.6, likely due organic carbon contamination as a result of operator error during sample handling (see Section 7.3.2). Nonetheless, the data provided valuable information since, for both sets of experiments, AOC values were being compared to that of CW which served as the control.

For CW treated by UV/H\( \text{O}_2 \), there was a clear increase in the AOC measured, increasing as the irradiation time increased (Figure 7.6). Speitel et al. (2000), Thomson et al. (2004), Toor & Mohseni (2007), and Section 2.3.4 reported an increase in the biodegradability of NOM for water treated by UV/H\( \text{O}_2 \). Toor & Mohseni (2007) reported AOC measurements of 62 µg L\(^{-1} \) and 100 µg L\(^{-1} \) for CW and CW treated by UV/H\( \text{O}_2 \) at 500 mJ cm\(^{-2} \) and 20 mg L\(^{-1} \) initial \( \text{H}_2\text{O}_2 \) concentration, respectively. AOC
measurements were done by a commercial laboratory according to SM 9217. The agreement with the values reported by Toor & Mohseni (2007) suggests that the values measured in this study are acceptable. Yet, clearly more data is required to solidify any claims and further experimentation and method testing is needed. Nonetheless, these preliminary results demonstrated that the developed AOC method could be used for identifying the impacts of UV/H$_2$O$_2$ on the assimilability of NOM.

7.4 Acknowledgments

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**Figure 7.1** Flow cytometer dot plot of sterilized CW with beads and fluorescent stain.

**Figure 7.2** Flow cytometer dot plot of CW with beads and fluorescent stain.
Figure 7.3 Cell concentration over hours for difference initial concentrations of acetate-C. Each bar is the average measurement for triplicate sample incubations. Error bars indicate the standard deviation for the triplicate sample incubations.

Figure 7.4 Stationary phase cell concentration in ultrapure water with varying levels of initial concentration of acetate-C. Each bar is the average measurement for triplicate sample incubations. Error bars indicate the standard deviation for the triplicate sample incubations.
Figure 7.5 Impact of quenching H₂O₂ by catalase, sodium thiosulfate, and manganese dioxide on the estimation of AOC for Capilano Water. Yield coefficient of 1E7 cells µg⁻¹ acetate-C used to convert cell concentration to AOC equivalent units. Each bar is the average measurement for triplicate sample incubations. Error bars indicate the standard deviation for the triplicate sample incubations.
Figure 7.6 Impact of UV/H₂O₂ (initial H₂O₂ concentration of 5 mg L⁻¹ and irradiation times of 30, 60, and 90 minutes) on the estimation of AOC for Capilano Water. Yield coefficient of 1E7 cells µg⁻¹ acetate-C used to convert cell concentration to AOC equivalent units. Each bar is the average measurement for triplicate sample incubations. Error bars indicate the standard deviation for the triplicate sample incubations.
Literature Cited


Chapter 8  
Conclusions

8.1 Overall Conclusions

This research investigated the changes in natural organic matter (NOM) characteristics during the UV/H$_2$O$_2$ advanced oxidation of raw surface water. Working with two different source waters, Capilano Water (CW) and Trepanier Water (TW), NOM concentration, structure, hydrophobicity, apparent molecular weight distribution (AMW), disinfection by-product formation potentials (DBP-FPs), and biodegradability were studied. CW was also treated by membrane ultrafiltration (UF) to remove a portion of NOM and subsequently treated by UV/H$_2$O$_2$. Also, a select fraction of the NOM, the very hydrophobic acids (VHA), was removed from CW and the impact of UV/H$_2$O$_2$ on NOM structure, concentration, and DBP-FPs was observed. Further, a dynamic kinetic model was developed to predict the extent of transformation of NOM as a result of reaction with hydroxyl radicals (‘OH). To determine the impact of UV/H$_2$O$_2$ treatment on assimilable organic carbon (AOC) a suitable method was developed.

Before presentation of the overall conclusions, it should be noted that some specific conclusions are based on the results from studies with CW and TW. NOM varies spatially and temporally, so there likely could be exceptions to the generalized conclusions stated below.

That being said, with full awareness of the inherent limitations encountered when studying a complex, variable material such as NOM, the overall conclusions from the UV/H$_2$O$_2$ treatment of raw water NOM are:

1. At fluences less than 2000 mJ cm$^{-2}$ and initial H$_2$O$_2$ concentrations less than or equal to 20 mg L$^{-1}$, NOM is not mineralized as indicated by no appreciable reduction in total organic carbon (TOC). This essentially demonstrates that under the fluence and initial H$_2$O$_2$ concentrations applied in commercial UV/H$_2$O$_2$ drinking water processes, raw water NOM is not likely to be mineralized.

2. ‘OH partially oxidizes NOM leading to ring opening of aromatic structures, cleavage of conjugated double bonded carbon structures, and reduction in the degree of aromatic substitution. These transformations are observed spectroscopically as a reduction in the chromophoric natural organic matter (CNOM) (i.e., NOM absorbing at 254 nm UV).

3. ‘OH preferentially reacts with and degrades higher apparent molecular weight (AMW) CNOM. This fragmentation of high AMW CNOM leads to the formation of smaller AMW
CNOM. These observations suggest that UV/H₂O₂ treatment can oxidize NOM to low molecular size, readily biodegradable constituents. To support this claim, it was observed that UV/H₂O₂ treatment oxidized recalcitrant NOM into more readily biodegradable compounds with increases in concentrations of formaldehyde and acetaldehyde, bioavailable, low molecular weight carbonyls. Additionally, using the developed AOC determination method, it was observed that the partially oxidized NOM was more assimilable by microorganisms than raw water NOM.

4. UV/H₂O₂ treatment leads to an appreciable reduction in the VHA fraction of NOM. However, while both CNOM and the VHA fraction are often considered to represent the large portion of DBP precursors, their reduction during UV/H₂O₂ does not lead to considerable reductions in DBP-FPs. Thus, one cannot expect substantial reduction in DBP precursors during commercial drinking water UV/H₂O₂ treatments.

5. The presence of alkalinity slows down the degradation of CNOM during UV/H₂O₂ since bicarbonate and carbonate act as an ’OH scavengers. Thus, for waters with increasing levels of alkalinity, the partial oxidation of NOM during UV/H₂O₂ decreases and in turn minimizes the transformation of NOM and subsequent impacts on biological stability.

The above conclusions generally address how NOM in raw surface water is transformed under commercial drinking water UV/H₂O₂ treatment conditions and the implications on related water quality parameters. Yet, most commercial drinking water UV/H₂O₂ applications are applied to water that has undergone some form of pre-treatment. To address this, NOM in CW was pre-treated so as to deduce how UV/H₂O₂ may impact NOM that has undergone transformation during pre-treatment. A similar deduction can be made for NOM that has lower amounts of high molecular size species, such as Nordic Reservoir NOM. For NOM that has undergone UF and/or lacks high molecular size species, the overall conclusions are:

6. UF removes a large portion of high AMW CNOM. Thus, the resulting water would not only represent a raw water that has undergone UF, but also raw water NOM that lacks high molecular size constituents.

7. NOM in water pre-treated by UF is readily mineralized during UV/H₂O₂ treatment. The increased reduction in TOC is likely due to the absence of high molecular size NOM, which leads to the increased reaction between ’OH and smaller molecular size NOM, leading to complete mineralisation.
8. 'OH reacts readily with all AMW CNOM fractions leading to a reduction in all but the smallest AMW fractions. So, when high molecular weight species are absent, 'OH is available to react with the remaining NOM leading to mineralisation. The mineralisation of Nordic Reservoir NOM during UV/H_2O_2 supports this claim as Nordic Reservoir NOM lacked high molecular size CNOM that was present in CW, TW, and Suwannee River NOM.

Alternate to the removal of high molecular size NOM by UF, the VHA fraction of NOM was removed to mimic pre-treatment processes capable of removing the VHA fraction, such as coagulation with alum. Key conclusions include:

9. UV/H_2O_2 treatment leads to mineralisation of NOM suggesting that, when coupled with a pre-treatment capable of removing a large portion of the VHA fraction, UV/H_2O_2 can achieve reductions in TOC. Further, this reduction in TOC leads to reductions in DBP-FPs demonstrating that DBP precursors are removed.

When UV/H_2O_2 is coupled with downstream biological activated carbon (BAC):

10. NOM removal by BAC improves when water is pre-treated by UV/H_2O_2. This demonstrates that UV/H_2O_2 increases the biodegradability of NOM, hence promoting NOM removal by BAC. Formaldehyde that is formed as a result of UV/H_2O_2 oxidation of NOM is effectively removed by BAC thus improving the biological stability of the water.

11. The BAC process is able to effectively remove residual H_2O_2 left behind after UV/H_2O_2 treatment. Thus, BAC has potential to be a low-cost, highly effective method for removing the residual H_2O_2.

The dynamic kinetic model developed in this research was unique and the first to attempt to predict the degradation of CNOM. The development and application of the model led to the following conclusions:

12. For both CW and TW, the model is able to accurately predict the degradation of CNOM as a function of initial H_2O_2 concentration and irradiation time (i.e., fluence). As tracking CNOM could be used as an indicator parameter for other metrics (i.e., formation of aldehydes, reduction in VHA, etc.), the kinetic model could be linked with empirical correlations to generate value for practical applications.

13. Although including the reduction in CNOM improves the modeling of H_2O_2 degradation, the model still under predicts H_2O_2 degradation. This indicates that there are other reaction mechanisms that need to be addressed.
14. The model adequately considers the impact of alkalinity on the degradation of CNOM during UV/H₂O₂ treatment.

Development of a method for the determination of AOC in UV/H₂O₂ treated water yielded the following key findings:

15. Manganese dioxide is a suitable agent for the removal of H₂O₂ prior to AOC analysis. Bovine liver catalase and sodium thiosulfate are inappropriate quenching agents.

16. The method was applied to show an increase in AOC as fluence increases during UV/H₂O₂ treatment of raw water. This finding is in line with the results from the complementary metrics of BDOC and aldehydes concentration which both indicate a reduction in biological stability of raw water treated by UV/H₂O₂.

8.2 Significance of the Research

With the growing number of commercial drinking water applications employing UV/H₂O₂ advanced oxidation for the removal of micropollutants, there is a growing need to fundamentally understand the numerous oxidation reactions taking place in such a system including the reaction between 'OH and NOM. NOM plays many key roles in drinking water treatment. Arguably, of utmost concern is that NOM serves as a precursor for chlorination DBPs. Additionally, due to its complex, polymeric structure NOM is capable of chelating heavy metals, binding organic pollutants, and shielding pathogens thus making it more difficult to remove these species from water. Also, as it is organic in nature, NOM serves as a substrate for microorganisms. Ozonation has been demonstrated to make NOM more bioavailable for microorganisms thus increasing the potential for biological regrowth in distribution systems. For membrane processes, NOM can contribute to membrane fouling thus reducing process efficiency. During UV disinfection, NOM screens photons which are required for inactivation of pathogens. Similarly, during UV based advanced oxidation processes, NOM absorbs photons that are needed for the generation of 'OH (i.e., photolysis of H₂O₂, activation of TiO₂, etc.). Further, NOM reacts with 'OH which is required for oxidation of micropollutants. As NOM is ubiquitously present in drinking water sources, this reaction is present in all advanced oxidation systems to some extent. Overall, it is clear that NOM plays an important role in drinking water applications and has impacts on almost every unit operation. Therefore, research towards understanding the fate of NOM during drinking water treatment and its impact on unit operations is valuable and necessary. This research specifically addressed this need for characterizing the reaction between 'OH and NOM and understanding what types of transformations NOM undergoes as a result of this reaction. It is clear that this research provides a significant contribution to understanding of
not only how NOM is transformed during UV/H₂O₂, but also how UV/H₂O₂ process efficiency is affected by NOM.

By understanding how NOM is transformed during UV/H₂O₂, this research provided information that can be applied toward engineering solutions that minimize undesirable transformations in NOM and for improving the quality of UV/H₂O₂ treated water. For example, this research revealed that during UV/H₂O₂ advanced oxidation, higher molecular size NOM is broken down to form smaller compounds. These products were shown to be more biodegradable which is undesirable from a biological regrowth standpoint. It was shown that these products are formed in greater concentrations as the fluence and/or initial H₂O₂ concentration are increased. Thus, by careful selection of process parameters (i.e., fluence and initial H₂O₂ concentration) deleterious impacts on water quality can be mitigated. This is just but one example of how the wealth of information within this research can help to improve the design and operation of UV/H₂O₂ systems. Following are the specific areas of strength and potential applications of the findings of this research. Later the limitations of the research and recommendations for moving forward are discussed.

8.3 Contributions to the Field

This research is the first comprehensive study to look at, in depth, the transformation of NOM under UV/H₂O₂ advanced oxidation conditions prior to mineralisation. The major scientific contributions of this research were revealing that (i) mineralization of raw water NOM is unlikely under practical UV fluences and H₂O₂ concentrations, (ii) NOM undergoes significant partial oxidation prior to mineralization including breakdown of aromatic rings, cleavage of carbon double bonds, and loss of high molecular size species, (iii) a marked formation of aldehydes and other readily biodegradable species takes place as a result of partial oxidation of NOM by ·OH, and (iv) a large change in chlorine reactivity and DBP-FPs of NOM after UV/H₂O₂ treatment is not possible when NOM is not mineralized. It was learned that raw water NOM must undergo extensive partial oxidation or other forms of pre-treatment before it can be mineralized by ·OH. This is primarily due to the presence of high molecular size species in raw water NOM. Once these species are removed or degraded, the remaining lower molecular size compounds can be mineralized.

The level of contribution is enhanced when the scope of commercial UV/H₂O₂ applications in drinking water treatment is considered. Working closely with industry leaders, the scope of this research was directed in order to provide relevant information for practical applications and to address industry concerns related to NOM transformation during UV/H₂O₂ treatment. As this research was carried out
under the umbrella of academia and industry, this research contributes heavily to both academic research as well as industrial practice.

As discussed earlier, NOM varies widely spatially and temporally. This research acknowledged this inherent challenge related to studying NOM, and subsequently went forth and studied two natural waters coming from very different geological regions and with markedly different characteristics. Further, isolated NOM from two sources was used in preparation of “synthetic” waters to closely study the reaction between \(^{\cdot}\text{OH}\) and NOM when other water constituents are absent. By comparing and contrasting results with different NOM sources, a broader perspective was achieved that enhanced the potential applications of the findings. Another related strength is that this research amended water characteristics by removing certain fractions of NOM as well as by adding alkalinity. These steps help to extend the findings beyond a specific water quality and NOM source to a much broader range where general NOM characteristics and water quality parameters can be used to infer the impact of UV/H\(_2\)O\(_2\) on NOM.

This research used a low pressure mercury lamp housed in a collimated beam apparatus as the irradiation source. While the collimated beam is very different from industrial UV reactors, it allows for maintaining a constant, reproducible irradiation source that avoids complications related to flow regimes and irradiation distribution within the reactor. Thus, other researchers can easily reproduce the findings as well as apply similar methods to other water qualities and NOM sources and directly compare results to the findings presented herein.

While the model is not entirely unique, it incorporates unique features such as a term to account for the change in water absorbance as well as the reduction in H\(_2\)O\(_2\) concentration. By including these features and considering all species dynamic, it comes closer to ideal characterization of the UV/H\(_2\)O\(_2\) system. Compared to existing literature models, it does the best at predicting the extent of degradation of H\(_2\)O\(_2\). Also, the model is presented such that it can be easily adopted, tested, and improved by others.

Determination of AOC is arguably one of the most informative metrics for water quality as it provides information towards the microbial quality of water. Yet, it is not widely applied due to the difficulties in the analytical technique. In this research recent developments in AOC determination were adopted, and advanced, for application to UV/H\(_2\)O\(_2\) treated water. The progress made towards this goal adds tremendous strength to the contributions of this work since a rapid, reproducible, low cost AOC determination method for UV/H\(_2\)O\(_2\) treated water is highly desired by industry.

Finally, this research employed rigour and repetition in both UV/H\(_2\)O\(_2\) treatment experiments as well as analytical techniques. UV/H\(_2\)O\(_2\) treatments were repeated in duplicate in most cases thus providing more reliable results. Further, drinking water analyses requires utmost quality control and clean sample
handling as analytes are typically at very low concentrations. This research employed a level of quality control comparable to that found in commercial laboratories, thus providing confidence in the results.

8.4 Potential Applications of Findings

First, it should be stated that although this study employed the UV/H₂O₂ AOP for generation of \(^•\)OH, the study focussed on the reaction between \(^•\)OH and NOM so the findings can essentially be applied to understand NOM transformation during other UV based AOPs. Whether \(^•\)OH are generated by photocatalysis, vacuum UV irradiation, or UV/H₂O₂, the reaction between \(^•\)OH and NOM exists in all these systems. The primary difference between these systems would be the level of exposure to \(^•\)OH, which this research addressed by investigating the impact of fluence and initial H₂O₂ concentration. Thus, as alternative AOPs start becoming more practical for drinking water applications, the findings herein provide a reference to compare with the impact of treatment parameters on the transformation of NOM.

Of high potential application is the model developed in this study. As residual H₂O₂ is present in all UV/H₂O₂ applications, and requires costly removal, accurate prediction is of high value for system design and cost reduction. As the model can also be applied to predict the degradation of micropollutants, it has applications beyond simply predicting the transformation of NOM. The model tracks the transformation of NOM by the surrogate parameter CNOM. Changes in CNOM correlated with other changes in NOM such as reduction in VHA and formation of aldehydes. Thus, this model could also be applied to predict changes in water quality by using empirical correlations linking degradation of CNOM to changes in water quality. Finally, the model can be integrated into computational fluid dynamics (CFD) photoreactor models. This chemical reaction model could be coupled with irradiation and hydrodynamic models to create a comprehensive CFD model for characterizing the UV/H₂O₂ process with industrial design UV reactors.

While the model predicts the degradation of CNOM, this surrogate parameter can also be used in actual process operation to track the transformation of NOM and to approximate the \(^•\)OH concentration. In practice, this would involve simple monitoring of CNOM upstream and downstream of the UV/H₂O₂ process. By monitoring the change in CNOM after UV/H₂O₂, the extent of formation of biodegradable compounds can be inferred. Further, since the reduction in CNOM is dependent on \(^•\)OH concentration, variation in its reduction would indicate a change in \(^•\)OH concentration. This could be due to a change in the concentration of water constituents, such as species contributing to alkalinity, affecting the concentration of \(^•\)OH scavengers or a variation in a process parameter such as fluence or initial H₂O₂ concentration. As \(^•\)OH concentration impacts the removal of target contaminants, this simple method has the potential to improve process performance.
Commercial drinking water UV/H\textsubscript{2}O\textsubscript{2} applications typically do not target the removal of NOM as it is cost prohibitive. However, it is acknowledged that there may be situations when NOM removal is desirable. In such cases UV/H\textsubscript{2}O\textsubscript{2} alone, or coupled with pre- and post-treatment, may be a feasible solution. The findings in this research demonstrated how NOM behaves prior to mineralisation by ’OH, how mineralisation can be achieved after removing specific fractions (i.e., VHA, high molecular size) of NOM, and how some raw water NOM may be able to be mineralized readily by UV/H\textsubscript{2}O\textsubscript{2}. In short, for when NOM removal is desired, the findings of this research provide indications of what steps can be taken to modify NOM so as to reduce the cost of removal by advanced oxidation processes.

Finally, the AOC determination method developed has far reaching applications for assessing the biological stability of current and future drinking water systems employing UV/H\textsubscript{2}O\textsubscript{2}. This will help to improve overall process performance such that organic contaminant removal can be achieved without compromising the microbial quality of the water.

8.5 Limitations of the Research and Recommendations for Future Investigations

- One limitation of this research is with respect to the impact of UV/H\textsubscript{2}O\textsubscript{2} on the molecular size distribution of NOM. HPSEC is an informative and widely applied tool for characterizing the molecular size distribution of NOM. But, when UV absorbance is the sole means of detection of NOM, only a specific fraction (i.e., chromophoric) of NOM is monitored. A more suitable approach for studying NOM would have been to employ an organic carbon detector in order to monitor the molecular size distribution of the entire NOM. By doing so, claims regarding the preferential reaction of ’OH with high molecular size NOM and the subsequent formation of low molecular size NOM would be better supported. Thus, it is recommended that future investigations couple HPSEC with online carbon detection in addition to UV absorbance detection. Her et al. (2002) provided details on an HPLC with downstream absorbance and DOC detection for HPSEC of NOM. Meanwhile, Huber & Frimmel (1994) developed a novel gel chromatography plus DOC detection instrument to characterize the molecular weight distribution of organic carbon in water. Allpike et al. (2005) compared these two instruments along with the simpler HPSEC with absorbance detection and concluded that absorbance detection yielded similar results to organic carbon detection so the analysis in this thesis is still highly relevant.

- When working with drinking water it is best to minimize sample handling. As this research employed grab sampling, the accuracies of absorbance and TOC measurements were reduced due to excessive sample handling. With some improvements to the experimental apparatus and
procedure, these limitations could be reduced. First, it is recommended that modifications be made such that UV absorbance can be measured continuously during UV/H$_2$O$_2$ treatment. This could be achieved easily by either placing a probe within the reactor or by setting up a flow loop through a spectrophotometer equipped with a flow cell. Thus, treatment would not have to be stopped and the sample would not have to be disturbed in order to collect UV absorbance data. Similarly, organic carbon detection could possibly be done online if the analytical instrument could be configured to accommodate this application. This would also provide continuous data rather than measurements at intervals. Secondly, it is recommended that the UV output (i.e., irradiance) of the collimated beam apparatus be increased by addition of a second lamp. This will reduce the treatment time required to achieve a desired fluence as well as increase the treatment capacity of the apparatus. Additionally, the apparatus should be modified such that the entire length of the lamp is utilized. Currently there is only one collimating tube which allows for photons only from the centre of the lamp to be used. By adding second and third collimating tubes on both sides of the current tube, more of the lamps’ output can be utilized. This will also allow for three simultaneous treatments, increasing treatment capacity and minimizing sample handling.

- This research focussed on transformations in NOM prior to mineralisation. The justification of this was because past research demonstrated that high fluences and/or initial H$_2$O$_2$ concentrations were required to achieve mineralisation. As commercial UV/H$_2$O$_2$ applications do not apply such strong conditions, it is unlikely mineralisation of NOM will take place. However, this research demonstrated that NOM can be mineralized even under low to moderate advanced oxidation conditions if it is pre-treated or the raw NOM lacks high molecular size constituents. This research fell short in that it did not provide an adequate picture of how NOM behaves in the region just before and after mineralisation. It is expected that partial oxidation continues, as was observed by the degradation of CNOM, but at some point NOM starts getting mineralized. After this instance, the reaction kinetics of the system is expected to change as the concentration of NOM is being reduced. Thus, it is recommended that future investigations aim to study this stage of the treatment. With the suggested improvements to the experimental apparatus (i.e., online UV absorbance and TOC detection), the transformation of NOM can be monitored continuously all the way from initial partial oxidation through to complete mineralisation. In this way the instance at which the system shifts to mineralisation of NOM can be observed. Also, how this instance changes for NOM from different sources and with different characteristics can be investigated.
The fractionation method applied in this study to investigate the impact of UV/H₂O₂ on the hydrophobic portions of NOM was time consuming and had poor accuracy for water with low TOC levels. The use of DAX/XAD fractionation was developed primarily for the isolation of NOM fractions rather than characterization. Of particular limitation is the method performs poorly with low TOC water, a primary characteristic of drinking water. The resins leach organic carbon as well as require extensive cleaning to minimize sample contamination. This limitation meant that in this research the impact of treatment on hydrophilic fractions, constituting less than 20% of the TOC, could not be investigated. It is recommended that DAX/XAD fractionation be continued for removal of specific fractions of NOM as a tool for mimicking pre-treatment processes but the method should not be used for characterizing NOM. Rather, the polarity rapid assessment method (PRAM), recently developed by Rosario-Ortiz et al. (2007), should be adopted as it has been demonstrated to yield similar information as conventional DAX/XAD fractionation while not requiring pH adjustment. Further the PRAM method appears to be more suitable for characterizing low TOC waters as leaching can be kept to less than 10% of the TOC of the water.

The developed AOC determination method was demonstrated to be adequate for AOC determination of UV/H₂O₂ treated water but the work requires optimization. Further work is recommended to improve the quenching method and to confirm the appropriateness of manganese dioxide. Quenching experiments should be repeated and the waters should be analyzed by the in house AOC method as well as by the standard method at a certified commercial laboratory. Also, the adequacy of using readily available manganese dioxide powder should be investigated as an alternative to the manganese dioxide based granules from Clack Corporation. Further, water should be treated by UV/H₂O₂ at varying fluences and initial H₂O₂ concentrations and the impact on AOC should be determined by both the standard method at a commercial lab as well as the in house method. Investigating the impact of additional alkalinity on the increase in AOC after UV/H₂O₂ is also recommended. Also, the concentration of aldehydes should be monitored concurrently with AOC so that a clear link between the two can be established. This should all be done with the improved experimental apparatus since UV absorbance can be measured throughout and linked with changes in AOC.

The model developed fell short in that it was not able to adequately predict the degradation of H₂O₂ as a function of irradiation time. This was hypothesized to be due to the reaction between H₂O₂ and carbon centred radical species formed as a result of reaction between °OH and NOM. However, this mechanism was neither investigated nor confirmed. Investigation should be done
to confirm or reject this hypothesis and, if confirmed, it should be included into the model to improve model performance. This hypothesis can be tested by conducting investigations into the degradation of H₂O₂ in pure water with and without dissolved oxygen, pure water with isolated NOM (i.e., the synthetic water used in this study) with and without dissolved oxygen, and pure water with a simple organic, such as formic acid, with and without dissolved oxygen.

- The model developed has potential to be adopted by other researchers as well as industry. However, in its current state the model employs commercial software (i.e., MATLAB) for solution. As this software is not readily available to many researchers, this may deter acceptance of this model. Alternatively, a model employing the pseudo-steady-state ·OH assumption can be easily solved with readily available software (e.g., Microsoft Excel, Octave) so may be more easily adopted. In the spirit of open-source software, it is recommended that the model be changed to assume a pseudo-steady-state for all radical species, recoded using Octave (open-source alternative to MATLAB) and distributed freely. By doing so, the model can be tested and improved by others and its performance can be compared to dynamic models (Chapter 5; Song et al. 2008) and steady-state ·OH models (Sharpless & Linden 2003). It can then be applied to a wider spectrum of water qualities and also organic pollutants.
Literature Cited


Appendix A
Supplementary Data

A.1 Influence of Alkalinity on the Aldehydes Concentration during UV/H$_2$O$_2$ of Capilano Water and Trepanier Water

![Figure A.1](image1)

**Figure A.1** Concentration of aldehydes during UV/H$_2$O$_2$ AO treatment of CW and CW with additional alkalinity over a range of fluence and initial H$_2$O$_2$ concentrations of 5 and 15 mg L$^{-1}$. Bars represent the average of two samples, each measured twice.

![Figure A.2](image2)

**Figure A.2** Concentration of aldehydes during UV/H$_2$O$_2$ AO treatment of TW and TW with additional alkalinity over a range of fluence and initial H$_2$O$_2$ concentrations of 5 and 15 mg L$^{-1}$. Bars represent the average of two samples, each measured twice.
Observations
- CW and TW responded similarly with respect to the impact of fluence, initial H$_2$O$_2$ concentration, and alkalinity on the aldehydes concentration during treatment.
- As fluence is increased, there was an increase in the concentration of aldehydes.
- As initial H$_2$O$_2$ concentration was decreased, there was a decrease in the concentration of aldehydes during treatment.
- As alkalinity is increased, there was a decrease in the concentration of aldehydes during treatment.

A.2 UV Absorbance as an Indicator Parameter for Change in Hydrophilic Fraction of Natural Organic Matter and Aldehydes Concentration

![Graph showing the relationship between very hydrophobic acids and change in 254 nm UV absorbance](image)

**Figure A.3** Very hydrophobic acids versus the change in 254 nm UV absorbance CW during UV/H$_2$O$_2$ treatment over a range of irradiation time and initial H$_2$O$_2$ concentration of 5 and 15 mg L$^{-1}$. 

\[
y = -459.74x + 61.48 \\
R^2 = 0.65
\]

Circle markers represent CW, 5 mg L$^{-1}$ H$_2$O$_2$; square markers represent CW, 15 mg L$^{-1}$ H$_2$O$_2$. 

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Observations

- The change in absorbance at 254 nm increased with increasing irradiation time and increasing initial H$_2$O$_2$ concentration while the very hydrophobic acids decreased. Thus, a negative correlation existed between the change in very hydrophobic acids and the change in the absorbance at 254 nm. It is clear that by monitoring only the absorbance at 254 nm, one could infer the impact on very hydrophobic acids.

- Both the change in absorbance at 254 nm and aldehydes concentration increased with increasing irradiation time, increasing initial H$_2$O$_2$ concentration. However, both decreased as alkalinity decreased. Similar observations were made for both CW and TW. There was a positive correlation between the change in absorbance at 254 nm and the aldehydes concentration. Therefore, it is clear that use of absorbance at 254 nm is an excellent indicator parameter for aldehydes and is appropriate for both CW and TW. Since aldehydes are an indicator of biological stability, one could essentially determine the impact of UV/H$_2$O$_2$ on biological stability by simply monitoring the absorbance at 254 nm during treatment.
A.3 Influence of Alkalinity on the Apparent Molecular Weight Distribution during UV/H$_2$O$_2$ of Capilano Water and Trepanier Water

Figure A.5 HPSEC chromatograms during UV/H$_2$O$_2$ AO treatment of CW and CW with additional alkalinity over a range of irradiation time and initial H$_2$O$_2$ concentration of 15 mg L$^{-1}$.

Figure A.6 HPSEC chromatograms during UV/H$_2$O$_2$ AO treatment of CW and CW with additional alkalinity over a range of irradiation time and initial H$_2$O$_2$ concentration of 5 mg L$^{-1}$. 
Figure A.7 HPSEC chromatograms during UV/H$_2$O$_2$ AO treatment of TW and TW with additional alkalinity over a range of irradiation time and initial H$_2$O$_2$ concentration of 15 mg L$^{-1}$.

Figure A.8 HPSEC chromatograms during UV/H$_2$O$_2$ AO treatment of TW and TW with additional alkalinity over a range of irradiation time and initial H$_2$O$_2$ concentration of 5 mg L$^{-1}$.

**Observations**

- As alkalinity was increased, the degradation of high AMW chromophores was impeded.
- Consequently, increasing alkalinity also reduced the formation of lower AMW chromophores.
A.4 Impact of UV/H$_2$O$_2$ on Nordic Reservoir Natural Organic Matter

Figure A.9 Degradation of chromophoric natural organic matter in Nordic Reservoir NOM synthetic water treated by UV/H$_2$O$_2$ at varying levels of TOC, initial H$_2$O$_2$ concentration, and irradiation time
Figure A.10 Degradation of pCBA in Nordic Reservoir NOM synthetic water treated by UV/H$_2$O$_2$ at varying levels of TOC, initial H$_2$O$_2$ concentration, and irradiation time.
Figure A.11 Degradation of H$_2$O$_2$ in Nordic Reservoir NOM synthetic water treated by UV/H$_2$O$_2$ at varying levels of TOC, initial H$_2$O$_2$ concentration, and irradiation time.

**Observations**

- The rate of scavenging of 'OH by Nordic Reservoir NOM was slightly higher than that of Suwannee River NOM (i.e., the rates of pCBA degradation were similar)
- The rate of degradation of CNOM was faster for Nordic Reservoir NOM than it was for Suwannee River NOM
- Mineralization of TOC was observed for Nordic Reservoir NOM under irradiation times and H$_2$O$_2$ concentrations that did not induce mineralization of TOC for the other NOMs studied.
A.5 Comparing Characteristics of Nordic Reservoir Natural Organic Matter and Suwannee River Natural Organic Matter

Table A.1 Characteristics of Suwannee River Natural Organic Matter and Nordic Reservoir Natural Organic Matter.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Suwannee River Natural Organic Matter</th>
<th>Nordic River Natural Organic Matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific UV absorbance (m L mg⁻¹ TOC)</td>
<td>3.4</td>
<td>4.2</td>
</tr>
<tr>
<td>Very hydrophobic acids (%)</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>Slightly hydrophobic acids (%)</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Charged and neutral hydrophilics (%)</td>
<td>16</td>
<td>22</td>
</tr>
</tbody>
</table>

Figure A.12 HPSEC chromatograms of Suwannee River Natural Organic Matter and Nordic Reservoir Natural Organic Matter. Each at a TOC concentration of 4.5 mg L⁻¹ in ultrapure water.

Observations
- The SUVA of Nordic Reservoir NOM was higher than Suwannee River NOM. This means that for a given concentration of TOC, there were more chromophores in Nordic Reservoir NOM than in Suwannee River NOM.
- Although there were more chromophores in Nordic Reservoir NOM, they were of lower molecular weight. This could explain why the rate of degradation of CNOM was faster for Nordic Reservoir NOM than it was for Suwannee River NOM. When high molecular weight CNOM is less, there will be less formation of low molecular weight CNOM when the high molecular weight CNOM react with •OH. This combination of less “pooling” of low molecular weight CNOM and more •OH available for reaction with low molecular weight CNOM, would increase the overall rate of degradation of CNOM.
- Since high molecular weight CNOM was less in Nordic Reservoir NOM, mineralization occurred sooner during treatment than it did for Suwannee River NOM.
- Nordic Reservoir NOM had less very hydrophobic acids and more hydrophilics than Suwannee River NOM. This supports the other data that suggested that Nordic Reservoir NOM consisted of smaller species that are more readily mineralized by OH.
Appendix B
Experimental Protocols

B.1 Iodide/Iodate Actinometry

Procedure
1.) Prepare 0.01M sodium borate buffer (1, 2)
   - 0.381g Na₂B₄O₇•10H₂O per 100 mL distilled water
2.) Measure pH of solution (pH ~ 9.25)
3.) Prepare 0.1M potassium iodate in borate buffer
   - 2.14g KIO₃ per 100mL borate buffer
   - This solution can be stored for several weeks in an opaque container.
4.) Prepare 0.6M potassium iodide in borate-iodate solution
   - 9.96g KI per 100mL borate-iodate solution
5.) Measure iodide-iodate-borate solution temperature in degrees Celsius. (T)
6.) Measure absorbance at 300nm (A₃₀₀) and 450 nm (A₄₅₀)
7.) Irradiate with UV under desired geometry.
8.) Measure absorbance at 450 nm (A₄₅₀)

Calculations

Quantum yield determination:
\[ \Phi = 0.75 \times [1 + 0.02 \times (T-20.7)] \times [1 + 0.23 \times (C-0.577)] \]

where:
\( \Phi \) = quantum yield (mol/einstein)
T = solution temperature in degrees Celsius
C = molar concentration of iodide
\( = [KI] = A_{300}/1.061 \)

Fluence determination:
\[ H' = \frac{4.72 \times 10^5 \times \Delta A_{450} \times V \times 1000}{\varepsilon_{450} \times \Phi \times A} \]

where:
\( H' \) = Fluence (mJ/cm²)
\( \Delta A_{450} \) = change in absorbance at 450 nm (cm⁻¹)
\( = (A_{450f} - A_{450i}) \)
V = solution volume (L)
\( \varepsilon_{450} \) = molar absorption coefficient of triiodide at 450 nm (M⁻¹ cm⁻¹)
\( = 1600 \ M^{-1} \ cm^{-1} \)
\( \Phi \) = quantum yield (mol/einstein)
A = area irradiated (cm²)
\( = \pi \times \text{radius of dish}^2 \)
4.72*10^5 = converting einsteins to joules
1000 = converting J to mJ
B.2 Concentration of H$_2$O$_2$

**Reagent A**
- 500ml Potassium hydrogen phthalate (KHP) 10g
  + Distilled water (DW)

**Reagent B**
- 500ml KI 33g
- NaOH 1g
- Ammonium molybdate tetrahydrate 0.1g
  +DW

**Analysis**
- Wavelength 351 nm
- Zero distilled water
- Blank ($A_o$) 2.5mL of each Reagent A and B
dilute with DW in 10mL volumetric flask
- Sample (A) 2.5mL of each A and B
  0.5 of sample
dilute with DW in 10mL volumetric flask

**Calculation**

Peroxide (ppm) : \[(A-A_o)*10*D/(0.7776*S)\]

D is additional dilution (1 if none)
S sample volume (=0.5mL)

**References**

B.3 Concentration of Free Chlorine

**Procedure**
1. Add 1 mL of sample to 10 mL volumetric flask and fill to mark with distilled water.
2. Add 1 packet of Hach DPD free chlorine reagent powder.
3. Invert 3 times and allow to sit for 1 minutes.
4. Measure absorbance @ 530 nm with spectrophotometer.

**Analysis**

| Wavelength | 530 nm |
| Zero       | distilled water |

**Calculation**

\[
[\text{Chlorine}] (\text{mg/L}) = \frac{A_{530} \text{ (cm}^\text{-1})}{0.1699}
\]

0.1699 is the slope obtained from calibration

**References**

Hach DPD Method 8021.
http://www.hach.com/fmmimghach/?CODE%3ADOC316.53.0102315566|1

B.4 Disinfection by-product formation potential

**Procedure**
1. Spike 30 mL of water sample with sodium hypochlorite (6% commercial bleach, Lavo Inc.) to achieve a free chlorine concentration about 3 times the TOC concentration. Use an initial chlorine spike that yields 1 mg L\text{-1} chlorine residual at the end of incubation.
2. Incubate for 7 days at 22 °C.

**References**


B.5 Trihalomethanes Analysis

**Procedure**
1. Start with the 30 mL of the water sample that underwent formation potential test or 30 mL calibration sample.
2. Add 10 g of NaCl and shake until dissolved.
3. Add 3 mL of working solvent (MTBE with internal standard).
4. Shake vigorously and consistently for 4 min.
5. Allow the phases to separate for approximately 2 min.
6. Using a disposable Pasteur pipet, transfer a portion of the solvent phase from the 40 mL vial to an autosampler vial. Ensure no water has carried over to the autosampler vial. If a dual phase appears in the autosampler vial, the bottom layer can be easily removed and discarded by using a Pasteur pipet.

Working solvent: \~400 μg L\text{-1} IS in MTBE - 40μL IS stock into 1L MTBE
Internal standard (IS) stock: 10000 μg mL\text{-1} 1,2-dibromopropane
Analysis

1. Analyse as soon as possible. The sample extract may be stored in a freezer (< -10°C) for a maximum of 14 days before chromatographic analysis but no more than 24 hours at room temperature (i.e., on an autosampler rack). Due to the volatility of the extraction solvent, if the septum on a vial has been pierced, the screw cap septum needs to be replaced
2. Analyse with GC/MS using defined “THM liquid May 06” method file.

Calibration

Calibration curve for all four THMs
- 150 μg L⁻¹ THMs: 22.5μL of stock solution into 30 mL DW
- 250 μg L⁻¹ THMs: 37.5μL of stock solution into 30 mL DW
- 350 μg L⁻¹ THMs: 52.5μL of stock solution into 30 mL DW
- 450 μg L⁻¹ THMs: 67.5μL of stock solution into 30 mL DW

Stock solution: 200 μg mL⁻¹ THMs in methanol

References

USEPA. (1995a) Method 551.1: Determination of chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron capture detection.

B.6 Haloacetic Acids Analysis

Procedure

1. Start with the 30 mL of the water sample that underwent formation potential test or 30 mL calibration sample.
2. Adjust the pH to less than 0.5 by adding at least 2 mL of concentrated acid
3. Cap and shake.
4. Quickly add 10 g of muffled sodium sulfate and shake for 3 to 5 min until almost is dissolved. Sodium sulphate is added to increase the ionic strength of the aqueous phase and thus further drive the HAA into the organic phase. The addition of this salt should be done quickly so that the heat generated from the addition of acid will help dissolve the salt.
5. Add 5 mL MTBE and place on the mechanical shaker for 30 min.
6. Allow the phases to separate for approximately 6 min.
7. Using a Pasteur Pipet, transfer approximately 3 mL of the upper MTBE layer to a 15 mL graduated conical centrifuge tube.
8. Add 1 mL 10% sulphuric acid in methanol to each centrifuge tube.
9. Cap the centrifuge tubes and place in water bath at 50°C and maintain for 2 hours. At this stage, methylation of the method analytes is attained.
10. Remove the centrifuge tubes from water bath and allow them to cool before removing the caps
11. Add 4 mL saturated sodium bicarbonate solution to each tube in 1 mL increments. Exercise caution when adding the solution because the evolution of CO₂ in this neutralization reaction is rather rapid.
12. Shake each tube for 2 min. As the neutralization reaction moves to completion, it is important to continue to exercise caution by venting frequently to released the evolved CO₂.
13. Transfer exactly 1 mL of the upper MTBE layer to an autosampler vial. A duplicate vial should be filled using the excess extract. Be certain no water has carried over onto the bottom of the autosampler vial. If a dual phase appears in the autosampler vial, the bottom layer can be easily removed and discarded by using a Pasteur pipet.
14. Add 10 μL of internal standard to the vial to be analysed.

Working solvent: MTBE
Internal standard (IS) stock: 100 μg mL⁻¹ 1,2,3-trichloropropane

Analysis
1. Analyse as soon as possible. The sample extract may be stored in a freezer (< -10°C) for a maximum of 14 days before chromatographic analysis but no more than 24 hours at room temperature (i.e., on an autosampler rack). Due to the volatility of the extraction solvent, if the septum on a vial has been pierced, the screw cap septum needs to be replaced

Calibration
Calibration curve for trichloroacetic acid (TCAA) and dichloroacetic acid (DCAA)
50 μg L⁻¹ HAAs: 1.5 μL of stock solution + 30 mL DW
100 μg L⁻¹ HAAs: 3 μL of stock solution + 30 mL DW
150 μg L⁻¹ HAAs: 4.5 μL of stock solution + 30 mL DW
200 μg L⁻¹ HAAs: 6 μL of stock solution + 30 mL DW

Stock solution: 1000 μg mL⁻¹ HAAs in MTBE

References
USEPA. (1995b) Method 552.2: Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatization and gas chromatography with electron capture detection.

B.7 Aldehydes Analysis

Procedure
1. Start with the 20 mL of the water sample that underwent treatment or 20 mL calibration sample.
2. Add 200 mg KHP to adjust the sample pH to approximately
3. Add 1 mL of freshly prepared PFBHA Reagent and swirl gently to mix.
4. Place samples in a constant-temperature water bath set at 35 ± 2 °C for 2 hours.
5. Remove vials and cool to room temperature for 10 minutes.
6. To each vial add approximately 0.05 mL (2 to 4 drops) of concentrated sulfuric acid. This prevents the extraction of excess reagent, which will cause chromatographic interferences.
7. Add 4 mL of hexane that contains the internal standard
8. Shake manually for 3 minutes. Let stand for approximately 5 minutes to permit phases to separate.
9. Draw off hexane layer (top layer) using a clean disposable Pasteur pipette for each sample into a smaller 8 mL vial containing 3 mL 0.2 N sulphuric acid. Shake for 30 seconds and let stand for 5 minutes for phase separation. NOTE: This acid wash step further reduces the reagent and other interferants from the final extract.
10. Draw off top hexane layer using another clean, disposable pipette for each sample and place in two 1.8 mL autosampler vials per sample. Store extra autosampler vials as a backup extract. Extracts may be stored for up to 14 days at 4 °C.

Working solvent: ~400 μg L⁻¹ IS in hexane - 40μL IS stock into 1L hexane
Internal standard (IS) stock: 10000 μg mL⁻¹ 1,2-dibromopropane
PFBHA Reagent: Prepare a fresh 15 mg mL\(^{-1}\) solution in reagent water daily. Prepare an amount appropriate to the number of samples to be derivatized. 1 mL of solution is added per sample. For a 15 mL volume of solution, weigh 0.225 grams of PFBHA into a dry 40 mL vial, add 15 mL water and shake to dissolve.

Analysis
1. Analyse as soon as possible. The sample extract may be stored in a freezer (< -10°C) for a maximum of 14 days before chromatographic analysis but no more than 24 hours at room temperature (i.e., on an autosampler rack). Due to the volatility of the extraction solvent, if the septum on a vial has been pierced, the screw cap septum needs to be replaced.

Calibration
Calibration curve for formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, heptanal, octanal, nonanal, decanal
- 10 µg L\(^{-1}\) aldehydes: 2 µL of stock solution + 20 mL DW
- 30 µg L\(^{-1}\) aldehydes: 4 µL of stock solution + 20 mL DW
- 50 µg L\(^{-1}\) aldehydes: 6 µL of stock solution + 20 mL DW
- 70 µg L\(^{-1}\) aldehydes: 8 µL of stock solution + 20 mL DW

Stock solution: 100 µg mL\(^{-1}\) aldehydes in acetonitrile

References

B.8 Biodegradable Organic Carbon Determination

Procedure
1. Turn on water bath to 50°C and allow it to equilibrate (~30min)
2. Measure out ~350 mL of sample in a graduated cylinder and place it in the round bottom flask
3. Put round bottom flask in a rotary evaporator
4. Turn on the vacuum pump, half turn on tap, turn knob on condenser
5. Turn on cooling water
6. Turn rotation speed to maximum
7. Wait ~ 30 min, volume should be ~100 mL
8. Prepare 30 mL for TOC analysis
9. Filter the remaining ~70 mL through 0.22 µL filter
10. Prepare duplicate 30 mL samples for BDOC analysis
11. Add 2 mL of raw water to each concentrated sterilized sample
12. Incubate at 25°C for 5 days at 100 rpm in the shaker incubator
13. After incubation analyze for TOC

References
B.9 Hydrophobic Fractionation (batch)

Resin Preparation
1. Put approximately 20 mg of DAX-8 and XAD-4 in a beaker.
2. Cover the DAX-8 and XAD-4 with methanol and mix the solution. Enough methanol should be added so that it is about 1-2 inches above the resin
3. Let the solution overnight.
4. Decant methanol and rinse resin with distilled water
5. Wash the resin with NaOH and HCl several times
6. Wash with distilled water until there is no residual TOC detected

Fractionation
1. 600 mL of water sample and 50 mL of DAX-8 are combined in an Erlenmeyer flask and stirred, with a magnetic stir bar and stir plate, for 3 hours
2. Decant water and measure the TOC concentration of DAX-8 treated water. Mix remainder of sample with 50 mL of XAD-4 in an Erlenmeyer flask and stir, with a magnetic stir bar and stir plate, for 3 hours
3. Decant water and measure the TOC concentration of XAD-4 treated water.

Calculation
The hydrophobic fraction is defined as the fraction of TOC that was adsorbed onto DAX-8. The hydrophilic fraction is defined as the fraction of TOC that was not adsorbed onto XAD-4 or DAX-8.

References

B.10 Hydrophobic Fractionation (continuous/column)

Resin Preparation
1. Submerse DAX-8 and XAD-4 in methanol and mix overnight
2. Decant methanol and resin fines
3. Submerse DAX-8 and XAD-4 in acetonitrile and mix overnight
4. Decant acetonitrile and resin fines
5. Submerse DAX-8 and XAD-4 in deionized water and mix
6. Decanted and repeat until there is no residual TOC measured
7. Load DAX-8 and XAD-4 onto a glass columns

Fractionation
1. Acidify 500 mL of sample to pH 2 using concentrated hydrochloric acid
2. Pass the sample through the column containing DAX-8 resin at a flowrate of 1 mL min⁻¹
3. Remove 60 mL of effluent for TOC analysis
4. Pass remaining 440 mL of sample through the column containing XAD-4 resin at a flowrate of 1 mL min⁻¹
5. Measure TOC of final effluent
6. Between fractionation of samples, clean resins to prevent sample cross-over due to leaching.
   a. Pass 1 L of DI water through the DAX-8 and XAD-4 resin columns.
b. Pass DI water at pH 2 through the columns until there is little trace of TOC (≤ 0.1 µg L\(^{-1}\)) in the effluent. After this the resins are deemed ready for the next sample.

**Calculation**

very hydrophobic acids (VHA): the percentage of the initial TOC adsorbed onto DAX-8, calculated by:

\[
\%\text{VHA} = \frac{\text{TOC}_{\text{initial}} - \text{TOC}_{\text{after DAX-8}}}{\text{TOC}_{\text{initial}}} \times 100
\]

slightly hydrophobic acids (SHA): the percentage of the initial TOC adsorbed onto XAD-4, calculated by:

\[
\%\text{SHA} = \frac{\text{TOC}_{\text{after DAX-8}} - \text{TOC}_{\text{after XAD}}}{\text{TOC}_{\text{initial}}} \times 100
\]

hydrophilic charged + hydrophilic NEU (CHA+NEU): the percentage of the initial TOC not adsorbed by either of the resins, calculated by:

\[
\%\text{(CHA + NEU)} = \frac{\text{TOC}_{\text{after XAD}}}{\text{TOC}_{\text{initial}}} \times 100
\]

**References**


**B.11 Assimilable Organic Carbon Determination**

**Equipment**

- *AOC free vials*: organic-carbon-free glass vials (40 mL) with TFE-lined silicone caps
- *Glass beakers*: organic-carbon-free glass beakers (200 mL)
- *Glass Erlenmeyer flasks*: organic-carbon-free glass beakers (200 mL)
- *Syringe*: 20 mL plastic syringe with filter attachment ability
- *Syringe filters*: Nalgene\textsuperscript{®} syringe filter units, disposable, polyethersulfone pore size 0.22 µm, filter diam. 25 mm, sterile; \(\gamma\)-irradiated (Sigma Aldrich: Z359904)
- *Cleaning vessel*: Glass or plastic container capable of holding 10 L of 0.1 N HCl solution
- *Incubator*: capable of 35 °C
- *Flow cytometer tubes*: BD Polystyrene Round-Bottom Test Tube, 5 ml, snap cap (VWR: CA60819-310)
- *Flow cytometer*
- *Muffle furnace*
- *Pipet tips and autoclavable box*: Pipet tips for 100 \(\mu\)L pipet and 1000 \(\mu\)L pipet
- *Microcentrifuge tube*: 1.5 mL microcentrifuge tube for storage of fluorochrome;

**Reagents**

- *Sodium acetate solution*: 400 mg/L CH\(_3\)COONa\(\cdot\)3H\(_2\)O (Sigma Aldrich: 229873); in MilliQ water
- *Bottled mineral water*: Containing no carbon dioxide and having received no chemical treatment (Evian);
- *Carbon free water*: MilliQ water
- **Mineral salts solution**: 171 mg/L K$_2$HPO$_4$ (Sigma Aldrich: 450200); 767 mg/L NH$_4$Cl (Sigma Aldrich: 254134); 1.44 g/L KNO$_3$ (Sigma Aldrich: 542040); in MilliQ water
- **10% Sodium persulphate solution**: 100 g/L Na$_2$S$_2$O$_8$ (Sigma Aldrich: 216232); in MilliQ water
- **Fluorochrome**: SYBR Green I; Invitrogen SYBR Green I nucleic acid gel stain *10,000X concentrate in DMSO*, 1 mL (Invitrogen: S-7567); 1:100 from original stock in DMSO; store at -20 °C
- **Fluorochrome diluent**: Dimethyl sulfoxide (Sigma Aldrich: D8418)
- **Flow cytometry bead count standards**: Duke Scientific Cyto-Cal 633 Alignment Beads, 3 um (Duke Scientific: FA3R)
- **Hydrochloric acid solution**: 0.1 N HCl
- **Inoculum**

**Preparation of AOC free equipment**
- **Glassware**: Wash with common detergent. Rinse at least 3x with MilliQ water. Submerge in 0.1 N HCl for overnight. Rinse with MilliQ water and air dry. Cap with aluminum foil and heat in Muffle furnace at 500 °C for 5 hours.
- **Caps and pipet tips**: Wash with common detergent. Rinse with MilliQ water. Soak in 10% sodium persulphate solution at 60 °C for at least 1 hour. Rinse at least 3x with MilliQ water and air dry.

**Maintaining AOC free environment**
- **VOCs**: Use of volatile organic compounds should be avoided (e.g. ethanol, etc.)
- **Gloves**: Gloves should be worn at all time and sample exposure to skin should be avoided.
- **Talking**: Keep conversation to a minimum when doing analysis.

**Sterilization**
- **Pipet tips**: Put in box and autoclave.

**Rinsing equipment to decrease chance of contamination**
- **Syringe**: Rinse syringe by flushing with MilliQ water at least 5x.
- **Syringe filters**: To remove AOC from syringe filters, rinse by flushing with at least 250 mL of MilliQ water. Follow by flushing with 20 mL of sample. Then use for sample filtration. A filter can be reused if the water being filtered is the same (e.g. Evian). If working with different water (e.g. Evian, lake water, water treated by UV/H$_2$O$_2$ at different conditions), then a new filter should be used for each sample and each filter is to be prepared as per above.
- **Pipet tips**: Rinse autoclaved pipet tips at least 3x with MilliQ before inserting into sample or other reagents. This is to minimize contamination from particles or AOC.

**Preparation of flow cytometry counting beads solution**
- **Dilution of beads**: Supplied beads have an approximate concentration of 5E6 beads/mL. Dilution is permitted by half. Thus add 3 mL of MilliQ water to the 3 mL of supplied beads solution.
- **Manual counting of beads**: To know beads concentration, count using haemocytometer and microscope. Pipet 10 µL of diluted beads onto haemocytometer. Under microscope, count beads in each square. Use the following equation to calculate the beads concentration: Concentration (beads/mL) = bead count * 10,000. Record beads concentration.
Preparation of AOC-free stock inoculum
- Sterilize 30 mL of Evian water into 40 mL glass vial by filtration through 0.22 μm filter using syringe and syringe filter. Inoculate Evian sample with 10 μL/mL of unfiltered/untreated water (e.g. PWN water obtained from Princess Juliana sand filter effluent). Cap and vortex. Incubate at 35 °C until stationary phase is maintained.

Preparation and incubation of samples for calibration/method testing
- Sterilize 30 mL of Evian water into 40 mL glass vial by filtration through 0.22 μm filter using syringe and syringe filter. Add 2.5 uL/mL mineral buffer. Add desired concentration of acetate-C (e.g. 50, 100, 150 µg/L using sodium acetate solution). Add 3.33 uL/mL of stock inoculum. Cap and vortex. Incubate at 35 °C until for 3-4 days.

Counting cell using flow cytometer
- Staining cells: Vortex incubated sample to ensure a thoroughly mixed sample. Pipet 1 mL of sample into round-bottom flow cytometer tube. Stain sample with 10 uL/30mL diluted SYBR Green in DMSO. Leave stained samples in dark for at least 20 min. Add 10 uL/mL counting beads. Analyze with flow cytometer within 2 hours.
- Flow cytometer analysis: Take samples to LRFCF at Robart Research Institute, UWO. Analyze using BD FacsCalibur. Record cell count after counting 500 beads.

References
Appendix C
Model Programming Code and Fisher Information Matrix Calculation

C.1 Code for Parameter Estimation

function SUM=CSRF(K)
format long;
function dy= mehdi_final(t,y)
dy=zeros(10,1);
k2 =2.7*10^7;
k3 =7.5*10^9;
k4 =8.5*10^6;
k5 =3.9*10^8;
k6 =6.6*10^9;
k7 =8*10^9;
k8 =5.5*10^9;
k9 =3*10^9;
k10 =0.13;
k11 =6.5*10^8;
k12 =9.7*10^7;
k13 =8.6*10^5;
k14 =3.7;
k15 =8*10^5;
k16 =3*10^7;
k17 =2*10^7;
k18=3.56e-2;
k19=2e10;
k20=7e5;
k21=4.5e10;
k22=1;
k23=5e10;
%ka1 = 10^(-11.6);
%ka2 = 10^(-10.36);
%ka3 = 10^(-4.86);
kCBA=5*10^9;
eh2o2 =19.6; % L/ mol.cm
eho2 =228;
H =10^(-6.8);

%ho2 = (ka1*y(1))/H;
%ho2r = (H*y(5))/ka3;

w = 2.95; %cm
A =eh2o2*w*y(1)+y(2)*w+eho2*w*y(9); %dimensionless
kah2o2 = (E0p*eh2o2*(1-10^(-A)))/A;
fih2o2 = 0.5; % mol (Es)-1
k1 = (kah2o2*fih2o2)*1000;
%CO32minus = (ka2*y(3))/H;

%------------------------------------------------------------------------%
dy(1) = -k1*y(1) - k2*y(y(4))^2*y(1) - k10*y(5)*y(1) - k14*y(9)*y(1) - k15*y(1)*y(6) -
k18*y(1) + k13*y(9)^2 + k19*H*y(8);  
k12*y(5)*y(9) + k13*y(9)^2 + k19*H*y(8);

dy(2) = -K(1)*y(2)*y(4);  

dy(3) = -k4*y(4)*y(3) - k22*y(3) + k23*H*y(10) + k15*y(6)*y(1) + k16*y(6)*y(8);  

dy(4) = 2*k1*y(1) + k10*y(5)*y(1) + k14*y(9)*y(1) - k2*y(1)*y(4) -
k3*y(8)*y(4) - k4*y(3)*y(4) - k5*y(10)*y(4) - k6*y(9)*y(4) -
k7*y(5)*y(4) - k8*(y(4)^2) - k9*y(6)*y(4) - K(2)*TOC*y(4) - kCBA*y(7)*y(4);  

dy(5) = k2*y(4)*y(1) + k3*y(4)*y(8) + k15*y(6)*y(1) + k16*y(6)*y(8) -
k7*y(4)*y(5) - k10*y(1)*y(5) - k11*y(6)*y(5) - k12*y(5)*y(9) -
k21*H*y(5) + k20*y(9);  

dy(6) = k4*y(4)^2*y(3) + k5*y(4)*y(10) - k9*y(4)*y(6) - k11*y(5)*y(6) -
k15*y(1)*y(6) - k16*y(8)*y(6) - k17*(y(6)^2);  

dy(7) = -K(1)*y(2)*y(4);  

dy(8) = -k4*y(4)*y(8) - k16*y(8)*y(6) - k19*H*y(8) + k18*y(1);  

dy(9) = -k6*y(9)*y(4) - k12*y(5)*y(9) - k13*y(9)^2 - k14*y(9)*y(1) -
k20*y(9) + k21*H*y(5);  

d(10) = -k5*y(4)*y(10) - k23*H*y(10) + k9*y(4)*y(6) + k11*y(5)*y(6) + 2*k17*(y(6)^2) + k22*y(3);  

end

%------------------------------------------------------------------------%-  
% options = odeset('RelTol',1e-5,'AbsTol',[1e-10 1e-10 1e-10 1e-10 1e-10 1e-10 1e-10 1e-10 1e-10 1e-10]);  
%------------------------------------------------------------------------%-  
y01=[1.57E-4 0.1069 0 0 0 0 1.18E-6 0 0 0]; % which is subject to change  
E0p=6.42E-10;  
TOC=0.0025666;  
[T1,Y1]= ode15s(@mehdi_final,tspan1,y01,options);  
a=Y1(:,2);  
H2O21=Y1(:,1);  
a1=[0.1069;0.0990;0.0934;0.0898;0.0842;0.0779];  
b1=[1.57E-04;1.49E-04;1.36E-04;1.26E-04;1.28E-04;1.20E-04];  
t1=[0;1800;3600;5400;7800;9600];
%--------------------------Second Experiment  ----------------------------%
tspan2=[0 900 1800 2700 3600 4500 5400 6300 7200 8100 9000];
y02=[4.54E-4 0.1099 0 0 0 1.20E-6 0 0 0];
E0p=6.42E-10;
TOC=0.00025666;
[T2,Y2]= ode15s(@mehdi_final,tspan2,y02,options);
b=Y2(:,2);
H2O22=Y2(:,1);
a2=[0.1099;0.0999;0.0963;0.0867;0.0771;0.0697];
b2=[4.54E-04;4.28E-04;3.94E-04;3.68E-04;3.71E-04;3.48E-04];
t2=[0;1800;3600;5400;7200;9000];
%--------------------------Third Experiment  -----------------------------%
tspan3=[0 900 1800 2700 3600 4500 5400 6300 7440 8100 9000];
y03=[1.43E-4 0.0510 0 0 0 1.17E-6 0 0 0];
E0p=6.42E-10;
TOC=0.00011083;
[T3,Y3]= ode15s(@mehdi_final,tspan3,y03,options);
c=Y3(:,2);
H2O23=Y3(:,1);
a3=[0.0510;0.0437;0.0381;0.0356;0.0305;0.0276];
b3=[1.43E-04;1.37E-04;1.40E-04;1.34E-04;1.23E-04;1.22E-04];
t3=[0;1800;3600;5400;7440;9000];
%------------------------ Fourth Experiment  -----------------------------%
tspan4=[0 900 1800 2700 3600 4500 5400 6300 7200 8100 9000];
y04=[4.36E-4 0.0473 0 0 0 1.24E-6 0 0 0];
E0p=6.42E-10;
TOC=0.00011083;
[T4,Y4]= ode15s(@mehdi_final,tspan4,y04,options);
d=Y4(:,2);
H2O24=Y4(:,1);
a4=[0.0473;0.0342;0.0269;0.0210;0.0164];
b4=[4.36E-04;4.26E-04;3.99E-04;3.86E-04;3.71E-04;3.52E-04];
t4=[0;1800;3600;5400;7200;9000];
%-------------------------- Fifth Experiment  ----------------------------%
tspan5=[0 900 1800 2700 3600 4500 5400 6300 7200 8100 9000];
y05=[1.47E-4 0.0769 0 0 0 1.30E-6 0 0 0];
E0p=6.42E-10;
TOC=0.00018916;
\[ T5, Y5 \] = ode15s(@mehdi_final, tspan5, y05, options);

e = Y5(:, 2);
H2O25 = Y5(:, 1);
a5 = [0.0769; 0.0724; 0.0678; 0.0636; 0.0580; 0.0530];
b5 = [1.47E-04; 1.33E-04; 1.19E-04; 1.24E-04; 1.17E-04; 1.12E-04];

t5 = [0; 1800; 3600; 5400; 7200; 9000];

% ----------------- [pCBA] part ---------------------------------------------

\[ T6, Y6 \] = ode15s(@mehdi_final, tspan6, y06, options);

f = Y6(:, 7);
a6 = [1.18E-06; 7.79E-07; 5.81E-07; 3.97E-07; 2.97E-07];
t6 = [0; 900; 1800; 2700; 3600];

% ----------------------------- Second Experiment -----------------------------

t8 = [0 450 1020 1350 1800 2250 2700 3150 3600];

\[ T8, Y8 \] = ode15s(@mehdi_final, tspan8, y08, options);

h = Y8(:, 7);
a8 = [1.17E-06; 6.77E-07; 4.06E-07; 2.26E-07; 1.31E-07];
t8 = [0; 1020; 1800; 2700; 3600];

% ----------------------------- Fourth Experiment -----------------------------

\[ T9, Y9 \] = ode15s(@mehdi_final, tspan9, y09, options);

h = Y9(:, 7);
a9 = [1.17E-06; 6.77E-07; 4.06E-07; 2.26E-07; 1.31E-07];
t9 = [0; 1020; 1800; 2700; 3600];
$$[T_9, Y_9] = \text{ode15s}(@mehdi_final, tspan_9, y_09, \text{options});$$

$$i = Y_9(:, 7);$$

$$a_9 = [1.24E-06; 4.35E-07; 1.85E-07; 7.61E-08; 2.87E-08];$$

$$t_9 = [0; 600; 1200; 1800; 2400];$$

%-------------------------- Fifth Experiment ----------------------------%

tspan_10 = [0 450 900 1350 1800 2250 2700 3150 3600];

$$y_{010} = [1.47E-4 \ 0.0769 \ 0 \ 0 \ 0 \ 1.30E-6];$$

$$E_{0p} = 6.42E-10;$$

$$\text{TOC} = 0.00018916;$$

$$[T_{10}, Y_{10}] = \text{ode15s}(@mehdi_final, tspan_{10}, y_{010}, \text{options});$$

$$j = Y_{10}(:, 7);$$

$$a_{10} = [1.30E-06; 7.99E-07; 4.84E-07; 3.49E-07; 2.30E-07];$$

$$t_{10} = [0; 900; 1800; 2700; 3600];$$

%-------------------Optimization-Error Minimization ----------------------%

$$\text{error} = \text{zeros}(55, 1);$$

%-------- Error values are relative for CpBA and Abs-------------------%

%{
sa = [1.22E-03; 4.04E-04; 9.29E-04; 7.09E-04; 1.87E-03; 1.15E-03; 2.54E-03; ...
  1.56E-03; 1.79E-03; 5.03E-04; 1.70E-03; 2.37E-03; 1.45E-03; ...
  5.86E-04; 4.18E-04; 8.18E-03; 1.21E-03; 5.86E-04; 1.01E-03; ...
  1.85E-03; 4.00E-04; 2.09E-03; 1.80E-03; 1.00E-03; 6.24E-04; 7.21E-04; ...
  1.00E-03; 1.08E-03;]
sp = [7.76E-09; 1.05E-09; 2.10E-08; 1.19E-08; 2.31E-09; 1.00E-08; 1.23E-08; ...
  1.00E-08; 1.00E-08; 6.75E-09; 8.09E-09; 2.59E-08; 1.00E-08; 2.04E-09; ...
  1.30E-09; 3.74E-09; 1.50E-08; 1.00E-08; 4.80E-09; 1.67E-09; 8.63E-09; ...
  1.45E-08; 1.00E-08; 1.26E-08; 1.97E-08];
%}

sa = [0.002; 0.002; 0.002; 0.002; 0.002; 0.002; 0.002; ...
  0.002; 0.002; 0.002; 0.002; 0.002; 0.002; ...
  0.002; 0.002; 0.002; 0.002; 0.002; 0.002; ...
  0.002; 0.002; 0.002; 0.002; 0.002; 0.002; ...
  0.002; 0.002; 0.002; 0.002; 0.002; 0.002; ...
  0.002; 0.002];
sp = [2e-8; 2e-8; 2e-8; 2e-8; 2e-8; 2e-8; ...
  2e-8; 2e-8; 2e-8; 2e-8; 2e-8; 2e-8; ...
  2e-8; 2e-8; 2e-8; 2e-8; 2e-8; 2e-8; ...
  2e-8; 2e-8; 2e-8; 2e-8; 2e-8; 2e-8; ...
  2e-8; 2e-8; 2e-8];

$$\text{error}(1) = (a_{10} - a(1))^2 / (sa(1)^2);$$

$$\text{error}(2) = (a_{10} - a(3))^2 / (sa(2)^2);$$

$$\text{error}(3) = (a_{10} - a(5))^2 / (sa(3)^2);$$

$$\text{error}(4) = (a_{10} - a(7))^2 / (sa(4)^2);$$

$$\text{error}(5) = (a_{10} - a(9))^2 / (sa(5)^2);$$

$$\text{error}(6) = (a_{10} - a(11))^2 / (sa(6)^2);$$

$$\text{error}(7) = (a_{10} - b(1))^2 / (sa(7)^2);$$

$$\text{error}(8) = (a_{10} - b(3))^2 / (sa(8)^2);$$

$$\text{error}(9) = (a_{10} - b(5))^2 / (sa(9)^2);$$

$$\text{error}(10) = (a_{10} - b(7))^2 / (sa(10)^2);$$

$$\text{error}(11) = (a_{10} - b(9))^2 / (sa(11)^2);$$
error(12)=(a2(6)-b(11))^2/(sa(12)^2);
error(13)=(a3(1)-c(1))^2/(sa(13)^2);
error(14)=(a3(2)-c(3))^2/(sa(14)^2);
error(15)=(a3(3)-c(5))^2/(sa(15)^2);
error(16)=(a3(4)-c(7))^2/(sa(16)^2);
error(17)=(a3(5)-c(9))^2/(sa(17)^2);
error(18)=(a3(6)-c(11))^2/(sa(18)^2);
error(19)=(a4(1)-d(1))^2/(sa(19)^2);
error(20)=(a4(2)-d(3))^2/(sa(20)^2);
error(21)=(a4(3)-d(5))^2/(sa(21)^2);
error(22)=(a4(4)-d(7))^2/(sa(22)^2);
error(23)=(a4(5)-d(9))^2/(sa(23)^2);
error(24)=(a4(6)-d(11))^2/(sa(24)^2);
error(25)=(a5(1)-e(1))^2/(sa(25)^2);
error(26)=(a5(2)-e(3))^2/(sa(26)^2);
error(27)=(a5(3)-e(5))^2/(sa(27)^2);
error(28)=(a5(4)-e(7))^2/(sa(28)^2);
error(29)=(a5(5)-e(9))^2/(sa(29)^2);
error(30)=(a5(6)-e(11))^2/(sa(30)^2);

error(31)=(a6(1)-f(1))^2/(sp(1)^2);
error(32)=(a6(2)-f(3))^2/(sp(2)^2);
error(33)=(a6(3)-f(5))^2/(sp(3)^2);
error(34)=(a6(4)-f(7))^2/(sp(4)^2);
error(35)=(a6(5)-f(9))^2/(sp(5)^2);
error(36)=(a7(1)-g(1))^2/(sp(6)^2);
error(37)=(a7(2)-g(3))^2/(sp(7)^2);
error(38)=(a7(3)-g(5))^2/(sp(8)^2);
error(39)=(a7(4)-g(7))^2/(sp(9)^2);
error(40)=(a7(5)-g(9))^2/(sp(10)^2);

error(41)=(a8(1)-h(1))^2/(sp(11)^2);
error(42)=(a8(2)-h(3))^2/(sp(12)^2);
error(43)=(a8(3)-h(5))^2/(sp(13)^2);
error(44)=(a8(4)-h(7))^2/(sp(14)^2);
error(45)=(a8(5)-h(9))^2/(sp(15)^2);

error(46)=(a9(1)-i(1))^2/(sp(16)^2);
error(47)=(a9(2)-i(3))^2/(sp(17)^2);
error(48)=(a9(3)-i(5))^2/(sp(18)^2);
error(49)=(a9(4)-i(7))^2/(sp(19)^2);
error(50)=(a9(5)-i(9))^2/(sp(20)^2);

error(51)=(a10(1)-j(1))^2/(sp(21)^2);
error(52)=(a10(2)-j(3))^2/(sp(22)^2);
error(53)=(a10(3)-j(5))^2/(sp(23)^2);
error(54)=(a10(4)-j(7))^2/(sp(24)^2);
error(55)=(a10(5)-j(9))^2/(sp(25)^2);

%--------------------------------------error for H2O2------------------------%
%
error(56)=(b1(1)-H2O21(1))/b1(1);
error(57) = (b1(2) - H2O21(3)) / b1(2);
error(58) = (b1(3) - H2O21(5)) / b1(3);
error(59) = (b1(4) - H2O21(7)) / b1(4);
error(60) = (b1(5) - H2O21(9)) / b1(5);
error(61) = (b1(6) - H2O21(11)) / b1(6);

error(62) = (b2(1) - H2O22(1)) / b2(1);
error(63) = (b2(2) - H2O22(3)) / b2(2);
error(64) = (b2(3) - H2O22(5)) / b2(3);
error(65) = (b2(4) - H2O22(7)) / b2(4);
error(66) = (b2(5) - H2O22(9)) / b2(5);
error(67) = (b2(6) - H2O22(11)) / b2(6);

error(68) = (b3(1) - H2O23(1)) / b3(1);
error(69) = (b3(2) - H2O23(3)) / b3(2);
error(70) = (b3(3) - H2O23(5)) / b3(3);
error(71) = (b3(4) - H2O23(7)) / b3(4);
error(72) = (b3(5) - H2O23(9)) / b3(5);
error(73) = (b3(6) - H2O23(11)) / b3(6);

error(74) = (b4(1) - H2O24(1)) / b4(1);
error(75) = (b4(2) - H2O24(3)) / b4(2);
error(76) = (b4(3) - H2O24(5)) / b4(3);
error(77) = (b4(4) - H2O24(7)) / b4(4);
error(78) = (b4(5) - H2O24(9)) / b4(5);
error(79) = (b4(6) - H2O24(11)) / b4(6);

error(80) = (b5(1) - H2O25(1)) / b5(1);
error(81) = (b5(2) - H2O25(3)) / b5(2);
error(82) = (b5(3) - H2O25(5)) / b5(3);
error(83) = (b5(4) - H2O25(7)) / b5(4);
error(84) = (b5(5) - H2O25(9)) / b5(5);
error(85) = (b5(6) - H2O25(11)) / b5(6);
%
SUM = norm(error, 1);
K
SUM
Y1;
Y2;
Y3;
Y4;
Y5;
Y6;
Y7;
Y8;
Y9;
Y10;

%---------------------------------------------------------------Absorbance-------------------------------------------%
%
figure(1)
plot(T1, a, '-', 'Color', 'r', 'LineWidth', 2)
hold on;
plot(t1, a1, '+', 'MarkerSize', 10, 'LineWidth', 2)
hold off;
figure(2)
plot(T2,b,'-','Color','b','LineWidth',2)
hold on;
plot(t2,a2,'rs','MarkerSize',10,'LineWidth',2)
hold off;
figure(3)
plot(T3,c,'-','Color','y','LineWidth',2)
hold on;
plot(t3,a3,'o','MarkerSize',10,'LineWidth',2)
hold off;
figure(4)
plot(T4,d,'-','Color','g','LineWidth',2)
hold on;
plot(t4,a4,'*','MarkerSize',10,'LineWidth',2)
hold off;
figure(5)
plot(T5,e,'-','Color','r','LineWidth',2)
hold on;
plot(t5,a5,'d','MarkerSize',10,'LineWidth',2)
hold off;
figure(6)
plot(T6,f,'-','Color','r','LineWidth',2)
hold on;
plot(t6,a6,'+','MarkerSize',10,'LineWidth',2)
hold off;
figure(7)
plot(T7,g,'-','Color','b','LineWidth',2)
hold on;
plot(t7,a7,'rs','MarkerSize',10,'LineWidth',2)
hold off;
figure(8)
plot(T8,h,'-','Color','y','LineWidth',2)
hold on;
plot(t8,a8,'o','MarkerSize',10,'LineWidth',2)
hold off;
figure(9)
plot(T9,i,'-','Color','g','LineWidth',2)
hold on;
plot(t9,a9,'*','MarkerSize',10,'LineWidth',2)
hold off;
figure(10)
plot(T10,j,'-','Color','r','LineWidth',2)
hold on;
plot(t10,a10,'d','MarkerSize',10,'LineWidth',2)
hold off;

%-----------------------------------pCBA----------------------------------%
figure(6)
plot(T6,f,'-','Color','r','LineWidth',2)
hold on;
plot(t6,a6,'+','MarkerSize',10,'LineWidth',2)
hold off;
figure(7)
plot(T7,g,'-','Color','b','LineWidth',2)
hold on;
plot(t7,a7,'rs','MarkerSize',10,'LineWidth',2)
hold off;
figure(8)
plot(T8,h,'-','Color','y','LineWidth',2)
hold on;
plot(t8,a8,'o','MarkerSize',10,'LineWidth',2)
hold off;
figure(9)
plot(T9,i,'-','Color','g','LineWidth',2)
hold on;
plot(t9,a9,'*','MarkerSize',10,'LineWidth',2)
hold off;
figure(10)
plot(T10,j,'-','Color','r','LineWidth',2)
hold on;
plot(t10,a10,'d','MarkerSize',10,'LineWidth',2)
hold off;

%%%-----------------------------------H2O2-----------------------------------%%
%\{ figure(11) plot(T1,H2O21,'-','Color','r','LineWidth',2) hold on; plot(t1,b1,'d','MarkerSize',10,'LineWidth',2) hold off; figure(12) plot(T2,H2O22,'-','Color','r','LineWidth',2) hold on; plot(t2,b2,'d','MarkerSize',10,'LineWidth',2) hold off; figure(13) plot(T3,H2O23,'-','Color','r','LineWidth',2) hold on; plot(t3,b3,'d','MarkerSize',10,'LineWidth',2) hold off; figure(14) plot(T4,H2O24,'-','Color','r','LineWidth',2) hold on; plot(t4,b4,'d','MarkerSize',10,'LineWidth',2) hold off; figure(15) plot(T5,H2O25,'-','Color','r','LineWidth',2) hold on; plot(t5,b5,'d','MarkerSize',10,'LineWidth',2) hold off; %\}

%-------------------Optimization-Error Minimization ----------------------%
end
%fminsearch(@CSR,[10^8,10^8])

function dy= CHBE(t,y)

C.2 Code for Model Function
%-----------------Well reported constants form literature----------------%

k2 =2.7*10^7;
k3 =7.5*10^9;
k4 =8.5*10^6;
k5 =3.9*10^8;
k6 =6.6*10^9;
k7 =8*10^9;
k8 =5.5*10^9;
k9 =3*10^9;
k10 =0.13;
k11 =6.5*10^8;
k12 =9.7*10^7;
\begin{verbatim}
194
k13 = 8.6 \times 10^5;
k14 = 3.7;
k15 = 8 \times 10^5;
k16 = 3 \times 10^7;
k17 = 2 \times 10^7;
k18 = 3.56e-2;
k19 = 2e10;
k20 = 7e5;
k21 = 4.5e10;
k22 = 1;
k23 = 2e10;
kCBA = 5 \times 10^9;
E0p = 6.42e-10;
TOC = 1.1083e-4;
eh2o2 = 19.6; \text{ L/ mol.cm}\%
H = 10^(-6.8);
b = 2.95; \text{ cm}
A = eh2o2 * b * y(1) + y(2) * b; \text{ dimensionless}
kah2o2 = (E0p * eh2o2 * (1 - 1 - 10^(-A))) / A;
fih2o2 = 0.5; \text{ %mol (Es)-1}
kA = kah2o2 * fih2o2 * 1000;
dy(1) = -kA*y(1) - k2*y(4) * y(1) - k10*y(5) * y(1) - k14*y(9) * y(1) - k15*y(1) * y(6) - k18*y(1) + k8*(y(4)^2) + ... 
k12*y(5)*y(9) + k13*y(9)^2 + k19*H*y(8);
dy(2) = -(3.04e8)*y(2)*y(4);
dy(3) = -k4*y(4)*y(3) - k22*y(3) + k23*H*y(10) + k15*y(6)*y(1) + k16*y(6)*y(8);
dy(4) = 2*kA*y(1) + k10*y(5)*y(1) + k14*y(9)*y(1) - k2*y(1)*y(4) - ... 
k3*y(8)*y(4) - k4*y(3)*y(4) - k5*y(10)*y(4) - k6*y(9)*y(4) - ... 
k7*y(5)*y(4) - k8*(y(4)^2) - k9*y(6)*y(4) - (1.37e8)*TOC*y(4) - kCBA*y(7)*y(4);
dy(5) = k2*y(4)*y(1) + k3*y(4)*y(8) + k15*y(6)*y(1) + k16*y(6)*y(8) - ... 
k7*y(4)*y(5) - k10*y(1)*y(5) - k11*y(6)*y(5) - k12*y(5)*y(9) - 
k21*H*y(5) + k20*y(9);
dy(6) = k4*y(4)*y(3) + k5*y(4)*y(10) - k9*y(4)*y(6) - k11*y(5)*y(6) - ... 
k15*y(1)*y(6) - k16*y(8)*y(6) - k17*(y(6)^2);
dy(7) = -kCBA*y(7)*y(4);
dy(8) = -k3*y(4)*y(8) - k16*y(8)*y(6) - k19*H*y(8) + k18*y(1);
dy(9) = -k6*y(9)*y(4) - k12*y(5)*y(9) - k13*y(9)^2 - k14*y(9)*y(1) - 
k20*y(9) + k21*H*y(5);
dy(10) = -k5*y(4)*y(10) - k23*H*y(10) + k9*y(4)*y(6) + k11*y(5)*y(6) + 2*k17*(y(6)^2) + k22*y(3);
\end{verbatim}
C.3 Code for Model Prediction

clear all
options = odeset('RelTol',1e-5,'AbsTol',[1e-10 1e-10 1e-10 1e-10 1e-10 1e-10
1e-10 1e-10 1e-10 1e-10]);

tspan=(linspace(0,16000,161))';
y0=[6.22e-4 0.0979 0 0 0 0 0 0 0 0];

[T,Y]= ode15s(@CHBE,tspan,y0,options);

H2O2=Y(:,1);
CNOM=Y(:,2);
HCO3=Y(:,3);
OH=Y(:,4);
O2=Y(:,5);
CO3R=Y(:,6);
CPBA=Y(:,7);
HO2=Y(:,8);
HO2R=Y(:,9);
CO3=Y(:,10);

%------------------------Drawing Absorbance Profile-----------------------%
figure(1)
plot(T,CNOM,'-','Color','b','LineWidth',2)
hold on;
absorbance=[0.0967;0.0835;0.0834;0.0749;0.0761];
time=[0;4175.5;7940.5;12527;15880];

plot(time,absorbance,'rs','MarkerSize',10,'LineWidth',2)
hold off;


### C.4 Fisher Information Matrix Calculation

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<th>Time</th>
<th>exp. value</th>
<th>model value</th>
<th>diff²</th>
<th>dCNOM/dk_CNOM</th>
<th>dCNOM/dk_TOC</th>
<th>dpCBA/dk_CNOM</th>
<th>dpCBA/dk_TOC</th>
<th>d^{2}_\text{CNOM}/d_\text{CNOM}^{2}</th>
<th>d^{2}_\text{pCBA}/d_\text{CNOM}^{2}</th>
<th>d^{2}_\text{pCBA}/d_\text{CNOM}^{2}</th>
<th>d^{2}_\text{CNOM}/d_\text{TOC}^{2}</th>
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Appendix D
List of Publications and Presentations

D.1 Publications


D.2 Presentations


Appendix E
Supplementary Report
Pilot Scale Investigation of the UV/H$_2$O$_2$ and BAC Processes: Effects on Natural Organic Matter in Surface Water

Project Report
Submitted to: Ted Mao, Trojan Technologies, Inc., London, ON, Canada

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April 20, 2006
Executive Summary

In this research, the effects of the UV/H\textsubscript{2}O\textsubscript{2} advanced oxidation process (AOP), combined UV/H\textsubscript{2}O\textsubscript{2} and biological activated carbon (BAC), and BAC on various water quality parameters were studied. The effects of UV source, hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) concentration, and electrical energy consumption (EEF) on NOM’s aromatic structure, degree of ring substitution, formaldehyde (FA) and acetaldehyde (AA) concentration, biodegradable organic carbon fraction (BDOC), and disinfection by-product formation potentials (DBP-FPs) were investigated. UV/H\textsubscript{2}O\textsubscript{2} as a standalone treatment had noticeable effects on water quality. Increases in EEF led to increases in the reduction of chromophoric NOM, reduction of degree of substitution of aromatic rings, and formation of FA and AA. Increases in H\textsubscript{2}O\textsubscript{2} concentration led to increases in the reduction of chromophoric NOM, reduction of degree of substitution of aromatic rings, and formation of FA. The low-pressure amalgam (LP-AM) lamp based reactor outperformed the medium-pressure (MP) lamp based reactor in terms of generating advanced oxidation conditions. Irrespective of the reactor, UV/H\textsubscript{2}O\textsubscript{2} treatment led to an increase in DBP precursors.

The combined UV/H\textsubscript{2}O\textsubscript{2}+BAC process outperformed BAC alone with respect to TOC and A\textsubscript{254} reduction. Additionally, combined treatment offered some advantages over BAC alone for the removal of DBP precursors. The combination of LP-AM UV/H\textsubscript{2}O\textsubscript{2}+BAC was observed to be better than MP UV/H\textsubscript{2}O\textsubscript{2}+BAC. In applications where UV/H\textsubscript{2}O\textsubscript{2} is employed for pollutant degradation, downstream BAC treatment would effectively remove residual H\textsubscript{2}O\textsubscript{2} and improve the overall water quality by removing unwanted UV/H\textsubscript{2}O\textsubscript{2} byproducts.

BAC treatment was demonstrated to be capable of removing FA and residual H\textsubscript{2}O\textsubscript{2}, by-products of UV/H\textsubscript{2}O\textsubscript{2} treatment.
E.1 Introduction

This report summarizes the work done at the ECT Research Facility and ECT Lab at Trojan Technologies, Inc. in London, ON, Canada. The research was conducted from June to November 2005. The focus of the project was to study the effects of UV/H\textsubscript{2}O\textsubscript{2} and integrated UV/H\textsubscript{2}O\textsubscript{2}+BAC treatments on natural organic matter in surface water. The report starts with providing a background into the research objectives. The main body of the report is divided into three main sections based on the nature of experimentation: (1) UV/H\textsubscript{2}O\textsubscript{2} treatment, (2) BAC treatment, and (3) UV/H\textsubscript{2}O\textsubscript{2}+BAC treatment. For each section the methodology of the experimental work and the key results of the research are presented with discussion. The report is completed with conclusions and recommendations for future work.

E.2 Background

Halogenated disinfection by-products (DBPs) are formed when chlorine chemically reacts with natural organic matter (NOM) in source drinking water. Trihalomethanes (THMs) and haloacetic acids (HAAs) are two common DBPs that are subject to increasingly stringent environmental and health regulations because of the concern over their health impacts (e.g. on human reproductive system). Advanced oxidation process (AOP) is a technology that partially oxidizes and converts NOM to intermediates that are more biodegradable and can be removed via biological activated carbon (BAC).

Previous research conducted in our lab has found that a combination of UV/H\textsubscript{2}O\textsubscript{2} and BAC is effective at reducing DBP formation potentials (DBP-FPs). While UV/H\textsubscript{2}O\textsubscript{2} as standalone treatment did not provide effective reduction of DBP-FPs under economically viable conditions, the integration of UV/H\textsubscript{2}O\textsubscript{2} with BAC resulted in the greatest reduction of DBP-FPs in all experimental runs. This was achieved at relatively moderate UV fluence of about 500 mJ/cm\textsuperscript{2} and a H\textsubscript{2}O\textsubscript{2} concentration of about 20 mg/L. Furthermore, under these conditions the combined treatment reduced the formation potential of THM to below upcoming regulations of 100 ppb (Toor 2005).

This research will focus on further understanding the UV/H\textsubscript{2}O\textsubscript{2} and BAC process by experimenting with different UV sources and studying the fate of NOM during the process under pilot scale operating setup.

E.2.1 Project Background

In this research, the effects of UV/H\textsubscript{2}O\textsubscript{2} and integrated UV/H\textsubscript{2}O\textsubscript{2}+BAC treatments on NOM in surface water were studied. The effect of these treatment processes on the structure, composition, and DBP-FPs
of NOM were investigated by varying the UV source, irradiation time, and H$_2$O$_2$ concentration for UV/H$_2$O$_2$ experimentation and UV source for integrated UV/H$_2$O$_2$+BAC treatment.

**E.2.2 Project Objectives**

The two specific objectives were as follows:

- Examine the effects of different UV sources, irradiation times, and H$_2$O$_2$ concentrations on the performance of the UV/H$_2$O$_2$ AOP.

- Examine the effects of different UV sources on the performance of the integrated UV/H$_2$O$_2$+BAC treatment process.

**E.3 UV/H$_2$O$_2$ Treatment**

In this section, the materials and methods used to carry out UV/H$_2$O$_2$ experimentation are presented followed by discussion of the experimental results.

**E.3.1 Materials and Methods**

Experimental work involved extensive and systematic pilot scale studies on a diluted surface water (DSW). Raw surface water (RSW) was transported (Mobile Striping and Sweeping) from Fanshawe Lake, London, Ontario. RSW was collected on three different occasions leading to the division of experimentation into three groups: Run 1, Run 2, and Run 3. Since the quality of RSW for Runs 1 and 2 was poor [Table 1], it was decided to dilute RSW with high quality, dechlorinated city water (>99% UVT, <900 ppb TOC). Therefore, prior to Runs 1 and 2, approximately 3,000 gallons of transported RSW was diluted with 7,000 dechlorinated city water to a final DSW volume of 10,000 gallons. RSW for Run 3 was collected in late fall after a heavy period of rain. Thus, the quality of RSW was significantly different than the RSW collected earlier. Therefore, prior to Run 3, approximately 900 gallons of RSW was diluted with 1500 gallons dechlorinated city water to a final DSW volume of 2400 gallons yielding DSW similar in quality to DSW from Runs 1 and 2.

The UV/H$_2$O$_2$ treatment process was carried out at Trojan’s ECT Research Facility. Figure E.1 presents a diagram of the experimental setup. DSW was fed from an 11,000 gallon holding tank into the reactor setup. The flowrate was adjusted using a butterfly valve upstream of the UV reactor. Before entering the UV reactor, DSW was spiked with a desired concentration of H$_2$O$_2$ (30% Fisher Scientific) using a peristaltic pump (Cole-Parmer). Treated water was sent to the drain. Two UV reactors were
employed in the study. A 4L12, consisted of 4 medium pressure (MP) Hg lamps with a power input of 11.7 kW at the 100% power setting, served as the polychromatic UV source. An 8AL20, equipped with 8 low pressure-amalgam (LP-AM) lamps, quartz sleeves, and a 2 kW power input at 100% power, acted as the monochromatic UV source. Figure E.2 illustrates the lamp emission spectra, relative to the LP-AM lamp, from 200 to 300 nm for the LP-AM and MP lamps. The treatment conditions were varied with respect to operating flowrate and H$_2$O$_2$ concentration. The 4L12 was operated at 100, 150, or 300 gpm while the 8AL20 was operated at 50, 70, or 100 gpm. The H$_2$O$_2$ concentration was varied between 0 and 15 mg/L. These conditions were selected based on the feasibility of their application in actual treatment processes.

Sample ports upstream and downstream of the reactors were used to collect untreated and treated DSW samples. Sample analysis was performed at Trojan’s ECT Laboratory. After measuring the H$_2$O$_2$ concentration, samples were quenched of H$_2$O$_2$ using 0.2 mg/L bovine liver catalase (Aldrich Canada) as recommended by Liu et al. (2003). The following parameters were monitored in the treated and untreated DSW samples: H$_2$O$_2$ concentration, total organic carbon (TOC), UV absorbance from 200 to 300 nm, THM formation potential (THM-FP), HAA formation potentials (HAA-FP), biodegradable dissolved organic carbon (BDOC), formaldehyde (FA) concentration, and acetaldehyde (AA) concentration.

H$_2$O$_2$ concentration was measured by reaction with iodide catalyzed by molybdate (Klassen et al. 1994). TOC was measured using a UV/Persulfate oxidation TOC analyzer (Sievers 800). UV absorbance was determined using a spectrophotometer (Cary 50/100) with a pathlength of 1 cm.

THM-FP and HAA-FP were maximum formation potential tests carried out by spiking a 80 mL water sample to 10 mg/L of free chlorine (Sodium hypochlorite, Sigma Aldrich) and incubating at 22°C for 7 days. After the chlorination period, according to the EPA Method 551.1 (USEPA 1995a), THMs were extracted and detected by GC/ECD (HP 6890) equipped with an HP-5 column (30 m x 0.32 mm x 0.25 μm) and an HP 6890 autosampler. Due to the absence of bromide in the DSW, chloroform was the primary THM reported. According to the EPA Method 552.2 (USEPA 1995b), HAAs were methylated, extracted, and detected by GC/MS (Varian Saturn 2000R) equipped with a CP-Sil 8 column (30 m x 0.25 mm x 0.25 μm) and a CTC Analytics Combi PAL autosampler. Dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were the primary HAAs reported because of their relatively high concentrations and the absence of brominated HAAs.

BDOC was determined following the method given be Servais et al. (1989). A 30 mL sample was seeded with 2 mL of RSW and incubated at 22°C for 7 days. The TOC before and after incubation was measured and the percent difference was recorded as BDOC.
FA and AA were derivatized and extracted, according to the EPA Method 556.1 (USEPA 1999). Detection was performed according to Standard Methods 6252 (Eaton et al. 1998) using the GC/ECD system described above.

E.3.2 Results and Discussion

For the UV/H₂O₂ experiments the two variables adjusted were flowrate and H₂O₂ concentration. Therefore, the results are reported with respect to the affect of electrical energy per flow (EEF) and H₂O₂ on the various water quality parameters stated above.

E.3.2.1 The Effect of EEF on Water Quality

Based on the flowrates and electrical energy values stated above the EEFs for each reactor were 0.039, 0.078, and 0.117 kW/gal/min for the 4L12 and 0.020, 0.029, and 0.040 for the 8AL20. To observe the affect of EEF, the results represent experiments done over the range of EEFs with H₂O₂ concentrations between 8 and 12 mg/L.

For all three DSWs, the change in TOC was insignificant over the range of EEFs for both reactors. Other researchers have observed a TOC reduction for NOM treated by UV/H₂O₂ with both monochromatic and polychromatic sources (Speitl et al. 2000; Thomson et al. 2004; Wang et al. 2000, 2001, 2005). However, these observations were made under strong advanced oxidation conditions facilitated by high H₂O₂ concentration and/or very long irradiation times, both of which were beyond the scope of this project.

Using a LP collimated beam apparatus, at a H₂O₂ concentration of 20 mg/L a significant TOC reduction in low molecular weight NOM (<10 kDa) was observed at fluences greater than 1000 mJ/cm², up to 27% reduction at a fluence of 1500 mJ/cm² (Sarathy et al. 2006). This suggests that in the absence of higher molecular weight species, the LP-AM UV/H₂O₂ process is capable of mineralizing low molecular weight organic carbon at higher fluences. Note that the fluence delivered by the 8AL20 at an EEF of 0.04 kW/gal/min was about 800 mJ/cm².

Although there was no significant reduction on the TOC of NOM, major changes in the structure of NOM were occurred. The absorbance of UV at 254 nm (A₂₅₄) by water gives an indication of the aromatic carbon content of NOM. Both the 8AL20 and the 4L12 continually reduced the chromophoric content of NOM as the EEF increased (Figure E.3). At an equal EEF, 0.04 kW/gal/min, the 8AL20 outperforms the 4L12 with respect to the reduction of A₂₅₄. In fact, even at an EEF of 0.12 kW/gal/min, the 4L12 does not reduce chromophoric content as significantly as the 8AL20 does at 0.04 kW/gal/min.
Thomson et al. (2002) found that the kinetics of A254 reduction during UV-photooxidation followed first order kinetics. This is observed here as well and the results show that the apparent first order rate constant for A254 reduction is greater for the 8AL20.

In addition to observing the changes in aromatic structure of NOM, the degree of activation of aromatic rings was interpreted by determining the ratio of absorbance at 254 nm to absorbance at 203 nm (A254/A203) (Korshin et al. 1997). A low A254/A203 value (< 0.027 for benzene) is representative of NOM for which the aromatic rings are substituted predominantly with aliphatic functional groups. A254/A203 is between 0.25 and 0.35 for catechols and phenolics, thus indicating the predominance of hydroxylic substitution. Values greater than 0.4 are typical of aromatic rings substituted with carboxyl groups (Korshin et al. 1997).

Increasing EEF had a marked reduction on the degree of substitution for most waters treated by both the 8AL20 and 4L12 (Figure E.3). Only the water treated by the 4L12 on the final run (Run 3) did not decrease in A254/A203. This could possibly be due to the relatively low initial degree of substitution. Yet, the 8AL20 still significantly altered the degree of substitution for this water (Run 3). As with aromaticity, the 8AL20 had a more significant effect on the degree of substitution while using less electrical energy.

Despite the reductions in aromatic structure and degree of substitution, the NOM’s potential to form disinfection by-products during chlorination was not reduced as EEF increased (Figure E.4). Rather, either increases or no changes in DBP-FPs, relative to the baseline, were observed for treated waters.

The THM-FPs (Figure E.4) for waters treated by the 8AL20 seemed to increase up to an EEF of 0.029 kW/gal/min and then reduce at an EEF of 0.04 kW/gal/min, to a concentration still greater than the THM-FP of untreated waters. This suggests that the THM-FP increases to a maximum and then decreases but this cannot be concluded due to the lack of data points. Two of the waters treated by the 4L12 (Runs 1 and 3) showed insignificant changes in THM-FP over the range of EEFs while the other water (Run 2) behaved similarly to the 8AL20 waters. That is, an increase in THM-FP, relative to the baseline, at an EEF of 0.04 kW/gal/min and then a continual decrease. HAA-FPs followed a similar trend as EEF increased (Figure E.4). All treated waters exhibited an increase in HAA-FPs while in some cases a maximum was reached and then a subsequent reduction. If the error in the analysis was factored in then the observed trends become less significant. In fact, statistical analysis by the t-test showed that there was no significant relationship between EEF and DBP-FPs besides the increase observed relative to the untreated water.

An increase in DBP-FPs has been observed in other research performed under similar conditions. Toor (2005) also observed an increase in HAA-FP for surface water treated by UV/H2O2 at fluences up to
1500 mJ/cm² and a H₂O₂ concentration of 23 mg/L. Liu et al. (2002) observed a 9% increase in HAA-FP up to fluences of 500 mJ/cm² using a low-pressure collimated beam apparatus with a H₂O₂ concentration of 100 mg/L. Paradis et al. (2005) presented 25% higher THM and 35% higher HAA concentrations for water previously exposed to UV/H₂O₂ advanced oxidation with a 4L12 reactor. Sarathy et al. (2006) also reported a continual increase in HAA-FPs for water treated up to 1500 mJ/cm² by LP collimated beam, at a H₂O₂ concentration of 20 mg/L. However, no significant change in THM-FPs was reported (Sarathy et al. 2006).

The UV/H₂O₂ AOP had a detrimental effect on water quality in that it led to the production of undesirable aldehydes. FA and AA were monitored and the concentration of both aldehydes increased as the EEF increased (Figure E.5). At the same EEF, the 8AL20 produced more aldehydes than the 4L12. Thomson et al. (2004) also reported an increase in FA and AA for high DOC water treated by UV/H₂O₂ using a 254 nm UV source. Using a synthetic water, Liu et al. (2002) also observed an increase in aldehydes as UV fluence increased. However, it was reported that the MP source produced twice as much aldehydes as the LP source. The reason MP produced more aldehydes in Liu’s work in comparison to our results can be attributed to the water’s characteristics and is discussed in Section E.3.3.

Since FA and AA are readily biodegradable, their increase would suggest an increase BDOC. However, it should be noted that aldehydes constitute only 25-30% of BDOC (Nawrocki et al. 2003) therefore an increase in aldehydes only partially explains an observed increase in BDOC. As expected, an increase in BDOC was observed as EEF increased (Figure E.6) but a well defined correlation with EEF was not observed. This lack of trend can be attributed to the inherent nature of the BDOC test which is highly variable and cannot be relied on to give accurate quantitative data. Factoring in the standard deviation of replicate analyses showed that a significant correlation between EEF and BDOC did not exists. However, the qualitative results are enough to conclude the UV/H₂O₂ process leads to an increase in BDOC. In addition to this, the data suggest the 8AL20 increased BDOC to a greater extent than the 4L12.

The above results showed that the 8AL20 and 4L12 performed significantly different with respect to changes in water quality parameters as EEF increased. Therefore, the lamps spectrum had an effect on the UV/H₂O₂ treatment but whether the differences were due to the photolysis of NOM or OH radical reaction with NOM cannot be determined with the above results. It is necessary to see how the two reactors performed at a constant EEF while the H₂O₂ concentration changed.
E.3.2.2 The Effect of H$_2$O$_2$ Concentration on Water Quality

H$_2$O$_2$ concentration was varied between 0 and 15 mg/L with a few experiments conducted at 20 and 28 mg/L. To analyze the effect of H$_2$O$_2$ concentration, the data presented below is for each reactor with the EEF held constant at 0.04 kW/gal/min. Only the results from Runs 1 and 2 are presented since Run 3 was performed at a constant H$_2$O$_2$ concentration.

When the H$_2$O$_2$ concentration was increased there was a noticeable decrease in chromophoric NOM for the 8AL20 treated waters (Figure E.7). Meanwhile, for the 4L12 treated waters, increased H$_2$O$_2$ concentration did not yield significant reduction of A$_{254}$. These observation suggests that the reduction of A$_{254}$ was due primarily to advanced oxidation since an increase in H$_2$O$_2$ concentration leads to the formation of more OH radicals. However, it is evident that the polychromatic source was not as effective at producing OH radicals since the 8AL20 reduced the chromophoric content to greater extents when compared to the 4L12. This suggests that the monochromatic source photolyzed H$_2$O$_2$ more effectively yielding a greater number of OH radicals available for reaction with NOM. Similar observations were made when looking at the effect of H$_2$O$_2$ concentration on the degree of substitution of aromatic rings (Figure E.7).

Changes in H$_2$O$_2$ concentration did not seem to affect DBP-FPs in the same way that increasing EEF did (Figure E.8). It may be that the observed increase in DBP-FPs after the UV/H$_2$O$_2$ AOP could be due mainly to alterations in NOM structure brought about by photolysis rather than reaction with OH radicals. This will be investigated in future work, in which factorial experiments will be employed, to identify which operating variables are responsible for the increase in DBP-FPs.

The effect of H$_2$O$_2$ concentration on the formation of aldehydes was significant and interesting (Figure E.9). As the dosage of H$_2$O$_2$ increased the expected increase in FA concentration was observed due to the stronger advanced oxidation conditions. Again, the 8AL20 led to the formation of more aldehydes, FA and AA, and this is likely due to the improved photolysis of H$_2$O$_2$ by the 8AL20. However, what stands out is that an increase in H$_2$O$_2$ concentration had no effect on the formation of AA. As previously stated, an increase in EEF increased the formation of AA. This suggests that AA is formed through a photolysis reaction rather than a OH radical reaction. This phenomenon needs to be further investigated since no literature can be found to either support or reject the hypothesis. Future work will determine if these results are reproducible. Also, attempts will be made to quantify other low molecular weight carbonyl species that might provide more information.

In general, BDOC and H$_2$O$_2$ concentration had a positive correlation (Figure E.10). However, an increase in H$_2$O$_2$ concentration from 5 to 15 mg/L did not seem to have a significant impact on BDOC.
But, when the H$_2$O$_2$ dosage was increased to 28 mg/L a substantial increase in BDOC was observed. Therefore, if the UV/H$_2$O$_2$ AOP were to be coupled with a downstream biological treatment for enhanced removal of NOM, high H$_2$O$_2$ dosages, upwards of 25 mg/L, may yield performance increases over the moderate H$_2$O$_2$ dosages addressed in this study.

E.3.2.3 The Effect of UV Source

As discussed above, the spectral emission of the reactors had a large impact on the UV/H$_2$O$_2$ process. At the same EEF and H$_2$O$_2$ concentration, the LP-AM reduced A$_{254}$ and A$_{254}$/A$_{203}$ and increased the formation of FA, AA, and BDOC to greater extents (Figures E.3, E.5, E.6, E.7, E.9, E.10). This suggests that the spectral emission of the LP-AM lamp was superior to the MP lamp with respect to the generation of OH radicals by the photolysis of H$_2$O$_2$. The cause of this phenomenon can be attributed to the UV absorbance of the DSWs.

Figure E.11 illustrates how the UV absorbance of the water can affect the performance of UV/H$_2$O$_2$ AOP. The figure shows the relative lamp emission spectra presented earlier overlaid with the absorbance from 200-300 nm of DSW from Run 1 and the calculated absorbance from 200-300 nm of a 10 mg/L H$_2$O$_2$. Clearly the high background absorbance of the DSW effectively screens out the majority of UV available for H$_2$O$_2$ photolysis.

Prior to experimentation, we hypothesized that the polychromatic source would improve performance of UV/H$_2$O$_2$ since the output of multiple wavelengths would increase the photolysis of H$_2$O$_2$ yielding more OH radicals. However, these additional wavelengths were screened out by the DSW leaving little UV available for the photolysis of H$_2$O$_2$. Additionally, the most powerful outputs of the MP lamp are at wavelengths greater than 254 nm, wavelengths at which H$_2$O$_2$ has a very low absorption coefficient. On the other hand, the LP-AM provided a strong monochromatic output at 254 nm that was able to effectively photolyze H$_2$O$_2$. Therefore, based on these results it is recommended that MP lamp technology should not be employed when dealing with highly absorbing waters.
**E.4 BAC**

In this section the materials and methods used to carry out BAC experimentation are presented followed by discussion of the experimental results.

**E.4.1 Materials and Methods**

For BAC experimentation three identical BAC columns were designed, constructed, and acclimated. Each column consisted of a PVC pipe, measuring 88 cm in height and 7.6 cm in diameter, with sealed end caps. Sample ports were located 16 cm and 40 cm from the base of the column. The packing material was a coconut shell based activated carbon (AC) with 12x30 mesh size and 0.6-0.85 mm effective size (USFilter Westates AC-1230-C). The AC bed height was 70 cm and was supported by a 10 cm high bed of glass beads (Potters Industries A-100-06/89) (Figure E.12).

Each BAC column had its own feed water storage tank with a volume of 1000 gallons. Water was fed into each column by peristaltic pumps (Cole-Palmer) at a flowrate of 150 mL/min. At this flowrate and with the above specified column dimensions, the empty bed contact time (EBCT) was 20 minutes.

After the columns were constructed, acclimation began to saturate the adsorption sites on the AC and develop a biofilm. DSW was collected from Waubuno Creek, London, ON and recirculated through the columns for up to 3 weeks and then drained and replaced with fresh RSW. Waubuno Creek water had an average TOC of 5 mg/L and UVT of 75% over the duration of acclimation. Acclimation was carried out for 4 months to ensure biological conditions were well developed. This was confirmed by heterotrophic plate counts of BAC influent and effluent (Figures E.13) and by monitoring the TOC removal capacity of the columns (Figure E.14).

Two experiments were conducted with BAC only. The first was carried out to study the ability of BAC to remove FA from water. This was investigated to determine if BAC was capable of removing the FA produced during the UV/H$_2$O$_2$ AOP. Here, RSW was collected from Fanshawe Lake and spiked to 30-35 µg/L FA. Over the course of a week, the effluent water was analyzed for FA concentration, TOC, and UV absorbance from 200 to 300 nm using the methods and instrumentation described in Section E.3.1.

The second experiment was carried out to study the ability of BAC to remove H$_2$O$_2$ from water. This was investigated to determine if BAC was capable of removing the residual H$_2$O$_2$ after the UV/H$_2$O$_2$ AOP. RSW from Fanshawe Lake was spiked to 10-12 mg/L H$_2$O$_2$. Over the course of a week, the effluent water was analyzed for H$_2$O$_2$ concentration, TOC, and UV absorbance from 200 to 300 nm using the methods and instrumentation described in Section E.3.1.
E.4.2 Results and Discussion

E.4.2.1 FA removal by BAC

BAC was highly effective at removing FA present in DSW (Figure E.15). Over the period of the experiment the BAC column was capable of removing on average 80% of FA present in the influent. The effluent’s FA concentration matched that of DSW without FA added. This simple experiment demonstrated that BAC is capable of removing FA that is formed as a by-product of UV/\(\text{H}_2\text{O}_2\) treatment.

E.4.2.2 \(\text{H}_2\text{O}_2\) by BAC

The ability of BAC to remove \(\text{H}_2\text{O}_2\) and the effects of \(\text{H}_2\text{O}_2\) on BAC performance were investigated. The results showed that BAC was capable of removing 95% of \(\text{H}_2\text{O}_2\) within the first 5 minutes of treatment and 100% after 20 minutes EBCT (Figure E.16). The presence of \(\text{H}_2\text{O}_2\) in the influent did not have any noticeable effects on BAC performance with respect to TOC removal or hydrodynamics.

E.5 UV/\(\text{H}_2\text{O}_2\)+BAC Treatment

In this section the materials and methods used to carry out combined UV/\(\text{H}_2\text{O}_2\)+BAC experimentation are presented followed by discussion of the experimental results.

E5.1 Materials and Methods

The UV/\(\text{H}_2\text{O}_2\)+BAC treatment process was carried out at Trojan’s ECT Research Facility. Figure E.17 presents a diagram of the experimental setup. After DSW was treated by UV/\(\text{H}_2\text{O}_2\), as described previously, it was stored in 3 separate storage tanks each with a volume of 1,000 gallons. Each of the storage tanks were hooked up to a BAC column and fed at an owrate of 150 mL/min, 20 min EBCT, with a peristaltic pump (Cole-Parmer). BAC-A column filtered LP-AM treated water, BAC-M column filtered MP treated water, and BAC-C column served as a control column that filtered the water that was not pretreated by UV/\(\text{H}_2\text{O}_2\). Each 14 days run consisted of a 7 days acclimation period to the new water and 7 days of sampling. During the sampling period, samples were collected every 2 days upstream and downstream of the BAC columns and the effluent was sent to the drain.

The objective of the experiments was to determine if the UV source had an effect on BAC performance. Therefore, the UV/\(\text{H}_2\text{O}_2\) treatment conditions were kept constant at a 10-12 mg/L \(\text{H}_2\text{O}_2\) dosage and a UVfluence of 800 -1000 mJ/cm\(^2\). This UVfluence range was selected because it was the
maximum achievable fluence for the 8AL20. This fluence range corresponded to an EEF of 0.04 kW/gal/min for the 8AL20 and 0.078 kW/gal/min.

The following parameters were monitored in the pre- and post-BAC samples: H$_2$O$_2$ concentration, total organic carbon (TOC), UV absorbance from 200 to 300 nm, THM formation potential (THM-FP), HAA formation potentials (HAA-FP), biodegradable dissolved organic carbon (BDOC), formaldehyde (FA) concentration, and acetaldehyde (AA) concentration. Analyses were performed as described in section 3.1.

E.5.2 Results and Discussion

The effects of UV source on BAC performance were noticeable but not wholly conclusive. With respect to TOC removal, the columns fed with pretreated UV/H$_2$O$_2$ waters (BAC-A and BAC-M) outperformed the control column (BAC-C) on average by about 10% (Figure E.18). However, no significant differences were observed between BAC fed with LP-AM treated water of MP treated water (Figure E.18). Toor (2005) reported that BAC, at 8.2 minutes EBCT, fed with water treated at 540 mJ/cm$^2$ of LP UV and 20 mg/L H$_2$O$_2$, on average, removed about 25% more TOC than a control BAC column fed with water not treated by UV/H$_2$O$_2$. It was proposed that this increase in performance was due to the increase in BDOC after UV/H$_2$O$_2$ treatment which subsequently facilitated further removal of TOC by BAC and also facilitated biological activity within BAC. This concept agrees with the results presented herein but the performance increase was not as substantial. The reason for this difference in observations could be due to several factors. One reason could be the relatively weak advanced oxidations conditions of this work, which were a result of screening of UV by NOM. Also, the difference in EBCT, 20 minutes vs. 8.2 minutes, could also have caused the difference in performances of BAC in this work and the previous. The longer EBCT employed in this work could have allowed the control column to remove additional TOC thus reducing the noticeable advantage over BAC fed with pretreated UV/H$_2$O$_2$. Also, it may be that the BAC columns used in the previous work were not fully acclimated since the acclimation phase last only 7 days (Toor 2005). For TOC removal, no significant differences were observed between BAC fed with LP-AM treated water of MP treated water (Figure E.18).

The reduction in A$_{254}$ was monitored and the results showed that BAC-A outperformed both the BAC-C and BAC-M by about 15% on average (Figure E.19). Interestingly, the BAC-M column did not demonstrate a significant advantage over BAC-C with respect to the removal of chromophoric NOM.

One of the hypotheses of this research was that the UV/H$_2$O$_2$+BAC process would lead to significant reduction in DBP-FPs when compared to water treated by BAC alone. The results of this research showed
evidence that UV/H$_2$O$_2$+BAC did lead to significant reductions in DBP-FPs but the observations were not consistent (Figure E.20). For Runs 1 BAC-A removed 3-50% more THM-FP while removing less HAA-FP than BAC-C. Meanwhile, BAC-M did not show any significant advantage over BAC-C for both THM-FP and HAA-FP. Similar, staggered results were observed for Run 2. The results from Run 3 seem quite irregular but it should be noted that the initial THM-FP and HAA-FP for Run 3 water were very low, in the range of 20 ppb for THM-FP and 100 ppb for HAA-FP. This low initial DBP-FP could be the cause of inconsistent observation for percent DBP-FPs removal.

E.5.3 The Potential of UV/H$_2$O$_2$ +BAC

Much of the data herein provided qualitative results with respect to the effectiveness of UV/H$_2$O$_2$+BAC as a combined treatment. It was observed that the two treatments naturally compliments one another. While UV/H$_2$O$_2$ degraded water quality by increasing BDOC, aldehydes concentration, and DBP-FPs, BAC effectively removed these by-products. On the other hand, UV/H$_2$O$_2$ facilitated the performance of BAC by increasing the BDOC and breaking down the structure of NOM. In applications where UV/H$_2$O$_2$ is employed for pollutant degradation, downstream BAC treatment would effectively remove residual H$_2$O$_2$ and improve the overall water quality by removing unwanted UV/H$_2$O$_2$ by-products.

The results herein support the recommendation of UV/H$_2$O$_2$+BAC as a primary treatment for the reduction of DBP precursors. However, large performance benefits over BAC alone were not observed and a synergistic effect was not clearly demonstrated. These results contrast with those of Toor (2005) and Speitel et al. (2000) which both demonstrated that UV/H$_2$O$_2$ combined with downstream biological treatment provided significant reduction in DBP-FPs over standalone biological treatment. It was suggested in Section E.5.2 that the long EBCT employed in this study may have improved the performance of BAC so much that more significant effects of UV/H$_2$O$_2$ pretreatment could not be observed.

In general, the combination of BAC+LP-AM was observed to offer advantages over the combination of BAC+MP and BAC alone. Although the UV/H$_2$O$_2$ treatment was carried out under similar fluences, the 8AL20 operated at half the EEF of the 4L12. This is significant to note since BAC+LP-AM still outperformed BAC+MP and much more significant advantages would have been observed if each reactor was operated at the same EEF. The improved performance of BAC+LP-AM can be attributed to the better UV/H$_2$O$_2$ performance of the 8AL20 discussed in Section E.3.3.
E.6 Conclusions and Future Work

In this report the work done at the ECT Research Facility at Trojan Technologies, Inc. was summarized. The key findings of this research were:

For the UV/H₂O₂ AOP:

- LP-AM lamp technology outperformed MP lamp technology in terms of generating advanced oxidation conditions.
- LP-AM lamp technology reduced the chromophoric NOM and degree of substitution of aromatic rings to a greater degree.
- LP-AM lamp technology increased the formation of aldehydes and BDOC to a greater degree.
- Increases in EEF led to increases in the reduction of chromophoric NOM, reduction of degree of substitution of aromatic rings, and formation of FA and AA.
- Increases in H₂O₂ concentration led to increases in the reduction of chromophoric NOM, reduction of degree of substitution of aromatic rings, and formation of FA.
- Increases in H₂O₂ had no effect on the formation of AA indicating AA is formed by the photolysis of NOM.
- AOP treatments by both UV sources led to an increase in DBP-FPs.
- Screening of UV by NOM may greatly decrease the performance of MP based processes.

For the BAC treatment process:

- BAC effectively removed FA and residual H₂O₂, by-products of UV/ H₂O₂ treatment. For the integrated UV/ H₂O₂+BAC treatment process:
  - The combined treatment outperformed BAC alone with respect to TOC and A₂₅₄ reduction.
  - The combined treatment offered some advantages over BAC alone for the removal of DBP precursors.
  - The combination of LP-AM UV/ H₂O₂+BAC was observed to be better than MP UV/ H₂O₂+BAC.
The results of the research have demonstrated that there is a lot to be understood for the UV/H₂O₂ AOP. Namely, the effects of UV source, irradiation time, and H₂O₂ dosage on various water quality parameters need to be further investigated to gain a better understanding of what exactly happens to NOM during the AOP. Future work will focus on:

- Conducting lab-scale experiments with multiple UV sources: 185+254 nm, 254 nm, and 200-300 nm.
- Study will consist of 5 factors (H₂O₂ concentration, spectral output, UV intensity, flowrate, and irradiation time), multi-level experimental design performed with two or more surface waters.
- Employ chemical actinometry to accurately determine fluences.
- Quantify OH radical concentration and OH radical demand of water.
- Statistical analysis of the factorial based experimental results will be used to:
  - Determine relative weighting of variables on performance of UV/H₂O₂ and their effects on various water quality parameters.
  - Develop a predictive model to fit the experimental data.

* For example, the predictive model would be able to determine the reduction in A₂₅₄ based on a given initial A₂₅₄, H₂O₂ concentration, spectral output, UV intensity, flowrate, and irradiation time.
### Table E.1. Water quality characteristics

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSW UVT</td>
<td>68%</td>
<td>65%</td>
<td>65%</td>
</tr>
<tr>
<td>RSW TOC</td>
<td>6.8 mg/L</td>
<td>6.5 mg/L</td>
<td>2.5 mg/L</td>
</tr>
<tr>
<td>DSW UVT</td>
<td>89%</td>
<td>92%</td>
<td>91%</td>
</tr>
<tr>
<td>DSW TOC</td>
<td>2.24 mg/L</td>
<td>1.85 mg/L</td>
<td>2.03 mg/L</td>
</tr>
</tbody>
</table>

**Figure E.1** UV/H$_2$O$_2$ experimental setup located at Trojan Technologies Inc.’s ECT Pilot Facility, London, ON.
Figure E.2 Relative lamp emission spectra from 200-300 nm for LP-amalgam and MP lamps used in 8AL20 and 4L12 reactors.

Figure E.3 The effect of EEF and UV source on the structure of NOM. [H_2O_2]=8-12 mg/L. Average values with standard deviations within 7%.
Figure E.4 The effect of EEF and UV source on DBP-FPs. \([\text{H}_2\text{O}_2]=8\text{-}12 \text{ mg/L. Average values with standard deviations within 20\%}.\]

Figure E.5 The effect of EEF and UV source on formation of aldehydes. \([\text{H}_2\text{O}_2]=8\text{-}12 \text{ mg/L. Average values with standard deviations within 10\%}.\)
Figure E.6  The effect of EEF and UV source on BDOC. $[\text{H}_2\text{O}_2]=8\text{-}12\text{ mg/L}$. Average values with standard deviations within 30%.

Figure E.7  The effect of $[\text{H}_2\text{O}_2]$ and UV source on the structure of NOM. EEF=0.4 kW/gal/min. Average values with standard deviations within 7%.
Figure E.8  The effect of [H$_2$O$_2$] and UV source on DBP-FPs. EEF=0.4 kW/gal/min. Average values with standard deviations within 20%.

Figure E.9  The effect of [H$_2$O$_2$] and UV source on formation of aldehydes. EEF=0.4 kW/gal/min; Average values with standard deviations within 10%.
Figure E.10  The effect of [H$_2$O$_2$] and UV source on BDOC. EEF=0.4 kW/gal/min. Average values with standard deviations within 30%.

Figure E.11  Absorbance from 200-300 nm of DSW from Run 1 and 10 mg/L H$_2$O$_2$ overlaid by relative lamp emission spectra.
Figure E.12 BAC acclimation phase photograph.

Figure E.13 Heterotrophic plate counts of BAC influent and effluent. 1:100 dilution.
Figure E.14 TOC removal capacity of BAC during acclimation phase.

Figure E.15 Removal of formaldehyde by BAC. EBCT = 20 min.
Figure E.16 Removal of H$_2$O$_2$ by BAC.

Figure E.17 UV/H$_2$O$_2$+BAC experimental setup located at Trojan Technologies Inc.’s ECT Pilot Facility, London, ON.
Figure E.18: The effect of UV source on the removal of TOC by BAC. \([\text{H}_2\text{O}_2]=10-12\ \text{mg/L, Fluence}=800-1000\ \text{mJ/cm}^2\). Average values with standard deviations of 3%.

Figure E.19: The effect of UV source on the removal of \(A_{254}\) by BAC. \([\text{H}_2\text{O}_2]=10-12\ \text{mg/L, Fluence}=800-1000\ \text{mJ/cm}^2\). Average values with standard deviations of 4%.
Figure E.20  The effect of UV source on the removal of DBP-FPs by BAC. \([\text{H}_2\text{O}_2]=10-12\ \text{mg/L}\). Fluence=800-1000 mJ/cm\(^2\). Average values with standard deviations of 10%.


