## Effect of Biological Activated Carbon (BAC) Filtration on the Removal and Biodegradation of Natural Organic Matter (NOM)

by

Kerry Elizabeth Black

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## ABSTRACT

Natural organic matter is a complex mixture of various organics including humic substances, carbohydrates, amino acids and carboxylic acids that exist in natural waters. Integrated treatment processes that combine oxidation processes and activated carbon biofilters have been shown to be effective at reducing natural organic matter (NOM) levels. The current research project investigated the effect of ozone and advanced oxidation at various doses on specific parameters including: biodegradability of NOM, formation of disinfection by-products (DBPs), change in apparent molecular weight (AMW) of NOM and dissolved organic carbon content (DOC).

Overall, ozonation of the raw water at 2mg O<sub>3</sub>/mg DOC resulted in significant reductions in aromatic material, resulting in lowered DBPFP. In addition, ozonation was successful at transforming NOM from high AMW to low AMW, rendering the organic material more biodegradable and preferentially removed during biofiltration.

While the high-dose oxidants (ozonation at 25mg  $O_3$ /mg DOC and AOP treatment at 4000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub>) were successful at reducing DOC, UVA, AMW and DBPFP, the elevated dose required make these options less realistic. Ozonation at 2mg O<sub>3</sub>/mg DOC and AOP treatment at 2000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub> provide good reduction of UVA, AMW and DBPFP.

The high dose oxidants are unsuitable as pre-treatment options for biofiltration given that they result in highly oxidized NOM that exhibited very little biodegradation during biofiltration. The lower dose oxidants are suitable pre-treatment options for biofiltration given the high reductions in UVA, AMW and DBPFP exhibited, and the similar biodegradation kinetics observed. Pre-oxidation prior to biofiltration is essential for removal of non-biodegradable DOC. The rate kinetics governing biodegradation were not sensitive to oxidant type or dose.

Overall, this project provided beneficial insight into the operation of integrated treatment processes and the effect of these on several NOM characteristics including biodegradation.

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# LIST OF EQUATIONS

# LIST OF ABBREVIATIONS

A <sub>254</sub>	Ultraviolet absorbance at 254nm wavelength
AMW	Apparent Molecular Weight
AOC	Assimilable Organic Carbon
AOP	Advanced Oxidation Process
BAC	Biologically Activated Carbon
BDOC	Biodegradable Dissolved Organic Carbon
BOM	Biodegradable Organic Matter
DBP	Disinfection By-Product
DBPFP	Disinfection By-Product Formation Potential
DOC	Dissolved Organic Carbon
EBCT	Empty Bed Contact Time
GAC	Granular Activated Carbon
$H_2O_2$	Hydrogen Peroxide
HAA	Haloacetic Acids
HAA <sub>5</sub>	Combined total of monochloroacetic acid, dichloroacetic acid, trichloroacetic
	acid, monobromoacetic acid, and dibromoacetic acid.
HPB	Hydrophobic Fraction
HPL	Hydrophilic Fraction
HPSEC	High Performance Size Exclusion Chromatography
HS	Humic Substances
MW	Molecular Weight
NOM	Natural Organic Matter
SUVA	Specific Ultraviolet Absorbance
THM	Trihalomethanes
TTHM	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
$UV/H_2O_2$	Advanced Oxidation Process Using Ultraviolet and Hydrogen Peroxide
UVA	Ultraviolet Absorbance
UV <sub>254</sub>	Ultraviolet Absorbance at 254 nm

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### **1.0 INTRODUCTION**

### **1.1 Overview**

Conventional water treatment processes combine coagulation, flocculation, filtration and chlorination as the key steps towards the creation of safe and good quality drinking water. However, these processes face extensive limitations as drinking water guidelines become more stringent. While chlorination represents an inexpensive and widely accepted form of disinfection, it may potentially lead to the formation of disinfection by-products (DBPs) which are currently regulated in both Canada and the United States. In Canada specifically, the Guidelines for Drinking Water Quality suggest maximum acceptable concentrations of 0.1 mg/L for trihalomethanes (THMs) and 0.08 mg/L for haloaceticacids (HAAs) (Health Canada, 2010). Water utilities are faced with the challenge of finding suitable and economical treatment processes that are able to meet these new rigorous guidelines.

Natural Organic Matter (NOM) is a complex mixture of organic materials found in most drinking water sources. There is no known direct negative health effects associated with the presence of NOM in drinking water. However, water quality and water treatment objectives may be significantly impacted by the presence of NOM, since it can lead to the formation of DBPs as well as the potential of biological regrowth within the distribution system (Hozalski et al., 1999). Many water treatment technologies are currently being developed to reduce levels of NOM in drinking water. Ozonation and advanced oxidation processes such as UV/H<sub>2</sub>O<sub>2</sub> have gained considerable attention as viable alternatives to the conventional treatment methods. In recent years, integrated treatment processes that combine the power of oxidation processes with subsequent treatment steps such as biological filtration have gained popularity as they can effectively reduce NOM levels in drinking water (van der Kooij et al., 1989; Hozalski et al., 1999; Toor and Mohseni, 2007). However, oxidation increases biodegradability of NOM, potentially enhancing biological growth within the distribution system (Hozalski et al., 1999; Sarathy and Mohseni, 2009). Therefore, biofiltration is necessary in order to remove biodegradable dissolved organic content (BDOC) matter prior to distribution.

This present research project investigated the effect of ozonation and advanced oxidation  $(UV/H_2O_2)$  on the characteristics of NOM, and its removal in an activated carbon biofilter. Of particular interest were the rate and extent of BDOC removal in activated carbon biofilters, and the effect of different oxidation doses on these rates. Initially, biodegradation of BDOC occurs rapidly in activated carbon biofilters (Yavich et al., 2004). However, a residual amount of BDOC typically remains in the effluent of the biofilter. This residual BDOC can result in microbial growth in water distribution systems. Very little is known regarding the effect of different types of oxidants and oxidant doses on the rate of change of biodegradable dissolved organic carbon (BDOC) with time in a biofilter.

### **1.2 Research Objectives**

The principle aim of the present research project was to investigate the extent and rate of removal of BDOC in a biofilter over time for different oxidation processes and doses. The overall objectives of this project were twofold:

Part 1 - Biofiltration Experiments: To assess the removal of NOM through biological activated carbon filtration.

Part 2 - Biodegradation Experiments: To assess the effect of oxidation on the rate of biodegradation.

The sub-objectives that contributed towards the aims of this project were:

Part 1:

- To assess the impact of ozonation and biofiltration on source water quality including TOC, UVA, SUVA, AMW and DBPFP.
- To acclimatize biomass in order to perform the biodegradation experiments in Part 2.

### *Part 2:*

 To establish the effect of ozonation or UV/ H<sub>2</sub>O<sub>2</sub> in combination with biological activated carbon filtration on the rate of biodegradation of organic matter and source water quality parameters including TOC, UVA, SUVA, AMW and DBPFP. • To develop a technique to evaluate biodegradation within activated carbon biofilters by determining the rate kinetics governing the removal of DOC over time.

A detailed schema of this research plan is illustrated in Figure 1-1.

### **1.3 Contributions**

This project was designed to evaluate the overall efficiency of integrated treatment processes that combine oxidation processes with biological filtration. Specifically, this project sheds light on operational advantages and limitations of ozonation, advanced oxidation and biofiltration. The results of this study will allow for a more in-depth understanding of the removal of biological organic matter (BOM) within a biofilter and the degradation of NOM throughout this treatment process. This study also provides insight from a water utility perspective on the viability of these new innovative treatment processes within the water sector.

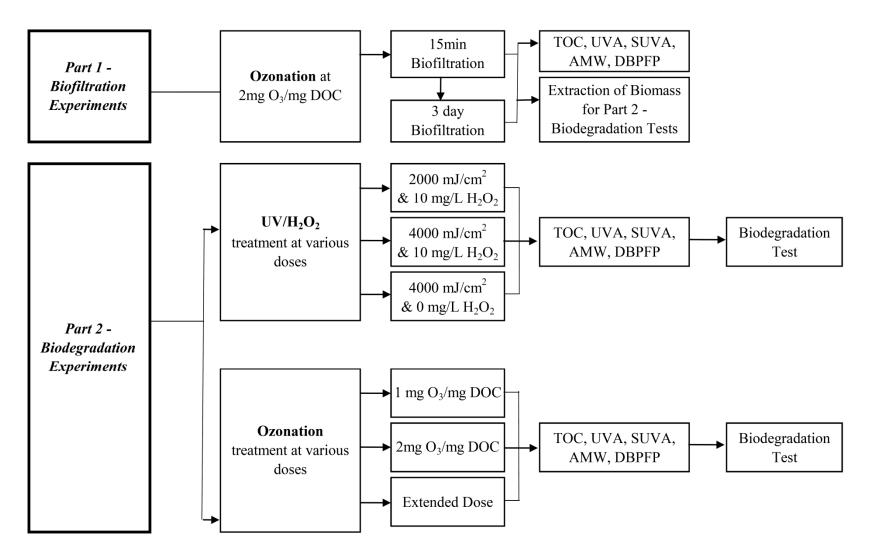


Figure 1-1- Research plan

## 2.0 LITERATURE REVIEW

### 2.1 Natural Organic Matter (NOM)

#### **2.1.1** Sources and Characteristics

Natural Organic Matter (NOM) is a complex mixture of organic materials found in most water sources. NOM can contain carbohydrates, lipids, amino acids, proteins, polysaccharides, and biopolymers. NOM can comprise organic materials from many different sources, including human activities. It can be classified into humic or non-humic substances. Sources are typically dominated by humic substances generated from biological activity within and surrounding a water source (Croue et al., 1999). Humic fractions can represent anywhere from 40 - 60% of the total dissolved organic carbon (DOC). Humic substances can be further subdivided into humic acids or fulvic acids (HA or FA). Humic acids contain many functional groups such as hydroxyl-, carbonyl-, methoxyl, phenolic and carboxyl groups (Wang and Hsieh, 2001). Furthermore, humic acids are typically hydrophobic, while non-humic acids are typically transphilic or hydrophilic (Juhna et al., 2006).

The non-humic fractions are typically present as amino acids, sugars and polysaccharides, though sugars and amino acids are less abundant due to their high biodegradation rates (Croue, 1999). The non-humic fractions are typically more biodegradable (Yavich, 1998). Non-humic substances are typically referred to as biodegradable organic matter (BOM).

#### 2.1.2 Problems Posed to Drinking Water

Due to the complexity of NOM, water quality and water treatment objectives can be significantly impacted by its presence in source waters. There is currently no known direct negative health effects associated with NOM in drinking water (Hozalski et al., 1999). However, NOM is a concern in drinking water treatment because it can potentially lead to other consequences including: taste and odour properties, disinfection by-products, high disinfection demand, membrane fouling, biological instability and other performance difficulties within treatment systems. Reduction in NOM levels before disinfection and distribution is vital for production of safe, high-quality drinking water (Hozalski et al., 1999). In terms of treatment in North America, NOM is typically removed through chemical coagulation, anion exchange, nanomembrane filtration and/or granular activated carbon (GAC) filtration (Juhna et al., 2006).

#### 2.1.2.1 Disinfection By-Products

Chlorine has been cited as one of the greatest public health advances of the 21<sup>st</sup> century (Okun, 2003). Chlorine is a simple and effective disinfectant for the inactivation of pathogens, as well as acting as valuable protection against further contamination within the distribution system by providing disinfection residual. Although chlorine is the most common disinfectant, ozone, chlorine dioxide, chloramines and UV radiation are also in use (USEPA, 2006).

As was mentioned in the previous Section, chlorine can react with NOM to form disinfection by-products (DBPs). DBPs have been a concern since the early 1970s because of their potential adverse health effects (Wang and Hsieh, 2001; Komulainen, 2004; USEPA, 2006). NOM is a precursor to most common DBPs such as trihalomethanes (THMs), haloacetic acids (HAAs), chlorinated ketones and haloacetonitriles, which are formed from the reaction of chlorine with naturally occurring organic precursors such as high molecular weight substances, humic and fulvic acids and aromatic structures (Rook, 1977; Reckhow et al., 1990; Singer, 1994; Croue et al., 1999; Kleiser and Frimmel, 2000; Wang and Hsieh, 2001; Nikolaou and Lekkas, 2001; Chin and Bérubé, 2005; Krasner et al., 2006; WHO, 2008; Sarathy and Mohseni, 2009).

In recent years, the USEPA has imposed maximum allowable concentrations for chloroform to 0.07mg/l, trichloroacetic acid (TCAA) at 0.02mg/L, and monochloroacetic acid (MCAA) at 0.07mg/L. The limits for total THMs (TTHM) is 0.08mg/L, and five of the nine known HAAs, HAA<sub>5</sub> is 0.06mg/L (USEPA, 2006). These values are based on its Stage 2 Disinfectant and DBP Rule. Health Canada regulates THMs at 0.1mg/L and HAAs at 0.08mg/L (2010). THMS and HAAs are a concern to human health because of their potential carcinogenic properties and suspected effects on reproductive and developmental health (Singer 1994; Toledano et al., 2005; USEPA, 2006, WHO 2008).

The formation of DBPs can be reduced by using non-chlorinated primary disinfectants, or by removing NOM prior to chlorination. A large portion of research has been devoted to the latter. Different treatment strategies alter NOM characteristics in various ways, thereby subsequently affecting its reactivity with chlorine. Although non-chlorinated primary disinfectants can be used, chlorine is always used for secondary disinfection, as it is long-lasting, and therefore present throughout the distribution system, preventing the growth of pathogens from source to tap. The WHO warns that disinfection should not be compromised in attempting to control DBPs as the health implications associated with inadequate disinfection are potentially far worse than the threat imposed by DBPs (WHO, 2008).

#### 2.1.2.2 Biological Stability

The creation of biologically stable drinking water is vital to the delivery of safe, high quality drinking water. Biologically stable drinking water can be defined as water in which the microbial quality does not change from treatment system to tap. Presence of microbial growth within the distribution system supports the reproduction of coliforms and bacteria, and leads to delivery of unsafe drinking water to the consumer. As was discussed previously, chlorine is applied as a secondary disinfectant to inhibit biological growth in the distribution system.

NOM is a precursor for biogrowth in water treatment and distribution systems (LeChevalier et al., 1996; Croue et al., 1999; Gottschalk et al., 2000; Sarathy and Mohseni, 2007). As discussed previously, the non-humic fraction of NOM is typically more biodegradable than the humic fractions, and therefore is typically the leading cause for bacterial regrowth within the distribution system (Yavich, 1998). Reduction in NOM prior to distribution reduces the potential for microbial growth.

The USEPA regulates chlorine residuals at a minimum of 0.2mg/L (2006). Health Canada however suggests an acceptable range of free chlorine, not to exceed 5mg/L (2010). In Canada, each drinking water authority stipulates a specific free chlorine residual requirement in its jurisdiction. Treatment processes that target the reduction of NOM, prior to distribution, lead to the formation of biologically stable drinking water.

#### 2.1.3 Characterization of NOM

#### 2.1.3.1 Total Organic Carbon (TOC)

NOM is typically measured as total organic carbon (TOC) in aquatic sources. TOC is composed of dissolved organic carbon (DOC) and particulate organic carbon (POC). DOC is defined as the organic carbon that passes through a  $0.45\mu m$  filter. Typically, NOM is present at low concentrations in water sources, between 2 to 10 mg/L DOC (Croue et al., 1999).

Another term important in this discussion is biodegradable dissolved organic carbon (BDOC). BDOC is the fraction of DOC that can be utilized as substrate by microorganisms (Allgiers et al., 1996). It typically represents between 10 to 20% of DOC (Servais et al., 1987). Similarly, assimilable organic carbon (AOC) refers to a fraction of the total organic carbon (TOC), which can be utilized by specific strains or defined mixtures of bacteria, resulting in an increase in biomass concentration that is quantifiable. AOC typically comprises just a small fraction (i.e. 0.1 to 9.0%) of the TOC (van der kooij et al., 1989).

#### 2.1.3.2 Ultraviolet Absorbance (UVA)

UV absorbance, measured at 254nm (UV<sub>254</sub>), in drinking water treatment analyses can provide insight into the composition of NOM in the source water. Light passes through a body of water and is absorbed by organic compounds leading to a reduction in transmitted light, the amount of which is proportional to the concentration of organic compounds in the solution.  $UV_{254}$  radiation is typically absorbed by aromatic rings and conjugated double bonds; therefore a reduction  $UV_{254}$  indicates a loss of aromatic and double-bonded structures.  $UV_{254}$  has been shown to correlate well with the content of aromatic material and DBP formation potential (Najm et al., 1994; Owen et al., 1995; Li et al., 2000; Kitis et al., 2001; Nikolaou and Lekkas, 2001). The value of the  $UV_{254}$  depends strongly on the concentration of humic acids in the water; when these are low, the  $UV_{254}$  is not accurate (Wang and Hsieh, 2001).

Specific UV absorbance (SUVA) is the ratio of  $UV_{254}$  absorbance to DOC. SUVA provides insight into the aromaticity and hydrophobicity of NOM (Krasner et al., 1993; Croue et al., 1999). A higher SUVA can be indicative of NOM with high aromaticity or

other unsaturated configurations, which is typically indicative of NOM that is poorly biodegradable (Goel et al., 1995).

#### 2.1.3.3 Polarity

Measurement of polarity allows for determination of the hydrophobic and hydrophilic fractions of NOM present in the source water. Hydrophobic fraction typically represents 30 - 50% of the DOC in natural waters (Kim et al., 2006).

#### 2.1.3.4 Molecular Weight (MW)

NOM molecular weight can vary from 100 to 10000 Da and is very diverse in nature (Pelekani et al., 1999. Apparent molecular weight (AMW) is an important property in drinking water treatment as changes can effect DBPFP and biological stability of the distribution system (Speitel et al., 2000; Thomson et al., 2002a; Parkinson et al., 2003; Buchanan et al., 2004; Buchanan et al., 2005; Wang et al., 2006). Higher AMW substances tend to be more aromatic in nature so may have a larger number of reaction sites (Westerhoff et al., 1999). The molecular weight of NOM is an important concept when discussing biodegradability. Lower molecular weight compounds tend to be more easily transported across cell membranes, attacked by metabolic enzymes and biodegraded (Leisinger et al., 1981). Kennedy et al., (2005) reported that NOM could be classified into different categories based on its AMW. According to this work, lower molecular weight organics would be on the order of less than 350Da, building blocks at 300-500Da, humic fractions at around 1000Da and biopolymers at greater than 20kDa.

#### **2.1.3.5** Disinfection By-Product Formation Potential (DBPFP)

As discussed previously, DBPs are an important element to consider in drinking water treatment. It can be difficult to characterize NOM and its tendency to form DBPs (Wang and Hsieh, 2001). The disinfection by-product formation potential (DBPFP) is a determination of the potential for formation of DBPs including THMs and HAAs. Factors affecting DBP formation include pH, temperature, chlorine concentration, bromide concentration, DOC, and chlorine reaction time (Ko et al., 2000).

Depending on the characteristics of NOM, DBPFP reduction can vary significantly. Chowdhury et al., (2008), observed that different NOM characteristics such as AMW and polarity are greatly impacted the DBPFP.

#### 2.2 Technologies for Removal of NOM

#### 2.2.1 Ozonation

#### 2.2.1.1 Principles of Ozonation

Ozone has been used in water treatment for over 100 years beginning in Nice France in 1906. Since then, it has seen widespread use across the world (Rakness, 1996; von Gunten 2003a). Ozone has been traditionally used as a disinfectant or oxidant. When used as an oxidant, ozone can help to reduce taste and odour compounds, colours and oxidize NOM. Recently it has been shown to be effective at the removal of micropollutants such as some antibiotics/antibacterials (Dodd et al., 2009).

Ozone is unstable in water. Ozone reacts with organic material by electrophillic addition to double bonds, producing carboxylic acids, alcohols and/or aldehydes. Ozone reaction kinetics are governed by a rapid first phase, commonly referred to as the instantaneous ozone demand (IOD), followed by a slower second phase that follows a first order rate (Cho et al., 2003; von Gunten, 2003a). The ozone reaction rates for both phases are dependent on water quality, pH, DOC and alkalinity (Cho et al., 2003).

Ozonation can occur via two pathways, direct or indirect. The direct pathway favours reactions primarily with unsaturated double bonds and aromatic compounds, though reaction with amines or sulphides is common (Gottschalk et al., 2000; von Gunten 2003a). The direct pathway is limited by the availability of dissolved molecular ozone in the water phase (Amirsadari et al., 2001). Alkalinity plays an important role in the direct pathway; at higher alkalinity, the direct pathway is favoured.

With the indirect pathway, hydroxyl radicals are formed and react with NOM. Hydroxyl radicals are strong, unselective oxidants. At higher pHs, the indirect pathway is favoured (Hoigne and Bader, 1975). There are many different ways for these OH radicals to react, a detailed description is provided elsewhere (Glaze et al., 1982). Alkalinity plays an important role in the indirect pathway. Carbonates are considered scavengers of hydroxyl radicals and as alkalinity increases, less hydroxyl radicals are available (AWWARF 1999). Depending on the alkalinity, production of OH radicals is typically much less than what is seen with advanced oxidation processes (AOPs) which is discussed in subsequent Sections.

If the goal of ozonation is disinfection, only enough ozone should be added to inactivate the microorganisms and the formation of BOM is undesirable. BOM can cause significant bacterial regrowth in the distribution system if it is not removed in subsequent treatment steps (Van der Kooij, 1989; Huang et al., 2004). If the goal of ozonation is to eliminate/reduce DBPS, then the production of BDOC should be maximized, so that it can be removed by subsequent degradation within a biofilter.

Disadvantages to the use of ozone are the formation of ozone-by-products (OBPs) such as aldehydes (formaldehyde, acetaldehyde, glyoxal, methyl glyoxal, etc.), ketoacids and carboxylic acids (Singer, 1999; von Gunten 2003a; von Gunten 2003b; Huang et al, 2004, Karnik et al., 2005a and Hammes et al, 2006). One of the main concerns is bromate formed during oxidation of bromide. (von Gunten, 2003b; WHO, 2008). Most of the ozonation by-products are highly biodegradable and can be removed through biofiltration prior to releasing the water into the distribution system (Krasner et al., 1993; Swietlik et al., 2004).

#### 2.2.1.2 Effect on NOM

During ozonation, NOM is oxidized and transformed into intermediates still present as DOC (Fahmi and Okada, 2003; Bérubé et al., 2004). Therefore, very little reduction in DOC is observed during low-dose ozonation. The reaction of ozone with the aromatic structures and double bonds of NOM results in a significant decrease in  $UV_{254}$  (Kim et al., 1997; Kleiser and Frimmel, 2000).

Ozonation greatly impacts the molecular weight of NOM. Ozone reacts with NOM resulting in fragmentation of organic material, and transformation from high to low AMW (Kaastrup and Halmo, 1987; Owen et al., 1995).

Ozone has been shown to be effective at removing certain DBP precursors naturally present in drinking water sources (Hu et al., 1999; Singer, 1999: Galapate et al., 2001; Chin and Bérubé, 2005). Some work has shown that ozonation typically reduces the DCAA, TCAA and THM formation potentials (Glaze et al., 1982; Owen et al., 1995; Kim et al., 1997; Chowdhury et al., 2008). However, other work has shown that ozonation can also

increase DBPFP (Langlais et al., 1991; Siddiqui et al., 1997; Goslan et al., 2007; Toor and Mohseni, 2007). Ozonation has also been shown to lead to the formation of bromoform, MBAA and DBAA (Huang et al., 2004; WHO, 2008).

The oxidation of NOM by ozone can enhance its biodegradability by reducing the size of NOM molecules, reducing aromaticity and increasing carboxylic acid functionality (Kaastrup and Halmo, 1987; Langlais et al., 1991; Westerhoff et al., 1999). In previous work, BDOC and AOC contents tended to increase after ozonation (Owen et al., 1995; (Rittman and Huck, 1989, Kim et al., 1997; Sarathy and Mohseni, 2009). Some work has shown that doses from 1 to 2 mg/mg TOC were optimal for enhancing biodegradation of NOM (Werner and Hambsh, 1986; Murphy, 1993; Siddiqui et al., 1997; Hozalski et al., 1999; AWWARF, 1999; Uhl, 2000; Kim et al., 2006; Melin et al., 2006). A summary of the reported effects of ozonation on NOM characteristics is presented in Table 2-1.

Parameter	Reported Effect
	Negligible effect (Kleiser and Frimmel, 2000; Ko et al, 2000; Chin and Bérubé, 2005; Chowdhury et al, 2008; Gunten et al., 2009)
	2-10% reduction (Westerhoff et al 1999)
	4% reduction (Amirsadari et al., 2001)
	10-30% reduction for ozone doses of 1 - 5mg/gmg DOC (Cipparone et al., 1997)
TOC	12% reduction of DOC at 1 mg $O_3$ /mg TOC (Kim et al., 2006).
	20% reduction in DOC following ozonation (Kim et al., 1997)
	16-33% TOC reduction (Hozalski et al., 1999) for 2-4 mg $O_3$ /mg TOC
	0-20% reduction in TOC (AWWARF 1999)
	6.4% reduction in DOC following ozonation (up to 1.5mg $O_3/mg$ DOC (Galapate et al, 2001)
	Reduction in UV and SUVA (Ko et al, 2000; Chin and Bérubé, 2005; Gunten et al., 2009)
	54% reduction in UVA260 (Galapate et al., 2001)
	45% reduction (Kaastrup and Halmo, 1989)
	50 - 75% reduction for doses of 0.5 - 1.5 mg $O_3$ /mg DOC(Kleiser and Frimmel, 2000)
UVA/SUVA	35-70% reduction (Chowdhury et al., 2008)
	28% reduction (Amirsadari et al., 2001)
	50% reduction at 1mg $O_3$ /mg DOC (Kim et al., 2006)
	50% reduction (Kim et al., 1997)
	56% reduction up to 1mg $O_3/mg$ DOC (Owen et al. 19950
Polarity	Decreased hydrophobicity, increased hydrophilicity (Westerhoff et al, 1999; Galapate et al 200;, Chowdhury et al 2008)

Table 2-1 - Summary of reporte	d effects of ozonation on NOM characteristics
Tuble 2 1 Summary of reports	

Parameter	Reported Effect
Polarity	Decrease in hydrophobic fraction from 54% to 5% following ozonation (Swietlik et al., 2004).
	Shift from higher MW to lower MW (von Gunten at al. 2003b)
MW	Higher MW oxidised preferentially, resultin in overall lowered MW (Swietlik et al., 2004)
	88% increase in compounds less than 500Da, large shift from HMW to LMW. (Hozalski et al., 1999)
	No effect (Kim et al., 1997)
	5% increase in HAAFP following ozonation (Siddiqui et al., 1997)
	Roughly 50% decreased in HAAFP and Chloroform formation potential (Chin and Bérubé, 2005)
HAAFP	Observed increases in DCAA following ozonation, however this could be the result of the formation of diketones and oxidation to aldehydes which has been shown to increase DCAA amounts (Reckhow and Singer, 1994).
	63% reduction in TCAA values at a dose of 3.5mg/L (Ko et al., 2000)
	34% reduction in HAAFP (Hu et al., 1999)
	10 - 60% reduction observed for ozone doses from 1 - 5 mg $O_3$ /mg DOC (Cipparone et al., 1997)
	-117% to 38% reduction of HAAFP, mostly due to reduction in DCAA and TCAA formation potentials of the hydrophilic NOM (Chowdhury et al., 2008)
	18-32% reduction observed (Kleiser and Frimmel 2000)
	8% reduction at low doses, higher removal of 43% at dose of 3 mg $O_3$ /mg DOC(Galapate et al., 2001)
	-21% to 47% reduction observed (Chowdhury et al., 2008)
	20-50% reduction in THMFP for 3.5mg/L preozonation (Ko et al., 2000)
THMFP	27% reduction (Hu et al., 1999)
	5-80% reduction for ozone doses of 1 -5 mg $O_3$ /mg DOC (Cipparone et al., 1997)
	5% increase in THMFP following ozonation (Siddiqui et al., 1997)
	50% reduction of chloroform (Bérubé et al., 2004)
	5-20% reduction in THMFP for 0.4 - 1.2 mg $O_3$ /mg DOC
	Increased BDOC and AOC content (Owen et al., 1995)
Biodegradability	Increased in BDOC by 5 - 50% (Hozalski et al., 1999; Cipparone et al., 1997; Digiano et al., 2001)
	NOM with a higher percentage of high molecular weight compounds experienced the greatest enhancement in biodegradability by ozonation (Hozalski et al., 1999).

## 2.2.2 UV/ H<sub>2</sub>O<sub>2</sub> Advanced Oxidation

## 2.2.2.1 Principles of UV/ $H_2O_2$ Oxidation

Processes that use OH radicals as the main oxidant are called advanced oxidation processes (AOPs). These hydroxyl radicals are very short lived and extremely strong

oxidizing agents. They react with double bonds, or H-atom abstraction to form carbon centred radicals.

 $UV/H_2O_2$  can be used to generate OH radicals, as presented in Equation 2-1. In this process, OH radicals are formed from cleavage of the hydrogen peroxide molecule.

#### Equation 2-1 $H_2O_2 + h \cdot v \rightarrow 2OH \bullet$

The units of UV are represented as  $mJ/cm^2$ . Most important wavelengths for UV when discussing water treatment are in the range of 200 - 280nm.

The rate of photolysis of  $H_2O_2$  is dependent on the pH, and increases in more alkaline conditions (Legrini et al., 1993). In addition, the rate of reaction is highly dependent on the concentration of  $H_2O_2$  and the UV light intensity, in addition to the chemical structure of the material being oxidized (Sundstrom et al., 1986). UV light tends to react with  $H_2O_2$  making less light photons available for the target pollutants at high  $H_2O_2$  doses (Wang et al., 2006). As a result, there exists an optimum  $H_2O_2$  dose, after which hydroxyl radicals become less available (Kleiser and Frimmel 2000; Litter, 2005; Wang et al., 2006; Sarathy 2009). Wang et al., reported that the formation of OH radicals was optimal at an  $H_2O_2$  dose of 1% (2000).

While UV/  $H_2O_2$  is not typically used for drinking water treatment, UV doses up to 1500mJ/cm<sup>2</sup> and  $H_2O_2$  doses up to 20mg/L have been suggested (Sarathy and Mohseni, 2009).

#### 2.2.2.2 Effect on NOM

At high doses, UV/  $H_2O_2$  can mineralize NOM and decrease the TOC concentration (Sundstrom et al., 1986; Langlais et al., 1991; Beltran et al., 1993; Gottschalk et al., 2000; Kleiser and Frimmel, 2000; Speitel et al., 2000; Thomson et al., 2004; Wang et al., 2006; Toor and Mohseni, 2007). However, the high amount of energy required to mineralize NOM makes this option economically unfeasible. At lower, more economically feasible doses, UV/  $H_2O_2$  does not mineralize NOM. Lower removal rates of DOC are observed at these doses given that NOM is partially oxidized and transformed into intermediates still present as DOC (Fahmi and Okada, 2003; Bérubé et al., 2004).

At the lower, more economically feasible doses, NOM is oxidized into intermediate compounds that are less aromatic and have been shown to lower the tendency to form DBPs

(Thomson et al., 2002b; Oppenlander, 2003; Thomson et al., 2004; Tuhkanen, 2004; Chin and Bérubé, 2005; Sarathy and Mohseni, 2007). High removal rates for UV254 have been observed (Goslan et al., 2006; Bond et al., 2009). Some work has shown that UV/  $H_2O_2$  is not efficient at removing DBPs and can lead to increased formation of DBPs (Toor & Mohseni, 2007). Transformations from high AMW to low AMW have been observed (Thomson et al., 2004; Sarathy, 2009)

AOPs can also lead to an increase in biodegradable organics (Speitel et al., 2000, Liu et al., 2002; Thomson et al., 2004; Toor and Mohseni, 2007) The lower dose treatments have been shown to increase the biodegradability of NOM (Liu et al., 2002; Toor and Mohseni, 2007). A summary of the reported effects of UV/ $H_2O_2$  on NOM characteristics is presented in Table 2-2.

Parameter	Reported Effect
тос	14.5 % reduction at 1500mJ/cm <sup>2</sup> and 20 mg/L $H_2O_2$ . Higher Reduction of 27% observed for a water with lower initial TOC concentration and absence of high molecular weight compounds (Sarathy and Mohseni, 2009)
	Up to 78% reduction for $UV/H_2O_2$ (Goslan et al, 2006)
	Up to 91% reduction for $UV/H_2O_2$ for 4700-4800 mJ/cm <sup>2</sup> and 78% reduction for 2100mJ/cm <sup>2</sup> (Bond et al., 2009).
UVA	55% reduction mostly due to the loss of aromatic and double bonded compounds (Sarathy and Mohseni, 2009)
UVA	Up to 94% reduction (Goslan et al 2006).
	Decrease in UV254 after AOP, especially at high UV doses (Toor and Mohseni, 2007)
	Higher MW oxidised preferentially, resulting in overall lowered MW (Sarathy, 2009; Thomson et al., 2004)
MW	Milder AOP conditions led to degradation of NOM and formation of smaller species, overall reduction in MW (Sarathy and Mohseni, 2007)
	At $H_2O_2$ of 5mg/L, and 1350UV reduction of 65, 53 & 29% for 850-1100, 1100-1400 and greater than 1400mJ/cm <sup>2</sup> . Greatest impact was achieved using 850 - 1400 mJ/cm <sup>2</sup> . (Sarathy and Mohseni, 2009)
	25 % hydrophobic compounds converted to hydrophilic compounds (Sarathy, 2009)
Polarity	Significant reduction in hydrophobic compounds following UV irradiaiton (Buchanan et al., 2005)
	AOPs are non selective oxidizers that don't necessarily preferentially remove hydrophobic compounds (Crittenden et al., 2005 & Bond et al., 2009).
	70(Chin Bérubé 2005) for Ozone UV
	No effect (Sarathy, 2009)
HAAFP	Observed increases in DCAA following AOP treatment could be the result of the formation of diketones and oxidation to aldehydes which has been shown to increase DCAA amounts (Reckhow and Singer, 1994).
	Upwards of 1000mJ/cm <sup>2</sup> and 100mg/L $H_2O_2$ required to reduce DBPs (Liu et al, 2002).

Table 2-2 - Summary of reported effects of UV/H<sub>2</sub>O<sub>2</sub> on NOM characteristics

Parameter	Reported Effect
	Increase of THMFP by 40% (Kleiser and Frimmel 2000)
	80% reduction for Ozone/UV (Chin and Bérubé 2005)
	<i>UV fluence greater than 1500 required for THMFP reduction (Toor and Mohseni, 2007)</i> woth $H_2O_2$ of 23
THMFP	No effect (Toor and Mohseni, 2007; Sarathy, 2009)
THMFP	Upwards of $1000mJ/cm^2$ and $100mg/L H_2O_2$ required to reduce DBPs (Liu et a.l, 2002).
	Upwards of 1500mJ/cm <sup>2</sup> and 23mg $H_2O_2$ required for reduction in THMFP (Toor and Mohseni, 2007)
	Limited reduction in chloroform potential (Bérubé et al., 2004)
Biodegradability	Increased in BDOC and biodgradability of NOM (Speitel et al., 2000; Liu et al., 2002; Toor and Mohseni, 2007)

#### 2.2.3 Oxidation/Biofiltration

#### 2.2.3.1 Principles of Combined Oxidation/Biofiltration

Conventional treatment processes may not necessarily meet current and future water quality requirements. Oxidation treatment processes alone may not necessarily be practical due to high energy demands, partial oxidation of NOM, insufficient reduction in DBPs and formation of biodegradable oxidation byproducts. Integrated treatment processes that combine oxidation processes and activated carbon biofilters have been shown to be very effective at reducing natural organic matter (NOM) levels by oxidising NOM in to more biodegradable DOC, which is subsequently removed by biofiltration (Owen et al., 1995).

The use of BAC following oxidation treatment processes has the advantage of preferentially removing biodegradable material formed during oxidation. Biological activated carbon (BAC) is a filtration system where granular activated carbon (GAC) is used as a growth medium, rather than for adsorption (AWWARF, 1994). GAC supports more dense populations than sand or anthracite (i.e. 4 to 8 times more biomass per gram of media), likely due to many factors including porosity, surface area, surface roughness, surface charge and adsorption capacity (Speitel 2000; Wang et al., 2006). GAC filtration has been shown to be effective at reducing DBP precursors, lowering nutrient availability for bacterial regrowth, and producing more biologically stable water (USEPA, 2006). It's also extremely good at reducing DOC levels and high AMW and humic fractions (Owen et al., 1995).

According to research, combined oxidation and biofiltration systems have the potential of resulting in the production of biological stable water, the minimization of the potential for bacterial regrowth within the distribution system; the removal of biodegradable

organic matter (BOM) and disinfection by-product precursors; the reduction in chlorine demand; and the potential removal/control of oxidation by-products (Cipparone et al., 1997; Wu et al., 2003; Fahmi and Okada, 2003).

Empty bed contact time (EBCT) is one of the single most important parameters for removal of BOM in biofilters. Many previous studies have found that removal of NOM was directly proportional to EBCT. (Lechevalier et al., 1992; Huck et al., 1994; Hozalski et al., 1995; Carlson and Amy, 1998). However, some research has shown that the EBCT has no effect on TOC removal (Hozalski et al., 1995). Typical EBCT can vary however, EBCTs of 15 - 20 minutes have been reported (Yavich et al., 2004; Wang et al., 1995).

Another important parameter to consider with biofiltration is acclimation. Acclimation of biofilters ensures the filters are operating at steady-state conditions, which allow filters to maximize the amount of BOM removed during filtration. Typical acclimation periods required to reach steady-state can vary widely and depend largely on source water characteristics and temperature. Acclimation periods in the range of 4 - 6 months have been reported (Wang et al., 1995; Yavich et al., 2004).

#### 2.2.3.2 Effect on NOM

The use of oxidation processes requires biofiltration since these processes increase the amount of BOM ((Speitel et al., 2000, Liu et al., 2002 and Thomson et al., 2004; Toor and Mohseni, 2007). Biologically-active filtration is an approach for removing NOM from water to limit both concerns of DBP formation and microbial regrowth (Hozalski et al., 1999; Thomson et al., 2002a; Buchanan et al., 2004).

Biologically active filtration has been shown to reduce the concentration of DOC (Krasner et al., 1993; Fonseca and Summers, 2003). Hozalski et al., (1999), found that removal of organic carbon by biodegradation was directly proportional to the percentage of low molecular weight compounds, and inversely proportional to SUVA.

BAC alone does not provide significant reduction in DCAA, TCAA or THM formation potentials (Toor and Mohseni, 2007). Standalone AOP or oxidation systems are generally not viable given that they results in partial oxidation of NOM, insufficient reduction in DBPs and formation of biodegradable oxidation byproducts. UV  $/H_2O_2$  followed by biofiltration has been shown to have a significant impact on removal of THMs

(Speitel et al., 2000; Xie and Zhou, 2002). However some research has shown that biological treatment can also increase HAAFP (Bond et al., 2009).

According to several researchers, there is presence of a rapidly biodegradable fraction of NOM that can be substantially removed in the biofiltration process (BDOCr), and a slowly biodegradable fraction that is largely released to the distribution system (BDOCs) (Prévost et al., 1992; Servais et al., 1994; Wang and Summers, 1994; Carlson et al., 1996, Carlson and Amy, 1997). BDOCr provides an indication of the DOC that can be removed during biofiltration and therefore its formation is desired. BDOCr can also potentially lead to the formation of DBPs when chlorinated. BDOCs gives an estimate of the NOM that is not significantly removed during biofiltration but can contribute to the biological instability of the treated water.

In previous work, the fraction of initial DOC that was converted to BDOCr during ozonation was reported not to be sensitive to DOC concentration for doses ranging from 0.2 - 1.4mgO<sub>3</sub>/mgDOC (Carlson and Amy, 1997).

On the other hand, the formation of BDOCs was almost always a function of source water composition rather than ozone dose (Carlson and Amy, 1997). BDOCs increased with source water DOC for ozone doses between 1 and 2 mgO<sub>3</sub>/mg DOC (Carlson and Amy, 1997).

With respect to the biodegradation kinetics, according to Huck et al. (1998), a first order relationship was found for BDOC removal through a full-scale GAC contactor. Yavich et al. (2001), found that biodegradation rates increased with increasing ozone dose (2004). Carlson and Amy found that there was some maximal value of ozone dosing, above which BDOCr rate of biodegradation was not increasing. A summary of the reported effects of combined oxidation and biofiltration on NOM characteristics is provided in Table 2-3.

Table 2-3 - Summary of reported	l effects of oxidation and	biofiltration on NOM	characteristics

Parameter	Reported Effect
	NOM with higher % of high MW had substantial improvement of TOC removal followed by biodegradation (Goel et al., 1995).
тос	30% reduction in DOC for ozone doses of 1.5 mgO <sub>3</sub> /mg DOC and subsequent biofiltration (Fonseca and Summers, 2003).
IOC	21-29% reduction (Wang et al., 1995)
	52% reduction (Toor and Mohseni, 2007)

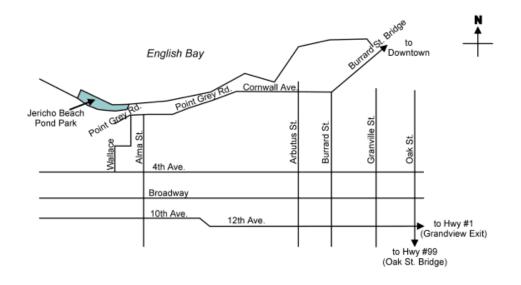
Parameter	Reported Effect
	15-40% reduction for ozone doses 1 - 5 mgO <sub>3</sub> /mg DOC with biofiltration (Cipparone et al., 1997)
TOC	14-15% (Servais et al., 1994)
	14-23% reduction (Klevens et al., 1996)
	20-40% reduction by biodegradation (with starting TOC of 4mg/L) (Hozalski et al., 1999)
T 137 A	<i>Further Decrease in UV254 after AOP and biofiltration - 59% reduction after 500Mj and 20mg/L in comparison to 22% reduction with BAC alone. (Toor and Mohseni, 2007)</i>
UVA	59% reduction (Toor and Mohseni 2007)
	60-80% reduction in SUVA (Hozalski et al., 1999)
Polarity	20% decrease in hydrophobicity (Fahmi et al., 2002)
MW	15-50% reduction in MW (Hozalski et al., 1999)
	37% reduction in DCAA to 50% reduction in TCAA for 500 mJ/cm <sup>2</sup> and 20mg/L $H_2O_2$ with BAC as compared to 0 and 7% with BAC alone (Toor and Mohseni, 2007).
	Observed increases in DCAA following AOP treatment (or ozonation) could be the result of the formation of diketones and oxidation to aldehydes which has been shown to increase DCAA amounts but this would be reduced by subsequent biofiltration (Reckhow and Singer, 1994).
	<i>Reduction in TCAA by 69%, and DCAA by 74% for 3000 mJ/cm<sup>2</sup> and 10-20mg/L H</i> <sub>2</sub> $O_2$ ( <i>Toor and Mohseni, 2007</i> ).
	38% of HAAFP following ozonation and biofiltration (Joslyn and Summers, 1992)
HAAFP	DBPFP was the lowest for biofilters treating ozonated wate, as compared to ozonation alone (Fonseca and Summers, 2003)
	No significant additional reduction over biotreatment alone (Wang et al., 1995)
	47% reduction of HAAFP (Siddiqui et al., 1997)
	Near complete removal of 5 HAAs with BAC (Xie and Zhou, 2001)
	46% reduction of HAAFP following ozonation and biofiltration (Joslyn and Summers, 1992)
	Additional 15% to almost 100% with ozone doses of 1 - 5 mgO <sub>3</sub> /mg DOC (Cipparone et al., 1997)
	42% reduction for 500mJ/cm <sup>2</sup> and 20mg/L $H_2O_2$ with BAC as compared to 11% with BAC alone (Toor and Mohseni, 2007).
	69% for high dose of $3000 \text{mJ/cm}^2$ and $10-20 \text{mg/L } H_2O_2$ (Toor and Mohseni, 2007)
	Significant Reduction in THMs (Speitel et al., 2000)
	Reduction in THMFP of 45% as compared to 25% with conventional treatment (AWWARF, 1994).
THMFP	50% removal (Wang et al., 1995)
	40-80% for ozone doses of 1 -5 mgO <sub>3</sub> /mg DOC (Cipparone et al., 1997)
	DBPFP was the lowest for biofilters treating ozonated water, as compared to ozonation alone (Fonseca and Summers, 2003)
	46% removal of THMFP (Siddiqui et al., 1997)
	40-59% removal of THMFP (Shukiary et al., 1992)
	Substantial reduction in BDOCr during oxidation and biofiltration (Carlson et al., 1996; Carlson and Amy, 1997).
Biodegradability	BDOCr formed during ozonation was sensitive to DOC concentration while BDOC s was not (Carlson and Amy, 1997)

# **3.0 MATERIALS AND METHODS**

# **3.1 Part 1: Biofiltration Experiments**

## 3.1.1 Raw Water Preparation

The raw water used for the study consisted of a mixture of pond water and tap water. The pond water was obtained from Jericho Beach Park, Vancouver, British Columbia (Figure 3-1).



#### Figure 3-1 - Jericho Beach pond park

Pond water was collected every 2 months throughout the duration of the project. The collected pond water was stored at 4°C for at least 1 week to allow for large particles to settle, and then filtered through binder-free borosilicate glass filters (Whatman Binder-Free Glass Microfiber Filters Type GF/D, Fisher Scientific). Tap water was added to the filtered pond water to achieve a DOC concentration of approximately 5mg/L. The resulting raw water had the characteristics outlined in Table 3-1.

Parameter	Value	
DOC (mg/L)	$5 \pm 0.2$	
pH	7 ± 0.3	
Temperature (°C)	21 ± 1	
Hardness (mg/L as CaCO <sub>3</sub> )	50 ± 10	
Alkalinity (mg/L as CaCO <sub>3</sub> )	50 ± 10	

Table 3-1 - Raw water characteristics

# 3.1.2 Feed Water Preparation

Feed water for the biofiltration system (Section 3.1.3) consisted of raw water treated with ozone to a dose of 2mg  $O_3$ /mg DOC. Ozone was generated by coronal discharge through compressed air. The  $O_3$  was bubbled using a stainless steel diffuser through a 2.5*L* amber bottle which was tightly fitted with a rubber fitting to limit off-gas release into the atmosphere. Exactly 2*L* of raw water was placed in the contactor for treatment. All tubing consisted of PTFE Teflon® tubing. Figure 3-2 illustrates a schematic of the ozonation system.

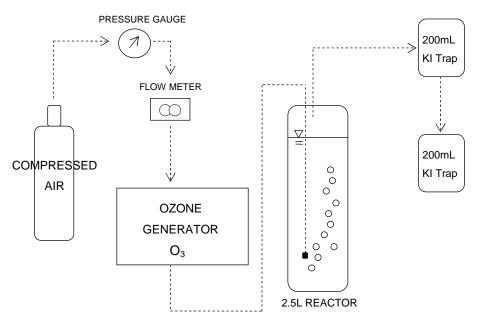


Figure 3-2 - Schematic of ozonation apparatus

To determine the ozone flow rate an initial calibration of the apparatus was necessary. The following procedure was used to calibrate the ozonation apparatus:

- A 2L potassium iodide (KI) calibration solution was prepared based on Standard Method 423.A (APHA, 1989). Exactly 40g of potassium iodide (Fisher Scientific) was dissolved in 2L of ultra-pure water. The Iodometric method for ozone concentration determination has also been used in previous studies (Galapate et al., 2001).
- Two secondary 200mL KI trap were prepared by dissolving 4g of potassium iodide in 200mL of ultra-pure water.
- 3. The 2L solution was placed in a 2.5L amber bottle contactor (the same vessel used for subsequent raw water treatment). A secure rubber stop was placed at the top of the vessel. Ozone off-gas was directed from the headspace to the secondary KI traps using PTFE Teflon® tubing.
- The 2L solution was ozonated for a specific time period and purged for a minimum of 5 minutes at a flow rate of 0.2 - 1L/min to ensure that all ozone was swept from the sample.
- 5. Ozone production is calculated based on the volume obtained from subsequent titration with sodium thiosulfate (Fisher Scientific). A 0.01N solution of sodium thiosulfate was prepared daily. Exactly 100ml of KI solution was placed in a 400ml beaker on a stir plate. 5ml of sulphuric acid (Pure, Fisher Scientific) was placed in the beaker with the sample. The sample was titrated with sodium thiosulfate until the yellow colour was almost discharged. 1ml of starch indicator solution was then added to impart a blue colour. The sample was then quickly titrated until the blue colour was discharged. Equation 3-1 was used to determine the ozone concentration.

Equation 3-1 
$$mg/L \cdot O_3 = \frac{(A \pm B) \times N \times 24,000}{mL \cdot sample}$$

where A = mL titration for sample, B = mL titration for blank and N is the normality of  $Na_2S_2O_3$ 

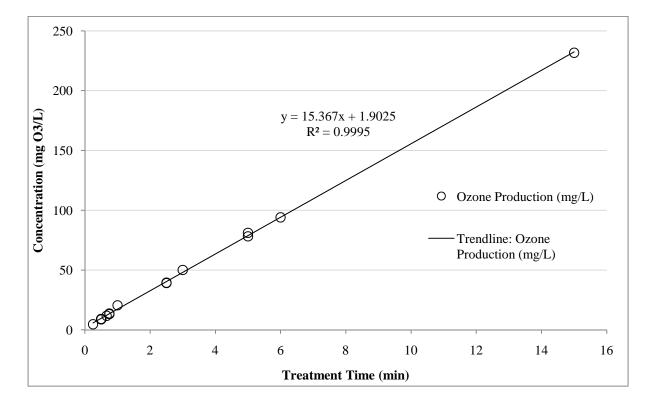
6. The final ozone production amount was determined as using Equation 3-2.

Equation 3-2 
$$\frac{M_{produced}}{V_{sample}} = \frac{M_{aqueous}}{V_{sample}} - \frac{M_{gaseous}}{V_{KI \cdot Trap \cdot 1}} - \frac{M_{gaseous}}{V_{KI \cdot Trap \cdot 2}}$$

where  $M_{aqueous}$  and  $M_{gaseous}$  are determined based on the KI method described above.

7. Calibration was repeated for several treatment times to determine the ozone production rate.

Figure 3-3 illustrates the calibration curve for ozonation concentration versus time. A full summary of raw data is provided in Appendix A.





Ozone consumption was then determined by treating a 2L raw water sample for a given time. Captured ozone in the secondary KI traps was subtracted from total ozone production to determine the final O<sub>3</sub> dose as described in Equation 3-3.

#### **Equation 3-3**

$$\frac{M_{consumed}}{V_{sample}} = \frac{M_{produced}}{V_{sample}} - \frac{M_{gaseous}}{V_{KI \cdot Trap \cdot 1}} - \frac{M_{gaseous}}{V_{KI \cdot Trap \cdot 2}}$$

where  $M_{produced}$  is determined during calibration (as described above) and  $M_{aqueous}$  and  $M_{gaseous}$  are determined based on the KI method described above.

Ozone consumption was highly dependent on the raw water matrix and varied substantially for a given dissolved organic carbon content. For this reason, it was necessary to calibrate and calculate the final ozone dose prior to each analysis.

# 3.1.3 Biofiltration System

A laboratory scale filtration apparatus was assembled in the Environmental Engineering Laboratory at the University of British Columbia. A schematic of the system is presented in Figure 3-4, and details of the system operation and geometry are summarized in Table 3-2.

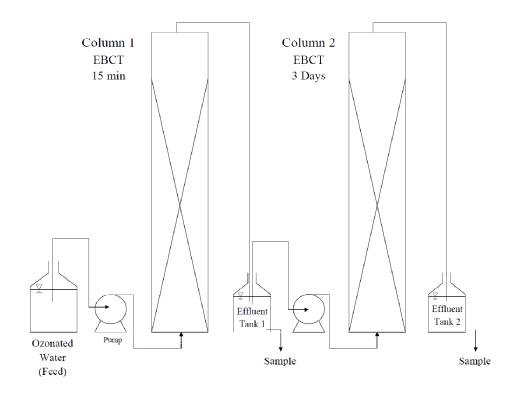


Figure 3-4 - A schematic of the laboratory scale apparatus.

Feed water (Section 3.1.2) was fed to the first column using a 1-100 RPM Masterflex L/S variable apeed console drive and multi-channel 8-cartridge pump head (Cole Parmer). Filtered water from Column 1 was then collected from effluent tank 1 for sampling and the remaining water was pumped to the second column using a 1-100 RPM Ismatec 4-channel compact pump (Cole Parmer). Filtered water from Column 2 was then collected for sampling.

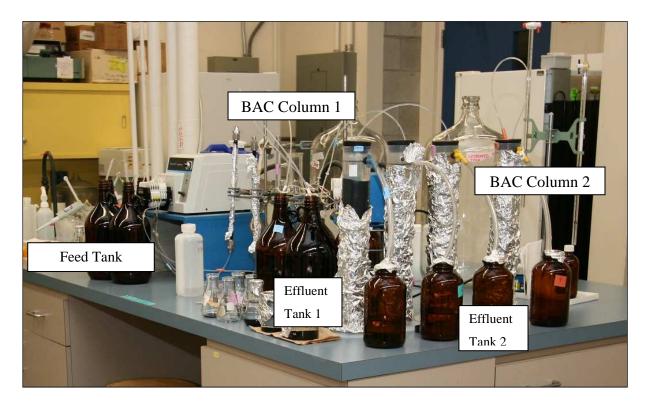
	Parameter	Setting
	Temperature (°C)	21 ± 1
∼ Volume (mL)		22 ± 1
Column I	Diameter (cm)	1
Colu	Flow Rate (ml//min)	1.1
0	EBCT	20 min
2	Volume (mL)	1000
un	Diameter (cm)	6.5
Column 2	Flow Rate (ml//min)	0.2
C	EBCT	3 Days

Table 3-2 - Laboratory apparatus characteristics

For quality control and assurance, a total of 4 separate filtration apparatuses were constructed and operated in parallel. The filtration apparatus was constructed using the following materials/

- 4 1 cm diameter glass Pyrex® columns, 30 cm long
- 4 1000mL plastic Nalgene® graduated cylinders
- 4 2L amber bottles for feed water
- 8 1L amber bottles for filtered water collection
- <sup>1</sup>/<sub>8</sub>" and <sup>1</sup>/<sub>4</sub>" PTFE Teflon® tubing for water circulation
- 4 3-stop Tygon® red/red/red tubing (1.14mm ID)
- 4 3-stop Tygon® yellow/blue/yellow tubing (1.5mm ID)
- 8 stainless steel Swagelok® fittings (½" to ½" diameter)
- 8 <sup>1</sup>/<sub>2</sub>" PTFE Teflon® ferrules
- 8 <sup>1</sup>/<sub>8</sub>" PTFE Teflon® ferrules
- 6- <sup>1</sup>/<sub>8</sub>" stainless steel compression fittings, union tees (Cole Parmer)

Amber bottles were used for feed and effluent tanks to minimize potential effects of exposure to light. In addition, all tubing, columns walls and openings were covered using aluminum foil. Feed water was replenished daily. An image of the bench-scale apparatus is shown in Figure 3-5.



# Figure 3-5 - Bench-scale apparatus

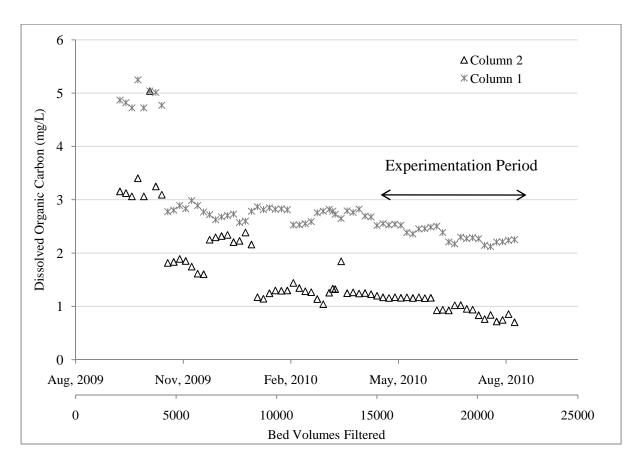
Each column contained wood-base Picabiol® granular activated carbon (PICA Carbon). Table 3-3 identifies the properties of the GAC used in this project.

Properties	Specification	Actual
Apparent Density (dry, g/mL)	0.18 - 0.26	0.22
Moisture (as packed, %)	5 Max	3.3
Ash (wt. %)	5% Max	3.4%
Iodine No. (mg I2/g GAC)	900 min	1125
Uniformity Coefficient	< 1.5	1.41
Effective Size	0.85 - 1.1 mm	1.04
	On 10 mesh	3.2%
	10x12 mesh	16.7%
	12x14 mesh	27.6%
Particle Size Distribution	14x16 mesh	27.2%
	16x18 mesh	18.5%
	18x20 mesh	5.4%
	Through 20 mesh	1.4%

Table 3-3 - Picabiol® granular activated carbon properties

The empty bed contact time (EBCT) of 20 minutes for Column 1 was selected based on the previous work of Allgeier et al. (1996), Carlson and Amy (1997) and Yavich et al. (2004) to remove the rapidly biodegradable fractions of NOM (BDOC<sub>r</sub>). An EBCT of 20 minutes is also representative of EBCTs at full-scale BAC treatment plants. The EBCT for Column 2 was selected to approximate the extent of biodegradation that occurs in distribution systems. The maximum average residence time in a distribution system was assumed to be approximately 3 days. In order to ensure consistency and ensure reproducible results, the EBCT was carefully monitored for each column. Equally important was biofilter acclimatization which can impact DOC removal rates. It was important to operate the biofilter process as close to steady-state as possible to achieve optimum results (Carlson and Amy, 1996; Prévost et al., 1997; Urfer et al., 1997).

Filter acclimatization can be roughly estimated by monitoring the removal efficiency of DOC, or the number of bed volumes filtered. Figure 3-6 illustrates the removal of DOC through the filter as a function of time to indicate when filter acclimatization was achieved. Figure 3-6 also illustrates the approximate number of bed volumes filtered prior to acclimatization.





Acclimatization or assurance that the filter was operating at steady-state was essential in order to begin any analysis. An excess of 4 months and approximately 10,000 bed volumes was necessary in order to ensure acclimatization of the filter.

As evidenced in other research, it was important to closely monitor and manage water temperature, NOM source and ozone dose in order to ensure constant biodegradation in the system (Hozalski et al., 1999). Though the NOM source remained consistent, seasonal changes may have affected the performance of the biofilters.

# **3.2 Biodegradation Experiments**

# 3.2.1 Raw water preparation

Please refer to Section 3.1.1 for relevant discussion regarding raw water preparation.

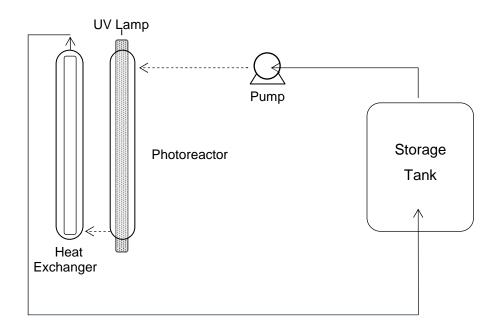
#### **3.2.2 Feed Water Preparation**

## 3.2.2.1 Ozonation

A description of the apparatus used for ozonation of the raw water is presented in Section 3.1.2. For the batch biodegradation experiments, the target ozone doses for the feed water were 1 mgO<sub>3</sub>/mg DOC, 2mg O<sub>3</sub>/mg DOC and an extended ozone dose. The extended ozone dose in this case was in the order of 25mg O<sub>3</sub>/mg DOC.

# 3.2.2.2 UV/H<sub>2</sub>O<sub>2</sub>

The UV/H<sub>2</sub>O<sub>2</sub> oxidation apparatus consisted of a semi-batch reactor comprising a storage tank, UV light source, recirculation line and heat exchanger illustrated in Figure 3-7. The low-pressure mercury lamp (Light Sources Inc., G10T5  $\frac{1}{2}$ L) was capable of an output of 5.7W at 254nm. The lamp was enclosed in a glass sleeve giving a net volume capacity of 85*mL*. Raw water was re-circulated through the reactor at a constant flow rate.



#### Figure 3-7 - Experimental semi-batch UV/H<sub>2</sub>O<sub>2</sub> reactor

UV fluence was calculated using potassium ferrioxalate actinometry as described elsewhere (Murov, 1993). Based on the desired UV dose and the characteristics of the source water,

irradiation times were calculated based on Equation 3-4 and Equation 3-5 as described in Bolten and Linden (2003).

Equation 3-4  $IT \cdot (\min) = D \times \frac{V_w}{V_r} \times \frac{1}{J_{UV} \times wf \times 60 \text{ s/min}}$ Equation 3-5  $wf = \frac{1 - 10^{-P_L \times Abs}}{P_L \times Abs \times \ln(10)}$ 

where D is the desired UV dose,  $V_w$  is the volume of water treated,  $V_r$  is the volume of the reactor,  $J_{UV}$  is the output of the lamp (*mw/cm*<sup>2</sup>), wf is the water factor,  $P_L$  is the path length (0.5*cm*) and Abs is the absorbance of the sample at 254*nm*.

The storage tank contained a 1*L* solution of raw water to which an  $H_2O_2$  solution (30%, Fisher Scientific) was added to achieve a final concentration of approximately 10mg/L.  $H_2O_2$  concentration was calculated using Equation 3-6 as described in Klassen et al. (1994).

# Equation 3-6 $H_2O_2[ppm] = (A - A_o) \times 10 \times D \times (0.7776 * S)$

where A is the absorbance of the prepared sample at 351nm, A<sub>o</sub> is the absorbance of the blank at 351nm, D is the additional dilution (1 if none), and S is the sample volume (0.5mL).

Following UV/H<sub>2</sub>O<sub>2</sub> treatment of the raw water samples, H<sub>2</sub>O<sub>2</sub> was quenched using 0.2mg/L bovine liver catalase (lyophilized powder,  $\geq 10,000$  *units/mg* protein, Sigma Aldrich Canada) as recommended by Liu et al. (2003). There was no observable increase in the DOC following the addition of 0.2mg/L of catalase.

For the batch biodegradation experiments, the target  $UV/H_2O_2$  doses for the feed water are summarized in. A full summary of raw data is provided in Appendix B.

Desired Dose, D (mJ/cm <sup>2</sup> )	H <sub>2</sub> O <sub>2</sub> Concentration ( <i>mg/L</i> )	Volume of Water Treated ( <i>mL</i> )	Irradiation Time , IT ( <i>min</i> )
4000	0	1000	65.5
2000	10	1500	49.1
4000	10	1500	99.0

Table 3-4 - UV/H<sub>2</sub>O<sub>2</sub> experiment conditions

## **3.2.3** Batch Biodegradation Experiments

#### 3.2.3.1 Batch System

The biodegradation experiments were completed based on similar work by Allgeier et al. (1996), Carlson and Amy (1997) and Yavich et al. (2004) and is described as follows.

1. GAC is first harvested from the acclimated filter bed. In order to ensure a representative sample of biomass was selected, the entire contents of the column were removed and mixed prior to harvesting. The amount harvested was selected to achieve a specific biomass load in the batch biodegradation test over a 24 hour period that was similar to that in BAC Column 1. Equation 3-7 describes this relationship:

Equation 3-7 
$$V_{harvest} = \left(\frac{V_{sample}}{Q_{Column\cdot 1}}\right) \times \frac{V_{Column\cdot 1}}{24hrs \times 60 \min/hr}$$

where  $V_{harvest}$  is the amount of GAC to be harvested (in mL),  $V_{sample}$  is the amount of sample used in the biodegradation experiment (50*mL*),  $Q_{Column1}$  is the flow rate of Column 1 (1.1*mL/min*) and  $V_{Column1}$  is the volume of GAC in Column 1.

Approximately 0.7*mL* of GAC was harvested for each batch biodegradation experiment. The same amount was used for biodegradation experiments performed on Column 2.

2. The harvested GAC was placed in a 150*mL* Erlenmeyer flask. Prior to analysis, the flasks were meticulously cleaned with detergent and rinsed at least three times with tap water, distilled water and ultra-pure water (Millipore Aqua-Q Ultra-Pure Water System) and baked in a muffle oven at 450°C for a minimum of 4 hours. Prior to use,

the muffled flasks were stored in a clean container with aluminum foil covering the openings.

- 3. Exactly 50*mL* of feed water was added to each Erlenmeyer flask. Table 3-5 describes the type of sample water that was considered for each biodegradation experiment.
- 4. Batch reactors were then placed in an incubated shaker (NBS 4230, GMI Inc.) at 100 RPM and temperature controlled at 21°C for each of the following times: 4, 8, 12, 18 hours and 1, 2, 3, 4, 5, 6 and 7 days. The temperature was selected to be consistent with the temperature observied during biofiltration (Section 3.1.3). A summary of each of the different scenarios is presented in Table 3-5.

Source of Biomass	Oxidant	Dose	Reaction Times	
	None	-		
Separate experiments performed using both BAC Column 1 & 2	Ozone	1 mg/ mg DOC		
	Ozone	2 mg/ mg DOC	4, 8, 12, 18	
	Ozone	Extended Dose (≈25 mg/mg DOC)	4, 8, 12, 18 hrs; 1, 2, 3, 4, 5, 6, 7 days	
	AOP	2000 mJ/cm2 & 10 mg/L $H_2O_2$	5, 6, 7 days	
	AOP	4000 mJ/cm2 & 10 mg/L $H_2O_2$		
	AOP	4000 mJ/cm2 & 0 mg/L $H_2O_2$		

Table 3-5 - Biodegradation experiment description

5. Once the reaction time was complete, the samples were removed and immediately filtered through 0.45µm filter paper (Millipore, Fisher Scientific) and stored at 4°C for subsequent analysis of DOC, UVA and molecular weight by HPSEC.

All batch biodegradation tests were fully randomized so as to minimize potential human and experimental error. For each of the conditions described in Table 3-5 a minimum of three replicates was performed.

A simple decay curve was used to analyze all data obtained from biodegradation experiments. Equation 3-8 was used for analysis of biodegradation curves.

# Equation 3-8 $y = a + b \exp(-cx)$

where, a represents the Concentration of non-biodegradable DOC ( $DOC_{non}$ ), b represents the initial Concentration of DOC, less the  $DOC_{non}$  ( $DOC_i$ ), c represents the kinetic rate constant for the biodegradation reaction (kinetic rate constant,  $k_{DOC}$ )

For each of the biodegradation curves obtained, the values of a, b and c were averaged for each scenario. This allowed for comparison of each of these values to determine whether any trends existed with respect to biodegradation. The most important parameter was of course the kinetic rate constant which was indicative of the rate at which DOC was biodegraded by the available biomass.

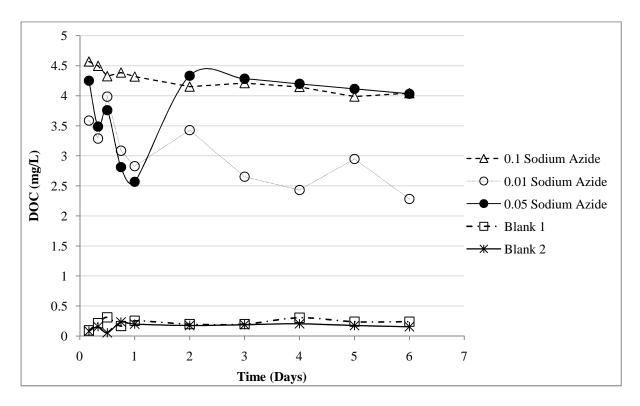
#### 3.2.3.2 Biomass Analysis

As a secondary confirmation of acclimatization, it was necessary to confirm the presence of biomass within the filter and to confirm that the removal of DOC was due to biodegradation and not adsorption to GAC. The biomass was qualitatively examined using acridine orange staining similar to the technique described in Hobbie et al. (1977). Samples of activated carbon from each of the columns were collected and stained with 0.01% acridine orange prepared with ultra-pure laboratory water and preserved with 2% formaldehyde. Samples were rinsed with ultra-pure water prior to analysis by fluorescing microscope. Because of the shape, size and contour of the granular activated carbon particles it was necessary to use a laser scanning confocal microscope capable of examining fluorescent emissions. A Zeiss Laser Scanning Microscope 510 DuoScan equipped with an LSM 5 Pascal Exciter and Zeiss AxioCam High Resolution camera was used. Results are provided in Appendix C.

In addition to analysis by microscopy, total volatile solids were also determined in accordance with Standard Methods 2540 (APHA, 2005) as an indicator of biomass growth. Biomass growth was also confirmed through visual inspection of the filtration apparatus. Results are provided in Appendix C.

Sample blanks were completed by repeating the biodegradation test with the harvested GAC using distilled and deionized ultrapure water (MilliQ water). In addition, sodium azide was used to kill the existing biomass so that any uptake by adsorption could be

accounted for. A solution of 0.1N Sodium Azide was required. No significant amount of DOC loss or gain can be attributed to the biomass and, therefore, it is expected that the biodegradation curves obtained in this study reflect the biodegradation potential of the harvested biomass. Results are illustrated in Figure 3-8.



#### Figure 3-8 - Quality control biodegradation curves

In addition, a secondary quality control method was employed. At random, double biomass or half of the biomass used in the original biodegradation experiment was used and these results were compared to the rest of the biodegradation test results. When double the amount of biomass was placed in the reactor, it was expected that it would removed the same amount of DOC, but in half the time. When half of the biomass was placed in the reactor, it was expected that it would take twice the time to remove the same amount of DOC. Results achieved during this process were as expected and repeated at random, to ensure good behaviour during the biodegradation test.

# **3.3 Analytical Methods**

#### 3.3.1 Glassware

Due to low concentrations of each of the various parameters examined in both the raw, feed, biofiltered and biodegraded water matrix, glassware was meticulously cleaned prior to use in order to minimize any potential contamination. All glassware, lids, Teflon-lined septa, lids and sampling vials were washed with detergent and rinsed at least three times with tap water, distilled water and ultrapure water (Millipore Aqua-Q Ultra-Pure Water System). In addition, all non-volumetric glassware and sampling vials were then baked in a muffle oven at 450°C for a minimum of 4 hours. Volumetric glassware was baked at 105°C in an oven for a minimum of 1 hour. After cleaning and baking, all glassware was stored in a clean, dry place with aluminum foil covering all openings.

# 3.3.2 pH

Throughout the duration of the experiments, pH was measured using an Accumet pH Meter 50 (Fisher Scientific). Prior to analysis, the pH meter was calibrated using three standard buffer solutions of pH 4.0, 7.0 and 10.0. The target pH of the prepared raw water was 7.0.

## 3.3.3 Temperature

Temperature was measured using a Fisherbrand\* general purpose thermometer (Fisher Scientific). Measurements were recorded to the nearest degree.

## 3.3.4 Alkalinity

Alkalinity was measured in accordance with Standard Methods 2320 (APHA, 2005) described below.

- 100ml of water sample was measured and place in Erlenmeyer flask. 1 drop of 0.1N sodium thiosulfate was then added to the sample.
- The sample was placed on stir plate with stir bar and one aliquot of phenolphthalein indicator was added.

- The sample was then titrated with standard acid solution until the red colour was almost discharged.
- One aliquot of bromcresol green was then added and the water sample was titrated until the colour changed from blue to yellow.

Alkalinity was calculated using Equation 3-9.

Equation 3-9 
$$mgCaCO_3 / L = \frac{V_{titred} \times N \times 50,000}{V_{sample}}$$

where  $V_{titred}$  is the volume of titrant used, N is the normality of the standard acid and  $V_{sample}$  is the volume of sample used (100*mL*).

The target alkalinity of the prepared raw water was 50mg/L as CaCO<sub>3</sub>.

## 3.3.5 Hardness

Total hardness was measured in accordance with Standard Methods 2340 C. EDTA Titrimetric Method (APHA, 2005) described below:

- 25*mls* of sample was diluted to 50*ml* with distilled water and placed in a 250ml Erlenmeyer flask. The flask was then placed on a stir plate with a stir bar.
- 1-2*ml* of buffer solution and one aliquot of Total Hardness Indicator were added to the sample.
- The sample was then titrated with EDTA until the reddish tinge was discharged and a pure blue colour remained. The entire titration was completed within 5 minutes to minimize CaCO<sub>3</sub> precipitation.

Total hardness was calculated using Equation 3-10.

Equation 3-10 
$$mgCaCO_3 / L = \frac{V_{titred} \times 1000}{V_{sample}}$$

where  $V_{titred}$  is the volume of titrant used, and  $V_{sample}$  is the volume of sample used (25*mL*).

The target total hardness of the prepared raw water was 50mg/L as CaCO<sub>3</sub>.

## **3.3.6** Total Organic Carbon (TOC)

For the raw, feed, biofiltered and biodegraded water analyzed in this experiment, nearly all (90%) of the TOC was present as DOC.

DOC concentrations were measured in accordance with the Persulfate-Ultraviolet Oxidation Method in Standard Methods 5310C (APHA, 2005). A Dohrman Pheonix 8000 UV-Persulfate Analyzer was used with a calculated method detection limit (MDL) of 0.1mg/L (Standard Methods 1030C, APHA 2005). Samples were filtered through  $0.45\mu$ m filter paper (Millipore, Fisher Scientific) prior to analysis. Due to the low concentrations of DOC present in the waters analyzed, the lowest analytical range of the instrument was employed (0.1 - 20mg/L). Three replicates of each sample were collected and each one was analyzed three times. A 5mg/L standard was analyzed for each instrument run. Blanks were prepared using ultra-pure laboratory water.

#### 3.3.7 Ultraviolet Absorbance (UVA) & Specific Ultraviolet Absorbance (SUVA)

Ultraviolet absorbance (UVA) was measured at 254nm (UV<sub>254</sub>) in accordance with Standard Methods 5910B (APHA, 2005). A UV 300 UV-Visible spectrometer (Spectronic Unicam) with a 1cm pathlength quartz cuvette was used. Samples were filtered through 0.45µm filter paper (Millipore, Fisher Scientific) prior to analysis. Three replicates of each sample were collected and each one was analyzed three times. A 5mg/L standard was analyzed for each instrument run. Blanks were prepared using ultra-pure laboratory water.

Specific UV was calculated based on the  $UV_{254}$  and DOC values using Equation 3-11. SUVA values were multiplied by 100 given that measurements were done with a 1*cm* UV cell (Xie, 2004).

**Equation 3-11** 

$$SUVA = \frac{UV_{254}}{DOC} \times 100 [L/mg \cdot m]$$

where UV254 is the absorbance at 254nm (cm-1) and DOC is the dissolved organic carbon content (mg/L).

# 3.3.8 Molecular Weight Determination by High Performance Size Exclusion Chromatography (HPSEC)

#### **3.3.8.1 HPSEC Analysis**

HPSEC analysis was performed using a Waters 2695 Separation Module HPLC system equipped with a Waters 2998 Photodiode Array Detector, set to detection at 260nm. 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 0.1M ionic strength and the column flowrate was 0.7 mL/min. Results from the HPSEC provided the detector response for a given retention time. AMW was correlated to the retention time by performing a calibration with Polystyrene Sulfonate Standards (American Polymer Standards Corporation) with defined molecular weights of 1100, 4000, 5000 and 7000 Da. A calibration curve with a coefficient of determination of 0.9975 is illustrated in Figure 3-9. Molecular weights of the standards did not cover the complete range of molecular weights considered in the present study; therefore the calibration curve was extrapolated using the equation displayed in Figure 3-9 for analysis.

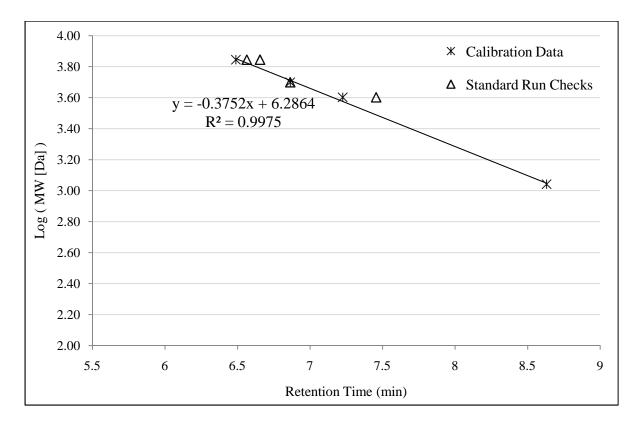


Figure 3-9 - HPSEC calibration curve

Each HPSEC run included standards that were verified against the original calibration curve to ensure consistency and are also shown in Figure 3-9.

A typical HPSEC chromatogram for the sample water is shown in Figure 3-10. The different NOM fractions are depicted in Figure 3-10, as described previously. The molecular weight estimates of these fractions were used for subsequent analysis.

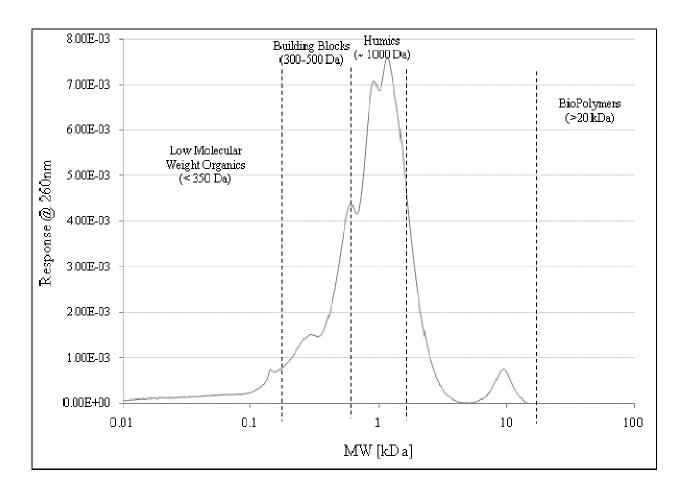


Figure 3-10 - Typical HPSEC chromatogram

It is important to note that baselines varied between runs, resulting in small shifts in chromatogram results. Baselines were therefore adjusted to normalise the data and allow for proper peak resolution. Baselines were adjusted using Systat's Peakfit version 4.12 "Baseline Fit and Subtract" function. To ensure reproducibility, results were confirmed through the analysis of replicates.

#### **3.3.8.2 Resolution of HPSEC Chromatograms**

Although the chromatograms provide insight into the characteristics of the NOM, it is difficult to quantitatively compare the chromatograms from different analyses. To overcome this limitation, the chromatograms were deconvoluted into a series of Gaussian peaks (Thomson et al., 2004; Sarathy and Mohseni, 2007). Using Systat's Peakfit software version 4.12, the "Autofit Peak III Deconvolution" function was applied with the parameters outlined in Table 3-6.

Parameter	Setting
Peak Type	Extreme Value 4 Parameter Tailed (Amplitude)
Response Width	20s
Response Width Defined at	Full Width at Half- Maximum
Frequency Domain Filter	60%
Amplitude Rejection Threshold	4%
Minimum R <sup>2</sup> Value	> 0.99

Table 3-6 - Autofit Peak III deconvolution parameters

The above settings were selected based on the minimum  $R^2$  of the fit and yielded a minimum  $R^2$  of 0.99 for all fitted chromatograms. These settings resulted in a 14-peak chromatogram that was used to fit all HPSEC data, presented in Figure 3-11. The summation of the 14 peaks corresponds to the original HPSEC chromatogram (Figure 3-11).

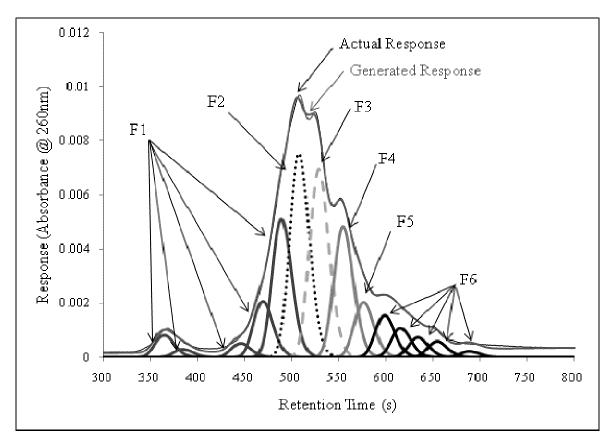


Figure 3-11 - HPSEC chromatogram resolution.

Showing the actual response, and the generated response from summation of the 14 peaks fitted. Peaks were categorized based on molecular weight (Da): >1350 (F1), 1050 - 1350 (F2), 750-1050 (F3), 500-750 (F4), 300-500 (F5), <300 (F6)).

The resolved peaks were categorized based on molecular weight and placed into apparent molecular weight (AMW) fractions based on their retention times using the calibration procedure discussed in Section 3.3.8.1. The largest fraction represented molecular weights greater than 1350Da and corresponded to the leading edge of the chromatogram (F1). The remaining peaks were resolved into the following fractions: 1050 - 1350 (F2), 750-1050 (F3), 500-750 (F4), 300-500 (F5), <300 (F6). The fractions F1, F2, F3, and F4 roughly corresponded to the humic substances, F5, to the building blocks and F6, to the lower molecular weight organics and neutrals, as depicted in Figure 3-10 (Kennedy et al., 2005). The areas of each individual peak were quantified to determine the area corresponding to each fraction.

# **3.3.9** Disinfection By-Product Formation Potential (DBPFP)

To quantify the disinfection by-product formation potential (DBPFP) of raw, treated and biodegraded waters the Uniform Formation Conditions (UFC) Method was performed (Summers et al., 1996). This method was chosen over the traditional seven-day formation potential test outlined in Standard Methods 5710 (APHA, 2005) as the traditional method applies high chlorine doses over long incubation time, which may lead to higher concentrations of DBPs, and higher chlorine-based over bromine-based DBPs (Symons et al., 1993; Symons et al., 1996; Shukairy and Summers, 1995). The UFC procedure targets conditions outlined in Table 3-7.

Uniform Formation Conditions		
pH	8.0 ± 0.2	
Temperature	20.0 ± 1.0	
Incubation Time	24 ± 1 hr	
Chlorine Residual (as Free Chlorine after 24 hrs)	$1.0 \pm 0.4 \ mg/L$	

 Table 3-7 - Uniform formation conditions

The UFC procedure used was as follows:

- 1. Samples were removed from storage at 4°C and allowed to equilibrate to room temperature (approximately 1 hour).
- 2. 2*mL/L* of pH 8 borate buffer (described in Summers et al., 1996) was added to the water sample and the pH was adjusted to 8.0 using sulphuric acid (Fisher Scientific)
- 3. An aliquot of the sample was placed into pre-cleaned 43*mL* amber glass vials until three quarters full.
- Dosing of the aliquot was then done using the combined hypochlorite-buffer solution (described in Summers et al., 1996), and inverted twice using a Teflon-lined screw cap.
- 5. Vials were then filled with remaining sample and capped headspace free. The vials were inverted a minimum of ten times.

6. Vials were incubated for 24 hours at 20.0°C. Following incubation, test vials were opened to measure the chlorine residual and pH, and quenched for subsequent analysis.

In order to determine the correct dosing amount, trial and error at various Cl<sub>2</sub>:TOC ratios was used to determine the required dose to allow for a  $1.0 \pm 4mg/L$  chlorine residual after 24 hours of incubation.

Prior to trihalomethane analysis, the aliquots of sample were quenched with 5g/50mL sodium thiosulfate (Fisher Scientific). Prior to haloacetic acid analysis, the aliquots of sample were quenched with 2.5g/50mL ammonium chloride (Fisher Scientific).

#### **3.3.10** Trihalomethanes (THMs)

Trihalomethane (THM) concentrations were measured based on the Liquid-Liquid Extraction Gas Chromatography Method described in Standard Methods 6232B (APHA, 2005). Pentane was used as the extraction solvent. Pentane was cleaned in accordance with the method developed at the UBC Environmental Engineering Laboratory which has been shown to produce pentane which is below the MDL for chloroform concentration (Bush, 2008). The following procedure was used to clean pentane:

- A gas chromatograph column was packed with basic alumina and placed in a Hewlett-Packard 5880A Series GC and heated to 220°C while passing helium carrier gas through the column. To ensure negligible concentrations of chloroforms, the column was heated for minimum of 24 hours.
- Pentane was then passed through the alumina-packed column with the help of a 100cc glass syringe (Benton Dickinson Luer-Lock Reusable Syringe, Fisher Scientific). Clean pentane was collected in a pre-cleaned amber bottle.

To minimize re-contamination of the pentane, cleaned pentane was used within 2 days, or it was necessary to repeat this procedure.

The following procedure was then used for trihalomethane extraction and analysis:

- 1. Pre-quenched samples were removed from storage at 4°C and allowed to equilibrate to room temperature (approximately 1 hour).
- Clean pentane was spiked with 1,2 dibromopropane as the internal standard to achieve a final concentration of 60µg/L.

- Calibration standards were prepared from commercially available THM calibration mixes (approximately 99% purity) in methanol (Supelco Analytical). A minimum of 5 standards covering the expected range of results were prepared.
- 4. Calibration standards and blanks were made using a commercially available brand of ozonated spring water (Safeway Select Refreshe, Canada Safeway Ltd) to reduce the potential for contamination from chloroform.
- 5. Exactly 5mL of sample was removed and discarded.
- Exactly 4mL of clean pentane was added to each sample vial. Each vial was then shaken vigorously for 5 minutes. Phases were allowed to separate for at least 2 minutes.
- 7. The upper layer was then removed from each vial and placed in a pre-cleaned GC vial using disposable Pasteur pipettes (Fisher Scientific).
- 8. Extracts were analyzed immediately or stored in the freezer at  $\leq 10^{\circ}$ C.

Extracts were analyzed for chloroform, bromoform, dibromochloromethane and bromodichloromethane using a Hewlett Packard 6890 Series GC with a Ni<sup>63</sup> electron capture detector (ECD) affixed with a Hewlett Packard 7672A autosampler. Helium was used as the carrier gas. One microliter ( $\mu$ L) of extract was injected in the GC column for each analysis. The GC-ECD properties for the THM analysis are outlined in Table 3-8.

Parameter	Setting	
Injector		
Туре	Splitless	
Temperature	90°C	
Detector		
Туре	ECD	
Temperature	260°C	
Oven		
Initial Temperature	30°C, hold for 2 minutes	
Ramp	6°C/min	
Final Temperature	120°C	

Table 3-8 -	GC-ECD	properties for	<b>THM analysis</b>
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Retention times for each of the compounds are summarized in Table 3-9.

Compound	Retention Time (min)
Chloroform	6.552
Bromodichloromethane	9.876
Dibromochloromethane	13.553
IS (1,2 DBP)	15.6
Bromoform	17.307

#### Table 3-9 - THM retention times (min)

The sum of each of the above compounds (excluding the internal standard), were used to determine the total THM (THM<sub>4</sub>) concentration in the source water.

# 3.3.11 Haloacetic Acids (HAAs)

Haloacetic acids (HAAs) were measured based on the Liquid-Liquid Microextraction Gas Chromatography Method described in USEPA 552.3 (USEPA, 2003).

The following procedure was used for haloacetic acid extraction and analysis:

- 1. Pre-quenched samples were removed from storage at 4°C and allowed to equilibrate to room temperature (approximately 1 hour).
- 2. 30*mL* of sample was measured in a pre-cleaned graduate cylinder. The remaining sample was discarded and exactly 30*mL* of sample was placed back in the vial. The graduate cylinder was rinsed with ultra-pure laboratory water between samples.
- Calibration standards were prepared from commercially available HAA calibration mixes (approximately 99% purity) in methanol (Supelco Analytical). A minimum of 5 standards covering the expected range of results were prepared.
- 4. Calibration standards and blanks were made using a commercially available brand of ozonated spring water (Safeway Select Refreshe, Canada Safeway Ltd) to reduce the potential for contamination.
- 5. An  $80\mu g/L$  surrogate solution of 2,3 dibromopropionic acid was prepared in methyl tert butyl ether (MTBE). Exactly  $80\mu L$  of surrogate standard was added to the water sample using a disposable-tip pipette. The tip was placed below the surface of the water and the vial was capped and inverted a minimum of 3 times.
- 6. The pH was adjusted through the addition of 2mL of concentrated sulphuric acid.

- Approximately 14g of sodium sulphate (muffled at 400°C for 4 hours and cooled) was added immediately after addition of sulphuric acid. The vial was capped and shaken using a Burrell Wrist-Action Shaker (Burrell Scientific) for approximately 1 minute.
- 8. A  $1\mu g/mL$  internal standard solution was prepared using 1,2,3 trichloropropane. Exactly 4mL of internal standard was added to the sample and shaken using a Burrell Wrist-Action Shaker for approximately 3 minutes.
- Phases were allowed to separate for 5 minutes. The upper layer was transferred to a pre-cleaned COD vial using a disposable Pasteur pipette.
- 10. 3*mL* of 10% sulphuric acid in methanol was added to each COD vial using a disposable-tip pipette. Vials were capped and inverted.
- 11. Vials were placed capped in an uncovered water bath at a temperature of 50°C for 2 hours. The water level was carefully monitored so as not to exceed half the depth of the COD vial. If the tube walls are heated, the tubes can evaporate some of the measured compounds, leading to higher variability in analytical results (EPA, 2003).
- 12. Vials were removed and allowed to cool.
- 13. 5*mL* of 150g/L sodium sulphate solution was added to each COD vial and vortexed using a vortex mixer (Fisher Scientific) for 5 seconds.
- 14. Phases were allowed to separate for no more than 2 minutes to limit loss of HAAesters.
- 15. The upper layer was then transferred to a second pre-cleaned COD vial.
- 16. 1mL of saturated sodium bicarbonate solution was added to the vial using a pipette. Each vial was then vortexted four times for five seconds each time. Phases were allowed to separate for 1 minute.
- 17. The upper layer was then removed from each vial and placed in a pre-cleaned GC vial using disposable Pasteur pipettes.
- 18. Extracts were analyzed immediately or stored in the freezer at  $\leq 10^{\circ}$ C.

Extracts were analyzed for all 9 HAAs including bromoacetic acid (MBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chloroacetic acid (MCAA), chlorodibromoacetic acid (CDBAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), tribromoacetic acid (TBAA), and trichloroacetic acid (TCAA). Analysis was performed using a Hewlett Packard 6890 Series GC affixed with a Hewlett Packard 5973 Mass Selective (MS) detector and Hewlett Packard 6890 Series autosampler. Helium was used as the carrier gas. One microliter ( $\mu$ L) of extract was injected in the GC column for each analysis. The GC-MS properties for the HAA analysis are outlined in Table 3-10.

Parameter	Setting		
Injector			
Туре	Splitless		
Temperature	200°C		
Detector			
Туре	MS		
Oven			
Initial Temperature	30°C, hold for 8 minutes		
Ramp	5°C/min for 16 minutes		
Final Temperature	110°C		

Table 3-10 - GC-MS properties for HAA analysis

Retention times for each of the compounds are summarized in Table 3-11.

Compound	Quantification Ion	Secondary Ions	Retention Time (min)
MCAA	105	64, 77	9.124
MBAA	152	93, 121	12.218
DCAA	83	87, 85	12.81
TCAA	117	119, 141	16.002
BCAA	127	129, 131	16.264
IS (1,2,3 TCP)	75	110, 112	16.481
DBAA	173	171, 175	19.27
BDCAA	163	141, 161	19.468
CDBAA	205	207, 209	22.658
Surrogate (2,3 DBPA)	165	167	22.72
TBAA	251	253, 231	25.65

Table 3-11 - HAA retention times (min)

The sum of each of the above compounds (excluding the internal standard and surrogate), were used to determine the total HAA (HAA<sub>9</sub>) concentration in the source water.

# **3.4 Quality Control/Quality Assurance**

#### **3.4.1** Sample Collection and Storage

QA/QC measures were implemented to verify integrity of the samples during collection and storage. All samples collected throughout the duration of the project were collected in amber glass vials and bottles to minimize any potential effects from exposure to light. All bottles were meticulously cleaned with detergent, tap water, distilled water, Millipore Aqua-Q Ultrapure water and baked at 400°C for a minimum of 1 hour prior to use. All samples were immediately stored at 4°C and analysed within one week of collection.

#### **3.4.2 Reagents and Laboratory Blanks**

All reagents used were laboratory quality unless otherwise stated. Storage blanks and laboratory blanks were used to determine if there was any contamination of the samples during sampling, storage or analysis. All blanks were made using Millipore Aqua-Q Ultrapure Water.

#### 3.4.3 Instrument Reproducibility

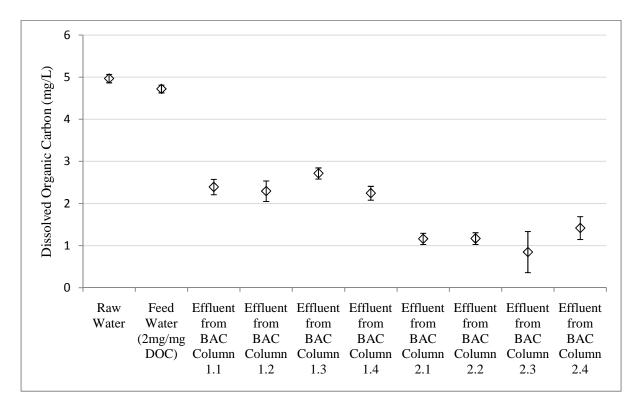
Instrument reproducibility was determined through the analysis of known standards for each of the analysis performed. The reproducibility of each of the analyses was validated by conducting recovery tests where an amount of known standard is spiked into one of the samples being analyzed. Recovery is expressed as the percentage (%) recovered from the initial spiked samples. Method detection limits were also performed according to Standard Methods 1030C (APHA, 2005).

# **4.0 RESULTS AND DISCUSSION**

# **4.1 Part 1 - Biofiltration Experiments**

# 4.1.1 Effect of Biofiltration on Dissolved Organic Carbon (DOC)

The effect of oxidation and subsequent biofiltration on DOC was determined throughout the course of this research project. Figure 4-1 illustrates the effect of oxidation and subsequent biofiltration on each of the four BAC Column 1 filters and the four BAC Column 2 filters. A full of summary of results obtained can be found in Appendix C. Note that the DOC reduction achieved by each of the replicates from BAC Column 1 and BAC Column 2 were similar.



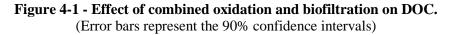
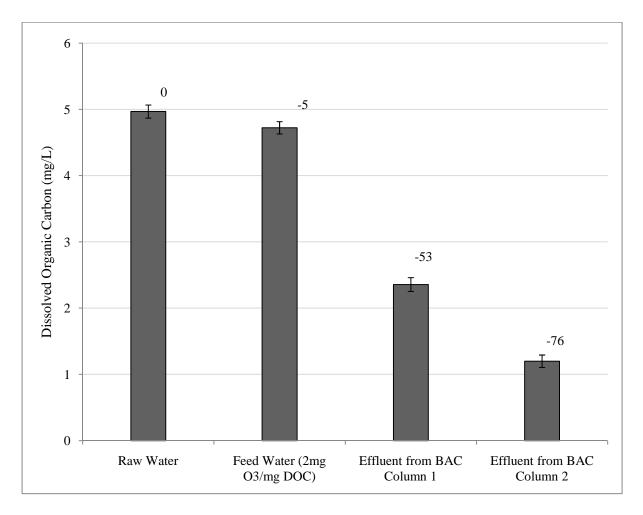
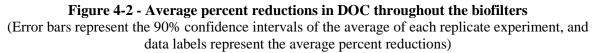


Figure 4-2 illustrates the average percent reductions in DOC throughout the biofiltration process.





Ozonation at 2 mgO<sub>3</sub>/mg DOC did not result in a significant reduction in DOC. These results are consistent with those from other research (Westerhoff et al., 1999; Amirsadari et al., 2001; AWWARF, 1999; Galapate et al., 2001). Biofiltration through BAC Column 1 resulted in significant removal of DOC of 48%. These results are consistent with those from other studies (Hozalski et al., 1999; Fonseca and Summers, 2003; Toor and Mohseni, 2007). The reduction in DOC observed is, however, 20% to 30% higher than that reported in other studies (Wang et al., 1995; Klevens et al., 1996; Cipparone et al., 1997). However, it is difficult to compare different studies that use different raw waters, EBCT, temperatures, etc. An additional 26% removal of DOC was observed following biofiltration through BAC Column 2. These results suggest that ozonation at the doses considered is not successful at reducing overall DOC levels, while biofiltration significantly reduces the DOC levels of the raw water.

## 4.1.2 Effect of Biofiltration on Specific Ultraviolet Absorbance (SUVA)

The effect of oxidation and subsequent biofiltration on SUVA was determined throughout the course of this research project. Figure 4-3 illustrates the effect of oxidation and subsequent biofiltration on SUVA on each of the four BAC Column 1 filters and the four BAC Column 2 filters. A full of summary of results obtained can be found in Appendix C.

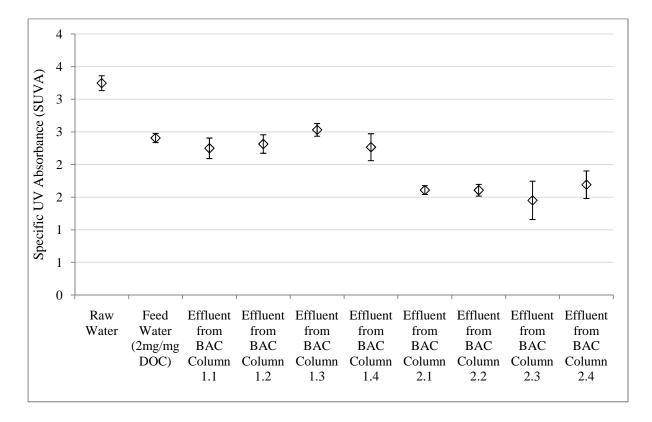


Figure 4-3 - Effect of combined oxidation and biofiltration on SUVA levels throughout the filter (Error bars represent the 90% confidence intervals)

Figure 4-4 illustrates the average percent reductions in DOC throughout the biofiltration process.

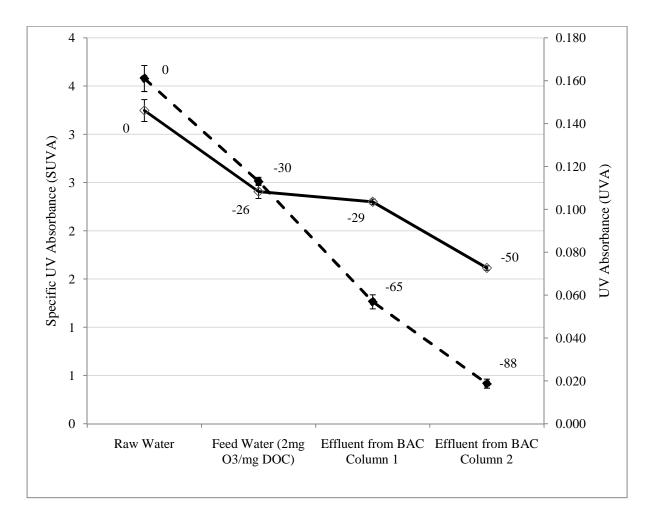
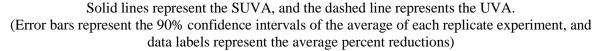


Figure 4-4 - Average percent reductions in SUVA throughout the biofilters.



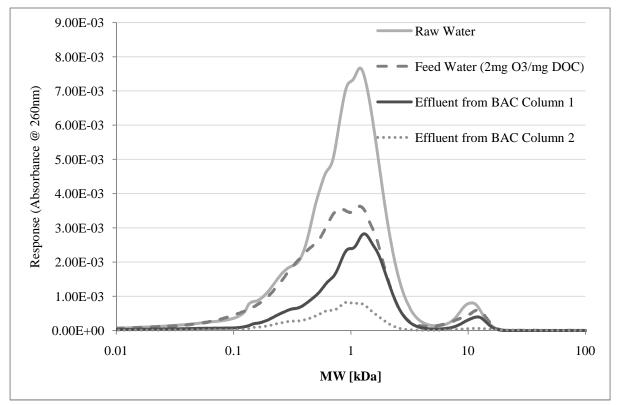
Ozonation at 2mgO<sub>3</sub>/mg DOC resulted in a significant reduction in SUVA of 30%. This result is consistent with those from previous work (Amirsadari et al., 2001; Gunten et al., 2009; Ko et al., 2000). Biofiltration through BAC Column 1 resulted in no significant additional reduction in SUVA, but an additional 35% reduction in UVA. These results are consistent with those from previous work (Hozalski et al., 1999; Toor and Mohseni, 2007). An additional 21% removal of SUVA and 23% removal in UVA was observed following biofiltration through BAC Column 2.

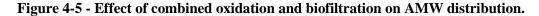
These results suggest that, while ozonation did not successfully reduce DOC levels (Section 4.1.1), it did significantly transform the NOM into less aromatic material. Although biofiltration in BAC Column 1 did not substantially change the fraction of the organic

material that was aromatic, it did significantly reduce the amount of aromatic material present in the feed water, given the high reduction in DOC observed in Section 4.1.1.

### 4.1.3 Effect of Biofiltration on Apparent Molecular Weight (AMW)

The effect of oxidation and biofiltration on the apparent molecular weight (AMW) was determined and is presented in Figure 4-5. The results are presented as averages of all replicate samples analyzed. Results from each of the replicate samples are presented in Appendix E.

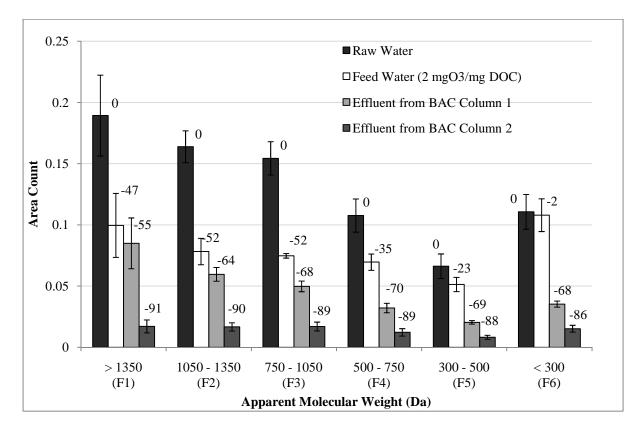




Ozonation at 2mgO<sub>3</sub>/mg DOC resulted in moderate reductions in the amount of NOM of most AMW. Further reduction in the amount of NOM of most AMW was observed following biofiltration through BAC Column 1 and BAC Column 2.

As discussed previously, although AMW chromatograms provide insight into the characteristics of NOM, it is difficult to quantitatively compare results from different analyses. For this reason, the AMW chromatograms were deconvoluted as discussed in Section 3.3.8.2. The area below each of the peaks provided a quantitative estimate of the

amount of organic material in that particular AMW range. The results from the deconvolution of AMW chromatograms are presented in Figure 4-6 and Table 4-1. Detailed results for each analysis is presented in Appendix F.



## Figure 4-6 - Effects of oxidation and biofiltration on AMW

(Error Bars represent the 90% confidence interval of the average of each of the replicate samples, data labels correspond to average percent reductions from raw water samples.)

### Table 4-1 - Summary of percent reduction in AMW fractions throughout biofiltration

(90% confidence intervals of the average of each of the replicates samples are shown in parentheses)

Source	> 1350 (F1)	1050 - 1350 (F2)	750 - 1050 (F3)	500 - 750 (F4)	300 - 500 (F5)	< 300 (F6)
Raw Water	0 (15)	0(7)	0(7)	0(11)	0 (13)	0(11)
2 mgO3/mg DOC	-47 (39)	-52 (20)	-52 (4)	-35 (14)	-23 (17)	-2 (18)
BAC Column 1	-55 (21)	-64 (8)	-68 (7)	-70 (10)	-69 (6)	-68 (6)
BAC Column 2	-91 (26)	-90 (17)	-89 (18)	-89 (21)	-88 (17)	-86 (16)

Ozonation at 2mgO<sub>3</sub>/mg DOC resulted in significant reductions in the amount of organic material for most of the AMW ranges, particularly the higher AMW NOM.

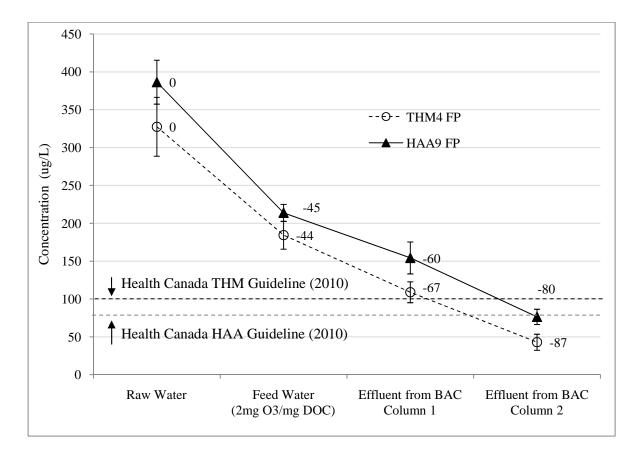
Biofiltration through BAC Column 1 resulted in overall reductions in the amount of organic material, in excess of 55%. A higher reduction in lower AMW content was observed. These results are consistent with previous work (Hozalski et al., 1999). A 19% to 36% reduction of organic material was observed following biofiltration through BAC Column 2. In contrast to BAC Column 1, larger reductions in the amount of AMW were observed for the larger AMW ranges for BAC Column 2.

These results suggest that BAC Column 1 preferentially biodegraded the smaller molecular weight NOM. Lower molecular weight compounds tend to be more biodegradable, therefore BAC Column 1 preferentially removed the lower AMW, more biodegradable organic compounds (Leisinger et al., 1981). The effluent of BAC Column 1 contained larger NOM that was less biodegradable (i.e. material that was not preferentially biodegraded in BAC Column 1). Although not readily biodegradable the greater amount of larger molecular weight NOM in the BAC Column 1 effluent, resulted in higher removal of this fraction in BAC Column 2, compared to the removal of lower molecular NOM.

It should be noted that the approach used to measure the molecular weight distribution of the NOM can only detect chromophoric NOM and ignored NOM that does not adsorb light at 200nm (such as biopolymers).

## 4.1.4 Effect of Biofiltration on Disinfection By-Produce Formation Potential (DBPFP)

The effect of oxidation and biofiltration on the disinfection by-product formation potential was determined and is presented in Figure 4-7. A full of summary of the raw data obtained can be found in Appendix G and Appendix H. THM4 formation potential corresponds to the formation potential of all four THMs; similarly, HAA9 formation potential corresponds to the formation potential of all nine known HAAs.

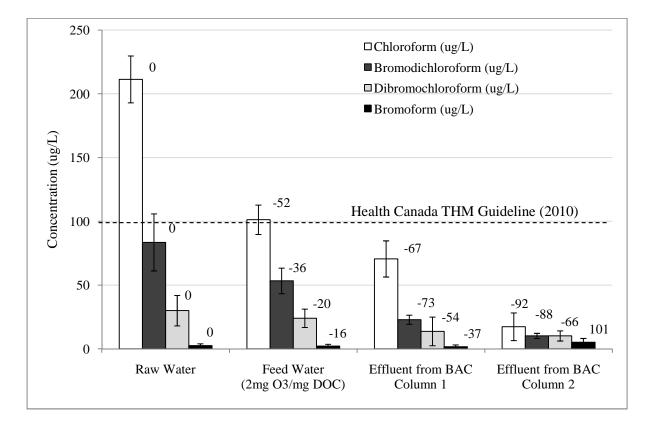


**Figure 4-7 - Reduction in THMFP and HAAFP throughout biofiltration** (Each point represents an average of at least 6 replicates, each chlorinated, incubated and analyzed separately. Data labels indicate the percent reduction based on average values. Error bars represent the 90% confidence interval for the average of the replicates analyzed.)

Ozonation at 2mgO<sub>3</sub>/mg DOC resulted in significant reductions in THMFP and HAAFP of 44% and 45% respectively. These results are consisted with those presented in other studies (Chin and Bérubé, 2004; Chowdhury et al., 2008). Biofiltration through BAC Column 1 resulted in additional reduction in THMFP and HAAFP of 23% and 15%, respectively. These results are consisted with previous work (Shukiary et al. .1992; Cipparone et al., 1997). However, these results are between 10% to 30% higher than previous work (Joslyn and Summer, 1992; Wang et al., 1995; Siddiqui et al., 1997). An additional 20% removal of HAAFP and THMFP was observed following biofiltration through BAC Column 2. Given the very high DBPFP in the raw water, only subsequent treatment by BAC Column 2 was able to lower the DBPFP under the Guidelines for Canadian Drinking Water Quality limits of 0.1(THMs) and 0.08 mg/L (HAAs).

These results suggest that ozonation caused a transformation in NOM, resulting in less aromatic compound (as discussed in Section 4.1.2) and therefore, ultimately significantly reduced the DBPFP. Similarly, BAC Column 1 and BAC Column 2 resulted in additional decreases IN DBPFP due to the reduction in aromatic compounds (as discussed in Section 4.1.2).

Further work was completed in order to determine the effect of oxidation and biofiltration on each of the DBPs. Figure 4-8 illustrates the removal efficiency of oxidation and biofiltration on the four known THMs.

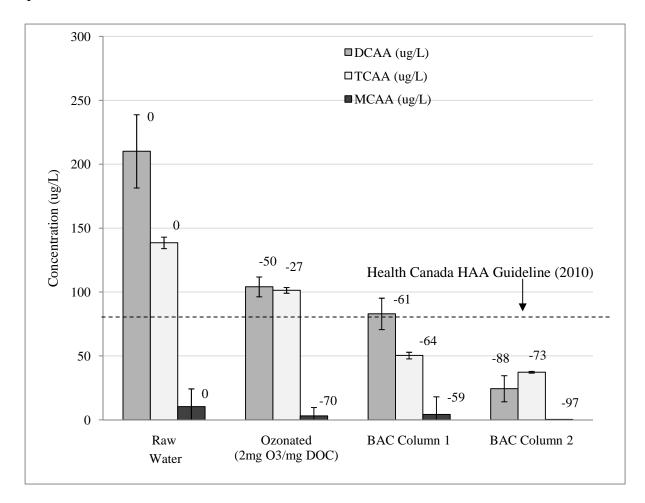


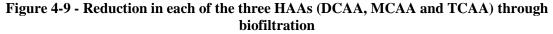
#### Figure 4-8 - Reduction of each of the four THMs through biofiltration

(Each point represents an average of at least 6 replicates, each chlorinated, incubated and analyzed separately. Data labels indicate the percent reduction based on average values. Error bars represent the 90% confidence interval for the average of the replicates analyzed.)

Ozonation at 2mgO3/mg DOC resulted in significant reductions in THMFP. Biofiltration through BAC Column 1 resulted in significant additional reductions in chloroform, bromodichloroform formation potential. An additional 25% removal of chloroform formation potential was observed following biofiltration through BAC Column 2. These results suggest that ozonation is successful at reducing THMFP; however, the overall reduction was not significant enough to meet current Guidelines for Canadian Drinking Water Quality limits. Subsequent biofiltration is necessary to lower the THMFP below guideline levels.

Figure 4-9 illustrates the removal efficiency of each oxidation condition on the three main HAAs; TCAA, MCAA and DCAA. Bromoacetic acids were not present in significant quantities, and have therefore been omitted from this discussion.





(Each point represents an average of at least 6 replicates, each chlorinated, incubated and analyzed separately. Data labels indicate the percent reduction based on average values. Errors bars represent the 90% confidence interval for the average of the replicates analyzed.)

Ozonation at 2mgO<sub>3</sub>/mg DOC resulted in significant reductions in HAAFP. A significant additional reduction of 33% was observed for TCAAFP levels following biofiltration through BAC Column 1. An additional 27% reduction of DCAAFP was

observed following biofiltration through BAC Column 2. No significant additional reduction of DCAAFP was observed following BAC Column 1.

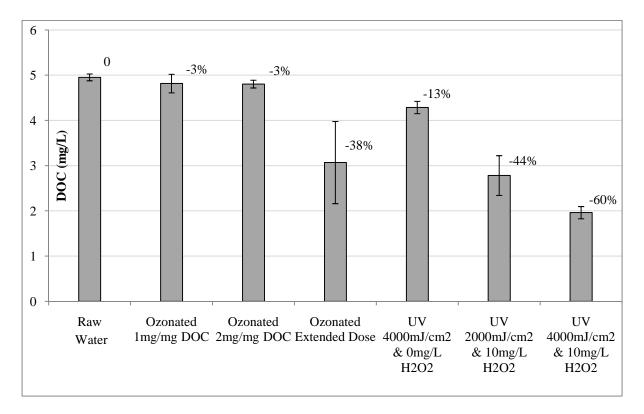
These results suggest that ozonation was successful at reducing HAAFP; however, the overall reduction was not significant enough to meet current Health Canada guidelines. Subsequent biofiltration is necessary to lower the HAAFP below guideline levels.

# 4.2 Part 2 - Biodegradation Experiments

# 4.2.1 Feed Water Analysis

## 4.2.1.1 Effect of Oxidation on Dissolved Organic Carbon (DOC)

The effect of oxidation on the dissolved organic carbon content was determined for the six conditions described previously and are presented in Figure 4-10. Raw data is provided in Appendix J.



## Figure 4-10 - Effect of oxidation on DOC (mg/L)

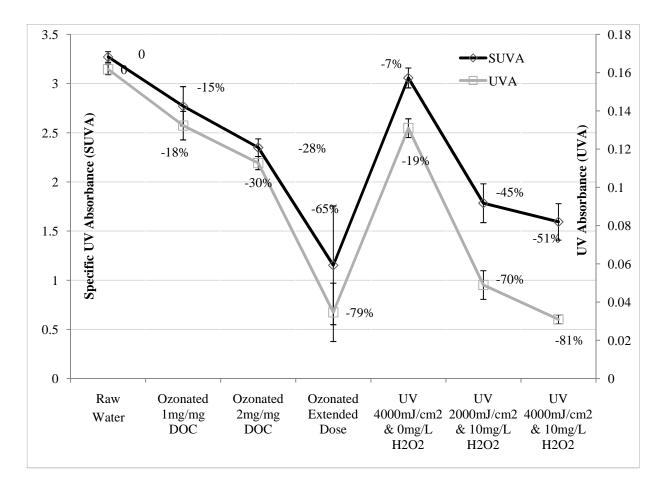
(Bars represent the average of all samples analyzed. Errors bars represent the 90% confidence interval and the data labels represent the average percent reduction.)

As expected, ozonation at 1 and 2 mgO<sub>3</sub>/mg DOC did not result in a significant reduction in DOC. These results are consistent with those from other research (Westerhoff et al., 1999; Amirsadari et al., 2001; AWWARF, 1999; Galapate et al., 2001). Ozonation at an extended dose of 25mgO<sub>3</sub>/mg DOC achieved a high removal of DOC, reducing the raw water DOC concentration by 38%. Compared to oxidation using ozone, oxidation using UV/H<sub>2</sub>O<sub>2</sub> resulted in greater reduction in DOC for the doses considered. UV/H<sub>2</sub>O<sub>2</sub> treatment at of 2000 and 4000 mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub>, resulted in significant reductions in DOC of 44% and 60% respectively. These results are consistent with those from other research (Goslan et al., 2006; Bond et al., 2009). UV/H<sub>2</sub>O<sub>2</sub> treatment at 4000mJ/cm<sup>2</sup> and 0mg/L H<sub>2</sub>O<sub>2</sub> resulted in a DOC reduction of 13%. This result was not expected, and the present study was unable to further determine the cause for this elevated DOC removal rate.

These results suggest that significant reduction in DOC is only observed following excessive oxidation of raw water, therefore at oxidation doses that are not economically feasible. In addition, high dose  $UV/H_2O_2$  was more successful at reducing the DOC levels of raw water than  $O_3$ , at the doses considered.

### 4.2.1.2 Effect of Oxidation on Specific Ultraviolet Absorbance (SUVA)

The effect of oxidation on the specific UV absorbance was determined for the six conditions described previously and are presented in Figure 4-11. A full of summary of results obtained can be found in Appendix J. For further comparison, a graph depicting UVA and SUVA removal resulting from oxidation is illustrated in Figure 4-11.



#### Figure 4-11 - Effect of oxidation on UVA and SUVA

(Data points represent the average of all samples analyzed. Errors bars represent the 90% confidence interval and the data labels represent the average percent reduction.)

Ozonation at 1 and 2 mgO<sub>3</sub>/mg DOC achieved overall UVA reductions of 18% and 30% respectively. These results are consistent with those from other research (Amirsadari et al., 2001; Gunten et al., 2009; Ko et al., 2000) as well as the results obtained in the biofiltration experiments (Section 4.1.2). However, these results are not consistent with those from some previous research, where UVA reductions in excess of 50% were achieved (Kim et al., 2006; Kim et al., 1997; Owen et al., 1995; Kaastrup and Halmo, 1989; Kleiser and Frimmel, 2000; Galapate et al., 2001). However, it is difficult to compare different studies that use different raw waters, EBCT, temperatures, etc. Ozonation at an extended dose of 25mgO<sub>3</sub>/mg DOC achieved an overall UVA reduction of 79%.

Compared to oxidation using ozone, oxidation using  $UV/H_2O_2$  resulted in greater reduction in UVA at the doses considered.  $UV/H_2O_2$  treatment at of 2000 and 4000 mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub>, resulted in reductions of UVA in excess of 70% and 81%, respectively.

These results are consistent with those from other research (Sarathy and Mohseni, 2009; Goslan et al., 2006; Toor and Mohseni, 2007).  $UV/H_2O_2$  treatment at 4000mJ/cm<sup>2</sup> and  $0mg/L H_2O_2$  resulted in a UVA reduction of 19%.

These results suggest that, while ozonation did not successfully reduce DOC levels (Section 4.2.1), it did significantly transform the NOM into less aromatic material. High dose ozonation, as well as AOPs, were successful at significantly lowering the fraction of the organic material that was aromatic, and the amount of aromatic material present in the feed water.

## 4.2.1.3 Effect of Oxidation on Apparent Molecular Weight (AMW)

The effect of oxidation on the apparent molecular weight (AMW) was determined for the six conditions described previously by HPSEC. Graphical results are shown in Figure 4-12. The results are presented as averages of all replicate samples analyzed. Results from each of the replicate samples are presented in Appendix E.

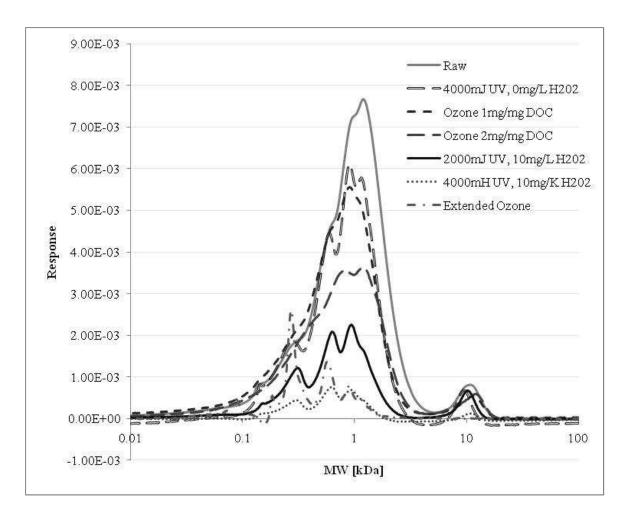


Figure 4-12 - Effect of oxidation on apparent molecular weight

Ozonation at 1 and  $2mgO_3/mg$  DOC resulted in moderate reductions in the amount of NOM of most AMW as observed in Figure 4-12. UV/H<sub>2</sub>O<sub>2</sub> treatment at of 2000 and 4000 mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub>, resulted in large reductions in the amount of NOM of most AMW. As expected, the 4000mJ/cm<sup>2</sup> and 0 mg/L H<sub>2</sub>O<sub>2</sub> resulted in what visually appeared to be the least impact on raw water levels.

As discussed previously, although AMW chromatograms provide insight into the characteristics of NOM, it is difficult to quantitatively compare results from different analyses. For this reason, the AMW chromatograms were deconvoluted, as discussed in Section 3.3.8.2. The area below each of the peaks provided a quantitative estimate of the amount of organic material in that particular AMW range. The results from the deconvolution of AMW chromatograms are presented in Figure 4-13 and Table 4-2. Detailed results for each analysis are presented in Appendix F.

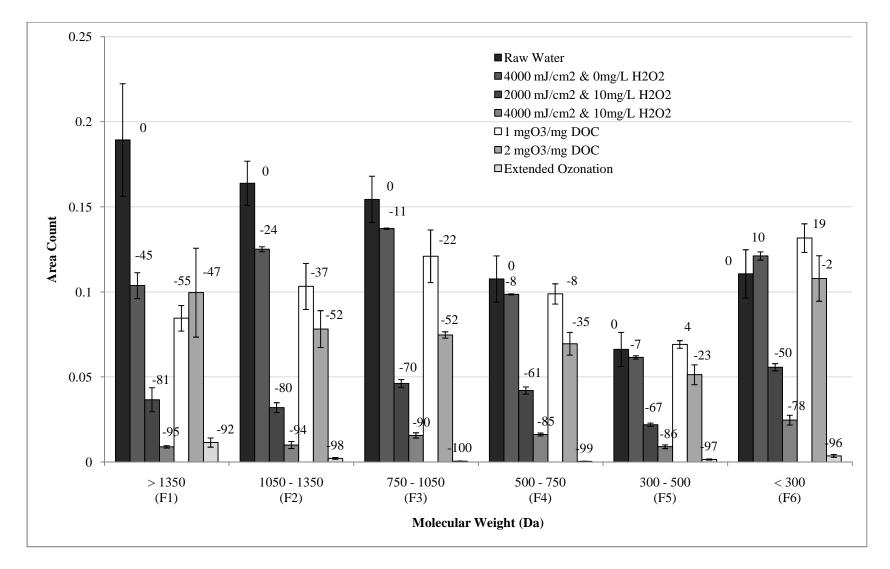


Figure 4-13 - Effects of oxidation on AMW.

Peaks were categorized based on molecular weight (Da): >1350 (F1), 1050 - 1350 (F2), 750-1050 (F3), 500-750 (F4), 300-500 (F5), <300 (F6)). Error Bars represent the 90% confidence interval, data labels correspond to average percent reductions.

Oxidation Scenario	> 1350 (F1)	1050 - 1350 (F2)	750 - 1050 (F3)	500 - 750 (F4)	300 - 500 (F5)	< 300 (F6)
Raw Water	0 (15)	0 (7)	0(7)	0 (11)	0 (13)	0(11)
1 mgO <sub>3</sub> /mg DOC	-55 (13)	-37 (19)	-22 (19)	-8 (9)	4 (5)	19 (9)
2 mgO <sub>3</sub> /mg DOC	-47 (39)	-52 (20)	-52 (4)	-35 (14)	-23 (17)	-2 (18)
$2000 \text{ mJ/cm}^2 \& 10 \text{mg/L H}_2\text{O}_2$	-80 (28)	-80 (13)	-70 (7)	-61 (7)	-67 (6)	-50 (6)
$4000 \text{ mJ/cm}^2 \& 10 \text{mg/L H}_2\text{O}_2$	-95 (13)	-94 (34)	-90 (16)	-85 (8)	-86 (20)	-78 (19)
$4000 \text{ mJ/cm}^2 \& 0 \text{mg/L H}_2\text{O}_2$	-45 (21)	-24 (10)	-11 (2)	-8 (3)	-7 (15)	10 (18)
Extended Ozonation	-92 (0)	-98 (0)	-100 (0)	-99 (0)	-97 (0)	-96 (0)

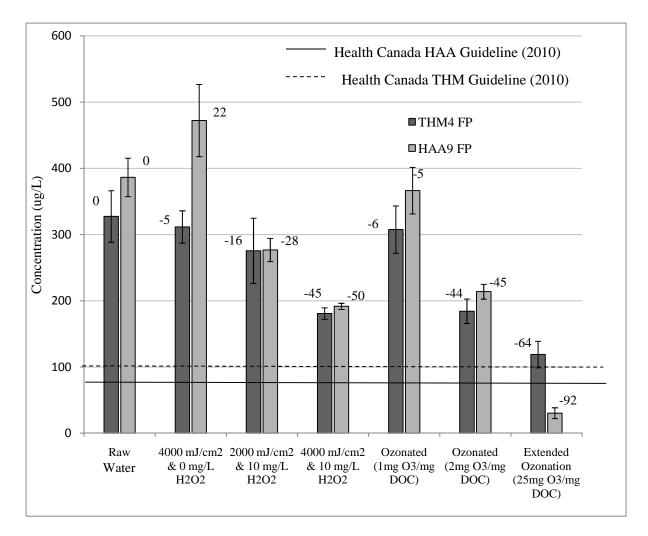
 Table 4-2 - Summary of average percent reduction in AMW fractions for each oxidation condition

(90% confidence intervals of reported reductions shown in parentheses)

Ozonation at 1 mgO<sub>3</sub>/mg DOC resulted in a shift from high molecular weight to low molecular weight NOM. Ozonation at 1mg resulted in a significant decrease in compounds greater than 750Da, while an increase in the smaller fractions was observed. However, this effect was not as noticeable at the higher dose of 2mgO<sub>3</sub>/mg DOC. This is most likely explained by the fact that the smaller organic material formed during oxidation was also oxidized at this higher dose. These results are consistent with those from other research (von Gunten et al., 2003b; Swietlik et al., 2004). Ozonation at an extended dose of 25 mgO<sub>3</sub>/mg DOC did not result in an apparent shift from high molecular weight to low molecular weight compounds, due to the high oxidation of NOM.  $UV/H_2O_2$  treatment at a dose of 2000mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub> resulted in a shift from high molecular weight to low molecular weight. These results are consistent with those from other research (Thomson et al., 2004; Sarathy, 2009) However, this effect was not as noticeable at the higher dose of  $4000 \text{mJ/cm}^2$  and 10 mg/L H<sub>2</sub>O<sub>2</sub>, and is most likely explained by the fact that the smaller material formed during oxidation was also oxidized at this higher dose. The results for average percent removals are somewhat higher than previous research (Sarathy and Mohseni, 2007; Sarathy, 2009). It should be noted that the approach used to measure the molecular weight distribution of the NOM can only detect chromophoric NOM and ignores NOM that does not absorb light at 200nm (such as biopolymers).

#### 4.2.1.4 Effect of Oxidation on Disinfection By-Produce Formation Potential (DBPFP)

The effect of oxidation on the disinfection by-product formation potential was determined for the six conditions described previously and are shown in Figure 4-14. A full of summary of results obtained can be found in Appendix G and Appendix H. THM4 formation potential corresponds to the formation potential of all four THMs; similarly, HAA9 formation potential corresponds to the formation potential of all nine known HAAs.



#### Figure 4-14 - Effect of oxidation on THMFP and HAAFP

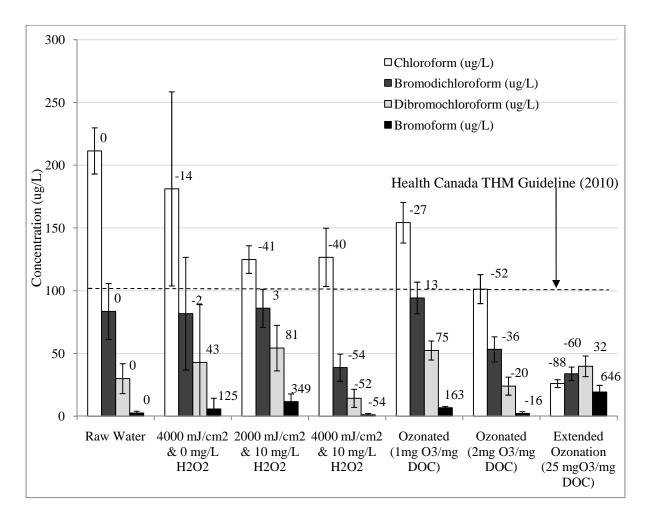
(Each bar represents an average of at least 3 replicates (in some cases, over 10 replicates were performed), each chlorinated, incubated and analyzed separately. Data labels indicate the percent reduction based on average values. Errors bars represent the 90% confidence interval).

Ozonation at  $1 \text{ mgO}_3/\text{mgDOC}$  resulted in no statistically significant reduction in either HAAFP or THMFP. This result is consistent with those from previous work that found either no effect or slight increases in both THM and HAA formation potential

following low-dose ozonation (Sidiqui et al., 1997; Galapate et al., 2001; Cipparone et al., 1997; Chowdhury et al., 2008). Ozonation at 2 mgO<sub>3</sub>/mgDOC resulted in an overall reduction of 45% for both THM and HAA formation potentials. These results are consistent with previous work that achieved between 30 - 60% removals at similar doses (Kleiser and Frimmel, 2000; Chin and Bérubé, 2005; Hu et al., 1999; Cipparone et al., 1997; Chowdhury et al., 2008; Ko et al., 2000). Ozonation at the extended dose of 25mgO<sub>3</sub>/mg DOC resulted in extremely high reductions in THMFP and HAAFP, achieving 64% and 92% removals, respectively. UV/ H<sub>2</sub>O<sub>2</sub> treatment at a dose of 2000mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub> did not result in a significant reduction in DBPFP. However, UV/ H<sub>2</sub>O<sub>2</sub> treatment at a dose of 4000 mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub> resulted in significant reductions in excess of 44% for both HAAFP and THMFP. UV/ H<sub>2</sub>O<sub>2</sub> treatment at a dose of 4000mJ/cm<sup>2</sup> and 0 mg/L H<sub>2</sub>O<sub>2</sub> resulted in significant with findings with those from previous work where HAAFP increased at low dose applications (Chowdhury et al., 2008).

Previous studies have reported quite varied results in terms of the effect of AOP on both HAAFP and THMFP, and therefore, further research is needed in order to confirm these findings. Total HAA and THM formation potentials were well above the Health Canada standards of 0.1mg/L for THMs and 0.08 mg/L for HAAs, with only the extended ozonation dose of 25mg/mg DOC resulting in concentrations of THMs and HAAs that met the current Guidelines for Canadian Drinking Water Quality limits for HAAs.

Further work was completed in order to determine the effect of oxidation on each of the DBPs. Figure 4-15 illustrates the removal efficiency of each oxidation condition on the four known THMs.



**Figure 4-15 - Effect of oxidation on the formation potential of each of the four THMs** (Each point represents an average of at least 6 replicates, each chlorinated, incubated and analyzed separately. Data labels indicate the percent reduction based on average values. Errors bars represent the 90% confidence interval for the average of the replicates analyzed.)

Ozonation at the lower dose of  $1mgO_3/mg$  DOC resulted in increases in all THMs with the exception of chloroform. Slight increases in all brominated THMs were observed, but results remain inconclusive. In contrast, ozonation at the higher dose of  $2mgO_3/mg$  DOC resulted in significant decreases for all four THMFPs. These results are consistent with those from previous work (Cipparone et al., 1997; Kleiser and Frimmel, 2000; Galapate et al., 2001; Bérubé et al., 2004). Ozonation at 25 mgO\_3/mg DOC resulted in significant decreases in bromodichloroform and chloroform formation potentials, but a substantial increase in bromoform formation potential levels was observed following ozonation. Compared to oxidation using ozone, oxidation using UV/ H<sub>2</sub>O<sub>2</sub> resulted in similar reductions in THMFP for all doses considered. UV/H<sub>2</sub>O<sub>2</sub> treatment at the lower dose of 2000mJ/cm<sup>2</sup>

and 10 mg/L H<sub>2</sub>O<sub>2</sub> resulted in no significant reduction in THMFP In contrast, UV/ H<sub>2</sub>O<sub>2</sub> treatment at the higher dose of 4000mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub> resulted in significant decreases in all four THMs with reductions in excess of 40%. These results are consistent with previous work (Toor and Mohseni, 2007). However, these results do not achieve similar reduction in THMFP as those from previous studies (Liu et al., 2002; Bérubé et al., 2004; Sarathy, 2009). UV/ H<sub>2</sub>O<sub>2</sub> treatment at 4000mJ/cm<sup>2</sup> and 0mg/L H<sub>2</sub>O<sub>2</sub> did not result in any significant reductions in THMFP.

Oxidation appeared to increase the brominated THMFP at the lower dose applications for ozonation and UV/  $H_2O_2$  treatment. However, the THMFP substantially decreased at the higher oxidation doses for ozonation and UV/  $H_2O_2$  treatment. Therefore, high-dose treatment is required in order to reduce THMFP levels to meet water quality guidelines.

Figure 4-16 illustrates the removal efficiency of each oxidation condition on the three main HAAs present; TCAA, MCAA, and DCAA. Bromoacetic acids were not present in significant quantities, and have therefore been omitted from this discussion.

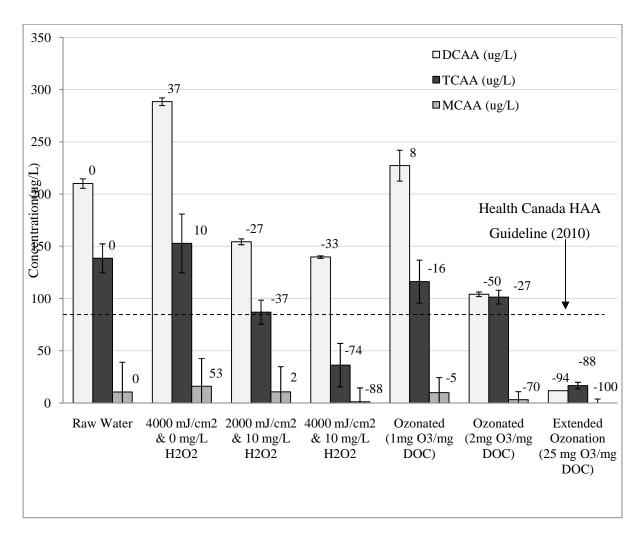


Figure 4-16 - Effect of oxidation on the formation potential of each of the three main HAAs (TCAA, MCAA, and DCAA).

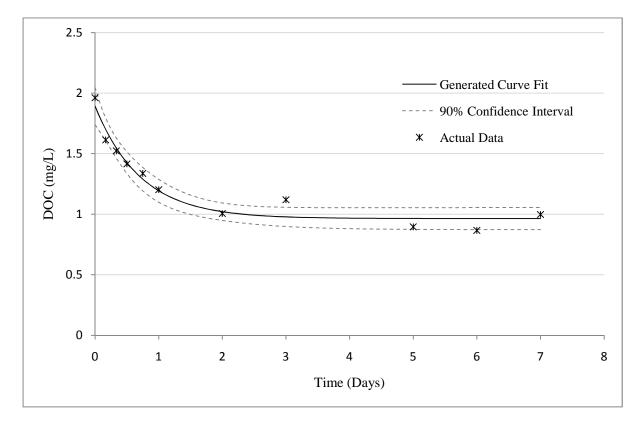
(Each point represents an average of at least 6 replicates, each chlorinated, incubated and analyzed separately. Data labels indicate the percent reduction based on average values. Errors bars represent the 90% confidence interval for the average of the replicates analyzed.).

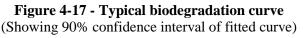
Ozonation at the lower dose of  $1mgO_3/mg$  DOC did not result in any significant reduction in HAAFP. An increase of 8% in DCAAFP levels was observed. These results are consistent with previous work (Siddiqui et al., 1997; Reckhow and Singer, 1994). In contrast, ozonation at the higher dose of  $2mgO_3/mg$  DOC resulted in significant decreases in DCAAFP levels. These results are consistent with previous work (Hu et al., 1999; Chin and Bérubé, 2004; Chowdhuyry et al., 2008). Ozonation at 25 mgO\_3/mg DOC resulted in significant decreases in all three HAAs. Compared to oxidation using ozone, oxidation using UV/ H<sub>2</sub>O<sub>2</sub> resulted in higher reductions in HAAFP. UV/H<sub>2</sub>O<sub>2</sub> treatment at the lower dose of 2000mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub> resulted in decreases in DCAAFP and TCAAFP of 27% and 37% respectively. UV/  $H_2O_2$ treatment at the higher dose of 4000mJ/cm<sup>2</sup> and 10 mg/L  $H_2O_2$  resulted in significant decreases in the FP of all three HAAs, with reductions of 33% to 88%. These results achieve much higher reductions than some reported in previous studies (Liu et al., 2002; Sarathy, 2009). UV/  $H_2O_2$  treatment at 4000mJ/cm<sup>2</sup> and 0mg/L  $H_2O_2$  resulted in increases in FP for each of the HAAs.

## 4.2.2 Batch Biodegradation Experiments

### 4.2.2.1 Effect of Oxidation on Biodegradation Kinetics

The effect of oxidation on biofiltration kinetics was examined for each of the oxidation scenarios outlined previously. Note that for all conditions investigated, the coefficient of correlation ( $\mathbb{R}^2$ ) obtained by fitting Equation 3-8 (see Section 3.2.3.1) using Systat software Table Curve 2D to the biodegradation data was 0.97. Typical results from the biodegradation experiments are presented in Figure 4-17. A full summary of results is provided in Appendix K.





The average values of a,b and c (see Section 3.2.3.1) for both BAC columns are summarized in Table 4-3, Figure 4-18 and Figure 4-19. Appendix L provides a full summary of the analysis of results.

	Oxidation	Average					
Oxidation		DOCnon (a)	DOCi (b)	kDOC(c)			
Biomass from BAC Column 1	Raw Water	2.546 (±0.182)	2.069 (±0.857)	1.857 (±0.505)			
	4000 mJ/cm <sup>2</sup> & 0 mg/L H <sub>2</sub> O <sub>2</sub>	2.464 (±0.248)	1.760 (±0.169)	1.751 (±0.834)			
	$\frac{2000 \text{ mJ/cm}^2 \& 10}{\text{mg/L H}_2\text{O}_2}$	1.288 (±0.227)	1.425 (±0.605)	2.300 (±0.668)			
	4000 mJ/cm <sup>2</sup> & 10 mg/L H <sub>2</sub> O <sub>2</sub>	0.878 (±0.136)	1.070 (±0.301)	2.604 (±0.389)			
	Ozonated (1mg O <sub>3</sub> /mg DOC)	2.942 (±0.320)	2.102 (±0.692)	1.632 (±0.686)			
	Ozonated (2mg O <sub>3</sub> /mg DOC)	2.816 (±0.105)	1.807 (±0.219)	1.632 (±0.462)			
	Extended Ozonation (25mg O3/mg DOC)	0.8467 (±0.018)	1.947 (±0.240)	0.626 (±0.062)			
	Raw Water	2.383 (±0.250)	2.680 (±0.280)	2.223 (±0.907)			
Biomass from BAC Column 2	$4000 \text{ mJ/cm}^2 \& 0 \text{ mg/L}$ $\text{H}_2\text{O}_2$	2.030 (±0.300)	2.087 (±0.076)	1.687 (±1.149)			
	2000 mJ/cm <sup>2</sup> & 10 mg/L H <sub>2</sub> O <sub>2</sub>	1.255 (±0.653)	1.302 (±0.419)	1.780 (±0.527)			
	4000 mJ/cm <sup>2</sup> & 10 mg/L H <sub>2</sub> O <sub>2</sub>	0.962 (±0.010)	0.863 (±0.417)	1.490 (±0.589)			
	Ozonated (1mg O <sub>3</sub> /mg DOC)	2.570 (±0.153)	2.509 (±0.563)	1.916 (±1.180)			
	Ozonated (2mg O <sub>3</sub> /mg DOC)	2.429 (±0.176)	2.127 (±0.101)	1.614 (±0.940)			
	Extended Ozonation (25mg O3/mg DOC)	0.650 (±0.250)	1.842 (±0.294)	0.449 (±0.096)			

 Table 4-3 - Biodegradation average curve parameters for BAC Column 1 and BAC Column 2

 (Error shown in parentheses corresponds to the 90% interval for the average of all replicates

analyzed).

Figure 4-18 illustrates the amount of non-biodegradable DOC remaining following biodegradation for each of the oxidation scenarios.

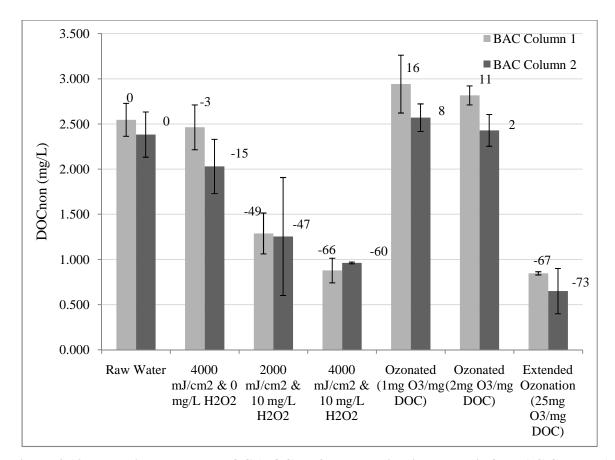


Figure 4-18 - Non-biodegradable DOC (DOC<sub>non)</sub> for each oxidation scenario for BAC Column 1 and BAC Column 2

(Bars represent the average of all replicates analyzed, error bars shown correspond to the 90% interval for the average of all replicates analyzed. Data labels indicate the average percent reduction).

Ozonation at  $1mgO_3/mg$  DOC and  $2 mgO_3/mg$  DOC did not result in a significant effect on the DOC<sub>non</sub> of the raw water. Extended ozonation at 25 mgO<sub>3</sub>/mg DOC did result in a 67% decrease in DOC<sub>non</sub>. Compared to oxidation using ozone, oxidation using UV/H<sub>2</sub>O<sub>2</sub> resulted in significant reductions in DOC<sub>non</sub>. UV/ H<sub>2</sub>O<sub>2</sub> treatment at 2000 mJ/cm<sup>2</sup> and 4000 mJ/cm<sup>2</sup> with 10mg/L H<sub>2</sub>O<sub>2</sub> resulted in 49% and 66% reductions in DOC<sub>non</sub>, respectively.

Similar results were obtained for BAC Column 2. Therefore, it can be concluded that the ability of the biomass present in both Column 1 and Column 2 biodegradable NOM was not significantly different despite the fact that they were each acclimated to different feed waters (as discussed in Section 3.1.3). Recall that the feed water fed to BAC Column 2 contained primarily the larger AMW, slow biodegradable material as discussed in Section 4.1.3. Therefore, the biomass acclimatized to the feed water containing the slowly biodegradable organic matter (BAC Column 2) was no better at biodegrading the nonbiodegradable material (DOCnon) than the biomass in BAC Column 1.

Overall, the extended ozonation dose, and the AOPs that combined 10 mg/L  $H_2O_2$ and both the 2000 and 4000 mJ/cm<sup>2</sup> UV doses were successful at sufficiently altering the NOM such that the removal of biodegradable organic matter was maximized during biodegradation, (i.e. the DOCnon levels were lowest). These results are consistent with those presented in Section 4.2.1, whereby it was concluded that these oxidation scenarios were superior at reducing DOC levels, reducing both the fraction and amount of aromatic content of the NOM, and decreasing the overall AMW of the NOM in the raw water. These results suggest that the non-biodegradable DOC, (DOC<sub>non</sub>), is a function of the type and dose of oxidation used. However, it is not a function of acclimation conditions of the biomass.

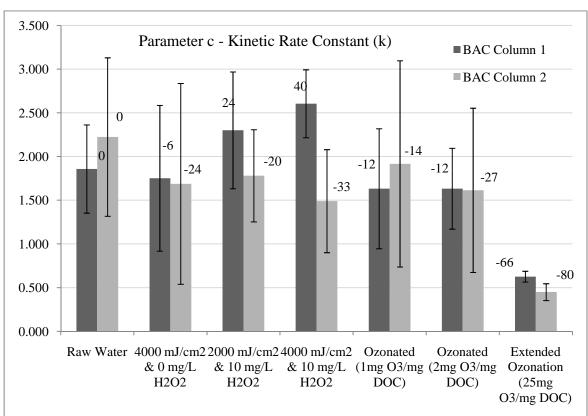


Figure 4-19 illustrates the kinetic rate constant for biodegradation for each of the oxidation scenarios.

### Figure 4-19 - Parameter c for each oxidation scenario for BAC Column 1

(Bars represent the average of all replicates analyzed, error bars shown correspond to the 90% interval for the average of all replicates analyzed. Data labels indicate the average percent reduction).

With the exception of the ozonation at 25 mgO<sub>3</sub>/mg DOC, the different oxidation types and doses did not have a significant effect on the rate of DOC biodegradation. Similar results were obtained for BAC Column 2. The low  $k_{doc}$  value obtained for ozonation at 25 mgO<sub>3</sub>/mg DOC may be due to the fact that most of the DOC is oxidised during extensive ozonation and only very slowly biodegradable DOC remained.

These results indicate that rate of biodegradation, or  $k_{DOC}$ , is not a function of the type and dose of oxidation, or to the acclimation conditions of the biomass.

## 4.2.2.2 Effect of Biodegradation on Ultraviolet Absorbance (UVA)

The effect of oxidation on biofiltration kinetics for UVA was examined for each of the oxidation scenarios outlined previously. The results obtained mirror those for DOC presented in Section 4.2.2.1. Full results are provided in Appendix M and Appendix N. Similar results were obtained for both BAC Column 1 and BAC Column 2.

These results provided further certainty that the ability of the biomass present in both BAC Column 1 and BAC Column 2 to biodegrade NOM, was not significantly different despite the fact that each were acclimated to different feed water as discussed in Section 3.1.3. Recall that the feed water fed to BAC Column 2 contained primarily the larger AMW, less aromatic, slowly biodegradable material (as discussed in Section 4.1.2 and 4.1.3). Therefore the biomass acclimatized to the feed water containing the less aromatic material (BAC Column 2) was no better at biodegrading the organic material than BAC Column 1.

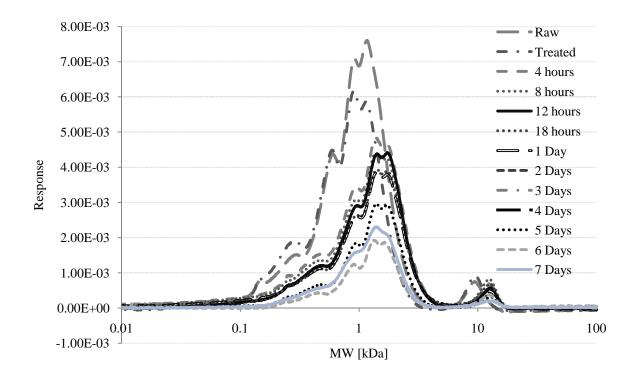
Overall, the high ozonation dose and the AOPs that combined  $10 \text{mg/L H}_2\text{O}_2$  and both the 2000 and 4000 mJ/cm<sup>2</sup> UV doses were successful at significantly lowering the aromaticity of the raw water (thereby increasing its biodegradability) such that removal of biodegradable organic material was maximized during biodegradation. These results are consistent with those presented in Section 4.2.2, whereby it was concluded that these particular oxidation scenarios were superior at lowering DOC, reducing both the fraction and amount of aromatic content of NOM, and decreasing the overall AMW of the NOM in the raw water. These results suggest that the amount of remaining UVA (present in NOM as DOC<sub>non</sub>) is sensitive to the type and dose of oxidation used.

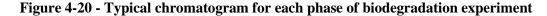
With the exception of the ozonation at 25mg O3/mg DOC, the different oxidation types and doses did not have a significant effect on the rate of UVA biodegradation. These

results indicate that the rate of biodegradation of UVA, or  $k_{UVA}$ , is not a function of the type and dose of oxidation or to the acclimation conditions of the biomass.

### 4.2.2.3 Effect of Biodegradation on Apparent Molecular Weight (AMW)

The effect of each oxidation and biodegradation was evaluated for each of the oxidation scenarios considered. Apparent Molecular Weight (AMW) was determined for each of the biodegradation samples. Figure 4-20 illustrates the HPSEC chromatograms that were obtained for each of the biodegradation experiments considered.





For the analysis that follows, results are presented for times of 0, 1 and 7 days. As discussed in Section 3.2.3.1, a batch test duration of 1 day is equivalent to an EBCT of approximately 15 minutes in a BAC Column (i.e. similar to BAC Column 1). Raw results for the batch biodegradation tests for each duration analyzed are presented in Appendix O. A typical chromatogram showing these three points is illustrated in Figure 4-21.

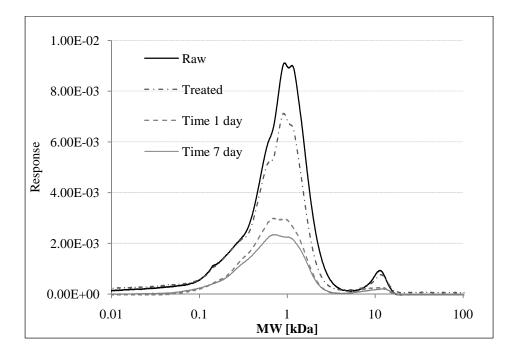
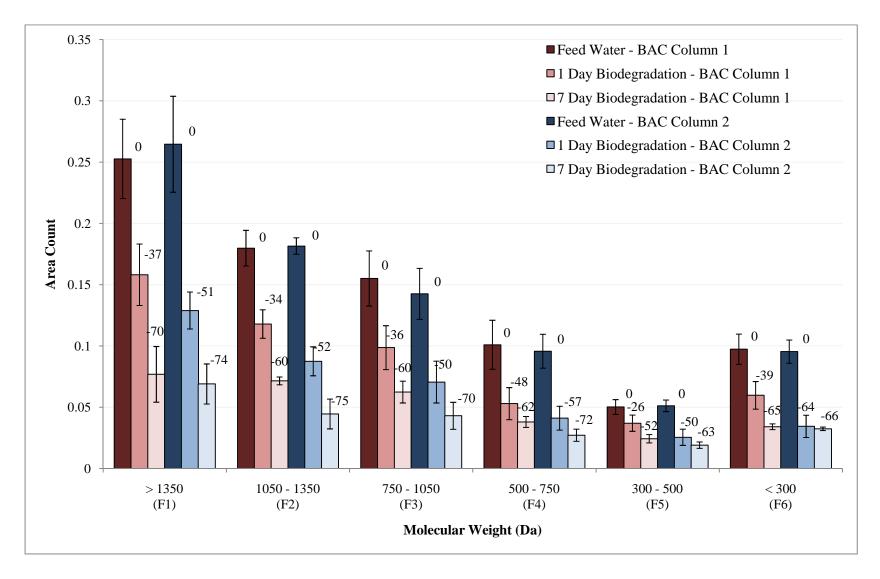


Figure 4-21 - Typical chromatogram result showing raw water, time 0 (treated), time 1 day and time 7 days.

As discussed previously, although AMW chromatograms provide insight into the characteristics of NOM, it is difficult to quantitatively compare results from different analyses. For this reason, the AMW chromatograms were deconvoluted as discussed in Section 3.3.8.2. The area below each of the peaks provided a quantitative estimate of the amount of organic material in that particular AMW range. The results from the deconvolution of AMW chromatograms are presented below. Detailed results for each analysis is presented in Appendix P, Appendix Q and Appendix R.

In the case of raw water samples (no treatment applied prior to biodegradation) results are presented in Figure 4-22.

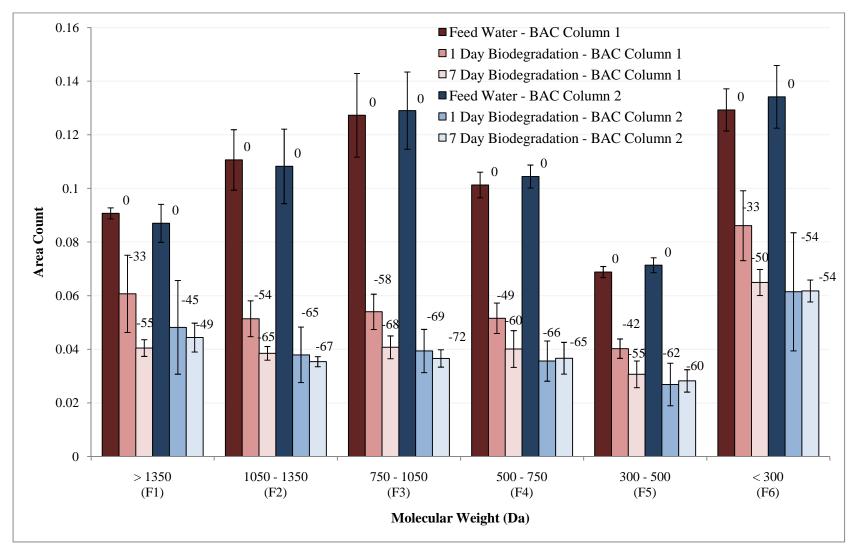


## Figure 4-22 - Deconvolution results for raw water biodegradation.

(Error bars represent the 90% confidence intervals. Data labels represent the percent reductions at time 1 day and time 7day.)

For each of the molecular weight ranges shown in Figure 4-22, significant reduction in the amount of NOM present in each AMW range was observed following both 1 day and 7 day biodegradation. High removal percentages were observed for the smaller molecular weight ranges during the 1 day biodegradation (also corresponding to BAC Column 1). Significant additional reduction in AMW was observed following the 7 day biodegradation, including biodegradation of the larger AMW material. These results suggest that insufficient removal of biodegradable compounds occurred during the 1 day biodegradation (corresponding to an EBCT of 15minutes) and therefore there exists a significant amount of residual biodegradable organic matter present following 1 day biodegradation. This residual organic matter, as discussed in Section 2.2.3, can lead to the formation of DBPs during chlorination and potential regrowth with the distribution system. The results for the raw water biodegradation provide a basis for comparison for the feed water biodegradation experiments with oxidized feed water.

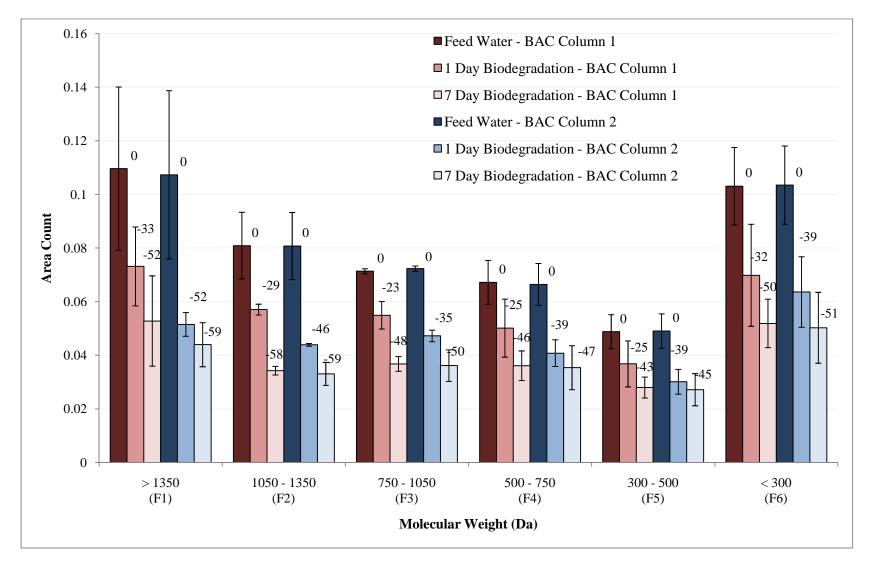
For ozonation at 1 mg  $O_3$ /mg DOC, results are presented in Figure 4-23.



**Figure 4-23 - Deconvolution results for ozonation at 1mg O<sub>3</sub>/mg DOC feed water biodegradation.** (Error bars represent the 90% confidence intervals. Data labels represent the percent reductions at time 1 day and time 7day.)

For each of the molecular weight ranges shown on Figure 4-23, significant reduction in the amount of NOM in each AMW range was observed following 1day biodegradation. In contrast to the raw water biodegradation experiments, in most cases, no significant additional reduction in AMW was observed following the 7 day biodegradation. These results suggest that ozonation at 1mg  $O_3$ /mg DOC successfully transformed the NOM present in the raw water (Section 4.2.1.2), such that this material was preferentially biodegraded within 1 day.

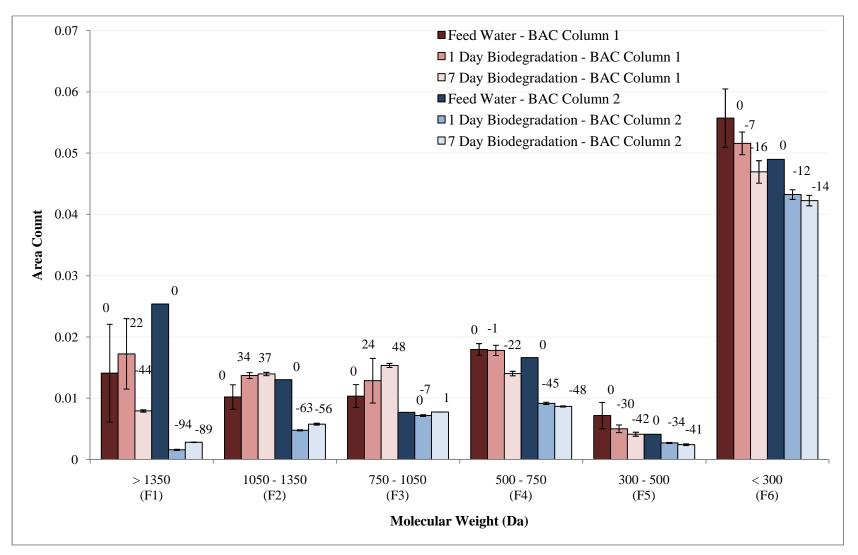
For ozonation at  $2 \text{ mg O}_3/\text{mg DOC}$ , results are presented in Figure 4-24.



**Figure 4-24 - Deconvolution results for ozonation at 2mg O<sub>3</sub>/mg DOC feed water biodegradation.** (Error bars represent the 90% confidence intervals. Data labels represent the percent reductions at time 1 day and time 7day.)

For each of the molecular weight ranges shown in Figure 4-24, significant reduction in the amount of NOM in each AMW range was observed following both 1day and 7 day biodegradation. In most cases, no significant additional reduction in AMW was observed following the 7 day biodegradation. These results suggest that ozonation at 2mg O<sub>3</sub>/mg DOC successfully transformed the NOM present in the raw water (Section 4.2.1.3), such that this material was preferentially biodegraded within 1 day. In contrast to the 1mg O<sub>3</sub>/mg DOC, lower removal percentages (in the order of 20% less removal) were observed following 1 day biodegradation for most fractions investigated (F2 - F5). These results suggest that the rapid phase biodegradation (BDOCr) is a function of the oxidant dose.

For ozonation at the extended dose of 25 mg  $O_3$ /mg DOC, results are presented in Figure 4-25.



**Figure 4-25 - Deconvolution results for ozonation at 25mg O<sub>3</sub>/mg DOC feed water biodegradation.** (Error Bars represent the 90% confidence intervals. Data labels represent the percent reductions at time 1 day and time 7day.)

For each of the molecular weight ranges shown in Figure 4-25, no significant reduction in the amount of NOM in each AMW range was observed following both 1 day and 7 day biodegradation. These results suggest that very little biodegradable organic matter remains prior to the start of biodegradation, and therefore no additional biodegradation is able to occur. These results are consistent with those presented in 4.2.1 whereby it was shown that the extended ozonation resulted in significant removal of DOC, UVA, SUVA and AMW.

For AOP oxidation using 4000mJ/cm<sup>2</sup> and 0 mg/L H<sub>2</sub>O<sub>2</sub>, results are presented in Figure 4-26.

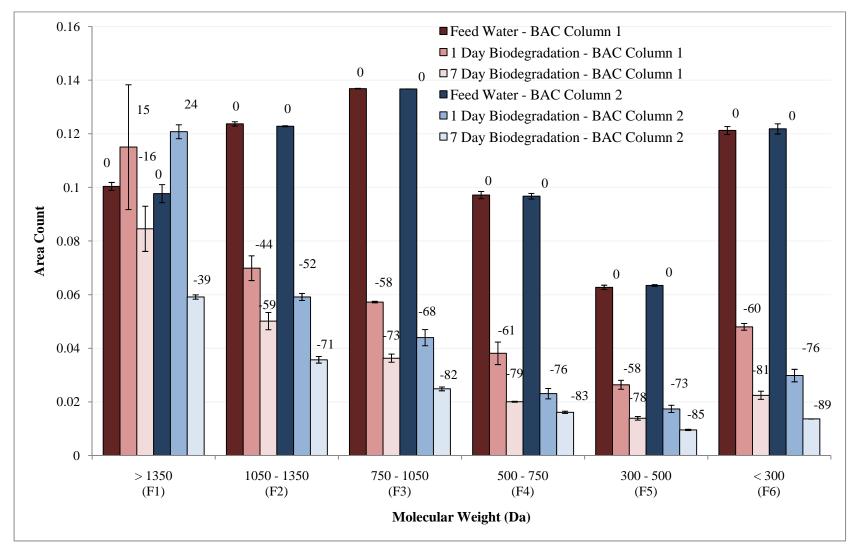


Figure 4-26 - Deconvolution results for for  $4000 \text{mJ/cm}^2$  and  $0 \text{ mg/L H}_2\text{O}_2$  feed water biodegradation. (Error Bars represent the 90% confidence intervals. Data labels represent the percent reductions at time 1 day and time 7day.)

For each of the molecular weight ranges shown in Figure 4-26, significant reduction in the amount of NOM in each AMW range was observed following both 1day and 7 day biodegradation. Higher removal percentages were observed for the smaller molecular weight ranges during the 1 day biodegradation (also corresponding to BAC Column 1) indicating that smaller AMW material is more easily biodegraded during the initial rapid phase of biodegradation. Significant additional reduction in AMW was observed following the 7 day biodegradation, including biodegradation of the larger AMW material. These results suggest that the smaller molecular weight material is more easily degraded during the initial biodegradation. These results correspond well with those obtained during biofiltration, as presented in Section 4.1.3.

For AOP oxidation using 2000mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub>, results are presented in Figure 4-27.

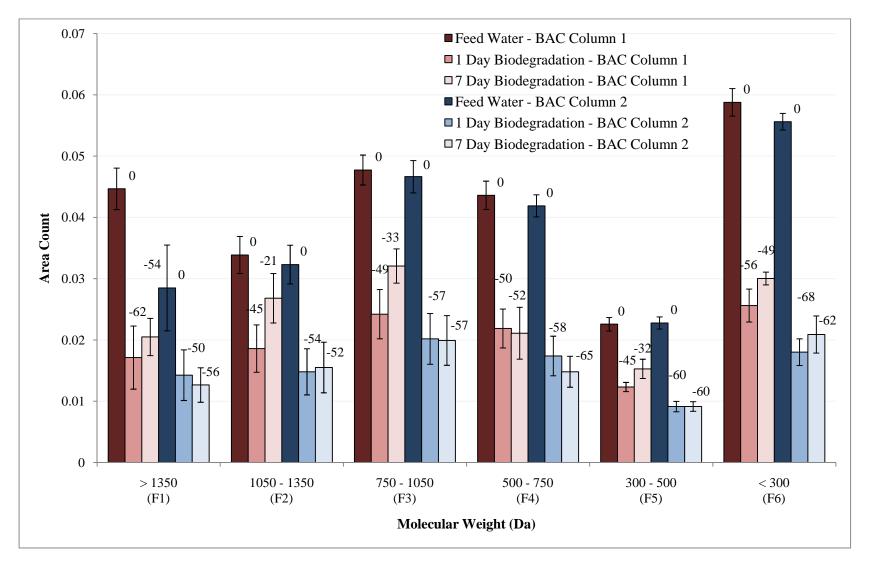


Figure 4-27 - Deconvolution results for 2000mJ/cm<sup>2</sup> and 10 mg/L  $H_2O_2$  feed water biodegradation. (Error bars represent the 90% confidence intervals. Data labels represent the percent reductions at time 1 day and time 7day.)

For each of the molecular weight ranges shown in Figure 4-27, significant reduction in the amount of NOM in each AMW range was observed following 1 day biodegradation. These results suggest that the oxidant used reduced the AMW of the NOM present in the raw water (Section 4.2.1.3), such that this material was preferentially removed during rapid biodegradation. The material present following 1 day biodegradation (BAC Column 1) was therefore less aromatic and biodegradable and was not preferentially removed during biodegradation. These results are not consistent with those obtained during biofiltration whereby BAC Column 2 removed the larger AMW substances during biofiltration (Section 4.1.3).

For AOP oxidation using 4000mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub>, results are presented in Figure 4-28.

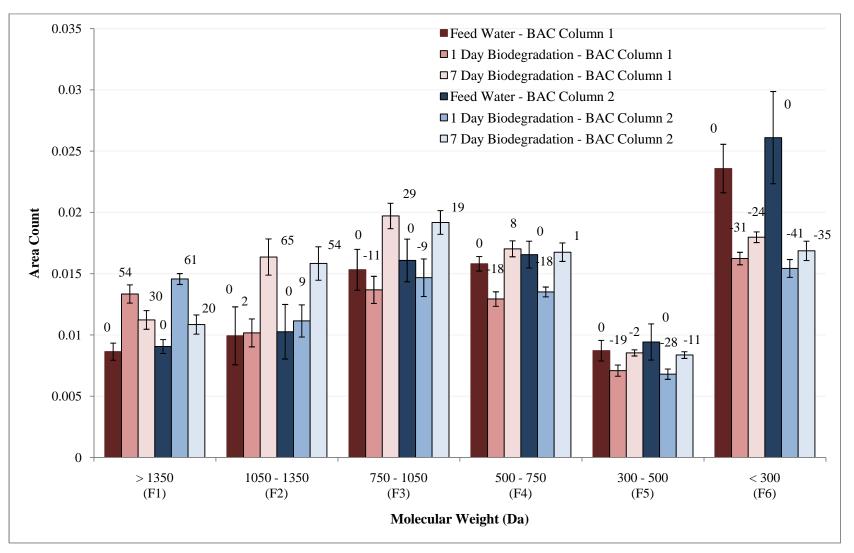


Figure 4-28 - Deconvolution results for  $4000 \text{mJ/cm}^2$  and  $10 \text{ mg/L H}_2\text{O}_2$  feed water biodegradation. (Error bars represent the 90% confidence intervals. Data labels represent the percent reductions at time 1 day and time 7day.)

For each of the molecular weight ranges shown in Figure 4-25, no significant reduction in the amount of NOM in each AMW range was observed following both 1 day and 7 day biodegradation. These results suggest that very little biodegradable organic matter remains prior to the start of biodegradation, and therefore no additional biodegradation is able to occur. These results are consistent with those presented in 4.2.1 whereby it was shown that the high dose AOP resulted in significant removal of DOC, UVA, SUVA and AMW. These results are similar to those of presented for the extended ozonation biodegradation experiment.

Overall these results suggest that the rapid phase biodegradation (1 Day biodegradation) is a function of the oxidant type and dose.

### 5.0 CONCLUSIONS AND RECOMMENDATIONS

### 5.1 Biofiltration Column Experiments

The objective of Part 1 of this project was to assess the removal of NOM through biological activated carbon filtration. Major conclusions from this work are presented below.

- Ozonation at 2 mg O<sub>3</sub>/mg DOC did not result in a significant reduction in DOC from the raw water. However, based on UVA and SUVA analysis, ozonation did successfully reduce the amount and fraction of the organic material that was aromatic. Ozonation also successfully reduced the AMW of the NOM present in the raw water. DBPFP was significantly reduced following ozonation; this was attributed to the decrease in aromatic material during ozonation. However, overall ozonation was unable to lower DBPFP below the Canadian Drinking Water Guideline values.
- 2. Subsequent biofiltration resulted in significant reduction in DOC levels. Biofiltration through BAC Column 1 did not result in a change in the fraction of organic material that was aromatic, but it significantly reduced the amount of aromatic material present. BAC Column 1 preferentially biodegraded the smaller molecular weight NOM that was more biodegradable. Effluent from BAC Column 1 contained higher AMW that was less biodegradable. The effluent of BAC Column 1 served as the feed water for BAC Column 2, and during biofiltration the larger AMW was successfully removed in BAC Column 2. Given the high reductions in aromatic content observed during biofiltration, a significant reduction in DBPFP was observed. However, only BAC Column 2 was able to lower the DBPFP and generate THM and HAA concentrations that were below the Health Canada Canadian Drinking Water Guideline values.

Overall, ozonation of the raw water at  $2 \text{mg O}_3/\text{mg DOC}$  resulted in significant reductions in aromatic material, resulting in lowered DBPFP. In addition, ozonation was successful at transforming NOM from high AMW to low AMW, rendering the organic material more biodegradable and preferentially removed during biofiltration.

### **5.2 Biodegradation Experiments**

#### 5.2.1 Raw Water Oxidation

The objective of Part 2 of this project was to assess the effect of oxidation on the rate of biodegradation. The first sub-objective was to determine the effect of different oxidation doses and types of oxidants on the removal of NOM. Major conclusions from this work are presented below.

- High dose oxidation is required to lower DOC levels significantly. In addition, treatment of raw water using UV/H<sub>2</sub>O<sub>2</sub> resulted in higher removal of DOC compared to ozonation at the doses considered. While ozonation did not significantly reduce DOC levels, it resulted in a decrease in aromatic material. High dose ozonation as well as UV/H<sub>2</sub>O<sub>2</sub> was successful at significantly lowering the fraction and amount of aromatic material present in feed water.
- 2. Ozonation at 2mg  $O_3$ /mg DOC and UV/H<sub>2</sub>O<sub>2</sub> treatment at 2000mJ/cm<sup>2</sup> and 10 mg/L resulted in a shift from high AMW to low AMW NOM. This effect was not as noticeable for the higher ozonation and AOP doses which was likely due to the fact that the smaller AMW organics formed during oxidation were also oxidized at the higher doses.
- 3. While significant reduction in DBPFP was observed for each of the scenarios investigated, only the extended ozonation dose of 25 mgO<sub>3</sub>/mg DOC was able to meet the Canadian Drinking Water Guideline limits for THMs and HAAs.

Overall, while the high-dose oxidants (ozonation at 25mg  $O_3/mg$  DOC and AOP treatment at 4000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub>) were successful at reducing DOC, UVA, AMW and DBPFP, the elevated dose required make these options less practically and economically feasible. Ozonation at 2mg  $O_3/mg$  DOC and AOP treatment at 2000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub> provide good removal of UVA and AMW and a reduction of the DBPFP.

### 5.2.2 Batch Biodegradation Experiments

The second sub-objective was to assess the effect of oxidation on the rate of biodegradation. Major conclusions from this work are presented below.

- 1. Ozonation at 1 and 2 mg  $O_3$ /mg DOC was not successful at reducing the amount of residual DOC (or non-biodegradable DOC) remaining following biodegradation. Extended ozonation and high dose AOPs at 2000 and 4000 mJ/cm<sup>2</sup> with 10mg/L H<sub>2</sub>O<sub>2</sub> were successful at lowering the amount of non-biodegradable DOC present following biodegradation. These results suggest that the amount of non-biodegradable DOC is a function of the type and dose of oxidant used. Reduction of non-biodegradable DOC can, therefore, be maximized by using the appropriate pre-oxidation treatment or dose.
- With the exception of the ozonation at 25mgO3/mg DOC, the different oxidation doses and types of oxidants used did not have a significant effect on the rate of DOC biodegradation. Therefore, k<sub>DOC</sub> is not a function of the type or dose of oxidant used.
- 3. Ozonation at 1 and 2mg O<sub>3</sub>/mg DOC, and AOP treatment using 2000 mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub>, was successful at reducing UVA and AMW of the NOM, rendering it more biodegradable, such that this material was preferentially removed during the rapid phase biodegradation (1 day biodegradation). This result suggests that potentials for DBPFP and regrowth within the distribution system are minimized, given the high reduction in biodegradable organic content.
- 4. Extended ozonation at 25 mgO3/mg DOC and AOP treatment using 4000 mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub>, oxidized most of the NOM, significantly reducing the DOC, UVA, AMW and DBPFP. However, very littler biodegradation occurred given the high oxidation of NOM, making oxidation at these doses unsuitable as pre-treatment for biofiltration systems.
- Results from both the raw water biodegradation experiment and the biodegradation experiment using only 4000mJ/cm<sup>2</sup> of UV light suggest that lower AMW NOM is preferentially biodegraded during biofiltration.
- 6. Biomass from BAC Column 1 and BAC Column 2 resulted in similar biodegradation kinetics and therefore both biomasses (regardless of the extended EBCT for BAC Column 2 and the different feed water) exhibited similar biodegradation rates. Therefore, this may indicate that the acclimation of biomass to highly biodegradable or slowly biodegradable NOM in the feed water would achieve similar biodegradation results.

Overall, the high dose oxidants (ozonation at 25mg  $O_3$ /mg DOC and AOP treatment at 4000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub>) are unsuitable as pre-treatment options for biofiltration given that they result in highly oxidized NOM that exhibits very little biodegradation during biofiltration. The lower dose oxidants are suitable pre-treatment options for biofiltration, given the high reductions in UVA, AMW and DBPFP exhibited, and the similar biodegradation kinetics observed. However, ozonation resulted in the lowest removals of non-biodegradable DOC and, therefore, the AOP dose of 2000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub> would maximize removal of non-biodegradable DOC, while also ensuring sufficient biodegradation of NOM during subsequent biofiltration.

#### **5.3 Engineering Significance and Future Work**

### 5.3.1 Significance

This work is useful to water utilities in evaluating the effect of oxidation on the biodegradability of NOM. Since sources of NOM vary widely in their chemical composition, and the degree to which they are able to be biodegraded will vary, it is important that water utilities considering biological treatment (or BAC treatment) perform batch biodegradation experiments, to obtain a preliminary estimate of the biodegradation potential of the NOM particular to their area. As an alternative, the SUVA may be a good indicator of the biodegradation potential, which is consistent with findings from Goel et al., (1995).

Because of the variability in NOM, it's also important that water utilities determine the optimum ozone dose or AOP dose to achieve maximum biodegradability by BAC, as demonstrated by this research. Pre-oxidation prior to biofiltration provides an opportunity to maximize the removal of the non-biodegradable fraction of NOM while biofiltration does not appear to affect the amount of non-biodegradable DOC. In addition, regardless of the preoxidant used, the rate kinetics appear to be constant when operating a steady-state biofiltration system.

For small water utilities, the complexity and cost of ozone based systems makes UV irradiation a more attractive alternative (AWWARF 1999). Given the results obtained in this

study, it may be more advantageous from a water quality perspective to employ advanced oxidation processes using UV. However, significant financial assessments would be required for any of the integrated treatment processes discussed in this report, given the potential for high capital and operating costs.

Despite the complexities involved in treating source water, BAC is simple and easy to operate and is a viable alternative for small and rural communities looking to achieved high water quality objectives with minimal operational requirements. Additional investigation into the feasibility of ozonation and AOPs in small and remote communities should be investigated.

### 5.3.2 Future work

- Investigation into the effect of different water sources with various types of NOM and AMW footprints on biodegradation kinetics is necessary as this study only used on type of raw water.
- Investigation of ozonation by-products removal efficiency within BAC would be beneficial, given that water quality standards may become more stringent with respect to these compounds.
- 3. Future work should explore other alternative integrated treatment processes. Exploring the feasibility of combined catalytic ozonation, or vaccum UV in combination with biofiltration biofiltration to determine whether this integrated treatment process is advantageous (see work by Chen et al., 2009).
- 4. It would be beneficial to explore more ozone dose ranges research has shown that the differences between ozone doses of 1 and 2 mg/mgDOC may not be significant enough to observe any differences (Cipparone et al., 1997; Buchanan et al., 2004).
- Future work should explore the effect of backwashing on BAC filter performance, even though some research with sand/glass beads has shown minimal effect on continuous flow biofilters after backwashing (Hozalski et al., 1999).
- 6. It would be advantageous to better articulate the degradation of ozone and hydrogen peroxide in BAC filters.

7. Future work should investigate the effect of these treatment processes on membrane fouling. It was shown by Karnik et al. (2005b), that ozone helped to increase recovery of permeate flux from 60 to 95%. However, additional work is still needed.

### REFERENCES

Allgeier, S.A., Summer, R.S. & Jacangelo, J.G. (1996). Simplified and rapid method for BDOC measurement. In *Proceedings 1996 AWWA Water Quality Technology Conference*. Boston, MA.

American Public Health Association (APHA). (2005). *Standard methods for the examination of water & wastewater*. (21<sup>st</sup> ed). Eds. Eaton, A. D., Franson, M. A. H., American Public Health Association., American Water Works Association., & Water Environment Federation. Washington, DC.

American Public Health Association (APHA). (1989). *Standard methods for the examination of water and wastewater* (17<sup>th</sup> ed). Washington, DC.

American Water Works Association Research Foundation (AWWARF). (1994). *Ozone and biological treatment for DBP control and biological stability*. Michael L Price (Eds). Denver, CO: AWWA Research Foundation.

American Water Works Association Research Foundation (AWWARF). (1999). Advanced oxidation and biodegradation processes for the destruction of TOC and DBP precursors. Denver, CO: AWWA Research Foundation.

Amirsardari, Y., Yu, Q., & Williams, P. (2001). Effect of ozonation and UV irradiation with direct filtration and disinfection byproduct precursors in drinking water treatment. *Environmental Technology*, 22(9), 1015–1023.

Beltran, F.J., Ovejero, G., & Acedo, B. (1993). Oxidation of atrazine in water by UV radiation combined with H<sub>2</sub>O<sub>2</sub>. *Water Research*, 27 (6), 1013–1021.

Bérubé, P.R., Mohseni, M., Chin, A. & Toor, R. (2004) Comparing UV-Ozone and UV-hydrogen peroxide for the reduction of the disinfection by-product formation potential. In *Proceedings from the 2004 AWWA Water Quality Technology Conference*. San Antonio, Texas.

Bond, T., Goslan, E.H., Jefferson, B., Roddick, F., Fan, L. & Parsons, S.A. (2009). Chemical and biological oxidation of NOM surrogates and effect on HAA formation. *Water Research*, *43*(10), 2615 - 2622.

Buchanan, W., Roddick, F., Porter, N., & Drikas, M. (2004). Enhanced biodegradability of UV and VUV pre-treated natural organic matter. *Water Science and Technology: Water Supply*, *4* (4), 103–111.

Buchanan, W., Roddick, F., Porter, N., & Drikas, M. (2005). Fractionation of UV and VUV pretreated natural organic matter from drinking water. *Environmental Science and Technology*, *39*(12), 4647–4654.

Bush, K. (2008). Assessment of Drinking Water Quality Using Disinfection By-Products in a Distribution System Following a Treatment Technology Upgrade. (Masters Dissertation). University of British Columbia, Vancouver, BC.

Carlson, K.H., & Amy, G.L. (1996). The relative importance of HLR and EBCT in biofiltration. In *Proceedings from the 1995 AWWA Water Quality Technology Conference*. New Orleans, LA.

Carlson, K.H. & Amy, G.L. (1997). The formation of filter-removable biodegradable organic matter during ozonation. *Ozone: Science & Engineering*. 19(2), 179-199.

Carlson, K.H. & Amy, G.L. (1998). BOM removal during biofiltration. *Journal of American Water Works Association*. 90 (12), 42 - 52.

Carlson, K.H., Amy, G.L, Garside, J., Blais, G. (1996). Ozone induced biodegradation and removal of NOM and ozonation by-products in biological filters. In M.R. Collins and N. J. D. Graham (Eds.), *Alternative Biological Filtration*, New York, NY: John Wiley and Sons.

Chen, K., Wang, Y., & Chang, Y. (2009). Using catalytic ozonation and biofiltration to decrease the formation of disinfection by-products. *Desalination*, 249 (3), 929 - 935.

Chin A., & Bérubé P. (2005). Removal of disinfection by-product precursors with ozone-UV advanced oxidation process. *Water Research 39*, 2136-2144.

Cho M., Haeshim, K., Cho S., &Yoon J. (2003). Investigation of ozone reaction in river water causing instantaneous ozone demand. *Ozone Science and Engineering* 25(4), 251 - 259.

Chowdury F.L., Bérubé P. R., Mohseni M. (2008). Characteristics of natural organic matter and formation of chlorinated disinfection by products from two source waters that respond differently to ozonation. *Ozone Science & Engineering 30* (5), 321-331.

Cipparone, L.A., Diehl, A.C., & Speitel Jr., G.E. (1997). Ozonation and BDOC removal: effect on water quality. J. Am. Water Works Assoc. 89 2 (1997), pp. 84–97.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., & Tchobanoglous, G. (2005). *Water treatment: Principles and design* (2<sup>nd</sup> ed.). New Jersey, NY: Wiley.

Croue J.-P., Korshin G., & Mark B. M. (1999). *Characterization of natural organic matter in drinking water*. American Water Works Association Research Foundation (AWWARF). Denver, CO.

Digiano, F.A., Singer, P.C., Parameswar, C. & Lecourt, T.D. (2001). Biodegradation kinetics of ozonated NOM and aldehydes. *Journal of American Water Works Association*, 98(8), 92 - 104.

Dodd M. C., Kohler H.P. E., & von Gunten U. (2009). Oxidation of antibacterial compounds by ozone and hydroxyl radical: elimination of biological activity during Aqueous ozonation processes. *Environmental Science & Technology* 43(7), 2498-2504.

Fahmi, N.W., & Okada, M. (2003). Improvement of DOC removal by multistage 22 AOP-biological treatment. *Chemosphere* 50(8), 1043–1048.

Fahmi, W.N. & Okada, M. (2002). Characterization of organic matter in ozonation and biological treatment. *Journal of Water Supply, Research & Technology - AQUA, 52* (4), 291 - 297.

Fonseca, A.C., & Summers, R.S. (2003). Evaluation of different ozonation strategies and of temperature effects on biological filter performance. In *Proceedings from the AWWA Water Quality and Technology Conference*. Philadelphia, PA.

Galapate, R., Baes, A., & Okada, M. (2001). Transformation of dissolved organic matter durin`g ozonation: effects on trihalomethane formation potential. *Water Research*, *35*, 2201–2206.

Glaze, W., Peyton, G., Lin, S., Huang, R., & Burieson, J. (1982). Destruction of pollutants in water with ozone in combination with ultraviolet radiation: Natural trihalomethane precursors. *Environmental Science and Technology*, *16*(8), 454–458.

Goel, S., Hozalski, R.M., &Bouwer, E.J. (1995). Biodegradation of NOM: effect of NOM source and ozone dose. *Journal of American Water Works Association*, 87 (1), 90-105.

Goslan E. H., Gurses F., Banks J., & Parsons S. A. (2006). An investigation into reservoir NOM reduction by UV photolysis and advanced oxidation processes. *Chemosphere* 65(7), 1113–1119.

Goslan, E., Jarvis, P., Bond, T., Bougeard, C., Jefferson, B., & Parsons, S. (2007). HAA precursor treatment: identifying characteristics for removal. In *Proceedings from the AWWA Water Quality Technology Conference*. Charlotte, NC.

Gottschalk, C., Libra, J., & Saupe, A. (2000). Ozonation of Water and Wastewater: A Practical Guide to Understanding Ozone and its Application. New York: Wiley-VCH.

Hammes, F., Salhi, E., Koster, O., Kaiser, H.P., Egli, T., & von Gunten, U. (2006). Mechanistic and kinetic evaluation of organic disinfection by-product and assimilable organic carbon (AOC) formation during the ozonation of drinking water. *Water Researc*, 40(12), 2275–2286

Health Canada. (2010). Guidelines for Canadian Drinking Water Quality. Federal-Provincial-Territorial Committee on Drinking Water. Available at <u>http://www.hc-sc.gc.ca/ewh-semt/alt\_formats/hecs-sesc/pdf/pubs/water-eau/2010-sum\_guide-res\_recom/sum\_guide-res\_recom-eng.pdf</u> [Accessed October 4, 2010]

Hobbie, J.E., Daley, R.J., & Jasper, S. (1977). Use of nucleopore filters for counting bacteria by fluorescent microscope. *Applied Environmental Microbiology*, *33*, 1225 - 1228.

Hoigne, J. & Bader, H. (1975). Ozonation of water - Role of hydroxyl radicals as oxidizing intermediates. *Science*, 190(4216), 782-784

Hozalski, R.M., Bouwer, E.J. & Goel, S. (1999). Removal of natural organic matter from drinking water supplies by ozone-biofiltration. *Water Science and Technology*, 40 (9), 157-163.

Hozalski, R.M., Goel, S. & Bouwer, E.J. (1995). TOC removal in biological filters. *Journal of American Water Works Association*, 87(12), 40 - 54.

Hu, J.Y., Wang, Z.A., Ng, W.J., & Ong, S.L. (1999) Disinfection by-products in water produced by ozonation and chlorination. *Environmental Monitoring and Assessment*, 59, 81-93.

Huang W.-J., Chen L.-Y., & Peng H.-S. (2004). Effect of NOM characteristics on brominated organics formation by ozonation. *Environment International*, 29 (2004), 1049-1055.

Huck, P.M., Zhang, S. & Price, M.L. (1994). BOM Removal during biological treatment: A first-order model. *Journal of American Water Works Association*, 86(6), 61 - 71.

Huck, P.M., Coffey, B.M., Amirtharajah, A. & Bouwer, E.J. (1998). Optimizing filtration in biological filters. In *Proceedings from the 1998 AWWA Water Quality Technology Conference*. San Diego, CA.

Joslyn, B. L., & Summers, R. S. (1992) Control of disinfection by-product precursors by ozonation, biofiltration, and carbon adsorption. In *Proceedings from the AWWA Annual Conference*. Vancouver, BC.

Juhna, T. & Melin, E. (2006). Ozonation & biofiltration in water treatment: operational status and optimization issues. *Techneau*.

Kaastrup, E. & Halmo, T.M. (1987). Removal of aquatic humus by ozonation and activated carbon adsoprtion. *Proc 193rd Mtg Div Envir Chem ACS*, 27(1), 355.

Karnik B., Davies S., Chen K., Jaglowski D., Baumann M., & Masten S. (2005a). The effects of combined ozonation and filtration on disinfection by-product formation. *Water Research 39*(13), 2839-2850.

Karnik, B.S., Davies, S.H.R., Chen, K.C., Jaglowski, D.R., Baumann, M.J. & Masten, S.J. (2005b). Effects of ozonation on the permeate flux of nanocrystalline ceramic membranes. *Water Research*, *39*, 728-734.

Kennedy, M.D., Chun, H.K., Quintanilla Yangal, V.A., Heijman, B.GJ., & Schisppers, J.C. (2005). Natural Organic Matter (NOM) fouling of ultrafiltration membranes: fractionation of surface water and characterisation by LC-OCD. *Desalination*, *178*(1-3), 73-83

Kim, W.H., Nishijima, W., Shoto, E., & Okada, M. (1997). Pilot plant study on ozonation and biological activated carbon process for drinking water treatment. *Water Science and Technology*, *35* (8), 21-28.

Kim, H.C., YU, M.J., Koo, J.Y. & Leo, S. (2006). Application of O<sub>3</sub>/GAC process for advanced and selective removal of NOM from conventionally treated water. *Water Science & Technology*, *16*(20), 101-108.

Kitis, M., Karanfil, T., Kilduff, J. E., Wigton, A. (2001). The reactivity of natural organicmatter to disinfection by-products formation and its relation to specific ultravioletabsorbance. *Water Science and Technology*, *43*(2), 9-16.

Klassen, N.V., Marchington, D. & McGowan, H.C.E. (1994). H<sub>2</sub>O<sub>2</sub> Determination by the I3- method and by KMnO4 titration. *Analytical Chemistry*, *66*, 2921-2925.

Kleiser, G. & Frimmel, F. H. (2000). Removal of precursors for disinfection byproducts (DBPs) - differences between ozone- and OH radical- induced oxidation. *Science of the Total Environment*, 256, 1–9.

Klevens, C.M., Collins M.R., Negm, R., Farrar M.F., & Fulton, G.P. (1996). Natural organic matter characterization and treatability by biological activated carbon filtration. In: *Disinfection by-products and NOM precursors: chemistry, characterization, control: Proceedings, ACS Symposium*, Washington, DC, p. 211–46.

Ko, Y.-W., Abbt-Braun, G., & Frimmel, F. (2000). Effect of preozonation on the formation of chlorinated disinfection by-products for River Ruhr. *Acta Hydrochimica et Hydrobiolica*, 28(5), 256–261.

Komulainen, H. (2004). Experimental cancer studies of chlorinated byproducts. *Toxicology*, 198, 239–248.

Krasner, S.W., Sclimenti, M.J., & Coffeey, B.M. (1993). Testing biologically active filters for removing aldehydes formed during ozonation. *Journal of American Water Works Association*, 85(5), 62 -70.

Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Sclimenti, M.J., Onstad, G.D., & Thruston Jr., A.D. (2006). Occurrence of a new generation of disinfection byproducts. *Environmental Science and Technology*, 40 (23), 7175–7185.

Langlais, B., Reckhow, D., & Brink, D. (Eds.). (1991). *Ozone in water treatment: Application and engineering*. Denver, CO: AWWA Research Foundation.

LeChevallier M.W., Becker W.C., Schorr P. & Lee R.G. (1992). Evaluating the performance of biologically active rapid filters. *Journal of American Water Works Association*, 84(4), 136 - 146.

LeChevalier, M.W., Welch, N.K., & Smith, D.B. (1996). Full-Scale studies of factors related to coliform regrowth in drinking water. *Applied Environmental Microbiology*, 62(7), 2201-2211.

Legrini, O., Oliveros, E., & Braun, A.M. (1993). Photochemical processes for water treatment. *Chemical Review*, *93*(2), 671–698.

Leisinger, T., Cook, A.M., Hütter, R., & Nüesch, J.M. (1981). *Microbial degradation of xenobiotics and recalcitrant compounds*. New York: Academic Press.

Li, C-W., Benjamin, M. M., Korshin, G. W. (2000). Use of UV spectroscopy to characterize the reaction between NOM and free chlorine. *Environmental Science and Technology*, *34* (12), 2570-2575.

Liao, C. H. & Gurol, M. D. (1995). Chemical oxidation by photolytic decomposition of hydrogen peroxide, *Environmental Science and Technology*, 29(12), 3007 – 3014

Litter M. I. (2005) Introduction to photochemical advanced oxidation processes for water treatment. In: Environmental Photochemistry Part II (Handbook of Environmental Chemistry), 325-366. Springer Verlag, Heidelberg

Liu, W., Andrews, S.A., Sharpless, C., Stefan, M., Linden, K.G., & Bolton, J.R. (2002). Bench-scale investigations into comparative evaluation DBP formation from different UV/H<sub>2</sub>O<sub>2</sub> technologies. In *Proceedings of the AWWA Water Quality Technology Conference*. Seattle, WA.

Liu, W., Andrews, S.A., Stefan, M.I. & Bolton, J.R. (2003) Optimal methods for quenching H<sub>2</sub>O<sub>2</sub> residuals prior to UFC testing. *Water Research*, *37*, 3697-3703.

Lucena, F., Frias, J. & Ribas, F. (1991). A new dynamic approach to the determination of BDOC in water. *Environmental Technology*, *12* (4), 343 - 347.

Melin, E., Skkog, R., & Odegaard, H. (2006). Ozonation/biofiltration with calcium carbonate as biofilter media. In: R. Gimbel, N.J.D. Graham, and M.R. Collins (Eds). *Recent progress in slow sand and alternative biofiltration processes*. (406-413). London: IWA Publishing.

Murov, S.L. (1993). Handbook of Photochemistry, (2<sup>nd</sup> ed), 299–313. New York: Marcel Dekker.

Murphy, B.M. (1993). Ozone-induced conversion of DBP precursors (DOC) to biodegradable by-products (BDOC). (Masters Dissertation), Department of Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, CO.

Najm, I.N., Patania, N.L., Jacangelo, J.G., & Krasner, S.W. (1994). Evaluating surrogates fordisinfection by-products. *Journal of American Water Works Association*, 86 (6), 98-106.

Nikolaou, A.D., & Lekkas, T.D. (2001). The role of natural organic matter during formation of chlorination byproducts: A review. *Acta Hydrochimica et Hydrobiolica*, 29 (2-3), 63–77.

Okun, D.A. (2003). Drinking water and public health protection. In F.W. Pontius (Ed), *Drinking Water Regulation and Health*, (3–24). New York, NY: John Wiley & Sons, Inc.

Oppenlander, T. (2003). *Photochemical purification of water and air*. New York:Wiley-VCH.

Owen, D.M., Amy, G.L., Chowdhury, Z.K., Paode, R., McCoy, G., & Viscosil, K. (1995). NOM characterization and treatability. *Journal of American Water Works Association*, 87(1), 46–63.

Parkinson, A., Roddick, F. A., Hobday, M. D. (2003). UV photooxidation of NOM: issues related to drinking water treatment. *Journal of Water Supply: Research and Technology.*—AQUA, 52(8), 577–586.

Pelekani, C., Newcombe, G., Snoeyink, V. L., Hepplewhite, C., Assemi, S., Beckett, R. (1999). Characterization of natural organic matter using high performance size exclusion chromatography. *Environmental Science and Technology*, *33*(16), 2807–2813.

Prévost, M., Coallier, J., Mailly, J., Desjardins, R. & Duchesne, D. (1992). Comparison of biodegradable organic carbon (BOC) techniques for process control. *Journal* of Water, Science & Technoglogy: AQUA, 41 (3) 141-150.

Prévost, M., Dubreuil, G., Desjardins, R. & Maclean, R. (1997). Bioreactors for the rapid determination of BDOC in drinking water - feed mode impact. In *Proceedings from the AWWA Water Quality Technology Conference*. Denver, CO.

Rakness, K.L., DeMers, L.D., Blank, B.D. (1996). Ozone system fundamentals for drinking water treatment. *Opflow*, 22(7), 4-5

Reckhow, D.A., & Singer, P.C. (1984). Mechanisms of organic halide formation during fulvic acid chlorination and implications with respect to pre-ozonation. In: R.L. Jolley, R.J. Bull, W.P. Davis, (Eds). *Water Chlorination: Chemistry, Environmental Impact and Health Effects*. (1229 - 1257). Chelsea, MI: Lewis Publishers Inc.

Reckhow, D.A., Singer, P.C., Malcom, R.L. (1990). Chlorination of humic materials: byproduct formation and chemical interpretations. *Environmental Science and Technology*, 24(11), 1655–1664.

Rittmann, B. & Huck, P. (1989). Biological treatment of public water supplies. *CRC Critical Review in Environmental Control*, *19*(2), 119-184.

Rook, J.J. (1977). Chlorination reactions of fulvic acids in natural waters. *Environmental Science and Technology*, 11(5), 478 - 482.

Sarathy, S. (2009). Effects of  $UV/H_2O_2$  advanced oxidation on physical and chemical characteristics of natural organic matter in raw drinking water sources. (Doctoral Dissertation). University of British Columbia, Vancouver, BC.

Sarathy, S., & Mohseni, M. (2007). The Impact of  $UV/H_2O_2$  advanced oxidation on molecular size distribution of chromophoric natural organic matter. *Environmental Science and Technology*, 41(24), 8315-8320

Sarathy, S., & Mohseni, M. (2009). The fate of natural organic matter during  $UV/H_2O_2$  advanced oxidation of drinking water. *Canadian Journal of Civil Engineering*, *36*, 160-169.

Servais, P., Billen, G. & Hascoet, M. (1987). Determination of the biodegradable fraction of dissolved organic matter in waters. *Water Research*, 21(4), 445-450.

Servais, P., Billern, G. & Bouillot, P. (1994). Biological colonization of granular activated carbon filters in drinking water treatment. *Journal of Environmental Engineering*, *120* (4), 888 - 899

Shukairy, H.M. & Summers, R.S. (1995). DBP speciation and kinetics as affected by ozonation and biotreatment disinfection by-products in water treatment: the chemistry of their formation and control. In Disinfection By-Products in Water Treatment, Eds. R.A. Minear and G.L. Amy. Boca Raton, FL: CRC Press Inc.,

Siddiqui, M.S., Amy, G.L. & Murphy, B.D., (1997). Ozone enhanced removal of natural organic matter from drinking water. *Water Research*, *31*(12), 3098-3106.

Singer P. C. (1994). Control of disinfection by-products in drinking water. *Journal of Environmental Engineering*, *120*(4), 727-744.

Singer, P.C. (1999). Formation and control of disinfection by-products in drinking water. AWWA Publishing, Denver, CO.

Speitel, G. E., Jr., Symons, J. M., Mialaret, J. M., & Wanielista, M. M. E. (2000). AOP/Biofilm process for DOX precursors. *Journal of American Water Works Association*, *92*, 59–73.

Summers, R.S., Hooper, S.M., Shukairy, H.M., Solarik, G., & Owen, D. (1996). Assessing DBP yield: uniform formation conditions. *Journal of American Water Works Association*, 88(6), 80-93.

Sundstrom, D.W., Klei, H.E., Nalette, T.A., Reidy, D.J., Weir, B.A., 1986. Destruction of halogenated aliphatics by UV catalyzed oxidation with  $H_2O_2$ . *Hazardous Waste Hazardous Materials*, 3(1), 101–110.

Swietlik J., Dabrowska A., Raczyk-Stanisławiak U., & Nawrocki J. (2004). Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Water Research* 38(3), 547-558.

Symons, J.M., Krasner, S.W., Sclimenti, M.J., Simms, L.A., Sorensen, H.W., Speitel, G.E., & Diehl, A.C. (1996). Influence of bromide ion on trihalomethane and haloacetic acid formation. In R.A. Minear & G.L.Amy (Eds), *Disinfection By-Products in Water Treatment: The Chemistry of Their Formation and Control.* (91–130). Boca Raton, FL:CRC.

Symons, J.M., Krasner, S.W., Simms, L.A., & Sclimenti, M. (1993). Measurement of THM and precursor concentration revisited: the effect of bromide ion. *Journal American Water Works Association*, 85(1), 51-62.

Thomson, J., Roddick, F.A., Drikas, M. (2002a). UV photooxidation facilitating biological treatment for the removal of NOM from drinking water. *Journal of Water Supply Research and Technology* – *AQUA*, *51* (6), 297–306.

Thomson, J., Roddick, F., & Drikas, M. (2002b). Natural organic matter removal by enhanced photo-oxidation using low pressure mercury vapor lamps. *Journal Water Science and Technology: Water Supply*, *2* (5-6), 435–443.

Thomson, J., Parkinson, A., & Roddick, F. A. (2004). Depolymerization of chromophoric natural organic matter. *Environmental Science Technology*, *38*, 3360–3369.

Toledano, M.B., Nieuwenhuijsen, M.J., Best, N., Whitaker, H., Hambly, P., de Hoogh, C., Fawell, J., Jarup, L., Elliott, P. (2005). Relation of trihalomethane concentrations in public water supplies to stillbirth and birth weight in three water regions in England. *Environmental Health Perspectives*, *113*, 225–232.

Toor R., & Mohseni M. (2007).  $UV/H_2O_2$  based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water. *Chemosphere*, 66 (11), 2087-2095.

Tuhkanen, T.A. (2004). UV/H<sub>2</sub>O<sub>2</sub> processes. In: S. Parsons (Ed.), *Advanced Oxidation Processes for Water and Wasterwater Treatment*. (86 - 110). London, UK: IWA Publishing.

Uhl, W. (2000). Biofiltration processes for organic matter removal. In: Rehm, H.J., & Reed, G. (eds). Biotechnology, 2nd completely revised ed. Vol 11c, Environmental Processes III. Wiley - VCH, New York. Pp. 457 - 478.

United States Environmental Protection Agency (USEPA). (2006). National primary drinking water regulations: stage 2 disinfectants and disinfection byproducts final rule. Fed. Regist. 71 (18), 388–492. <u>http://www.epa.gov/fedrgstr/EPA-WATER/2006/January/Day-04/w03.pdf</u>. Accessed: June 24, 2010.

Urfer, D. & Huck, P.M. (2001). Measurement of biomass activity in drinking water biofilters using a respirometric method. Water Research. 35 (6) pp.1469-1477.

van der Kooij, D., Hijnen, W.A.M., & Kruithof, J.C. (1989). The effect of ozonation, biological filtration and distribution on the concentration of easily assimilable organic carbon (AOC) in drinking water. *Ozone: Science and Engineering*, *11*(3), 297–311.

von Gunten, U. (2003a). Ozonation of drinking water: Part I.Oxidation kinetics and product formation. *Water Research*, *37*(7), 1443-1467.

von Gunten, U. (2003b). Ozonation of drinking water: Part II. Disinfection and byproduct formation in presence of bromide, iodide or chlorine. *Water Research*, *37*(7), 1469-1487.

Wang, J.Z., & Summers, R.S. (1994). Modeling of biofiltration of natural organic matter in drinking water treatment. In Proceedings of the 1994 ASCE Environmental Engineering Conference. Boulder, CO.

Wang, J.Z., Summers, R.S. & Miltner, R.J. (1995). Biofiltration performance: Part 1, relationship to biomass. *Journal American Water Works Association*, 87(12), 55 - 63.

Wang G. S., Hsieh S. T., & Hong C. S. (2000). Destruction of humic acid in water by UV light - catalyzed oxidation with hydrogen peroxide. *Water Research*, *34*, 3882-3887.

Wang G.-S., & Hsieh S.-T.: (2001). Monitoring natural organic matter in water with scanning spectrophotometer. *Environmental International*, 26(4), 205-212.

Wang, G.-S., Liao, C.-H., Chen, H.-W., & Yang, H.-C. (2006). Characteristics of natural organic matter degradation in water by  $UV/H_2O_2$  treatment. *Environmental Technology*, 27(3), 277–287.

Werner, P.; Hambsch, B. (1986). Investigations on the growth of bacteria in drinking water. *Water Supply*, *4*(3), 227 - 235.

Westerhoff, P., Debroux, J., Aiken, G., & Amy, G. (1999). Ozone induced changes in natural organic matter (NOM) structure. *Ozone Science and Engineering*, *21*, 551–570.

World Health Organization (WHO). (2008). Guidelines for drinking-water quality: incorporating 1st and 2nd addenda, Vol.1, Recommendations. (3<sup>rd</sup> Ed). <u>http://www.who.int/water\_sanitation\_health/dwq/fulltext.pdf</u> [Accessed June 6, 2010].

Wu, J.J., Wu, C., & Chuang, W. (2003). Evaluation of oxidation byproducts and control of organic matters using advanced oxidation processes (AOPs) combined with biological fluidized bed for the treatment of eutrophicated raw water. In *Proceedings of the 16th International Ozone Congress*, Las Vegas, NV.

Xie, Y.F. & Zhou, H. (2001). Biologically active carbon for HAA removal: Column study. In *Proceedings from the 2001 AWWA Water Quality Technology Conference*. Nashville, TN.

Xie, Y.F., & Zhou, H., (2002). Use of BAC for HAA removal, Part 2: Column study. *Journal of American Water Works Association*, 94(5), 126 - 135.

Xie, Y. F. (2004). Disinfection Byproducts in Drinking Water: Formation, analysis, and control. New York, NY: Lewis Publishers.

Yavich, A.A. (1998). The use of ozonation and biological fluidized bed treatment for the control of NOM in drinking water. (Doctoral Dissertation), Michigan State University, East Lansing, MI.

Yavich, A.A., Lee, K.H., Chen, K.C., Papa, L. & Masten, S.J. (2004). Evaluation of biodegradability of NOM after ozonation. *Water Research*, *38*(12), 2839 - 2846.

ID	Date	Time (min)	<i>N</i> Sodium Thiosulfate	Titration 1	Titration 2	Blank Titration	Primary KI Trap Titration	Calculated O <sub>3</sub> Produced (mg/L)	Calculated O <sub>3</sub> Produced in 2L (mg)	mg O <sub>3</sub> (200ml Trap 1)	Total O <sub>3</sub> Produced (mg)	Total O <sub>3</sub> Produced (mg/L)
	July 19th, 2010	3.00	0.01	20.8	21	0	0.2	50.16	100.32	0.096	100.224	50.112
	July 19th, 2010	6.00	0.01	38.7	39.7	0	0.3	94.08	188.16	0.144	188.016	94.008
	July 20th, 2010	2.50	0.01	16.1	16.5	0	0.2	39.12	78.24	0.096	78.144	39.072
	July 20th, 2010	5.00	0.01	31.7	33.5	0	0.3	78.24	156.48	0.144	156.336	78.168
	July 21st, 2010	2.50	0.01	16.5	16.4	0	0.2	39.48	78.96	0.096	78.864	39.432
	July 21st, 2010	1.00	0.01	8.5	8.6	0	0.1	20.52	41.04	0.048	40.992	20.496
0 <b>n</b>	July 21st, 2010	0.50	0.01	3.8	3.7	0	0.1	9	18	0.048	17.952	8.976
Calibration	July 21st, 2010	0.25	0.01	1.9	2	0	0	4.68	9.36	0	9.36	4.68
alib	July 21st, 2010	0.50	0.01	3.8	3.6	0	0.1	8.88	17.76	0.048	17.712	8.856
Ü	July 22nd, 2010	0.50	0.01	3.7	3.6	0	0.1	8.76	17.52	0.048	17.472	8.736
	July 22nd, 2010	0.75	0.01	5.4	5.6	0	0.1	13.2	26.4	0.048	26.352	13.176
	July 23rd, 2010	0.75	0.01	5.6	5.8	0	0.1	13.68	27.36	0.048	27.312	13.656
	July 25th, 2010	0.67	0.01	5	4.8	0	0.1	11.76	23.52	0.048	23.472	11.736
	July 25th, 2010	0.50	0.01	3.8	3.8	0	0.1	9.12	18.24	0.048	18.192	9.096
	July 31st, 2010	15.00	0.01	96.4	96.7	0	0.1	231.72	463.44	0.048	463.392	231.696
	August 8th, 2010	5.00	0.01	33.7	33.9	0	0.1	81.12	162.24	0.048	162.192	81.096

## APPENDIX A. OZONATION CALIBRATION DATA

Table A-1 - Ozone calibration data

	ID	Date	Time (min)	N Sodium Thiosulfate	Primary KI Trap Titration	Secondary Trap KI Titration	mg O <sub>3</sub> (200ml Trap 1)	mg O <sub>3</sub> (200ml Trap 2)	Total O <sub>3</sub> Produced (mg)	Total O <sub>3</sub> Produce d (mg/L)	DOC Raw Water (mg/L)	Total O <sub>3</sub> Produced (mg O <sub>3</sub> /mg DOC )
	703 1.1	July 3rd, 2010	0.75	0.01	1.9	0.1	0.888	0.048	20.1456	10.0728	4.8763	2.0657
	704 1.1	July 4th, 2010	0.75	0.01	1.7	0.1	0.792	0.048	20.2416	10.1208	5.1247	1.9749
	705 1.1	July 5th, 2010	0.75	0.01	1.4	0.1	0.648	0.048	20.3856	10.1928	4.9957	2.0403
	706 1.1	July 6th, 2010	0.75	0.01	1.9	0.1	0.888	0.048	20.1456	10.0728	4.9875	2.0196
	710 1.1	July 10th, 2010	0.75	0.01	2.3	0.1	1.08	0.048	19.9536	9.9768	5.3112	1.8784
	714 1.1	July 14th, 2010	0.75	0.01	3	0.1	1.416	0.048	19.6176	9.8088	4.8865	2.0073
	715 1.1	July 15th, 2010	0.75	0.01	2.6	0.1	1.224	0.048	19.8096	9.9048	4.9876	1.9859
	718 1.1	July 18th, 2010	0.75	0.01	3.2	0.1	1.512	0.048	20.1936	10.0968	4.8995	2.0608
	719 1.4	July 19th, 2010	0.5	0.01	19	0.1	9.12	0.048	9.024	4.512	5.164	0.8737
	720 1.1	June 20th, 2010	0.75	0.01	2.8	0.1	1.32	0.048	19.7136	9.8568	5.0134	1.9661
	721 1.1	July 21st, 2010	2.5	0.01	65	0.1	31.32	0.048	47.496	23.748	5.2443	4.5283
	721 2.1	July 21st, 2010	0.5	0.01	13.7	0.1	6.624	0.048	11.52	5.76	5.2853	1.0898
<u>ب</u>	721 2.2	July 21st, 2010	0.5	0.01	4.3	0.1	2.088	0.048	16.056	8.028	4.8346	1.6605
Treatment	721 2.3	July 21st, 2010	0.5	0.01	0.9	0.1	0.408	0.048	17.736	8.868	4.7217	1.8781
ne	721 2.4	July 21st, 2010	0.5	0.01	3.1	0.1	1.488	0.048	16.656	8.328	4.596	1.8120
ntı	723 1.1	July 23rd, 2010	0.75	0.01	2.8	0.1	1.32	0.048	22.39344	11.19672	5.0646	2.2108
ee	723 1.1	July 23rd, 2010	0.75	0.01	3.4	0.1	1.608	0.048	19.4256	9.7128	4.9876	1.9474
Ľ	723 1.2	July 23rd, 2010	0.75	0.01	3.8	0.1	1.872	0.048	25.392	12.696	5.1337	2.4731
•	724 1.1	July 24th, 2010	0.75	0.01	2.8	0.1	1.32	0.048	19.7136	9.8568	5.0646	1.9462
	725 1.1	July 25th, 2010	0.75	0.01	25.1	0.1	12.096	0.048	11.328	5.664	4.7393	1.1951
	725 1.2	July 25th, 2010	0.75	0.01	23.9	0.1	11.424	0.048	12	6	4.6721	1.2842
	730 1.1	June 30th, 2010	0.75	0.01	2.5	0.1	1.176	0.048	19.8576	9.9288	5.2347	1.8967
	731 1.1	July 31st, 2010	15	0.01	46.2	0.8	22.728	0.384	440.28	220.14	4.4398	49.5833
	731 1.2	July 31st, 2010	0.75	0.01	3.4	0.1	1.608	0.048	25.656	12.828	4.8264	2.6579
	731 1.3	July 31st, 2010	30	0.01	220	80	106.56	38.4	781.824	309.576	4.0277	76.8617
	801 1.1	August 1st, 2010	45	0.01	305	105	147.6	50.4	1192.176	434.568	5.7945	74.9966
	803 1.1	August 2nd, 2010	0.5	0.01	3.6	0.1	1.752	0.048	16.392	8.196	4.8913	1.6756
	808 1.1	August 8th, 2010	5	0.01	230	0.8	110.88	0.384	50.928	25.464	4.9583	5.1356
	815 1.1	August 25th, 2010	0.75	0.01	1.8	0.1	0.84	0	20.1936	10.0968	4.8995	2.0608
	825 1.1	August 25th, 2010	2.5	0.01	74	75	35.76	0.24	42.864	21.432	5.1225	4.1839
	825 1.2	August 25th, 2010	5	0.01	236	234	112.8	0.288	49.104	24.552	4.6883	5.2369

Table A-2 - Ozone treatment data

# APPENDIX B. UV/H<sub>2</sub>O<sub>2</sub> TREATMENT DATA

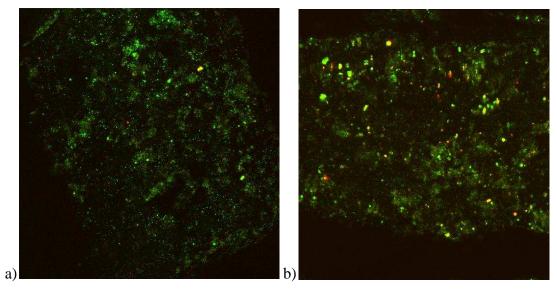
ID	UVA <sub>254</sub> (cm <sup>-1</sup> )	wf	UV Dose ( <i>mJ/cm</i> <sup>2</sup> )	Volume (mL)	Irradiation Time, IT ( <i>min</i> )	H <sub>2</sub> O <sub>2</sub> Dose	Bovine Liver Stock Concentration (mg/L)	Bovine Liver Dosing (mL)
Jphh 06/23 1.1	0.155	0.91585	2000	1000	32.7	0 mg/L	500	0.4
Jphh 06/23 1.2	0.157	0.91483	2000	1000	32.7	0 mg/L	500	0.4
Jphh 06/23 1.3	0.157	0.91483	4000	1000	65.4	0 mg/L	500	0.4
Jphh 06/23 1.4	0.159	0.91381	4000	1000	65.5	0 mg/L	500	0.4
Jphh 06/23 2.1	0.151	0.9179	2000	1000	32.6	10 mg/L	500	0.4
Jphh 06/23 2.2	0.155	0.91585	2000	1000	32.7	10 mg/L	500	0.4
Jphh 06/23 2.3	0.157	0.91483	4000	1000	65.4	10 mg/L	500	0.4
Jphh 06/23 2.4	0.152	0.91739	4000	1000	65.3	10 mg/L	500	0.4
Jphh 06/26 1.1	0.154	0.91637	2000	900	29.4	10 mg/L	500	0.36
Jphh 06/26 1.2	0.153	0.91688	2000	900	29.4	10 mg/L	500	0.36
Jphh 06/26 1.3	0.142	0.92254	4000	900	58.4	10 mg/L	500	0.36
Jphh 06/26 1.4	0.149	0.91893	4000	900	58.6	10 mg/L	500	0.36
Jphh 06/26 2.1	0.172	0.90721	2000	1500	49.5	10 mg/L	500	0.6
Jphh 06/26 2.2	0.169	0.90873	4000	1500	98.8	10 mg/L	500	0.6
Jphh 06/26 2.3	0.148	0.91944	4000	1500	97.7	0 mg/L	500	0
Jphh 06/26 2.4	0.157	0.91483	4000	1500	98.2	0 mg/L	500	0
Jphh 06/26 3.1	0.156	0.91534	2000	1500	49.1	0 mg/L	500	0
Jphh 06/26 3.2	0.156	0.91534	4000	1500	98.1	0 mg/L	500	0
Jphh 06/27 1.1	0.175	0.9057	4000	1500	99.2	10 mg/L	500	0.6
Jphh 06/27 1.2	0.172	0.90721	4000	1500	99.0	10 mg/L	500	0.6
Jphh 06/27 1.3	0.158	0.91432	2000	1500	49.1	10 mg/L	500	0.6
Jphh 06/27 1.4	0.157	0.91483	2000	1500	49.1	10 mg/L	500	0.6

Table B-1- UV/  $H_2O_2$  experiment conditions

## APPENDIX C. BIOMASS ANALYSIS AND VOLATILIZATION

## RESULTS

The three biomass analysis techniques were described in the previous Section. The first was through the use of a modified acridine orange staining method. Results are illustrated in Figure C-1 - Image of stained fluorescing GAC.



**Figure C-1 - Image of stained fluorescing GAC** (a is GAC from BAC Column 1, b is GAC from BAC Column 2)

Given the constraints of the microscope and the complexity of the surface of GAC particles, it was difficult to observe the presence of rod-shaped (bacteria) fluorescing elements. The virgin GAC did not respond similarly to this treatment, and produced no fluorescence under the microscope. Given that both particles underwent similar procedures, this provides a qualitative confirmation of the presence of biomass on the GAC particles.

The second analysis involved the determination of volatile solids on the granular activated carbon extracted from the columns. This analysis proved difficult given the medium used. It was necessary to perform a volatile solids test on both virgin GAC and GAC extracted from the columns. Results are presented in Figure C-2 and Table C-1.

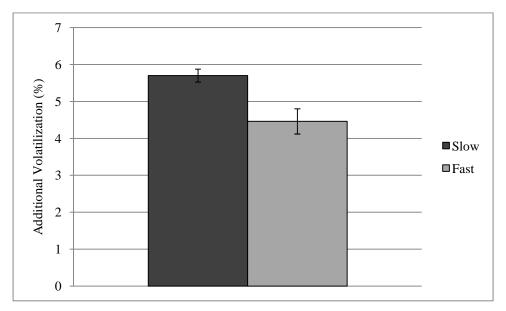


Figure C-2 - Percent additional volatilization of harvested GAC compared to virgin GAC

The value of percent additional volatization provides a semi-quantitative confirmation that biomass was present on the filter media. Given the complexity in analyzing results from this test, it is important that secondary tests be performed in order to confirm presence of biomass within filters.

The tests performed provided confirmation of presence of biomass growth within biofilters.

### Table C-1 - Volatilization of harvested GAC

Virgin GAC Volatilization

I	D	Dish Weight	Dish + GAC	After 40°C	After 105°C	After 550°C	Weight of Dry GAC	Weight of GAC after 105°C	Weight of GAC after 550°C	% Virgin GAC Volatilized	Aver	age
Virgir	n GAC	1.1080	3.6082	3.2279	3.2440	1.4803	2.1199	2.1360	0.3723	82.5702		
Virgin	n GAC	1.0791	2.7499	2.4750	2.5583	1.3025	1.3959	1.4792	0.2234	84.8972	86.2	026
Virgir	n GAC	1.1087	2.1020	1.8805	1.8140	1.1887	0.7718	0.7053	0.0800	88.6573	80.2	930
Virgir	n GAC	1.0804	1.8907	1.7017	1.7644	1.1553	0.6213	0.6840	0.0749	89.0497		
Filter (	GAC Vol	atilizatio	n									
ID	Dish Weight	Dish + GAC	After 40°C	After 105°C	After 550°C	Weight of Dry GAC	Weight of GAC after 105°C	Weight of GAC after 550°C	Remaining weight if Virgin GAC only	Additional amount volatilized	Additional % volatilized	Average
Slow	1.1018	5.4954	3.9964	2.0057	1.1784	2.8946	0.9039	0.0766	0.1239	0.0766	5.2320	
Slow	1.0904	4.9891	3.5212	1.9736	1.1632	2.4308	0.8832	0.0728	0.1211	0.0728	5.4636	
Slow	1.0962	4.6407	3.1389	1.8791	1.1611	2.0427	0.7829	0.0649	0.1073	0.0649	5.4167	
Slow	1.0760	4.9307	3.2027	1.9158	1.1466	2.1267	0.8398	0.0706	0.1151	0.0706	5.2996	
Slow	1.0753	2.1236	1.5761	1.3323	1.0946	0.5008	0.2570	0.0193	0.0352	0.0193	6.1830	
Slow	1.1074	2.0499	1.5153	1.3559	1.1268	0.4079	0.2485	0.0194	0.0341	0.0194	5.9166	5.6976
Slow	1.0786	2.2287	1.5821	1.3652	1.1019	0.5035	0.2866	0.0233	0.0393	0.0233	5.5639	
Slow	1.1014	5.7544	4.1847	2.2448	1.1926	3.0833	1.1434	0.0912	0.1567	0.0912	5.7302	
Slow	1.0900	4.8918	3.4525	1.9876	1.1604	2.3625	0.8976	0.0704	0.1230	0.0704	5.8632	
Slow	1.0957	3.5090	2.3734	1.6688	1.1397	1.2777	0.5731	0.0440	0.0786	0.0440	6.0288	
Slow	1.0758	4.5127	2.9312	1.9011	1.1396	1.8554	0.8253	0.0638	0.1131	0.0638	5.9759	
Fast	1.1008	1.8131	1.3852	1.2878	1.1177	0.2844	0.1870	0.0169	0.0256	0.0169	4.6929	
Fast	1.0895	2.1716	1.6189	1.3245	1.1115	0.5294	0.2350	0.0220	0.0322	0.0220	4.3273	4.4597
Fast	1.0952	2.4319	1.8488	1.3813	1.1219	0.7536	0.2861	0.0267	0.0392	0.0267	4.3588	

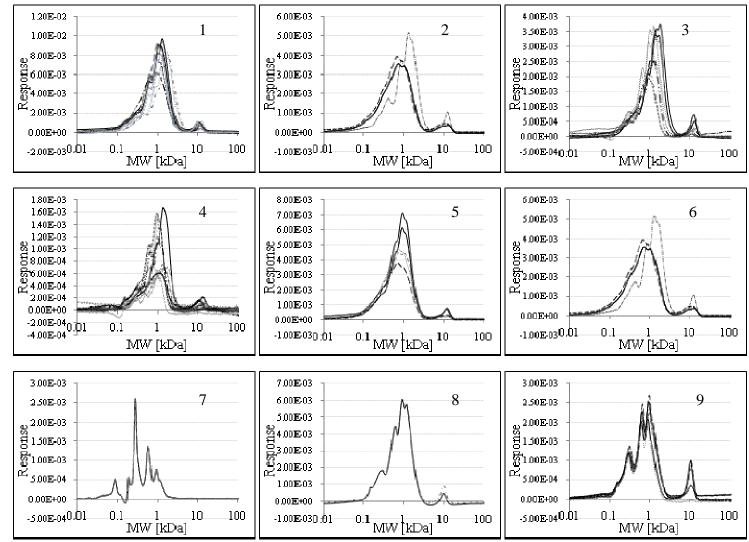
## APPENDIX D. BIOFILTRATION RESULTS FOR TOC AND UVA

	ŀ	Raw Water				Treated W	ater (2mg/m	g DOC)	
ID	DOC	(Std Dev)	UVA	SUVA	ID	DOC	(Std Dev)	UVA	SUVA
7/03 1.1	4.8763	0.062566	0.173	3.548	7/03 1.1	4.632485	0.077607	0.112	2.417709
7/04 1.1	5.1247	0.075093	0.156	3.038	7/04 1.1	4.868465	0.072941	0.116	2.382681
7/05 1.1	4.9957	0.073391	0.125	2.493	7/05 1.1	4.745915	0.034136	0.112	2.359924
7/06 1.1	4.9875	0.059522	0.162	3.247	7/06 1.1	4.738125	0.064205	0.117	2.469331
7/07 1.1	5.1104	0.0673	0.194	3.802	7/07 1.1	4.85488	0.030808	0.11	2.265761
7/07 1.2	4.9583	0.0489	0.136	2.743	7/07 1.2	4.710385	0.080567	0.12	2.547562
7/10 1.1	5.3112	0.068035	0.190	3.585	7/10 1.1	5.04564	0.09385	0.1	1.981909
7/14 1.1	4.8865	0.08278	0.163	3.334	7/14 1.1	4.642175	0.08996	0.118	2.541912
7/15 1.1	4.9876	0.034424	0.130	2.598	7/15 1.1	4.73822	0.065116	0.104	2.194917
7/18 1.1	4.8995	0.061799	0.166	3.396	7/18 1.1	4.654525	0.055671	0.112	2.406261
7/19 1.1	5.0896	0.1007	0.173	3.399	7/19 1.1	4.7845	0.0555	0.109	2.27819
7/19 1.4	5.6839	0.0821	0.176	3.096	7/19 1.4	4.837635	0.048563	0.103	2.12914
7/20 1.1	5.0134	0.0827	0.127	2.527	7/20 1.1	4.7154	0.1029	0.115	2.438817
7/21 1.1	5.2853	0.0576	0.181	3.425	7/21 1.1	5.021035	0.003186	0.111	2.2107
7/21 2.1	4.91	0.0704	0.162	3.299	7/21 2.1	4.6411	0.0346	0.108	2.327035
7/21 2.2	4.8346	0.1403	0.128	2.648	7/21 2.2	4.7154	0.1029	0.115	2.438817
7/21 2.3	4.7217	0.132	0.163	3.452	7/21 2.3	4.391181	0.014173	0.106	2.413929
7/21 2.4	4.596	0.0673	0.160	3.481	7/21 2.4	4.45812	0.062726	0.117	2.624425
7/23 1.1	5.0646	0.0543	0.158	3.120	7/23 1.1	4.8959	0.0523	0.119	2.430605
7/23 1.2	5.1337	0.0446	0.160	3.117	7/23 1.2	5.0439	0.0918	0.118	2.33946
7/24 1.1	5.0646	0.000525	0.203	4.004	7/24 1.1	4.834086	0.062503	0.116	2.399626
7/25 1.1	4.7393	0.1165	0.163	3.439	7/25 1.1	4.765542	0.099263	0.105	2.203317
7/25 1.2	4.6721	0.0547	0.169	3.617	7/25 1.2	4.578658	0.017186	0.105	2.293248
7/30 1.1	5.2347	0.070709	0.153	2.923	7/30 1.1	5.339394	0.029089	0.108	2.022701
7/31 1.1	4.4398	0.006	0.141	3.176	7/31 1.1	4.7633	0.077378	0.119	2.498268
7/31 1.2	4.8264	0.0809	0.174	3.605	7/31 1.2	4.8694	0.0209	0.12	2.464369
7/31 1.3	4.0277	0.1319	0.150	3.724	7/31 1.3	3.62493	0.036364	0.111	3.062128
8/01 1.1	5.7945	0.1627	0.193	3.331	8/01 1.1	5.21505	0.000985	0.11	2.10928
8/03 1.1	4.8913	0.1422	0.159	3.251	8/03 1.1	4.40217	0.076535	0.125	2.839509
803 1.1	4.9223	0.056908	0.152	3.088	803 1.1	4.43007	0.065962	0.122	2.753907
825 1.1	4.8995	0.007096	0.153	3.123	825 1.1	4.40955	0.077968	0.121	2.744044

## Table D-1- DOC, UVA data for biofiltration

		Column 1.1			Column 1.2					
ID	DOC	(Std Dev)	UVA	SUVA	ID	DOC	(Std Dev)	UVA	SUV	
c1.1	2.5585	0.056	0.052	2.032	c1.2	1.4105	0.0082	0.028	1.98	
c1.1	2.845	0.0896	0.071	2.496	c1.2	2.1604	0.0059	0.04	1.85	
c1.1	2.915	0.0307	0.069	2.367	c1.2	2.7963	0.0471	0.063	2.25	
c1.1	2.8739	0.0222	0.066	2.297	c1.2	1.3516	0.0234	0.025	1.85	
c1.1	2.7396	0.0102	0.069	2.519	c1.2	1.8969	0.0357	0.035	1.84	
c1.1	2.6032	0.0278	0.07	2.689	c1.2	1.8712	0.0295	0.041	2.19	
c1.1	2.9943	0.1883	0.07	2.338	c1.2	2.1581	0.0174	0.053	2.45	
c1.1	2.8505	0.0563	0.033	1.158	c1.2	1.7933	0.0033	0.052	2.90	
c1.1	1.8807	0.0353	0.037	1.967	c1.2	1.3208	0.0513	0.023	1.74	
c1.1	2.0768	0.0375	0.034	1.637	c1.2	2.6759	0.0305	0.069	2.57	
c1.1	2.567	0.0038	0.058	2.259	c1.2	2.8325	0.0286	0.065	2.29	
c1.1	2.8731	0.0387	0.066	2.297	c1.2	2.8851	0.0411	0.067	2.32	
c1.1	1.6374	0.0251	0.031	1.893	c1.2	2.0382	0.0394	0.056	2.74	
c1.1	1.868	0.0265	0.032	1.713	c1.2	1.81	0.0349	0.05	2.76	
c1.1	1.858	0.0146	0.036	1.938	c1.2	3.0689	0.1246	0.074	2.4	
c1.1	2.4749	0.0263	0.058	2.344	c1.2	3.1687	0.0044	0.074	2.33	
c1.1	1.8673	0.0086	0.051	2.731	c1.2	2.7536	0.0616	0.057	2.0	
c1.1	1.6415	0.0202	0.046	2.802	c1.2	2.8848	0.2498	0.078	2.70	
c1.1	2.1401	0.0658	0.054	2.523	c1.2	2.7341	0.0464	0.073	2.6	
c1.1	1.9782	0.0106	0.054	2.730			Column 1.4			
c1.1	3.0086	0.1572	0.075	2.493	ID	DOC	(Std Dev)	UVA	SUV	
		Column 1.3			c1.4	2.5487	0.0096	0.062	2.43	
ID	DOC	(Std Dev)	UVA	SUVA	c1.4	2.0699	0.035	0.051	2.40	
c1.3	2.4422	0.0174	0.058	2.375	c1.4	2.7137	0.0279	0.072	2.65	
c1.3	2.8445	0.0388	0.078	2.742	c1.4	1.7791	0.0495	0.039	2.19	
c1.3	2.8857	0.0093	0.072	2.495	c1.4	1.863	0.0088	0.066	3.54	
c1.3	2.7753	0.0197	0.07	2.522	c1.4	2.0976	0.0214	0.038	1.8	
c1.3	2.6879	0.0721	0.068	2.530	c1.4	2.4814	0.0263	0.051	2.05	
c1.3	2.658	0.0341	0.067	2.521	c1.4	3.0319	0.0246	0.07	2.30	
					c1.4	2.8797	0.0748	0.07	2.43	
					c1.4	2.1572	0.021	0.034	1.5	
					c1.4	2.0717	0.0316	0.04	1.93	
					c1.4	2.2008	0.0137	0.052	2.30	
					c1.4	1.9851	0.0209	0.053	2.6	
					c1.4	2.0756	0.0087	0.045	2.10	
					c1.4	2.1134	0.0218	0.041	1.94	
					c1.4	1.873	0.0237	0.032	1.70	

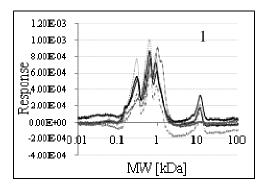
		Column 2.1					Column 2.2		
ID	DOC	(Std Dev)	UVA	SUVA	ID	DOC	(Std Dev)	UVA	SUV
c2.1	1.7927	0.0046	0.026	1.450	c2.2	1.4958	0.0031	0.021	1.40
c2.1	0.6786	0.0407	0.011	1.621	c2.2	0.5745	0.0109	0.01	1.74
c2.1	0.9522	0.031	0.014	1.470	c2.2	0.7179	0.0148	0.011	1.53
c2.1	1.497	0.0367	0.029	1.937	c2.2	0.937	0.0271	0.016	1.70
c2.1	1.3036	0.0107	0.019	1.458	c2.2	1.5214	0.0223	0.022	1.44
c2.1	1.4422	0.0196	0.023	1.595	c2.2	1.4938	0.0285	0.022	1.47
c2.1	1.1268	0.0636	0.018	1.597	c2.2	1.1601	0.057	0.02	1.72
c2.1	0.9713	0.0345	0.016	1.647	c2.2	1.779	0.0416	0.029	1.63
c2.1	0.9121	0.0203	0.014	1.535	c2.2	1.1613	0.0299	0.022	1.89
c2.1	0.7126	0.0224	0.011	1.544	c2.2	1.2679	0.0282	0.023	1.81
c2.1	1.3294	0.0223	0.024	1.805	c2.2	0.8409	0.0185	0.013	1.54
c2.1	1.3034	0.012	0.022	1.688	c2.2	1.0364	0.0258	0.016	1.54
c2.1	1.099	0.0109	0.02	1.820	c2.2	1.0935	0.0421	0.011	1.00
c2.1	1.8723	0.0323	0.035	1.869	c2.2	1.0643	0.0085	0.019	1.78
c2.1	0.8101	0.057	0.01	1.234	c2.2	1.6923	0.0628	0.031	1.83
c2.1	0.7984	0.0025	0.012	1.503	c2.2	0.9251	0.0362	0.013	1.40
c2.1	1.1518	0.0102	0.018	1.563	c2.2	0.8752	0.0384	0.014	1.60
c2.1	1.2449	0.0154	0.021	1.687	c2.2	1.4174	0.0087	0.026	1.83
c2.1	1.1038	0.0333	0.017	1.540			Column 2.4		
		Column 2.3			ID	DOC	(Std Dev)	UVA	SUV
ID	DOC	(Std Dev)	UVA	SUVA	c2.4	1.2809	0.0024	0.017	1.32
c2.3	1.3626	0.0099	0.019	1.394	c2.4	0.9609	0.01	0.02	2.08
c2.3	0.9923	0.0105	0.012	1.209	c2.4	1.7212	0.0101	0.037	2.15
c2.3	0.4287	0.0196	0.006	1.400	c2.4	1.2298	0.0261	0.013	1.05
c2.3	0.6108	0.0096	0.011	1.801	c2.4	0.9502	0.018	0.012	1.26
					c2.4	0.8915	0.0127	0.015	1.68
					c2.4	0.975	0.0321	0.015	1.53
					c2.4	2.142	0.0279	0.051	2.38
					c2.4	0.9851	0.0103	0.014	1.42
					c2.4	1.5226	0.0089	0.023	1.5
					c2.4	1.9644	0.0018	0.037	1.88
					c2.4	2.3996	0.045	0.048	2.00

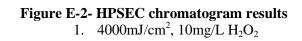


## APPENDIX E. OXIDATION HPSEC CHROMATOGRAMS

**Figure E-1- HPSEC chromatogram results** 

1. Raw Water; 2. Influent Water (Ozonated); 3. BAC Column 1; 4. BAC Column 2; 5. Ozonated 1mg; 6. Ozonated 2mg; 7. Extended Ozonation; 8. 4000mJ/cm<sup>2</sup>, 0mg/L H<sub>2</sub>O<sub>2</sub>; 9. 2000mJ/cm<sup>2</sup>, 10mg/L H<sub>2</sub>O<sub>2</sub>







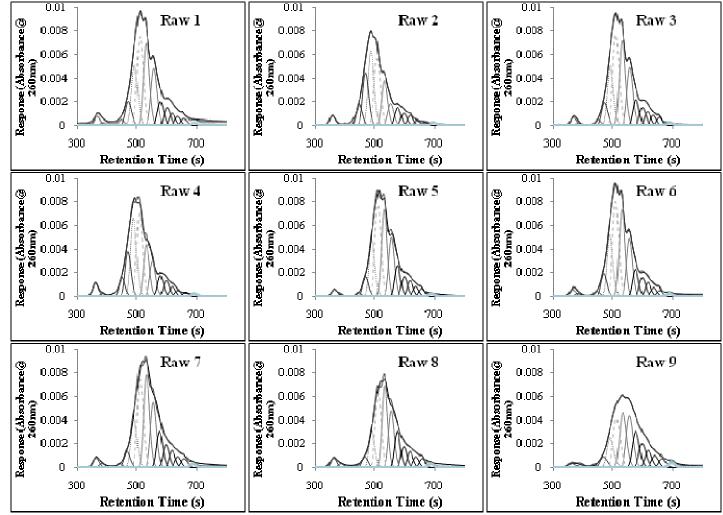


Figure F-1 - Peakfit analysis results for each of the raw water (ID 1-9) HPSEC chromatograms. Using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

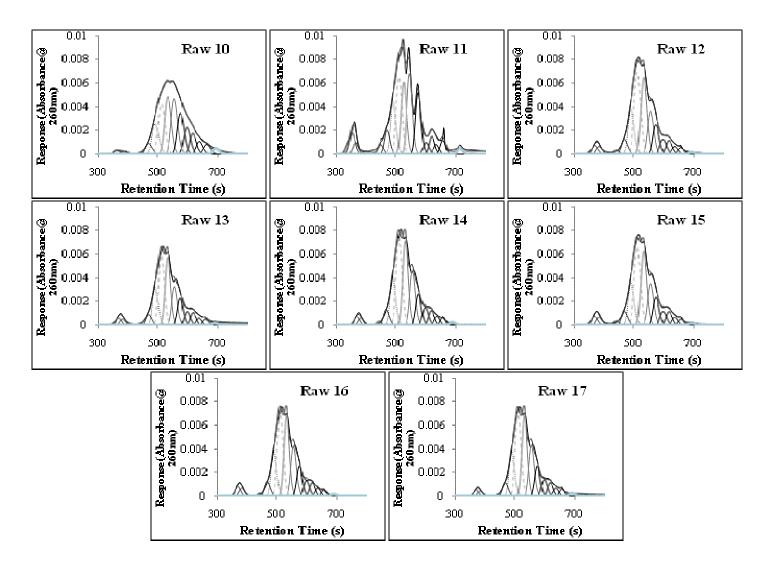


Figure F-2 - Peakfit analysis results for each of the raw water (ID 10 -17) HPSEC chromatograms. Using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

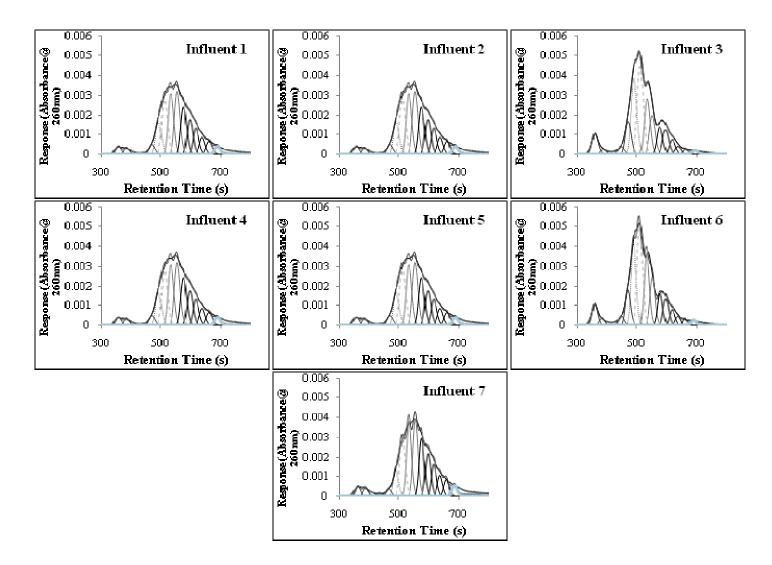


Figure F-3 - Peakfit analysis results for each of the influent BAC column ozonated at 2mgO<sub>3</sub>/mgDOC (ID 1 to 7) water HPSEC chromatograms. Using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

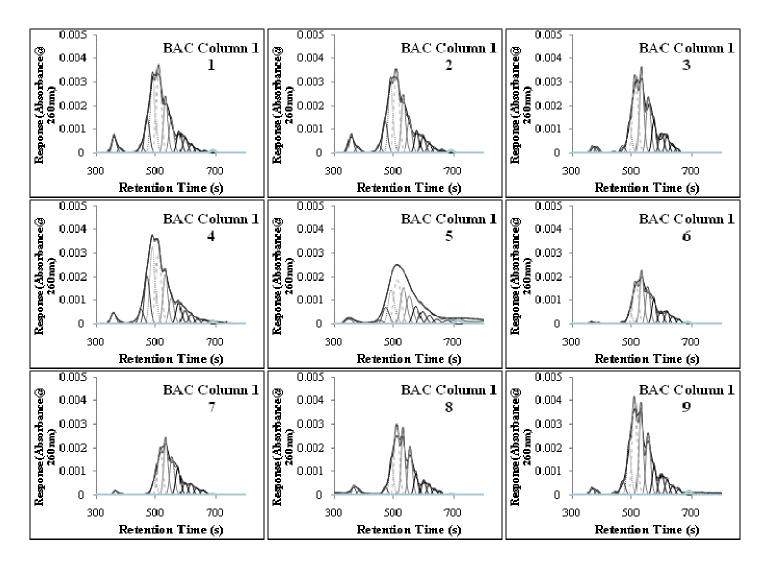


Figure F-4 - Peakfit analysis results for each of the influent BAC Column 1 effluent (ID 1 to 9) water HPSEC chromatograms. Using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

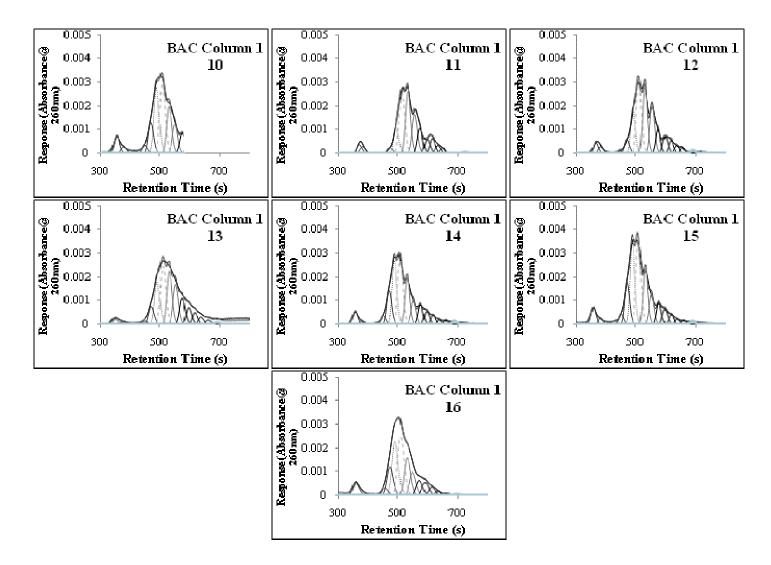


Figure F-5 - Peakfit analysis results for each of the influent BAC Column 1 effluent (ID 10 to 16) water HPSEC chromatograms. Using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

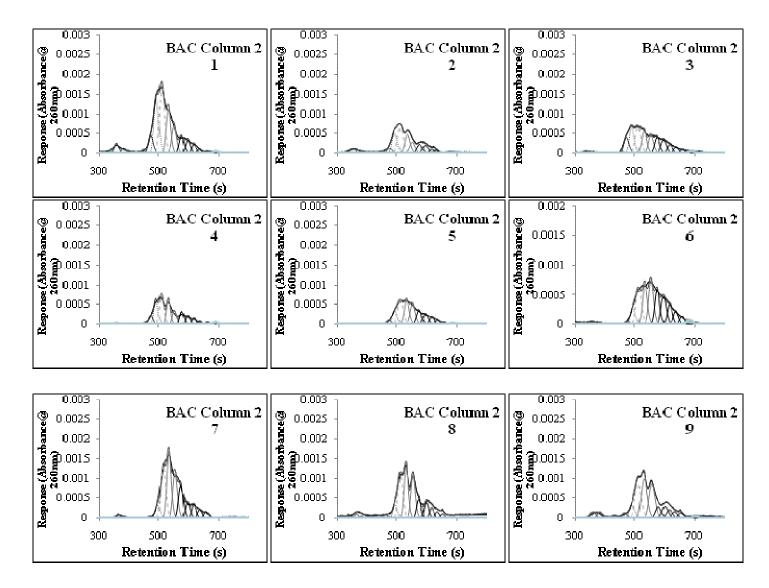


Figure F-6 -Peakfit analysis results for each of the influent BAC Column 2 effluent (ID 1 to 9) water HPSEC chromatograms. Using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

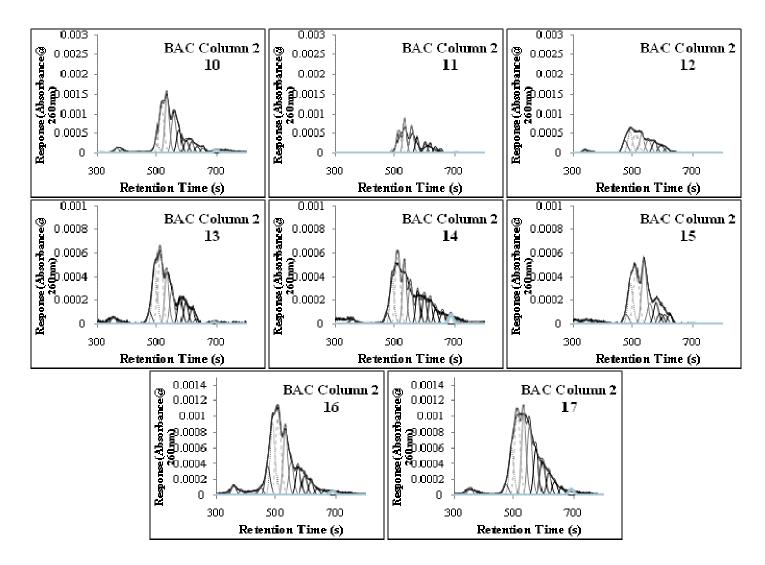


Figure F-7 -Peakfit analysis results for each of the influent BAC Column 2 effluent (ID 10 to 17) water HPSEC chromatograms. Using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

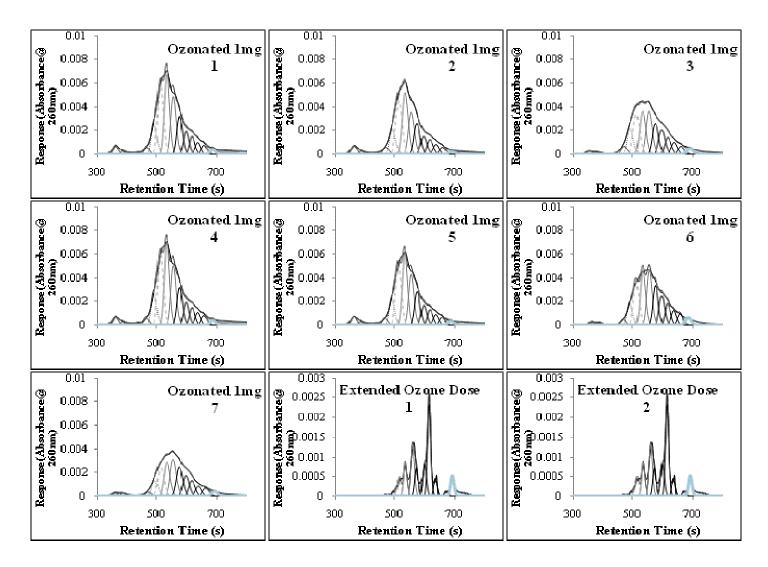


Figure F-8 - Peakfit analysis results for each of the Ozonated at 1mgO<sub>3</sub>/mgDOC water (ID 1-7) and extended dose (ID 1 to 2) HPSEC chromatograms. Using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

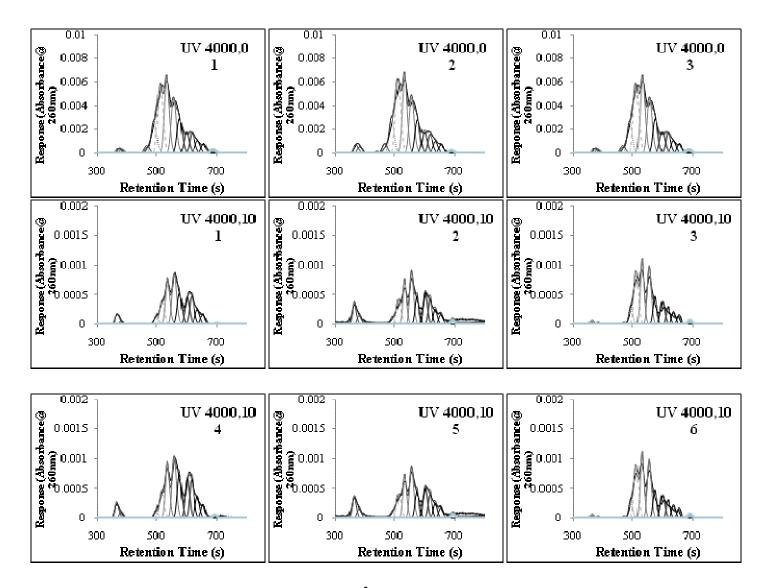
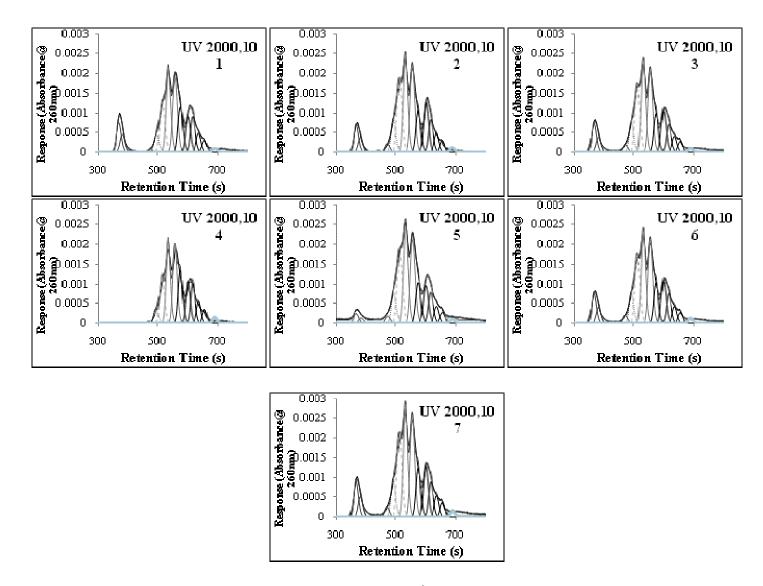


Figure F-9 - Peakfit analysis results for each of the UV 4000mJ/cm<sup>2</sup> and 0 mg/L H<sub>2</sub>O<sub>2</sub> (ID 1 to 3) and 10mg/L H<sub>2</sub>O<sub>2</sub>treated (ID 1 to 6) HPSEC chromatograms. Systat Peakfit v4.12 using Autofit Peak III Deconvolution.



**Figure F-10 -Peakfit analysis results for each of the UV 2000mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub> (<b>ID 1 to 7**) **HPSEC chromatograms.** Systat Peakfit v4.12 using Autofit Peak III Deconvolution.

Description	Sample ID	TBAA (ug/L)	CDBAA (ug/L)	BDCAA (ug/L)	DBAA (ug/L)	BCAA (ug/L)	TCAA (ug/L)	MCAA (ug/L)	DCAA (ug/L)	MBAA (ug/L)	HAA9 (ug/L)
4000,10 626 1.4	1	0.000	0.000	0.000	0.000	13.218	20.706	0.191	156.429	0.000	190.545
4000,10 626 1.3	3	0.000	0.000	0.000	0.000	12.630	21.419	1.780	159.922	0.000	195.751
Extended 805 1.1	4	0.000	0.000	0.000	0.000	1.681	14.225	0.000	9.441	0.000	25.347
c2.1 705	5	23.673	0.000	0.000	6.238	1.651	16.900	0.091	11.707	17.810	78.069
Extended 805 1.3	6	0.000	0.000	0.000	0.000	1.743	14.551	0.000	10.321	0.000	26.614
Extended 805 1.4	7	0.000	0.000	0.000	0.000	1.511	16.615	0.000	11.789	0.000	29.915
Extended 805 1.2	8	0.000	0.000	1.040	0.152	1.591	21.269	0.000	15.571	0.000	39.622
c1.2 707	9	0.000	0.000	1.606	0.000	1.907	63.269	0.000	62.623	0.000	129.405
2mg 715	11	0.000	0.000	2.956	0.000	2.746	98.658	0.000	93.285	0.000	197.645
2mg 713	12	0.000	0.000	1.937	0.000	2.665	98.687	0.000	100.573	0.000	203.862
c1.2 710	13	0.000	0.000	1.197	0.000	2.154	49.044	4.318	64.708	0.000	121.422
4000,10 627 1.1	14	32.074	0.000	0.000	0.463	3.659	67.848	0.000	80.288	0.000	184.331
4000,10 627 1.2	14 DUP	0.000	0.000	0.000	0.000	13.072	18.071	2.106	152.449	0.000	185.698
1mg 718	15	0.000	0.000	3.597	0.346	11.659	119.225	0.000	229.185	0.000	364.012
2000,10 626 2.1	16	0.000	0.000	2.608	0.227	7.605	73.330	12.357	152.103	0.000	248.230
c1.1 707	17	0.000	0.000	2.457	0.477	31.605	39.841	0.000	115.856	0.000	190.237
4000,10 627 1.2	18	0.000	0.000	0.000	0.450	31.712	45.784	0.000	128.032	0.000	205.978
4000,10 623 1.3	19	0.000	0.000	3.072	0.331	3.479	34.942	0.000	155.932	0.000	197.756
Raw 721 2.1	20	0.000	0.000	21.567	7.238	59.843	123.438	0.000	223.440	3.484	439.010
Raw 723 1.2	21	0.000	0.000	4.902	0.281	6.998	144.009	11.926	210.777	0.000	378.893
Raw 719 1.4	22	0.000	0.000	0.000	0.416	15.614	115.425	14.919	233.696	0.000	380.070
Raw 719 1.4	22 DUP	0.000	0.000	3.988	0.000	14.540	105.479	14.964	208.757	0.000	347.728
1mg 713	24	0.000	0.000	2.596	0.000	11.372	122.908	13.069	238.396	0.000	388.341
1mg 712	25	0.000	0.000	0.000	0.000	9.448	106.585	16.637	214.176	0.000	346.846
15 Spike (6	50)	576.828	314.808	102.60429	73.17381	145.35918	197.51118	180.516	374.00598	113.8041	
15 Recover	(%)	98	104	88	121	110	110	98	92	<i>93</i>	
60 STD		588.6	302.7	112.59	60.18	120	59.79	184.2	178.98	122.37	

# APPENDIX G. HAA RESULTS

Table G-1 - HAA data run 1

Description	Sample ID	TBAA	CDBAA	BDCAA	DBAA	BCAA	TCAA	MCAA	DCAA	MBAA	HAA9
L.	ł	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)
c2.2 801	26	0.000	0.000	3.038	0.000	4.074	40.979	0.000	27.590	0.000	75.681
c2.2 804	27	0.000	0.000	3.317	0.429	3.660	42.650	0.000	23.293	0.000	73.349
c2.2 806	28	0.000	0.000	3.259	0.308	3.986	46.280	0.000	31.693	0.000	85.525
c2.1 801	29	0.000	0.000	4.061	0.398	3.919	49.236	0.000	33.139	0.000	90.753
c2.1 803	30	0.000	0.000	3.117	0.234	2.577	27.838	2.012	19.300	0.000	55.079
2000,10 626 1.2	31	0.000	0.000	3.052	0.325	8.823	85.144	11.950	168.803	0.000	278.095
c1.2 806	32	0.000	0.000	1.508	0.000	2.163	74.766	3.953	71.941	0.000	154.330
2mg 801	33	0.000	0.000	2.288	0.314	3.085	119.049	5.575	104.904	0.000	235.214
2mg 802	33	0.000	0.000	2.735	0.000	2.854	103.478	2.345	100.035	0.000	211.447
4000,10 627	34	0.000	0.000	0.000	0.000	1.381	45.084	4.399	145.094	0.000	195.958
2000,10 627 1.3	35	0.000	0.000	1.146	0.256	3.540	144.853	4.600	135.714	0.000	290.108
2mg 803	36	0.000	0.000	0.000	0.000	3.603	91.748	5.425	110.487	0.000	211.263
2mg 804	37	0.000	0.000	1.823	0.239	3.766	96.803	5.475	115.504	0.000	223.610
4000,0 626 2.3	38	0.000	0.000	4.211	0.488	13.087	155.531	17.998	302.787	0.000	494.101
4000,0 626 2.4	39	0.000	0.000	0.000	0.355	12.487	135.827	16.292	270.210	0.000	435.171
c1.1 801	40	0.000	0.000	2.336	0.422	30.549	32.661	8.597	95.381	0.000	169.946
c1.1 804	40 DUP	0.000	0.000	3.2654	0.000	32.465	31.185	8.655	86.789	0	162.359
2000,10 627 1.3	41	0.000	0.000	2.418	0.692	36.720	61.574	11.592	172.901	0.000	285.897
c1.1 801	42	0.000	0.000	4.962	0.246	5.085	61.890	4.594	83.475	0.000	160.252
2000,10 626 1.2	43	0.000	0.000	19.609	4.835	40.771	80.563	8.815	146.367	2.426	303.386
Raw 721 2.1	44	0.000	0.000	5.017	0.408	9.460	203.217	10.511	188.253	0.000	416.866
Raw 721 2.1	45	0.000	0.000	4.037	0.222	6.244	139.430	10.321	195.777	0.000	356.031
4000,0 623 1.1	46	0.000	0.000	0.352	0.426	13.782	167.094	13.650	292.436	0.000	487.740
2000,10 627 1.4	47	0.000	0.000	3.478	0.000	10.425	76.543	14.321	150.478	0.000	255.245
34 Spike (2	0)	174.618	118.053	35.654	18.656	42.540	59.500	65.361	98.060	39.566	
34 Recover (		89	117	95	93	103	92	99	48	97	
20 STD		196.2	100.9	37.53	20.06	40	19.93	61.4	59.66	40.79	

# APPENDIX H. THM RESULTS

Description	Sample ID	Chloroform (ug/L)		Dibromochloroform	Bromoform (ug/L)
			(ug/L)	(ug/L)	
Raw 802	39	250.804535	51.10706977	6.063689458	0
Raw 731 1.2	33	206.9451227	31.63243132	2.778186312	0
Raw 731 1.2	32	204.7230835	27.16993318	2.279237894	0
Raw 731 1.1	31	264.4803594	19.13325392	0	0
Raw 725 1.2	30	157.3051628	72.78095509	25.23699774	0
Raw 725 1.1	27	211.784019	101.553403	35.16377021	2.573537148
Raw 725 1.1	27 DUP	196.9861091	95.54887981	33.31593809	2.461003698
Raw 719 1.4	3	178.574	95.684	35.985	3.121
Raw 719 1.4	3 DUP	167.030	90.174	33.964	2.979
Raw 719 1.2	76	205.498856	117.8887309	65.75337216	8.836802552
Raw 719 1.1	2	271.333	155.969	61.869	5.467
Raw 719 1.1	1	206.043	119.455	44.448	4.047
Raw 707 1.4	9	170.137	95.855	36.794	3.146
Raw 707 1.2	7	208.882	114.091	43.657	3.842
Extended 806	44 DUP	24.00932068	27.38452356	28.38760902	13.27881389
Extended 806	44	21.76928435	24.99147686	27.80790972	12.39275519
Extended 805	46	23.30938468	26.61728637	27.85598276	12.83999739
Extended 804	45	32.37661894	34.88766049	43.09139428	16.15064574
Extended 803	47	28.3646767	35.85088398	40.39216478	21.00848481
Extended 802	48	24.67935672	40.10804452	47.78671664	26.41884547
Extended 801	79	25.66645486	40.43240802	51.56573015	26.9162005
c2.2 806	62	54.45040949	12.3848969	2.961951409	0
c2.2 724	71	10.65838967	12.48548776	16.0913155	10.0547004
c2.2 723	70	9.20241938	10.63496849	14.00835355	8.642110457
c2.2 719	69	11.07243045	12.80789526	15.88505235	9.231351688
c2.2 719	69 DUP	9.639340614	11.06313313	14.28986189	8.821460881
c2.2 717	68	8.559610743	9.910030354	12.95782043	8.035877997
c2.1 806	67	26.19423468	11.90137728	10.56963021	0
c2.1 717	65	12.21923085	4.323988733	0	0
c2.1 708	63	6.566480383	7.037528097	8.953098529	5.623485762
c1.3 721	13	63.941	28.919	9.514	0.000
c1.3 719	40	42.92812524	33.39187239	23.46873248	5.801638462
c1.2 805	61	67.57416301	15.35265811	3.648219675	0
c1.2 803	60 DUP	67.96797626	16.78824546	4.107742649	0
c1.2 803	60	59.55193203	14.3952766	3.529976065	0
c1.2 801	72	17.51249287	20.95193513	26.70045751	12.78411784
c1.2 725	59	78.80912886	19.95684368	4.52851584	0
c1.2 713	58	134.0903971	35.95916834	9.295534404	0
c1.2 713	58 DUP	120.5987487	32.42883821	8.389534854	0
c1.2 707	57	100.2366471	26.20468464	6.749745782	0
c1.1 806	56	78.25103799	19.13770853	4.349084878	0
c1.1 805	55	64.51433342	13.34929493	0	0
c1.1 801	54	89.10700381	21.96673422	0	0
c1.1 801	66	59.24951559	23.39366873	0	0
c1.1 801	66 DUP	42.91749782	18.3151619	8.025130576	0
c1.1 723	53	136.5448694	37.42827607	7.856443882	0
c1.1 718	11 DUP	64.073	37.602	20.474	2.189
c1.1 718	11	58.826	33.977	18.305	2.246
c1.1 715	52	56.7601021	15.7898895	3.527770076	0 .

#### Table H-1 - THM data run 1

Description	Sample ID	Chloroform (ug/L)	Bromodichloroform (ug/L)	Dibromochloroform (ug/L)	Bromoform (ug/L)
c1.1 710	64	9.063877698	9.751668923	111.9087153	6.806400828
c1.1 707	51	82.81542359	19.53688122	0	0
4000,10 6301.4	18	100.097	53.831	19.970	0.000
4000,10 6301.4	16	121.961	54.528	18.432	0.000
4000,10 628 1.2	12	91.088	53.968	29.279	3.665
4000,10 628 1.2	75	93.67730639	54.51220053	28.3604886	4.014777014
4000,10 628 1.2	12 DUP	66.271	38.555	20.862	2.576
4000,10 628 1.1	38 DUP	160.9202888	32.35952543	3.694472598	0
4000,10 628 1.1	38	152.24346	30.24480897	3.441213521	0
4000,10 627 1.3	23	81.67231363	51.95056201	28.16341428	4.102771205
4000,10 627 1.3	23 DUP	73.65376382	47.16427986	25.64689683	3.731376557
4000,10 626 1.4	37	150.2098969	16.9799564	0	0
4000,10 626 1.4	36	175.4308497	10.76951614	0	0
4000,10 626 1.3	81	198.3206802	14.15201661	0	0
4000,10 626 1.3	26	101.5351401	46.2841196	15.54093654	0
4000,0 731 1.2	35	234.06108	51.14474629	11.40636839	0
4000,0 723 1.2	22	156.5054694	99.52207248	60.46156947	9.014687415
4000,0 723 1.2	21	152.837	94.684	56.779	8.428
2mg 803	6 DUP	124.295	67.713	25.265	2.029
2mg 803	6	114.457	61.110	22.808	0.000
2mg 803	80	61.336	79.147	29.897	2.462
2mg 731 1.2	78	114.3666571	36.61431523	11.48246322	0
-	78 34		24.51691957		
2mg 731 1.2	34 20	116.0322474 116.520	72.016	5.260213764 42.792	0 6.477
2mg 723 1.2					
2mg 723 1.1	24	117.8779411	70.5704658	41.12016985	5.695010945
2mg 723 1.1	25 17	75.83086314	44.69755575	25.6838767	3.417264377
2mg 713		94.709	42.827	14.493	0.000
2mg 712	14	111.095	48.608	16.276	0.000
2mg 703	28	90.59996746	53.14386964	30.45344812	3.717114248
2mg 703	28 DUP	62.59834194	35.85652179	20.5421347	2.59409317
2000,10 627 1.4	8 DUP	135.786	71.283	26.571	2.141
2000,10 627 1.4	10	125.994	61.227	22.450	0.000
2000,10 627 1.4	8	131.299	68.275	25.107	2.000
2000,10 627 1.3	15	132.575	61.402	21.516	0.000
2000,10 628 1.4	50	142.4026778	114.4578269	79.80530419	17.57563913
2000,10 626 1.2	43	120.4717811	97.41789612	73.71977376	18.83953007
2000,10 626 1.2	42 DUP	108.5744702	90.39805444	68.53048874	17.95469006
2000,10 626 1.2	42	95.08601854	77.10942042	58.19514044	15.05775365
2000,10 626 1.1	41	142.5217178	117.7229605	85.33129985	21.38335835
1mg 725 1.1	77	158.7835577	91.30627225	50.63579869	6.823898321
1mg 725 1.1	29	153.6594333	90.94253809	53.25132562	6.49110536
1mg 721 2.1	73	176.5813409	101.8294673	53.99799587	6.72268539
1mg 721 2.1	74	121.6692871	69.24695982	36.6252595	4.668102388
1mg 719 1.1	5	170.342	115.781	65.386	8.725
1mg 719 1.1	4	144.161	96.347	54.614	7.315
15 mg 802	81	94.30235287	56.45637264	24.67210191	4.556008756
15 mg 803	82	72.03931998	51.40218912	25.17019917	2.733811501
15 mg 804	83	75.76708134	44.1113371	14.05863986	0
0	65 Spike (20)	33.062	21.912	19.879	21.859
	65 Recover (%)		95	106	121
	20 STD	18.54884	18.85581	18.75349	18.06512

## APPENDIX I. OXIDATION TOC AND UVA DATA

reatment	ID	DOC	Std. Dev.	UVA
	JP 7/25 1.1	4.7393	0.1165	0.163
	JP 7/25 1.1 TREATED	4.6681	0.0655	0.134
	JP 7/25 1.2	4.6721	0.0547	0.169
	JP 7/25 1.2 TREATED	4.4361	0.01514	0.11
	JP 7/21 2.3	4.7217	0.132	0.163
	JP 7/21 2.3 TREATED	4.6922	0.0386	0.152
	JP 7/21 2.4	4.596	0.0673	0.16
	JP 7/21 2.4 TREATED	4.5131	0.0039	0.11
	JP 7/21 2.1	4.91	0.0704	0.162
C	JP 7/21 2.1 TREATED	4.3941	0.0417	0.159
0	JP 7/21 2.2	4.8346	0.1403	0.128
D	JP 7/21 2.2 TREATED	4.6293	0.0814	0.127
a B	JP 7/19 1.4	5.6839	0.0821	0.176
u/u	JP 7/19 1.4 TREATED	5.683	0.0943	0.124
Õ	JP 7/19 1.4	5.6839	0.0821	0.176
60	JP 7/19 1.4 TREATED	5.683	0.0943	0.124
ш	JP 7/21 2.1	4.91	0.0704	0.162
1	JP 7/21 2.1 TREATED	5.0749	0.101	0.1298
Ozone 1mg O <sub>3</sub> /mg DOC	JP 7/25 1.2	4.6721	0.0547	0.169
ZO	JP 7/25 1.2 TREATED	4.4361	0.01514	0.11
Õ	JP 7/25 1.1	4.7393	0.1165	0.163
	JP 7/25 1.1 TREATED	4.7028	0.0612	0.132
	JP 7/25 1.1	4.7393	0.1165	0.163
	JP 7/25 1.1	4.7854	0.0436	0.131
	JP 7/19 1.4	5.6839	0.0821	0.176
	JP 7/19 1.4 TREATED	5.4763	0.0399	0.149
	JP 7/21 2.1	4.91	0.0704	0.162
	JP 7/21 2.1 TREATED	4.3941	0.0417	0.159
	JP 7/25 1.1	4.7393	0.1165	0.163
	JP 7/25 1.1 TREATED	4.6681	0.0655	0.134
	JP 7/23 1.1	5.0646	0.0543	0.158
	JP 7/23 1.1 TREATED	4.8959	0.0523	0.109
ບ	JP 7/23 1.2	5.1337	0.0446	0.16
Ŏ	JP 7/23 1.2 TREATED	5.0439	0.0918	0.107
D	JP 7/23 1.1	5.0646	0.0543	0.158
<b>5</b> 0	19.0 JP 7/23 1.1 TREATED	4.7154	0.1029	0.115
/m	JP 7/23 1.1	5.0646	0.0543	0.158
õ	20.0 JP 7/23 1.1 TREATED	4.7154	0.1029	0.115
50	JP 7/23 1.2	5.1337	0.0446	0.16
Ozone 2mg O <sub>3</sub> /mg D(	21.0 JP 7/23 1.2 TREATED	4.7845	0.0555	0.109
0	JP 7/23 1.2	5.1337	0.0446	0.16
ne	22.0 JP 7/23 1.2 TREATED	4.6411	0.0346	0.108
[0Z	JP 731 1.2 RAW	4.8264	0.0809	0.174
Ö	36.0 JP 731 1.2 TREATED	4.8694	0.0209	0.12
-	JP 731 1.2 RAW	4.8264	0.0809	0.174
	JP 731 1.2 TREATED	4.7633	0.0609	0.119

#### Table I-1 - Raw TOC and UVA data for oxidation conditions

Treatment	D	DOC	Std. Dev.	UVA
	JP 6/26 2.3	4.8775	0.0948	0.148
	JP 6/26 2.3 TREATED	4.2048	0.1682	0.123
2 & )2	JP 6/26 2.4	5.1373	0.0341	0.157
4000 mJ/cm <sup>2</sup> 0 mg/L H <sub>2</sub> O	JP 6/26 2.4 TREATED	4.4845	0.0303	0.134
J/c	JP 6/26 2.3	4.9335	0.0955	0.156
m, M	JP 6/26 2.3 TREATED	4.3566	0.0561	0.133
0 Ü	JP 6/26 2.3 2	4.8775	0.0948	0.148
0000	JP 6/26 2.3 TREATED 2	4.112	0.0304	0.129
7	JP 6/26 2.4 2	4.9288	0.0442	0.156
	JP 6/26 2.4 TREATED 2	4.269	0.0249	0.136
	JP 6/26 1.1	4.7135	0.029	0.142
8	JP 6/26 1.1 TREATED	3.6977	0.0314	0.053
	JP 6/27 1.3	5.0687	0.0143	0.158
Ĥ	JP 6/27 1.3 TREATED	2.9073	0.0316	0.065
Ţ	JP 6/27 1.4	4.8559	0.0493	0.157
ng	JP 6/27 1.4 TREATED	2.2997	0.0536	0.047
0 r	JP 6/26 2.1	4.8595	0.1124	0.172
-	JP 6/26 2.1 TREATED	1.9949	0.0391	0.033
Š	JP 6/26 2.1	4.8595	0.1124	0.172
2000 mJ/cm <sup>2</sup> & 10 mg/L H <sub>2</sub> O <sub>2</sub>	JP 6/26 2.1 TREATED	1.9763	0.012	0.034
[/ci	JP 6/27 1.3 2	5.0687	0.0143	0.158
lu	JP 6/27 1.3 TREATED 2	3.2331	0.0133	0.059
0 1	JP 6/27 1.4 2	4.8559	0.0493	0.157
00	JP 6/27 1.4 TREATED 2	2.6893	0.0061	0.053
5	JP 6/26 1.2	4.9293	0.0779	0.153
	JP 6/26 1.2 TREATED	3.4552	0.0154	0.048
	JP 6/26 1.3	4.7135	0.029	0.142
02	JP 6/26 1.3 TREATED	2.1466	0.0326	0.027
H <sub>2</sub> (	JP 6/27 1.2	5.0434	0.091	0.172
	JP 6/27 1.2 TREATED	1.778	0.0307	0.031
lm ( mg/]	JP 6/26 1.4	4.7874	0.0311	0.149
000 m 10 mg/	JP 6/26 1.4 TREATED	2.7439	0.0061	0.029
8 9	JP 6/27 1.1	5.0602	0.0852	0.175
4 ''	JP 6/27 1.1 TREATED	1.9613	0.012	0.034
ىھ	JP 731 1.3 RAW	4.0277	0.1319	0.15
Extended Ozone Dose	JP 731 1.3 T(extended)	2.6255	0.0315	0.028
P Q	JP 801 1.1 RAW	5.7945	0.1627	0.193
ter ne	JP 801 1.1 T(45 min)	3.6678	0.0121	0.031
Extended Zone Dos	JP 803 1.1 RAW	4.8913	0.1422	0.159
$\neg$	JP 803 1.1 T(2 hours)	2.9117	0.0321	0.045
	× /			

D	DOC Average	TOC standard deviation	UV254	D	DOC Awerage	TOC standard deviation	UV254	D	DOC Average	TOC standard deviation	
1.1	1.7211	0.0086	0.019	3.1	2.7633	0.0262	0.037	5.1	1.6276	0.0125	0.029
1.10	1.221	0.0068	0.026	3.10	1.645	0.0111	0.029	5.10	1.3584	0.0287	0.02
1.11	1.2351	0.0099	0.024	3.11	1.4202	0.0027	0.033	5.11	0.9495	0.0104	0.014
1.2	1.4859	0.0102	0.018	3.2	2.4929	0,0198	0.035	5.2	1.5137	0.0066	0.026
1.3	1.2606	0.0109	0.017	3.3	2.2112	0.0289	0.031	5.3	1.4139	0.0097	0.024
1.4	1.1053	0.011	0.017	3.4	1.1844	0.0164	0.031	5.4	1.2717	0.0028	0.022
1.5	0.9156	0.0126	0.016	3.5	1.651	0.0139	0.025	5.5	1.1454	0.0082	0.021
1.6	0.7993	0.0247	0.016	3.6	1.281	0.0166	0.022	5.6	1.3972	0.1682	0.017
1.7	0.7692	0.0105	0.017	3.7	1.3545	0.0089	0.024	5.7	1.2346	0.044	0.014
1.8	1.1608	0.0136		3.8	1.5377	0.0133	0.024	5.8	1.1352	0.0075	0.017
1.9	1.057	0.097	0.015	3.9	1.8212	0.0056	0.026	5.9	1.1861	0.0159	0.016
2.1	1.6282	0.0153	0.018	4.1	2.0119	0.0029	0.026	6.1	1.5288	0.0085	0.019
2.10	1.0065	0.0024	0.014	4.10	1.0989	0.001	0.017	6.10	0.9266	0.171	0.015
2.11	1.0853	0.0157	0.016	4.11	1.1266	0.0073	0.016	6.11	1.0185	0.0151	0.016
2.12	1.0705	0.0089	0.014	4.2	1.7643	0.0063	0.024	6.12	1.1932	0.0081	0.015
2.2	1.1039	0.02	0.016	4.3	1.5557	0.0083	0.022	6.2	1.3434	0.0176	0.02
2.3	1.2059	0.0148	0.016	4.4	1.384	0.0216	0.023	6.3	1.2189	0.0047	0.016
2.4	1.1896	0.0059	0.018	4.5	1.1572	0.0081	0.018	6.4	1.1277	0.0091	0.014
2.5	1.0814	0.0078	0.015	4.6	1.0305	0.011	0.019	6.5	0.9405	0.0086	0.012
2.6	0.9359	0.0046	0.016	4.7	0.9172	0.0082	0.015	6.6	0.9073	0.062	0.014
2.7	0.7839	0.0072	0.013	4.8	1.1822	0.0098	0.014	6.7	1.0143	0.008	0.016
2.8	1.0864	0.0076	0.014	4.9	1.1714	0.0154	0.014	6.9	0.7799	0.0212	0.013
2.9	1.1875	0.0114	0.015								

## APPENDIX J. BIODEGRADATION TOC/UV RESULTS

Table J-1 - TOC/UV data for biodegradation tests

ID	DOC Average	TOC standard deviation	UV254	ID	DOC Awerage	TOC standard deviation	UV254	ID	DOC Average	TOC standard deviation	UV254
7.1	1.6137	0.0019	0.016	9.1	2.3005	0.0098	0.037	11.10	0.9819	0.0368	0.019
7.10	0.8666	0.0329	0.011	9.10	1.3997	0.0485	0.019	11.1	1.2846	0.0167	0.017
7.11	0.9981	0.0236		9.11	1.3304	0.0196	0.019	11.11	0.9114	0.0113	0.014
7.12	1.3962	0.0079	0.014	9.12	1.2377	0.0556	0.011	11.12	0.7586	0.0128	0.011
7.2	1.5228	0.0174	0.017	9.2	2.1872	0.0092	0.036	11.2	1.2921	0.0061	0.016
7.3	1.4156	0.0026	0.015	9.3	1.9324	0.0076	0.03	11.3	1.1752	0.0186	0.016
7.4	1.337	0.0057	0.013	9.4	1.8218	0.0045	0.028	11.4	0.85	0.0082	0.012
7.5	1.2029	0.0103	0.011	9.5	1.7725	0.0056	0.026	11.5	0.8496	0.1034	0.011
7.6	1.0057	0.0038	0.012	9.7	1.3011	0.0101	0.018	11.6	0.791	0.0136	0.01
7.7	1.1195	0.0148	0.015	9.8	1.4311	0.0377	0.019	11.7	0.756	0.0209	0.014
7.9	0.8956	0.0119	0.013	9.9	1.355	0.0122	0.026	11.8	0.7962	0.0266	0.016
8.1	2.4882	0.0074	0.042	10.10	1.1613	0.0344	0.016	11.9	0.8273	0.0159	0.017
8.10	1.3585	0.0425	0.025	10.1	1.5574	0.0058	0.018	12.10	1.412	0.053	0.026
8.11	1.4505	0.0545	0.026	10.11	1.0343	0.0138	0.012	12.1	2.0747	0.0087	0.039
8.12	1.3751	0.0166	0.021	10.2	1.3533	0.1151	0.015	12.11	1.3804	0.0226	0.021
8.2	2.4184	0.0076	0.044	10.3	1.3843	0.0203	0.014	12.2	1.9219	0.0241	0.031
8.3	1.9468	0.0066	0.033	10.4	1.2426	0.0138	0.013	12.3	1.5975	0.0383	0.026
8.4	1.7156	0.0068	0.031	10.5	1.118	0.0251	0.012	12.4	1.5917	0.0183	0.026
8.5	1.6777	0.027	0.029	10.6	0.9766	0.0096	0.012	12.5	1.4865	0.007	0.023
8.7	1.4379	0.0588	0.025	10.7	0.8365	0.0293	0.011	12.6	1.3521	0.0247	0.017
8.8	1.1641	0.0162	0.018	10.8	0.9852	0.0538	0.015	12.7	1.2762	0.0087	0.021
8.9	1.2958	0.0069	0.024	10.9	0.9891	0.0694	0.016	12.8	1.3958	0.0068	0.025
								12.9	1.2938	0.0204	0.024

ID	DOC Average	TOC standard deviation	UV254	ID	DOC Awerage	TOC standard deviation	UV254	ID	DOC Average	TOC standard deviation	
13.10	1.0863	0.0716	0.01	15.10	2.945	0.0298	0.064	17.1	4.3308	0.059	0.074
13.1	1.4699	0.0253	0.018	15.1	4.5976	0.0124	0.125	17.10	2.5984	0.0418	0.054
13.11	1.154	0.0143	0.023	15.11	2.9911	0.0057	0.062	17.2	3.9203	0.0674	0.06
13.2	1.4235	0.0163	0.014	15.2	4.1334	0.0754	0.113	17.3	3.5959	0.0188	0.074
13.3	1.1877	0.0134	0.016	15.3	4.0656	0.1076	0.105	17.4	3.4498	0.0277	0.068
13.4	1.0841	0.0406	0.011	15.4	3.638	0.024	0.092	17.5	3.222	0.0692	0.062
13.5	0.8675	0.022	0.013	15.5	3.6558	0.0451	0.093	17.6	2.7184	0.0273	0.055
13.6	1.0622	0.0641	0.016	15.6	3.6121	0.0595	0.077	17.7	2.7288	0.0247	0.059
13.7	0.896	0.0207	0.015	15.7	3.468	0.0294	0.073	17.8	2.8023	0.0988	0.065
13.8	1.2024	0.0358	0.014	15.8	3.1172	0.1046	0.067	17.9	2.8324	0.0318	0.052
13.9	1.2493	0.0137	0.016	15.9	2.9474	0.0508	0.067	18.1	4.5944	0.0059	
14.10	0.8251	0.0316	0.011	16.10	2.4517	0.0283	0.056	18.10	2.507	0.0088	0.036
14.1	1.4756	0.0078	0.014	16.1	4.2561	0.066	0.111	18.11	2.5418	0.0015	0.049
14.11	0.8524	0.0418	0.012	16.11	2.5174	0.0162	0.046	18.2	4.0905	0.1866	0.092
14.2	1.363	0.0098	0.009	16.2	3.7525	0.1157	0.095	18.3	3.7093	0.0357	0.083
14.3	1.2497	0.0341	0.011	16.3	3.4011	0.0571	0.084	18.4	3.5722	0.0423	0.075
14.4	1.0894	0.068	0.009	16.4	3.3019	0.0288	0.089	18.5	3.6135	0.0708	0.081
14.5	0.9978	0.0142	0.008	16.5	3.0653	0.0099	0.068	18.6	2.7099	0.062	0.06
14.6	0.8421	0.0225	0.01	16.6	2.764	0.0327	0.054	18.7	2.6921	0.0326	0.062
14.7	0.7335	0.0388	0.01	16.7	2.7639	0.0093	0.062	18.8	2.5523	0.0549	0.055
14.8	0.985	0.0021	0.009	16.8	2.6266	0.1351	0.06	18.9	2.7944	0.0552	0.054
14.9	1.0045	0.0125	0.009	16.9	2.4932	0.0173	0.058				

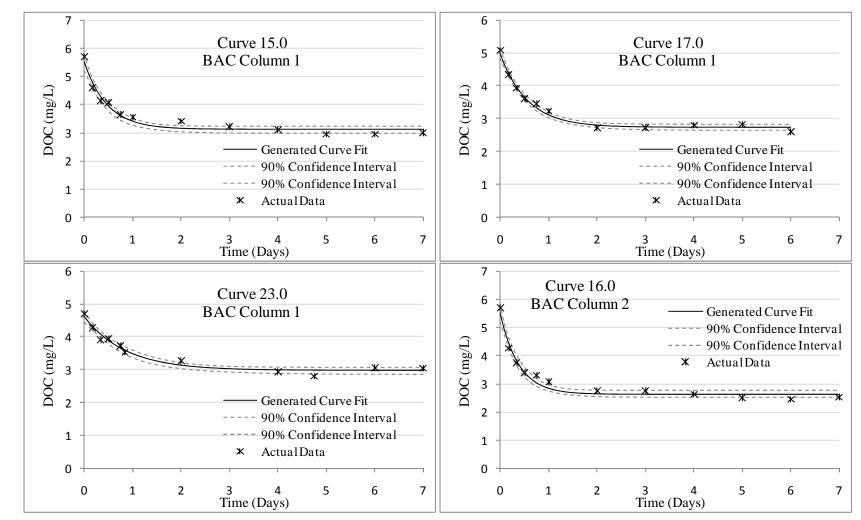
ID	DOC Average	TOC standard deviation	UV254	ID	DOC Awerage	TOC standard deviation	UV254	ID	DOC Average	TOC standard deviation	
19.10	2.8091	0.0638	0.062	21.10	2.5881	0.0617	0.052	23.10	3.0524	0.0202	0.074
19.1	3.9903	0.0341	0.094	21.1	3.9295	0.081	0.088	23.1	4.2801	0.0847	0.113
19.11	2.6918	0.2917	0.056	21.11	2.6384	0.0195	0.056	23.11	3.0381	0.0452	0.075
19.2	3.7961	0.0202	0.091	21.2	3.6171	0.0284	0.081	23.2	3.9105	0.11	0.102
19.3	3.4684	0.0506	0.082	21.3	3.45	0.0456	0.079	23.3	3.9433	0.0615	0.1
19.4	3.3863	0.0141	0.07	21.4	3.5809	0.0813	0.074	23.4	3.733	0.0139	0.095
19.5	3.4979	0.0858	0.069	21.5	3.5027	0.0313	0.078	23.5	3.5321	0.0276	0.09
19.6	3.083	0.0311	0.069	21.6	2.9661	0.033	0.068	23.6	3.2662	0.0472	0.055
19.7	2.9624	0.062	0.065	21.7	2.8455	0.0242	0.065	23.7	2.6045	0.0293	0.071
19.8	3.2581	0.0094	0.063	21.8	2.9546	0.0153	0.058	23.8	2.931	0.0512	0.072
19.9	2.8207	0.0275	0.065	21.9	2.6175	0.0312	0.055	23.9	2.798	0.0267	0.06
20.10	2.3525	0.0904	0.043	22.10	2.4007	0.0152	0.038	24.10	2.2729	0.0428	0.045
20.1	3.8379	0.0687	0.088	22.1	4.0184	0.0537	0.085	24.1	4.0677	0.0427	0.104
20.11	2.1587	0.0589	0.042	22.11	2.3551	0.1722	0.043	24.11	2.4317	0.0386	0.049
20.2	3.4167	0.0292	0.078	22.2	3.8281	0.1229	0.079	24.2	3.4376	0.0294	0.088
20.3	3.1835	0.0468	0.073	22.3	3.3906	0.0364	0.07	24.3	3.3787	0.0301	0.085
20.4	3.0144	0.0784	0.068	22.4	3.1962	0.0702	0.063	24.4	3.1355	0.0294	0.077
20.5	3.0861	0.0329	0.067	22.5	3.3918	0.0122	0.066	24.6	2.6308	0.0091	0.061
20.6	2.6976	0.0327	0.056	22.6	2.7616	0.049	0.057	24.7	2.5192	0.0162	0.054
20.7	2.4808	0.0148	0.05	22.7	2.5125	0.0669	0.049	24.8	2.6205	0.0383	0.052
20.8	2.6255	0.0065	0.047	22.8	2.4396	0.0688	0.048	24.9	2.3591	0.0989	0.048
20.9	2.18	0.068	0.043	22.9	2.3514	0.0121	0.049				

D	DOC Average	TOC standard deviation	UV254	ID	DOC Average	TOC standard deviation	UV254	ID	DOC Average	TOC standard deviation	UV254
25.10	2.43	0.0407	0.058	27.10	2.6334	0.0098	0.059	31.10	2.3971	0.0323	0.049
25.1	4.0642	0.0861	0.133	27.1	4.3956	0.0676	0.142	31.1	3.7289	0.0834	0.084
25.11	1.8741	0.0928		27.11	2.4792	0.0306		31.11	2.3745	0.04	0.049
25.2	4.1683	0.0413	0.127	27.2	4.3513	0.039	0.134	31.2	3.3778	0.0288	0.092
25.3	3.7683	0.0532	0.104	27.3	4.1297	0.024	0.114	31.3	3.2189	0.0306	0.084
25.4	3.4682	0.0221	0.097	27.4	4.0908	0.0298	0.157	31.4	3.0494	0.0327	0.078
25.5	3.1568	0.0175	0.095	27.5	3.5716	0.04	0.1	31.6	2.5456	0.0205	0.061
25.6	2.9713	0.0154	0.083	27.6	3.5124	0.0416	0.07	31.7	2.58	0.041	0.056
25.7	2.8446	0.0312	0.077	27.7	3.1599	0.0094	0.068	31.8	2.7371	0.0307	0.051
25.8	2.8201	0.0706	0.061	27.8	2.8396	0.0123	0.066	31.9	2.4094	0.1142	0.051
25.9	2.4995	0.0321	0.058	27.9	2.6344	0.0088	0.059	32.1	3.5608	0.0439	0.096
26.10	2.4048	0.0644	0.059	28.10	1.8863	0.0435	0.039	32.10	1.9789	0.0495	0.011
26.1	4.0836	0.0362	0.095	28.1	4.0397	0.0363	0.127	32.11	1.8688	0.0245	0.034
26.11	2.2964	0.0255	0.053	28.11	1.8793	0.0234		32.2	3.1568	0.0343	0.083
26.2	3.7604	0.0608	0.12	28.2	3.5867	0.0199	0.104	32.3	2.9731	0.0327	0.078
26.3	3.6107	0.0407	0.105	28.3	3.6126	0.0561	0.099	32.4	3.1864	0.0426	0.073
26.4	3.3684	0.0111	0.095	28.4	3.2752	0.0228	0.109	32.5	2.5287	0.0731	0.065
26.5	3.18	0.0404	0.092	28.5	2.8356	0.0353	0.071	32.6			0.029
26.6	2.7132	0.0447	0.074	28.6	2.0176	0.0517	0.061	32.7	1.969	0.2038	0.036
26.7	2.6367	0.0289	0.073	28.7	2.3916	0.023		32.8	2.0413	0.037	0.038
26.8	2.571	0.0068	0.062	28.8	2.081	0.0269	0.078	32.9	2.0517	0.0054	0.036
26.9	2.5422	0.0351	0.06	28.9	2.0254	0.0519	0.041				

ID	DOC Average	TOC standard deviation	UV254	ID	DOC Awerage	TOC standard deviation	UV254	ID	DOC Average	TOC standard deviation	UV254
33.1	3.7655	0.0572	0.106	35.10	2.5557	0.042	0.068	37.1	4.207	0.0842	0.103
33.10	2.3261	0.0445	0.026	35.1	3.8837	0.0838	0.112	37.10	2.7472	0.0167	0.056
33.11	2.055	0.006	0.043	35.11	2.4554	0.0935	0.064	37.11	2.6708	0.0171	0.057
33.2	3.4	0.076	0.094	35.3	3.6077	0.0659	0.111	37.2	3.7943	0.0475	0.098
33.3	3.2089	0.0464	0.087	35.4	3.4793	0.045	0.078	37.3	3.6244	0.0468	0.09
33.4	3.3497	0.0388	0.079	35.5	3.3378	0.0565	0.092	37.4	3.4318	0.0748	0.087
33.5	3.0381	0.0416	0.076	35.6	3.0293	0.0201	0.086	37.5	3.1491	0.0628	0.063
33.6	2.8636	0.0292	0.057	35.7	2.8223	0.0691	0.076	37.6	3.0506	0.0394	0.069
33.7	2.5918	0.1329	0.055	35.8	2.8172	0.0918	0.035	37.7	2.895	0.0599	0.065
33.8	2.3829	0.0311	0.049	35.9	2.5355	0.0105	0.07	37.8	3.0334	0.0579	0.067
33.9	2.401	0.0328	0.051	36.1	3.8298	0.0697	0.085	37.9	2.658	0.1279	0.061
34.10	1.9434	0.0395	0.035	36.10	2.4859	0.0158	0.044	38.1	3.9209	0.0791	0.13
34.1	3.4642	0.0374	0.092	36.11	2.4142	0.0099	0.043	38.10	2.4143	0.005	0.054
34.11	1.8268	0.0523	0.033	36.2	3.4169	0.0256	0.077	38.11	2.1325		0.044
34.3	2.8847	0.0368	0.07	36.3	3.3375	0.0608	0.059	38.2	3.2038	0.045	0.103
34.4	2.6919	0.1416	0.06	36.4	3.1394	0.0125	0.071	38.3	3.1053	0.0318	0.109
34.5	2.4311	0.0569	0.056	36.5	2.8951	0.1197	0.051	38.4	3.1344	0.0253	0.101
34.6	2.1687	0.0317	0.045	36.6	2.655	0.035	0.055	38.5	2.7083	0.0906	0.07
34.7	2.1447	0.024	0.04	36.7	2.4744	0.0452	0.05	38.6	2.6764	0.0186	0.076
34.8	2.2618	0.1773	0.035	36.8	2.7024	0.1745	0.051	38.7	2.4735	0.0262	0.067
34.9	1.8985	0.0223	0.035	36.9	2.4162	0.0685	0.048	38.8	2.617	0.0665	0.047
								38.9	2.3019	0.0466	0.056

D	DOC Average	TOC standard deviation	UV254	D	DOC Average	TOC standard deviation	UV254	D	DOC Average	TOC standard deviation	UV254
39.1	3.9402	0.0697	0.136	42.2	1.9468	0.0353	0.018	14.12 (half 12 hr)	1.4117	0.0227	0.012
39.10	2.467	0.0161	0.055	42.3	2.0398	0.0395	0.019	15.0 JP 7/19 1.4 T	5.683	0.0943	0.124
39.11	2.3382	0.0046	0.052	42.4	2.0164	0.0223	0.017	15.12 (half 4 hr)	4.8306	0.0724	0.134
39.2	3.4349	0.0329	0.114	42.6	2.3904		0.021	16.0 JP 7/19 1.4 T	5.683	0.0943	0.124
39.3	3.2178	0.0488	0.111	42.7	1.3878	0.054	0.016	16.12 (half 4hr)	4.5109	0.0775	0.139
39.4	3.2159	0.0466	0.106	42.8	0.8671	0.0087	0.021	17.0 JP 7/21 2.1 T	5.0749	0.101	0.1298
39.5	2.685	0.0968	0.074	42.9	0.8011	0.0143	0.014	17.12 (Double 12 hr)	3.116	0.0232	0.062
39.7	2.4261	0.0154	0.064	43.1	2.2747	0.0406	0.026	18.0 JP 7/21 2.1 T	5.0749	0.101	0.1298
39.8	2.5873	0.0707	0.064	43.2	2.0469	0.0215	0.019	18.12 (Double 12 hr)	3.2784	0.0304	0.067
39.9	2.4742	0.0838	0.063	43.3	1.9509	0.0124	0.018	19.0 JP 7/23 1.1 T	4.7154	0.1029	0.115
40.1	2.487	0.1102	0.033	43.4	2.0319	0.0109	0.019	19.12 (half 24 hr)	3.7066	0.0827	0.088
40.2	2.278	0.0257	0.028	43.6	1.5804	0.007	0.019	2.0 JP 6.26 1.4	2.7439	0.0061	0.029
40.3	2.2552	0.0328	0.028	43.7	1.1366	0.0346	0.015	20.0 JP 7/23 1.1 T	4.7154	0.1029	0.115
40.4	2.3193	0.0091	0.028	43.8	0.895	0.04	0.015	20.12 (half 24 hr)	3.3969	0.1189	0.081
40.6	1.2257	0.0214	0.034	43.9	0.8029	0.0212	0.014	21.0 JP 7/23 1.2 T	4.7845	0.0555	0.109
40.8	1.0203	0.0033	0.022	1.0 JP 6/26 1.3	2.1466	0.0326	0.027	21.12 (half 8hr)	3.8569	0.2011	0.091
40.9	0.9703	0.0104	0.021	1.12 (Dup 24hr)	0.9597	0.0023	0.016	22.0 JP 7/23 1.2 T	4.6411	0.0346	0.108
41.1	2.4898	0.0925	0.034	10.0 JP 6/27 1.2	1.778	0.0307	0.031	22.12 (Half 8 hour)	4.0394	0.0865	0.078
41.2	2.641	0.0317	0.031	10.12 (half, 10.7)	0.784	0.0111	0.011	23.0 JP 7/25 1.1 T	4.7028	0.0612	0.132
41.4	2.189	0.0304	0.027	11.0 JP 6/27 1.2	1.778	0.0307	0.031	23.12 (Dup 4 hr)	4.2439	0.0516	0.123
41.6	1.2314	0.0211	0.026	12.0 JP 6/27 1.4	2.2997	0.0536	0.047	34.0 JP 626 2.4	4.4845	0.0303	0.134
41.7	1.1726	0.0411	0.022	12.12 (Double 24hr)	1.1783	0.0425	0.019	24.0 JP 7/25 1.1	4.7854	0.0436	0.131
41.8	0.9857	0.0208	0.013	13.0 JP 6/26 2.1	1.9949	0.0391	0.033	24.12 (Dup 4 hr)	4.0437	0.0258	0.105
41.9	0.9917	0.0413	0.021	13.12 (half 12 hr)	1.3599	0.0298	0.016	25.0 JP 7/7 1.1	5.1719	0.0814	0.177
42.1	2.2532	0.0227	0.025	14.0 JP 6/26 2.1	1.9763	0.012	0.034	25.12 (half 24 hr)	3.676	0.0669	0.111
								4.12 (Dup 24hr)	1.2618	0.0091	0.021

D	DOC Average	TOC standard deviation	UV254	D	DOC Average	TOC standard deviation	UV254	ID	DOC Average	TOC s tandard deviation	
20.12 (half 24 hr)	3.3969	0.1189	0.081	35.0 JP 728 1.1 RAW	3.9812	0.0165	0.161	22.0 JP 7/23 1.2 T	4.6411	0.0346	0.108
21.0 JP 7/23 1.2	4.7845	0.0555	0.109	36.0 JP 731 1.2 T	4.8694	0.0209	0.12	22.12 (Half 8 hour)	4.0394	0.0865	0.078
21.12 (half 8hr)	3.8569	0.2011	0.091	37.0 JP 731 1.2 T	4.8694	0.0209	0.12	23.0 JP 7/25 1.1 T	4.7028	0.0612	0.132
22.0 JP 7/23 1.2	4.6411	0.0346	0.108	38.0 JP 801 1.1 RAW	5.2779	0.1281	0.175	23.12 (Dup 4 hr)	4.2439	0.0516	0.123
22.12 (Half 8 hour)	4.0394	0.0865	0.078	39.0 JP 801 1.1 RAW	5.2779	0.1281	0.175	34.0 JP 626 2.4	4.4845	0.0303	0.134
23.0 JP 7/25 1.1	4.7028	0.0612	0.132	4.0 JP 6.26 1.2	3.4552	0.0154	0.048	24.0 JP 7/25 1.1	4.7854	0.0436	0.131
23.12 (Dup 4 hr)	4.2439	0.0516	0.123	4.12 (Dup 24hr)	1.2618	0.0091	0.021	24.12 (Dup 4 hr)	4.0437	0.0258	0.105
34.0 JP 626 2.4	4.4845	0.0303	0.134	40.0 JP 805 T	2.7905	0.0348	0.036	25.0 JP 7/7 1.1	5.1719	0.0814	0.177
24.0 JP 7/25 1.1	4.7854	0.0436	0.131	41.0 JP 805 T	2.7905	0.0348	0.036	25.12 (half 24 hr)	3.676	0.0669	0.111
24.12 (Dup 4 hr)	4.0437	0.0258	0.105	42.0 JP 805 T	2.7905	0.0348	0.036	26.0JP 7/7 1.2	5.1375	0.0462	0.176
25.0 JP 7/7 1.1	5.1719	0.0814	0.177	6.0 JP 6/27 1.1	1.9613	0.012	0.034	26.12 (Double 12 hr)	3.1102	0.0717	0.084
25.12 (half 24 hr)	3.676	0.0669	0.111	7.0 JP 6/27 1.1	1.9613	0.012	0.034	27.0 JP 7/7 1.3	5.0133	0.0591	0.169
43.0 JP 805 T	2.7905	0.0348	0.036	8.0 JP 6/27 1.3	2.9073	0.0316	0.065	27.0 JP 7/7 1.3	5.0414	0.0128	0.176
5.0 JP 6/27 1.3	3.2331	0.0133	0.059	9.0 JP 6/27 1.4	2.6893	0.0061	0.053	27.12 (Double 24 hr)	2.8886	0.0387	0.079
5.12 (Dup 24hr)	0.9605	0.0019	0.017	14.12 (half 12 hr)	1.4117	0.0227	0.012	28.0 JP 7/7 1.4	5.3385	0.0569	0.181
26.0JP 7/7 1.2	5.1375	0.0462	0.176	15.0 JP 7/19 1.4 T	5.683	0.0943	0.124	28.0 JP 7/7 1.4	5.3562	0.0339	0.187
26.12 (Double 12 hr)	3.1102	0.0717	0.084	15.12 (half 4 hr)	4.8306	0.0724	0.134	28.12 (Half 12 hr)	3.8895	0.0137	0.11
27.0 JP 7/7 1.3	5.0133	0.0591	0.169	16.0 JP 7/19 1.4 T	5.683	0.0943	0.124	3.0 JP 6.26 1.1	3.6977	0.0314	0.053
27.0 JP 7/7 1.3	5.0414	0.0128	0.176	16.12 (half 4hr)	4.5109	0.0775	0.139	3.12 (Dup 3.7)	1.1505	0.0122	0.02
27.12 (Double 24 hr)	2.8886	0.0387	0.079	17.0 JP 7/21 2.1 T	5.0749	0.101	0.1298	31.0 JP 626 2.3	4.3566	0.0561	0.0133
28.0 JP 7/7 1.4	5.3385	0.0569	0.181	17.12 (Double 12 hr)	3.116	0.0232	0.062	31.12 (Half 48 hr)	2.9457	0.0457	0.075
28.0 JP 7/7 1.4	5.3562	0.0339	0.187	18.0 JP 7/21 2.1 T	5.0749	0.101	0.1298	32.0 JP 626 2.3	4.112	0.0304	0.129
28.12 (Half 12 hr)	3.8895	0.0137	0.11	18.12 (Double 12 hr)	3.2784	0.0304	0.067	32.12 (Half 48hr)	1.8698	0.0158	0.03
3.0 JP 6.26 1.1	3.6977	0.0314	0.053	19.0 JP 7/23 1.1 T	4.7154	0.1029	0.115	33.0 JP 626 2.4	4.269	0.0249	0.136
3.12 (Dup 3.7)	1.1505	0.0122	0.02	19.12 (half 24 hr)	3.7066	0.0827	0.088	35.0 JP 728 1.1 RAW	3.9812	0.0165	0.161
31.0 JP 626 2.3	4.3566	0.0561	0.0133	2.0 JP 6.26 1.4	2.7439	0.0061	0.029	36.0 JP 731 1.2 T	4.8694	0.0209	0.12
31.12 (Half 48 hr)	2.9457	0.0457	0.075	20.0 JP 7/23 1.1 T	4.7154	0.1029	0.115	37.0 JP 731 1.2 T	4.8694	0.0209	0.12
32.0 JP 626 2.3	4.112	0.0304	0.129	20.12 (half 24 hr)	3.3969	0.1189	0.081	38.0 JP 801 1.1	5.2779	0.1281	0.175
32.12 (Half 48hr)	1.8698	0.0158	0.03	21.0 JP 7/23 1.2 T	4.7845	0.0555	0.109	39.0 JP 801 1.1	5.2779	0.1281	0.175
33.0 JP 626 2.4	4.269	0.0249	0.136	21.12 (half 8hr)	3.8569	0.2011	0.091	4.0 JP 6.26 1.2	3.4552	0.0154	0.048
42.0 JP 805 T	2.7905	0.0348	0.036	40.0 JP 805 T	2.7905	0.0348	0.036	41.0 JP 805 T	2.7905	0.0348	0.036



### APPENDIX K. BIODEGRADATION CURVES FOR DOC

Figure K-1 - Biodegradation test results for 1mgO<sub>3</sub>/mg DOC

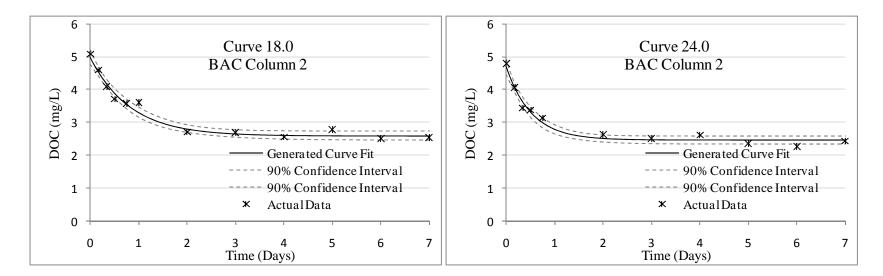


Figure K-2 - Biodegradation test results for 1mgO<sub>3</sub>/mg DOC

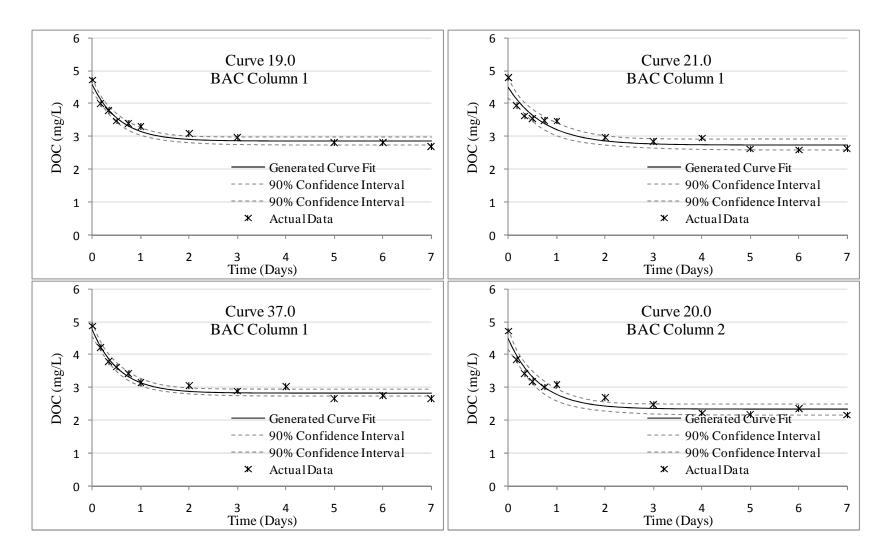


Figure K-3 - Biodegradation test results for 2mgO<sub>3</sub>/mg DOC

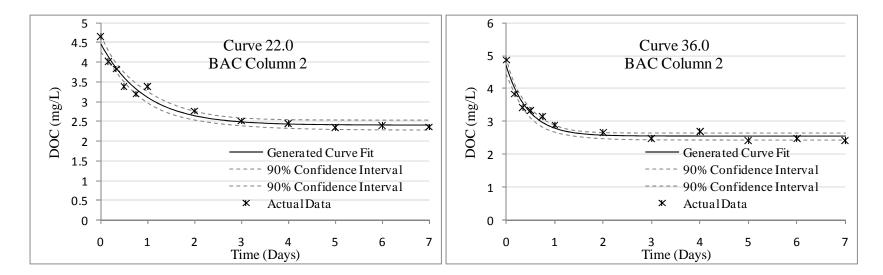


Figure K-4 - Biodegradation test results for 2mgO<sub>3</sub>/mg DOC

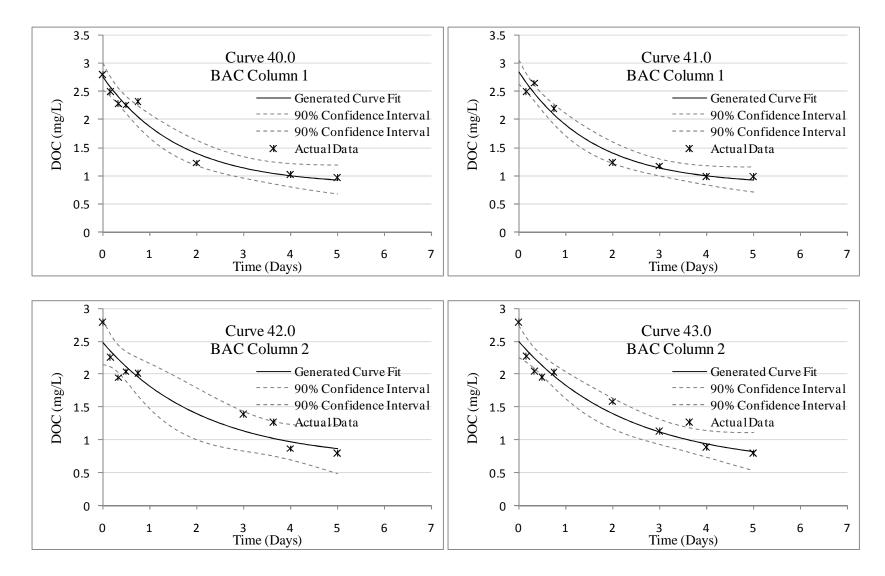


Figure K-5 - Biodegradation test results for extended ozonation

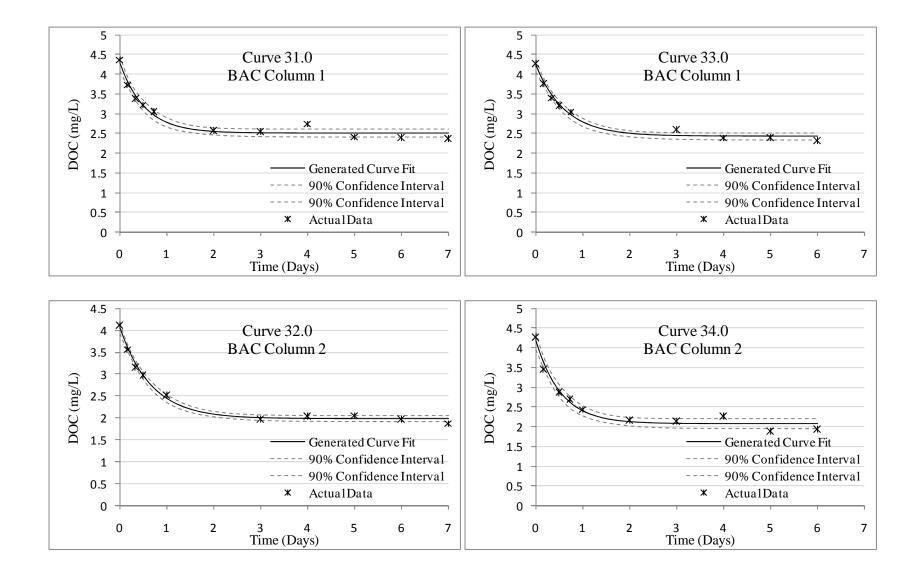


Figure K-6 - Biodegradation test results for 4000mJ/cm<sup>2</sup> and 0 mg/L  $\rm H_2O_2$ 

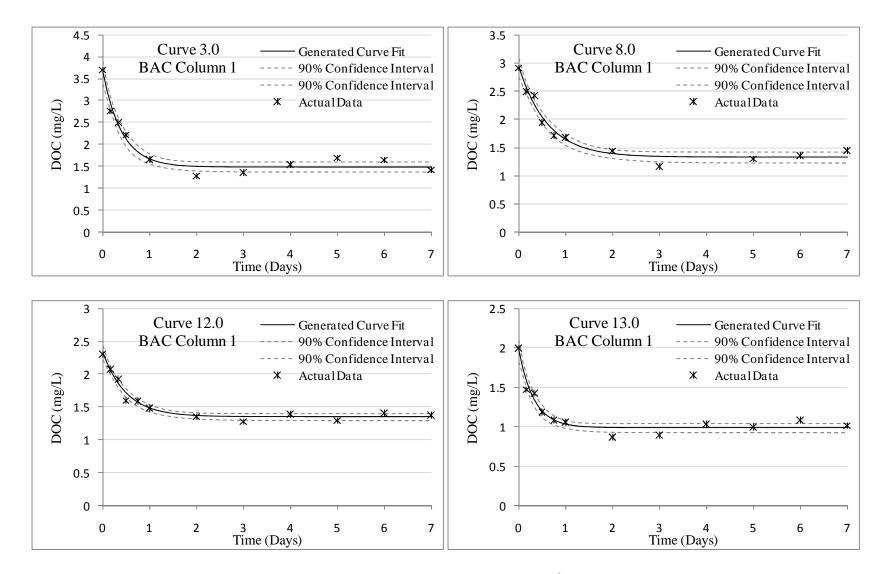


Figure K-7 - Biodegradation test results for 2000mJ/cm<sup>2</sup> and 10 mg/L  $H_2O_2$ 

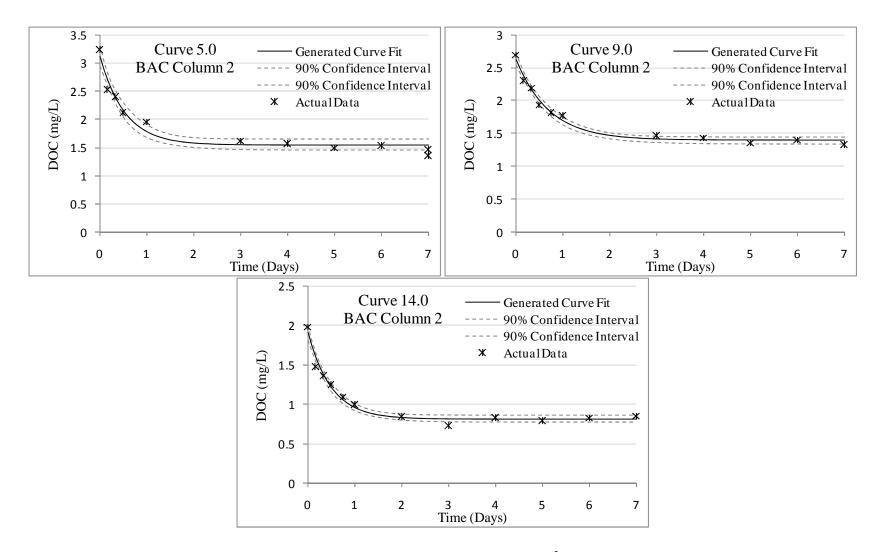


Figure K-8 - Biodegradation test results for 2000mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub>

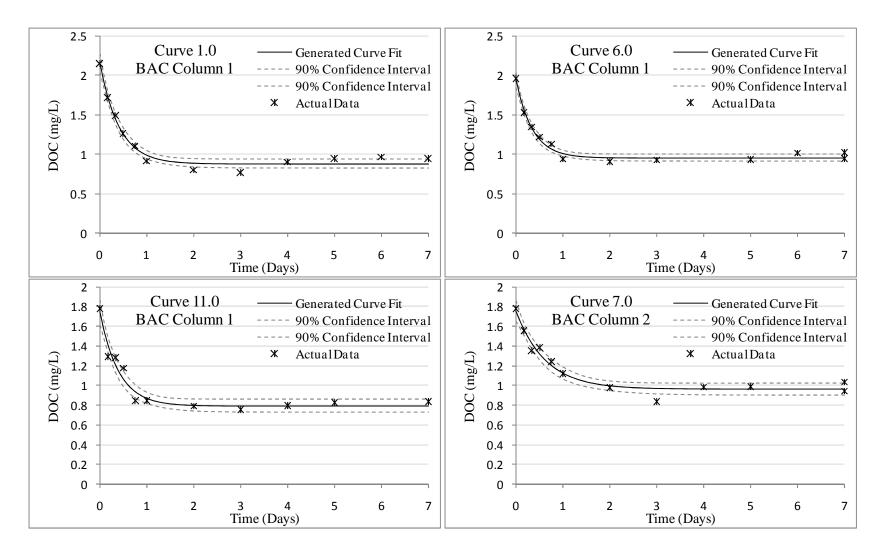


Figure K-9 - Biodegradation test results for 4000mJ/cm<sup>2</sup> and 10 mg/L  $H_2O_2$ 

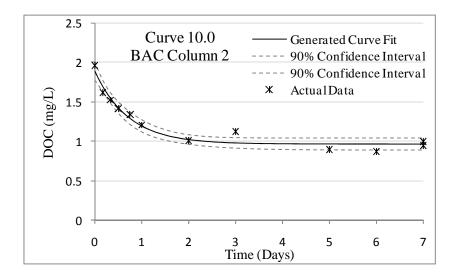


Figure K-10 - Biodegradation test results for 4000mJ/cm<sup>2</sup> and 10 mg/L  $H_2O_2$ 

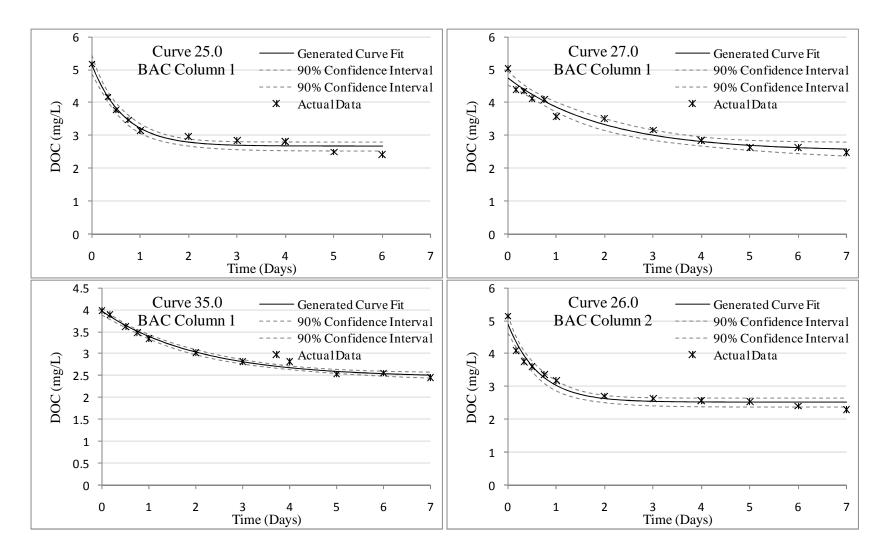


Figure K-11 - Biodegradation test results for raw water samples

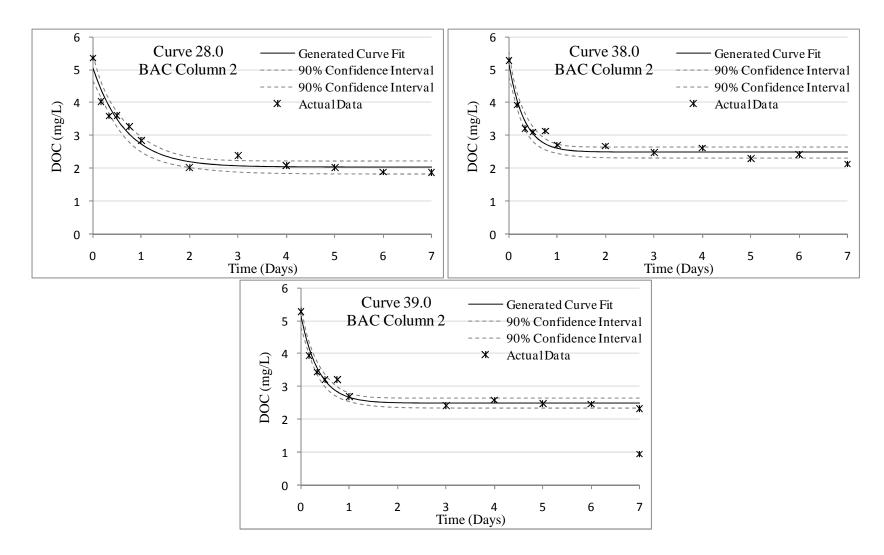


Figure K-12 - Biodegradation test results for raw water samples

### APPENDIX L. BIODEGRADATION TEST ANALYSIS RESULTS FOR DOC

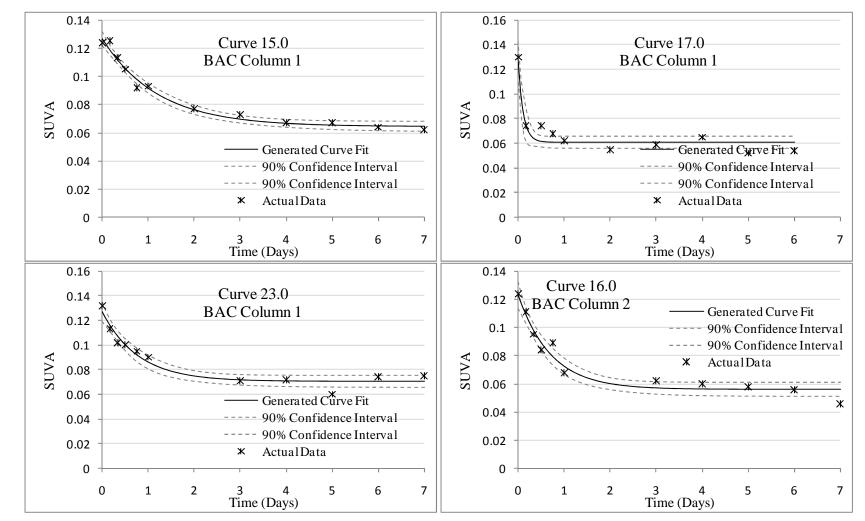
Oxidation	ID	Variables		Average			Standard Deviation			# of	t test	Emer (a)	Eman (b)	Eman (a)	
Oxidation	ш	a	b	с	а	b	c	a stdev	b stdev	c stdev	n	t	Error (a)	Error (b)	Error (c)
1mg, Column 1	15	3.114	2.412	1.942							3	2.92			
1mg, Column 1	17	2.738	2.257	1.782	2.942	2.102	1.632	0.190	0.410	0.407	3	2.92	0.3201	0.6915	0.6862
1mg, Column 1	23	2.973	1.637	1.171							3	2.92			
1mg, Column 2	16	2.642	2.884	2.612							3	2.92			
1mg, Column 2	18	2.599	2.402	1.213	2.570	2.509	1.916	0.091	0.334	0.700	3	2.92	0.1530	0.5627	1.1798
1mg, Column 2	24	2.468	2.243	1.924							3	2.92			
2mg, Column 1	19	2.870	1.716	1.772							3	2.92		-	
2mg, Column 1	21	2.747	1.748	1.316	2.816	1.807	1.632	0.063	0.130	0.274	3	2.92	0.1054	0.2193	0.4623
2mg, Column 1	37	2.832	1.956	1.808							3	2.92 2.92			
2mg, Column 2	20	2.336	2.155	1.567						3	2.92				
2mg, Column 2	22	2.409	2.058	1.081	2.429	2.127	1.614	0.104	0.060	0.557	3	2.92	0.1760	0.1014	0.9397
2mg, Column 2	36	2.542	2.168	2.193	.316         2.816         1.807           .808         .567						3	2.92			
Extended, Column 1	40	0.84394	1.90845	0.61641	0 847	1 0 17	0.626	0.004	0.054	0.014	2	6.314	0.0176	0.2404	0.0621
Extended, Column 1	41	0.84951	1.98462	0.63608	0.047	1.74/	0.020	0.004	0.054	0.014	2	6.314	0.0170	0.2404	0.0021
Extended, Column 2	42	0.68948	1.79511	0.46431	0 650	1 8/12	0.449	0.056	0.066	0.022	2	6.314	0.2505	0 2941	0.0963
Extended, Column 2	43	0.61014	1.88826	0.43379	0.050	1.042	0.77)	0.050	0.000	0.022	2	6.314	0.2303	0.2941	0.0903
4000,0 Column 1	31	2.50299	1.78627	1.88347	2.464	1.760	1.751	0.056	0.038	0.187	2	6.314	0.2480	0.1686	0.8337
4000,0 Column 1	33	2.42443	1.73288	1.6194	2.404	1.700	1.751	0.050	0.058	0.107	2	6.314	0.2480	0.1000	0.8337
4000,0 Column 2	32	1.98264	2.07546	1.50524	2.030	2.087	1.687	0.067	0.017	0.257	2	6.314	0.2998	0.0750	1.1485
4000,0 Column 2	34	2.0776	2.09951	1.86904	2.050	2.007	1.007	0.007	0.017	0.237	2	6.314	0.2998	0.0759	1.1483
4000,10 Column 1	1	0.88089	1.27537	2.44539							3	2.92			
4000,10 Column 1	6	0.95692	0.98943	2.8685	0.878	1.070	2.604	0.081	0.179	0.230	3	2.92	0.1360	0.3013	0.3885
4000,10 Column 1	11	0.79569	0.94663	2.4986							3	2.92			

#### Table L-1 - Biodegradation curve analysis results for DOC

Oxidation	D	Variables			Average			Standard Deviation			# of	t test	Error (a)	Error (b)	Error (c)
Oxidation	Ш	a	b	с	а	b	c	a stdev	b stde v	c stdev	n	t	EITOI (a)	EITOR (D)	EITOR (C)
4000,10 Column 2	7	0.96049	0.79719	1.58339	0.962	0.863	1.490	0.002	0.093	0.132	2	6.314	0.0098	0.4169	0.5895
4000,10 Column 2	10	0.96361	0.92925	1.39666	0.902	0.005	1.470	0.002	0.075	0.152	2	6.314	0.0078	0.4107	0.5675
2000,10 Column 1	3	1.49012	2.15492	2.47212							4	2.132			
2000,10 Column 1	8	1.32546	1.59285	1.63663	1.288	1.425	2.300	0.213	0.567	0.627	4	2.132	0.2267	0.6046	0.6685
2000,10 Column 1	12	1.34841	0.97498	2.00203	1.200	1.425	2.300	0.215	15 0.507	0.027	4	2.132	0.2207	0.0040	0.0085
2000,10 Column 1	13	0.98829	0.9759	3.08819							4	2.132			
2000,10 Column 2	5	1.55115	1.57668	1.89486							3	2.92			
2000,10 Column 2	9	1.39649	1.2366	1.42665	1.255	1.302	1.780	0.387	0.249	0.312	3	2.92	0.6530	0.4191	0.5267
2000,10 Column 2	14	0.81642	1.09256	2.0191							3	2.92			
Raw, Column 1	25	2.66683	2.48096	1.51736							3	2.92			
Raw, Column 1	27	2.51378	2.22517	0.50666	2.546	2.069	0.835	0.108	0.508	0.591	3	2.92	0.1821	0.8566	0.9967
Raw, Column 1	35	2.45825	1.50135	0.48051							3	2.92			
Raw, Column 2	26	2.51434	2.38034	1.54561							4	2.132			
Raw, Column 2	28	2.03146	3.02042	1.46405	2.383	2.680	2.223	0.235	0.263	0.851	4	2.132	0.2502	0.2804	0.9067
Raw, Column 2	38	2.4875	2.68266	3.16743	2.305	2.000	2.225	0.235	0.203	0.631	4	2.132	0.2302	0.2804	0.9007
Raw, Column 2	39	2.49896	2.63664	2.71658							4	2.132			

		Variables			% non-					
Oxidation	ID					Average	Std Dev	Ν	Т	Error
		a	b	с	dable					
1mg, Column 1	15	3.114	2.412	1.942	56%					
1mg, Column 1	17	2.738	2.257	1.782	55%	59%	5%	3	2.92	9%
1mg, Column 1	23	2.973	1.637	1.171	64%					
1mg, Column 2	16	2.642	2.884	2.612	48%					
1mg, Column 2	18	2.599	2.402	1.213	52%	51%	3%	3	2.92	4%
1mg, Column 2	24	2.468	2.243	1.924	52%					
2mg, Column 1	19	2.870	1.716	1.772	63%					
2mg, Column 1	21	2.747	1.748	1.316	61%	61%	2%	3	2.92	3%
2mg, Column 1	37	2.832	1.956	1.808	59%					
2mg, Column 2	20	2.336	2.155	1.567	52%					
2mg, Column 2	22	2.409	2.058	1.081	54%	53%	1%	3	2.92	2%
2mg, Column 2	36	2.542	2.168	2.193	54%				2.92 2.92 2.92	
Extended, Column 1	40	0.84394	1.90845	0.61641	31%	2004				
Extended, Column 1	41	0.84951	1.98462	0.63608		30%	0%	2	6.314	2%
Extended, Column 2	42	0.68948	1.79511	0.46431	28%	• • • •				
Extended, Column 2	43	0.61014	1.88826			26%	2%	2	6.314	11%
4000,0 Column 1	31	2.50299		1.88347	58%		_			
4000,0 Column 1	33	2.42443	1.73288	1.6194		58%	0%	2	6.314	0%
4000,0 Column 2	32	1.98264	2.07546	1.50524		10.07				
4000,0 Column 2	34	2.0776	2.09951	1.86904	50%	49%	1%	2	6.314	3%
4000,10 Column 1	1	0.88089	1.27537	2.44539	41%					
4000,10 Column 1	6	0.95692	0.98943	2.8685	49%	45%	4%	3	2.92	7%
4000,10 Column 1	11	0.79569	0.94663	2.4986	46%					
4000,10 Column 2	7	0.96049	0.79719	1.58339	55%	53%	3%	2	6 214	12%
4000,10 Column 2	10	0.96361	0.92925	1.39666	51%	5570	370	Z	0.314	1270
2000,10 Column 1	3	1.49012	2.15492	2.47212	41%					
2000,10 Column 1	8	1.32546	1.59285	1.63663	45%	49%	7%	4	2 132	8%
2000,10 Column 1	12	1.34841	0.97498	2.00203	58%	.,,,,	770	-	2.152	070
2000,10 Column 1	13	0.98829	0.9759	3.08819	50%					
2000,10 Column 2	5	1.55115	1.57668	1.89486	50%					
2000,10 Column 2	9	1.39649	1.2366	1.42665		48%	5%	3	2.92	9%
2000,10 Column 2	14	0.81642		2.0191	43%					
Raw, Column 1	25	2.66683	2.48096	1.51736						
Raw, Column 1	27	2.51378		0.50666		56%	6%	3	2.92	9%
Raw, Column 1	35	2.45825	1.50135	0.48051	62%					
Raw, Column 2	26	2.51434		1.54561	51%					
Raw, Column 2	28	2.03146		1.46405		47%	5%	4	2.132	5%
Raw, Column 2	38	2.4875	2.68266	3.16743						
Raw, Column 2	39	2.49896	2.63664	2.71658	49%					

Table L-2 - Biodegradation analysis of % non-biodegradable for DOC



### APPENDIX M. BIODEGRADATION CURVES FOR SUVA

Figure M-1 - Biodegradation test results for 1mgO<sub>3</sub>/mg DOC

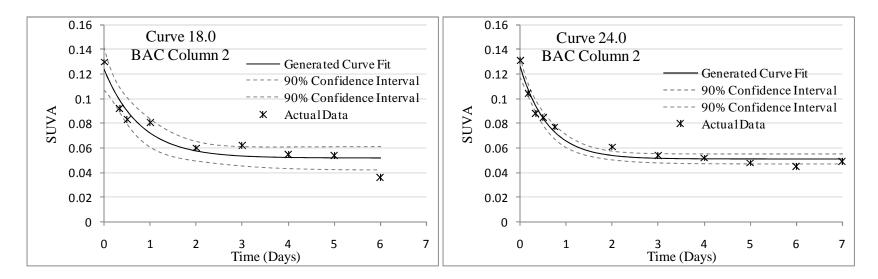


Figure M-2 - Biodegradation test results for 1mgO<sub>3</sub>/mg DOC

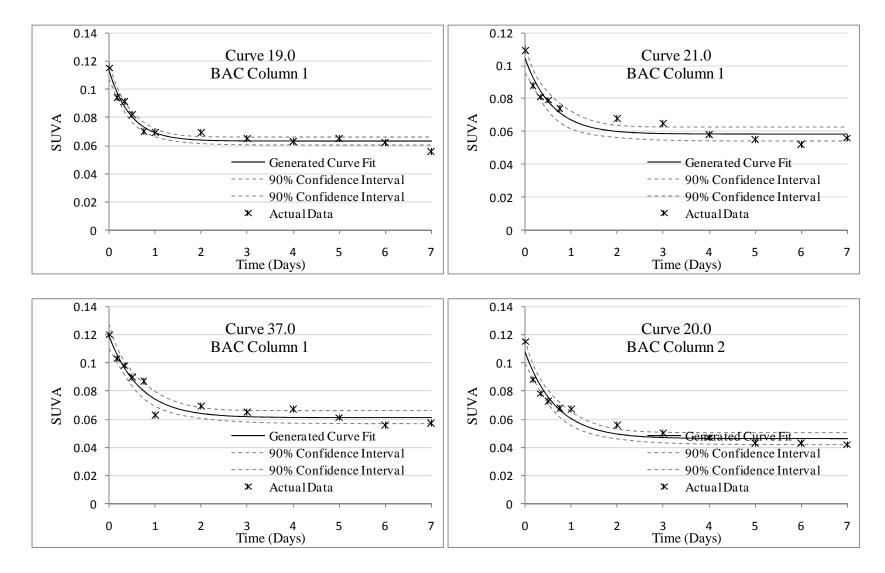


Figure M-3 - Biodegradation test results for 2mgO<sub>3</sub>/mg DOC

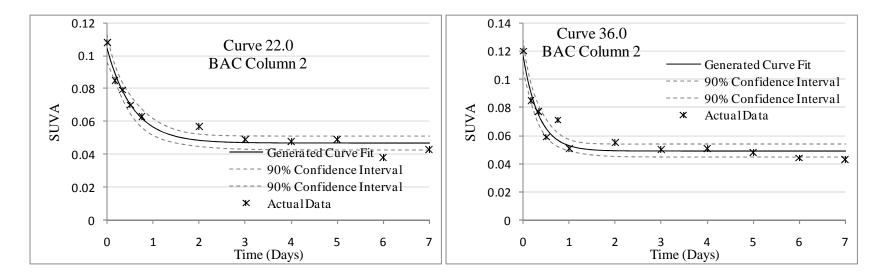


Figure M-4 - Biodegradation test results for 2mgO<sub>3</sub>/mg DOC

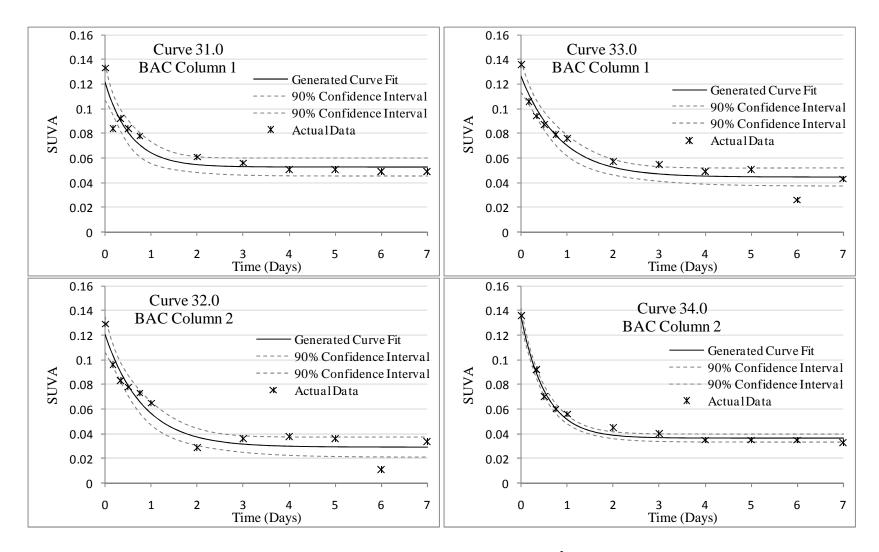


Figure M-5 - Biodegradation test results for 4000mJ/cm<sup>2</sup> and 0mg/L  $H_2O_2$ 

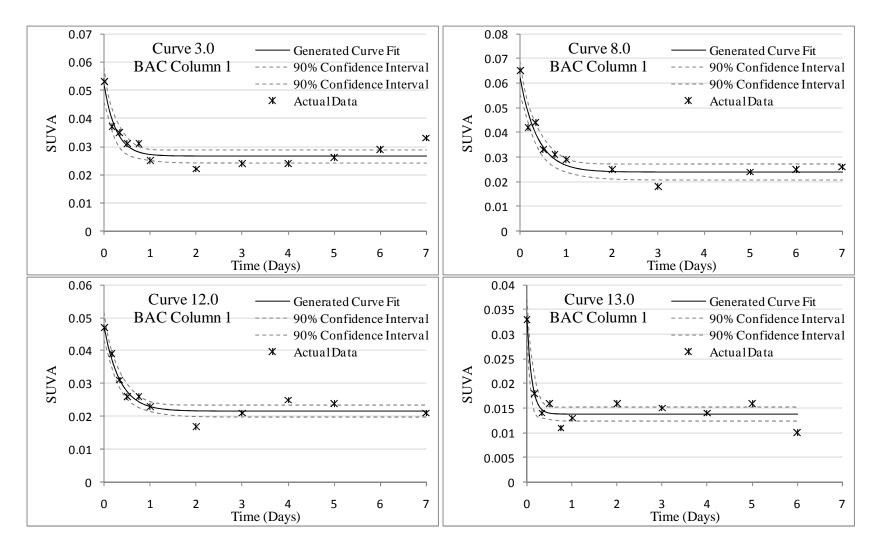


Figure M-6 - Biodegradation test results for 2000mJ/cm<sup>2</sup> and 10mg/L  $H_2O_2$ 

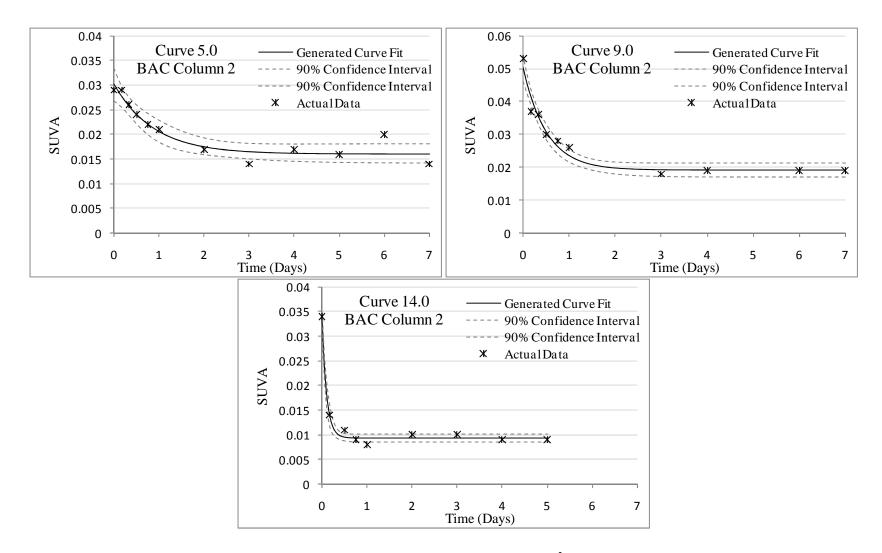


Figure M-7 - Biodegradation test results for 2000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub>

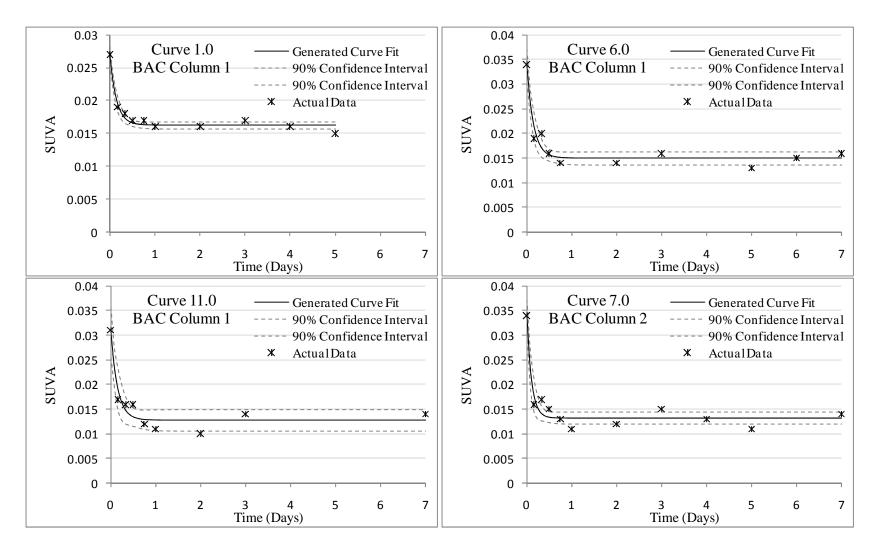


Figure M-8 - Biodegradation test results for 4000mJ/cm<sup>2</sup> and 10mg/L  $\rm H_2O_2$ 

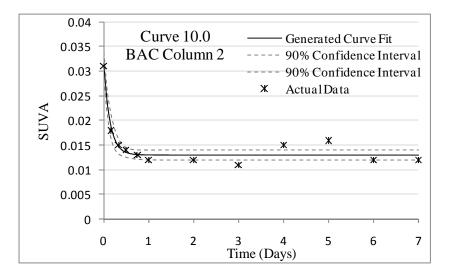


Figure M-9 - Biodegradation test results for 4000mJ/cm<sup>2</sup> and 10mg/L  $H_2O_2$ 

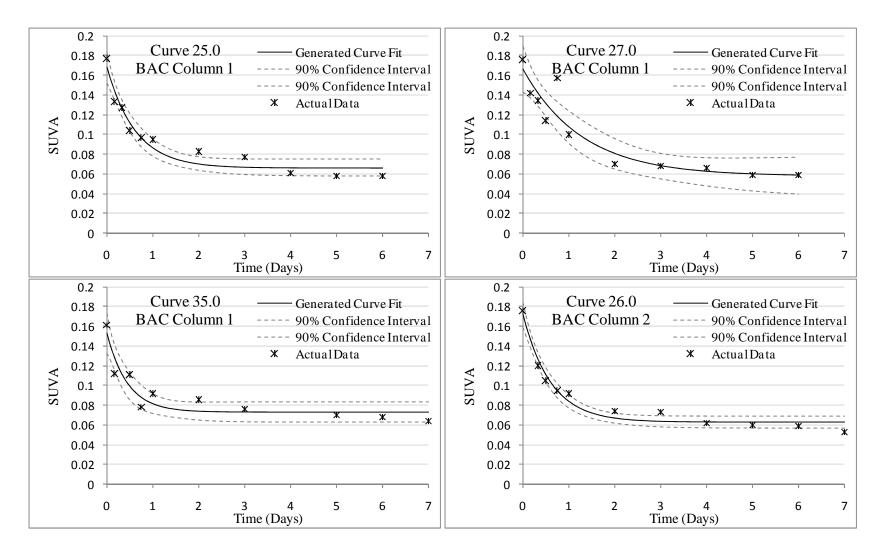
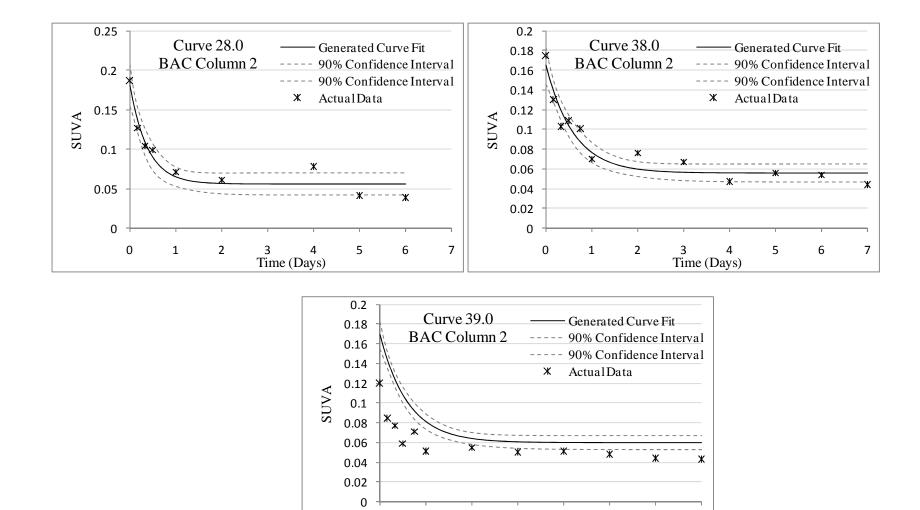


Figure M-10 - Biodegradation test results for raw water samples



**Figure M-11 - Biodegradation test results for raw water samples** 

3 4 Time (Days)

## APPENDIX N. BIODEGRADATION TEST ANALYSIS RESULTS FOR SUVA

Oxidation	ID	Variables		Average		Standard Deviation			# of	t test	Emon (a)	Eman (b)	Error (c)		
Ostuation	Ш	a	b	с	a	b	С	a stdev	b stdev	c stdev	n	t	Error (a)	Error (b)	Error (c)
1mg, Column 1	15	0.06455	0.06255	0.83051							2	6.314			
1mg, Column 1	17	<del>0.06081</del>	<del>0.06869</del>	<del>9.0581</del>	0.067	0.060 1.05	1.058	0.004	0.004	0.322	2	6.314	0.0185	0.0173	1.4380
1mg, Column 1	23	0.07041	0.05706	1.286							2	6.314			
1mg, Column 2	16	0.05602	0.06725	1.40967	0.053			0 0.003			3	2.92	0.0046	0.0069	
1mg, Column 2	18	0.05183	0.07232	1.26796		0.072	1.440		0.004	0.190	3	2.92			0.3200
1mg, Column 2	24	0.05085	0.07531	1.64377							3	2.92			
2mg, Column 1	19	0.06302	0.05054	2.1454							3	2.92			
2mg, Column 1	21	0.05852	0.04584	1.68405	0.061	0.051 1.773	0.002	0.006	0.337	3	2.92	0.0038	0.0101	0.5682	
2mg, Column 1	37	0.06123	0.05778	1.4891							3	2.92			
2mg, Column 2	20	0.04622	0.06134	1.46622							3	2.92			
2mg, Column 2	22	0.04681	0.0579	1.77716	0.047	0.062 2.042	2.042	0.002	0.005	0.745	3	2.92	0.0027	0.0084	1.2559
2mg, Column 2	36	0.04922	0.06775	2.88359						3	2.92				
4000,0 Column 1	31	0.05271	0.06916	1.78344	0.049	0.076 1.474	1.474	0.006	0.009	0.438	2	6.314	0.0256	0.0411	1.9540
4000,0 Column 1	33	0.04459	0.08218	1.16448	0.049	0.076	1.4/4	0.000			2	6.314			
4000,0 Column 2	32	0.02958	0.09117	1.20847	0.033	0.095	<b>1.543</b> 0.005	0.005	0.005	0.474	2	6.314	0.0225	0.0242	2.1143
4000,0 Column 2	34	0.0367	0.09885	1.8782	0.033	0.095 1.	1.545	0.005	0.003	0.474	2	6.314			
4000,10 Column 1	1	0.01626	0.01064	6.93199			6.777	0.002			3	2.92	0.0030	0.0075	0.2352
4000,10 Column 1	6	0.01494	0.01873	6.73574	0.015	0.016			0.004	0.140	3	2.92			
4000,10 Column 1	11	0.0127	0.01799	6.66209							3	2.92			
4000,10 Column 2	7	0.01319	0.02066	9.54416	0.013	0.019 8.30	0.260	0.000	0.002	1.675	2	6.314	0.0008	0.0084	7.4779
4000,10 Column 2	10	0.01294	0.01799	7.1755	0.015		0.300		0.002	1.075	2	6.314	0.0008		

## Table N-1 - Biodegradation curve analysis results for SUVA

Oxidation	ID	Variables		Average			Standard Deviation			# of	t test Error (a)	Error (b)	Error (c)		
GAUATION		a	b	с	a	b	с	a stdev	b stdev	c stdev	n	t			
2000,10 Column 1	3	0.02651	0.02553	3.83604							3	2.92			
2000,10 Column 1	8	0.02407	0.03834	2.64703	0.024	0.030	<b>3.135</b> 0.002	0.002	0.007	0.622	3	2.92	2.92 2.92 0.0041	0.0123	1.0493
2000,10 Column 1	12	0.02165	0.02586	2.92244		0.050		0.002	0.007		3	2.92			
2000,10 Column 1	13	<del>0.0138</del>	<del>0.0192</del>	<del>9.1839</del>							3	2.92			
2000,10 Column 2	5	0.01608	0.01408	1.13352							3	2.92			
2000,10 Column 2	9	0.01918	0.03117	1.96156	0.015	0.023	4.311	0.005	0.009	4.804	3	2.92	0.0084	0.0145	8.0996
2000,10 Column 2	14	0.00938	0.0246	9.83805							3	2.92			
Raw, Column 1	25	0.06637	0.1017	1.61297							3	2.92			
Raw, Column 1	27	0.05746	0.10843	0.77662	0.066	0.097	1.544	0.008	0.015	0.736	3	2.92	0.0134	0.0253	1.2407
Raw, Column 1	35	0.07332	0.07971	2.24371							3	2.92			
Raw, Column 2	26	0.06282	0.10931	1.64948							4	2.132			
Raw, Column 2	28	0.05606	0.12548	2.62282	0.059	0.113 1.891	0.003	0.008	0.488	4	2.132	0.0034	0.0087	0.5199	
Raw, Column 2	38	0.05615	0.10883	1.66028			1.091	0.005	0.008	0.400	4	2.132	0.0034	0.0087	0.5199
Raw, Column 2	39	0.05957	0.10929	1.63307							4	2.132			

		Variables			% non-					
Oxidation	D	a	b	с	1	Awrage	Std Dev	Ν	Т	Error
1mg, Column 1	15	0.06455	0.06255	0.83051	51%					
1mg, Column 1	17	0.06081	0.06869	9.0581	47%	51%	4%	3	2.92	7%
1mg, Column 1	23	0.07041	0.05706	1.286	55%					
1mg, Column 2	16	0.05602	0.06725	1.40967	45%					
1mg, Column 2	18	0.05183	0.07232	1.26796	42%	<i>43%</i>	3%	3	2.92	4%
1mg, Column 2	24	0.05085	0.07531	1.64377	40%					
2mg, Column 1	19	0.06302	0.05054	2.1454	55%					
2mg, Column 1	21	0.05852	0.04584	1.68405	56%	54%	3%	3	2.92	4%
2mg, Column 1	37	0.06123	0.05778	1.4891	51%					
2mg, Column 2	20	0.04622	0.06134	1.46622	43%					
2mg, Column 2	22	0.04681	0.0579	1.77716	45%	43%	1%	3	2.92	2%
2mg, Column 2	36	0.04922	0.06775	2.88359	42%					
4000,0 Column 1	31	0.05271	0.06916	1.78344	43%	20.0/	604	2	0.00	100/
4000,0 Column 1	33	0.04459	0.08218	1.16448	35%	39%	6%	3	2.92	10%
4000,0 Column 2	32	0.02958	0.09117	1.20847	24%	269/	0.07	2		201
4000,0 Column 2	34	0.0367	0.09885	1.8782	27%	26%	2%	3	2.92	3%
4000,10 Column 1	1	0.01626	0.01064	6.93199	60%					
4000,10 Column 1	6	0.01494	0.01873	6.73574	44%	49%	10%	3	2.92	17%
4000,10 Column 1	11	0.0127	0.01799	6.66209	41%					
4000,10 Column 2	7	0.01319	0.02066	9.54416	39%	40%	2%	2	6.314	9%
4000,10 Column 2	10	0.01294	0.01799	7.1755	42%	40 /0	2%	Z	0.514	9%
2000,10 Column 1	3	0.02651	0.02553	3.83604	51%					
2000,10 Column 1	8	0.02407	0.03834	2.64703	39%	44%	5%	4	2.132	6%
2000,10 Column 1	12	0.02165	0.02586	2.92244	46%		570	-	2.132	070
2000,10 Column 1	13	0.0138	0.0192	9.1839	42%					
2000,10 Column 2	5	0.01608	0.01408	1.13352	53%					
2000,10 Column 2	9	0.01918	0.03117	1.96156	38%	40%	13%	3	2.92	22%
2000,10 Column 2	14	0.00938	0.0246	9.83805	28%					
Raw, Column 1	25	0.06637	0.1017	1.61297	39%	4.4.6.4	7%			11%
Raw, Column 1	27	0.05746	0.10843	0.77662	35%	41%		3	2.92	
Raw, Column 1	35	0.07332	0.07971	2.24371	48%					
Raw, Column 2	26	0.06282	0.10931	1.64948	36%					
Raw, Column 2	28	0.05606	0.12548	2.62282	31%	34%	2%	4	2.132	3%
Raw, Column 2	38	0.05615	0.10883	1.66028	34%					
Raw, Column 2	39	0.05957	0.10929	1.63307	35%					

Table N-2 - Biodegradation analysis of % non-biodegradable for SUVA

Oxidation	Average							
	DOCnon (a)	DOCi (b)	kDOC (1/c)					
Raw, BAC Column 1	0.066 (±0.013)	0.097 (±0.025)	0.784 (±0.749)					
4000,0 BAC Column 1	0.049 (±0.026)	0.076 (±0.041)	0.709 (±0.941)					
2000,10 BAC Column 1	0.024 (±0.004)	0.030 (±0.012)	0.327 (±0.101)					
4000,10 BAC Column 1	0.015 (±0.003)	0.016 (±0.008)	0.147 (±0.005)					
1mg, BAC Column 1	0.067 (±0.019)	0.060 (±0.017)	0.991 (±1.34)					
2mg, BAC Column 1	0.061 (±0.004)	0.051 (±0.010)	0.577(±0.174)					
Raw, BAC Column 2	0.059 (±0.003)	0.113 (±0.009)	0.551 (±0.120)					
4000,0 BAC Column 2	0.033 (±0.022)	0.095 (±0.024)	0.680 (±0.932)					
2000,10 BAC Column 2	0.015 (±0.008)	0.023 (±0.015)	0.498 (±0.658)					
4000,10 BAC Column 2	0.013 (±0.003)	0.019 (±0.008)	0.122 (±0.005)					
1mg, BAC Column 2	0.053 (±0.005)	0.072 (±0.007)	0.702 (±0.152)					
2mg, BAC Column 2	0.047 (±0.003)	0.062 (±0.008)	0.53 (±0.286)					

Table N-3 - Biodegradation average curve parameters for BAC Column 1 and BAC Column 2

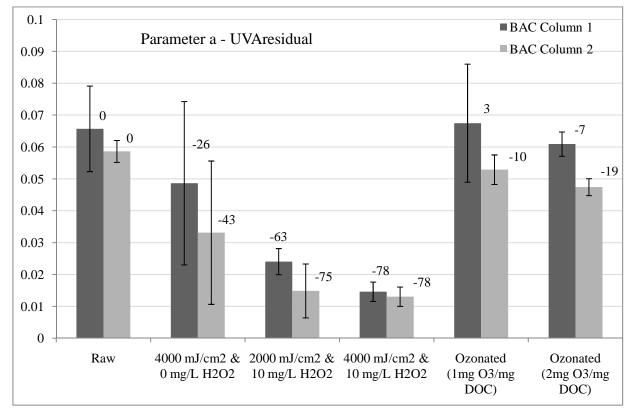


Figure N-1 - Parameter a for each oxidation scenario for BAC Column 1 and 2

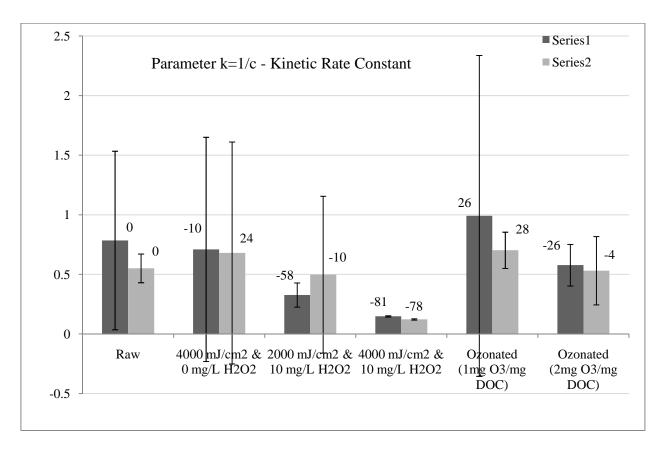
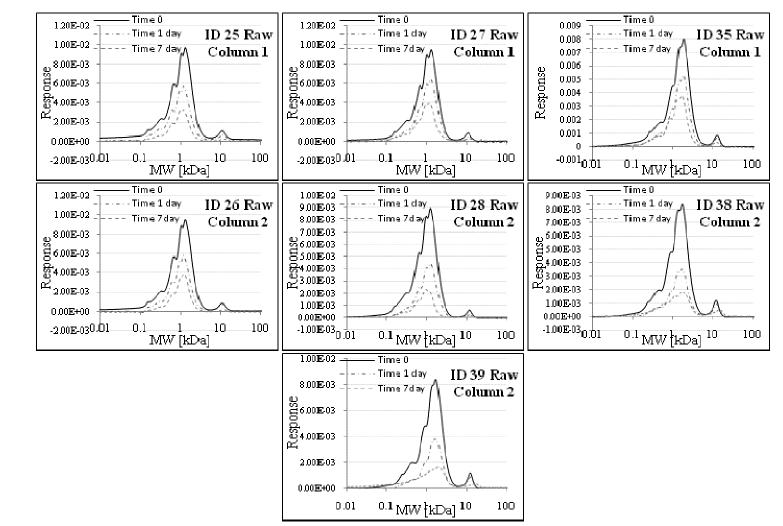
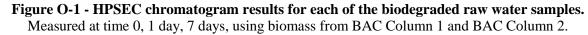
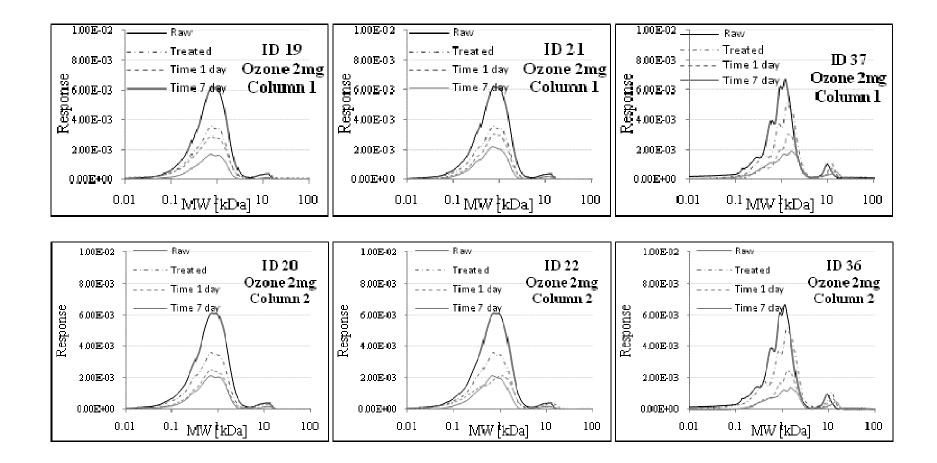


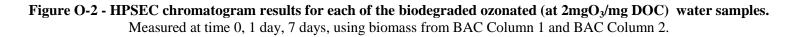
Figure N-2 - Parameter c for each oxidation scenario for BAC Column 1

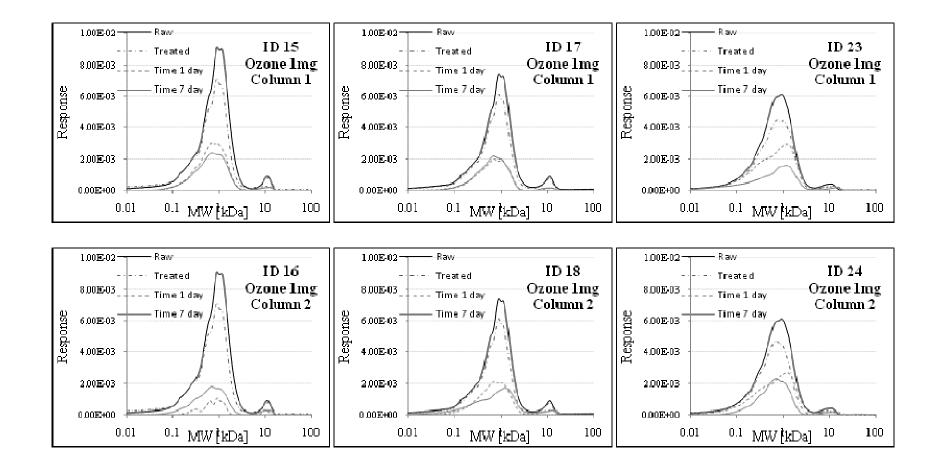


## APPENDIX O. BIODEGRADATION HPSEC CHROMATOGRAMS









**Figure O-3 - HPSEC chromatogram results for each of the biodegraded ozonated (at 1mgO<sub>3</sub>/mg DOC) water samples.** Measured at time 0, 1 day, 7 days, using biomass from BAC Column 1 and BAC Column 2.

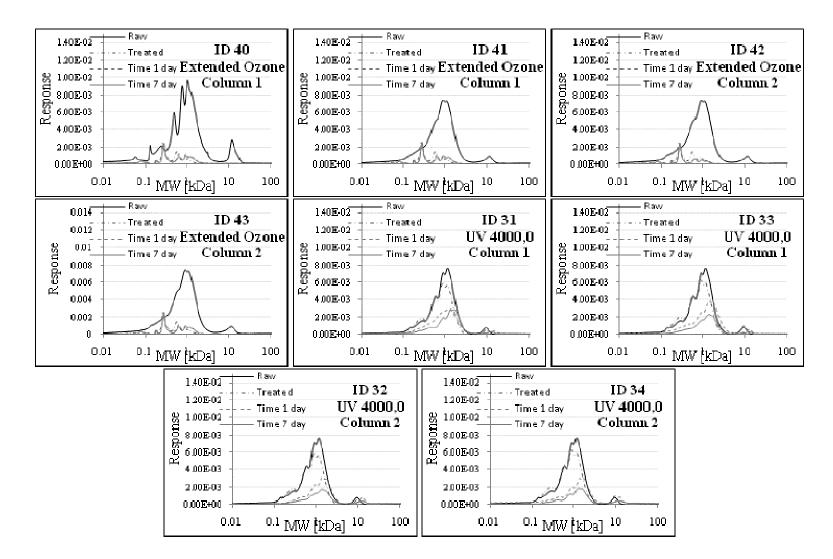
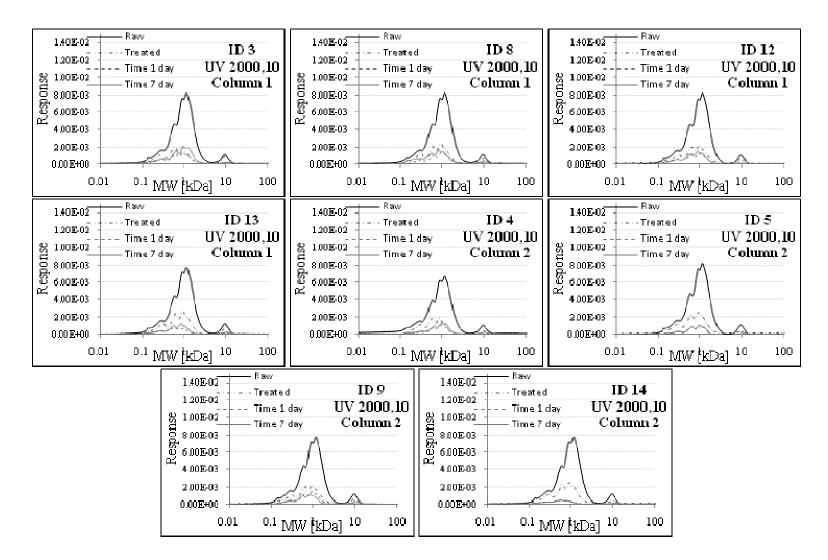
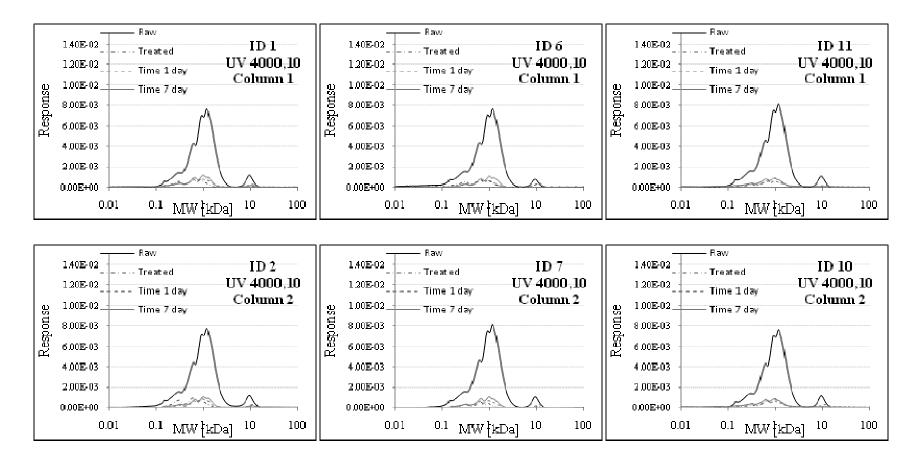


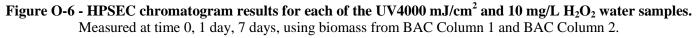
Figure O-4 - HPSEC chromatogram results for each of the biodegraded ozonated (at the extended dose) and each of the UV4000 mJ/cm<sup>2</sup> and 0 mg/L H<sub>2</sub>O<sub>2</sub> water samples.

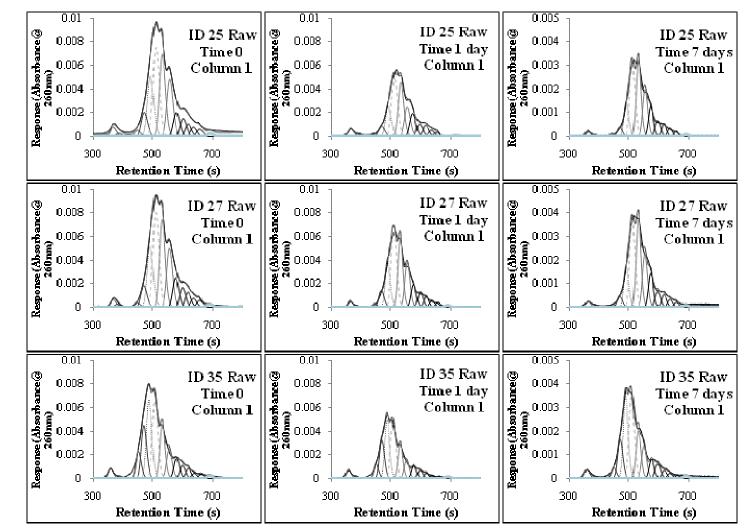
Measured at time 0, 1 day, 7 days, using biomass from BAC Column 1 and BAC Column 2.



**Figure O-5 - HPSEC chromatogram results for each of the UV2000 mJ/cm<sup>2</sup> and 10 mg/L H<sub>2</sub>O<sub>2</sub> water samples. Measured at time 0, 1 day, 7 days, using biomass from BAC Column 1 and BAC Column 2.** 

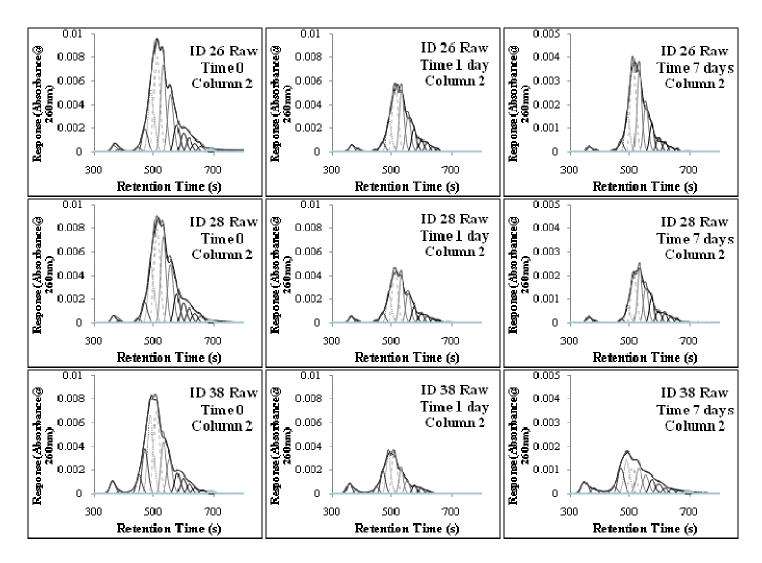




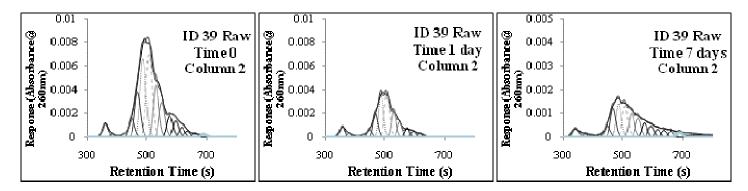


APPENDIX P. PEAKFIT ANALYSIS FOR BIODEGRADED CHROMATOGRAMS

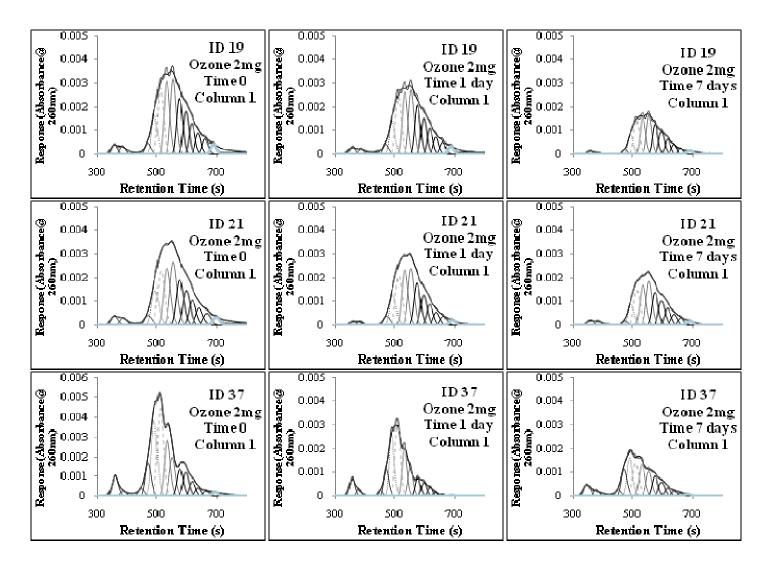
**Figure P-1 - Peakfit analysis results for each of the raw water biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.



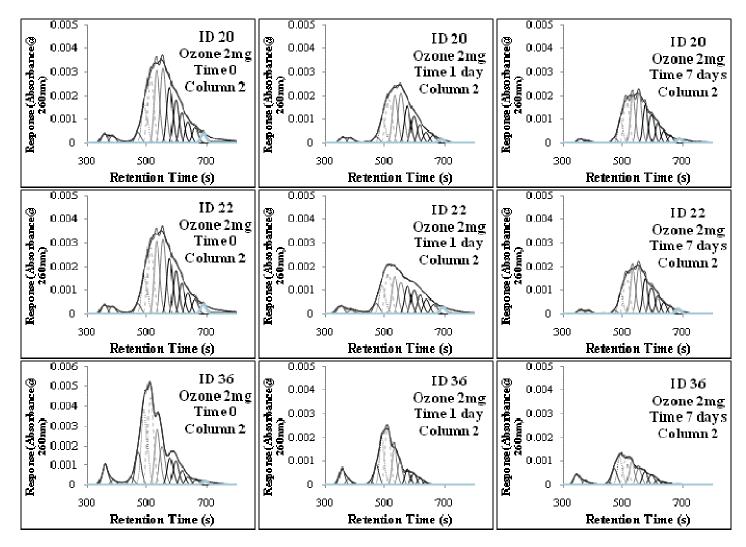
**Figure P-2 - Peakfit analysis results for each of the raw water biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.



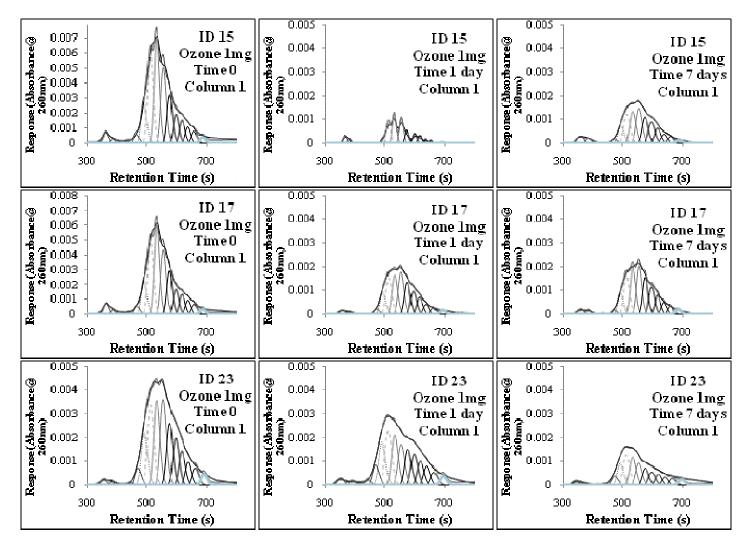
**Figure P-3 - Peakfit analysis results for each of the raw water biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.



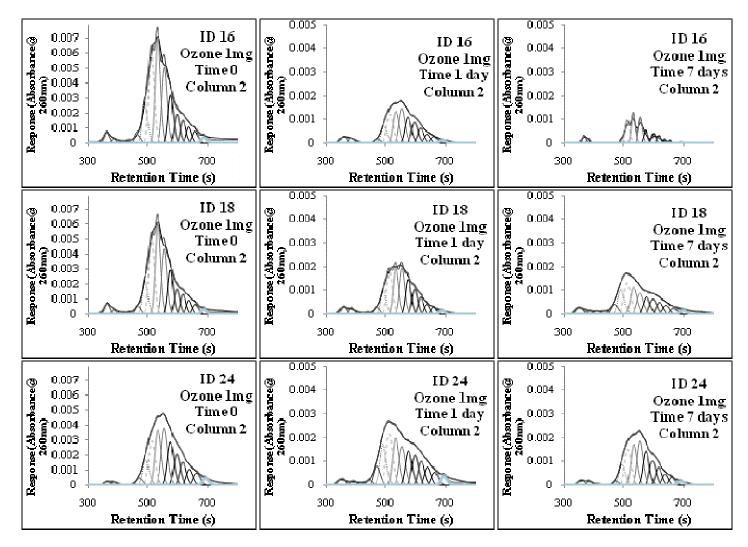
**Figure P-4 - Peakfit analysis results for each of the ozonated at 2mgO<sub>3</sub>/mg DOC and biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.



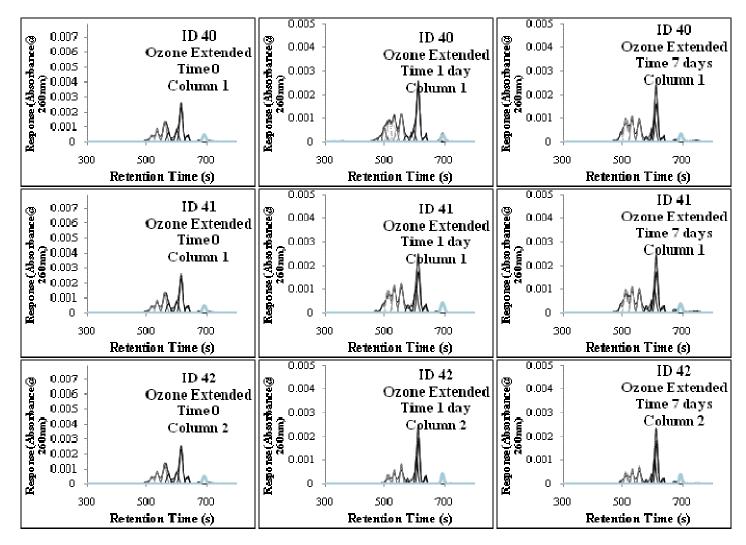
**Figure P-5 - Peakfit analysis results for each of the ozonated at 2mgO<sub>3</sub>/mg DOC and biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.



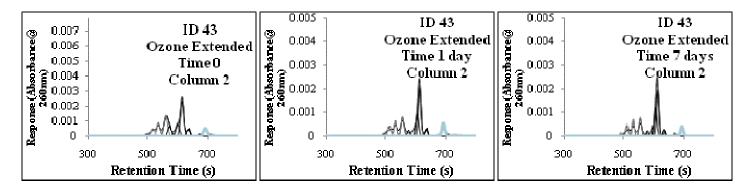
**Figure P-6 - Peakfit analysis results for each of the ozonated at 1mgO<sub>3</sub>/mg DOC and biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.



**Figure P-7 - Peakfit analysis results for each of the ozonated at 1mgO<sub>3</sub>/mg DOC and biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.



**Figure P-8 - Peakfit analysis results for each of the ozonated at the extended dose and biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.



**Figure P-9 - Peakfit analysis results for each of the ozonated at the extended dose and biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

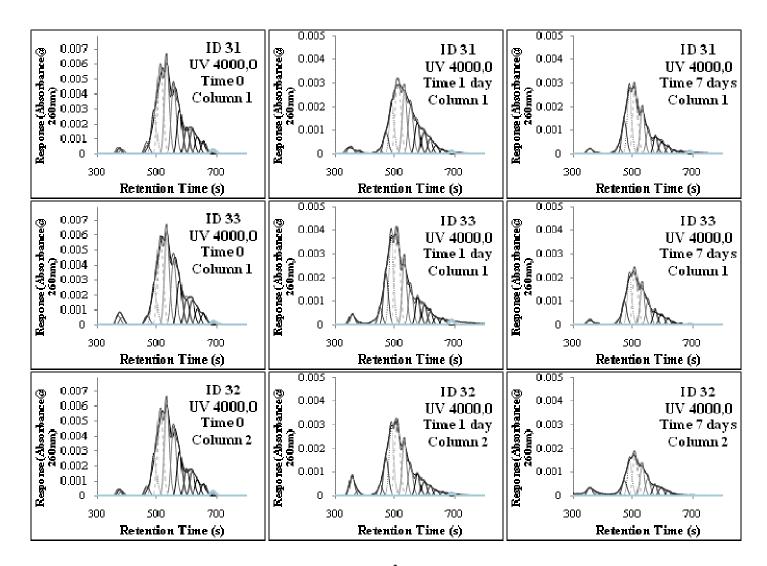
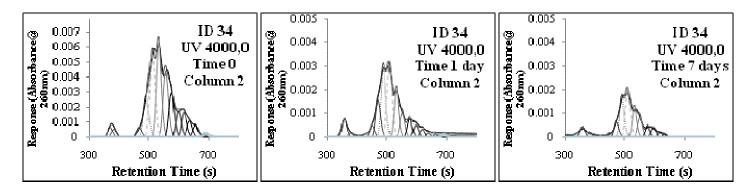


Figure P-10 - Peakfit analysis results for each of UV4000mJ/cm<sup>2</sup> and 0mg/L H<sub>2</sub>O<sub>2</sub> and biodegraded HPSEC chromatograms. Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.



**Figure P-11 - Peakfit analysis results for each of UV4000mJ/cm<sup>2</sup> and 0mg/L H<sub>2</sub>O<sub>2</sub> and biodegraded HPSEC chromatograms.** Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

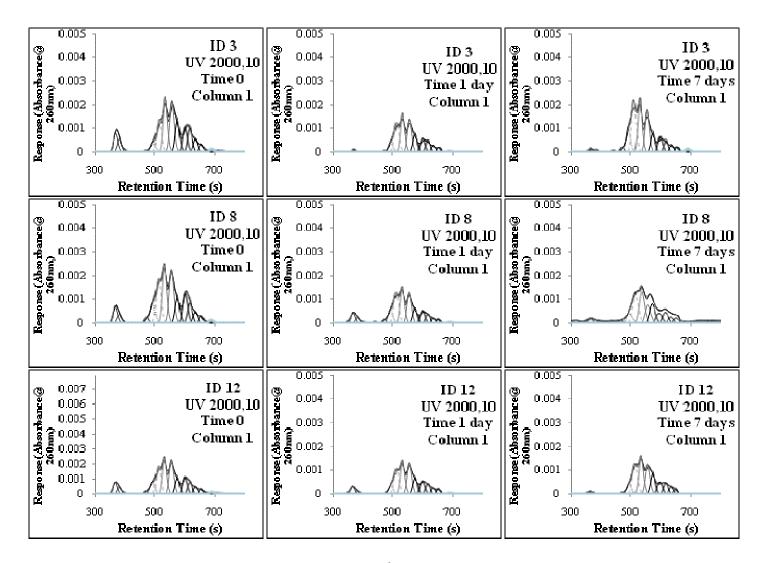


Figure P-12 - Peakfit analysis results for each of UV2000mJ/cm<sup>2</sup> and 10mg/L  $H_2O_2$  and biodegraded HPSEC chromatograms. Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

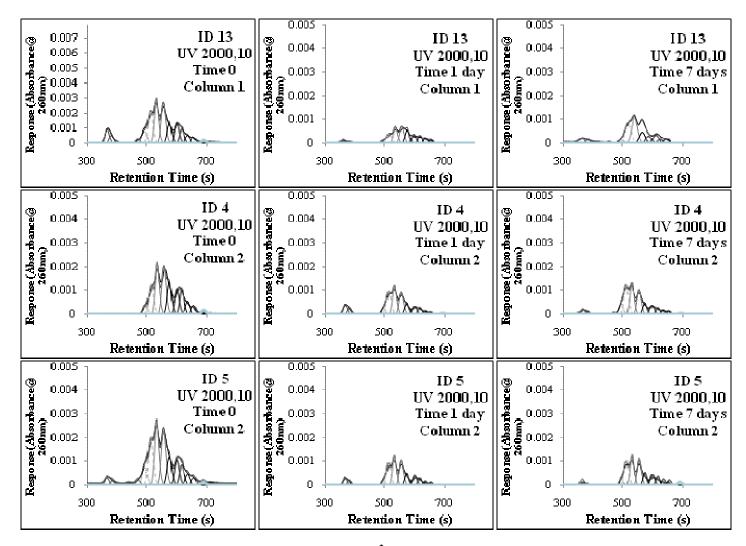


Figure P-13 - Peakfit analysis results for each of UV2000mJ/cm<sup>2</sup> and 10mg/L  $H_2O_2$  and biodegraded HPSEC chromatograms. Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

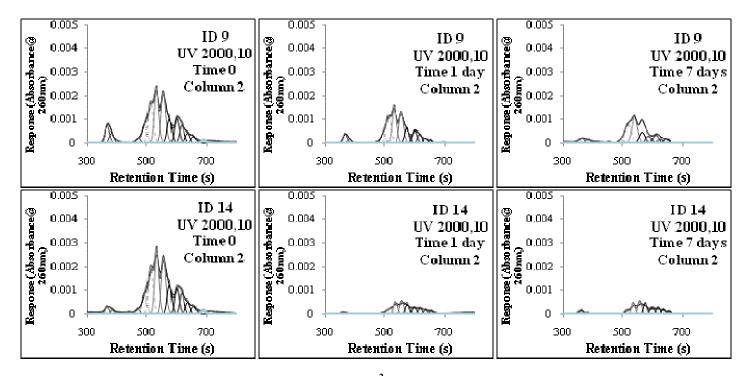


Figure P-14 - Peakfit analysis results for each of UV2000mJ/cm<sup>2</sup> and 10mg/L  $H_2O_2$  and biodegraded HPSEC chromatograms. Showing time 0, 1 day and 7 days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

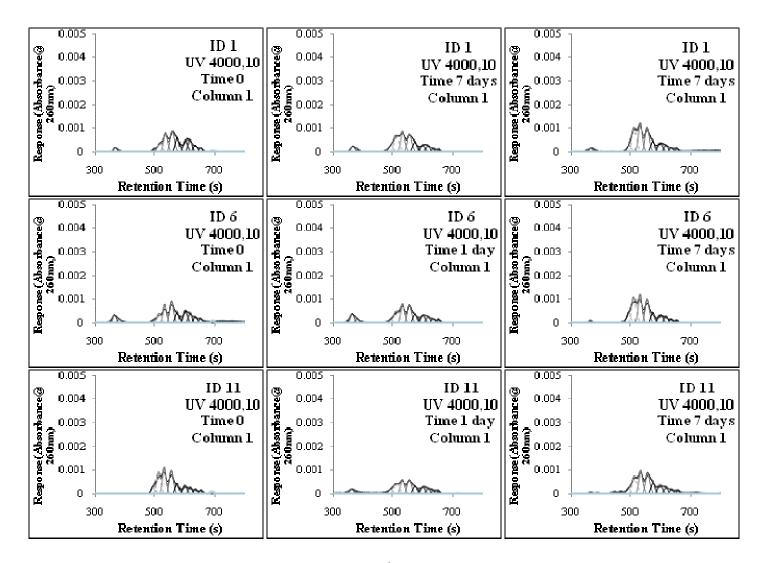


Figure P-15 - Peakfit analysis results for each of UV4000mJ/cm<sup>2</sup> and 10mg/L  $H_2O_2$  and biodegraded HPSEC chromatograms. Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

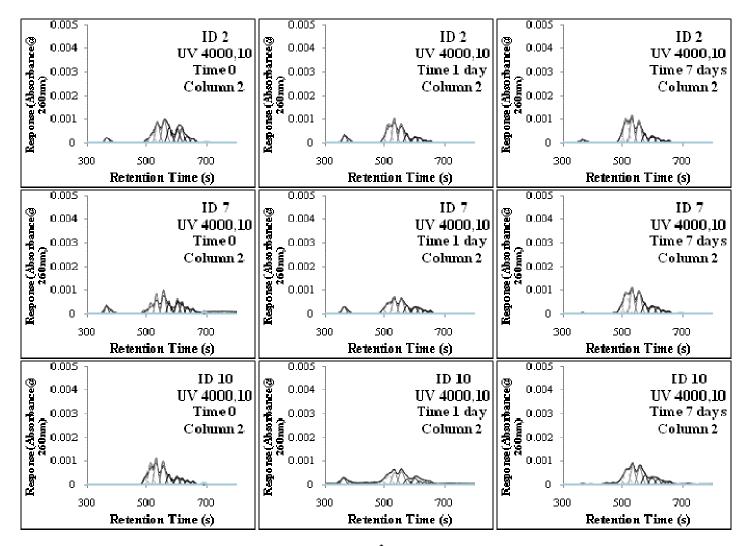
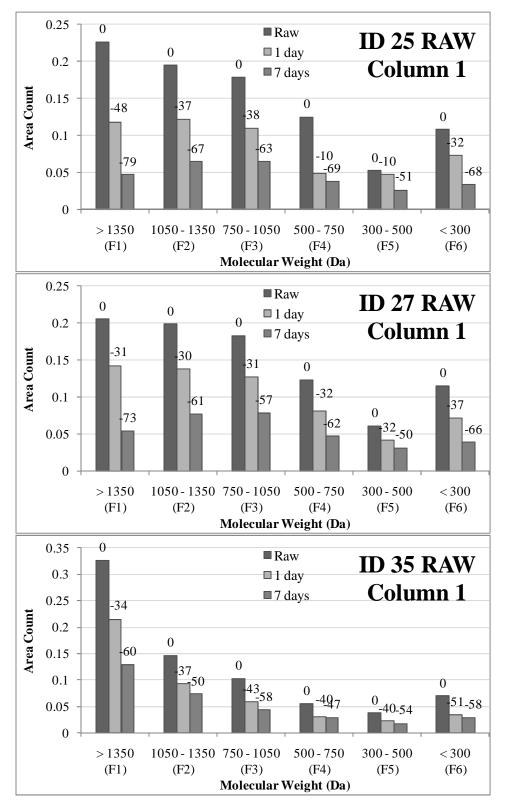
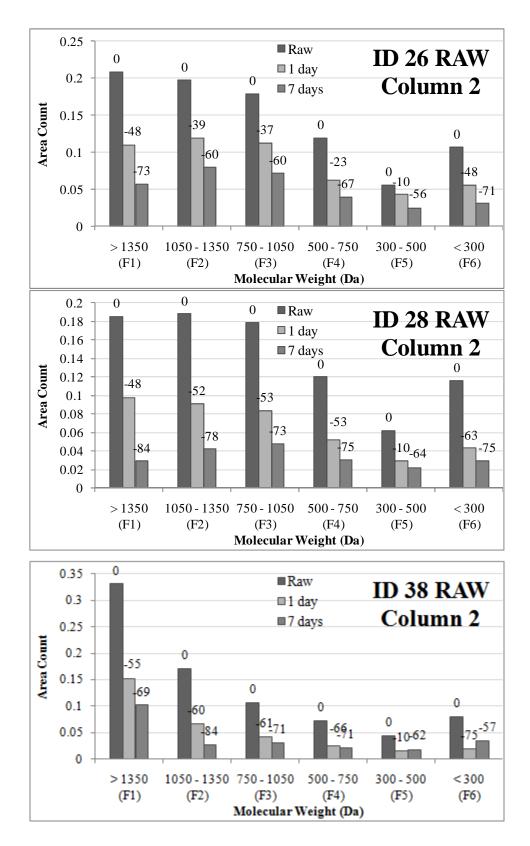


Figure P-16 - Peakfit analysis results for each of UV4000mJ/cm<sup>2</sup> and 10mg/L  $H_2O_2$  and biodegraded HPSEC chromatograms. Showing time 0, 1 day and 7days for both BAC Column 1 and BAC Column 2 using Systat Peakfit v4.12, Autofit Peak III Deconvolution.

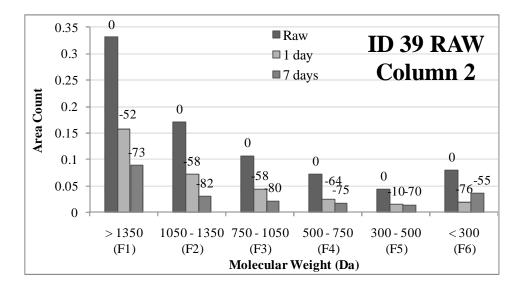
## APPENDIX Q. BIODEGRADATION BAR GRAPH RESULTS



**Figure Q-1 - Bar graph results for each of the raw water Peakfit analyzed HPSEC chromatograms.** Showing time 0, 1 day, 7day for BAC Column 1.



**Figure Q-2 - Bar graph results for each of the raw water Peakfit analyzed HPSEC chromatograms.** Showing time 0, 1 day, 7day for BAC Column 2.



**Figure Q-3 - Bar graph results for each of the raw water Peakfit analyzed HPSEC chromatograms.** Showing time 0, 1 day, 7day for BAC Column 2.

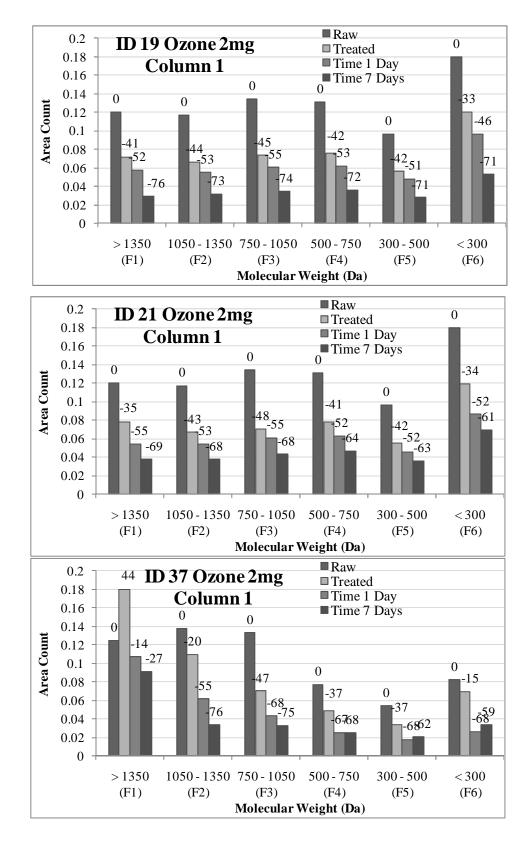


Figure Q-4 - Bar graph results for each of the ozonated 2 mgO<sub>3</sub>/mg DOC Peakfit analyzed HPSEC chromatograms.

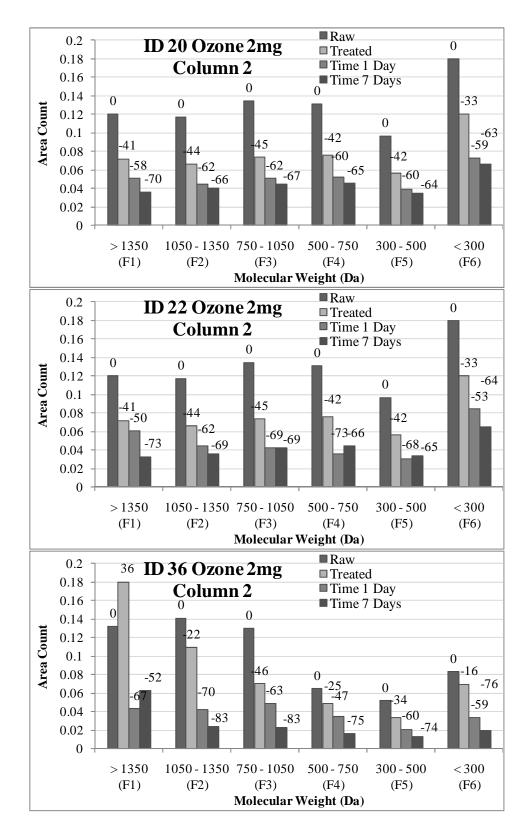


Figure Q-5 - Bar graph results for each of the ozonated 2 mgO<sub>3</sub>/mg DOC Peakfit analyzed HPSEC chromatograms.

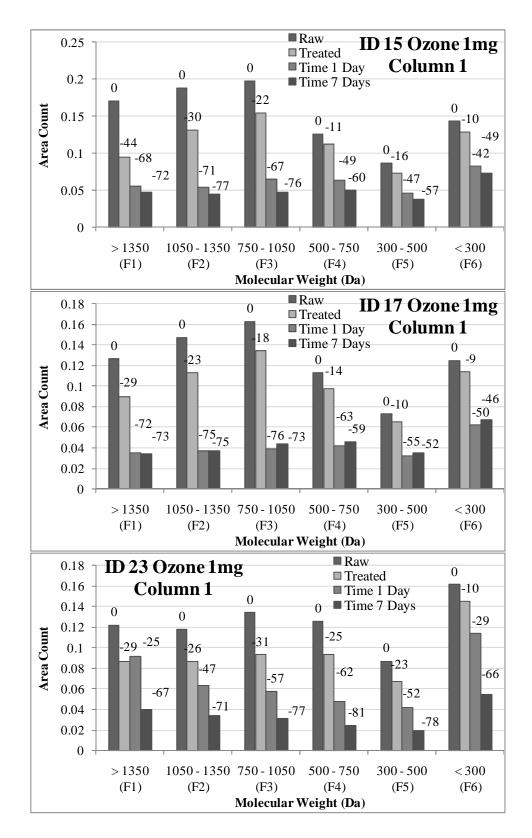


Figure Q-6 - Bar graph results for each of the ozonated 1 mgO<sub>3</sub>/mg DOC Peakfit analyzed HPSEC chromatograms.

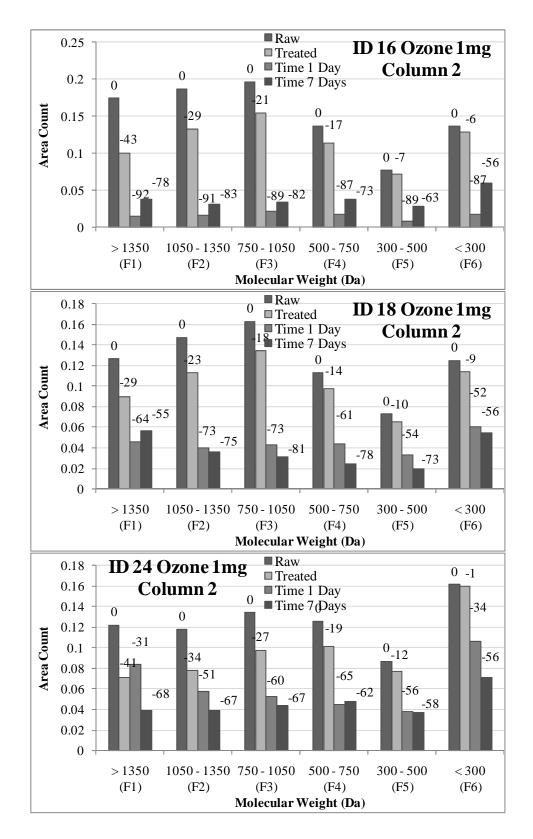


Figure Q-7 - Bar graph results for each of the ozonated 1 mgO<sub>3</sub>/mg DOC Peakfit analyzed HPSEC chromatograms.

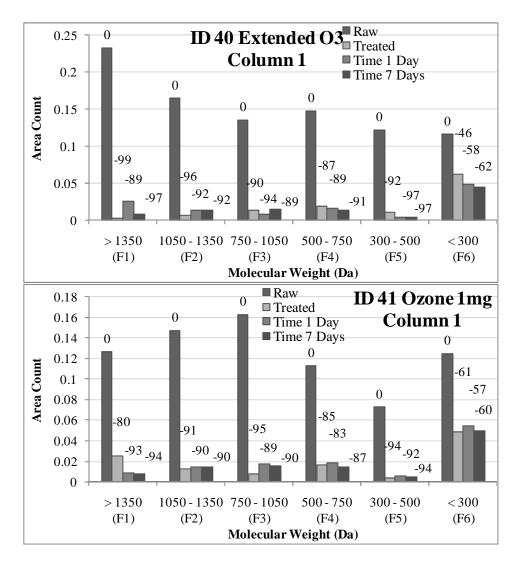


Figure Q-8 - Bar graph results for each of the extended ozonated 25 mgO<sub>3</sub>/mg DOC Peakfit analyzed HPSEC chromatograms.

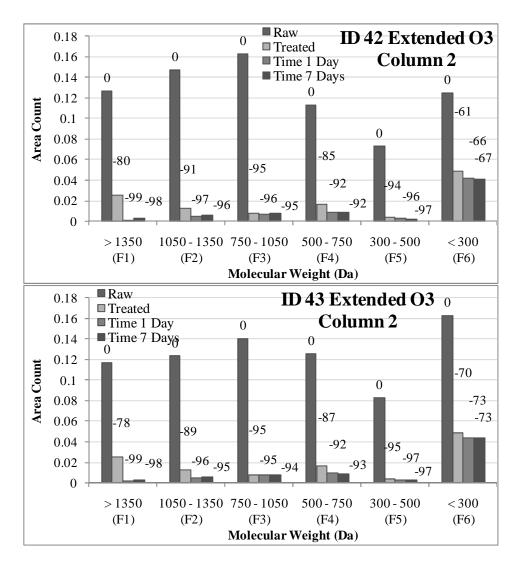


Figure Q-9- Bar graph results for each of the extended ozonated 25 mgO<sub>3</sub>/mg DOC Peakfit analyzed HPSEC chromatograms.

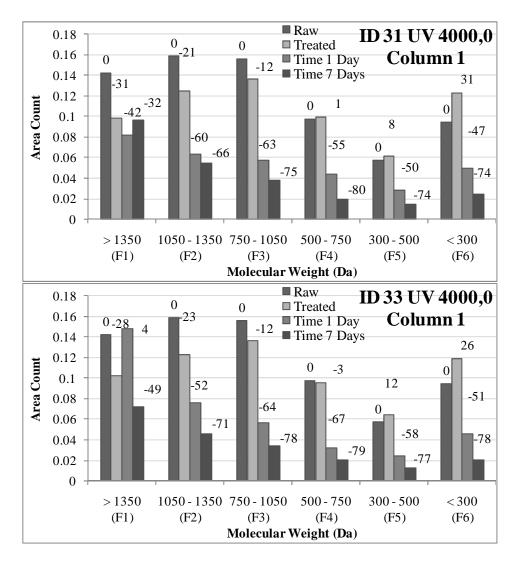


Figure Q-10 - Bar graph results for each of the UV4000mJ/cm<sup>2</sup> and 0mg/L  $H_2O_2$  Peakfit analyzed HPSEC chromatograms.

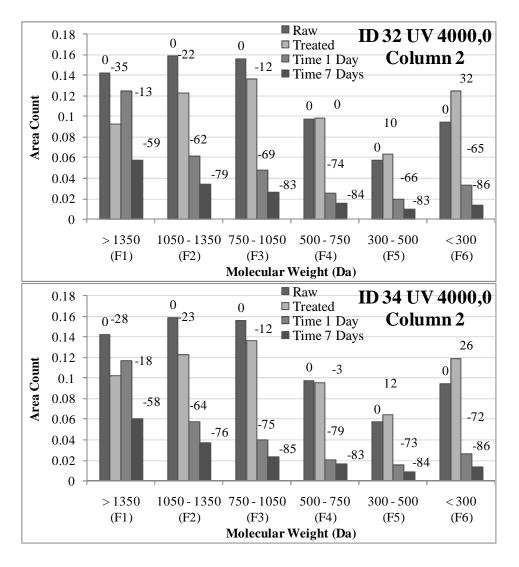


Figure Q-11 - Bar graph results for each of the UV4000mJ/cm<sup>2</sup> and 0mg/L  $H_2O_2$  Peakfit analyzed HPSEC chromatograms.

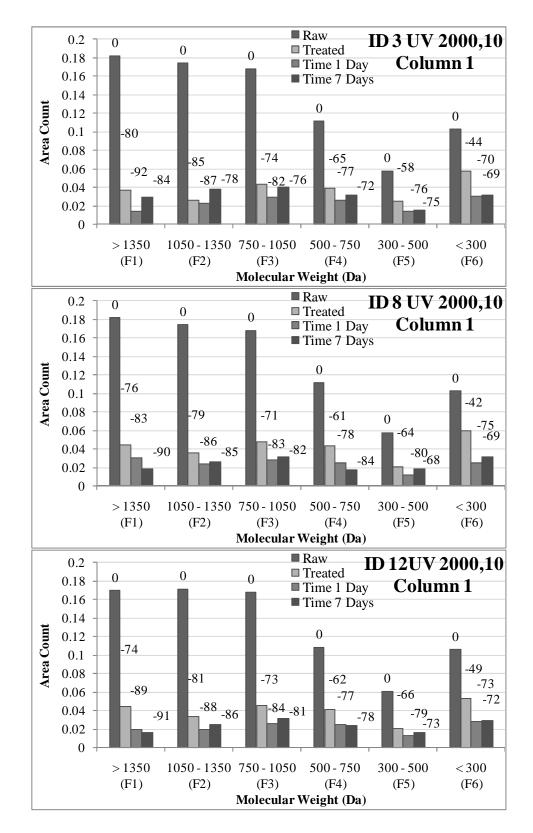


Figure Q-12 - Bar graph results for each of the UV2000mJ/cm<sup>2</sup> and 10mg/L  $H_2O_2$  Peakfit analyzed HPSEC chromatograms.

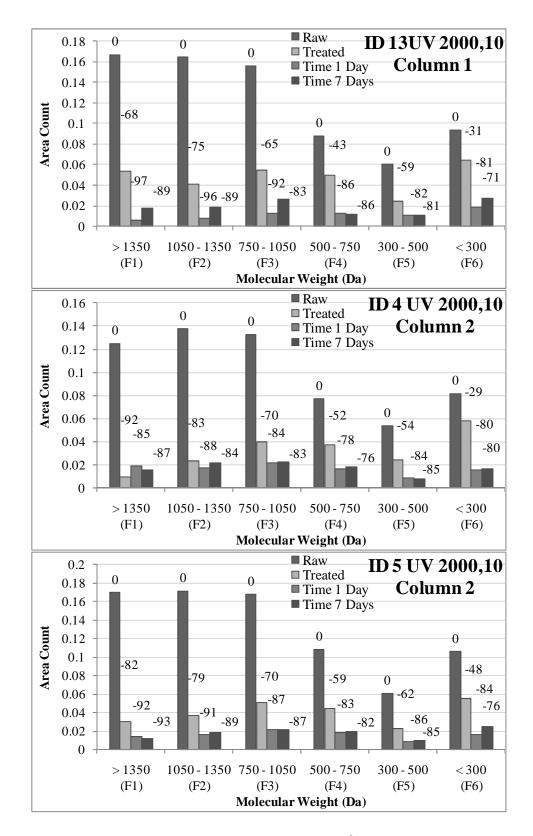


Figure Q-13 - Bar graph results for each of the UV2000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub> Peakfit analyzed HPSEC chromatograms.

Showing raw, time 0, 1 day, 7day for both BAC Column 1 and BAC Column 2.

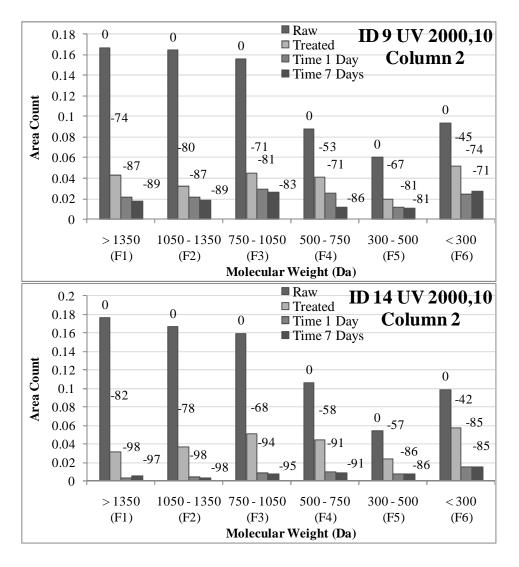


Figure Q-14 - Bar graph results for each of the UV2000mJ/cm<sup>2</sup> and 10mg/L  $H_2O_2$  Peakfit analyzed HPSEC chromatograms.

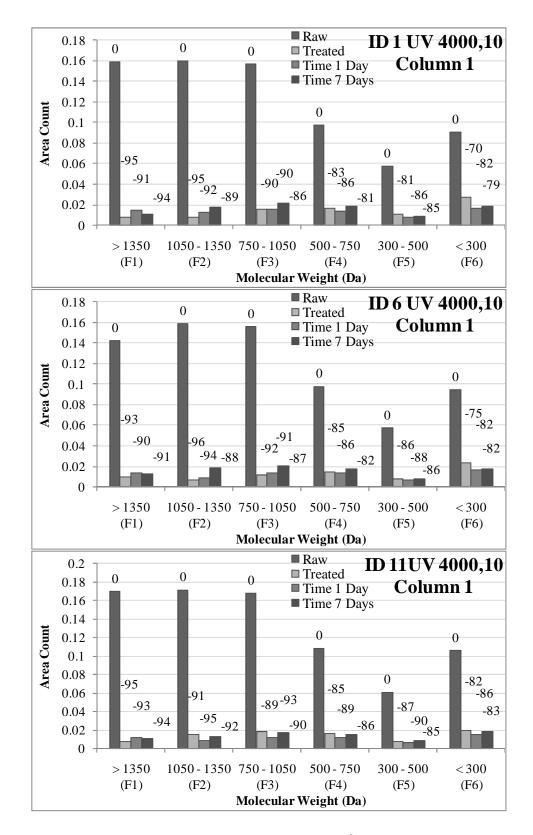


Figure Q-15 - Bar graph results for each of the UV4000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub> Peakfit analyzed HPSEC chromatograms.

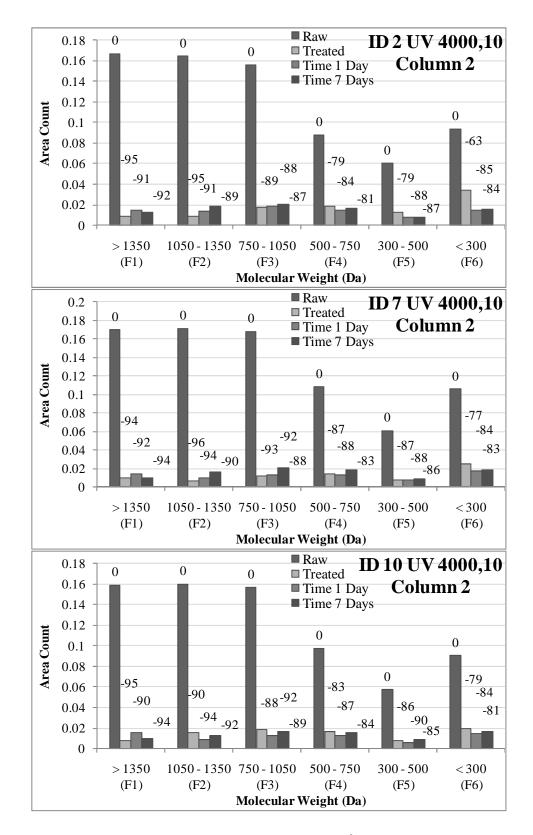
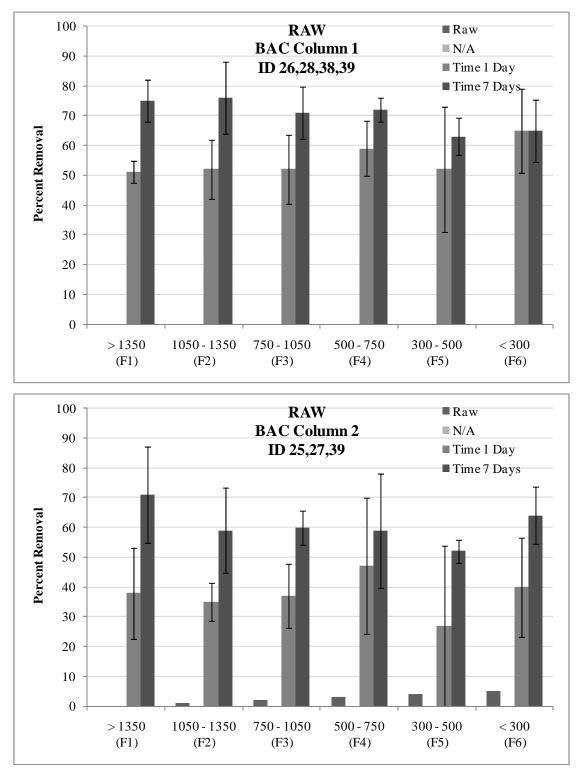


Figure Q-16 - Bar graph results for each of the UV4000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub> Peakfit analyzed HPSEC chromatograms.

APPENDIX R. BIODEGRADATION PERCENT REMOVAL RESULTS



## Figure R-1 - Percent removal results for each of the Peakfit analysed HPSEC chromatograms raw water samples.

Showing raw, time 0, 1 day, 7day for both BAC Column 1 and BAC Column 2.

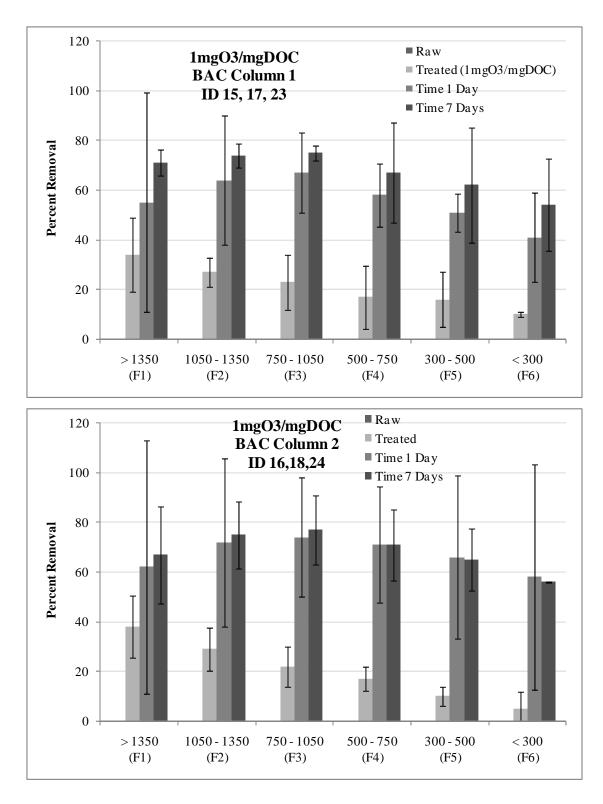


Figure R-2 - Percent removal results for each of the Peakfit analysed HPSEC chromatograms ozonated 1 mgO<sub>3</sub>/mg DOC water samples. Showing raw, time 0, 1 day, 7day for both BAC Column 1 and BAC Column 2.

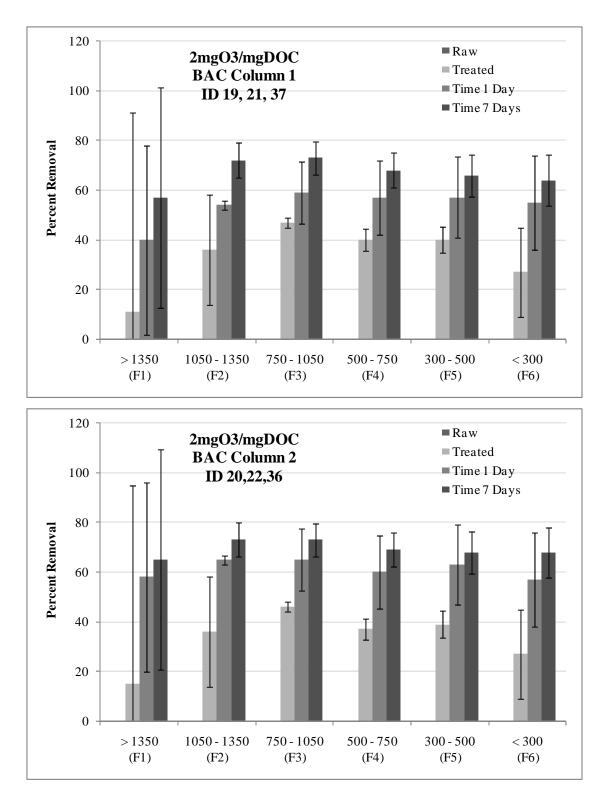


Figure R-3 - Percent removal results for each of the Peakfit analysed HPSEC chromatograms ozonated 2 mgO<sub>3</sub>/mg DOC water samples. Showing raw, time 0, 1 day, 7day for both BAC Column 1 and BAC Column 2.

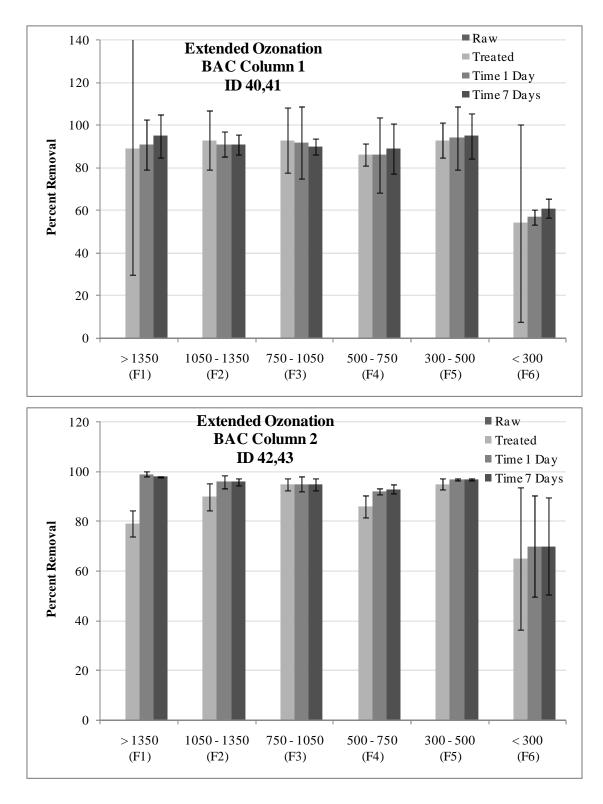


Figure R-4 - Percent removal results for each of the Peakfit analysed HPSEC chromatograms ozonated 25 mgO<sub>3</sub>/mg DOC water samples. Showing raw, time 0, 1 day, 7day for both BAC Column 1 and BAC Column 2.

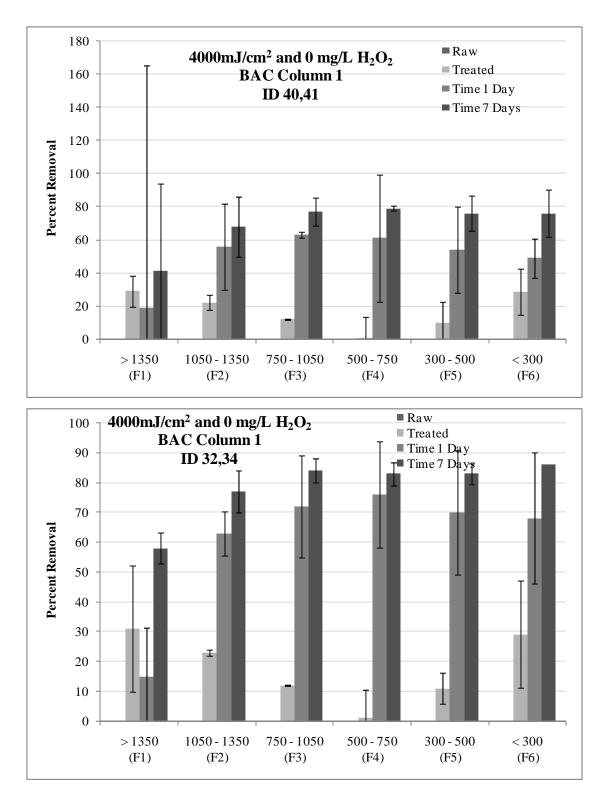


Figure R-5 - Percent removal results for each of the Peakfit analysed HPSEC chromatograms UV4000mJ/cm<sup>2</sup> and 0mg/L H<sub>2</sub>O<sub>2</sub> water samples. Showing raw, time 0, 1 day, 7day for both BAC Column 1 and BAC Column 2.

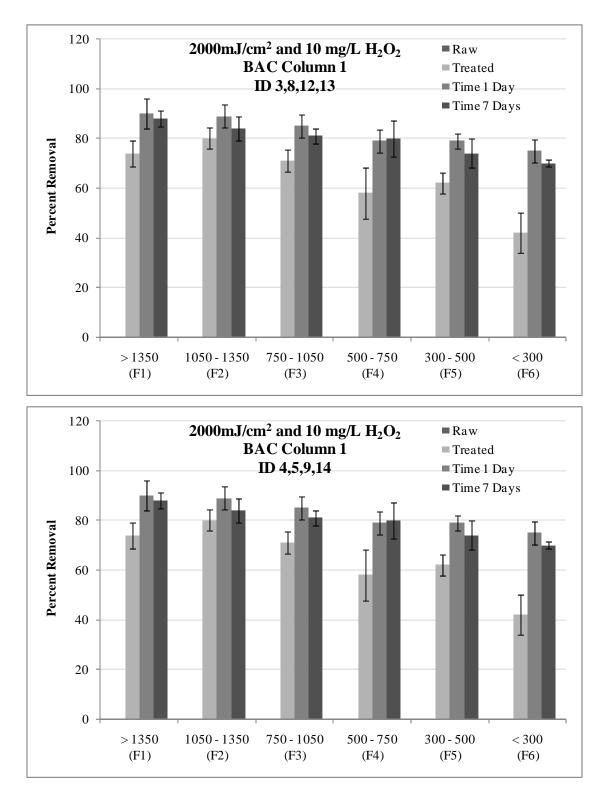


Figure R-6 - Percent removal results for each of the Peakfit analysed HPSEC chromatograms UV2000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub> water samples. Showing raw, time 0, 1 day, 7day for both BAC Column 1 and BAC Column 2.

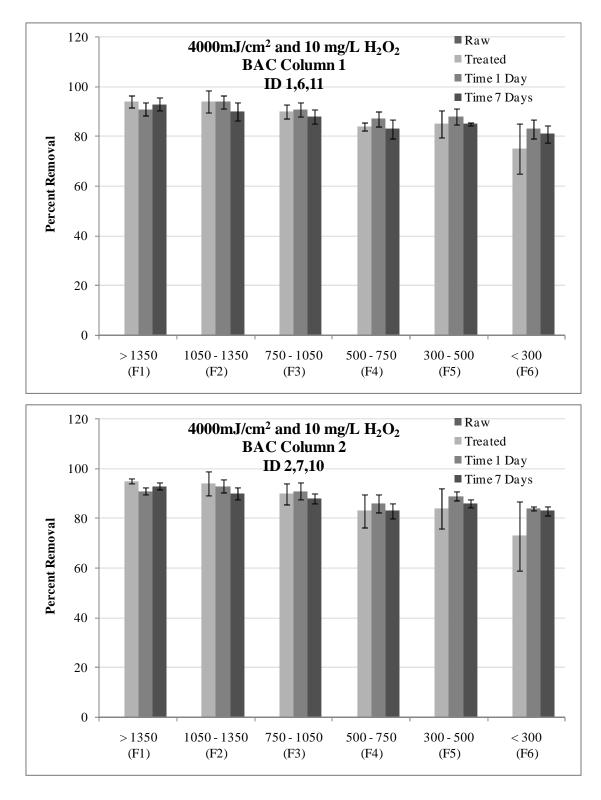


Figure R-7 - Percent removal results for each of the Peakfit analysed HPSEC chromatograms UV2000mJ/cm<sup>2</sup> and 10mg/L H<sub>2</sub>O<sub>2</sub> water samples. Showing raw, time 0, 1 day, 7day for both BAC Column 1 and BAC Column