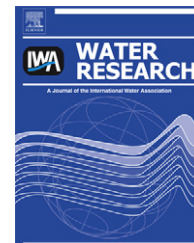


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# Comparison of advanced oxidation processes for the removal of natural organic matter

Rupa Lamsal, Margaret E. Walsh, Graham A. Gagnon\*

Department of Civil & Resource Engineering, Dalhousie University, Halifax, NS B3J 1Z1, Canada

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## ABSTRACT

This study examined the impact of UV, ozone (O<sub>3</sub>), advanced oxidation processes (AOPs) including O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> in the change of molecular weight distribution (MWD) and disinfection by-product formation potential (DBPFP). Bench-scale experiments were conducted with surface river water and changes in the UV absorbance at 254 nm (UV<sub>254</sub>), total organic carbon (TOC), trihalomethane and haloacetic acid formation potential (THMFP, HAAFP) and MWD of the raw and oxidized water were analyzed to evaluate treatment performance. Combination of O<sub>3</sub> and UV with H<sub>2</sub>O<sub>2</sub> was found to result in more TOC and UV<sub>254</sub> reduction than the individual processes. The O<sub>3</sub>/UV process was found to be the most effective AOP for NOM reduction, with TOC and UV<sub>254</sub> reduced by 31 and 88%, respectively. Application of O<sub>3</sub>/UV and H<sub>2</sub>O<sub>2</sub>/UV treatments to the source waters organics with 190–1500 Da molecular weight resulted in the near complete alteration of the molecular weight of NOM from >900 Da to <300 Da. H<sub>2</sub>O<sub>2</sub>/UV was found to be the most effective treatment for the reduction of THM and HAA formation under uniform formation conditions. These results could hold particular significance for drinking water utilities with low alkalinity source waters that are investigating AOPs, as there are limited published studies that have evaluated the treatment efficacy of five different oxidation processes in parallel.

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## 1. Introduction

Natural organic matter (NOM) is a complex heterogeneous mixture of different organic compounds with varying molecular size and properties. A common drinking water treatment goal is to remove NOM as it is a precursor for unwanted disinfection by-products (DBPs) during chemical disinfection processes, such as chlorine (Edzwald et al., 1985; Mosteo et al., 2009) and ozone (Gagnon et al., 1997; Schechter and Singer, 1995). NOM has also been shown to contribute to fouling on membrane surfaces (e.g., Hong and Elimelech, 1997; Her et al., 2008), the production of biologically unstable water (Rittmann and Snoeyink, 1984) and other unwanted water quality issues

such as metal complexes (Ravichandran et al., 1998; Schmitt et al., 2002).

The application of advanced oxidation processes (AOPs) has gained significant interest in the drinking water industry as an additional tool for removing NOM and minimizing the formation of DBPs in drinking water (Zhou and Smith, 2001; Chin and Bérubé, 2005). Previous studies have focused on ozone (O<sub>3</sub>) (e.g. Gagnon et al., 1997), ultraviolet radiation (UV) (e.g. Chin and Bérubé, 2005; Thomson et al., 2002) and AOPs including hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in combination with UV (H<sub>2</sub>O<sub>2</sub>/UV) (e.g. Toor and Mohseni, 2007; Wang et al., 2006), O<sub>3</sub> in combination with UV (O<sub>3</sub>/UV) (Amirsardari et al., 2001; Chin and Bérubé, 2005) and H<sub>2</sub>O<sub>2</sub> in combination with O<sub>3</sub> (H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>)

\* Corresponding author. Tel.: +1 902 494 3268; fax: +1 902 494 3108.

E-mail address: [graham.gagnon@dal.ca](mailto:graham.gagnon@dal.ca) (G.A. Gagnon).

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(e.g. Kleiser and Frimmel, 2000) to evaluate the potential for NOM reduction and the mitigation of DBP formation in finished water. Matilainen and Sillanpää (2010) have provided a thorough review of published oxidation and AOPs studies that have been conducted on both natural and synthetic test waters. However, these studies have primarily focused on evaluating one or two oxidation or AOPs for NOM reduction. This study goes beyond the previously published studies by directly comparing the treatment efficacy of five different oxidation processes in parallel, in terms of changes to molecular weight distribution (MWD) of the source water, NOM reduction and subsequent minimization of disinfection by-product formation potential (DBPFP) from a low turbidity, highly colored surface water.

During advanced oxidation treatment, hydroxyl radicals ( $\text{HO}^\bullet$ ) are formed which act as a strong oxidant and transform NOM. Westerhoff et al. (2007) directly measured the rate constants for reactions between  $\text{HO}^\bullet$  radicals and seven dissolved organic matter (DOM) isolates from different sources and observed rate constants in range from  $1\text{--}5 \times 10^8 \text{ M}^{-1}\text{S}^{-1}$ , which is three to four orders of magnitude higher than for chlorine and ozone (Crittenden et al., 1999). Hydroxyl radicals produced during AOPs are capable of reducing total organic carbon (TOC) concentrations and DBPFP of raw water (Amirsardari et al., 2001; Chin and Bérubé, 2005; Kusakabe et al., 1990; Sierka and Amy, 1985; Glaze et al., 1982). Under strong advanced oxidation conditions (i.e. long irradiation time and/or higher  $\text{H}_2\text{O}_2$  concentrations) NOM is mineralized, indicated by a decrease in TOC and DBPFP (Kleiser and Frimmel, 2000; Wang et al., 2006; Toor and Mohseni, 2007). However, such strong treatment conditions may not be economically feasible, and in commercial applications, low or moderate advanced oxidation conditions are applied. Under these conditions, NOM is partially oxidized and higher molecular weight compounds are transformed into smaller and more biodegradable compounds such as aldehydes and carboxylic acids (Backlund, 1992; Edwards and Benjamin, 1992; Gagnon et al., 1997; Sarathy and Mohseni, 2007). Such changes in the chemical characteristic of NOM also result in reducing TOC concentrations and/or alter the characteristics of the DBP precursor material potentially reducing its reactivity with chlorine.

The objective of this study was to compare  $\text{O}_3$ , UV and three AOPs including  $\text{H}_2\text{O}_2/\text{O}_3$ ,  $\text{H}_2\text{O}_2/\text{UV}$  and  $\text{O}_3/\text{UV}$  for NOM

removal and assess the impact on modifying the MWD of NOM following treatment. This study was conducted using laboratory-controlled conditions with a natural surface water source that has a low alkalinity ( $<5 \text{ mg/L}$  as  $\text{CaCO}_3$ ) and moderate level of total organic carbon (TOC of  $3\text{--}4 \text{ mg/L}$ ). The effectiveness of each treatment process was evaluated by traditional metrics for NOM; namely, UV absorbance at  $254 \text{ nm}$  ( $\text{UV}_{254}$ ), TOC concentration, specific UV absorbance (SUVA), trihalomethane formation potential (THMFP), and haloacetic acid formation potential (HAAFP). In addition, the MWD following each treatment was assessed using high performance size exclusion chromatography (HPSEC) analysis. HPSEC has been demonstrated to be an effective technique for determining the MWD of NOM (Pelakani et al., 1999). Determination of the MWD of NOM provides information on the specific fraction of NOM that plays important role in DBP formation (Amy et al., 1987; Chang and Young, 2000) and membrane fouling potential during water treatment (e.g. Her et al., 2008).

## 2. Materials and methods

### 2.1. Source water characterization

Surface water collected from the French River, which provides the drinking water in a northern shore community in Nova Scotia, Canada, was used for the bench-scale study. The French River water is characterized by its low alkalinity ( $<5 \text{ mg CaCO}_3/\text{L}$ ), low turbidity ( $<1.5 \text{ NTU}$ ), and high color level ( $>35 \text{ Pt-Co}$ ). The French River has general characteristics that are similar to other surface water sources in Nova Scotia and Atlantic Canada (Waller et al., 1996).

### 2.2. Experimental set-up

The laboratory scale batch set-up for the ozone experiments used in this study is shown in Fig. 1. It consists of a compressed air system, ozone generator, a contactor (reactor) and off-gas collection system. The reactor was a glass tank with a working volume of  $10 \text{ L}$  ( $0.305 \text{ cm diameter} \times 0.41 \text{ cm height}$ ). The inflow and outflow of the ozone gas line in the reactor was fitted with a laboratory stopper (Fisher scientific # 14141R) at the top of the reactor and sample was

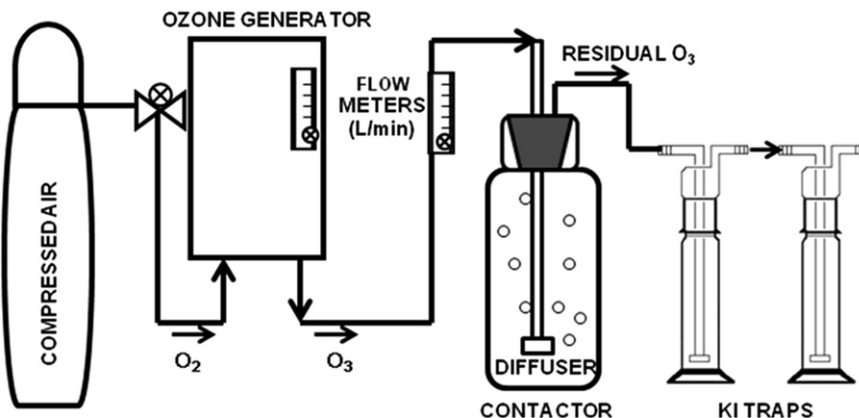


Fig. 1 – Schematic of laboratory set-up for ozone experiment.

taken from the bottom of the reactor. Compressed air with a flow rate of 2 L/min was passed into the ozone generator (VMUS-4), where high voltage corona discharge causes break down of oxygen molecules into radicals that combine with oxygen molecules to form ozone. Ozone was bubbled into the base of the reactor using a fine bubble diffuser at a flow rate of 2 L/min and pressure of 15 psi. A potassium iodide solution (20 g KI in 1 L water) was used to collect the residual ozone in the off-gas from the reactor. The ozone experiments were conducted in a semi-batch mode by continuously passing O<sub>3</sub> gas in a 10 L reactor directly with 3 L sample volume at room temperature (23 °C) for 30 min. Ozonation for 30 min showed better performance than for lower treatment times (e.g., 5 and 15 min) and similar performance to higher treatment times (45 min and 60 min). The concentration of ozone consumed during the 30 min reaction time was  $4.04 \pm 0.11$  mg/L. The detailed procedure for ozone dose calculation is provided in the supplementary material. For the H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> experiments, 23 mg/L of hydrogen peroxide solution (50% Fisher Scientific) was mixed with 3 L of the raw water for approximately 5 min and the mixture was ozonated for 30 min, similar to the treatment times used in the ozone experiments. The concentration of H<sub>2</sub>O<sub>2</sub> was chosen following previous studies using surface water (Sarathy and Mohseni, 2007; Goslan et al., 2006; Toor and Mohseni, 2007). Toor and Mohseni (2007) have reported that at lower concentrations of H<sub>2</sub>O<sub>2</sub>, the H<sub>2</sub>O<sub>2</sub>/UV AOP was not effective for reducing DBP precursors.

A low pressure ultraviolet lamp (Trojan UV Max.) with 43 W power was used during the UV experiment. The dimension of the chamber assembly was 0.495 m × 0.09 m, and the length of the lamp (i.e., sleeve length) was 0.405 m. The UV reactor is a glass tube with a working volume of approximately 2 L. Raw water was pumped into the reactor at a flow rate of 167 mL/min using a masterflex pump to achieve the maximum UV dose delivered by the lamp (e.g., >1000 mJ/cm<sup>2</sup>). The delivered UV dose in the UV and UV based AOP experiments was 1140 mJ/cm<sup>2</sup>, which was determined by using potassium ferrioxalate actinometer. Additional information on the UV dose calculation is provided in the supplementary material. For the H<sub>2</sub>O<sub>2</sub>/UV AOP experiments, 23 mg/L of H<sub>2</sub>O<sub>2</sub> was first mixed with 3 L of the raw water for 5 min. The mixture was then pumped through the UV reactor at the same flow rate as that of UV process experiments. For the O<sub>3</sub>/UV combined AO process, the raw water sample was ozonated for 30 min and then pumped through the UV reactor to achieve the 1140 mJ/cm<sup>2</sup> UV dosage. The oxidation processes evaluated in this study utilized higher dosages of oxidants than typically applied in drinking water treatment for optimum removal of

NOM and DBPFP, consistent with earlier studies (Chin and Bérubé, 2005; Toor and Mohseni, 2007).

### 2.3. Analytical methods

In this study, NOM was quantified by measuring UV<sub>254</sub>, TOC concentrations, and dissolved organic carbon (DOC) concentrations. Specific UV absorbance (SUVA) which can be used as a surrogate parameter to monitor the changes in aromatic nature of NOM in water was calculated from UV<sub>254</sub> and DOC as outlined by Edzwald et al. (1985). In addition, DBPFP was determined for THMs and HAAs using the uniform formation conditions (UFC) methodology (Summers et al., 1996). Finally, NOM characterization included analysis using high performance size exclusion chromatography (HPSEC) (PerkinElmer, Series 200) with a UV/VIS detector to determine the molecular weight distribution of NOM. A detailed description of the analytical test procedures used for this research is provided in the supplementary material. Also, included in the supplementary material is a methodology for the general water quality parameters (e.g., pH, turbidity) that were measured as part of this study.

## 3. Results and discussion

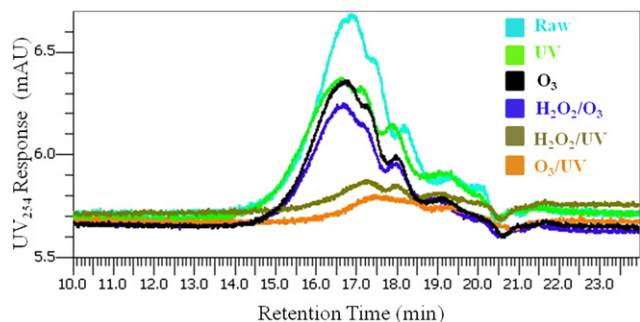
### 3.1. Characterization of the source water

The majority of organic carbon of the French River was in the dissolved fraction, as demonstrated by the TOC ( $3.10 \pm 0.3$  mg/L) and DOC ( $2.85 \pm 0.13$  mg/L) measurements. The UV<sub>254</sub> value was  $0.090 \pm 0.003$  cm<sup>-1</sup> (Table 1). The SUVA for the French River water was 3.2 m<sup>-1</sup>/(mg/L), which indicates that the source water contained a mixture of hydrophobic and hydrophilic NOM fractions (Owen et al., 1995).

The chromatogram used to determine the MWD of the source water is presented in Fig. 2. The total area of the sample was integrated using Totalchrom software (PerkinElmer, Ontario, Canada) to obtain the entire MWD of NOM in the sample (Fig. 3). The relationship between the molecular weight of organic compounds and their retention time was determined by log-linear regression between log molecular weight and retention time. HPSEC analysis showed that the French River raw water consists of four different MW fractions: 1246, 690, 478 and 292 Da. The highest percentage area of chromatogram (i.e., 66%) was observed with the 1246 Da MW fraction. Earlier studies have proposed that compounds having 1000–1500 Da MW range likely represent

**Table 1 – Mean and standard deviations of water quality parameters and dosages used in each treatment processes.**

	Raw	UV	O <sub>3</sub>	O <sub>3</sub> /UV
UV <sub>254</sub> (cm <sup>-1</sup> )	$0.092 \pm 0.003$	$0.080 \pm 0.003$	$0.039 \pm 0.007$	$0.011 \pm 0.004$
TOC (mg/L)	$3.10 \pm 0.325$	$2.99 \pm 0.049$	$2.92 \pm 0.053$	$2.12 \pm 0.116$
DOC (mg/L)	$2.85 \pm 0.131$	$2.73 \pm 0.072$	$2.79 \pm 0.175$	$2.0 \pm 0.723$
SUVA (m <sup>-1</sup> /(mg/L))	$3.16 \pm 0.170$	$2.93 \pm 0.131$	$1.43 \pm 0.023$	$0.55 \pm 0.006$
Dosages		1140 mJ/cm <sup>2</sup>	$4.04 \pm 0.110$ mg/L	$4.04 \pm 0.110$ mg/L 1140 mJ/cm <sup>2</sup>



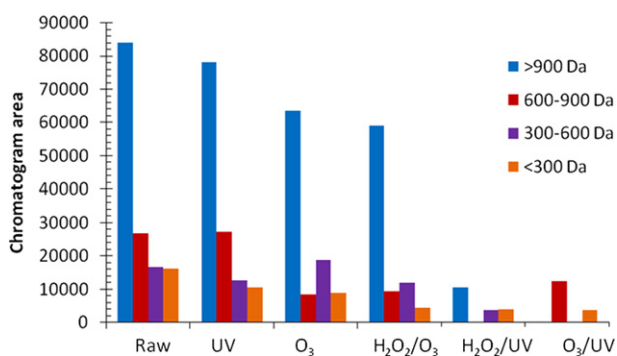
**Fig. 2 – High performance size exclusion chromatography (HPSEC) chromatograms of raw and oxidized waters.**

humic and fulvic acids (e.g. Huber and Frimmel, 1996), which is supported by the measured SUVA value ( $3.19 \text{ m}^{-1}/\text{mg/L}$ ) in the French River. The lower proportion of intermediate and low MW fractions present in the French River water may represent simple aromatic compounds or fulvic acids as described by Her et al. (2002, 2008).

### 3.2. Impact of advanced oxidation on TOC and SUVA

In the AOP experiments, the reduction of NOM was attributed to chemical oxidation of NOM present in the raw water by hydroxyl radicals ( $\text{HO}^\bullet$ ). However, these  $\text{HO}^\bullet$  can also react with carbonate and bicarbonate ions which are typically present in raw water. This reaction significantly reduces the amount of  $\text{HO}^\bullet$  radicals available for oxidation of NOM (Gottschalk et al., 2000). Since the source water used in this study has low alkalinity, the impact of carbonate and bicarbonate ions on the resulting concentration of  $\text{HO}^\bullet$  was expected to be negligible.

A reduction in  $\text{UV}_{254}$  absorbance was observed after each treatment process is presented in Table 1. UV radiation at 254 nm is mainly absorbed by aromatic compounds and conjugated double bonds (Singer, 1999). Therefore, reduction in  $\text{UV}_{254}$  indicates a loss of aromatic and conjugated double bond structures of NOM (Owen et al., 1995). However, the observed impact of the treatment processes on TOC concentration was less because of the partial oxidation of NOM to other intermediate by-products (Table 1). UV treatment on its own had minor impact upon the  $\text{UV}_{254}$  absorbance and almost no impact on TOC concentration. The impact of UV or  $\text{H}_2\text{O}_2$



**Fig. 3 – Chromatogram area counts for raw and oxidized waters for different molecular weight compounds.**

alone has been found to be negligible for NOM reduction in other studies (Chin and Bérubé, 2005). The rate of  $\text{UV}_{254}$  and TOC reduction increased significantly when  $\text{H}_2\text{O}_2$  was combined with UV. UV in combination with  $\text{H}_2\text{O}_2$  promotes the formation of  $\text{HO}^\bullet$ , as reported by other researchers (Wang et al., 2006; Toor and Mohseni, 2007). The  $\text{UV}_{254}$  absorbance and TOC concentrations decreased from 11 to 60% and 3–23%, respectively, with UV treatment in the presence of  $\text{H}_2\text{O}_2$  compared to UV treatment on its own. Sarathy and Mohseni (2007) also observed significant reduction of  $\text{UV}_{254}$  without TOC reduction in experiments with  $\text{H}_2\text{O}_2/\text{UV}$  AOP with a UV dose of  $1500 \text{ mJ}/\text{cm}^2$  and  $\text{H}_2\text{O}_2$  concentrations up to  $20 \text{ mg/L}$ .

The ozone and  $\text{H}_2\text{O}_2/\text{O}_3$  treatment processes reduced the raw water TOC concentration by 6 and 10%, respectively. However, as presented in Table 1,  $\text{UV}_{254}$  absorbance was observed to be reduced by 57% with  $\text{O}_3$  treatment and 59% with  $\text{H}_2\text{O}_2/\text{O}_3$  treatment. The higher reduction of  $\text{UV}_{254}$  absorbance with less reduction of TOC demonstrates the removal of conjugated double bonds with minimal mineralization. Increased NOM oxidation in  $\text{H}_2\text{O}_2/\text{O}_3$  process, as compared to the  $\text{O}_3$  process alone, was a result of more  $\text{HO}^\bullet$  formation.

Combination of ozone with UV ( $\text{O}_3/\text{UV}$ ) reduced TOC and  $\text{UV}_{254}$  by 31 and 88%, respectively. The higher reduction of  $\text{UV}_{254}$  achieved can be explained by the NOM reaction with  $\text{O}_3$ . In all  $\text{O}_3$  experiments, the samples were treated with high doses of  $\text{O}_3$ , and as a result, double bonds were oxidized and  $\text{UV}_{254}$  was reduced. Moreover, since the ozone concentration evaluated in this study is much higher than hydroxyl radical levels, ozone is expected to be the main degradation pathway for NOM. In  $\text{O}_3/\text{UV}$  AOP systems evaluated in other studies, mineralization of organic carbon was also observed (Amirsardari et al., 2001; Kusakabe et al., 1990; Glaze et al., 1982; Sierka and Amy, 1985). Chin and Bérubé (2005) evaluated the  $\text{O}_3/\text{UV}$  AOP with an  $\text{O}_3$  dose of  $4 \text{ mg/L}$  and a UV dose of  $0.13 \text{ W}/\text{cm}^2$  on raw water characterized with  $1.3\text{--}3.2 \text{ mg/L}$  TOC concentrations. That study found approximately 15% mineralization of the TOC in the raw water after  $\text{O}_3/\text{UV}$  treatment, although the UV dose evaluated (approx.  $130 \text{ mJ}/\text{cm}^2$ ) was much lower than that used in this study (i.e.,  $1140 \text{ mJ}/\text{cm}^2$ ). The increased mineralization observed in  $\text{O}_3/\text{UV}$  AOP compared to  $\text{H}_2\text{O}_2/\text{O}_3$  and  $\text{H}_2\text{O}_2/\text{UV}$  AOPs may be due to a larger yield of hydroxyl radical per oxidant compared to other advanced oxidation processes (Gottschalk et al., 2000; Oh et al., 2003). Since production yields of  $\text{HO}^\bullet$  in each oxidation process were not measured during this study, further work would be required to verify this theory.

### 3.3. Impact of oxidation on NOM molecular weight

HPSEC chromatograms for the AOP test waters are presented in Fig. 2. Higher MW organics are eluted from the column first and lower MW organics are eluted later. The peak area of chromatogram represents the intensity of UV absorbance of the sample detected by the UV detector at 254 nm. Therefore, these peaks are indication of the presence of aromatic or double bond organic compounds. Prior to application of the treatments evaluated in this study, the HPSEC chromatogram of raw water featured a large peak, and the total area under the HPSEC chromatogram decreased with the application of the different

treatment processes. These results demonstrate the oxidation of aromatic or double bond organic matter into lower molecular weight compounds after treatment.

The MWD of each process observed in Fig. 2 was translated into quantitative terms using Totalchrom software available with the HPSEC instrument and is presented in Fig. 3. The UV treatment process showed minor impact on the MWD of the source water NOM. Ozone was found to reduce the >900 Da and 600–900 Da MW fractions of organics by 25 and 68%, respectively. As described earlier,  $UV_{254}$  and TOC were found to be reduced by 57 and 6%, respectively, after  $O_3$  treatment, demonstrating that NOM oxidation occurred with removal of conjugated double bonds with minimal mineralization. Frimmel et al. (2000) also observed that ozone treatment decreased the absorbance of Ruhr River water with minimal mineralization and found decreases in the higher MW fractions with concomitant increase in the lower MW fractions. However, minimal increase in the lower MW (i.e. 13% of 300–600 Da) fraction of NOM was observed during this study.

Fig. 3 shows that the reduction of larger MW NOM was higher than that of lower MW NOM. The preferential reduction of larger MW organic matter, in comparison to lower MW organic matter, could be a result of the higher reaction rate constant between  $HO^\bullet$  and the larger MW compounds (Thomson et al., 2004). Higher MW compounds tend to be more aromatic in nature, so they may have a larger number of reaction sites than smaller MW compounds. Thomson et al. (2004) also explained that higher MW compounds react fastest as they have higher molar absorptivities than lower MW compounds. Westerhoff et al. (1999) observed the positive correlation between molecular weights and aromaticity and the reaction rate constant between  $HO^\bullet$  and NOM.

Ozone in combination with UV showed complete removal of MW NOM >900 Da. However, there was no observed increase in the formation of lower MW NOM. Similarly, when  $H_2O_2$  was combined with the UV process, the  $H_2O_2/UV$  AOP reduced the >900 Da MW fractions by 85% and the 600–900 Da MW fractions by 100% without any observed increase in lower MW fractions of the NOM. This is in contrast to previous studies that have shown significant reduction of larger MW NOM in combination with an increase in lower MW NOM (Sarathy and Mohseni, 2007). However, that study performed HPSEC analysis at 260 nm to detect the chromophoric NOM only. Observation of 23% TOC reduction versus 60%  $UV_{254}$  reduction with the  $H_2O_2/UV$  AOP implies increase in lower MW NOM. However, the HPSEC analysis used in this study did not provide further information for single bond organic carbon since the UV detector of the HSPEC instrument only measures the aromatic or double bond organics, making the direct relationship and quantification between HPSEC and TOC results difficult.

### 3.4. Impact of advanced oxidation on DBP formation

The total trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP) of the raw and oxidized waters are shown in Figs. 4 and 5, respectively. In general, THMFP removal was greater than HAAFP in the oxidation processes studied. The precursor materials for THMs tend to be aromatic whereas HAAs precursor materials

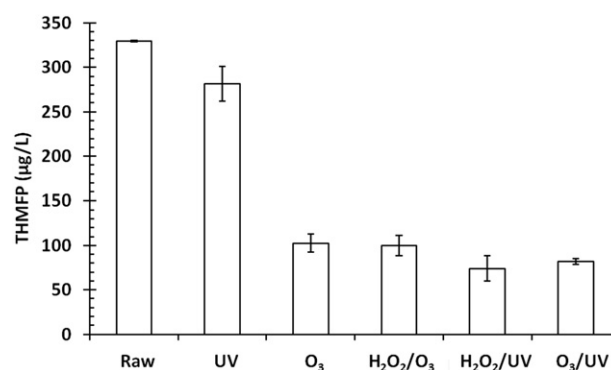


Fig. 4 – THMs for raw and oxidized waters (Vertical bars represent  $2\sigma$  levels).

are aliphatic as discussed in detail in Bond et al. (2009) and Hong et al. (2009). The treatment by AOPs tends to decrease the aromaticity of NOM, therefore, the decrease in THMFP is greater than that of HAAFP caused by the larger removal of THMs precursor materials. In both the raw and oxidized waters, chloroform formed the majority of trihalomethane species, followed by dichlorobromomethane and dibromochloromethane. The concentrations of bromoform were below the detection limit (zero) in all samples. The majority of HAA species measured in the raw water were dichloroacetic acid, bromochloroacetic acid, chloroacetic acid. Dibromoacetic acid and bromodiacyetic acid concentrations were found to be below detection limit.

The results of the UV treatment process showed 15% reduction of THMFP and no reduction of HAAFP. The little to no reduction of THMFP and HAAFP may be due to the minor impact of UV radiation on  $UV_{254}$  reductions and changes in MWD of organics. These observations are consistent with those found in other studies (e.g., Chin and Bérubé, 2005), where it has also been demonstrated that UV treatment on its own is ineffective at reducing THMFP and HAAFP. When  $H_2O_2$  was combined with UV, THMFP and HAAFP were reduced by 77 and 62%, respectively. The increased reduction of THMFP and HAAFP observed with the  $H_2O_2/UV$  AOP agrees with the increased reduction of  $UV_{254}$  achieved with  $H_2O_2/UV$  treatment (e.g., 60%) compared to the moderate 11% reduction in

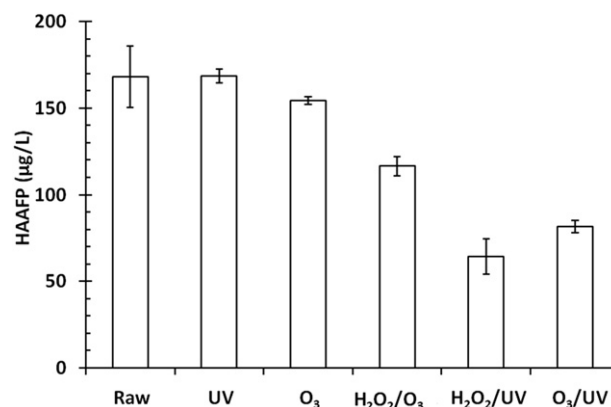


Fig. 5 – HAAs of raw and oxidized waters (Vertical bars represent  $2\sigma$  levels).

UV<sub>254</sub> achieved with UV treatment alone. MWD results also showed that H<sub>2</sub>O<sub>2</sub>/UV AOP resulted in increased reduction of >900 Da MW fractions by 85% and the complete reduction of 600–900 Da MW fractions of NOM. Such a decrease in THMFP and HAAFP was also observed with 23 mg/L initial H<sub>2</sub>O<sub>2</sub> concentration and UV dose higher than 1500 mJ/cm<sup>2</sup> in a study conducted by Toor and Mohseni (2007) with similar source water qualities. Liu et al. (2002) reported reduction of both THMFP and HAAFP with UV dose of 1000 mJ/cm<sup>2</sup> or higher and initial H<sub>2</sub>O<sub>2</sub> concentration of 100 mg/L. These studies have suggested that a combination of high UV dose and H<sub>2</sub>O<sub>2</sub> concentration is required for the potential generation of higher levels of HO• radicals and hence the reduction of THMFP and HAAFP. The study conducted by Toor and Mohseni (2007) also demonstrated a significant reduction of H<sub>2</sub>O<sub>2</sub> concentration in the solution, indicating the generation of HO• radicals that consequently oxidized DBP precursors and reduced the THMFP and HAAFP of the source water. Significant reduction of THMFP and HAAFP with H<sub>2</sub>O<sub>2</sub>/UV treatment was also observed in this study, which indicates a decrease in H<sub>2</sub>O<sub>2</sub> concentration in the solution.

In contrast to UV treatment alone, ozone treatment showed a higher reduction of THMFP and HAAFP (i.e., 69 and 8%, respectively). The increased percent reduction of THMFP with the O<sub>3</sub> process is supported by increased reduction of UV<sub>254</sub> (57%), indicating strong correlation between UV<sub>254</sub> and THMFP reductions (Edzwald et al., 1985). The MWD results also showed the increased reduction of UV absorbing organics. These results are consistent with previous studies (e.g., Hu et al., 1999; Westerhoff et al., 1999; Galapate et al., 2001). The reduction of THMFP and HAAFP of the ozonated samples can be explained by the reaction pathway for DBPs. Similar to chlorine, ozone reacts by addition to the aromatic system and once the aromatic double bonds are consumed by ozone, fewer sites are available for chlorine addition. Chlorine addition to the double bond is a main pathway for DBP production.

In the H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> AOP experiments, the THMFP and HAAFP were reduced by 70 and 31%, respectively. For treatments involving O<sub>3</sub> in combination with UV, THMFP was reduced by 75% and HAAFP was reduced by 52%. Glaze et al. (1982) observed that the combined application of O<sub>3</sub> and UV was more effective than ozone alone for the destruction of THM precursors in two southern U.S. surface water sources. Other researchers have also reported significant reduction of THMFP and HAAFP during treatment with the O<sub>3</sub>/UV process (Sierka and Amy, 1985; Chin and Bérubé, 2005). Overall, the results of this study found that H<sub>2</sub>O<sub>2</sub>/UV showed improved precursor reduction of 77% for THMFP and 62% for HAAFP, compared to the reduction of 75% for THMFP and 52% for HAAFP in O<sub>3</sub>/UV, and the reduction of 70% for THMFP and 31% for HAAFP in H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>.

#### 4. Conclusions

This study evaluated O<sub>3</sub>, UV, and three advanced oxidation processes including H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/UV for the removal of natural organic matter and reduction in DBP formation potential of the treated source water. Bench-scale experiments demonstrated that the ozone and UV treatment

processes alone showed less impact on TOC reduction compared to the combined AOPs of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>/UV. However, O<sub>3</sub> showed significant reduction of UV<sub>254</sub>. The O<sub>3</sub>/UV AOP showed increased performance reducing UV<sub>254</sub> by 88% and TOC by 31% compared to the other oxidation processes evaluated. The H<sub>2</sub>O<sub>2</sub>/UV process reduced UV<sub>254</sub> by 60% and TOC by 23%, achieving somewhat lower reductions than the O<sub>3</sub>/UV process. Further study with measurement of product yield in each oxidation process would help for better explanation of the results.

The HPSEC analysis showed that the molecular weight (MW) of the organic compounds that are able to absorb UV light at 254 nm in the source water ranged from 190 to 1500 Da. Overall, the application of the oxidation processes evaluated in this study resulted in the reduction of higher MW NOM, with the O<sub>3</sub>/UV and H<sub>2</sub>O<sub>2</sub>/UV AOPs having the largest impact on MW transformation of the source water. Treatment with the H<sub>2</sub>O<sub>2</sub>/UV AOP resulted in the largest reduction of THMFP (77%) and HAAFP (62%) compared to the other treatment processes evaluated. Similarly, treatment with the O<sub>3</sub>/UV AOP showed comparable reduction of THMFP (75%) and HAAFP (52%). Results from this study suggest that O<sub>3</sub>/UV and H<sub>2</sub>O<sub>2</sub>/UV are viable options for maximum reduction of NOM from low alkalinity drinking water sources characterized with low turbidity and medium SUVA, and could hold particular significance for plants that are investigating alternative AOPs currently available in the drinking water marketplace. However, further studies that focus on measurement of product yield and include cost analysis for each oxidation process would be necessary for appropriate selection of AOPs.

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#### REFERENCES

- Amirsardari, Y., Yu, Q., Williams, P., 2001. Effect of ozonation and UV irradiation with direct filtration and disinfection byproduct precursors in drinking water treatment. *Environ. Technol.* 22, 1015–1023.
- Amy, G.L., Collins, M.R., Kuo, C.J., King, P.H., 1987. Comparing gel permeation chromatography and ultrafiltration for the molecular weight characterization of aquatic organic matter. *J. Am. Water Works Assn.* 79 (1), 43–49.
- Backlund, O., 1992. Degradation of aquatic humic materials by ultraviolet light. *Chemosphere* 25 (12), 1869–1878.
- Bond, T., Henriot, O., Goslan, E., Parsons, S.A., Jefferson, B., 2009. Disinfection by-product formation and fractionation behaviour of natural organic matter surrogates. *Environ. Sci. Technol.* 43 (15), 5982–5989.
- Chang, P.B.L., Young, T.M., 2000. Kinetics of methyl tert-butyl ether degradation and by-product formation during UV/

- hydrogen peroxide water treatment. *Water Res.* 34, 2233–2240.
- Chin, A., Bérubé, P.R., 2005. Removal of disinfection by-product precursors with ozone-UV advanced oxidation process. *Water Res.* 39 (10), 2136–2144.
- Crittenden, J.C., Hu, S., Hand, D.W., Green, S.A., 1999. A kinetic model for H<sub>2</sub>O<sub>2</sub>/UV process in a completely mixed batch reactor. *Water Res.* 33, 2315–2328.
- Edwards, M., Benjamin, M.M., 1992. Transformation of NOM by ozone and its effect on iron and aluminum solubility. *J. Am. Water Works Assn.* 84 (6), 56–66.
- Edzwald, J.K., Becker, W.C., Wattier, K.L., 1985. Surrogate parameters for monitoring organic matter and trihalomethane precursors. *J. AWWA.* 4, 122–128.
- Frimmel, F.H., Hesse, S., Kleiser, G., 2000. In natural organic matter and disinfection byproducts - Characterisation and control in drinking water. ACS Symposium Series. 761.
- Gagnon, G.A., Booth, S.D., Peldszus, S., Mutti, D., Smith, F., Huck, P.M., 1997. Carboxylic acids: formation and removal in full-scale plants. *J. Am. Water Works Assn.* 89, 88–97.
- Galapate, R., Baes, A., Okada, M., 2001. Transformation of dissolved organic matter during ozonation: effects on trihalomethane formation potential. *Water Res.* 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. 2. Natural trihalomethane precursors. *Environ. Sci. Technol.* 16, 454–458.
- 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.
- Gottschalk, C., Libra, J., Saupe, A., 2000. *Ozonation of Water and Wastewater: A Practical Guide to Understanding Ozone and Its Application.* Wiley-VCH, New York.
- Her, N., Amy, G., Foss, D., Cho, J., Yoon, Y., Kosenka, P., 2002. Optimization of method for detecting and characterizing NOM by HPLC-size exclusion chromatography with UV and on-line DOC detection. *Environ. Sci. Technol.* 36 (5), 1069–1076.
- Her, N., Amy, G., Chung, J., Yoon, J., Yoon, Y., 2008. Characterizing dissolved organic matter and evaluating associated nanofiltration membrane fouling. *Chemosphere* 70 (3), 495–502.
- Hong, S., Elimelech, M., 1997. Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *J. Membr. Sci.* 132, 159–181.
- Hong, H.C., Wong, M.H., Liang, Y., 2009. Amino acids as precursors of trihalomethane and haloacetic acid formation during chlorination. *Arch. Environ. Contam. Toxicol.* 56 (4), 638–645.
- Hu, J., Wang, Z., Ng, W., Ong, S., 1999. Disinfection byproducts in water produced by ozonation and chlorination. *Environ. Monit. Assess.* 59, 81–93.
- Huber, S.A., Frimmel, F.H., 1996. Size-Exclusion Chromatography with Organic Carbon Detection (LC-OCD): A Fast and Reliable Method for the Characterization of Hydrophilic Organic Matter in Natural Waters. *Vom Wasser* 86, 277–290.
- Kleiser, G., Frimmel, F.H., 2000. Removal of precursors for disinfection by-products (DBPs)-differences between ozone- and OH-radical-induced oxidation. *Sci. Total Environ.* 256 (1), 1–9.
- Kusakabe, K., Aso, S., Hayashi, J., Isomura, K., Morooka, S., 1990. Decomposition of humic acid and reduction of trihalomethane formation potential in water by ozone with UV irradiation. *Water Res.* 24, 781–785.
- Liu, W., Andrews, S.A., Sharpless, C., Stefan, M., Linden, K.G., Bolton, J.R., 2002. Bench-scale investigations into comparative evaluation of DBP formation from different UV/H<sub>2</sub>O<sub>2</sub> technologies. Proceedings, AWWA Water Quality Technology Conference, Seattle, WA.
- Matilainen, A., Sillanpää, M., 2010. Removal of natural organic matter from drinking water by advanced oxidation processes. *Chemosphere* 80 (4), 351–365.
- Mosteo, R., Miguel, N., Martín-Muniesa, S., Ormad, M.P., Ovelleiro, J.L., 2009. Evaluation of trihalomethane formation potential in function of oxidation processes used during the drinking water production process. *J. Hazard. Mater.* 172 (2–3), 661–666.
- Oh, H.J., Kim, W.J., Choi, J.S., Gee, C.S., Hwang, T.M., Kang, J.G., Kang, J.W., 2003. Optimization and control of ozonation plant using raw water characterization method. *Ozone Sci. Eng.* 25, 383–392.
- Owen, D.M., Amy, G.L., Chowdhury, Z.K., Paode, R., McCoy, G., Viscosil, K., 1995. NOM characterization and treatability. *J. Am. Water Works Assn.* 87, 46–63.
- Pelakani, C., Newcombe, G., Snoeyink, V.L., Hepplewhite, C., Assemi, S., Beckett, R., 1999. Characterization of natural organic matter using high performance size exclusion chromatography. *Environ. Sci. Technol.* 33, 2807–2813.
- Ravichandran, M., Aiken, G.R., Reddy, M.M., Ryan, J.N., 1998. Enhanced dissolution of cinnabar (mercury sulfide) by dissolved organic matter isolated from the Florida Everglades. *Environ. Sci. Technol.* 32, 3305–3311.
- Rittmann, B.E., Snoeyink, V.L., 1984. Achieving biologically stable drinking water. *J. Am. Water Works Assn.* 76 (10), 106–114.
- Sarathy, S.R., Mohseni, M., 2007. The impact of UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation on molecular size distribution of chromophoric natural organic matter. *Environ. Sci. Technol.* 41, 8315–8320.
- Schechter, D.S., Singer, P.C., 1995. Formation of aldehydes during ozonation. *Ozone Sci. Eng.* 17 (1), 53–59.
- Schmitt, D., Taylor, H.E., Aiken, G.R., Roth, D.A., Frimmel, F.H., 2002. Influence of natural organic matter on the adsorption of metal ions onto clay minerals. *Environ. Sci. Technol.* 36, 2932–2938.
- Singer, P.C., 1999. Humic substances as precursors for potentially harmful disinfection byproducts. *Water Sci. Technol.* 40 (9), 25–30.
- Sierka, R., Amy, G., 1985. Catalytic effects of UV light and/or ultrasound on the ozone oxidation of humic acid and THM precursors. *Ozone Sci. Eng.* 7, 47–62.
- Summers, R.S., Hooper, S.M., Solarik, G., Owen, D., 1996. Assessing DBP yield: uniform formation conditions. *J. Am. Water Works Assn.* 81 (7), 80–93.
- Thomson, J., Roddick, F., Dirkas, M., 2002. UV photooxidation facilitating biological treatment for the removal of NOM from drinking water. *J. Water Supply Res. Technol. AQUA* 51, 297–306.
- Thomson, J., Parkinson, A., Roddick, F.A., 2004. Depolymerization of chromophoric natural organic matter. *Environ. Sci. Technol.* 38, 3360–3369.
- Toor, R., Mohseni, M., 2007. UV/H<sub>2</sub>O<sub>2</sub> based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water. *Chemosphere* 66, 2087–2095.
- Waller, D.H., Macphee, M.J., Prendiville, P.W., McCurdy, R.F., Gates, A.W., D'Eon, W.J., 1996. Characteristics of Nova Scotia surface waters and treatment options for removal of color and trihalomethane precursors. *Can. J. Civ. Eng.* 23, 1316–1325.
- Wang, G.S., Liao, C.H., Chen, H.W., Yang, H.C., 2006. Characteristics of natural organic matter degradation in water by UV/H<sub>2</sub>O<sub>2</sub> treatment. *Environ. Technol.* 27 (3), 277–287.
- Westerhoff, P., Debroux, J., Aiken, G., Amy, G., 1999. Ozone induced changes in natural organic matter (NOM) structure. *Ozone Sci. Eng.* 21, 551–570.
- Westerhoff, P., Mezyk, S.P., Cooper, W.J., Minakata, D., 2007. Electron pulse radiolysis determination of hydroxyl radical rate constants with Suwannee River fulvic acid and other dissolved organic matter isolates. *Environ. Sci. Technol.* 41 (13), 4640–4646.
- Zhou, H., Smith, D., 2001. Advanced technologies in water and wastewater treatment. *Can. J. Civ. Eng.* 28, 49.