Ozonation of natural organic matter and aquatic humic substances: the effects of ozone on the structural characteristics and subsequent trihalomethane formation potential

Mehrnaz Sadrnourmohammadi IWA, Kenneth Brezinski
and Beata Gorczyca IWA

ABSTRACT

The effect of ozonation on the structural and chemical characteristics of natural organic matter (NOM) and its isolated humic fractions, humic acid (HA) and fulvic acid, were studied using Fourier transform infrared coupled to attenuated total reflectance (FTIR-ATR), ultraviolet/visible (UV/Vis) spectroscopy, and synchronous scanning fluorescence (SSF) spectroscopy. The results were linked to the effect of ozonation on trihalomethane formation potential (THMfp) reduction for water standards with high THM precursors. Results showed that ozonation at a dose of 1 mg ozone/mg dissolved organic carbon (DOC) was capable of reducing DOC, UV absorbance at 254 nm (UV_{254}), and THMfp by up to 42%, 95%, and 89% for the HA water standard, respectively. The study of UV/Vis, FTIR-ATR, and SSF revealed trends showing that ozone can alter the composition of DOC in the water standards, causing a significant reduction in aromaticity. The reduction of UV_{254} for each ozonated sample also affirms that ozone mainly targets aromatic moieties contained in NOM. FTIR-ATR results showed that the reduction of unsaturated functional groups, including aromatic rings and $C = C$ bonds in the water standards tested, were the main components impacted by ozone application. SSF results also revealed that ozonation decreases the fluorescence intensity of the maximum peak – as well as the whole spectra.

Key words | FTIR-ATR, humic substances, natural organic matter, ozone, synchronous fluorescence
spectroscopy, trihalomethane formation potential

Mehrnaz Sadrnourmohammadi IWA
(corresponding author)
WSP,
1600 Buffalo Pl, Winnipeg, Manitoba,
Canada,
R3T 6B8
and
Department of Civil Engineering,
University of Manitoba,
Winnipeg,
Canada
E-mail: mehrnaz.sad@gmail.com

Kenneth Brezinski
Beata Gorczyca IWA
Department of Civil Engineering,
University of Manitoba,
15 Gillson Street, Winnipeg, Manitoba,
Canada
R3T 5V6

INTRODUCTION

Natural organic matter (NOM) is a complex and heterogeneous mixture of organic compounds with varying functional and structural characteristics (Lamsal *et al.* 2011). It consists of particulate organic matter and dissolved organic matter (DOM); with DOM typically measured in terms of dissolved organic carbon (DOC). DOC, the poorly defined complex and heterogeneous mixture of organic compounds with varying functional and structural characteristics, is separated into two major classes: humic and non-humic. Humic substances (HSs) are defined as a diverse group of organic materials resulting from the degradation of plant and animal tissues (Yu *et al.* 2005). The composition of HS is site specific, strongly impacted by the local environment, and influenced by parameters such as water temperature, alkalinity, and pH (Chow *et al.* 2005). HSs form the major fraction of DOC in surface

waters, representing 40–80% by some estimates (Thurman 1985; Zhao et al. 2006). Our recent studies of the DOC composition in two major rivers in southern Manitoba, the Red River and Assiniboine River, have found them to be rich in aquatic HSs (AHSs) (Sadrnourmohamadi et al. 2013; Sadrnourmohamadi & Gorczyca 2015a, 2015b). AHSs consist of humic acids (HAs), which are compounds insoluble at a pH of less than 2 and fulvic acids (FAs), which are soluble at all pH levels (Zhao et al. 2006; Rodríguez & Núñez 2011). HAs are characterized by their aromatic structure with extended conjugation and can be described as a heterogeneous polyfunctional polymer with a polymeric network that can entrap volatile organic compounds (Kerc et al. 2003). FA comprises the dominant fraction of HSs with lower molecular weight and lower levels of aromaticity, as compared to their HA counterparts (Amy et al. 1986; Matilainen et al. 2011; Brezinski & Gorczyca 2019a). Recently, increased attention has been paid to the removal of the HS (FA and HA) fraction of DOC, since they are known to be the main precursors toward the formation of carcinogenic trihalomethanes (THMs) (Kerc et al. 2003; Zhao et al. 2006; Brezinski & Gorczyca 2019b).

Ozonation has been reported to be an effective treatment for THM reduction in drinking water, even without a significant decrease in the initial total organic carbon content (TOC). In these cases, ozone transforms high molecular weight organic compounds into smaller ones, which are resistant to reactions involving chlorine as a disinfectant (Camel & Bermond 1998; Galapate et al. 2001; Chiang et al. 2002; Black & Bérubé 2014; Mao et al. 2014). However, several studies have demonstrated cases where ozone had a deteriorative effect on THM reduction (Toor & Mohseni 2007; Chowdhury et al. 2008). It has been reported that DOC composition and distribution in natural waters determine the efficiency of ozone in terms of the reduction in THM precursors (Camel & Bermond 1998; Galapate et al. 2001). Moreover, more recent studies have investigated several other parameters associated with THM precursors, such as NOM polarity (Yan et al. 2010), which are impacted prior to ozonation. Conventional ozonation has even been shown to be preferable over more advanced techniques such as electro-peroxone pretreatment, on waters with high NOM and high UV_{254} absorbance (Mao et al. 2018). This is in line with others

who note that the hydrophobic fraction of NOM is mainly targeted by ozone, contributing almost twice as much to THM formation potential (THMfp) as the hydrophilic fraction (Chiang et al. 2009).

The reactions following the application of ozone on natural waters, especially those with high levels of DOC and calcium hardness as found in Canadian Prairies waters, are especially complex. Moreover, the heterogeneous and complex structure of DOC makes ozone treatment extremely challenging. Therefore, fundamental studies tracking the effects of different parameters, such as ozone dose and DOC type under controlled laboratory conditions, are needed. Studies reporting similar experimental conditions have tested DOC levels as high as $7.8 \, mg \, L^{-1}$ (Chiang et al. 2009), with other studies not exceeding $3.2 \, mg \, L^{-1}$ DOC in their raw and synthetic waters (Yan et al. 2010; Deeudomwongsa et al. 2017; Mao et al. 2018). Additionally, the work of Yan et al. (2010) was the only such study that looked at alkalinity exceeding $75 \, mg \, L^{-1}$ as $CaCO_3$. The transformation in the functional characteristics of NOM after ozonation at varying ozone doses needs to be further investigated for high DOC waters, as it will lead to a better understanding of how ozone impacts DOC concentration, and consequently, THM formation for prairie waters.

Objectives

The effect of ozone on the structural composition of THM precursors depends on several parameters such as DOC composition and ozone dosage. This study investigated the effects of ozone on THMs precursors of NOM and both HA and FA separately. The results were also linked to the change in the formation potential of THMs after ozonation.

The effect of ozone on the functional and structural properties of each source of organic compound was assessed by different physical (DOC and ultraviolet absorbance at 254 nm (UV_{254})) and spectroscopic techniques (Fourier transform infrared coupled to attenuated total reflectance (FTIR-ATR), ultraviolet/visible (UV/Vis), and fluorescence spectroscopy).

Humic species are found to be the dominant fractions of DOC in two Manitoba surface waters (Goss & Gorczyca 2012; Goss et al. 2017). It has been reported that 50–70% of

Manitoba potable water treatment plants that use these surface water sources are not in compliance with THM regulations set by provincial regulators. Therefore, the results of this study would be beneficial for local drinking water treatment operators and industry alike, in order to help meet requirements set by provincial regulators.

MATERIALS AND METHODS

Water sources

Synthetic water samples prepared in the laboratory were used in this study. Three different commercial organic compounds, including Suwannee River NOM, Suwanee River HA, and Suwanee River FA standards – provided by the International Humic Substance Society (IHSS) (St. Paul, Minnesota, USA) – were used to simulate the three different types of organic compounds. These standards, considered as the reference material, were selected because of their widespread use in the literature (Averett *et al.* 1994; Leenheer *et al.* 1995; Ratpukdi *et al.* 2009); and their ability to act as representative surrogates for NOM based on their acidity content (Ritchie & Perdue 2003; Adusei-Gyamfi *et al.* 2019) and size and conformation (Baalousha *et al.* 2006).

As a result, this work can be compared with those found in the literature and with future studies. Synthetic water was prepared by dissolving NOM, HA, and FA IHSS standards in deionized water and diluting to approximately 15 mg L^{-1} with the pH adjusted to 7.0 – a typical DOC and pH range of source water used by Manitoba water treatment plants. The solution was stirred overnight and then filtered through a 0.45 μm nitrocellulose filter paper to remove any residual, non-dissolved NOM.

Ozonation tests

Ozonation was conducted on a semi-batch basis by bubbling the desired amount of ozone through the 2 L water sample following the method described in Sadrnourmohamadi & Gorczyca (2015a). Ozone was generated by a laboratory generator (Model OZO 1VTTL, Ozomax Ind., Canada); this unit is employing the corona discharge method using dehumidified atmospheric air as the feed gas to generate ozone.

All experiments were conducted at a constant flow rate of 0.23 L/min, and ozone dosage was adjusted by changing the ozonation time.

Ozone output from the generator and ozone concentration in the reactor off-gas were determined by the iodometric method (APHA 2012), while the indigo method was used for ozone measurement in the aqueous phase (Bader & Hoigne 1981). Nitrogen gas was bubbled into the water sample after each ozonation runs for at least 10 min to purge the unreacted ozone gas.

Throughout this study, ozone dose refers to the transferred ozone dose (the difference of the mass of applied ozone and the mass of ozone in the off-gas). The most commonly used ozone doses in drinking water pretreatment are <1.0 mg ozone/mg DOC (Agbaba *et al.* 2004; Bose & Reckhow 2007). This work investigates ozone doses of 0.2, 0.6, and 1.0 mg ozone/mg DOC.

Analytical methods

The effectiveness of ozonation was evaluated by measuring DOC and UV$_{254}$ values. Water samples were filtered through a 0.45 μm nitrocellulose filter paper, and DOC concentrations were measured using a total organic carbon analyzer (Phoenix 8000, Tekmar Dohrmann, USA). UV$_{254}$ of the filtered samples were measured using an Ultrospec 2100 pro UV/visible spectrophotometer, (GBC Scientific Equipment, Australia) with a 1 cm quartz cell.

THM formation potential

THM formation potential measurements were conducted according to *Standard Methods 5710B* (APHA 2012), with further details of this procedure having been described elsewhere (Sadrnourmohamadi *et al.* 2013; Sadrnourmohamadi & Gorczyca 2015a). 50 mg L^{-1} of sodium hypochlorite was added to each filtered sample to ensure that there was a sufficient residual amount of chlorine available to react with all organics present in the water sample. All samples were buffered to a pH of 7 using a phosphate buffer. Sample vials were sealed with TFE caps and were kept in the dark at 4 °C for 7 days. After 7 days, all samples were found to have >1.0 mg L^{-1} (3–5 mg L^{-1}) free chlorine, which shows that all THM formation reactions were

driven to completion. An alteration to the *5710B* procedure was the chlorinated water incubation temperature. In this study, chlorinated water samples were incubated at 4 °C to simulate the water temperature in distribution systems, which is representative of the cold Canadian Prairie region.

THMs concentrations were determined with a liquid–liquid extraction method according to *Standard Methods 6232B* (APHA 2012). All experiments were run in triplicate to ensure experimental reproducibility.

Spectroscopic analysis

UV/Vis spectra

UV/Vis spectra of water samples were recorded on an Ultrospec 2100 pro UV/visible spectrophotometer, (GBC Scientific Equipment, Australia) using 1 cm cuvettes in the 190–800 nm wavelength range.

FTIR-ATR spectroscopy

All FTIR-ATR spectra were recorded on freeze-dried samples using a Bruker Alpha FTIR spectrometer (Bruker, MS, USA) equipped with ALPHA's Platinum ATR single reflection diamond ATR module, recorded in the 4,000–500 cm^{-1} region.

Fluorescence

Fluorescence spectra in the synchronous scan mode were obtained by a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies, CA, USA). Synchronous scan excitation spectra were acquired by recording the fluorescence intensity, while simultaneously scanning over both the emission (λ_{em}) and excitation (λ_{ex}) wavelengths and keeping a constant optimized wavelength difference (offset: $\Delta\lambda = \lambda_{em} - \lambda_{ex}$) (Chen *et al.* 2003; Rodríguez *et al.* 2014a). Synchronous excitation spectra can improve peak resolution and reduce overlapping interferences. It also can identify the effect of ozone on structural signatures such as intensity, position, and shift of the fluorescence peak for each sample (Uyguner & Bekbolet 2005a, 2005b; Zhang *et al.* 2008). Synchronous scan spectra were recorded in the excitation wavelength range of 360–650 nm using the

$\Delta\lambda = 44$ nm bandwidth between the excitation and emission monochromators. Although most studies on HS use a synchronous fluorescence of $\Delta\lambda = 18$–20 nm, some researchers have reported that an offset value of 44 nm acts as a powerful tool for DOC characterization before and after oxidation with chlorine dioxide and ozone (Swietlik & Sikorska 2004; Zhang *et al.* 2008). In this study, both the excitation and emission slits of the instrument were set at a 10 nm bandwidth, and a 600 nm/min scan speed was used.

RESULTS AND DISCUSSION

Effect of ozone on water characteristics

Dissolved organic carbon and UV_{254}

Figure 1 shows the effect of ozonation on the removal efficiencies of DOC and UV_{254}, for all water samples. Generally, increased ozone dosage resulted in an increased reduction of DOC and UV_{254} values for all water samples. However, HA water samples show the highest reduction of these parameters compared to NOM and FA standards. For this sample, 1 mg ozone/mg DOC resulted in a 42% reduction of DOC and a 96% reduction in UV_{254}, respectively. Generally, more available ozone molecules and hydroxyl radicals are produced as ozone dosage increases – leading to an increase in organic carbon removal (Ratpukdi *et al.* 2010). Chang *et al.* (2002) had investigated the effect of ozone on HA removal at different ozone doses, in which they reported a 47% DOC reduction at an ozone dosage of 1.5 mg ozone/mg DOC. Tuhkanen *et al.* (1994) and Molnar *et al.* (2012) have both shown DOC reduction ranged between 5% and 25% under typical ozone doses of 0.4–1 mg ozone/mg DOC. Pryor *et al.* (2002) have also reported up to a 25% DOC reduction at lower applied ozone doses of 0.3–0.5 mg ozone/mg DOC. Water samples used in these studies were natural waters; however, our reported DOC removal values can still be comparable with these published works.

UV_{254} is a parameter that indicates the unsaturated and/or aromatic carbon content of water samples (Edzwald & Tobiason 1999). For all the water samples studied, UV_{254} values decreased following ozone application. This can be
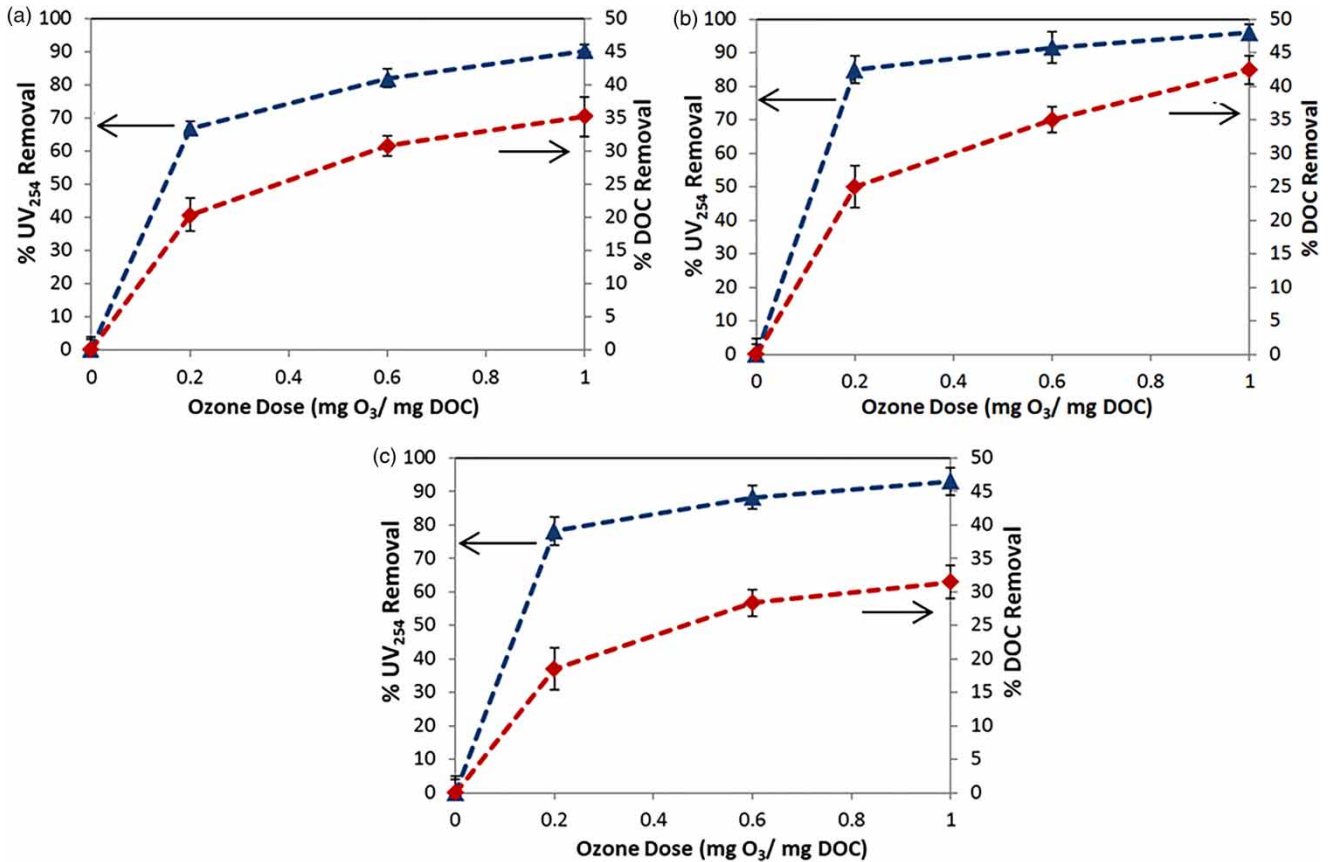
Figure 1 │ Water quality parameters for samples under different doses of ozone: (a) NOM, (b) HA, and (c) FA.

due to oxidation of unsaturated and/or aromatic carbon molecules, which is in accordance with previously reported results (Gilbert 1988; Camel & Bermond 1998; Swietlik *et al.* 2004; Sadrnourmohamadi & Gorczyca 2015a). Figure 1 shows a higher reduction in UV_{254} values compared to DOC. This indicates the oxidation of a large portion of conjugated species by ozone, even with a low reduction in DOC. (Chang & Singer 1991; Chang *et al.* 2002; Ratpukdi *et al.* 2010). This is indicative of a targeting of aromatic, conjugated species rather than aliphatic groups.

THM formation potential

Table 1 indicates the results of total THMfp (TTHMfp) for different water samples pre- and post-ozonation. In Table 1, it is clear that chloroform (CH_3Cl) is the major detected species of THMs since NaOCl was used for chlorination. No brominated species were detected since the

simulated water samples did not contain bromide. Results indicate that prior to ozonation, HA yielded a higher TTHMfp, followed by NOM and FA standards. Upon ozonation, this value reduces significantly, with the highest reduction (89%) observed for HA water samples (Table 1). A lower ozone dose accomplished a relatively significant reduction in TTHMfp; however, by increasing the ozone dose, a small incremental reduction was achieved. This indicates that ozone can eliminate a large portion of the precursors that promote THM formation quickly, while it has a lesser effect on other portions of the precursors under these experimental conditions (Amy *et al.* 1986). As shown in Figure 1, ozone can oxidize/decompose aromatic, UV absorbing moieties of NOM resulting in a higher reduction of THMfp relative to DOC, which is consistent with previous studies (Amy *et al.* 1986, 1991; Galapate *et al.* 2001). Improved reduction of TTHMfp at higher ozone doses is related to an increased reduction of HS as the

**Table 1** │ TTHMFP for different water samples pre- and post-ozonation

Organic compound type	Ozone dose (mg O_3/mg DOC)	CH_3Cl ($\mu g\ L^{-1}$)	$CHBrCl_2$ ($\mu g\ L^{-1}$)	$CHBr_2Cl$ ($\mu g\ L^{-1}$)	$CHBr_3$ ($\mu g\ L^{-1}$)	TTHMFP ($\mu g\ L^{-1}$)
NOM	0	95.5 ± 0.3	ND	ND	ND	95.5 ± 0.3
	0.2	51.6 ± 0.2	ND	ND	ND	51.6 ± 0.2
	0.6	40.7 ± 0.3	ND	ND	ND	40.7 ± 0.3
	1.0	27.7 ± 0.1	ND	ND	ND	27.7 ± 0.1
HA	0	134.0 ± 1.3	ND	ND	ND	134.0 ± 1.3
	0.2	35.3 ± 2.0	ND	ND	ND	35.3 ± 2.0
	0.6	25.0 ± 0.2	ND	ND	ND	25.0 ± 0.2
	1.0	14.6 ± 0.9	ND	ND	ND	14.6 ± 0.9
FA	0	89.4 ± 2.3	ND	ND	ND	89.4 ± 2.3
	0.2	51.6 ± 1.0	ND	ND	ND	51.6 ± 1.0
	0.6	22.5 ± 0.13	ND	ND	ND	22.5 ± 0.13
	1.0	18.1 ± 0.7	ND	ND	ND	18.1 ± 0.7

main precursor to form THMs (Rodríguez & Núñez 2011). HAs are reported to have high levels of aromaticity, and consequently, a high UV absorbance (Amy *et al.* 1986). As reported, UV_{254} removal can be related to TTHMfp (Uyak & Toroz 2007). Figure 2 shows a plot of UV_{254} removal against TTHMfp data from this study. A good correlation of $R^2 = 0.82$ was achieved between UV_{254} removal and TTHMfp reduction.

Spectroscopy characterization

UV/Vis spectroscopic analysis

Figure 3 shows the UV/Vis spectra of each water sample before and after a series of ozone applications. All non-ozonated samples show quite similar UV/Vis absorption spectra
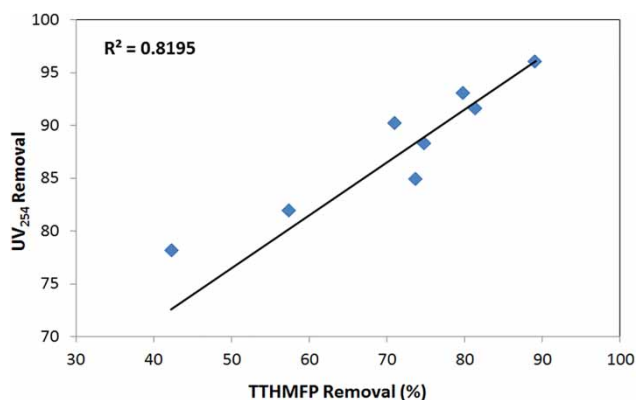
Figure 2 │ Removal of UV_{254} against TTHMFP for three ozonated water samples.

with a featureless decrease in absorption intensity with increasing wavelength. Due to the complex structure of organic compounds in each water sample, the UV spectra did not exhibit many distinctive features. However, in the case of non-ozonated samples, a shoulder in the wavelength range of 260–290 nm indicates the presence of π-π* electron transitions from polycyclic aromatic hydrocarbons, benzoic acids, and phenolic substances (Fukushima & Tatsumi 2001). It can also be related to general unsaturated and aromatic compounds, attributed to the broader conjugated structure (Chin *et al.* 1994; Purmalis 2013). Moreover, UV_{280} provides important clues regarding the extent of humification, degree of aromaticity, and possible estimations of molecular weight (Chin *et al.* 1994). Figure 3(b) shows that non-ozonated HA has the highest UV_{280} absorbance values compared to those recorded by NOM and FA. This behavior is expected since HA contains a relatively high amount of aromatic and functional groups, and hence UV absorbing moieties. The difference decreases with an increase in wavelength (Chen *et al.* 2002).

UV spectra of ozonated water samples showed that UV absorbance decreased with increasing ozone dosage. The shoulder in the range of 260–290 nm for non-ozonated water samples disappeared as a result of ozone application. Also, the absorptivity at 280 nm decreased with increasing ozone dosage. This is to be expected since ozone can remove or oxidize the moieties responsible for UV absorbance in this wavelength range (Rositano *et al.* 2001). Ozonation is found to target NOM at all wavelengths, with a sharp decrease at shorter wavelengths which is in
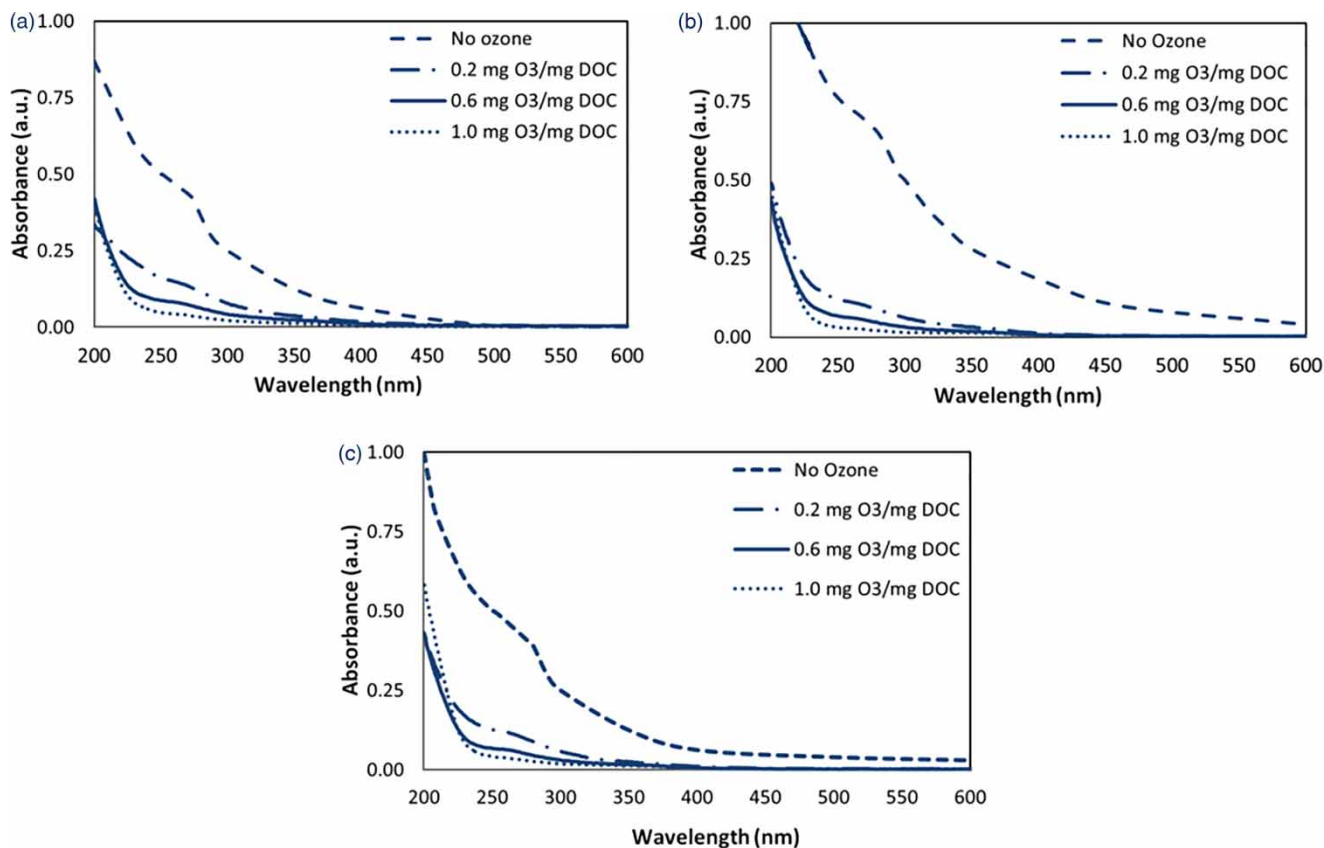
Figure 3 │ UV/Vis spectra of Suwannee River: (a) NOM, (b) HA, and (c) FA, before and after ozonation (pH = 7 and total organic carbon concentration = 15 mg L^{-1}).

agreement with the previous work (Rositano *et al.* 2001; Ho *et al.* 2013). The absorptivity of ozonated water samples approaches zero within the visible range (400–700 nm).

Fluorescence spectroscopic analysis

The effect of ozonation on NOM, HA, and FA samples was also studied by synchronous scan spectra recorded at $\Delta\lambda = 44$. Figure 4 shows the spectra of non-ozonated samples, as well as ozonated samples at 0.2, 0.6, and 1 mg ozone/mg DOC doses. The three non-ozonated samples showed a well-defined maximum peak at $\lambda = 380$–400 nm and a small shoulder-like peak at $\lambda = 260$. The non-ozonated HA sample exhibited a fluorescence peak with half intensity compared to the FA sample, which is in agreement given the higher molecular weight of HA. The intensity of the fluorescence peak is affected by the molecular structure of NOM and decreases with an increase in the molecular weight of the analyzed organic matter fractions (Chen

et al. 2003; Swietlik & Sikorska 2004; Rodríguez *et al.* 2014a). Although HA is known to be rich in aromatic character, its low fluorescence intensity can also be related to HA inter-, and intra-molecular bonding, and re-absorption of the emitted radiation by other absorption centers of humic macromolecules (Miano *et al.* 1988; Senesi 1990; Chen *et al.* 2003). Moreover, the peak of the maximum intensity of HA occurred at a higher excitation wavelength compared to FA. According to Rodríguez *et al.* (2014a, 2014b) the maximum peaks located at higher wavelengths are indicative of aromatic or conjugated unsaturated systems, characteristics that fit well with HA. Peaks of maximum intensity at lower wavelengths are related to a low degree of aromatic and conjugated chromophores and are in agreement with the typical characteristics of the FA. Some additional small sub-peaks also can be seen at an excitation λ of 270–290 nm and 270–290 nm for HA and FA, respectively. These peaks are indicative of the polydispersive structure of HSs (Rodríguez *et al.* 2014a). Upon ozonation,
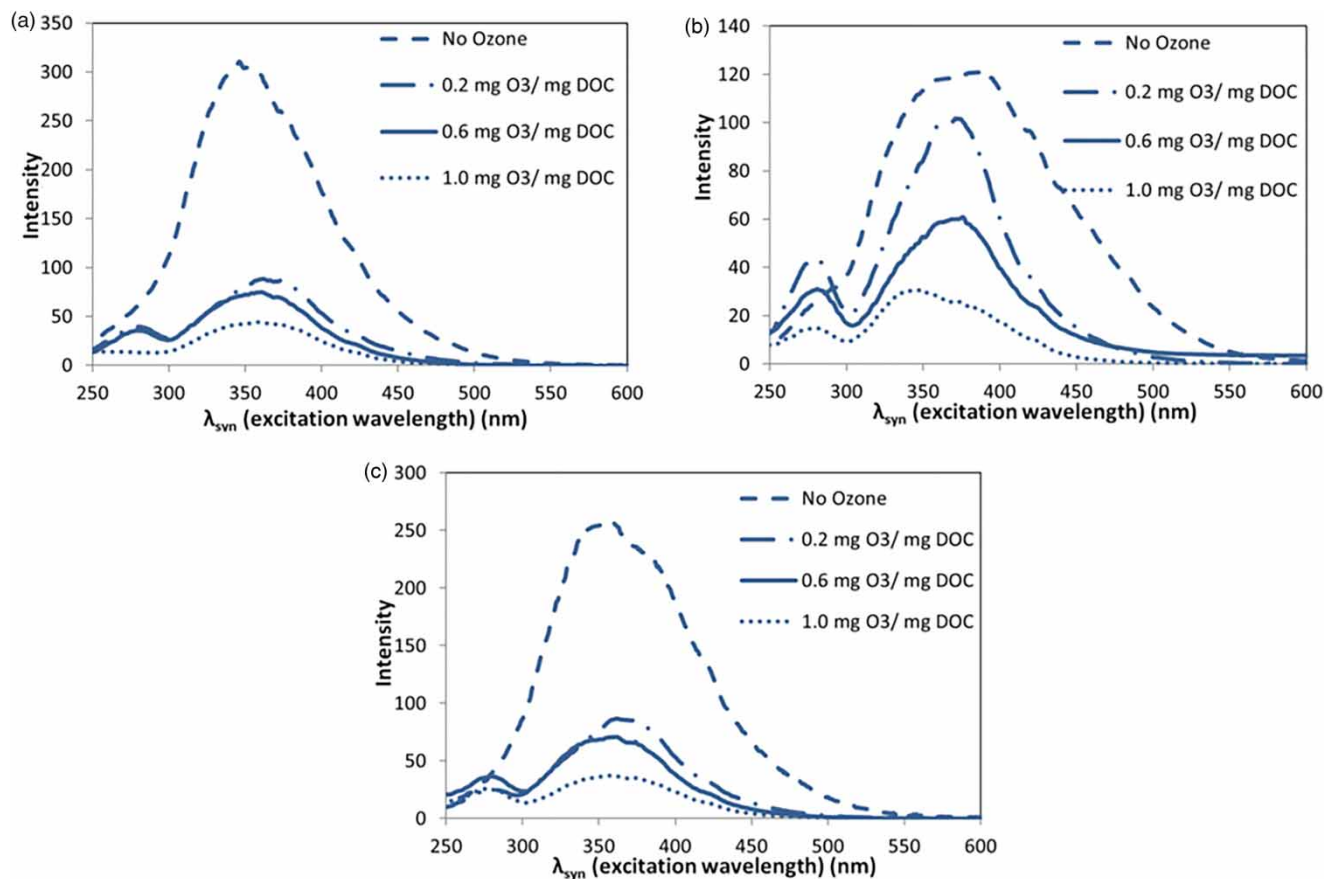
Figure 4 │ Synchronous fluorescence spectra of Suwannee River: (a) NOM, (b) HA, and (c) FA (pH = 7 and total organic carbon concentration = 15 mg L^{-1}).

the fluorescence intensity of the maximum peak as well as the whole spectra decreased for all samples. This can be attributed to a lower degree of aromaticity and a lower level of conjugation (Uyguner & Bekbolet 2005a; Zhang *et al.* 2008; Rodríguez *et al.* 2014a).

A protein-like peak at a shorter wavelength of 260 nm with low intensity increased when 0.2 mg ozone/mg DOC ozone dosage was applied. According to the literature, this peak can be attributed to aromatic amino acids (Coble 1996; Zhang *et al.* 2008; Rodríguez *et al.* 2014a). By increasing the ozone dose, the intensity of this peak decreased significantly, even below the non-ozonated sample due to the extensive structural degradation of the humic macromolecule at high ozone dosages (Rodríguez *et al.* 2014b). The results obtained in this study can be compared to those achieved by Zhang *et al.* (2008) (ozone dose = 1 mg ozone/mg TOC and synchronous spectra recorded at $\Delta\lambda = 66$ nm). A reported increase in the fluorescence of the

protein-like peak was followed by a decrease in the fluorescence of the maximum peak of the spectrum for both FA and HA extracted from river water samples. The disappearance of these characteristic peaks, which is accompanied by a reduction in DOC, UV$_{254}$, and TTHMfp, can be attributed to the destruction of aromatic moieties (Uyguner & Bekbolet 2005a, 2005b).

FTIR-ATR spectroscopic analysis

The FTIR-ATR spectra of HS and FA samples obtained pre- and post-ozonation are shown in Figure 5. The change in functional group composition after ozone application can be the main case for THM reduction (Chang *et al.* 2002). All the spectra for the two non-ozonated HSs (HA and FA) were similar. The absorption bands of all samples were interpreted based on the literature (Senesi *et al.* 1989; Silverstein & Webster 1998).
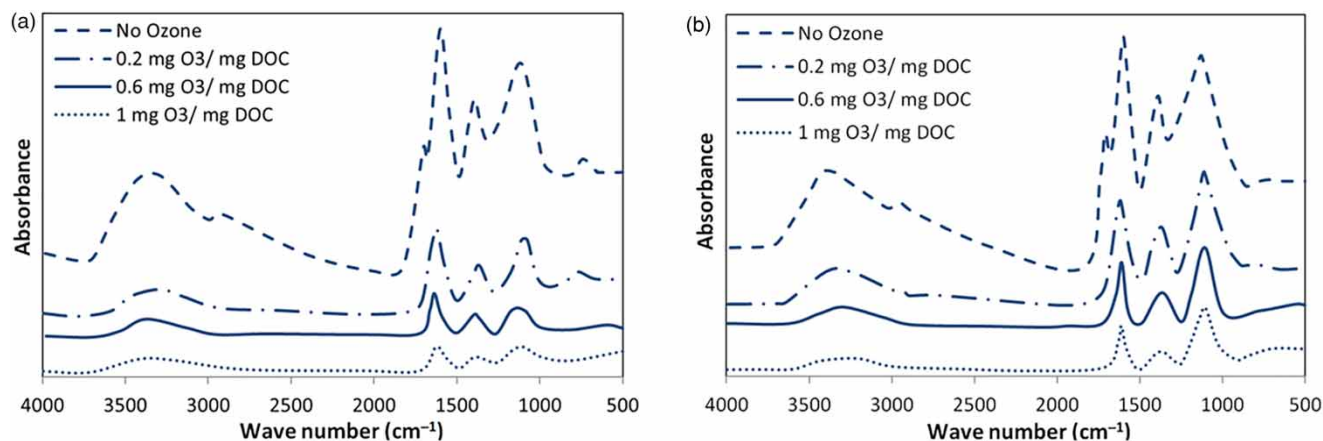
Figure 5 | FTIR-ATR spectra of Suwannee River: (a) HA and (b) FA (pH = 7 and total organic carbon concentration = 15 mg L^{-1}).

A broad peak at the 3,700–3,200 cm^{-1} region is generally assigned to O–H groups, and the shoulder present in the 3,000–2,800 cm^{-1} region can be attributed to aliphatic CH, CH$_2$, CH$_3$ stretching. The peak in the range of 1,720–1,700 is indicative of carbonyl groups (C = O stretching mainly due to carboxylic acids and ketones). The peak at 1,637 cm^{-1} is a typical peak for aromatic C = C vibration and C = O conjugation within the aromatic ring. The peak at 1,380–1,400 cm^{-1} is assigned to C–H deformation of aliphatic and CH$_3$ groups. In addition, a peak in the range of 1,150 cm^{-1} is indicative of C–O stretching and O–H deformation of COOH (Li *et al.* 2008). The C–O stretching of alcoholic compounds, esters, ethers, and phenols is shown at 1,066 cm^{-1}. Also, aromatic C–H bending can be observed at 850 cm^{-1}. Carboxylic character (an O–H band at 3,400–3,300 cm^{-1} and a C = O band at 1,730–1,700 cm^{-1}) was found for all samples. The O–H peak (3,700–3,200 cm^{-1}) is more intense for HA samples than for FA which is consistent with the literature (Senesi *et al.* 1989). HA shows a relatively higher absorption intensity at ~1,620 cm^{-1} and 2,920 cm^{-1}. These results suggest that the untreated HA sample is richer in aromatic compounds and aliphatic CH$_2$/CH$_3$ groups than the FA sample, which is consistent with our UV/Vis spectroscopy analysis. After 0.2 mg ozone/mg DOC application, the peak area of the O–H band decreases. Further increase in ozone dosage results in the removal of this peak and the shoulder located at 2,900 cm^{-1} (attributed to C–H functional groups). A reduction is also observed for aromatic C = C vibration and C = O conjugation attached to an aromatic ring

(1,600 cm^{-1}). Moreover, in HA samples, the absorbance of aromatic C–H bending (850 cm^{-1}) was reduced. In summary, FTIR results indicate that after ozonation, O–H, C–H, and CO/OH peaks are still present; however, the peak prominence of aromatic C = C and C = O conjugation with aromatic rings (1,600 cm^{-1}) and O–H (3,200 cm^{-1}) decrease remarkably. The degradation of these functional groups, which is more significant for the HA samples – in line with UV/Vis spectral data (Figure 3) – likely accounts for the TTHMfp reduction following ozonation (Chang *et al.* 2002; Kanokkantapong *et al.* 2006).

CONCLUSION

In this study, the composition and chemical characteristics of NOM and isolated HSs, HA, and FA (provided by the IHSS), before and after ozone application were studied by means of FTIR-ATR, UV/Vis, and synchronous scanning fluorescence (SSF) measurements. The main objective of this study was to show the effect of ozone oxidation on the structural and chemical composition of three types of aquatic organic standards. The results were also linked to the effects of the ozonation process on reducing THMfp of water samples with high levels of THM precursors present. The following conclusions can be made from this study:

1. Ozonation at a dose of 1 mg ozone/mg DOC was capable of reducing DOC, UV$_{254}$, and THMfp by up to 42%, 95%, and 89% for the HA water standard – the main THM precursor – respectively.

2. The results of the UV/Vis, FTIR-ATR, and SSF work reveal a consistent trend showing that ozone can alter the composition of DOC in the water samples, causing a significant reduction in aromaticity. The reduction of UV_{254} for each ozonated sample also reaffirms the notion that ozone mainly targets aromatic moieties present in organic carbon molecules.

3. FTIR-ATR results showed that the reduction of unsaturated functional groups, such as aromatic rings and $C = C$ bonds in the water standards, are the main targets of ozone application.

4. SSF results also revealed that ozonation decreases the fluorescence intensity of the maximum peak as well as for the whole spectra. Ozonation reduced the concentration of aromatic and highly conjugated compounds in the water. This is the main reason why ozonation is effective in reducing water THMfp levels, as they contain the bulk of highly reactive THM precursors.

REFERENCES

Adusei-Gyamfi, J., Ouddane, B., Rietveld, L., Cornard, J.-P. & Criquet, J. 2019 Natural organic matter-cations complexation and its impact on water treatment: a critical review. *Water Research* **160**, 130–147. https://doi.org/10.1016/j.watres. 2019.05.064.

Agbaba, J., Ivancev-Tumbas, I., Dalmacija, B. & Klasnja, M. 2004 Formation by-products in the course of intermediate ozonation of groundwater pretreated with ozone and polyaluminium chloride. *Water Science and Technology* **49**, 63–68.

Amy, G. L., Chadik, P. A. & Sierka, R. A. 1986 Ozonation of aquatic organic matter and humic substances: an analysis of surrogate parameters for predicting effects on trihalomethane formation potential. *Environmental Technology Letters* **7**, 99–108.

Amy, G. L., Tan, L. & Davis, M. K. 1991 The effects of ozonation and activated carbon absorption on trihalomethane speciation. *Water Research* **25**, 191–202.

APHA 2012 *Standard Methods for the Examination of Water and Waste Water*. American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, DC, USA.

Averett, R. C., Leenheer, J. A., McKnight, D. M. & Thorn, K. A. 1994 *Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures, U.S. Geological Survey Water-Supply Paper 2373*. U.S. Geological Survey, Denver, Colorado.

Baalousha, M., Motelica-Heino, M. & Coustumer, P. L. 2006 Conformation and size of humic substances: effects of major cation concentration and type, pH, salinity, and residence time. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **272** (1), 48–55. https://doi.org/10.1016/j.colsurfa.2005.07.010.

Bader, H. & Hoigne, J. 1981 Determination of ozone in water by the indigo method. *Water Research* **15**, 449–456.

Black, K. E. & Bérubé, P. R. 2014 Rate and extent NOM removal during oxidation and biofiltration. *Water Research* **52** (Supplement C), 40–50. https://doi.org/10.1016/j.watres. 2013.12.017.

Bose, P. & Reckhow, D. A. 2007 The effect of ozonation on natural organic matter removal by alum coagulation. *Water Research* **41**, 1516–1524.

Brezinski, K. & Gorczyca, B. 2019a An overview of the uses of high performance size exclusion chromatography (HPSEC) in the characterization of natural organic matter (NOM) in potable water, and ion-exchange applications. *Chemosphere* **217**, 122–139. https://doi.org/10.1016/j.chemosphere.2018. 10.028.

Brezinski, K. & Gorczyca, B. 2019b Multi-spectral characterization of natural organic matter (NOM) from Manitoba surface waters using high performance size exclusion chromatography (HPSEC). *Chemosphere* **225**, 53–64. https://doi.org/10.1016/j.chemosphere.2019.02.176.

Camel, V. & Bermond, A. 1998 The use of ozone and associated oxidation processes in drinking water treatment. *Water Research* **32**, 3208–3222.

Chang, S. D. & Singer, P. C. 1991 The impact of ozonation on particle stability and the removal of TOC and THM precursors. *Journal American Water Works Association* **83**, 71–79.

Chang, C. N., Ma, Y. S. & Zing, F. F. 2002 Reducing the formation of disinfection by-products by pre-ozonation. *Chemosphere* **46**, 21–30.

Chen, J., Gu, B., LeBooeuf, E., Pan, H. & Dai, S. 2002 Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. *Chemosphere* **48**, 59–68.

Chen, J., LeBooeuf, E., Pan, H., Dai, S. & Gu, B. 2003 Fluorescence spectroscopic studies of natural organic matter fractions. *Chemosphere* **50**, 639–647.

Chiang, P. C., Chang, E. E. & Liang, C. H. 2002 NOM characteristics and treatabilities of ozonation processes. *Chemosphere* **46**, 929–936.

Chiang, P.-C., Chang, E.-E., Chang, P.-C. & Huang, C.-P. 2009 Effects of pre-ozonation on the removal of THM precursors by coagulation. *Science of the Total Environment* **407** (21), 5735–5742. https://doi.org/10.1016/j.scitotenv. 2009.07.024.

Chin, Y. P., Aiken, G. & O'Loughlin, E. 1994 Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environmental Science & Technology* **28**, 1853–1858.

Chow, A. T., Gao, S. & Dahlgren, A. 2005 Physical and chemical fractionation of dissolved organic matter and trihalomethane

precursors: a review. *Journal of Water Supply: Research and Technology – AQUA* **54**, 475–507.

Chowdhury, F. L., Berube, 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 and Engineering* **30**, 321–331.

Coble, P. G. 1996 Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy. *Marine Chemistry* **51**, 325–346.

Deeudomwongsa, P., Phattarapattamawong, S. & Andrew Lin, K.-Y. 2017 Control of disinfection byproducts (DBPs) by ozonation and peroxone process: role of chloride on removal of DBP precursors. *Chemosphere* **184**, 1215–1222. https://doi.org/10.1016/j.chemosphere.2017.06.105.

Edzwald, J. K. & Tobiason, J. E. 1999 Enhanced coagulation: US requirements and a broader view. *Water Science and Technology* **40**, 63–70.

Fukushima, M. & Tatsumi, K. 2001 Degradation characteristics of humic acid during photo-fenton processes. *Environmental Science & Technology* **35**, 3683–3690.

Galapate, R. P., Baes, A. U. & Okada, M. 2001 Transformation of dissolved organic matter during ozonation: effects on trihalomethane formation potential. *Water Research* **35**, 2201–2206.

Gilbert, E. 1988 Biodegradability of ozonation products as a function of COD and DOC elimination by the example of humic acids. *Water Research* **22**, 123–126.

Goss, C. & Gorczyca, B. 2012 Trihalomethane formation potential of DOC fractions isolated from two Canadian Prairie surface water sources. *Water Science and Technology: Water Supply* **13** (1), 114–122. https://doi.org/10.2166/ws.2012.093.

Goss, C., Wiens, R., Gorczyca, B. & Gough, K. 2017 Comparison of three solid phase extraction sorbents for the isolation of THM precursors from manitoban surface waters. *Chemosphere* **168** (Supplement C), 917–924. https://doi.org/10.1016/j.chemosphere.2016.10.118.

Ho, L., Hainthaler, M. & Newcombe, G. 2013 Using UV spectroscopy and molecular weight determinations to investigate the effect of various water treatment processes on NOM removal: Australian case study. *Journal of Environmental Engineering* **139** (1), 117–126.

Kanokkantapong, V., Marhaba, T. F., Panyapinyophol, B. & Pavasant, P. 2006 FTIR evaluation of functional groups involved in the formation of haloacetic acids during the chlorination of raw water. *Journal of Hazardous Materials B* **136**, 188–196.

Kerc, A., Bekbolet, M. & Saatci, A. M. 2003 Effect of partial oxidation by ozonation on the photocatalytic degradation of humic acids. *International Journal of Photoenergy* **5** (2), 75–80.

Lamsal, R., Walsh, M. E. & Gagnon, G. A. 2011 Comparison of advanced oxidation processes for the removal of natural organic matter. *Water Research* **45**, 326–3269.

Leenheer, J. A., Wershaw, R. L. & Reddy, M. M. 1995 Strong-acid, carboxyl- group structures in fulvic acid from the Suwannee River, Georgia. 1. Minor structures. *Environmental Science & Technology* **29**, 393–398.

Li, J., Liu, H., Zhao, X., Qu, J., Liu, R. & Ru, J. 2008 Effect of preozonation on the characteristic transformation of fulvic acid and its subsequent trichloromethane formation potential: presence or absence of bicarbonate. *Chemosphere* **71**, 1639–1645.

Mao, Y., Wang, X., Yang, H., Wang, H. & Xie, Y. F. 2014 Effects of ozonation on disinfection byproduct formation and speciation during subsequent chlorination. *Chemosphere* **117**, 515–520. https://doi.org/10.1016/j.chemosphere.2014.08.083.

Mao, Y., Guo, D., Yao, W., Wang, X., Yang, H., Xie, Y. F. & Wang, Y. 2018 Effects of conventional ozonation and electro-peroxone pretreatment of surface water on disinfection by-product formation during subsequent chlorination. *Water Research* **130**, 322–332. https://doi.org/10.1016/j.watres.2017.12.019.

Matilainen, A., Gjessing, E. T., Lahtinen, T., Hed, L., Bhatnagar, A. & Sillanpaa, M. 2011 An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment, review. *Chemosphere* **83**, 1431–1442.

Miano, T. M., Sposito, G. & Martin, J. P. 1988 Flourescence spectroscopy of humic substances. *Soil Science Society of America Journal* **52**, 1016–1019.

Molnar, J., Agbaba, J., Dalmacija, B., Klasnja, M., Watson, M. & Kragul, M. 2012 Effects of ozonation and catalytic ozonation on the removal of natural organic matter from groundwater. *Journal of Environmental Engineering* **138**, 804–808.

Pryor, M. J., Naidoo, P. S., Bahrs, P. & Freese, S. D. 2002 Ozone experience at Umgeni Water. In: *Presented at the Biennial Conference of the Water Institute of Southern Africa*. Available from: http://www.ewisa.co.za/misc/WISAConf/WISA2002/Abstracts/094%20Abstract.pdf (accessed April 2015).

Purmalis, O. 2013 Comparative study of humic acids by using spectroscopy. In: *1st Annual International Interdisciplinary Conference, AIIC 2013*, April 24–26 Azores, Portugal.

Ratpukdi, T., Rice, J. A., Chilom, G., Bezbaruah, A. & Khan, E. 2009 Rapid fractionation of natural organic matter in water using a novel solid-phase extraction technique. *Water Environment Research* **81** (11), 2299–2308.

Ratpukdi, T., Siripattanakul, S. & Kahn, E. 2010 Mineralization and biodegradability enhancement of natural organic matter by ozone-VUV in comparison with ozone, VUV, ozone UV, and UV: effects of pH and ozone dose. *Water Research* **44**, 3531–3543.

Ritchie, J. D. & Perdue, E. M. 2003 Proton-binding study of standard and reference fulvic acids, humic acids, and natural organic matter. *Geochimica et Cosmochimica Acta* **67** (1), 85–96.

Rodríguez, F. & Núñez, L. A. 2011 Characterization of aquatic humic substances. *Water and Environment Journal* **25**, 163–170.

Rodríguez, F. J., Schlenger, P. & García-Valverde, M. 2014a A comprehensive structural evaluation of humic substances using several fluorescence techniques before and after ozonation. Part I: structural characterization of humic substances. *Science of the Total Environment* **476–477**, 718–730.

Rodríguez, F. J., Schlenger, P. & García-Valverde, M. 2014b A comprehensive structural evaluation of humic substances using several fluorescence techniques before and after ozonation. Part II: evaluation of structural changes following ozonation. *Science of the Total Environment* **476–477**, 731–742.

Rositano, J., Newcombe, G., Nicholson, B. & Sztajnbok, P. 2001 Ozonation of NOM and algal toxins in four treated waters. *Water Research* **35** (1), 23–32.

Sadrnourmohamadi, M. & Gorczyca, B. 2015a Effects of ozone as a stand-alone and coagulation-aid treatment on the reduction of trihalomethanes precursors from high DOC and hardness water. *Water Research* **73**, 171–180.

Sadrnourmohamadi, M. & Gorczyca, B. 2015b Removal of dissolved organic carbon (DOC) from high DOC and hardness water by chemical coagulation – relative importance of monomeric, polymeric and colloidal aluminum species. *Journal of Separation Science and Technology* In Press. doi:10.1080/01496395.2015.1014494.

Sadrnourmohamadi, M., Goss, C. D. & Gorczyca, B. 2013 Removal of DOC and its fractions from the high DOC and hardness surface waters of the Canadian Prairie. *WST: Water Supply* **13**, 864–870.

Senesi, N. 1990 Molecular and quantitative aspects of the chemistry of fulvic acid and its interactions with metal ions and organic chemicals. Part II: the fluorescence spectroscopy approach. *Analytica Chimica Acta* **232**, 77–106.

Senesi, N., Miano, T. M., Provenzano, M. R. & Brunetti, G. 1989 Spectroscopic and compositional characterization of IHSS reference and standard fulvic and humic acids of various origin. *Science of the Total Environment* **81/82**, 143–156.

Silverstein, R. M. & Webster, F. X. 1998 *Spectrometric Identification of Organic Compounds*. John Wiley, New York.

Swietlik, J. & Sikorska, E. 2004 Application of fluorescence spectroscopy in the studies of natural organic matter fractions reactivity with chlorine dioxide and ozone. *Water Research* **38**, 3791–3799.

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

Thurman, E. M. 1985 *Organic Geochemistry of Natural Waters*. W. Junk Press, Boston, MA.

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**, 2087–2095.

Tuhkanen, T. A., Kainulainen, T. K., Vartiainen, T. K. & Kalliokoski, P. J. 1994 The effect of preozonation, ozone/hydrogen peroxide treatment, and nanofiltration on the removal of organic matter from drinking water. *Ozone Science and Engineering* **16**, 367–383.

Uyak, V. & Toroz, I. 2007 Disinfection by-product precursors reduction by various coagulation techniques in Istanbul water supplies. *Journal of Hazardous Materials* **141**, 320–328.

Uyguner, C. S. & Bekbolet, M. 2005a Evaluation of humic acid photocatalytic degradation by UV–vis and fluorescence spectroscopy. *Catalysis Today* **101**, 267–274.

Uyguner, C. S. & Bekbolet, M. 2005b Implementation of spectroscopic parameters for practical monitoring of natural organic matter. *Desalination* **176**, 47–55.

Yan, M., Wang, D., Ma, X., Ni, J. & Zhang, H. 2010 THMs precursor removal by an integrated process of ozonation and biological granular activated carbon for typical Northern China water. *Separation and Purification Technology* **72** (3), 263–268. https://doi.org/10.1016/j.seppur.2010.02.015.

Yu, M. J., Kim, Y. H., Han, I. & Kim, H. C. 2005 Characterization of humic substances isolated from Han River water and change in the structural and chemical characteristics by ozonation. *Environmental Technology* **26** (9), 1033–1041.

Zhang, T., Lu, J., Ma, J. & Qiang, Z. 2008 Fluorescence spectroscopic characterization of DOM fractions isolated from a filtered river water after ozonation and catalytic ozonation. *Chemosphere* **71**, 911–921.

Zhao, Z.-Y., Gu, J.-D., Fan, X.-J. & Li, H.-B. 2006 Molecular size distribution of dissolved organic matter in water of the Pearl River and trihalomethane formation characteristics with chlorine and chlorine dioxide treatments. *Journal of Hazardous Materials* **134**, 60–66.