

Characterization of disinfection byproduct formation and associated changes to dissolved organic matter during solar photolysis of free available chlorine

Tessoro R. Young ^a, Wentao Li ^b, Alan Guo ^a, Gregory V. Korshin ^a, Michael C. Dodd ^{a,*}

^a Dept. of Civil and Environmental Engineering, University of Washington, Seattle, WA, USA

^b State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Nanjing, 210023, China

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ABSTRACT

Solar irradiation of chlorine-containing waters enhances inactivation of chlorine-resistant pathogens (e.g., *Cryptosporidium* oocysts), through in situ formation of ozone, hydroxyl radical, and other reactive species during photolysis of free available chlorine (FAC) at UVB–UVA wavelengths of solar light (290–400 nm). However, corresponding effects on regulated disinfection byproduct (DBP) formation and associated dissolved organic matter (DOM) properties remain unclear. In this work, when compared to dark chlorination, sunlight-driven FAC photolysis over a range of conditions was found to yield higher DBP levels, depletion of DOM chromophores and fluorophores, preferential removal of phenolic groups versus carboxylic acid groups, and degradation of larger humic substances to smaller molecular weight compounds. Control experiments showed that increased DBP levels were not due to direct DOM photolysis and subsequent dark reactions with FAC, but to co-exposure of DOM to FAC and reactive species (e.g., O₃, HO•, Cl•, Cl₂•, ClO•) generated by FAC photolysis. Because solar chlorine photolysis can enable inactivation of chlorine-resistant pathogens at far lower CT_{FAC} values than chlorination alone, the increases in DBP formation inherent to this approach can likely be offset to some extent by the ability to operate at significantly decreased CT_{FAC}. Nonetheless, these findings demonstrate that applications of solar chlorine photolysis will require careful attention to potential impacts on DBP formation.

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1. Introduction

Free available chlorine (FAC) is the most commonly applied chemical disinfectant worldwide (WHO, 2017). However, some important waterborne microorganisms are chlorine-resistant and persist after disinfection with FAC. For instance, highly chlorine-resistant oocysts of the protozoan parasites *Cryptosporidium hominis* and *Cryptosporidium parvum* are a frequent cause of waterborne illness in the United States and worldwide (Medema et al., 2009; Painter et al., 2015). Ultraviolet (UV) irradiation and ozonation are both recognized alternative disinfection strategies that can be applied to achieve inactivation of protozoan (oo)cysts and other chlorine-resistant microorganisms; nevertheless, monetary and

energy expenses may prevent their use in small-scale drinking water treatment applications (Cho et al., 2006; EPA, 2005).

Exposing chlorinated water to sunlight has been reported to dramatically enhance inactivation of chlorine-resistant *Bacillus subtilis* endospores and highly chlorine-resistant *Cryptosporidium* oocysts when compared to chlorination alone (Forsyth et al., 2013; Zhou et al., 2014). Photolysis of free available chlorine by solar wavelengths of UV light (i.e., UVB and UVA wavelengths from 290 to 400 nm, which overlap with the absorption spectra for HOCl and OCl[−]; Fig. S2a) produces hydroxyl radical (HO•), chlorine atom (Cl•), and atomic oxygen (O(³P)); the latter of which reacts with dissolved oxygen (O₂) to form ozone (O₃) (Table 1, Equations (1)–(4)) (Buxton and Subhani, 1972; Forsyth et al., 2013; Nowell and Hoigne, 1992a; b; Oliver and Carey, 1977; Zhou et al., 2014). O₃ and HO• in particular are strong oxidants that can enhance disinfection during chlorination by damaging or penetrating protective spore and cyst coats (Cho and Yoon, 2007, 2008; Forsyth et al., 2013; Zhou et al., 2014). Considering the low cost and widespread availability of FAC and sunlight, solar FAC photolysis could provide a uniquely

* Corresponding author. contact details: 305 More Hall, Box 352700; Seattle, WA, 98195

E-mail addresses: try4@uw.edu (T.R. Young), liwentao@nju.edu.cn (W. Li), ahg8@uw.edu (A. Guo), korshin@uw.edu (G.V. Korshin), doddmc@uw.edu (M.C. Dodd).

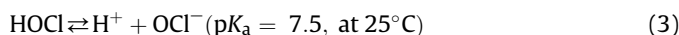
Table 1

Summary of chlorine photolysis reactions and quantum yields.

		$\Phi(254\text{ nm})$	$\Phi(313\text{ nm})$	$\Phi(365\text{ nm})$
$\text{HOCl} + h\nu \rightarrow \text{HO}^\bullet + \text{Cl}^\bullet$	(1a)	0.46–1.4 ^{a,c}	1 ^{d*}	N/A
$\text{OCl}^- + h\nu \rightarrow \text{O}^\bullet + \text{Cl}^\bullet$	(1b)	0.278 ^e	0.127 ^e	0.08 ^e
$\text{OCl}^- + h\nu \rightarrow \text{O}(\text{}^3\text{P}) + \text{Cl}^\bullet$	(2)	0.074 ^e	0.075 ^e	0.28 ^e

N/A = not available, ^a(Watts and Linden, 2007), ^b(Jin et al., 2011), ^c(Wang et al., 2012), ^dAt approximately 310 nm, ^e(Molina et al., 1980), ^f(Buxton and Subhani 1972).

effective option for enhancing disinfection in decentralized and point-of-use treatment, especially in low-resource settings – for example, by combining chlorination with conventional solar disinfection (SODIS) (McGuigan et al., 2012).



While the potential of solar FAC photolysis for mitigating acute health risks (by enabling inactivation of chlorine-susceptible and chlorine-resistant pathogens) has been established (Forsyth et al., 2013; Zhou et al., 2014), the possible long-term health implications of using it as a potable water treatment approach (e.g., effects on disinfection byproduct formation) must also be explored before recommending its practical application.

FAC and the various oxidants generated during FAC photolysis also react with inorganic and organic water constituents, such as bromide and dissolved organic matter (DOM), that can serve as disinfection byproduct (DBP) precursors. An abundance of investigations have evaluated DBP formation in DOM-containing waters during UVC-driven (200–280 nm) FAC photolysis – in which HOCl and OCl[−] undergo primarily homolytic cleavage to form HO[•] and Cl[•] (Eq. 1a,b). However, conflicting results have been reported regarding whether FAC + UVC treatment leads to increased DBP formation (e.g., due to precursor formation via hydroxylation and aromatic ring opening by hydroxyl radical or other radical species (Pisarenko et al., 2013; Wang et al., 2015; Xiang et al., 2016)) or decreased DBP formation due to precursor degradation (Li et al., 2016; Wang et al., 2017), when compared to chlorination alone (Liu et al., 2012; Remucal and Manley, 2016; Yang et al., 2016).

Comparatively little information is available regarding the potential impacts of sunlight-driven FAC photolysis on DBP formation (Nowell and Hoigne, 1992b; Oliver and Carey, 1977; Pisarenko et al., 2013; Simard et al., 2013). In comparison to UVC-driven FAC photolysis, solar FAC photolysis ($\lambda > 290\text{ nm}$) proceeds to a much greater extent through OCl[−] heterolysis (particularly at pH above the pK_a of HOCl; Eq. (3)) – yielding ground-state atomic oxygen (Eq. (2)), in addition to O₃ under oxic conditions (Eq. (4)) (Buxton and Subhani, 1972). Previous work investigating sequential exposure of DOM to O₃ and chlorine has shown that high O₃ doses can decrease DBP formation by degrading DBP precursors, whereas low O₃ doses can actually result in increased DBP formation, especially under conditions favoring HO[•] formation (De Vera et al., 2015; Mao et al., 2014; Riley and Mancy, 1978). The impacts of simultaneous DOM exposure to FAC, O₃, and HO[•] or other radicals during solar FAC photolysis are less clear, and to the authors' knowledge, a comprehensive evaluation of this reaction chemistry has yet to be undertaken. Several groups have noted decreases in total organic halogens (TOX) within reclaimed water (Lv et al., 2017), and degradation of naphthenic acids within oil sand process water (Shu et al., 2014) after sunlight-driven FAC photolysis. Others have

reported increasing formation of organochlorine, trihalomethanes (THMs), and haloacetic acid (HAAs), coupled with significant degradation of chromophores and fluorophores, during treatment of organic precursors with FAC and artificial UVA light sources ($\lambda_{\text{peak}} \sim 350\text{--}365\text{ nm}$) when compared to dark chlorination (Oliver and Carey, 1977; Pisarenko et al., 2013). However, there is limited data available on formation of specific classes of DBPs associated modifications to DOM and DBP precursors, during broadband simulated or natural solar irradiation of chlorinated water.

Furthermore, available data on DBP formation during UV or sunlight-driven FAC photolysis have generally been reported only for conditions in which water samples were subjected to either (i) varying initial FAC concentrations for fixed irradiation times, or (ii) fixed initial FAC concentrations for variable irradiation times, without accounting for variations in FAC concentration and consequent effects on cumulative FAC exposure ($CT_{\text{FAC}} = \int_0^t [\text{FAC}] dt$) during irradiated and dark treatment. This is an important limitation, as DBP formation is dependent on both FAC concentration and reaction time and is expected to be strongly influenced by variations in FAC concentrations during irradiation. Without the availability of measurements of CT_{FAC} (which normalizes for variations in FAC concentration and reaction time) from the prior studies, it remains unclear how CT_{FAC} -specific DBP formation potentials are affected by sunlight-driven FAC photolysis, in turn hindering direct comparison of DBP formation under dark and light conditions.

The principal objectives of this work were to (a) quantify formation of regulated organic DBPs (THMs and HAAs) during sunlight-driven FAC photolysis, and (b) correlate DBP formation with characteristic changes to DOM during dark chlorination, solar irradiation, and sunlight-driven FAC photolysis. DBP formation was investigated under a variety of conditions (e.g., varying pH, temperature, bromide concentration, or O₂ concentration; w/ and w/o added oxidant scavengers). The effects of variations in FAC exposure were normalized to CT_{FAC} to enable comparison of CT_{FAC} -specific DBP formation under the range of conditions investigated. Corresponding changes in DOM character were investigated by monitoring changes in DOC, fluorescence excitation-emission matrices (EEMs), UV absorbance (UV₂₅₄ specifically), differential absorbance spectra, and size-exclusion chromatographs of the DOM present in treated solutions. An overarching objective of this work was to utilize these analyses to provide an improved understanding of how DOM modifications resulting from solar irradiation in the presence of FAC influence DBP yields, and how this knowledge may be applied to mitigate such impacts during the use of this approach to enhance inactivation of chlorine-resistant microorganisms for drinking water treatment applications.

2. Materials and methods

2.1. Materials

The reverse osmosis isolate of Suwannee River natural organic matter (SRNOM) was obtained from the International Humic Substance Society (batch number 2R101N). All other chemicals, unless specified otherwise, were obtained from Sigma Aldrich and were of at least reagent-grade purity. All aqueous stock solutions were prepared in Milli-Q ultrapure water with resistivity $\geq 18.2\text{ M}\Omega\text{ cm}$. Detailed descriptions of chemical and natural water sample sources and stock solution preparation are provided in the Supplementary Material, Text S1.

2.2. Chlorine and simulated sunlight treatment procedures

Experiments were undertaken in duplicate using buffered reagent water solutions (10 mM phosphate unless otherwise

specified, at pH 8.0 or 6.0) or natural water samples (details and characterization in Text S1 and Table S1) according to four treatment protocols: (i) dark chlorination (FAC only), (ii) simulated solar irradiation without FAC followed by a dark FAC period (Light only/FAC only), (iii) simulated solar irradiation of FAC-containing water for varying times followed by dark FAC treatment (FAC + light/FAC only), and (iv) simulated solar irradiation of FAC-containing water for varying times *without* subsequent dark FAC treatment (FAC + light). All simulated solar irradiations were conducted within an Atlas Material Testing Solutions SUNTEST XLS + solar simulator equipped with a 1700-W, O₃-free, Xe arc lamp with daylight filter (cutoff below 290 nm) and infrared radiation filter. Irradiations of samples in quartz reactor tubes were undertaken at either 10 or 25 °C (maintained by means of a recirculating water bath). Detailed descriptions of reactor configurations and experimental procedures (including rationale for selection of FAC concentrations, irradiation times, and CT_{FAC} values utilized in experiments) are provided in Text S2–S3 and Fig. S1.

Chemical actinometry experiments, using *para*-nitroanisole and pyridine (Dulin and Mill, 1981; Laszakovits et al., 2017), were performed in quartz reactor tubes alongside sample irradiation experiments (Text S4). Periodic spectral irradiance measurements were obtained using a USB2000+ XR spectroradiometer (Ocean Optics) equipped with a 200 $\mu\text{m} \times 2\text{ m}$ optical fiber and CC-3-UV-S cosine corrector (see Fig. S2b for representative spectral irradiance curves).

2.3. Natural sunlight experiments

Experiments using natural sunlight followed the same general procedures as simulated sunlight experiments, except that samples were exposed to sunlight on the roof of More Hall at the University of Washington. Incident fluence data are included in Fig. S3 and a representative spectral irradiance curve is included in Fig. S2b.

2.4. Ozone experiments

One-hundred mL volumes of 2 mg/L SRNOM solutions (pH 8, 0.5-mM phosphate buffer, w/ or w/o 50-mM *tert*-butanol (*t*-BuOH)) were dosed in duplicate with aqueous O₃ at concentrations ranging from 0.25 to 1 g O₃/g DOC, and allowed to react to complete O₃ consumption prior to analyses. See Text S1 for details on O₃ stock solution preparation.

2.5. Analytical methods

2.5.1. DBP extraction and analysis

Twenty mL volumes of Na₂S₂O₃-quenched samples were acidified to pH < 2 with 98% purity H₂SO₄. After increasing the aqueous ionic strength with sodium sulfate, THMs and protonated HAAs were then extracted into 4 mL of MTBE amended with internal standards (100 $\mu\text{g/L}$ 1,2,3-trichloropropane and 2,3-dibromopropanoic acid) via vigorous mixing. Subsequently, the supernatant MTBE layer containing THMs and HAAs was separated from the underlying aqueous phase via pipetting and transferred into a separate conical-bottom borosilicate glass vial. HAAs were esterified by adding 1 mL of acidified methanol (10% volume H₂SO₄) to 3 mL of the MTBE extract and heating at 50 °C for 2 h. After esterification, excess acid was neutralized with 4 mL of saturated aqueous sodium bicarbonate, and 1 mL of neutralized MTBE supernatant was transferred to autosampler vials for analysis (Hodgeson et al., 1995). THMs and HAAs were analyzed using a Shimadzu GC-2010 with HP-1MS U column and electron-capture detector.

2.5.2. Absorbance and fluorescence measurements

Samples quenched with As(III), a fast-reacting inorganic FAC quencher (Dodd et al., 2006) with negligible UV absorbance at $\lambda > 220\text{ nm}$, were analyzed by UV and fluorescence spectrophotometry. UV-Visible absorbance spectra were recorded from 224 to 800 nm and fluorescence EEMs recorded over an excitation range of 240–600 nm and an emission range of 245.2–826.6 nm. Both measurements were collected within a 1 cm quartz cuvette using a HORIBA Aqualog 800-C spectrofluorometer (details in Text S5).

2.5.3. UV-Visible differential absorbance spectrophotometry (DAS)

As per established methods (Dryer et al., 2008; Gao and Korshin, 2013), after completion of experiments, 40 mL volumes of 0.5-mM phosphate-buffered samples were quenched with Na₂S₂O₃ in two-fold excess of FAC and acidified to pH ~2.9 by addition of 1 M HClO₄. Samples were gradually titrated with NaOH (1 M) at 0.5-unit pH intervals, and absorbance spectra recorded in a 5-cm quartz cell within a Shimadzu UV2700 spectrophotometer (details in Text S6). DAS spectra were obtained using Equation (5), where $A_{pH(\lambda)}$ is the absorbance (measured between 200 and 600 nm) at varied pH, $A_{pH_Ref(\lambda)}$ is the reference absorbance acquired at pH ~2.9, and l_{cell} is the quartz cell path length.

$$\Delta A_{pH(\lambda)} = \frac{A_{pH(\lambda)} - A_{pH_Ref(\lambda)}}{l_{cell} \times DOC}; \text{ units of } L/(mg \cdot cm) \quad (5)$$

2.5.4. Size exclusion chromatography (SEC)

As(III)-quenched samples were also analyzed by SEC with inline UV, fluorescence, and DOC detection. One-hundred μL injection volumes of each sample were resolved by size/molecular weight using a Tosoh Toyopearl HW-50S (250 mm $\times$ 20 mm, 3 μm) column installed on a Dionex UltiMate3000 HPLC operated at 1 mL/min with a mobile phase of 13.8 mM phosphate buffer at pH 6.8 and 0.1 M ionic strength (with ionic strength adjustment using NaClO₄). The HPLC-SEC system was equipped with a UV diode array detector, fluorescence detector, and GE Sievers 900 Series Turbo online organic carbon detector equipped with an inline inorganic carbon remover (additional details in Text S7).

3. Results and discussion

3.1. Disinfection byproduct formation

3.1.1. General effects of FAC photolysis on DBP formation

Fig. 1 compares concentrations of HAA5 (mono-, di-, and tri-chloroacetic acids, and mono- and dibromoacetic acids) and TTHM (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) formed during exposure of phosphate buffered solutions containing 2 mg/L of SRNOM and 8 mg/L as Cl₂ of FAC to varying irradiation times (0, 15, 30, and 45 min of simulated sunlight, equal to 0, 6.2, 12.4, and 18.6 J/cm² fluence), coupled with post-irradiation dark FAC exposure up to a cumulative CT_{FAC} of 400 (mg/L) $\times$ min. As shown in Fig. 1, there is a clear increase in DBP formation during FAC + light/FAC only treatment when compared to FAC only treatment for all conditions. Elevated temperature resulted in further increases in DBP formation at each condition (Fig. 1), which appears to be due primarily to increased rates of dark DOM chlorination (Text S8). Direct DOM photolysis did not appear to be an important contributor to DBP formation. Even at the highest fluence investigated (18.6 J/cm²), HAA5 and TTHM yields after light only/FAC only treatment were similar to those measured following FAC only treatment (Table S3). Similar trends were also observed when using natural sunlight to photolyze FAC (Fig. S3).

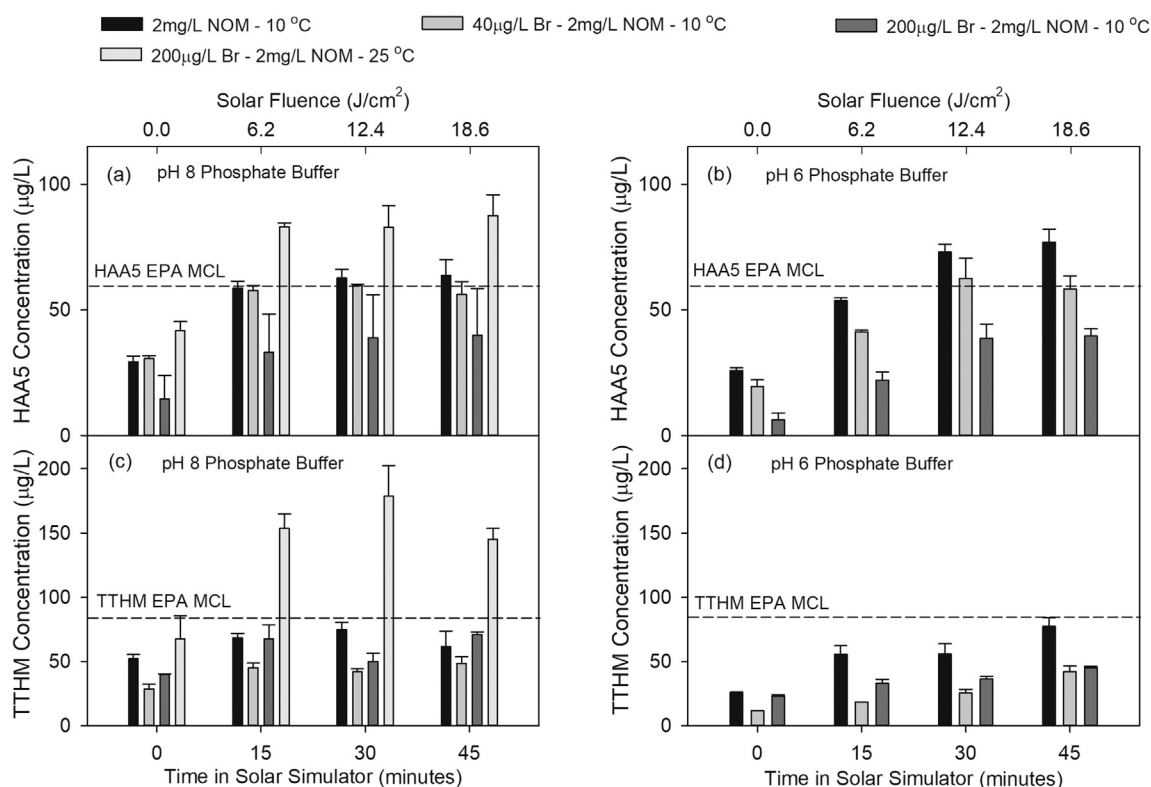


Fig. 1. (a) HAA5 and (c) TTHM formation in pH 8 (10 mM) phosphate buffer with 2 mg/L SRNOM comparing FAC only treatment (0 min in the solar simulator) with FAC + light/FAC only treatment at varying bromide concentration (0–200 µg/L) and temperature (10 °C or 25 °C); and (b) HAA5 and (d) TTHM formation in pH 6 (10 mM) phosphate buffer with 2 mg/L SRNOM at 10 °C comparing FAC only treatment with FAC + light/FAC only treatment at varying bromide concentration (0–200 µg/L). All samples utilized $[FAC]_0 = 8$ mg/L as Cl_2 and targeted $CT_{FAC} = 400$ (mg/L) × min.

As discussed in more detail below, the increases in THM and HAA formation during solar FAC photolysis may result from DOM modifications predisposing certain DBP precursor constituents to increased halogenation during co-exposure to FAC, O_3 , and various reactive oxygen or halogen species (ROS or RHS) generated by FAC photolysis. While prior work has shown that pre-ozonation of DOM at ~0.4–1 mg O_3 /mg C and circumneutral pH can decrease THM formation during chlorination (Gallard and von Gunten, 2002; Hua and Reckhow, 2013), pre-oxidative treatment at lower O_3 exposures and/or elevated $HO^\bullet$ exposures (e.g., during O_3 treatment at high pH or AOPs such as UV/ H_2O_2) – similar to the conditions of solar FAC photolysis – has actually been shown to increase THM formation during chlorination (De Vera et al., 2015; Dotson et al., 2010; Mao et al., 2014; Riley and Mancy, 1978). This is thought to be due to degradation of higher molecular weight humic-like substances to smaller, chlorine-reactive alcohol or ketone-containing aromatic or aliphatic groups (De Vera et al., 2015; Dotson et al., 2010; Mao et al., 2014; Riley and Mancy, 1978).

In additional experiments, bromide was added to reaction solutions at concentrations of 40 or 200 µg/L, in order to evaluate formation of brominated DBPs under conditions representative of relatively pristine or human-influenced surface waters, respectively (Flury and Papritz, 1993; Soltermann et al., 2016). Addition of bromide led to suppression of HAA5 and TTHM yields during both FAC only and FAC + light/FAC only treatments (Fig. 1). In contrast, HAA9 – which includes additional mixed Cl- and Br-containing HAAs not captured by HAA5 – remained relatively constant at elevated bromide levels during FAC only treatment (Fig. S6a) (consistent with prior observations (Chellam and Krasner, 2001; Cowman and Singer, 1996)), and increased at elevated bromide

levels during FAC + light/FAC only treatment (Fig. S6a). In addition, bromine substitution factor (BSF) – a measure of the fraction of total DBP halogen content attributable to bromine (Text S9) – increased for TTHM and HAA9 during FAC only and FAC + light/FAC only treatments at elevated bromide levels, with a relatively larger increase in BSF observed during FAC + light/FAC only treatment (Fig. S6). This suggests increased bromination during FAC + light/FAC only treatment compared to FAC only treatment – potentially due to modifications to DOM during FAC photolysis (leading to greater susceptibility of DBP precursors to bromination), or direct bromination of DBP precursors by photochemically-generated reactive bromine species such as $Br^\bullet$ or $BrCl^\bullet$.

pH effects on FAC speciation or photolysis pathway (Eqs. (1)–(3)) did not seem to have a clear influence on HAA formation, as variation of pH did not have a strong effect on HAA5 (Fig. 1a and b) or HAA9 (Fig. S6a) yields during either FAC only or FAC + light/FAC only treatment. Prior investigations have also reported variability in the pH-dependence of overall HAA formation during dark chlorination and FAC photolysis processes, though trihaloacetic acid formation generally appears to correlate inversely with pH during dark chlorination (Korshin et al., 2002; Liang and Singer, 2003; Remucal and Manley, 2016; Wang et al., 2015). In contrast, TTHM yields in the present work increased with increasing pH for both FAC only and FAC + light/FAC only treatment (Fig. 1c and d), consistent with prior observations (Gallard and von Gunten, 2002; Pisarenko et al., 2013; Rook, 1977). In addition to an increased importance of OH^- in the haloform reaction at higher pH, increased TTHM yields during FAC + light/FAC only treatment may be in part related to solar FAC photolysis kinetics, as the rate of FAC photolysis increases with pH at wavelengths above 260 nm due to increased

UV absorbance by FAC with the shift in speciation from HOCl to OCl⁻ (Eqs. (1)–(3), Fig. S2a) (Nowell and Hoigne, 1992a; b).

3.1.2. Effects of dissolved O₂ removal and radical scavenger addition

In order to evaluate the relative importance of O₃ and radical species in driving DBP formation during FAC + light/FAC only treatment, concentrations of O₂ were varied from ~0 to 1.6 mmol/L and the radical scavengers *t*-BuOH or carbonate (as NaHCO₃) were added separately at concentrations of 50 mM to selected reaction solutions (Fig. 2). Initially anoxic conditions are expected to limit formation of O₃ by preventing the reaction of photochemically-generated O(³P) with O₂, whereas saturation with O₂ is anticipated to increase O₃ formation relative to ambient conditions (as per Eq. (4)). Addition of 50 mM concentrations of *t*-BuOH or carbonate is anticipated to lead to 97% or 41% scavenging of HO[•], 95% or 88% scavenging of Cl[•], and 53% or 4% scavenging of O(³P) under the experimental conditions investigated here (Text S10 and Table S4).

The absence of O₂ did not appear to lead to significant differences in HAA5 yields, whereas O₂ saturation led to moderate decreases in HAA5 yields, indicating that O₃ may contribute to destruction of HAA precursors during FAC photolysis (Fig. 2a). Fig. 2b shows that the absence of O₂ resulted in a small increase in TTHM yields during FAC + light/FAC only treatment, possibly due to decreased destruction of THM precursors (e.g., dihydroxybenzenes) by O₃ (Gallard and von Gunten, 2002; Hua and Reckhow, 2013). O₂ saturation had no clear effect on THM yields during FAC + light/FAC only treatment.

Addition of *t*-BuOH and carbonate each appeared to result in modest decreases in HAA5 yields (Fig. 2a) during FAC + light/FAC

only treatment, due in large part to decreases in di- and tri-chloroacetic acid formation (Fig. 2a and Fig. S6a). This indicates that radical reactions with DOM may contribute to HAA precursor formation. Carbonate and *t*-BuOH addition did not have a clear effect on TTHM yields during FAC + light/FAC only treatment (Fig. 2b). Overall, variations in dissolved O₂ concentrations and addition of radical scavengers resulted in at most modest changes to organic DBP formation, making it difficult to distinguish direct effects of O₃ and radical species (e.g., HO[•], Cl[•], Cl₂^{•-}, ClO[•], O(³P)) on DBP precursors.

3.1.3. Importance of photochemical versus dark reactions in driving DBP formation

Fig. 3 compares DBP formation versus CT_{FAC} during FAC only treatment and FAC + light treatment (labeled 15, 30, and 45 min) without and with post-irradiation dark FAC treatment. Compared to FAC only treatment, FAC + light treatment resulted in substantially greater yields of TTHM and HAA5 at a given CT_{FAC} value, confirming that yields of DBPs are elevated during sunlight-driven FAC photolysis. Fig. 3 also highlights the change in DBP formation resulting from continued FAC only treatment after sunlight-driven FAC photolysis by comparing the results for FAC + light treatment (open symbols) with those for FAC + light/FAC only treatment (half-filled symbols), with the same irradiation times used in each case. It appears that the CT_{FAC}-normalized rate of HAA5 formation during dark chlorination (Fig. 3, solid lines) increases modestly after FAC + light treatment (regression slopes increase by factors of 2 and 3 for pH 8 and 6, respectively), whereas the rate of TTHM formation during dark chlorination (Fig. 3, dashed lines) is similar after FAC + light and FAC only pretreatment when normalized by CT_{FAC}. Taken together, these data indicate that most (if not all) of the relative increases in DBP yields observed during FAC + light/FAC only experiments are due to DBP formation during FAC photolysis, rather than to post-irradiation reactions in the dark. This in turn suggests that increases in DBP formation during sunlight-driven FAC photolysis are driven primarily by halogenation reactions during irradiation (consistent with (Oliver and Carey, 1977)), though it is unclear if this is due to (i) direct halogenation of DOM by RHS (e.g., Cl[•], Br[•], BrCl[•], Cl₂^{•-}, ClO[•]), (ii) oxidative modifications to DOM resulting in generation of precursor moieties with higher susceptibility toward halogenation by FAC (or RHS), or (iii) a combination of both.

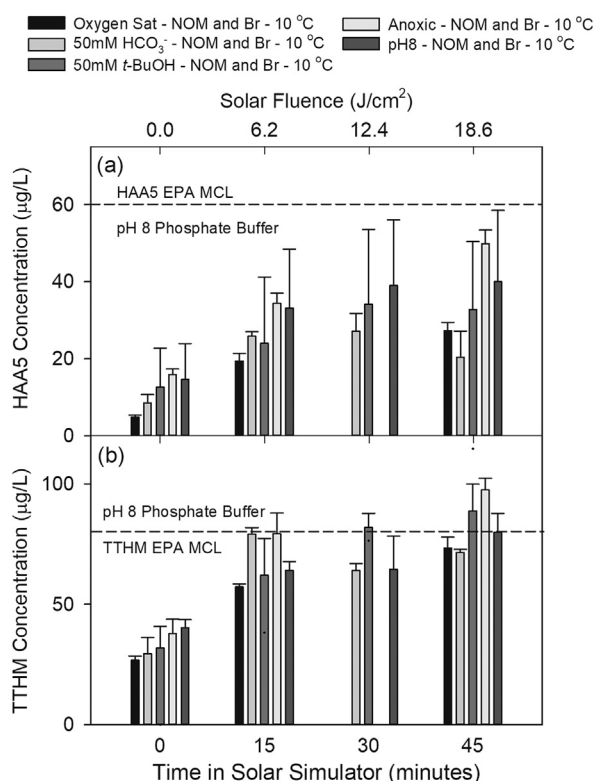


Fig. 2. (a) HAA5 and (b) TTHM formation with saturated (1.6 mM) dissolved O₂ (black), 50 mM HCO₃⁻ (red), 50 mM *t*-BuOH (green), initially anoxic conditions (yellow), or no alteration (blue) after exposure to FAC only or FAC + light/FAC only treatment with variable irradiation times. All solutions were prepared in 10 mM phosphate buffer at pH 8 and 10 °C with 2 mg/L SRNOM, 200 µg/L bromide, [FAC]₀ ~ 8 mg/L as Cl₂, and targeted CT_{FAC} = 400 (mg/L) × min.

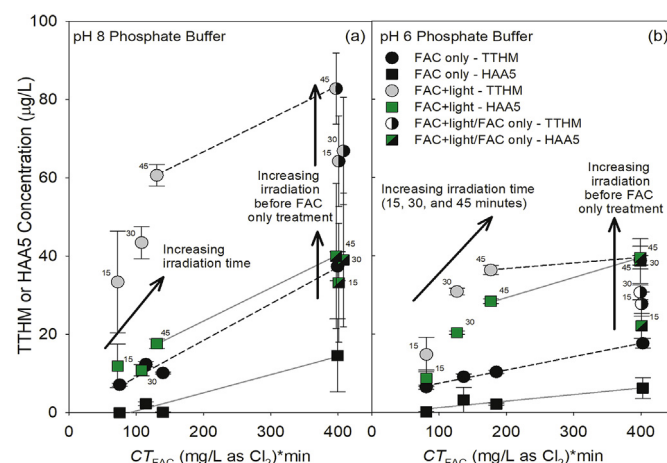


Fig. 3. Comparison of TTHM and HAA5 formation during FAC only, FAC + light, and FAC + light/FAC only treatment targeting CT_{FAC} = 400 (mg/L) × min at 10 °C for (a) pH 8; and (b) pH 6. All samples were prepared in 10 mM phosphate buffer with 2 mg/L SRNOM, 200 µg/L bromide, and [FAC]₀ ~ 8 mg/L as Cl₂.

3.1.4. DBP formation during treatment of natural waters

Fig. 4 shows HAA5 and TTHM yields in two natural freshwaters – Lake Washington and a local reservoir; with and without addition of 200 $\mu\text{g/L}$ of bromide – subjected to (i) FAC only, (ii) Light only/FAC only, and (iii) FAC + light/FAC only treatment. FAC only and Light only/FAC only treatment (at fluences up to 18.6 J/cm^2) resulted in similar DBP yields, indicating that direct photolysis of the DOM does not impact DBP formation during chlorination. HAA5 concentrations associated with Lake Washington remained well below the EPA MCL of $60 \mu\text{g/L}$ and were not detected within the local reservoir water. TTHM formation was compliant with the EPA MCL of $80 \mu\text{g/L}$ at natural bromide concentrations for each water, though at higher bromide concentrations, formation of bromodichloromethane and dibromochloromethane increased during solar FAC photolysis, and TTHM levels exceeded the MCL. These results indicate that sunlight-driven FAC photolysis can likely be applied for disinfection of natural waters with relatively low DOM and bromide concentrations, though further work is needed to evaluate its applicability over a wider range of water qualities.

3.2. Analyses of changes to dissolved organic matter

3.2.1. UV-Visible absorbance and fluorescence

The results summarized in Fig. 5a, Fig. S7a, and Table S5 show that SRNOM after FAC + light treatment has substantially lower 254 nm UV absorbance than after FAC only treatment. Addition of *t*-BuOH results in preservation of chromophores during solar FAC photolysis (31% and 51% losses in 254 nm absorbance with and without *t*-BuOH respectively, after 45 min of FAC + light). Anoxic

conditions also result in preservation of chromophores during solar FAC photolysis treatment, but to a lesser extent than *t*-BuOH addition (40% loss after 45 min of FAC + light); indicating that radical species and O_3 contribute to decreases in absorbance and destruction of associated aromatic compounds.

Untreated SRNOM has characteristic fluorescence features, including two peaks located near $250 \text{ nm}_{\text{Ex}}/450 \text{ nm}_{\text{Em}}$ and $330 \text{ nm}_{\text{Ex}}/450 \text{ nm}_{\text{Em}}$, that are typically associated with terrestrial humic constituents (Hua et al., 2010; Ishii and Boyer, 2012). DOM with high fluorescence intensity in these regions has been positively correlated to THM formation during chlorination (Hua et al., 2010; Li et al., 2016). Fig. S8 depicts the change to fluorescence EEMs after FAC only, Light only, Light only/FAC only, FAC + light, and FAC + light/FAC only treatment. FAC + light and FAC + light/FAC only treatments resulted in significantly greater losses in the fluorescence signals associated with humic constituents when compared to FAC only, Light only, or Light only/FAC only treatments (Figs. 5a and S7a). Previous research has also demonstrated greater fluorophore destruction during FAC-UVA treatment when compared to FAC-UVC AOP treatment (Pisarenko et al., 2013) and FAC-only treatment (Shu et al., 2014).

Introducing *t*-BuOH as a radical scavenger during solar chlorine photolysis significantly inhibited degradation of humic-like fluorophores, to an extent greater than observed by limiting O_3 formation under anoxic conditions (Figs. 5a and S7a and Table S5). These trends indicate that photochemically-generated $\text{HO}^\bullet$, $\text{Cl}^\bullet$, or other ROS/RHS, and – to a lesser degree – O_3 , all play important roles in the degradation of fluorophores during FAC + light treatment.

3.2.2. UV-Visible differential absorbance spectra (DAS)

The pH titration DAS analysis method provides an in situ approach to quantifying behavior of ionizable chromophores, which reflects contributions of carboxylic and phenolic functional groups in DOM (Dryer et al., 2008; Gao and Korshin, 2013). A monotonic increase in UV absorbance (240–450 nm) of DOM is typically observed with increasing pH, which is primarily associated with deprotonation of aromatic DOM chromophores (Korshin et al., 1997). From the DAS results of raw SRNOM (Fig. 6a) there are two prominent feature bands: a narrow band centered at $\sim 280 \text{ nm}$ (DA280) associated with carboxylic acid groups, and a broad band centered at $\sim 340 \text{ nm}$ (DA340) associated with phenolic groups (Dryer et al., 2008; Gao and Korshin, 2013).

FAC only treatment of SRNOM-containing solutions at pH 8 and 6 resulted in moderate decreases in sample absorbance (Figs. 6b, S9a,b), indicating that FAC reacted directly with chromophores within the DOM. The DA340/DA280 ratio for samples subjected to FAC only treatment at pH 8 and 6 did not change during titration from pH 6 to 10, indicating suppression of the phenol deprotonation feature compared to the untreated sample (Fig. S9a,b). Light only treatment had no significant impact on DAS spectra (Fig. S9a,b).

Exposing SRNOM-containing solutions to FAC + light treatment using natural (FAC + light_{NS}) or simulated sunlight (FAC + light_{SS}) at pH 6 and 8 resulted in substantially greater bleaching of UV absorbance compared to FAC only treatment, and particularly enhanced removal at 340 nm, indicating preferential modification of phenolic groups (Figs. 6c, S9a,b). FAC + light treatment at pH 8 resulted in a lower average DA340/DA280 ratio than at pH 6, likely due to increased deprotonation of phenolic groups to more reactive phenolate forms and higher FAC photolysis rates at pH 8 (Fig. S9a,b). The addition of bromide was found to have no significant effect on changes to the DA340/DA280 ratio before or after treatment (Fig. S9b,c).

Changes in DAS spectra observed during FAC + light treatment

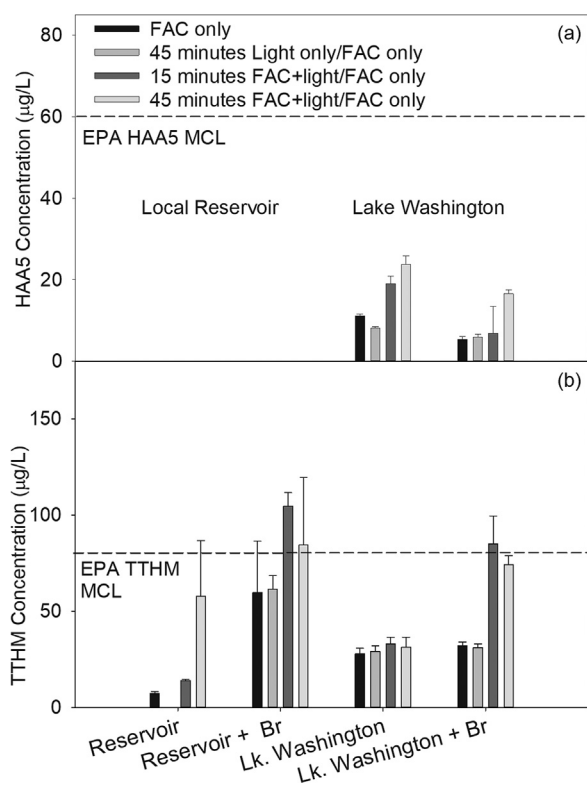


Fig. 4. (a) HAA5 and (b) TTHM formation in natural waters during FAC only, Light only/FAC only, and FAC + light/FAC only treatment. For all samples the temperature was 10°C , $[\text{FAC}]_0 \sim 8 \text{ mg/L}$ as Cl_2 , and $\text{CFAC} = 400 (\text{mg/L}) \times \text{min}$. Local Reservoir – pH = 8.05, 0.5 mg/L as C, $24.5 \mu\text{g/L}$ bromide, and 30.7 mg/L as CaCO_3 alkalinity. Lake Washington – pH = 8.10, 2.4 mg/L as C, $23.7 \mu\text{g/L}$ bromide, and 38.0 mg/L as CaCO_3 alkalinity. Samples labeled “+ Br” included an additional $200 \mu\text{g/L}$ of bromide in excess of natural levels.

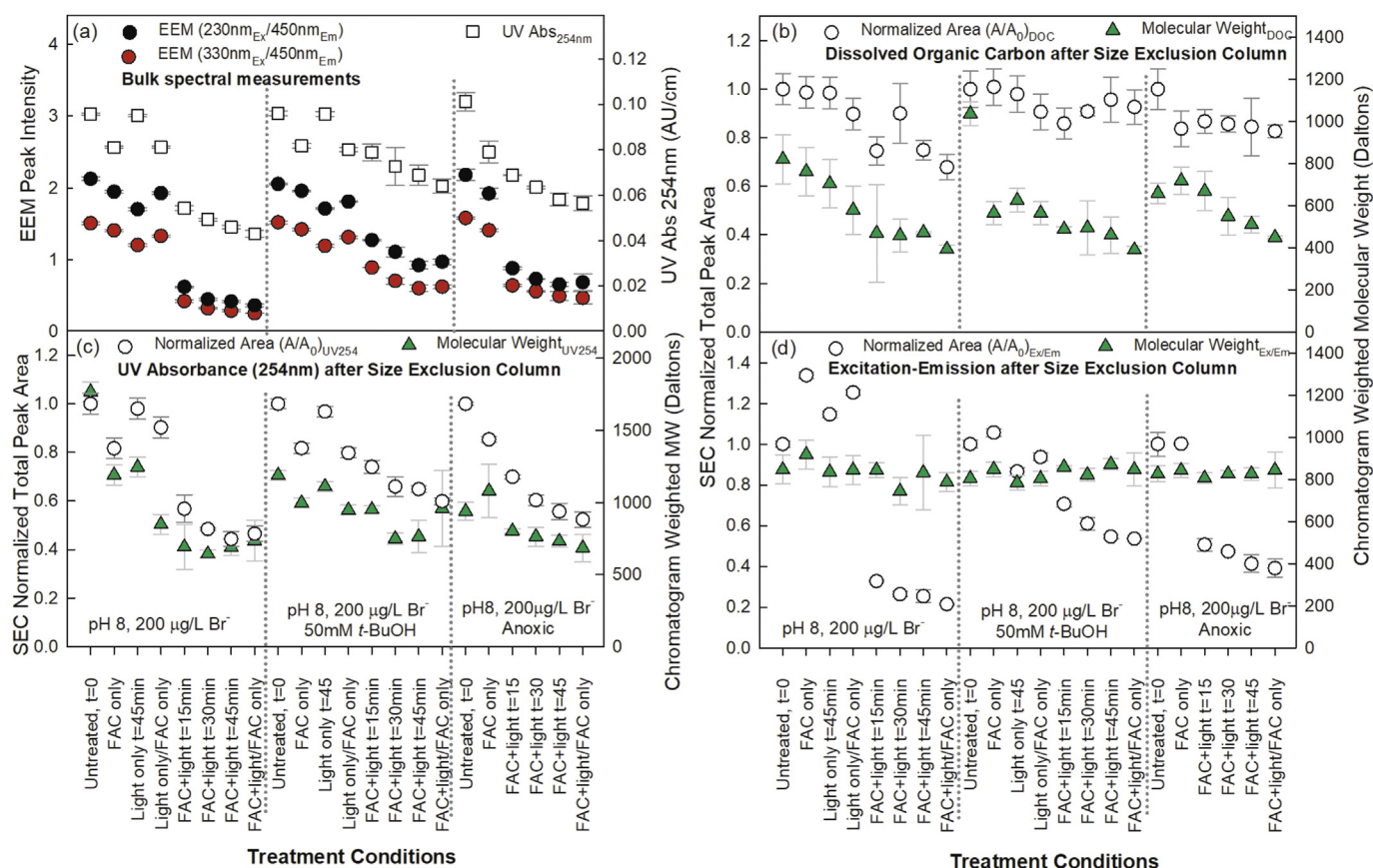


Fig. 5. (a) Bulk UV absorbance at 254 nm (white squares) and fluorescence (filled circles). (b)–(d) SEC data for (b) DOC, (c) UV absorbance at 254 nm, and (d) fluorescence (Ex: 320 nm, Em: 450 nm), summarizing total chromatographic peak areas normalized by untreated samples (white circles), and MW estimated from signal intensity-weighted retention times (green triangles; Text S7 for details). Data is from experiments with pH 8, 10 mM phosphate buffered solutions containing 2 mg/L SRNOM, 200 µg/L Br⁻, and [FAC]₀ ~ 8 mg/L as Cl₂ (when applicable) at 10 °C, after Light only, FAC only, Light only(45 min irr.)/FAC only, FAC + Light, and FAC + Light(45 min irr.)/FAC only treatment (x-axis represents treatment conditions, not time series). FAC only, Light only/FAC only, and FAC + light/FAC only experiments targeted $CT_{FAC} = 400$ (mg/L) × min. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

at pH 8 were similar to those observed during treatment of samples with increasing O₃ doses (O₃/DOC > 0.75) (Fig. 6c,f), where addition of *t*-BuOH had little effect on DAS changes during direct O₃ treatment (Fig. S9e). This is consistent with the proposed role of O₃ in contributing to direct degradation of phenolic groups in DOM during FAC + light treatment. However, purging O₂ from solution to limit the formation of O₃ during FAC + light treatment at pH 8 did not have a significant effect on DA340/DA280 ratios in comparison to FAC + light_{SS} treatment at ambient O₂ levels (Figs. 6d and S9d), suggesting either that O₃ plays a significantly less important role in driving phenol degradation compared to O(³P), HO[•], Cl[•], and other radical species, or that increased degradation of phenols by O(³P) (which would be elevated in the absence of O₂, as per Eq. (4)) compensates for the absence of O₃. Adding *t*-BuOH as a radical scavenger limited decreases in DA340/DA280 ratios during FAC + light treatment to a moderate extent (Figs. 6e and S9d), indicating some preservation of phenol groups due to suppression of ROS, RHS, and/or O₃ (via scavenging of O(³P) (Zhou et al., 2014)).

3.2.3. Size exclusion chromatography with UV-fluorescence-DOC detection (SEC-UV-FLD-DOC)

Size exclusion chromatography enables fractionation of DOM by size and/or molecular weight (MW), resulting in discrimination of two major peaks in the SRNOM comprising (1) a larger peak (Peak 1 here) assigned to higher MW humic substances and (2) a second, smaller peak (Peak 2 here) generally assigned to lower MW acidic compounds (Her et al., 2003; Huber et al., 2011) (see Fig. S10 for

example chromatograms). Fig. 5b–d and S7b–d summarize results from chromatographic analyses of treated samples, including normalized total chromatogram area ((Peak 1 + Peak 2)_{area}/(Peak 1 + Peak 2)_{area, untreated}) and average DOM MW estimates – each obtained using UV, fluorescence, and DOC detection (see Text S7 for analytical details and MW calculations and Fig. S11 for plots of fractional peak areas).

FAC only treatment generally resulted in a decrease of <20% for UV chromatogram areas and 5–10% for total DOC areas, while a slight (~5%) increase in total fluorescence was visible – an effect associated with halogenation of DOM (Korshin et al., 1999). Increasing periods of irradiation during FAC + light treatment resulted in decreases in overall MW as measured by UV and DOC detection, as well as 40–60% decreases in total UV chromatogram areas and up to 25% decreases in DOC chromatogram areas (Fig. 5b,c, S7b–d). By comparison, fluorescence peak area decreased 20–80% with minimal changes to overall MW as measured by fluorescence (Figs. 5d and S7d). These observations for FAC + light treatment are likely attributable to degradation of higher MW humic substances comprising Peak 1 to lower MW byproducts comprising Peak 2 (with little corresponding mineralization of DOC to CO₂), coupled with degradation of chromophores associated primarily with higher MW humic substances, and degradation of fluorophores associated with both higher and lower MW organics. Low MW byproducts that contribute to Peak 2 in DOC chromatograms after treatment appear to have a modest UV signal and very little fluorescence character (Fig. S10).

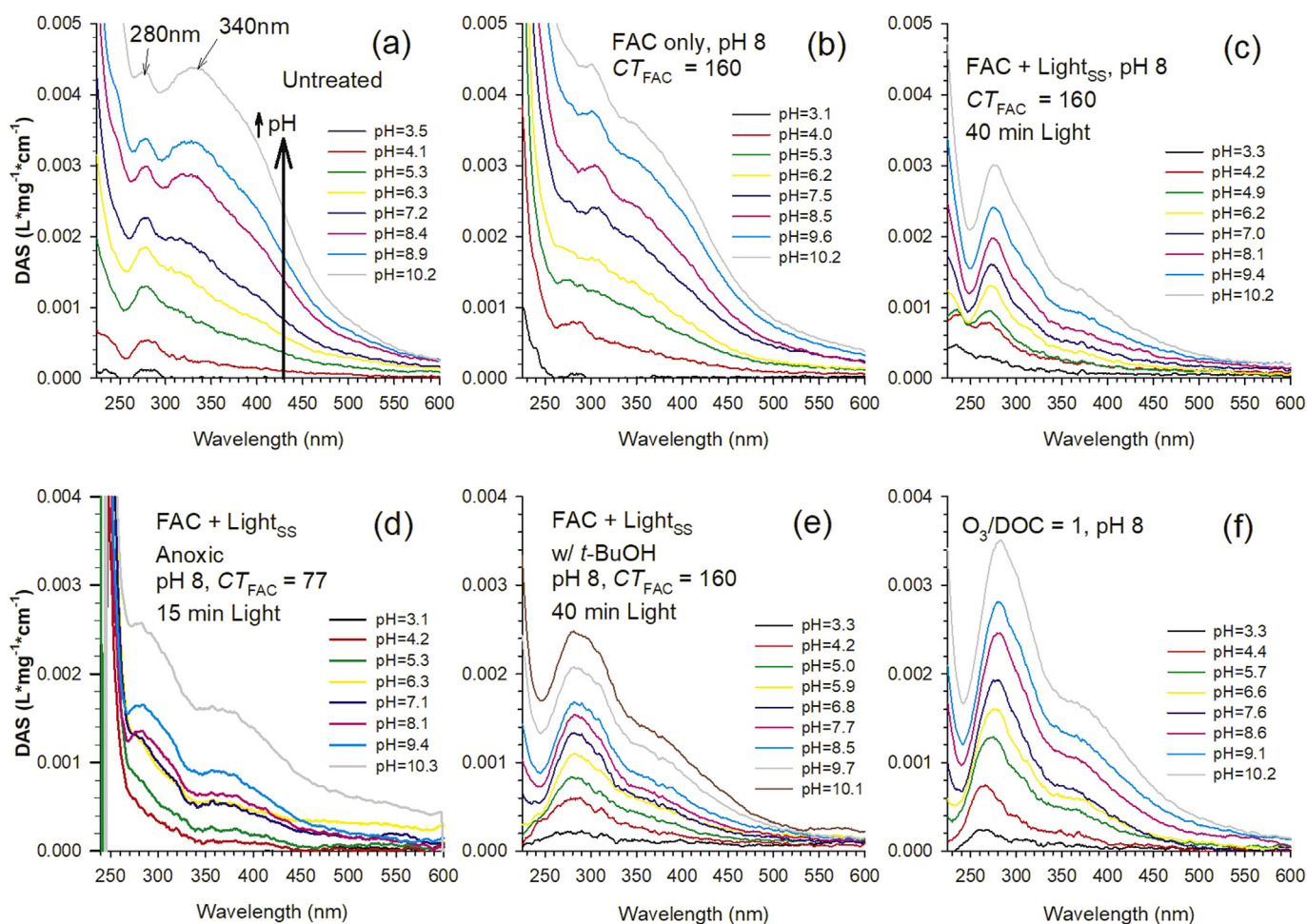


Fig. 6. Sample DAS spectra for 2 mg/L SRNOM in 0.5 mM phosphate buffer subjected to (a) no treatment; (b) FAC only treatment at pH 8 to $CT_{FAC} = 160$ (mg/L) $\times$ min; (c) FAC + light treatment at pH 8 to $CT_{FAC} = 160$ (mg/L) $\times$ min; (d) FAC + light treatment at pH 8 with initially anoxic conditions, $CT_{FAC} = 77$ (mg/L) $\times$ min; (e) FAC + light treatment at pH 8 with 50 mM *tert*-butanol to $CT_{FAC} = 160$ (mg/L) $\times$ min; and (f) O_3 only treatment at pH 8. All solutions prepared in 0.5 mM phosphate buffer at 25 °C with 2 mg/L SRNOM and $[FAC]_0 \sim 8$ mg/L as Cl_2 .

Changes observable by DOC and UV detection were similar for each treatment at pH 8 and 6 (Figs. 5b,c, S7b,c). Similar to bulk sample fluorescence and UV absorbance measurements, addition of *t*-BuOH resulted in preservation of chromophores and fluorophores and appeared to hinder degradation of larger MW compounds to lower MW compounds. This implies that $HO^\bullet$, $Cl^\bullet$, and other RHS species likely play an important role in breaking down aromatic molecules contained within larger DOM size fractions, though it should be noted that *t*-BuOH also scavenges $O(^3P)$ to a limited extent (Zhou et al., 2014), so some of the decreases in chromophore and fluorophore destruction may also have been due to blockage of reactions between $O(^3P)$ or O_3 and DOM. Suppressing O_3 formation by deoxygenation of reaction solutions prior to FAC + light treatment also resulted in decreased destruction of chromophores and fluorophores, but not to the same extent as *t*-BuOH addition. This suggests that O_3 may target a subset of primarily electron-rich aromatic functional groups such as phenols and activated aromatic rings, whereas $HO^\bullet$, $Cl^\bullet$, and other radical species may less selectively attack a larger pool of aromatic components within the DOM.

3.3. Linkages between observed DOM modifications and increased DBP formation during sunlight-driven FAC photolysis

Decreases in fluorescence and UV absorbance of SRNOM exhibited clear correlations with TTHM and HAA9 yields during FAC + light

treatment (Fig. S12), whereas correlations for HAA5 yields were weaker (likely due to the smaller group of HAAs encompassed by HAA5 relative to HAA9). There were no clear trends between DBP formation and fluorescence or absorbance changes during FAC only treatment, providing additional evidence that modifications of DOM by ROS, RHS, and/or O_3 produced during FAC photolysis are associated with the observed increases THM and HAA yields.

The findings discussed to this point suggest that O_3 generated during solar FAC photolysis contributes to preferential elimination of SRNOM's humic-like fluorescence properties, which are likely attributable in part to activated/electron-rich aromatic rings (e.g., phenolic groups) (Cory and McKnight, 2005; Sharpless and Blough, 2014). Similarities in DA340/DA280 losses during FAC + light treatment and O_3 only treatment also indicate a role for O_3 in preferential phenolic degradation during FAC photolysis. Previous work has shown that treatment of DOM by O_3 results in degradation of aromatics within the DOM (e.g., ring cleavage of dihydroxybenzenes and phenolic-like compounds) and to decreased DBP formation during subsequent chlorination, highlighting the role of phenolic moieties in DOM as DBP precursors (Gallard and von Gunten, 2002; Li et al., 2016). However, it is possible that under the conditions of FAC + light treatment, O_3 levels are low enough relative to DOM concentrations that activated aromatic DBP precursors are generated by oxygenation and/or hydroxylation reactions to a greater extent than they are destroyed (Mao et al., 2014;

Riley and Mancy, 1978). In this work, HAA and THM formation during FAC + light/FAC only treatment seemed to correlate negatively with conditions favoring higher in situ O_3 levels, supporting the hypothesis that increasing O_3 exposure contributes to the net degradation of organic DBP precursors.

Experiments undertaken here with added radical scavengers indicate that ROS and RHS contribute to both chromophore and fluorophore destruction and non-selective attack and degradation of high molecular weight humic-like substances to form lower molecular weight organic acids. $HO^\bullet$ has been found to react rapidly via hydroxylation of olefins and aromatic compounds and hydrogen abstraction from aliphatic compounds (Dotson et al., 2010; Mvula and von Sonntag, 2003; Pan et al., 1993; Varanasi et al., 2018). $Cl^\bullet$ may also react with a variety of aliphatic, aromatic, and olefinic moieties, as well as alcohol groups in DOM via addition, electron-transfer, and/or H-abstraction (Alegre et al., 2000; Martire et al., 2001; Varanasi et al., 2018; Wang et al., 2017). Overall, ROS and/or RHS reactions appear to contribute to the generation of additional DBP precursors. It is hypothesized that $HO^\bullet$ in particular activates aromatic groups by hydroxylation and generates lower MW aldehydes, ketones, and carboxylic acids as transformation products after reacting with higher MW fractions of DOM (Varanasi et al., 2018; Wang et al., 2017). HAA formation increases moderately during FAC only treatment after FAC + light pretreatment when compared to FAC only treatment at equivalent CT_{FAC} , supporting the hypothesis that molecules generated via ROS and RHS reactions with DOM act as HAA precursors (specifically for DCAA and TCAA) during the residual dark chlorination period of FAC + Light/FAC only experiments. Increased THM and HAA formation during FAC + light treatment may also be due to direct attack of DOM by radical species such as $HO^\bullet$, $Cl^\bullet$, $Br^\bullet$, $BrCl^\bullet$, $Cl_2^\bullet$, or $ClO^\bullet$ – initiating radical chain reactions leading to Cl-addition or C-centered radical recombination with $Cl^\bullet$ or other halogen radicals (Alegre et al., 2000; Li et al., 2016; Martire et al., 2001; Wang et al., 2015).

One possible explanation for the increases in DBP yields observed during FAC + light treatment, even in the presence of added radical scavengers or under anoxic conditions, is that O_3 and radical species contribute to varying degrees to both degradation and generation of DBP precursors (De Vera et al., 2015; Mao et al., 2014), with precursor generation generally outweighing precursor degradation. Consequently, limiting O_3 formation does not prevent increases in DBP formation due to radical reactions (Li et al., 2016), and limiting $HO^\bullet$ and $Cl^\bullet$ levels does not prevent increases in DBP formation due to $O(^3P)$ and/or O_3 reactions (Mao et al., 2014; Riley and Mancy, 1978).

4. Conclusions

- Application of simulated and natural sunlight-driven FAC photolysis in SRNOM solutions and natural waters resulted in increased yields of regulated organic DBPs (THMs and HAAs), degradation of DOM chromophores and fluorophores, and decreases in average DOM MW due to degradation of higher MW humic substances to lower MW organic acids with minimal mineralization of DOC.
- Subjecting DOM-containing solutions to FAC + light treatment resulted in substantial changes in the ratios of differential absorbances at 280 and 340 nm (corresponding to carboxylic and phenolic DOM moieties), with preferential removal of the 340 nm band, indicating depletion of phenol groups relative to carboxylic groups in the bulk DOM.
- Taken together, these results indicate that FAC + light treatment results in enhanced degradation of UV-absorbing and fluorescent aromatic constituents (phenolic moieties in particular) of higher MW humic substances by photochemically-generated

oxidants including O_3 , $HO^\bullet$, and possibly $Cl^\bullet$, $ClO^\bullet$, $Cl_2^\bullet$, and $O(^3P)$. Oxidants are expected to participate in aromatic and aliphatic electron transfer, addition, and H-abstraction reactions, in addition to aromatic ring cleavage, resulting in formation of lower MW organic acid byproducts. This process likely results in enhanced formation of DBPs through (a) increased dark halogenation of DBP precursors derived from aromatic ring-cleavage and other DOM degradation pathways; (b) direct halogenation of DBP precursors by RHS such as $Cl^\bullet$, $Br^\bullet$, $BrCl^\bullet$, $Cl_2^\bullet$, or $ClO^\bullet$; or (c) a combination of the two. The fact that DBP formation during FAC only treatment subsequent to FAC + light treatment was only moderately higher (for HAAs) than during FAC only treatment suggests that direct halogenation by photochemically-generated RHS may contribute substantially to the enhanced DBP yields observed during sunlight-driven FAC photolysis. It is recommended that future investigations expand on these findings by utilizing model compounds representing various types of DOM constituent groups to evaluate the relative importance of reaction pathways involving ROS, RHS, and O_3 in driving DBP formation during solar FAC photolysis (and UV-driven FAC photolysis in general).

- Application of sunlight-driven FAC photolysis for disinfection is anticipated to lead to increased DBP formation, and will require careful attention to potential impacts on THM and HAA levels. However, because this process can enable inactivation of chlorine resistant pathogens (e.g., *Cryptosporidium* oocysts) at far lower CT_{FAC} values than chlorination alone, the increases in DBP formation inherent to FAC + light treatment may be offset by the ability to operate at significantly decreased CT_{FAC} . In addition, risks of increased DBP formation could be mitigated by limiting applications of sunlight-driven FAC photolysis to short-term (e.g., emergency) use and/or to appropriate source waters (e.g., those with low DOM and bromide levels, as observed here for treatment of two samples collected from natural surface water sources).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2018.09.022>.

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