**Ozone and chlorine reactions with dissolved organic matter -
assessment of oxidant-reactive moieties by optical measurements and
the electron donating capacities**

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Abstract

Oxidation processes are impacted by the type, concentration and reactivity of the dissolved organic matter (DOM). In this study, the reactions between various types of DOM (Suwannee River fulvic acid, Nordic Reservoir NOM and Pony Lake fulvic acid) and two oxidants (ozone and chlorine) were studied in the pH range 2-9 by using a combination of optical measurements and electron donating capacities.

The relationships between residual electron donating capacity (EDC) and residual absorbance showed a strong pH dependence for the ozone-DOM reactions with phenolic functional groups being the main reacting moieties. Relative EDC and absorbance abatements (UV_{254} or UV_{280}) were similar at pH 2. At pH 7 or 9, the relative abatement of EDC was more pronounced than for absorbance, which could be explained by the formation of UV-absorbing products such as benzoquinone from the transformation of phenolic moieties. An increase in fluorescence abatement with increasing pH was also observed during ozonation. The increase in fluorescence quantum yields could not be attributed to formation of benzoquinone, but related to a faster abatement of phenolic moieties relative to fluorophores with low ozone reactivity.

The overall $\cdot OH$ yields as a result of DOM-induced ozone consumption increased significantly with increasing pH, which could be related to the higher reactivity of phenolic moieties at higher pH. The $\cdot OH$ yields for SRFA and PLFA were proportional to the phenolic contents, whereas for NNOM, the $\cdot OH$ yield was about 30% higher.

During chlorination of DOM at pH 7 an efficient relative EDC abatement was observed whereas the relative absorbance abatement was much less pronounced. This is

due to the formation of chlorophenolic moieties, which exert a significant absorbance, and partly lose their electron donating capacity.

Pre-ozonation of SRFA leads to a decrease of chloroform and haloacetic acid formation, however, only after an threshold of $> \sim 50\%$ abatement of the EDC and under conditions which are not precursor limited. The decrease in chloroform and haloacetic acid formation after the threshold EDC abatement was proportional to the relative residual EDC.

Keywords: Dissolved organic matter, electron donating capacity, oxidant reactivity, ozone, chlorine, disinfection by-products

1. Introduction

1.1 Role and properties of DOM in natural and engineered aquatic systems

Dissolved organic matter (DOM) plays an important role in numerous natural and engineered aquatic processes. DOM consists of a mixture of heterogeneous compounds with a continuum of functional groups and molecular sizes (Leenheer and Croue 2003). DOM contains organic molecular structure with a wide size range, including humic substances, biopolymers, building blocks and low molecular weight organic acids (Huber et al. 2011, Leenheer and Croue 2003).

In water treatment, DOM is typically characterized by measurements of concentration (dissolved organic carbon, DOC) and/or optical properties (absorbance or fluorescence). Absorbance has been used as a surrogate for DOM concentration and as a process control parameter for the oxidation of organic contaminants in water and wastewater treatment (Gerrity et al. 2012, Wittmer et al. 2015). DOM is often characterized by the specific ultraviolet absorbance at 254 nm ($SUVA_{254}$, UV absorbance divided by the DOC), a surrogate for DOM aromaticity (Weishaar et al.

2003). Over the last years, the use of DOM fluorescence measurements has become more common. These measurements were used to quantify both DOM concentration and character in natural and engineered systems (Gerrity et al. 2012, Osburn et al. 2012, Stedmon et al. 2003).

1.2. Role and change of the DOM in oxidative water treatment processes

During oxidative processes (e.g., application of ozone or chlorine), DOM is the main sink for the added oxidants. Specific functional groups within the DOM (e.g. poly(phenols), amines, olefins, anilines, etc.) are susceptible to chemical modifications during exposure of the DOM to oxidants (Lee and von Gunten 2010). The reactivities and concentrations of such moieties in the DOM determine the extent of the DOM-oxidant interactions and their effects on the targeted oxidation/disinfection processes (Lee and von Gunten 2010).

Some understanding of the interactions between the oxidants and DOM can be gained by considering reaction rate constants between a specific oxidant and known DOM moieties. For example, the apparent second order rate constant for the reaction between ozone and phenol is on the order of $10^6 \text{ M}^{-1}\text{s}^{-1}$ at pH 7, whereas for chlorine (HOCl) it is $20 \text{ M}^{-1}\text{s}^{-1}$ (Deborde and von Gunten 2008, Gallard and von Gunten 2002). Given that the aromaticity (i.e., average proportion of aromatic moieties including phenolic moieties to the total carbon) varies between 12-22 % for DOM isolates, a phenol concentration of approximately $2 \times 10^{-6} \text{ M}$ can be estimated for a 1 mg C/L solution of SRFA. This suggests that an equimolar concentration of ozone will be consumed within seconds, whereas the HOCl consumption will take five hours.

Changes in selected physicochemical properties of DOM during its reaction between ozone or HOCl are well-characterized. For example, the overall absorbance

and fluorescence intensities decrease with increasing extent of chemical oxidation (Gerrity et al. 2012). Concomitantly, the reaction of the oxidants with DOM result in the formation of disinfection by-products (DBPs) (Lee et al. 2007, Mitch and Sedlak 2002, von Gunten 2003), and also changes in the redox properties of the DOM (Wenk et al. 2013). Depending on the oxidant applied, different types of DBPs can be formed. Primary products from the attack of phenolic by ozone are benzoquinones, catechols, muconic acids, etc. (Mvula and von Sonntag 2003, Ramseier and von Gunten 2009, Tentscher 2018), which can be further oxidized to aldehydes, ketones and carboxylic acids (Hammes et al. 2006). For chlorination, primary products from phenolic moieties are chlorophenols, which are then further transformed to trihalomethanes (e.g., chloroform) or haloacetic acids (Gallard and von Gunten 2002, Ge et al. 2014). In addition, both ozone and chlorine can react with amines, forming e.g., nitroso- and nitro-compounds or *N*-oxides or organic and inorganic halamines, respectively (de Vera et al. 2017b, Heeb et al. 2017, McCurry et al. 2016, von Sonntag and von Gunten 2012).

1.3 Characterizing the redox properties of the DOM and assessing DBPs formation

Recently, there has been a growing interest in the electrochemical properties of DOM in water treatment applications. A method based on mediated electrochemical oxidation employing ABTS^{•+} - the one-electron oxidation product of ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonicacid) – as an electron transfer mediator to facilitate electron transfer from oxidizable moieties in the DOM to the working electrode of the electrochemical cell (Aeschbacher et al. 2010). The outcome of this measurement is the so-called electron donating capacity (EDC). A further development of this method involved automation by implementing flow-injection analysis in which electron donation from the DOM to ABTS^{•+} under formation of ABTS was quantified chronoamperometrically in an electrochemical flow cell (Walpen et al. 2016). In

another study, EDC was measured employing size-exclusion chromatography for DOM size separation, followed by the same approach involving ABTS^{•+} for EDC quantification by a post-column reaction and spectrophotometric analysis of the decolourization of ABTS^{•+} to ABTS (Chon et al. 2015, Önnby et al. 2018).

EDC measurements allow for an assessment of the redox properties or the antioxidant capacity of the DOM (Aeschbacher et al. 2010). Known electron-donating moieties of the DOM include phenols such as mono- and poly-hydroxylated benzene rings, amines, aniline, sulfur or olefinic moieties. Previous work has shown that the EDC values of ten DOM isolates were positively correlated with their titrated phenol contents, strongly suggesting that phenolic moieties of the DOM are major contributors to the EDC of DOM samples (Aeschbacher et al. 2012).

Taken together, the extent of the oxidant consumption and the formation of DBPs from the oxidant-DOM reactions depend on the concentrations and types of the reactive moieties in DOM. Combined EDC and absorbance measurements have advanced the understanding of the DOM-ozone and the DOM-chlorine reactions (Wenk et al. 2013), including the effects on micropollutant abatement (Chon et al. 2015, de Vera et al. 2017a).

The main objective of this paper is to advance our understanding of the reactions between oxidants (ozone and chlorine) and DOM. To investigate changes in the DOM during oxidation, changes in EDC and optical properties (absorbance and fluorescence) were assessed at various pH values for dosage and kinetic experiments. Furthermore, the formation of hydroxyl radicals ($\cdot\text{OH}$) was investigated during ozonation of DOM. Finally, the formation of chloroform and chloroacetic acids without or with pre-ozonation followed by chlorination was measured and related to the abatement of the

140 EDC.

141 2. Material and methods

142 2.1. Chemicals, natural organic matter isolates, preparation of solutions

143 A list of the chemicals and standards used in this study is provided in Text S1, in
144 the supplementary data.

145 Model DOM isolates including Suwanee River fulvic acid (SRFA), Nordic
146 Reservoir NOM (NNOM) and Pony Lake fulvic acid (PLFA) were obtained from the
147 International Humic Substances Society (IHSS) (details are given in Table S1). The
148 type and composition of all solutions used in this study, including preparation details,
149 are provided in Text S2 and Table S2.

150 2.2 Oxidation experiments

151 Ozonation was performed as dosage experiments (50 mL) or kinetic experiments
152 (5 to 250 mL), in absence or in presence of 100 mM *t*-BuOH as a hydroxyl radical
153 ($\cdot\text{OH}$) scavenger (Staehelin and Hoigné 1985). Control experiments showed that the
154 added *t*-BuOH did not interfere with absorbance measurements at 254 nm nor with the
155 quantification of the EDC (Table S3).

156 For ozone dosage experiments, samples that had been ozonated were stored at
157 room temperature overnight to ensure complete ozone depletion. For kinetic
158 experiments, 5 mL samples were collected using a dispenser system (Hoigné and Bader
159 1994) and immediately quenched by various quenchers (see below) at pre-determined
160 reaction times up to 3000s. Samples corresponding to 5, 10 and 15s were obtained from
161 separate experiments performed in 15 mL glass vials with a 5 mL reaction volume and
162 direct quenching (see below).

Chlorine dosage experiments were performed with 40 mL samples. After chlorine addition, the samples were stored for 48h at room temperature for complete depletion of chlorine. The samples were stored in the dark to avoid photo-decomposition of chlorine (Nowell and Hoigné 1992).

In dosage experiments, specific ozone doses of 0 - 0.5 mmol O₃/mmol C or specific chlorine doses of 0 - 0.2 mmol HOCl/mmol C were applied. The specific oxidant doses lie within the typical range applied in water and wastewater treatment (Bourgin et al. 2018, Garcia-Villanova et al. 1997, Zimmermann et al. 2011). For some selected experiments, SRFA was pre-ozonated with higher specific ozone doses than above (0 - 2.0 mmol O₃/mmol C) to obtain an EDC abatement of $\leq 95\%$. Thereafter, the samples were treated with the above specific chlorine doses, to follow the conventional treatment step undertaken at water treatment plants with pre-ozonation and post-chlorination.

Kinetic ozone experiments were performed with a specific ozone dose of 0.25 mmol O₃/mmol C. Depending on the subsequent measurements (see sections 2.4.1 - 2.4.4), ozone in the kinetic experiments was quenched by either (i) indigo to quantify residual ozone, (ii) maleic acid to quantify the EDC, or (iii) sulfite to quench ozone to quantify $\cdot\text{OH}$ formation and to measure solution absorbance spectra (control measurements are shown in Table S3).

2.2.1 Quantification of the formation of $\cdot\text{OH}$ during ozone depletion

$\cdot\text{OH}$ is formed by various pathways during ozone decomposition in water (von Sonntag and von Gunten 2012). The use of *t*-BuOH as $\cdot\text{OH}$ quencher results in the formation of formaldehyde (Flyunt et al. 2003). Two moles of formaldehyde are formed from the reaction of one mole of $\cdot\text{OH}$ with *t*-BuOH (Flyunt et al. 2003).

2.2.2 Optical measurements

Absorbance spectra (200 to 600 nm) were measured on Uvikon 940 (Kontron Instruments) or Varian Cary 100 (Agilent Technologies) instruments in quartz cuvettes (1 and 5 cm path lengths). The spectra were collected at least two hours after addition of the oxidant (kinetic experiments) or after resting overnight (ozone) or 48h (chlorine), to ensure that the oxidants were completely consumed. Fluorescence absorbance was collected in duplicate with a Fluoromax-4 spectrofluorometer (Horiba, USA) for ozonated or non-ozonated samples. Fluorescence emission was collected between 300-700 nm at excitation wavelengths between 240-550 nm using a 0.25s integration time and a 5 nm bandpass. Spectra were corrected for inner filter effects and normalized to Raman area (at $\text{Ex}=350$ nm) in Matlab. Fluorescence quantum yields were calculated using quinine sulfate (in 0.05 M H_2SO_4) as a reference based on a previously reported method (Cawley et al. 2014). To confirm that measurements from ozone-dosed samples prepared in the two involved laboratories resulted in identical conditions, the respective absorbance spectra were compared. This comparison indicated good agreement between the experimental protocols of the two laboratories (Figure S1) allowing for comparison of EDC and fluorescence spectra collected in the first and second laboratory, respectively.

2.2.3 Quantification of the EDC by SEC-EDC

EDC was quantified following the method described in detail elsewhere (Chon et al. 2015, Önnby et al. 2018). In brief, the method consists of size exclusion chromatography (SEC) followed by a post-column reaction (PCR) of DOM with the radical cation of ABTS ($\text{ABTS}^{*\cdot+}$) as a chemical oxidant, which was pre-formed by oxidation of ABTS with chlorine (Pinkernell 2000). The SEC-EDC system leads to a

molecular size fractionation of DOM prior to its oxidation of electron-donating moieties in the DOM by ABTS^{•+}. The resulting reductive decolorization of ABTS^{•+} (absorbance maximum at 405 nm) to ABTS (no absorbance at 405 nm) is then quantified by monitoring absorbance at this wavelength using a spectrophotometric flow-through detector. A more detailed description of the method is given in Text S3 and in (Önnby et al. 2018).

2.2.4 Analytical methods

The concentration of formaldehyde was determined colorimetrically using the Hantzsch reaction (Nash 1953). The quantified samples were in the concentration range of 5-200 μM , with a quantification limit of 0.5 μM formaldehyde. The obtained molar absorption coefficient at 412 nm of formaldehyde was 7207 $\text{M}^{-1}\text{cm}^{-1}$. Reported concentrations were average values from triplicate measurements with a residual standard deviation (RSD) < 5%. The exact concentration of a commercial formaldehyde solution used as a calibration standard for the colorimetric method was determined by volumetric titration with sulfuric acid in a solution containing formaldehyde and sodium sulfite (Walker 1944).

Ozone depletion was followed by measuring the residual ozone concentration using the indigo method (Bader and Hoigné 1981). Briefly, a 2 mM indigo solution and a 0.02 M phosphate buffer reagent was added and diluted prior to use by ensuring that indigo was present in a stoichiometric excess (at least twofold) to ozone and measured at 600 nm in quartz cuvettes (1 and 5 cm path lengths).

Chloroform formed during reaction of DOM with HOCl was quantified by gas chromatography-mass spectrometry (GC-MS, GC-8000 Fisons) with head-space injection (Combi-PAL). Samples (5 mL) were filled in 10 mL head space vials, which

were pre-equilibrated at 80°C for 30 min prior to injection, following a previous protocol (Shah et al. 2015). Haloacetic acids (HAAs) were measured using a capillary ion chromatography (Thermo Dionex ICS-4000) coupled to tandem mass spectrometry (Thermo TSQ-Vantage) with an injection volume of 100 μ L (Shah et al. 2015). More details about the two analytical methods for chloroform and HAAs quantification, including method detection limits, measuring ranges and RSD values (%) are given in Text S4.

3. Results and discussion

3.1. Estimation of phenol concentrations

The aromaticity for the chosen DOM isolates was obtained from the IHSS (cf. Table S1) and a certain fraction of the aromatic units are phenolic moieties. In this study, we quantified the EDC abatement for DOM isolates treated with specific ozone doses between 0.05 and 0.15 mmol O_3 /mmol C. A linear response in EDC abatement (EDC/EDC_0) as a function of the specific ozone dose was observed (Figure S2). The calculated EDC abatement was then correlated with the previous relationship between EDC and phenol (Aeschbacher et al. 2012) according to Text S5.

Table 1 summarizes the phenol content determined from EDC measurements, the aromaticity obtained from the IHSS, respectively, and the nitrogen content for SRFA, NNOM and PLFA. The quantified phenol contents based on EDC measurements show a similar trend as the aromaticity from the IHSS. The quantified phenolic content for SRFA and PLFA were well correlated with the values for phenolic content given by IHSS (IHSS 2017). It is observed that the phenol content decreased in the order SRFA > NNOM > PLFA. Table 1 shows that the absolute EDC of PLFA is lower (2.43 mmol e^- /g C) compared to the EDC of SRFA or NNOM, respectively (5.98 and 4.16 mmol e^- /g

259 C) (Aeschbacher et al. 2012).

260 (Table 1)

261 3.2 pH dependence of the ozone consumption kinetics upon reaction with the three model

262 DOM isolates

263 Figure 1 shows the kinetics of the ozone depletion in solutions containing either
 264 SRFA, NNOM or PLFA as a function of pH in presence of *t*-BuOH to quench $\cdot\text{OH}$.
 265 Generally, the rates of the ozone depletion decreased with decreasing pH, which is a
 266 consequence of the lower reactivity of protonated organic moieties with ozone (von
 267 Sonntag and von Gunten 2012). At pH 2, ozone was still detectable after 3000s (roughly
 268 ~10% for SRFA, ~20% for NNOM and PLFA (overlapping data points) of the initially
 269 added ozone). For pH 3, less than 5% of the initially added ozone was detectable after
 270 3000s of reaction with SRFA and NNOM, whereas the ozone residual was still about
 271 20% of the initially added ozone for PLFA. At pH 7 or 9, ozone depletion was
 272 significantly faster. At pH 9, ozone was completely consumed within 60s of its addition
 273 to SRFA and NNOM solutions, respectively, and only 10% residual ozone was detected
 274 for PLFA. The pronounced decrease in ozone reactivity with increasing pH can be
 275 rationalized by DOM moieties that undergo acid-base speciation (e.g., phenols and/or
 276 amines). These are typically less or non-reactive in their neutral/protonated forms,
 277 which is the case at pH 2 (Lee and von Gunten 2010). For example, apparent second
 278 order rate constants for the reaction between ozone and phenol increases from 10^3 to 10^8
 279 $\text{M}^{-1}\text{s}^{-1}$ when the pH is increased from pH 2 to 9 (Lee and von Gunten 2010). For
 280 amines, the apparent second order rate constants are very low for the protonated species,
 281 whereas they are much higher (between 10^4 and $10^6 \text{M}^{-1}\text{s}^{-1}$) for neutral amines (Lee and
 282 von Gunten 2016, von Sonntag and von Gunten 2012).

Based on the higher phenolic/aromatic and the lower nitrogen proportion of SRFA and NNOM compared to PLFA (Table 1), we hypothesize that the observed increase in ozone depletion rate with increasing pH was due to the reaction with deprotonated phenolic moieties. In contrast, PLFA has lower phenol contents and more nitrogen-containing moieties such as amines, which are present in higher proportions (6.51 %N, Table 1) and might play a certain role for the pH-dependence of the slower observed ozone depletion kinetics in the PLFA experiments. To this end, it was demonstrated in a recent study that the nitrate formation from amine moieties in PLFA increased relative to the absorbance abatement (phenolic moieties) with increasing pH (Song et al. 2017). This finding indicated that there was a higher contribution of nitrogen-containing moieties to the ozone consumption in PLFA as compared to SRFA. Regardless of similar concentrations between phenol and amine moieties, phenolic moieties will always outcompete amines in the DOM-ozone interactions. However, due to the high amine reactivity at higher pH, it will be difficult to resolve the two individual effects kinetically in batch-type experiments with ozone.

(Figure 1)

3.3 Kinetics of EDC/EDC₀ abatement during oxidation

Figure S3 shows the kinetics of the relative EDC (EDC/EDC₀) abatement during ozonation of SRFA, NNOM and PLFA in the pH range 2 - 9. The decrease in EDC/EDC₀ during ozonation increased with increasing pH. These results suggest that EDC-active sites react more efficiently at a higher pH, which is in accordance with the faster ozone depletion discussed in section 3.2. Based on the correlation of EDC with DOM phenolic content, this result provides additional evidence for the importance of phenolic moieties in DOM in the consumption of ozone by DOM.

3.4. Kinetics of absorbance abatement during oxidation

Changes in absorbance spectra during ozonation of SRFA, NNOM and PLFA are shown in Figures S4 – S7 for experiments at pH 2, 3, 7 and 9, respectively. The largest absorbance changes were observed over the wavelength range 220-280 nm. Although experiments at all pHs showed a fast initial abatement in DOM absorbance, the abatement was strongly pH dependent. At pH 2 and 3, the absorbance decreases occurred over the entire reaction time of 3000s (Figures S4 and S5). At pH 7, the absorbance abatement is significant for the initial 100s, followed by a slower and gradual decrease until 1000s (Figure S6). For pH 9, the absorbance abatement occurred very rapidly after ozone addition, with no further decrease in absorbance at longer reaction times (Figure S7).

319 3.5 Relationships between changes in EDC and absorbance

320 Previous studies investigated the relationships between the relative abatements
321 of EDC and absorbance during DOM chemical oxidation only at circumneutral pH
322 (Chon et al. 2015, Önnby et al. 2018, Wenk et al. 2013). Figures 2a-d show the relative
323 abatement in both EDC and absorbances during ozonation of SRFA in the pH range 2-9.
324 Figures S8 and S9 show the analogous relationships for the same pH range for NNOM
325 and PLFA (absorbance at 254 nm) and for SRFA, NNOM and PLFA (absorbance at
326 280 nm), respectively. At low pH, ozonation resulted in comparable relative decreases
327 of EDC and absorbance (i.e., data close to the 1:1 line in Figures 2a-b). By comparison,
328 at high pH the relative EDC abatement increases compared to the relative absorbance
329 abatement (data to the left of the 1:1 line in Figures 2c-d).

The decrease in EDC/EDC_0 compared to the relative absorbance abatement with increasing pH may have resulted from a higher extent of benzoquinone formation from phenolic moieties at higher than lower pH (Mvula and von Sonntag 2003, Ramseier and von Gunten 2009, Tentscher and von Gunten 2017, Tentscher et al. 2018). These benzoquinone moieties in the DOM also absorb light at 254 nm and would therefore have led to a smaller decrease in the absorbance at 254 nm at high pH. The formation of benzoquinones would thus be consistent with the observed shifts in the correlations (EDC/EDC_0 vs A/A_0) towards smaller decreases in absorbance values in these plots. At lower pH, the yield of benzoquinones from the phenol-ozone reaction is smaller with a higher yield of ring-opening products such as acetic, formic and maleic acids with low UV absorbance (Ramseier and von Gunten 2009). Hence, ozonation of DOM at the low pH resulted in limited formation of UV-absorbing moieties and thus a comparable relative decrease of the absorbance (total aromatics) and EDC (phenols, a subset of the aromatic moieties). Consistent with this explanation, the data collected for SRFA, NNOM and PLFA at low pH fell close to the 1:1 lines in Figures 2, S8 and S9.

(Figure 2)

To further elucidate the reasons for the observed correlations between the relative abatements of EDC and absorbance, changes in absorbance spectra were investigated with phenol as a surrogate for phenolic moieties in the DOM. For these experiments, we did not quantify EDC for phenol as this low-molecular weight compound will not be detectable in the SEC-EDC set-up due to its small molecular size. Figures 3a-c show the changes in absorbance spectra for the reactions between ozone (52 μM) and phenol (34 μM) yielding a similar molar ozone:carbon ratio as in Figure 2 (0.25:1.0). Absorbance spectra for reaction times of 0 and 60s are shown (completion of the reaction) in Figure 3 for pH 2, 3 and 7. Figures 3b and 3c also include the spectra of 1,4-benzoquinone at pH 3 and pH 7 for comparison. The added 1,4-benzoquinone concentrations in Figures 3b and 3c are 10 μM for pH 3 and 21 μM for pH 7, respectively.

Figures 3a-c show that, as the pH increased, oxidation of phenol via ozone led to an enhanced formation of an absorbance peak centered at a maximum of about 252 nm. The good agreement with lambda max at 252 nm suggest that 1,4-benzoquinone was formed in these experiments, both at pH 3 and pH 7. This conclusion is supported by an earlier study which used HPLC analyses to demonstrate that the ozonation of phenols results in 1,4-benzoquinone formation (Ramseier and von Gunten 2009, Tentscher et al. 2018). Based on the above-mentioned concentrations of formed benzoquinone, the calculated yields relative to the initial phenol concentration were 17% at pH 3 and 40% at pH 7, which is comparable to previous findings (Mvula and von Sonntag 2003, Ramseier and von Gunten 2009, Tentscher et al. 2018).

In parallel with the development of an absorbance peak at 252 nm, the absorbance at 272 nm increased at pH 7, while it decreased at pH 3 during ozonation of phenol (compare Figures 3b-c). These results suggest that phenolic polymerization products are possibly formed during ozonation of phenol at pH 7 giving rise to the absorbance increase at 272 nm.

Overall, the absorbance at 254 nm increases during ozonation of phenol at all pH values and under the experimental conditions used herein. However, the increase was smaller at lower pH values. Because phenols are only a subset of chromophores in DOM, the results obtained from phenol ozonation can only be applied to the ozonation of DOM in a qualitative manner. Despite this limitation, the overall trend of the DOM experiments above, where an increased absorbance peak was formed at 254 nm at high pH due to formation of 1,4-benzoquinone from phenolic moieties in DOM, can partially be explained by the smaller formation of UV-absorbing moieties at lower pH. Overall, a deviation from the 1:1 correlation (Figures 2c-d) is partially caused by the formation of benzoquinone-type compounds, which still absorb light but are more electron deficient and hence, lead to an enhanced relative EDC abatement compared to the absorbance.

(Figure 3)

3.6 Changes of fluorescence of DOM during DOM ozonation

3.6.1 Changes in fluorescence intensity as a function of ozone dose and experimental pH

In addition to evaluating the absorbance, the changes in fluorescence were also considered. Fluorescence offers an additional tool to assess the contribution of different moieties of the DOM towards the observed reactivity with ozone. The fluorescence intensity of DOM has previously been shown to decrease with increased ozone dose

(Gerrity et al. 2012). As an example, oxidation of phenols and formation of benzoquinone should result in a decrease in fluorescence intensity due to the very weak fluorescence of benzoquinones (Ma et al. 2010). The decrease is explained by destruction of chromophoric (aromatic) moieties (Swietlik and Sikorska 2004). Figure S10 shows that both the relative fluorescence intensity and the relative absorbances for SRFA and PLFA decreased with an increasing specific ozone dose at pH 3, 7 and 9, respectively. Overall, the decrease in fluorescence was less pronounced compared to the loss in absorbance, indicating that light-absorbing moieties were more sensitive to ozone oxidation than fluorescent moieties (see below).

3.6.2 Changes in fluorescence quantum yields of DOM with increasing ozonation

The de-coupling of the absorbance and fluorescence responses to oxidation by ozone was further studied by measuring the fluorescence quantum yields (Φ_f). The Φ_f describes the probability of the excited singlet state within DOM to be deactivated through fluorescence, relative to non-radiative pathways (Lakowicz 2006). Φ_f was calculated as the integrated emission spectrum divided by the absorbance at a particular excitation wavelength (Cawley et al. 2014). The Φ_f were investigated for ozonated SRFA and PLFA in the pH range 3 - 9. Figure S11, shows how Φ_f generally increase continuously with specific ozone doses for SRFA and PLFA at all pH values. The extent of the observed Φ_f increase depends on both the type of DOM as well as the pH. In contrast to PLFA, an induction period was apparent for SRFA at pH 7 and 9 (but not at pH 3). The values for Φ_f did not significantly change compared to non-ozonated DOM up to a specific ozone dose of 0.05 mmol O_3 /mmol C.

Figures 4a and 4b show the relative changes in absorbance and Φ_f (at $\lambda_{ex} = 350$

nm, relative to samples without ozonation) for PLFA and SRFA as a function of the specific ozone dose or the residual EDC, respectively. For PLFA, absorbance and Φ_f respond immediately to changes in specific ozone doses (Figure 4a). For SRFA, the Φ_f increases more steadily as a function of the specific ozone dose or the relative EDC abatement (Figures 4a and b).

(Figure 4)

The increase in Φ_f with increasing ozone exposure seemingly contradicts the prediction based on current models of DOM photophysics (Sharpless and Blough 2014). Benzoquinones are known not to fluoresce, and it could be expected that a conversion of phenolic moieties to benzoquinones as a result of ozone-DOM reactions as discussed above, would lead to lower Φ_f . Additionally, considering the charge transfer (CT) model for fluorescence, the overall quantum yield would decrease due to the loss of electron donors (i.e., phenols), thereby reducing the abundance of CT bands. However, a recent study suggests that CT interactions are not the main photophysical mechanism within DOM, and therefore the observed results should be considered in the context of individual compounds (McKay et al. 2018).

The effect of ozone on both absorbance and fluorescence (i.e., decrease in intensity while observing an increase in Φ_f) can be explained as follows. Ozone treatment of the DOM resulted in the loss of both light absorbing and fluorescent moieties, including phenols. In the case of absorption, the abatement of these moieties still leaves residual absorbance from the transformation products, and the EDC is reduced more efficiently due to the conversion of phenols into non-electron donating moieties (see discussion above). The overall fluorescence intensity decreased as fluorescent moieties are removed by reaction with O_3 . The increase in Φ_f can be

explained by a model where absorbing moieties that are not fluorescing are degraded faster than fluorescing moieties, therefore the overall Φ_f values increase. For example, electron-poor aromatic moieties (e.g., but not limited to, hydroxy aromatic ketones, aldehydes, or acids) may not be abated efficiently by ozone under the chosen experimental conditions due to their low second-order rate constants in comparison to phenol (von Sonntag and von Gunten 2012). Fluorescence by these refractory components would be less “diluted” from absorbance by non-fluorescing chromophores that have reacted with ozone. Overall, this results in an increased Φ_f for higher specific ozone doses. These data indicate that a fraction of fluorophores within DOM are not very reactive to ozone, and the overall fraction of fluorescent moieties in DOM is lower than for absorbance.

3.7 OH radical formation from ozone-DOM interaction

Upon reaction of ozone with electron rich moieties of DOM (e.g., phenolic moieties, amines, etc.), $\cdot\text{OH}$ can be formed by direct or indirect electron transfer reactions to ozone (von Sonntag and von Gunten 2012). Table S4 summarizes published $\cdot\text{OH}$ yields for a range of compounds: the $\cdot\text{OH}$ yield (amount of $\cdot\text{OH}$ formed relative to consumed ozone) for e.g., both phenol and catechol was found to be 24% at pH 7 (Nöthe et al. 2009).

The cumulative $\cdot\text{OH}$ concentration was measured by formaldehyde formation during ozonation of SRFA, NNOM and PLFA in presence of *t*-BuOH as a $\cdot\text{OH}$ scavenger. Under these conditions, the stability of ozone is enhanced because chain reactions are suppressed (Staehelin and Hoigné 1985). Therefore, these measurements correspond to the primary $\cdot\text{OH}$ formation only and do not include chain reactions.

Figure 5 shows the cumulative $\cdot\text{OH}$ concentration as a function of time for

SRFA, NNOM, PLFA and phenol in the pH-range of 2-9 (data is shown for an ozone residual > 10% of initial ozone addition). In Figure S12, the cumulative $\cdot\text{OH}$ concentration is shown for longer reaction times. Generally, the cumulative $\cdot\text{OH}$ concentration increased during the first phase of the reaction, whereafter, it leveled off due to the depletion of the reactive moieties that lead directly to $\cdot\text{OH}$ formation. In absence of *t*-BuOH, re-formation of phenolic-type and other $\cdot\text{OH}$ -forming moieties could be expected by the reaction of $\cdot\text{OH}$ with aromatic sites (Nöthe et al. 2009). However, these reactions were suppressed under the applied experimental conditions.

Because the ozone depletion was slow both at pH 2 and 3, the consumption of the sites leading to $\cdot\text{OH}$ formation was slower and started to level off after 120s. Phenol was consumed in a relatively similar reaction time, faster at pH 3 than at pH 2. For pH 3, this leads to an earlier termination of the phenol-induced $\cdot\text{OH}$ formation (Figures 5a and b). At pH 7, the cumulative $\cdot\text{OH}$ concentration increased initially very sharply. The rate of depletion of the sites responsible for $\cdot\text{OH}$ formation decreased in the order phenol > SRFA > NNOM > PLFA (Figure 5c). At pH 9 the maximum cumulative $\cdot\text{OH}$ concentration was observed at 15s for both SRFA and NNOM, whereas for PLFA it gradually increased until 90s (Figure 5d).

The cumulative $\cdot\text{OH}$ formation can be compared with the ozone depletion kinetics in Figure 1: an initial drop in ozone depletion shown at 120s (pH 2 and 3) and at 90 and 15s (pH 7 and 9, respectively), corresponded to time points in Figure 5 where the cumulative $\cdot\text{OH}$ formation leveled off. These observations can be explained by the reactions between ozone and phenolic moieties consuming ozone instantly (Figure 1) and yielding $\cdot\text{OH}$ radicals (Figure 5).

(Figure 5)

Table 2 shows the $\cdot\text{OH}$ yields (maximum $\cdot\text{OH}$ concentration observed normalized to the ozone dose) as a function of the pH for SRFA, NNOM, PLFA and phenol, respectively and for a complete depletion of ozone. At pH 2, the $\cdot\text{OH}$ yields are 6.7%, 12.4% and 13.6% for SRFA, NNOM or PLFA, respectively. The yields observed at pH 3 (7.3%, 14.2%, 9.6% for SRFA, NNOM or PLFA, respectively) were all in reasonable agreement with the obtained yields for phenol at pH 2 and 3. At pH 7, the $\cdot\text{OH}$ yields were 27%, 30.5% or 21% for SRFA, NNOM or PLFA, respectively and at pH 9, they were about 33.7 and 38.6% for SRFA and NNOM, whereas for PLFA it was 28.5%. Hence, overall the $\cdot\text{OH}$ yields increase with increasing pH. This is in agreement with the higher $\cdot\text{OH}$ yields for phenol at pH 7 (37.5%) than at the lower pHs. Compared to a previous study the yields in this study were higher (compare 24% obtained before with 28% obtained in this study, Table S4) (Flyunt et al. 2003).

At pH 7 and 9, the observed $\cdot\text{OH}$ yields for NNOM, SRFA and PLFA were quite similar. The trend for these yields are similar to the estimated phenol content of the respective DOM isolate (Table 1). However, it could be expected that NNOM, which only has about 70% of the phenol content of SRFA (compare 2.05 (NNOM) with 2.86 mmol phenol/g C (SRFA), respectively, Table 1), should have a smaller $\cdot\text{OH}$ yield for the same ozonation conditions. In the case of PLFA (1.77 mmol phenol/g C), the $\cdot\text{OH}$ yield corresponded to about 80% of the $\cdot\text{OH}$ yield of SRFA. The relatively high $\cdot\text{OH}$ yield for PLFA could be due to the higher content of amine-containing moieties, which may also be important sources for an indirect $\cdot\text{OH}$ formation via a superoxide radical-induced pathway (Buffle and von Gunten 2006).

(Table 2)

Figure S13 shows a correlation between the relative EDC abatement and the cumulative $\cdot\text{OH}$ yields for SRFA, NNOM and PLFA in the pH range 2-9. It is shown that the $\cdot\text{OH}$ yields are within certain limits proportional to the relative EDC abatement for all DOM types.

In summary, the results show that the $\cdot\text{OH}$ yields from ozone-DOM interactions significantly increase with increasing pH. Since the $\cdot\text{OH}$ yields do not vary significantly with varying pH amines may partly explain this trend (Mvula and von Sonntag 2003).

3.8 Effect of chlorination on EDC abatement

3.8.1 Changes in EDC as a function of the specific chlorine doses

We determined the changes in EDC and absorbance (254 and 280 nm) of SRFA, NNOM and PLFA as a function of an increasing chlorine dose at pH 7 (Figure S14). For all DOM isolates, the relative abatement of EDC is significantly more enhanced compared to the loss in the relative absorbance in comparison to the ozonation

experiments (compare Figure S14 with Figure 2 and Figures S8-S9). This is consistent with previous findings (Wenk et al. 2013) and has been explained by the formation of chlorinated phenolic moieties, which still have a significant UV absorbance while being less redox active (Criquet et al. 2015, Deborde and von Gunten 2008, Wenk et al. 2013). To this end, Table S5 shows the molar absorption coefficients (ϵ) of the expected chlorinated reaction products (Gallard and von Gunten 2002, Lee and Morris 1962) at 254 or 280 nm, respectively, which were determined from the UV/Vis spectra in this study (Figure S15). Despite the unknown product distribution during chlorination, a strong absorbance can be expected, because most molar absorption coefficients (ϵ_{254} or $\epsilon_{280\text{nm}}$) are $>2000 \text{ M}^{-1}\text{cm}^{-1}$ (Table S5). Compared to phenols, chlorophenols react more slowly with chlorine to form non-absorbing products (Deborde and von Gunten 2008) and because chlorophenols have significant UV absorbances, the slopes in plots of the relative abatements of EDC versus UV absorbance are < -1 .

3.8.2 EDC abatement and correlation with chloroform formation

During chlorination, phenols and other activated aromatic moieties, such as resorcinol (Norwood et al. 1980, Rebenne et al. 1996, Rook 1977, Theruvathu et al. 2001), but also β -diketo acid type moieties and β -diketones (Dickenson et al. 2008) can serve as precursor for trihalomethanes (THMs, e.g., chloroform) formation. As discussed above, the same activated aromatic compounds such as hydroxybenzenes react readily with ozone (Hoigné and Bader 1983, von Sonntag and von Gunten 2012). As hydroxybenzenes (including phenol/resorcinol moieties) also play an important role for the EDC, the effect of EDC abatement on THM formation was assessed. To change the EDC, pre-ozonation experiments were performed to abate $\text{EDC} \leq 95\%$ in SRFA. Chloroform and HAAs were then measured after post-chlorination of these samples.

Figure 6 shows the chloroform formation during post-chlorination as a function of the relative EDC abatement. In most experiments (except 40 μM HOCl, Figure 6a), a pronounced decrease in chloroform formation, was observed only for the pre-ozonated samples with a relative EDC of 50%. Similar observations were also apparent for the formation of the haloacetic acids monochloroacetic acid (MCAA), dichloroacetic acid (DCAA) or trichloroacetic acid (TCAA) (Figure S16). Once an abatement of EDC of about 50% was reached, the CHCl_3 formation decreased. This threshold was reached earlier for a higher chlorine dose (40 μM) because under these conditions chloroform formation was precursor-limited and small changes in precursor concentrations led to a decrease. In contrast, for smaller chlorine doses ($\leq 25 \mu\text{M}$) this effect was no longer visible until a threshold EDC abatement was reached, because of the excess of precursors relative to chlorine. In agreement to the current observations, no effect on DBP formation (chloroform, TCAA and adsorbable organic chlorine) could be observed from a DBP formation potential test during chlorination, after 10-40% EDC abatement by ozone in a previous study (de Vera et al. 2017a). Therefore, the above-mentioned results might be explained by a low extent of precursor abatement during pre-ozonation for low relative EDC abatements.

The presence of *t*-BuOH during pre-ozonation blocks hydroxyl radical oxidation, but also leads to higher ozone exposures compared to the absence of a scavenger. The higher exposure may affect the chloroform formation during post-chlorination, as demonstrated in a previous study in which an identical ozone dose was applied with and without *t*-BuOH (De Vera et al. 2015). In contrast to these previous results, the results obtained in presence and absence of *t*-BuOH are very similar in the current study (Figures 6a and b). Based on these results, we conclude that $\cdot\text{OH}$ only has a limited effect on chloroform formation during post-chlorination. Similar conclusions

can be drawn from the formation of HAAs in presence and absence of *t*-BuOH (Figure S16).

(Figure 6)

4. Conclusions

Based on results from ozone-DOM interactions in the pH-range 2-9 and chlorine-DOM interactions at pH 7, it can be concluded that phenolic moieties play a dominant role for the DOM reactivity.

- The ozone depletion kinetics during ozonation of DOM was greatly affected by changes in degree of protonation: The ozone depletion kinetics increased in the pH-range 2-9, which could be explained by an important contribution of phenolic moieties in the DOM.
- The pH-dependence of EDC-absorbance correlations during (i) ozonation indicate a higher benzoquinone yield from the DOM oxidation at higher pH, which is in agreement with results from ozone-phenol reactions. (ii) For chlorine, a more efficient EDC abatement as compared to absorbance was observed and could be explained by formation of strongly UV-absorbing mono-, di- and/or trichlorophenols, which are not oxidized by the ABTS radical cation.
- The fluorescence intensity decreased during ozonation, while an increase in fluorescence quantum yield (Φ_f) was observed. The increase in Φ_f could not be explained by benzoquinone formation, it is suggested to take place due to the fast abatement of phenolic moieties relative to fluorophores with low ozone reactivity.
- During ozonation, increasing $\cdot\text{OH}$ yields were observed with increasing pH (2-

600 9), as a result of the higher amine reactivity at higher pH.

601 • The relative abatement of EDC by pre-ozonation did not influence the

602 chloroform/chloroacetic acids formation during post-chlorination for relative

603 EDC abatements $\leq \sim 50\%$ as long as the chloroform/chloroacetic acids

604 formation is not precursor limited. For EDC abatements $> 50\%$, the

605 chloroform/chloroacetic acids (from post-chlorination) decrease was strongly

606 correlated with the ozone-induced EDC abatement.

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Figure captions

Figure 1. Ozone depletion kinetics at an ozone:carbon molar ratio of 0.25:1 for SRFA, NNOM and PLFA at (a) pH 2, (b) pH 3, (c) pH 7, and (d) pH 9. Experimental conditions: 208 μM initial carbon concentration from the different model DOM isolates, 52 μM ozone, 100 mM *t*-BuOH and pH-adjusted H_2SO_4 (pH 2), 10 mM phosphate (pH 3, 7), 10 mM borate (pH 9). Samples were quenched with indigo at the specified reaction times to quantify the remaining concentration of ozone.

Figure 2. Relationship between the relative abatements of EDC and absorbance at 254 nm during the reaction of ozone with SRFA for a molar ozone:carbon ratio of 0.25:1 at (a) pH 2, (b) pH 3, (c) pH 7, and (d) pH 9. Samples were quenched with 0.1 mM sulfite (to measure changes in absorbance) or 1.0 mM maleic acid (to quantify EDC). Initial concentrations were 52 μM for ozone, 208 μM for carbon and 100 mM *t*-BuOH, respectively in pH-adjusted solutions with H_2SO_4 (pH 2), 10 mM phosphate (pH 3, 7), 10 mM borate (pH 9).

Figure 3. Absorbance spectra for phenol (34 μM) before (0 s) and after (60 s) reaction with ozone (52 μM) for an ozone:carbon molar ratio of 0.25:1 for (a) pH 2, (b) pH 3 and (c) pH 7 and with 100 mM *t*-BuOH. In (b) and (c) the spectra for 1,4-benzoquinone are also shown (with concentrations of (b) 10 μM , (c) 21 μM). The samples were quenched with 0.1 mM sulfite and adjusted for pH with H_2SO_4 (pH 2) or 10 mM phosphate (pH 3, 7). The absorbance at 254 nm is marked in the plots by a vertical line.

Figure 4. Relative changes in absorbance at 350 nm (values < 1) and the fluorescence quantum yield Φ_f/Φ_{f0} (values > 1), as a function of (a) the specific ozone dose, and (b) the relative residual EDC. The experimental data represent the average of duplicates and error bars represent propagated standard deviations. Experimental conditions: 100 mM *t*-BuOH, 10 mM phosphate buffer (pH 7), initial carbon concentration 208 μM .

Figure 5. Evolution of the cumulative hydroxyl radical ($\cdot\text{OH}$) concentrations (μM) for SRFA, NNOM, PLFA and phenol at an ozone:carbon molar ratio of 0.25:1. (a) pH 2, (b) pH 3, (c) pH 7 and (d) pH 9. Samples were quenched with 0.1 mM sulfite (1 mM sulfite for phenol). Experimental conditions: 208 μM initial carbon concentration, 100 mM *t*-BuOH, ozone dose = 52 μM , initial phenol concentration 34 μM , pH-adjusted with H_2SO_4 (pH 2), 10 mM phosphate (pH 3, 7) or 10 mM borate (pH 9).

Figure 6. Relative EDC abatements during pre-ozonation and the corresponding chloroform formation during post-chlorination of SRFA. Post-chlorination doses: 8, 16, 25 and 40 μM HOCl. (a) Presence of *t*-BuOH during pre-ozonation (closed circles), (b) absence of *t*-BuOH (open circles). Experimental conditions: DOC concentration = 208 μM , 10 mM phosphate buffer (pH=7), 100 mM *t*-BuOH. Data on EDC abatement are presented in Table S6.

Tables

Table 1. Phenol or aromaticity content (weight %) from EDC measurements^a and IHSS^b, respectively. The ratio between phenol and the aromaticity, the absolute EDC (mmol e⁻/g C) and the nitrogen and carbon content^b (weight %) are also shown.

	SRFA	NNOM	PLFA
Phenol, %^a	26.9±6.72	19.3±3.57	16.7±2.29
Phenol, mmol phenol/g C^b	2.86±0.71	2.05±0.38	1.77±0.24
Aromaticity, %^c	22.0	19.0	12.0
(Phenol/aromaticity)	1.22	1.01	1.39
EDC, mmol e⁻/g C^d	5.98	4.16	2.43
C, %^e	52.3	53.2	52.5
N, %^e	1.17	1.10	6.51

^aPhenol content from EDC measurements was calculated by using the approach from (Aeschbacher et al. 2012), details on calculations are found in Text S5), ^bPhenol content from the phenol estimates from the EDC measurements in this study, ^cdetermined by ¹³C-NMR estimates of carbon distribution and obtained from IHSS: www.humicsubstances.org, ^dEDC values recalculated from (Aeschbacher et al. 2012), ^ecarbon and nitrogen content from elemental composition in % (w/w) of a dry, ash-free sample, elemental composition obtained from IHSS: www.humicsubstances.org.

Table 2. [•]OH yields from the reactions of SRFA, NNOM, PLFA or phenol with ozone in the pH range 2-9 at an ozone:carbon molar ratio of 0.25:1.0. Initial carbon concentration 208 μM, ozone dose 52 μM, and in presence of 100 mM *t*-BuOH. The presented values are averaged for triplicate measurements and the standard deviations are rounded off to one significant digit.

	[•] OH yield, (%) ^a			
	pH 2	pH 3	pH 7	pH 9
SRFA	6.7±0.8	7.3±0.4	27.0±1.2	33.7±1.5
NNOM	12.4±1.4	14.2±1.5	30.5±0.9	38.6±0.7
PLFA	13.6±0.4	9.6±1.1	21.0±0.1	28.5±0.3
Phenol	6.6±0.0	6.6±0.0	37.5±0.1	na ^b

^aOH radical yield normalized to the ozone dose, ^bna: not applicable.

Absorbance in 1 cm

EDC/EDC₀

Highlights

- Ozone (O_3)- and chlorine-DOM reactions were assessed in the pH range 2-9
- For O_3 , the relationship between EDC and absorbance is pH dependent
- For O_3 , benzoquinone formation explained low absorbance/high EDC loss at pH>7
- For chlorine, UV-absorbing chlorophenols were formed while EDC decreased
- $CHCl_3$ formation during chlorination of DOM decreased for > ~50% EDC abatement