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1 **Manuscript**

2 **Chemical oxidation of dissolved organic matter by chlorine dioxide,**
3 **chlorine, and ozone: Effects on its optical and antioxidant properties**

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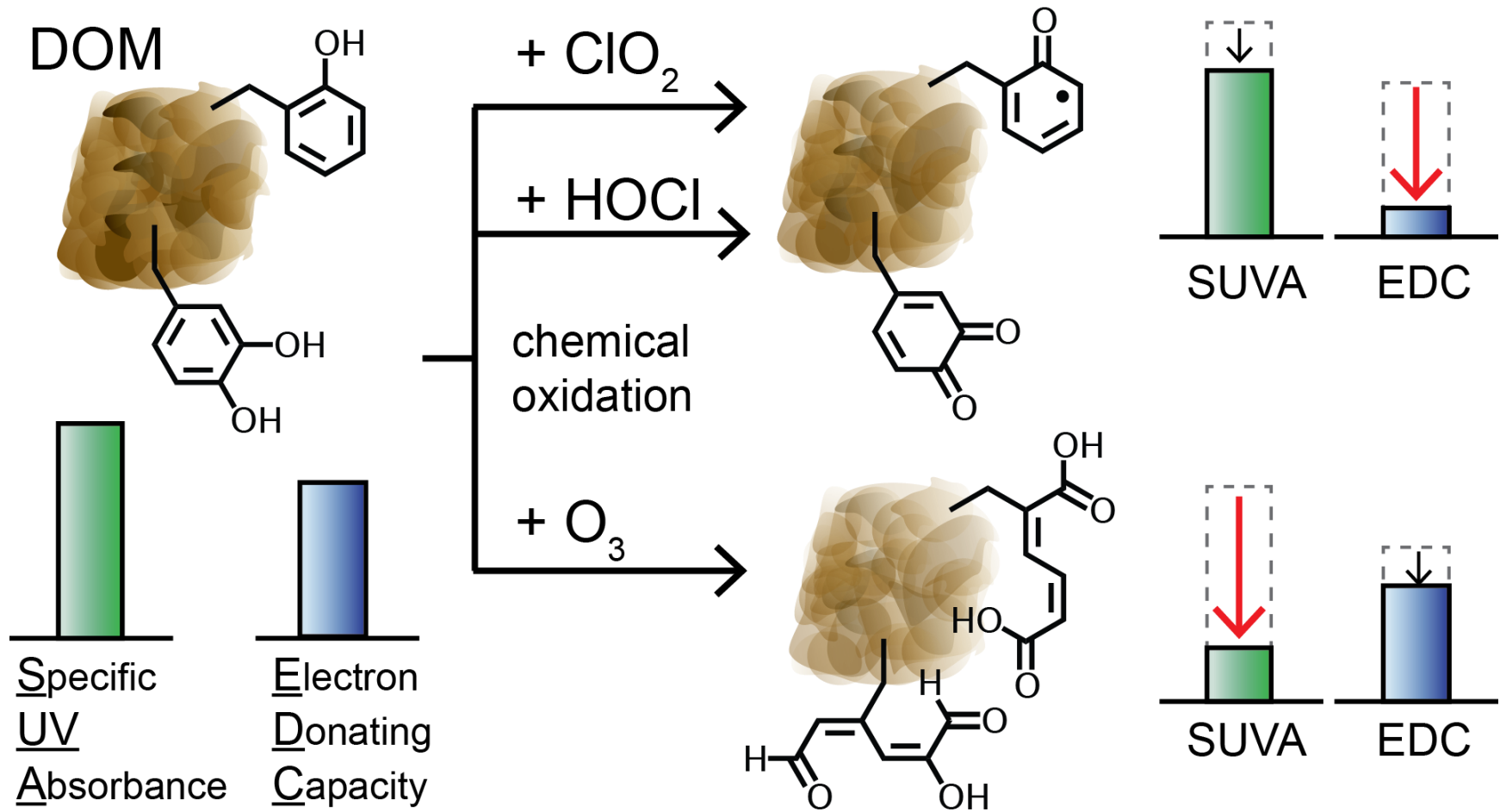
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TOC Art

34 **Abstract**

35 In water treatment dissolved organic matter (DOM) is typically the major sink for
36 chemical oxidants. The resulting changes in DOM, such as its optical properties have
37 been measured to follow the oxidation processes. However, such measurements contain
38 only limited information on the changes in the oxidation states of and the reactive
39 moieties in the DOM. In this study, we used mediated electrochemical oxidation to
40 quantify changes in the electron donating capacities (EDCs), and hence the redox states,
41 of three different types of DOM during oxidation with chlorine dioxide (ClO_2), chlorine
42 (as HOCl/OCl^-), and ozone (O_3). Treatment with ClO_2 and HOCl resulted in comparable
43 and prominent decreases in EDCs, while the UV absorbances of the DOM decreased only
44 slightly. Conversely, ozonation resulted in only small decreases of the EDCs but
45 pronounced absorbance losses of the DOM. These results suggest that ClO_2 and HOCl
46 primarily reacted as oxidants by accepting electrons from electron-rich phenolic and
47 hydroquinone moieties in the DOM, while O_3 reacted via electrophilic addition to
48 aromatic moieties, followed by ring cleavage. This study highlights the potential of
49 combined EDC-UV measurements to monitor chemical oxidation of DOM, to assess the
50 nature of the reactive moieties and to study the underlying reaction pathways.

51

52 **Introduction**

53 Drinking water and wastewater treatment facilities often have a chemical oxidation
54 step for disinfection, the removal of organic micropollutants, color removal and taste and
55 odor control. Among the most commonly used oxidants are chlorine dioxide (ClO_2),
56 chlorine (as hypochlorous acid, HOCl and OCl^-), and ozone (O_3).¹ For a number of

57 reasons, the efficiency of the oxidation step and the quality of the treated water largely
58 depend on the reaction of the chemical oxidant with dissolved organic matter (DOM).
59 First, DOM is a major contributor to drinking water color, which negatively affects the
60 acceptance of the water among consumers.² Second, the reaction of DOM with the
61 chemical oxidants accelerates their consumption and, thus, may reduce the efficiency of
62 the oxidation step for disinfection and micropollutant oxidation.^{3,4} Third, the reaction of
63 the oxidants with DOM may result in the formation of potentially harmful
64 disinfection/oxidation by-products.⁵⁻⁷ Fourth, chemical DOM oxidation results in the
65 generation of low molecular weight assimilable organic carbon (AOC)^{8,9}. Following the
66 oxidation step, the AOC needs to be removed by biological filtration to improve the
67 biological stability of drinking waters.^{4,10,11} For these reasons, information on the DOM
68 concentration and its reactivity is indispensable to find the appropriate dose of an oxidant
69 to meet the various requirements on oxidative water treatment processes and to avoid
70 underperformance, higher costs, and undesired by-product formation during the oxidation
71 step.

72 As a consequence, there is considerable interest in simple and readily measurable
73 parameters that provide information on the concentration and reactivity of the DOM in
74 the water.^{12,13} Two commonly measured parameters are the dissolved organic carbon
75 (DOC) content, which captures the concentration of DOM, and the specific UV
76 absorbance of the water at the wavelength of 254 nm (SUVA₂₅₄, expressed in L mgC⁻¹ m⁻¹)
77 ¹), which is a proxy for DOM aromaticity.¹⁴ Previous work showed that both the
78 consumption of chemical oxidants by DOM and the occurrence of some
79 disinfection/oxidation by-products are positively correlated to SUVA₂₅₄.¹⁵⁻¹⁹ These

80 correlations suggest activated aromatic moieties as major oxidizable functional groups in
81 DOM, consistent with the high reactivity of low-molecular weight activated aromatic
82 moieties, including phenols, methoxybenzenes and anilines, with ClO_2 , chlorine, and
83 O_3 .²⁰⁻²⁹ However, despite the positive correlations with chemical oxidant consumption,
84 SUVA_{254} alone was found to be a relatively poor predictor of DOM reactivity and
85 disinfection byproduct formation with chlorine.^{14,30} Other methods that have been used to
86 determine the concentration and reactivity of oxidizable moieties in DOM are difficult to
87 adapt for routine water analysis or provide only indirect information on the redox states
88 of DOM.³¹⁻³⁷ Therefore, an analytical method is desirable that allows for a direct
89 quantification of changes in DOM oxidation states caused by reaction with chemical
90 oxidants.³⁸

91 Mediated electrochemical oxidation (MEO), an analytical technique recently
92 developed in our research group, fulfills these requirements. MEO allows for a fast and
93 reliable quantification of the electron donating capacities (EDC) (i.e., the number of
94 electrons that are donated by a given amount of DOM) of dilute DOM samples in
95 electrochemical cells with well-controlled pH and E_h conditions.^{39,40} We previously
96 demonstrated that MEO quantifies activated phenolic moieties in DOM: EDC values of a
97 set of chemically diverse humic substances (HS) were positively correlated with their
98 titrated phenol contents and showed dependencies on E_h and pH comparable to those of
99 low molecular weight phenols and hydroquinones.⁴⁰ We expect that chemical oxidants
100 oxidize these activated phenolic moieties in DOM, resulting in decreasing EDC values of
101 the DOM during treatment. MEO may therefore be a powerful technique to quantify

102 DOM reactivity with chemical oxidants and to directly monitor changes in DOM
103 oxidation states during chemical oxidation in water treatment.

104 The goal of this study was to explore the potential of combined MEO and UV-
105 visible absorbance measurements to selectively quantify the oxidation states of DOM
106 during chemical oxidation and to elucidate the underlying oxidant-dependent reaction
107 pathways. We measured the UV-vis absorbance spectra and the EDC values of three HS
108 (Suwannee River Humic and Fulvic Acids (SRHA and SRFA) and Pony Lake Fulvic
109 Acid (PLFA)) during dose-dependent treatment with ClO₂, chlorine, and O₃. HS, in
110 general, make up the major fraction of DOM. We specifically chose SRHA, SRFA, and
111 PLFA because these materials are commercially available and have been used in previous
112 oxidation studies,^{18,41} and their key physicochemical properties are known. Furthermore,
113 SRHA/FA and PLFA represent allochthonous and autochthonous aquatic HS with
114 terrestrial higher plant-derived and with microbially-derived precursor materials,
115 respectively. This study addresses fundamental questions on the changes in DOM
116 antioxidant properties and reactivities during chemical oxidation, and, in the implication
117 section, highlights the potential of combining MEO and SUVA₂₅₄ measurements to
118 monitor chemical oxidant demand in water treatment facilities.

119 **Materials and Methods**

120 **Chemicals.** All chemicals were from commercial sources and used as received:
121 *tert*-butanol (t-BuOH) (≥99.7%), 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid)
122 diammonium salt (ABTS) (>99%), potassium peroxodisulfate (≥99%), sodium chlorite
123 (NaClO₂) (puriss. p.a. 80%), sodium chlorate (NaClO₃) (≥99%), ortho-phosphoric acid
124 (85%), sodium dihydrogen phosphate dihydrate (≥99%), disodium hydrogen phosphate

125 dodecahydrate ($\geq 98.0\%$) and hypochlorite solution 6-14% were from Sigma-Aldrich,
126 sodium dihydrogen phosphate monohydrate (99–102%) was from Merck.

127 **Humic substances.** Suwannee River Humic Acid Standard II (SRHA; catalogue
128 number: 2S101H), Suwannee River Fulvic Acid Standard II (SRFA; 2S101F), and Pony
129 Lake Fulvic Acid Reference (PLFA; 1R109F) were obtained from the International
130 Humic Substances Society (IHSS, St. Paul, MN) and used as received. Selected
131 physicochemical properties of the HS, including elemental compositions, aromaticities
132 and phenol contents, are provided in **Table S1** in the Supporting Information.

133 **Preparation of aqueous solutions.** Aqueous solutions were prepared using
134 deionized water either from Milli-Q (Millipore) or Barnsteadt water purification systems.
135 HS stock solutions (100 mg C L^{-1}) were prepared in 5 mM phosphate buffer (pH 8) or in
136 deionized water. The DOC of the HS stock solutions was determined after 25-fold
137 dilution on a Shimadzu V-CPH TOC analyzer (Kyoto, Japan) and used to calculate
138 SUVA_{254} and carbon-normalized EDC values.

139 Chlorine dioxide (ClO_2) stock solutions ($\sim 10 \text{ mM}$) were produced by mixing
140 potassium peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$, 2 g in 50 mL water) with sodium chlorite (NaClO_2 , 4
141 g in 50 mL).⁴² The stock solution of chlorine (Cl_2 ; $\sim 10 \text{ mM}$) was prepared by diluting a
142 sodium hypochlorite solution with water. Ozone (O_3) stock solutions (~ 1.3 to 1.5 mM)
143 were prepared by sparging ozone gas through water cooled in an ice bath.⁴³ The O_3 gas
144 was formed from pure oxygen with an Apaco CMG 3-3 ozone generator (Grellingen,
145 Switzerland). The exact concentrations of oxidants in the stock solutions were quantified
146 spectrophotometrically using molar absorption coefficients of $\varepsilon = 1200 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda =$

147 359 nm for ClO_2 ,⁴⁴ $\epsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 290 \text{ nm}$ for chlorine (as ClO^-),⁴⁵ and $\epsilon = 3000$
148 $\text{M}^{-1} \text{ cm}^{-1}$ at $\lambda = 258 \text{ nm}$ for ozone.⁴⁶

149 **ClO_2 , chlorine, and O_3 oxidation of DOM.** Oxidation experiments were carried
150 out in a series of identical glass reaction vessels (50 or 100 mL) (Schott, Germany). The
151 vessels contained either DOM solutions (nominal concentrations of $0.83 \text{ mmol C L}^{-1}$ (=10
152 mg C L^{-1}) after reagent mixing) or DOM-free blank solutions at pH 7 (50 mM phosphate
153 buffer). Oxidant stock solutions were added to the vessels under vigorous mixing on a
154 magnetic stirrer plate. The employed oxidant doses were in the ranges of 0–0.36 mmol
155 $\text{ClO}_2/\text{mmol C}$, 0–0.85 mmol chlorine/mmol C, and 0–1.12 mmol $\text{O}_3/\text{mmol C}$, which
156 cover the ranges commonly used for water treatment.^{28,47,48} Ozonation experiments were
157 performed in the presence (5 mM) and absence of t-BuOH as a scavenger for formed
158 hydroxyl radicals ($\bullet\text{OH}$). After oxidant addition, the vessels were closed, removed from
159 the stirrer and stored at 22°C for 12h for chlorine dioxide, 3d for chlorine, and 2h for
160 ozone. Subsequently, un-reacted ClO_2 and O_3 were removed from the solution by gently
161 purging with helium for 20 min. In selected experiments, residual chlorine (max. $0.5 \mu\text{M}$)
162 was measured using the DPD colorimetric method.⁴² The ozone exposure in the DOM-
163 containing systems in the presence and absence of t-BuOH was measured according to
164 previously described methods.^{49,50} Control experiments in which t-BuOH was added to
165 the solutions after depletion of ozone showed that t-BuOH did not affect UV-visible
166 absorption and EDC measurements.

167 **UV/visible light absorbance measurements.** Absorbance spectra of untreated and
168 oxidized HS were collected on Uvikon 940 (Kontron Instruments) or Varian Cary 100
169 (Agilent Technologies) spectrophotometers in quartz glass cuvettes (Hellma) (10 or 100

170 mm path lengths). All sample spectra were corrected for the spectrum of the HS-free
 171 phosphate buffer (pH 7). The carbon-specific absorption coefficients of untreated and
 172 treated HS, $a(\lambda)$ [L / (mg C · m)], were calculated according to eq. 1, where $A(\lambda)$ is the
 173 sample absorption at a given wavelength λ , b [m] is the path length, and C_{HS} [mg C / L] is
 174 the organic carbon concentration of the untreated HS.

$$175 \quad a(\lambda) = \frac{A(\lambda)}{b \times C_{\text{HS}}} \quad \text{Eq. 1}$$

176 The values $a(254 \text{ nm})$ and $a(280 \text{ nm})$ are referred to as SUVA_{254} and SUVA_{280} ,
 177 respectively.. The spectral slope coefficients of the HS absorbance spectra, S [1/nm],
 178 were obtained by nonlinear least-square fitting of DOM absorption data from $\lambda = 300$ to
 179 600 nm with a single exponential decay function,⁵¹ where $a(\lambda_{\text{ref}})$ is the specific absorption
 180 coefficient at the reference wavelength of $\lambda_{\text{ref}} = 350 \text{ nm}$.⁵²

$$181 \quad a(\lambda) = a(\lambda_{\text{ref}}) \times \exp\left\{-S \times (\lambda - \lambda_{\text{ref}})\right\} \quad \text{Eq. 2}$$

182 The parameter S describes the steepness of DOM absorbance spectra on a logarithmic
 183 scale: The relative decrease in absorbance with increasing wavelength becomes steeper as
 184 S increases. Changes in the spectral slopes were also determined over narrower
 185 wavelength ranges (i.e., from 275-295 nm, $S_{275-295}$, and from 350-385 nm, $S_{350-385}$)
 186 following the approach suggested by Helms and coworkers.⁵³ Data fitting and
 187 integrations were performed using Origin 8.0 software (OriginLab).

188 **Quantification of electron donating capacities.** EDC values of untreated and
 189 oxidant-treated HS solutions were quantified by MEO using 2,2'-azino-bis(3-

190 ethylbenzthiazoline-6-sulfonic acid) (ABTS) as electron transfer mediator.^{39,40} MEO
191 measurements were conducted in an electrochemical cell containing a reticulated vitreous
192 carbon working electrode (WE), a Pt counter electrode, and an Ag/AgCl reference
193 electrode. The electrochemical cells were first filled with 60-65 mL of buffer solution
194 (0.1 M KCl, 0.1 M phosphate, pH 7) and the WE was polarized to an oxidizing potential
195 of $E_h = +0.725$ V vs. the Standard Hydrogen Electrode (SHE), controlled by a potentiostat
196 (either an Autolab PG302 (EcoChemie B.V.) or a 630C instrument (CH Instruments)). A
197 volume of 2 mL of an aqueous ABTS solution (5 mM) was added to the cell, resulting in
198 an oxidative current peak due to the oxidation of ABTS to its radical cation $ABTS^{*\cdot+}$
199 (standard reduction potential $E_h^0(ABTS^{*\cdot+}/ABTS) = 0.68$ V vs. SHE⁵⁴). Upon attainment
200 of redox equilibrium between $ABTS^{*\cdot+}/ABTS$ and the WE (and hence stable current
201 readings), HS samples (5-7 mL) were successively spiked to the cell. Oxidation of
202 electron donating moieties in the added HS by $ABTS^{*\cdot+}$ resulted in the formation of
203 reduced ABTS, which was subsequently re-oxidized at the WE to $ABTS^{*\cdot+}$ to re-establish
204 redox equilibrium. The resulting oxidative current peak was integrated to yield the EDC
205 values of the added HS:

$$206 \quad EDC = \frac{\int_0^t I dt}{F m_{HS}} \quad \text{Eq. 3}$$

207 where I [A] is the baseline-corrected current and F ($=96485$ s A/mol_e⁻) is the
208 Faraday constant, and m_{HS} [mg_C or mmol_C] is the mass/amount of HS analyzed. Most HS
209 samples were analyzed in triplicates and some in duplicates with $t = 50$ min between
210 replicate analysis to ensure baseline-separation of individual current peaks.

211 **Results and Discussion**

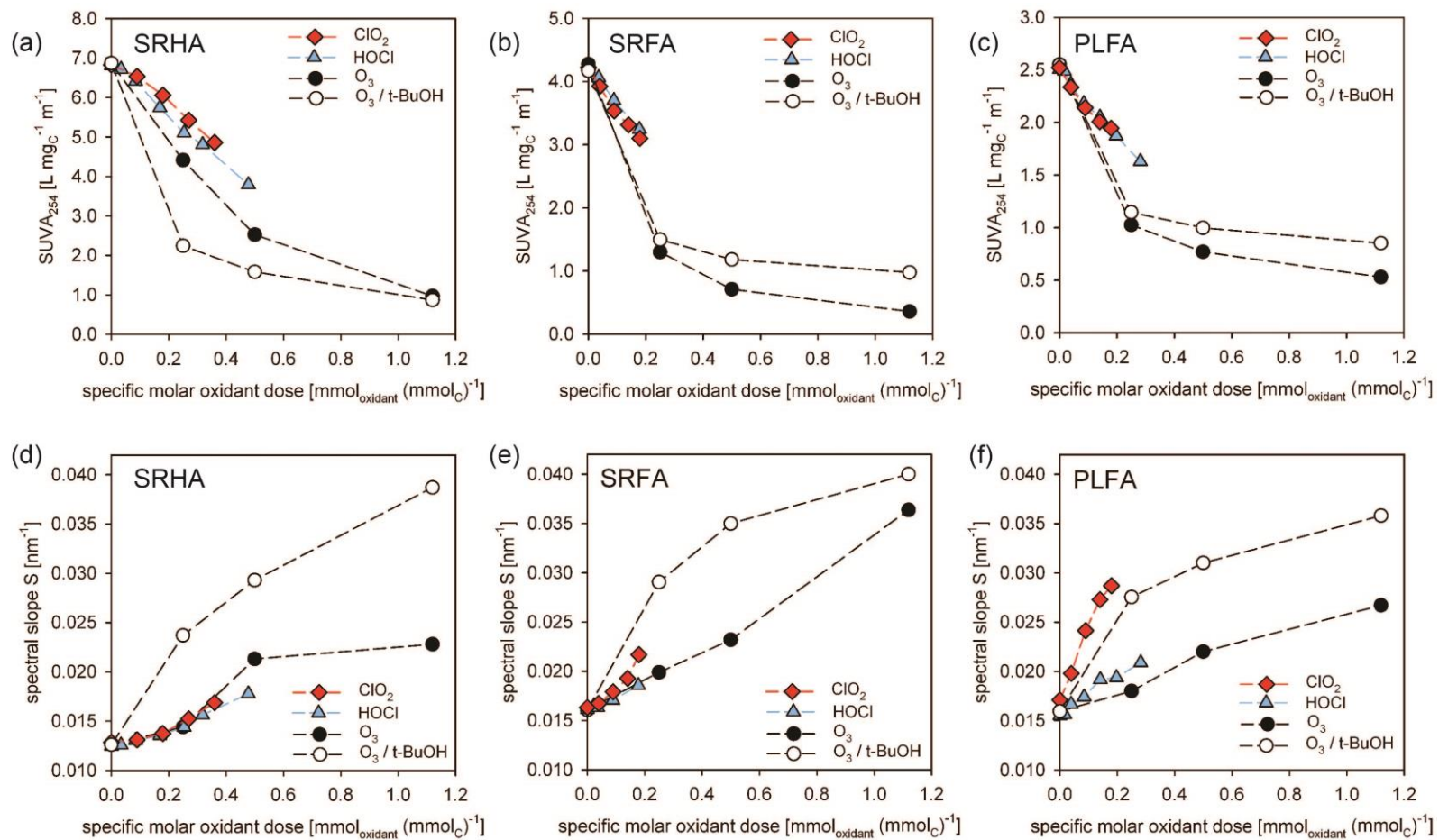
212 *Effects of oxidant treatments on DOM optical properties.* The specific absorption
213 coefficients of the untreated samples decreased in the order SRHA > SRFA > PLFA over
214 the entire measured wavelength range from 220 to 600 nm (**Figures S1** and **S2**). The
215 trend in the absorption coefficients follows the decrease in HS aromaticity⁵⁵ from 31%
216 for SRHA to 22% for SRFA and 12% for PLFA (**Table S1**).⁵⁶ The absorbance spectrum
217 of untreated SRHA extended further into the red than the spectra of both SRFA and
218 PLFA, which is reflected by the smaller *S* values for SRHA than for SRFA and PLFA.
219 Longer wavelength absorbance of HS has been ascribed to charge transfer complexes
220 between electron donor and acceptor pairs in HS,^{55,57,58} which may be more abundant in
221 HA than FA.

222 Treatment of the HS with all oxidants resulted in decreasing specific absorption
223 coefficients at all collected wavelengths (**Figures 1a-c**) and increasing *S* values (**Figure**
224 **1d-f**) with increasing oxidant doses, consistent with previous reports.^{8,37,59,60} The
225 absorbance spectra, the differential spectra, and the spectral slopes $S_{275-295}$ and $S_{350-385}$ of
226 untreated and oxidant-treated HS are shown in **Figures S1** to **S5**. Overall, the decreases
227 in the specific absorption coefficients suggest a decrease in aromaticity of the treated HS.
228 The increase in *S* values with increasing oxidant dose indicates that moieties/complexes
229 absorbing at longer wavelengths were preferentially removed and/or transformed into
230 shorter wavelength-absorbing components. The increase in *S* and $S_{275-295}$ values with
231 increasing oxidant doses may also reflect decreases in the average molecular weights of
232 the DOM upon reaction with the chemical oxidants, as detailed in the Supporting
233 Information. Consistent with previous observations,^{30,61} the differential spectra for HOCl

234 treated HS show a local maximum in absorption loss at around 270-272 nm, indicating a
235 selective removal of chromophores in this wavelength region by reaction with chlorine. A
236 similar maximum loss in absorbance around 270 nm was also observed for ClO₂-treated
237 PLFA. This feature was absent from the differential spectra of ClO₂-treated SRHA and
238 SRFA as well as of the O₃-treated SRHA, SRFA, and PLFA both in absence and presence
239 of t-BuOH.

240 A detailed analysis of the absorbance and differential absorbance spectra revealed
241 that ClO₂ and HOCl treatments had different effects on DOM optical properties than the
242 O₃ treatments. The SUVA₂₅₄ and SUVA₂₈₀ values of all three HS decreased linearly with
243 increasing doses of ClO₂ and HOCl and followed similar dose-dependencies for the two
244 oxidants (**Figures 1a-c** and **Figure S6**, respectively). ClO₂ and HOCl treatment of SRHA
245 and SRFA also resulted in comparable increases in *S* with increasing oxidant doses, while
246 PLFA showed larger increases in *S* upon treatment with ClO₂ than HOCl at the same
247 specific molar oxidant doses (**Figure 1d-f**). In comparison to the ClO₂ and HOCl
248 treatments, ozonation resulted in much larger decreases in the specific absorption
249 coefficients of the HS, both in the absence and presence of t-BuOH (**Figures 1a-c** and
250 **S6d-f**). The larger decreases in SUVA₂₅₄ and SUVA₂₈₀ upon treatment with O₃ than ClO₂
251 and HOCl at the same specific molar oxidant doses demonstrates that UV-light absorbing
252 aromatic moieties in the HS were more efficiently removed (or transformed to less
253 efficiently absorbing moieties) by O₃ than by both ClO₂ and HOCl. Note that narrower
254 dose ranges were used for ClO₂ and HOCl than for O₃ based on the effects of the three
255 oxidants on the antioxidant properties of the HS, as detailed below.

256 Ozonation in the presence of t-BuOH resulted in larger losses in HS absorbance at
257 wavelengths > 315 nm and larger increases in *S* than in the absence of t-BuOH. These
258 effects of t-BuOH can be ascribed to two factors. First, t-BuOH scavenges •OH which are
259 formed by DOM–ozone reactions and which catalytically degrade O₃.^{16,62} Quenching of
260 •OH by t-BuOH therefore enhanced O₃ lifetimes and, hence, resulted in higher O₃
261 exposures of the HS. Enhanced O₃ exposure in the presence compared to the absence of t-
262 BuOH was verified experimentally with PLFA solutions (see **Figures S3, S4**). Second,
263 by scavenging •OH, t-BuOH shifted the overall oxidation pathway from unselective,
264 diffusion-controlled •OH additions, •H abstraction (and electron transfer reactions),⁶² to
265 more selective, direct reactions of O₃ with moieties such as olefins, activated aromatics
266 and amines in the DOM.⁶² The presence of t-BuOH therefore enhanced O₃-reaction
267 induced cleavage of light absorbing olefinic and aromatic systems,⁶³ resulting in larger
268 changes in HS optical properties than in the absence of t-BuOH.



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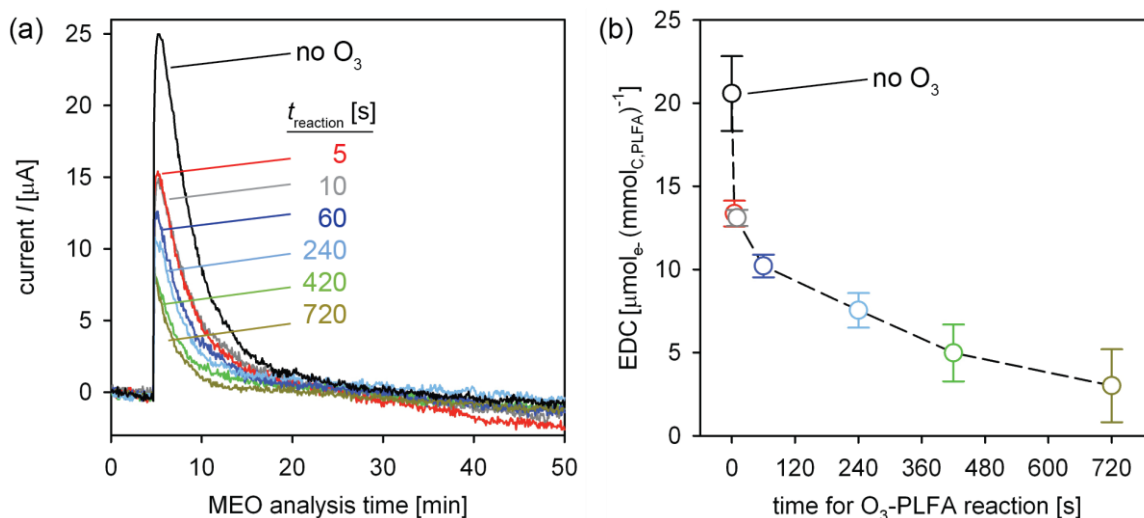
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Figure 1. Changes in the optical properties of Suwannee River Humic Acid (SRHA), Suwannee River Fulvic Acid (SRFA), and Pony Lake Fulvic Acid (PLFA) upon treatment with chlorine dioxide (ClO₂), chlorine (as HOCl), and ozone (O₃) (both in the absence and presence of t-BuOH). Panels (a)-(c): Changes in the specific UV absorption at 254 nm (i.e., SUVA₂₅₄) of (a) SRHA, (b) SRFA, and (c) PLFA as a function of the specific molar oxidant dose (mmol_{oxidant} (mmol_C)⁻¹). Panels (d)-(f): Changes in the spectral slope S (from 300 to 600 nm) of (d) SRHA, (e) SRFA, and (f) PLFA as a function of the specific molar oxidant dose.

275 *Effects of oxidant treatments on DOM antioxidant properties.* In a first set of
276 experiments we evaluated the sensitivity of MEO to detect oxidant-induced changes in
277 the EDCs of HS by quantifying the kinetics of PLFA oxidation by O₃ at a constant initial
278 dose of 0.5 mmol O₃/ mmol C. We chose PLFA because it has the lowest EDC values of
279 several DOMs previously tested.⁴⁰ **Figure 2a** shows the evolution of the oxidative current
280 responses in MEO for PLFA samples after reaction with O₃ for various times. The
281 corresponding EDC values, obtained by integration of the oxidative current peaks (Eq. 3),
282 show fast oxidation of the electron donating moieties in PLFA by O₃ (**Figure 2b**): Within
283 one minute and 12 minutes of reaction, the EDC of PLFA decreased to approximately
284 50% and 15% of its original value, respectively. The results of this experiment
285 demonstrate the suitability of MEO to quantify changes in the oxidation state of HS
286 during treatments with chemical oxidants. Based on the reaction kinetics, the dose-
287 dependent ozonation experiments were run for 2h to guarantee completion of HS-O₃
288 reactions.

289 **Figure 3** shows that the EDCs of SRHA, SRFA, and PLFA decreased with
290 increasing doses of ClO₂, HOCl and O₃ (both in the presence and absence of t-BuOH)
291 and, hence, dose-dependent removal of electron donating moieties in the HS for all three
292 oxidants. Normalized to the same specific molar oxidant dose, the decreases in EDC were
293 largest for ClO₂, intermediate for HOCl and O₃ in the presence of t-BuOH, and smallest
294 for O₃ in the absence of t-BuOH: Linear fits of the decreases in EDC values of SRHA and
295 SRFA at low specific molar oxidant doses had the steepest slopes for ClO₂ (i.e., -0.69 and
296 -0.46 mmol_e.(mmol ClO₂)⁻¹), intermediate slopes for HOCl (i.e., -0.38 and -0.36 mmol_e.
297 (mmol HOCl)⁻¹) and for O₃ in the presence of t-BuOH (i.e., -0.35 and -0.29 mmol_e.(mmol

298 $\text{O}_3)^{-1}$), and the shallowest slopes for O_3 in the absence of t-BuOH (i.e., -0.15 and -0.08
299 $\text{mmol}_e\cdot(\text{mmol O}_3)^{-1}$) (**Figure S5, Table S2**). The PLFA data did not show a linear
300 decrease in EDC with increasing specific molar oxidant dose and could therefore not be
301 fitted.

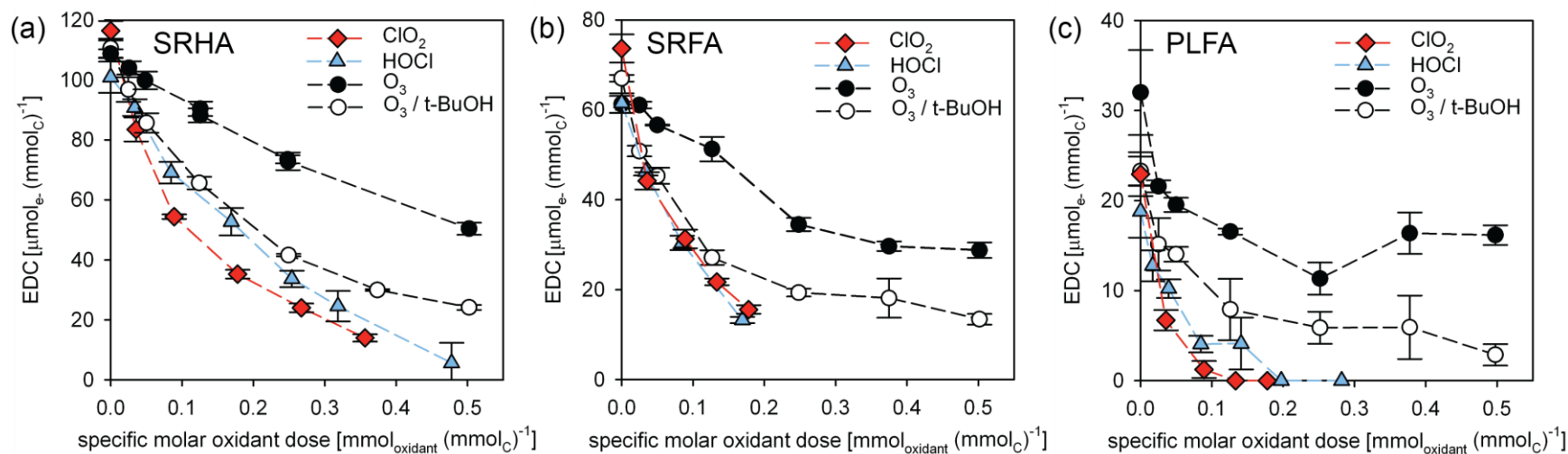


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303 **Figure 2.** Ozonation of Pony Lake Fulvic Acid (PLFA). Effects of the reaction time on
304 (a) the oxidative current responses in mediated electrochemical oxidation (MEO) and (b)
305 the corresponding electron donating capacities (EDC) of PLFA. Experimental conditions:
306 0.5 mmol $\text{O}_3/\text{mmol C}$; 5 mM t-butanol; 50 mM PO_4 -buffer, pH 7.0. The samples were
307 quenched with 1 mM maleic acid at selected reaction times.

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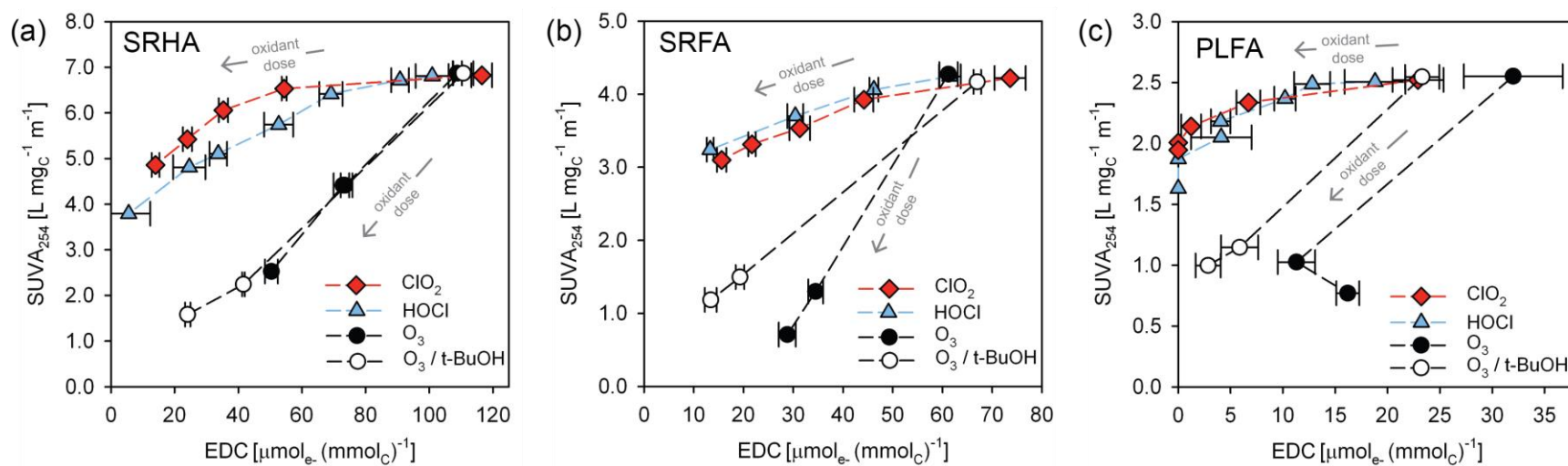
309 Treatments with high doses of ClO_2 and HOCl resulted in complete loss of EDC in
310 some of the systems, including a replicate SRFA- ClO_2 experiment (**Figure S6**), whereas
311 all HS retained some EDC during ozonation even at the highest O_3 doses. The removal of
312 electron-donating moieties in the tested HS was therefore more efficient by ClO_2 and
313 HOCl treatments than by ozonation. The larger decreases in EDCs by O_3 in the presence
314 than in the absence of t-BuOH can be assigned to $\bullet\text{OH}$ quenching by t-BuOH and hence
315 higher O_3 exposures of HS and more selective oxidations of electron donating moieties
316 by O_3 .



298

299 **Figure 3.** Dependencies of the electron donating capacities (EDCs) of (a) Suwannee River Humic Acid (SRHA), (b) Suwannee River
 300 Fulvic Acid (SRFA), and (c) Pony Lake Fulvic Acid (PLFA) on the specific molar doses of the chemical oxidants chlorine dioxide
 301 (ClO_2), chlorine (as HOCl), and ozone (in the absence and presence of t-BuOH).

302 *Mechanistic interpretation.* In the following, the changes in the optical and the
303 antioxidant properties of the HS will be further explored by plotting the oxidant-induced
304 decreases in the SUVA₂₅₄ values versus the corresponding decreases in the EDC values
305 (**Figure 4**). Treatments of the HS with ClO₂ and HOCl resulted in comparable SUVA₂₅₄-
306 EDC dependencies for these two oxidants with larger relative decreases in the EDC than
307 in the SUVA₂₅₄ values. This finding implies a more efficient removal of electron
308 donating phenolic moieties than UV-light absorbing aromatic moieties upon treatment of
309 the HS with ClO₂ and HOCl. Compared to the ClO₂ and HOCl treatments, ozonation in
310 the presence and absence of t-BuOH led to distinctly different SUVA₂₅₄-EDC
311 dependencies with larger relative losses in the SUVA₂₅₄ than in the EDC values.
312 Ozonation therefore caused a more efficient removal of UV-light absorbing aromatic
313 moieties than electron donating phenolic moieties. Ozonation of SRHA in the presence
314 and absence of t-BuOH resulted in comparable SUVA₂₅₄-EDC dependencies. Conversely,
315 ozonation of SRFA in the presence of t-BuOH resulted in smaller decreases in SUVA₂₅₄
316 and larger decreases in the EDC values as compared to ozonation in the absence of t-
317 BuOH at the same initial ozone dose. We note that the EDC measurements of PLFA
318 samples at high O₃ doses were close to the quantification limit of MEO. The apparent
319 increase in the EDC value of PLFA at the highest O₃ dose (**Figure 3c**) therefore likely
320 reflected uncertainties in the EDC quantification.



321

322 **Figure 4.** Effect of chemical oxidant treatments on the specific UV absorbances (SUVA₂₅₄) and the electron donating capacities
 323 (EDCs) of (a) Suwanee River Humic Acid (SRHA), (b) Suwanee River Fulvic Acid (SRFA), and (c) Pony Lake Fulvic Acid (PLFA).
 324 The chemical oxidants used were chlorine dioxide (ClO₂), chlorine (as HOCl), and ozone (O₃; in the absence and presence of tertiary
 325 butanol (t-BuOH)). The chemical oxidant dose increased in the direction indicated by the grey arrows.

326 The effects on the optical and antioxidant properties of the HS shown in **Figure 4**
327 can be rationalized on the basis of known major reaction pathways of ClO₂, HOCl, and
328 O₃ with light-absorbing and electron donating phenolic moieties in the HS (**Figure 5**).
329 ClO₂ reacts as a one-electron transfer oxidant with low molecular weight phenols forming
330 chlorite and the corresponding phenoxyl radicals.²¹ At circumneutral pH, this reaction
331 proceeds mostly via the phenolate species because of its oxidation rate constants with
332 ClO₂ that are about six orders of magnitude higher than those for the non-dissociated
333 phenol species.²⁶ Analogously to low molecular weight phenols, phenolic moieties in HS
334 are expected to undergo one electron oxidation by ClO₂. We have previously shown that
335 HS contain electron donating phenolic and hydroquinone moieties with apparent
336 oxidation potentials^{40,64} much lower than the standard reduction potential of ClO₂,
337 $E_h^0(\text{ClO}_2(\text{aq})/\text{ClO}_2^-) = 0.954 \text{ V}$.⁶⁵ SRHA and SRFA are derived from higher-plant
338 precursor materials, including lignin, which is rich in methoxylated phenols.⁶⁶ Generally,
339 methoxylation activates phenols for electrophilic attack and leads to faster oxidation
340 kinetics.²⁶ Phenoxyl radicals resulting from a first one electron oxidation^{26,67,68} may either
341 be further oxidized by reacting with another ClO₂ to form ortho- or para-quinones or
342 undergo irreversible coupling reactions. Hydroquinone moieties present in the untreated
343 HS are expected to be oxidized by ClO₂ to semiquinone intermediates and subsequently
344 to the respective quinone moieties. These reaction pathways involving ClO₂ as the
345 oxidant have in common that electron donating phenolic moieties are oxidized while their
346 UV-light absorbing aromatic structure is preserved. In fact, based on the higher extinction
347 coefficient of benzoquinone than hydroquinone at 254 nm, the oxidation of hydroquinone
348 to quinone moieties in the DOM may have resulted in higher SUVA₂₅₄ values than

349 measured if no hydroquinone moieties had been oxidized. These pathways are therefore
350 fully consistent with the pronounced decreases in the EDC and the relatively small losses
351 in $SUVA_{254}$ values observed for HS treatment with ClO_2 .

352 Phenolic moieties in HS may react with HOCl in an electrophilic substitution
353 reaction (**Figure 5**). At circumneutral pH, this reaction proceeds via the phenolate due to
354 its much higher reactivity compared to the phenol.²⁸ In this reaction, HOCl attacks at the
355 *ortho* and *para* positions to the hydroxyl substituent, resulting in the formation of (poly)-
356 chlorinated phenols. Such an initial chlorination should not lead to a decrease in the
357 electron donating capacities of the phenolic moieties.^{69,70} The reaction of low molecular
358 weight phenols with HOCl has been demonstrated to proceed via polychlorinated phenols
359 which ultimately undergo ring cleavage to form non-aromatic, chlorinated products
360 (**Figure 5**).²⁸ However, the small changes in the $SUVA_{254}$ values of HS upon HOCl
361 treatment do not support ring cleavage as a significant reaction pathway for phenolic, or
362 more general, aromatic moieties present in HS. Alternatively, the smaller relative
363 decreases in the $SUVA_{254}$ than EDC values upon HOCl treatment are consistent with the
364 two-electron oxidation of hydroquinone and/or catechol moieties by HOCl to form the
365 respective quinone moieties and chloride. These reactions are thermodynamically
366 favorable given that the standard reduction potentials for the two electron reductions of
367 HOCl and OCl^- ($pK_a(HOCl)= 7.54$ at $25^\circ C$) (i.e., $HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$; $E_h^0 =$
368 $1.48 V^{71}$ and $OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2 OH^-$; $E_h^0 = 0.84 V^{71}$) are much higher than the
369 oxidation potentials of hydroquinones. This is in agreement with the high second order
370 rate constants for the reaction of HOCl with hydroxyphenols.⁷² This reaction pathway

371 may therefore result in similar changes in the optical and antioxidant properties as ClO₂,
372 which acts almost exclusively by an electron transfer mechanism.

373 The reaction of phenolic moieties with O₃ at circumneutral pH is dominated by
374 phenolate and initiated by an ozone adduct, which may react further by (i) loss of
375 ozonide, O₃⁻, to form a phenoxy radical, (ii) loss of H₂O₂ to form an *ortho*
376 benzoquinone, (iii) loss of singlet oxygen, ¹O₂, to form a catechol-type compound, and
377 (iv) a Criegee-type reaction with a cleavage of the aromatic ring.^{23,24,62} The formations of
378 phenoxy radicals (pathway (i)) and catechols (pathway (ii)) are important but minor
379 pathways for the oxidation of phenol with ozone.²³ If these would be the dominant
380 reaction pathways of phenolic moieties during ozonation, this would lead to
381 comparatively large decreases in the EDC and small decreases in the SUVA₂₅₄ values,
382 while the opposite effect was observed experimentally (**Figure 4**). Instead, the
383 pronounced decreases in SUVA₂₅₄ support ring cleavage of phenols and hydroquinones
384 via the Criegee mechanism (pathway (iv)) to form muconic-type compounds and
385 eventually aliphatic aldehydes (**Figure 5**). Ring cleavage reactions may have involved
386 non-phenolic aromatic moieties such as anisoles and polymethoxybenzenes, as
387 demonstrated for low-molecular weight methoxylated compounds.²² The loss of these
388 moieties would have resulted in decreasing SUVA₂₅₄ without affecting the EDC values of
389 the HS, as both the target compounds and products would not be oxidizable in MEO.

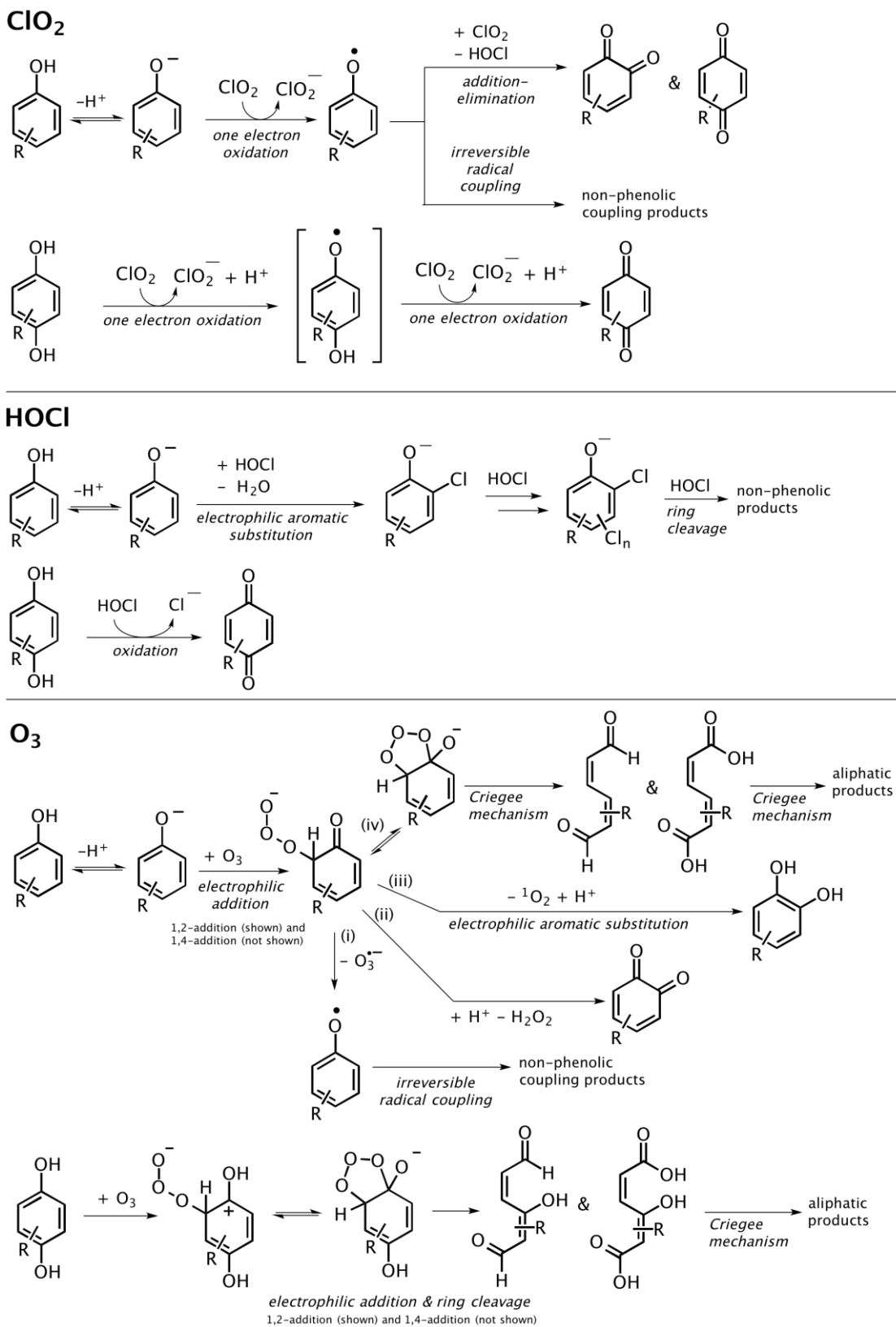


Figure 5. Proposed reaction pathways of phenolic moieties in the humic substances during reaction with chlorine dioxide (ClO₂), chlorine (HOCl), and ozone (O₃).

393 **Implications**

394 This study establishes that the EDC of DOM is a parameter that directly relates to
395 the DOM redox state. The EDC is highly sensitive to changes in DOM occurring during
396 chemical oxidation processes and can be readily quantified by mediated electrochemical
397 oxidation (MEO). If combined with measurements of complementary optical parameters,
398 such as $SUVA_{254}$, the changes in the EDC values provide information on the kinetics and
399 the dose-dependent oxidation of electron donating moieties in DOM. The combined
400 analysis of optical and antioxidant properties also provides insight into which moieties in
401 the DOM react with the chemical oxidants and helps identifying the major oxidant-
402 dependent reaction pathways of DOM.

403 In addition to advancing the fundamental understanding of chemical DOM
404 oxidation, the results from this study are also relevant from a more applied, water
405 treatment perspective. MEO has potential to be used in water treatment facilities to
406 monitor DOM oxidation during a chemical oxidation step. Combined determination of
407 changes in the EDC and $SUVA_{254}$ (or other suitable optical parameters) in close to real-
408 time can be used to control chemical oxidant doses. The resulting refined dosing
409 operation can minimize overdosing which may have negative impacts on water quality,
410 such as the enhanced formation of disinfection/oxidation by-products. Future work needs
411 to assess the potential of EDC- $SUVA_{254}$ measurements as a new tool to advance the
412 understanding of and the capability to predict other important processes occurring during
413 chemical oxidation of DOM, such as the formation of disinfection by-products, the
414 generation of assimilable carbon, and the efficiency of disinfection.

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420 Supporting Information

421 This material is available free of charge via the internet at <http://pubs.acs.org>.

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