Inhibitory Effect of Dissolved Organic Matter on the Transformation of Selected Anilines and Sulfonamide Antibiotics Induced by the Sulfate Radical

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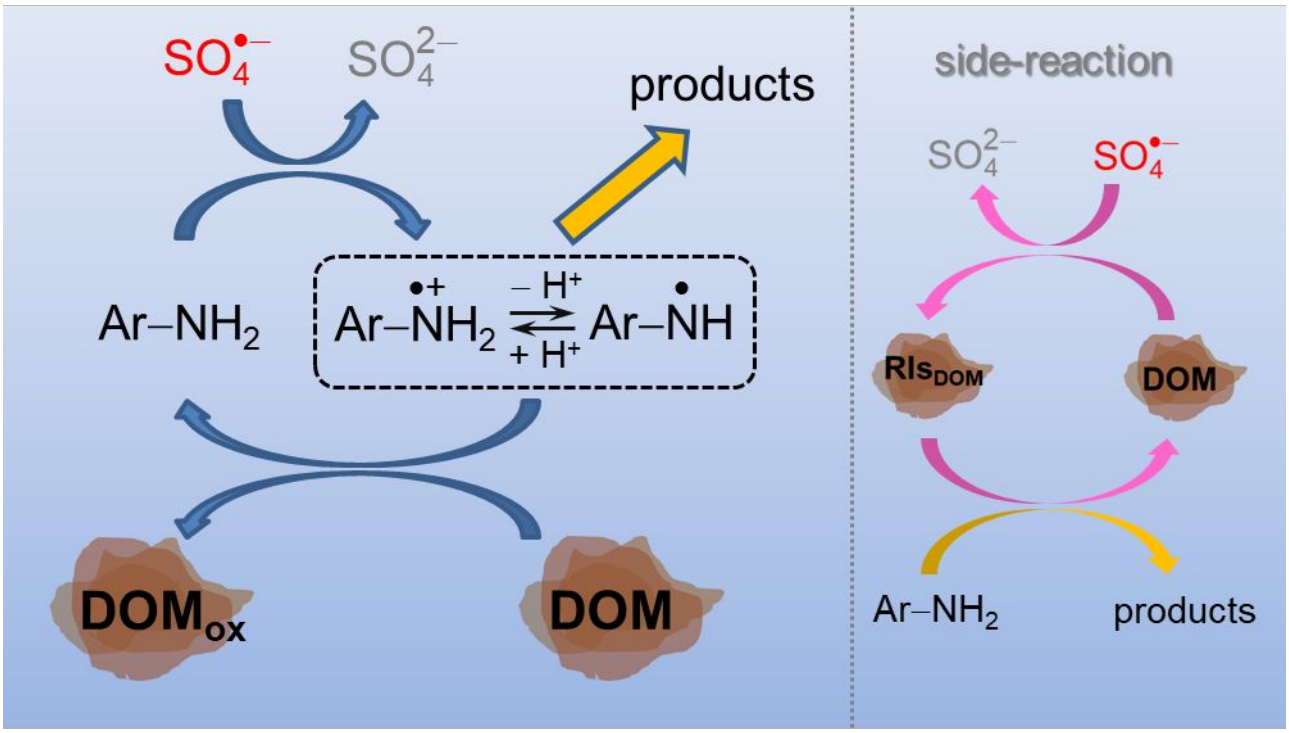
Graphical Abstract



Abstract

Dissolved organic matter (DOM) has been shown to inhibit the oxidation of aromatic amines initiated by excited triplet states, an effect that was attributed to the reduction of oxidation intermediates back to their parent compounds. The present study focuses on the quantification of an analogous inhibitory effect of DOM on aqueous oxidations induced by the sulfate radical ($SO_4^{\bullet-}$). Second-order rate constants for the $SO_4^{\bullet-}$-induced transformation of selected anilines and sulfonamide antibiotics were determined by competition kinetics in the presence and absence of DOM from three different isolates at pH 8. In the presence of 1 mg_C L^{-1} of DOM, a significant reduction in the rate constant was observed for most of the compounds compared to DOM-free solutions, but for two electron-rich anilines increases in rate constant were measured. For 4-cyanoaniline and sulfamethoxazole, the DOM concentration dependence of the rate constant consisted in a sharp decrease up to ≈1.0 mg_C L^{-1} of DOM, followed by a region of slight changes or even increases for higher DOM concentrations (up to 5 mg_C L^{-1}). This behavior was attributed to the occurrence of the aforementioned inhibitory effect and a counteracting accelerated transformation of the contaminants due to reactions with secondary radical oxidants resulting from DOM oxidation by $SO_4^{\bullet-}$. Both effects of inhibition and secondary oxidants should be considered when assessing the abatement of aromatic amines in $SO_4^{\bullet-}$-based advanced oxidation processes.

Introduction

Advanced oxidation processes (AOPs) based on the sulfate radical ($SO_4^{\bullet-}$) as the primary oxidizing species have been extensively investigated for their possible use in the remediation of contaminated waters and soils. Various papers provide a rich collection of bibliography on this research area that has been rapidly developing during the past few years.[1-4] $SO_4^{\bullet-}$ is a stronger one-electron oxidant than the hydroxyl radical ($^{\bullet}OH$); their standard reduction potentials vs. SHE in aqueous solution being $E^0_{\mathrm{red}}\left(\mathrm{SO_4}^{\bullet-}/\mathrm{SO_4}^{2-}\right)$ = 2.44 V and E^0_{red} $\left(^{\bullet}\mathrm{OH}/\mathrm{OH}^{-}\right)$ = 1.90 V.[5] However, its reaction kinetics and mechanisms are different from those of $^{\bullet}OH$, making it overall a more selective oxidant than $^{\bullet}OH$. In particular, $SO_4^{\bullet-}$ reacts much slower than $^{\bullet}OH$ in hydrogen abstraction reactions[6] and with electron-deficient aromatic compounds such as nitrobenzene.[7] Since $SO_4^{\bullet-}$ can oxidize water and the hydroxide anion to $^{\bullet}OH$, the hydrogen carbonate and carbonate anions to the carbonate radical ($CO_3^{\bullet-}$), and halides to a suite of highly reactive halide-containing radicals,[8-10] these radicals coexist in waters treated by $SO_4^{\bullet-}$-based AOPs, which may complicate the study of the oxidative degradation of organic water contaminants.[11-13] As for $^{\bullet}OH$ and $CO_3^{\bullet-}$, dissolved organic matter (DOM) is expected to be a major scavenger of $SO_4^{\bullet-}$ in various waters. A second-order rate constant of 6.8×10^3 L mg_C^{-1} s^{-1} was determined for its reaction with a humic acid,[2] which is lower by a factor of ≈2–5 than typical scavenging rate constants of $^{\bullet}OH$ by DOM.

Studies performed during the last decade have revealed the occurrence of an inhibitory effect of DOM on the photosensitized transformation of organic contaminants.[14-18] This inhibitory effect, detected during the oxidative transformation of several aromatic contaminants (in particular aromatic amines) induced by excited triplet states of model photosensitizers or DOM itself, was ascribed to the reduction of oxidation intermediate radicals brought about by antioxidant moieties of the DOM. The formation of an intermediate radical that can be

transformed (through reduction) back to its parent compound appears to be the crucial condition for such an inhibitory effect to occur. It is obvious that this condition is expected to be satisfied not only in the case of triplet-induced oxidations, but also for a suite of oxidation reactions initiated by radical oxidants. In investigations performed on $^{\bullet}OH$-induced oxidations of fifteen selected aromatic contaminants, no inhibitory effect of the aforementioned type could be detected.[15] This was explained by the formation of radical-type adducts of the aromatic contaminants with $^{\bullet}OH$ which could not undergo reduction to yield the parent compound.[15]

The present study was performed to detect and quantify inhibitory effects possibly occurring in oxidations of organic contaminants induced by $SO_4^{\bullet-}$. Second-order rate constants for the oxidation of several selected anilines and sulfonamide antibiotics by $SO_4^{\bullet-}$ were measured for aqueous solutions in the presence and absence of humic substances. Steady-state ultraviolet irradiation (308 nm < λ < 410 nm) of persulfate was used to generate $SO_4^{\bullet-}$, and the rate constants were measured by competition kinetics using as a competitor isoproturon, a compound previously shown not to be affected by inhibitory effects in triplet-induced oxidations.[14]

Materials and Methods

List of Chemicals and Humic Substances. All chemicals in the following list (supplier and purity grade given in parentheses) were purchased from common commercial sources and used without purification. (A) Anilines: Aniline (Aldrich, ≥ 99.5%), 4-cyanoaniline (Fluka, ≥ 97%), 3,4-dichloroaniline (Aldrich, 98%), *N,N*-dimethylaniline (Fluka, ≥ 99.5%), *N*-ethylaniline (Fluka, ≥ 99%), *N*-methylaniline (Fluka, ≥ 98%); (B) Sulfonamides: Sulfachloropyridazine (Sigma, ≥ 98%), sulfadiazine (Sigma, 99.0%), sulfadimethoxine (Fluka, ≥ 98.5%), sulfamethoxazole (Sigma-Aldrich, analytical standard), sulfathiazole (Sigma-Aldrich, 99%); (C) Miscellaneous compounds: Potassium persulfate ($K_2S_2O_8$, Fluka, ≥ 99.0%), disodium hydrogen phosphate dihydrate ($Na_2HPO_4 \cdot 2\ H_2O$, Merck, ≥ 99.5%), sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$, Merck, ≥ 99.0%), phosphoric acid (Fluka, ≥ 85%), *t*-butanol (Sigma-Aldrich, ≥ 99.7%), isoproturon (IPU, Sigma-Aldrich, Pestanal®, ≥ 99.8%), 2,4,6-trimethylphenol (TMP, EGA-Chemie, 99%). Ultrapure water (resistivity > 18 MΩ cm, organic carbon < 2 ppb) was obtained from a Barnstead Nanopure purification system and used for all aqueous solutions and chromatography. Humic substances, purchased from the International Humic Substances Society, comprised Pony Lake fulvic acid (PLFA, code 1R109F), Suwannee River fulvic acid (SRFA, code 1S101F) and Suwannee River humic acid (SRHA, code 1S101H).

Competition Kinetics Experiments. Aqueous solutions containing potassium persulfate (5.0×10^{-4} M), a single target compound (1.0×10^{-6} M), isoproturon as a competitor (1.0×10^{-6} M), phosphate buffer (5.0×10^{-4} M, solution pH = 8.0), *t*-butanol (2.5×10^{-4} M) as a hydroxyl radical scavenger, and a given amount of one of the three humic substances were made in quartz glass tubes (18 mm external diameter, 15 mm internal diameter) using appropriate stock solutions of the various components. The employed phosphate buffer concentration was low to reduce the formation of phosphate radicals.[19] Using the rate

101 constants summarized in Table S4 of the SI, the contribution of phosphate radicals to the
102 transformation of a target compound was estimated not to exceed 10 %, which is not expected
103 to significantly affect the results and conclusions of this study. The use of *t*-butanol as a
104 hydroxyl radical scavenger (with a second-order reaction rate constant of 6.0×10^8 M^{-1} s^{-1})[20]
105 ensured that the fraction of target or reference compound reacting with $^{\bullet}OH$ (both assumed to
106 react with $^{\bullet}OH$ with rate constants of 1×10^{10} M^{-1} s^{-1}) was less than 3% compared to $SO_4^{\bullet-}$
107 and thus negligible. The tubes were closed with glass stoppers, shaken by hand, placed in a
108 water bath and kept 15 minutes at a temperature of 25.0 °C. They were then submitted to
109 irradiation in a temperature-controlled (25.0 ± 0.2 °C) DEMA (Hans Mangels GmbH,
110 Bornhein-Roisdorf, Germany) model 125 merry-go-round photoreactor which was equipped
111 with a Heraeus Noblelight model TQ718 medium-pressure mercury lamp operated at an input
112 power of 500 W. The lamp was placed in a cooling jacket consisting of a quartz glass inner
113 wall, a borosilicate glass outer wall and a UVW-55 glass filter (supplied by DEMA) in
114 between. The combination of these glasses resulted in a band-pass filter for the wavelength
115 range of 308–410 nm. This setup was chosen, in analogy to a previous study on the
116 determination of hydroxyl radical rate constants,[21] to limit the phototransformation of the
117 target compounds and the competitor while allowing for photolysis of persulfate, mainly
118 induced by the 313 nm emission line of the mercury lamp. A more detailed description of the
119 photoreactor and its operation is given elsewhere.[22] Samples (400 μL) were taken just before
120 irradiation and during irradiation at regular time intervals, filled into vials and immediately
121 transferred to the refrigerated autosampler (5.0 °C) of the chromatographic equipment. All
122 kinetic experiments were performed in duplicate. Control irradiation experiments were
123 performed with persulfate-free solutions to check for possible interferences by direct or
124 indirect phototransformation reactions of the target compounds and isoproturon. Within the
125 time range employed for competition kinetics experiments and in the absence as well as in the

126 presence of one of the three studied humic substances up to a concentration of 5 $mg_C\ L^{-1}$, no
127 significant depletion of target compounds or isoproturon could be detected, indicating that
128 these side-reactions can be neglected in the frame of this study.
129 Apparent second-order rate constants for the reaction of $SO_4^{\bullet-}$ with a target compound (TC)
130 leading to the transformation of TC, $k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}}$, were determined based on the following
131 competition kinetics expression (see SI, Text S1 for its derivation):

132 $$\ln\frac{[\mathrm{TC}]_0}{[\mathrm{TC}]} = \frac{k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}}}{k^{\mathrm{tr}}_{\mathrm{SO_4^{\bullet-}},\mathrm{IPU}}}\ln\frac{[\mathrm{IPU}]_0}{[\mathrm{IPU}]} \quad (1)$$

133 where $k^{\mathrm{tr}}_{\mathrm{SO_4^{\bullet-}},\mathrm{IPU}}$ is the second-order rate constant for the reaction of $SO_4^{\bullet-}$ with the competitor
134 IPU leading to the transformation of IPU. The term *apparent* ("app" as a superscript in the
135 rate constant) was used to allow for possible side-reactions in the transformation of TC. From
136 the slope α of a regression line of $\ln\frac{[\mathrm{TC}]_0}{[\mathrm{TC}]}$ vs. $\ln\frac{[\mathrm{IPU}]_0}{[\mathrm{IPU}]}$, the target rate constant was obtained as:
137 $k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}} = \alpha \times k^{\mathrm{tr}}_{\mathrm{SO_4^{\bullet-}},\mathrm{IPU}}$, with $k^{\mathrm{tr}}_{\mathrm{SO_4^{\bullet-}},\mathrm{IPU}} = 2.9 \times 10^9\ M^{-1}s^{-1}$ (value set equal to the mean of
138 the second-order rate constant determined by pulse radiolysis).[23] In consideration of the
139 absence of inhibitory effect during the excited-triplet induced oxidation of phenylureas,
140 including IPU,[14] we made the assumption that $k^{\mathrm{tr}}_{\mathrm{SO_4^{\bullet-}},\mathrm{IPU}}$ remains unaffected by the presence
141 of DOM in the studied solutions.
142 **Analytical Methods.** The concentration of target compounds and isoproturon during kinetic
143 runs was followed by high-performance liquid chromatography (HPLC) using an Agilent
144 1100 system equipped with a quaternary low-pressure mixing gradient pump, a refrigerated
145 autosampler, a temperature-controlled column compartment, a diode array detector and an
146 Agilent 1200 fluorescence detector. Alternatively, an analogous Thermo Fischer Ultimate
147 3000 HPLC system was used. A detailed list of HPLC analysis methods is given in the
148 Supporting Information (SI), Table S2.
149

150 ## Results and Discussion

151 **Transformation and Competition Kinetics.** Typical transformation kinetics runs showing
152 the depletion of 3,4-dichloroaniline (an example of TC) and the competitor (IPU) in the
153 presence and absence of DOM are shown in Figure 1a. The transformation kinetics of TCs
154 and IPU was well described by a first order-model and was significantly affected by the
155 presence of DOM, which slowed down the transformation of both TC and IPU. The decrease
156 of the TC and IPU transformation rates observed in the presence of DOM is primarily
157 attributed to scavenging of $SO_4^{\bullet-}$ by DOM, which reduces the steady-state concentration of
158 $SO_4^{\bullet-}$, $[SO_4^{\bullet-}]_{ss}$. The latter is related to the transformation rates by the following equations.

159 $$-\frac{d[\mathrm{TC}]}{dt} = k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}}\left[\mathrm{SO_4^{\bullet-}}\right]_{\mathrm{ss}}[\mathrm{TC}] \quad (2a)$$

160 $$-\frac{d[\mathrm{IPU}]}{dt} = k^{\mathrm{tr}}_{\mathrm{SO_4^{\bullet-}},\mathrm{IPU}}\left[\mathrm{SO_4^{\bullet-}}\right]_{\mathrm{ss}}[\mathrm{IPU}] \quad (2b)$$

161 The dependence of $[SO_4^{\bullet-}]_{ss}$ on DOM concentration is treated below when discussing the
162 determination of the scavenging rate constant of $SO_4^{\bullet-}$ by DOM. Besides, there is a further
163 effect of DOM on the transformation rate of a TC that influences the second-order rate
164 constant, $k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}}$, and is central to the present study. Such an effect was quantified by
165 competition kinetics as shown in Figures 1b–c. For DCA the slope of the competition kinetics
166 regression line was smaller in the presence of 1.0 $mg_C\ L^{-1}$ of the added DOM isolate (PLFA,
167 SRFA or SRHA) than in its absence, indicating a decreased $k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{DCA}}$ in the presence of
168 DOM.
169

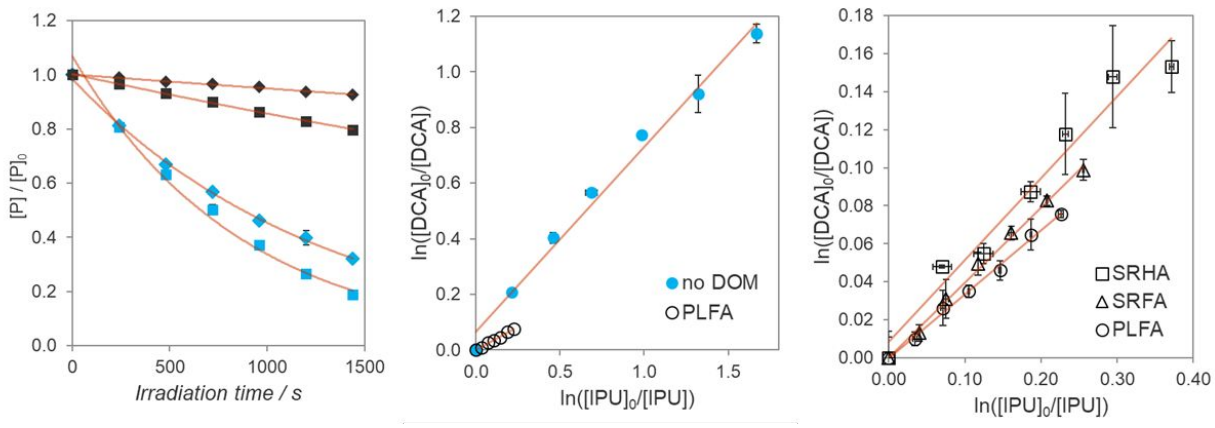


Figure 1. a. Example of transformation kinetics plots showing the decrease in relative residual concentration $[P]/[P]_0$ of isoproturon (IPU, squares) and 3,4-dichloroaniline (DCA, diamonds) vs. irradiation time, in the absence (blue symbols) and presence (black symbols) of DOM (PLFA, 1.0 mg_C L^{-1}). Lines represent first-order kinetics fits. **b.** Example of competition kinetics plots with corresponding linear regression lines (according to eq 1) for DCA vs. IPU in the absence (blue symbols) and in the presence of 1.0 mg_C L^{-1} of PLFA (open symbols). **c.** Competition kinetics plots as in panel b for 1.0 mg_C L^{-1} of either SRHA (squares), SRFA (triangles) or PLFA (circles). All irradiated solutions contained initially 1.0×10^{-6} M IPU, 1.0×10^{-6} M DCA, 5.0×10^{-4} M $K_2S_2O_8$, 5.0×10^{-4} M phosphate buffer (pH 8.0), and 2.5×10^{-4} M *t*-butanol. Error bars indicate standard errors related to HPLC analysis.

Second-Order Rate Constants Determined in the Absence of DOM. The competition kinetics method, applied to DOM-free solutions, yielded rate constants that are collected in Table 1. For the six substituted anilines, the rate constants were comprised in the relatively narrow range of $(1.8 – 3.3) \times 10^9$ $M^{-1}s^{-1}$, whereas for the sulfonamides the variation spanned about one order of magnitude ($8.7 \times 10^8 – 8.6 \times 10^9$ $M^{-1}s^{-1}$). For all compounds, the determined rate constant values are consistent with literature values for aromatic compounds lacking strongly electron-withdrawing groups [24, 25] and similar to those measured for several

190 pharmaceuticals that occur as aquatic contaminats. [26, 27] According to the pK_a values collected
191 in Table 1, all anilines are largely present in their molecular, neutral form at pH 8.0, while the
192 anionic form of the sulfonamides dominates their speciation at this pH. No obvious influence
193 of electric charge of the TCs on the measured rate constants could be inferred. Also, for the
194 group of the anilines, no evident correlation between the one-electron oxidation potential of
195 the TCs (- 1.32,[28] - 1.02 [28] and - 0.87 [29] V vs. SHE for 4-cyanoaniline, aniline and *N,N*-
196 dimethylaniline, respectively) and the rate constants could be observed. The lack of clear
197 dependence of the rate constants on the substituent of the anilines is analogous to the behavior
198 of phenylureas,[23] suggesting that, for both classes of compounds, even those members bearing
199 electron-withdrawing substituents have sufficiently high oxidation potentials to undergo a
200 diffusion-controlled oxidation by $SO_4^{\bullet-}$.
201

Table 1. Second-order rate constants for the reaction of the sulfate radical with target compounds determined in this study by competition kinetics (in the absence of dissolved organic matter). [a]

Target compound	α (rate constant relative to isoproturon) [b]	$k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}}([\mathrm{DOM}]=0)$ / 10^9 M^{-1} s^{-1} [c]	pK_a [d] (from literature)
Aniline	0.614 ± 0.022	1.78 ± 0.06	4.60 [e]
4-Cyanoaniline	0.943 ± 0.040	2.73 ± 0.12	1.74 [e]
3,4-Dichloroaniline	0.669 ± 0.050	1.94 ± 0.15	2.97 [f]
N,N-Dimethylaniline	1.149 ± 0.032	3.33 ± 0.09	5.15 [e]
N-Ethylaniline	0.824 ± 0.023	2.39 ± 0.07	5.11 [e]
N-Methylaniline	0.918 ± 0.031	2.66 ± 0.09	4.85 [e]
Sulfachloropyridazine	1.98 ± 0.21	5.74 ± 0.61	5.5,[g] 5.9 [h]
Sulfadiazine	2.98 ± 0.37	8.6 ± 1.1	6.5,[g] 6.4 [h]
Sulfadimethoxine	0.314 ± 0.032	0.911 ± 0.093	6.2,[g] 6.1 [h]
Sulfamethoxazole	0.299 ± 0.024	0.868 ± 0.069	5.6,[i] 5.7 [h]
Sulfathiazole	0.431 ± 0.025	1.25 ± 0.07	7.2,[i] 7.2 [g]
2,4,6-Trimethylphenol	1.210 ± 0.027	3.51 ± 0.08	10.88 [e]

[a] Composition of the solutions used for competition kinetics experiments: initial target compound and isoproturon concentrations 1.0×10^{-6} M; potassium persulfate concentration 5.0×10^{-4} M; *t*-butanol concentration 2.5×10^{-4} M; phosphate buffer concentration 5.0×10^{-4} M, pH 8.0. [b] Slope α of the competition kinetics plots according to eq 1, obtained by linear regression. The average values from two independent experiments are given. The errors represent 95% confidence intervals obtained from linear regression and by applying Gaussian error propagation. [c] Calculated as $\alpha \times k^{\mathrm{tr}}_{\mathrm{SO_4^{\bullet-}},\mathrm{IPU}}$, where the second-order rate constant for the reaction of the sulfate radical with isoproturon was set to be $k^{\mathrm{tr}}_{\mathrm{SO_4^{\bullet-}},\mathrm{IPU}} = 2.9 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$. The error in $k^{\mathrm{tr}}_{\mathrm{SO_4^{\bullet-}},\mathrm{IPU}}$ ($0.2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$)[23] was not considered in the calculation of the errors, which represent 95% confidence intervals. [d] pK_a values refer to the following deprotonation equilibria: a) for the anilines (An): AnH^+/An; b) for the sulfonamides (SA): SA/SA(-H)$^-$ (i.e., second pK_a); for 2,4,6-trimethylphenol (TMPhOH): TMPhOH/TMPhO$^-$. [e] Ref. 30. [f] Ref. 31. [g] Ref. 32. [h] Ref. 33. [i] Ref. 34.

219 **Effect of DOM on Second-Order Rate Constants.** For all TCs and DOM isolates
220 considered in this study, second-order rate constants for solutions containing 1.0 mg_C L^{-1} of
221 DOM were determined in duplicate. The representation of the effect of DOM on these rate
222 constants (see Figure 2) was done by utilizing the previously defined "inhibition factor",
223 *IF*([DOM]), [14, 15] which is the ratio of the rate constants measured in the presence of a given
224 concentration of DOM and in the absence of DOM, respectively. In this study, the inhibition
225 factor is defined by eq 3.

226 $$IF([\mathrm{DOM}]) = k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}}([\mathrm{DOM}])/k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}}([\mathrm{DOM}]=0) \quad (3)$$

227 For the anilines (Figure 2a) there are important compound-specific differences in
228 *IF*([DOM] = 1.0 mg_C L^{-1}). The lowest *IF* values (≈0.2) can be observed for 4-cyanoaniline.
229 These low values express a strong inhibitory effect on the reaction of $SO_4^{\bullet-}$ with this
230 compound exerted by all three organic matter isolates. Important but less strong inhibitory
231 effects are also observed for aniline and 3,4-dichloroaniline. *N,N*-dimethylaniline exhibits
232 almost no inhibitory effect (*IF* slightly lower than 1), while for *N*-ethylaniline and
233 *N*-methylaniline the presence of DOM does not inhibit, but, on the contrary, enhances the
234 $SO_4^{\bullet-}$-induced transformation of these compounds, with *IF* values in the range of ≈1.1 – 1.6.
235 The behavior of the sulfonamides (Figure 2b) is less variable than for the anilines, with all
236 compounds showing a significant inhibitory effect in the presence of any of the three DOM
237 isolates, except for sulfathiazole in the presence of SRHA (*IF* ≅ 1.1). Considering each
238 individual compound separately and comparing the effect of the three different DOM isolates,
239 it is difficult to infer a general trend for the magnitude of the inhibition factor. In the cases of
240 measured inhibitory effect (i.e. for *IF* < 1), SRFA and PLFA exhibit on average almost the
241 same inhibitory effect, while SRHA significantly appears to be the weakest inhibitor (with the
242 highest *IF* values). This ranking of DOM isolates with respect to their inhibitory effect is

contrary to the expectation drawn from studies on the inhibitory effect of DOM on triplet-induced transformations of organic

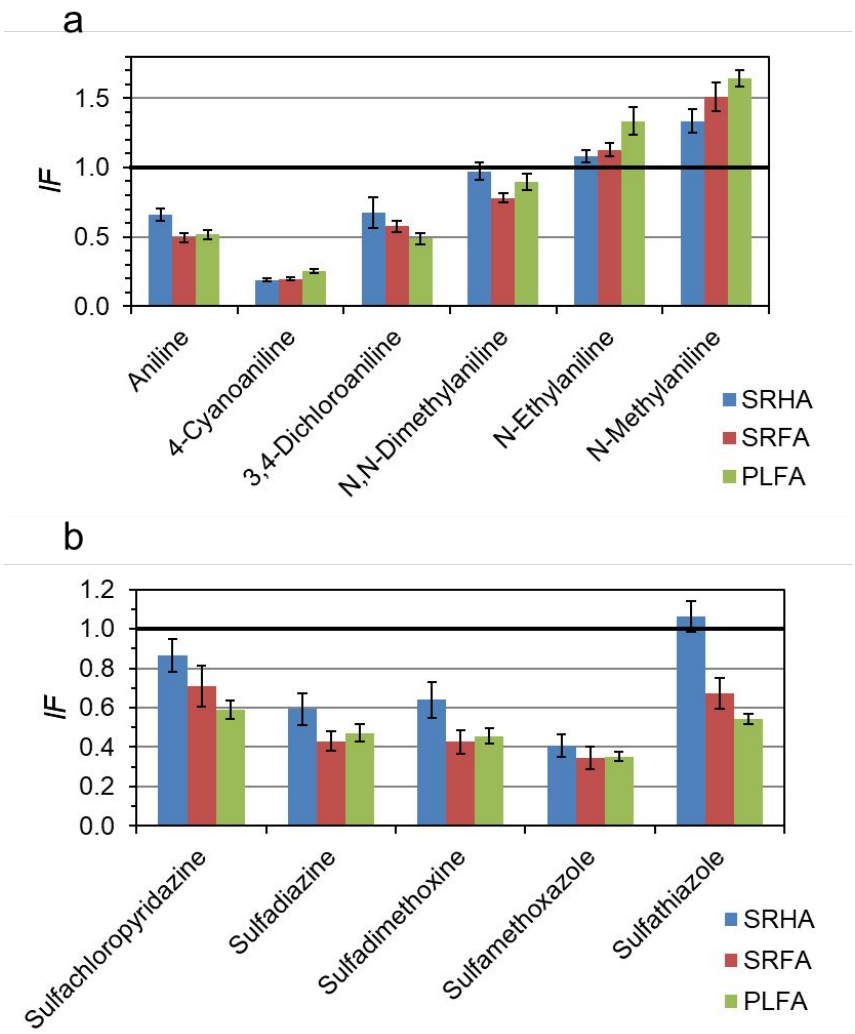


Figure 2. Determined inhibition factors $IF\left([\mathrm{DOM}] = 1.0\ \mathrm{mg_C\ L^{-1}}\right)$ (eq 3) for aqueous solutions (pH 8.0) of Suwannee River humic acid (blue bars), Suwannee River fulvic acid (red bars) and Pony Lake fulvic acid (green bars), for the studied (**a**) anilines and (**b**) sulfonamides. The values represent the mean of *IF* obtained from two independent experiments and the error bars are 95% confidence intervals obtained from linear regression and by applying Gaussian error propagation.

contaminants. [15, 17, 18] The inhibitory effect on triplet-induced transformations resulted to be stronger for terrestrially derived DOM isolates, such as SRHA and SRFA, compared to

255 PLFA, an aquatic DOM isolate of mainly autochtonous origin, and to be positively correlated
256 to the antioxidant capacity of DOM. This antioxidant capacity, quantified using an
257 electrochemical techniques as electron donating capacity (EDC), [35] increases in the order
258 PLFA < SRFA < SRHA, and therefore one would have predicted a clear increase of the
259 inhibitory effect (and therefore a decrease in *IF*) in the same order also in the case of $SO_4^{\bullet-}$-
260 induced oxidation. Obviously, this is not the case for the results presented in Figure 2. We
261 suspect that this unexpected outcome may be caused by side-reactions of the target compound
262 and/or the competitor, for instance by the reaction of these compounds with secondary
263 reactive intermediates (RIs) produced by the reaction of $SO_4^{\bullet-}$ with DOM. The presence of
264 such secondary RIs would also provide an explanation for the enhancement of transformation
265 observed for *N*-ethylaniline and *N*-methylaniline in the presence of DOM.
266 For both studied compound classes, the compounds with the most pronounced inhibitory
267 effect, namely 4-cyanoaniline and sulfamethoxazole, were selected to investigate the
268 dependence of *IF* on the concentration of DOM. The corresponding results are shown in
269 Figure 3. Data for 4-cyanoaniline show less scattering than for sulfamethoxazole, which we
270 attribute to a higher accuracy in the HPLC analysis of 4-cyanoaniline. For both target
271 compounds, there is a sharp decrease in *IF* when increasing [DOM] from 0 to ≈0.5 – 1.0 mg_C
272 L^{-1}. Thereby, the steepness of the function *IF*([DOM]) is less pronounced for PLFA than for
273 SRHA and SRFA. This is in line with the expectations from our previous studies on the
274 inhibitory effect occurring for excited triplet-induced transformations and the fact that PLFA
275 has less antioxidant moieties than SRHA and SRFA (see the above discussion concerning the
276 different concentration of antioxidant moieties in the studied DOM isolates). With increasing
277 DOM concentration above 0.5 – 1.0 mg_C L^{-1}, only a further slight decrease in *IF* is observed,
278 and for DOM concentration values exceeding 1.5 mg_C L^{-1}, *IF* even appears to increase with
279 increasing [DOM] in several cases. This observed increase in *IF* at higher DOM

concentrations, which is more important for sulfamethoxazole than for 4-cyanoaniline, is compatible with the suggestion made above that secondary RIs formed from reactions of $SO_4^{\bullet-}$ with DOM may create additional transformation routes for the TCs. We believe that the competitor, IPU, is less affected by these secondary RIs because of its higher resistance to oxidation due to the presence of the phenylurea group instead of the aniline group (which is common to both compound classes of the anilines and sulfonamides).

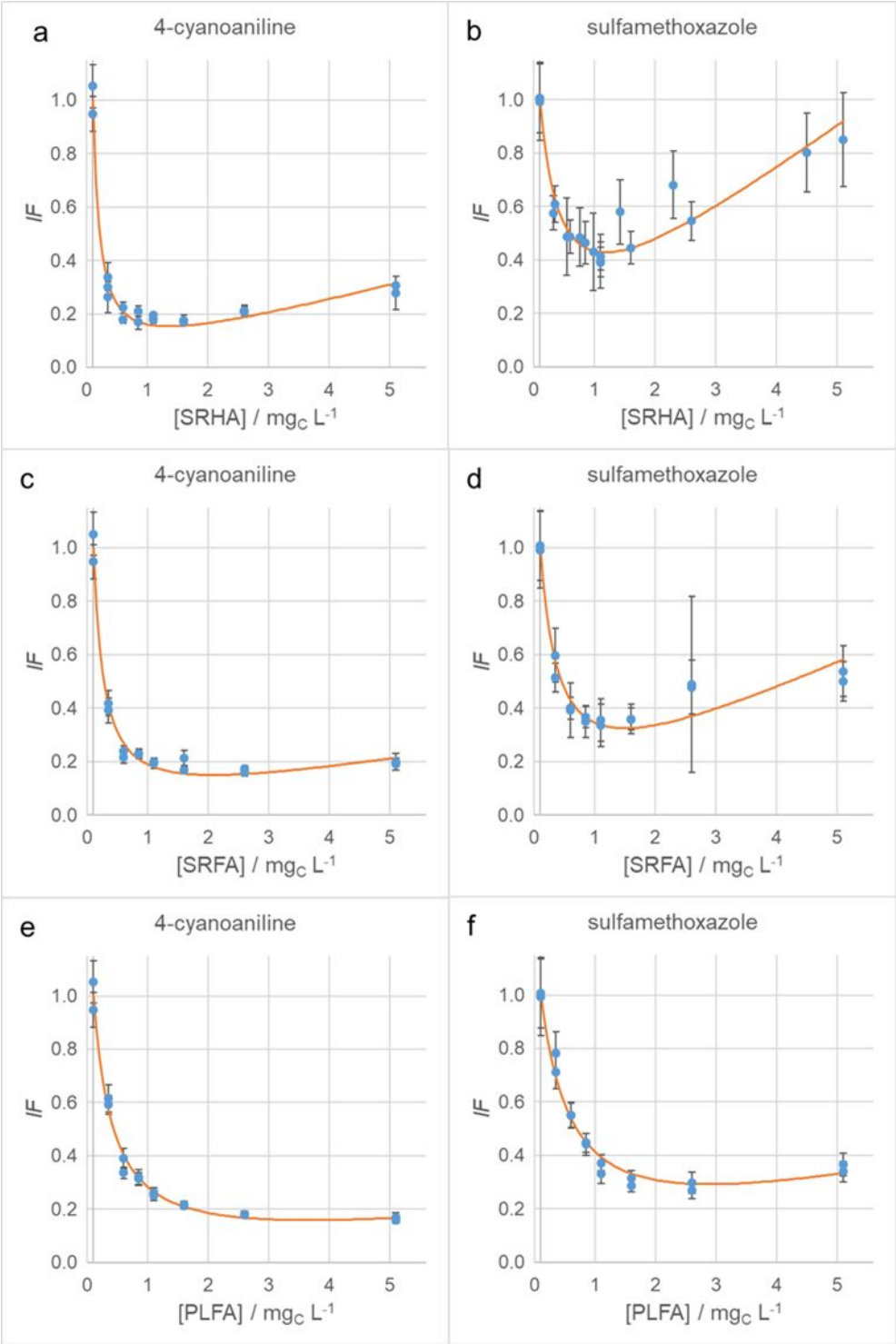


Figure 3. Inhibition factors (*IF*, eq 3) measured at various DOM concentrations in the range of 0.0 – 5.0 mg_C L^{-1} for aqueous solutions (pH 8.0) of Suwannee River humic acid (**a, b**), Suwannee River fulvic acid (**c, d**) and Pony Lake fulvic acid (**e, f**). Target compounds: 4-cyanoaniline (**a, c, e**) and sulfamethoxazole (**b, d, f**). Data points correspond to *IF* values obtained by applying eq 3 to $k_{SO_4^-,TC}^{tr,app}([DOM])$ values from individual experiments and using

the mean value of $k^{\mathrm{tr,app}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}}([\mathrm{DOM}]=0)$ from two independent experiments. Error bars represent 95% confidence intervals obtained from linear regression and by applying Gaussian error propagation. The continuous lines represent best fitting functions according to eq 11 and the fitting parameter values given in Table 2.

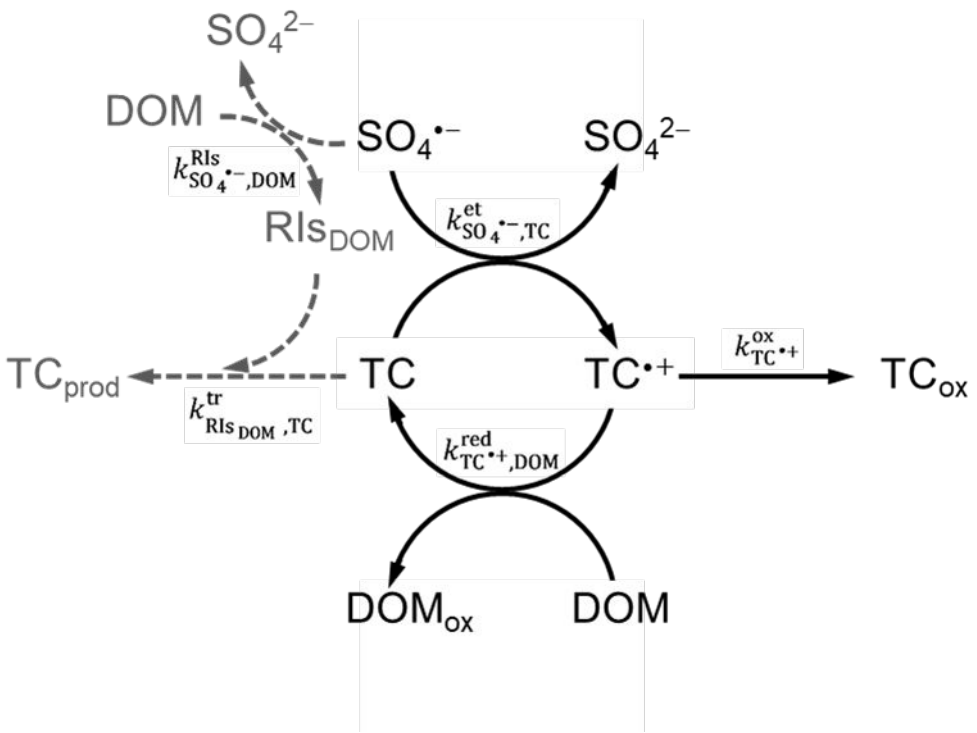
In the following, we develop a model to describe the dependence of *IF* on DOM concentration. The chemical reactions used in this model are also represented in Scheme 1. The basic assumption, which was also employed to develop kinetic models for the excited triplet-induced transformation of TCs and its inhibition by DOM,[14] implies the formation of a reactive radical intermediate, $TC^{\bullet+}$, through a one-electron transfer from TC to $SO_4^{\bullet-}$ (eq 4). This intermediate can then either transform to a stable oxidation product, TC_{ox} (eq 5), or be reduced by DOM (which is oxidized to DOM_{ox}) yielding the parent compound, TC (eq 6).

$$SO_4^{\bullet-} + TC \rightarrow SO_4^{2-} + TC^{\bullet+} \qquad k^{\mathrm{et}}_{\mathrm{SO_4^{\bullet-}},\mathrm{TC}} \qquad (4)$$

$$TC^{\bullet+} \rightarrow TC_{ox} \qquad k^{\mathrm{ox}}_{\mathrm{TC^{\bullet+}}} \qquad (5)$$

$$TC^{\bullet+} + DOM \rightarrow TC + DOM_{ox} \qquad k^{\mathrm{red}}_{\mathrm{TC^{\bullet+}},\mathrm{DOM}} \qquad (6)$$

Note that in the above and all the following reaction equations, the corresponding first- or second-order rate constants are given on the right.



311

312 **Scheme 1.** Representation of the key reactions involved in the oxidation of a target compound

313 (TC) induced by the sulfate radical in the presence of DOM. Species, reactions and

314 corresponding rate constants are described in the text.

315

316 In the absence of further reactions involving TC, the kinetic treatment of the above reaction

317 equations leads to the following expression for the inhibition factor (see derivation in the SI,

318 Text S2):

319 $$IF([\mathrm{DOM}]) = \frac{1}{1 + \left(k^{\mathrm{red}}_{\mathrm{TC}^{\bullet+},\mathrm{DOM}} / k^{\mathrm{ox}}_{\mathrm{TC}^{\bullet+}}\right) \times [\mathrm{DOM}]} \quad (7)$$

320 Equation 7 has the same form as analogous relationships derived for pseudo-first-order rate

321 constants of excited triplet-induced transformations inhibited by DOM.[14, 15] Defining

322 $[\mathrm{DOM}]_{1/2} = k^{\mathrm{ox}}_{\mathrm{TC}^{\bullet+}} / k^{\mathrm{red}}_{\mathrm{TC}^{\bullet+},\mathrm{DOM}}$ and substituting into eq 7, one obtains:

323 $$IF([\mathrm{DOM}]) = \frac{1}{1 + [\mathrm{DOM}]/[\mathrm{DOM}]_{1/2}} \quad (8)$$

324 In eqs 7 and 8, *IF* is a hyperbolic function of [DOM], and the parameter $[\mathrm{DOM}]_{1/2}$ is the

325 concentration of DOM at which *IF* = 0.5. $[\mathrm{DOM}]_{1/2}$ is inversely related to the steepness of the

326 function IF([DOM]) and to the inhibitory strength of the DOM under consideration.[15] The
327 monotonically decreasing functions, eqs 7 and 8, are obviously not capable to mimic the
328 experimental results presented in Figure 3. We hypothesize that the deviation from the basic
329 model is due to the formation of secondary RIs from the reaction of $SO_4^{\bullet-}$ with DOM,
330 according to eq 9.

331 $$SO_4^{\bullet-} + DOM \rightarrow SO_4^{2-} + RIs_{DOM} \qquad k^{RIs}_{SO_4^{\bullet-},DOM} \qquad (9)$$

332 RIs_{DOM} is a collective term defining secondary reactive intermediates formed through this
333 reaction (eq 9) and able to react with, and presumably oxidize, a TC. Transient signals
334 resulting from the reaction of $SO_4^{\bullet-}$ with DOM and exhibiting lifetimes in the order of
335 0.1 – 1 ms have been recently detected in a laser flash photolysis study.[36] They were
336 tentatively attributed to phenoxyl radicals resulting from one-electron oxidation of phenolic
337 moieties in the DOM.[36] For the kinetic treatment of interest to the present study, we consider
338 the simple case in which these RIs induce the transformation of TC to a stable product TC_{prod}
339 (see eq 10).

340 $$RIs_{DOM} + TC \rightarrow TC_{prod} \qquad k^{tr}_{RIs_{DOM},TC} \qquad (10)$$

341 Considering RIs_{DOM} as a single species, whose reaction with TC is characterized by a lumped
342 rate constant, $k^{tr}_{RIs_{DOM},TC}$, and assuming a dominating first-order kinetic pathway for the
343 depletion of RIs_{DOM}, with rate constant $k^{d}_{RIs_{DOM}}$, as well as no reaction of IPU with RIs_{DOM}, one
344 obtains the following expression for the inhibition factor defined above (see SI, Text S2 for
345 the derivation).

346 $$IF([DOM]) = \frac{1}{1 + [DOM]/[DOM]_{1/2}} + \frac{K_{RIs}}{k^{et}_{SO_4^{\bullet-},TC}} \times [DOM] \qquad (11)$$

347 Where K_{RIs} is defined by eq 12 and contains information about the formation and depletion of
348 RIs_{DOM} as well as the reactivity of RIs_{DOM} with TC.

349 $$K_{RIs} = \frac{k^{tr}_{RIs_{DOM},TC} \times k^{RIs}_{SO_4^{\bullet-},DOM}}{k^{d}_{RIs_{DOM}}} \qquad (12)$$

For each [DOM] series as presented in Figure 3, *IF* data were fitted to eq 11 using *IF* and [DOM] as the dependent (y) and independent (x) variable, respectively, and $[DOM]_{1/2}$ and $D_{RIs} = \frac{K_{RIs}}{k^{et}_{SO_4^{\bullet-},TC}}$ as fitting parameters. D_{RIs} expresses the relative reactivity of a given target compound with the secondary reactive intermediates, RIs_{DOM}, compared to the sulfate radical. The obtained best-fitting parameters are presented in Table 2. As can be deduced from the diagrams in Figure 3 and the determination coefficients (see Table 2), the quality of the fittings is satisfactory, supporting the validity of the adopted model. With 4-cyanoaniline as a TC, obtained $[DOM]_{1/2}$ values clearly increase in the order SRHA < SRFA < PLFA, which means a decrease of the inhibitory effect in the direction SRHA > SRFA > PLFA, in accordance with the aforementioned expectation from previous studies on excited triplet-induced oxidation. High correlations of these $[DOM]_{1/2}$ values were found with published EDC values[35] (r = 0.98) and phenolic moieties content[37] (r = 1.00) of the three DOM isolates. For sulfamethoxazole as a TC, the trend is different in that SRHA presents a higher $[DOM]_{1/2}$ value than SRFA, but PLFA still exhibits the highest $[DOM]_{1/2}$ value, as for 4-cyanoaniline. Despite this anomaly, correlations with EDC (r = 0.80) and phenolic moieties content (r = 0.64) were also relevant. When comparing the two TCs, $[DOM]_{1/2}$ values for sulfamethoxazole are on average a factor of ≈2 higher than those for 4-cyanoaniline, meaning that for the latter the reduction of $TC^{\bullet+}$ back to the parent compound has a higher efficiency than for sulfamethoxazole. The values of $[DOM]_{1/2}$ determined here are in general quite low when compared with the ones determined in excited triplet-induced oxidation studies.[14, 15] The only direct comparison that can be made for an identical TC (sulfamethoxazole) and an identical DOM (SRFA) indicate a $[DOM]_{1/2}$ value for the $SO_4^{\bullet-}$ system that is only 14 – 20 % of the values obtained for excited triplet-induced oxidation (the results of the "one-channel model" were used).[15] This large difference might be related to the production of the superoxide radical anion under the conditions of an excited triplet-induced oxidation.

375 Superoxide would act as an additional reductant of the oxidation intermediate, especially in
376 the absence of DOM, thus causing an increase of the measured $[DOM]_{1/2}$ value.
377
378 **Table 2. Parameter values for the inhibitory and secondary reactive intermediates**
379 **effects obtained by fitting the inhibition factor dependence on DOM concentration to eq**
380 **11.**

Target compound	DOM isolate	$[DOM]_{1/2}$ [a] / mg_C L^{-1}	D_{RIs} [a] / 10^{-1} L mg_C^{-1}	K_{RIs} [a] / 10^8 L mg_C^{-1} M^{-1} s^{-1}	r^2
4-Cyanoaniline	SRHA	0.109 ± 0.008	0.58 ± 0.04	1.61 ± 0.12	0.985
	SRFA	0.166 ± 0.011	0.36 ± 0.04	1.00 ± 0.12	0.986
	PLFA	0.321 ± 0.016	0.21 ± 0.04	0.58 ± 0.11	0.988
Sulfamethoxazole	SRHA	0.348 ± 0.034	1.71 ± 0.01	1.49 ± 0.08	0.901
	SRFA	0.302 ± 0.028	1.05 ± 0.01	0.91 ± 0.06	0.934
	PLFA	0.526 ± 0.029	0.48 ± 0.05	0.42 ± 0.04	0.980

381 [a] Standard errors are used.
382
383 The values of K_{RIs} obtained from the second fitting parameter, D_{RIs}, (see Table 2) consistently
384 decrease in the order SRHA > SRFA > PLFA for both TCs. K_{RIs} values for SRHA are on
385 average ≈3.2 times larger than for PLFA. Moreover, they were found to be highly correlated
386 with the EDC (r = 0.98) and the phenolic moieties content (r = 1.00) of the DOM isolates.
387 This means that the production efficiency of RIs_{DOM} increases proportionally with the
388 phenolic moieties content of the DOM. The values of K_{RIs} for sulfamethoxazole are on
389 average only ≈15% smaller than for 4-cyanoaniline, possibly indicating that both compounds
390 have a very similar second-order rate constant for their reaction with RIs_{DOM} (eq 10).

To reinforce the hypothesis that K_{RIs} is related to the formation of secondary oxidants RIs_{DOM}, an additional series of competition kinetics experiments utilizing 2,4,6-trimethylphenol (TMP) as a TC was performed (see SI, Figure S1). This phenol was selected for two main reasons. First, it is an electron-rich, easily oxidizable compound ($E^0_{red}(TMP^{\bullet +}/TMP)$ = 1.22 V vs. SHE)[38] and therefore a suitable candidate probe compound to measure radical oxidants such as the RIs_{DOM}. Second, it is not likely to undergo inhibition of oxidation, as such an inhibition was not observed in previous studies on excited triplet-induced oxidation,[14, 16] which is favorable to the unbiased measurement of RIs_{DOM}. Moreover, in the present study TMP was found to be stable in the presence of persulfate in the dark. In contrast to the results obtained for 4-cyanoaniline and sulfamethoxazole (Figure 3), *IF* values for TMP were never smaller than unity and steadily increased with increasing [DOM] for all investigated dissolved humic substances (SI, Figure S1). The increase in *IF* was linear up to [DOM] = 1.5 $mg_C\ L^{-1}$ and appeared to level off at higher [DOM] values. The linear increase concurs with the behavior of *IF* expected from eq 11, which reduces to a linear function of [DOM] in the absence of inhibitory effect (the first fraction on the right-hand side becomes equal to unity). The deviation from linearity observed at [DOM] > 1.5 $mg_C\ L^{-1}$ possibly arises from an increasingly important scavenging of the secondary radicals RIs_{DOM} by DOM. D_{RIs} values for TMP (see SI Table S3) were determined as the slopes of linear regression lines of the *IF* vs. [DOM] series in the range 0 < [DOM] < 1.5 $mg_C\ L^{-1}$, and the corresponding K_{RIs} values were derived. The variation of K_{RIs} for TMP among the three DOM types is similar as for 4-cyanoaniline and sulfamethoxazole, with high correlations to the EDC (r = 0.95) and the phenolic moieties content (r = 1.00). However, K_{RIs} values are on average by a factor of ≈23 larger compared to sulfamethoxazole and ≈20 larger compared to 4-cyanoaniline. Since K_{RIs} values for the aromatic amines were obtained by fitting *IF* values over the whole studied [DOM] range, a quantitative comparison to the values for TMP has to be made with caution.

We estimate that, if measured under the same conditions, K_{RIs} values for TMP would be about an order of magnitude higher than for the aromatic amines. These findings are in line with the assumption that the increase of *IF* with increasing [DOM] is caused by secondary oxidants as hypothesized above. In view of the large difference in reactivity between TMP on the one hand and the two aromatic amines on the other hand, these secondary oxidants appear to be more selective than $SO_4^{\bullet-}$, which concurs with their proposed identification as phenoxyl radicals.[36] The phenoxyl radical hypothesis is reasonable, since phenolic moieties of the DOM are expected to be readily oxidized by $SO_4^{\bullet-}$ to phenoxyl radicals. Moreover, part of these phenoxyl radicals are anticipated to bear electron withdrawing groups, such as carbonyl groups, as can be deduced from the low phenolic pK_a values obtained by titration of various humic substances.[39] This would imply that part of the phenoxyl radicals are effective oxidants, with one-electron reduction potentials of up to ≈ 1.1 – 1.3 V vs. SHE,[40, 41] thus probably capable of oxidizing the studied aromatic amines and the electron-rich phenol TMP. However, in view of the limited kinetic data available on the reactivity of phenoxyl radicals with organic compounds,[42] much remains to be done to verify the phenoxyl radical hypothesis.

We would like to point out that the kinetic analyses of the inhibitory and secondary oxidants effects performed in this study are strictly quantitative under the assumption that IPU is not subject to these effects. The assumption regarding the inhibitory effect is based, as explained in the Materials and Methods section, on the absence of inhibitory effect for excited triplet-induced oxidation reactions [14] and the fact that both excited triplet- and $SO_4^{\bullet-}$-induced oxidations are expected to form the same radical intermediates. The second assumption appears to be safe in that the secondary oxidants are expected to have a much lower one-electron oxidation potential than the absolute value of the oxidation potential of IPU, which is not known but can be estimated based on excited triplet-induced oxidation of phenylureas.[43]

441 The presented data support the validity of these hypotheses. In the purely hypothetical case in
442 which IPU would also be subject to a (possibly minor) inhibitory effect, the actual inhibitory
443 effect on the $SO_4^{\bullet-}$-induced oxidation of the studied anilines and sulfonamides would even be
444 larger than assessed in our analysis.

445 **Second-Order Rate Constants for the Reaction of the Sulfate Radical with DOM.** The
446 kinetic data collected for the determination of *IF* in the presence of DOM at various
447 concentrations were utilized to assess the scavenging of $SO_4^{\bullet-}$ by DOM and thus quantify the
448 corresponding second-order rate constants, $k^{s}_{SO_4^{\bullet-},DOM}$. The determination of these rate
449 constants, based on the decrease of the initial rate of transformation of the competitor IPU
450 with increasing DOM concentration, is described in detail in the SI, Text S3. The following
451 average values of $k^{s}_{SO_4^{\bullet-},DOM}$ from three independent data series (DOM concentration series
452 for the three TCs 4-cyanoaniline, sulfamethoxazole and 2,4,6-trimethylphenol) were obtained
453 (see SI, Figure S2 and Table S5): $(1.15 \pm 0.43) \times 10^4$ L mg_C^{-1} s^{-1} for SRHA, $(7.1 \pm 4.0) \times 10^3$
454 L mg_C^{-1} s^{-1} for SRFA, and $(3.1 \pm 1.2) \times 10^3$ L mg_C^{-1} s^{-1} for PLFA. Despite the relatively large
455 standard deviations, these values are well correlated to the EDC ($r = 0.98$) and phenolic
456 moieties content ($r = 1.00$) of the DOM isolates. They are also consistent with $k^{s}_{SO_4^{\bullet-},DOM}$
457 values determined for a humic acid[2] and for effluent organic matter,[13] but above the range of
458 values ($(1.53 - 3.50) \times 10^3$ L mg_C^{-1} s^{-1}) measured using laser flash photolysis for some aquatic
459 and terrestrial humic substances.[36]
460

Environmental implications

The present study has shown that DOM can have three different effects on the oxidation rate of aromatic amines induced by the sulfate radical: decreases of the oxidation rate by (1) $SO_4^{\bullet-}$ scavenging and (2) the inhibitory effect due to reduction of oxidation intermediates may be partially compensated by (3) an increase in oxidation rate through DOM-derived secondary oxidants. While $SO_4^{\bullet-}$ scavenging affects the rate of oxidation of any organic contaminant at the same extent, the inhibitory effect is expected to occur with compounds showing relatively stable oxidation intermediate radicals that are prone to reduction. In addition, increased oxidation rates caused by reaction with secondary oxidants are anticipated to be important for compounds that are easily oxidized (i.e. those possessing a high oxidation potential). Depending on the presence or absence of inhibitory effect and/or enhancement of oxidation due to secondary radicals, contaminants may be classified in the following four categories. (A) Compounds having low oxidation potential and not forming reducible radical intermediates: for these compounds, which are likely to comprise the great majority of non-aromatic contaminants, but also aromatic contaminants such as phenylureas or benzene derivatives (but excluding anilines or phenols), only $SO_4^{\bullet-}$ scavenging will play a role. (B) Compounds having low oxidation potential and forming reducible radical intermediates: in addition to $SO_4^{\bullet-}$ scavenging, the inhibitory effect will further reduce the oxidation rates of these compounds, which are predicted to include highly electron-poor aromatic amines and possibly phenols. (C) In the case of compounds with high oxidation potential and forming reducible radical intermediates, as exemplified by the anilines and sulfonamides investigated in this study, both the inhibitory effect and oxidation by secondary radicals will complicate their oxidation kinetics. (D) Finally, for compounds showing high oxidation potential and not forming reducible radical intermediates, such as electron-rich phenols, the rates of oxidation by $SO_4^{\bullet-}$ will be higher than those predicted solely on the base of $SO_4^{\bullet-}$ scavenging, due to the

action of secondary radicals. To assess abatement rates of organic contaminants in $SO_4^{\bullet-}$-based AOPs, the inhibitory effect of DOM and/or the production of secondary radicals from DOM will have to be considered for those compounds falling under the aforementioned categories B – D. This further complicates the prediction of abatement rates in the presence of $SO_4^{\bullet-}$, which is notoriously very complex as a consequence of $SO_4^{\bullet-}$ scavenging by various water matrix components (water itself, DOM and inorganic anions, such as OH^-, HCO_3^-/CO_3^{2-}, Cl^- or Br^-) and the corresponding formation of reactive inorganic radicals (e.g. $^{\bullet}OH$, $CO_3^{\bullet-}$, $Cl^{\bullet}$, $Cl_2^{\bullet-}$).[11-13]

Analogous effects caused by the presence of DOM, as observed here for oxidations induced by $SO_4^{\bullet-}$, are expected to occur in the oxidation of aromatic amines induced by other radicals, such as the ones just mentioned. Systematic studies in this area are planned. The observed enhancement of oxidation rates attributed to DOM-derived secondary oxidants, possibly phenoxyl radicals, opens new perspectives for comparative studies of radical species derived from the DOM during oxidative and photochemical processes.[44-46]

Associated content

The Supporting Information is available free of charge on the ACS Publications website at DOI: ...

List of abbreviations, HPLC analysis parameters, additional figures and tables, and derivation of equations.

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