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1 **Effect of solution pH on the dual role of dissolved organic matter in**
2 **sensitized pollutant photooxidation**

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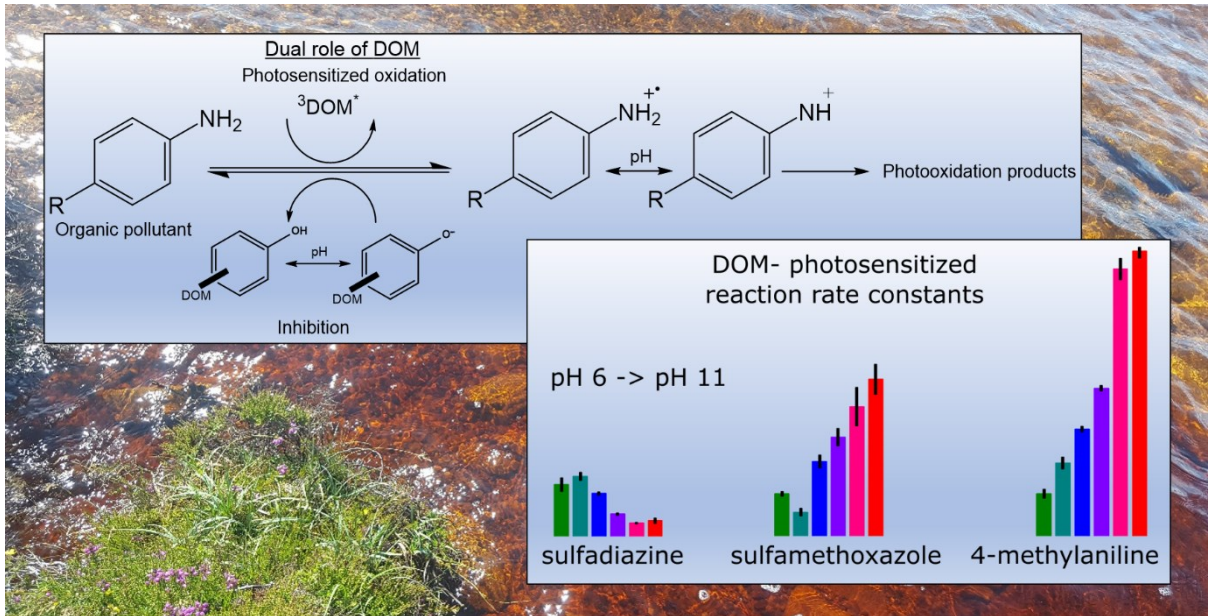
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22 **Graphical Abstract**

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25

26 **Abstract**

27 Dissolved organic matter (DOM) has a dual role in indirect phototransformations of aquatic
28 contaminants by acting both as photosensitizer and inhibitor. Herein, the pH dependence of
29 the inhibitory effect of DOM as well as the underlying mechanisms, were studied in more
30 than 400 kinetic irradiation experiments over the pH range of 6 – 11. Experiments employed
31 various combinations of one of three DOM isolates, one of two model photosensitizers, the
32 model antioxidant phenol and one of nine target compounds (TCs), comprising several
33 aromatic amines, in particular anilines and sulfonamides, and 4-cyanophenol. Using model
34 photosensitizers without antioxidants, the phototransformation of most TCs increased with
35 increasing pH, even for TCs for which pH did not affect speciation. This trend was attributed
36 to pH-dependent formation yields of TC-derived radicals and their re-formation to the parent
37 TC. Analogous trends were observed with DOM as photosensitizer. Comparison of model
38 and DOM photosensitizer datasets showed increasing inhibitory effects of DOM on TC
39 phototransformation kinetics with increasing pH. In systems with anilines as TC and phenol
40 as model antioxidant, pH-trends of the inhibitory effect could be rationalized based on the
41 reduction potential difference (ΔE_{red}) of phenoxyl/phenol and aniliny/ aniline couples. Our
42 results indicate that the light-induced transformation of aromatic amines in the aquatic
43 environment is governed by pH-dependent inhibitory effects of antioxidant phenolic moieties
44 of DOM and pH-dependent processes related to the formation of amine oxidation
45 intermediates.

46 **Synopsis:** This study improves the understanding and assessment of organic contaminants
47 abatement that is induced by sunlight in surface waters.

48 **Keywords:** Excited triplet states, radicals, speciation, reduction potential, photolysis, humic
49 substances, antibiotics.

50 **Introduction**

51 Direct and indirect photochemical reactions are important transformation pathways of
52 biomolecules and contaminants in the aquatic environment¹⁻³, leading for example to
53 detoxification of halogenated disinfection by-products.^{4,5} Dissolved organic matter (DOM) is
54 a chemically complex and structurally diverse component of natural water bodies that plays
55 critical roles in a wide range of environmentally relevant processes.⁶⁻⁸ In clear surface waters,
56 DOM is the main absorber of sunlight in the upper water layer. Photon absorption by DOM
57 can trigger both indirect phototransformation of contaminants and photoinactivation of
58 pathogens but also result in DOM photobleaching.⁹⁻¹⁸ Photochemical processes in surface
59 waters involve various short-lived reactive species and different reaction pathways,¹⁹⁻²³ with
60 DOM and its excited triplet states (³DOM*) as key participants.²⁴⁻²⁹ In fact, DOM plays a dual
61 role in photochemical transformation reactions by acting both as photosensitizer, enhancing
62 photochemical transformations, and as antioxidant, slowing down photochemical
63 transformations by quenching reactive intermediates.

64 Excited triplet states, including ³DOM*, are generally known to undergo electron transfer
65 reactions.³⁰ According to equation 1, ³DOM* may withdraw an electron from an oxidizable
66 organic target compound (TC) to form a DOM radical anion DOM*⁻ and a one-electron
67 oxidized contaminant radical cation TC*⁺. The latter are short-lived intermediates that may
68 further react to stable oxidation products TC_{ox} (equation 2). However, TC*⁺ may itself
69 abstract an electron from an electron-rich antioxidant (AO) moiety, a reaction that
70 reconstitutes the parent TC (equation 3). Reaction with the antioxidant thus quenches TC
71 oxidation.





72

73 The inhibition of triplet-induced reactions through antioxidants lowers the rate of TC
74 transformation. Phenolic moieties, which are abundant in DOM,^{31,32} are considered a major
75 reservoir of antioxidant capacity in natural waters.

76 The effect of DOM and model antioxidants on triplet-induced oxidations of organic
77 compounds has been investigated in several recent studies.³³⁻⁴² These studies showed that
78 DOM inhibits the oxidative transformation of a wide range of environmentally relevant
79 compounds, particularly when containing aniline functional groups, such as sulfonamide
80 antibiotics, and phenolic groups.³³ The inhibitory effect of terrestrial DOM was found to be
81 substantially higher than that of aquatic DOM.³⁴ The antioxidant properties of DOM were
82 characterized using electrochemical techniques which provided evidence for phenolic
83 moieties within DOM as main antioxidants.^{43,44} The role of phenolic moieties as antioxidants
84 in DOM was further characterized by kinetic irradiation experiments in model systems with
85 triplet photosensitizers and either phenolic antioxidants or DOM as antioxidant.³⁵ Partial pre-
86 oxidation of DOM by ozone diminished its antioxidant activity³⁸ and also decreased the
87 inhibitory effect of DOM on triplet induced transformations.³⁶ Quenching of triplet states by
88 DOM was ruled out as a potential cause of the inhibitory effect.⁴⁵ The inhibitory effect of
89 DOM has been reported for radical cations induced by direct absorption of light.³⁹ However,
90 reformation of initial compounds from metastable transformation products may also occur for
91 other types of photochemical reaction pathways, such as reversible photohydrations and
92 photooxygenations.⁴⁶⁻⁴⁹

93 The aims of this study were (1) to investigate how the inhibitory effect of DOM changes with
94 pH and (2) to compare this effect to other pH-dependent effects on triplet-induced
95 transformation kinetics. We anticipated that varying the pH would largely alter the inhibitory
96 effect due to causing speciation shifts of the phenolic antioxidant moieties within the DOM.
97 These phenolic moieties deprotonate to phenolates over a wide pH range centred at ≈ 9.7 .^{32, 50}
98 Phenolates are more readily oxidized than undissociated phenols because their one-electron
99 oxidation potential is ≈ 0.7 V higher compared to their protonated counterparts.⁵¹ Therefore,
100 the working hypothesis for this study was that the inhibitory effect of DOM, as well as of
101 phenolic model antioxidants, increases with pH from neutral to basic solution pH conditions.
102 However, this working hypothesis may be simplistic because more complex pH dependencies
103 are conceivable. pH effects on radical intermediates might weaken or even reverse the trend
104 expected based on our working hypothesis. pH affects not only the equilibrium speciation of
105 aniline radical cations,^{52, 53} which are key intermediates for the inhibitory effect (see equation
106 3), but also the rates of the corresponding deprotonation and protonation reactions.⁵⁴ With
107 increasing pH, the deprotonation rates of the radical cations $TC^{*\cdot+}$ are expected to increase and
108 the protonation equilibrium is shifted to the deprotonated species. The latter are weaker
109 oxidants than the radical cations, and a decrease in reduction rate of the radicals and thus a
110 smaller inhibitory effect is expected. Furthermore, $TC^{*\cdot+}$ and their deprotonated counterparts,
111 are possibly involved in other pH-dependent reactions leading to their further transformation
112 to oxidized products or to reduction back to their parent compounds. Finally, pH may also
113 alter transformation kinetics by changing light absorption characteristics of DOM, production
114 rates and reactivities of $^3DOM^*$ (generated from a variety of different precursor
115 chromophores) and changes in TC ground state speciation. Despite the importance of pH on
116 DOM photochemistry in aquatic photochemical reactions, most studies considering the effect
117 of pH on surface water photochemistry focus on indirect photodegradation of specific target

118 compounds, while providing an explanatory framework around pH-induced shifts of reactive
119 species steady-state concentration and target compound speciation,⁵⁵⁻⁵⁷ but without
120 considering the photochemical or photophysical processes, such as changes in fluorescence
121 intensity with pH,⁵⁸ within DOM in detail. pH is an important driver in DOM
122 photobleaching, which increases towards both lower and higher pH exhibiting a minimum
123 around pH 6 – 6.5.⁵⁹ Increased photobleaching at higher pH has been explained with the
124 expansion of DOM and its chromophores⁶⁰, along with increasing light absorption with
125 increasing pH⁶¹ and enhanced internal charge transfer due to deprotonated phenolic
126 moieties.⁶²

127 The irradiation experiments for this study were carried out with photosensitizers, antioxidants
128 and TCs chosen based on previous studies^{34-36, 51, 63, 64} in solutions covering a range of pH 6 –
129 11. This pH range was selected to include the pH of most natural surface waters (~ 7 – 9) and
130 to cover protonation equilibria of phenolic moieties of DOM. Lower pH within the range of
131 pH ~ 2 – 6, which are for example occurring in atmospheric water⁶⁵ and acid mine
132 drainage⁶⁶, were not included due to the additional complexity arising by protonation
133 equilibria of TCs and carboxylic moieties within DOM ($pK_a \approx 4$).^{32, 50} In the studied pH
134 range, carboxylic moieties of DOM are not expected to play an important role for the
135 investigated kinetic changes, because they are mostly deprotonated.

136 Aromatic ketones and DOM isolates were employed as photosensitizers. Suwannee River
137 fulvic acid (SRFA) and Nordic aquatic fulvic acid (NAFA) served as representative DOMs of
138 terrestrial origin, derived from higher plants, while Pony Lake fulvic acid (PLFA) served as
139 representative aquatic DOM derived mostly from microbial sources.⁶⁷ Anilines, including
140 sulfonamides, and 4-cyanophenol served as TCs. Choice of TCs was based on previous
141 studies characterizing the inhibitory effect of DOM on anilines and sulfonamides at fixed pH

142 ³³⁻³⁵, the importance of anilines and their derivatives as aquatic contaminants^{68, 69}, including
 143 their frequent use as model pollutants,⁷⁰ and the availability of radical cation standard one-
 144 electron reduction potential data. Sulfonamides are a broad class of high-usage classic
 145 antibiotics with various ecotoxicological effects in the environment that can be frequently
 146 detected in surface waters, including at above micromolar concentrations.⁷¹ 4-cyanophenol
 147 was chosen as a representative phenolic compound without antioxidant properties. Both
 148 unsubstituted phenol and DOM isolates were used as antioxidants. Four different types of
 149 experimental systems were utilized to study TC phototransformation, namely: System 1,
 150 employing either a model photosensitizer or DOM (in the latter case, DOM acted both as
 151 photosensitizer and antioxidant); System 2, employing a model photosensitizer and DOM as
 152 antioxidant; System 3, employing DOM as photosensitizer and a model antioxidant; System
 153 4, employing a model photosensitizer and a model antioxidant.

154

155 **Materials and Methods**

156 **Chemicals.** A list of target compounds, photosensitizers, antioxidants and DOMs used in this
 157 study is provided in Table 1. Supplier and purity details, including information on additional
 158 chemicals used and preparation of stock solutions, are provided in Supporting Information (SI)
 159 Text S1.

160

161 **Table 1.** Target compounds, model photosensitizers, model antioxidant and DOM isolates,
 162 with acid dissociation constants (pK_a) and one-electron standard reduction potentials (E°_{Red})
 163 of their relevant reactive species.

Compound	Abbreviation	CAS-RN IHSS No.	$pK_a^{(a)}$	$pK_a^{*(b)}$	$E^\circ_{\text{Red}}^{(c)}$ [V vs. SHE]
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Model photosensitizers	2-acetonaphthone	2AN	93-08-3	-	1.7 ⁷²	1.10 ^{45, 73} , 1.34 ⁷⁴
	4-carboxbenzophenone	CBBP	611-95-0	4.57 ⁷⁵	n.a. ^{76(d)}	1.83 ^{45, 77}
Target compounds	aniline	ANI	62-53-3	4.87 ⁷⁵	7.05 ⁵²	1.02 ⁵³
	4-methoxyaniline	4MtA	104-94-9	5.36 ⁷⁵	9.6 ⁵³	0.79 ⁵³
	4-methylaniline	4MA	106-49-0	5.08 ⁷⁵	8.5 ⁵³	0.92 ⁵³
	<i>N,N</i> -dimethylaniline	DMA	121-96-7	5.07 ⁷⁵	n.a.	0.87 ⁷⁸
	sulfamethoxazole	SMX	723-46-6	1.6±0.2, 5.7±0.2 ⁸¹	n.a.	n.a.
	sulfachloropyridazine	SCPD	80-32-0	2±3, 5.9±0.3 ⁸¹	n.a.	n.a.
	sulfadiazine	SD	38-35-9	2±1, 6.4 ± 0.6 ²⁸	2.9 ⁸²	1.30 ^(c) , 1.09 ^{82(c)}
	4-cyanophenol	4CNP	767-00-0	7.97 ⁷⁵	< 0 ⁸³	1.71 ^{51(c)} , 1.12 ^{84(f)}
Model antioxidant	phenol		108-95-2	9.99 ⁷⁵	-2 ^{83, 85}	1.5 ^{51(c)} , 0.79 ^{84(f)}
DOM isolates	Suwannee River fulvic acid	SRFA	2S101F	3.76, 9.84 ⁵⁰	n.a.	n.a.
	Pony Lake fulvic acid	PLFA	1R109F	4.52, 9.48 ⁸⁶	n.a.	n.a.
	Nordic aquatic fulvic acid	NAFA	1R105F	3.79, 9.67 ³²	n.a.	n.a.

164 ^a Titration fitting parameters for proton binding of IHSS extracts assuming two main types of proton binding
165 sites within humic substances, namely carboxylic acids and phenols.³²

166 ^b Dissociation constant of relevant reactive species: protonated excited triplet state (photosensitizer), radical
167 cation (target compound) or protonated phenoxy radical (target compound or model antioxidant).

168 ^c Standard one-electron reduction potential of the excited triplet state (photosensitizer) or radical cation
169 (TC^{•+}/TC), except where noted [Unit: V vs. standard hydrogen electrode, SHE]

170 ^d n.a.: not available

171 ^e Standard one-electron reduction potential of sulfadiazine radical / sulfadiazine anion (SD^{•-}/SD⁻)

172 ^f Standard one-electron reduction potential of phenoxy radical / phenolate (PhO^{•-}/PhO⁻).

173 **Preparation of solutions.** All aqueous solutions were prepared using ultrapure water (Milli-
174 Q, Millipore). Solutions for irradiations were prepared in 20 mL (final volume) capped quartz-
175 glass tubes with a headspace of approximately 2 mL and contained 5 mM phosphate buffer,
176 which was used throughout the investigated pH range of 6 – 11. Phosphate buffered solutions
177 for all experiments were used to avoid possible effects on TC transformation kinetics due to
178 the increasing importance of carbonate radicals in carbonate buffered systems at elevated pH.^{26,}
179 ^{55, 56} Note that experiments conducted at pH 9 and 10 were not in the optimum buffer range of
180 phosphate. However, pH measurements before and after each set of irradiations showed that
181 the pH values drifted by ≤ 0.05 pH units, even under these alkaline conditions. Solutions
182 contained different combinations of a single TC, a model photosensitizer or DOM as
183 photosensitizer, and a model antioxidant or DOM as antioxidant. The initial TC concentration
184 was 5 μM. Concentrations of model photosensitizers were 50 μM for CBBP and 10 – 100 μM
185 for 2AN (Table S5a/b for different TCs). TC, model photosensitizer and phenol addition to the
186 solutions did not change its pH. The DOM concentration was 2.5 mg C L⁻¹ (applied in most

187 cases) or 1.0 mg C L^{-1} . Addition of DOM stock solutions decreased the solution pH by $0.1 \pm$
188 0.02 units at pH 9 – 11. Possible changes in TC phototransformation kinetics resulting from
189 this slight pH decrease were assumed to be within experimental error. Thus, we report target
190 integer pH values in the results section. The concentrations of the model antioxidant phenol
191 were $10 \text{ }\mu\text{M}$ or $25 \text{ }\mu\text{M}$. The added phenol concentration is reasonably comparable to the
192 concentration of both phenolic moieties and electron donating groups within solutions
193 containing $1 - 2.5 \text{ mg C L}^{-1}$ DOM.³⁵ SRFA and NAFA phenolic content has been measured
194 via titration and 1 mg C L^{-1} corresponds to $3 \text{ }\mu\text{M}$ phenolic moieties, while not all phenolic
195 moieties act as antioxidants.³² Similarly, the electron donating capacity (EDC) for a variety of
196 humic substances was measured at an applied potential of $E_h = 0.61 \text{ V}$, pH 7, and ranged
197 approximately from $0.6 - 1.8 \text{ }\mu\text{M EDC per mg humic substance}$.⁴³

198 **Irradiation experiments.** The irradiation setup consisted of a merry-go-round photoreactor
199 (Hans Mangels, Germany) that was equipped with a 500 W medium-pressure lamp, a
200 borosilicate glass cooling jacket, a 0.15 M sodium nitrate filter solution which cut off lamp
201 emission wavelengths $\leq 320 \text{ nm}$, to minimize direct phototransformation of TCs, and a
202 cooling system adjusted to 25°C ($\pm 0.2^\circ\text{C}$). Further details on the setup are provided
203 elsewhere.³⁴ Model and DOM photosensitizer concentrations and irradiation times for
204 complete kinetics experiments (SI Tables S2, S3, S5 – S8) were optimized according to
205 preliminary trials and results of previous studies,³⁴⁻³⁶ irradiation times ranged from 5 min to
206 90 min. Differences in model photosensitizer concentration across different experiments and
207 pH are not expected to affect normalized reaction rate constants. To determine transformation
208 kinetics of the TCs, six samples of $400 \text{ }\mu\text{L}$ were withdrawn from each quartz-tube in
209 equidistant time intervals during photoirradiation. Samples were immediately stored at 4°C
210 and analysed by high-performance liquid chromatography (HPLC) within 36 h. Most
211 experiments were performed in duplicate (a few in triplicate) and were found to yield

212 reproducible results with a deviation in reaction rate constants of <10% between repetition
213 experiments, except for a few experiments conducted at pH 10 and 11 with higher deviations.
214 Details on analytical methods, including HPLC analysis, UV-vis absorption and pH-
215 measurements are provided in Text S2 and Table S1.

216 **Data analysis.** The depletion of TCs was fitted assuming pseudo-first-order reaction kinetics
217 (i.e., reaction rate constants k [s^{-1}] equalled the linear slopes of TC concentrations, expressed
218 in natural logarithmic units, vs. irradiation times). To achieve comparable results across all
219 TC/photosensitizer/inhibitor/pH combinations, reaction rate constants were first corrected for
220 direct phototransformation of the TC (see Text S3 for discussion on effect of pH on direct
221 phototransformation for single TCs and Table S2/S3 for measured direct phototransformation
222 rate constants) and, for System 2 experiments (i.e., for solutions with model photosensitizers
223 and DOM as antioxidant), to compensate for the photosensitizing effect of DOM. These
224 corrections were performed separately for separate pH values by subtracting reaction rate
225 constants for each TC in pure water or in solutions containing only DOM without model
226 sensitizers from rate constants obtained with model sensitizers (either in the absence or
227 presence of DOM). Light-screening correction was applied in a second step using the factors
228 for different photosensitizer and inhibitor combinations listed in Tables S9 – S14. Details on
229 the determination of correction factors are provided elsewhere.³⁶ Consistent with previous
230 publications, the corrected rate constants are labelled with the superscript (2) (i.e. $k^{(2)}$) to
231 indicate that two corrections were made.³⁴⁻³⁶ In no case did the corrections alter trends that
232 were apparent already in the uncorrected data. UV-absorption spectra of TCs and phenol are
233 shown in Figures S1 and S2. UV-vis absorption spectra of model and DOM photosensitizers,
234 molar (model photosensitizers) and specific absorption coefficients (DOM) at the relevant
235 wavelengths of the irradiation system are provided in Figure S4 and Table S4, alongside a
236 discussion on the effect of spectral changes of both model photosensitizers and DOM on the

237 observed rate constants in this study, as well as the importance of pH-induced changes in
238 photophysical processes (Text S4).

239 **Results and Discussion**

240 **Transformation of TCs by model photosensitizers and DOM (System 1).** We determined
241 rate constants of indirect phototransformation for nine TCs in combination with two model
242 photosensitizers, 2AN (Figure 1a) and CBBP (Figure 1b), and two DOM isolates, PLFA
243 (Figure 1c) and SRFA (Figure 1d) over the pH range of 6 – 11. To facilitate comparison
244 between different TCs and photosensitizers, the displayed rate constants, $k_{TC,pH,norm}^{(2)}$, were
245 corrected rate constants ($k_{TC,pH}^{(2)}$) normalized to the value obtained at the lowest tested pH of 6
246 ($k_{TC,pH\ 6}^{(2)}$), i.e., $k_{TC,pH,norm}^{(2)} = k_{TC,pH}^{(2)} / k_{TC,pH\ 6}^{(2)}$. Numerical values of all these rate constants
247 are provided in Tables S2, S3, S5 – S8, in the SI.

248 The rate constants in systems containing a model sensitizer (either 2AN or CBBP) reflect
249 only the effect of pH on photosensitized TC transformation as there were no antioxidants in
250 these solutions, and thus no inhibitory effects. Rate constants of TC phototransformation in
251 the presence of PLFA and SRFA reflect the combined effect of DOM photosensitization and
252 inhibitory effects through DOM antioxidant moieties. Concerning the effect of reactive
253 oxygen species with changing pH, Text S5 discusses the role of superoxide and in detail the
254 possible impact of singlet oxygen (1O_2) on the observed rate constants. In summary, the
255 impact of 1O_2 is expected minor based on its available reaction rate constants with TCs.

256 In the systems containing the model photosensitizers 2AN or CBBP, the transformation rate
257 constants of anilines (ANI, 4MA, 4MtA and DMA) strongly increased with increasing pH,
258 between a factor of 2.1 (4MA) and 9.3 (DMA), relative to the lowest rate constant measured
259 at pH 6. This pH trend for anilines may be rationalized by aniline radical cations formed

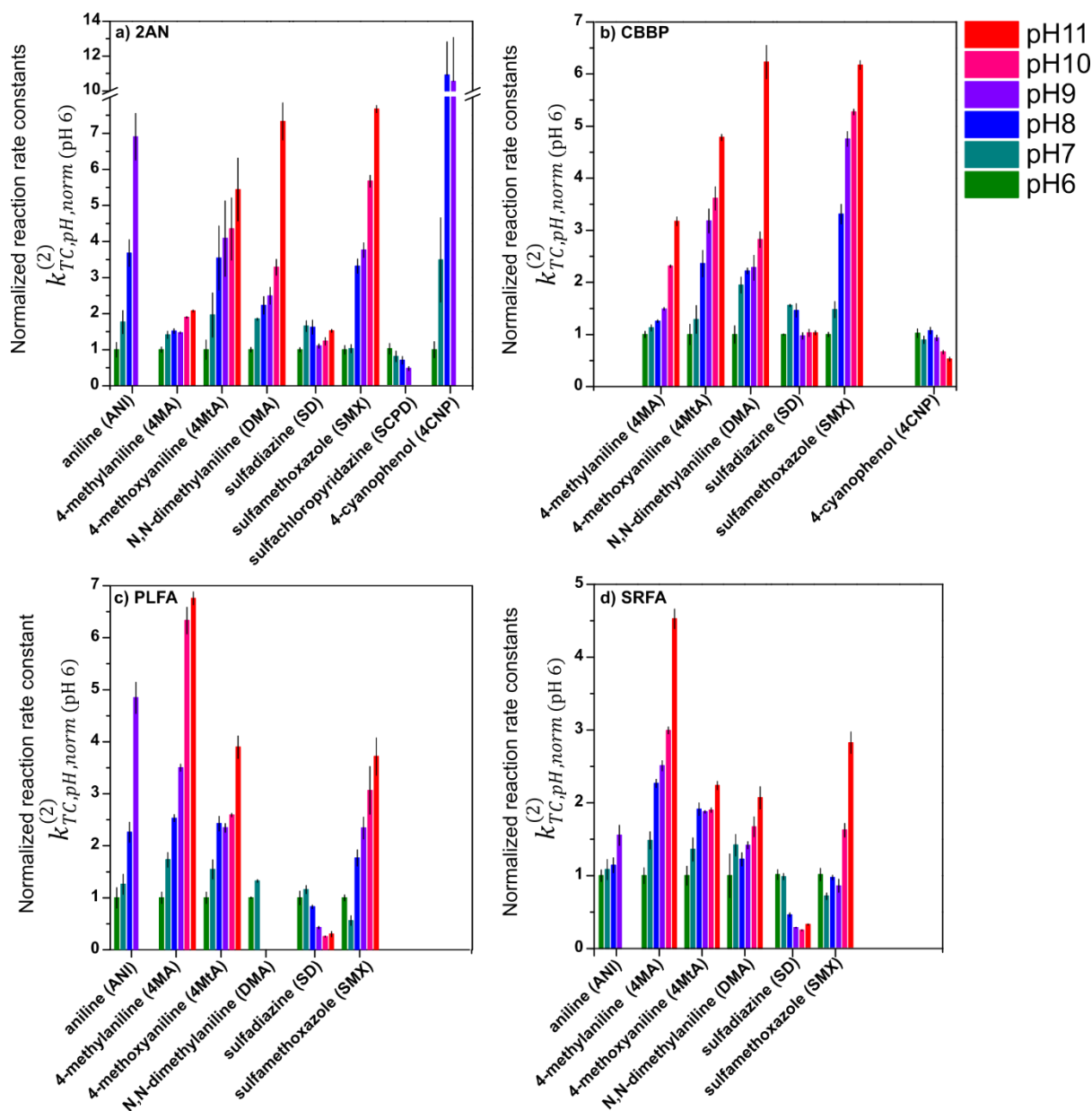
260 through one-electron oxidation deprotonating at higher pH. For ANI, 4MA and 4MtA the
261 resulting aniliny radicals are expected to be more prone to coupling reactions, which would
262 compete with a possible reduction by superoxide (Text S5). For DMA, deprotonation of the
263 radical cation would lead to a carbon centered radical on one of the methyl groups and further
264 degradation, also competing with a possible reduction by superoxide (Text S5). As compared
265 to the anilines, there was no consistent pH trend for the sulfonamides SMX, SCPD and SD.
266 With increasing pH, the phototransformation rate constants strongly increased for SMX,
267 moderately decreased for SPCD, while no clear pH trend was observed for SD.

268 When comparing transformation by the two photosensitizers 2AN and CBBP, the effect of
269 pH on the normalized pseudo-first-order rate constants for each individual TC was similar
270 with a single exception: For 4CNP (pKa: 7.97), the normalized rate constants strongly
271 increased with pH for 2AN but not for CBBP. This observation can be explained by the
272 different one-electron reduction potentials of the photosensitizers in their excited triplet states
273 ($E_{red}^{0*}({}^3\text{Sens}^*/\text{Sens}^{\bullet-})$). Assuming that the phototransformation of 4CNP is initiated by a one-
274 electron transfer to the excited triplet state of the photosensitizer⁵¹, excited triplet CBBP
275 ($E_{red}^{0*}({}^3\text{CBBP}^*/\text{CBBP}^{\bullet-}) = 1.83 \text{ V vs. standard hydrogen electrode (SHE)}$) is expected to
276 undergo a diffusion-controlled reaction with both the undissociated and deprotonated forms
277 of 4CNP (having one-electron oxidation potentials of -1.71 and -1.12 V vs SHE,
278 respectively), which explains the lack of pH effect on the transformation rate of 4CNP. In
279 contrast, for ${}^3\text{2AN}^*$ with a lower one electron reduction potential ($E_{red}^{0*}({}^3\text{2AN}^*/\text{2AN}^{\bullet-}) =$
280 1.10 – 1.34 V vs. SHE), a fast reaction is only expected to occur with the deprotonated form
281 of 4CNP, explaining the enhancement in transformation rate of 4CNP with increasing pH.

282 In qualitative terms, the TC reaction rate constants with DOM as a photosensitizer (Figure 1c
283 and d) had a similar pH dependence as those observed with the model photosensitizers. This

284 finding supports that both 2AN and CBBP are suitable model photosensitizers to mimic the
285 ³DOM*-induced TC oxidation over the studied pH range. However, compared to the
286 experimental series with model photosensitizers only, we expected decreased photosensitized
287 transformation rate constants with increasing pH due to the presence of DOM antioxidant
288 moieties that inhibit transformation. Given the two competing processes of photosensitization
289 and inhibition in the systems containing DOM, the similar pH trends observed in the presence
290 and absence of DOM antioxidant moieties suggest that inhibition by DOM generally played a
291 minor role. The only exception to this conclusion is the reaction of SD: its rate constants were
292 not strongly affected by pH for model sensitizers but decreased with increasing pH when
293 DOM was the photosensitizer. The latter finding concurs with the expectation that the
294 inhibition caused by antioxidant moieties of DOM increases with increasing pH. The absence
295 of a significant pH effect for SD transformation without antioxidants agrees with previous
296 observations.²⁸ This difference to the behavior of the anilines and SMX is possibly related to
297 the particular pathway of triplet-sensitized phototransformation of sulfonamides exhibiting a
298 six-membered heterocyclic substituent (such as SD, but not SMX), which leads to the
299 formation of SO₂ extrusion products.²⁸ The limited amount of data available for SCPD
300 appear to indicate a pH dependence of the rate constants more similar to SD than SMX,
301 which concurs with the same type of substituent carried by SD and SCPD.

302 Note, for DOM as photosensitizer, electrostatic attraction between negatively charged DOM
303 and TC compounds can be neglected over the whole pH range, since none of the TCs is
304 present as a positively charged (cationic) species at pH \geq 6. This includes SD, exhibiting a
305 significant speciation change between pH 6 and pH 7 from neutral (zwitterionic) to anionic,
306 while changes on the photosensitized rate constant of SD are small in this pH span compared
307 to those observed for pH 7 – 11.



308

309 **Figure 1.** Pseudo-first-order rate constants, normalized to the corresponding values at pH 6,
 310 for the transformation of target compounds photosensitized by model photosensitizers (a) 2-
 311 acetophenone (2AN), (b) benzophenone-4-carboxylate (CBBP), or dissolved organic matter
 312 isolates (c) Pony Lake fulvic acid (PLFA), and (d) Suwannee River fulvic acid (SRFA) at
 313 several different pH values indicated in the legend. Error bars show 95% confidence intervals
 314 (Tables S4-S8).
 315

316 **Assessing the individual inhibition and photosensitization contribution in DOM-induced**
 317 **phototransformations.** Due to the intrinsic coexistence of photosensitizing and antioxidant
 318 moieties in DOM, the individual contribution of the two types of **moieties** can be determined

319 using comparative irradiation experiments. In previous studies we expressed inhibition by
320 DOM based on a calculated inhibition factor (*IF*).³⁴⁻³⁶ *IF* was defined as the ratio of rate
321 constants for the transformation of a TC in the presence and absence of antioxidants obtained
322 with the same photosensitizer (under identical irradiation conditions). Here we use an
323 analogous concept: the normalized reaction rate constants for the transformation of a TC
324 photosensitized by a given DOM at a certain pH are divided by the corresponding normalized
325 rate constants obtained using a given model photosensitizer (in the absence of inhibitors).
326 This ratio, termed here as “comparative inhibition factor” (*CIF*), expressed as:
327 $CIF = k_{TC,pH,norm,DOM}^{(2)} / k_{TC,pH,norm,Sens}^{(2)}$. This parameter is a less precise indicator of the
328 inhibitory effect than *IF* because it is based on rate constants obtained using two different
329 photosensitizers (i.e., a given DOM and a given model sensitizer). In addition, DOM
330 photosensitizer moieties are subject to changes in absorbance and possibly in intersystem
331 crossing quantum yields with varying solution pH (Texts S4 and S5), while we do not expect
332 such pH effects to occur for the used model photosensitizers.

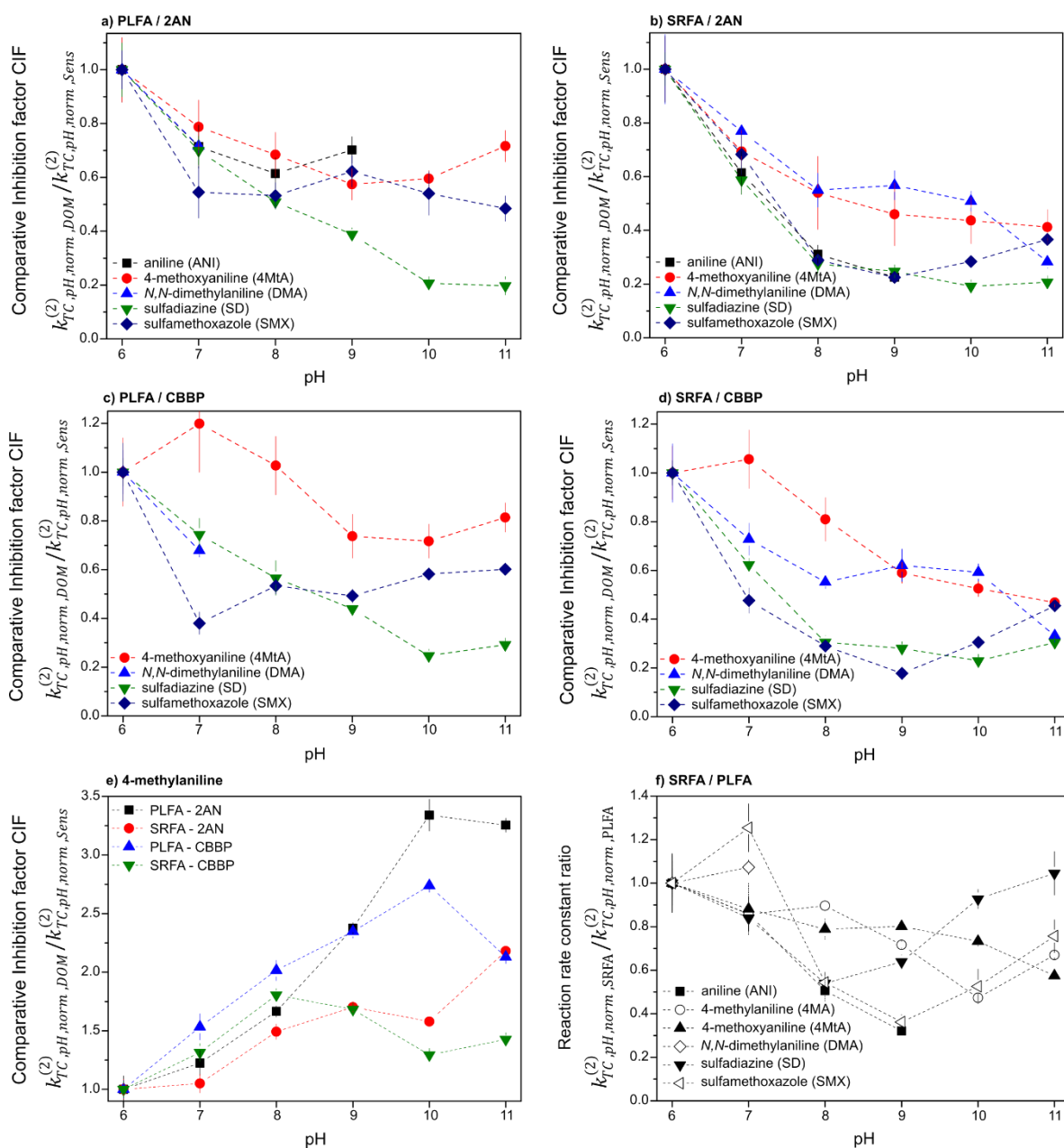
333 Figure 2a-e shows calculated *CIF* of the four DOM-model sensitizer combinations and six
334 TCs. Note that, the values of *CIF* at pH 6 are always one (by definition). Therefore, *CIF* is
335 not able to reveal an inhibitory effect at pH 6 but is useful to describe the changes in
336 inhibitory effect with increasing pH. We used the lowest tested pH value as the reference
337 point for data evaluation primarily based on our initial hypothesis that phenolic antioxidant
338 activity increases with increasing pH. For most target compounds, *CIF* decreased as the pH
339 increased (Figure 2a-d), supporting the hypothesis that the inhibitory effect of DOM
340 increases with increasing pH because of an increased fraction of deprotonated phenolic
341 moieties in the DOM. We observed the opposite trend for 4MA for which we currently have
342 no explanation (Figure 2e): *CIF* increased with increasing pH.

343 When evaluating datasets across different TCs, the decrease in *CIF* was largest over the
344 circumneutral pH range between pH 6 and 8. At mildly alkaline conditions from pH 8 the
345 increase in inhibition subsided or reversed. Also considering the observed exception for
346 4MA, these pH trends indicate that *CIF* changes with pH might depend on various factors,
347 such as protonation equilibria involving TC^{*+} , the reactions of transformation intermediates of
348 the TCs with superoxide radical anion to form transformation products or leading to
349 reformation of the parent compound, or with DOM, yielding addition of the oxidized TCs to
350 DOM. The latter reaction, which was suggested to occur for aniline in oxidative aqueous
351 environment,⁸⁷ possibly affects in particular the transformation of 4MA, whose *CIF* exhibits a
352 very distinct pH dependence.

353 Comparing Figure 2a/c and Figure 2b/d suggests that *CIF* tends to be lower for SRFA
354 compared to PLFA. A direct comparison is provided in Figure 2f based on the normalized
355 reaction rate constants $k_{TC,pH,norm,SRFA}^{(2)}/k_{TC,pH,norm,PLFA}^{(2)}$. For most TCs, this ratio is smaller
356 than unity for any pH value ≥ 7 , the lowest values being observed at $8 \leq \text{pH} \leq 10$. This can be
357 interpreted as an enhanced inhibitory effect of SRFA in the latter pH range compared to
358 PLFA. In general, a higher inhibitory effect of SRFA compared to PLFA is expected based
359 on previous studies and the higher concentration of antioxidant moieties in SRFA.³⁴⁻³⁶ The
360 fact that the minimum values in *CIF* ratios are found in this pH range, but not exactly at the
361 same pH value for any TC, suggests that the inhibitory effect is related to the protonation
362 equilibria of the phenolic moieties in DOM and the radical intermediates of each TC (i.e.,
363 TC^{*+}). These aspects will be discussed in more detail when addressing results from **System 4**
364 experiments (*vide infra*).

365 A possible explanation for the different behavior of 4MtA in systems with CBBP and 2AN at
366 pH below $\sim 7 - 8$ could be that, due to the high reduction potential of excited triplet CBBP,
367 secondary DOM-derived photo-oxidants are formed, which can transform the readily

368 oxidizable 4MtA and would mask DOM-induced inhibition observed in the systems with
 369 2AN.

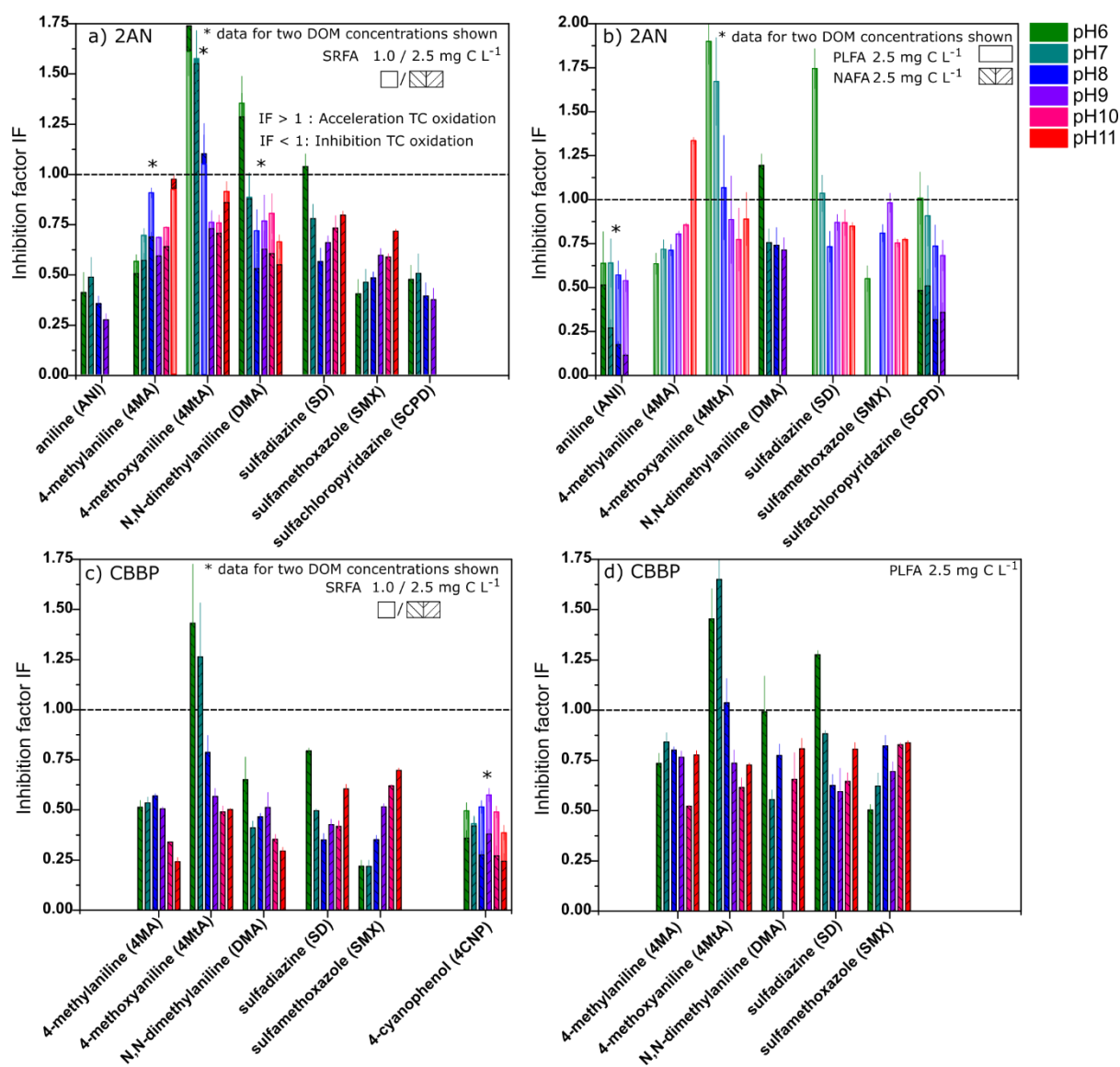


370
 371 **Figure 2.** Comparative inhibition factors of photosensitized transformation of target
 372 compounds (TCs) for the DOM isolates [2.5 mg C L⁻¹] Pony lake fulvic acid (PLFA) and
 373 Suwannee River fulvic acid (SRFA) in relation to the model sensitizers 2-acetonaphthone
 374 (2AN) and benzophenone-4-carboxylate (CBBP) [a-e] and reaction rate constant ratio of SRFA
 375 and PLFA photosensitized transformations of TCs [f] at different pH. Experimental error bars
 376 were determined by the error propagation law using 95% confidence intervals of pseudo-first
 377 order transformation rate constants of single photosensitizer/TC systems.
 378

379 **Transformation of TCs by model photosensitizers in the presence of DOM as**
380 **antioxidant (System 2).** Figure 3 shows results for irradiations with model photosensitizers
381 and DOM to assess the role of DOM as antioxidant. Data are presented as inhibition factor
382 (*IF*), which is the ratio of pseudo-first-order reaction rate constants with and without added
383 DOM as antioxidant (i.e., $IF = k_{TC,pH,Sens,AO}^{(2)} / k_{TC,pH,Sens}^{(2)}$). The corrected reaction rate
384 constants used in the calculation of *IF* are provided in Figures S8 – S16. For most of the
385 studied systems across all TCs and pH values, there was a significant inhibitory effect (*IF* <
386 1). The determined *IF* values are like those reported previously at pH 8 for the same model
387 photosensitizer, TC and DOM combinations.^{33,34} The inhibitory effect at 2.5 mg_C L⁻¹ DOM
388 addition was stronger than at 1.0 mg_C L⁻¹ across the whole pH range. Higher *IF* values (i.e.,
389 weaker inhibitory effect) for microbially derived PLFA compared to terrestrially derived
390 SRFA and NAFA confirm previously measured *IF* data at pH 8.³⁴

391 Regarding the pH dependence of the inhibitory effect, four out of eight TCs (ANI, 4MtA,
392 DMA and SCPD) with 2AN as photosensitizer showed a decreasing *IF* with increasing pH.
393 For 4MA, SMX, and SD there was either an increase in *IF* or no obvious trend with pH. The
394 results for the latter TCs appear to not support the initial hypothesis that *IF* decreases (i.e.,
395 inhibition increases) with increasing pH, considering that the antioxidant capacity of DOMs
396 (measured as electron donating capacity, EDC) almost doubles by increasing the pH from 7
397 to 9.⁴³ *IF* trends were similar for both 2AN and CBBP, except for 4MA. The data of 4-CNP,
398 which show an almost constant inhibitory effect over the studied pH range (Figure 3c), could
399 be explained by the high reduction potential (i.e., strongly oxidizing character) of the 4-
400 cyanophenoxyl radical (1.12 V, see Table 1). This may cause a very efficient reduction of this
401 radical by both undissociated and deprotonated phenolic antioxidant moieties of DOM
402 leading to re-formation of the parent compound and hence inhibited reaction. Furthermore,
403 especially for 4MtA, but also for DMA and SD, some *IF* values > 1 were observed in the

404 lower pH range, meaning that for these TCs and these pH conditions an enhancement effect
 405 of DOM was dominant over a possible inhibitory effect. Analogous enhancements have been
 406 observed previously and attributed to the formation of oxidizing species resulting from the
 407 reaction of DOM with the primary oxidant, specifically, the triplet state of a model
 408 photosensitizer^{33,34} but also for the sulfate, radical which was studied separately.⁸⁸ This
 409 enhancement effect could explain the unclear trends observed for System 2.



410 **Figure 3.** Inhibition factors (*IF*) for the transformation of target compounds (TCs; x axis)
 411 photosensitized by 2-acetonaphthone (2AN) (a-b) and benzophenone-4-carboxylate (CBBP)
 412 (b-d) with the DOM isolates SRFA, PLFA and NAFA in their role as natural antioxidants.
 413

414 **Transformation of TCs by DOM as photosensitizer in the presence of phenol as**
415 **antioxidant (System 3).** Experiments were performed using aniline as TC, DOM isolates as
416 photosensitizers, and phenol as antioxidant in the pH range from 6 to 9. Their results are
417 represented in terms of IF in Figure S17. While the inhibitory effect of phenol was almost
418 absent at pH 6 (i.e., $IF \cong 1$), it was significant at higher pH, with an increase in inhibition
419 (i.e., decrease in IF) observed for PLFA and SRFA, and a pH independent IF for NAFA. The
420 effect of phenol addition on IF was more pronounced for PLFA than for SRFA or NAFA,
421 which can be ascribed to the lower intrinsic phenol content of PLFA^{32, 50} and concurs with the
422 results of previous studies performed at pH near 8.^{35, 37}

423 **Transformation of TCs in the presence of 2-acetonaphthone as a model photosensitizer**
424 **and phenol as a model antioxidant (System 4).** For this part of the study, four anilines
425 (ANI, 4MA, 4MtA, and DMA) and three sulfonamides (SD, SMX, and SCPD) were tested as
426 TCs (Figure S18). The IF of all anilines decreased with increasing pH up to pH 9, in
427 agreement with the basic hypothesis that the phenolate ion is a better inhibitor of these
428 photosensitized reactions than the undissociated phenol. At pH 6, 4MA and DMA
429 transformation was not inhibited, while for 4MtA even an enhanced reaction ($IF > 1$) is
430 observed at pH 6 and 7. At the highest pH of 11, a reversal in trend is observed for 4MA and
431 4MtA, i.e., IF is higher compared to pH 10. An extended discussion of the behaviour of the
432 anilines including transformation data is given in the next sub-section. For the sulfonamides
433 there is no obvious pH trend. SD exhibited the lowest IF at circumneutral pH as observed
434 with natural antioxidants, while IF for SMX decreased with increasing pH.

435 For a rough comparison of the relative changes in IF with pH with phenol and the natural
436 antioxidants SRFA, PLFA and NAFA, the ratio of the corresponding IF s was calculated (i.e.
437 $IF_{\text{natural AO,pH}}/IF_{\text{phenol,pH}}$, Figure S19). We note that such a comparison needs to be interpreted

438 carefully since antioxidant concentration and type are different. For 4MtA, SCPD and for SD,
439 except at pH 7, the ratios are ~ 1 over the whole pH range. This confirms the qualitative
440 observation from above that IF values behave similarly with changing pH in the presence of
441 either natural or model antioxidants. IF ratios for ANI, 4MA and DMA increase with pH
442 indicating a relative increase of inhibition with increasing pH in systems with phenol as
443 model antioxidant.

444 **Correlation between inhibitory effect and pH-dependent redox potentials.** In systems
445 consisting of both a model photosensitizer and a model antioxidant (System 4), pH-dependent
446 redox potentials were used to rationalize the inhibitory effect across different TCs in the
447 studied pH range. Both the model antioxidant phenol and the four aniline target compounds
448 (ANI, 4MA, 4MtA, and DMA) have pH-dependent redox potentials, which are represented in
449 Figure 4a. The one-electron reduction potential of the redox couple consisting of the
450 phenoxyl radical (both protonated and neutral form) and the phenol (both molecular and
451 deprotonated form) decreases linearly (slope of -0.059 V per pH unit) with increasing pH
452 from 0 to 10, reaching a constant value of 0.79 V vs. SHE above pH 10 at which reduction of
453 the radical to the phenolate is not coupled to proton uptake.

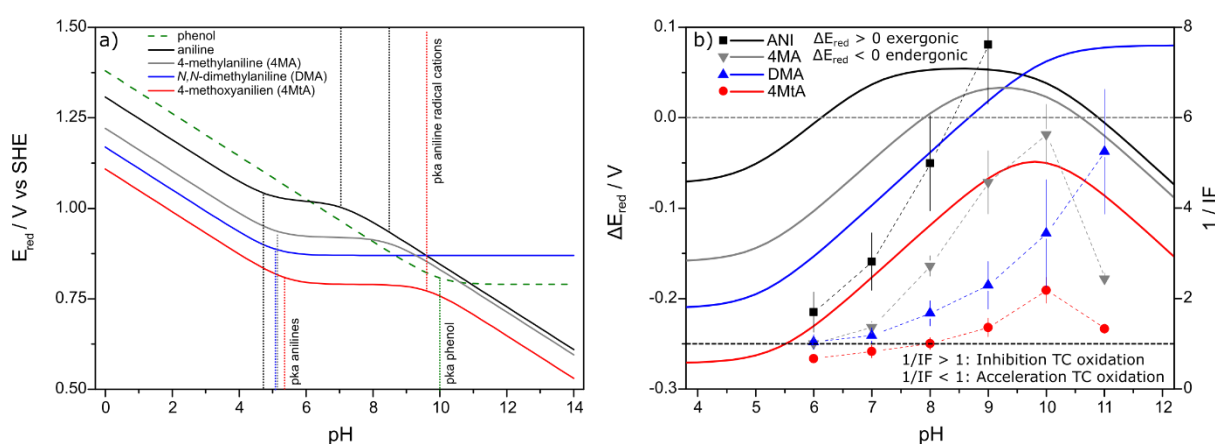
454 For the aniliny radicals (protonated and neutral forms are considered), the one-electron
455 reduction potentials decrease in the same way as for phenol in the pH range from 0 to the pK_a
456 values of the individual anilines (4.9 to 5.4), remain constant (i.e., pH independent) in the pH
457 range between these values and the pK_a values of the aniline radical cations, and then
458 decrease linearly with pH (slope of -0.059 V per pH unit) in the higher pH range. The only
459 exception to this additional decrease in E_{red} with pH is DMA, which maintains a constant
460 reduction potential even at high pH since its radical cation does not deprotonate over the
461 studied pH range. Except for 4MtA, $E_{red}(pH)$ functions for the aniliny radicals, which for $0 <$

462 pH < 5 are lower than the corresponding function for the phenoxy radical, cross at some pH
463 value the $E_{\text{red}}(\text{pH})$ function of the latter, meaning that the oxidation of phenol by the aniliny
464 radicals (cationic or neutral forms) becomes thermodynamically favourable above this pH. A
465 second crossing of the reduction potentials of anilines and phenol occurs for ANI and 4MA at
466 pH values well above the $\text{p}K_{\text{a}}$ of phenol, and the oxidation of phenol by the corresponding
467 aniliny radicals becomes thermodynamically unfavourable above these pH values.

468 To better illustrate the thermodynamics of this redox reactions, Figure 4b shows the
469 difference of reduction potential between each aniliny and phenoxy radicals (i.e., $\Delta E_{\text{red}} =$
470 $E_{\text{red,aniliny}} - E_{\text{red,phenoxy}}$). The diagram also contains data on the inhibitory effect, expressed as
471 inverse inhibition factor (1/IF: high 1/IF corresponds to high inhibitory effect) for the four
472 anilines. The magnitude of the inhibitory effect clearly correlates with increasing ΔE_{red} in the
473 order of ANI > 4MA > DMA > 4MtA and follows, for each of the anilines, the pH-
474 dependence of ΔE_{red} . It can be concluded that the inhibition is determined by the pH (and
475 speciation)-dependent reduction potential difference between the phenoxy/phenol and the
476 aniliny/aniline couples. Interestingly, inhibition (1/IF > 1) of aniline oxidation was observed
477 even for thermodynamically unfavourable conditions, i.e., negative ΔE_{red} . For $\Delta E_{\text{red}} < 0$ V the
478 reaction rate constant for the reduction should be smaller and eventually become insignificant
479 compared to conditions with positive ΔE_{red} . Simultaneously, for $\Delta E_{\text{red}} < 0$ V the back
480 reaction, i.e., the oxidation of the aniline via the phenoxy radical is expected to be faster than
481 the forward reaction.

482 To explain the observed IF under these conditions, scavenging of the phenoxy radical, which
483 outcompetes the back reaction, must be assumed. Possible scavengers of the phenoxy radical
484 include the phenoxy radical itself, superoxide, and phenol,⁸⁹ the latter reaction leading to
485 radical adducts.⁹⁰ The aforementioned thermodynamic considerations also offer arguments to

486 explain the reaction enhancement ($IF > 1$) observed for 4MtA at pH 6 and 7 (see the
 487 preceding sub-section). Phenoxy radicals, which may be formed by oxidation of phenol by
 488 the excited triplet state of 2-AN, may cause an effective oxidation of 4MtA, since this
 489 reaction is the most favourable among the ones considered (see Figure 4b). In turn, the
 490 aniliny radicals of 4MtA cannot be reduced by phenol. As a result, the oxidation of 4MtA by
 491 phenoxy radicals prevails, causing an enhancement of the photosensitized transformation of
 492 4MtA.



493
 494 **Figure 4.** (a) One-electron reduction potentials E_{red} (V vs. standard hydrogen electrode
 495 (SHE)) for phenoxyl and aniliny radicals as a function of pH. Acid dissociation constants of
 496 the relevant species (see Table 1) are indicated by vertical dotted lines. (b) Difference in
 497 reduction potential ΔE_{red} of each aniliny radical and phenoxyl radical for the pH range of 4 –
 498 12, and inverse inhibition factors ($1/IF$) for anilines with 2AN as model photosensitizer and
 499 phenol (10 μ M) as model antioxidant. Calculations for E_{red} and ΔE_{red} are available as
 500 supplementary .xlsx data file, with further consideration on the dependence of redox
 501 potentials of phenol and anilines, including redox equations provided in SI, Text S6.

502
 503 The ΔE_{red} vs pH trends presented in Figure 4b, which exhibit maxima in correspondence of
 504 $1/IF$ maxima, can explain qualitatively the occurrence of the minima in IF (corresponding to
 505 maxima in $1/IF$) observed in several cases for System 2 data (see Figure 3). This observation
 506 can be extended by analogy to the minima in CIF observed for System 1 data (see Figure 2).
 507 The fact that, for DOM acting as antioxidant, the minima in IF or CIF occur at lower pH than
 508 for phenol might be due to the lower pK_a of phenolic moieties of DOM³² compared to phenol.

509 For the sulfonamides, predictions about IF based on ΔE_{red} can only be made at the level of
510 guesses due to the missing knowledge on the reduction potentials of their radicals and the
511 complex speciation behaviour of the latter.⁸² Radicals of the anilinium type would have a
512 higher one-electron reduction potential (e.g., ~ 1.3 V vs SHE for SD)⁹¹ and are also expected
513 to have lower pK_a^* values (e.g., ~ 6.3 estimated for SD using quantum chemical
514 computations)⁸² than the corresponding radicals of the anilines studied here. The higher
515 reduction potentials can explain the generally lower IF values (more efficient inhibition)
516 observed, especially in the lower pH range, for the sulfonamides compared to the anilines.
517 Lower pK_a^* values would explain why the IF minima and onsets to increasing IF would occur
518 at lower pH for the sulfonamides compared to the anilines.

519

520 **Environmental Implications**

521 This study presents the first comprehensive collection of kinetic data on the pH dependence
522 of the photosensitized transformation of aromatic amines under conditions relevant to sunlit
523 surface waters. Pseudo-first-order rate constants for aromatic amines photosensitized by
524 PLFA and SRFA, as surrogates of dissolved organic matter present in surface waters, varied
525 depending on the specific target compound by a factor of up to ~ 7 in the 6 – 11 pH range. For
526 the realistic situation encountered in most freshwaters buffered by bicarbonate/carbonate, pH
527 varies between 7 and 9, and the pH-induced variability of pseudo-first-order rate constants
528 reduces significantly for several of the studied compounds. However, at the smaller range of
529 environmentally occurring pH the maximum observed variability factor of ~ 5 remains high.
530 Therefore, to accurately predict the fate of aromatic amines in surface waters, investigations
531 on the pH dependence of their photosensitized transformation may be required.

532 It is generally assumed that the transformation kinetics and abatement of contaminants in the
533 aquatic environment can be described in terms of their speciation by using corresponding rate
534 constants (independent of the water matrix composition) for each species and, when
535 applicable, the steady-state concentration of aquatic reactive species (such as $^3\text{DOM}^*$, $^1\text{O}_2$ or
536 the hydroxyl radical). However, this approach has limitations, and the present study has
537 highlighted, for the studied aromatic amines, the existence of a pH-dependent photosensitized
538 transformation kinetics beyond a simple speciation effect.

539 The hypothesis of an increased inhibitory effect of DOM on photosensitized transformation
540 of aromatic amines at higher pH could not be confirmed for several studied compounds. A
541 possible explanation for this failure is the important increase in the efficiency of
542 photosensitized transformation with increasing pH, observed for several compounds.
543 Moreover, other not yet well understood compound-specific effects, such as protonation
544 equilibria, lifetimes and reactions (possibly addition to and reduction by superoxide radical
545 anion, and addition to DOM) of the radicals derived from oxidation of the compounds, might
546 affect transformation rates of these compounds. Beyond oxidations induced by excited triplet
547 states, the inhibitory effect of DOM may also occur for radical-induced reactions of organic
548 contaminants, as recently shown for the sulfate radical⁸⁸ produced by photolysis of persulfate.
549 For the latter system, a clearer response of the inhibitory effect of DOM with increasing pH is
550 expected due to the absence of significant superoxide sources that would compete with
551 DOM-induced inhibition.

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556 anonymous reviewers that helped to improve this manuscript.

557 **Supporting Information**

558 6 Texts specifying chemicals used, preparation of stock solutions, analytical details,
559 discussing direct phototransformation of target compounds, effects of changes in absorption
560 spectra, role of singlet oxygen and superoxide, relationships of redox potentials of phenol and
561 anilines with pH. 14 Tables showing HPLC analysis parameters, direct phototransformation
562 rates, measured and corrected photosensitized transformation rates, absorption coefficients of
563 photosensitizers, including for DOMs, and light attenuation factors of experimental solutions.
564 19 Figures showing UV-Vis absorption spectra of photosensitizers, DOMs, and target
565 compounds, depletion kinetics of target compounds and phenol, and phototransformation
566 rates with model sensitizers in the presence of model and natural antioxidants. One .xlsx data
567 file with E_{red} and ΔE_{red} calculations.

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