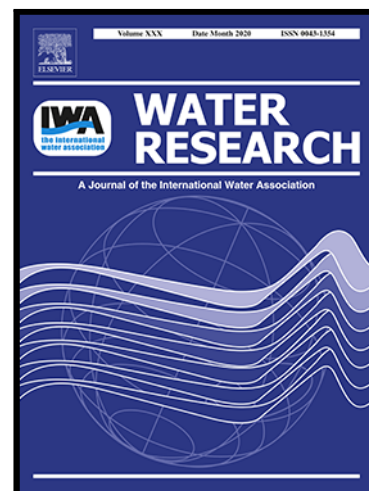


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**Highlights**

- Transformation kinetics of several organic compounds photosensitized by DOM
- Enhanced transformation of electron-rich compounds at lower initial concentration
- Effect attributed to DOM-derived long-lived photooxidants (LLPO)
- Reduction potential of LLPO estimated in the range of 1.0 – 1.3 V vs. SHE
- Photochemically produced phenoxyl radicals mimic LLPO effect

# Enhanced transformation of aquatic organic compounds by long-lived photooxidants (LLPO) produced from dissolved organic matter

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## Keywords

DOM, aquatic photochemistry, transformation kinetics, photosensitizer, phenoxyl radicals, organic contaminants

## Abstract

Dissolved organic matter (DOM) plays a crucial role in the photochemical transformation of organic contaminants in natural aquatic systems. The present study focuses on the characterization of a specific effect previously observed for electron-rich phenols, consisting in an acceleration of the DOM-photosensitized transformation of target compounds at low concentrations ( $< 1 \mu\text{M}$ ). This effect was hypothesized to be caused by DOM-derived "long-lived" photooxidants (LLPO). Pseudo-first-order rate constants for the transformation of several phenols, anilines, sulfonamide antibiotics and phenylureas photosensitized by Suwannee River fulvic acid were determined under steady-state irradiation using the UVA and visible wavelengths from a medium-pressure mercury lamp. A significant enhancement (by a factor of 2.4 – 16) of the first-order transformation rate constant of various electron-rich target compounds was observed for an initial concentration of  $0.1 \mu\text{M}$  compared to  $5 \mu\text{M}$ . This effect points to a relevant reactivity of these compounds with LLPO. For phenols and anilines the enhancement effect occurred only above certain standard one-electron oxidation potentials. From these data series the standard one-electron reduction potential of LLPO was estimated to be in the range of 1.0 – 1.3 V versus the standard hydrogen electrode. LLPO are proposed to mainly consist of phenoxyl radicals formed by photooxidation of electron-poor phenolic moieties of the DOM. The plausibility of this hypothesis was successfully tested by studying the photosensitized transformation kinetics of 3,4-dimethoxyphenol in aqueous solutions containing a model photosensitizer (2-acetonaphthone) and a model electron-poor phenol (4-cyanophenol) as DOM surrogates.

## Abbreviations

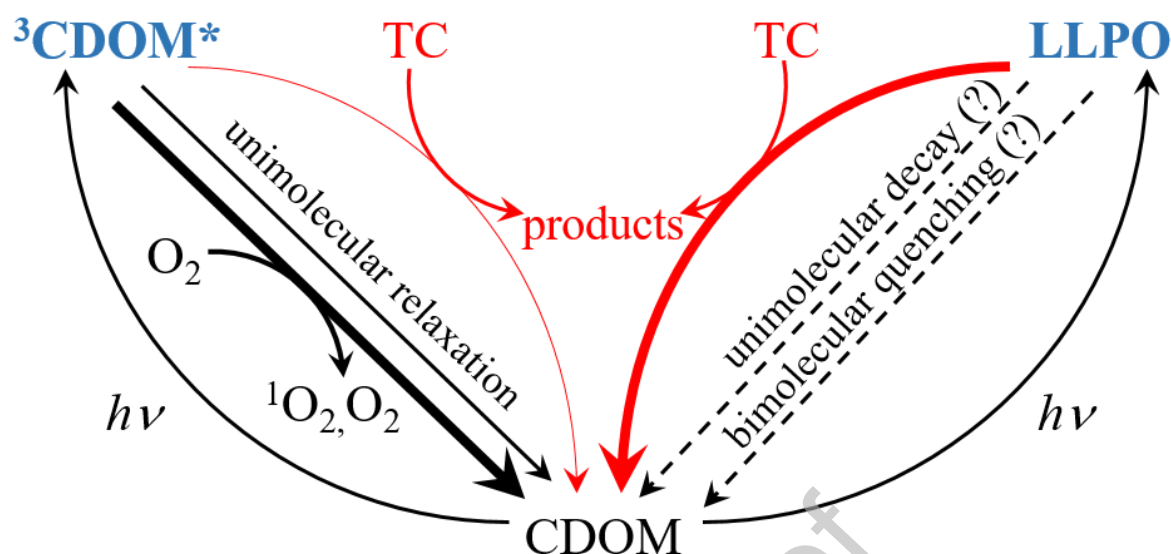
2-AN	2-acetonaphthone
4-CN-PhOH	4-cyanophenol
4-CN-PhO <sup>-</sup>	4-cyanophenoxide ion
4-CN-PhO <sup>•</sup>	4-cyanophenoxy radical
CDOM	chromophoric dissolved organic matter
<sup>3</sup> CDOM*	excited triplet states of CDOM
DMABN	4-(dimethylamino)benzonitrile
DMOP	3,4-dimethoxyphenol
DMP	3(2,5-dimethoxyphenyl)-1,1-dimethylurea
DOM	dissolved organic matter
$E_{\text{red},1}^0$	standard one-electron reduction potential (unit: V vs. SHE)
$E_{\text{ox},1}^0$	standard one-electron oxidation potential (unit: V vs. SHE)
<i>EF</i>	enhancement factor
HPLC	high-performance liquid chromatography
$k^{\text{obs}}$	pseudo-first-order rate constants for the transformation of a TC
$k^{\text{obs},c}$	$k^{\text{obs}}$ , corrected for direct photolysis and light screening effects
$k_{0.1}^{\text{obs},c}$	$k^{\text{obs},c}$ for [TC] <sub>0</sub> = 0.1 μM
$k_{5.0}^{\text{obs},c}$	$k^{\text{obs},c}$ for [TC] <sub>0</sub> = 5.0 μM
LLPO	long-lived photooxidants
SHE	standard hydrogen electrode
PLFA	Pony Lake fulvic acid
PPRI	photochemically produced reactive intermediates
R-PhOH <sub>ep</sub>	model electron-poor phenol
R-PhO <sub>ep</sub> <sup>-</sup>	model electron-poor phenoxide ion
R-PhO <sub>ep</sub> <sup>•</sup>	model electron-poor phenoxy radical
Sens	photosensitizer
<sup>3</sup> Sens*	excited triplet states of Sens
SRFA	Suwannee River fulvic acid
SRHA	Suwannee River humic acid
TC	target compound
TMP	2,4,6-trimethylphenol

## 1. Introduction

The ubiquitous and in its chemical composition extremely complex dissolved organic matter (DOM) (Leenheer and Croué 2003) is a source of various photochemically produced reactive intermediates (PPRI) when exposed to sunlight (Richard and Canonica 2005, Rosario-Ortiz and Canonica 2016, Vione et al. 2014, Zafiriou et al. 1984). PPRI are produced through absorption of sunlight, especially its ultraviolet (UV) portion, by chromophoric constituents of the DOM, the so-called CDOM, (Rosario-Ortiz and Canonica 2016, Sharpless and Blough 2014) and contribute to the transformation of many aquatic contaminants in sunlit surface waters (Richard and Canonica 2005). PPRI derived from CDOM irradiation comprise well-defined chemical entities, such as the hydroxyl radical, carbonate radical or singlet oxygen, as well as excited states or radical species that are often elusive to precise chemical identification because they are derived from and still attached to the DOM (Richard and Canonica 2005, Sharpless and Blough 2014, Vione et al. 2014). Excited triplet states of the CDOM ( $^3\text{CDOM}^*$ ) have been recognized as pivotal photooxidants affecting the fate of organic contaminants in surface waters (Caponica 2007, Canonica et al. 1995, McNeill and Canonica 2016).

Besides  $^3\text{CDOM}^*$ , the existence of DOM-derived photooxidants having longer lifetimes than  $^3\text{CDOM}^*$  and therefore termed "long-lived" photooxidants (LLPO) was postulated (Caponica and Freiburghaus 2001, Canonica and Hoigné 1995). This assumption was used to explain the observed increase in pseudo-first-order CDOM-photosensitized transformation rate constants of electron-rich phenols (i.e., phenols bearing electron-donating substituents) with decreasing initial phenol concentrations in the range of  $10^{-6} - 10^{-7}$  M (Caponica and Freiburghaus 2001, Canonica and Hoigné 1995, Kawaguchi 1993). This observation is highly relevant, since concentrations of many organic contaminants in natural surface waters are even lower than this concentration range (Moschet et al. 2014, Ruff et al. 2015). So far, 2,4,6-trimethylphenol (TMP) (Caponica and Freiburghaus 2001, Kawaguchi 1993), 4-methoxyphenol (Caponica and Hoigné

1995), 3,4-dimethoxyphenol (DMOP) (Canonica and Freiburghaus 2001, Canonica and Hoigné 1995), and *N,N*-dimethylaniline (Canonica and Freiburghaus 2001) were reported to undergo this effect, while for 4-methylphenol the effect was absent at the lowest investigated initial concentration of  $10^{-7}$  M (Canonica and Freiburghaus 2001). A conceptual model and corresponding kinetic equations were developed to explain the observed increase in pseudo-first-order transformation rate constants with decreasing initial concentration of the target compound (Canonica and Hoigné 1995, Canonica and Freiburghaus 2001). An updated version of this model is visualized in Fig. 1. Two pools of CDOM-derived photooxidants in aerated aqueous solution are assumed. For the first pool, the presence of a target compound at concentrations  $\leq 5 \times 10^{-6}$  M does not significantly affect the steady-state concentration of the photooxidants. With the current knowledge on CDOM photochemistry and using target compounds that are not significantly transformed by singlet oxygen, these photooxidants are assumed to mainly represent  $^3\text{CDOM}^*$ . For the second pool, the presence of a target compound at concentrations in the range of  $1 \times 10^{-7} - 5 \times 10^{-6}$  M significantly affects the steady-state concentration of the photooxidants. The increasing steady-state concentration of this pool of photooxidants with decreasing target compound concentration results in an increasing pseudo-first-order rate constant for the transformation of the target compound. Assuming a maximum second-order rate constant of  $\approx 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the reaction of these photooxidants with a target compound and a reduction in steady-state concentration of the photooxidants by at least 50% upon addition of a target compound at  $5 \times 10^{-6}$  M concentration, the photooxidants of this second pool can be estimated to have on average lifetimes longer than  $\approx 67 \text{ } \mu\text{s}$  (see the Supplementary Information (SI), Text S1 for a detailed calculation). An estimation made in the original study lead to lifetimes in the order of  $100 \text{ } \mu\text{s}$  (Canonica and Hoigné 1995). This lifetime is much longer than estimates for  $^3\text{CDOM}^*$  in aerated water ( $1.6 - 6.3 \text{ } \mu\text{s}$ , see SI, Text S2), which justifies the use of the term "long-lived photooxidants" (LLPO) in the present paper.



**Fig. 1.** Reactions controlling the deactivation and lifetime of long-lived photooxidants (LLPO) compared to excited triplet states of chromophoric dissolved organic matter ( $^3\text{CDOM}^*$ ) in aerated water in the presence of a target compounds (TC). The thickness of the arrows illustrates the relative importance of the various deactivation processes of LLPO and  $^3\text{CDOM}^*$  in the presence of an electron-rich phenol as TC at a concentration of  $5 \times 10^{-6}$  M.

The knowledge on the deactivation pathways and rate constants of  $^3\text{CDOM}^*$  has been substantially improving during the last decade (Golanoski et al. 2012, Schmitt et al. 2017, Sharpless 2012), yielding the aforementioned average lifetimes of  $^3\text{CDOM}^*$  in aerated water at 25 °C that match well with the early lifetime estimate of 2  $\mu\text{s}$  (Zepp et al. 1985). The main groups of reactions of  $^3\text{CDOM}^*$  with organic contaminants, namely one-electron oxidation and triplet–triplet energy transfer, and the energetics of such reactions are also fairly well understood (McNeill and Canonica 2016, Rosario-Ortiz and Canonica 2016). In contrast, during the last twenty years, no substantial advances in the characterization of the hypothesized LLPO were made, despite their potentially decisive contribution to the phototransformation of some aquatic organic contaminants in surface waters which may even override the contribution



of  $^3\text{CDOM}^*$ , due to the often very low concentrations of these contaminants. Since LLPO are formed in an oxic environment and are capable of oxidizing electron-rich phenols, they are expected to be oxidizing radicals that are part of the photochemically transformed DOM. These radicals possibly include peroxy radicals (Mill et al. 1980), or phenoxy radicals, which are plausible due to abundance of phenolic moieties in the DOM (Ritchie and Perdue 2003) and could result from a one-electron oxidation of these moieties by  $^3\text{CDOM}^*$ . LLPO have been suggested to have a higher selectivity than  $^3\text{CDOM}^*$  in their reaction with phenols (Canonica and Hoigné 1995), and therefore, assuming one-electron oxidation of the phenols (or any other compound) in both cases, LLPO should have lower standard one-electron reduction potentials ( $E_{\text{red},1}^0$ ) than  $^3\text{CDOM}^*$  (note that in the following all potentials are given vs. standard hydrogen electrode (SHE)). The reduction potentials of the latter were estimated to lie in the range of 1.36 – 1.90 V vs. SHE (Canonica et al. 2000) and, more recently, 1.6 – 1.8 V vs. SHE (Parker and Mitch 2016). The reduction potentials of various substituted phenoxy radicals have been measured and cover a wide range (Jonsson et al. 1993, Lind et al. 1990), which extends from values near zero for very electron-rich species to 1.22 V for the 4-nitrophenoxy radical (Lind et al. 1990), with the unsubstituted phenoxy radical having 0.79 V (Lind et al. 1990). Moreover, estimations of  $E_{\text{red},1}^0$  are available for alkyl peroxy radicals,  $\text{ROO}^\bullet$  (0.71 – 0.83 V) and alkyl percarboxyl radicals,  $\text{RC(O)OO}^\bullet$ , (1.05 – 1.19 V) (Merényi et al. 1994). Considering the estimated standard one-electron oxidation potentials,  $E_{\text{ox},1}^0$ , of electron-rich phenols in their undissociated form (-1.17 V for DMOP and -1.22 V for TMP) (Canonica et al. 2000) both electron-poor phenoxy radicals and  $\text{RC(O)OO}^\bullet$  would be efficient oxidants of these phenols and therefore plausible candidates for LLPO.

The primary goal of this study was to evaluate the propensity of several organic compounds, belonging to various chemical classes, to undergo photosensitized transformation induced by LLPO. To this end, the pseudo-first-rate constants for the DOM-photosensitized transformation

of each target compound at initial concentrations of  $1.0 \times 10^{-7}$  M and  $5.0 \times 10^{-6}$  M was measured. The lower initial concentration was designated to allow precise quantification of the rate constants without the need of sample pre-concentration and to be consistent with a previous study (Canonica and Freiburghaus, 2001). The resulting rate constant difference was interpreted in terms of LLPO reactivity. For substituted phenols and anilines as target compounds, their reactivity with LLPO was related to the standard one-electron oxidation potentials of the compounds for estimating the reduction potential of LLPO. Using DMOP as an LLPO probe compound, the dependence of LLPO reactivity on DOM type and concentration was investigated. Finally, a chemical model system consisting of a photosensitizer and an electron-poor phenol (i.e., a phenol bearing electron-withdrawing substituents) was employed to mimic the effect of DOM-derived LLPO on the pseudo-first-order transformation rate constant of the electron-rich phenol DMOP.

## 2. Experimental section

**2.1. Materials and solutions.** The following chemicals were obtained from common commercial sources and used as received: (A) Target compounds: phenol (Fluka, >99.5%), 4-methylphenol (Fluka, >99 %), 2,4,6-trimethylphenol (TMP, Ega Chemie, 99%), 3,4-dimethoxyphenol (DMOP; Alfa Aesar, 98%), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (trolox, Sigma Aldrich, 97%), aniline (Sigma Aldrich,  $\geq 99.5\%$ ), 4-cyanoaniline (Fluka,  $\geq 97\%$ ), 4-methylaniline (Sigma Aldrich, 99.6%), 4-(dimethylamino)benzonitrile (DMABN, Sigma Aldrich, 98%), isoproturon (Sigma Aldrich, pestanal®), diuron (Sigma Aldrich, pestanal®), 3-(2,5-dimethoxyphenyl)-1,1-dimethylurea (DMP, Sigma Aldrich), sulfamethoxazole (Sigma Aldrich), sulfadiazine (Sigma Aldrich,  $\geq 99\%$ ), and sulfadimethoxine (Sigma Aldrich,  $\geq 98.5\%$ ); (B) Model photosensitizer: 2-acetonaphthone (2-AN, Sigma Aldrich, 99%); (C) Model electron-poor phenol: 4-cyanophenol (4-CN-PhOH, Fluka, >97%); (D) Buffer

components:  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  (Sigma Aldrich/Merck,  $\geq 98.5\%$ ) and  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (Merck, for analysis). The DOM isolates Suwannee River fulvic acid (SRFA, type “standard III”, 3S101F), Suwannee River humic acid (SRHA, type “standard III”, 3S101H), Pony Lake fulvic acid (PLFA, type “reference”, 1R109F) were purchased from the International Humic Substances Society (IHSS).

Ultrapure water was obtained from a Barnstead NANOpure system (Skin AG, Allschwil, Switzerland). Stock solutions of all target compounds (100 or 500  $\mu\text{M}$ ) and the model electron-poor phenols (500  $\mu\text{M}$ ) were made in ultrapure water. The stock solutions of the photosensitizer (500  $\mu\text{M}$ ) were prepared in acetonitrile and further diluted to 50  $\mu\text{M}$  using ultrapure water. Phosphate buffer stock solutions (50 mM, pH 7.76) were prepared in ultrapure water by dissolving appropriate amounts of  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ . DOM isolates stock solutions ( $\approx 50$  or  $100 \text{ mg C L}^{-1}$ ) were made in ultrapure water by dissolving an estimated target amount of the hygroscopic isolates. All solutions were stored in the dark at  $4^\circ\text{C}$ .

**2.2. Irradiation experiments.** Solutions to be irradiated were prepared by mixing appropriate amounts of the aforementioned stock solutions, and 16 mL thereof were transferred to quartz tubes (18 mm external diameter, 15 mm internal diameter, 250 mm height) sealed with glass stoppers. The final concentration of phosphate buffer was 5 mM, resulting in a pH of  $8.0 \pm 0.1$ . The quartz tubes were shaken by hand and placed in a water bath at  $25.0^\circ\text{C}$  for 15 minutes. Thereafter, irradiations were performed using a temperature-controlled DEMA (Hans Mangel GmbH, Bornheim-Roisdorf, Germany) model 125 merry-go-round photoreactor equipped with a Heraeus Noblelight model TQ718 medium-pressure mercury lamp. The latter was positioned in a borosilicate cooling jacket and operated with an input power of 500 W. The geometry of the photoreactor was described in detail elsewhere (Wegelin et al. 1994). Light from the mercury lamp was filtered by the double wall of the cooling jacket and additionally by a 0.15 M sodium nitrate filter solution, which was recirculated in the photoreactor to maintain a

constant temperature of  $25.0 \pm 0.2$  °C. This resulted in a cut-off filter transmitting light with wavelength  $\lambda > 320$  nm. Total irradiation times varied in the range of 3 minutes to 8 hours depending on the rates of transformation of the various target compounds, and 360  $\mu$ L samples were withdrawn from the quartz tubes at six equidistant time intervals. The photon fluence rate in the quartz tubes was checked weekly by chemical actinometry using an aqueous solution of 4-nitroanisole ( $5.0 \times 10^{-6}$  M) and pyridine ( $1.0 \times 10^{-2}$  M) (Laszakovits et al. 2017, Leresche et al. 2016). It was determined for the relevant wavelength band of 334 – 436 nm using the methods detailed by Leresche et al., 2016, and found to vary in the range of  $(4.1 - 5.6) \times 10^{-3}$  einstein  $\text{m}^{-2} \text{s}^{-1}$  over the duration of the whole study.

**2.3. Analytical methods.** Concentrations of the target compounds were determined by high-performance liquid chromatography (HPLC) using an Agilent 1100 HPLC system, equipped with a quaternary low-pressure mixing gradient pump, a photodiode array detector, and a fluorescence detector (Agilent 1200 series), or an analogous Dionex 3000 Ultimate system. The photodiode array detector was mainly used to analyze samples taken from solutions with 5.0  $\mu$ M initial target compound concentration. For solutions with 0.1  $\mu$ M initial target compound concentration, the fluorescence detector was often preferred to the photodiode array detector because of the higher sensitivity that could be achieved for the analysis of some target compounds. Typically, duplicate injections of 100  $\mu$ L samples were performed. A reverse-phase  $\text{C}_{18}$  column (Cosmosil 5 $\text{C}_{18}$  –MS-II) was used. Details on HPLC analytical conditions are described in the SI, Table S1.

The pH of the samples was measured before and after each irradiation experiment using a pH meter (either a Metrohm Model 605 equipped with a Metrohm pH electrode Model 6.02341.110, or a Thermo Scientific Model Orion Star A111 equipped with a Thermo Scientific pH electrode Model Orion 8115BNUWP ROSS Ultra). Typically, a small pH decrease ( $<0.1$  pH units) was observed during the irradiation experiment. Concentrations of DOM stock

solutions were measured, after appropriate dilution, using a Shimadzu TOC-L CSH total organic carbon (TOC) analyzer (limit of quantification 0.5 mgC L<sup>-1</sup>, accuracy 0.2 mgC L<sup>-1</sup>, measuring range 0.5 – 30 mgC L<sup>-1</sup>). An Agilent Cary 100 UV-vis spectrophotometer was used to measure absorption spectra of the DOM isolates and to calculate light screening factors.

**2.4. Determination of rate constants.** Pseudo-first-order rate constants,  $k^{\text{obs}}$ , for the transformation of a given target compound were determined using the following relationship:

$$\ln \left( \frac{[\text{TC}]_t}{[\text{TC}]_0} \right) = -k^{\text{obs}}t \quad (1)$$

where  $[\text{TC}]_t$  and  $[\text{TC}]_0$  are the target compound concentrations at irradiation time  $t$  and before irradiation, respectively. For DOM-containing samples, light screening corrections were performed according to the SI, Text S3. To determine the net contribution of DOM photosensitization to the transformation of TCs, the observed rate constants measured for DOM-containing solutions were further corrected, when applicable, by subtracting the pseudo-first-order rate constant obtained for the corresponding blank experiments (i.e., for DOM-free solutions). This correction compensates for the possible contributions of direct phototransformation or other effects of the water matrix. All corrected rate constants are termed  $k^{\text{obs,c}}$ , details of the calculation are given in the SI, Text S4.

**2.5. Determination of the enhancement factor.** For the representation of the enhancement in  $k^{\text{obs,c}}$  observed for the transformation of target compounds at the low initial concentration of  $1.0 \times 10^{-7}$  M (0.1  $\mu\text{M}$ ) compared to the high initial concentration of  $5.0 \times 10^{-6}$  M (5.0  $\mu\text{M}$ ), an enhancement factor,  $EF$ , was defined as:

$$EF = \frac{k_{0.1}^{\text{obs,c}}}{k_{5.0}^{\text{obs,c}}} \quad (2)$$

where the subscripts of the rate constants indicate the initial TC concentration in  $\mu\text{M}$ .

## 2.6. Kinetic models and simulations

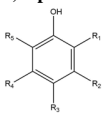
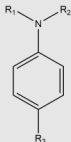
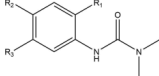
The software Kintecus© (Ianni 2017) was employed to simulate the photosensitized transformation kinetics of 3,4-dimethoxyphenol in solutions containing 2-acetonaphthone as a model photosensitizer and 4-cyanophenol as a model electron-poor phenol. Details of these simulations are given in the SI, Text S6 and Table S7.

### 3. Results and discussion

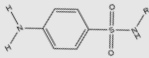
#### 3.1. Screening of target compounds potentially subject to LLPO-induced transformation.

Based on a literature review, organic target compounds were selected for a screening study according to the following criteria: (1) Indirect phototransformation photosensitized by CDOM is, or is expected to be, their dominant photochemical transformation pathway; (2) excited triplet states of the CDOM ( $^3\text{CDOM}^*$ ) acting as photooxidants play, or are expected to play, a major role in their indirect phototransformation under the employed irradiation conditions ( $\lambda > 320 \text{ nm}$ ); (3) LLPO are known to, or might, significantly contribute to their CDOM-photosensitized transformation. A few target compounds not satisfying the third criterion were also investigated as negative controls. The selected target compounds potentially fulfilling the above criteria (see Table 1) belong to four distinct chemical classes, namely phenols, anilines, sulfonamides, and phenylureas.

Table 1. Selected target compounds to test the long-lived photooxidant (LLPO) effect

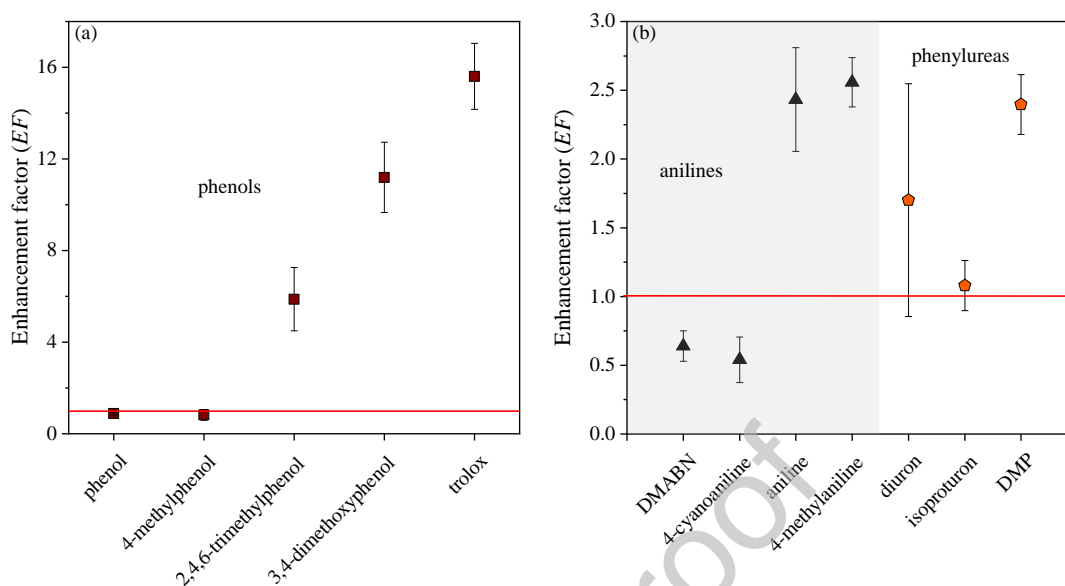
Compound class	Target compound	$E_{\text{ox},1}^0$ / V vs. SHE	pK <sub>a</sub>	Information on LLPO effect prior to this study	References on CDOM-photosensitized transformation
<b>a) phenols</b> 	phenol	-1.50 <sup>a</sup>	10.0 <sup>b</sup>	Tested, not observed This study: negative control	(Canonica and Hoigné 1995, Canonica et al. 1995)
	4-methylphenol	-1.38 <sup>a</sup>	10.3 <sup>b</sup>	Tested, not observed This study: negative control	(Canonica and Hoigné 1995, Canonica et al. 1995)
	2,4,6-trimethylphenol (TMP)	-1.22 <sup>a</sup>	10.9 <sup>b</sup>	Tested, observed	(Aguer et al. 2005, Canonica and Freiburghaus 2001, Canonica and Hoigné 1995, Canonica et al. 1995, Halladja et al. 2007, Kawaguchi 1993, Rosario-Ortiz and Canonica 2016)
	3,4-dimethoxyphenol (DMOP)	-1.17 <sup>a</sup>	9.9 <sup>c</sup>	Tested, observed	(Canonica and Freiburghaus 2001, Canonica and Hoigné 1995, Canonica et al. 1995)
	6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (trolox)	-0.95 <sup>a</sup>	11.9 <sup>d</sup>	Expected	(Canonica and Hoigné 1995, Canonica et al. 1995)
<b>b) anilines</b> 	4-(dimethylamino)benzonitrile (DMABN)	-1.34 <sup>e</sup>		Unknown	(Leresche et al. 2016)
	4-cyanoaniline	-1.32 <sup>f</sup>	1.74 <sup>b</sup>	Unknown	(Canonica and Laubscher 2008, Leresche et al. 2016)
	4-acetylaniline	-1.14 <sup>f</sup>		Unknown	
	aniline	-1.02 <sup>f</sup>	4.62 <sup>b</sup>	Unknown	(Canonica and Laubscher 2008, Wenk and Canonica 2012)
	4-methylaniline	-0.92 <sup>f</sup>	5.08 <sup>b</sup>	Unknown	
<b>c) phenylureas</b> 	diuron	$\sigma_{\text{tot}}^+$ <sup>g</sup> 0.48		Not expected This study: negative control	(Canonica et al. 2006, Gerecke et al. 2001, Zeng and Arnold 2013)
	isoproturon	-0.28		Tested, not observed This study: negative control	(Canonica et al. 2006, Gerecke et al. 2001, Karpuzcu et al. 2016, Langlois et al. 2014)
	3(2,5-dimethoxyphenyl)-1,1-dimethylurea (DMP)	-0.54		Unknown	
<b>d) sulfonamides</b>	sulfamethoxazole		1.8 <sup>h</sup> ; 5.6 <sup>h</sup>	Unknown	(Bahnmüller et al. 2014, Boreen et al. 2005, Canonica and Laubscher 2008, Ryan et al. 2011, Wenk and Canonica 2012)



	sulfadiazine	2.1 <sup>h</sup> ; Unknown	(Bahnmüller et al. 2014, Canonica and Laubscher 2008, Wenk and Canonica 2012)
	sulfadimethoxine	6.3 <sup>h</sup> ; Unknown	
		1.9 <sup>h</sup> ; Unknown	(Guerard et al. 2009, Leresche et al. 2016)
		5.9 <sup>h</sup>	

<sup>a</sup> Standard one-electron oxidation potential of the substituted phenol (undissociated form) calculated using the experimentally determined standard one-electron oxidation potential of the corresponding phenoxide ion and the  $pK_a$  values of the phenol and the corresponding protonated phenoxyl radical (Caponica et al. 2000). Note that negative values are used here to comply with thermodynamic conventions. <sup>b</sup> (Dean 1999). <sup>c</sup> (Caponica et al. 2000). <sup>d</sup> (Steenken and Neta 1982). <sup>e</sup> Estimated using excited triplet state quenching data of several photosensitizers (Leresche et al. 2019). <sup>f</sup> Standard one-electron oxidation potential of the substituted aniline (non-protonated form) set equal to the negative value of the experimentally determined reduction potentials of the corresponding aniline radical cation (Jonsson et al. 1994). <sup>g</sup> Overall Hammett  $\sigma^+$  substituent constant calculated as the sum of the individual substituent constants at each position ( $\sigma^+$  for the ortho and para positions,  $\sigma$  for the meta position) (Caponica and Tratnyek 2003, Hansch et al. 1991). Negative values indicate higher electron-donating character with respect to the parent compound fenuron. <sup>h</sup>  $pK_a$  values of the protonated and neutral form of the sulfonamide, respectively (Lin et al. 1997).

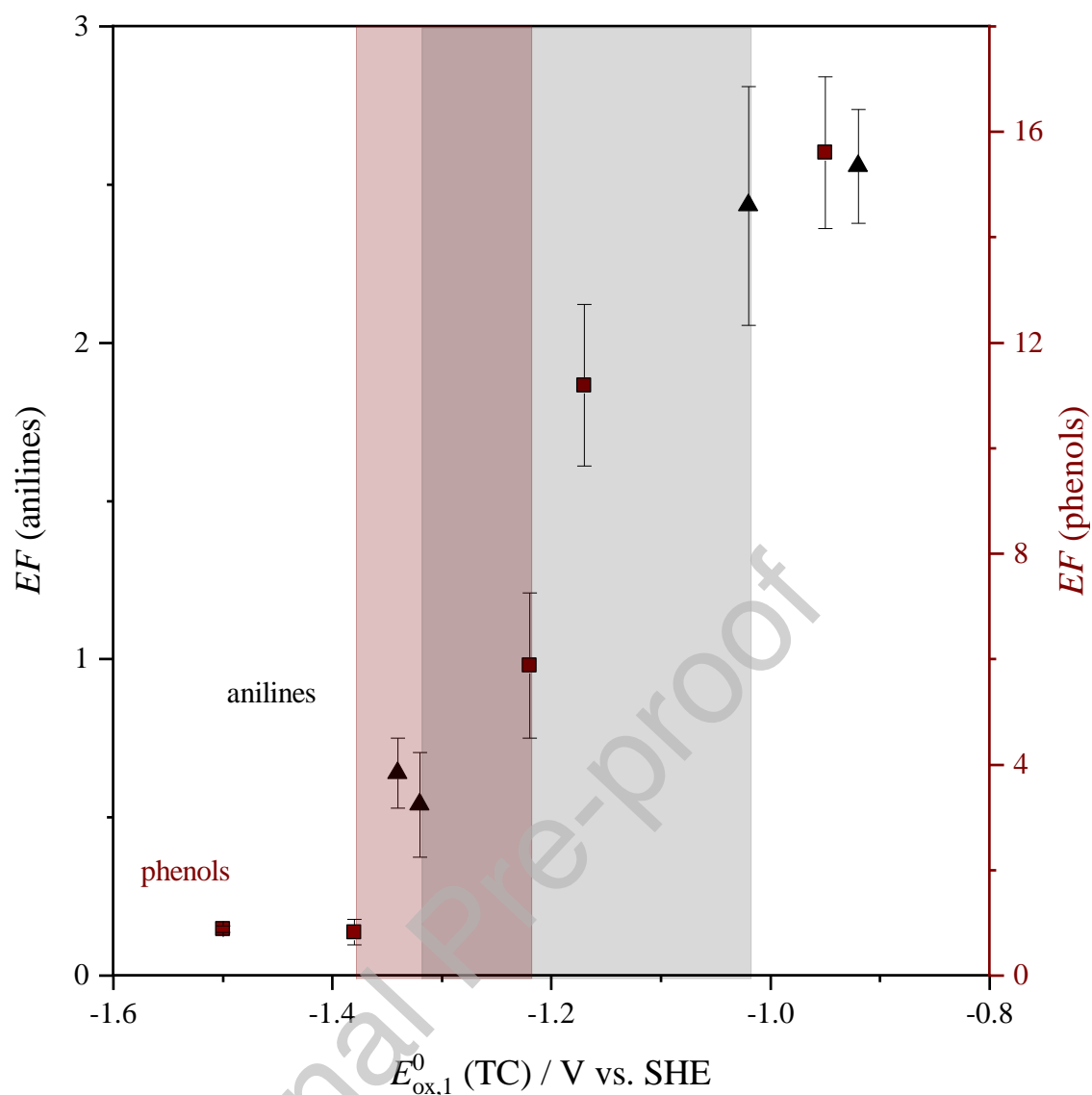
The experimental rate constant data for all investigated target compounds are summarized in Table S4 (SI) and represented in Fig. 2 utilizing the enhancement factor ( $EF$ , eq. (2)). For the sulfonamides and 4-acetylaniline, the determination of  $EF$  was not possible because direct photolysis appeared to dominate their transformation (see SI, Text S4 and Table S4). For six target compounds,  $EF$  was  $\leq 1$ , within the experimental accuracy, meaning that there is no enhancement in the rate constant by reducing the initial target compound concentration. This is interpreted as a negligible impact of LLPO on the phototransformation of these target compounds. For all other compounds, including TMP, DMOP, trolox, aniline, 4-methylaniline, and DMP,  $EF$  was  $> 1$ , meaning that at the low initial target compound concentration a significantly higher rate constant was determined compared to the higher initial target compound concentration. For these compounds, the enhancement in the rate constants at the low initial concentration is attributed to the effect of LLPO. The compounds with  $EF > 1$  belonging to the phenols, anilines, and phenylureas are among the most electron-rich representatives of each class, as can be deduced from their oxidation potentials or Hammett substituent constants (see Table 1). The three electron-rich phenols TMP, DMOP and trolox exhibit by far the highest  $EF$  values, which lie in the range of 6 – 16. For anilines and phenylureas,  $EF$  values do not exceed  $\approx 2.6$ .



**Fig. 2.** Observed enhancement factors ( $EF$ , eq. (2)) for the transformation of (a) phenols (brown squares), and (b) anilines (black triangles), and phenylureas (orange pentagons), photosensitized by Suwannee River fulvic acid ( $2.5 \text{ mgC L}^{-1}$ ) at pH 8.0. High and low initial concentrations of the target compounds were  $5.0$  and  $0.1 \text{ }\mu\text{M}$ , respectively. Note the different y-axis scales. The horizontal red straight lines indicate  $EF = 1$ . Error bars (when not visible, smaller than the symbols) represent standard deviations of duplicate experiments.

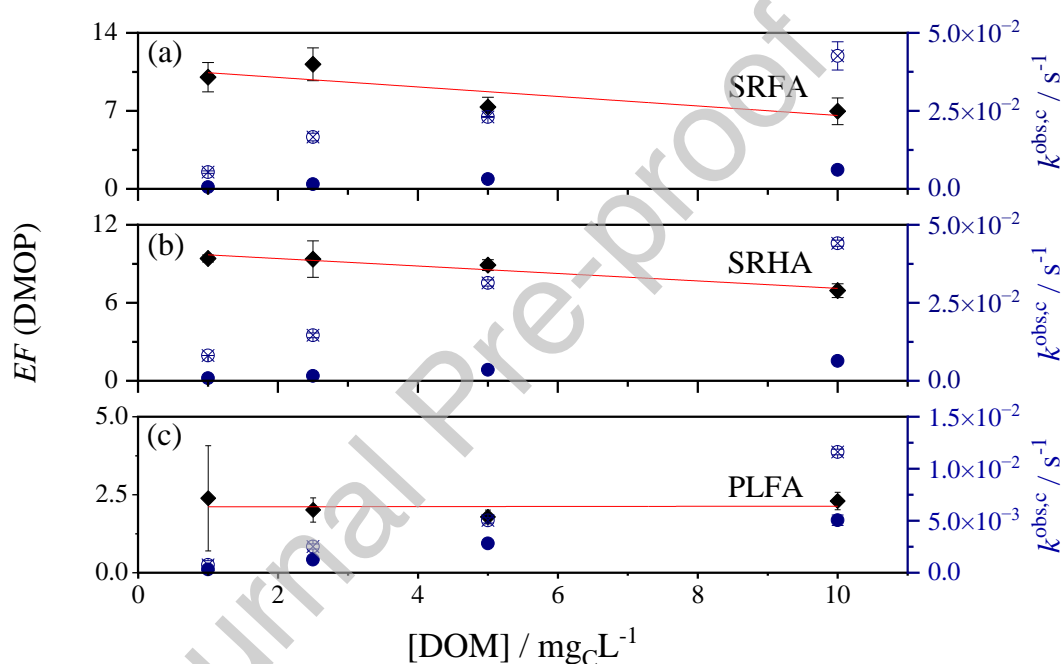
**3.2. Estimation of the reduction potential of LLPO.** The above  $EF$  data for phenols and anilines, for which standard one-electron oxidation potentials ( $E_{\text{ox},1}^0$ ) are known (see Table 1), can be used to evaluate the oxidative character of LLPO, in particular the standard one-electron reduction potential ( $E_{\text{red},1}^0$ ). Fig. 3 displays  $EF$  values for these two compound classes (as from Fig. 2) as a function of the corresponding oxidation potentials. For the phenols,  $EF$  is close to unity up to a value of  $E_{\text{ox},1}^0 = -1.38 \text{ V}$  and increases steadily with  $E_{\text{ox},1}^0$  above this value. The onset of  $EF > 1$  is located between  $-1.38$  and  $-1.22 \text{ V}$ . For the anilines, the change in  $EF$  as a

function of  $E_{\text{ox},1}^0$  follows a similar trend as for the phenols, with  $EF \approx 1$  for  $E_{\text{ox},1}^0 \leq -1.32$  V and an onset of  $EF > 1$  located between -1.32 and -1.02 V. These onset ranges overlap (from -1.32 to -1.22 V), but the onset range for the anilines is shifted by  $\approx 0.2$  V towards higher oxidation potentials compared to the phenols. Assuming a pure one-electron transfer reaction of LLPO with anilines, it can be concluded that the maximum  $E_{\text{red},1}^0$  values for LLPO lie in the range of 1.02 – 1.32 V. The case of phenols is more complex to evaluate, since phenols are known to undergo proton-coupled electron transfer reactions (Sjödín et al. 2006, Warren et al. 2010, Weinberg et al. 2012), which may lower the potential required for their oxidation compared to a pure electron-transfer reaction. Therefore, we consider that the range of maximum  $E_{\text{red},1}^0$  values for LLPO that can be deduced from the phenol series (1.22 – 1.38 V) overestimates the actual maximum reduction potential of LLPO. At the experimental pH, a small fraction of the phenols (between 1.2% for phenol and 0.013% for trolox, as can be calculated from their  $pK_a$  values) is present as phenoxide ion. The latter, which has a standard one-electron reduction potential that is on average about 0.7 V higher compared to the corresponding undissociated phenol, is expected to react with LLPO at a very high rate. The fact that neither 4-methylphenol nor phenol exhibit an LLPO effect demonstrates that the reaction of phenoxides with LLPO can be neglected in the frame of the present experiments.



**Fig. 3.** Dependence of the enhancement factor on the oxidation potential of the target compounds (see Table 1). *EF* (data as in Fig. 2) was measured at pH 8.0 for the photosensitized transformation of phenols (brown squares) and anilines (black triangles). Photosensitizer: Suwannee River fulvic acid (2.5 mg<sub>C</sub> L<sup>-1</sup>). Error bars (when not visible, smaller than the symbols) represent standard deviations of duplicate experiments. Shaded areas (red for phenols, grey for anilines) indicate the  $E^0_{ox,1}$  ranges used to estimate the LLPO reduction potential.

**3.3. Dependence of enhancement effect on type and concentration of DOM.** Using DMOP as a target compound, its photosensitized transformation kinetics at the two initial concentrations of  $1.0 \times 10^{-7}$  and  $5.0 \times 10^{-6}$  M was measured in the presence of various concentrations of the three selected DOM isolates. Figure 4 displays the DOM concentration dependence of the corrected pseudo-first-order rate constants,  $k^{\text{obs},c}$ , and the enhancement factors ( $EF$ ) derived from these rate constants, for the three isolates (a) Suwannee River fulvic acid, (b) Suwannee River humic acid, and (c) Pony Lake fulvic acid.



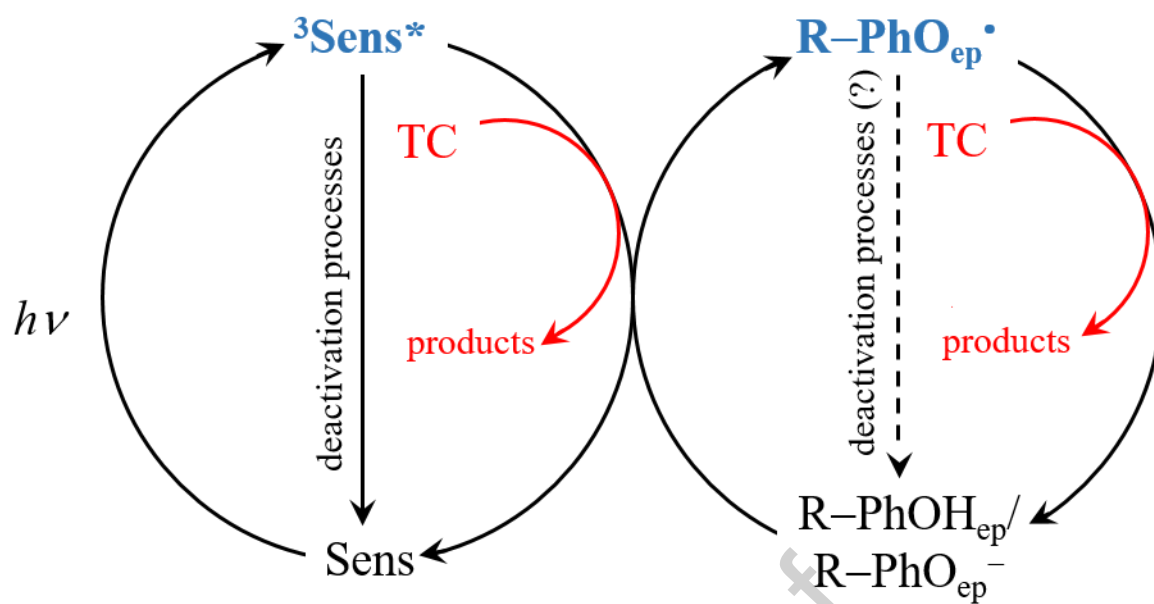
**Fig. 4.** Corrected pseudo-first-order rate constants (right y-axes) for the DOM-photosensitized transformation of 3,4-dimethoxyphenol (DMOP) (initial concentrations  $1.0 \times 10^{-7}$  M, open crossed circles, and  $5.0 \times 10^{-6}$  M, closed blue circles) at pH 8.0 as a function of the concentration of (a) Suwannee River fulvic acid, (b) Suwannee River humic acid, and (c) Pony Lake fulvic acid. The corresponding enhancement factors ( $EF$ , black diamonds, left y-axis) with linear fits (red lines) are also shown. Error bars (when not visible, smaller than the symbols) represent standard deviations of duplicate experiments.

At  $[\text{DMOP}]_0 = 5.0 \times 10^{-6} \text{ M}$  and for all three DOM isolates,  $k^{\text{obs,c}}$  is always much lower than for  $[\text{DMOP}]_0 = 1.0 \times 10^{-7} \text{ M}$  and increases proportionally with increasing DOM concentrations. This indicates that, up to  $[\text{DOM}] = 10 \text{ mg}_\text{C} \text{ L}^{-1}$ , DOM does not significantly quench the photooxidants responsible for the transformation of DMOP. This conclusion concurs with the assumption that the photooxidants are mainly  $^3\text{CDOM}^*$ , which, in analogy to the excited triplet states of model aromatic ketones (Wenk et al. 2013), are expected to be free from quenching by DOM at these DOM concentration levels. Moreover, for  $[\text{DMOP}]_0 = 5.0 \times 10^{-6} \text{ M}$ , all three DOM isolates exhibit similar rate constants at equal DOM concentration. For the lower initial DMOP concentration, PLFA exhibit a linear increase in  $k^{\text{obs,c}}$  with increasing DOM concentrations, while for SRFA and SRHA the initially linear increase in  $k^{\text{obs,c}}$  tends to level off at  $[\text{DOM}] > \approx 5 \text{ mg}_\text{C} \text{ L}^{-1}$ .

For increasing DOM concentrations, the enhancement factors tend to decrease for SRFA and SRHA and to remain constant for PLFA. For PLFA,  $EF$  is essentially independent of the DOM concentration, with an average value of 2.1, which is significantly lower than the values determined for SRFA and SRHA. The lower  $EF$  is interpreted as lower impact of LLPO in the transformation of DMOP. Interestingly, the Suwannee River DOM isolates also have a higher aromaticity, phenolic content, and electron donating capacity than PLFA (Aeschbacher et al. 2012, Senesi et al. 1989). The fact that the LLPO effect is positively correlated with the concentration of phenolic moieties in the DOM supports the hypothesis that LLPO include phenoxyl radicals of the DOM formed during photoinduced oxidation of the corresponding phenolic moieties of the DOM. The decrease in  $EF$  observed at the higher SRFA and SRHA concentrations (also revealed by the linear fit line slopes of  $(-0.4 \pm 0.1)$  and  $(-0.29 \pm 0.05) \text{ L mg}_\text{C}^{-1}$ , respectively) is attributed to partial LLPO scavenging by DOM itself. Such a scavenging coincides with the higher concentration of electron donating moieties for the two Suwannee River DOM isolates compared to PLFA.

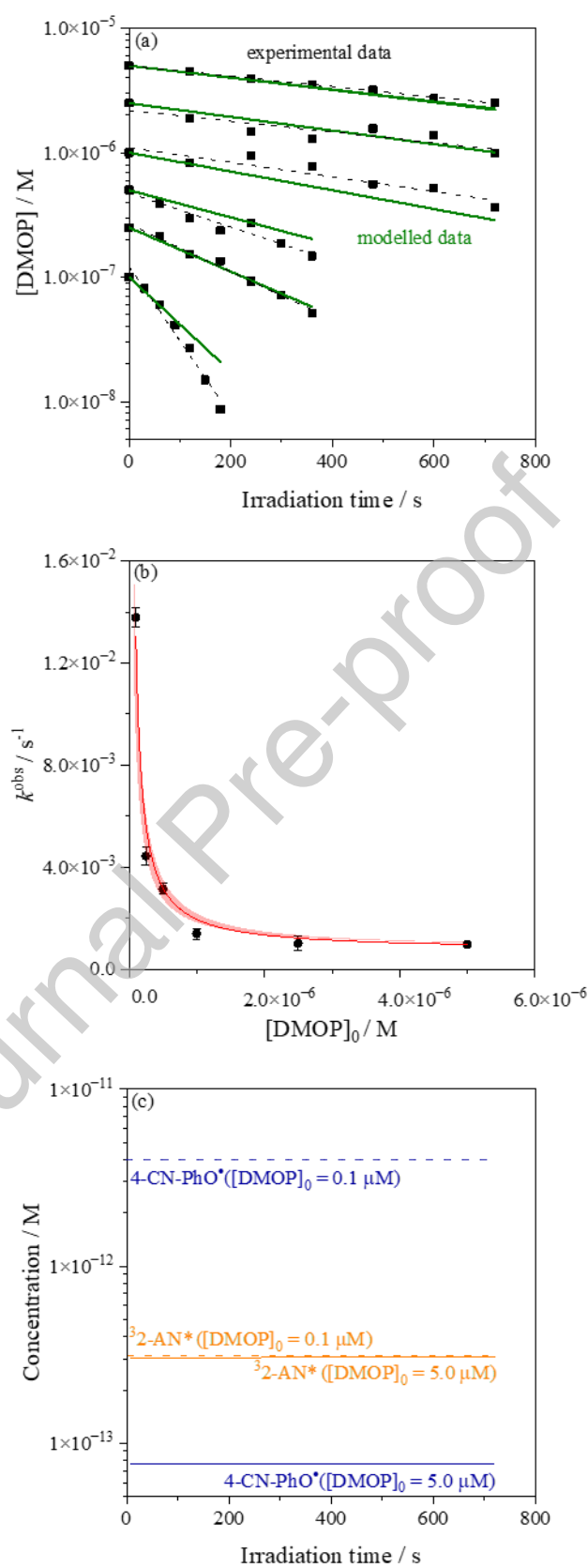
**3.4. Chemical model systems to mimic DOM-derived LLPO.** Model aromatic ketones and quinones have been widely used in aquatic photochemistry to mimic the reactivity of  $^3\text{CDOM}^*$  with an oxidative character (Canonica et al. 2006, Canonica et al. 2000, Canonica et al. 1995, Canonica and Laubscher 2008, Carena et al. 2019, Maurino et al. 2008, Minella et al. 2018, Werner et al. 2005). Moreover, phenol and phenolic compounds bearing electron-donating substituents have been utilized as model antioxidants, in combination with DOM or model photosensitizers, to investigate the dual role of DOM as a photosensitizer and inhibitor of  $^3\text{CDOM}^*$ -induced oxidations of aquatic organic contaminants (Bahnmüller et al. 2014, Leresche et al. 2016, Wenk and Canonica 2012). Here, we use a model photosensitizer (Sens) in combination with a model electron-poor phenol ( $\text{R-PhOH}_{\text{ep}}$ ) to photogenerate both oxidizing excited triplet states ( $^3\text{Sens}^*$ ) and electron-poor phenoxyl radicals ( $\text{R-PhO}_{\text{ep}}^\bullet$ ), which are formed upon one-electron oxidation of the model phenol by  $^3\text{Sens}^*$ . In such model systems with well-defined chemicals (see Fig. 5),  $^3\text{Sens}^*$  and  $\text{R-PhO}_{\text{ep}}^\bullet$  are used to mimic  $^3\text{CDOM}^*$  and LLPO, respectively. As in the case of irradiated CDOM, both short-lived excited triplet states and longer-lived radicals coexist under irradiation in these model systems.





**Fig. 5.** Reaction scheme for a model system including a photosensitizer (Sens) and a partly dissociated electron-poor phenol ( $\text{R-PhOH}_{\text{ep}}/\text{R-PhO}_{\text{ep}}^-$ ) used to photogenerate short-lived excited triplet states ( $^3\text{Sens}^*$ ) and longer-lived phenoxyl radicals ( $\text{R-PhO}_{\text{ep}}^\bullet$ ), both contributing to the transformation of a target compound (TC).

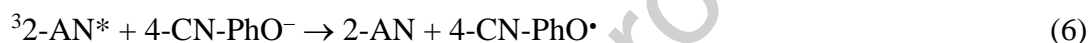
Irradiation experiments were performed using aqueous solutions buffered at pH 8.0 and containing 2-AN ( $1.5 \times 10^{-6}$  M) as Sens, 4-CN-PhOH ( $5.0 \times 10^{-6}$  M) as an electron-poor phenol (R-PhOH<sub>ep</sub>), and DMOP as a target compound at different initial concentrations in the range of  $1.0 \times 10^{-7}$  M –  $5.0 \times 10^{-6}$  M. The photosensitized transformation kinetics of DMOP was found to slow down with increasing initial concentration of DMOP between  $1.0 \times 10^{-7}$  and  $1.0 \times 10^{-6}$  M, while it remained constant above the latter concentration (Fig. 6a). First-order fitting of the kinetic data yielded pseudo-first-order rate constants that increased by a factor of 3, 4, and 10 for initial DMOP concentrations of  $5.0 \times 10^{-7}$  M,  $2.5 \times 10^{-7}$  M, and  $1.0 \times 10^{-7}$  M, respectively (see Fig. 6b), compared to the average rate constant observed for the higher initial DMOP concentrations ( $1.0 - 5.0 \times 10^{-6}$  M). The decrease in the first order rate constant with increasing initial concentrations of the target phenol is analogous to the one observed in the original study, in which DOM was used as a photosensitizer (Canonica and Hoigné 1995). This indicates that the model system is able to qualitatively reproduce the kinetic effect attributed to LLPO. The concentrations of 2-AN and 4-CN-PhOH were also monitored during these experiments and found to be essentially constant (see SI, Text S5 and Fig. S1).



**Fig. 6.** (a) Photosensitized transformation kinetics of 3,4-dimethoxyphenol (DMOP), in the presence of 2-acetonaphthone (2-AN,  $1.5 \times 10^{-6}$  M) and 4-cyanophenol (4-CN-PhOH,  $5.0 \times 10^{-6}$  M) at pH 8.0, for different initial concentrations of DMOP. Note the logarithmic scale of the y-axis. Black filled squares represent experimental data (average values from duplicate experiments), black thin lines are the corresponding first-order kinetics fits (yielding  $k^{\text{obs}}$ ), and green lines represent simulated DMOP transformation kinetics runs obtained from kinetic modelling (see SI, Text S6 and Table S7). (b) Pseudo-first-order rate constants ( $k^{\text{obs}}$ ) for the photosensitized transformation of DMOP as a function of  $[\text{DMOP}]_0$ . The red line with 95% confidence interval band represents a fit to eq. (10). (c) Time runs for the concentrations of  $^3\text{2-AN}^*$  (orange lines), and  $4\text{-CN-PhO}^\bullet$  (blue lines), for  $[\text{DMOP}]_0 = 5.0 \times 10^{-6}$  M (continuous lines) and  $1.0 \times 10^{-7}$  M (dashed lines), obtained from kinetic simulations (see SI, Text S6 and Table S7). Note the logarithmic scale of the y-axis.

Kinetic modelling was used to rationalize the observed DMOP transformation kinetics for the different initial concentrations of DMOP. The reactions considered in the model correspond to those represented in Fig. 5. The primary reaction (eq. (3)) consists in the excitation of 2-AN by photons of UV light to form its excited triplet state,  $^3\text{2-AN}^*$ . Note that this reaction includes several elementary photophysical steps (see e.g. (Rosario-Ortiz and Canonica 2016)), which do not have to be considered in detail because they occur on a very short time scale compared to the lifetime of  $^3\text{2-AN}^*$ . A second reaction (eq. (4)) describes the deactivation of  $^3\text{2-AN}^*$  in the absence of a target compound or an electron-poor phenol. This is also a lumped reaction comprising unimolecular deactivation and quenching by oxygen, but an overall deactivation rate constant can be employed because the oxygen concentration remains constant during the irradiation experiments. Further relevant reactions of  $^3\text{2-AN}^*$  involve DMOP (eq. (5)), leading to an oxidation product of DMOP,  $\text{DMOP}_{\text{ox}}$ , and  $4\text{-CN-PhO}^-$  (eq. (6)), which is present at pH 8.0 at equimolar concentration compared to the undissociated form of 4-CN-PhOH, leading to

the formation of the phenoxyl radical of the latter, 4-CN-PhO $\cdot$ . Both reactions also lead to ground-state 2-AN. The reaction of  $^3\text{2-AN}^*$  with the undissociated form of 4-CN-PhOH was neglected because it is too slow (Canonica et al. 2000). Finally, 4-CN-PhO $\cdot$  reacts with DMOP leading to 4-CN-PhO $^-$  and DMOP $_{\text{ox}}$  (eq. (7)). Note that for simplicity no distinction was made between the oxidation products of DMOP from eqs. (5) and (7).



Kinetic modelling was performed using the rate constants presented in Text S6 and Table S7 (SI). Kinetic simulations based on the above five reactions failed to reproduce adequately the experimental data shown in Fig. 6a. Also, the inclusion of an additional first-order deactivation reaction of 4-CN-PhO $\cdot$  in the kinetic model was not able to mimic the observed kinetics for DMOP in the micromolar range. Finally, the inclusion of a reaction of 4-CN-PhO $\cdot$  with DMOP $_{\text{ox}}$  (note that for simplicity no distinction was made between various generations of oxidation products), eq. (8), lead to a satisfactory reproduction of the experimental kinetics (see simulation results in Fig. 6a).



The fractions of DMOP transformed by the individual reactive species (after the whole irradiation periods) were also estimated utilizing the kinetic simulations. For  $[\text{DMOP}]_0 = 5.0 \times 10^{-6}$  M, 86% of the initial DMOP is transformed by  $^3\text{2-AN}^*$ , while for  $[\text{DMOP}]_0 = 1.0 \times 10^{-7}$  M, 89% of DMOP is transformed by 4-CN-PhO $\cdot$ .

To better understand the role of  $[\text{DMOP}]_0$  for the kinetics of DMOP transformation, the concentrations of the key reactive species, namely  $^3\text{2-AN}^*$  and  $4\text{-CN-PhO}^\bullet$ , obtained from kinetic simulations are represented in Fig. 6c as a function of irradiation time for the highest and lowest  $[\text{DMOP}]_0$  values ( $5.0 \times 10^{-6}$  M and  $1.0 \times 10^{-7}$  M, respectively). For the duration of the DMOP transformation experiments, both  $^3\text{2-AN}^*$  and  $4\text{-CN-PhO}^\bullet$  exhibit a constant steady-state concentration. This steady-state condition can be used to express the pseudo-first-order rate constant for the transformation of DMOP as the sum of the individual contributions of each reactive species (eq. (9)).

$$k_{\text{DMOP}}^{\text{obs}} = k_{^3\text{2-AN}^*, \text{DMOP}}^r \times [^3\text{2-AN}^*]_{\text{ss}} + k_{4\text{-CN-PhO}^\bullet, \text{DMOP}}^r \times [4\text{-CN-PhO}^\bullet]_{\text{ss}} \quad (9)$$

where the second-order rate constants  $k^r$  refer to the reactions of the species indicated in the subscripts leading to a transformation of DMOP, and the subscript "ss" stands for steady-state. The simulation results show that, while  $[^3\text{2-AN}^*]_{\text{ss}}$  has essentially the same value for both initial DMOP concentrations,  $[4\text{-CN-PhO}^\bullet]_{\text{ss}}$  for  $[\text{DMOP}]_0 = 1.0 \times 10^{-7}$  M is 50 times higher than for  $[\text{DMOP}]_0 = 5.0 \times 10^{-6}$  M, suggesting an inverse proportionality between  $[4\text{-CN-PhO}^\bullet]_{\text{ss}}$  and  $[\text{DMOP}]_0$  (i.e.,  $[4\text{-CN-PhO}^\bullet]_{\text{ss}} \propto 1/[\text{DMOP}]_0$ ). Utilizing this relationship, eq. (9) can be expressed as:

$$k_{\text{DMOP}}^{\text{obs}} = k_{^3\text{2-AN}^*, \text{DMOP}}^{\text{obs}} + \beta_{4\text{-CN-PhO}^\bullet, \text{DMOP}}^r / [\text{DMOP}]_0 \quad (10)$$

where the factor  $k_{^3\text{2-AN}^*, \text{DMOP}}^{\text{obs}} = k_{^3\text{2-AN}^*, \text{DMOP}}^r \times [^3\text{2-AN}^*]_{\text{ss}}$  is the pseudo-first-order rate constant for the transformation of DMOP in the absence of 4-CN-PhOH, and  $\beta_{4\text{-CN-PhO}^\bullet, \text{DMOP}}^r$  is an inverse proportionality factor related the reaction of 4-CN-PhO $^\bullet$  with DMOP. Both factors are independent of the DMOP concentration. Eq. (10) has a similar form as the original equation developed to explain the kinetic effect attributed to LLPO (Canonica and Hoigné 1995). A non-linear fitting of the  $k_{\text{DMOP}}^{\text{obs}}$  vs  $[\text{DMOP}]_0$  data to eq. (10) was successful (see Fig. 6b), yielding

$k_{32\text{-AN}^*,\text{DMOP}}^{\text{obs}} = (7.25 \pm 0.07) \times 10^{-4} \text{ s}^{-1}$ ,  $\beta_{4\text{-CN-PhO}^*,\text{DMOP}}^{\text{r}} = (1.23 \pm 0.03) \times 10^{-9} \text{ M s}^{-1}$  and a determination coefficient of 0.98.

#### 4. Conclusions

This study provides new insights into the kinetics of transformation of several target compounds and actual or potential aquatic contaminants photosensitized by CDOM. The principal objective of the study was to show that an enhancement of such a photosensitized transformation may occur at target compound concentrations of  $1 \times 10^{-7} \text{ M}$  compared to concentrations of a few  $10^{-6} \text{ M}$ . A concentration of  $1 \times 10^{-7} \text{ M}$  is closer to actual concentrations of contaminants occurring in sunlit surface waters compared to the concentrations used in the great majority of the studies in literature. The main outcomes of this study are:

- Electron-rich compounds belonging to the chemical classes of phenols, anilines, and phenylureas showed an enhanced CDOM-photosensitized transformation at  $1 \times 10^{-7} \text{ M}$  initial concentration compared to  $5 \times 10^{-6} \text{ M}$ . For phenols, enhancement factors (*EF*) are  $> 10$  in some cases, while for the other compound classes maximum *EF* of  $\approx 2.6$  were observed.
- The enhancement effect was attributed to DOM-derived long-lived photooxidants (LLPO). Using the enhancement effect of selected anilines and phenols, which was shown to increase with oxidation potential of the compounds, the one-electron reduction potential of LLPO derived from Suwannee River fulvic acid was estimated to be in the range of 1.02 – 1.32 V vs. SHE.
- Using 3,4-dimethoxyphenol as an LLPO probe compound, the highly aromatic and phenolic-rich Suwannee River humic and fulvic acids exhibited a much higher LLPO effect than Pony Lake fulvic acid, which has a significantly lower aromaticity and phenolic content.

- The same probe compound exhibited an analogous enhancement effect in a model system consisting of the photosensitizer 2-acetonaphthone and the electron-poor phenol 4-cyanophenol. The results from this model system support the hypothesis that LLPO comprise electron-poor phenoxyl radicals photochemically produced from DOM. This conclusion is corroborated by the aforementioned correlation between the LLPO effect and the phenolic content of different DOM types.

The findings of this study call for a reexamination of the predictions concerning the rates of indirect photochemical transformation of electron-rich aquatic contaminants, such as several phenols and anilines. Since such predictions are mostly based on laboratory irradiation experiments with spiked contaminants, it is recommended that future experiments are performed using various initial concentrations of the target compounds in the range  $\leq 1 \times 10^{-6}$  M.

#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### **Appendix A. Supplementary Data**

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

Journal Pre-proof

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## Graphical abstract

