

**Electronic Supplementary Information for**

**Assessing the Source of the Photochemical Formation of**

**Hydroxylating Species from Dissolved Organic Matter Using Model**

**Sensitizers**

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**Table S1.** List of chemicals, vendors, and chemical purities.

<i>Chemical</i>	<i>CAS</i>	<i>Source</i>	<i>Purity</i>
Benzene	71-43-2	Alfa Aesar	99.8
Phenol	108-95-2	Alfa Aesar	≥ 99
Benzoic acid	65-85-0	Alfa Aesar	Recrystallized
Salicylic acid	69-72-7	EMD	≥ 99
p-Benzoquinone	106-51-4	Alfa Aesar	Sublimated
Anthraquinone-2-sulfonate	131-08-8	Aldrich	97%
2,6-Dimethoxy-p-benzoquinone	530-55-2	Alfa Aesar	98%
4-Benzoylbenzoic acid	611-95-0	Aldrich	99%
3-Methoxyacetophenone	586-37-8	Acros Organics	98%
Umbelliferone	93-35-6	Aldrich	99%
trans-Cinnamic acid	140-10-3	Aldrich	≥ 99%
2,4-Dihydroxybenzoic acid	89-86-1	Aldrich	97%
4-Hydroxybenzoic acid	99-96-7	Aldrich	≥ 99%
Sodium Nitrate	7631-99-4	Fisher Scientific	99.7%
Sodium Nitrite	7632-00-0	Aldrich	≥ 97%
Hydrogen peroxide	7722-84-1	BDH	30% w/w
Methanol	67-56-1	VWR	99.8%
Acetonitrile	75-05-8	VWR	99.95%
Phosphoric acid	7664-38-2	EMD	85% w/w
Sodium hydroxide	1310-73-2	Sigma Aldrich	≥ 97%

**Text S1. Actinometry****254 nm Irradiations**

Uridine was used as an actinometer following the procedure of Jin et al.<sup>1</sup> In brief, a stock uridine solution of 1.2 μM was prepared in 1 mM phosphate buffer (pH 7.0). For actinometry experiments, uridine stock was added to a set of vials and irradiated. At regular time intervals vials were withdrawn from the reactor and the uridine concentration measured spectrophotometrically using the molar extinction coefficient of 8593 M<sup>-1</sup> cm<sup>-1</sup> at λ=262 nm. Photon irradiance was calculated according to eq S1 with the irradiance typically being about 1.7 × 10<sup>-8</sup> Einstein cm<sup>-2</sup> s<sup>-1</sup>,

$$I_{0,254nm} = \frac{k'[\text{uridine}]_0 l}{1000\Phi_{\text{uridine}}(1 - 10^{-\epsilon_{\text{uridine}}[[\text{uridine}]_0]l})} \quad \text{eq S1}$$

where  $I_{0,254nm}$  is the photon irradiance (Einstein cm<sup>-2</sup> s<sup>-1</sup>) for the 254 nm lamps, which are treated as a monochromatic light source,  $k'$  is the observed first-order rate constant for uridine decay (s<sup>-1</sup>),  $[\text{uridine}]_0$  is the initial concentration of uridine (M),  $l$  is the path length,  $\Phi_{\text{uridine}}$  is the quantum yield for uridine photodegradation (0.020), and  $\epsilon_{\text{uridine}}$  is the molar extinction coefficient for uridine (10 185 M<sup>-1</sup> cm<sup>-1</sup>) at 254 nm.<sup>1</sup>

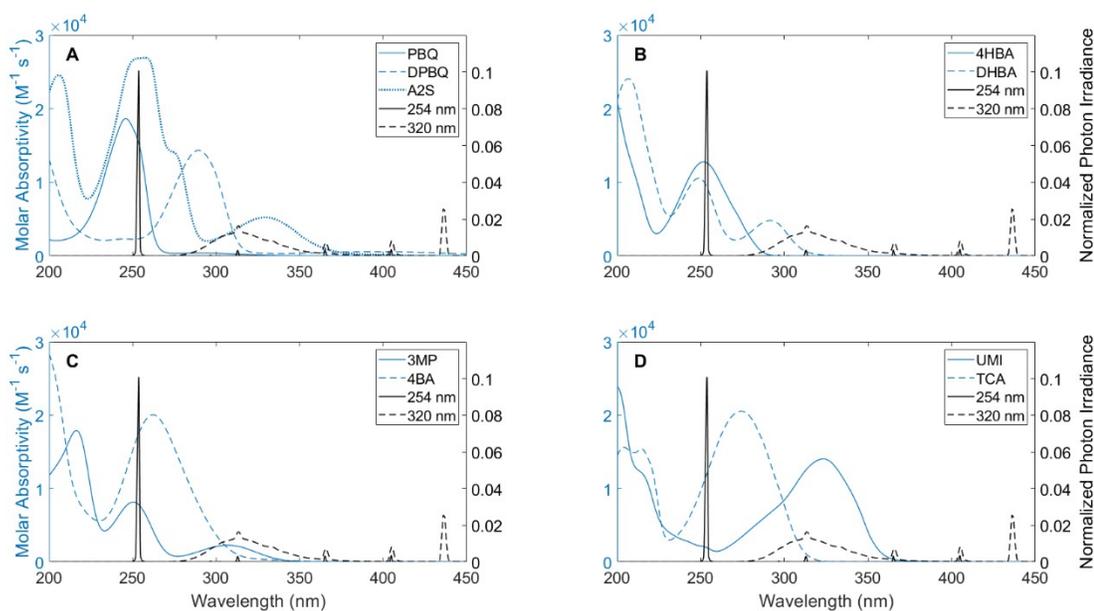
### 320 nm Irradiations

*p*-Nitroanisole (PNA) / pyridine (PYR) actinometry was used following the procedure of Laszakovits et al using a solution containing 10  $\mu$ M PNA and 5 mM PYR.<sup>2</sup> The disappearance of PNA was monitored throughout irradiation time using HPLC for detection, employing 50% 10 mM phosphoric acid/50% acetonitrile mobile phase with UV detection at 300 nm. The typical retention time of PNA in the system was approximately 2.3 min. These data were fitted to a first-order kinetic model. Eq S2 was used to calculate the photon irradiance, with the irradiance typically being about  $1.3 \times 10^{-7}$  Einstein  $\text{cm}^{-2} \text{s}^{-1}$ ,

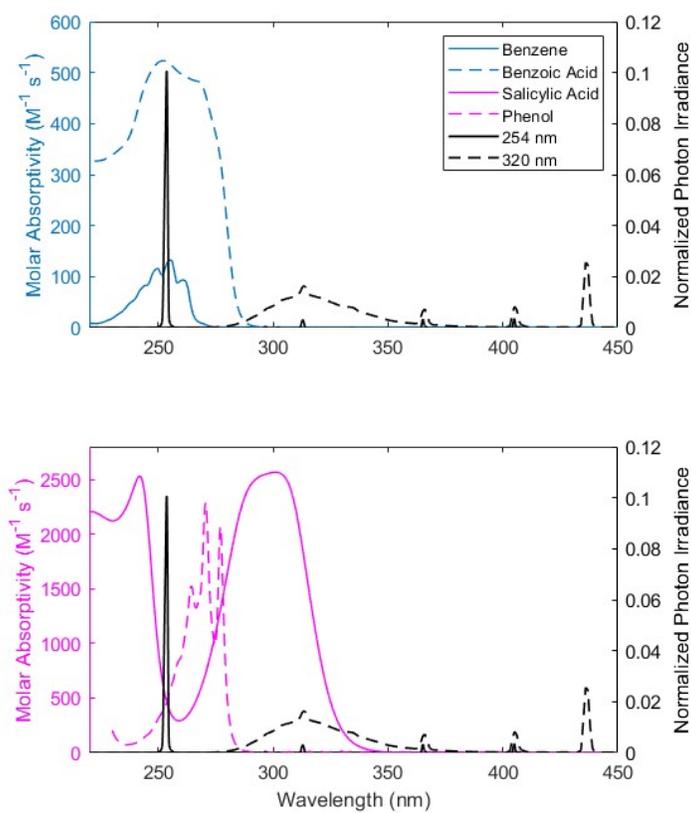
$$I_{0,320\text{nm}} = \frac{k[\text{PNA}]_0 l}{1000\Phi_{\text{PNA}} \sum_{\lambda} (1 - 10^{-\epsilon_{\text{PNA},\lambda}[\text{PNA}]_0 l})} \quad \text{eq S2}$$

$$\Phi_{\text{PNA}} = 0.29[\text{PYR}] + 0.00029 \quad \text{eq S3}$$

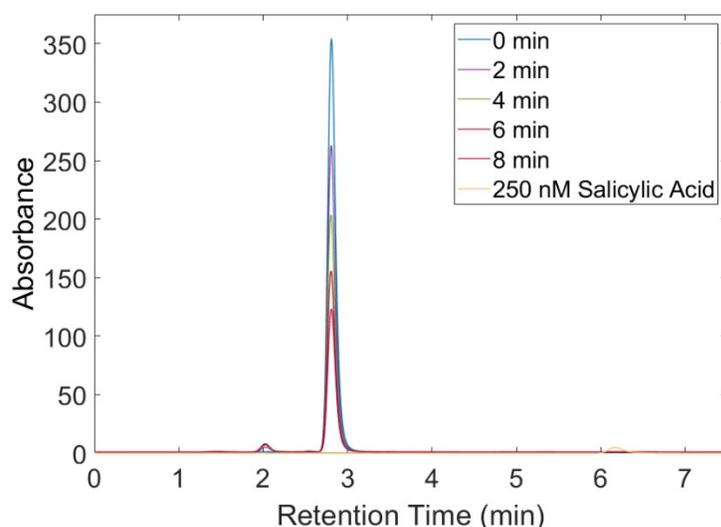
where  $I_{0,320\text{nm}}$  is the photon irradiance (Einstein  $\text{cm}^{-2} \text{s}^{-1}$ ) for the 320 lamps, which emit light over a spectrum seen in Figure S1,  $k$  is the observed first-order rate constant for PNA decay ( $\text{s}^{-1}$ ),  $[\text{PNA}]_0$  is the initial concentration of PNA (M),  $l$  is the path length,  $\Phi_{\text{PNA}}$  is the PNA quantum yield and is calculated using eq 3, and  $\epsilon_{\text{PNA},\lambda}$  is the molar extinction coefficient for PNA over the wavelengths emitted by the 320 nm lamps, which can be found in the study by Laszakovits et al<sup>2</sup>.



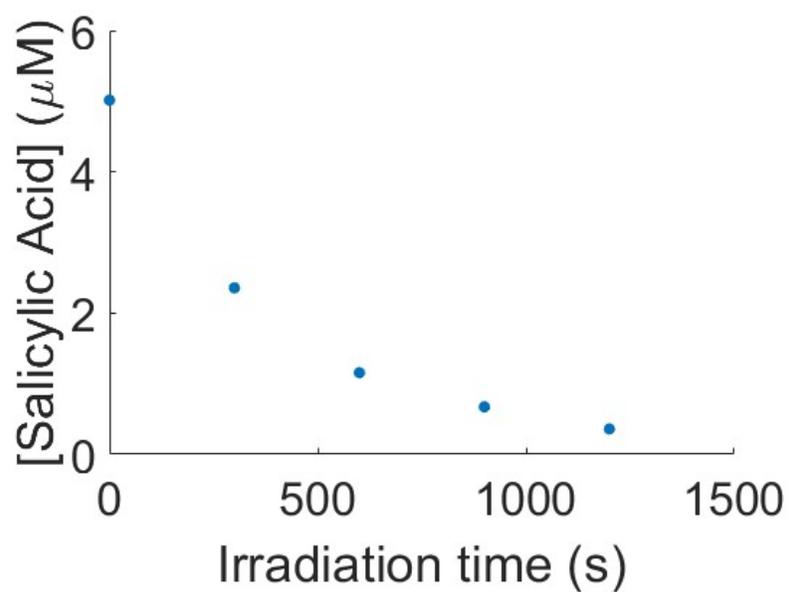
**Figure S1.** Molar absorptivity of sensitizers on the left y-axis and normalized (total area = 1) lamp spectra on the right y-axis. A: Quinones, B: Hydroxybenzoic acids, C: Aromatic ketones, and D: Other triplet forming species.



**Figure S2.** Molar absorptivity of probes (benzene and benzoic acid) and hydroxylated probes (phenol and salicylic acid) on the left y-axis and normalized (total area = 1) lamp spectra on the right y-axis. Benzene and phenol molar absorptivity data is from literature.<sup>3</sup>



**Figure S3.** Chromatograms for irradiation of DHBA with 254 nm lamps at 0, 2, 4, 6, and 8 minutes. Shown in light orange is a 250 nM salicylic acid standard.



**Figure S4.** Direct photolysis of salicylic acid at 320 nm results in rapid first order decrease in salicylic acid concentration.

**Text S2.** Contribution of H<sub>2</sub>O<sub>2</sub> to the production of hydroxylating species

Estimated rate of formation of •OH from H<sub>2</sub>O<sub>2</sub> photolysis for varying concentrations of H<sub>2</sub>O<sub>2</sub> under 254 and 320 nm irradiation conditions. The following equation was used.

$$R_{\bullet OH} = \Phi_{\bullet OH}[H_2O_2] \sum_{\lambda} k_{a\lambda} \quad \text{eq S4}$$

where  $k_{a\lambda}$  was calculated using eq 3 from the main text and values for  $\epsilon_{H_2O_2}$  and  $\Phi_{\bullet OH}$  were found in literature.<sup>4,5</sup> The concentration of H<sub>2</sub>O<sub>2</sub> was estimated using experimental data from other studies.<sup>6,7</sup>

**Table S2.** Rate of formation of •OH from H<sub>2</sub>O<sub>2</sub> photolysis.

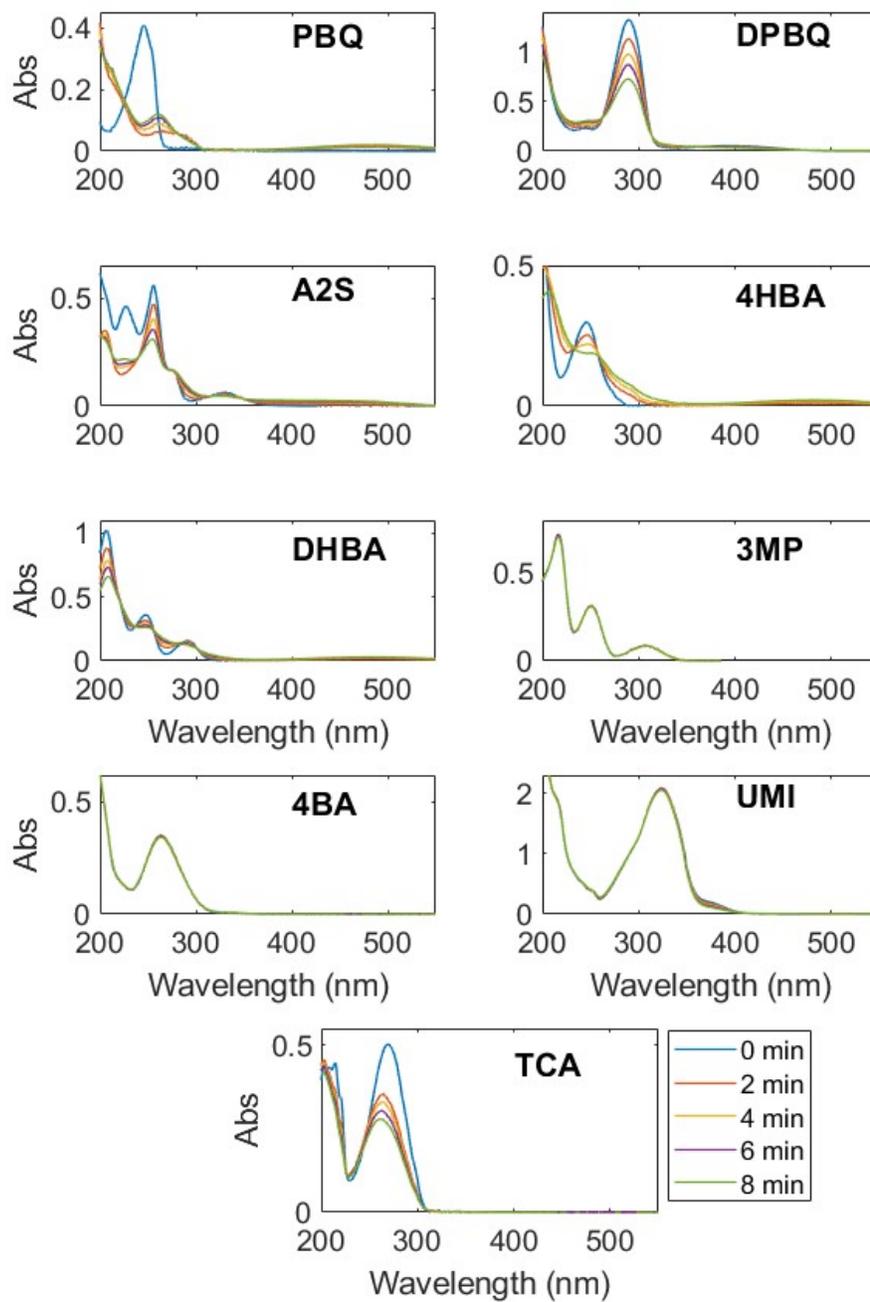
[H <sub>2</sub> O <sub>2</sub> ]	$R_{\bullet OH, 254nm}$ (M s <sup>-1</sup> )	$R_{\bullet OH, 320nm}$ (M s <sup>-1</sup> )
100 nM**	$7.6 \times 10^{-15}$	$9.1 \times 10^{-15}$
1000 nM**	$7.6 \times 10^{-14}$	$9.1 \times 10^{-14}$
20 uM*	$1.5 \times 10^{-12}$	$1.8 \times 10^{-12}$

\*Approximate concentration of Sens used in photochemistry experiments reported in this study.

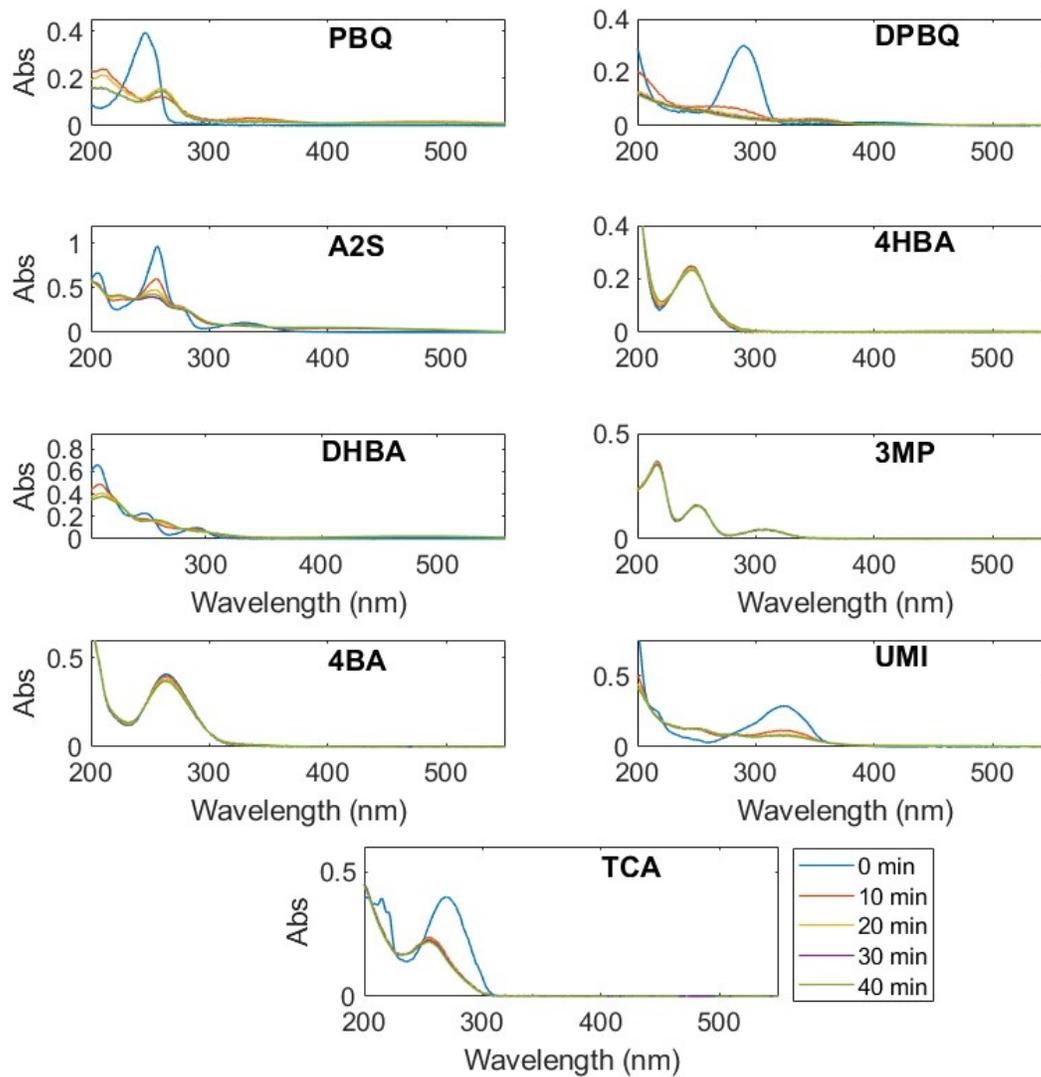
\*\*Within concentration range of measured H<sub>2</sub>O<sub>2</sub> from photochemistry experiments with DOM and quinones.<sup>6,7</sup>

**Table S3.** List of formation rates (nM s<sup>-1</sup>) of salicylic acid and phenol for experimental conditions 254 nm/benzoic acid and 320 nm/benzene, respectively. This data can be found in Figures 2 and 3 in the main text. ND = No data in the case of A2S because the formation of phenol is not linear.

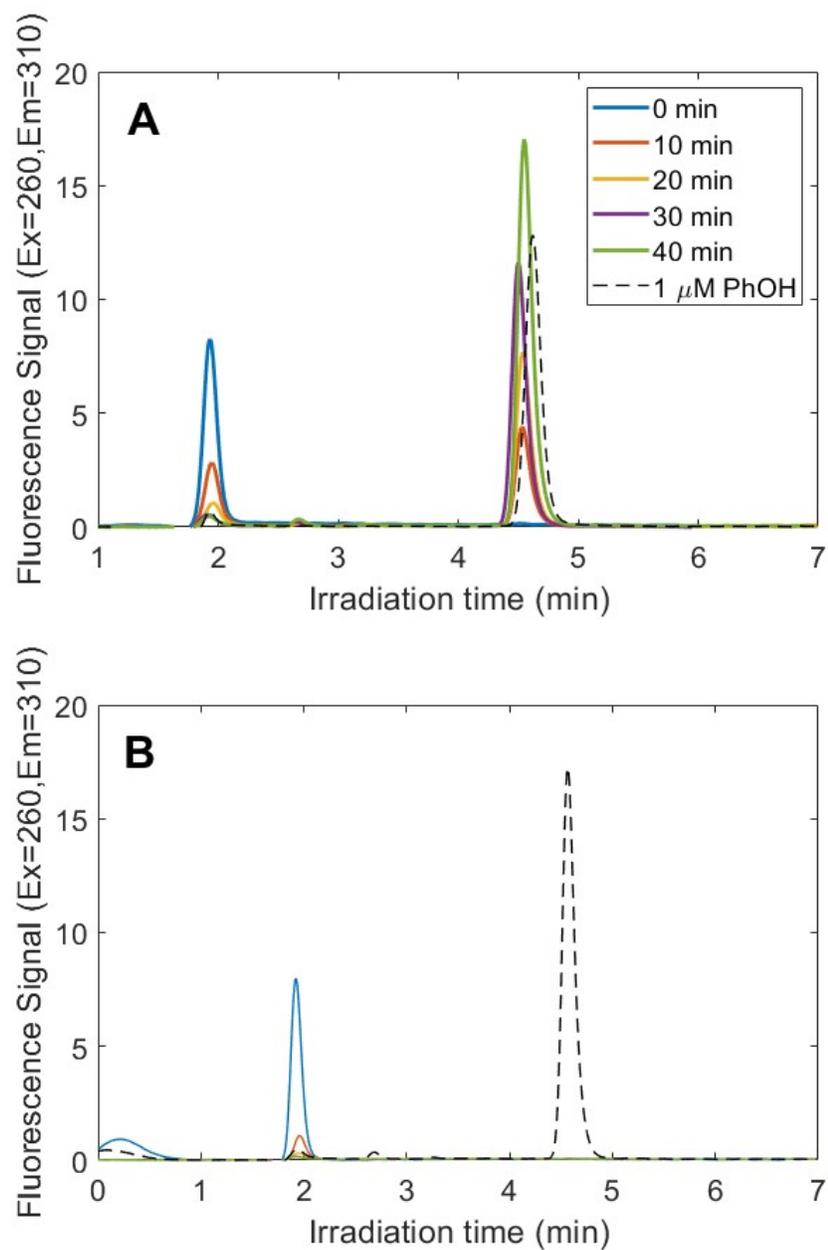
Sensitizer	254 nm/Benzoic acid (nM s <sup>-1</sup> )	320 nm/Benzene (nM s <sup>-1</sup> )
PBQ	5.9 ± 0.46	0.95 ± 0.07
DPBQ	8.1 ± 0.46	2.2 ± 0.19
A2S	26 ± 1.73	ND
4HBA	3.0 ± 0.13	1.3 ± 0.13
DHBA	3.4 ± 0.83	1.9 ± 0.27
4BA	1.0 ± 0.05	0.60 ± 0.08
3MP	0.45 ± 0.10	0.43 ± 0.07
TCA	0.51 ± 0.13	0.39 ± 0.01
UMI	0.31 ± 0.11	0.49 ± 0.06
Direct photolysis of probe	1.4 ± 0.08	0.19 ± 0.04



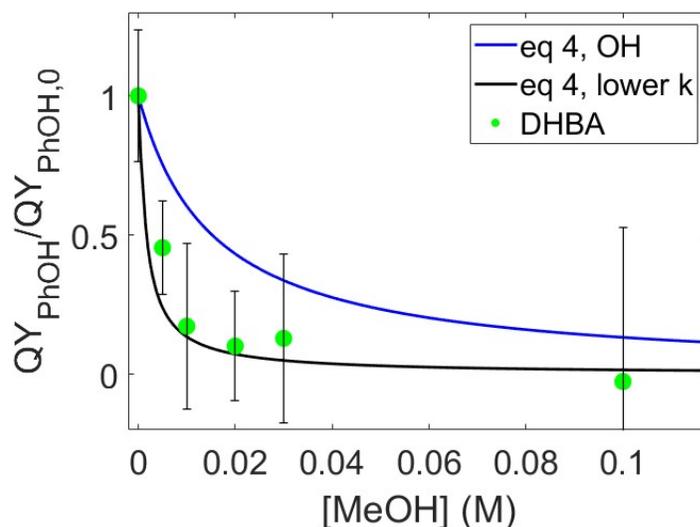
**Figure S5.** Absorbance spectra of Sens at 0, 2, 4, 6, and 8 minutes irradiation times, exposed to 254 nm lamps.



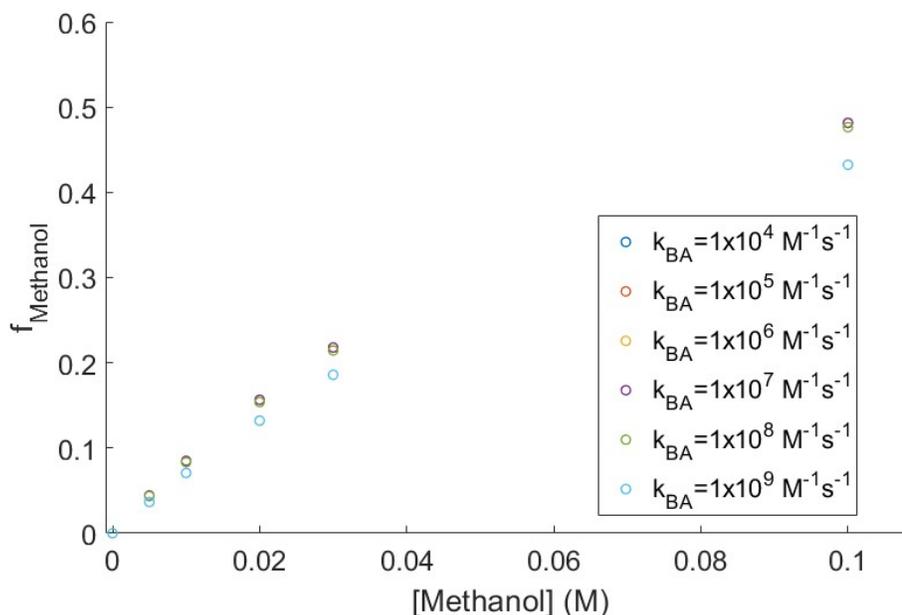
**Figure S6.** Absorbance spectra of Sens at 0, 10, 20, 30, and 40 minutes irradiation times, exposed to 320 nm lamps.



**Figure S7.** A: Chromatograms for detection of phenol from the photolysis of hydroquinone using 320 nm with benzene as a probe compound. B: Chromatograms for direct photolysis of hydroquinone using the phenol method for HPLC analysis.



**Figure S8.** DHBA methanol quenching data in the system using benzene and 320 nm irradiation, compared to the model, eq 4 (main text), using two different values for  $k_{PC,\bullet OH}$ . In blue is the model where the rate constant for  $\bullet OH$  was employed, in black is the model where a rate constant an order of magnitude lower than that of  $\bullet OH$ , and in green is the methanol quenching data for DHBA.



**Figure S9.** Fraction of triplet quinone reacting with methanol, as described by eq 6 in the main text, in an aqueous aerobic system containing benzoic acid and varying concentrations of methanol. Concentrations of methanol used in quenching experiments ranged between 0.005 – 0.1 M.

### **Text S3. Absorption of light by quinones and hydroxybenzoic acids in dissolved organic matter (DOM)**

*Quinones.* Electron accepting capacity (EAC) used to calculate the concentration of quinones in sample containing DOM and using this value the fraction of light absorbed by quinones was calculated. For these calculations, we utilized Suwannee River fulvic acid (SRFA) as a model DOM sample.

The concentration of quinones in SRFA was calculated using the EAC value of  $671 \mu\text{mol}_e \cdot \text{g}_{\text{HS}}^{-1}$  measured by Aeschbacher et al. (2010):

$$[\text{quinone}] = 671 \mu\text{mol}_e \cdot \text{g}_{\text{HS}}^{-1} \times 1 \mu\text{mol}_{\text{quinone}} / 2 \mu\text{mol}_e = 335.5 \mu\text{mol}_{\text{quinone}} \cdot \text{g}_{\text{HS}}^{-1}$$

For a 10 mg/L SRFA solution, this give a concentration of:

$$[\text{quinone}] = 0.010 \text{ g}_{\text{HS}} \text{ L}^{-1} \times 335.5 \mu\text{mol}_{\text{quinone}} \cdot \text{g}_{\text{HS}}^{-1} = 3.35 \mu\text{mol} \text{ L}^{-1}$$

Finally, the absorbance at a specific wavelength was calculated by selecting a quinone model sensitizer (MS) (e.g., *p*-benzoquinone), assuming that the entire [quinone] calculated above is attributable to that specific quinone and multiplying by the molar extinction coefficient. For example, for *p*-benzoquinone at 246 nm:

$$\text{Abs}_{\text{pBQ},246} = 3.35 \mu\text{mol}_{\text{pBQ}} \text{ L}^{-1} \times 22,000 \text{ M}^{-1} \text{ cm}^{-1} = 0.074 \text{ cm}^{-1}$$

To determine the fraction of light absorbed by quinone in the SRFA mixture, the above absorbance value is divided by that of the DOM isolate at the chosen excitation wavelength. For our purposes, the DOM solution absorbance was calculated using a measured  $\text{SUVA}_{254}$  ( $4.2 \text{ L mg}_C^{-1} \text{ m}^{-1}$ ) and spectral slope ( $S$ ,  $0.0152 \text{ nm}^{-1}$ ) for SRFA:

$$\text{Abs}_{\text{SRFA},246} = \text{SUVA}_{254} \times \exp(-S(246-250)) \times 0.01 \text{ cm m}^{-1} \times 5 \text{ mg}_C \text{ L}^{-1} = 0.24 \text{ cm}^{-1}$$

The fraction of light absorbed by *p*-benzoquinone at 246 nm is therefore equal to  $0.074/0.24 = 0.31$ .

*Hydroxybenzoic acids.* Similar calculations were performed for hydroxybenzoic acids by employing the electron donating capacities (EDC) of SRFA. Although the contribution of hydroxybenzoic acids to the EDC is unknown, recent reports suggest that these moieties may be involved as electron donors within DOM.<sup>8</sup> By assuming that the entire EDC is due to hydroxybenzoic acids, the calculations shown here represent an upper limit for the contribution of hydroxybenzoic acids to DOM absorbance, with the actual contribution probably being less. The equation used for calculating the concentration of hydroxybenzoic acid is shown below:

$$[\text{hydroxybenzoic acid}] = [\text{DOM}] \times \text{EDC} \times 1 \mu\text{mol}_{\text{hydroxybenzoic acid}} / 2 \mu\text{mol}_e$$

**Table S4.** Fractional absorbance of quinone and hydroxybenzoic acid MS in SRFA (2S101F) calculated based on electron accepting capacity and electron donating capacity, respectively.

<b>Quinone MS</b>	<b>Wavelength (nm)</b>	<b>Epsilon (<math>M^{-1} cm^{-1}</math>)</b>	<b>Abs SRFA (<math>cm^{-1}</math>)</b>	<b>Abs MS (<math>cm^{-1}</math>)</b>	<b>Abs MS/Abs SRFA <math>\times 100</math></b>
p-benzoquinone	246	22000	0.24	0.074	31.1%
	296	320	0.11	0.001	1.0%
	424	20	0.02	0.000	0.4%
2,6-dimethoxy-p-benzoquinone	258	17000	0.20	0.057	28.9%
	332	280	0.06	0.001	1.5%
	424	30	0.02	0.000	0.6%
1,4-napthoquinone	252	16700	0.22	0.056	25.9%
	342	2490	0.06	0.008	15.2%
4-hydroxybenzoic acid	254	12676	0.21	0.181	86.0%
	300	11	0.10	0.000	0.2%
2,4-dihydroxybenzoic acid	254	9296	0.21	0.132	63.0%
	300	3510	0.10	0.050	47.9%

## References for the Electronic Supplementary Information

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