Electronic Supplementary Information for

The Effect of Probe Choice and Solution Conditions on the Apparent Photoreactivity of Dissolved Organic Matter

Andrew C. Maizel[1] *and Christina K. Remucal*[1, 2]*

[1]Department of Civil and Environmental Engineering

University of Wisconsin - Madison

Madison, Wisconsin

[2]Environmental Chemistry and Technology Program

University of Wisconsin - Madison

Madison, Wisconsin

Submitted to: *Environmental Science: Processes and Impacts,* May 25, 2017.

Contents (28 pages): Figures: S1-S9, Tables: S1-S22.

* Corresponding author address: 660 N. Park St., Madison, WI 53706; e-mail: remucal@wisc.edu; telephone: (608) 262-1820; fax: (608) 262-0454.

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S1. Sample Characterization

After filtration, all waters were analyzed for Ca, Fe, K, Mg, and Na concentrations under ambient conditions by inductively coupled plasma-optical emission with a Perkin Elmer 4300 DV and results are presented in Table S1. Waters were analyzed for chloride, nitrite, nitrate, and sulfate by anion exchange chromatography with a Dionex ICS-2100 and results are presented in Table S2. UV-vis absorbance measurements were collected with a Shimadzu UV-2401 PC, using quartz 1 cm cuvettes. Measurements were collected at 1 nm increments against a Milli-Q water reference and were corrected for blank and long wavelength (700-800 nm) absorption. E_2:E_3 is defined as the ratio of absorbance at 250 nm and 365 nm.[1] $SUVA_{254}$ is defined as the ratio of absorbance at 254 nm to the concentration of dissolved organic carbon.[2] Spectral slopes ($S_{275-295}$, $S_{300-700}$, and $S_{350-400}$) are determined with a least squares regression of exponential functions that have the absorbance at the shortest relevant wavelength as a reference.[1] Spectral slope ratio (S_R) is the ratio of $S_{275-295}$ to $S_{350-400}$. UV-vis results are presented in Table S3. Dissolved organic and dissolved inorganic carbon were quantified with a GE Sievers M5310C TOC analyzer and results in ambient waters are presented in Table S4. pH was determined with a Mettler Toledo EL20, and results in ambient waters are presented in Table S4.

Table S1. Inductively couple plasma-optical emission spectroscopy results for ambient waters. K in Western Lake Superior Sanitary District (WLSSD) effluent was calculated with a different wavelength (404.72 nm) than the other waters (766.49 nm) due to an unknown interference.

	Ca (μM)	Fe (μM)	K (μM)	Mg (μM)	Na (μM)
Oligotrophic Lakes					
Big Muskellunge Lake	169 ± 2	< 1.8	11.9 ± 0.1	82.5 ± 0.6	38 ± 0.8
Sparkling Lake	296 ± 3	< 1.8	19.4 ± 0.1	140.8 ± 1.1	146.9 ± 3.1
Terrestrially Influenced Waters					
Allequash Lake	303 ± 3	< 1.8	16.0 ± 0.1	136.3 ± 1.0	83.5 ± 1.8
St. Louis River	456 ± 4	20.4 ± 0.2	161.4 ± 1.0	418.9 ± 3.1	211.5 ± 4.5
Surface Wetlands					
Toivola Swamp	226 ± 2	31.1 ± 0.3	8.0 ± 0.1	94 ± 0.7	81.4 ± 1.7
Trout Bog	121 ± 1	3.6 ± 0.0	10.3 ± 0.1	13.2 ± 0.1	16.9 ± 0.4
Wastewater Effluents					
WLSSD	1431 ± 13	3.6 ± 0.0	222.2 ± 1.3	418.9 ± 3.1	8327.6 ± 177.9
Madison Metropolitan Sewerage District (MMSD)	2123 ± 13	1.1 ± 0.01	2.8 ± 0.6	1804.3 ± 17.0	8454.2 ± 59.0

Table S2. Ion chromatography results for all waters under ambient conditions.

	Cl^- (μM)	NO_2^- (μM)	NO_3^- (μM)	SO_4^- (μM)
Oligotrophic Lakes				
Big Muskellunge Lake	13	<28	<14	93
Sparkling Lake	313	<28	<14	91
Terrestrially Influenced Waters				
Allequash Lake	27	<28	<14	119
St. Louis River	144	<28	<14	315
Surface Wetlands				
Toivola Swamp	49	<28	<14	10
Trout Bog	35	<28	<14	20
Wastewater Effluents				
WLSSD	2560	<140	<70	6822
MMSD	8582	<28	1166	1417

Table S3. UV-visible spectroscopy results for all waters under ambient conditions.

	E_2:E_3 (-)	$SUVA_{254}$ (L m^{-1} mg-C^{-1})	$S_{275\text{-}295}$ (nm^{-1})	$S_{300\text{-}700}$ (nm^{-1})	$S_{350\text{-}400}$ (nm^{-1})	S_R (-)
Oligotrophic Lakes						
Big Muskellunge Lake	10.51	0.964	0.0255	0.0196	0.0233	1.097
Sparkling Lake	9.63	1.375	0.0249	0.0198	0.0224	1.112
Terrestrially Influenced Waters						
Allequash Lake	5.97	3.061	0.0172	0.0170	0.0178	0.969
St. Louis River	4.68	4.431	0.0129	0.0152	0.0166	0.775
Surface Wetlands						
Toivola Swamp	5.07	3.972	0.0145	0.0156	0.0177	0.818
Trout Bog	4.86	3.720	0.0143	0.0152	0.0173	0.826
Wastewater Effluents						
WLSSD	5.98	2.781	0.0134	0.0171	0.0191	0.703
MMSD	5.36	2.464	0.0114	0.0164	0.0169	0.675

Table S4. Dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and pH measurements in ambient waters.

	[DOC] (mg-C L^{-1})	[DIC] (mg-C L^{-1})	pH
Oligotrophic Lakes			
Big Muskellunge Lake	4.05 ± 0.03	5.68 ± 0.03	7.64 ± 0.06
Sparkling Lake	3.41 ± 0.02	8.07 ± 0.01	7.67 ± 0.02
Terrestrially Influenced Waters			
Allequash Lake	5.67 ± 0.07	10.03 ± 0.06	7.55 ± 0.04
St. Louis River	28.82 ± 0.37	15.51 ± 0.22	7.81 ± 0.08
Surface Wetlands			
Toivola Swamp	44.12 ± 0.65	4.6 ± 0.24	6.73 ± 0.19
Trout Bog	19.72 ± 0.11	1.04 ± 0.16	5.67 ± 0.16
Wastewater Effluents			
WLSSD	21.44 ± 0.42	58.33 ± 1.53	8.51 ± 0.05
MMSD	6.83 ± 0.17	65.72 ± 1.18	8.27 ± 0.02

S2. Solid Phase Extraction

The solid phase extraction (SPE) protocol is based on similar protocols used to concentrate dissolved organic matter (DOM) prior to mass spectrometry analysis.[3,4] Approximately 500 mL of each sample was acidified with 1 M HCl to pH 2. Agilent Bond Elut-PPL SPE cartridges (500 mg, 6 mL) were attached to a vacuum manifold and prepared by rinsing with 5 mL methanol. Acidified samples were pumped through the SPE cartridges at approximately 5 drops per second until the entire sample volume had passed through. SPE cartridges were then rinsed with 5 mL 0.01 M HCl and dried with HEPA filtered air for 5 minutes. DOM isolates were eluted from the SPE cartridges with 5 mL methanol. Methanol eluents were dried under HEPA filtered air, and the DOM isolates were diluted in 10 mM pH 8 borate buffer solution prepared in ultrapure water. [DOC] recovery was calculated as the fraction of the mass of dissolved organic carbon recovered in the final aqueous solutions compared with the calculated mass of dissolved organic carbon that was in the ambient water, and is presented in Table S5. UV-vis results of SPE isolates are presented in Table S5.

Table S5. Optical properties data and DOC recovery for SPE isolates.

	E_2:E_3 (-)	$SUVA_{254}$ (L m^{-1} mg-C^{-1})	$S_{275-295}$ (nm^{-1})	$S_{300-700}$ (nm^{-1})	$S_{350-400}$ (nm^{-1})	S_R (-)	DOC recovery %
Oligotrophic Lakes							
Big Muskellunge Lake	10.43	1.24	0.0222	0.0211	0.0218	1.0195	48.8
Sparkling Lake	9.93	1.50	0.0218	0.0211	0.0224	0.9743	50.8
Terrestrially Influenced Waters							
Allequash Lake	5.65	3.38	0.0185	0.0165	0.0184	1.0043	54.3
St. Louis River	5.04	4.15	0.0130	0.0158	0.0182	0.7129	65.3
Surface Wetlands							
Toivola Swamp	5.40	3.75	0.0143	0.0163	0.0190	0.7550	70.0
Trout Bog	4.84	3.79	0.0131	0.0153	0.0177	0.7441	68.6
Wastewater Effluents							
WLSSD	6.34	2.83	0.0124	0.0179	0.0203	0.6094	63.0
MMSD	4.73	2.60	0.0120	0.0149	0.0165	0.7279	53.5

S3. Photochemistry Experiments

Solution rates of light absorbance (R_{abs}), [DOC], pH and ionic strength for experiments conducted under ambient conditions are presented in Table S6, for standardized [DOC] and pH in Table S7, for SPE isolates in Table S8, for variable [DOC] with constant pH in Table S9 and Figure S1, and for variable pH with constant [DOC] in Table S10 and Figure S2. UV-vis spectra collected under ambient conditions, with standardized [DOC] and pH, and with SPE isolates are presented in Figure S3. Quantum yield coefficients and pseudo-steady state concentrations for experiments conducted under ambient conditions are presented in Table S11, for standardized [DOC] and pH in Table S12, for SPE isolates in Table S13, for experiments with variable [DOC] and constant pH in Table S14, and for experiments with variable pH and constant [DOC] in Table S18. Quantum yield coefficients measured in SPE isolates are presented in Figure S4. Apparent quantum yields measured in SPE isolates are presented in Figure S5. Psuedo-steady state concentrations measured in SPE isolates are presented in Figure S6. Apparent quantum yields measured in experiments with variable [DOC] but constant pH are shown in Figure S7. Apparent quantum yields measured in experiments with variable pH, but constant [DOC] are shown in Figure S8. Linear regressions of quantum yield coefficients vs. [DOC] in experiments with variable [DOC] and constant pH are shown in Table S15. Linear regressions of apparent quantum yields vs. [DOC] in experiments with variable [DOC] and constant pH are shown in Table S16. Linear regressions of pseudo-steady state concentrations vs. [DOC] in experiments with variable [DOC] and constant pH are shown in Table S17. Linear regressions of quantum yield coefficients vs. pH in experiments with variable pH and constant [DOC] are shown in Table S19. Linear regressions of apparent quantum yields vs. pH in experiments with variable pH and constant [DOC] are shown in Table S20. Linear regressions of pseudo-steady state concentrations vs. pH in experiments with variable pH and constant [DOC] are shown in Table S21. Linear regressions of quantum yield coefficients vs. E_2:E_3 under ambient and standardized conditions are shown in Table S22. Ratios of pseudo-steady state concentrations observed under ambient conditions, standardized conditions, and in SPE isolates are shown in Figure S9.

Photoreactivity of SPE Isolates. [DOC] recovery was 49 – 70% and the re-diluted isolates had similar $SUVA_{254}$ (101 ± 7%), E_2:E_3 (106 ± 11%), and R_{abs} (99 ± 12%, excluding oligotrophic lakes, which have [DOC] < 4 mg – C L^{-1} under standardized conditions; Tables S5 and S8) to corresponding waters under standardized [DOC] and pH.

Quantum yield coefficients and apparent quantum yields are slightly elevated in SPE isolate solutions compared with standardized conditions (Figures S4 and S5). The largest average increases are in f_{TMP} and $\Phi_{3DOM,TMP}$ (+24 ± 18%), followed by f_{FFA} and Φ_{1O2} (+21 ± 15%) and f_{HDA} and $\Phi_{3DOM,HDA}$ (+8 ± 22%). Despite the shifts in average quantum yield terms, identical trends are observed as under standardized [DOC] and pH. For example, all probes show increasing quantum yield terms from surface wetlands to terrestrially influenced waters to oligotrophic lakes. Additionally, ratios of quantum yields terms measured in SPE isolates are similar to those recorded with standardized [DOC] and pH, with Φ_{1O2} : $\Phi_{3DOM,TMP}$ ranging from 0.8 – 2.0 and Φ_{1O2} : $\Phi_{3DOM,HDA}$ ranging from 7.2 – 17.9. The distinctive photoreactivity of the wastewater effluents is maintained as well, with wastewater effluents exhibiting higher Φ_{1O2}, but lower $\Phi_{3DOM,TMP}$, than the oligotrophic lakes, as well as mutually similar Φ_{1O2} and $\Phi_{3DOM,TMP}$ but dissimilar $\Phi_{3DOM,HDA}$.

Pseudo-steady state concentrations in irradiated SPE isolates are also similar to values measured in corresponding whole waters under standardized conditions. Excluding the oligotrophic lakes, $[^1O_2]_{ss}$ decreases 11 ± 7 %, $[^3DOM]_{ss,TMP}$ increases 1 ± 12%, and $[^3DOM]_{ss,HDA}$ decreases 1 ± 14 % (Figure S6). [DOC] in SPE isolates from the oligotrophic lakes are higher than in the standardized conditions, which partially represent the increased [DOC] in these waters relative to standardized conditions ($[^3DOM]_{ss,TMP}$ + 55%, $[^3DOM]_{ss,HDA}$ +39%, $[^1O_2]_{ss}$ +24%; [DOC]: Big Muskellunge Lake = +2%, Sparkling Lake = + 21%). Additionally, SPE isolates exhibit similar ratios of pseudo-steady state concentrations as observed under standardized conditions. For example, $[^3DOM]_{ss,TMP}$: $[^3DOM]_{ss,HDA}$ are 4.3 – 5.5 in wastewaters, 7.7 – 8.3 in oligotrophic lakes, and 9.4 – 10.4 in terrestrially influenced waters and surface wetlands.

Table S6. R_{abs}, [DOC], pH, and ionic strength of sample waters, as irradiated under ambient conditions

	R_{abs} (10^9 E cm^{-3} s^{-1})	[DOC] (mg-C L^{-1})	pH	Ionic Strength (mM)
Oligotrophic Lakes				
Big Muskellunge Lake	0.146 ± 0.005	4.05 ± 0.03	7.64 ± 0.06	1.0
Sparkling Lake	0.190 ± 0.008	3.41 ± 0.02	7.67 ± 0.02	1.6
Terrestrially Influenced Waters				
Allequash Lake	1.142 ± 0.003	5.67 ± 0.07	7.55 ± 0.04	1.6
St. Louis River	8.513 ± 0.010	28.82 ± 0.37	7.81 ± 0.08	3.3
Surface Wetlands				
Toivola Swamp	9.991 ± 0.005	44.12 ± 0.65	6.73 ± 0.19	1.0
Trout Bog	5.229 ± 0.005	19.72 ± 0.11	5.67 ± 0.16	0.4
Wastewater Effluents				
WLSSD	3.758 ± 0.014	21.44 ± 0.42	8.51 ± 0.05	25.4
MMSD	1.321 ± 0.003	6.83 ± 0.17	8.27 ± 0.02	22.5

Table S7. R_{abs}, [DOC], pH, and ionic strength of sample waters, as irradiated under standardized conditions.

	R_{abs} (10^9 E cm^{-3} s^{-1})	[DOC] (mg-C L^{-1})	pH	Ionic Strength (mM)
Oligotrophic Lakes				
Big Muskellunge Lake	0.15 ± 0.007	3.93	7.99 ± 0.03	1.43
Sparkling Lake	0.182 ± 0.003	3.30	7.94 ± 0.01	2.11
Terrestrially Influenced Waters				
Allequash Lake	0.805 ± 0.005	4.00	7.97 ± 0.02	1.61
St. Louis River	1.474 ± 0.021	4.00	8.00 ± 0.03	0.94
Surface Wetlands				
Toivola Swamp	1.248 ± 0.002	4.00	8.01 ± 0.03	0.57
Trout Bog	1.309 ± 0.006	4.00	8.04 ± 0.02	0.56
Wastewater Effluents				
WLSSD	0.713 ± 0.007	4.00	7.97 ± 0.04	5.21
MMSD	0.759 ± 0.011	4.00	7.93 ± 0.02	13.67

Table S8. R_{abs}, [DOC], pH, and ionic strength of diluted SPE isolates.

	R_{abs} (10^9 E cm^{-3} s^{-1})	[DOC] (mg-C L^{-1})	pH	Ionic Strength (mM)
Oligotrophic Lakes				
Big Muskellunge Lake	0.208 ± 0.005	4.0	7.98 ± 0.07	0.48
Sparkling Lake	0.249 ± 0.006	4.0	7.98 ± 0.06	0.48
Terrestrially Influenced Waters				
Allequash Lake	0.939 ± 0.002	4.0	7.97 ± 0.08	0.48
St. Louis River	1.324 ± 0.003	4.0	7.96 ± 0.09	0.48
Surface Wetlands				
Toivola Swamp	1.114 ± 0.005	4.0	7.99 ± 0.08	0.48
Trout Bog	1.271 ± 0.007	4.0	7.96 ± 0.09	0.48
Wastewater Effluents				
WLSSD	0.742 ± 0.001	4.0	8.00 ± 0.04	0.48
MMSD	0.878 ± 0.005	4.0	8.01 ± 0.04	0.48

Table S9. R_{abs}, [DOC], pH, and ionic strength of sample waters for experiments with variable [DOC] and constant pH.

	R_{abs} (10^9 E cm^{-3} s^{-1})	[DOC] (mg-C L^{-1})	pH	Ionic Strength (mM)
WLSSD				
4 mg-C L^{-1}	0.71 ± 0.01	4.0	7.97 ± 0.04	5.2
8 mg-C L^{-1}	1.41 ± 0.01	8.0	7.98 ± 0.04	9.9
12 mg-C L^{-1}	2.08 ± 0.01	12.0	7.96 ± 0.01	14.7
16 mg-C L^{-1}	2.76 ± 0.02	16.0	7.95 ± 0.03	19.4
20 mg-C L^{-1}	3.42 ± 0.02	20.0	7.94 ± 0.03	24.1
St. Louis River				
4 mg-C L^{-1}	1.47 ± 0.02	4.0	8.00 ± 0.03	0.9
8 mg-C L^{-1}	2.83 ± 0.02	8.0	7.90 ± 0.09	1.4
12 mg-C L^{-1}	4.07 ± 0.02	12.0	7.91 ± 0.08	1.9
16 mg-C L^{-1}	5.27 ± 0.01	16.0	7.92 ± 0.06	2.3
20 mg-C L^{-1}	6.34 ± 0.02	20.0	7.94 ± 0.06	2.8

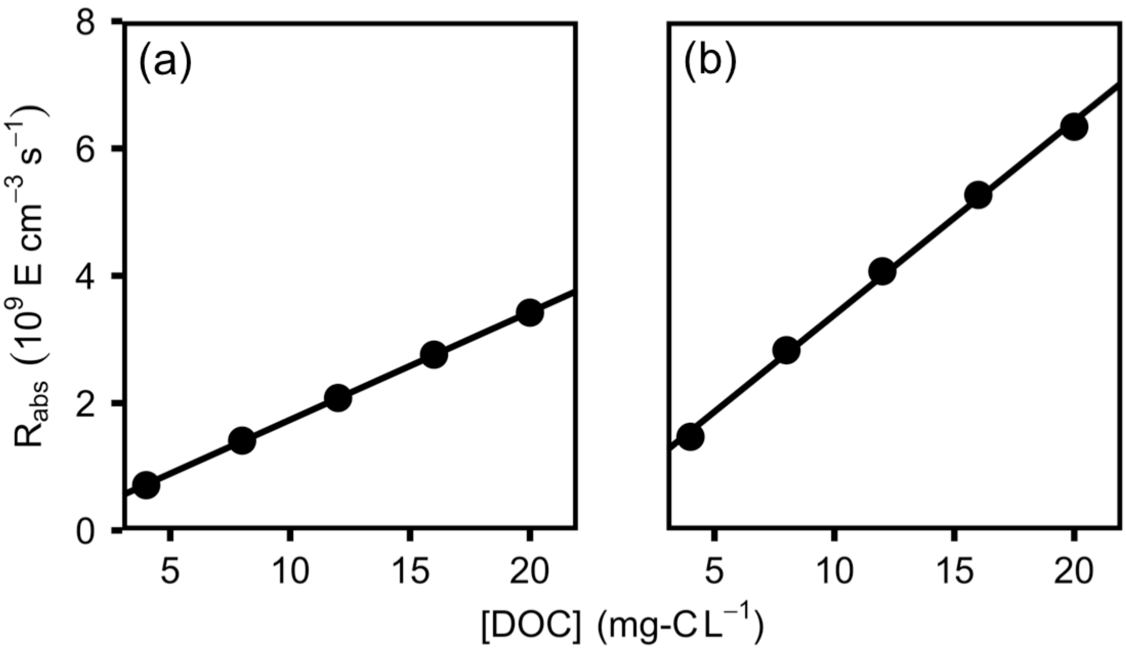

Figure S1. Solution rates of light absorption vs. [DOC] in (a) WLSSD ($r^2 > 0.99$, $p < 0.001$) and (b) St. Louis River water ($r^2 > 0.99$, $p < 0.001$) in experiments conducted with variable [DOC] and constant pH. Trend lines indicate least squares linear regressions.

Table S10. R_{abs}, [DOC], pH, and ionic strength of sample waters for experiments with variable pH and constant [DOC].

	R_{abs} (10^9 E cm^{-3} s^{-1})	[DOC] (mg-C L^{-1})	pH	Ionic Strength (mM)
MMSD				
pH 6	0.73 ± 0.01	4.0	6.06 ± 0.02	19.7
pH 7	0.78 ± 0.01	4.0	6.99 ± 0.04	27.9
pH 8	0.76 ± 0.004	4.0	7.98 ± 0.08	13.7
pH 9	0.78 ± 0.01	4.0	8.96 ± 0.06	16.5
Toivola Swamp				
pH 6	1.14 ± 0.01	4.0	5.96 ± 0.06	6.6
pH 7	1.15 ± 0.02	4.0	7.02 ± 0.05	14.8
pH 8	1.22 ± 0.02	4.0	7.97 ± 0.04	0.57
pH 9	1.29 ± 0.05	4.0	9.01 ± 0.07	3.4

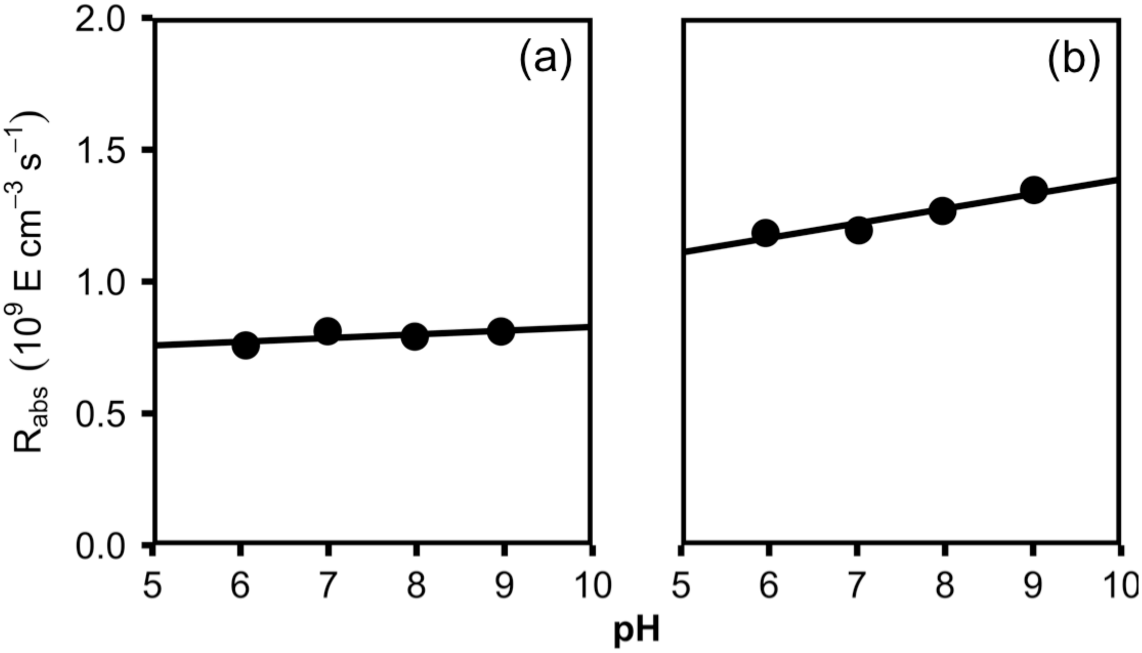

Figure S2. Solution rates of light absorption vs. pH in (a) MMSD (r^2 = 0.50, p = 0.29) and (b) Toivola Swamp (r^2 = 0.92, p = 0.04) in experiments conducted with variable pH and constant [DOC]. Trend lines indicate least squares linear regressions.

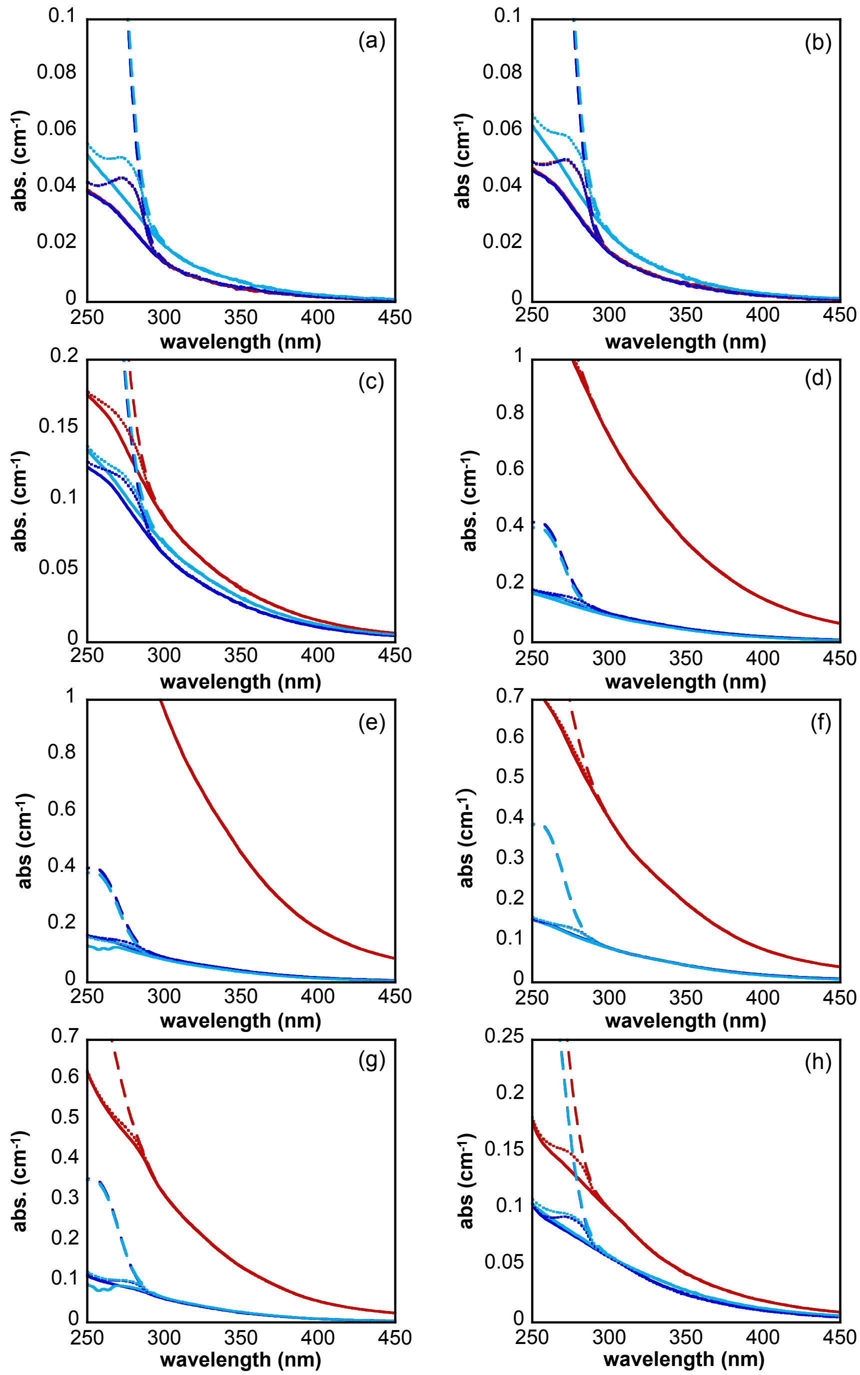

Figure S3. UV-vis spectra for (a) Big Muskellunge Lake, (b) Sparkling Lake, (c) Allequash Lake, (d) St. Louis River, (e) Toivola Swamp, (f) Trout Bog, (g) WLSSD, and (h) MMSD. Red lines indicate samples under ambient conditions, dark blue lines indicate samples under standardized conditions, and light blue lines indicate diluted SPE isolates. Solid lines indicate samples prepared with 10 µM FFA, long dashes indicate samples prepared with 10 µM HDA, and short dashes indicate samples prepared with TMP.

Table S11. Quantum yield coefficients and reactive intermediate pseudo-steady state concentrations under ambient conditions.

	f_{FFA} (M^{-1})	f_{HDA} (M^{-1})	f_{TMP} (M^{-1})	$[^1O_2]_{ss}$ (10^{-15} M)	$[^3DOM]_{ss,HDA}$ (10^{-15} M)	$[^3DOM]_{ss,TMP}$ (10^{-15} M)
Oligotrophic Lakes						
Big Muskellunge Lake	5.5 ± 0.3	19.1 ± 0.1	67.1 ± 2.0	74 ± 3	5.8 ± 0.1	35.7 ± 0.8
Sparkling Lake	5.3 ± 0.1	15.9 ± 0.1	61.3 ± 0.7	98 ± 1	6.0 ± 0.03	40.7 ± 0.7
Terrestrially Influenced Waters						
Allequash Lake	4.2 ± 0.2	6.4 ± 0.3	27.7 ± 1.5	450 ± 20	15.5 ± 0.7	110 ± 5
St. Louis River	5.1 ± 0.9	3.9 ± 0.2	9.3 ± 0.3	4027 ± 675	69.8 ± 2.8	276 ± 11
Surface Wetlands						
Toivola Swamp	5.7 ± 0.6	3.1 ± 0.2	5.2 ± 0.3	5574 ± 504	66.1 ± 3.8	187 ± 8
Trout Bog	3.1 ± 0.1	5.5 ± 0.1	6.7 ± 0.1	1604 ± 54	61.2 ± 1.9	126 ± 2
Wastewater Effluents						
WLSSD	6.0 ± 0.3	10.5 ± 0.4	16.2 ± 0.1	2108 ± 96	83.5 ± 2.5	212 ± 3
MMSD	5.9 ± 0.1	20.7 ± 0.5	34.7 ± 1.3	772 ± 20	58.1 ± 0.7	165 ± 5

Table S12. Quantum yield coefficients and reactive intermediate pseudo-steady state concentrations under standardized [DOC] and pH.

	f_{FFA} (M^{-1})	f_{HDA} (M^{-1})	f_{TMP} (M^{-1})	$[^1O_2]_{ss}$ (10^{-15} M)	$[^3DOM]_{ss,HDA}$ (10^{-15} M)	$[^3DOM]_{ss,TMP}$ (10^{-15} M)
Oligotrophic Lakes						
Big Muskellunge Lake	5.9 ± 0.6	17 ± 0.5	70.2 ± 0.8	81.3 ± 8.3	5.8 ± 0.2	39.9 ± 0.3
Sparkling Lake	5.4 ± 1.3	15.6 ± 0.2	68.9 ± 2.9	93.4 ± 21.4	6.3 ± 0.1	46.4 ± 1.7
Terrestrially Influenced Waters						
Allequash Lake	4.1 ± 0.1	7.4 ± 0.3	37.7 ± 0.8	319.9 ± 7	13.6 ± 0.5	110.1 ± 1.5
St. Louis River	3.61 ± 0.02	4.6 ± 0.2	36.3 ± 1.0	503.9 ± 3.9	15.7 ± 0.8	196.2 ± 5.1
Surface Wetlands						
Toivola Swamp	3.4 ± 0.1	5.4 ± 0.3	32.3 ± 1.4	393.6 ± 12.4	15.1 ± 0.2	158.8 ± 7.9
Trout Bog	2.61 ± 0.01	3.8 ± 0.1	24.6 ± 0.5	322.9 ± 0.4	11.2 ± 0.1	125.9 ± 2.6
Wastewater Effluents						
WLSSD	6.8 ± 0.2	13.8 ± 0.2	48.3 ± 0.9	466.4 ± 10.4	22.9 ± 0.3	123 ± 2.7
MMSD	6.6 ± 0.2	24.2 ± 1.1	55 ± 0.6	473.7 ± 14.2	42 ± 1.2	161.2 ± 1.6

Table S13. Quantum yield coefficients and reactive intermediate pseudo-steady state concentrations for experiments with SPE isolates.

	f_{FFA} (M^{-1})	f_{HDA} (M^{-1})	f_{TMP} (M^{-1})	$[^1O_2]_{ss}$ (10^{-15} M)	$[^3DOM]_{ss,HDA}$ (10^{-15} M)	$[^3DOM]_{ss,TMP}$ (10^{-15} M)
Oligotrophic Lakes						
Big Muskellunge Lake	5.9 ± 0.7	17.5 ± 1.2	97.7 ± 3.6	88 ± 9.9	7.8 ± 0.4	60.2 ± 2.3
Sparkling Lake	7.4 ± 0.7	18.3 ± 0.6	95.8 ± 1.9	130.6 ± 12.0	8.9 ± 0.4	73.8 ± 1.3
Terrestrially Influenced Waters						
Allequash Lake	4.7 ± 0.2	7.3 ± 0.4	48.1 ± 0.8	321.6 ± 9.2	14.3 ± 1.0	135.9 ± 1.8
St. Louis River	5.2 ± 0.3	6.4 ± 0.5	46.1 ± 0.7	462.5 ± 29.4	17.7 ± 1.0	183.9 ± 2.4
Surface Wetlands						
Toivola Swamp	4.2 ± 0.4	7.2 ± 0.1	47.1 ± 0.9	329.8 ± 23.6	16.8 ± 0.4	167.5 ± 4.0
Trout Bog	3.4 ± 0.2	4.0 ± 0.4	28.0 ± 1.2	277 ± 20.5	11.4 ± 1.1	107.6 ± 4.0
Wastewater Effluents						
WLSSD	7.8 ± 0.9	12.7 ± 0.8	48.8 ± 0.2	412 ± 40.8	21 ± 1.0	115.7 ± 0.1
MMSD	7.0 ± 0.2	17.4 ± 0.1	52.4 ± 2.1	389.5 ± 10.7	34.3 ± 0.8	146 ± 4.9

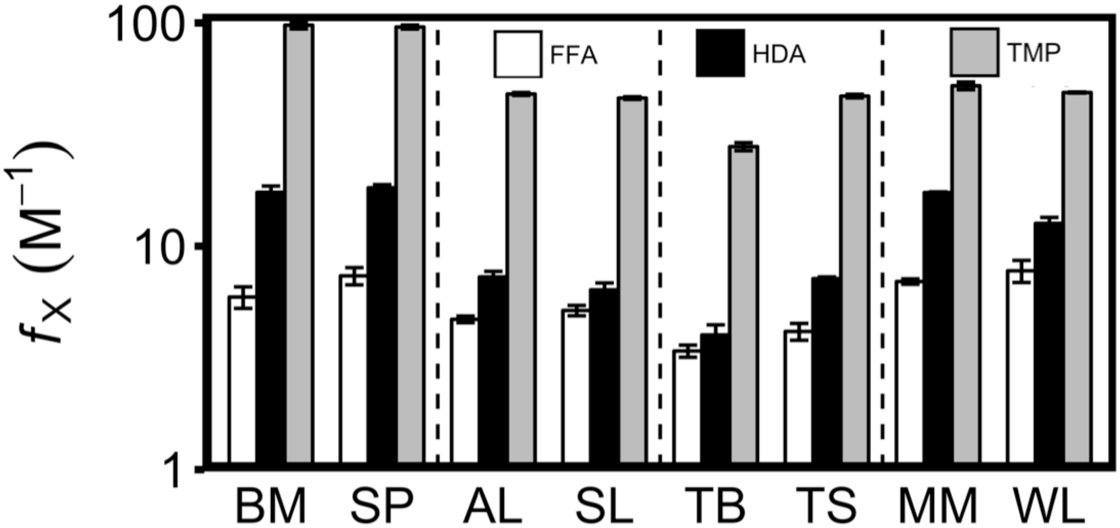

Figure S4. Quantum yield coefficients calculated with (white) FFA, (black) HDA, and (grey) TMP in SPE isolates of Big Muskellunge Lake (BM), Sparkling Lake (SP), Allequash Lake (AL), St. Louis River (SL), Trout Bog (TB), Toivola Swamp (TS), MMSD effluent (MM), and WLSSD effluent (WL). Error bars represent the standard deviation of triplicate experiments.

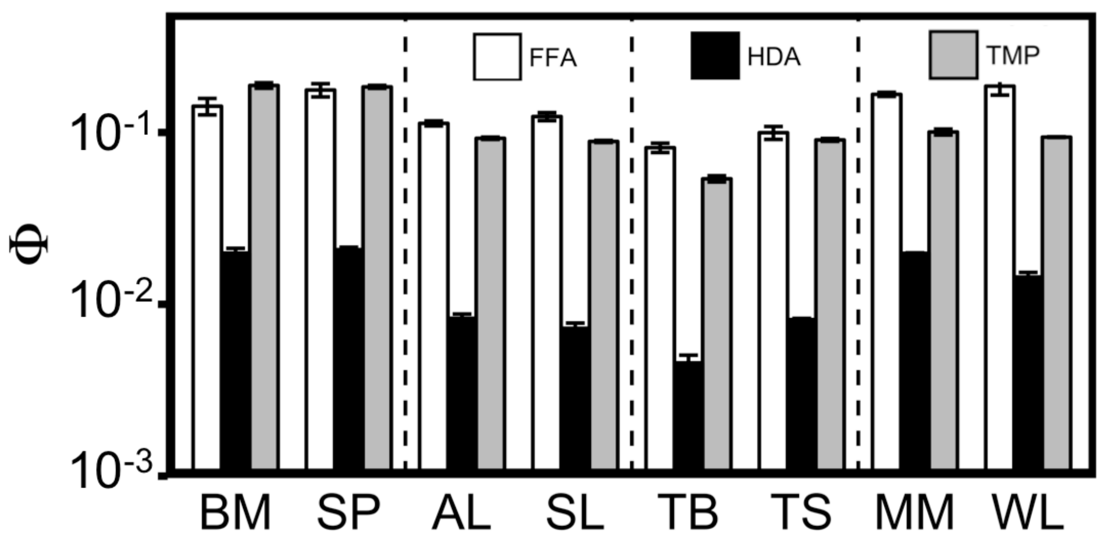

Figure S5. Apparent quantum yields calculated with (white) FFA, (black) HDA, and (grey) TMP in SPE isolates of Big Muskellunge Lake (BM), Sparkling Lake (SP), Allequash Lake (AL), St. Louis River (SL), Trout Bog (TB), Toivola Swamp (TS), MMSD effluent (MM), and WLSSD effluent (WL). Error bars represent the standard deviation of triplicate experiments.

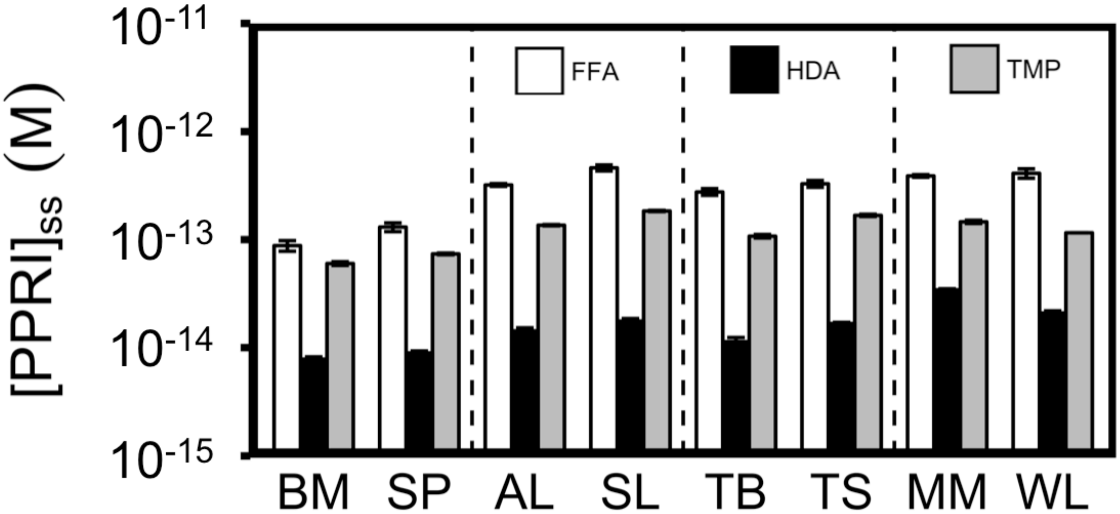

Figure S6. Pseudo-steady state concentrations calculated with (white) FFA, (black) HDA, and (grey) TMP in SPE isolates of Big Muskellunge Lake (BM), Sparkling Lake (SP), Allequash Lake (AL), St. Louis River (SL), Trout Bog (TB), Toivola Swamp (TS), MMSD effluent (MM), and WLSSD effluent (WL). Error bars represent the standard deviation of triplicate experiments.

Table S14. Quantum yield coefficients and reactive intermediate pseudo-steady state concentrations for experiments with variable [DOC] and constant pH.

	f_{FFA} (M^{-1})	f_{HDA} (M^{-1})	f_{TMP} (M^{-1})	$[^1O_2]_{ss}$ (10^{-15} M)	$[^3DOM]_{ss,HDA}$ (10^{-15} M)	$[^3DOM]_{ss,TMP}$ (10^{-15} M)
WLSSD						
4 mg-C L^{-1}	6.8 ± 0.2	13.8 ± 0.2	48.3 ± 0.9	466.4 ± 10.4	22.9 ± 0.3	123 ± 2.7
8 mg-C L^{-1}	5.68 ± 0.02	15.1 ± 1.4	26.3 ± 0.3	607 ± 12.2	44.2 ± 3.7	130.6 ± 1
12 mg-C L^{-1}	5.27 ± 0.2	13.11 ± 0.1	20.6 ± 0.7	830 ± 15.3	56.5 ± 0.3	151.5 ± 4.4
16 mg-C L^{-1}	5.10 ± 0.1	14 ± 1.5	17.98 ± 0.6	1070.1 ± 10.8	79.8 ± 8.3	175.5 ± 3.7
20 mg-C L^{-1}	4.89 ± 0.1	11.58 ± 0.8	16.1 ± 0.3	1271.2 ± 25.2	82.1 ± 5.3	194.8 ± 1.7
St. Louis River						
4 mg-C L^{-1}	3.61 ± 0.02	4.6 ± 0.2	36.3 ± 1	503.9 ± 3.9	15.7 ± 0.8	196.2 ± 5.1
8 mg-C L^{-1}	3.85 ± 0.04	4.6 ± 0.3	29.0 ± 0.3	727.3 ± 9.2	26 ± 1.2	238.4 ± 3.2
12 mg-C L^{-1}	3.53 ± 0.06	4.3 ± 0.1	21.6 ± 0.3	966.7 ± 21.4	36.3 ± 1.1	264.3 ± 6.5
16 mg-C L^{-1}	3.29 ± 0.04	4.46 ± 0.3	17.1 ± 0.3	1169.4 ± 13.1	48.7 ± 3.3	271.8 ± 5.1
20 mg-C L^{-1}	3.28 ± 0.09	4.58 ± 06	14.7 ± 0.1	1415.1 ± 38.3	60 ± 6.4	281.8 ± 2.5

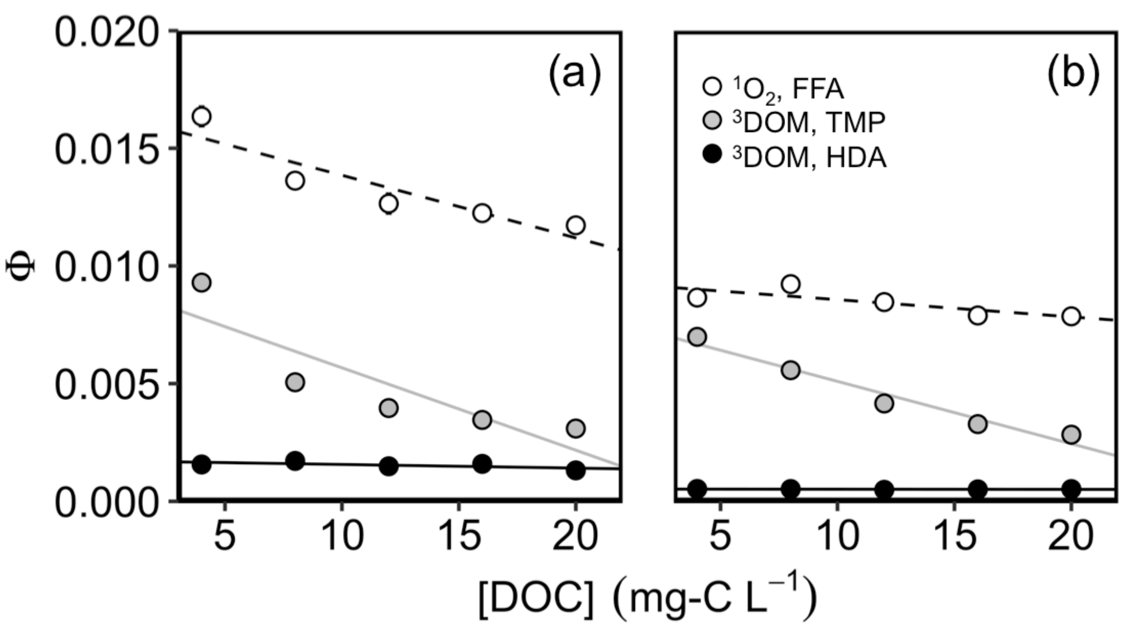

Figure S7. Apparent quantum yields as a function of [DOC] in (a) WLSSD and (b) St. Louis River, pH 8.1 ± 0.1. Error bars represent the standard deviation of triplicate experiments. Trend lines represent least squares linear regressions. Descriptions of linear regressions are presented in Table S17.

Table S15. Linear regression of quantum yield coefficients vs. [DOC] in experiments with variable [DOC] but constant pH.

	Slope **(M^{-1} * L mg-C^{-1})**	***y-Intercept*** **(M^{-1})**	***r^2*** **(-)**	***p*** **(-)**
St. Louis River				
f_{FFA}	-0.031	3.877	0.660	0.095
f_{HDA}	-0.006	4.578	0.068	0.673
f_{TMP}	-1.378	40.269	0.961	0.003
WLSSD				
f_{FFA}	-0.111	6.884	0.841	0.028
f_{HDA}	-0.138	15.168	0.450	0.215
f_{TMP}	-1.819	47.683	0.768	0.051

Table S16. Linear regression of apparent quantum yields vs. [DOC] in experiments with variable [DOC] but constant pH.

	Slope **(L mg-C^{-1})**	***y-Intercept*** **(-)**	***r^2*** **(-)**	***p*** **(-)**
St. Louis River				
Φ_{1O2}	-0.73×10^{-4}	92.96×10^{-4}	0.660	0.095
$\Phi_{3DOM, HDA}$	-0.006×10^{-7}	5.20×10^{-4}	0.068	0.673
$\Phi_{3DOM, TMP}$	-2.65×10^{-4}	77.44×10^{-4}	0.961	0.003
WLSSD				
Φ_{1O2}	-2.66×10^{-4}	165.07×10^{-4}	0.841	0.028
$\Phi_{3DOM, HDA}$	-0.16×10^{-4}	17.24×10^{-4}	0.450	0.215
$\Phi_{3DOM, TMP}$	-3.50×10^{-4}	91.70×10^{-4}	0.768	0.051

Table S17. Linear regression of pseudo-steady state concentrations vs. [DOC] in experiments with variable [DOC] and constant pH.

	Slope **($M \times L$ mg-C^{-1})**	***y-Intercept*** **(-)**	***r^2*** **(-)**	***p*** **(-)**
St. Louis River				
$[^1O_2]_{ss}$	5.67×10^{-14}	2.77×10^{-13}	0.999	< 0.001
$[^3DOM]_{ss,HDA}$	2.78×10^{-15}	3.96×10^{-15}	0.999	< 0.001
$[^3DOM]_{ss,TMP}$	5.11×10^{-15}	1.89×10^{-13}	0.887	0.0167
WLSSD				
$[^1O_2]_{ss}$	5.18×10^{-14}	2.27×10^{-13}	0.993	< 0.001
$[^3DOM]_{ss,HDA}$	3.66×10^{-16}	1.09×10^{-14}	0.957	0.004
$[^3DOM]_{ss,TMP}$	4.71×10^{-15}	9.86×10^{-14}	0.977	0.001

Table S18. Quantum yield coefficients and reactive intermediate pseudo-steady state concentrations for experiments with variable pH and constant [DOC].

	f_{FFA} (M^{-1})	**f_{HDA} (M^{-1})**	**f_{TMP} (M^{-1})**	**$[^1O_2]_{ss}$ (10^{-15} M)**	**$[^3DOM]_{ss,HDA}$ (10^{-15} M)**	**$[^3DOM]_{ss,TMP}$ (10^{-15} M)**
MMSD						
pH 6	7.5 ± 0.26	22.42 ± 0.86	48.0 ± 1.2	408.8 ± 13.8	34.6 ± 1.1	101.4 ± 1.9
pH 7	6.49 ± 0.13	20.64 ± 1.67	41.0 ± 0.5	387.7 ± 9.7	33.8 ± 2.8	93.7 ± 2.4
pH 8	6.83 ± 0.1	22.61 ± 0.73	47.3 ± 0.6	391.5 ± 4.5	36.7 ± 1.1	105.3 ± 1.1
pH 9	5.25 ± 0.04	20.53 ± 0.94	48.9 ± 2.3	310.5 ± 3.6	33.9 ± 1.9	111.5 ± 5.3
Toivola Swamp						
pH 6	3.85 ± 0.04	4.36 ± 0.44	9.8 ± 0.4	356.1 ± 35	25.1 ± 1.1	113.7 ± 2
pH 7	3.53 ± 0.06	3.57 ± 0.13	7.1 ± 0.5	294.1 ± 14.7	19.4 ± 1.4	109.6 ± 8.1
pH 8	3.29 ± 0.04	3.35 ± 0.05	4.5 ± 0.2	290.9 ± 9.2	12.8 ± 0.4	114.1 ± 1
pH 9	3.28 ± 0.09	2.98 ± 0.01	4.3 ± 0.3	298.6 ± 3.4	13.1 ± 0.9	108.4 ± 3

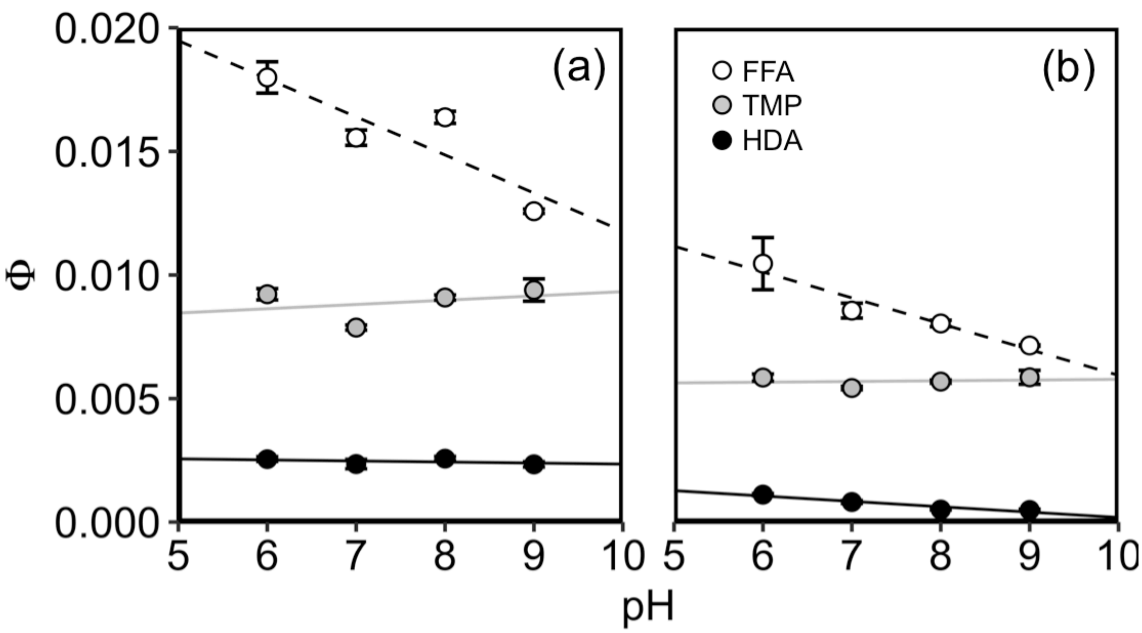

Figure S8. Apparent quantum yields as a function of pH in (a) MMSD and (b) Toivola Swamp, [DOC] = 4 mg-C L^{-1}. Error bars represent the standard deviation of triplicate experiments. Trend lines represent least squares linear regressions.

Table S19. Linear regression of quantum yield coefficients vs. pH in experiments with variable pH and constant [DOC].

	Slope **(M^{-1})**	***y-Intercept*** **(M^{-1})**	***r^2*** **(-)**	***p*** **(-)**
MMSD				
f_{FFA}	-0.64	11.33	0.769	0.123
f_{HDA}	-0.37	24.32	0.181	0.575
f_{TMP}	0.90	39.53	0.104	0.678
Toivola Swamp				
f_{FFA}	-0.44	6.84	0.930	0.035
f_{HDA}	-1.91	20.72	0.907	0.048
f_{TMP}	0.15	28.55	0.034	0.815

Table S20. Linear regression of apparent quantum yields vs. pH in experiments with variable pH and constant [DOC].

	Slope (-)	*y-Intercept* (-)	r^2 (-)	*p* (-)
MMSD				
Φ_{1O2}	-1.54×10^{-3}	2.72×10^{-2}	0.769	0.123
$\Phi_{3DOM,\ HDA}$	-4.19×10^{-5}	2.76×10^{-3}	0.181	0.575
$\Phi_{3DOM,\ TMP}$	1.73×10^{-4}	7.60×10^{-3}	0.104	0.678
Toivola Swamp				
Φ_{1O2}	-1.05 × -03	1.64×10^{-2}	0.930	0.035
$\Phi_{3DOM,\ HDA}$	-2.17 × -04	2.35×10^{-3}	0.907	0.048
$\Phi_{3DOM,\ TMP}$	2.89 × -05	5.49×10^{-3}	0.034	0.815

Table S21. Linear regression of pseudo-steady state concentrations vs. pH in experiments with variable pH and constant [DOC].

	Slope (M)	*y-Intercept* (M)	r^2 (-)	*p* (-)
MMSD				
$[^1O_2]_{ss}$	$-2.91\ 10^{-14}$	5.93×10^{-13}	0.738	0.141
$[^3DOM]_{ss,HDA}$	7.31×10^{-17}	3.42×10^{-14}	0.005	0.931
$[^3DOM]_{ss,TMP}$	4.19×10^{-15}	7.15×10^{-14}	0.528	0.273
Toivola Swamp				
$[^1O_2]_{ss}$	-1.76×10^{-14}	4.42×10^{-13}	0.536	0.268
$[^3DOM]_{ss,HDA}$	-4.26×10^{-15}	4.96×10^{-14}	0.882	0.061
$[^3DOM]_{ss,TMP}$	-1.16×10^{-15}	1.20×10^{-13}	0.268	0.483

Table S22. Linear regression of quantum yield coefficients vs. E_2:E_3 under standardized and ambient conditions. Regressions were calculated with and without the wastewater effluents.

	Slope **(M^{-1})**	***y-Intercept*** **(M^{-1})**	**r^2 (-)**	***p*** **(-)**
Ambient Conditions				
f_{FFA}	0.107	4.393	0.06	0.553
f_{FFA} (w/o WW effluents)	0.171	3.646	0.20	0.365
f_{HDA}	2.033	-2.586	0.43	0.079
f_{HDA} (w/o WW effluents)	2.582	-8.536	0.98	<0.001
f_{TMP}	10.084	-37.101	0.88	<0.001
f_{TMP} (w/o WW effluents)	10.673	-42.908	0.97	<0.001
Standardized [DOC], pH				
f_{FFA}	0.309	2.785	0.20	0.271
f_{FFA} (w/o WW effluents)	0.453	1.085	0.90	0.003
f_{HDA}	1.544	1.427	0.23	0.233
f_{HDA} (w/o WW effluents)	2.237	-6.223	0.99	<0.001
f_{TMP}	6.536	4.134	0.76	0.005
f_{TMP} (w/o WW effluents)	7.330	-4.742	0.95	0.001

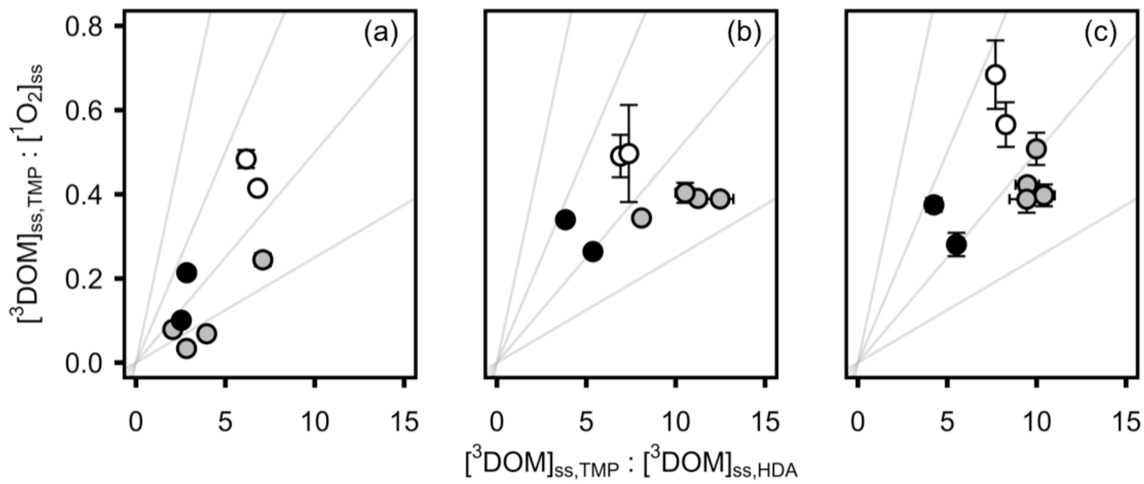

Figure S9. Ratios of $[^3DOM]_{ss,TMP}$: $[^1O_2]_{ss}$ versus ratios of $[^3DOM]_{ss,TMP}$: $[^3DOM]_{ss,HDA}$ under (a) ambient conditions, (b) standardized ([DOC] = 4 mg-C L^{-1}, pH = 8) conditions, and (c) using SPE isolates. Ratios of $[^3DOM]_{ss,HDA}$: $[^1O_2]_{ss}$ are visualized with grey lines that correspond to 5, 10, 20, and 40. Error bars represent the standard deviation of triplicate experiments.

S4. References

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