Electronic Supplementary Information

Photochemical Fate of Quaternary Ammonium Compounds in River Water

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S1 Experimental Section

Materials and Methods

Absorption spectra

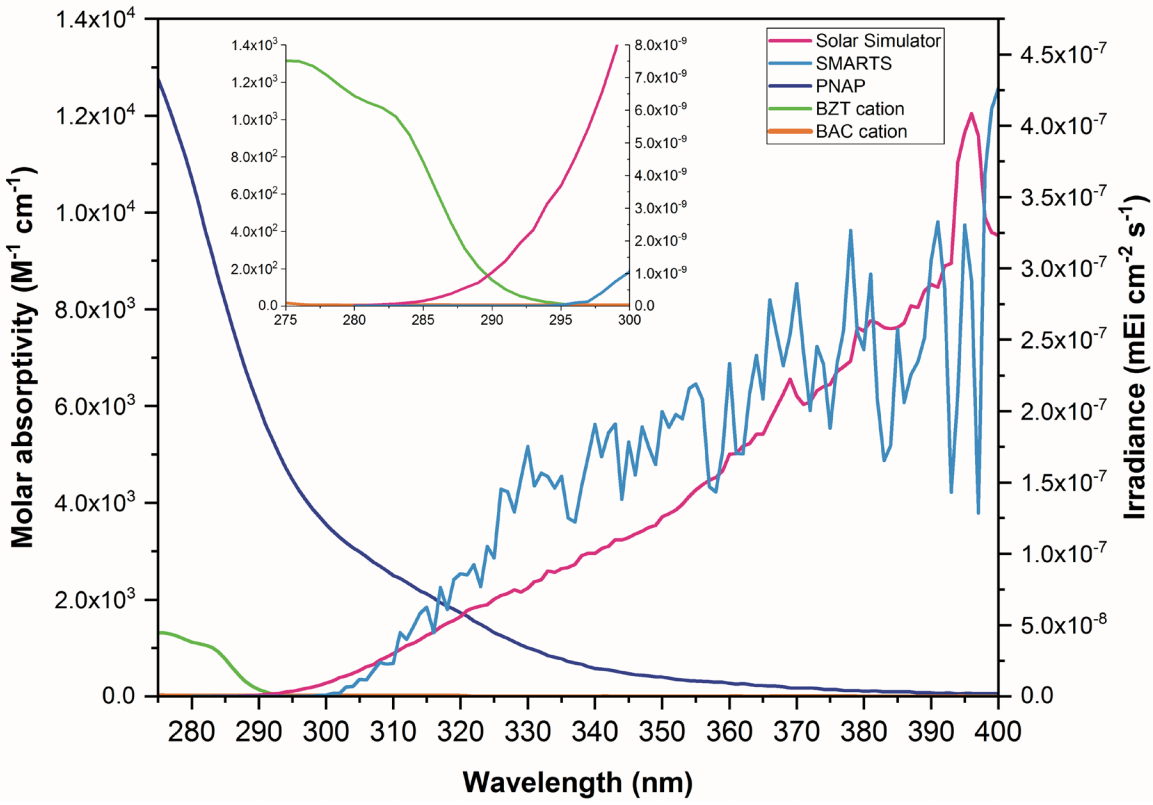
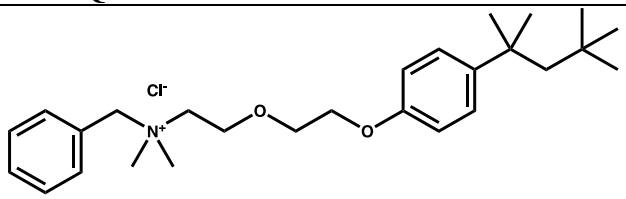
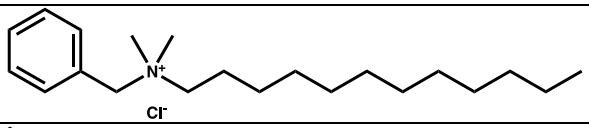
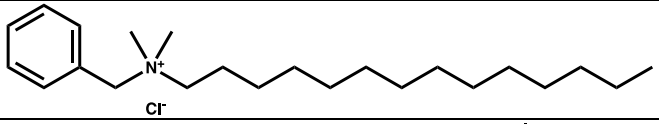
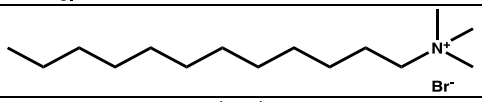
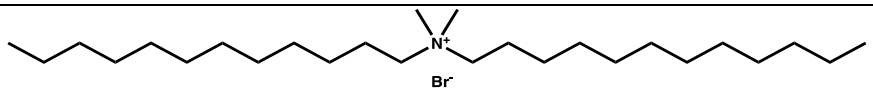


Figure S1: Solar simulator and sunlight spectral irradiances and molar absorption coefficients.

Chemicals and reagents.

Table S1: QAC Structures	
Benzethonium Chloride (BZT)	
C_{12}-Benzalkonium Chloride (BAC)	
C_{14}-BAC	
C_{12}-Alkyltrimethylammonium (ATMA) Bromide	
C_{12}-Dialkyldimethylammonium (DADMA) Bromide	

River water sample collection and analysis

Table S2: Water quality parameters of the Mississippi river water used in photochemical study			
Water Quality Parameter	**Method**	**6/5/18**	**2/27/19**
Nitrite (NO_2^- mg of N/L)	Metrohm ion chromatograph	<0.1	<0.1
Nitrate (NO_3^- mg of N/L)	Metrohm ion chromatograph	0.7	0.8 ± 0.1
Dissolved organic carbon (NPOC mg-C/L)	Shimadzu TOC-L analyzer	9.8	9.2
Dissolved inorganic carbon (DIC mg-C/L)	Shimadzu TOC-L analyzer	32	39
pH	Thermo Orion pH meter	8.5 ± 0.1	8.2

Analytical methods

Concentrations of BACs and BZT were measured by high-pressure liquid chromatography (HPLC) on an Agilent 1100 LC with a variable wavelength detector set at 210 nm with 50 µL injection volume. An Eclipse XDB column (4.6 × 150 mm, 3.5 or 5 µm, Agilent) was used with isocratic mixtures of methanol and 10 mM ammonium acetate with 0.1% glacial acetic acid or formic acid and 10% methanol at a flow rate of 1 mL min^{-1}.

Table S3: RP-HPLC Methods

Compound	Column[a]	Mobile Phase (v:v)[b]	Injection V (µL)	Flow Rate ($mLmin^{-1}$)	Detector λ (nm)
C_{12}-BAC	Eclipse XDB-C18 (4.6×150 mm, 3.5 µm)	90% 9:1 methanol:10mM ammonium acetate with 0.1% acid 10% 9:1 10mM ammonium acetate with 0.1% acid:methanol	50	1.0	210
C_{14}-BAC	Eclipse XDB-C18 (4.6×150 mm, 3.5 µm)	95% 9:1 methanol:10mM ammonium acetate with 0.1% acid 5% 9:1 10mM ammonium acetate with 0.1% acid:methanol	50	1.0	210
BZT	Eclipse XDB-C18 (4.6×150 mm, 3.5 µm)	90% 9:1 methanol:10mM ammonium acetate with 0.1% acid 10% 9:1 10mM ammonium acetate with 0.1% acid:methanol	50	1.0	210
pCBA	Eclipse XDB-C18 (4.6×150 mm, 3.5 µm)	45% acetonitrile 55% 10mM pH3 phosphate buffer with 10% acetonitrile	40	1.0	238
PNAP	Eclipse XDB-C18 (4.6×150 mm, 3.5 µm)	65% acetonitrile 35% 10 mM pH 3 phosphate buffer with 10% acetonitrile	35	1.0	220
FFA	Eclipse XDB-C18 (4.6×150 mm, 3.5 µm)	10% acetonitrile 90% 10mM pH3 phosphate buffer with 10% acetonitrile	35	1.0	219
[a]Columns were at room temperature (~20 °C)					
[b]All mobile phases were isocratic					

Photochemical experiments: simulated and outdoor photolysis in river water

Table S4: Rooftop experiment dates and times

Date	Time out	Time in	Cumulative Hours
6/28/18	12:04 PM	5:00 PM	4.9
6/29/18	10:09 AM	3:40 PM	10.5
7/2/18	10:00 AM	3:50 PM	16.3
7/5/18	12:00 PM	5:00 PM	21.3
7/6/18	11:30 AM	5:00 PM	26.8

Table S5: SMARTS inputs

Parameter	Value	Units
Site pressure	Calculated from latitude and altitude	
Latitude	44.975	decimal degrees (DD)
Altitude	0.262128	km
Height	0	
Default atmosphere	Mid-latitude summer	
Water vapor	Calculated from reference atmosphere and altitude	
Ozone abundance[a]	0.3125	atm-cm
Ozone column altitude correction	Vertical profile correction	

Gaseous absorption	Light pollution	
Carbon dioxide[b]	Mauna Loa daily or weekly averages	ppm
Extraterrestrial spectrum	1366.1	Wm^{-2}
Aerosol model	Shettle and Fenn rural	
Aerosol optical depth at 500 nm	0.1	
Albedo	Light soil	
Tilt	30	degrees
Surface azimuth	218	degrees SW
Solar constant	1361	Wm^{-2}
Longitude	-93.233611	DD
[a]Average value from Apell and McNeill (2019)[1] for June and September at 40° N and 50° N (converted from Dobson units)		
[b]https://www.esrl.noaa.gov/gmd/ccgg/trends/graph.html		

S2 Results and Discussion

Reactivity of QACs with hydroxyl radical from hydrogen peroxide sensitizer experiments

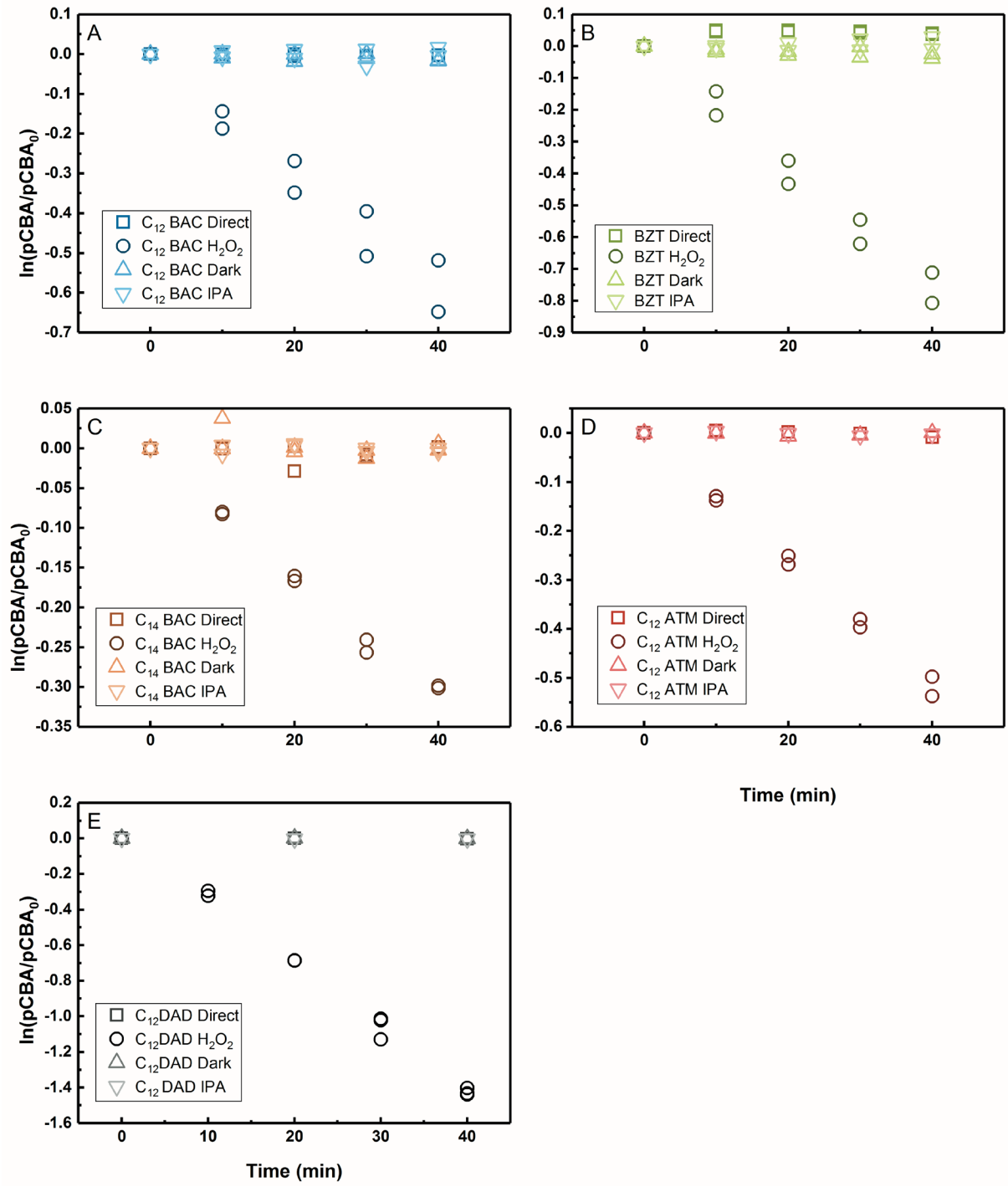


Figure S2: Log plot of pCBA concentration over time in H_2O_2 sensitizer experiments for: A) C_{12}-BAC, B) BZT, C) C_{14}-BAC, D) C_{12}-ATMA, E) C_{12}-DADMA. Squares are direct photolysis controls, circles are hydrogen peroxide, triangles are dark controls, and upside down triangles are IPA quenched controls.

Table S6: Steady-state hydroxyl radical concentrations in experiments with hydrogen peroxide.[a]

QAC	$[^{\bullet}OH]_{ss}$ (M)
C_{12}-DADMA	$(1.17 \pm 0.03) \times 10^{-13}$
C_{12}-BAC	$(5.0 \pm 0.5) \times 10^{-14}$
C_{14}-BAC	$(2.6 \pm 0.2) \times 10^{-14}$
BZT	$(6.4 \pm 0.2) \times 10^{-14}$
C_{12}-ATMA	$(4.3 \pm 0.1) \times 10^{-14}$
[a]Errors represent 95% confidence intervals	

Assessing reactivity with other PPRIs

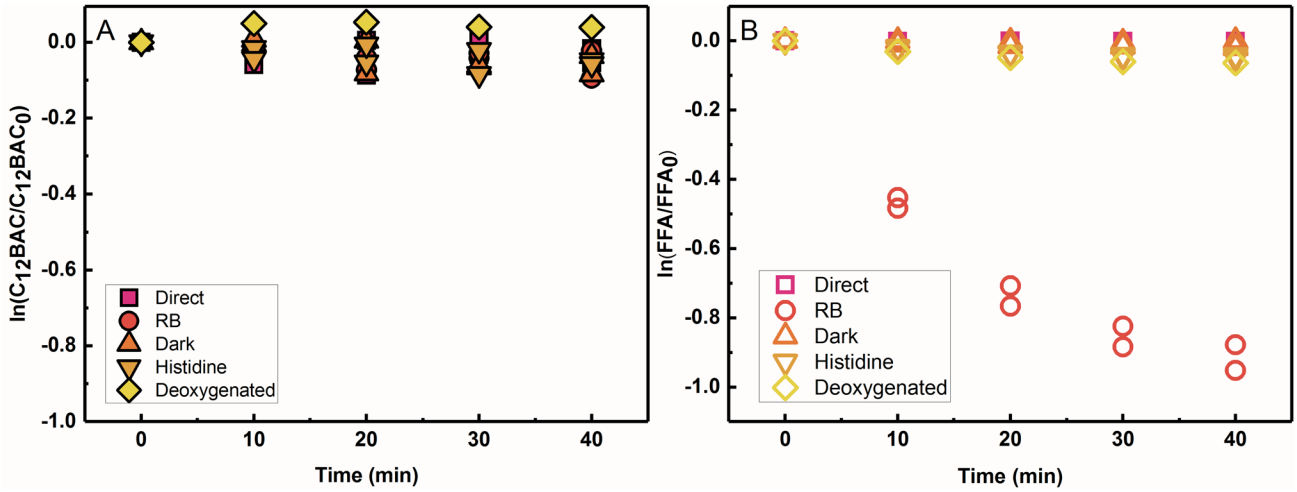


Figure S3: Log-concentration over time of: C_{12}-BAC (A) and FFA (B) under simulated sunlight in phosphate buffer (Direct, pink squares), with rose bengal (RB, red circles), dark control (orange triangle), histidine quenched control (light orange upside down triangle), deoxygenated control (yellow diamond).

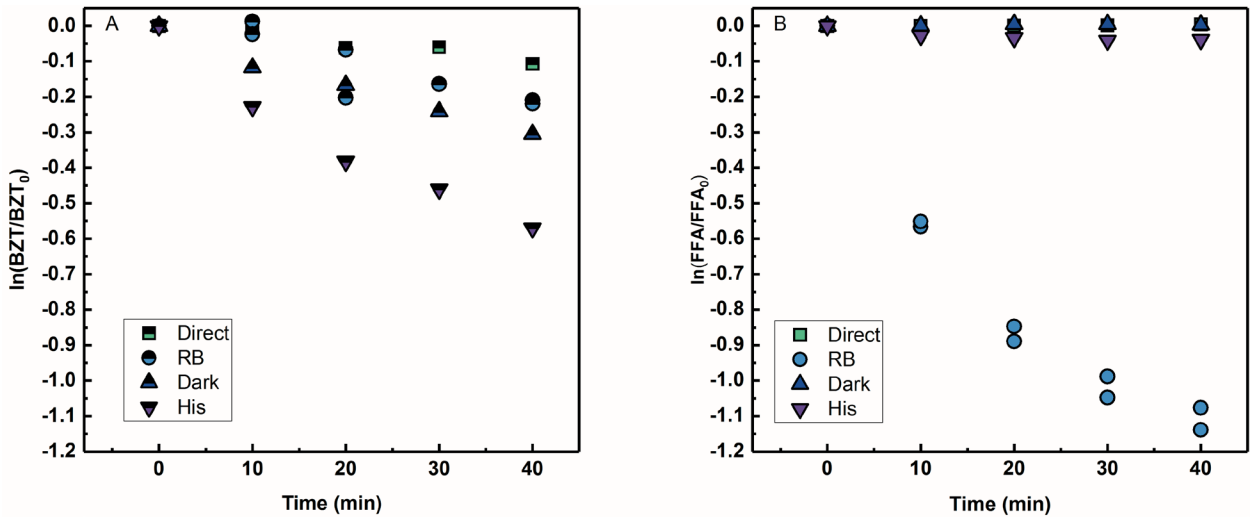


Figure S4: Log-concentrations over time of: BZT (A) and furfuryl alcohol (B) under simulated sunlight in phosphate buffer (Direct, green squares), with rose bengal (RB, light blue circles),

dark control (Dark, dark blue triangle), histidine quenched control (His, purple upside down triangle).

Additional experiments in which 10 μM BZT was spiked into 6 mL buffer and then BZT and 2 μM of RB were spiked into 6 mL buffer and 6 mL river water and wrapped in foil and kept on the bench top under ambient conditions. These tests showed 2% decrease in BZT concentration over 5 days alone in buffer, 20% decrease in buffer with rose bengal, and 18% decrease in river water with rose bengal.

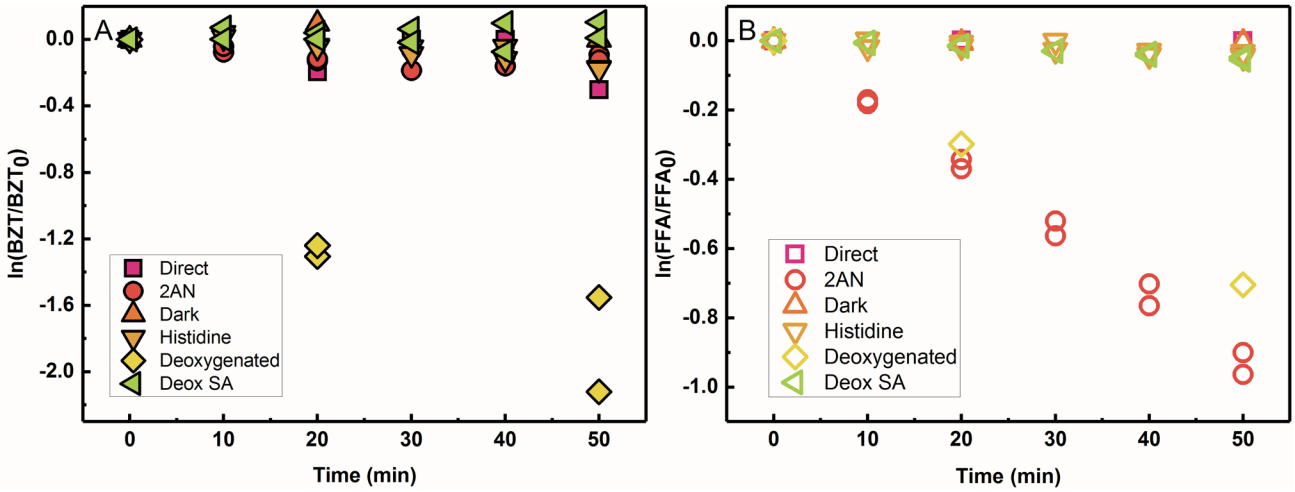


Figure S5: Log-concentration over time of: BZT (A) and FFA (B) under simulated sunlight in phosphate buffer (Direct, pink squares), with 2-acetylnaphthalene (2AN, red circles), dark control (orange triangle), histidine quenched control (light orange upside down triangle), deoxygenated control (yellow diamond), and sorbic acid quenched deoxygenated control (green left triangle).

Table S7: Pseudo-first-order rate constants, k_{obs} (s^{-1}), for FFA irradiated under simulated sunlight in singlet oxygen sensitizer experiments and singlet oxygen steady-state concentrations, $[^1O_2]_{ss}$ (M)[a]

	FFA with BZT		FFA with C_{12}-BAC	
Sample	**k_{obs}**	**$[^1O_2]_{ss}$**	**k_{obs}**	**$[^1O_2]_{ss}$**
Direct	N/A	N/A	$(1.2 \pm 0.5) \times 10^{-6}$	$(10 \pm 4) \times 10^{-15}$
2-acetylnaphthalene	$(3.06 \pm 0.08) \times 10^{-4}$	$(2.62 \pm 0.05) \times 10^{-12}$	N/A	N/A
Rose Bengal	N/A	N/A	$(4.5 \pm 0.8) \times 10^{-4}$	$(3.9 \pm 1.2) \times 10^{-12}$
Dark	$(0.2 \pm 0.3) \times 10^{-6}$	$(2 \pm 2) \times 10^{-14}$	$(5 \pm 3) \times 10^{-6}$	$(4 \pm 3) \times 10^{-14}$
Histidine	$(1.2 \pm 0.3) \times 10^{-5}$	$(1.1 \pm 0.3) \times 10^{-13}$	$(2.3 \pm 0.3) \times 10^{-5}$	$(2.0 \pm 0.3) \times 10^{-13}$
Deoxygenated	$(2.4 \pm 0.1) \times 10^{-4}$	$(2.03 \pm 0.05) \times 10^{-12}$	$(3.1 \pm 0.8) \times 10^{-5}$	$(2.7 \pm 0.7) \times 10^{-13}$
Deoxygenated with sorbic acid	$(1.6 \pm 0.1) \times 10^{-5}$	$(1.4 \pm 0.1) \times 10^{-13}$	N/A	N/A

[a]Error bars represent 95% confidence intervals

Photochemical transformation of BACs & BZT in river water under simulated and natural sunlight

Table S8: Pseudo-first-order rate constants, k_{obs} (h^{-1}) [a], for QACs irradiated under simulated sunlight

	BZT	C_{12}-BAC	C_{14}-BAC
MRW	$(9.7 \pm 0.3) \times 10^{-2}$	$(2.9 \pm 0.4) \times 10^{-2}$	$(2.8 \pm 0.6) \times 10^{-2}$
MRW_{corr}	$(2.0 \pm 0.3) \times 10^{-2}$	-	-
Direct	$(7.2 \pm 0.7) \times 10^{-2}$	$(2 \pm 1) \times 10^{-3}$	$(-6 \pm 3) \times 10^{-3}$
IPA	$(7.7 \pm 0.4) \times 10^{-2}$	$(1.7 \pm 0.3) \times 10^{-3}$	$(5 \pm 3) \times 10^{-3}$
Dark	$(6 \pm 2) \times 10^{-2}$	$(-2 \pm 3) \times 10^{-3}$	$(3 \pm 3) \times 10^{-3}$

[a]Error bars represent 95% confidence intervals

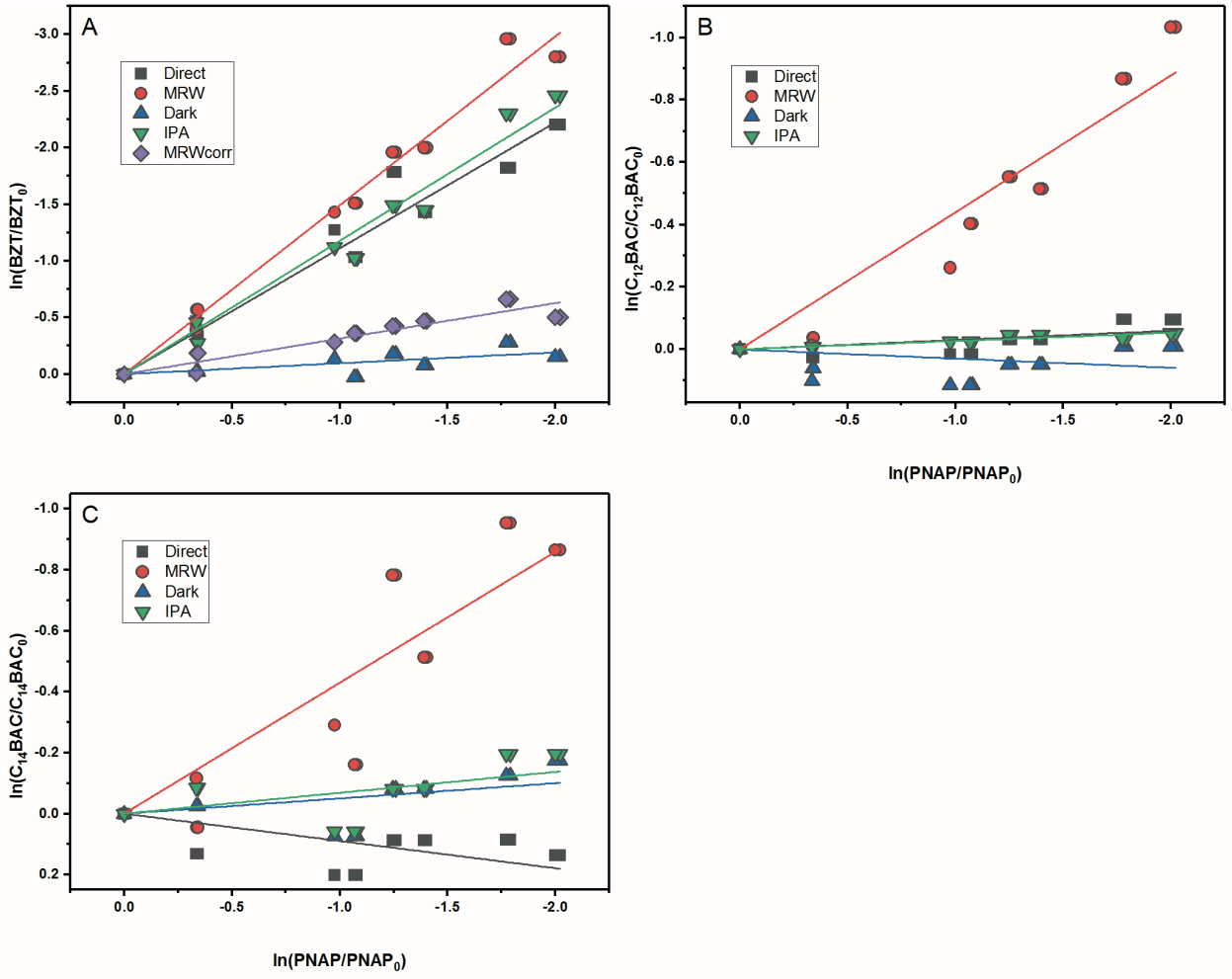


Figure S6: Logarithmic plots of BZT (A), C_{12}-BAC (B), and C_{14}-BAC (C) solar simulator photolysis versus actinometer loss in phosphate buffer (Direct, black squares), Mississippi River water (MRW, red circles), MRW dark controls (Dark, blue diamonds), and MRW with 1% isopropanol (IPA, green upside down triangles). Purple diamonds are MRW time points corrected for direct photolysis to show BZT indirect photochemical loss in MRW (MRW_{corr}). Solid lines represent linear regressions.

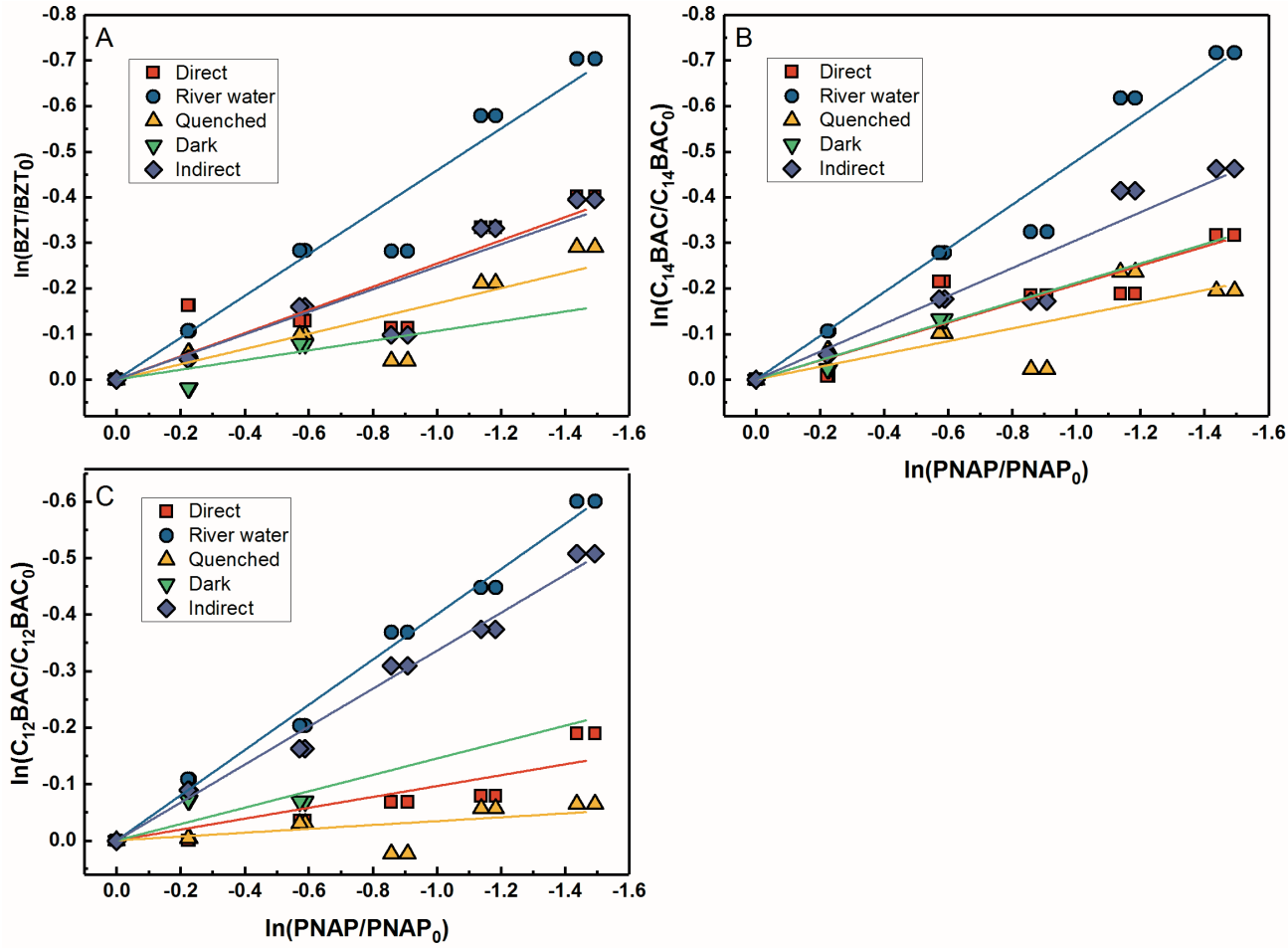


Figure S7: Logarithmic plots of BZT (A), C_{14}-BAC (B), and C_{12}-BAC (C) natural sunlight photodegradation versus actinometer loss in phosphate buffer (Direct, red squares), Mississippi River water (River water, blue circles), river water with 1% isopropanol (Quenched, yellow triangles), river water dark controls (Dark, green upside down triangles), total photochemical loss in river water minus other abiotic losses (Indirect, purple diamonds). Solid lines represent linear regressions.

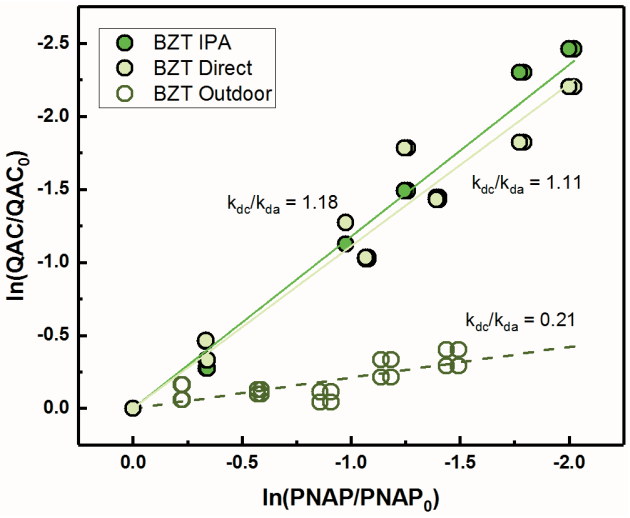


Figure S8: Log-log plot of BZT versus PNAP for solar simulator (solid symbols) and natural sunlight (open symbols) quantum yield determinations in river water. Solid and dashed lines represent linear regressions for solar simulator and natural sunlight experiments, respectively.

S3 Additional tables and figures

Photochemical transformation of BACs & BZT in river water under simulated and natural sunlight

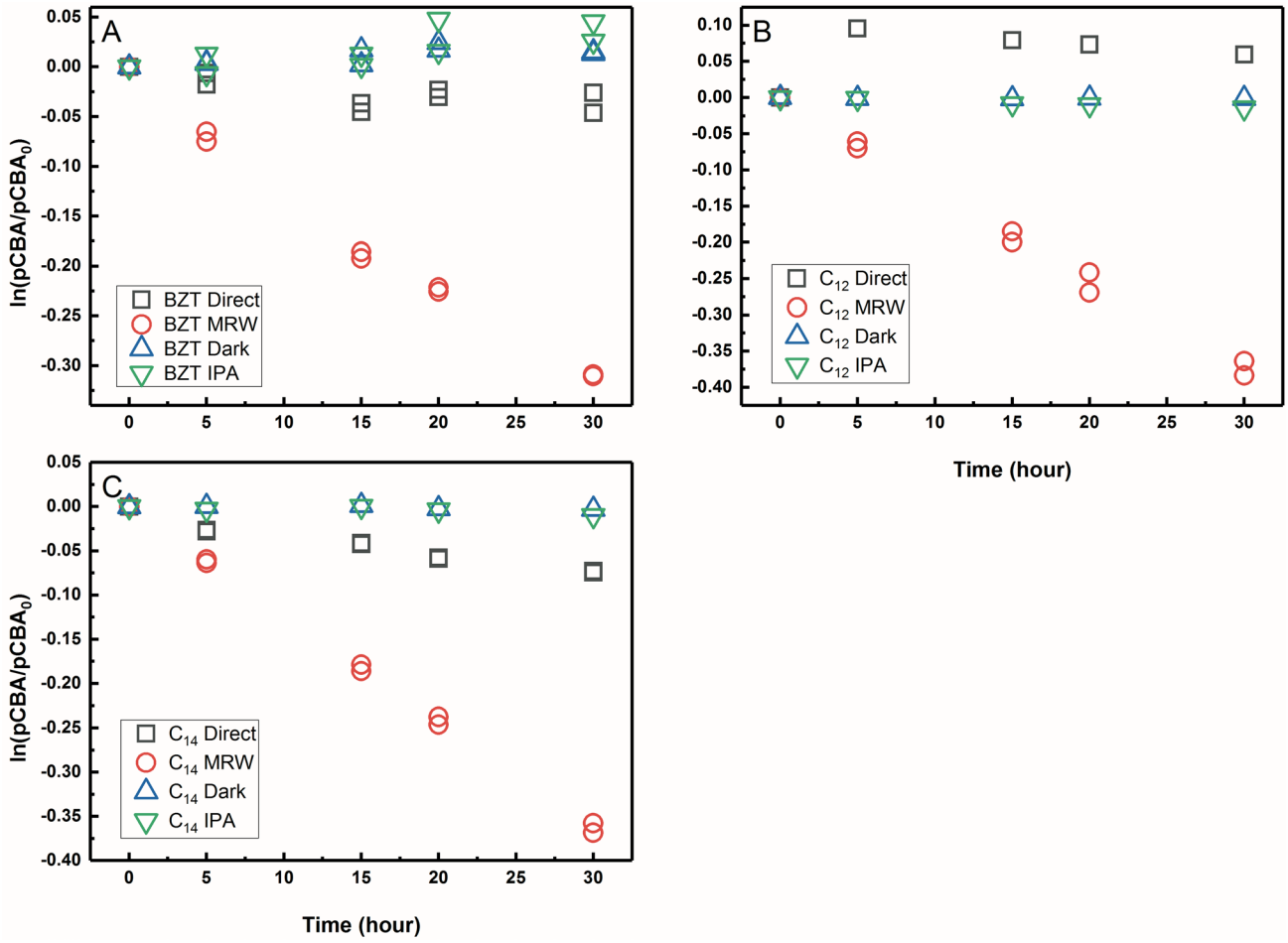


Figure S9: Logarithmic plot of pCBA loss over time in river water solar simulator experiments for: A) BZT, B) C_{12}-BAC, and C) C_{14}-BAC. Black squares are direct photolysis controls, red circles are river water samples, blue triangles are dark controls, and green triangles are IPA quenched controls.

Half-life estimate

$$k_c = 2.303\Phi_c \sum_\lambda (\varepsilon_{\lambda,c} I_\lambda) \quad (1)$$

$$t_{1/2} = \frac{ln(2)}{k_c} \quad (2)$$

Literature Cited

1. Apell, J. N. & McNeill, K. Updated and validated solar irradiance reference spectra for estimating environmental photodegradation rates. *Environ. Sci. Process. Impacts* **21**, 427–437 (2019).