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>
<thead>
<tr>
<th>Table S1: QAC Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzethonium Chloride (BZT)</strong></td>
</tr>
<tr>
<td><img src="image1" alt="Benzethonium Chloride (BZT) structure" /></td>
</tr>
<tr>
<td><strong>C₁₂-Benzalkonium Chloride (BAC)</strong></td>
</tr>
<tr>
<td><img src="image2" alt="C₁₂-Benzalkonium Chloride (BAC) structure" /></td>
</tr>
<tr>
<td><strong>C₁₄-BAC</strong></td>
</tr>
<tr>
<td><img src="image3" alt="C₁₄-BAC structure" /></td>
</tr>
<tr>
<td><strong>C₁₂-Alkyltrimethylammonium (ATMA) Bromide</strong></td>
</tr>
<tr>
<td><img src="image4" alt="C₁₂-Alkyltrimethylammonium (ATMA) Bromide structure" /></td>
</tr>
<tr>
<td><strong>C₁₂-Dialkyltrimethylammonium (DADMA) Bromide</strong></td>
</tr>
<tr>
<td><img src="image5" alt="C₁₂-Dialkyltrimethylammonium (DADMA) Bromide structure" /></td>
</tr>
</tbody>
</table>

**River water sample collection and analysis**

<table>
<thead>
<tr>
<th>Table S2: Water quality parameters of the Mississippi river water used in photochemical study</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water Quality Parameter</strong></td>
</tr>
<tr>
<td>Nitrite ($\text{NO}_2^-$ mg of N/L)</td>
</tr>
<tr>
<td>Nitrate ($\text{NO}_3^-$ mg of N/L)</td>
</tr>
<tr>
<td>Dissolved organic carbon (NPOC mg-C/L)</td>
</tr>
<tr>
<td>Dissolved inorganic carbon (DIC mg-C/L)</td>
</tr>
<tr>
<td>pH</td>
</tr>
</tbody>
</table>

**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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Columna</th>
<th>Mobile Phase (v:v)b</th>
<th>Injection V (μL)</th>
<th>Flow Rate (mL min⁻¹)</th>
<th>Detector λ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂-BAC</td>
<td>Eclipse XDB-C18 (4.6×150 mm, 3.5 μm)</td>
<td>90% 9:1 methanol:10mM ammonium acetate with 0.1% acid 10% 9:1 10mM ammonium acetate with 0.1% acid:methanol</td>
<td>50</td>
<td>1.0</td>
<td>210</td>
</tr>
<tr>
<td>C₁₄-BAC</td>
<td>Eclipse XDB-C18 (4.6×150 mm, 3.5 μm)</td>
<td>95% 9:1 methanol:10mM ammonium acetate with 0.1% acid 5% 9:1 10mM ammonium acetate with 0.1% acid:methanol</td>
<td>50</td>
<td>1.0</td>
<td>210</td>
</tr>
<tr>
<td>BZT</td>
<td>Eclipse XDB-C18 (4.6×150 mm, 3.5 μm)</td>
<td>90% 9:1 methanol:10mM ammonium acetate with 0.1% acid 10% 9:1 10mM ammonium acetate with 0.1% acid:methanol</td>
<td>50</td>
<td>1.0</td>
<td>210</td>
</tr>
<tr>
<td>pCBA</td>
<td>Eclipse XDB-C18 (4.6×150 mm, 3.5 μm)</td>
<td>45% acetonitrile 55% 10mM pH3 phosphate buffer with 10% acetonitrile</td>
<td>40</td>
<td>1.0</td>
<td>238</td>
</tr>
<tr>
<td>PNAP</td>
<td>Eclipse XDB-C18 (4.6×150 mm, 3.5 μm)</td>
<td>65% acetonitrile 35% 10 mM pH 3 phosphate buffer with 10% acetonitrile</td>
<td>35</td>
<td>1.0</td>
<td>220</td>
</tr>
<tr>
<td>FFA</td>
<td>Eclipse XDB-C18 (4.6×150 mm, 3.5 μm)</td>
<td>10% acetonitrile 90% 10mM pH3 phosphate buffer with 10% acetonitrile</td>
<td>35</td>
<td>1.0</td>
<td>219</td>
</tr>
</tbody>
</table>

aColumns were at room temperature (~20 °C)
bAll mobile phases were isocratic

Photochemical experiments: simulated and outdoor photolysis in river water

Table S4: Rooftop experiment dates and times

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

Table S5: SMARTS inputs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site pressure</td>
<td>Calculated from latitude and altitude</td>
<td></td>
</tr>
<tr>
<td>Latitude</td>
<td>44.975</td>
<td>decimal degrees (DD)</td>
</tr>
<tr>
<td>Altitude</td>
<td>0.262128</td>
<td>km</td>
</tr>
<tr>
<td>Height</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Default atmosphere</td>
<td>Mid-latitude summer</td>
<td></td>
</tr>
<tr>
<td>Water vapor</td>
<td>Calculated from reference atmosphere and altitude</td>
<td></td>
</tr>
<tr>
<td>Ozone abundancea</td>
<td>0.3125</td>
<td>atm-cm</td>
</tr>
<tr>
<td>Ozone column altitude correction</td>
<td>Vertical profile correction</td>
<td></td>
</tr>
<tr>
<td>Gaseous absorption</td>
<td>Light pollution</td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide(^b)</td>
<td>Mauna Loa daily or weekly averages</td>
<td></td>
</tr>
<tr>
<td>Extraterrestrial spectrum</td>
<td>1366.1 ppm</td>
<td></td>
</tr>
<tr>
<td>Aerosol model</td>
<td>Shettle and Fenn rural</td>
<td></td>
</tr>
<tr>
<td>Aerosol optical depth at 500 nm</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Albedo</td>
<td>Light soil</td>
<td></td>
</tr>
<tr>
<td>Tilt</td>
<td>30 degrees</td>
<td></td>
</tr>
<tr>
<td>Surface azimuth</td>
<td>218 degrees SW</td>
<td></td>
</tr>
<tr>
<td>Solar constant</td>
<td>1361 Wm(^-2)</td>
<td></td>
</tr>
<tr>
<td>Longitude</td>
<td>-93.233611 DD</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)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 H₂O₂ sensitizer experiments for: A) C₁₂-BAC, B) BZT, C) C₁₄-BAC, D) C₁₂-ATMA, E) C₁₂-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.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>['OH]\textsubscript{ss} (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{12}-DADMA</td>
<td>$(1.17 \pm 0.03) \times 10^{-13}$</td>
</tr>
<tr>
<td>C\textsubscript{12}-BAC</td>
<td>$(5.0 \pm 0.5) \times 10^{-14}$</td>
</tr>
<tr>
<td>C\textsubscript{14}-BAC</td>
<td>$(2.6 \pm 0.2) \times 10^{-14}$</td>
</tr>
<tr>
<td>BZT</td>
<td>$(6.4 \pm 0.2) \times 10^{-14}$</td>
</tr>
<tr>
<td>C\textsubscript{12}-ATMA</td>
<td>$(4.3 \pm 0.1) \times 10^{-14}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Errors represent 95% confidence intervals

Assessing reactivity with other PPRIs

Figure S3: Log-concentration over time of: C\textsubscript{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, \( k_{\text{obs}} \) (s\(^{-1}\)), for FFA irradiated under simulated sunlight in singlet oxygen sensitizer experiments and singlet oxygen steady-state concentrations, \([{}^1\text{O}_2]_{\text{ss}}\) (M)\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>FFA with BZT</th>
<th>FFA with C(_{12})-BAC</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>N/A</td>
<td>(1.2 ± 0.5) x 10(^{-6})</td>
<td>(10 ± 4) x 10(^{-15})</td>
<td></td>
</tr>
<tr>
<td>2-acetylnaphthalene</td>
<td>(3.06 ± 0.08) x 10(^{-4})</td>
<td>(2.62 ± 0.05) x 10(^{-12})</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Rose Bengal</td>
<td>N/A</td>
<td>(4.5 ± 0.8) x 10(^{-4})</td>
<td>(3.9 ± 1.2) x 10(^{-12})</td>
<td></td>
</tr>
<tr>
<td>Dark</td>
<td>(0.2 ± 0.3) x 10(^{-6})</td>
<td>(2 ± 2) x 10(^{-12})</td>
<td>(5 ± 3) x 10(^{-6})</td>
<td>(4 ± 3) x 10(^{-14})</td>
</tr>
<tr>
<td>Histidine</td>
<td>(1.2 ± 0.3) x 10(^{-5})</td>
<td>(1.1 ± 0.3) x 10(^{-13})</td>
<td>(2.3 ± 0.3) x 10(^{-5})</td>
<td>(2.0 ± 0.3) x 10(^{-13})</td>
</tr>
<tr>
<td>Deoxygenated</td>
<td>(2.4 ± 0.1) x 10(^{-4})</td>
<td>(2.03 ± 0.05) x 10(^{-12})</td>
<td>(3.1 ± 0.8) x 10(^{-5})</td>
<td>(2.7 ± 0.7) x 10(^{-13})</td>
</tr>
<tr>
<td>Deoxygenated with sorbic acid</td>
<td>(1.6 ± 0.1) x 10(^{-5})</td>
<td>(1.4 ± 0.1) x 10(^{-13})</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^a\)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, \( k_{\text{obs}} \) (h\(^{-1}\))\(^a\), for QACs irradiated under simulated sunlight

<table>
<thead>
<tr>
<th>Sample</th>
<th>BZT</th>
<th>C(_{12})-BAC</th>
<th>C(_{14})-BAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRW</td>
<td>(9.7 ± 0.3) x 10(^{-2})</td>
<td>(2.9 ± 0.4) x 10(^{-2})</td>
<td>(2.8 ± 0.6) x 10(^{-2})</td>
</tr>
<tr>
<td>MRW(_{\text{corr}})</td>
<td>(2.0 ± 0.3) x 10(^{-2})</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Direct</td>
<td>(7.2 ± 0.7) x 10(^{-2})</td>
<td>(2 ± 1) x 10(^{-3})</td>
<td>(-6 ± 3) x 10(^{-3})</td>
</tr>
<tr>
<td>IPA</td>
<td>(7.7 ± 0.4) x 10(^{-2})</td>
<td>(1.7 ± 0.3) x 10(^{-3})</td>
<td>(5 ± 3) x 10(^{-3})</td>
</tr>
<tr>
<td>Dark</td>
<td>(6 ± 2) x 10(^{-2})</td>
<td>(-2 ± 3) x 10(^{-3})</td>
<td>(3 ± 3) x 10(^{-3})</td>
</tr>
</tbody>
</table>

\(^a\)Error bars represent 95% confidence intervals
Figure S6: Logarithmic plots of BZT (A), C\textsubscript{12}-BAC (B), and C\textsubscript{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\textsubscript{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) C₁₂-BAC, and C) C₁₄-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**

\[ k_c = 2.303 \Phi_c \sum \epsilon_{\lambda} l_{\lambda} \]  
\[ t_{1/2} = \frac{\ln(2)}{k_c} \]
Literature Cited