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1 **Photoinduced transformation of pyridinium-based ionic**
2 **liquids, and implications for their photochemical**
3 **behavior in surface waters**

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10 **Abstract**

11 The photochemical reactivity of three ionic liquids (1-ethylpyridinium tetrafluoroborate, 1-butyl-4-
12 methylpyridinium tetrafluoroborate, and 1-(3-cyanopropyl)pyridinium chloride) was studied by combining
13 laboratory experiments and photochemical modeling, to get insight into the possible behavior in surface-
14 water environments. Among the studied compounds, phototransformation in sunlit surface waters could
15 be an important attenuation pathway for 1-butyl-4-methylpyridinium tetrafluoroborate (BMPOTFB). In this
16 case the reaction with the carbonate radicals ($\text{CO}_3^{\cdot-}$) would prevail at low values of the dissolved organic
17 carbon (DOC), while the direct photolysis would be important at intermediate to high DOC values. The
18 sensitization by the triplet states of chromophoric dissolved organic matter could play a significant role at
19 high DOC, especially in the presence of a considerable fraction of highly photoreactive pedogenic organic
20 matter derived from soil runoff. The main processes that account for the phototransformation of BMPOTFB
21 and produce the main detected transformation products (TPs) are hydroxylation, detachment/shortening
22 of the butyl chain and double bond formation. Interestingly, there is a considerable overlap between the
23 intermediates formed by direct photolysis and those produced by indirect photochemistry. Some of the TPs
24 formed from BMPOTFB are more toxic than the parent compound towards *Vibrio fischeri* bacteria, and
25 account for the increase in toxicity of the irradiated mixtures. Differently from BMPOTFB, in the case of the
26 other two studied ionic liquids the photodegradation would play a negligible role in environmental
27 attenuation, with the possible exception of very shallow waters with low DOC.

28 **Keywords:** pollutants in surface waters; environmental attenuation of pollution; sunlight-induced
29 reactions; direct and indirect photochemistry.
30

31 **1. Introduction**

32 Ionic liquids (ILs) have several interesting properties such as good thermal stability, wide
33 electrochemical potential window, high electric conductivity and miscibility with water or organic
34 solvents, which permit application mainly as solvents for organic synthesis and as electrolytes
35 (Plechkova and Seddon, 2008; Holbrey and Seddon, 1999). Room-temperature ILs have received
36 huge attention as green and high-tech reaction media (Stepnowski and Zaleska, 2005) because,
37 differently from conventional organic solvents, they have negligible vapor pressure and do not emit
38 toxic vapors (Kralisch et al 2005).

39 However, a broad implementation of the use of ILs in industry may have some drawbacks. For
40 instance, due to their high stability, significant amounts of ILs are expected to occur in natural
41 waters and soil in the near future (Bubalo et al. 2014; Czerwicka et al. 2009; Richardson and
42 Ternes, 2014). Surface water is a major environmental compartment in which ILs may be emitted as
43 industrial wastes, and the most hydrophilic of these compounds should preferentially be found in
44 aqueous phases. Therefore, information concerning the fate of ILs in the aquatic environment is
45 crucial. Some studies have shown that ILs are more toxic to cells than conventional solvents
46 (Stepnowski and Zaleska, 2005), and the most common imidazolium-based compounds also
47 showed high resistance against microbial degradation (Czerwicka et al, 2009).

48 Photochemistry is a potentially important attenuation route for ILs in surface waters (Calza et al.,
49 2015). Generally speaking, phototransformation in surface waters can be divided into direct
50 photolysis (a xenobiotic absorbs sunlight, which triggers its degradation) and indirect
51 photochemistry. In the latter, sunlight is absorbed by naturally-occurring photosensitizers (most
52 notably nitrate, nitrite and chromophoric dissolved organic matter, CDOM) to produce reactive
53 transient species ($\bullet\text{OH}$, $^1\text{O}_2$ and CDOM triplet states, $^3\text{CDOM}^*$) (Dong et al., 2015; Rosario-Ortiz
54 and Canonica, 2016). More precisely, nitrate and nitrite yield $\bullet\text{OH}$, while irradiated CDOM
55 produces $^3\text{CDOM}^*$, which can form $^1\text{O}_2$ by reaction with oxygen (McNeill and Canonica, 2016).

56 Irradiated CDOM yields $\bullet\text{OH}$ as well (Lee et al., 2013; Page et al., 2014), at least partially through a
57 photo-Fenton process (Chiwa et al., 2015; Mostofa and Sakugawa, 2016; Giannakis et al., 2016a/b).
58 An additional transient, the carbonate radical $\text{CO}_3^{\bullet-}$, is produced by oxidation of carbonate and
59 bicarbonate by $\bullet\text{OH}$ and of carbonate by $^3\text{CDOM}^*$ (Canonica et al., 2005; Bahnmuller et al., 2014;
60 Janssen et al., 2014; Trivella et al., 2015; Bintou et al., 2015). These transients are then involved
61 into the phototransformation of xenobiotics (Silva et al., 2015), including the xenobiotics that do
62 not undergo direct photolysis (Janssen et al., 2015). Dissolved organic matter (DOM, not
63 necessarily chromophoric), which is usually quantified as the dissolved organic carbon (DOC), is
64 the main sink of both $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ (Huang and Mabury, 2000; Canonica et al., 2005; Keen et al.,
65 2014). This issue, combined with the fact that CDOM is a major radiation absorber, explains why
66 $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ are usually more concentrated in low-DOC waters. In contrast, the highest levels of
67 $^3\text{CDOM}^*$ and $^1\text{O}_2$ usually occur in high-DOC environments, because organic matter is involved in
68 the production of these transients but not in their scavenging. Actually, the quenching of $^3\text{CDOM}^*$
69 occurs by reaction with O_2 or interval conversion, while $^1\text{O}_2$ is quenched by collision with the water
70 solvent (Wenk et al., 2013; Vione et al., 2014).

71 Within this framework, we studied the photofate of three pyridinium-based ILs under conditions
72 that are relevant to sunlit environmental waters: 1-ethylpyridinium tetrafluoroborate (EPTFB), 1-(3-
73 cyanopropyl)pyridinium chloride (CPPC) and 1-butyl-4-methylpyridinium tetrafluoroborate
74 (BMPOTFB). The known physical properties of the studied ILs (Zhao et al., 2003; Bandres et al.,
75 2008; Guerrero et al., 2012) are summarized in **Table SM1** in the Supplementary Material
76 (hereafter SM). We paid attention to the identification of the intermediate products formed during
77 ILs degradation, by using the HPLC-MS/MS technique. The identification of transformation
78 products (TPs) is a crucial aspect because, in addition to providing important information on the
79 mechanism of degradation, the formed TPs may have a very different impact on the environment

80 compared to the parent molecules. To our knowledge, this is the first study about the photochemical
81 transformation of EPTFB, CPPC and BMPOTFB.

82

83 **2. Experimental section**

84 *2.1. Materials and Reagents*

85 1-Ethylpyridinium tetrafluoroborate (**EPTFB**) (98%), 1-(3-cyanopropyl)pyridinium chloride
86 (**CPPC**) (98.5%), 1-butyl-4-methylpyridinium tetrafluoroborate (**BMPOTFB**) ($\geq 97,0\%$), sodium
87 nitrate ($\geq 99,9\%$), sodium bicarbonate ($\geq 99,7\%$), acetonitrile ($\geq 99\%$), acetaminophen (APAP),
88 anthraquinone-2-sulfonic acid, sodium salt (98%), hydrogen peroxide (35%), formic acid (98%),
89 sodium 1-hexanesulfonate (98%), and phosphoric acid (85%) were purchased from Sigma Aldrich,
90 Italy. Rose Bengal (80%) was purchased from Alfa Aesar. All aqueous solutions were prepared
91 with ultra-pure water (Millipore Milli-Q™).

92 *2.2. Irradiation Experiments*

93 Irradiation experiments were performed in magnetically stirred cylindrical closed cells (Pyrex glass,
94 40 mm i.d. \times 25 mm), on 5 mL aqueous solutions containing each studied IL at 20 μ M initial
95 concentration. The goal of these experiments was not to directly reproduce environmental
96 conditions in the laboratory (which is indeed problematic, in particular as far as the water depth is
97 concerned), but rather to obtain reasonably accurate measurements of the main photochemical
98 parameters such as direct photolysis quantum yields and second-order reaction rate constants. These
99 data, used as input values for a photochemical model, allow inferences to be made on the
100 photochemical fate of the studied compounds in environmental waters. Direct photolysis
101 experiments were carried out on each IL taken separately, under UVB irradiation with a Philips TL
102 20W/01 RS lamp having emission maximum at 313 nm. The lamp radiation reached the irradiated
103 solutions mainly from the top.

104 Indirect photolysis experiments followed the competition kinetics approach (Puskas et al., 2005;
105 Dantas et al., 2007; Katsoyiannis et al., 2011; Sun et al., 2016). They were run on systems
106 containing a mixture of all the studied ILs and acetaminophen (APAP), each at 20 μM initial
107 concentration. The rationale for the use of APAP as reference compound is that its second-order
108 reaction rate constants are known for all the transient species relevant to this study ($\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$
109 and $^3\text{CDOM}^*$; De Laurentiis et al., 2014). An important issue in these competition kinetics
110 experiments is the need to minimize the occurrence of multiple reaction pathways, which are
111 problematic for the assessment of the reaction rate constants. For the competition approach to work,
112 one needs a single prevailing reaction pathway to be operational. Therefore, the radical $\bullet\text{OH}$ was
113 produced by irradiating 100 mM NaNO_3 under the TL 01 RS lamp described above, which was also
114 used to produce $\text{CO}_3^{\bullet-}$ upon irradiation of 100 mM NaNO_3 + 100 mM NaHCO_3 . In both cases, a
115 high concentration of nitrate was used to minimize the IL direct photolysis. Elevated bicarbonate
116 was needed to scavenge the majority of photogenerated $\bullet\text{OH}$, thereby minimizing the interference of
117 $\bullet\text{OH}$ on the $\text{CO}_3^{\bullet-}$ reactions. Anthraquinone-2-sulfonate (AQ2S) was used as CDOM proxy to study
118 the reactivity of $^3\text{CDOM}^*$. The use of AQ2S has pros and cons: on the one side it does not yield
119 $\bullet\text{OH}$ or $^1\text{O}_2$ upon irradiation, which allows for the study of a pure triplet-sensitized process
120 (Maddigapu et al., 2010). In the case of atrazine, a remarkably good agreement has also been found
121 between the reaction rate constants with $^3\text{AQ2S}^*$ and with natural $^3\text{CDOM}^*$ (Marchetti et al, 2013;
122 Zeng and Arnold, 2013). However, the triplet state $^3\text{AQ2S}^*$ may be more reactive than average
123 $^3\text{CDOM}^*$, which could lead to an overestimation of the triplet-sensitization rate constants when
124 using AQ2S as CDOM proxy (De Laurentiis et al., 2014; Avetta et al., 2016). The latter issue
125 should be (and was here) taken into account when using kinetic data derived from AQ2S
126 photochemistry. In the AQ2S experiments, solutions containing 0.2 mM AQ2S and 20 μM
127 ILs/APAP mixtures were irradiated under a Philips TLK 05 lamp, with emission maximum at 365
128 nm. Finally, measures of reactivity with $^1\text{O}_2$ were performed using a lamp Philips TL D 18W/16

129 with emission maximum at 545 nm. The dye Rose Bengal (10 μ M initial concentration) was chosen
130 as the $^1\text{O}_2$ source. The irradiation conditions already described were also used for the study of IL
131 transformation products (TPs) *via* the aforementioned photochemical pathways. In this case,
132 however, each IL was irradiated separately and at a relatively high loading (20 mg L⁻¹), to simplify
133 TPs detection and identification.

134 **2.3. Analytical Procedures**

135 *2.3.1. Liquid Chromatography - UV detection (HPLC-UV)*

136 After the scheduled irradiation times the cells were withdrawn from the lamp, and their content
137 was analyzed by HPLC-UV to monitor the time evolution of the studied ILs and, when relevant, of
138 APAP as well. The instrument used was a Merck-Hitachi HPLC equipped with AS-2000A
139 autosampler (100 μ L injection volume), L-6200 and L-6200A pumps for high-pressure gradients,
140 L-4200 UV-Vis detector and a reverse-phase column Phenomenex Kinetex® 100Å C18 (250 mm \times
141 4.6 mm \times 5 μ m). The eluent consisted of an aqueous solution of the ionic coupler sodium 1-
142 hexanesulfonate 0.01 M (eluent A) and acetonitrile (eluent B). After 3 min of isocratic conditions
143 (90/10 v/v A/B), the acetonitrile fraction was increased up to 60/40 v/v in 19 min. For the tests with
144 the dye Rose Bengal these conditions were followed by a second gradient up to 40/60 v/v A/B over
145 4 min, which was held for 5 min to allow elution of the photosensitizer. Re-equilibration of the
146 HPLC column was achieved by going back to the starting conditions, which were held for 5 min
147 before the next injection. The mobile phase flow rate was 1 mL/min and the detection wavelength
148 was 210 nm. With these elution conditions the retention times were 5.3 min for APAP, 6.2 min for
149 EPTFB, 6.8 min for CPPC, and 14.6 min for BMPOTFB.

150 *2.3.2. Liquid Chromatography - High Resolution Mass Spectrometry (HPLC-HRMS)*

151 This technique was used to detect and identify the TPs of the studied ILs under irradiation. For
152 HPLC-HRMS analyses of the irradiated aqueous solutions, the chromatographic separations were
153 carried out with a Phenomenex C18 Gemini® NX 110-Å column, 150 mm \times 2.1 mm \times 3 μ m

154 particle size (Phenomenex, Bologna, Italy), using a Ultimate 3000 HPLC instrument (Dionex,
155 Thermo Scientific, Milan, Italy). The injection volume was 20 μ L and the flow rate 200 μ L/min. A
156 gradient mobile phase composition was used, going from 5/95 v/v of acetonitrile/
157 heptafluorobutyric acid (5 mM in water) to 20/80 v/v in 15 min, followed by a second gradient step
158 up to 95/5 v/v in 5 min.

159 A LTQ Orbitrap mass spectrometer (Thermo Scientific, Milan, Italy) was interfaced to the HPLC
160 instrument through an ESI ion source. The HPLC column effluent was delivered into the ion source
161 using nitrogen as both sheath and auxiliary gas. The capillary voltage and tube lens voltage in the
162 ESI source were maintained at 28 V and 70 V, respectively. The source voltage was set to 4.5 kV in
163 the positive ion mode. The capillary temperature was maintained at 270°C. The acquisition method
164 was optimized beforehand in the tuning sections (capillary, magnetic lenses and collimating
165 octapole voltages) for the parent compound, to achieve maximum sensitivity. Mass accuracy of the
166 recorded ions (vs calculated) was \pm 5 millimass units (mmu, without internal calibration).

167 The MS spectra were acquired using full scan MS (50-1000 m/z range) and MS² acquisition in the
168 positive ion mode, with a resolution of 30000 (500 m/z FWHM) in FTMS (full transmission) mode.
169 The ions submitted to MS² acquisition were chosen on the basis of full MS spectra abundance,
170 without using automatic dependent scan. Collision energy was set to 30% for all of the MS²
171 acquisition methods, and the MS² acquisition range was between the value of ion trap cut-off and
172 the m/z value of the (M+H)⁺ ion. Xcalibur software (Thermo Scientific, Milan, Italy) was used for
173 both acquisition and data analysis.

174 2.3.3. Toxicity Measurements

175 The toxicity of the reaction mixtures collected at different irradiation times was measured with a
176 Microtox® Model 500 Toxicity Analyzer (Milan, Italy). Acute toxicity was assessed with a
177 bioluminescence inhibition assay using the marine bacterium *Vibrio fischeri*, by monitoring changes
178 in the natural emission of the luminescent bacteria when challenged with toxic compounds. Freeze-

179 dried bacteria, reconstitution solution, diluent (2% NaCl) and an adjustment solution (non-toxic
 180 22% sodium chloride) were purchased from Azur (Milan, Italy). Samples were tested in five
 181 dilutions in a medium containing 2% sodium chloride, and luminescence was recorded after 5, 15,
 182 and 30 min of incubation at 15°C. Because no substantial changes in luminescence were observed
 183 between 5 and 30 minutes, only the percent toxicity recorded at 15 minutes will be discussed.
 184 Inhibition of luminescence, compared with a toxic-free control to give the percentage inhibition,
 185 was calculated following the established protocol of the Microtox® calculation program.

186 **2.4. Kinetic data treatment**

187 The time evolution of the studied ILs was fitted with a pseudo-first order equation of the form
 188 $C_t^{IL} = C_o^{IL} e^{-k_{IL} t}$, where C_t^{IL} is the IL concentration at the time t , C_o^{IL} the initial concentration, and k_{IL}
 189 the pseudo-first order degradation rate constant. The IL initial degradation rate was calculated as
 190 $R_o^{IL} = k_{IL} C_o^{IL}$. The initial degradation rate of APAP (R_o^{APAP}) was calculated in a similar way.

191 With a mixture of APAP and of the studied ILs, under conditions where a reactive species X is
 192 generated (with $X = \bullet\text{OH}, \text{CO}_3^{\bullet-}, {}^1\text{O}_2$ or ${}^3\text{AQ2S}^*$), if reaction with X only is operational, the initial
 193 rate is $R_o^{IL} = k_{X,IL}[X]C_o^{IL}$ for each relevant IL, and $R_o^{APAP} = k_{X,APAP}[X]C_o^{APAP}$ for APAP. Here, $k_{X,IL}$
 194 and $k_{X,APAP}$ are the respective second-order reaction rate constants of X with each studied IL and
 195 with APAP, and $[X]$ is the steady-state concentration of the transient species. Because ILs and
 196 APAP occur together in the same mixture, $[X]$ is the same in all the relevant expressions of R_o^{IL} and
 197 R_o^{APAP} . Moreover, we chose the initial conditions so that $C_o^{IL} = C_o^{APAP}$. On this basis it is possible to
 198 derive $R_o^{IL}(R_o^{APAP})^{-1} = k_{X,IL}(k_{X,APAP})^{-1}$, from which the second-order rate constant of the reaction
 199 between each IL and X can be obtained as follows: $k_{X,IL} = k_{X,APAP}R_o^{IL}(R_o^{APAP})^{-1}$ (Herrmann et al.,
 200 2010). Note that the initial rates are derived from the experimental data, while $k_{X,APAP}$ is known
 201 from a previous study (De Laurentiis et al., 2014).

202 For the determination of the direct photolysis quantum yields, the photon flux absorbed by each IL
203 (P_a^{IL}) was calculated as follows: $P_a^{IL} = \int_{\lambda} p^{\circ}(\lambda)[1 - 10^{-\varepsilon_{IL}(\lambda)b[IL]}]d\lambda$, where $p^{\circ}(\lambda)$ is the incident
204 spectral photon flux density of the used UVB lamp, $\varepsilon_{IL}(\lambda)$ is the IL molar absorption coefficient, b
205 = 0.4 cm is the optical path length inside the solution, and $[IL] = 20\mu\text{L}$ is the initial molar
206 concentration of the relevant IL. The values of $p^{\circ}(\lambda)$ were determined by combining spectral
207 measurements with a calibrated Ocean Optics USB2000 CCD spectrophotometer, and chemical
208 actinometry with 2-nitrobenzaldehyde. The detailed procedure has been reported by Marchisio et al.
209 (2015). The wavelength trends of $p^{\circ}(\lambda)$ and $\varepsilon_{IL}(\lambda)$ are shown in **Figure 1A**. The direct photolysis
210 quantum yield was calculated as $\Phi_{IL} = R_o^{IL}(P_a^{IL})^{-1}$.

211 **2.5. Photochemical modeling**

212 The model assessment of ILs photodegradation was carried out with the APEX software (Aqueous
213 Photochemistry of Environmentally-occurring Xenobiotics), available for free as Electronic
214 Supplementary Information of Bodrato and Vione (2014). APEX predicts photochemical reaction
215 kinetics from photoreactivity parameters of xenobiotics (absorption spectra, direct photolysis
216 quantum yields and second-order reaction rate constants with transient species), and from data of
217 water chemistry and depth (Bodrato and Vione, 2014). APEX predictions have been validated by
218 comparison with field data of pollutant phototransformation kinetics in surface freshwaters
219 (Marchetti et al., 2013; Avetta et al., 2016). The standard solar spectrum used in APEX is referred
220 to fair-weather conditions during summertime at mid latitude (Frank and Klöpffer, 1988). Sunlight
221 irradiance is not constant in the natural environment, due to fluctuations in meteorological
222 conditions (not included in APEX) and to diurnal and seasonal cycles. To allow easier comparison
223 between model results and environmental conditions, taking the day-night cycle into account,
224 APEX uses a summer sunny day (SSD) as time unit, equivalent to fair-weather 15 July at 45° N
225 latitude. The absorption of radiation by the photosensitisers (CDOM, nitrate and nitrite) and the

226 studied substrates is calculated based on competition for sunlight irradiance in a Lambert-Beer
227 approach (Bodrato and Vione, 2014; Braslavsky, 2007). APEX applies to well-mixed waters and
228 gives average values over the water column, with contributions from the well-illuminated surface
229 layer and from darker water in the lower depths, where irradiance is very low (Loiselle et al., 2008).

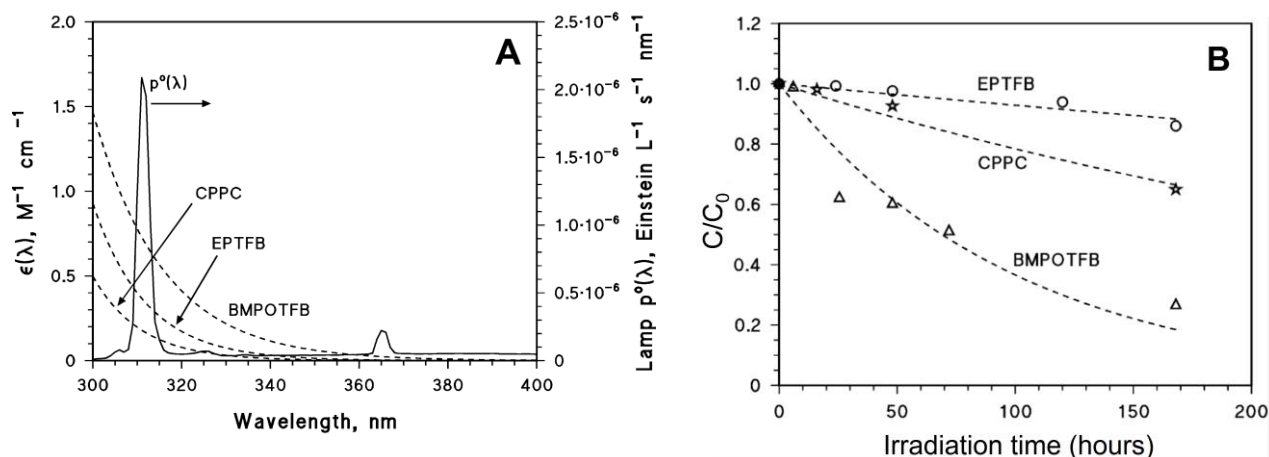
230

231 **3. Results and Discussion**

232 *3.1. Photochemical reactivity of the studied ILs*

233 First of all, the direct photolysis of **EPTFB**, **CPPC** and **BMPOTFB** was studied by irradiating the
234 relevant compounds taken separately (no mixtures were used in this case) under a UVB lamp. The
235 ILs time trends are reported in **Figure 1B**, which shows that the photochemical degradation rates
236 followed the order **BMPOTFB** > **CPPC** > **EPTFB**. The relevant direct photolysis quantum yields
237 are reported in **Table 1**. The comparison between quantum yield values (**Table 1**) and
238 photodegradation kinetics (**Figure 1B**) suggests that **EPTFB** was the compound featuring both the
239 lowest quantum yield of direct photolysis (about one order of magnitude smaller than the other two
240 ILs) and the slowest direct phototransformation. Compared with the other studied ILs, **EPTFB**
241 featured an intermediate degree of UVB radiation absorption (**Figure 1A**). **CPPC** was the studied
242 IL with the highest quantum yield of direct photolysis but, because of relatively low radiation
243 absorption, its photodegradation was slower compared to **BMPOTFB**.

244 The reactivity between the studied ILs and the transient species under consideration ($X = \bullet\text{OH}$,
245 $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ or $^3\text{AQ2S}^*$) was studied in mixtures of **EPTFB**, **CPPC**, **BMPOTFB** and APAP
246 (hereafter, substrates). All of the four substrates had the same initial concentration in the mixture
247 ($[\text{Substrate}]_0 = 20 \mu\text{M}$). The reaction with $\bullet\text{OH}$ was studied upon UVB irradiation of the mixture in
248 the presence of 0.10 M NaNO_3 , and the reactivity order was **BMPOTFB** > **EPTFB** > **CPPC**. The
249 substrates time evolution is shown in **Figure 2A**, while the second-order reaction rate constants of
250 the studied ILs with $\bullet\text{OH}$ are listed in **Table 1**.



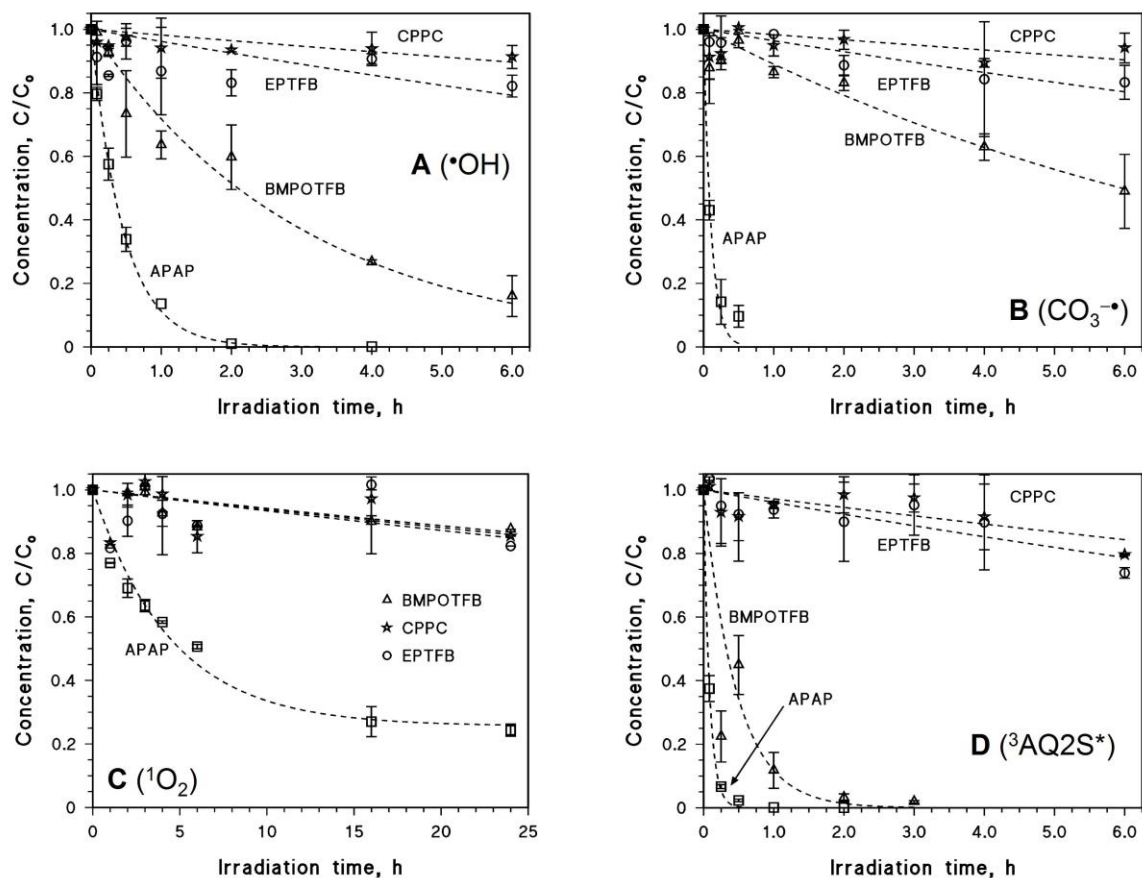
251
 252 **Figure 1.** (A) Absorption spectra ($\epsilon(\lambda)$) of the studied ILs, and emission spectrum ($p^\circ(\lambda)$) of the
 253 used UVB lamp (Philips TL 01). (B) Time trends of the studied ILs (each had a 20 μM initial
 254 concentration in a distinct one-component solution) upon UVB irradiation in Milli-Q water (direct
 255 photolysis experiments).

256

257 **Table 1.** Photoreactivity parameters (direct photolysis quantum yields and second-order reaction
 258 rate constants with photoinduced transients) of the studied ILs and of APAP. For modeling
 259 purposes, the range of $k_{IL,^3CDOM^*}$ was varied between $0.05 k_{IL,^3AQ2S^*}$ and $k_{IL,^3AQ2S^*}$ as explained in the
 260 text. Note that Substrate = EPTFB, BMPOTFB, CPPC, or APAP. The APAP data are taken from
 261 De Laurentiis et al. (2014). Φ_{APAP} is reported for a sake of completeness, but it was not used to
 262 calculate Φ_{IL} . The error bounds, representing the σ -level uncertainty, were taken from the literature
 263 in the case of APAP. For the studied ILs, they were derived from duplicate experiments.

	EPTFB	BMPOTFB	CPPC	APAP
$\Phi_{Substrate}$, unitless	$(4.81 \pm 0.62) \cdot 10^{-2}$	$(4.53 \pm 0.62) \cdot 10^{-1}$	$(7.77 \pm 0.67) \cdot 10^{-1}$	$(4.57 \pm 0.17) \cdot 10^{-2}$
$k_{Substrate^{\bullet}OH}$, $\text{M}^{-1} \text{s}^{-1}$	$(3.33 \pm 2.23) \cdot 10^7$	$(2.84 \pm 1.22) \cdot 10^8$	$(1.55 \pm 0.91) \cdot 10^7$	$(1.87 \pm 0.56) \cdot 10^9$
$k_{Substrate^{\bullet}CO_3^-}$, $\text{M}^{-1} \text{s}^{-1}$	$(7.04 \pm 5.97) \cdot 10^5$	$(4.85 \pm 2.59) \cdot 10^6$	$(1.52 \pm 0.86) \cdot 10^6$	$(3.8 \pm 1.1) \cdot 10^8$
$k_{Substrate^{\bullet}O_2}$, $\text{M}^{-1} \text{s}^{-1}$	$(1.40 \pm 1.30) \cdot 10^6$	$(1.50 \pm 1.10) \cdot 10^6$	$(1.30 \pm 1.10) \cdot 10^6$	$(3.68 \pm 0.73) \cdot 10^7$
$k_{Substrate^{\bullet}AQ2S^*}$, $\text{M}^{-1} \text{s}^{-1}$	$(3.71 \pm 1.17) \cdot 10^7$	$(1.99 \pm 1.18) \cdot 10^9$	$(2.64 \pm 0.99) \cdot 10^7$	$(1.08 \pm 0.16) \cdot 10^{10}$

264



265

266 **Figure 2.** Time trends of APAP and the three studied ILs in the same mixture (20 μM initial
 267 concentration for each substrate), in the presence of: **(A)** 0.1 M NaNO_3 under UVB irradiation; **(B)**
 268 0.1 M NaNO_3 + 0.1 M NaHCO_3 under UVB irradiation; **(C)** 10 μM Rose Bengal under yellow-
 269 lamp irradiation; **(D)** 0.2 mM AQ2S under UVA irradiation. The error bars represent the standard
 270 error of duplicate experiments.

271

272

273 The reaction with $\text{CO}_3^{\bullet-}$ was studied upon UVB irradiation of 0.1 M NaNO_3 + 0.1 M NaHCO_3 ,
 274 under which conditions the $\bullet\text{OH}$ radicals generated by nitrate photolysis would be largely (>95%)
 275 scavenged by the HCO_3^- and CO_3^{2-} ions to produce $\text{CO}_3^{\bullet-}$. The $\bullet\text{OH}$ scavenging fractions were
 276 assessed on the basis of the known $\bullet\text{OH}$ reaction rate constants of HCO_3^- and CO_3^{2-} (Buxton et al.,
 277 1988), of the rate constants of the studied substrates (**Table 1**), and on the initial concentrations in

278 solution. The ILs order of reactivity with $\text{CO}_3^{\bullet-}$ was **BMPOTFB** > **EPTFB** > **CPPC**. The relevant
279 time evolutions are shown in **Figure 2B**, and the second-order reaction rate constants are listed in
280 **Table 1**.

281 The transient $^1\text{O}_2$ was generated by irradiation of 10 μM Rose Bengal under yellow light. The three
282 ILs showed comparably low reactivity with $^1\text{O}_2$, much lower than for APAP (see **Figure 2C** and
283 **Table 1**). Finally, the reactivity by triplet sensitization was studied upon UVA irradiation of 0.2
284 mM AQ2S, a concentration value that was chosen to minimize the reaction between excited and
285 ground-state AQ2S (Bedini et al., 2012). Also in this case the reactivity order was **BMPOTFB** >
286 **EPTFB** > **CPPC** (see **Figure 2D** and **Table 1**).

287 As explained before, $^3\text{AQ2S}^*$ may be more reactive than natural $^3\text{CDOM}^*$ and may provide an
288 overestimation of the $^3\text{CDOM}^*$ rate constants (De Laurentiis et al., 2014; Avetta et al., 2016). For
289 this reason, and based on the results of a recent study (Avetta et al., 2016), the $^3\text{AQ2S}^*$ rate
290 constants ($k_{IL,^3\text{AQ2S}^*}$) were taken as upper limits for those with $^3\text{CDOM}^*$ ($k_{IL,^3\text{CDOM}^*}$). The
291 corresponding lower limits were taken as $k_{IL,^3\text{CDOM}^*} = 0.05 k_{IL,^3\text{AQ2S}^*}$. By assuming that $k_{IL,^3\text{CDOM}^*}$
292 varies between $0.05 k_{IL,^3\text{AQ2S}^*}$ and $k_{IL,^3\text{AQ2S}^*}$, one gets some insight into the potentially variable
293 reactivity of $^3\text{CDOM}^*$. Indeed, triplet sensitisation processes are quite fast when triggered by
294 runoff-derived soil organic matter, and they are much slower in the presence of aquatic CDOM
295 (De Laurentiis et al., 2012).

296 In the above experiments of indirect photochemistry it was generally found that **BMPOTFB** had a
297 significantly higher reactivity than the other studied ILs, but it was less reactive than APAP. All
298 three ILs have an electron-poor pyridinium ring, which might account for lower reactivity with
299 oxidizing transient species when compared to the electron-rich phenolic ring of APAP. However,
300 differently from the other ILs, **BMPOTFB** also has an electron-donating methyl substituent that

301 could somewhat increase the electron density on the aromatic ring and, therefore, make it more
302 reactive than the other studied ILs.

303 **3.2. Modeling of ILs phototransformation in surface waters**

304 The photoreactivity parameters reported in **Table 1** were used as input data for the APEX software,
305 using either $k_{IL,^3CDOM^*} = k_{IL,^3AQ2S^*}$ or $k_{IL,^3CDOM^*} = 0.05 k_{IL,^3AQ2S^*}$ in different sets of calculations.

306 Because depth and dissolved organic carbon (DOC) are the water body features that most influence
307 photochemical reactions (Vione et al., 2014), the ILs half-life times were computed as a function of
308 these two variables. Reasonable values were assumed for other water parameters of photochemical
309 significance, *i.e.*, 0.1 mM nitrate, 1 μ M nitrite, 1 mM bicarbonate, and 10 μ M carbonate (Vione et
310 al., 2014). On this basis and for fair-weather summertime irradiation, APEX returned the half-life

311 times reported in **Figure 3 (3A,D: BMPOTFB; 3B,E: EPTFB; 3C,F: CPPC; 3A,B,C:**
312 $k_{IL,^3CDOM^*} = k_{IL,^3AQ2S^*}$; **3D,E,F:** $k_{IL,^3CDOM^*} = 0.05 k_{IL,^3AQ2S^*}$). First of all, note that all the half-life times

313 increase with increasing depth and that they also increase with DOC, with the partial exception of a
314 trend with a maximum (**EPTFB** with $k_{EPTFB^3CDOM^*} = k_{EPTFB^3AQ2S^*}$, see **Figure 3B**). The rationale of

315 the depth trend is that the lower depths of deep water bodies are poorly illuminated by sunlight, a
316 phenomenon that offsets the elevated photoreactivity at the water surface. Increasing DOC means

317 increasing DOM and CDOM. The occurrence of CDOM inhibits the direct photolysis (due to
318 competition for irradiance between CDOM and the substrate(s)), while DOM causes an even larger

319 inhibition of the \bullet OH/CO₃⁻ reactions (due to scavenging of the radicals) (Vione et al., 2014). The
320 inhibition of direct photolysis, of \bullet OH and CO₃⁻ processes is often not offset by the enhancement

321 of the reactions triggered by ³CDOM* and ¹O₂, of which CDOM is the only source. Actually,
322 CDOM tends to reach absorption saturation in deep waters with high DOC, in which case the

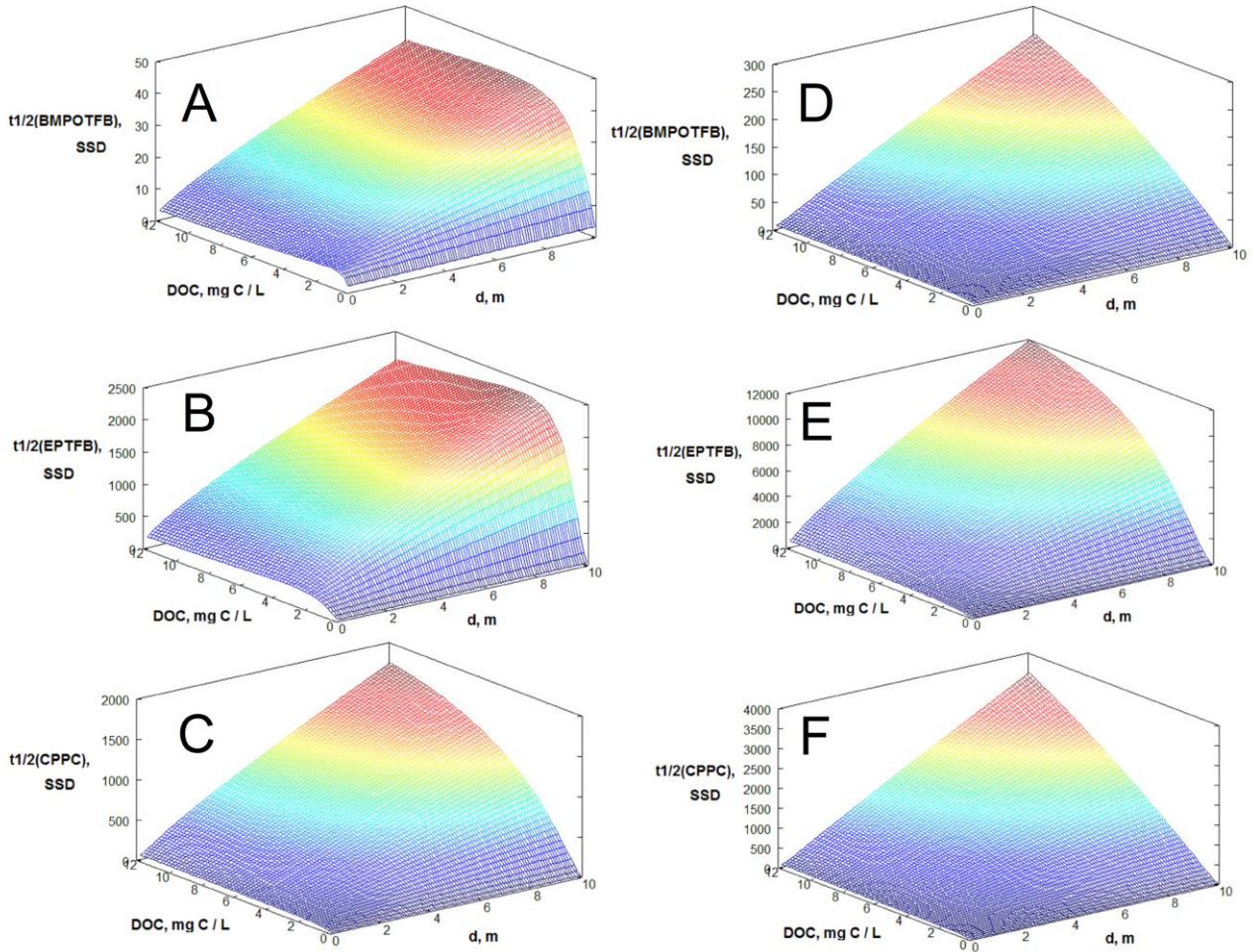
323 production of ³CDOM* is little enhanced by a CDOM increase. In contrast, the scavenging of
324 \bullet OH/CO₃⁻ and the competition for irradiance do not undergo saturation effects (Avetta et al.,

325 2016). There are some exceptions, however: if the reactivity of a substrate with $^3\text{CDOM}^*/^1\text{O}_2$ is
326 remarkably high, these processes can significantly increase the degradation kinetics at elevated
327 DOC. In this case one can observe a maximum in the half-life times as a function of the DOC
328 (Fabbri et al., 2015), which happened here with **EPTFB** if $k_{\text{EPTFB}^3\text{CDOM}^*} = k_{\text{EPTFB}^3\text{AQ2S}^*}$ (**Figure 3B**).

329 Among the studied ILs, **BMPOTFB** is predicted to be by far the most photolabile compound in the
330 natural environment. This prediction follows the results of the irradiation experiments, which
331 already suggested that **BMPOTFB** was more photoreactive than **EPTFB** or **CPPC** via both direct
332 photolysis and indirect photochemistry. If $k_{\text{BMPOTFB}^3\text{CDOM}^*} = k_{\text{BMPOTFB}^3\text{AQ2S}^*}$, phototransformation
333 would be an important attenuation pathway for **BMPOTFB** under all the water conditions
334 considered in **Figure 3** (depth = 0-10 m, DOC = 0-12 mg C L⁻¹). If $k_{\text{BMPOTFB}^3\text{CDOM}^*} =$
335 $0.05 k_{\text{BMPOTFB}^3\text{AQ2S}^*}$, the photodegradation half-life times would be quite long in deep and high-DOC
336 waters. When considering the half-life time data reported in **Figure 3**, it should be noted that one
337 cannot have year-long fair-weather summertime conditions in mid-latitude environments.
338 Therefore, the longer lifetimes are certainly underestimated.

339 Differently from **BMPOTFB**, the predicted photochemical half-life times of **EPTFB** and **CPPC**
340 are very high and they can reach years to decades in deep water bodies with high DOC. Under such
341 circumstances, other processes will prevail over phototransformation in the environmental
342 attenuation of these ILs. Photochemistry could still play some role for **EPTFB** and **CPPC**, but only
343 in water bodies that are shallow and have low DOC at the same time.

344



345

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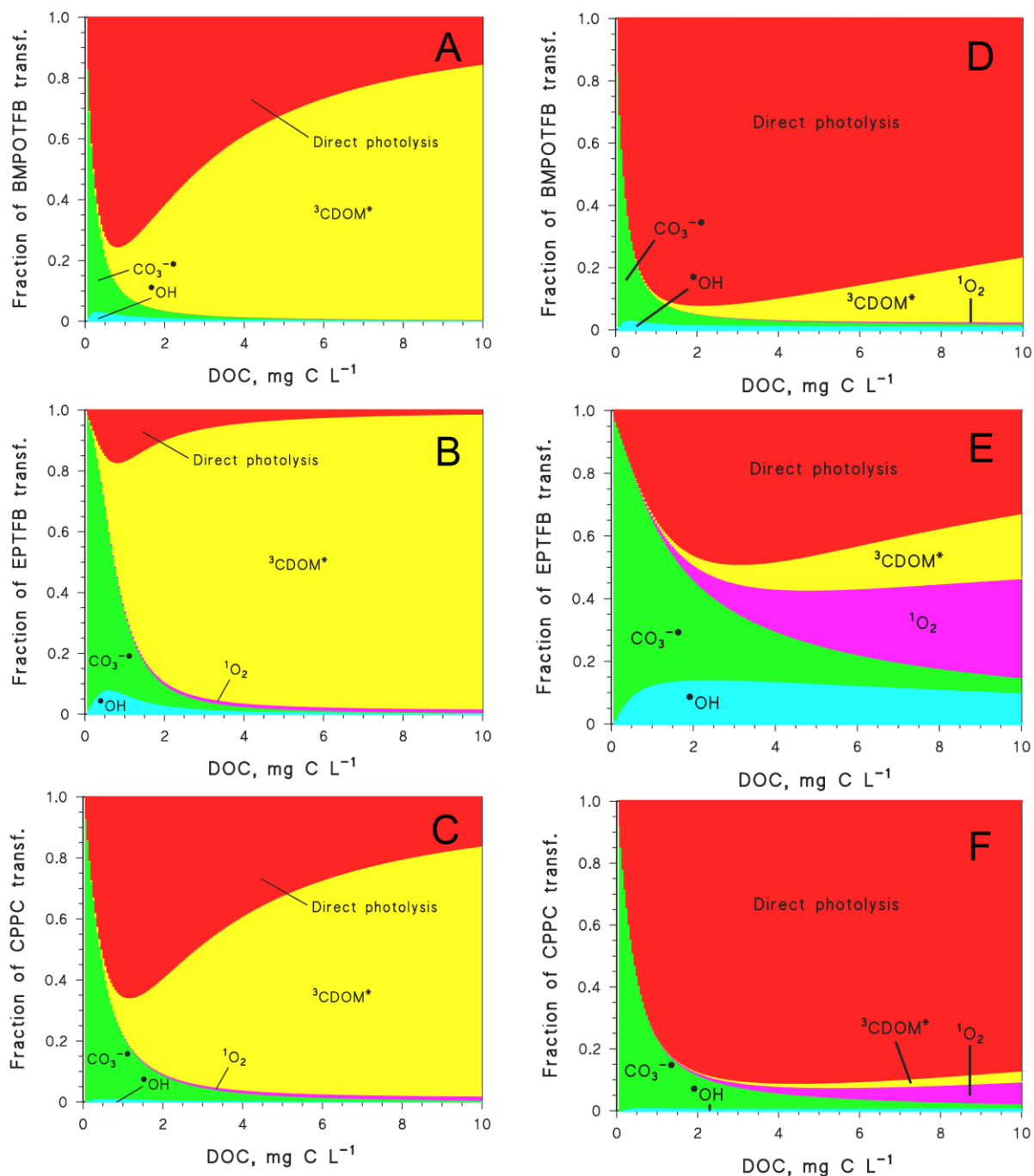
347 **Figure 3.** Half-life times predicted by APEX (SSD = summer sunny days equivalent to fair-weather
 348 15 July at 45°N latitude), as a function of the DOC and the water depth d , for: (A) **BMPOTFB**,
 349 with $k_{BMPOTFB^3CDOM^*} = k_{BMPOTFB^3AQ2S^*}$; (B) **EPTFB**, with $k_{EPTFB^3CDOM^*} = k_{EPTFB^3AQ2S^*}$; (C) **CPPC**, with
 350 $k_{CPPC^3CDOM^*} = k_{CPPC^3AQ2S^*}$; (D) **BMPOTFB**, with $k_{BMPOTFB^3CDOM^*} = 0.05 k_{BMPOTFB^3AQ2S^*}$; (E) **EPTFB**,
 351 with $k_{EPTFB^3CDOM^*} = 0.05 k_{EPTFB^3AQ2S^*}$; (F) **CPPC**, with $k_{CPPC^3CDOM^*} = 0.05 k_{CPPC^3AQ2S^*}$. Other water
 352 conditions: 0.1 mM nitrate, 1 μ M nitrite, 1 mM bicarbonate, 10 μ M carbonate.

353

354 **Figure 4** reports, as a function of the DOC, the fractions of ILs phototransformation that are
355 accounted for by the different photoreaction pathways, for a water depth of 5 m and other
356 conditions as per the above discussion (**4A,D: BMPOTFB; 4B,E: EPTFB; 4C,F: CPPC; 4A,B,C:**
357 $k_{IL,^3CDOM^*} = k_{IL,^3AQ2S^*}$; **4D,E,F:** $k_{IL,^3CDOM^*} = 0.05 k_{IL,^3AQ2S^*}$). The model predicts that the reactions with
358 $CO_3^{\bullet-}$ can be important for all ILs at low DOC (usually below 2 mg C L⁻¹), while $\bullet OH$ and 1O_2 can
359 be important only in the case of **EPTFB**. The reactions with $^3CDOM^*$ can be major pathways at
360 high DOC if $k_{IL,^3CDOM^*} = k_{IL,^3AQ2S^*}$, while they become secondary processes if
361 $k_{IL,^3CDOM^*} = 0.05 k_{IL,^3AQ2S^*}$. In the latter case, the direct photolysis is expected to strongly dominate the
362 phototransformation of both **BMPOTFB** and **CPPC**.

363 By crossing these results with the half-life time data, which show the environmental water
364 conditions where photochemistry can be important in IL attenuation, one gets that: (i) the direct
365 photolysis is very relevant for **BMPOTFB**, especially in water bodies where the occurrence of
366 CDOM of mainly aquatic origin would limit the triplet-sensitized processes. Other significant
367 **BMPOTFB** transformation pathways are $CO_3^{\bullet-}$ at low DOC and possibly $^3CDOM^*$ at high DOC,
368 in the presence of significant amounts of soil-derived organic matter that would enhance the
369 reactions of triplet sensitization (De Laurentiis et al., 2012); (ii) the photodegradation of **EPTFB**
370 may only be significant in low-DOC waters, and in these conditions the prevailing pathways are the
371 direct photolysis and the reactions with $\bullet OH$ and $CO_3^{\bullet-}$. The exact value of $k_{EPTFB^3CDOM^*}$ is of
372 limited interest because, for the $^3CDOM^*$ processes to play a significant role, one needs relatively
373 high-DOC conditions where **EPTFB** photochemistry cannot be important; (iii) a similar issue holds
374 for **CPPC**, although in this case the $\bullet OH$ process can be neglected and the only important low-DOC
375 pathways are the direct photolysis and the $CO_3^{\bullet-}$ reaction.

376



377

378 **Figure 4.** Fractions of ILs phototransformation accounted for by the different photoinduced
 379 pathways, as predicted by the APEX software for summertime irradiation conditions. (A)
 380 **BMPOTFB**, with $k_{BMPOTFB^3CDOM^*} = k_{BMPOTFB^3AQ2S^*}$; (B) **EPTFB**, with $k_{EPTFB^3CDOM^*} = k_{EPTFB^3AQ2S^*}$; (C)
 381 **CPPC**, with $k_{CPPC^3CDOM^*} = k_{CPPC^3AQ2S^*}$; (D) **BMPOTFB**, with $k_{BMPOTFB^3CDOM^*} = 0.05 k_{BMPOTFB^3AQ2S^*}$;
 382 (E) **EPTFB**, with $k_{EPTFB^3CDOM^*} = 0.05 k_{EPTFB^3AQ2S^*}$; (F) **CPPC**, with $k_{CPPC^3CDOM^*} = 0.05 k_{CPPC^3AQ2S^*}$.
 383 Other water conditions: 5 m depth, 0.1 mM nitrate, 1 μM nitrite, 1 mM bicarbonate, 10 μM
 384 carbonate.

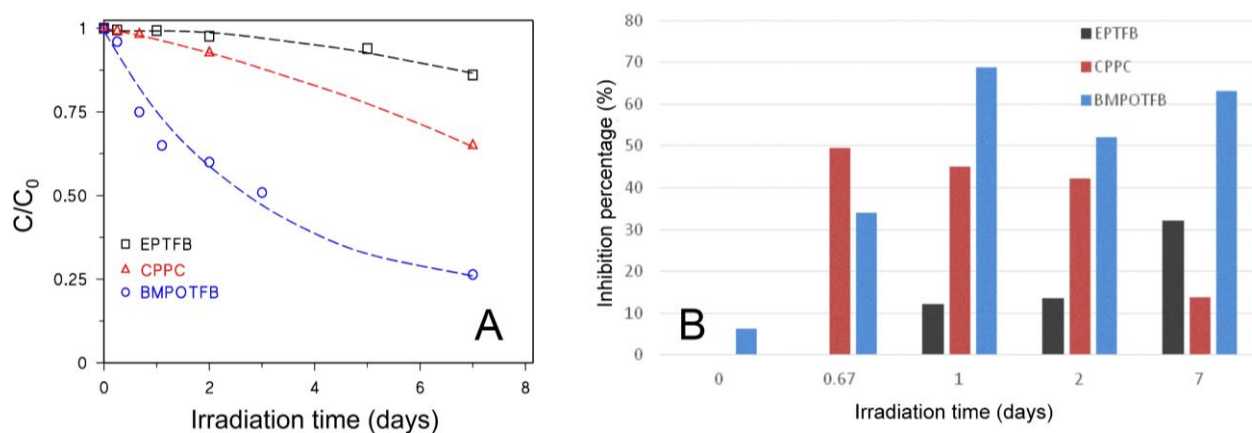
385 3.3. ILs toxicity assessment upon photoinduced degradation

386 Acute toxicity was monitored over time upon UVB direct photolysis of the studied ILs. The choice
387 of the direct photolysis pathway for the toxicity study has two reasons: (i) experimental simplicity,
388 because the assessment of toxicity in indirect phototransformation is complicated by the possible
389 production of toxic species/intermediates from the photosensitizers (De Luis et al., 2010). The
390 indirect phototransformation processes might be incompletely accounted for in control experiments
391 carried out without the substrates, because the substrates themselves are major scavengers of
392 transient species (e.g. in the case of $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$), and the transient steady-state concentrations
393 may vary dramatically when the substrates are absent; (ii) environmental significance. The direct
394 photolysis is an important process in the phototransformation of **BMPOTFB**, for which
395 photochemistry may be a significant attenuation pathway in surface waters. The direct photolysis is
396 less important for **EPTFB** (see **Figure 4**), but the phototransformation kinetics of this compound
397 are predicted to be very slow except for low-DOC waters (**Figure 3**). In these conditions, the direct
398 phototransformation pathway could play a remarkable role. The phototransformation of **CPPC** can
399 only be significant under low-DOC conditions, where the direct photolysis is an important
400 degradation pathway.

401 The acute toxicity tests were carried out by monitoring changes in the natural emission of the
402 luminescent bacteria *Vibrio fischeri*, when exposed to potentially toxic compounds. Out of the
403 various available bioassays, this test is sensitive, rapid, cost-effective, reproducible, and it can be
404 used for almost all kinds of toxic compounds (Parvez et al., 2006, Matsushita et al., 2015). The
405 toxicity is here expressed as the percentage of inhibition of the bacteria luminescence. Results
406 obtained on samples subjected to different irradiation times are plotted in **Figure 5** (**5A**: time trend
407 of ILs in the irradiated solutions; **5B**: time trend of the toxicity in the same solutions). The studied
408 ILs are not toxic, as shown by the absence or near absence of a toxic effect before irradiation. Under
409 UVB light the photoinduced transformation of **EPTFB** proceeded through the formation of almost

410 harmless TPs, and a slight toxicity increase was only observed after 7 days of irradiation.
411 Unfortunately, this compound is the studied IL for which phototransformation (either direct or
412 indirect) is expected to play the least important role in the natural environment (see **Figure 3**). In
413 contrast, the toxicity of irradiated **CPPC** and **BMPOTFB** increased over time, thereby suggesting
414 that their phototransformation proceeded through the formation of moderately toxic compounds.

415



416

417 **Figure 5.** (A) Time trends of **BMPOTFB**, **EPTFB** and **CPPC** (20 mg L⁻¹ initial loading in
418 separate solutions) upon direct photolysis under UVB irradiation. (B) Toxicity evolution (inhibition
419 of *Vibrio fischeri* emission) in the same irradiated solutions shown in the (A) panel.

420

421

422 3.4. Characterization of the transformation products

423 The direct photolysis of **EPTFB**, **CPPC** and **BMPOTFB** yielded several transformation products
424 (TPs), which were detected in ESI positive mode *via* HPLC-HRMS. **Tables SM2-SM4** in the SM
425 report the measured m/z ratios and the most probable empirical formulas for all the detected TPs.
426 The relevant time evolution profiles are provided in **Figure 6**. Among the TPs of **BMPOTFB**, a
427 few of them were formed at early reaction times and disappeared during the course of the irradiation
428 experiments, which lasted for up to eight days. Several other TPs appeared at relatively long

429 irradiation times, and their concentration increased during irradiation. The various TPs could be
430 formed upon direct photolysis through three different pathways shown in **Scheme 1** and involving:
431 (a) hydroxylation; (b) detachment/shortening of the butyl chain; (c) double bond formation.

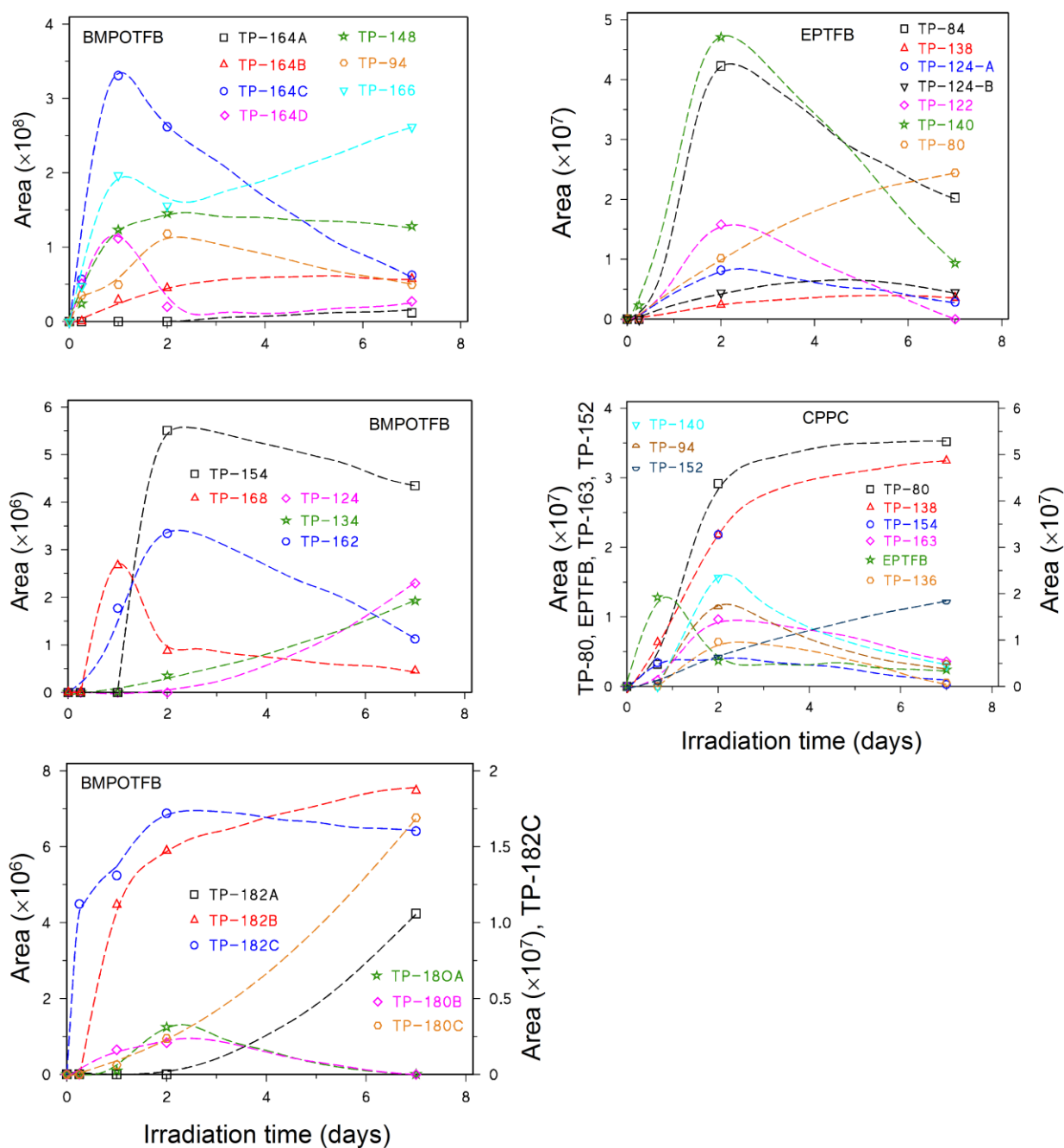
432 The MS² spectrum of **BMPOTFB** has a product ion at 94.0652 *m/z*, presumably produced by the
433 loss of the butyl chain (see **Table SM2**). This peculiar loss was helpful in attributing the structures
434 of unknown TPs. A TP having 166.1233 *m/z* (**TP-166**) is consistent with a monohydroxyderivative.
435 The formation of a product ion at 71.0447 *m/z* (hydroxylated butyl moiety) in the MS² spectrum of
436 **TP-166**, combined with the loss of C₂H₆, permits to locate the OH group on the butyl chain and to
437 confine it on C1 or C2.

438 Four species with 164.1077 *m/z* (**TP-164A** through **D**) were detected and attributed to keto
439 derivatives. For **TP-164A** it was not possible to acquire enough structural information, while for the
440 other compounds the presence of the product ion at 94.0634 *m/z* allows the placement of the
441 hydroxyl group on the butyl chain. Additionally, **TP-164B** presents the structural diagnostic loss of
442 formaldehyde that allows the keto group to be located on C4 (McLafferty and Turecek, 1993).

443 Three species with 182.1184 *m/z* (**TP-182A** through **C**) are consistent with **BMPOTFB**
444 dihydroxyderivatives. All these TPs show the product ion at 94.0652 *m/z* in their MS² spectrum,
445 thereby allowing the two OH groups to be located on the butyl chain. **TP-182C** should have one
446 OH group on the C4 atom of the butyl chain, as suggested by the loss of methanol.

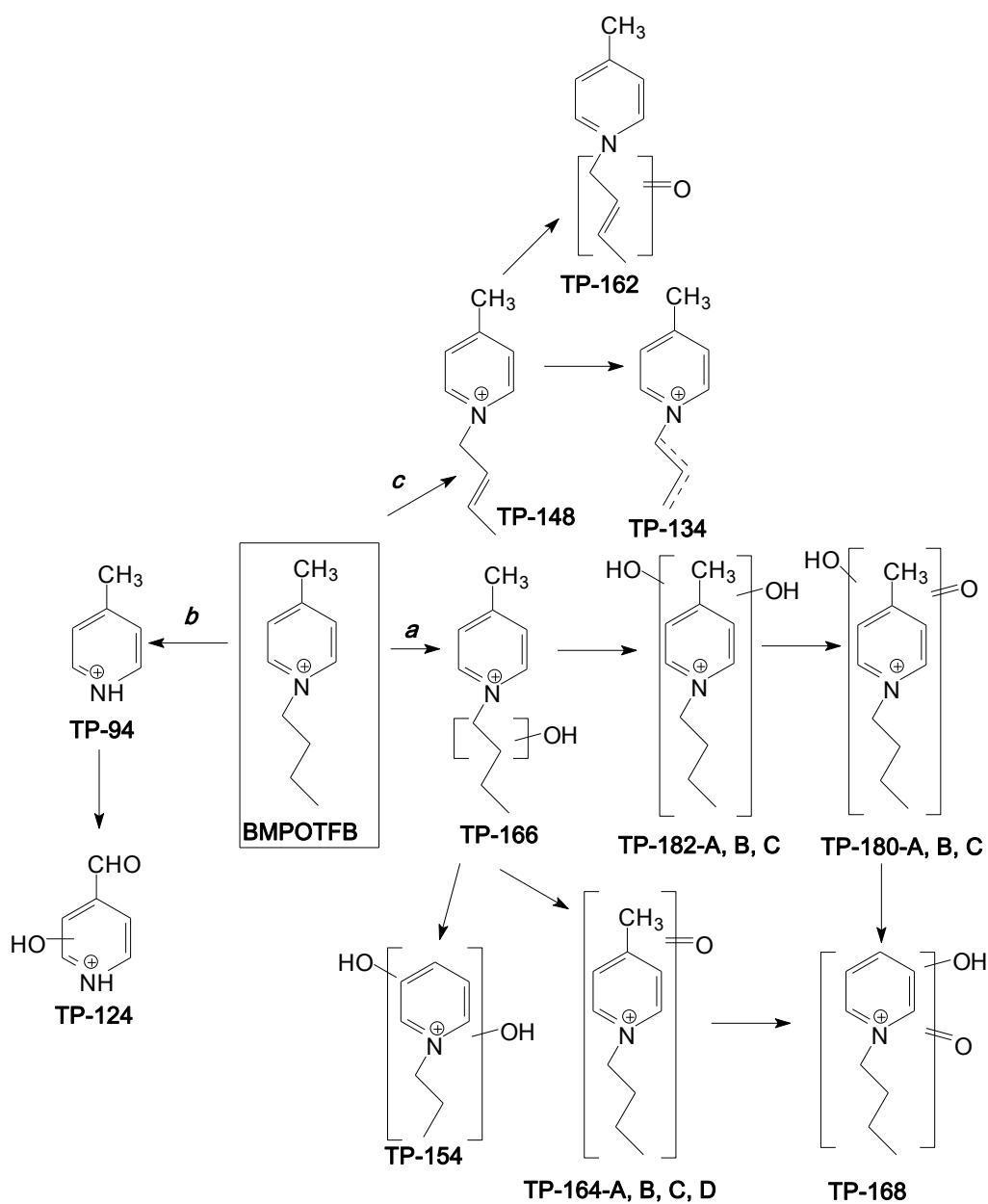
447 Three species with 180.0995 *m/z* (**TP-180A** through **C**) should be dihydroxylated/oxidized
448 compounds. In the case of **TP-180C**, the loss of formic acid and the formation of the precursor ion
449 at 94.0634 *m/z* suggest the presence of a carboxylic group on the butyl chain.

450



451

452 **Figure 6.** Time evolution of the TPs formed upon UVB irradiation of (left side) **BMPOTFB** and of
 453 (right side) **EPTFB** (top) and **CPPC** (bottom). Multiple plots are provided for **BMPOTFB** to show
 454 TPs with different peak areas, and for readability issues as well. The dashed curves are just a guide
 455 for the eye. In a couple of cases data are plotted against different Y-axes, located on the right hand
 456 and on the left hand of each plot. The least numerous group of compounds is listed on the given
 457 axis. The remaining compounds, not explicitly mentioned, are plotted against the other axis.



458

459 **Scheme 1.** Proposed transformation pathways followed by **BMPOTFB** under direct photolysis.

460

461 Three compounds at 162.0891, 148.1126 and 134.0967 m/z with empirical formulas $C_{10}H_{12}ON$,
 462 $C_{10}H_{14}ON$ and $C_9H_{12}N$, respectively, are consistent with progressive dealkylation and with
 463 formation of a double bond on the alkyl chain. For **TP-162**, the most abundant ion in MS^2 exhibits a
 464 C_4H_6O loss that suggests the occurrence of a keto group on the butyl chain.

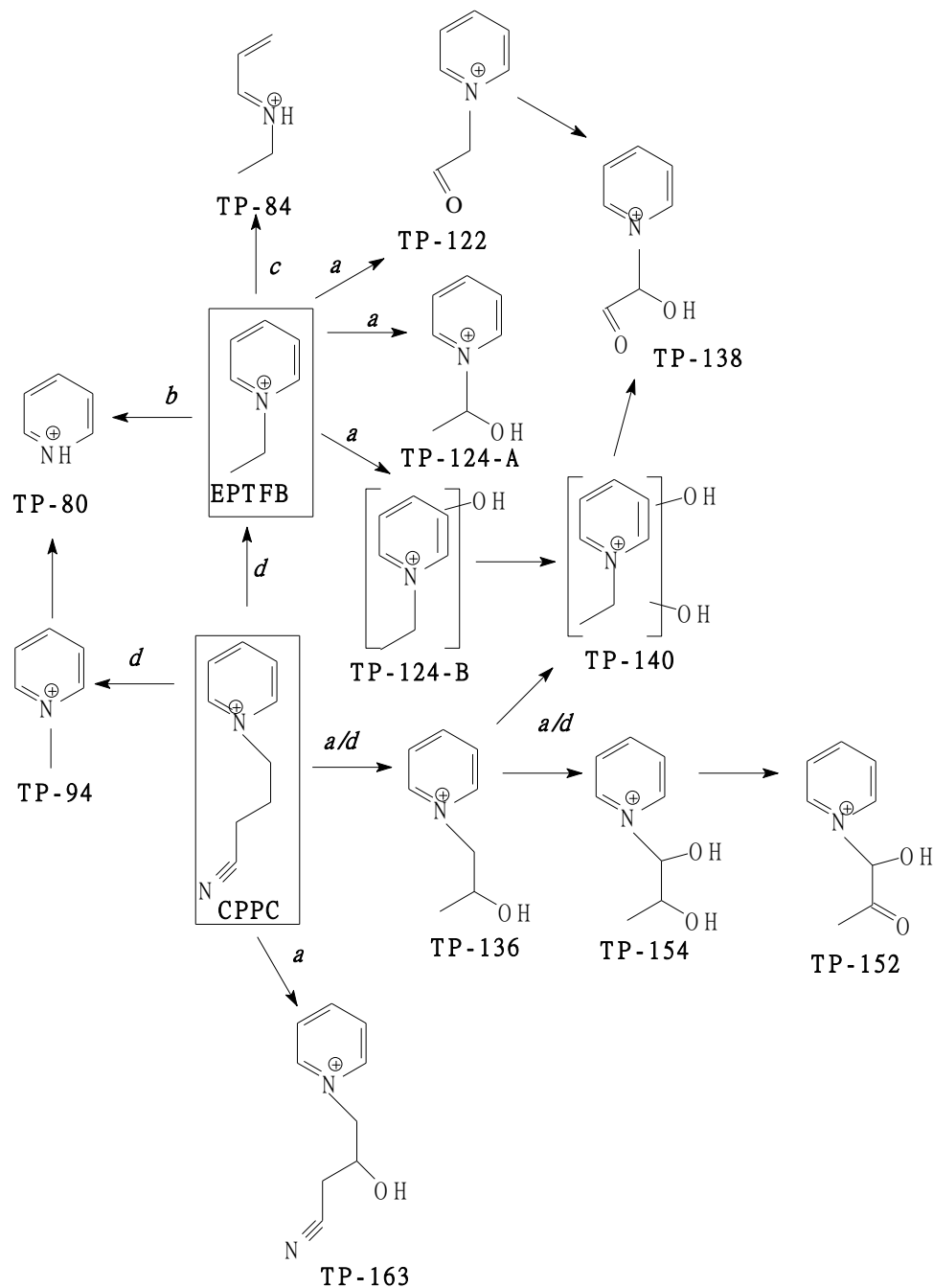
465 **TP-168** and **TP-154** may be formed *via* the detachment of a methyl group and/or *via* side-chain
466 shortening, but insufficient mass information was available to propose a univocal structure.

467 **TP-94** and **TP-124** are formed upon detachment of the butyl chain. **TP-94** is consistent with 4-
468 methylpyridine, while **TP-124** would involve methyl oxidation and possibly ring hydroxylation.
469 Unfortunately, the information contained in the MS spectra did not allow for the proposal of a
470 proper location for the OH group in **TP-124**.

471 As far as the indirect photochemistry processes are concerned, **TP-148** was also detected upon
472 reactions with $\bullet\text{OH}$, $\text{CO}_3^-\bullet$ and $^3\text{AQ2S}^*$, **TP-164 B,D** with $\bullet\text{OH}$, **TP-164 C,D** and **TP-166 C,D** with
473 $^3\text{AQ2S}^*$, and **TP-94** with $\text{CO}_3^-\bullet$. The formation of partially overlapping TPs in different pathways
474 is quite common in phototransformation reactions (De Laurentiis et al., 2014).

475 In the case of **EPTFB**, three main transformation pathways could be detected under direct
476 photolysis conditions. These pathways involve: (*a*) hydroxylation; (*b*) detachment of the ethyl
477 chain, and (*c*) ring opening (see **Scheme 2**). The MS² spectrum of **EPTFB** has the ion at 80.0492
478 *m/z* as base peak, formed through the detachment of the ethyl chain (C₂H₄, see **Table SM3**). Upon
479 photolysis, pathway *a* likely yields two isobaric species with 124.0757 *m/z* and empirical formula
480 C₇H₁₀ON, which can be attributed to hydroxyderivatives. In the case of **TP-124A**, the loss of
481 C₂H₄O in the MS² spectrum suggests that the OH substituent occurs on the alkyl chain. Moreover,
482 the absence of methanol loss tentatively suggests that OH is located on the ethyl carbon atom bound
483 to nitrogen (C1). For **TP-124B**, the absence of MS² product ions prevented any hypothesis
484 concerning the OH position. The formation of **TP-122**, with empirical formula C₇H₈ON, likely
485 involved the oxidation of the alcoholic group to a keto one. The loss of C₂HON in the MS²
486 spectrum supports the occurrence of a keto group on the alkyl chain, which should be located on C2
487 as suggested by the CO loss (McLafferty and Turecek, 1993). Pathway *a* also involved the
488 formation of TPs with empirical formula C₇H₁₀O₂N (**TP-140**) and C₇H₈O₂N (**TP-138**), which are

489 well-matched with dihydroxylated and dihydroxylated/oxidized derivatives, respectively. However,
 490 the absence of MS² product ions prevented any hypothesis about the location of the two OH groups.
 491



492

493 **Scheme 2.** Proposed transformation pathways followed by compounds **EPTFB** and **CPPC** upon
 494 direct photolysis.

495

496 Further transformation (pathway *b*) involved the detachment of the alkyl chain with formation of
497 pyridine (**TP-80**). An alternative route (pathway *c*) would proceed through ring opening to yield
498 compound **TP-84**. The most abundant compounds (as far as peak areas are concerned) were **TP-**
499 **140**, **TP-84** and **TP-80**, thereby suggesting that the three pathways had similar importance.
500 Interestingly, the compound **TP-84** was also detected upon reactions with $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$ and $^3\text{AQ2S}^*$,
501 and **TP-140** upon reaction with $\bullet\text{OH}$ as well.

502 In a close analogy with **EPTBF**, the MS^2 spectrum of **CPPC** presents as base peak the pyridinium
503 ion at 80.0492 m/z . This ion is likely formed through the detachment of the cyano-propyl chain (see
504 **Table SM4**). The direct photolysis of **CPPC** involved hydroxylation (see pathway *a* in **Scheme 2**).
505 **TP-163** is well-matched with a monohydroxylated derivative, and the detected MS^2 product ions
506 are consistent with losses of $\text{C}_2\text{H}_3\text{N}$ and $\text{C}_3\text{H}_3\text{ON}$. Therefore, the OH substituent should not occur
507 on the cyano carbon (C4) or on the carbon attached to the cyano group (C3) (McLafferty and
508 Turecek, 1993). The occurrence of OH on the carbon atom bound to the ring nitrogen (C1) also
509 looks little likely, leaving C2 as the most reasonable position for the OH group. The MS data are
510 also consistent with chain shortening (pathway *d*) and with a combined chain
511 shortening/hydroxylation (pathway *a/d*). The detachment of the methylcyano group accounts for the
512 formation of a compound with 108.0809 m/z , recognized as **EPTFB** and confirmed by standard
513 match. A further chain shortening would produce **TP-94**, which was identified as 1-methylpyridine.
514 The latter could yield **TP-80**, matched with pyridine (also detected during **EPTFB** photolysis),
515 through detachment of the methyl group. Pathway *a/d* yields **TP-136**, **TP-154** and **TP-152** through
516 cyano group detachment and hydroxylation. In all cases, the OH groups were added to the propyl
517 chain as assessed by the product ion at 80.0478 m/z (pyridinium ion) in the relevant MS^2 spectra.
518 The presence of some structurally-diagnostic ions allowed a univocal location of the oxygen atoms
519 on the alkyl chain. **TP-136** formation would imply the detachment of the cyano group and the

520 oxidation of the alkyl chain. Actually, the absence of formaldehyde loss combined with C₂H₂O and
521 C₃H₄O losses allowed the location of the keto group on C2.

522 Based on its exact mass, **TP-152** might have an OH group and a keto one. The oxygen-containing
523 functions should be both located on the alkyl chain, as suggested by the occurrence of the
524 pyridinium ion in the MS² spectrum. The absence of any methanol loss is not consistent with the
525 occurrence of OH on C3. Together with the loss of ketene, this suggests that the keto group should
526 be located on C2 and the hydroxyl one on C1. Therefore, **TP-152** could be tentatively identified as
527 the oxidized form of **TP-154**. The formation of **TP-138** and **TP-140** likely involved methylcyano-
528 group detachment and hydroxylation. The retention times and fragmentation spectra of the TPs
529 derived from **CPPC** matched well with the TPs formed from **EPTFB** photolysis. As far as peak
530 areas are concerned, the main TPs were **TP163**, formed through pathway *a*, **TP108** and **TP80**,
531 involving pathway *d*. While **EPTFB** was formed from **CPPC** at early reaction times and reached its
532 maximum concentration after 1 day of irradiation, all the other TPs were more persistent and either
533 peaked at two days irradiation, or continued accumulating up to at least eight days. No TPs were
534 detected upon indirect phototransformation of **CPPC**, probably because of the scarce reactivity of
535 this substrate with the studied transient species.

536 The occurrence of definite chemical functions allows some hypotheses to be advanced concerning
537 the potential toxicity of TPs (Mayo-Bean et al., 2012). On this basis and from the above discussion
538 one may assume that among the detected TPs of **BMPOTFB**, those for which a univocal chemical
539 structure could be proposed are unlikely to be more toxic than the parent compound, because no
540 potentially toxic functionalities were added (Mayo-Bean et al., 2012). A toxicity increase could be
541 expected in the (possible but not confirmed) circumstance that dihydroxylation involved the
542 aromatic ring, especially if two OH groups occurred in para position (hydroquinone derivatives)
543 (Mayo-Bean et al., 2012). Similar considerations hold for **CPPC** and **EPTFB**.

544

545 **4. Conclusions**

- 546 • Phototransformation in sunlit surface waters is a potentially important attenuation pathway for
547 **BMPOTFB** but not for **EPTFB** and **CPPC**, with the possible exception of shallow water
548 bodies with very low DOC.
- 549 • The phototransformation of **BMPOTFB** is expected to proceed through $\text{CO}_3^{\bullet-}$ reactions at
550 low DOC and *via* direct photolysis at higher DOC. In water bodies that are rich in pedogenic
551 organic matter (humic and fulvic substances), also the $^3\text{CDOM}^*$ reactions could play an
552 important role at elevated DOC.
- 553 • The phototransformation of **EPTFB** and **CPPC** is extremely slow in high-DOC waters, thus
554 the most relevant photochemical attenuation pathways (provided that the water body is
555 shallow) are those prevailing at low DOC: $\text{CO}_3^{\bullet-}$, direct photolysis and, for **EPTFB** alone,
556 $\bullet\text{OH}$.
- 557 • The direct photolysis of **BMPOTFB** and **CPPC** yields TPs that are more toxic than the parent
558 compound. The main identified reaction pathways upon direct photolysis are hydroxylation,
559 lateral-chain shortening and ring opening, and toxic TPs might be formed by multiple
560 hydroxylation if this process yields hydroquinone-like derivatives.

561

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