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(Article begins on next page)

1 **The role of direct photolysis in the photodegradation of the herbicide**
2 **bentazone in natural surface waters**

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10

11 **Abstract**

12 The photochemical fate of the herbicide bentazone was assessed by lab experiments and modeling
13 tools. Experimental and modeling results showed that bentazone is mainly photodegraded by direct
14 photolysis in natural water samples, even in the presence of dissolved organic matter (DOM) that
15 can act as light-screening agent, photosensitizer and scavenger of reactive species. Even when it
16 was dissolved in natural water samples containing different DOM amounts, the phototransformation
17 kinetics of bentazone was unchanged compared to irradiation runs in ultrapure water. This finding
18 suggests that the DOM and the other components of our samples did not affect the direct photolysis
19 of bentazone by light-absorption competition, at least at the experimental optical path lengths, and
20 did not induce significant indirect photodegradation by producing reactive transient species.
21 Photochemical modeling in a lake-water photoreactivity scenario corroborated the observed
22 experimental results, showing the predominant role of direct photolysis in the overall (direct +
23 indirect) photodegradation of bentazone at different water depths and DOM contents. However, the
24 model predicted a minor but non-negligible contribution of indirect photochemistry (i.e., reactions
25 triggered by HO[•], CO₃^{•-} and ³CDOM*) to the herbicide degradation. This contribution (especially

26 by ³CDOM*) could become crucial in deep and DOM-rich water bodies. Finally, several
27 photoproducts formed by direct photolysis and HO[•]-induced photodegradation were identified,
28 which should not be particularly toxic for aquatic organisms and *Vibrio fischeri* bacteria.

29

30 **Keywords:** Photochemistry; Pesticides; Photochemical modeling; APEX; Photodegradation
31 intermediates.

32

33

34 **1. Introduction**

35 Pesticides are widespread micropollutants in surface and groundwaters (Luo et al., 2014; Masiá et
36 al., 2015; Metcalfe et al., 2019), and they cause considerable environmental concern because of
37 their toxic effects on aquatic ecosystems (Ccanccapa et al., 2016; Silva et al., 2015). After
38 application on crops, pesticides can reach groundwaters and surface waters, including streams and
39 lakes, because of leaching and soil runoff processes (Battaglin et al., 2003; Lupi et al., 2019; Milan
40 et al., 2015; Riise et al., 2004). Moreover, water contamination by pesticides is favored by the close
41 link between some crops and the aquatic systems. The latter provide water used for irrigation
42 purposes or, in the case of some paddies, for fish-farming activities (Clasen et al., 2018; Milan et
43 al., 2012). Fortunately, many pesticides are not recalcitrant in water environments and they can be
44 transformed through chemical (e.g., hydrolysis) and biological processes, as well as photochemical
45 reactions in sunlit surface waters (Fenner et al., 2013). Hydrolysis often depends upon water pH and
46 it is faster in acidic and basic conditions, which means that the pH values of natural waters often
47 coincide with a minimum in the hydrolysis kinetics. However, this process can still be an important
48 dissipation pathway for some pesticides (Liu et al., 2001; Ramesh and Balasubramanian, 1999;
49 Tebes-Stevens et al., 2017; Williams and Tjeerdema, 2016). Compared to hydrolysis, biotic and
50 abiotic photochemical degradations usually play a more important role in the environmental fate of

51 pesticides. Biodegradation is often a key dissipation route (Fenner et al., 2013), but it strongly
52 depends upon the considered xenobiotic and aquatic system (Katagi, 2013). Photochemical
53 reactions may be major transformation pathways for several pesticides and their metabolites
54 (Adachi et al., 2018; Burrows et al., 2002; Konstantinou et al., 2001; Remucal, 2014). These
55 reactions can be distinguished into direct photolysis and indirect photochemistry. Direct photolysis
56 refers to the transformation of a molecule upon direct light absorption. Indeed, some pollutants are
57 able to absorb sunlight, reach excited molecular states and then undergo chemical transformation
58 (Katagi, 2018). Direct photolysis can be inhibited by competitive light-absorbing compounds,
59 including most notably the dissolved organic matter (DOM) that naturally occurs in surface waters.
60 The DOM chromophoric moieties (CDOM) can both screen radiation and act as photosensitizers to
61 trigger the indirect photodegradation of water pollutants. Indeed, upon sunlight absorption CDOM
62 forms the so-called *Photochemically Produced Reactive Intermediates* (PPRIs), which react with
63 water contaminants and cause their degradation. The most important PPRIs are hydroxyl and
64 carbonate radicals (HO^\bullet and $\text{CO}_3^{\bullet-}$, respectively, which are also generated by the photolysis of
65 nitrate and nitrite), the excited triplet states of CDOM (${}^3\text{CDOM}^*$), as well as singlet oxygen (${}^1\text{O}_2$)
66 (Vione et al., 2014). Despite their effectiveness in degrading several pollutants including many
67 pesticides (Remucal, 2014), photoreactions yield in some cases photoproducts of considerable
68 environmental concern, which may be toxic to aquatic organisms (Bavcon Kralj et al., 2007; Carena
69 and Vione, 2018; Dong and Hu, 2016). Furthermore, also the biotic degradation processes can be
70 problematic as shown in the case of the herbicide propanil (Carena et al., 2017; Kanawi et al., 2016;
71 Roehrs et al., 2012).

72 In the present study, the role of direct and indirect photolysis was assessed towards the
73 photodegradation of bentazone (hereinafter BNTZ) in surface water samples. BNTZ is a post-
74 emergence herbicide used in different crops such as wheat, rice and beans, to control weed growth.
75 Because of soil leaching phenomena (Lammoglia et al., 2018), BNTZ has been detected in rivers,
76 coastal waters and groundwaters (Palma et al., 2018; Papadakis et al., 2018; Kock-Schulmeyer et

77 al., 2019). As shown in previous studies, BNTZ is photolabile in natural waters (coastal lagoon),
78 and it has been degraded in laboratory experiments by 81% via direct photolysis and by 17% via
79 photosensitized processes (Al Housari et al., 2011). In that case, the predicted photochemical
80 lifetime of BNTZ was ~12 days by considering only direct photolysis and HO[•] reactions (Al
81 Housari et al., 2011). Here we assessed the transformation of BNTZ by all the potentially important
82 photoreaction pathways in fresh waters (direct photolysis, HO[•] radicals, ³CDOM*, ¹O₂ and CO₃^{•-};
83 Katagi, 2018; Vione et al., 2014). Moreover, we identified the BNTZ photoproducts formed by the
84 main processes, evaluating their environmental importance by means of photochemical modeling,
85 and assessing the time evolution of acute toxicity.

86

87 **2. Materials and Methods**

88

89 **2.1 Reagents**

90 Gradient-grade methanol for HPLC analysis was purchased from VWR Chemicals BDH®. All the
91 other compounds were bought from Sigma-Aldrich (analytical grade) and used as received, without
92 further purification. Ultra-pure water was produced by a Milli-Q system (Millipore, 18.2 MΩ cm
93 resistivity, 2 ppb TOC).

94 The stock solutions of BNTZ (pK_a ~ 3.3 at 24 °C; O'Neil, 2013) were prepared weekly by
95 dissolving the compound in ultra-pure water under magnetic stirring. Their natural acidic pH (<4.5,
96 thereby outside the environmental significance range) was adjusted to 7.0 with NaOH 0.1 mol L⁻¹.

97 The stock solutions were stored in the dark at ~5 °C.

98

99 **2.2 Lake and paddy water samples**

100 The real water samples used in this work were taken from four small- to medium-sized lakes and a
101 rice field, all located in the Piedmont region (NW Italy). The paddy water was sampled during the

102 2016 spring season, while the lake water samples were collected in February 2017. After collection,
103 the samples (~1 L) were transported to the lab refrigerated and in the dark. Upon arrival, they were
104 immediately vacuum-filtered with polyamide filters (0.45 μm pore size, Sartorius). The filtered
105 samples were kept in the dark at ~ 5 $^{\circ}\text{C}$ till the irradiation experiments, to prevent modifications
106 caused by residual biological activity. The origin of the samples and their dissolved organic carbon
107 (DOC) and pH values were as follows: Lake Maggiore (DOC = 0.44 $\text{mg}_\text{C} \text{L}^{-1}$, pH 6.6), Avigliana
108 Lake (3.1 $\text{mg}_\text{C} \text{L}^{-1}$, 7.8), Candia Lake (4.0 $\text{mg}_\text{C} \text{L}^{-1}$, 7.5), Viverone Lake (4.1 $\text{mg}_\text{C} \text{L}^{-1}$, 7.5), Santhià
109 rice-field (2.4 $\text{mg}_\text{C} \text{L}^{-1}$, 7.3). The absorption spectra of the natural water samples are shown in **Fig.**
110 **SM-1** in the Supplementary Material (SM).

111

112 **2.3 Irradiation experiments**

113 Spiked solution aliquots (20 mL, 20 $\mu\text{mol} \text{L}^{-1}$ BNTZ) in both ultra-pure water adjusted to pH 7.0
114 and real water samples were irradiated in cylindrical Pyrex glass cells, under a Philips TL K05 lamp
115 (40 W) that mainly emits UVA radiation. The rationale for using this lamp was the following: (i)
116 BNTZ mostly absorbs radiation in the UV region, thus most of its photochemistry would take place
117 where the lamp emits; (ii) the majority of the photoprocesses triggered by sunlit CDOM take place
118 in the UV and especially the UVA region (see SM for details). The chosen initial BNTZ
119 concentration was the lowest that still allowed for reliable quantification by liquid chromatography
120 (*vide infra*). This concentration level was also low enough to avoid self-sensitization processes
121 (photodegradation of a compound, triggered by the excited states of the same molecule; Bedini et
122 al., 2012).

123 The UV irradiance of the lamp ($12.3 \pm 0.9 \text{ W m}^{-2}$ in the 290-400 nm range) was measured with an
124 irradiance meter by CO.FO.ME.GRA. (Milan, Italy). The solutions were magnetically stirred during
125 irradiation. A detailed description of the irradiation system can be found in the SM of Carena et al.
126 (2017).

127 The lamp radiation reached the solutions mainly from the top. However, to properly take into
128 account the multiple reflection phenomena that typically occur in photoreactors, chemical
129 actinometry was used to measure the spectral photon flux density in solution. 2-Nitrobenzaldehyde
130 (2NBA, $100 \mu\text{mol L}^{-1}$ initial concentration) was used as chemical actinometer (Galbavy et al., 2010;
131 Marchisio et al., 2015; Willet and Hites, 2000). The detailed method has been reported by
132 Marchisio et al. (2015). The 2NBA solutions were irradiated in the same cells used for BNTZ
133 irradiation, under the same lamp and using the same irradiation volume.

134 **Fig. SM-2** shows the spectral photon flux density of the used lamp, together with the UV-visible
135 absorption spectrum of BNTZ. The two spectra overlap between 300 and 390 nm, which is also the
136 spectral range where BNTZ absorbs sunlight. The BNTZ photodegradation profiles followed
137 pseudo-first order kinetics (note that the reactions with PPRI follow second-order kinetics, but
138 PPRI themselves are in steady-state; their concentrations being constant during irradiation, the
139 second order reduces to a pseudo-first order). The time trends were fitted with the equation $C_t =$
140 $C_o \cdot \exp(-k' \cdot t)$. Here, k' is the experimental pseudo-first order degradation rate constant, calculated by
141 fitting the relevant degradation curves, t is the irradiation time, C_o the initial BNTZ concentration
142 ($20 \mu\text{mol L}^{-1}$), and C_t the BNTZ concentration at the irradiation time t . The initial degradation rates
143 of BNTZ were computed as $R = k' C_o$.

144 To quantify the BNTZ concentration at each scheduled irradiation time (C_t), solutions aliquots (1.2
145 mL) were sampled through the lateral neck of the glass cells, which were otherwise kept tightly
146 closed during irradiation. Aliquots were then analyzed by High-Performance Liquid
147 Chromatography coupled with Diode Array Detection (HPLC-DAD, *vide infra*). In order not to
148 affect too much the initial optical depth (1.6 cm), each solution was sampled only twice causing ~
149 12% maximum volume variation. This is well within the typical variability of this kind of
150 experiments.

151 The kinetic assessment of the dark BNTZ degradation (blank experiments) caused by, e.g.,
152 hydrolysis and/or biodegradation was carried out by placing both synthetic and real water samples,
153 spiked with BNTZ, in glass cells wrapped with double aluminum foil, under the irradiation lamp.
154 The rationale for placing them under the lamp was to achieve comparable temperature and stirring
155 conditions as for the irradiated samples.
156 All the irradiation experiments were carried out in duplicate, and the data points were then plotted
157 as average values plus-or-minus the standard error.

158

159 **2.4 Identification of the BNTZ photoproducts**

160 Aqueous BNTZ solutions (1 mmol L^{-1}) at pH 7 were irradiated inside a total of three cylindrical
161 Pyrex glass cells as reported in paragraph 2.3. Analysis by Gas Chromatography-Mass
162 Spectrometry (GC-MS) then followed, after SPME (Solid Phase Micro-Extraction) of samples at
163 different irradiation times ($t = 0, 24\text{h}, 48\text{h}$ and 72h). The sample solutions (total pooled volume of
164 60 mL) were divided into three aliquots of 20 mL each, and the pH was adjusted to 4, 7 and 10. The
165 goal was to maximize the SPME extraction of photoproducts with different acid-base properties.
166 The SPME procedure was as follows: a DVB/CAR/PDMS, 57914-U fiber was immersed into the
167 sample solution at $24 \text{ }^\circ\text{C}$ under magnetic stirring. After 30 min, the fiber was introduced into the GC
168 injector where the adsorbed compounds were thermally desorbed and injected into the GC column
169 (ZB-624, 30 m length, 0.25 mm ID, $1.4 \text{ }\mu\text{m}$ Film Thickness).

170 A similar procedure was applied to identify the indirect photoproducts of BNTZ. In this case, an
171 aqueous solution of bentazone (1 mmol L^{-1}) and H_2O_2 (0.1 mol L^{-1}) at pH 7 was exposed to light as
172 reported in paragraph 2.3, and analyzed by SPME GC-MS as before (including the pH adjustment
173 to 4, 7 and 10), after 0h, 4h, 16h and 30h of irradiation. H_2O_2 was used as HO^\bullet source, and the
174 irradiated solutions containing H_2O_2 in ultra-pure water are virtually free of $^3\text{CDOM}^*$ and $\text{CO}_3^{\bullet-}$ as
175 potentially interfering PPRIs.

176

177 **2.5 Assessment of the BNTZ toxic effects with experimental (*Vibrio fischeri*) and *in-silico***
178 **methods**

179 The assessment of the toxicity towards aquatic microorganisms of both BNTZ and its
180 photoproducts was carried out experimentally by using *Vibrio fischeri* bacteria, and *in silico* by
181 QSAR modeling.

182 Acute toxicity of samples collected at different irradiation times was evaluated with a Microtox
183 Model 500 Toxicity Analyzer (Milan, Italy). This assay exploits the bioluminescence changes of the
184 marine bacterium *Vibrio fischeri* by monitoring the inhibition in the natural emission of the
185 luminescent bacteria when challenged with toxic compounds. Freeze-dried bacteria, reconstitution
186 solution, diluent (2% NaCl) and an adjustment solution (non-toxic 22% sodium chloride) were
187 obtained from Azur (Milan, Italy). Samples were tested in a medium containing 2% sodium
188 chloride, and luminescence was recorded after 5, 15 and 30 min of incubation at 15 °C. No
189 substantial differences were found between the three contact times. Inhibition of luminescence,
190 compared with a toxic-free control to give the percentage inhibition, was calculated following the
191 established protocol and using the Microtox calculation program.

192 QSAR modeling was performed by means of the freely available ECOSAR V2.0 software
193 [Ecological Structure Activity Relationships (ECOSAR) Class Program], developed by the U.S.
194 Environmental Protection Agency (EPA) (Mayo-Bean et al., 2012). ECOSAR computes both acute
195 (LC₅₀ and EC₅₀) and chronic (ChV = Chronic Value) toxicity parameters toward aquatic organisms
196 on the basis of the molecular structure of the considered neutral organic compound. In particular,
197 toxicity outputs are fish 96h - LC₅₀, daphnid 48h – LC₅₀ and green algae 96h – EC₅₀. In contrast, the
198 ChV is computed as the geometric mean of NOEC (no-observed-effect concentration) and LOEC
199 (lowest-observed-effect concentration) (Mayo-Bean et al., 2012). Furthermore, the computed LC₅₀,
200 EC₅₀ and ChV values related to Log K_{ow} > 5, > 6.4 and > 8, respectively, were here neglected
201 (Mayo-Bean et al., 2017a).

202

203 **2.6 HPLC-DAD, GC-MS, DOC, pH and UV-Vis absorption measurements**

204 The HPLC-DAD instrument used to quantify BNTZ during the irradiation experiments was a
205 VWR-Hitachi LaChrom Elite chromatograph equipped with L-2200 autosampler (injection volume
206 60 μL), L-2130 quaternary pump for low-pressure gradients, Duratec vacuum degasser, L-2300
207 column oven (set at 40 $^{\circ}\text{C}$), and L-2455 photodiode array detector. The column was a VWR
208 LiChroCART 125-4 Cartridge, packed with LiChrospher 100 RP-18 (125mm \times 4mm \times 5 μm). Elution
209 was carried out in isocratic mode with a mixture of 58% ultrapure water (acidified at pH \sim 2.8 with
210 phosphoric acid) and 42% methanol, with a total flow rate of 1.0 mL min^{-1} (column dead time \sim 1.0
211 min). The BNTZ elution time was 8.9 min and the detection wavelength was 221 nm.

212 GC-MS analytical determinations were performed using an Agilent 6890N Network GC System
213 coupled with an Agilent 5973 Inert Mass Spectrometer, operating in the electron impact ionization
214 mode. Source was kept at a temperature of 270 $^{\circ}\text{C}$. The oven temperature was programmed as
215 follows: initial column temperature was 40 $^{\circ}\text{C}$ for 5 min, then increased by 15 $^{\circ}\text{C min}^{-1}$ to 260 $^{\circ}\text{C}$,
216 and finally keeping it steady at 260 $^{\circ}\text{C}$ for 8.33 min, for a total run time of 28 min. The carrier gas
217 was ultra-pure He (1.0 mL min^{-1} ; SIAD, Bergamo, Italy). Full mass spectra were acquired from m/z
218 29 to m/z 500.

219 The total dissolved organic carbon (DOC) of lake and paddy water samples was determined by
220 using a Shimadzu TOC-VCSH instrument, equipped with an ASI-V autosampler. The DOC was
221 calculated as the difference between total (dissolved) carbon (TC) and inorganic carbon (IC).

222 The pH of the samples was measured with a combined glass electrode, connected to a Metrohm 602
223 pH meter.

224 The UV-Vis absorption spectra of the lake and paddy water samples were measured with a V-550
225 Jasco spectrophotometer, using a 5.0 cm optical path quartz cuvette (Hellma).

226

227 **2.7 Photochemical modeling**

228 The photochemical fate of BNTZ in environmental waters (namely, its pseudo-first order
229 photodegradation rate constants and the corresponding half-life times) was modeled with the APEX
230 software (Bodrato and Vione, 2014). APEX can model the direct and indirect photochemistry of
231 pollutants in well-mixed surface waters, such as the whole water column of lakes during overturn,
232 but also their epilimnion during summer stratification, and even the floodwater of rice fields (e.g.
233 Carena and Vione, 2018).

234 Briefly, APEX requires as input data the chemical and photochemical features of the water body
235 (i.e., concentration of photosensitizers and scavengers of the PPRIs, water absorption spectrum and
236 water depth), as well as the photoreactivity parameters of the considered xenobiotic (i.e., the UV-
237 visible absorption spectrum, the direct photolysis quantum yield and the second-order rate constants
238 for the reactions with the different PPRIs). **Table SM-2** shows the relevant parameters of BNTZ
239 photoreactivity used in the modeling. The output values of the photodegradation kinetics are
240 averaged over the entire water column depth.

241 Here, the software was run supposing a clear-sky scenario corresponding to July 15th at 45°N
242 latitude. The corresponding time unit (default in APEX), the so-called Summer Sunny Day (SSD),
243 is equivalent to 10h of continuous irradiation at 22 W m⁻² UV irradiance under clear-sky sunlight.

244

245 **3. Results and Discussion**

246

247 **3.1 BNTZ photodegradation and its photochemical modeling**

248 **Fig. 1a** shows the experimental degradation profiles of BNTZ under irradiation. No dark
249 degradation of BNTZ was observed (data not shown) in either ultrapure water or lake/paddy water
250 samples. This finding agrees with previous works showing no BNTZ hydrolysis or biodegradation,
251 in either synthetic or real water samples (Al Housari et al., 2011; Song et al., 2019; Zeng and

252 Arnold, 2013). No significant difference between the BNTZ direct photolysis in ultrapure water and
 253 its phototransformation in natural waters was observed. The BNTZ photodegradation rate in natural
 254 water samples (R_{DOM}) and that in ultrapure water (R_{H2O}) yielded $R_{DOM} = 0.90-0.95 R_{H2O}$ (see **Fig.**
 255 **1b**). Several previous works have shown that some pollutants undergo inhibition of direct
 256 photodegradation in the presence of DOM, basically because of competition for irradiance with the
 257 chromophoric DOM moieties (CDOM) (e.g., Dimou et al., 2004; Malouki et al., 2004; Walse et al.,
 258 2004). To assess the possible role of light screening by CDOM on BNTZ photodegradation, the
 259 ratio between the photon absorption rate of BNTZ in both real samples ($P_{a,DOM}$) and ultrapure water
 260 ($P_{a,H2O}$) was computed as follows (**Eq.1**):

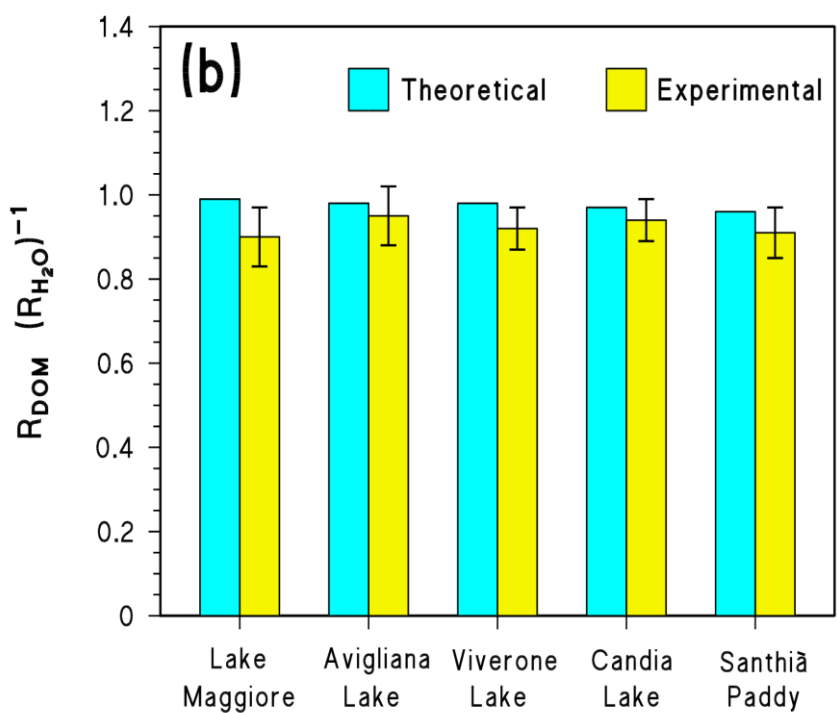
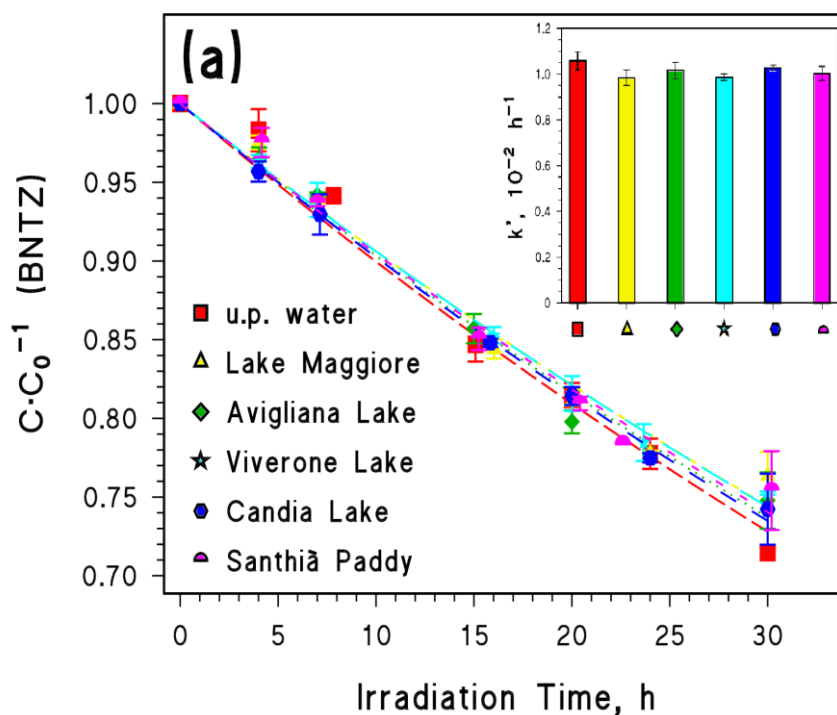
$$\frac{R_{DOM}}{R_{H2O}} = \frac{P_{a,DOM}}{P_{a,H2O}} = \frac{\int_{\lambda_1}^{\lambda_2} p^0(\lambda) \frac{A_{\lambda,BNTZ}}{A_{\lambda,tot}} [1 - 10^{-A_{\lambda,tot}}] d\lambda}{\int_{\lambda_1}^{\lambda_2} p^0(\lambda) [1 - 10^{-A_{\lambda,BNTZ}}] d\lambda} \quad (\text{Eq. 1})$$

261 where $p^0(\lambda)$ is the spectral photon flux density of the lamp in solution (**Fig. SM-2**), while $A_{\lambda,BNTZ}$
 262 and $A_{\lambda,tot}$ are the Lambert-Beer absorbance values of, respectively, BNTZ and the whole irradiated
 263 solution (*i.e.*, $A_{\lambda,tot} = A_{\lambda,CDOM} + A_{\lambda,BNTZ}$). The choice of λ_1 and λ_2 was linked to the spectral-
 264 range overlap of lamp emission and BNTZ absorption (300-392 nm).
 265 range overlap of lamp emission and BNTZ absorption (300-392 nm).

266 The theoretical values of $R_{DOM} (R_{H2O})^{-1}$ calculated with **Eq. (1)** are reported in **Fig. 1b** (blue bars),
 267 showing 1-5% difference with the experimental ratios (yellow bars). This difference is well within
 268 the typical uncertainty of the irradiation technique. Therefore, at least at the optical path lengths of
 269 the irradiation experiments BNTZ was mainly degraded by direct photolysis, and it can be safely
 270 assumed that light screening by CDOM can account for the small differences between ultra-pure
 271 and natural water samples.

272 However, UV radiation that illuminates laboratory solutions, and that is efficiently absorbed by
 273 both CDOM and several organic compounds such as BNTZ, poorly penetrates in real deep water
 274 columns in the presence of CDOM (Bracchini et al., 2004; Rose et al., 2009).

275

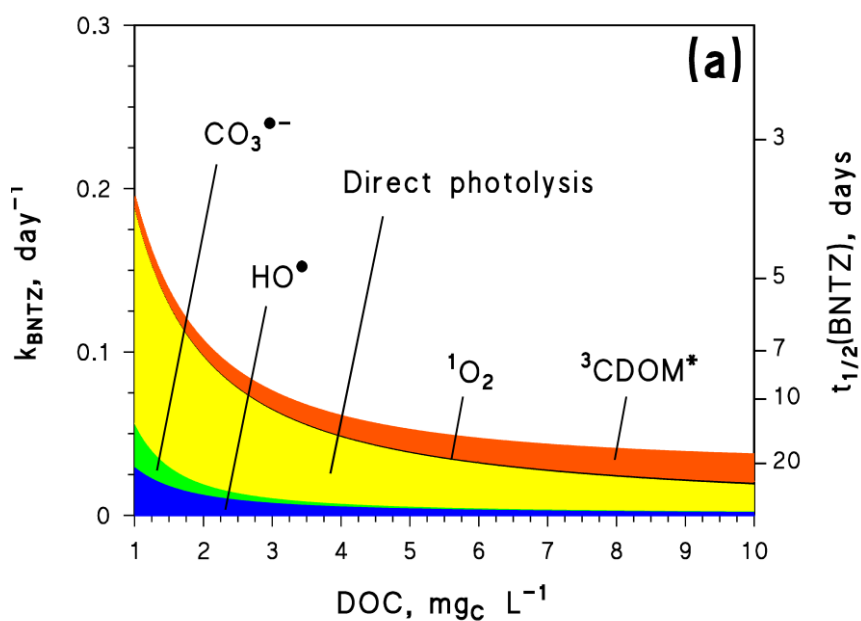


279 **Fig. 1.** (a) BNTZ photodegradation profiles in different aqueous matrices. Inset: experimental k' values for
 280 BNTZ photodegradation. (b) DOM-induced inhibition (light screening) of BNTZ photodegradation assessed
 281 as both theoretical and experimental ratio between the BNTZ degradation rate in real water samples and in
 282 ultrapure water ('u.p. water').

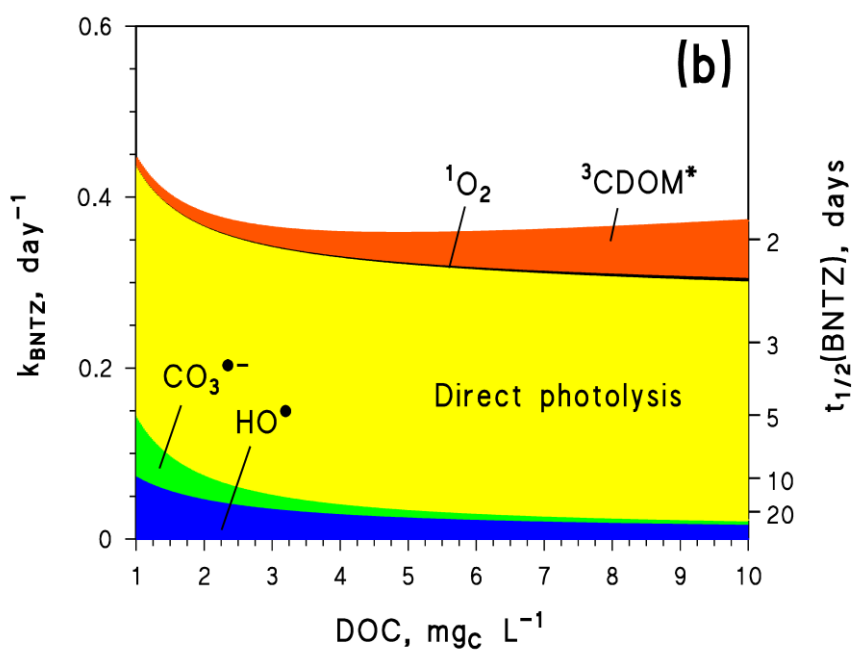
284 In contrast, visible light penetrates more deeply in water and it is absorbed by CDOM as well,
285 thereby increasing the importance of CDOM-related photoprocesses (including $^3\text{CDOM}^*$ reactions)
286 vs. direct photolysis in deep water bodies (Canonica, 2007; McNeill and Canonica, 2016).
287 Consequently, the relative importance of the $^3\text{CDOM}^*$ reactions is often higher in the natural
288 environment than in laboratory irradiation systems, because of differences in the water column
289 depth and the related optical path length (Bianco et al., 2015; **Fig SM-4**). Therefore, because the
290 second-order rate constant of the reaction between BNTZ and $^3\text{CDOM}^*$ has been estimated to be
291 quite high with steady-state irradiations experiments in real water samples (Zeng and Arnold, 2013;
292 see also **Table SM-2**), $^3\text{CDOM}^*$ could play an important role in the overall phototransformation of
293 BNTZ. Because elevated water depths are hardly accessible to experimentation, it is interesting to
294 model the photochemical behavior of BNTZ in natural water bodies.

295 The modeling of BNTZ photodegradation in lake water (3 m lake water depth, 15th of July at 45°N)
296 agrees reasonably well with the experimental findings (**Fig. 2a**). The direct photolysis is predicted
297 to be the main phototransformation pathway of the herbicide, while the roles of HO^\bullet and $\text{CO}_3^{\bullet-}$ are
298 quite low between 1 and 5 $\text{mg}_\text{C} \text{L}^{-1}$. The importance of HO^\bullet and $\text{CO}_3^{\bullet-}$ reactions becomes even
299 negligible for $\text{DOC} > 5 \text{ mg}_\text{C} \text{L}^{-1}$. $^1\text{O}_2$ is not important as well in our scenario, although $^1\text{O}_2$ can be
300 the major PPRI photodegrading BNTZ in prairie potholes with high DOM content between 20 and
301 38 $\text{mg}_\text{C} \text{L}^{-1}$. In these environments, direct photolysis is limited to 40-45% of the total BNTZ
302 photodegradation (Zeng and Arnold, 2013). According to our model results, at so high DOC levels
303 the main role in BNTZ degradation would be played by $^3\text{CDOM}^*$ instead of $^1\text{O}_2$, which is expected
304 to give a minor contribution to the process. The main reason for this difference could be due to the
305 fact that CDOM in prairie potholes has very different photoreactivity than that assumed by the
306 APEX software, which has been designed around lake-water CDOM and its photoreactivity.
307 Coming back to the modeled lake-type environment (**Fig. 2**), the results also suggest that BNTZ
308 could be significantly degraded by $^3\text{CDOM}^*$ at $\text{DOC} > 2 \text{ mg}_\text{C} \text{L}^{-1}$. This makes a difference with the

309 irradiation experiments, where lake/paddy water from Avigliana, Viverone, Candia and Santhià had
310 $\text{DOC} > 2 \text{ mg}_C \text{ L}^{-1}$. However, the optical path length of the irradiated samples was much shorter (1.4
311 - 1.6 cm) than the water column depths found in the most reasonable environmental scenarios,
312 including the modeled one. We can thus speculate that differences in water-column depth may
313 account for the different relative roles of direct photolysis and $^3\text{CDOM}^*$ reaction between model
314 output and experimental results. Indeed, by lowering the water depth to 1.5 cm (**Fig. 2b**), which is
315 comparable to the optical path length of our experiments, the direct photolysis assumes much higher
316 importance than in the 3-m depth scenario. The model still predicts some minor role for HO^\bullet , $\text{CO}_3^{\bullet-}$
317 and $^3\text{CDOM}^*$ in BNTZ degradation, which might or might not be highlighted experimentally given
318 the uncertainties in both model results and irradiation runs. The fact that the irradiation experiments
319 seem to exclude a significant role of indirect photochemistry (**Fig. 1b**) may have the following
320 explanations: (i) the importance of indirect photoreactions is comparable to the experimental
321 uncertainty, and it is thus not or hardly appreciable; (ii) the CDOM photoreactivity assumed in the
322 model (average freshwater conditions) is higher compared to that of the studied samples; (iii) DOM
323 inhibits the BNTZ degradation because of back-reduction processes due to its intrinsic antioxidant
324 activity (Canonica and Laubscher, 2008; Leresche et al., 2016; Wenk and Canonica, 2012).
325 However, the indirect photochemistry of $^3\text{CDOM}^*$ could become the main BNTZ
326 phototransformation pathway in a deep water body with a high DOM content ($\text{DOC} = 10 \text{ mg}_C \text{ L}^{-1}$,
327 depth $> 3 \text{ m}$, see **Fig. SM-4**). In that case, the BNTZ direct photolysis would be overcome by
328 $^3\text{CDOM}^*$ photochemistry because of the light penetration issues explained above. However, in deep
329 and DOM-rich water bodies the photoreaction kinetics would be quite slow, and other non-
330 photoinduced processes could become important or even dominate the degradation of BNTZ.
331 The reactions with HO^\bullet and $\text{CO}_3^{\bullet-}$ could be the second most important photodegradation pathway of
332 BNTZ at low DOC. Their importance could be increased in the presence of elevated nitrate and/or
333 nitrite concentration values (see **Fig. SM-5**).



334



335

336

337 **Fig. 2.** Pseudo-first order rate constants (left Y-axis) and half-life times (right Y-axis) of BNTZ in a lake
 338 water column of (a) 3 m and (b) 1.5 cm depth. The assumed water chemical composition was: $100 \mu\text{mol L}^{-1}$
 339 NO_3^- , $1 \mu\text{mol L}^{-1} \text{NO}_2^-$, $1 \text{mmol L}^{-1} \text{HCO}_3^-$, and $10 \mu\text{mol L}^{-1} \text{CO}_3^{2-}$. The day time unit refers to fair-weather
 340 15 July at 45°N latitude.

341

342 Our model results agree well with the reported photochemical half-life time of BNTZ, which has
343 been predicted by Al Housari et al. (2011) to be ~12 days in a coastal lagoon on the basis of
344 irradiation experiments. In the same work, field data suggested the BNTZ lifetime to be about 5-15
345 days, which is compatible as well with the range predicted by APEX (**Fig. 2a**). Because BNTZ
346 biodegradation can be slow (Al Housari et al., 2011; Song et al., 2019), and because we did not
347 observe significant BNTZ degradation in natural waters in the dark, we can predict that
348 photochemistry (and in particular the direct photolysis) could play an important role in the total
349 BNTZ dissipation in lake water.

350

351 **3.2 BNTZ degradation products**

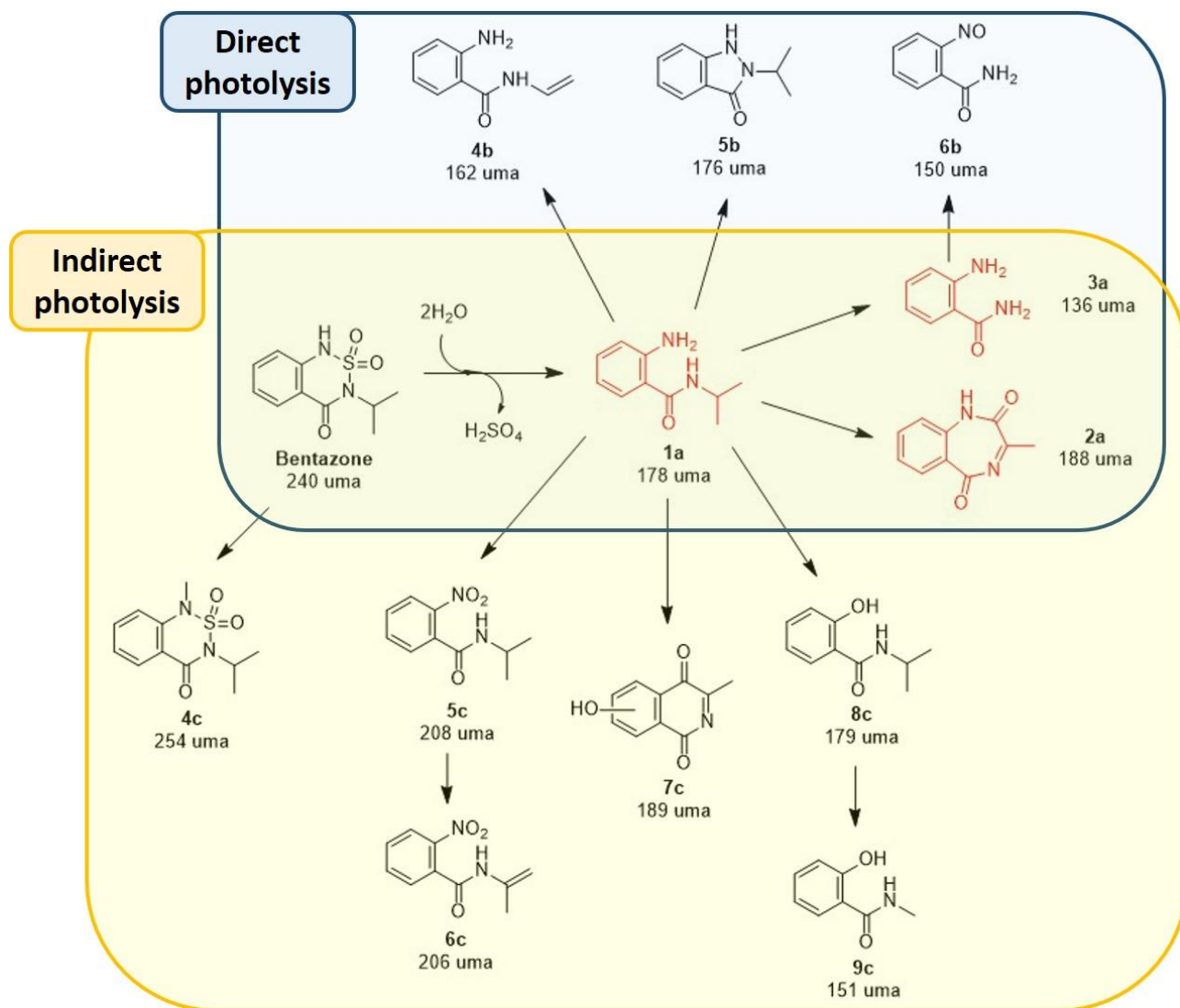
352 GC-MS analyses were carried out on irradiated solutions of BNTZ to identify the photoproducts.
353 Their characterization may provide further information about the transformation mechanisms of the
354 herbicide, and it can also be useful to assess and explain the time trend of toxicity. Indeed, it has
355 been shown for some pollutants that the degradation products may be more persistent and toxic than
356 the parent compound (Bavcon Kralj et al., 2007; Erickson et al., 2012; Isidori et al., 2009;
357 Passananti et al., 2015; Vogna et al., 2004). This issue is often underestimated, but it should be
358 taken into account in order to properly assess the environmental impact of a pollutant.

359 The products derived by direct and indirect photolysis were identified by GC-MS. Some
360 photoproducts were identified in all the extraction conditions (pH 4, 7 and 10), while others were
361 adsorbed on the fiber only at specific pH values.

362 **Fig. 3** shows the possible molecular structures of the BNTZ photodegradation products in pure
363 water and in the presence of HO[•] radicals, generated by H₂O₂ photolysis, proposed on the basis of
364 the GC-MS analysis. The rationale for the choice of the two processes is that direct photolysis is the
365 main BNTZ photoreaction, while HO[•] may play an important role at low DOC and low water depth,
366 where photoreactions are fast and thus very competitive with additional processes (**Fig. 2a**). The
367 compounds detected in both conditions (direct and indirect photolysis) are highlighted in red. The

368 main BNTZ photoproduct observed after 72h of irradiation (direct photolysis) is the
369 photohydrolysis compound **1a**, derived by the cleavage of the amide N-S and amine N-S bonds.
370 This compound has been identified previously as a BNTZ degradation product (Nilles and Zabik,
371 1975; Song et al., 2019), and its formation generates sulfuric acid that could further catalyze
372 degradation reactions. 2-Amino-*N*-isopropylbenzamide (**1a**) may absorb light and undergo a
373 Norrish type II reaction to produce the benzamide **3a** (White et al., 1996). A di-radical species
374 photogenerated by **1a** could also produce compound **4b**, as well as the bicyclic compound **5b**
375 through an intramolecular reaction. Also the bicycle **2a** could derive from **1a** via intramolecular
376 recombination with the isopropyl chain and further oxidation. Finally, the oxidation of the aromatic
377 amine may lead to the nitroderivative **6b**.

378 The irradiation of BNTZ in the presence of H₂O₂ (indirect photolysis) for 30h yielded several
379 products, some of which (**1a**, **2a** and **3a**) were also observed in direct photolysis. Except for *N*-
380 methylbentazone (**4c**), all the detected compounds do not contain sulfur in the molecular structure.
381 This finding suggests that photohydrolysis to **1a** is the main degradation pathway also in the case of
382 HO•. However, we cannot exclude the possibility that compound **1a** actually derives from BNTZ
383 direct photolysis rather than exclusively from the HO•-induced reactions. Indeed, although the H₂O₂
384 concentration was 100-fold higher than that of BNTZ, the molar absorption coefficient of the latter
385 species is nevertheless higher of the same order of magnitude. Therefore, BNTZ absorbs light at
386 least as well as H₂O₂, and in irradiated H₂O₂ solutions its direct photolysis can occur at the same
387 time as degradation by HO•. Another evidence of the loss of sulfur from BNTZ was the solution pH
388 decrease from 7 to 4 during light exposure, presumably because of the formation of H₂SO₄. These
389 findings are quite in contrast with the results obtained by Peschka et al. (2007), who have not
390 observed the loss of sulfur from BNTZ during irradiation in water enriched with inorganic salts and
391 organic matter. *N*-methylbentazone (**4c**) has been already identified as a transformation product of
392 BNTZ by Song et al. (2019), during irradiation of water/methanol and water/ethyl acetate solutions.
393 Those conditions could have allowed the BNTZ methylation by the solvent itself.



395

396

397 **Fig. 3.** Possible degradation pathways of BNTZ under UV irradiation in water (inside the blue box, direct
 398 photolysis) and in the presence of UV + H_2O_2 (inside the yellow box, indirect photolysis by HO^\bullet). The
 399 products included in the overlapping area of the yellow and blue boxes, highlighted in red for higher clarity,
 400 were observed in both conditions. The recorded mass spectra are reported in the SM (from **Fig. SM-7 to Fig.**
 401 **SM-10**).

402

403

404 In our case, however, BNTZ was irradiated in water (without organic solvent) at quite a high
405 concentration (1 mmol L⁻¹). Such conditions might perhaps trigger some cross-reactions between
406 different BNTZ molecules, leading to the formation of **4c**. Consequently, the formation of **4c** in our
407 samples might be an artifact and it should be still verified in environmentally relevant conditions,
408 where BNTZ occurs at lower concentration values. To our knowledge, compounds **6c**, **7c** and **9c**
409 have never been identified as products of BNTZ degradation, and they have thus been observed in
410 this work for the first time.

411 It has already been reported in the literature that **5c** and **8c** are BNTZ transformation products
412 obtained under photolytic (Nilles and Zabik, 1975), photocatalytic (UV + TiO₂) and HO[•]-induced
413 degradation conditions (Mir et al., 2014; Guelfi et al., 2019). Product **5c** derives from the oxidation
414 of the aromatic amine group, while the substitution of this latter with OH could lead to **8c**. In
415 particular, **6c** and **9c** could derive from **5c** and **8c**, respectively, upon transformation of the
416 isopropyl chain. Subsequent oxidation of **1a** could lead to the bicycle **7c** that is stabilized by
417 resonance. Finally, we did not observe BNTZ dimerization products as in previous works
418 (Berberidou et al., 2017; Eyheraguibel et al., 2009; Nilles and Zabik, 1975), probably due to our
419 analysis conditions. Indeed, the BNTZ retention time was 25.6 min and the total chromatographic
420 run time was 28 min. Therefore, since dimerization products should have higher retention time
421 compared to BNTZ, it is reasonable that we did not observe these products. Our goal was to identify
422 the BNTZ degradation products rather than the large dimerization products, which are usually less
423 important under environmental conditions because their formation requires substrate concentration
424 values higher than those occurring in surface waters.

425

426 **3.3 Toxicity assessment of BNTZ photoproducts towards aquatic organisms**

427 The LC₅₀/EC₅₀ and ChV parameters towards aquatic organisms were evaluated for BNTZ and the
428 identified photoproducts reported in **Fig. 3** with the ECOSAR software. When considering the same
429 chemical class as the parent compound, no formation of peculiarly toxic intermediates was

430 predicted during either direct or HO[•]-induced photodegradation (**Table SM-3**). Note that when
431 using ECOSAR, the difference of toxicity between two compounds can be deemed significant when
432 the predicted values differ by at least one order of magnitude (Mayo-Bean et al., 2012). It should be
433 pointed out that some molecules (i.e., **1a**, **5b**, **8c** and **9c**) also belong to different chemical classes
434 than BNTZ, because photodegradation introduces further functional groups. Actually, some toxicity
435 parameters relative to hydrazines and phenol amines satisfied the above rule of increased toxicity.
436 However, when using the traditional approach that considers only the chemical class with the most
437 conservative effect level (Mayo-Bean et al., 2017b), an important toxicity increase seems to be
438 ruled out.

439 The measurements with *Vibrio fischeri* did not show important acutely toxic effects of either BNTZ
440 or its photodegradation mixtures after 4, 16 and 23h of irradiation at the adopted initial BNTZ
441 concentration (20 μmol L⁻¹, **Fig. SM-6**). Our findings are quite different from those reported by
442 Berberidou et al. (2017), which observed an increase of toxicity towards *Vibrio fischeri* during the
443 early stages of the BNTZ photocatalytic degradation. This probably because direct photolysis and
444 photocatalytic degradation of the compound proceed with different mechanisms, and because we
445 adopted a lower BNTZ concentration. Therefore, both *in-silico* methods and experimental
446 assessments suggest that BNTZ photodegradation does not yield toxic species. The reason might be
447 that (i) the detected intermediates are not particularly toxic, including **1a**, **5b**, **8c** and **9c**, or (ii) toxic
448 compounds are formed at very low concentration.

449 Although both models and experiments suggest that the BNTZ photoproducts are not more toxic
450 than the parent compound, at least at the formed concentration values, further and more sensitive
451 toxicological assessments should be carried out in order to ensure that photodegradation really leads
452 to BNTZ attenuation.

453

454 **4. Conclusion**

455 Direct photolysis is here shown to be the main photolytic pathway for BNTZ in natural water
456 samples. The prevalence of direct photolysis was confirmed by photochemical modeling, and it
457 should be more marked if the water body is shallow. The computed half-life time agreed well with
458 the values reported in the literature for field conditions, thereby suggesting that the direct photolysis
459 can be the major dissipation pathway for BNTZ in most surface waters. Indirect photochemistry
460 might play a non-negligible role, both in shallow and DOM-poor waters where HO[•]-induced
461 reactions are important, or in deep and DOM-rich waters, where ³CDOM* could become the main
462 actor in BNTZ photodegradation. However, in the latter case photodegradation is predicted to be
463 quite slow, and additional reaction pathways (e.g., biodegradation) could take on a major
464 importance.

465 Several BNTZ photoproducts were identified for the direct photolysis and the HO[•]-induced
466 transformation of the herbicide, thereby allowing for the proposal of a photodegradation pathway.
467 Important toxic effects of the detected photoproducts towards aquatic organisms and *Vibrio fischeri*
468 bacteria could be excluded, with the use of QSAR modeling and toxicity tests.

469

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473

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475

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