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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<sup>•</sup>, CO<sub>3</sub><sup>•-</sup> and <sup>3</sup>CDOM\*) to the herbicide degradation. This contribution (especially

26 by <sup>3</sup>CDOM\*) could become crucial in deep and DOM-rich water bodies. Finally, several  
27 photoproducts formed by direct photolysis and HO<sup>•</sup>-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 ( $\text{HO}^\bullet$  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<sup>•</sup> 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<sup>•</sup> radicals, <sup>3</sup>CDOM\*, <sup>1</sup>O<sub>2</sub> and CO<sub>3</sub><sup>•-</sup>;  
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<sub>a</sub> ~ 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<sup>-1</sup>.

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  $\mu\text{m}$  pore size, Sartorius). The filtered  
105 samples were kept in the dark at  $\sim 5$   $^{\circ}\text{C}$  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  $\sim$   
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 ( $1 \text{ mmol L}^{-1}$ ) 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  $72\text{h}$ ). The sample solutions (total pooled volume of  
164  $60 \text{ mL}$ ) were divided into three aliquots of  $20 \text{ mL}$  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 ( $1 \text{ mmol L}^{-1}$ ) and  $\text{H}_2\text{O}_2$  ( $0.1 \text{ mol L}^{-1}$ ) 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.  $\text{H}_2\text{O}_2$  was used as  $\text{HO}^\bullet$  source, and the  
174 irradiated solutions containing  $\text{H}_2\text{O}_2$  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 (LC<sub>50</sub> and EC<sub>50</sub>) 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 - LC<sub>50</sub>, daphnid 48h – LC<sub>50</sub> and green algae 96h – EC<sub>50</sub>. 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 LC<sub>50</sub>,  
200 EC<sub>50</sub> and ChV values related to Log K<sub>ow</sub> > 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  $\mu\text{L}$ ), 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 $\mu\text{m}$ ). 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  $\text{mL min}^{-1}$  (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  $\text{mL min}^{-1}$ ; 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 15<sup>th</sup> 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<sup>-2</sup> 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**):

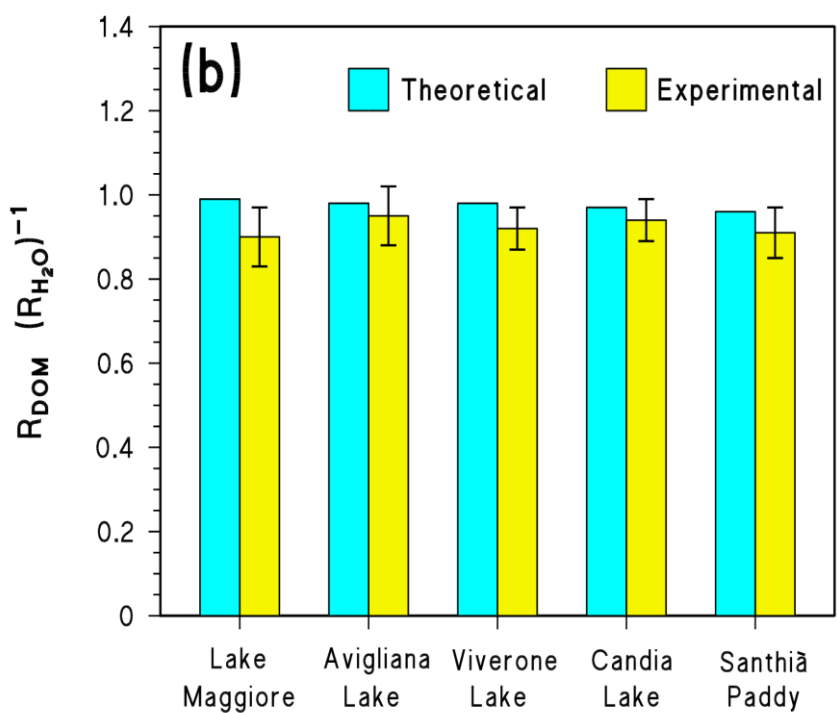
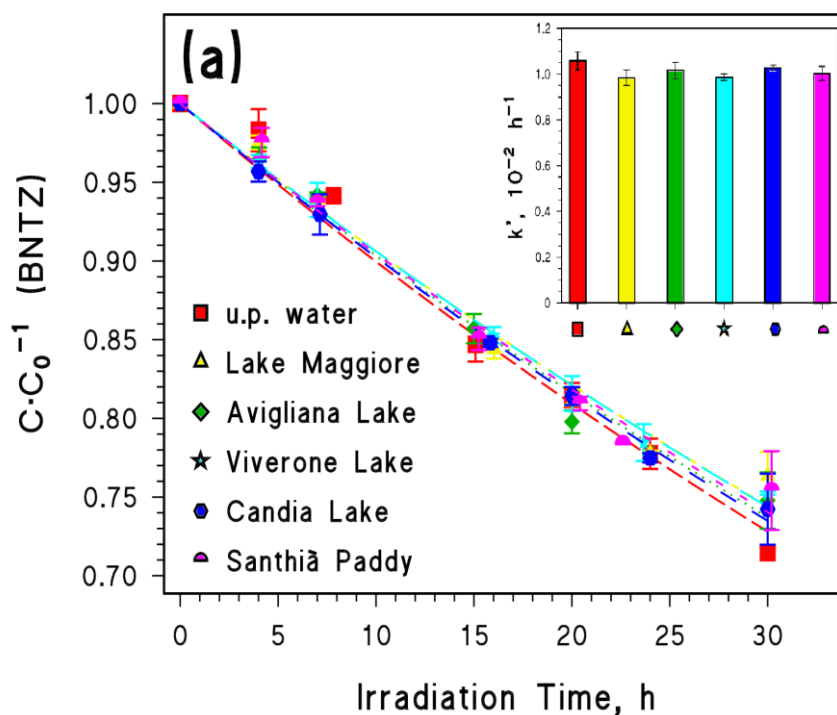
$$\frac{R_{DOM}}{R_{H2O}} = \frac{P_{a,DOM}}{P_{a,H2O}} = \frac{\int_{\lambda_1}^{\lambda_2} p^0(\lambda) \frac{A_{\lambda,BNTZ}}{A_{\lambda,tot}} [1 - 10^{-A_{\lambda,tot}}] d\lambda}{\int_{\lambda_1}^{\lambda_2} p^0(\lambda) [1 - 10^{-A_{\lambda,BNTZ}}] d\lambda} \quad (\text{Eq. 1})$$

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  $\lambda_1$  and  $\lambda_2$  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

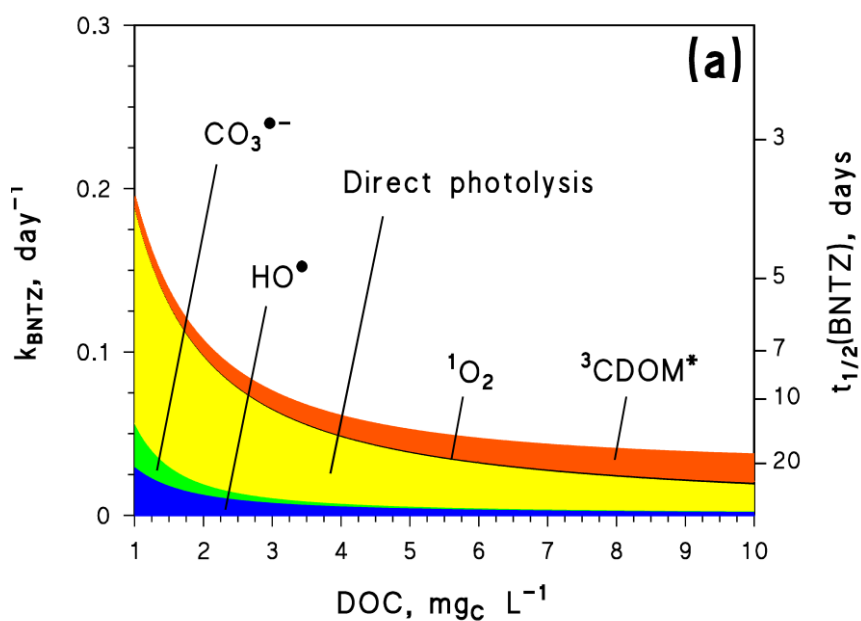


279 **Fig. 1.** (a) BNTZ photodegradation profiles in different aqueous matrices. Inset: experimental  $k'$  values for  
 280 BNTZ photodegradation. (b) DOM-induced inhibition (light screening) of BNTZ photodegradation assessed  
 281 as both theoretical and experimental ratio between the BNTZ degradation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

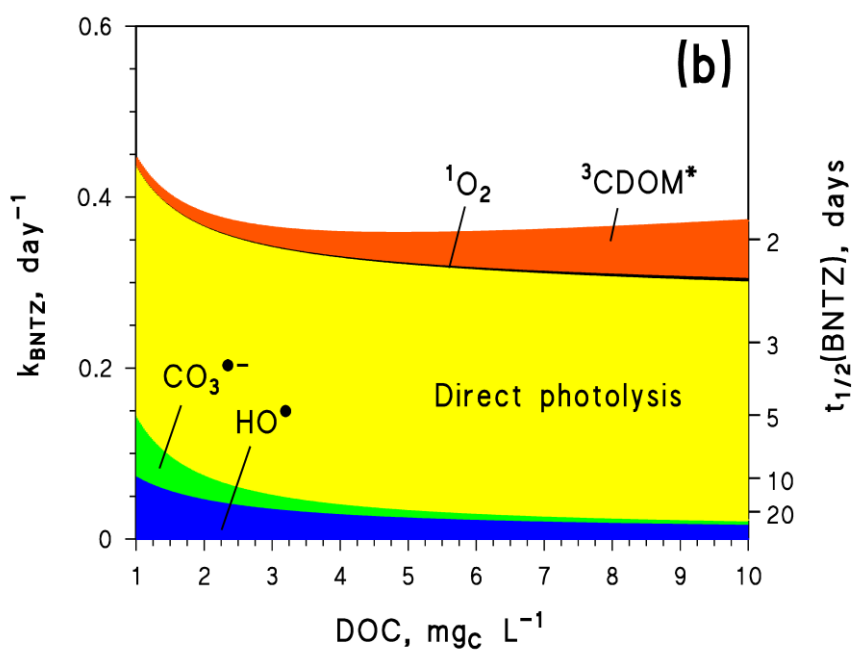
284 In contrast, visible light penetrates more deeply in water and it is absorbed by CDOM as well,  
285 thereby increasing the importance of CDOM-related photoprocesses (including  $^3\text{CDOM}^*$  reactions)  
286 vs. direct photolysis in deep water bodies (Canonica, 2007; McNeill and Canonica, 2016).  
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, 15<sup>th</sup> 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  $\text{HO}^\bullet$  and  $\text{CO}_3^{\bullet-}$  are  
298 quite low between 1 and 5  $\text{mg}_\text{C} \text{L}^{-1}$ . The importance of  $\text{HO}^\bullet$  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  $\text{HO}^\bullet$ ,  $\text{CO}_3^{\bullet-}$   
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  $\text{HO}^\bullet$  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  $\text{NO}_3^-$ ,  $1 \mu\text{mol L}^{-1} \text{NO}_2^-$ ,  $1 \text{mmol L}^{-1} \text{HCO}_3^-$ , and  $10 \mu\text{mol L}^{-1} \text{CO}_3^{2-}$ . The day time unit refers to fair-weather  
 340 15 July at  $45^\circ\text{N}$  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**

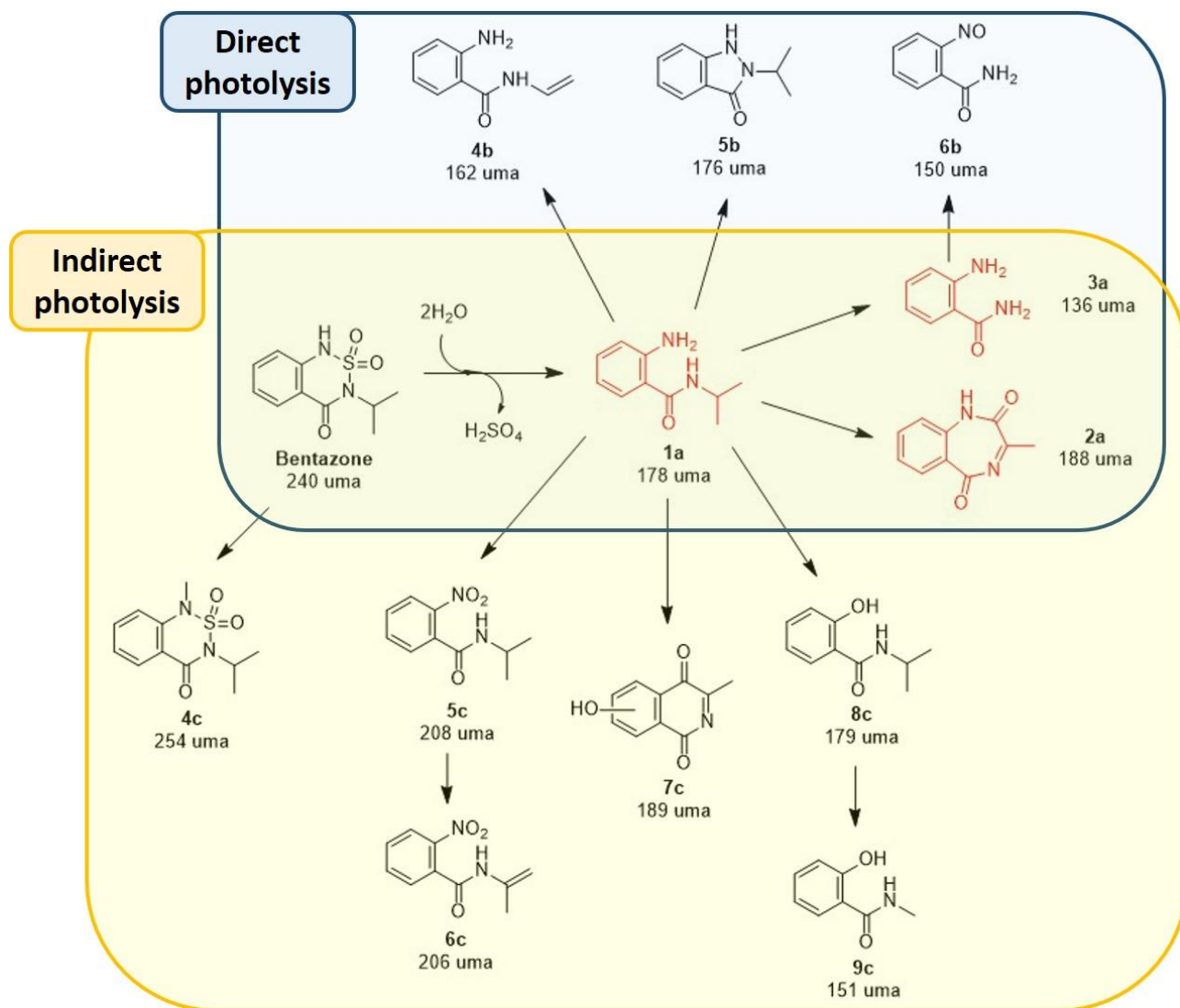
352 GC-MS analyses were carried out on irradiated solutions of BNTZ to identify the photoproducts.  
353 Their characterization may provide further information about the transformation mechanisms of the  
354 herbicide, and it can also be useful to assess and explain the time trend of toxicity. Indeed, 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<sup>•</sup> radicals, generated by H<sub>2</sub>O<sub>2</sub> 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<sup>•</sup> 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 H<sub>2</sub>O<sub>2</sub> (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 H<sub>2</sub>O<sub>2</sub>  
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 H<sub>2</sub>O<sub>2</sub>, and in irradiated H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>SO<sub>4</sub>. 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 +  $\text{H}_2\text{O}_2$  (inside the yellow box, indirect photolysis by  $\text{HO}^\bullet$ ). 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<sup>-1</sup>). 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 + TiO<sub>2</sub>) and HO<sup>•</sup>-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 LC<sub>50</sub>/EC<sub>50</sub> 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<sup>•</sup>-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<sup>-1</sup>, **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<sup>•</sup>-induced  
461 reactions are important, or in deep and DOM-rich waters, where <sup>3</sup>CDOM\* 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<sup>•</sup>-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

476 **References**

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