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

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Abstract

The photochemical fate of the herbicide bentazone was assessed by lab experiments and modeling tools. Experimental and modeling results showed that bentazone is mainly photodegraded by direct photolysis in natural water samples, even in the presence of dissolved organic matter (DOM) that can act as light-screening agent, photosensitizer and scavenger of reactive species. Even when it was dissolved in natural water samples containing different DOM amounts, the phototransformation kinetics of bentazone was unchanged compared to irradiation runs in ultrapure water. This finding suggests that the DOM and the other components of our samples did not affect the direct photolysis of bentazone by light-absorption competition, at least at the experimental optical path lengths, and did not induce significant indirect photodegradation by producing reactive transient species. Photochemical modeling in a lake-water photoreactivity scenario corroborated the observed experimental results, showing the predominant role of direct photolysis in the overall (direct + indirect) photodegradation of bentazone at different water depths and DOM contents. However, the model predicted a minor but non-negligible contribution of indirect photochemistry (i.e., reactions triggered by $HO^{\bullet}$, $CO_3^{\bullet-}$ and $^3CDOM^*$) to the herbicide degradation. This contribution (especially

by ^{3}CDOM*) could become crucial in deep and DOM-rich water bodies. Finally, several photoproducts formed by direct photolysis and $HO^{\bullet}$-induced photodegradation were identified, which should not be particularly toxic for aquatic organisms and *Vibrio fischeri* bacteria.

Keywords: Photochemistry; Pesticides; Photochemical modeling; APEX; Photodegradation intermediates.

1. Introduction

Pesticides are widespread micropollutants in surface and groundwaters (Luo et al., 2014; Masiá et al., 2015; Metcalfe et al., 2019), and they cause considerable environmental concern because of their toxic effects on aquatic ecosystems (Ccanccapa et al., 2016; Silva et al., 2015). After application on crops, pesticides can reach groundwaters and surface waters, including streams and lakes, because of leaching and soil runoff processes (Battaglin et al., 2003; Lupi et al., 2019; Milan et al., 2015; Riise et al., 2004). Moreover, water contamination by pesticides is favored by the close link between some crops and the aquatic systems. The latter provide water used for irrigation purposes or, in the case of some paddies, for fish-farming activities (Clasen at al., 2018; Milan et al., 2012). Fortunately, many pesticides are not recalcitrant in water environments and they can be transformed through chemical (e.g., hydrolysis) and biological processes, as well as photochemical reactions in sunlit surface waters (Fenner et al., 2013). Hydrolysis often depends upon water pH and it is faster in acidic and basic conditions, which means that the pH values of natural waters often coincide with a minimum in the hydrolysis kinetics. However, this process can still be an important dissipation pathway for some pesticides (Liu et al., 2001; Ramesh and Balasubramanian, 1999; Tebes-Stevens et al., 2017; Williams and Tjeerdema, 2016). Compared to hydrolysis, biotic and abiotic photochemical degradations usually play a more important role in the environmental fate of pesticides. Biodegradation is often a key dissipation route (Fenner et al., 2013), but it strongly depends upon the considered xenobiotic and aquatic system (Katagi, 2013). Photochemical reactions may be major transformation pathways for several pesticides and their metabolites (Adachi et al., 2018; Burrows et al., 2002; Konstantinou et al., 2001; Remucal, 2014). These reactions can be distinguished into direct photolysis and indirect photochemistry. Direct photolysis refers to the transformation of a molecule upon direct light absorption. Indeed, some pollutants are able to absorb sunlight, reach excited molecular states and then undergo chemical transformation (Katagi, 2018). Direct photolysis can be inhibited by competitive light-absorbing compounds, including most notably the dissolved organic matter (DOM) that naturally occurs in surface waters. The DOM chromophoric moieties (CDOM) can both screen radiation and act as photosensitizers to trigger the indirect photodegradation of water pollutants. Indeed, upon sunlight absorption CDOM forms the so-called *Photochemically Produced Reactive Intermediates* (PPRIs), which react with water contaminants and cause their degradation. The most important PPRIs are hydroxyl and carbonate radicals ($HO^{\bullet}$ and $CO_3^{\bullet-}$, respectively, which are also generated by the photolysis of nitrate and nitrite), the excited triplet states of CDOM ($^3CDOM^*$), as well as singlet oxygen ($^1O_2$) (Vione et al., 2014). Despite their effectiveness in degrading several pollutants including many pesticides (Remucal, 2014), photoreactions yield in some cases photoproducts of considerable environmental concern, which may be toxic to aquatic organisms (Bavcon Kralj et al., 2007; Carena and Vione, 2018; Dong and Hu, 2016). Furthermore, also the biotic degradation processes can be problematic as shown in the case of the herbicide propanil (Carena et al., 2017; Kanawi et al., 2016; Roehrs et al., 2012).

In the present study, the role of direct and indirect photolysis was assessed towards the photodegradation of bentazone (hereinafter BNTZ) in surface water samples. BNTZ is a post-emergence herbicide used in different crops such as wheat, rice and beans, to control weed growth. Because of soil leaching phenomena (Lammoglia et al., 2018), BNTZ has been detected in rivers, coastal waters and groundwaters (Palma et al., 2018; Papadakis et al., 2018; Kock-Schulmeyer et al., 2019). As shown in previous studies, BNTZ is photolabile in natural waters (coastal lagoon), and it has been degraded in laboratory experiments by 81% via direct photolysis and by 17% via photosensitized processes (Al Housari et al., 2011). In that case, the predicted photochemical lifetime of BNTZ was ~12 days by considering only direct photolysis and $HO^{\bullet}$ reactions (Al Housari et al., 2011). Here we assessed the transformation of BNTZ by all the potentially important photoreaction pathways in fresh waters (direct photolysis, $HO^{\bullet}$ radicals, $^{3}CDOM^{*}$, $^{1}O_2$ and $CO_3^{\bullet-}$; Katagi, 2018; Vione et al., 2014). Moreover, we identified the BNTZ photoproducts formed by the main processes, evaluating their environmental importance by means of photochemical modeling, and assessing the time evolution of acute toxicity.

2. Materials and Methods

2.1 Reagents

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

The stock solutions of BNTZ (pK_a ~ 3.3 at 24 °C; O'Neil, 2013) were prepared weekly by dissolving the compound in ultra-pure water under magnetic stirring. Their natural acidic pH (<4.5, thereby outside the environmental significance range) was adjusted to 7.0 with NaOH 0.1 mol L^{-1}. The stock solutions were stored in the dark at ~5 °C.

2.2 Lake and paddy water samples

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

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

2.3 Irradiation experiments

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

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

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

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

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

The kinetic assessment of the dark BNTZ degradation (blank experiments) caused by, e.g., hydrolysis and/or biodegradation was carried out by placing both synthetic and real water samples, spiked with BNTZ, in glass cells wrapped with double aluminum foil, under the irradiation lamp. The rationale for placing them under the lamp was to achieve comparable temperature and stirring conditions as for the irradiated samples.

All the irradiation experiments were carried out in duplicate, and the data points were then plotted as average values plus-or-minus the standard error.

2.4 Identification of the BNTZ photoproducts

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

A similar procedure was applied to identify the indirect photoproducts of BNTZ. In this case, an 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 reported in paragraph 2.3, and analyzed by SPME GC-MS as before (including the pH adjustment to 4, 7 and 10), after 0h, 4h, 16h and 30h of irradiation. H_2O_2 was used as $HO^{\bullet}$ source, and the irradiated solutions containing H_2O_2 in ultra-pure water are virtually free of $^3CDOM^*$ and $CO_3^{\bullet-}$ as potentially interfering PPRIs.

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

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

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

QSAR modeling was performed by means of the freely available ECOSAR V2.0 software [Ecological Structure Activity Relationships (ECOSAR) Class Program], developed by the U.S. Environmental Protection Agency (EPA) (Mayo-Bean et al., 2012). ECOSAR computes both acute (LC_{50} and EC_{50}) and chronic (ChV = Chronic Value) toxicity parameters toward aquatic organisms on the basis of the molecular structure of the considered neutral organic compound. In particular, toxicity outputs are fish 96h - LC_{50}, daphnid 48h – LC_{50} and green algae 96h – EC_{50}. In contrast, the ChV is computed as the geometric mean of NOEC (no-observed-effect concentration) and LOEC (lowest-observed-effect concentration) (Mayo-Bean et al., 2012). Furthermore, the computed LC_{50}, EC_{50} and ChV values related to Log K_{ow} > 5, > 6.4 and > 8, respectively, were here neglected (Mayo-Bean et al., 2017a).

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

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

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

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

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

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

2.7 Photochemical modeling

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

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

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

3. Results and Discussion

3.1 BNTZ photodegradation and its photochemical modeling

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

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

$$\frac{R_{DOM}}{R_{H2O}} = \frac{P_{a,DOM}}{P_{a,H2O}} = \frac{\int_{\lambda 1}^{\lambda 2} p^0(\lambda)\frac{A_{\lambda,BNTZ}}{A_{\lambda,tot}}[1-10^{-A_{\lambda,tot}}]d\lambda}{\int_{\lambda 1}^{\lambda 2} p^0(\lambda)[1-10^{-A_{\lambda,BNTZ}}]d\lambda} \qquad (Eq.1)$$

where $p^0(\lambda)$ is the spectral photon flux density of the lamp in solution (**Fig. SM-2**), while $A_{\lambda,BNTZ}$ and $A_{\lambda,tot}$ are the Lambert-Beer absorbance values of, respectively, BNTZ and the whole irradiated 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-range overlap of lamp emission and BNTZ absorption (300-392 nm).

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

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

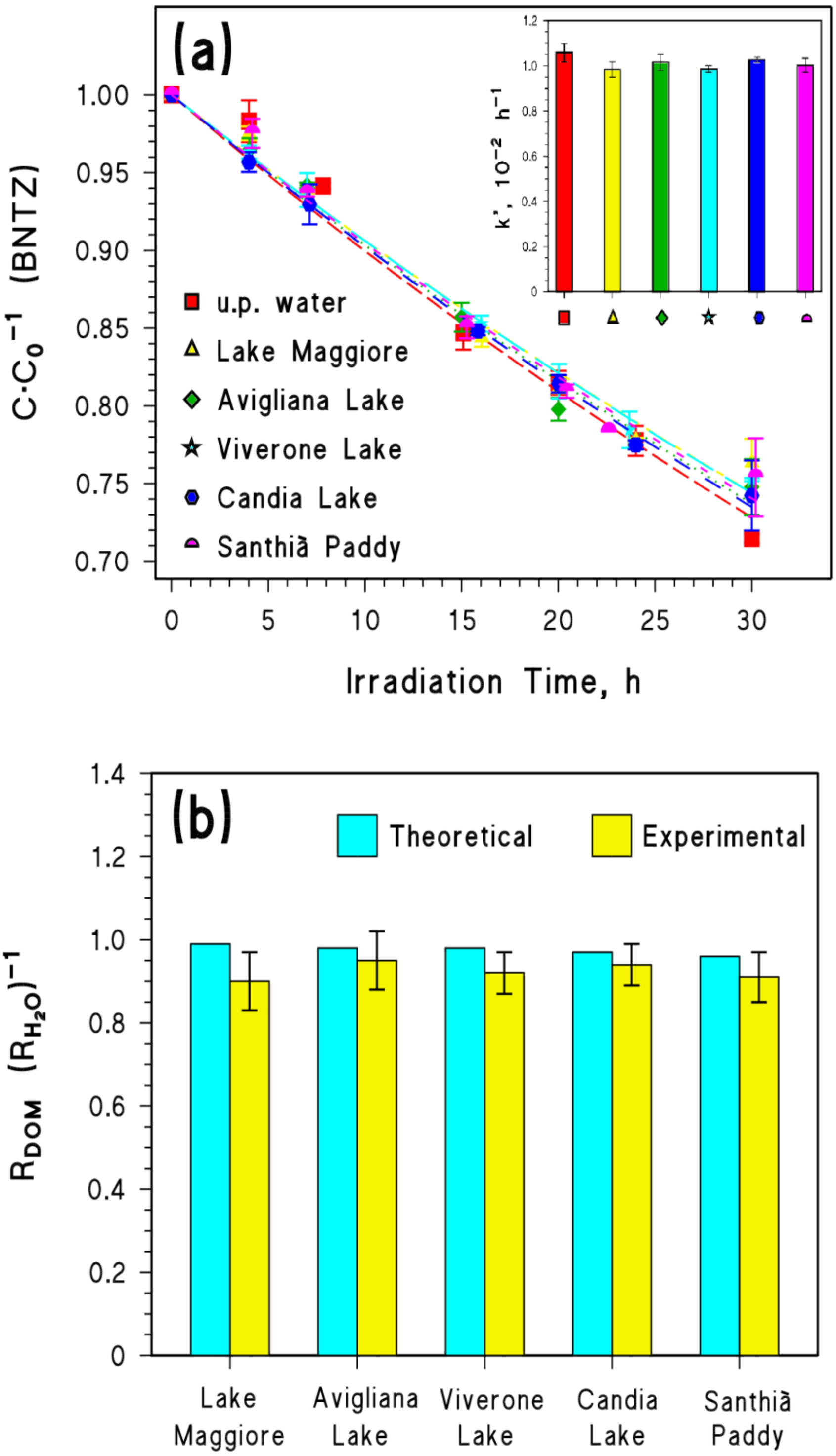

Fig. 1. (a) BNTZ photodegradation profiles in different aqueous matrices. Inset: experimental k' values for BNTZ photodegradation. (b) DOM-induced inhibition (light screening) of BNTZ photodegradation assessed as both theoretical and experimental ratio between the BNTZ degradation rate in real water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

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

The modeling of BNTZ photodegradation in lake water (3 m lake water depth, 15th of July at 45°N) agrees reasonably well with the experimental findings (**Fig. 2a**). The direct photolysis is predicted to be the main phototransformation pathway of the herbicide, while the roles of $HO^•$ and $CO_3^{•-}$ are quite low between 1 and 5 mg$_C$ L^{-1}. The importance of $HO^•$ and $CO_3^{•-}$ reactions becomes even negligible for DOC > 5 mg$_C$ L^{-1}. $^1O_2$ is not important as well in our scenario, although $^1O_2$ can be the major PPRI photodegrading BNTZ in prairie potholes with high DOM content between 20 and 38 mg$_C$ L^{-1}. In these environments, direct photolysis is limited to 40-45% of the total BNTZ photodegradation (Zeng and Arnold, 2013). According to our model results, at so high DOC levels the main role in BNTZ degradation would be played by ^{3}CDOM* instead of $^1O_2$, which is expected to give a minor contribution to the process. The main reason for this difference could be due to the fact that CDOM in prairie potholes has very different photoreactivity than that assumed by the APEX software, which has been designed around lake-water CDOM and its photoreactivity.

Coming back to the modeled lake-type environment (**Fig. 2**), the results also suggest that BNTZ could be significantly degraded by ^{3}CDOM* at DOC > 2 mg$_C$ L^{-1}. This makes a difference with the irradiation experiments, where lake/paddy water from Avigliana, Viverone, Candia and Santhià had DOC > 2 mg_C L^{-1}. However, the optical path length of the irradiated samples was much shorter (1.4 - 1.6 cm) than the water column depths found in the most reasonable environmental scenarios, including the modeled one. We can thus speculate that differences in water-column depth may account for the different relative roles of direct photolysis and $^3CDOM^*$ reaction between model output and experimental results. Indeed, by lowering the water depth to 1.5 cm (**Fig. 2b**), which is comparable to the optical path length of our experiments, the direct photolysis assumes much higher importance than in the 3-m depth scenario. The model still predicts some minor role for $HO^•$, $CO_3^{•-}$ and $^3CDOM^*$ in BNTZ degradation, which might or might not be highlighted experimentally given the uncertainties in both model results and irradiation runs. The fact that the irradiation experiments seem to exclude a significant role of indirect photochemistry (**Fig. 1b**) may have the following explanations: *(i)* the importance of indirect photoreactions is comparable to the experimental uncertainty, and it is thus not or hardly appreciable; *(ii)* the CDOM photoreactivity assumed in the model (average freshwater conditions) is higher compared to that of the studied samples; *(iii)* DOM inhibits the BNTZ degradation because of back-reduction processes due to its intrinsic antioxidant activity (Canonica and Laubscher, 2008; Leresche et al., 2016; Wenk and Canonica, 2012). However, the indirect photochemistry of $^3CDOM^*$ could become the main BNTZ phototransformation pathway in a deep water body with a high DOM content (DOC = 10 mg_C L^{-1}, depth > 3 m, see **Fig. SM-4**). In that case, the BNTZ direct photolysis would be overcome by $^3CDOM^*$ photochemistry because of the light penetration issues explained above. However, in deep and DOM-rich water bodies the photoreaction kinetics would be quite slow, and other non-photoinduced processes could become important or even dominate the degradation of BNTZ.

The reactions with $HO^•$ and $CO_3^{•-}$ could be the second most important photodegradation pathway of BNTZ at low DOC. Their importance could be increased in the presence of elevated nitrate and/or nitrite concentration values (see **Fig. SM-5**).

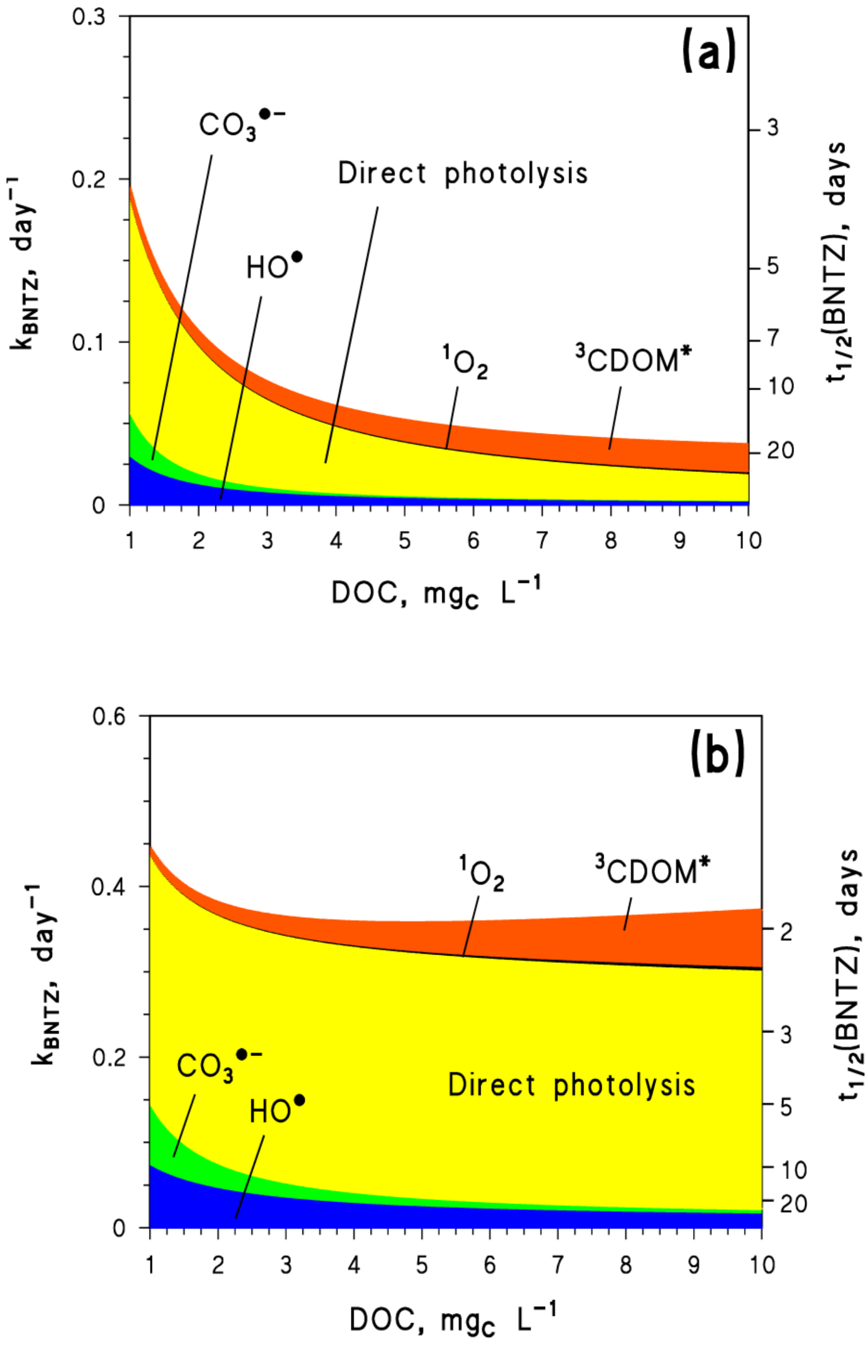

Fig. 2. Pseudo-first order rate constants (left Y-axis) and half-life times (right Y-axis) of BNTZ in a lake water column of (a) 3 m and (b) 1.5 cm depth. The assumed water chemical composition was: 100 μmol L^{-1} NO_3^-, 1 μmol L^{-1} NO_2^-, 1 mmol L^{-1} HCO_3^-, and 10 μmol L^{-1} CO_3^{2-}. The day time unit refers to fair-weather 15 July at 45°N latitude.

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

3.2 BNTZ degradation products

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

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

Fig. 3 shows the possible molecular structures of the BNTZ photodegradation products in pure water and in the presence of $HO^{\bullet}$ radicals, generated by H_2O_2 photolysis, proposed on the basis of the GC-MS analysis. The rationale for the choice of the two processes is that direct photolysis is the main BNTZ photoreaction, while $HO^{\bullet}$ may play an important role at low DOC and low water depth, where photoreactions are fast and thus very competitive with additional processes (**Fig. 2a**). The compounds detected in both conditions (direct and indirect photolysis) are highlighted in red. The main BNTZ photoproduct observed after 72h of irradiation (direct photolysis) is the photohydrolysis compound **1a**, derived by the cleavage of the amide N-S and amine N-S bonds. This compound has been identified previously as a BNTZ degradation product (Nilles and Zabik, 1975; Song et al., 2019), and its formation generates sulfuric acid that could further catalyze degradation reactions. 2-Amino-*N*-isopropylbenzamide (**1a**) may absorb light and undergo a Norrish type II reaction to produce the benzamide **3a** (White et al., 1996). A di-radical species photogenerated by **1a** could also produce compound **4b**, as well as the bicyclic compound **5b** through an intramolecular reaction. Also the bicycle **2a** could derive from **1a** via intramolecular recombination with the isopropyl chain and further oxidation. Finally, the oxidation of the aromatic amine may lead to the nitroderivative **6b**.

The irradiation of BNTZ in the presence of H_2O_2 (indirect photolysis) for 30h yielded several products, some of which (**1a**, **2a** and **3a**) were also observed in direct photolysis. Except for *N*-methylbentazone (**4c**), all the detected compounds do not contain sulfur in the molecular structure. This finding suggests that photohydrolysis to **1a** is the main degradation pathway also in the case of $HO^{\bullet}$. However, we cannot exclude the possibility that compound **1a** actually derives from BNTZ direct photolysis rather than exclusively from the $HO^{\bullet}$-induced reactions. Indeed, although the H_2O_2 concentration was 100-fold higher than that of BNTZ, the molar absorption coefficient of the latter species is nevertheless higher of the same order of magnitude. Therefore, BNTZ absorbs light at least as well as H_2O_2, and in irradiated H_2O_2 solutions its direct photolysis can occur at the same time as degradation by $HO^{\bullet}$. Another evidence of the loss of sulfur from BNTZ was the solution pH decrease from 7 to 4 during light exposure, presumably because of the formation of H_2SO_4. These findings are quite in contrast with the results obtained by Peschka et al. (2007), who have not observed the loss of sulfur from BNTZ during irradiation in water enriched with inorganic salts and organic matter. N-methylbentazone (**4c**) has been already identified as a transformation product of BNTZ by Song et al. (2019), during irradiation of water/methanol and water/ethyl acetate solutions. Those conditions could have allowed the BNTZ methylation by the solvent itself.

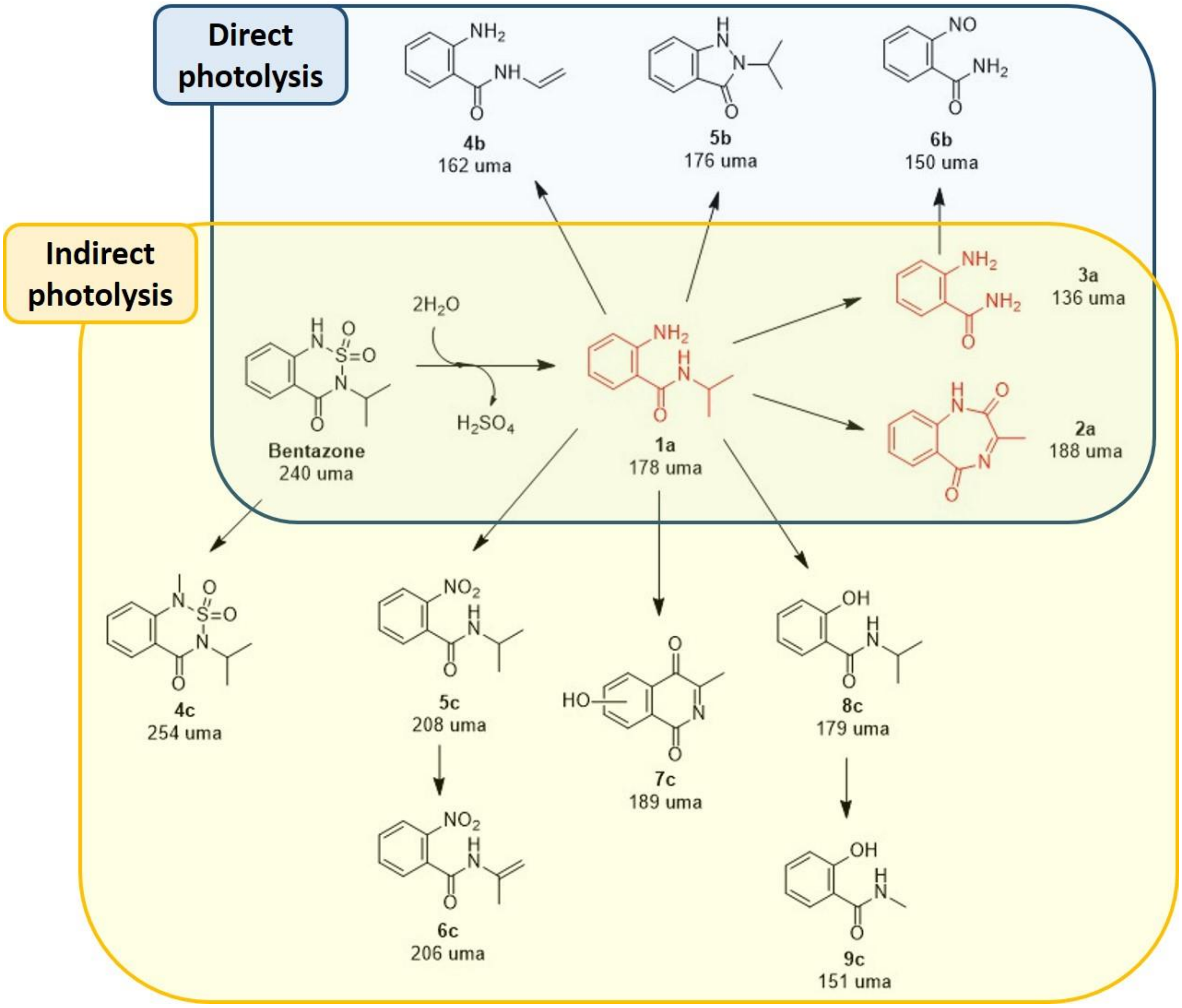

Fig. 3. Possible degradation pathways of BNTZ under UV irradiation in water (inside the blue box, direct photolysis) and in the presence of UV + H_2O_2 (inside the yellow box, indirect photolysis by $HO^{\bullet}$). The products included in the overlapping area of the yellow and blue boxes, highlighted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

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

It has already been reported in the literature that **5c** and **8c** are BNTZ transformation products obtained under photolytic (Nilles and Zabik, 1975), photocatalytic (UV + TiO_2) and $HO^{\bullet}$-induced degradation conditions (Mir et al., 2014; Guelfi et al., 2019). Product **5c** derives from the oxidation of the aromatic amine group, while the substitution of this latter with OH could lead to **8c**. In particular, **6c** and **9c** could derive from **5c** and **8c,** respectively, upon transformation of the isopropyl chain. Subsequent oxidation of **1a** could lead to the bicycle **7c** that is stabilized by resonance. Finally, we did not observe BNTZ dimerization products as in previous works (Berberidou et al., 2017; Eyheraguibel et al., 2009; Nilles and Zabik, 1975), probably due to our analysis conditions. Indeed, the BNTZ retention time was 25.6 min and the total chromatographic run time was 28 min. Therefore, since dimerization products should have higher retention time compared to BNTZ, it is reasonable that we did not observe these products. Our goal was to identify the BNTZ degradation products rather than the large dimerization products, which are usually less important under environmental conditions because their formation requires substrate concentration values higher than those occurring in surface waters.

3.3 Toxicity assessment of BNTZ photoproducts towards aquatic organisms

The LC_{50}/EC_{50} and ChV parameters towards aquatic organisms were evaluated for BNTZ and the identified photoproducts reported in **Fig. 3** with the ECOSAR software. When considering the same chemical class as the parent compound, no formation of peculiarly toxic intermediates was predicted during either direct or $HO^{\bullet}$-induced photodegradation (**Table SM-3**). Note that when using ECOSAR, the difference of toxicity between two compounds can be deemed significant when the predicted values differ by at least one order of magnitude (Mayo-Bean et al., 2012). It should be pointed out that some molecules (i.e., **1a**, **5b**, **8c** and **9c**) also belong to different chemical classes than BNTZ, because photodegradation introduces further functional groups. Actually, some toxicity parameters relative to hydrazines and phenol amines satisfied the above rule of increased toxicity. However, when using the traditional approach that considers only the chemical class with the most conservative effect level (Mayo-Bean et al., 2017b), an important toxicity increase seems to be ruled out.

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

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

4. Conclusion

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

Several BNTZ photoproducts were identified for the direct photolysis and the $HO^{\bullet}$-induced transformation of the herbicide, thereby allowing for the proposal of a photodegradation pathway. Important toxic effects of the detected photoproducts towards aquatic organisms and *Vibrio fischeri* bacteria could be excluded, with the use of QSAR modeling and toxicity tests.

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