

Photolysis of herbicide butafenacil and toxicity of its products on marine microalgae

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Abstract: Photolysis plays a critical role in the elimination of herbicides in the environment. Butafenacil (BFA) is a protoporphyrinogen oxidase-inhibiting herbicide regarded as eco-friendly, but the toxicity of BFA photolysis products remains unclear. Natural light was found to enhance the degradation of BFA across different aqueous matrices. In particular, 10 mg/L BFA in ultrapure water could be completely degraded within 1 h under ultraviolet (UV) light. Natural organic matter (fulvic acid) and nitrate could inhibit, while alkaline conditions (pH 9) could accelerate the photolysis process. After UV photolysis of BFA, a significant reduction in acute toxicity towards two marine microalgae (*Chlorella pyrenoidosa* and *Phaeodactylum tricornutum*) was observed. Using liquid chromatography-high-resolution tandem mass spectrometry, nine previously unreported photolysis products were identified, which were distinct from those generated by hydrolysis. Toxicity predictions from a computational model indicated that the major photolysis products were remarkably less toxic to algae than their precursor BFA, suggesting that photolysis was key to BFA detoxification. Notably, one major photolysis product with high stability was predicted to bear a high potential risk to daphnia and fish. Given the complexity of environmental aqueous conditions, the persistent toxicity of BFA photolysis products is likely more complex, calling for further in-depth investigation.

Key words: LC-HRMS; QSAR; hydrolysis products; computational toxicity; acute toxicity

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1. Introduction

The global reliance on herbicides results in an annual influx exceeding 700,000 tons into marine ecosystems through runoff and fluvial transport[1-3]. In these waters, hydrolysis and photolysis drive the formation of complex mixtures of degradation products (DPs), creating compounded risks for marine organisms[4-6]. Marine microalgae are especially susceptible to herbicides, owing to the targeting of their photosynthetic apparatus by these compounds. Indeed, residual photosystem II (PSII) inhibitors compromise zooxanthellae physiology, driving coral bleaching in sensitive ecosystems such as the Great Barrier Reef[7, 8]. The threat extends to primary production, with herbicide residuals and DPs suppressing productivity by >10% in some seas, compromising marine ecosystem function[9]. Recent studies revealed that the toxicity of photolysis products from herbicides to non-target organisms was equal to or exceeded their precursors[10, 11], which were frequently overlooked in risk assessment and raised great concern about herbicide residuals on the marine ecosystem [12]. As most herbicides are photosensitive and undergo photolysis in the environment [13], the toxicity of the photolysis products to non-target organisms, e.g., microalgae, should be investigated.

Uracil derivatives, such as butafenacil (BFA), have attracted sustained interest owing to their high efficacy, low mammalian toxicity, and favorable environmental compatibility[14, 15]. In herbicide design, the introduction of a trifluoromethyl ($-CF_3$) group can markedly improve stability against enzymatic, chemical, and environmental degradation[16-18]. But the increased persistence in the environment was unwanted. Since its commercialization in 2001, BFA has been used for weed control in cereals (e.g., wheat), orchards (e.g., citrus), and non-crop areas, particularly in major agricultural markets such as Australia[19, 20]. Notably, China issued its first registration for BFA export in 2022, although its use is prohibited domestically and within the European Union. Given the frequent detection of legacy herbicides (e.g., atrazine) in marine ecosystems, regulations now require stricter ecotoxicological assessment for novel herbicides[21]. Although BFA dissipates rapidly via hydrolysis, the persistence of its DPs undermines its regulatory acceptance and practical deployment[22]. This regulatory bottleneck, coupled with limited field application, leaves baseline monitoring data for BFA notably sparse. While uracil derivatives are occasionally detected, BFA occurrence in authentic field samples remains undocumented in the peer-reviewed literature.

Current risk assessments for BFA are grounded primarily in regulatory frameworks centered on hydrolysis kinetics and standard biotic endpoints. Specifically, BFA exhibits marked pH-dependent hydrolytic kinetics: while hydrolysis proceeds sluggishly at neutral pH (half-life of 100–117 days at pH 7), it accelerates sharply under alkaline conditions (half-life < 2 days at pH 9), yielding two products CGA-293731 and CGA-293730

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with high toxicity to microalgae, which retain the CF₃-substituted uracil (pyrimidinedione) core[22]. BFA undergoes relatively slow aqueous photolysis (half-life ~ 25–30 days) and dissipates rapidly in soil primarily via microbial degradation (aerobic DT₅₀ ≈ 0.5–2.2 days). However, systematic investigations into its photolysis mechanisms remain conspicuously scarce. Despite evidence that some herbicide photolyzed products can be more environmentally hazardous than their parent compounds[23–26], the photolysis pathways of BFA and the associated toxicity of its products are unclear. Therefore, investigations of BFA photolysis and microalgal toxicity assays are essential for a comprehensive ecological risk assessment upon its entry into marine systems.

As the standards of photolysis products were usually not commercially available, the traditional toxicity test was not applicable[27]. Recently, quantitative structure–activity relationship (QSAR) modeling offers a valuable alternative for preliminary toxicity estimation of compounds without standards[28]. By linking molecular structure to biological activity based on chemical similarity[10, 29], QSAR enables toxicity prediction and prioritizes the new compounds for further evaluation in experimental toxicity testing[30].

In this work, we compared the photolysis of BFA under sunlight and UV in 4 different water samples, and tested the toxicity of photolyzed BFA using two marine microalgae. The photolyzed products were identified using liquid chromatography-high-resolution tandem mass spectrometry (LC-HRMS/MS), and their acute and chronic toxicities against microalgae were evaluated using an ecological structure-activity relationships (ECOSAR) predictive model, which revealed that the decreased toxicity was probably owing to the less toxic products.

2. Experimental

2.1. Chemicals and materials

Butafenacil (BFA, ≥98%) was purchased from Yuanye (Shanghai, China). Sodium nitrate (NaNO₃, ≥99%), ethanol (EtOH), and acetonitrile (ACN) of HPLC grade were purchased from Aladdin (Shanghai, China). Fulvic acid (FA, 95%) was obtained from Shifeng (Shanghai, China). Ultrapure water (>18.25 MΩ·cm) was prepared using a Milli-Q Direct-Q-8 system (Millipore, Bedford, MA, USA). Axenic strains of *Phaeodactylum tricornutum* were obtained from the Laboratory of Marine Pollution Ecochemistry, Ocean University of China, while *Chlorella pyrenoidosa* was kindly provided by China Guanghe Crab Industry Co., Ltd. The UV photolysis experiments were conducted using a CEL-LAB500 photolysis apparatus (Beijing China Education Au-light Co., Ltd., Beijing, China). A xenon lamp light source (PLS-SXE300C, Beijing Perfectlight Technology Co., Ltd.) was employed in this study.

2.2. Photolysis kinetics of BFA

2.2.1. Photolysis of BFA under sunlight

To investigate the hydrolysis and photolysis behavior of BFA in different matrices, ultrapure water, lake water (from the Panjin campus, filtered), seawater (from the Liaodong Bay, Baohai Sea, filtered), and tap water were used to simulate natural aquatic environments with different water compositions. Tap water represents a common water source for preparing herbicide solutions in agricultural irrigation. The BFA water sam-

ples were prepared at 5 mg/L, sealed, and placed in quartz test tubes. To distinguish the contributions of photolysis and hydrolysis, a dark control group was set up, with tubes completely wrapped in aluminum foil to block sunlight. The experiments were conducted between September and October (40.7°N, 122.13°E). The light-exposure group received 9 h of sunlight daily (8:30 am–5:30 pm) to simulate the real solar radiation. At 0, 1, 2, 3, 4, 5, 7, 9, and 11 days during the exposure, 0.2 mL aliquots were collected from each sample and immediately stored at –20°C for LC-HRMS/MS analysis. All treatments were performed in triplicate.

2.2.2. BFA photolysis under UV Light at different conditions

A BFA solution was prepared in ultrapure water and irradiated in sealed quartz tubes for 2 h under UV. To simulate real environmental conditions, the effects of naturally dissolved organic matter (DOM, e.g., humic substances) were evaluated by adding fulvic acid (FA) at concentrations of 1, 2, 5, and 10 mg/L, and the pH values were adjusted to pH 4, 7, and 9. A series of nitrate working solutions (0–40 mg/L NO₃[–]) were prepared in ultrapure water (with negligible pH variation). To differentiate photolytic from hydrolytic degradation pathways, parallel dark controls were established by wrapping reactors in aluminum foil. All treatments were conducted in triplicate and irradiated at a constant 20°C via a circulating water bath.

2.3. Acute toxicity tests of BFA and its photolysis products

A green alga *C. pyrenoidosa* and a diatom *P. tricornutum* were selected as test organisms, which are representative marine microalgae commonly employed as model organisms in ecotoxicological research, and their physiological status is also an indicator of potential pollution impact on primary producers.

All algal tests were conducted in accordance with the Organization for Economic Co-operation and Development (OECD) Guidelines for the Testing of Chemicals (Algal Growth Inhibition Test, Test Guideline 201)[31]. The culture medium with F/2 nutrients was prepared using seawater (from Liaodong Bay, salinity 28 ± 1‰, pH 7.9–8.2). The medium was filtered through a 0.22 μm membrane (cellulose acetate) and autoclaved (at 121°C for 20 min), and the pH was adjusted to approximately 8.0. Axenic algal cultures were maintained at a temperature of 21 ± 1°C under a 12 h:12 h light-dark cycle at an intensity of approximately 80 μmol m^{–2} s^{–1} (white fluorescent lamps). To prevent cell adhesion and mitigate localized oxygen depletion, the culture vessels were manually shaken at intervals of 6–8 h to prevent the cell adhesion and oxygen depletion.

Based on preliminary range-finding tests, the concentrations for 5–85% growth inhibition were selected for these two marine microalgae. Specifically, a six-concentration gradient was established: 0, 50, 100, 200, 500, and 1000 μg/L for *P. tricornutum*, and 0, 1, 2, 5, 10, and 20 μg/L for *C. pyrenoidosa*.

2.4. Screening and identification of the photolysis products

The screening and identification of BFA photolysis products were performed using LC-HRMS/MS. The detailed analytical method is summarized in Supporting Information (Text S1).

Putative photolysis products were screened using the non-targeted metabolomics software MS^{Dial} 5.0. The screening was based on the difference in signal intensity between the irradiated and initial (time-zero) samples. Ions exhibiting a significant increase in intensity (10-fold increase in MS¹) were picked as potential photolysis products, and their product ion spectra (MS²) were further collected. Due to the lack of authentic standards and matching entries in mass spectral libraries, manual interpretation of MS² spectra was conducted, and tentatively identified compounds had to meet (1) mass error < 5 ppm in MS¹ and (2) explainable characteristic ions in MS².

2.5. ECOSAR analysis

Acute and chronic toxicity profiles for nine BFA photolysis products were predicted using the ECOSAR (Ecological Structure-Activity Relationships) module within EPI Suite 4.1[30, 32]. Three representative aquatic taxa: fish (*Actinopterygii*), daphnia (*Branchiopoda*), and green algae were assessed. The model provided predicted acute toxicity (reported as 96 h-LC₅₀ for fish, 48 h-EC₅₀ for daphnia, and 96 h-EC₅₀ for green algae) and chronic toxicity (Chronic Value, ChV). The ChV was calculated as the geometric mean of the predicted No Observed Effect Concentration (NOEC) and the Lowest Observed Effect Concentration (LOEC).

3. Results and Discussion

3.1. Photolysis kinetics of BFA

3.1.1. Photolysis of BFA under natural sunlight

As shown in Figure 1 and Table S1, the degradation rate of BFA varied substantially across the different aqueous matrices. Under both light and dark conditions, the degradation rates were: seawater > lake water > tap water > ultrapure water. This trend correlated strongly with the inherent alkalinity of the aqueous matrices, following the order: seawater (pH 8.4) > lake water (pH 8.3) > tap water (pH 7.8) > ultrapure water (pH 5.8). The enhanced degradation observed in seawater was due to the higher pH, as basic conditions were reported to promote the hydrolysis of susceptible functional groups (e.g., ester bonds) within the BFA structure[22, 33]. This pH-dependent mechanism was further verified by ultrapure water with different pH (pH 4, 7, and 9), and the fastest degradation was observed at pH 9 (Figure 2b, under UV).

Hydrolysis dominated the degradation in the dark,

whereas sunlight exposure substantially accelerated the process in all water samples (tap, lake, and seawater). For instance, in spiked seawater (5 mg/L BFA), sunlight irradiation reduced the half-life from 5.52 days (dark control) to 3.5 days (Table S1), which indicated that photolysis played a significant role in enhancing the degradation rate of BFA in natural aquatic environments.

3.1.2. Effects of pH, nitrate, and fulvic acid on BFA photolysis

To minimize interference from hydrolysis, ultrapure water with the slowest BFA hydrolysis rate was used to prepare the BFA solutions for investigating its photolytic mechanism under UV irradiation. Without fulvic acid (FA), BFA (10 mg/L) was rapidly degraded within 1 h under UV light. In contrast, under the solar light with a UV-blocking filter, little degradation of BFA was observed (Figure S1). These results confirmed that UV radiation was the primary driver for BFA photolysis under natural sunlight.

Natural DOM and pH are key factors influencing the photolysis of herbicides. The photolysis profiles of BFA under UV irradiation were examined at different FA concentrations and different pH values. Figure 2a and Table S2 confirm that FA addition impeded BFA photolysis in all treatment groups, and inhibitory potency increased proportionally with FA loading. For instance, 10 ppm FA increased the photolytic half-life of BFA by approximately 13 min in ultrapure water, indicating that natural DOM hindered the BFA photolysis. Similar inhibitory effects of DOM on photolysis were reported for other herbicides, such as atrazine[34–37], and were largely due to the inner-filter effect (referred to as light-shielding) of FA absorbing a portion of UV light, thereby reducing the available photon flux[35, 38]. Collectively, these results indicate that elevated DOM levels in natural waters (e.g., lakes and rivers) can suppress the BFA photolysis, thereby extending its environmental lifetime.

The degradation rates of BFA in acidic and neutral conditions (pH 4 and 7) were lower than in basic conditions, as the half-life decreased from 20.1 min to 13.1 min at pH 9 (Figure 2b). This enhancement likely stems from UV-promoted hydrolysis of BFA, supported by the detection of known hydrolysis products under UV light, such as CGA 293731[22]. The concentration of these hydrolysis products substantially exceeded that in dark controls, but gradually decreased with prolonged irradiation.

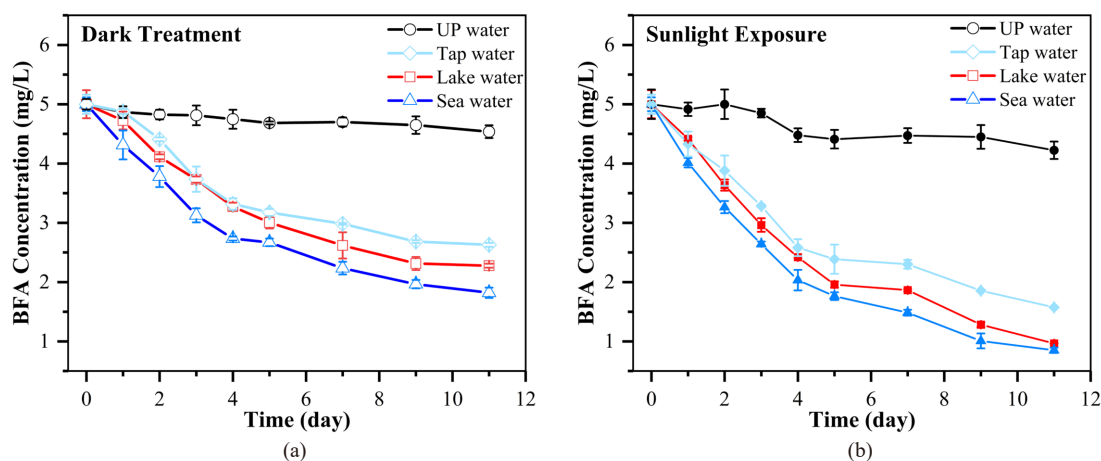


Fig. 1. Degradation of BFA in different aqueous matrices under natural light irradiation.

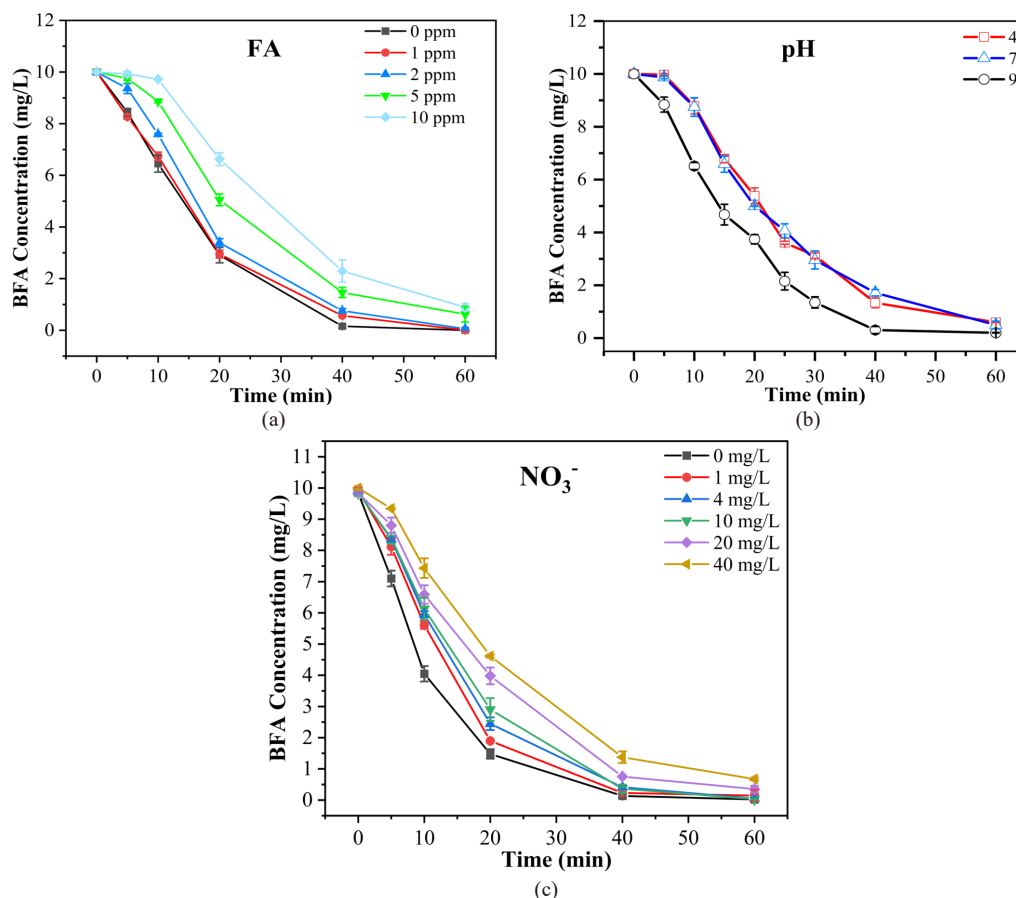


Fig. 2. Effects of A) fulvic acid concentration, B) pH, and C) nitrate on the photolysis of BFA.

tion to undetectable. In alkaline environments, UV light not only induces the direct photolysis of BFA but also facilitates hydrolysis through the attack of abundant nucleophilic species such as hydroxide ions (OH^-) on hydrolyzable sites (e.g., ester and amide bonds) in the molecule[33]. Meanwhile, the resulting hydrolysis products undergo further photolytic degradation. Therefore, the enhanced degradation of BFA under alkaline conditions arises from the synergistic effects of hydrolysis and photolysis.

Nitrate is a key environmental factor that exhibits a dual effect of "promotion at low concentrations and inhibition at high concentrations" on herbicide photolysis. At low nitrate concentrations, hydroxyl radicals ($\cdot\text{OH}$) generated from nitrate under light exposure can accelerate the degradation of most herbicides[39]; whereas at high nitrate concentrations, the strong absorption of nitrate in the UV band, especially 250–350 nm, competes with target pollutants for photons, causing a "light-shielding effect" that inhibits photolysis[40]. Research has shown that when the nitrate concentration in water exceeds 1 mg/L, its absorption of UV light can significantly suppress the photodegradation of organic pollutants[41]. Our findings align with this: within the tested concentration range (1–40 mg/L), nitrate consistently inhibited the photolysis of BFA (Figure 2c). As nitrate concentration increased, the inhibition became more pronounced. Even at a low concentration of 1 mg/L, the half-life of BFA photolysis was extended by about 25%.

The nitrate concentration used in this experiment (1 mg/L) is higher than the background levels in open oceans (typically < 0.1 mg/L) and most coastal seawaters (0.1–1.0

mg/L)[42–44]. Therefore, in offshore marine environments, the inhibitory effect of nitrate on BFA photolysis should be negligible. However, in eutrophic estuaries or coastal waters subjected to agricultural runoff, in which nitrate concentrations often exceed 1–2 mg/L[45], such photolytic retardation can prolong persistence of BFA in the environment, thereby elevating its potential ecological risks.

3.2. Acute toxicity tests of BFA and its photoproducts

The acute toxicities of BFA photolyzed solutions with different UV irradiation times were evaluated using two microalgae, *P. tricornutum* and *C. pyrenoidosa*. The BFA showed significantly different toxicities to *P. tricornutum* and *C. pyrenoidosa*, with 96 h- EC_{50} values of $188 \pm 21 \mu\text{g/L}$ and $2.1 \pm 0.7 \mu\text{g/L}$, respectively, and UV irradiation remarkably reduced the toxicity of BFA to both species (Table 1, Figures S2 and S3). With prolonged irradiation time, the 96 h- EC_{50} of the photolyzed BFA solution increased from 188 $\mu\text{g/L}$ to > 1000 $\mu\text{g/L}$ for *P. tricornutum*, and from 2.13 $\mu\text{g/L}$ to > 20 $\mu\text{g/L}$ for *C. pyrenoidosa*, respectively. For the cell growth inhibition near the 96 h- EC_{50} concentrations of BFA, the inhibitory effect was greatly alleviated by UV irradiation on both microalgae (Figure 3). After 120 min of irradiation, little growth inhibition of both species was observed in the photolyzed BFA solution, suggesting that the photolyzed products were substantially less toxic than their precursor BFA.

3.3. Identification of BFA Photoproducts and Photodegradation Pathways

To identify the photolysis products contributing to the detoxification effect on microalgae, LC-HRMS/MS was

Table 1. 96 h-EC₅₀ (Cell Density Inhibition Rate) of BFA towards the Two Algal Species under Different UV Irradiation Times (Figure S2-3).

	96 h-EC ₅₀ (μg/L)					
UV irradiation time (min)	0	10	20	40	60	120
<i>P. tricornutum</i>	188	228	263	399	1099	>1000
<i>C. pyrenoidosa</i>	2.13	2.43	5.61	9.4	>20	>20

Note: EC₅₀ values marked with ">" indicate that no 50% mortality was observed at the highest tested concentration (1000 μg/L for *P. tricornutum*; 20 μg/L for *C. pyrenoidosa*).

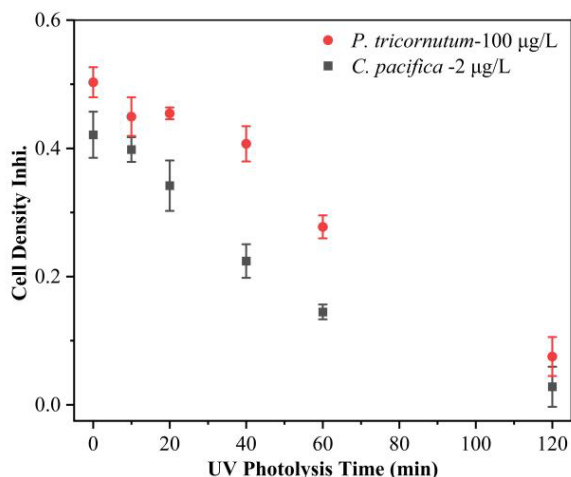


Fig. 3. Changes in the toxicity of BFA to two microalgal species (96 h cell density inhibition rate) with UV photolysis time.

employed to analyze the photolyzed BFA solution, and 9 photoproducts were tentatively identified (the structures and retention times (RT) were summarized in Table S3). The elucidation of these photoproducts was presented in Text S2 and Figure S4-S10. Notably, all nine photoproducts were only generated via photolysis as they were undetectable in dark controls. Moreover, their chemical structures differ from those in historical regulatory evaluations, revealing a previously unreported transformation profile of BFA. In the absence of commercial standards and comprehensive mass spectral libraries, compound identification was achieved through manual interpretation based on HRMS fragmentation patterns (MS²). The fitting errors were less than 5 ppm for all molecular ions, and the identification confidence levels were assigned as Level 2 (library

match or diagnostic evidence) or Level 3 (tentative candidate)[46].

DP-331 and DP-127 were taken as two representative photolysis products and analyzed in detail in Figures 4 and 5. The blue dashed lines highlight specific bond cleavages, thereby visualizing the structural basis for their mass spectral fragmentation.

For DP-331, m/z 331.05301 matched the composition of C₁₃H₉F₃N₂O₅⁺ (Figure 4). The ion at m/z 313.04242 corresponded to the loss of H₂O from C₁₃H₉F₃N₂O₅⁺, confirming the presence of a carboxylic acid moiety. The subsequent fragment at m/z 287.06380 was identified as C₁₂H₁₀N₂O₃F₃⁺. Further neutral loss of NH₃ generated the ion at m/z 274.06799, which then lost H₂O to yield the fragment at m/z 256.05627. The fragment at m/z 162.01857 fit the formula C₈H₄NO₃⁺. Notably, construction of the conjugated C=N=O moiety presumably arises from pyrimidine ring cleavage, a fragmentation pathway corroborated by characteristic neutral loss patterns in the MS² spectrum of the parent BFA.

For DP-127, the protonated molecule at m/z 127.1117 matched the formula of C₈H₁₅O⁺ (Figure 5). A distinctive feature of the spectrum is the successive loss of H₂O (m/z 109.10135), indicative of a hydroxyl group. The precursor ion readily eliminated H₂O to yield the dominant fragment C₈H₁₃⁺ at m/z 109.1014. Subsequent fragmentation via C–C bond cleavages generated a series of smaller diagnostic ions, including C₆H₉⁺ (m/z 81.0703) and C₅H₇⁺ (m/z 67.0548). Notably, the concurrent ions of C₄H₇⁺ (m/z 55.0549) and C₄H₉⁺ (m/z 57.0704) arising from the specific chain cleavage supported the proposed structure.

Based on the identified photolysis products, the BFA tends to proceed through two distinct photolysis pathways (Fig-

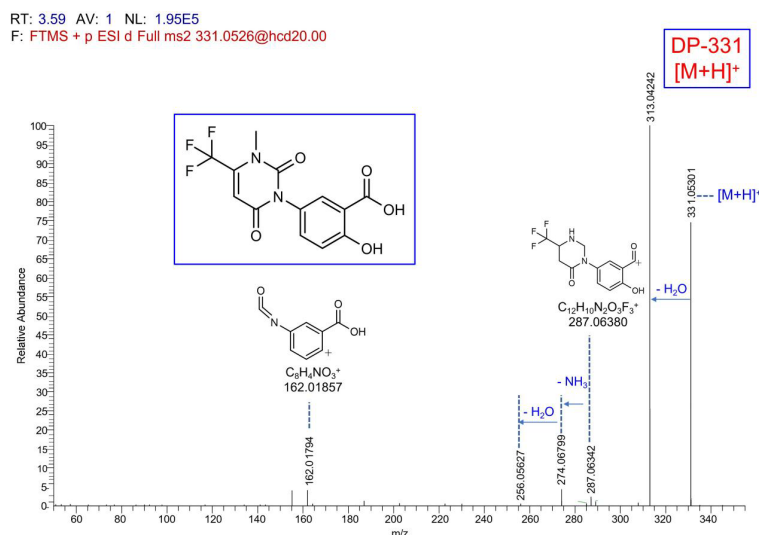


Fig. 4. Fragmentation pattern of DP-331

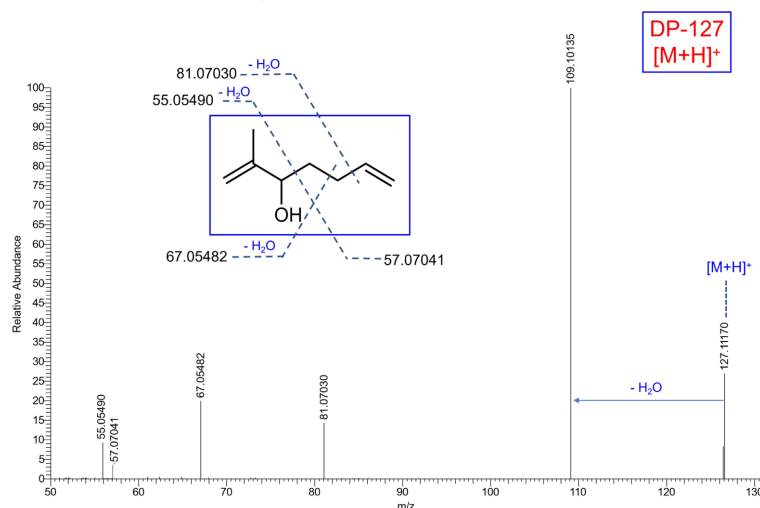
RT: 3.64 AV: 1 NL: 4.60E4
F: FTMS + p ESI d Full ms2 127.1117@hcd20.00

Fig. 5. Fragmentation pattern of DP-127

ure 6). Pathway I is initiated by the oxidative rearrangement and cleavage of the side-chain alkene and adjacent ester bond, yielding low-molecular-weight products such as DP-230, DP-127, and DP-143. This fragmentation pathway is corroborated by diagnostic ions at m/z 101.05896 (from DP-143) and m/z 55.05490 (from DP-127), which indicate homolytic cleavage of the BFA side chain mediated by carbon-centered radicals. Among these, DP-230 likely results from ester hydrolysis accompanied by reductive amination, whereas DP-143 and DP-127 contain a short-chain ketone and hydroxyl moiety, respectively, reflecting cleavage, recombination, and hydroxylation of the side chain. Pathway II relates to the degradation of the core heterocycle: the pyrimidinedione ring of BFA first undergoes hydroxylation to form DP-331, followed by ring-opening cleavage to generate DP-319. DP-319 is then converted to DP-187 via the loss of benzaldehyde, followed by oxidation/demethylation to yield DP-157.

In summary, BFA photolysis is governed by side-chain cleavage, splitting into Pathway I (formation of stable, accumulating derivatives) and Pathway II (gradual degradation of the heterocyclic core). Although both pathways happen simultaneously, the main products of side-chain derivatives (e.g., DP-143 and DP-127) indicate that Pathway I is the major photolytic

route.

The environmental fate of BFA is governed by both hydrolytic and photolytic pathways. Under ambient conditions, hydrolysis is the predominant transformation route, particularly under alkaline conditions. This process is characterized by the cleavage of the ester linkage, leading to the release of the side chain, accompanied by uracil-ring modification and N-demethylation. This pathway retains the integrity of the pyrimidinedione core and the trifluoromethyl (CF_3) moiety, yielding highly persistent, fluorinated residues such as CGA-293731, which are documented in regulatory assessments[22].

UV irradiation triggers a different degradation paradigm. Photochemical energy induces oxidative rearrangement and cleavage of the side-chain alkene, as well as the adjacent ester bond. This process actively disrupts the fluorinated pyrimidine moiety, explaining why the photoproducts identified in this study are structurally distinct from hydrolysis products[22]. However, the efficiency of this photolytic breakdown is highly sensitive to the aqueous matrix. In natural waters characterized by high levels of DOM and nitrate (NO_3^-), the shielding and quenching effects significantly inhibit BFA photolysis[40]. Consequently, in complex environmental matrices (e.g., estuaries with high DOM, low pH, and high nitrate), the suppression of the primary photolytic pathway is likely to prolong the persistence of BFA.

3.4. ECOSAR analysis

Notably, unlike those from hydrolysis, photolysis predominantly generated BFA derivatives without the trifluoromethyl group, suggesting a reduction in potential ecological hazard. As demonstrated by the concentration dynamics (Figure 7), the levels of the photoproducts DP-127 and DP-143 increased continuously throughout the 120 min light exposure. This result indicated that they were the primary stable end products, possessing the potential for long-term persistence and accumulation in water bodies. In contrast, products such as DP-157, DP-187, and DP-185 accumulated during the initial period of time, and then declined following the complete degradation of BFA, indicating they were photolytic intermediates. Other products that remained at consistently low concentra-

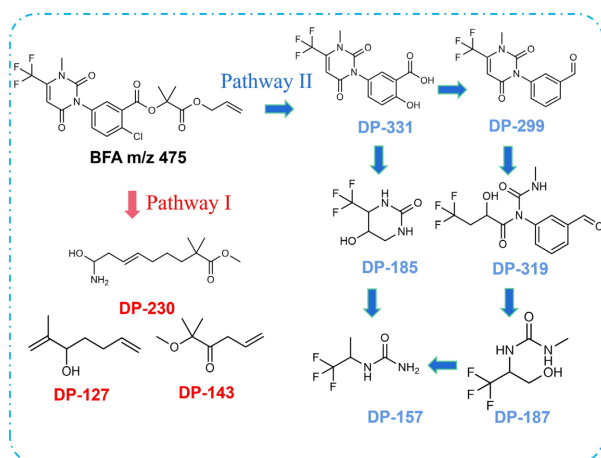


Fig. 6. Proposed photolysis pathways of BFA under UV irradiation (see Table S3 for details).

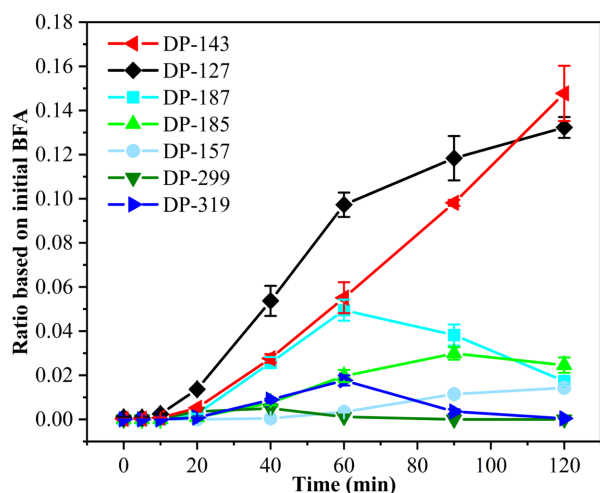


Fig. 7. Temporal changes in the relative concentrations of major BFA photolysis products (peak area normalized to the initial BFA concentration).

tions, such as DP-299 and DP-319, were also supposed to be intermediates. It should be noted that the total peak area of the identified products did not fully recover the initial BFA mass, as products of poorly ionized or low-molecular-weight ($m/z < 50$ Da) were undetectable in this ESI-LC-HRMS.

Toxicity prediction results from the ECOSAR model indicated that the acute toxicity of most photolysis products was lower than that of BFA. Only DP-319 and DP-229 exhibited slightly higher toxicity to green algae, whereas DP-127 showed significantly greater toxicity to daphnids and fish compared to BFA (Figure 8, Table S4).

For green algae, the toxicity of major products, e.g., DP-127 and DP-143, was markedly reduced. For fish and daphnia, the LC_{50} values of nearly all the products increased substantially (indicating lower toxicity). ECOSAR predictions indicated that the LC_{50} of DP-331 for fish was roughly 47-fold that of BFA, while the LC_{50} of DP-185 for daphnia was approximately 10,000-fold higher, demonstrating that photolysis of BFA was

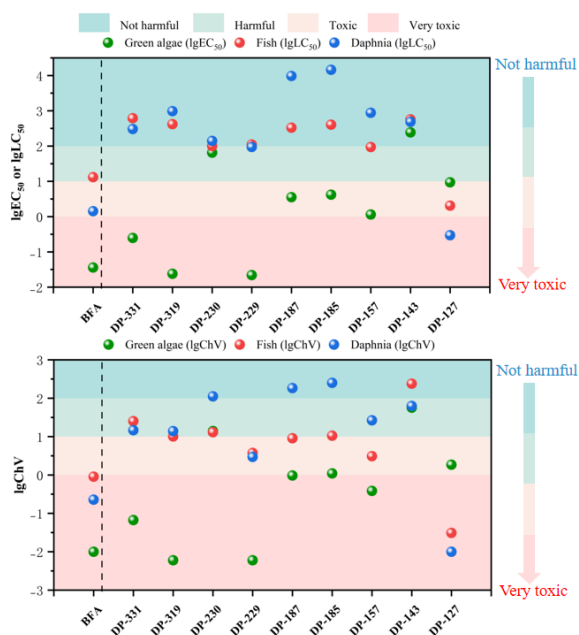


Fig. 8. Predicted toxicity of the major photolysis products of butafenacil (BFA) to three aquatic organisms based on the ECOSAR model.

an effective detoxification pathway towards daphnia and fish.

Regarding green algae, the toxicity of most products was much lower than that of BFA. For example, the toxicity of DP-143 and DP-230 was reduced by three to four orders of magnitude compared to BFA. Although the EC_{50} values of DP-319 and DP-229 for green algae were comparable to BFA, their concentrations were remarkably lower, thus leading to a net reduction in overall toxicity.

DP-127 is a notable exception with a 48 h- LC_{50} of only 0.297 mg/L for daphnids and a 96 h- LC_{50} of 2.046 mg/L for fish, significantly lower (i.e., more toxic) than those of BFA. This suggests that the photochemical rearrangement and cleavage of the alkene side chain and ester bond in BFA can generate intermediates with enhanced acute toxicity to small crustaceans and fish. Given that DP-127 was a major photolysis product with high stability to UV, it might pose a high potential risk to daphnia and fish populations, and further animal tests should be necessary.

The prediction results from ECOSAR modeling indicate that photolysis can significantly reduce the acute toxicity of BFA to algae, fish, and daphnia. Two predominant products of DP-127 and DP-143 are likely responsible for the observed reduction in acute toxicity to algae. However, the complete photolysis of BFA does not equate to perfect detoxification, as "high-risk products" with substantial toxicity were generated, indicating that some photolysis products should be included in the environmental risk assessment in addition to the parent compound.

4. Conclusion

This study demonstrated that solar radiation, particularly UV photolysis, was an effective detoxification factor of BFA to microalgae in surface aquatic environments. Furthermore, low concentrations of natural DOM and nitrate were sufficient to inhibit BFA photolysis, whereas alkaline conditions accelerated the process. The primary stable photolysis products without the $-CF_3$ moiety, such as DP-127 and DP-143, were considered as key contributors to the reduced toxicity of BFA towards algae. However, ECOSAR modeling predicted that DP-127 exhibits high acute toxicity to daphnids and fish. Therefore, while photolysis mitigates risk to primary producers, it may potentially increase the ecological risk to higher trophic levels.

While QSAR prediction models worked well for screening out high-risk structures, they can't replace actual toxicology experiments. Future work should focus on the chemical synthesis or preparative isolation of key DPs to confirm their ecotoxicological effects. In conclusion, marine ecological risk assessments should not focus solely on the parent herbicide but should also consider the hazards posed by its persistent, toxic transformation products.

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Conflicts of Interest

The authors declare that they have no conflicts of interest.

Electronic Supplementary Material (ESM)

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