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Dissolved black carbon mediated photo-transformation of tetrachlorantraniliprole: Kinetics, pathways, and adverse effects of the photoproduct

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ABSTRACT

The combustion of agricultural and forestry residues, along with subsequent runoff, can lead to the production of a significant quantities of dissolved black carbon (DBC), which plays a pivotal role in the photo-transformation of organic pesticides. As a result, the photochemical activity of DBC and its associated photo-transformation mechanisms must elucidate. This study investigated the effect of DBC on tetrachlorantraniliprole (TCTP) photo-transformation, a new type of pesticide independently developed and widely used in China, using photochemical simulation experiments. The results revealed that the prepared DBC had a smaller molecular weight and higher aromaticity, generating $^3\text{DBC}^*$, $\cdot\text{OH}$, and $^1\text{O}_2$, with apparent quantum yields of 4.75×10^{-2} , 4.35×10^{-5} , and 4.01×10^{-2} , respectively. $^3\text{DBC}^*$ was the dominant intermediate reactive responsible for accelerating TCTP photolysis by determining its direct photolysis rate constant as 0.278 min^{-1} . The degradation pathway of TCTP mainly involved nucleophilic substitution, dechlorination, and cleavage of the C–N bond. Notably, TCTP can photo-generate the cross-condensation products only in the presence of DBC. Ecotoxicity and organ-specific toxicity analysis demonstrated reduced environmental risks compared to TCTP for both direct photoproducts, as well as those mediated by DBC. These findings highlighted how DBC altered the photo-transformation pathway leading to decreased environmental risk-associated amide pesticides.

1. Introduction

Black carbon (BC) is a carbon-rich residue produced by the combustion of fossil fuels and biomass [1,2]. Globally, agricultural activity significantly contributes to the quantity of agricultural waste, which releases substantial quantities of BC into the soil, atmosphere, and aquatic environments. Estimates have shown that the worldwide production of BC ranges from 114 to 383 Tg per year [3]. BC can store carbon elements in long-term carbon reservoirs, alleviating global climate change, and serving as a key element in the global carbon budget [4–6]. The water-soluble fraction of BC continuum is defined as dissolved black carbon (DBC), which acts as a key link connecting the two

main black carbon reservoirs of land soil and ocean sediment and comprises an important component of natural dissolved organic matter (DOM) pools [3,7]. In recent years, researchers have extensively focused on the photochemistry of DBC, which has had a significant impact on the fate of contaminants in aquatic environments [3,8–10]. Therefore, it is important to appreciate the photochemical activity effect of DBC on the migration and transformation of contaminants.

Research has shown that photo-transformation can cause irreversible changes to the molecular structure of contaminants, which will determine their persistence in surface water, and making it critical to assess ecological risks [11,12]. DOM is a widely present organic molecule mixture in water, with a dual influence on the photo-transformation of

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contaminants. DOM can serve as a photosensitizer for the degradation of organic contaminants by producing various reaction intermediates (RIs) through photochemistry, such as singlet oxygen ($^1\text{O}_2$), hydroxyl radicals ($\cdot\text{OH}$), superoxide anion ($\text{O}_2^{\cdot-}$), and the excited triplet state ($^3\text{DOM}^*$) [13,14]. In addition, DOM can suppress the photo-transformation of contaminants by competing for the absorption of photons and consuming RIs [15]. As a prominent component of DOM, DBC exhibits similar characteristics to DOM, however, its chemical and structural properties significantly differ from DOM.

DBC is a mixture that contains functional groups such as phenolic and carboxyl groups, with a relatively uniform structure [16]. Because of this unique chemical structure, DBC may exhibit stronger photochemical properties under sunlight irradiation. The investigation conducted by Fu et al. [17] suggested that simulated DBC sunlight irradiation can generate $^1\text{O}_2$, and its quantum yield may surpass many well-studied DOM types. Hence, it is necessary to consider the impact of DBC on the photo-transformation processes of pollutants in surface water. Some studies have suggested that DOM can affect the photo-transformation pathways of emerging pollutants, alter the toxicity of the photoproduct mixture that forms, and ultimately affect their environmental fate [18]. The effects of DBC on photolysis of emerging pollutants and variation in risk posed by their photoproducts need to further elucidated.

Natural constituents in water (NO_3^- , HCO_3^- , Cl^-) can produce photoactive species, which will obviously affect the photo-transformation of the contaminants [19]. NO_3^- , HCO_3^- , and Cl^- are widely present in lakes and oceans, and will react with $\cdot\text{OH}$ or $^3\text{DOM}^*$ producing ($\text{NO}_2^{\cdot-}$), carbonate radicals ($\text{CO}_3^{\cdot-}$), and dichlorine radicals ($\text{Cl}_2^{\cdot-}$). These products will be reactive toward electron-rich organic micro pollutants [20].

Pesticides are widely used to prevent and eliminate plant diseases and pests. The excessive use and uncontrolled release of pesticides can lead to chronic poisoning, infertility, abortions, malformations, and neurotoxicity in humans and biota. The impact of pesticides on non-target organisms has become a global crisis over the past decades [21–23]. Tetrachlorantraniliprole (TCTP), invented by the Shenyang Research Institute of Chemical Industry, was the first diamide pesticide product developed with independent intellectual property rights in China. TCTP can act on the ry-anodinerreceptors of insects, causing muscle contraction, paralysis, and death of the insects. Currently, TCTP is being used in China to control certain emblem Lepidoptera insects such as *Adoxophyes orana*, and *Pieris rapae*. However, the photo-transformation mechanism of TCTP and the toxicity of the photoproducts on aquatic organisms under the influence of DBC remain unclear. This limits the accurate analysis of TCTP photo-transformation behavior and ecological risks.

This investigation aimed to reveal the photo-transformation behavior of TCTP, focusing on the contribution of DBC to this process. The ecotoxicity and organ-specific toxicities of TCTP photo-transformation products formed with and without DBC were discussed. The photo-transformation and photolysis pathway mechanisms were assessed, and the photo-transformation products were analyzed and identified. The effects of DBC concentrations on photo-transformation were analyzed, and we discussed its mechanism through quenching experiments. Furthermore, the quantum yields and steady-state concentrations of the RIs were calculated in order to evaluate the role of RIs in TCTP photo-transformation and we elucidated the mechanism controlling the reaction. TCTP contained rich electronic structure (e.g., $-\text{NH}-$), which we postulated made TCTP reactive against $\text{NO}_2^{\cdot-}$, $\text{CO}_3^{\cdot-}$, and $\text{Cl}_2^{\cdot-}$. However, the effects of NO_3^- , HCO_3^- , and Cl^- on the photo-transformation of TCTP have rarely been determined, and additional studies as performed in this work.

2. Material and methods

2.1. Chemicals

Tetrachlorantraniliprole (TCTP, 99.6 % purity) was obtained from Alta Scientific Ltd. (China), while Sigma-Aldrich (U.S.A.) provided the following materials: tetrahydrofuran (THF, >99.5 %), furfuryl alcohol (FFA, 98 %), isopropyl alcohol (IPA, 99 %), acetonitrile (99.9 %), and methanol (99.9 %). The following chemicals were provided by Aladdin, Shanghai: phenol (>99 %), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 97 %), 2,4,6-trimethylphenol (TMP, >98 %), and 2,2,6,6-tetramethylpiperidine (TEMP, 98 %). Suwannee River humic acid (SRHA, C, 35.06 %; H, 3.77 %; O, 60.11 %; N, 1.06 %) was obtained from International Humic Substance Society (IHSS) (<https://humicsubstances.org/>). An ultra-pure water system (UPTA-10, Shanghai Lichen Bangxi Instrument Technology Co., Ltd., China) was used to produce the experimental water with a resistivity of 18.3 M Ω ·cm at 25 °C.

2.2. Preparation and characterization of DBC

Rice straw has been chosen as the preferred material for DBC preparation based on the following considerations: Firstly, China, being a prominent agricultural nation, accounts for approximately 35 % of the total food crop planting area, thereby resulting in an abundant yield of rice straw. Secondly, rice straw is commonly employed for field burning and subsequent incorporation into soil to enhance its fertility through biochar formation. Thereafter, the leaching and other effects of biochar contribute to the release of DBC. The feedstock for the rice straw was provided by a farm situated in the suburbs of Suqian City, Jiangsu Province, China.

The biochar commonly found in nature is typically formed through the high-temperature pyrolysis of biomass under strictly anaerobic or anoxic conditions [8]. Therefore, in this study, DBC was prepared via oxygen-limited pyrolysis at high temperature as described by Fu et al. [17]. Specifically, biomass pyrolysis was conducted for 3 h at a temperature of 400 °C and a heating rate of 15 °C/min in a tube furnace with oxygen limitation [3,7]. Following powdered grinding, the resulting biochar was sieved through a 100-mesh (0.15 mm) sieve. Subsequently, a KS-5200DE bath sonicator (Kunshan Jielimei Ultrasonic Instrument, China) was used to sonicate 10 g of rice biochar in 1000 mL of deionized water at an intensity of 100 W for 30 min. To aid in the release of DBC, the mixture was stirred at 200 rpm for 48 h at a temperature of 25 °C in the dark with an HJ-4 magnetic stirrer (Changzhou Ronghua Instrument, China) [2]. The resulting DBC solution, which consisted of the filtrate that passed through the 0.45 μm membranes, was collected and extracted after 3 freeze-drying cycles. After 48 h, the filtrate was freeze-dried under vacuum at -80°C . The resulting DBC powder was kept out of direct sunlight and at room temperature in a desiccator.

The UV–vis spectrum of DBC (200–500 nm) was determined using deionized water as a blank solution and an Envolution201 UV–vis spectrophotometer (Thermo Scientific Instrument, China) in a quartz cuvette with a 1 cm path length. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) and Fourier transform infrared (FT-IR, Thermo Nicolet is 10) spectroscopy were used to examine the precise chemical composition and structure of DBC. The excitation-emission matrix (EEM) spectrum of fluorescence was obtained by scanning the excitation wavelengths between 200 and 500 nm, using an F-7000 fluorescence spectrophotometer, under emission detection between 300 and 600 nm at 5-nm intervals. Total organic carbon (TOC, Shimadzu CPH CN200) measurements were used to calculate the DBC concentration.

To investigate the production and strength of the radiation induced RIs, electron paramagnetic resonance (EPR) spectra were also obtained. Using DMPO and TEMP as a spin trap to generate spin adducts at room temperature, an EPR spectrometer was utilized to monitor $\cdot\text{OH}$ and $^1\text{O}_2$ [24]. For 30 min, the DBC solutions were exposed to artificial sunshine.

Subsequently, TEMP and DMPO were used with DBC solutions to trap $^1\text{O}_2$ and $\cdot\text{OH}$, respectively, and the solution samples were used to determine the RIs after mixing. Main RIs ($\cdot\text{OH}$, $^1\text{O}_2$, and $^3\text{DBC}^*$) that generated by the DBCs under irradiation has been detected utilizing molecular probe techniques [3,25].

2.3. Photochemical reaction experiments

Using 50 mL quartz colorimetric tubes, the photolysis kinetics of TCTP was investigated using batch studies, at a reaction temperature of $25 \pm 1^\circ\text{C}$. To eliminate interference from other factors, all the experiments on the photodegradation of TCTP with or without DBC were conducted in pure water. Tube insertion into photochemical reactor (XPA-1, Nanjing Xujiang Electromechanical Plant, Nanjing, China), which were subsequently rotated. The 500 W high-pressure mercury lamp fitted with 290 nm cut-off filters was placed under refrigeration (Fig. S1). Previous studies [7,26,27] have demonstrated that the spectral characteristics of sunlight on surface water can be effectively simulated using a 500 W mercury lamp in conjunction with a 290-nm filter. Consequently, numerous photochemical simulation experiments of organic pollutants have been conducted under these specific light source conditions [26,27]. The same reaction conditions were also used for the control tests without DBCs, and aluminum foil was used to cover the tubes for the dark control trials. Under predetermined time intervals, a 0.5 mL sample volume was collected from the reaction solution for the analysis of the concentration variation of TCTP. All irradiation experiments were performed in triplicate.

Text S1 describes the pseudo-first-order rate constants (k_{obs}) for photodegradation of TCTP. Equations (1)–(4) demonstrate how the indirect photo-transformation rate constant (k_{ip} , min^{-1}) of TCTP was determined using the attenuated direct photo-transformation rate constant (k_{dp} , min^{-1}) with DBC and the measured apparent photo-transformation rate constant (k_{obs} , min^{-1}). We determined k_{dp} by measuring the direct photo-transformation rate constant ($k_{\text{H}_2\text{O}}$, min^{-1}) of TCTP without DBC and the accumulated light screening coefficient of DBC from 290 to 320 nm, k_{dp} was determined.

$$k_{\text{obs}} = k_{\text{dp}} + k_{\text{ip}} \quad (1)$$

$$k_{\text{dp}} = k_{\text{H}_2\text{O}} * S\lambda_{\lambda} \quad (2)$$

$$S_{\lambda} = \frac{1 - e^{-2.303\alpha_{\lambda}L}}{2.303\alpha_{\lambda}L} \quad (3)$$

$$S_{290-320} = \frac{\int_{290}^{320} S_{\lambda} dS_{\lambda}}{320 - 290} \quad (4)$$

where S_{λ} is the light-screen factor, L (2 cm) is the route length of the tubes in the photochemical investigations, and α_{λ} (cm^{-1}) denotes is the attenuation coefficient particular to a wavelength.

Scavenging tests were carried out using IPA (10 μM) as a quencher of $\cdot\text{OH}$, THF (20 μM) as a quencher of $^1\text{O}_2$, and TMP (20 μM) as a quencher of $^3\text{DBC}^*$ in order to clarify the contributions of the RIs photodegradation of TCTP. Text S2 in the [Supplementary Material](#) contains a thorough description of the procedures used to determine the steady-state concentrations of $\cdot\text{OH}$ ($[\cdot\text{OH}]_{\text{ss}}$), $^1\text{O}_2$ ($[^1\text{O}_2]_{\text{ss}}$), and $^3\text{DBC}^*$ ($[^3\text{DBC}^*]_{\text{ss}}$).

The quantum yield of RIs (Φ_{RI}) could be determined by:

$$\Phi_{\text{RI}} = \frac{R_{\text{RI}}}{\sum k\alpha(\lambda)[\text{DBC}]} \quad (5)$$

$$k\alpha(\lambda) = \frac{I\lambda\varepsilon(\lambda)(1 - 10^{-\varepsilon(\lambda)[\text{DBC}]z})}{\varepsilon(\lambda)[\text{DBC}]z} \approx 2.303I\lambda\varepsilon(\lambda) \quad (6)$$

where $k\alpha(\lambda)$ is the characteristic light absorption coefficient of DBC ($\text{einstein}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}\cdot\text{nm}^{-1}$), $[\text{DBC}]$ is the dissolved concentration of DBC

(mg C/L), $\varepsilon(\lambda)$ is the molar absorption coefficient of DBC ($\text{L mgC}^{-1}\text{cm}^{-1}$), z is the depth of the solution (m).

The steady-state concentration of $\cdot\text{OH}$ ($[\cdot\text{OH}]_{\text{ss}}$, M), $^1\text{O}_2$ ($[^1\text{O}_2]_{\text{ss}}$, M), and $^3\text{DBC}^*$ ($[^3\text{DBC}^*]_{\text{ss}}$, M) could be determined by:

$$[\cdot\text{OH}]_{\text{ss}} = \frac{R_{\cdot\text{OH}}}{k_{\text{benzene}, \cdot\text{OH}}[\text{benzene}]} \quad (7)$$

$$[^1\text{O}_2]_{\text{ss}} = \frac{R^1\text{O}_2}{k_{\text{FFA}, ^1\text{O}_2}[\text{FFA}] + S^1\text{O}_2} \quad (8)$$

$$[^3\text{DBC}^*]_{\text{ss}} = \frac{R^3\text{DBC}^*}{k_{\text{TMP}, ^3\text{DBC}^*}[\text{TMP}] + S^3\text{DBC}^*} \quad (9)$$

where R_{RI} denotes the RI generation rate, $k_{\text{benzene}, \cdot\text{OH}}$ is the second-order reaction rate of benzene reacting with $\cdot\text{OH}$ ($7.8 \times 10^9 \text{ s}^{-1}$), $k_{\text{FFA}, ^1\text{O}_2}$ is the second-order reaction rate constant of FFA with $^1\text{O}_2$ ($1.2 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$), $S^1\text{O}_2$ is the solvent quenching reaction rate constant of $^1\text{O}_2$ ($2.5 \times 10^5 \text{ s}^{-1}$), $k_{\text{TMP}, ^3\text{DBC}^*}$ is the second-order reaction rate constant of TMP with $^3\text{DBC}^*$ ($8.1 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$), and $S^3\text{DBC}^*$ ($3.1 \times 10^5 \text{ s}^{-1}$) is the sum of the reaction rate constant of $^3\text{DBC}^*$ reaction with ground state dissolved oxygen ($2.2 \times 10^5 \text{ s}^{-1}$) and quenching constant of $^3\text{DBC}^*$ caused by other factors ($9.0 \times 10^4 \text{ s}^{-1}$).

The initial concentrations of TCTP were set at 15 μM to facilitate the investigation of the degradation products and aid in their identification. The photodegradation products of TCTP in the presence of DBC has been investigated by using ultra-high performance liquid chromatography–mass spectrometry (UPLC-MS). During the simulated sunlight irradiation, samples were collected at specific time intervals (0, 2, and 10 min) for analysis.

2.4. Prediction of photoproduct toxicity

2.4.1. Ecotoxicity evaluations

To establish a foundation for the ecological risk evaluation of the pollutants in this work, the ecotoxicity information of the produced pollutants were assessed using EPIWEB 4.1 Software. The environmental toxicity of TCTP and its photo-transformation products were estimated by ECOSAR 2.2. To achieve this objective, the chronic toxicity (Chv), half effect concentration (EC_{50}), and half lethal concentration (LC_{50}) of three aquatic organisms (green algae, daphnia, and fish) were computed.

2.4.2. Organ-specific toxicity predictions

A web-based ProTox-II database was used to forecast the toxicological outcomes associated with the molecular architecture. ProTox-II predicted the potential toxicity of known and unknown chemicals using machine learning models trained on published document data, either in vitro or in vivo [28,29]. Verifying and screening out three different degrees of toxicity of photo-transformation products was conducted by (a) hepatotoxicity, carcinogenicity, immunotoxicity (inhibition of B cell growth), mutagenicity, and cytotoxicity; (b) toxicological pathways, evaluated by nuclear receptor signaling pathways (aryl hydrocarbon receptor (AhR), androgen receptor (AR), androgen receptor ligand binding domain (AR-LBD), aromatase, estrogen receptor alpha (ER), estrogen receptor ligand binding domain (ER-LBD), and peroxisome proliferator-activated receptor gamma (PPAR-Gamma); (c) stress response pathways evaluated by nuclear factor (erythroid-derived 2)-like 2/antioxidant responsive element (nrf2/ARE), heat shock factor response element (HSE), mitochondrial membrane potential (MMP), phosphoprotein (tumor suppressor) p53 and ATPase family AAA domain-containing protein 5 (ATAD5).

2.5. Analytical methods

The contents of TCTP, FFA, and TMP during the experimental process were analyzed by High Performance Liquid Chromatography

(HPLC) with a 4.6×250 mm Kromasil 100–5–C18 column (Wukong-K2025 Technologies, Shandong, China). The flow phase composition, detection wavelengths, and flow rates are shown in Table S1. The intermediate products of TCTP photodegradation were determined using Ultra Performance Liquid Chromatography Tandem Mass Spectrometry (UPLC-MS), and the detailed analysis methods are shown in Text S3. When conducting the photo-transformation experiments, an equal volume solution of 0.5 mL was removed and filtered through $0.22 \mu\text{m}$ membranes before HPLC analysis. Statistical analysis and graphic construction were conducted using IBM SPSS Statistics 27 and Origin 2021 software, respectively, and the differences between the different experimental groups were evaluated by one-way analysis of variance, then separated using a least significant difference (LSD) test.

3. Results and discussion

3.1. Optical performance of DBC

The DBC spectrum was wide and non-characteristic, indicating the presence of a conjugated system in the molecule (Fig. 1a). The characteristic free spectra of DBC indicated that various chromophores were present, with an absorbance overlap and charge transfer phenomenon between the chromophores. The optical performance (i.e., E_2/E_3 , E_4/E_6 , and SUVA_{254}) of the DBC samples was calculated. DBC had higher E_2/E_3 (4.39) and SUVA_{254} values (4.21) than well-studied natural dissolved organic matter (NOM) [8,10], indicating that it had a higher degree of aromatization and lower relative molecular weight. The E_4/E_6 of DBC (3.5) was significantly lower than that of DOM (4.7–14.5), possibly because DBC contained more conjugated structures [30]. This suggested that DBC had higher photoreactivity than NOM.

FT-IR analysis (Fig. 1b) showed that DBC contained an obvious characteristic peak at 3400 cm^{-1} , which was caused via O–H vibrations in the carboxyl group [31], indicating a rich distribution of carboxyl groups. The vibration peaks of DBC at 1600 cm^{-1} and 1380 cm^{-1} were due to the stretching vibration of the aromatic C=C double bond [32] and in-plane bending vibration of CH_3 , respectively. The band strength was weak, indicating low aromaticity. The vibration peak of DBC at 1100 cm^{-1} was the result of C–O single bond stretching vibrations [31], while the characteristic peaks at 790 cm^{-1} and 540 cm^{-1} represented different benzene ring substitutions. These results indicated that the DBC surface contained many hydrophilic functional groups.

The XPS peak of C1s measured (Fig. 2b) could be deconvoluted into four surface constituents, which corresponded to C–C/C–H at a binding energy of 284.8 eV , C–O at 286.3 eV , and C=O at 288.03 eV . This indicated the coexistence of aliphatic carbon domains (CC and CO) and aromatic carbon domains (C=C) in DBC, and these structures

contributed to the generation of more reactive intermediates by DBC [25].

The EEM spectrum of DBC contained a strong peak at the excitation/emission wavelength pair of $\text{Ex/Em} = (200\text{--}250) \text{ nm}/(>400) \text{ nm}$ and $(250\text{--}380) \text{ nm}/(>400) \text{ nm}$ (Fig. 2d). This has been commonly associated with the presence of fulvic acid-like and humic acid-like compounds [33]. Similar results have also been found in the EEM spectra of DBC derived from bamboo biomass [17]. The EEM spectra of DBC samples were simpler than DOM, and DOM demonstrated peaks in multiple EEM regions [34], indicating the presence of fewer complex fluorophore components. According to the UV–vis, FT-IR, XPS, and EEM characterization results, we speculated that DBC had promoting effects on TCTP degradation.

3.2. Photo-transformation kinetics

The photo-transformation rate constants (k_{obs}) of TCTP were determined in pure water and solutions containing anions (Cl^- , NO_3^- , and HCO_3^-). As indicated by the results in Fig. 3, no significant decrease in the concentration of TCTP was observed under dark conditions, declaring that the decrease in TCTP concentration was primarily caused by photo-transformation. The k_{obs} results of TCTP were $0.278 \pm 0.001 \text{ min}^{-1}$ in pure water, $0.309 \pm 0.002 \text{ min}^{-1}$ in the solution contained NO_3^- , $0.221 \pm 0.001 \text{ min}^{-1}$ in the solution contained HCO_3^- , and $0.326 \pm 0.002 \text{ min}^{-1}$ in the solution contained Cl^- .

NO_3^- is a photosensitizer that can produce photoreactive transient species ($\cdot\text{OH}$ or $\text{NO}_2^{\cdot-}$) under irradiation [35]. In the range of $\lambda = 315\text{--}320 \text{ nm}$, NO_3^- will exhibit strong light absorption [36]. Research has demonstrated that NO_3^- (5 mM) will prompt faster TCTP photo-transformation, possibly due to the photosensitization effect by the NO_3^- . However, HCO_3^- exhibits no light absorption, but can react with hydroxyls and other oxidative free radicals, consuming RIs [37]. Therefore, due to this scavenging effect, expected that HCO_3^- could inhibit the photo-transformation of TCTP. The results of this study showed that HCO_3^- inhibits TCTP photodegradation, which could be explained by reaction with oxidizing radicals.

In comparison to NO_3^- or HCO_3^- , Cl^- significantly enhance the photolysis of TCTP. Previous studies [38] have also demonstrated that the presence of Cl^- can enhance the photolysis of organic pollutants. The enhancement can be attributed to Cl^- acting as a scavenger for $\cdot\text{OH}$ and its ability to generate $\text{Cl}_2^{\cdot-}$ while trapping $\cdot\text{OH}$ [39]. It has been found that $\text{Cl}_2^{\cdot-}$ promotes the photo-transformation of contaminants by reacting with electron rich chromophores. TCTP contains several electron rich chromophores such as benzene ring, pyridine ring, and pyrazole ring. Therefore, it is possible that the reaction between $\text{Cl}_2^{\cdot-}$ and TCTP contributes to the enhanced influence on Cl^- for TCTP photo-transformation.

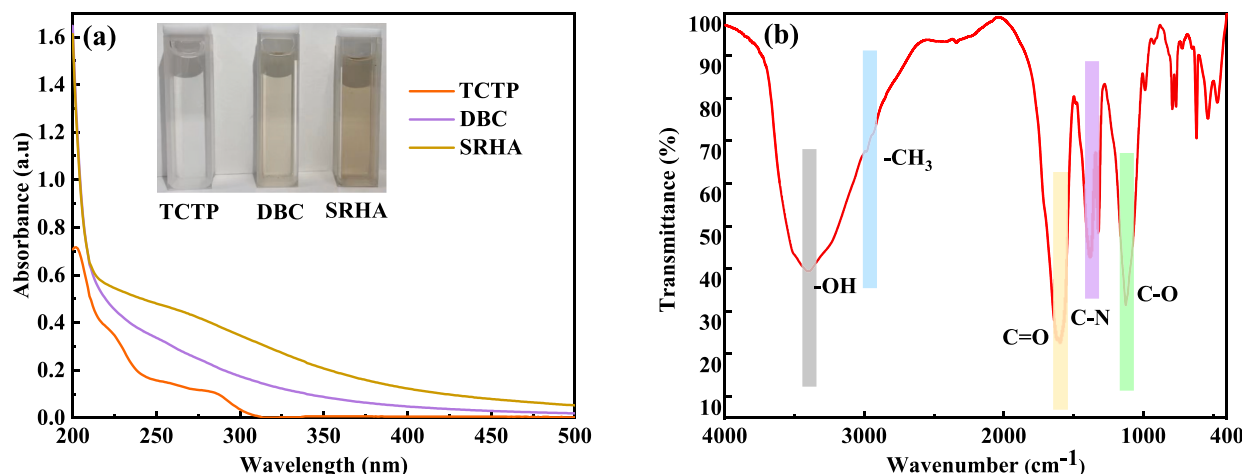


Fig. 1. (a) The UV–vis spectrum of the DBC solution, (b) the FT-IR spectrum of DBC.

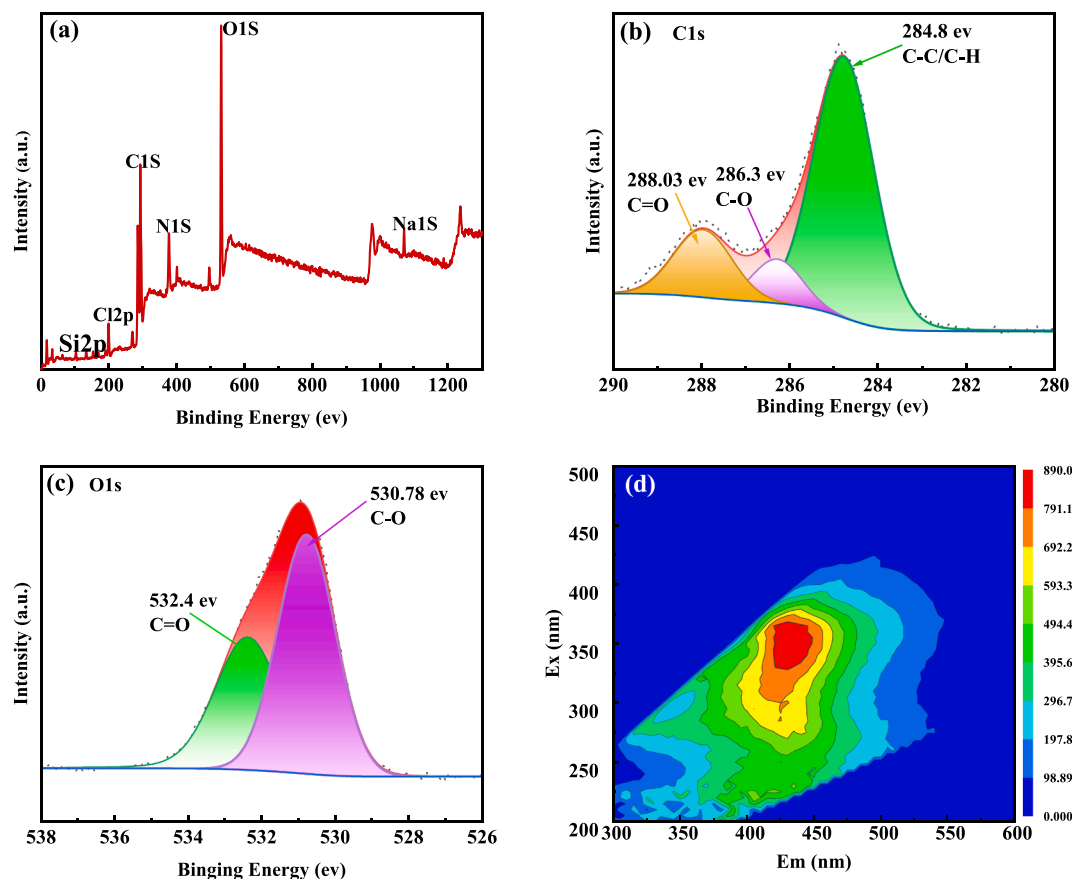


Fig. 2. (a) The XPS spectrum of DBC, (b) the XPS peak of C1s, (c) the XPS peak of O1s, (d) the EEM spectra of 2 mg C/L DBC.

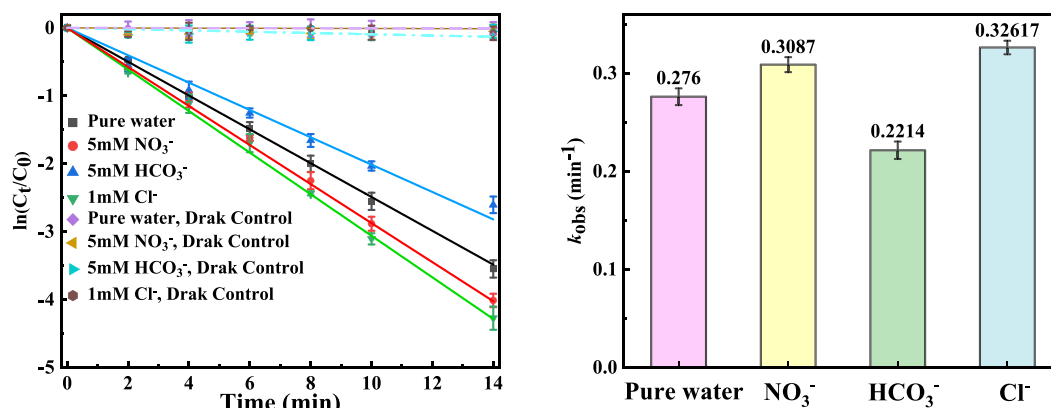


Fig. 3. Plots of degradation kinetics of TCTP in pure water and in solutions containing specific anions, as well as the determined k_{obs} of the TCTP.

3.3. Photo-transformation of TCTP in the presence of DBC

The k_{obs} of TCTP in the presence of DBC is studied (Fig. 4). The addition of 2 mg C/L of DBC significantly enhanced the photo-transformation of TCTP, and the k_{obs} value increased to 0.323 min⁻¹. Under dark conditions, the removal of TCTP in 2 mg of C/L DBC solution was negligible (Fig. S2), indicating that DBC had almost no adsorption effect on TCTP. Therefore, DBC could promote the indirect photo-transformation of TCTP and accelerate its photo-transformation.

At a low DBC concentration (<2 mg C/L), the k_{obs} of TCTP increased from 0.285 to 0.323 min⁻¹ when the DBC concentration increased from 0.5 to 2 mg C/L. However, the TCTP photo-transformation decreased to 0.156 min⁻¹ when the DBC concentration was further increased to 10

mg C/L (Table S2). The k_{obs} of TCTP with DBC (0.5–2 mg C/L) was found to be higher than without DBC. Notably, as the concentration of DBC increased, the enhancing effect of DBC on TCTP photo-transformation gradually weakened, and inhibition was even observed. This observation was similar to observations for chiral pesticides triadimefon and triadimenol [40].

The following analysis was used to explain the observed phenomenon. DBC could generate RIs (i.e., ³DBC*, ¹O₂, and ·OH) by absorbing light, which could accelerate the photo-transformation of TCTP. As the concentration of DBC increased, it competed with TCTP to absorb photons, causing a lower observed k_{obs} and the clearing effect of ³DBC* by DBC was more pronounced at high concentrations. Previous studies also reported that high concentrations of DOM had a scavenging effect

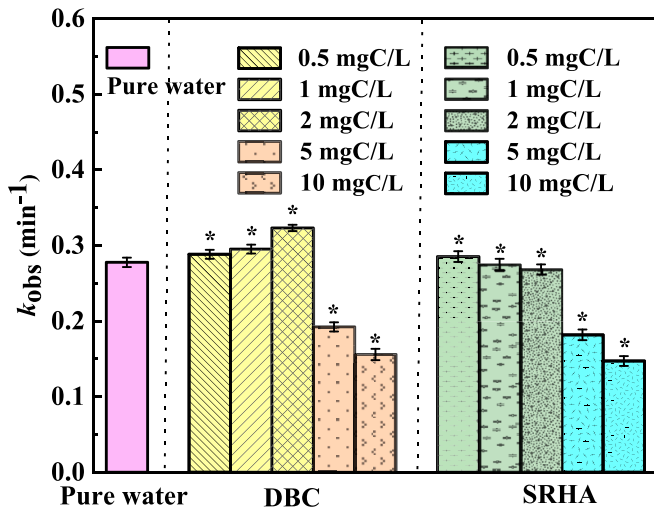


Fig. 4. Photo-transformation of TCTP in the solutions containing DBC and SRHA.

on $^3\text{DOM}^*$ [41].

The comparison included SRHAs with well-studied photochemical activity [10] and at the same concentration, the k_{obs} of TCTP with SRHA was found to be lower than that of DBC (Fig. 4). These results indicated that DBC had a lighter inhibitory effect on TCTP and higher photochemical activity compared to SRHA, which was possibly related to their structure [10]. The ability of DOM to generate RIs was related to its chemical and structural properties, where the higher the aromaticity and lower the molecular weight, the stronger its ability to generate RIs [42,43]. UV-vis and EEM characterization of DBC indicated that DBC contained more aromatic structures and humic components, with a lower molecular size than SRHA. Therefore, DBC was expected to generate more $^3\text{DBC}^*$ and $^1\text{O}_2$, promoting the effect on TCTP photo-transformation.

SRHA had a stronger inhibitory effect on TCTP compared to DBC. This was possibly due to the competitive absorption of photons by TCTP (Fig. 1a). Due to light competition between chromogenic DBC, SRHA, and TCTP, the k_{obs} rate of TCTP was affected by DBC and SRHA. Because the absorption wavelengths of DBC, SRHA, and TCTP overlapped at 290–320 nm, DBC and SRHA functioned as an inner filter to reduce photon availability for the direct photo-transformation of TCTP. To further assess the inhibition degree of TCTP photo-transformation through the light shielding effect induced by DBC or SRHA, the light

screening factor (S_{λ}) was calculated to correct the direct photolysis rate constants (k_{dp} , Table S3). A significant difference was observed in the contribution of indirect photo-transformation in the DBC or SRHA solutions (Table S3). The light shielding effect and photosensitization effect become more pronounced with the increase in DBC concentration. At higher DBC concentration (>2 mg C/L), the light shielding effect surpasses the photosensitization effect. When the DBC concentration reaches 10 mg C/L, light shielding contributes to -60.2% of TCTP photolysis, while the photosensitization effect contributes 29.4% .

3.4. Mechanism of TCTP photodegradation in the presence of DBC

The three characteristic peaks with 1:1:1 intensities of the $\text{TEMP-}^1\text{O}_2$ adducts, and typical four-line (1:2:2:1) EPR signals of DMPO-OH adducts were detected, indicating the production of $^1\text{O}_2$ and $\cdot\text{OH}$ (Fig. 5).

The chemical probe experiment was performed to confirm the generation of $\cdot\text{OH}$ and $^1\text{O}_2$ in the DBC solutions. Under simulated sunlight irradiation, the concentration of FFA significantly decreased with DBC, indicating the generation of $^1\text{O}_2$ (Fig. S3a). The calculated $[\text{O}_2]_{\text{ss}}$ and $\Phi_{1\text{O}_2}$ values are listed in Table 1, where the $\cdot\text{OH}$ concentrations were measured using a benzol probe compound. As the irradiation time changed, phenol was generated in the system, indicating the production of $\cdot\text{OH}$ (Fig. S3b). The concentration of TMP in the presence of DBC was greatly reduced, indicating the production of $^3\text{DBC}^*$ (Fig. S3c).

The inclusion of dissolved humus (DHS) obtained from IHSS allowed for a more comprehensive assessment of the photoreactivity of DBC, encompassing SRHA, Suwannee River fulvic acid (SRFA), and Suwannee River NOM (SRNOM). The results indicated that the ability of DBC to produce RIs was superior to the ability of DHS to generate RIs.

Table 1

Steady-state concentration and apparent quantum yield of $\cdot\text{OH}$, $^1\text{O}_2$, and excited triplet state for DBC and DHS.

[RI] _{ss} ($\times 10^{-14}$ M)			Φ ($\times 10^{-2}$)			Sort
$\cdot\text{OH}$	$^1\text{O}_2$	$^3\text{DBC}^*/^3\text{DHS}^*$	$\cdot\text{OH}$	$^1\text{O}_2$	$^3\text{DBC}^*/^3\text{DHS}^*$	
0.015	29.1	23.8	0.004	4.01	4.75	DBC (this study)
0.011	25.3	27.6	0.006	3.91	7.10	Rice DBC [3,10]
0.004	23.4	8.9	0.001	3.78	1.14	SRHA [46]
0.003	19.9	9.4	0.002	6.30	2.45	SRFA [10]
0.002	16.3	12.1	0.003	9.85	4.65	SRNOM [47]

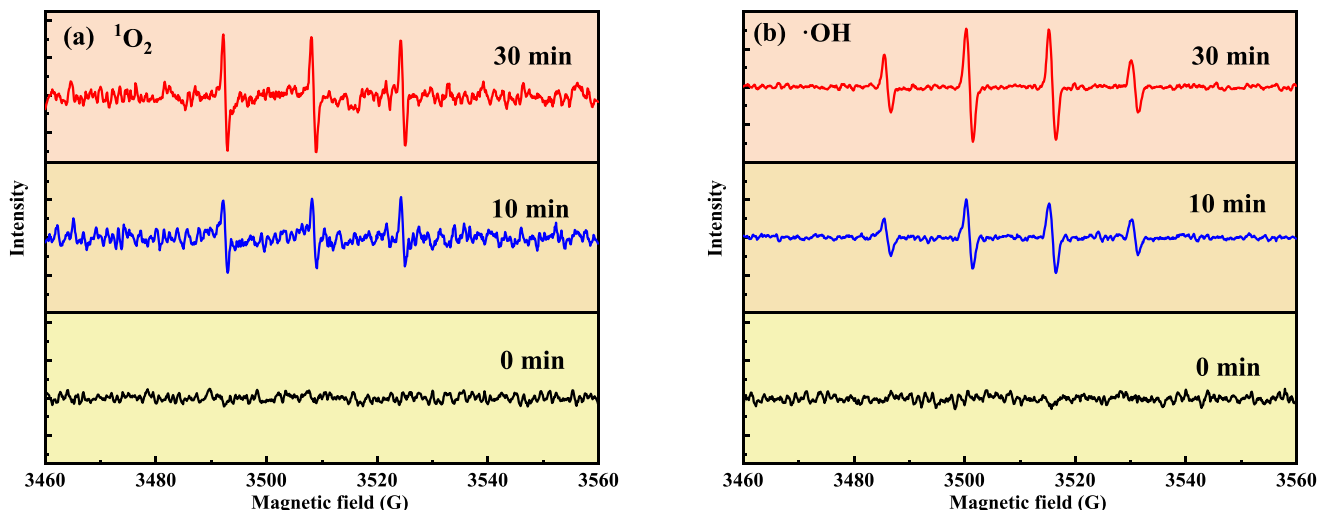


Fig. 5. The EPR spectra of (a) $^1\text{O}_2$ trapped by TEMP, and (b) $\cdot\text{OH}$ trapped by DMPO.

Differences compared to other rice derived DBC were possibly caused by different biomass sources and pyrolysis temperatures [44]. Lin et al. proposed that a lower pyrolysis temperature (250 °C–450 °C) was conducive to the formation of humic acids and neutral low molecular weight substances in DOM, while a higher pyrolysis temperature (450 °C–900 °C) promoted the formation of low molecular weight acids and neutral substances [45], which was related to the quantum yield of RIs [46]. The quantum yield of $^3\text{DOM}^*$ and $^1\text{O}_2$ was positively correlated with the carbonyl content. As a precursor material for $^1\text{O}_2$ and $\cdot\text{OH}$ production, the carbonyl content of $^3\text{DOM}^*$ also affected the quantum yield of $^1\text{O}_2$ and $\cdot\text{OH}$ [47].

The role of RIs in the DBC-mediated photo-transformation of TCTP was verified through quenching experiments (Fig. 6). The results indicated that the photo-transformation of TCTP was significantly reduced after TMP (12.9 %) addition, followed by THF (8.0 %), and IPA (4.1 %). This verified the more important role of $^3\text{DBC}^*$ in the photo-transformation of TCTP. In addition, $^1\text{O}_2$ slightly contributed to the degradation of TCTP. Thus, it was very likely that $^3\text{DBC}^*$ significantly contributed to the photo-transformation of TCTP by DBC.

In addition to the RIs discussed above involved in the photo-transformation of TCTP, superoxide anion ($\text{O}_2^{\cdot-}$) is also a key RIs that can significantly affect the photolysis of organic pollutants [9,25]. Previous study [17] has demonstrated DBC can transfer electron to O_2 and then generate $\text{O}_2^{\cdot-}$, using the probe of XTT reactions with $\text{O}_2^{\cdot-}$ formation of XTT formazan to verify the formation of $\text{O}_2^{\cdot-}$. $\text{O}_2^{\cdot-}$ is a transient precursor for the indirect formation of $\cdot\text{OH}$. From the perspective of mineralization of organic pollutants, the efficacy of $\text{O}_2^{\cdot-}$ falls short compared to that of $\cdot\text{OH}$ [3,16]. Therefore, the impact of $\text{O}_2^{\cdot-}$ was not further considered in the photolysis of TCTP. On the other hand, $\text{O}_2^{\cdot-}$ can alter the molecular structure of organic pollutants through reductive dehalogenation [48–50], thereby modifying their environmental risks. It is necessary to consider the changes in TCTP molecular structure induced by DBC-induced generation of $\text{O}_2^{\cdot-}$ in future studies, thus altering its environmental risk.

Further quantitative evaluation was conducted on the contribution of $^3\text{DBC}^*$ in the photoreaction. Due to the unknown rate constant of the secondary reaction between $^3\text{DBC}^*$ and TCTP, it was difficult to directly evaluate the contribution of $^3\text{DBC}^*$ in the reaction. Therefore, the contribution of $^3\text{DBC}^*$ was estimated by examining the quenching effect [51]. The value of k_{obs} for the reaction of TMP with $^1\text{O}_2$ was nearly an order of magnitude lower than the value of k_{obs} for the reaction of TMP with $^3\text{DBC}^*$, and we expected that the $^1\text{O}_2$ mediated photoreaction was not significantly inhibited by TMP [52]. The k_{obs} value for the photo-

transformation of TCTP in the DBC solutions noticeably decreased from 0.332 to 0.281 min^{-1} as the TMP concentration increased from 0 to 0.5 mM. The predominant role of $^3\text{DBC}^*$ in the indirect photoreaction was confirmed based on the maximum decrease of k_{obs} in the presence of TMP.

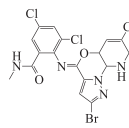
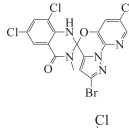
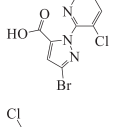
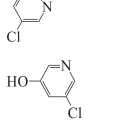
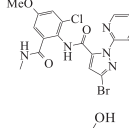
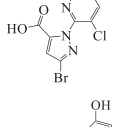
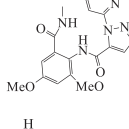
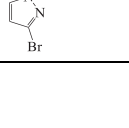
3.5. Analysis of the photo-transformation pathways of TCTP with DBC

The photo-transformation products (PTPs) of TCTP in deionized water and DBC solutions were determined by UPLC-MASS, and the structural identification of the intermediates was determined by MS/MS spectral analysis. The PTPs and possible degradation pathways of TCTP in DBC are presented in Table 2 and Fig. 7. PTPs with m/z values of 501.6/501.55/334.1/149.0/130.1/512.0/318.1/808.2/145.6 were detected in the DBC solution, and the MS/MS spectra of the PTPs are shown in Fig. S4.

The main transformation processes involved the cleavage of the C–N bond, substitution reactions, hydrolysis, addition reactions, and cross-condensation. The degradation pathway of TCTP in the DBC solution occurred via three routes, as depicted in Fig. 7. In pathway I, the C–N bond of TCTP was attacked, followed by hydrolysis, forming small molecular products P334.1 (m/z : 334.1), which were further C–N bond

Table 2

Photoproducts of TCTP in pure water and in solutions containing DBC.

PTPs	ESI (+) MS, m/z	Structural formula	Photolysis	
			without DBC	with DBC
P1	501.6		✓	ND
P2	501.55		✓	ND
P3	334.1		✓	ND
P4	149.0		✓	✓
P5	130.1		✓	ND
P6	512.0		ND	✓
P7	318.1		ND	✓
P8	808.2		ND	✓
P9	145.6		ND	✓

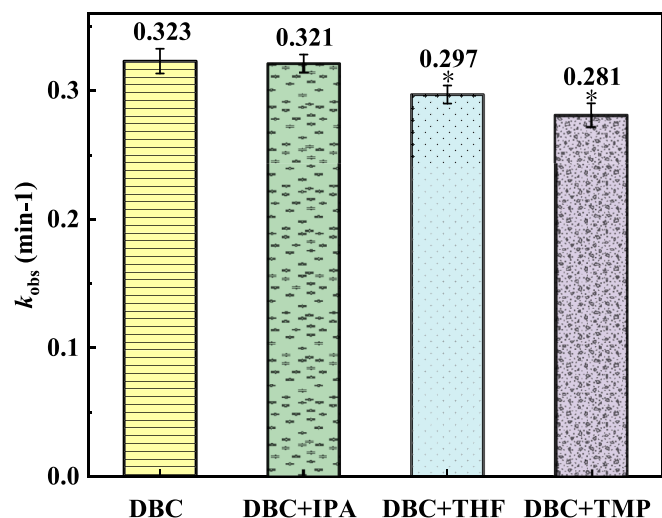


Fig. 6. DBC (2.0 mg C/L) mediated the photo-transformation of TPTC upon the addition of quenchers (IPA, THF and TMP, 20 μM).

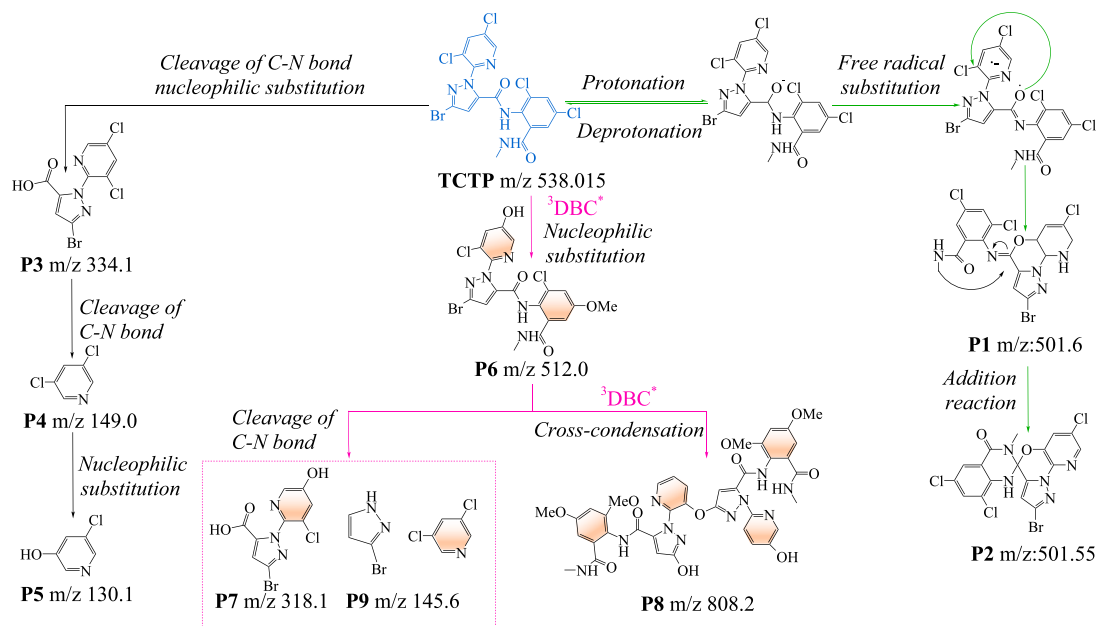


Fig. 7. Proposed TCTP photo-transformation pathways in pure water (P1–P5) and in the solution contained DBC (P1–P9).

cleaved and hydrolyzed to form simple compounds P149.0 and P130.1, respectively. More importantly, as the photo-transformation process continued, the aforementioned small organic compounds would eventually decompose into CO₂ and H₂O. Meanwhile, in pathway II, TCTP generated photo-transformation products with an *m/z* of 501.6 due to dechlorination. This included free radical substitution, which was followed by addition reactions to form compound P501.55.

Notably, in the TCTP solution containing DBC, some new photo-products with *m/z* values of 512.0, 318.1, 808.2, and 145.6 were identified, and the reaction between TCTP and ³DBC* possibly generated these additional intermediate products. In pathway III, the irradiation of TCTP in the presence of DBC induced a direct substitution reaction after photolysis, and the chlorine free radicals were replaced by

hydroxyl and methoxy groups to form P512.0 products, which have rarely been reported in previous studies [7,9]. ³DBC* was confirmed to have a redox effect [13,53], and P808.2 was derived from the cross condensation of P512.0, while P145.6 and P318.1 formed from P512.0 via the cleavage of the C–N bond.

3.6. Ecotoxicity of TCTP and its PTPs

The changes in toxicity of the TCTP solutions during light experiments are shown in Fig. 8 and Table S4. TCTP has shown toxic effects on aquatic organisms, especially lower trophic organisms. P1 forms through dechlorination of the TCTP benzene ring, forming P2 through a subsequent addition reaction. The photoproduct P1 was found to be 1–2

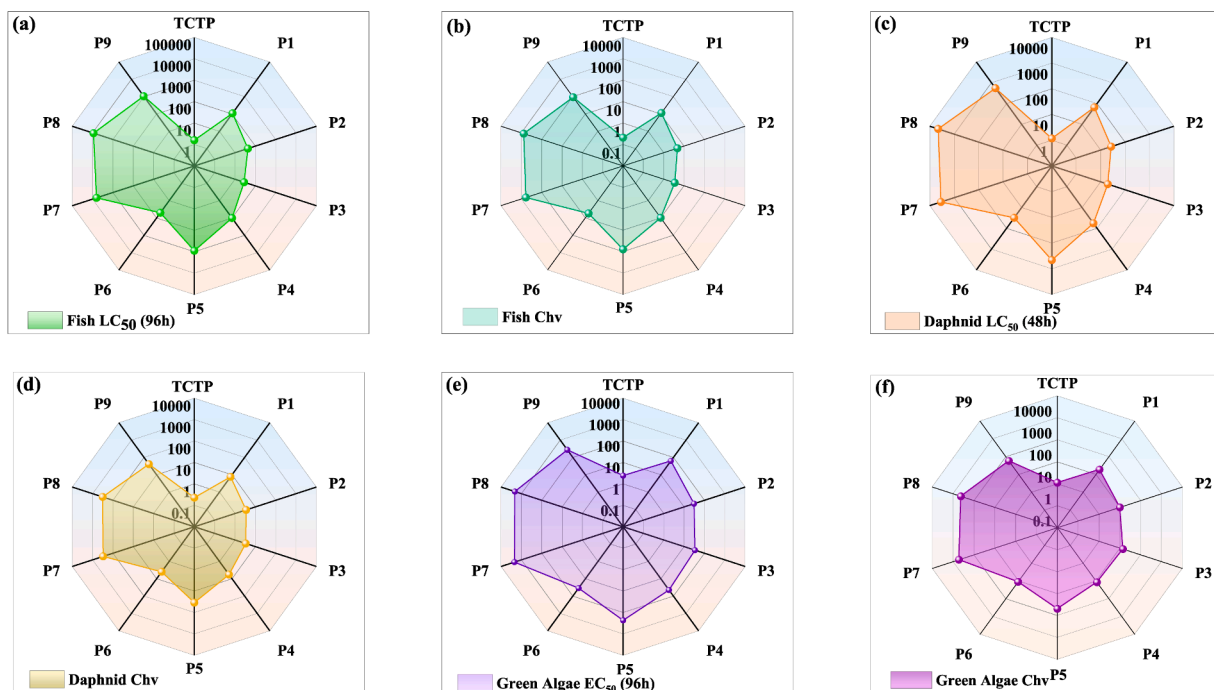


Fig. 8. Acute and chronic toxicity of TCTP and its degradation products on fish, daphnia and green algae (a–f).

orders of magnitude more toxic than TCTP, while the acute and chronic toxicity of P2 were found to be lower than P1. Predictive data showed that the elimination of chlorine on the benzene ring structure reduced the toxicity of its products, and intramolecular addition reaction would lead to increased toxicity. Previous investigations showed a toxicity enhancement with an increase in unsaturated bonds in the molecule [54].

The C–N bond of TCTP was easy to cleave, where later chlorine groups were substituted with hydroxyl radicals, and the reaction pathway followed TCTP-P3-P4-P5. With a decrease in the number of carbon chains and chlorine groups on the benzene ring, the acute and chronic toxicity of TCTP and its products on *fish*, *daphnia*, and *green algae* gradually decreased. P6 was the dechlorination product of TCTP, and chlorine functional groups were substituted with hydroxyl radicals and methoxy groups, respectively. This resulted in the cleavage of the C–N bond and a coupled reaction, and the reaction products consisted of P7, P9, and P8, with toxicity that was more than two orders of magnitude lower than that of P6. This was possibly because the carbon chain length was shorter and chlorine groups were substituted.

The log k_{ow} values of TCTP, P1, P2, P3, P4, P5, P6, P7, P8, and P9 were 4.72, 2.65, 3.09, 2.69, 2.09, 0.97, 3.03, 1.57, 0.74, and 0.95, respectively, where the higher the log k_{ow} value of the pollutants, the stronger their hydrophobicity, making it easier for them to enter the cell membrane. This was possibly the reason why the toxicity of PTPs on all three organisms was lower than that of TCTP.

3.7. Organ-specific toxicity prediction through ProTox-II

The organ-specific toxicity prediction results are presented in Fig. 9 and Table S5. The hepatotoxicity activity has been predicted for TCTP and its photoproducts, excluding P4, P5, and P8. Previous study had demonstrated that bromine-containing aromatic compounds exhibit a tendency to accumulate and persist, thereby disrupting endocrine function, inducing neurotoxic effects, and causing harm to the reproductive system leading to fetal malformations and liver toxicity [55–57]. Interestingly, the molecular structures of TCTP and its photoproducts (excluding P4, P5, and P8) contain a bromine-containing aromatic ring.

P4 was predicted to induce carcinogenicity, P5 was found to be active for MMP, and prolonged exposure to P5 possibly altered the stress response pathways, while the PTPs of TCTP (except P2) were predicted not to show AhR. This indicated that the degradation products had no

effect on the nuclear receptor signaling pathways. These results indicated that the overall toxicity of the degradation products was reduced compared to TCTP.

4. Conclusions

TCTP could undergo direct photo-transformation and indirect photo-transformation, while DBC could accelerate the photo-transformation of TCTP, with $^3\text{DBC}^*$ playing an important role. At low DBC concentrations (<2.0 mg C/L), the TCTP photo-transformation k_{obs} value increased from 0.285 to 0.3110 min^{-1} with increasing DBC concentration (0.5 mg C/L–2 mg C/L). However, the k_{obs} value of TCTP decreased to 0.1557 min^{-1} at a DBC concentration of 10 mg C/L due to higher screening and self-quenching effects. This indicated that in the presence of DBC, the persistence of TCTP in the illuminated water environment was reduced. Nine PTPs of TCTP in pure water and DBC-amended solutions were identified. Hydroxyl addition, dechlorination, cleavage of the C–N bond, addition reactions, and cross-condensation were the main degradation pathways. The presence of DBC led to the generation of new photo-degradation products derived from TCTP, and toxicity assessment showed that the toxicity of TCTP degradation products did not exceed the toxicity of TCTP.

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CRediT authorship contribution statement

Yaling Li: Writing – original draft, Methodology, Investigation, Formal analysis. **Tianlie Luo:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Formal analysis. **Minhui Yang:** Investigation, Data curation. **Guo Liu:** Supervision, Project administration. **Xian Chen:** Validation, Software. **Yihua Li:** Supervision, Data curation. **Chengzhi Zhou:** Methodology. **Willie J.G.M. Peijnenburg:** Writing – review & editing.

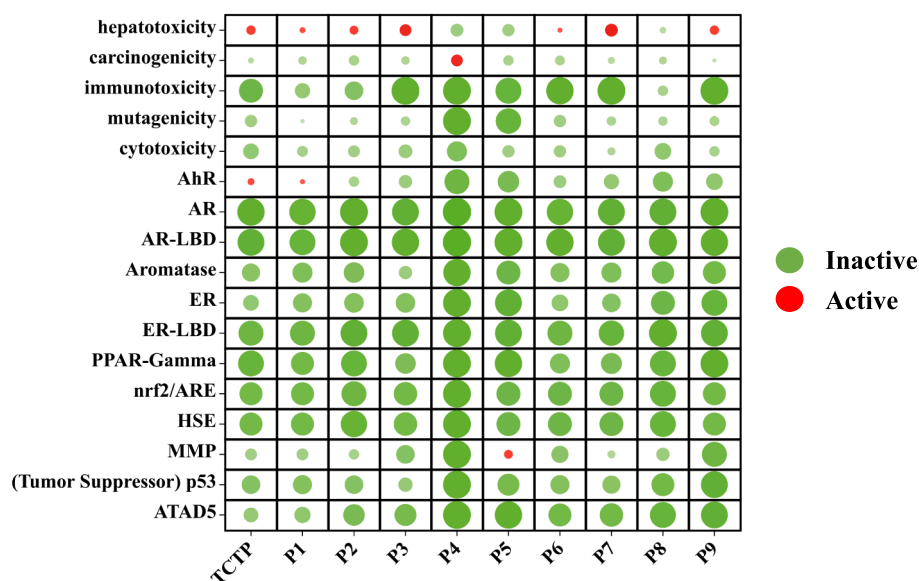


Fig. 9. Organ-specific toxicity analysis of the PTPs, where the red and green circles represent active and inactive, respectively, and the larger circles represent greater probability.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2024.126957>.

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