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Photolysis- and Dissolved Organic Matter-Induced Toxicity of Triclocarban to *Daphnia magna*

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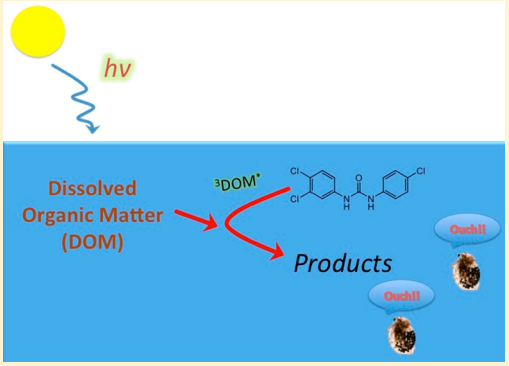
Supporting Information

ABSTRACT: Triclocarban (TCC) is a common antimicrobial compound used in soaps and other household products and is found globally in many surface waters. This study investigated the acute toxicity of TCC and its photolyzed products to *Daphnia magna* using 50% 96-h lethal concentration (LC_{50}) tests. The effects of dissolved organic matter (DOM) on the toxicity of TCC photoproducts to *D. magna* were also studied. Direct photolysis of TCC formed photoproducts that were significantly less toxic (LC_{50} value of 2.67 ± 0.6 μM) than the parent TCC compound (LC_{50} value of 0.087 ± 0.3 μM). In contrast, the indirect photolysis of TCC in the presence of DOM produced photoproducts that were significantly more toxic (LC_{50} value of 0.032 ± 0.015 μM). Chlorinated anilines and isocyanates, identified by mass spectrometry, were formed in the presence of DOM as indirect photolysis products of TCC and were shown to be partially responsible for the observed toxicity.



INTRODUCTION

Pharmaceuticals and personal care products (PPCPs) continue to be an emerging concern because their usage has increased dramatically over recent decades and little is known about their impact on the environment. Because many of these PPCPs enter receiving waters through wastewater treatment plant (WWTP) effluents and to a lesser degree from septic systems, understanding their environmental fate has gained interest due to their potential toxicity and other deleterious modes of action, e.g., endocrine disrupting properties and antibiotic resistance.[1]

Triclocarban (TCC; 3,4,4′-trichlorocarbanilide) is an antimicrobial compound that is commonly found in many household products, including bar soaps, deodorants, detergents, and cosmetics.[2] Triclocarban is lipophilic, with a log K_{ow} value of 4.2,[3] and has the potential to bioaccumulate in organisms. It has indeed been detected in a variety of organisms including algae,[4] New Zealand mudsnails,[5] and fish,[6] and its lethal and sublethal toxicity in fathead minnows (*Pimephales promelas*) has been investigated.[7] While the Food and Drug Administration (FDA) has recently moved to ban TCC in the United States, TCC is still used in many other countries.

The photolysis of triclosan (TCS), a similar antimicrobial compound, has been extensively studied because it photodegrades into potentially toxic photoproducts, including chlorophenols and dioxin congeners,[8−16] TCC has garnered much less attention. Guerard et al.[17] and Trouts and Chin[18] reported significant indirect photolysis mediated by dissolved organic matter (DOM), and only one study has identified photochemically derived products (4-chloroaniline, 3,4-dichloroaniline, 4-chlorophenyl isocyanate, and 3,4-dichlorophenyl isocyanate) after photolysis.[19] Nonetheless, to date, there have been no studies that have examined the toxicity of TCC photoproducts on aquatic organisms and only one that we are aware of for triclosan.[20] For these reasons, we investigated the photoinduced toxicity of TCC and the influence of DOM on the formation of photoproducts.

We investigated the lethal toxicity to *Daphnia magna* using US EPA Method 821-R-12-012[21] for TCC and TCC photodegradation products formed in the presence and absence of DOM in a standardized solution (US EPA moderately hard water, a standard used in aquatic toxicity testing).[20] Photolyzed TCC solutions, with and without DOM, were analyzed by gas chromatography−mass spectrometry (GC-MS) to identify the photoderivatives formed. TCC photolysis experiments were conducted using DOM originating from different WWTP effluent waters collected from four different sites around central

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Ohio as well as DOM from the International Humic Substances Society (IHSS) isolated by chromatography, i.e., XAD-8 and reverse osmosis. To determine which of the four photoproducts are most likely responsible for the observed toxicity, we created de novo solutions with each of the four photoproducts and performed 96-h lethality toxicity tests on *D. magna*.

EXPERIMENTAL SECTION

Materials. Triclocarban (99%) was purchased from Sigma-Aldrich (St. Louis, MO). $NaHCO_3$ (99−100%), KCl (99.4%), $MgSO_4$ (99%), and $CaSO_4$ (98%) were purchased from Fisher Scientific (Waltham, MA). HPLC grade acetonitrile was purchased from Fisher Scientific (Waltham, MA). Suwannee River natural organic matter (SRNOM) (RO Isolation), Pony Lake fulvic acid (PLFA), and Suwannee River fulvic acid (SRFA) (XAD-8 isolation) were purchased from IHSS (St. Paul, MN). Old Woman Creek fulvic acid (OWC) (XAD-8 isolation) was isolated from a wetland surface water near Huron, OH and used for this study. Wastewater treatment plant (WWTP) effluent (pH range 7.0 to 7.1) was collected from four central Ohio WWTPs: Jackson Pike (68 MGD) and Southerly (114 MGD: both in Columbus, OH), and from two rural sites: London, OH (5.8 MGD) and Plain City, OH (0.75 MGD).

Solution Compositions. EPA water was prepared by dissolving $NaHCO_3$, KCl, and $MgSO_4$ in Milli-Q water (Millipore).[20] This water was shaken and allowed to aerate overnight to achieve a final nominal concentration of 96 mg/L $NaHCO_3$, 4 mg/L KCl, 60 mg/L $MgSO_4$, and 60 mg/L $CaSO_4$ with a pH of 7.4. To determine the effect of DOM on TCC photolysis and product formation, lyophilized fulvic acids or RO isolates were added to EPA water at a concentration of 12 mg DOM/L to yield DOC levels of 4−6 mg/L. Actual DOC concentrations were measured using a Shimadzu TOC-V_{CPN} total organic carbon analyzer. SRNOM was used in toxicity testing solutions because it is obtained from a reliable source (Suwannee River) and is readily available for purchase in large quantities, which is necessary for the large volumes needed in our toxicity study.

Photolysis Experiments. To determine the amount of time needed to degrade compounds for toxicity tests, degradation kinetics tests were used to determine the photolysis rates and half-lives of our compounds. We formulated solutions of the desired compound by dissolving a high concentration of the compound in methanol, evaporating off the methanol, and adding EPA water in the absence and presence of DOM or WWTP effluent to achieve the desired nominal concentration of 10 μM TCC. Solutions were thoroughly mixed and then pipetted into quartz phototubes and exposed in a Sun Test CPS solar simulator (Atlas Testing), a type of solar simulator that is commonly used to study photochemical reactions. The filter used in our solar simulator blocked wavelengths less than 290 nm and mimics the spectrum of natural sunlight. Phototubes, representing each time point, were removed at various times and left in the dark until all tubes were removed. Irradiation was monitored with a VWR UV light meter/ultraviolet radiometer. TCC was measured using a Waters 1515 HPLC pump and 717 Plus autosampler with a Waters 2487 dual beam absorbance UV detector set at a wavelength of 257 nm. Analytes were separated using a Restek Pinnacle DB C18 column (5 μm particle size, 250 mm × 4.6 mm) at a flow rate of 0.8 mL/min. The mobile phase consisted of 70:30 acetonitrile:Milli-Q water (v:v) adjusted to pH 3−4 (retention time = 9 min).

Acute Toxicity Testing. *D. magna* were purchased from Aquatic Biosystems, Inc. (Fort Collins, CO) and maintained in EPA water until testing time. Organisms were fed a yeast/trout chow/algae (YTC/algae) mix and ground alfalfa. *D. magna* culture tanks were kept at 20 °C over a 12-h light/dark photoperiod under constant aeration.

Acute (96-h) toxicity tests were performed using six concentrations, spanning 5 orders of magnitude (i.e., 10 μM−0.0001 μM), of the compounds dissolved in EPA water or EPA water containing SRNOM. For photolyzed solutions, the initial TCC concentration was considered the "concentration" of photoproducts so the relative toxicities of the parent and its derivatives in the photolyzed solutions would be comparable. Due to the large volume of sample needed to conduct each toxicity assay, we were unable to test the other DOM samples because of the limited amounts available for this study. Test solution (prepared as described for photolysis studies) (25g) was added to 150 mL beakers, and five *D. magna* less than 24 h old were gently pipetted from the culture tank into each beaker. Test beakers containing *D. magna* were left in the dark during the duration of the tests due to the photosensitivity of the compounds. After 48 h, the *D. magna* were fed for 2 h, then live organisms were gently removed from the beakers and allowed to remain in a small amount of solution while waters were renewed. After renewal, *D. magna* were replaced into the test chambers and monitored for another 48 h (96 h total). Mortality was monitored and recorded every 24 h, and 96 h-LC_{50} values were calculated using Solver in Microsoft Excel. Details regarding blanks and controls are provided in the Supporting Information (SI).

Photoproduct Identification. Gas chromatography−mass spectrometry (GC-MS) analyses were used to identify photoproducts and confirm the complete degradation of the parent. Samples (500 μL) were added to 500 μL of CH_2Cl_2, vortexed for 20 s, and repeated. Here, 350 μL of the extract was transferred to a new glass tube, dried completely under N_2, and reconstituted in 35 μL of CH_2Cl_2. Then, 1 μL of this solution was injected into a Thermo Trace GC Ultra GC coupled to a Thermo DSQII single quadrupole mass spectrometer. The initial hold was at 40 °C for 2 min, then increased to 300 °C at a rate of 10 °C/min, and then held at 300 °C for 2 min. The ion source temperature was 250 °C, using an ES+ ionization method and a full scan m/z of 10−750. Split injection mode was used, with a split flow of 15 mL/min, a split ratio of 10, an inlet temperature of 225 °C, and a transfer line temperature of 300 °C.

Data Analysis. Dose−response curves were analyzed using TCC, and photoproduct concentrations and were fitted by the log-logistic[22] using the Newton optimization method (Solver, Microsoft Excel, 2007). LC_{50} values were considered different if there was no 95% confidence interval overlap, and if confidence limits did overlap, differences between LC_{50} values in different treatments were calculated using a single-sided student-t test (p = 0.05).

RESULTS AND DISCUSSION

Initial experiments were conducted only with parent TCC to establish a baseline toxicity level. Further, solutions of TCC in the presence and absence of DOM were photolyzed until the parent compound was below the observed no mortality concentrations in the test solution. Complete loss of TCC by

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photolysis was confirmed by gas chromatography mass spectrometry (Figure S1). The 96-h LC_{50} values for photoderivatives formed from the direct photolysis (EPA water only) of TCC increased; i.e., the photoproducts are significantly less toxic than the parent compound with a LC_{50} of 2.67 ± 0.6 μM relative to a value of 0.087 ± 0 to 0.3 μM for TCC (Figure 1).

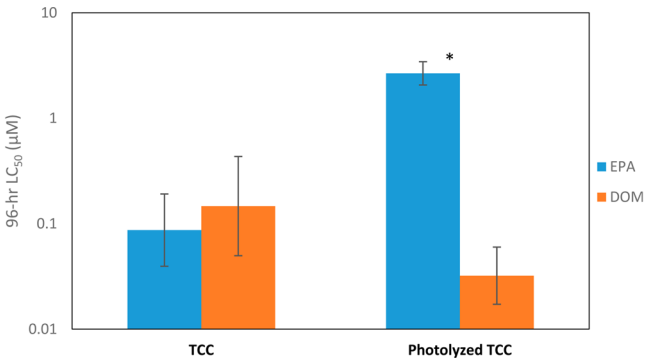

Figure 1. 96-h LC_{50} values (shown with 95% CI error bars) for triclocarban, both parent and photolyzed, with and without DOM. Triclocarban without DOM was less toxic after photolysis than TCC in US EPA water without photolysis (LC_{50}s of 0.087 and 2.67 μM, respectively). In the presence of SRNOM, toxicity was the same as TCC in US EPA water regardless of the presence of DOM or photolysis (LC_{50}s of 0.146 and 0.032 μM, respectively). Asterisk (*) indicates significant difference from all other LC_{50} values ($p \leq 0.05$).

In contrast, the photoproducts of TCC irradiated in 6 mg/L-DOC SRNOM EPA water solutions exhibited similar or higher toxicity relative to the parent compound with an LC_{50} value of 0.032 ± 0.015 μM. Further, dark TCC controls prepared in SRNOM solutions exhibited less toxicity than the parent compound in the absence of DOM (0.146 ± 0.06 μM). It is possible that partitioning of TCC into SRNOM could potentially detoxify this compound, but based upon its octanol−water partition coefficient, the actual fraction bound to DOM is very small and is less than 10% if one assumes that K_{ow} is similar in magnitude to the TCC DOM partition coefficient (K_{DOM}). Typically, however, K_{DOM} is significantly smaller than K_{ow}, and our estimates of TCC bound to DOM are very conservative. Regardless of the exact mechanism, DOM's ubiquity in natural waters may offer some protection for this organism from the toxic effects of TCC and possibly other deleterious synthetic organic compounds.

Due to the low toxicity of direct photolysis products and the high toxicity of indirect photolysis products, we focused on the products of the indirect photolysis pathway. The DOM-mediated photosensitized pathway for TCC degradation lead to the formation of photoproducts that differ from those formed by direct photolysis. Indeed, we observed persistent toxicity even after the parent compound was below detection limits in the SRNOM solutions (Figure S1). Further, we believe that DOM is also capable of shielding the photoproducts through a combination of processes such as light screening and possible interactions with DOM moieties. Given that DOM is ubiquitous to all aquatic systems in sunlit natural surface waters, TCC photodegrades into these more toxic products that could be persistent in the environment.

We detected four compounds, 4-chloroaniline (4-CA), 3,4-dichloroaniline (3,4-DCA), 4-chlorophenyl isocyanate (4-CPI), and 3,4-dichlorophenyl isocyanate (3,4-DCPI), by GC-MS in the photolyzed TCC solution containing SRNOM (Figure S2). These substances are identical to the ones reported by Ding et al.[19] for TCC photolysis in their system. In contrast, none of the products were detected in the solutions, which were photolyzed *without* DOM, which suggest that the direct photolytic degradation of TCC yields unknown, less toxic photoproducts (Figure S3). Indeed, as discussed elsewhere, DOM appears to play a critical role in the formation of the photoderivatives identified in this study. Further, DOM also appears to play a role in shielding these toxic photoproducts thereby making them more persistent in the environment. The photoproducts persisted even after the parent compound was photodegraded to below its limits of detection as assayed by GC-MS. It is unclear, however, whether these photoderivatives are more labile in natural surface waters where they may be metabolized by microorganisms.

We assessed the photoproduct toxicity of the individual compounds with *D. magna* and demonstrated that 4-CA likely exerts the majority of the toxic effects observed for our photolyzed TCC in SRNOM solutions (LC_{50} value of 0.082 ± 0.05 μM), while the other compounds were less toxic (3,4-DCA LC_{50} of 1.03 ± 0.6 μM, 4-CPI LC_{50} of >10 μM, 3,4-DCPI LC_{50} of 2.03 ± 0.7 μM) (Table 1). While the chlorophenyl isocyanate products exhibited significantly less toxicity to *D. magna*, together these compounds may induce synergistic effects that cannot be easily assessed and are likely manifested in the observed toxicity of the TCC photoproducts formed in SRNOM solutions. Further, it is plausible that other photoproducts not determined by our approach, e.g., photoderivatives of the chloro-anilines and -isocyanates, may also play a role in the observed toxicity.

Table 1. LC_{50} Values of Products of TCC Photolyzed in SRNOM[a]

Product	4-CA	3,4-DCA	4-CPI	3,4-DCPI
96-h LC_{50} (μM)	0.082 ± 0.05	1.03 ± 0.6	>10	2.03 ± 0.7

[a]4-CA exhibited the highest toxicity, while the toxicity of 4-CPI was not calculated as the LC_{50} was higher than the highest test concentration.

In an effort to assess the *potential* toxicity of the other DOM samples without having to conduct separate toxicity experiments (refer to our methods), we screened the photoproducts formed by GC-MS. Surprisingly, the chloro-aniline photoproducts were detected in the SRNOM and wastewater effluent DOM but *not* in the fulvic acids (Table 2). We attribute this to the XAD-8 isolation method, which likely removed the fraction of DOM responsible for the formation of chloro-aniline products. The wastewater effluent samples also did not produce any of the isocyanate compounds, but they were all present in SRNOM (Table 2). As noted by other investigators,[23,24] DOM present in wastewater is compositionally different from DOM originating from natural sources, and as a result the photochemistry of these two types of organic matter are noticeably different.

Based upon our results, we proposed a scheme whereby initial absorption of light occurs by the DOM, and then, the excited state DOM (presumably triplets) donates an electron to form a TCC radical anion. This radical anion can then lead to the rearrangement of the molecule and cleavage at either of the bonds between the NH and C═O groups. This in turn will form either a chloro-aniline radical or chlorophenyl isocyanate, depending on bond cleavage, and these radicals will undergo

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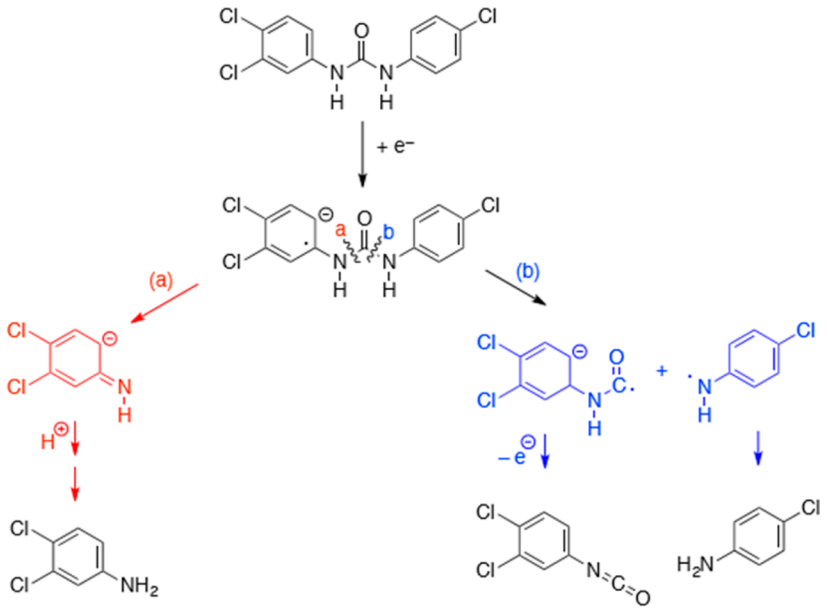
Table 2. Detection of Four Photoproducts of Triclocarban Photolyzed in the Presence of DOM in Four Wastewater Treatment Plant Waters and Seven Different DOM Solutions[a]

water	DOM type	derivation	DOM isolation method	TOC (mg/L)	4-CA	3,4-DCA	4-CPI	3,4-DCPI
Jackson Pike	WWTPE	allochthonous/ autochthonous	None	5.34	Y	Y	N	N
Southerly	WWTPE	allochthonous/ autochthonous	None	4.81	Y	Y	N	N
London	WWTPE	allochthonous/ autochthonous	None	4.76	Y	Y	N	N
Plain City	WWTPE	allochthonous/ autochthonous	None	3.25	Y	Y	N	N
Old Woman Creek	FA	allochthonous/ autochthonous	XAD8	6.14	N	N	Y	Y
Pony Lake	FA	autochthonous	XAD8	5.54	N	N	Y	Y
Suwannee River	FA	allochthonous	XAD8	4.79	N	N	Y	Y
Suwannee River	NOM	allochthonous	RO	6.00	Y	Y	Y	Y
EPA	None	N/A	N/A	0.00	N	N	N	N

[a]Either 4-chloraniline (4-CA) and 3,4-dichloroaniline (3,4-DCA) or 4-chlorophenyl isocyanate (4-CPI) and 3,4-dichlorophenyl isocyanate (3,4-DCPI) or all four were detected in all of the solutions, regardless of DOM type (WWTPE = wastewater treatment plant effluent, HA = humic acid, FA = fulvic acid, NOM = natural organic matter) or DOM derivation. XAD8 = a poly-methylmethacrylate resin.

Scheme 1. Proposed Mechanism of DOM-Mediated Photolysis of Triclocarban to 4-Chloroaniline, 3,4-Dichloroaniline, 4-Chlorophenyl isocyanate, and 3,4-Dichlorophenyl Isocyanate[a]



[a]TCC is transferred an electron from UV-irradiation-excited DOM, forming a radical anion that cleaves between the C═O and either NH group, forming a set of chloro-aniline and chlorophenyl isocyanate radicals, which will undergo rearrangement to form stable molecules.

rearrangement to form stable photolysis products (Scheme 1). While photoreduction by triplet DOM is not a common process due to the presence of oxygen (the primary oxidant), it has been observed for a number of compounds including simple halogenated organic molecules and chorothalonil.[25,26] A recent review by McNeill and Canonica[27] summarizes recent work on photoreduction pathways by triplet DOM. With respect to wastewater effluent, it is possible that the isocyanate radical may undergo side reactions with moieties unique to this DOM that prevents it from forming in sufficient quantities. We cannot, however, explain why the chloro-anilines were not observed for the FA samples using the proposed pathway. Finally, we believe that the hydroxyl radical plays a relatively unimportant role in TCC's photo fate due to the possible presence of trace methanol associated with the plating–volatilization process used to make our analyte working solutions. Under these circumstances, it becomes the dominant hydroxyl radical scavenger in our system.

In conclusion, our study is the first to demonstrate TCC's acute toxicity to *D. magna*. This study also found that photolyzed TCC in solution without DOM is detoxified due to the photodegradation of TCC to unknown, less toxic

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products. When photolyzed in solution with DOM, TCC breaks down to form 4-CA, 3,4-DCA, 4-CPI, and 3,4-DCPI, and together these products exert a toxicity that is greater than the parent TCC or as individual compounds. It is plausible that once these compounds are formed, DOM also then shields the photoproducts from further photodegradation. While four photoproducts were detected, the LC_{50} of 4-CA is at least an order of magnitude lower than the three other photoproducts and likely exerts the majority of the toxicity observed in TCC-photolyzed DOM solutions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00429.

These include blank toxicity test details, selection of irradiation times, GC-MS spectra of triclocarban and photoproducts, and lethal concentration 50 curves. (PDF)

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Notes

The authors declare no competing financial interest.

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