



Direct and indirect photolysis of triclocarban in the presence of dissolved organic matter

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Abstract

Photolysis is an important attenuation pathway for the removal of wastewater effluent organic micropollutants from surface waters. In this work, direct and indirect processes leading to the degradation of the disinfectant, triclocarban were studied. Photo-irradiation experiments were conducted in water collected from Old Woman Creek (OWC) a tributary of Lake Erie near Huron, OH, USA and in solutions of fulvic acids isolated from the Suwannee River, Georgia, USA (SRFA), Old Woman Creek (OWCFA) and Pony Lake, Antarctica (PLFA). Photodegradation of triclocarban proceeded faster in the presence of all three fulvic acids relative to deionized water. PLFA, an autochthonous dissolved organic matter (DOM) was found to be more reactive than the other fulvic acids, while the mostly allochthonous SRFA exhibited the lowest reactivity toward triclocarban. The later observation can be in part explained by anti-oxidant moieties present in SRFA. Photosensitized triclocarban degradation in whole water DOM from OWC was entirely attributable to the fulvic acid fraction and suggests that this component is the most photo-reactive fraction of the DOM. Anoxic and methanol-quenched experiments revealed unexpected results whereby the former suggests oxidation through reaction with triplet DOM, while the later is indicative of reaction with photo-generated hydroxyl radicals. It is possible that methanol can quench excited DOM species, which would shut down the triplet oxidation pathway. Finally, we observed no enhancement of triclocarban-photosensitized degradation through the addition of iron.

Introduction

Triclocarban (TCC) is a disinfectant used in a variety of household and personal care products including soaps, shampoos, creams, and cosmetics (Chu and Metcalfe, 2007). In the United States 500,000–1,000,000 pounds of triclocarban is produced annually (Halden and Paull, 2004). Triclocarban has been in widespread use since the 1950s, but its environmental fate has been less studied than the other common disinfectant triclosan, which is found predominantly in liquid soaps (Halden and Paull, 2005). TCC has a high octanol-water partition coefficient, ($\log K_{ow} = 4.9$) and can readily bioaccumulate in organisms. It is known to interfere with mammalian reproduction leading to reduced conception, fewer offspring, and decreased survival of offspring (Halden and Paull, 2004). It has also been shown to amplify the natural action of androgens and may possibly impact the use of hormones for birth control and hormone replacement therapy (Chen et al., 2008). It is also a potential carcinogen due to the possibility of carbon-nitrogen bond cleavage, which would generate N-hydroxylated metabolites (Halden and Paull, 2004). In addition, TCC yields mono- and dichloro- anilines as attenuation byproducts in the environment, which are hematotoxic, genotoxic, and persistent (Heidler et al., 2006; Ding et al., 2014).

The photofate of triclosan has been investigated in artificial UV light (Ding et al., 2013) and sunlight (Guerard et al., 2009; Ding et al., 2014). The direct photolytic half-life of TCC under simulated sunlight is ~ 24 hours (Guerard et al., 2009). In natural waters, however, a number of substances known as photosensitizers can promote the degradation of TCC through side reactions with reactive photo-generated species i.e., indirect photolysis. Dissolved organic matter (DOM) is the most ubiquitous photosensitizer in natural sunlit surface waters and when irradiated generates both reactive oxygen species (ROS) and other non-ROS transients

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such as triplet DOM (^3DOM). Further, DOM's chromophoric composition can vary depending on its source, which ultimately determines its photo-reactivity and ability to generate ROS and other transients. For example autochthonous materials derived from algal or microbial products are typically aliphatic to olefinic in character while allochthonous materials are derived from the degradation of higher plant materials (Guerard et al., 2009). As such allochthonous DOM precursors contain significant amounts of lignins and are characterized by high levels of aromaticity. In our previous studies we demonstrated that allochthonous DOM is effective at generating ROS such as the hydroxyl radical ($\text{OH}\cdot$), while autochthonous organic matter is effective at forming ^3DOM (Guerard et al., 2009; Cawley et al., 2009). Subsequent research by Wenk et al. (2011, 2012) demonstrated that the presence of unknown anti-oxidant moieties (presumably phenolic compounds) present in allochthonous DOM (and much less prevalent in autochthonous DOM) maybe responsible for this dichotomy in DOM photo-reactivity. These investigators postulated that anti-oxidants prevent the oxidation of aniline contaminants by ^3DOM by reverting the analyte intermediate back to the parent compound.

With respect to the indirect photolysis of TCC few studies exist that directly examine the role of DOM (Guerard et al., 2009; Ding et al., 2014). These studies only examined the humic fraction of DOM and little is known about the other components that maybe responsible for sensitizing the photodegradation of TCC. Ding et al. (2014) showed that, contrary to fulvic acids, humic acids actually inhibited the direct photolysis of TCC. The concentrations of humic acids used in the Ding et al. (2014) study, however, were exceedingly high (50 mg/L), which could have resulted in a significant amount of light screening. Further the humic substances used in that study were of a commercial variety of unknown origin, which may not be representative of humics present in aquatic dissolved organic matter.

In this study, we examined the photolytic degradation of TCC as a follow-up to our previous paper (Guerard et al., 2009) whereby reaction rates in filtered whole water i.e., unaltered DOM were compared to those measured in solutions of fulvic acids. Further we examined the addition of chemical amendments (specifically iron) to assess possible interactive effects i.e., assessing the importance of the photo-Fenton reaction for generating $\text{OH}\cdot$. For this study we used surface water from Old Woman Creek (Huron, OH), which is a eutrophic wetland adjacent to Lake Erie. DOM from this site is derived from a mixture of both autochthonous and allochthonous precursors. Land use in the watershed is predominantly row crop agriculture (Miller and Chin, 2005). Our autochthonous end member is a fulvic acid derived from Pony Lake, Antarctica, which is completely free of inputs from higher plants, while the allochthonous end member is from the Suwannee River, GA, USA, an acidic "blackwater" swamp. It was our intention to investigate to what extent these chemical differences in DOM would impact the degradation kinetics of tricloarban.

Materials and methods

Reagents and chemicals

All chemicals and reagents were purchased commercially and used without further purification. Chemicals and reagents were acquired from the following: tricloarban (99.5%) from Chem Services West Chester, PA; isopropanol (Optima), acetonitrile (Optima), sodium hydroxide (NaOH; analytical reagent) from Mallinckrodt; potassium hydrogen phthalate (KHP), sodium nitrate, *p*-nitroanisole, and pyridine from Aldrich (Milwaukee, WI); AG-50W-X8 resin from Bio-Rad (Hercules, CA); argon (4.8 grade) from Praxair. The reference fulvic acids Suwannee River Fulvic Acid (SRFA) Lot #1R101F-1 and Pony Lake Fulvic Acid Lot #1R109F were purchased from the International Humic Substance Society (IHSS). All glassware was washed with NOCHROMIX Cleaning Reagent (Godax Laboratories, Inc.) in concentrated sulfuric acid and all plastics were washed with 10% HCl prior to use.

Photolysis experiments

Stock solutions of TCC were prepared in methanol. From this stock solution, photolysis solutions were prepared by evaporating an aliquot of stock (to remove the co-solvent, which can participate in side reactions) and reconstituted in the appropriate matrix (Milli-Q water, filtered OWC water, or fulvic acid solutions). Final concentrations were 0.5 μM tricloarban, and fulvic acid at ~ 5 mg/L as dissolved organic carbon (DOC). To probe the role of hydroxyl radical and other possible ROS photolysis experiments with excess methanol (25mM) as a radical scavenger were performed. Sub-oxic experiments were purged with argon for 90 minutes (1min/mL) and transferred to quartz tubes in a glove box under a 95% N_2 /5% H_2 atmosphere.

In all cases, solutions were irradiated in airtight quartz tubes sealed with Teflon caps with no headspace. Photolysis experiments were performed in a CPS+ Solar Simulator (Atlas Electric Devices) equipped with a xenon arc lamp. By using the "Solar standard" filter, the output of the simulator is able to mimic the spectrum of natural sunlight for wavelengths from 290 to 800 nm. Initial pH was 7.0 and was constant over the course of the reaction. Dark controls were run concurrently for each photolysis experiment and did not deviate more than 1% of the initial concentration. Temperature was measured using a black standard temperature probe

and maintained at 30°C. Total photolysis time for each experiment was 24 hours. Kinetic data were fitted to a pseudo-first order equation.

In order to monitor photon flux and to check for changes in the light intensity of the lamp, chemical actinometry was conducted periodically using the p-nitroanisole (PNA)/pyridine (PYR) system (Dulin and Mill, 1982). Over the course of this research, no significant changes in light intensity were observed. The following equation is used to compare reaction rates between the solar simulator and natural sunlight using PNA's equivalent rate constant (k) at solar noon in June at 40° N, which is the exact latitude at Ohio State University:

$$k = \phi_{\lambda} \sum \epsilon_{\lambda} \Lambda_{\lambda} \quad (1)$$

where ϕ is PNA's quantum yield, ϵ is the molar absorption coefficient of PNA, and Λ is sunlight irradiance for a specific wavelength (Leifer, 1988). The rate constant for this set of data was calculated to be 3.1 times faster in the simulator. Thus, the TCC degradation rates presented here are significantly faster than would be observed in natural sunlight due to both the intensity of the light source used and the lack of variance due to cloud cover and changes in sun angle over a diurnal cycle.

Light screening in the whole water and fulvic acid solutions, was calculated using a UV-Vis absorbance scan for each sample and the following equation:

$$S_{\lambda} = [1 - 10^{-(1.2)(A)}] / (2.3)(1.2)(A) \quad (2)$$

where A is absorbance, 1.2 is an average distribution function of light in natural waters, (Schwarzenbach et al., 2003; Zepp and Cline, 1977). We plotted S_{λ} versus wavelength and integrated the area under the curve to determine the overall screening factor over the wavelengths of interest (290 to 350 nm), the region in which DOM has the highest absorption. At the DOC levels used in this study light screening effects ranged from (0.92 to 0.96).

Analytical methods

Individual samples were sacrificed every three hours and analyzed by high-pressure liquid chromatography (HPLC) analysis to determine loss of the parent compound. A direct aqueous injection (200 μ L) was made from each vial into the HPLC and separation was achieved using a Novapak Waters C-18 reverse-phase chromatography column and detected using a Waters 2487 absorbance detector at 257nm. Mobile phase for the analysis was 80% methanol/20% Milli-Q (v/v) and the flow rate was 1.0 mL/min. Kinetic data were analyzed using Microsoft Excel and SigmaPlot 10.0. Rate coefficients for triclocarban degradation were determined using a least-squares fit of the observed data to a pseudo-first order kinetics model with $R^2 > 0.97$ for all reactions.

Results

Direct photolysis of 0.5 μ M TCC was observed in Milli-Q with an observed degradation rate constant (k_{obs}) of 0.029 hr^{-1} and is similar to what we reported previously (0.028 hr^{-1}) (Guerard et al., 2009). This is consistent with TCC's UV-Vis absorbance spectrum of TCC, which has sufficient light absorption above 290nm to promote direct photolysis. Dark controls were run concurrently for all experiments, and no depletions were observed.

We observed an enhancement in TCC photolysis rates in the presence of OWC whole water samples ($k_{\text{obs}} = 0.040 \text{ hr}^{-1}$), which is similar to solutions of OWC fulvic acid made at comparable DOC levels ($k_{\text{obs}} = 0.046 \text{ hr}^{-1}$). As reported before (Guerard et al., 2009) this value falls approximately midway between the geochemical endmember fulvic acids (Figure 1). The levels of non-DOM photosensitizers present in OWC whole water appears to not play an important role. For example nitrate levels (71 μ M) are below where it can contribute to the photolytic formation of $\text{OH}\cdot$ (typically $> 100 \mu\text{M}$) (Zepp et al., 1987; Miller and Chin, 2005). Further total iron levels (21 μ M) maybe sufficiently high to produce antagonistic effects as discussed elsewhere in this paper at the pH levels used in this study. Thus, statistically it appears that in the OWC whole water all the photosensitized effects for the transformation of TCC can be attributed to the fulvic acid fraction alone and that the presence of other DOM components does not play any significant role.

We conducted experiments to assess the possible reaction pathways that may be responsible for the observed TCC photosensitized degradation. For this study we investigated methanol as a more "general" ROS scavenger because of its reactivity toward both $\text{OH}\cdot$ and the hydroperoxyl radical (Altarawneh et al., 2011). In the presence of methanol and fulvic acids we observed complete to almost complete quenching of the indirect TCC photolytic pathway (Figure 2) for two of the fulvic acid solutions. The Pony Lake fulvic acid sample appeared to be the only one that still possessed significant indirect photolytic capabilities to degrade

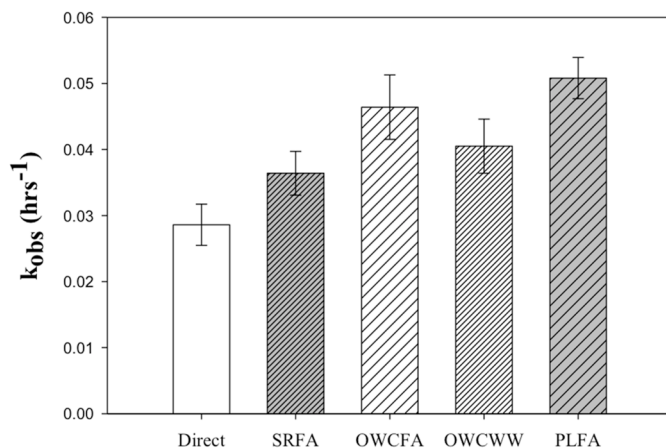


Figure 1

Triclocarban measured pseudo first order photo-degradation rate constants (k_{obs}).

Photolysis experiments were conducted in deionized water, Old Woman Creek whole water (OWC WW), and fulvic acid solutions from the Suwannee River (SRFA), Old Woman Creek (OWC FA), and Pony Lake (PLFA). All rate constants are corrected for light screening and are reported at the 95% confidence interval. Rate constants for OWC FA, PLFA, and SRFA were previously reported in Guerard et al., (2009).

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TCC in the presence of methanol. In contrast to our previous study, where isopropanol was employed as the OH^\bullet scavenger it appears that side reactions involving other ROS is participating in the indirect photolysis of TCC, and/or the methanol is quenching other important pathways.

Whole water OWC DOM conducted under anoxic conditions significantly increased TCC reaction rates (0.061 hr^{-1}) relative to experiments equilibrated with atmospheric oxygen (0.040 hr^{-1}). These results corroborated the results of Guerard et al. (2009) who observed a similar effect for experiments conducted in OWC fulvic acid. These results strongly suggest that TCC is susceptible to oxidation by triplet DOM and as stated earlier it appears that the triplet moieties appear to be associated with the fulvic acid fraction as oppose to other DOM components for this sample.

We also examined the possibility of iron-mediated indirect photolysis in natural waters to enhance contaminant degradation from the production of $\bullet\text{OH}$ through the photo-Fenton pathway. Fulvic acid solutions were spiked with $20 \mu\text{M FeCl}_3$. Surprisingly, all the TCC rate constants decreased to or slightly less than the value reported for direct photolysis (Figure 3). Thus, while it is apparently clear that the photo-Fenton process does not appear to be important the reduction in TCC reaction rates is unexpected and discussed below.

Discussion

Direct photolysis of TCC is an important and possibly the dominant pathway for its attenuation in the environment. Work by Ding et al. (2014) showed that the degradation of TCC results in the formation of chloroanilines (mono and dichloro) as well as chloroiso-cyanatobenzene compounds. Based upon electron spin resonance spectroscopy in the presence of spin traps these authors showed that TCC photolysis is a self-sensitized reaction and that singlet oxygen appears to play an important role in the absence of photosensitizers. As will be discussed elsewhere our data suggest that singlet oxygen does not appear to be an important species in the presence of DOM.

The increase in reaction rate beyond direct photolysis was observed in the presence of DOM and demonstrates the importance of indirect pathways in TCC's photofate. Further it is clearly apparent that the degree to which this occurs is highly dependent upon the composition of the dissolved organic matter pool. The least reactive DOM in this study was the predominantly allochthonous Suwannee River fulvic acid.

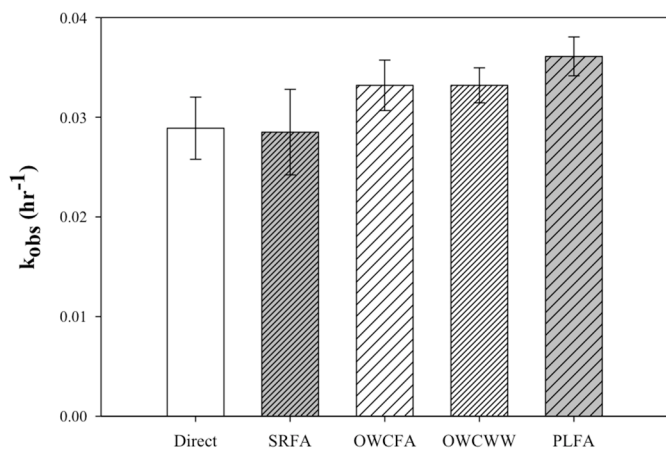


Figure 2

Triclocarban pseudo first order photo-degradation rate constants measured in the presence of methanol for SRFA, OWC FA, PLFA and OWC WW.

Direct photolysis rate constant is included as a reference to assess the extent of methanol quenching.

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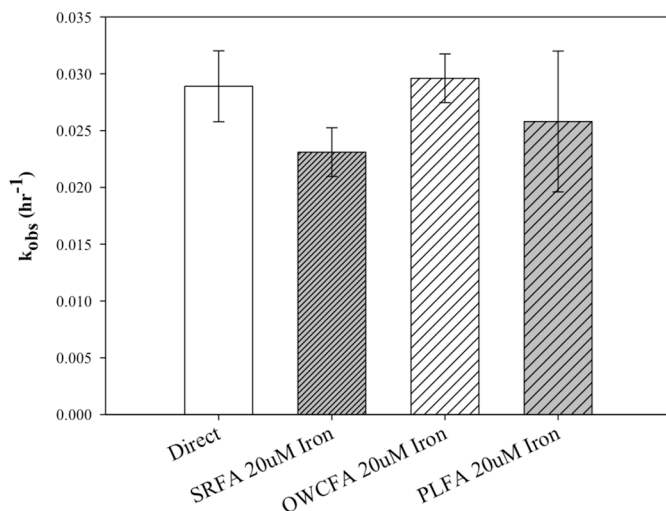


Figure 3

Triclocarban observed pseudo first order photo-degradation rate constants measured in FeCl_3 -spiked fulvic acid solutions.

Direct photolysis rate constant is included to show the significant quenching effect of iron on the photofate of triclocarban.

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As shown in our earlier studies (Miller and Chin, 2005; Guerard et al., 2009) we observed that indirect organic contaminant pathways involving ROS appear to be most effective for allochthonous derived DOM. In contrast those compounds that are susceptible to oxidation by ^3DOM react more readily with organic matter derived from autochthonous sources i.e., from phytoplankton and other microorganisms. Research by Wenk et al. (2011, 2012) has demonstrated that the presence of anti-oxidants such as phenolic compounds in allochthonous DOM is responsible for this disparity. The presence of these anti-oxidants could result in the reversion of meta-stable photo-intermediates back to the parent compound, which is manifested as “slower” reaction kinetics. Finally, more recent work by Wenk et al. (2013) showed that excited triplet state ketones could be quenched by DOM, but not at the DOC concentrations used in this study. It is conceivable that this later process could be more important in high DOC waters (> 22 mg/L as DOC).

The experiments conducted for both fulvic acid solutions (Guerard et al., 2009) and whole water DOM suggest the importance of ^3DOM as a reactive intermediate in TCC's photofate. Triplet DOM can react with ground state TCC through electron or energy transfer (Figure 4), and can concurrently generate singlet oxygen. Removal of O_2 in the anoxic experiments allows us to assess the importance of singlet oxygen because ground state triplet oxygen is an important scavenger of ^3DOM . In all cases we observed faster TCC reaction kinetics by as much as > 50% in the anoxic solutions relative to air-equilibrated samples. This data suggests that singlet oxygen is not important in the indirect mediated degradation of TCC in the presence of DOM as the sensitizer, and is in contrast to the results of Ding et al. (2014). These researchers demonstrated that singlet oxygen is the responsible ROS in the self-sensitized direct photolysis of TCC based upon ESR data. While the direct photolysis of TCC is significant, we believe that oxidation of TCC by triplets becomes the dominant transformation pathway in the presence of irradiated-DOM. We suspect that in the presence of DOM singlet oxygen can be scavenged beyond quenching by water, and the dominant attenuation pathway switches to reaction with ^3DOM . Evidence for this has been reported by Cory et al. (2008) who found that 64–70% of the uptake of oxygen in irradiated solutions of fulvic acid could be explained through interactions with singlet oxygen.

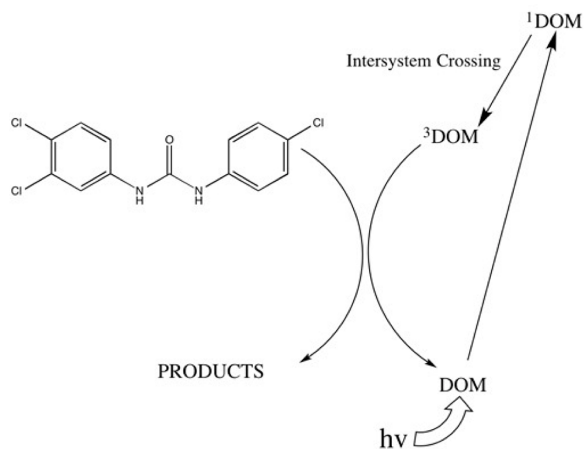


Figure 4

Proposed reaction pathway for the reaction between triclocarban and photo-excited triplet state dissolved organic matter (^3DOM).

Side reactions involving other reactive oxygen species were found to be insignificant relative to oxidation by ^3DOM .

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The complete quenching of the fulvic acids (with the exception of Pony Lake) and OWC whole water (Figure 2) by methanol strongly suggest that the hydroxyl radical appears to play an important role in the degradation of TCC. While methanol is also reactive toward the hydroperoxyl radical at our pH (7.0) only ~ 3% exists as hydroperoxyl with the remainder being the superoxide conjugate base. This runs contrary to our anoxic experimental data, which showed that ^3DOM is the dominant reactive transient. Further we also reported significant quenching of TCC indirect photolysis by isopropanol in an earlier paper (Guerard et al., 2009). Recent research has demonstrated that simple alcohols are capable of quenching both $\text{OH}\cdot$ and reactive transients. Vione et al. (2010) showed that isopropanol is capable of quenching ^3DOM involved in the indirect oxidation of 4-chloro-2-methylphenoxy-acetic acid (MCPA). They demonstrated by laser flash photolysis that the absorbance of the second transient species (presumably the triplet) is quenched significantly by approximately a factor of 3 at alcohol concentrations (25 mM) used in this and our previous study (Guerard et al., 2009) at pH = 7.8. Ding et al. (2014) also reported that isopropanol is capable of quenching the direct photolysis of TCC even though $\text{OH}\cdot$ was not identified in their ESR data. Like Vione et al. (2010) they attribute this anomaly to the scavenging of ^3TCC by the alcohol. Thus, it is conceivable that the complete quenching of the indirect pathway is caused by reaction between the excited state DOM and methanol. While reaction with $\text{OH}\cdot$ is still possible we believe that it is a secondary process relative to oxidation by ^3DOM .

We examined the possibility of additional $\text{OH}\cdot$ production from the photo-Fenton mechanism by spiking our solutions with μM levels of iron. Research by Vermilyea and Voelker (2009) suggest that this process could be important in the indirect photo-attenuation of organic contaminants by $\text{OH}\cdot$ at neutral pH. Surprisingly, the addition of $20\mu\text{M}$ iron significantly quenched the reaction to that observed for direct photolysis rates (or slightly lower) for all samples (Figure 3). While we cannot offer an explanation for our results, one possibility is the formation of amorphous iron oxides that are capable of sorbing chromophoric components of the DOM pool. Recent work by Porcal et al. (2014) showed an analogous effect for the photobleaching of DOM whereby they propose a similar explanation. Thus, it appears that addition of iron in our system suppressed the indirect TCC photolytic pathway significantly. Finally iron levels in our OWC whole water samples were similar in concentration to the levels spiked into the fulvic acid solutions and the rate constants were slightly lower than the equivalent OWC fulvic acid solution suggesting that the photo-Fenton process at this pH is not important and that iron oxides may suppress the indirect photolytic pathway for TCC degradation.

Direct photolysis is a significant degradation pathway for TCC, but our OWC whole water and fulvic acid experiments show that DOM contributes to the degradation of TCC. Indeed this study demonstrated that the fulvic acid fraction of OWC DOM is an important photosensitizer. We speculate that ^3DOM directly interacts with TCC through either energy transfer or electron transfer. Previous research suggests that the first step of the sensitization pathway is most likely an electron transfer from TCC to DOM (Canonica et al., 2006). Unlike our previous results (Guerard et al., 2009) we believe that DOM generated $\cdot\text{OH}$ may not play as important a role (if any) in the photosensitized degradation of TCC. Finally, DOM composition matters with SRFA being the least reactive relative to either OWC whole water and fulvic acid or PLFA. We suspect that anti-oxidant moieties associated with allochthonous DOM maybe responsible for reversion of meta-stable intermediates back to the parent compound.

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Contributions

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- Experimental execution: TT
- Data interpretation: TT and YPC
- Paper write up: YPC and TT

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Competing interests

There are no competing or conflict of interests from either author.

Data accessibility statement

Data for this paper can be made available by contacting the corresponding author.

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