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16 October 2023

New insights into the environmental photochemistry of 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan): Reconsidering the importance of indirect photoreactions

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Abstract

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is a widely used antimicrobial agent that undergoes fairly slow biodegradation. It is often found in surface waters in both the acidic (HTric) and basic (Tric⁻) forms (pK_a ~ 8), and it can undergo direct photodegradation to produce several intermediates including a dioxin congener (2,8-dichlorodibenzodioxin, hereafter 28DCDD). The latter is formed from Tric⁻ and causes non-negligible environmental concern. Differently from current literature reports, in this paper we show that the direct photolysis would not be the only important transformation pathway of triclosan in surface waters. This is particularly true for HTric, which could undergo very significant reactions with •OH and, if the laser-derived quenching rate constants of this work are comparable to the actual reaction rate constants, with the triplet states of chromophoric dissolved organic matter (³CDOM*). Model calculations suggest that reaction with ³CDOM* could be the main HTric phototransformation pathway in deep waters with high dissolved organic carbon (DOC), while reaction with •OH could prevail in low-DOC waters. In the case of Tric⁻ the direct photolysis is much more important than for HTric, but triplet-sensitised transformation could produce 28DCDD + 27DCDD with higher yield compared to the direct photolysis, and it could play some role as dioxin source in deep waters with elevated DOC.

Keywords: triclosan; environmental photochemistry; direct photolysis; emerging pollutants; sensitised photochemistry; dioxins; pharmaceuticals and personal care products (PPCPs).

1. Introduction

Triclosan is an antimicrobial agent that is frequently used in personal care products such as liquid soaps and bath foams, as well as several other consumer and surgical products (Bahrgava et al., 1996; Jones et al., 2000; Wong-Wah-Chung et al., 2007). It is fairly resistant to biodegradation, which accounts for its incomplete removal in wastewater treatment plants (WWTPs). Triclosan abatement in WWTPs consists of several processes, including actual biodegradation, sorption to sediments and formation of chloroderivatives, if chlorination is used in the disinfection stage (Singer et al., 2002; Buth et al., 2009; Lee et al., 2012). Triclosan is a weak acid with $pK_a \sim 8$, thus both the protonated form (HTric) and the dissociated one ($Tric^-$) occur in environmental waters (Singer et al., 2002). The behaviour of both species should be taken into account when assessing the environmental fate of this compound.

Phototransformation is a very important degradation pathway for triclosan in surface waters. It is also a very interesting example of a process in which a transformation intermediate is more harmful than the parent compound, because the direct photolysis of triclosan yields 2,8-dichlorodibenzodioxin (28DCDD) as well as chlorophenols (Latch et al., 2003; Mezcua et al., 2004; Latch et al., 2005; Sanchez-Prado et al., 2006; Aranami et al., 2007; Wong-Wah-Chung et al., 2007). Although 28DCDD is not the most toxic among dioxin congeners, its environmental impact is considerably higher than that of triclosan (Buth et al., 2009).

Photochemical processes in surface waters are usually divided into direct and indirect photolysis. In the former case, sunlight absorption by a substrate triggers transformation *via* bond breaking, photoionisation or reactivity of the excited states (Canle et al., 2005; Rajam et al., 2011; Burdzinski et al., 2013; Da Silva et al., 2013; Xiao et al., 2014). In contrast, indirect photochemistry involves reactive transients such as $^\bullet OH$, $CO_3^{-\bullet}$, $^1O_2$ and the triplet states of chromophoric dissolved organic matter ($^3CDOM^*$). Such transients are formed upon sunlight absorption by photoactive compounds (photosensitisers) that naturally occur in surface waters. Important photosensitisers include for instance CDOM (which produces $^3CDOM^*$, $^1O_2$ and $^\bullet OH$), nitrate and nitrite (both being $^\bullet OH$ sources) (Kohn and Nelson, 2007; Peterson et al., 2012; Keen et al., 2012; Zeng and Arnold, 2013; Fernandez-Gomez et al., 2013; Lee et al., 2013; Mostafa and Rosario-Ortiz, 2013). Moreover, $CO_3^{-\bullet}$ is produced upon oxidation of carbonate and bicarbonate by $^\bullet OH$, and (usually to a lesser extent) through oxidation of carbonate by $^3CDOM^*$ (Huang and Mabury, 2000; Canonica et al., 2005; Wallace et al., 2010). Dissolved organic matter (DOM, either chromophoric or not) is the main sink of $^\bullet OH$ and $CO_3^{-\bullet}$, while $^1O_2$ is mainly deactivated upon collision with water. Moreover, $^3CDOM^*$ undergoes thermal deactivation as well as reaction with dissolved oxygen to produce $^1O_2$ (Donham et al., 2014; Keen et al., 2014; Vione et al., in press).

In most of the available scientific literature, the transformation of triclosan in surface waters is unquestioningly attributed to direct photolysis, while indirect photoreactions are neglected as potential transformation pathways. In this paper we show that, although this assumption can be acceptable for Tric⁻, it is questionable in the case of HTric (which is the main triclosan species at pH < 8). In addition to the $^\bullet$OH process that can be quite significant under some conditions, reaction with ^{3}CDOM* has been completely neglected as a potential transformation pathway of triclosan in the natural environment.

2. Experimental

Reagents and materials. The stock solution of triclosan (99%, purchased from Dr. Ehrenstorfer) was prepared in acetonitrile (gradient grade, VWR International). 1-Nitronaphthalene (1NN), anthraquinone-2-sulphonic acid (sodium salt), H_2O_2, NaOH and $HClO_4$ (all of analytical grade) were purchased from Sigma-Aldrich and used without further purification. Water used to prepare the solutions was purified with a Millipore water system (Millipore RQ, resistivity 18 MΩ cm, DOC < 0.01 mg L^{-1}). All solutions were stored in the dark at 4 °C and mixed before each experiment to obtain the desired concentrations.

Laser flash photolysis experiments. Mixtures of triclosan and 1NN underwent laser shot irradiation at 355 nm, to excite 1NN and limit the excitation of triclosan itself. For 355 nm excitation, experiments were carried out using the third harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser system instrument, used in a right-angle geometry with respect to the monitoring light beam. The single pulses were *ca.* 9 ns in duration and pulse energy was set to ∽65 mJ. Individual cuvette samples (3 mL volume) were used for a maximum of four consecutive laser shots. The transient absorbance at the pre-selected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator and photomultiplier (1P28). A spectrometer control unit was used for synchronising the pulsed light source and programmable shutters with the laser output. The signal from the photomultiplier was digitised by a programmable digital oscilloscope (HP54522A). A 32 bits RISC processor kinetic spectrometer workstation was used to analyse the digitised signal.

Irradiation experiments. Triclosan aqueous solutions were irradiated under a Xenon lamp (Philips) in a 40 mL thermostated cylindrical reactor, cooled by water circulation at a temperature of 15 °C. The reactor was located at one focal point of the lamp to maintain a constant irradiation of the whole sample, and it was equipped on top with a Pyrex filter to remove wavelengths lower than ~285 nm. Samples were continuously stirred with a magnetic stirrer and a Teflon bar to ensure homogeneity. The emission spectrum of the lamp was

recorded using a fibre optics coupled with a CCD spectrophotometer (Ocean Optics USD 2000+UV-VIS), calibrated with a reference lamp (DH-2000-CAL, Ocean Optics). The irradiance reaching the reactor surface was calculated to be 34 W m^{-2} in the range of 290-400 nm. Figure 1 reports the lamp spectrum as well as the absorption spectra of HTric and Tric$^-$.

Analysis by liquid chromatography (UPLC-DAD and LC-MS). The disappearance of triclosan and the evolution of intermediates were monitored by ultra-high performance liquid chromatography, using a Waters Acquity UPLC instrument equipped with a diode array detector and a Waters 2695 separation module. The mobile phase was a mixture of water and acetonitrile (50/50 v/v) at 0.3 mL min^{-1} flow rate. The column was a Water Acquity UPLC C18 (100 mm × 2.1 mm × 1.7 µM). The triclosan retention time was 8.0 min, detection wavelength 220 nm.

A LC-MS system (Agilent 1100 Series, binary pump), equipped with an ESI ion source (negative ion mode), an ion-trap mass selective detector (MSD VL) and a UV detector, was used to identify 28DCDD among the transformation intermediates of triclosan. The adopted column was a Sphere Clone C18 (Phenomenex, 4.6 × 250 mm × 5 µm) and the gradient elution was as follows: initially 5 % acetonitrile and 95 % water, followed by a linear gradient to 95 % acetonitrile within 11 min, keeping constant the latter conditions for a further 20 min. The flow rate was 0.4 mL min^{-1} and the UV detector was set at 254 nm.

The initial rates of triclosan transformation and intermediates formation were determined with the initial slope method.

Photochemical modelling. The model used in this work has been described in detail in several previous publications (see for instance Minella et al., 2013 or Ruggeri et al., 2013). Recently, a software application has been developed from the model (APEX: Aqueous Photochemistry of Environmentally-occurring Xenobiotics). Based on the Octave open-source software (Eaton, 2012), APEX (including its User's Guide that contains a comprehensive account of the model equations) can be downloaded for free from the author's site (*http://chimica.campusnet.unito.it/do/didattica.pl/Quest?corso=7a3d*) or as electronic supporting information of Bodrato and Vione (2014). Model validation was carried out by comparison with field data, including the phototransformation of pharmaceuticals (Vione et al., 2011; De Laurentiis et al., 2012a).

APEX predicts steady-state concentrations of $^\bullet$OH, $CO_3^{-\bullet}$, $^1O_2$ and $^3CDOM^*$, based on water chemistry and depth and on the spectral photon flux density of sunlight. In the case of $^3CDOM^*$, the software includes formation quantum yields from CDOM that have been measured upon irradiation of natural water samples with concentrated 2,4,6-trimethylphenol as probe (Al Housari et al., 2010). Such an approach is suitable to determine the most reactive and short-lived triplet states, while longer-lived and poorly reactive species could escape

detection. The latter transients could include oxygen-containing radicals in addition to triplet states (Canonica and Freiburghaus, 2001), which are also expected to show low reactivity towards refractory organic pollutants.

APEX predicts the reaction kinetics of pollutants by direct photolysis and indirect photochemistry. Required input data are absorption spectra of xenobiotics, photolysis quantum yields and second-order reaction rate constants with $^\bullet OH$, $CO_3^{-\bullet}$, $^1O_2$ and $^3CDOM^*$. Formation yields of intermediates *via* the relevant photochemical pathways are required to model formation rate constants and total yields. APEX uses as standardised time unit a summer sunny day (SSD), equivalent to fair-weather 15 July at 45°N latitude (Vione et al., 2011). While keeping a standard unit of definite duration, it is possible to take into account the day-night cycle and to relate results to outdoor conditions.

Sunlight is not vertically incident over the water surface. The solar zenith angle should be considered, as well as the fact that refraction deviates the light path in water towards the vertical. Because of this phenomenon, the path length l of light in water is longer than the water depth d: on 15 July at 45°N it is $l = 1.05\ d$ at noon, and $l = 1.17\ d$ at ±3 h from noon. The latter is a reasonable daily average for 15 July.

There are a couple of further issues: *(i)* APEX applies to well-mixed surface waters, including the epilimnion of stratified lakes; *(ii)* results are integral values over the water column, thus they are average values for the given depth. The average takes into account contributions from both the sunlit portion next to the surface and the darker deep layers.

3. Results and Discussion

3.1. *Laser flash photolysis experiments*

The triplet-sensitised kinetics of triclosan transformation can be assessed by use of photoactive molecules as CDOM proxies. The Stern-Volmer approach allows the determination of the second-order rate constant between triclosan and a triplet state, based on the effects that variable triclosan concentrations have on the kinetics of triplet decay. Preliminary experiments were carried out to identify a suitable proxy molecule for CDOM. One possibility could be anthraquinone-2-sulphonate (AQ2S), based on the fact that quinones are very common CDOM components (Cory and McKnight, 2005). However, laser irradiation of triclosan + AQ2S proved impractical due to important spectral interference between the species formed from triclosan and the AQ2S excited state. Looking for a triplet sensiser not undergoing such interference, it was finally determined that 1-nitronaphthalene (1NN) is a suitable molecule to investigate the kinetics of triclosan transformation in aqueous media.

The choice of 1NN was largely motivated by experimental convenience. This compound is actually more representative of the photosensitisers occurring in atmospheric aerosols (Maddigapu et al., 2011; De Laurentiis et al., 2013) than of those present in surface waters. However, the reduction potential of the 1NN triplet state (^{3}1NN*) is around 2 V (Zugazagoitia et al., 2008), thus it is not very far from those of benzophenones and acetophenones that are often used as CDOM proxies (1.6-1.8 V; Canonica et al., 2006). Moreover, the triplet state of 1NN is considerably less reactive compared to that of AQ2S (Brigante et al., 2010; De Laurentiis et al., 2012b; Brigante et al., 2014), which makes 1NN even more appropriate in a study aimed (among other issues) at assessing the environmental importance of triplet-sensitised triclosan transformation.

For the laser flash photolysis experiments, pH was set at 3.5 and 9.5 where the main triclosan forms are HTric and Tric$^-$, respectively. The decay of ^{3}1NN* was monitored at 620 nm as previously reported (Brigante et al., 2010), to avoid interference from radical species such as 1NN$^{-\bullet}$ or the triclosan phenoxy radical. The latter has two absorption maxima at 375 and 421 nm (Wong-Wah-Chung et al., 2007). The ^{3}1NN* state was efficiently quenched by triclosan, and its pseudo-first order decay constant increased from ~6.5×10^5 s^{-1} in pure water (at both pH values) to 1.7×10^6 s^{-1} and 2.0×10^6 s^{-1} in the presence of 0.15 mM triclosan at pH 3.5 and 9.5, respectively.

The spectra of excited 1NN when alone in solution, at both pH 3.5 (Figure 2A) and 9.5 (Figure 2C) showed two main absorption bands at ~400 and 620 nm, which can be assigned to ^{3}1NN* (Brigante et al., 2010). The addition of triclosan caused the appearance of further absorption signals below 400 nm (Figure 2B, D), which are probably due to phenoxy radicals and/or 1NN$^{-\bullet}$ (De Laurentiis et al., 2013). The absorption of the transient peak around 380 nm was much higher at pH 9.5 compared to pH 3.5 at t > 2 µs. Such a difference may suggest that HTric and Tric$^-$ could take part in different oxidation mechanisms with ^{3}1NN*. At pH 9.5 the high absorption signal could be attributed to 1NN$^{-\bullet}$ (Brigante et al., 2010), which would be generated by an electron-transfer pathway. At pH 3.5, the lower absorption could be the consequence of a different reaction pathway (*e.g.* hydrogen transfer) that might yield *e.g.* 1NN-H$^\bullet$.

The second-order rate constant between ^{3}1NN* and triclosan was obtained by linear fit, plotting the pseudo-first order rate constant of ^{3}1NN* decay as a function of triclosan concentration (see Figure SM1 in the Supplementary Material, hereafter SM). The ^{3}1NN* + triclosan second-order rate constant was thus determined as $(3.08 \pm 0.73) \times 10^9$ M^{-1} s^{-1} at pH 3.5 (HTric) and as $(4.34 \pm 0.62) \times 10^9$ M^{-1} s^{-1} at pH 9.5 (Tric$^-$). The reaction rate constants of both HTric and Tric$^-$ with ^{3}1NN* are quite elevated, which suggests that triclosan has high potential to undergo triplet-sensitised transformation (which is, by the way, quite reasonable for a phenolic compound). However, one should consider the fact that the laser flash photolysis experiments give the rate constant of ^{3}1NN* quenching by HTric/Tric$^-$. Such a

quenching could be due to chemical reactivity, but also to physical issues. Moreover, reactions between phenolic compounds and excited triplet states would yield phenoxyl radicals, which could be reduced back to the starting molecules upon *e.g.* reaction with the superoxide anion (Canonica et al., 2000). Therefore, the laser-derived flash photolysis rate constants are upper limits for the actual reaction rate constants between triplet states and substrates (Canonica et al., 2000; Canonica et al., 2006).

3.2. Irradiation experiments

The photoinduced formation of dioxins from triclosan is a process of potentially high environmental concern. The modelling of such a reaction by means of APEX requires the dioxin formation yield(s) from triclosan, which are unfortunately available only for the direct photolysis of Tric¯ (Latch et al., 2003, Kliegman et al., 2013). For this reason, the photochemical production of 28DCDD was monitored here in all the main transformation processes that both HTric and Tric¯ are expected to undergo in surface waters (direct photolysis and reaction with $^\bullet$OH and ^{3}CDOM*). Hydrogen peroxide was used as photochemical $^\bullet$OH source and 1NN as CDOM proxy. No formation of 28DCDD was observed, under any condition, in the presence of HTric. The 28DCDD was also not formed upon reaction between Tric¯ and $^\bullet$OH. A new peak with retention time of 2.1 min, which could be compatible with 28DCDD (Wong-Wah-Chung et al., 2007), appeared upon irradiation of Tric¯ alone and of Tric¯ + 1NN (pH 10.8 in both cases). LC-MS analysis indicated that, in both cases, the peak contained two dioxin congeners, 28DCDD and 27DCDD, which probably coeluted under the adopted conditions (typical fragment ions from both structures were present, see Table SM1 in SM). The formation of 27DCDD upon triclosan photodegradation had already been described (Mezcua et al., 2004).

Quantification of the dioxin peak (28DCDD + 27DCDD, hereafter DCDD) was carried out by UPLC-DAD, but spectral deconvolution was prevented by the lack of commercial standards. Figure 3 reports the time evolution of triclosan (Tric¯) concentration and dioxin peak area, upon irradiation of 50 µM triclosan alone or in mixture with 50 µM 1NN (pH 10.8). The absolute yields of dioxin formation cannot be calculated but, under the hypothesis that the two congeners have similar absorption coefficients at 220 nm and a constant ratio of the formation yields in the two processes, one gets that the dioxin yield with Tric¯ + 1NN (triplet-sensitised transformation) might be ~3.5 times higher than for the direct photolysis. Considering that the literature reports a 4% formation yield of 28DCDD upon direct photolysis (Kliegman et al., 2013), it might be tentatively assumed that the corresponding yield in triplet-sensitised transformation could be as high as 14%.

3.3. Photochemical modelling

Table 1 summarises the photochemical reactivity parameters of triclosan in its acidic (HTric) and basic (Tric⁻) forms (direct photolysis quantum yields and second-order reaction rate constants with $^\bullet OH$, $^1O_2$ and triplet states, using 1NN as CDOM proxy). It should again be recalled that the quenching rate constant with ^{3}1NN*, derived by laser flash photolysis, is actually an upper limit for the reaction rate constant between $^3CDOM*$ and HTric/Tric⁻. The values reported in Table 1 can be used as input data for the APEX software, to predict environmental lifetimes as a function of water parameters such as depth and chemical composition. APEX also allows the assessment of the relative role of different photochemical pathways in the transformation of the substrate. The latter issue is important, because different photoreactions are characterised by different values of the dioxin yield from Tric⁻. The solution pH is also important because HTric, differently from Tric⁻, does not yield DCDD upon photochemical transformation. Moreover, the model showed that the reaction between triclosan (either HTric or Tric⁻) and $^1O_2$ is unimportant under most environmental conditions (with the partial exception of very $^1O_2$-rich waters: see Latch et al., 2005).

The direct photolysis quantum yield $\Phi_{Triclosan}$ deserves a comment because different literature references report different values (in the 0.1-0.7 range), obtained with light sources emitting under different intervals (simulated sunlight or narrow UV bands). However, there is no clear indication that $\Phi_{Triclosan}$ varies with wavelength, or that it is much different for HTric and Tric⁻ (Latch et al., 2005; Buth et al., 2009). For this reason, model simulations will take into account the effects of varying $\Phi_{Triclosan}$ between 0.1 and 0.7 (assuming equal values for HTric and Tric⁻), and using in other cases an intermediate value of 0.4.

Figure 4 reports the modelled half-life times of triclosan (assuming $\Phi_{Triclosan} = 0.4$) as a function of water depth and of the dissolved organic carbon (DOC), which in the model measures both DOM and CDOM. Figure 4a reports the data for HTric, Figure 4b those of Tric⁻. A first noteworthy issue is that the lifetime of the basic form is much lower compared to HTric, implying that Tric⁻ is more photolabile under surface-water conditions. This happens because Tric⁻ absorbs a much larger fraction of sunlight compared to HTric. The half-life times of both forms increase with depth, because the bottom layers of deeper water bodies are poorly illuminated by sunlight and, as a consequence, photochemical reactions have lower importance in deeper water columns.

The half-life time of HTric has a maximum as a function of DOC, while that of Tric⁻ continuously increases with increasing DOC. A key issue is that both DOM and CDOM would increase with increasing DOC. DOM scavenges $^\bullet OH$, and its importance as scavenger is higher compared to that of CDOM as source. Therefore, [$^\bullet OH$] decreases as DOC increases. Moreover, CDOM absorbs sunlight and competes with triclosan for irradiance, which would inhibit direct photolysis in high-DOC waters. Contrary to $^\bullet OH$ and photolysis, the reactions

induced by ^{3}CDOM* are enhanced if DOC increases. To explain the DOC trends reported in Figure 4, one should consider that the direct photolysis is much more important in the case of Tric$^-$ than for HTric. For the basic form the inhibition of direct photolysis (and, with a lesser impact, of $^•$OH) with increasing DOC is more important than the corresponding enhancement of ^{3}CDOM*, thus the half-life time of Tric$^-$ increases with DOC. Considering HTric, the initial increase of the half-life time with increasing DOC is accounted for by the inhibition of direct photolysis and $^•$OH reaction that are the main degradation pathways in low-DOC waters. After the maximum (*e.g.* above ~ 2 mg C L^{-1} DOC), ^{3}CDOM* becomes the main degradation pathway and the half-life time decreases with increasing DOC.

Figure 5 reports the fraction of triclosan degradation that is accounted for by direct photolysis, for both HTric (5a) and Tric$^-$ (5b), as a function of depth and DOC. In the case of HTric, photolysis accounts for up to 50% of the overall degradation. The photolysis process is favoured in shallow waters with low DOC, because: *(i)* HTric absorbs UVB radiation, which undergoes poor penetration in the water column due to efficient absorption by CDOM, and *(ii)* high-DOC water contains elevated CDOM, which competes with HTric for sunlight irradiance. Reaction with $^•$OH could be important in low-DOC water; on the contrary, high DOC implies elevated DOM that scavenges $^•$OH. The inhibition effect of DOM is higher for $^•$OH than for the direct photolysis, which accounts for the initial increase of the photolysis fraction at low DOC. On the other hand, reaction with ^{3}CDOM* could be the main process (accounting for up to 90% of the overall HTric transformation) in deep waters with elevated DOC. It should be underlined that the 90% degradation of HTric by ^{3}CDOM*, as returned by the model, is an average value over a whole water column of, say, 10 m depth, and not the point value at 10 m. Therefore, it is suggested that reaction with ^{3}CDOM* is a potentially very important pathway for HTric degradation in the natural aquatic environment. The ^{3}CDOM* process is understandably favoured in high-DOC waters, and in deep ones because CDOM absorbs visible radiation that shows considerable penetration in the water column.

In the case of Tric$^-$ (Figure 5b), it is shown that direct photolysis would always account for the majority (> 75%) of the overall transformation. The relative weight of reaction with ^{3}CDOM* would approach ~20% in the most favourable conditions (deep waters with high DOC), while $^•$OH would account for no more than 1-2% of total transformation.

The data reported in Figures 4 and 5 allow the interpretation of the literature reports concerning the effect of organic matter on the photolysis of triclosan, while putting them in an environmental context. First of all, it can be seen that triclosan undergoes faster degradation in the absence of organic matter (DOC $\rightarrow$ 0) than in its presence (Figure 4), independently of the details of the DOC trend of HTric or Tric$^-$ transformation. The inhibition of the transformation of triclosan by organic matter, when compared to high-purity water, is both predicted by our model and reported in laboratory results from the literature, with an overall agreement between model and experiments (Tixier et al., 2002). However, literature studies

have probably not investigated the details of what was going on in DOM-rich water samples and have made the (reasonable) hypothesis that slower photodegradation was occurring by direct photolysis, partially inhibited by competition for irradiance between CDOM and triclosan. Under such circumstances, it is possible that photolysis was inhibited more than expected (*i.e.*, almost totally quenched) and replaced (but only partially) by the ^{3}CDOM* reaction, ending in an overall slower degradation. It is also possible that the ^{3}CDOM* process escaped detection because it would be enhanced in deep waters, which cannot be reproduced by laboratory experiments, or because transformation was attributed to $^1O_2$ that would be unimportant under most environmental conditions (with some minor exceptions: Latch et al., 2005).

APEX results suggest that the main HTric transformation pathway under high-DOC and high-depth conditions would be the reaction with ^{3}CDOM*. Therefore, at low water pH, the direct photolysis might not always be the main process of triclosan transformation. This marks a considerable difference with most literature reports that consider direct photolysis as the only important triclosan transformation pathway in environmental waters (although very often the elucidation of direct and indirect photoreaction pathways was not the primary paper goal; see for instance Chen et al., 2010; Fang et al., 2010; Halden, 2014). For this reason, we believe that the present study opens up the way for a reconsideration of the relative importance of direct and indirect photochemistry in the environmental fate of triclosan, which is very important for fate prediction under conditions where ^{3}CDOM* reactions are enhanced. Of course, the model predictions here presented are based on the measured quenching rate constant of ^{3}1NN* by HTric, which is an upper limit for the reaction rate constant between HTric and ^{3}CDOM*.

The results reported so far were obtained under the hypothesis that the direct photolysis quantum yield of triclosan is 0.4 for both HTric and Tric$^-$. Figure 6 reports the substrate half-life time as a function of pH (which influences the equilibrium HTric $\leftrightarrows$ Tric$^-$ + H$^+$) and of the photolysis quantum yield $\Phi_{Triclosan}$, under the assumption that $\Phi_{Triclosan}$ does not vary between HTric and Tric$^-$. The decrease of the half-life time with increasing pH is accounted for by the higher photolability of Tric$^-$ compared to HTric. The half-life time also decreases with increasing $\Phi_{Triclosan}$. In the case of HTric, which prevails at pH < 8, the variation of $\Phi_{Triclosan}$ has limited impact on the half-life time because the direct photolysis accounts for no more than 50% of HTric degradation (in comparison, $^\bullet$OH accounts for up to 50% and ^{3}CDOM* for up to 90%). In the case of Tric$^-$ the direct photolysis accounts for an important fraction of the overall trasformation ($\geq$75%), and the half-life time is almost inversely proportional to $\Phi_{Triclosan}$. Anyway, although important, the uncertainty on the $\Phi_{Triclosan}$ value does not hamper model predictions dramatically.

Figure 7 reports the fraction of triclosan transformation that is accounted for by direct photolysis, as a function of pH and $\Phi_{Triclosan}$. The direct photolysis process is understandably enhanced at elevated pH (prevalence of Tric⁻) and elevated $\Phi_{Triclosan}$.

To see if the reaction between Tric⁻ and [3]CDOM* may be important in dioxin formation, we have modelled the production of 28DCDD (the only dioxin for which a definite yield value from triclosan is available in the literature). Unfortunately, our experimental data are referred to 28DCDD + 27DCDD. To enable modelling, we assumed that no dioxin is formed from HTric (as per our experimental data) and that the 28DCDD yield from Tric⁻ is 4% for the direct photolysis and 14% for the reaction with [3]CDOM*. The latter value was derived on the basis of the literature yield of 28DCDD upon Tric⁻ photolysis (4%; Kliegman et al., 2013), and on the fact that the DCDD yield with Tric⁻ + [3]CDOM* was 3.5 times higher than for the direct photolysis. Here one has to formulate the additional hypothesis that the formation yields of both 27DCDD and 28DCDD undergo a comparable increase when passing from photolysis to [3]CDOM*.

Figure 8 reports the modelling of 28DCDD formation from triclosan as a function of pH and DOC, as far as both formation kinetics (first-order formation rate constant, 8a) and formation yield (8b) are concerned. Because the phototransformation of HTric does not yield 28DCDD, the kinetics and yield of dioxin formation increase with increasing pH. The formation rate constant decreases with increasing DOC, because CDOM competes with Tric⁻ for sunlight irradiance and inhibits its direct photolysis. Elevated DOC would favour [3]CDOM*, but in a 5-m deep water column CDOM tends to saturate absorption and [[3]CDOM*] would not increase much with increasing DOC. Because the enhancement of [3]CDOM* could not compensate for the inhibition of the direct photolysis, one observes that both Tric⁻ transformation and 28DCDD formation would be slower at high DOC. In contrast, the formation yield of 28DCDD increases with increasing DOC, because the relevant yield was assumed to be higher upon [3]CDOM* reaction than upon direct photolysis. If this assumption is valid, the [3]CDOM* process (although a secondary one for Tric⁻ degradation) could play a non-negligible role in the formation of 28DCDD in deep waters with elevated DOC.

4. Conclusions

- Triclosan shows elevated second-order rate constants for the quenching of [3]1NN*: they are $(3.08 \pm 0.73) \times 10^9$ M⁻¹ s⁻¹ for the acid form (HTric) and $(4.34 \pm 0.62) \times 10^9$ M⁻¹ s⁻¹ for the basic one (Tric⁻). These quenching rate constants are upper limits for the reaction rate constants between HTric/Tric⁻ and [3]CDOM*.

- The reaction between Tric⁻ and irradiated 1NN gives the dioxins 28DCDD and 27DCDD, with a yield that is probably higher compared to the direct photolysis.
- According to the model results, if the rate constants with ^{3}1NN* are representative of those with ^{3}CDOM*, direct photolysis would not be the only important process that accounts for HTric transformation in surface waters. Photolysis would prevail at intermediate DOC values (1-2 mg C L^{-1}), but $^\bullet$OH would be more important at lower DOC and ^{3}CDOM* at high DOC. Reaction with ^{3}CDOM* could prevail in deep and DOM-rich water bodies, at pH < 8. In contrast, the phototransformation of Tric⁻ (pH > 8) would be mainly accounted for by direct photolysis.
- The considerable uncertainty on the photolysis quantum yield of triclosan (which could vary in the 0.1 - 0.7 range) has a significant impact on the modelled half-life times, but its impact is not so large as to prevent photochemical modelling.

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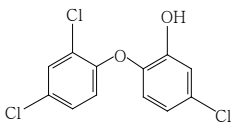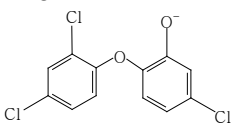
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Table 1. Data concerning the photochemical reactivity of triclosan (HTric and Tric⁻ forms, pKa ~ 8).

	HTric	Tric⁻
Photolysis quantum yield (mol Einstein^{-1})	0.1 - 0.7 [a, b]	0.1 - 0.7 [a,b]
Reaction rate with $^1O_2$ (M^{-1}·s^{-1})	$3 \cdot 10^6$ [b]	$1.1 \cdot 10^8$ [b]
Reaction rate with $^\bullet$OH (M^{-1}·s^{-1})	$5.4 \cdot 10^9$ [a]	$1 \cdot 10^{10}$ (*)
Reaction rate with ^{3}1NN* (M^{-1}·s^{-1})	$3.1 \cdot 10^9$ [c]	$4.3 \cdot 10^9$ [c]
28DCDD formation yield, direct photolysis	Negligible	0.04 [d]
28DCDD formation yield, ^{3}1NN*	Negligible	0.14 (**)

[a] Buth et al., 2009.

[b] Latch et al., 2005.

[c] This work.

[d] Kliegman et al., 2013.

(*) This rate constant was not reported in the literature. We have assumed a reasonable upper limit, under the (arbitrary) hypothesis that Tric⁻ might be more reactive than HTric towards $^\bullet$OH. Despite its fully arbitrary nature, this assumption is of little effect because the $^\bullet$OH process would account for no more than 1-2% of Tric⁻ transformation.

(**) This value was assumed on the hypothesis that 28DCDD and 27DCDD have similar absorption coefficients at 220 nm, and that the formation yields of both compounds increase by a comparable amount between direct photolysis and ^{3}CDOM* reaction.
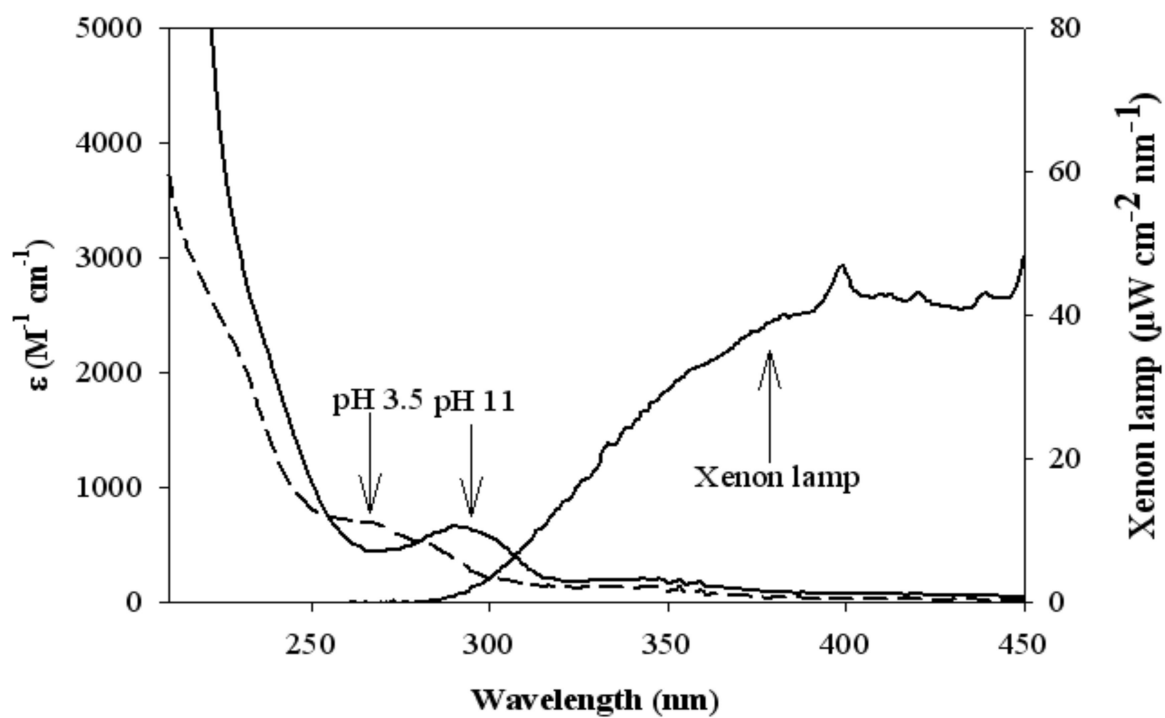
Figure1. UV-vis absorption spectra of triclosan at pH 3.5 (Htric) and 11 (Tric⁻) (molar absorption coefficient ε). Emission spectrum of the xenon lamp (irradiance on top of the solutions).
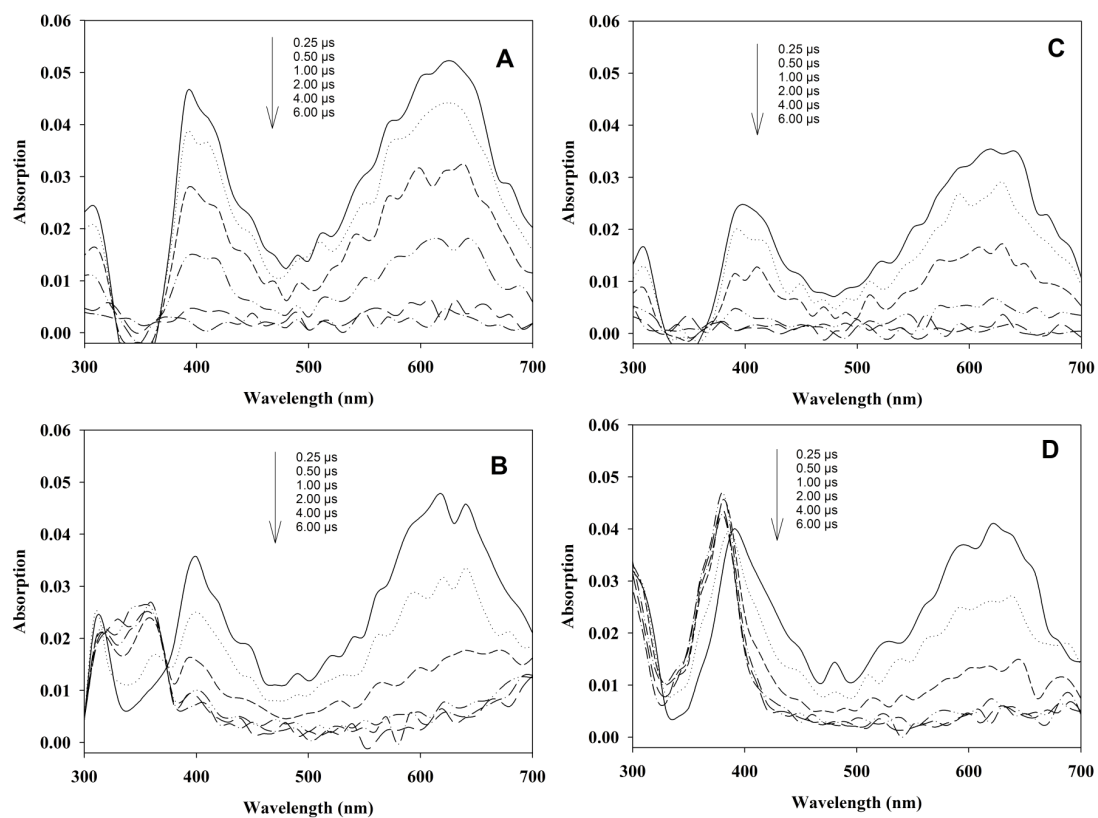
Figure 2. Transient absorption spectra obtained after 355 nm excitation of 5×10^{-5} M 1NN, in pure water at pH 3.5 (**A**) and 9.5 (**C**), and in the presence of triclosan (1.5×10^{-4} M) at pH 3.5 (**B**) and 9.5 (**D**). In all the experiments the temperature was 295 ± 2 K.
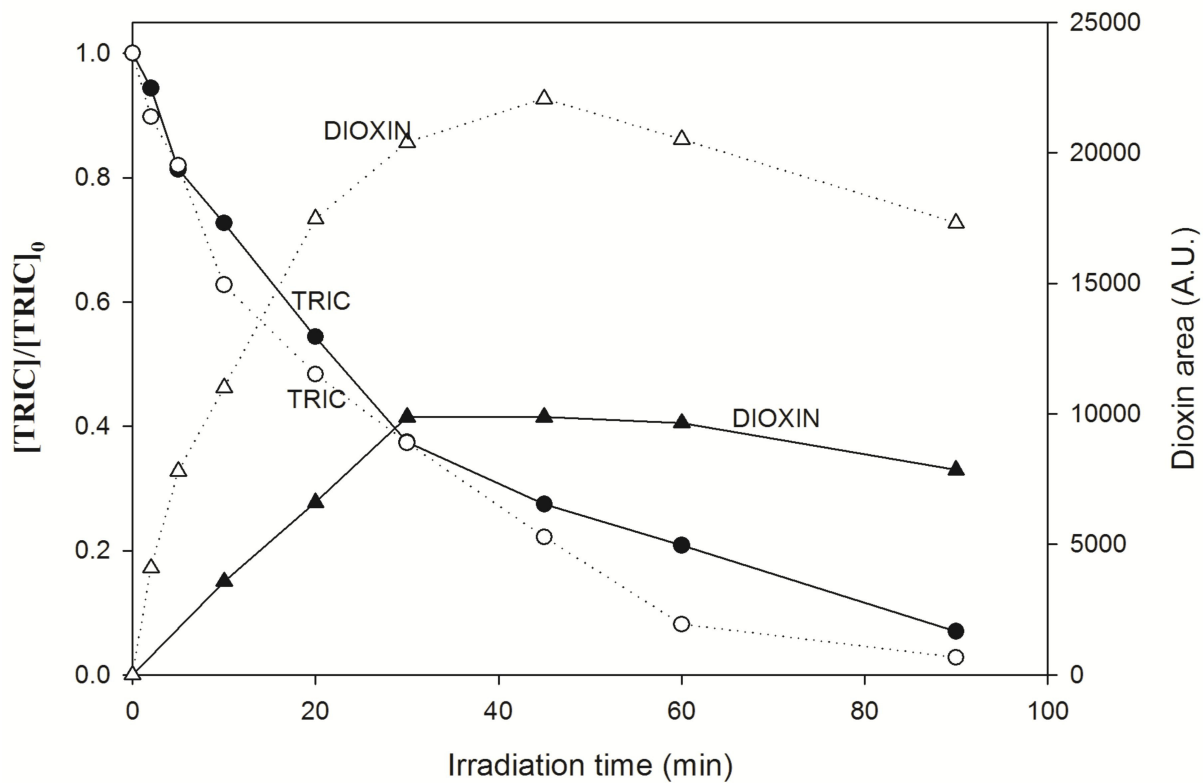
Figure 3. Polychromatic irradiation of 5×10^{-5} M triclosan (TRIC) at pH 10.8, without (solid symbols) and with (open symbols) 1NN addition (5×10^{-5} M): time evolution of Tric$^-$ (circles) and of DCDD (triangles).
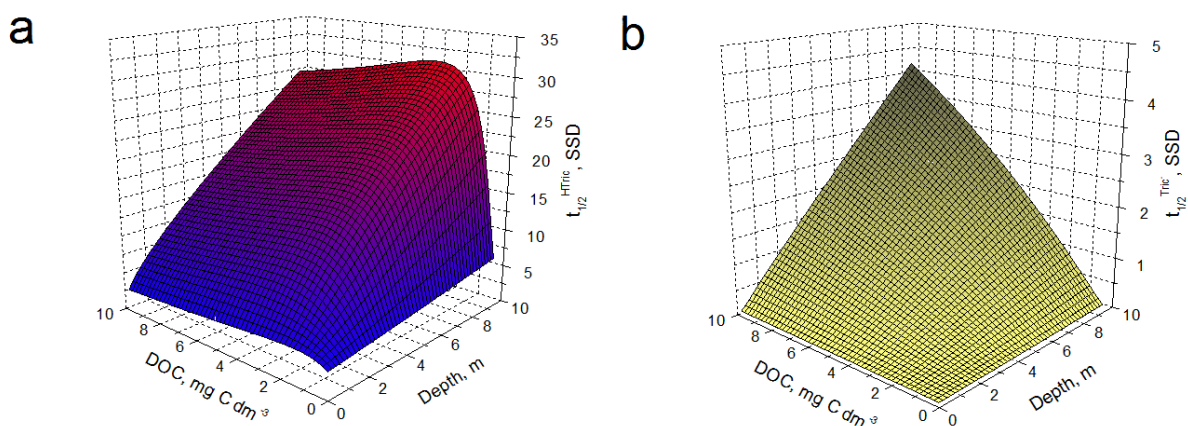
Figure 4. Half-life times (SSD = solar sunny days equivalent to 15 July at 45° latitude) of HTric **(a)** and Tric⁻ **(b)**, as a function of water depth and DOC. Other water conditions: 0.1 mM nitrate, 1 µM nitrite, 1 mM bicarbonate, 30 µM carbonate; $\Phi_{triclosan} = 0.4$.
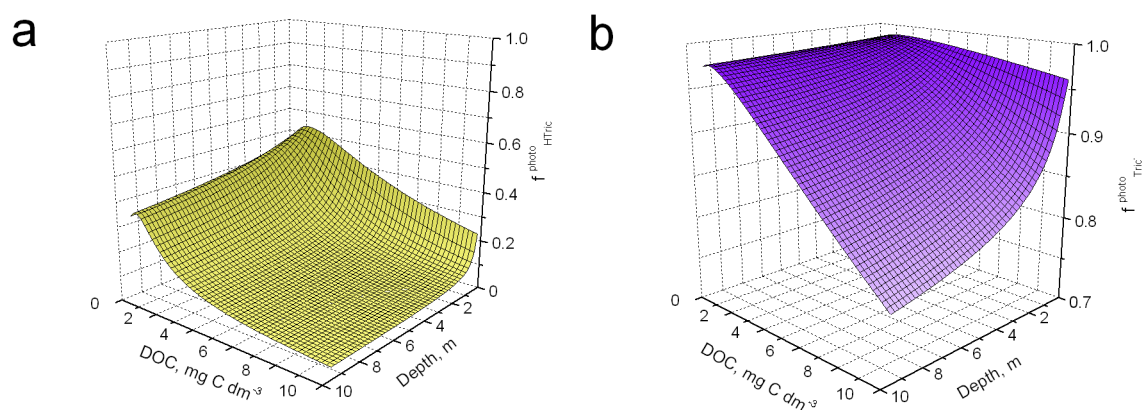
Figure 5. Fractions of the overall transformation accounted for by direct photolysis, for both HTric **(a)** and Tric⁻ **(b)**, as a function of water depth and DOC. Other water conditions: 0.1 mM nitrate, 1 µM nitrite, 1 mM bicarbonate, 30 µM carbonate; $\Phi_{triclosan} = 0.4$.
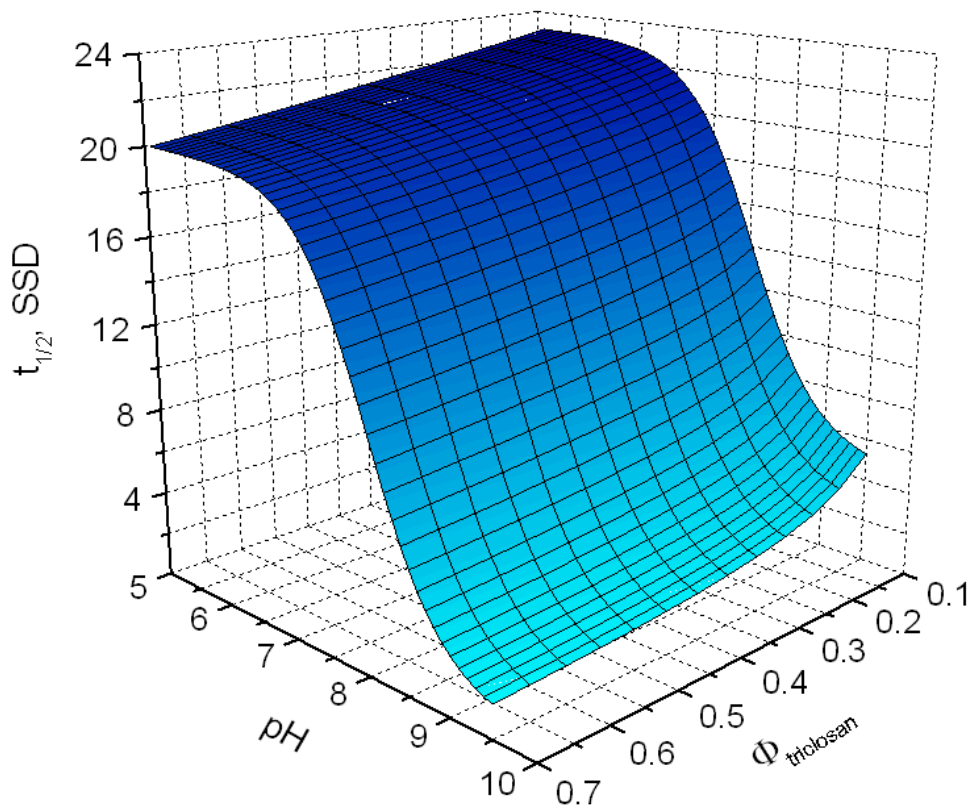
Figure 6. Half-life time of triclosan, as a function of pH and of the direct photolysis quantum yield $\Phi_{triclosan}$. Other water conditions: 0.1 mM nitrate, 1 µM nitrite, 1 mM bicarbonate, 30 µM carbonate, 5 mg C L^{-1} DOC, 5 m depth.
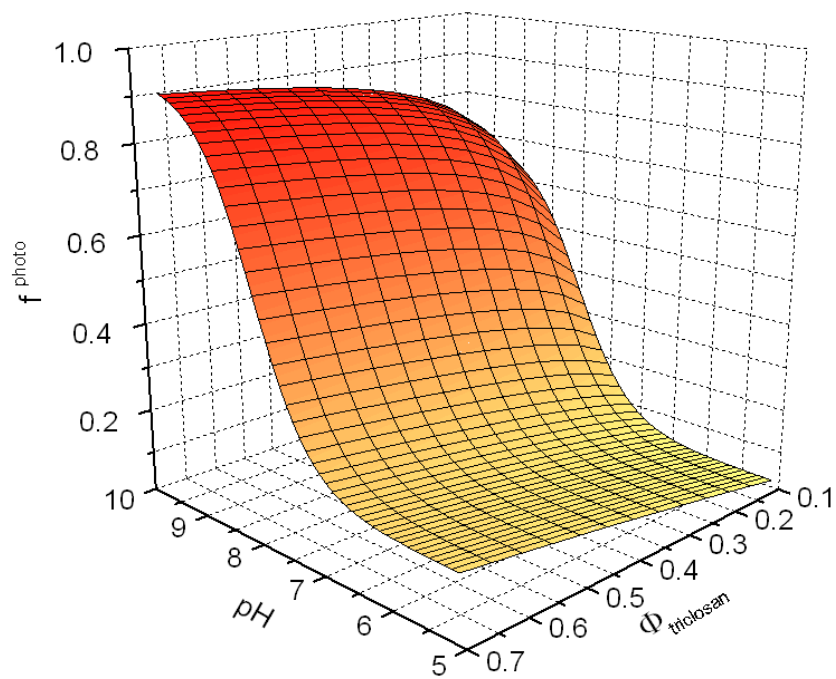
Figure 7. Fraction of triclosan transformation accounted for by direct photolysis, as a function of pH and $\Phi_{triclosan}$. Other water conditions: 0.1 mM nitrate, 1 µM nitrite, 1 mM bicarbonate, 30 µM carbonate, 5 mg C L^{-1} DOC, 5 m depth.
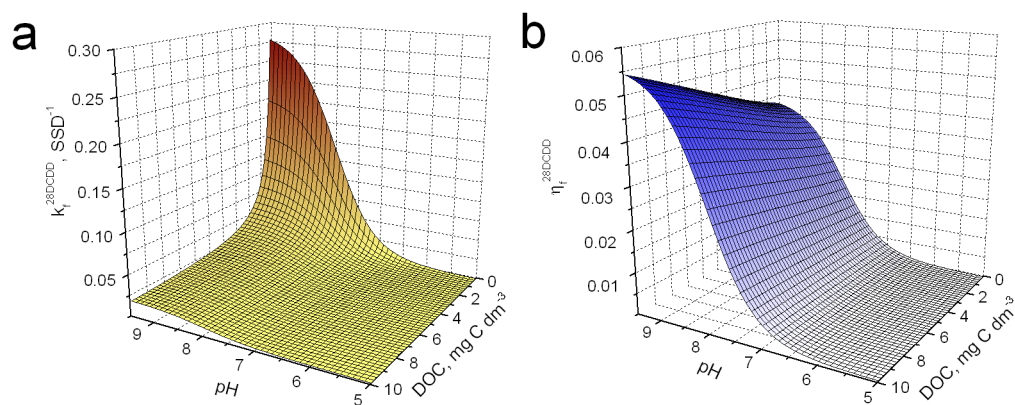
Figure 8. (a) Formation rate constant of 28DCDD from triclosan, as a function of pH and DOC. **(b)** Formation yield of 28DCDD from triclosan, as a function of pH and DOC. Other water conditions: 0.1 mM nitrate, 1 µM nitrite, 1 mM bicarbonate, 30 µM carbonate, 5 m depth; $\Phi_{triclosan} = 0.4$.