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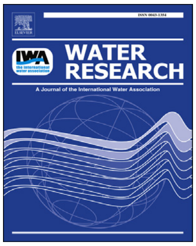

New insights into the environmental photochemistry of 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan): Reconsidering the importance of indirect photoreactions

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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 $^{\bullet}OH$ 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 $^{\bullet}OH$ 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.

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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 ~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 $^3CDOM^*$ has been completely neglected as a potential transformation pathway of triclosan in the natural environment.

2. Experimental

2.1. 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.

2.2. 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.

2.3. 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 USB 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

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