



Insights into reductive dechlorination of triclocarban in river sediments: Field measurements and in vitro mechanism investigations



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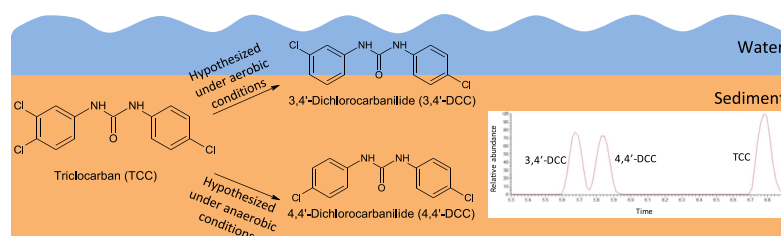
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HIGHLIGHTS

- TCC reductive dechlorination led to formation of two DCC isomers in river sediments.
- Potential dechlorination mechanisms were studied in vitro using biomimetic systems.
- Anaerobic nucleophilic addition reaction might explain 4,4'-DCC formation on field.
- 3,4'-DCC might be formed *in situ* upon a two steps radical aerobic mechanism.
- In situ TCC attenuation may not require strict anaerobic conditions to occur.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 3 June 2015

Received in revised form

19 August 2015

Accepted 29 August 2015

Available online xxx

Keywords:

Triclocarban

Sediment

Reductive dechlorination

Nucleophilic substitution

Nucleophilic addition

ABSTRACT

Triclocarban (TCC) reductive dechlorination was investigated using a combination of field and laboratory experiments. Field monitoring revealed that TCC reductive dechlorination in river sediments leads to formation of two isomers of its lesser chlorinated congener namely 3,4'-dichlorocarbanilide and 4,4'-dichlorocarbanilide. Monochlorocarbanilide was not detected in sediments supporting that transformation of dichlorocarbanilide into monochlorocarbanilide is the rate limiting step of TCC dechlorination. In vitro experiments were conducted to study TCC potential reductive dechlorination mechanisms. These experiments demonstrated that 4,4'-dichlorocarbanilide was specifically formed upon a nucleophilic addition reaction under anaerobic conditions. The 3,4'-dichlorocarbanilide was formed upon a two steps radical mechanism under aerobic conditions which includes TCC activation by one electron oxidation followed by a nucleophilic substitution reaction with glutathione. In vitro results suggested that strict anaerobic conditions might not be required for TCC reductive dechlorination in the environment. Moreover, in vitro reactions were performed using biomimetic or enzymatic systems supposing that TCC dechlorination might occur through microbial action *in situ*. Measured dichlorocarbanilide isomers/triclocarban ratios were used to evaluate the relative significance of both dechlorination pathways and the pathway leading to 3,4'-dichlorocarbanilide was found significant in all investigated river sediment samples.

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1. Introduction

Triclocarban (TCC) is a polychlorinated high-production volume antimicrobial chemical mostly used as an additive to antimicrobial soaps, cosmetics and other personal care products at levels of 0.2–1.5% (w/w). Due to incomplete removal in biological wastewater treatment plants (WWTPs) and long term persistence upon environmental release, TCC is actually one of the most frequently detected emerging contaminant at the ng- μ g range in water resources (Gautam et al., 2014), sludges (Pycke et al., 2014), biosolids amended soils (Cha and Cupples, 2009) and sediments (Souchier et al., 2014), especially in the US or in China where it ranks now in the list of top contaminants of concern (Halden and Paull, 2005; Zhao et al., 2010). Indeed, bioaccumulation of TCC in biota (Higgins et al., 2011) together with potential adverse effects of this compound in wildlife and humans have been recently highlighted (Chen et al., 2008; Sood et al., 2013).

In addition to TCC monitoring, studies have been performed during the last decade to elucidate the fate of this compound in the environment. TCC biodegradation in WWTPs is believed to be low (<20%) and accumulation in sewage sludge mainly occurs (Heidler et al., 2006; Lozano et al., 2013). An aerobic wastewater bacteria potentially involved in TCC biodegradation during sewage treatment through the hydrolysis of the urea bridge has been recently evidenced (Miller et al., 2010). In soil, half-lives ranging from 80 to 231 d were measured under aerobic conditions (Cha and Cupples, 2010; Wu et al., 2009) and no significant biodegradation was observed in anaerobic conditions within 70 d experiments (Ying et al., 2007). Detection of 3,4-dichloroaniline and 4-chloroaniline at trace levels in soil column spiked with TCC suggested occurrence of urea bridge hydrolysis but this degradation pathway remained minor (<1%) or further degradation of transformation products (TPs) occurred (Kwon and Xia, 2012). Interestingly, in sediment downstream from WWTPs where TCC tends to accumulate, TCC reductive dechlorination process was evidenced leading to significant formation of mainly dichlorocarbanilide (DCC) together with monochlorocarbanilide (MCC) and carbanilide (NCC), even if these two latter were formed only to a lesser extent (Miller et al., 2008; Venkatesan et al., 2012). If DCC provides specifically from TCC biodegradation, this metabolite is also known to occur as an impurity at levels of about 0.2% by weight in technical grade TCC. However, amounts of DCC measured in sediment were far too high to be only a consequence of its presence as an impurity (Souchier et al., 2014).

TCC reductive dechlorination processes in sediments have been speculated to occur through the action of strict anaerobic dechlorinating microorganisms even though bacterial strains involved in these transformations and degradation mechanisms have not clearly been identified yet (Miller et al., 2010). Halorespiration has been anticipated as a plausible TCC anaerobic reductive dehalogenation process (Miller et al., 2008). This cobalt corrinoid-dependent anaerobic reductive dehalogenation is thought to be involved in the reductive dehalogenation of highly halogenated persistent aromatic pollutants such as decabromodiphenyl ether (BDE-209) (Robrock et al., 2008) but also the reductive dehalogenation of lower halogenated aromatic compounds such as chlorobenzene or chlorotoluene isomers (Nelson et al., 2014). TCC aerobic reductive dehalogenation has also been hypothesized (Venkatesan et al., 2012) without providing with any transformation mechanisms or degradation conditions. Even though reductive dehalogenation is originally thought to rarely occur in aerobes, detection of a dehalogenated TP of triclosan in alga cell cultivation (Wang et al., 2013) and dechlorination products of polychlorobiphenyls in partially-oxygenated soils (Meggo et al., 2013) suggest existence of an alternate aerobic reductive dechlorination pathway for chlorinated

aromatic compounds. Recently, diclofenac (DCF), a chlorinated amine derivative similarly to TCC, has shown to undergo aerobic reductive dechlorination leading to formation of a glutathione-adduct (DDF-SG) when incubated with horseradish peroxidase (HRP), glutathione S-transferases (GST) and reduced glutathione (GSH) (Boerma et al., 2014). DCF dechlorination was supposed to occur through a GST-catalyzed nucleophilic aromatic substitution reaction after one-electron oxidation process obtained in reaction with HRP. Similarly, dechlorination and GSH conjugation of a series of chlorinated anilines including dichlorinated anilines were also reported in human liver microsomes (Zhang et al., 2011). Surprisingly, this aerobic transformation pathway, which might occur in environment because HRP and GST are environmental widespread enzymes, has not been investigated yet in the case of TCC despite the closely related structures of TCC and DCF. Then, it still remains uncertain if TCC dechlorination reactions occur abiotically or biotically and if the latter, what organisms are carrying them out and under what conditions. The determination of TCC reductive dechlorination mechanisms is needed because it may help to elucidate these different points.

The main contribution of this work is then (i) to identify the regioselectivity of TCC reductive dehalogenation in the environment by monitoring the two potential dehalogenated metabolites, 3,4'- and 4,4'-dichlorocarbanilide in river sediments and (ii) to propose dechlorination mechanisms to explain field observations using in vitro mechanistic experiments. Investigating TCC reductive dechlorination in sediments was thought to be relevant since TCC dehalogenation probably reduces its toxicity and constitutes a clear remediation pathway for this persistent contaminant.

2. Material and methods

2.1. Chemicals and reagents

Triclocarban (TCC, 99%), diclofenac (DCF, 99%), pentachlorophenol (PCP, 99%), 3,4'-dichlorocarbanilide (3,4'-DCC, 99%), ketoprofen, peroxidase type II from horseradish (HRP), hydrogen peroxide (H_2O_2), sodium citrate, titanium(II) chloride solution (TiCl_3 15% in 10% HCl), reduced glutathione (GSH), oxidized glutathione (GSSG), tris(hydroxymethyl)aminomethane (TRIS), glutathione S-transferase from equine liver (GST), bis(triphenylphosphine)nickel(II) dichloride ($\text{NiCl}_2(\text{PPh}_3)_2$) and sodium borohydride (NaBH_4) were obtained from Sigma Aldrich (St Quentin Fallavier, France). 4,4'-dichlorocarbanilide (4,4'-DCC, 99%) was purchased from Apollo (Manchester, UK). Deuterated triclocarban (TCC- d_4 , 99%) was provided from CDN Isotopes (Quebec, Canada), Cyanocobalamin (96%) from Acros Organic (Geel, Belgium) and Fontainebleau sand was purchased from Prolabo (Paris, France).

2.2. Study area

Sediment grab samples were collected twice in summer and fall 2013 from the upper 10 cm layer of the bed sediment at 3 sites (Sed1, Sed2 and Sed3) within 100 m downstream from three French WWTPs (WWTP1, WWTP2 and WWTP3). Each of the three biological WWTPs included nitrogen and phosphorus removal steps. In addition, WWTP3 was equipped with a membrane bioreactor. Characteristics and operating conditions of the WWTPs are provided as [Supplementary Material \(SM\) \(Table SM1\)](#). Sed2 and Sed3 were collected in small streams with flow rate < $1\text{--}5\text{ m}^3\text{ s}^{-1}$ and Sed1 was sampled in a 2 m deep shipping channel. In this latter case, core sediment was extracted with free fall gravity corer while in the first case sediments were collected with a shovel. Site characteristics and other physicochemical properties (pH, temperature,

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