



## Screening triclocarban and its transformation products in river sediment using liquid chromatography and high resolution mass spectrometry



Marine Souchier<sup>a,b</sup>, Dael Benali-Raclot<sup>b</sup>, David Benanou<sup>b</sup>, Véronique Boireau<sup>b</sup>, Elena Gomez<sup>a</sup>, Claude Casellas<sup>a</sup>, Serge Chiron<sup>a,\*</sup>

<sup>a</sup> UMR HydroSciences 5569, Montpellier Université, 15 Avenue Ch. Flahault, 34093 Montpellier cedex 5, France

<sup>b</sup> Veolia Recherche et Innovation, 36, Avenue Kleber, 75116 Paris 16ème arrondissement, France

### HIGHLIGHTS

- LC-HRMS method was validated to quantify TCC and transformation products in sediment
- TCC, DCC and 3-Cl-TCC were ubiquitously detected in the 1-500 ng/g range
- DCC/TCC ratio increase highlighted reductive dechlorination in anoxic sediment
- 3-Cl-TCC is probably more persistent than TCC
- Other suspected chlorinated biocides were also detected in sediment

### ARTICLE INFO

#### Article history:

Received 18 July 2014

Received in revised form 27 August 2014

Accepted 27 August 2014

Available online 26 September 2014

Editor: Damia Barcelo

#### Keywords:

Triclocarban

Sediment

Reductive dechlorination

Tetrachlorocarbanilides

High resolution mass spectrometry

### ABSTRACT

An analytical method was developed and validated for the target screening of triclosan (TCS), triclocarban (TCC) and its lesser and higher chlorinated congeners namely, 4,4'-dichlorocarbanilide (DCC) 3,3',4,4'-tetrachlorocarbanilide (3-Cl-TCC) and 2,3',4,4'-tetrachlorocarbanilide (2-Cl-TCC) in river sediment. Sediment samples were extracted by pressurized liquid extraction and quantification and identification of target compounds were carried by liquid chromatography high resolution mass spectrometry (LC-HRMS). The overall method recoveries were 89% with relative standard deviations below 6%. Method detection limits ranged from 0.01 to 0.12 ng/g. The usefulness of the method was demonstrated on sediment samples collected downstream of three wastewater treatment plants in an attempt to provide with a set of occurrence data of these biocides in France and for a better understanding of their fate in river. Major results are the following: TCC, DCC and 3-Cl-TCC were ubiquitously detected demonstrating that these emerging contaminants have been probably overlooked in France. Reductive dechlorination of TCC into DCC was also ubiquitous but predominated in anoxic sediment. 3-Cl-TCC is probably more persistent than TCC and LC-HRMS enabled the detection and identification of a suite of other chlorinated biocides in river sediment.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Triclocarban (TCC) is a polychlorinated high-production volume antimicrobial substance still in use. Even though TCC has probably more limited applications than triclosan (TCS), mostly as an additive to antimicrobial soap, cosmetics and other personal care products at levels of 0.2–1.5% (w/w), co-occurrence of TCC and TCS residues in water resource can be easily understood from their similar usage and chemical structure and due to their incomplete removal in biological

wastewater treatment plants (WWTPs). TCC is actually one of the most frequently detected emergent contaminant at the ng-µg range in water resources (Carmona et al., 2014; Gautam et al., 2014; Halden and Paull, 2005; Sapkota et al., 2007; Zhao et al., 2010), sludges (Chu and Metcalfe, 2007; Heidler et al., 2006; Lozano et al., 2013), bio-solids-amended soils (Cha and Cupples, 2009; Ying et al., 2007) and in river sediments (Venkatesan et al., 2012; Wang et al., 2014) or in estuarine sediment (Miller et al., 2008) especially in the US or in China where it ranks in the list of top contaminants of concern (Halden and Paull, 2005; Zhao et al., 2010). Indeed, bioaccumulation in biota (Coogan and La Point, 2008; Higgins and Paesani, 2009; Higgins et al., 2011) together with its potential adverse effects in wildlife have been recently highlighted (Chen et al., 2008; Sood et al., 2013; Yueh et al., 2012). In

\* Corresponding author. Tel.: +33 4 11 75 94 15; fax: +33 4 11 75 94 61.  
E-mail address: [Serge.Chiron@msem.univ-montp2.fr](mailto:Serge.Chiron@msem.univ-montp2.fr) (S. Chiron).

WWTPs, TCC biodegradation is believed to be minimal and elimination mainly due to accumulation in sewage sludge prevails (Heidler et al., 2006; Lozano et al., 2013). However, under anaerobic and reducing conditions, dechlorination process was evidenced and was supposed to be operated through the activity of exclusively anaerobic dechlorinating microorganisms leading to the formation of transformation products (TPs), namely dichlorocarbanilide (DCC), monochlorocarbanilide (MCC) and carbanilide (NCC) (Chiaia-Hernandez et al., 2013; Higgins and Paesani, 2009; Miller et al., 2008, 2010; Venkatesan et al., 2012). DCC is also a manufacturing by-product together with 3,4,3',4'-tetrachlorocarbanilide (3-Cl-TCC) at levels of about 0.2% by weight in technical grade TCC (Sapkota et al., 2007). If these impurities are not eliminated during wastewater treatment, they may also contribute to the levels of contamination found in environment (Sapkota et al., 2007). Environmental fate and toxicity of TPs of TCC remain mostly unknown. Consequently, warning exists concerning TCC and this situation has drawn an increased scrutiny by US EPA and TCC regulating in the US is currently questioned (EPA, 2002; Halden, 2014). In contrast, in EU and more particularly in France, the issue of TCC in water cycle has been probably overlooked until now because this compound is scarcely monitored since it is not included in priority monitoring list for water quality control. Consequently, the major contribution of this work is: 1) to develop and validate an analytical method for the screening of TCC and its TPs in river sediment and 2) to provide a first record of sediment contamination levels collected downstream of domestic WWTP outlet in France and to discuss it with respect to TCS contamination levels and situations in other countries. River sediment compartment has been selected in this study for monitoring purposes because TCC and its TPs tend to sorb and accumulate in sediment due to high octanol water coefficient values ( $\log K_{ow}$ , calculated using  $K_{ow}$  WIN) of 4.3, 4.9, 5.6 and low water solubilities of 3.7, 0.65 and 0.11 mg/L (calculated using Solaris V4.67) for DCC, TCC and 3-Cl-TCC, respectively (Gautam et al., 2014; Miller et al., 2008; Venkatesan et al., 2012). In addition, for these persistent hydrophobic organic contaminants which rapidly sorb to sediment and suspended particles, river sediments are excellent archives of environmental contaminants since sediment can act as integrators of many inputs within rivers. This represents a relevant advantage compared to water analysis. TCC and its TPs have then been already detected in lake sediment and estuarine sediment at concentration levels in the ng- $\mu$ g/g dry weight (dw) range (Chiaia-Hernandez et al., 2013; Miller et al., 2008; Venkatesan et al., 2012). However, their investigation in river sediments is rather scarce and river sediment is probably an under-investigated compartment. Since TCC is not amenable by gas chromatography mass spectrometry (GC-MS) techniques even with a derivatization step (Bisceglia et al., 2010), liquid chromatography-mass spectrometry (LC-MS) in association with an extraction step employing either an ultrasonic extraction, a pressurized liquid extraction (PLE) or a QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) extraction together with a clean-up including either solid phase extraction or a dispersive solid-phase extraction (dSPE) method has turned out to be the most reliable techniques for TCC and its TP detection at trace levels in environmental samples. Until now, triple quadrupole tandem mass spectrometry with an electrospray interface in the negative ionization mode has been mostly used because of its high selectivity in the Selected Reaction Monitoring (SRM) mode of detection allowing limits of detection down to 0.01 ng/g dw in sediment (Cha and Cupples, 2009; Higgins et al., 2011; Pycke et al., 2014; Sapkota et al., 2007; Zhao et al., 2010). The use of high resolution Orbitrap mass spectrometry in our study has been selected because it allows for studying parent compounds and TPs with and without reference standards based on accurate mass and fragmentation patterns (e.g.; MCC which is not commercially available). The most common HRMS instruments have resolving power in the 20,000–100,000 range with a high mass accuracy (<5 ppm) and still a sensitivity down to the picogram range in the

full scan mode of detection. This increase in selectivity allows for a reliable screening of molecular ions and their MS/MS fragments against a complex matrix background such as in sediment.

## 2. Material and methods

### 2.1. Chemicals and reagents

Standards of triclosan (TCS,  $\geq 97\%$ ), triclocarban (TCC, 99%); 3,3',4,4'-tetrachlorocarbanilide (3-Cl-TCC); 2,3',4,4'-tetrachlorocarbanilide (2-Cl-TCC) and carbanilide (NCC, 98%) were obtained from Sigma Aldrich (St Quentin Fallavier, France). 4,4'-dichlorocarbanilide (4,4'-DCC) was purchased from Apollo (Manchester, UK). Deuterated TCC (TCC-d<sub>4</sub>, 99%) and deuterated TCS (TCS-d<sub>3</sub>, 98.5%) were from CDN Isotopes (Quebec, Canada). Fontainebleau sand was purchased from Prolabo (Paris, France). HPLC grade methanol and pesticide analytical grade methanol and acetone were obtained from Carlo Erba (Val De Reuil, France). All chemicals were used as received without further purification. All aqueous solutions were prepared with UHQ milliQ water (Millipore, Bedford, USA).

### 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 WWTPs (WWTP1, WWTP2 and WWTP3) located in France. All these 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 (Table S1). Sed2 and Sed3 were collected in small streams with a flow rate of <1–5 m<sup>3</sup>/s 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, dissolved oxygen) at the time of sampling are provided in Table S2. Sediments were stored in the dark at –20 °C before extraction. The organic matter rate in sediments was measured after calcination of dried sediment at 550 °C in a furnace during 4 h, in accordance with the “NF EN 12879 Standard dated May 1997”.

### 2.3. Sample preparation and extraction

Sed1, Sed2 and Sed3, were freeze-dried, gently disaggregated, and sieved to a particle size <2 mm. TCC-d<sub>4</sub> and TCS-d<sub>3</sub> surrogates (10 ng/g) were added to the dried sediments. 5 g of sediment was mixed with 25 g of Fontainebleau sand to increase solvent channeling and placed into 34 mL stainless steel extraction cells equipped with glass fiber filters. The prepared cells were extracted by pressurized liquid extraction (PLE) using an ASE 350 system (Dionex, Sunnyvale, USA). The same operating conditions than those used by Wu et al., 2009 to extract TCC and TCS from soil samples were applied: preheat, 0 min; static, 5 min; flush, 60%; cycles, 2; purge, 120 s; oven temperature, 80 °C; and pressure, 1500 psi. Several solvents, employed in the literature for extraction of TCC from sediments or soils, were evaluated using PLE including extraction with 100% methanol (Wu et al., 2009), 30:70 acetone/ethyl acetate (Chiaia-Hernandez et al., 2013) and 50:50 acetone/methanol (Miller et al., 2008). Finally, a mix of 50:50 methanol/acetone allowed for the best recoveries and was then selected (data not shown). After extraction, a purification step is usually performed using solid phase extraction procedure (Chu and Metcalfe, 2007; Lozano et al., 2013) or more recently using a dispersive solid-phase extraction (dSPE) (Chiaia-Hernandez et al., 2013). The dSPE method was tested. Briefly, the dried extract was resuspended in acetonitrile and water followed by the addition of ammonium chloride and magnesium sulfate to promote partitioning of less polar compounds

Download English Version:

<https://daneshyari.com/en/article/6328412>

Download Persian Version:

<https://daneshyari.com/article/6328412>

[Daneshyari.com](https://daneshyari.com)