

Short Communication

Sonochemical degradation of triclosan in water and wastewater

Lucia Sanchez-Prado^a, Ruth Barro^a, Carmen Garcia-Jares^a, Maria Llompart^a,
Marta Lores^a, Christos Petrakis^b, Nicolas Kalogerakis^c, Dionissios Mantzavinos^c,
Eleftheria Psillakis^{c,*}

^a Department of Analytical Chemistry, Nutrition and Bromatology, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain

^b Mediterranean Agronomic Institute of Chania (MAICh), P.O. Box 85, GR-73100 Chania, Greece

^c Department of Environmental Engineering, Technical University of Crete, Polytechniopolis, GR-73100 Chania, Greece

Received 6 August 2007; accepted 21 January 2008

Available online 2 February 2008

Abstract

The sonochemical degradation of $5 \mu\text{g l}^{-1}$ triclosan, a priority micro-pollutant, in various environmental samples (seawater, urban runoff and influent domestic wastewater) as well as in model solutions (pure and saline water) was investigated. Experiments were conducted with a horn-type sonicator operating at 80 kHz frequency and a nominal applied power of 135 W, while solid-phase microextraction coupled with gas chromatography–electron capture detector (SPME/GC–ECD) was employed to monitor triclosan degradation. The latter followed pseudo-first order kinetics with the rate constant being (min^{-1}): 0.2284 for seawater > 0.1051 for 3.5% NaCl in deionised water > 0.0597 for centrifuged urban runoff ~ 0.0523 for untreated urban runoff > 0.0272 for deionised water > 0.0063 for wastewater influent. SPME/GC–ECD and SPME coupled with gas chromatography–mass spectrometry (SPME/GC–MS) were also used to check for the formation of chlorinated and other toxic by-products; at the conditions in question, the presence of such compounds was not confirmed.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Degradation; SPME; Triclosan; Ultrasound; Water matrix

1. Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is an antimicrobial agent listed by the 76/768/EEC European Union council directive as a preservative for cosmetic products. Its widespread use in consumer products such as toothpastes, antiperspirants, detergents, cosmetics, antimicrobial creams, lotions and hand soaps is due to its bacteriostatic performance against a broad spectrum of microorganisms as well as its favourable human safety profile. Triclosan is typically transported through a waste disposal conveyance system to a sewage treatment facility. Trace levels of triclosan not removed during wastewater treatment are released to the receiving waters as part of

the effluent matrix. Accordingly, the presence of triclosan in wastewater, surface water, seawater and sediments has been frequently reported in Europe and the United States and this is of concern given the fact that under certain conditions (such as in presence of hypochlorite or due to photochemical reactions), the native species can be converted into more toxic and persistent polar compounds, such as chlorinated phenols (mainly 2,4-dichloro and 2,3,4-trichlorophenol) polychlorinated biphenyl ethers and dihydroxylated derivatives as well as non-polar and bio-accumulative species such as methyl triclosan and polychlorinated dibenzodioxins [1–6].

The use of high power ultrasound with frequencies in the range 20–1000 kHz induces the so-called acoustic cavitation. In general, cavitation can be defined as the phenomena of the formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small

* Corresponding author. Tel.: +30 28210 37810; fax: +30 28210 37852.
E-mail address: elia.psillakis@enveng.tuc.gr (E. Psillakis).

intervals of time and releasing large magnitudes of energy over a very small location [7]. Today, there are several publications reporting the successful removal of a wide range of organic pollutants from relatively dilute aqueous solutions [7,8]. However and to the best of our knowledge, sonolysis of triclosan in waters and wastewaters has not been reported before. Moreover, triclosan degradation by advanced oxidation processes other than sonolysis has received mere attention. In recent reports, Yu et al. [9] studied the TiO₂-mediated photocatalytic degradation in model aqueous solutions, while Suarez et al. [10] investigated triclosan oxidation by means of ozone.

The aim of this work is to investigate for the first time the sonolysis of triclosan, a priority micro-pollutant, in aqueous samples of environmental importance. It is well known that the presence of matrix components (such as salt, natural organic and particulate matter) may dramatically alter the efficiency of sonochemical and other advanced oxidation processes. Accordingly, the present work investigates the effect of real sample matrix (seawater, urban runoff and influent domestic wastewater) upon triclosan sonolysis. For the purpose of the present investigations solid-phase microextraction (SPME) was used as a viable analytical tool for monitoring the degradation of triclosan as well as the possible formation of chlorinated by-products.

2. Experimental

2.1. Chemicals and sample preparation

Triclosan (Irgasan, 97%) was obtained from Fluka, Sigma–Aldrich (Steinheim, Germany). Pesticide grade methanol and sodium chloride (>99.8% purity) were obtained from Merck (Darmstadt, Germany) and Riedel de Haen (Seelze, Germany) respectively. Deionised water was prepared on a water purification system from Labconco Water Pro™ PS (Kansas City, Missouri, USA). In those cases where samples had to be centrifuged prior to sonication, this was done for 10 min at 4000 rpm with a Heraeus Megafuge centrifuge. For sample preparation, a 1000 mg l⁻¹ standard stock solution of triclosan was initially prepared in methanol. Spiked aqueous solutions were prepared daily by spiking water with the organic stock solution of triclosan at the concentration levels of interest.

2.2. Aqueous samples

Sonication experiments were conducted with model solutions prepared in deionised water as well as with (i) seawater collected from Chania, Western Crete, Greece, (ii) urban runoff collected from one of the exits of the municipal stormwater drain system of Chania discharging in coastal water and (iii) wastewater collected from the inlet of the secondary treatment of the domestic wastewater treatment plant of Chania. Real samples, whose properties are summarised in Table 1, were collected the day before the sonication experiment was performed and were ana-

Table 1
Properties of real samples used in this study (measured at 20 °C)

Sample	Initial triclosan contamination (µg l ⁻¹)	pH	Salinity (% w:v)	TDS (mg l ⁻¹)	TOC (mg l ⁻¹)
Seawater	<0.01	8	3.5	51	3.5
Urban runoff	0.07	7.7	0.018	397	6.7
Influent domestic wastewater	0.4	7.6	0.029	644	256

lysed for their total organic carbon (TOC) content using a Shimadzu TOC 5000A instrument and total dissolved solids (TDS) dried at 180 °C according to the Standard Method 2540 C [11]. pH and salinity were measured using a portable instrument (pH/Cond340i) supplied by WTW GmbH (Weilheim, Germany).

2.3. SPME extraction procedure

The SPME method used is described in detail elsewhere [12,13]. In brief, a commercially available 100 µm polydimethylsiloxane SPME fibre, housed in a manual SPME holder (Supelco, Bellefonte, PA, USA) was used for all extractions. Each time, aliquots of water samples (5 ml) were placed in 7 ml vials and direct SPME was performed by exposing the fibre to the solution. The extraction was carried out for 30 min at room temperature while stirring at 1250 rpm.

2.4. Gas chromatographic analyses

A Hewlett–Packard (HP 5890 Series II) gas chromatography–electron capture detector (GC–ECD) system equipped with a split/splitless injector was used for all analyses. The system was operated by HP ChemStation A03.04 software. Experimental conditions were column HP5-MS, 30 m × 0.25 mm i.d. × 0.25 µm film; oven temperature programme: 60 °C, hold 2 min, rate 15 °C min⁻¹ to 210 °C then 10 °C min⁻¹ to 270 °C, hold 10 min. The injector was maintained at 280 °C and operated in the splitless mode with the split closed for 2 min (split ratio 50:1). The detector temperature was 290 °C. Helium (>99.999 % purity) was used as the carrier gas at a constant head pressure of 130 kPa. The linearity of the SPME method was evaluated for triclosan concentrations between 0.1 and 50 µg l⁻¹ and was found to be very good having a 0.996 correlation coefficient (*r*). The method's detection limit was estimated to be 0.01 µg l⁻¹.

Samples were also analysed by means of SPME/GC–mass spectrometry (MS). These analyses were carried out on a Shimadzu GC-17A, Version 3, QP-5050A Gas Chromatograph/Mass Spectrometer system (Shimadzu Corporation, Kyoto, Japan) equipped with the same capillary column (HP5-MS, 30 m × 0.25 mm i.d. × 0.25 µm film) and having identical injector conditions and oven temperature programme. The ionization mode was electron impact (70 eV), the interface temperature was set at 300 °C with 1.40 kV detector voltage

and the selected ion monitoring (SIM) mode of operation was used as a sensitive analytical tool.

2.5. Sonication experiments

An Ultrason 250 (LabPlant, Huddersfield, UK) horn-type sonicator capable of operating either continuously or in pulse mode at a fixed frequency of 80 kHz and a variable electric power output up to 150 W was used. Reactions were carried out in a 250-ml round-bottom cylindrical all-glass reaction vessel equipped with a cooling jacket, connected to a temperature control unit (Polystat cc2 model manufactured by Huber, Germany). The reaction vessel was covered with aluminium foil, avoiding thus any photochemical reactions. In all cases, 200 ml solutions containing $5 \mu\text{g l}^{-1}$ of triclosan were subjected to ultrasonic irradiation at a nominal power output of 135 W with the sonicator operating in pulse mode (30 s “on”, 30 s “off”). It should be mentioned here, that the extremely low methanolic content did not alter the physicochemical properties of the synthetic samples. Results are quoted with respect to the actual sonication time (i.e. the ‘on’ period of the duty cycle) rather than the overall treatment time (i.e. the ‘on’ and ‘off’ period of the duty cycle) which was twice as much as the sonication time. Pulse operation was chosen to minimise heat dissipation during sonication, thus facilitating temperature control. Moreover, preliminary experiments were conducted either leaving the reactor’s temperature uncontrolled or keeping it constant at 20 °C; in either case, triclosan degradation remained practically unchanged. Hence, in all subsequent experiments the temperature of the reaction vessel was left uncontrolled.

3. Results and discussion

Fig. 1 shows triclosan normalised concentration–time profiles for the various samples subjected to ultrasonic irradiation. As seen, nearly complete triclosan removal could be achieved within 120 min of irradiation for all samples but the influent domestic wastewater for which only 60% degradation was recorded after 180 min of reaction. Conversely, degradation in seawater proceeded rapidly yielding over 95% conversion in 15 min. For all samples, control experiments were run, where $5 \mu\text{g l}^{-1}$ aqueous solutions of triclosan were left in the dark at ambient temperature for the same period of time and in the absence of ultrasonic irradiation, revealing that the decrease in triclosan concentration was due to the effect of sonication alone.

Sonochemical degradation of organic compounds at low concentrations usually follows pseudo-first order kinetics regarding substrate concentration, i.e.

$$-\frac{dC_i}{dt} = kC_i \iff \ln\left(\frac{C_{i,0}}{C_i}\right) = kt \quad (1)$$

where k is an apparent reaction rate constant, and $C_{i,0}$ and C_i is the substrate concentration at time zero and t respectively. If the data of Fig. 1 are plotted in the form of Eq. (1), straight lines passing through the origin fit the experimental data well and rate constants can be calculated from the slopes of the respective straight lines (plots are not shown for brevity). The computed rate constants are 0.0272 (0.983), 0.1051 (0.996), 0.2284 (0.944), 0.0523 (0.994), 0.0597 (0.997) and 0.0063 min^{-1} (0.982) for deionised water, 3.5% NaCl in deionised water, seawater, urban runoff water, centrifuged urban runoff water and influent wastewater

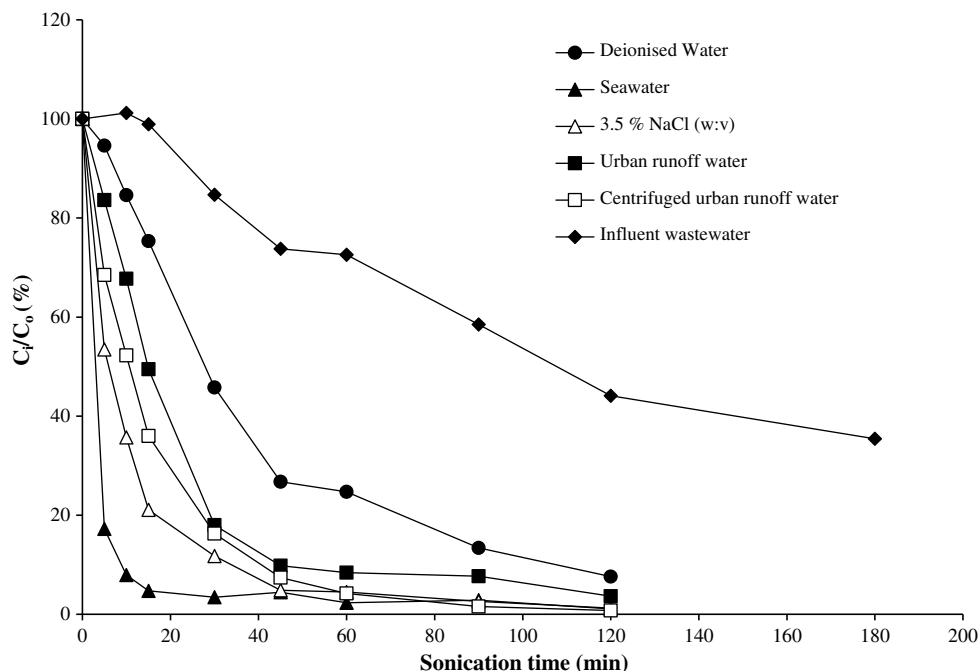


Fig. 1. Normalised concentration–time profiles during sonication of various samples spiked with $5 \mu\text{g l}^{-1}$ triclosan.

untreated urban runoff, centrifuged urban runoff and influent domestic wastewater respectively with numbers in brackets showing the correlation coefficients (r) for the linear regression of the logarithm of concentration against time.

As clearly seen, increasing the ionic strength of the sample had a beneficial effect on degradation; a four to eight-fold increase in the reaction rate was recorded when triclosan was treated in deionised water in the presence of 3.5% NaCl or seawater compared to the run without salt. Seymour and Gupta [14] who investigated the effect of sodium chloride addition upon the sonochemical degradation of aqueous solutions of chlorobenzene, *p*-ethylphenol and phenol at 20 kHz found out that the presence of NaCl improved substantially degradation rates. The enhancement in degradation rates was attributed to the salting-out effect, where fewer water molecules are available for dissolving the analyte molecules. Therefore, the solute is expected to migrate from the liquid bulk inside or near the cavitation bubble where degradation via pyrolysis and/or hydroxyl radical-induced reactions is likely to occur fast [15,16]. The fact that degradation in seawater was faster than in artificial saline water may be associated with the water matrix of the former. Inorganic and organic species can serve as extra nuclei for cavitation as well as alter the gas and interfacial properties of the cavitation bubble influencing thus the temperature, pressure and chemical species present during the bubble collapse [17].

In further runs, triclosan degradation in urban runoff water was studied. Non-point source pollution, unlike pollution from industrial and sewage treatment plants, comes from many diffuse sources and is caused by rainfall or snowmelt moving over and through the ground. As the runoff moves, it washes natural and human-made pollutants, finally depositing them into lakes, rivers, wetlands, coastal waters, or even in underground sources of drinking water. According to the USEPA, urban runoff waters represent one of the leading sources of water quality impairment. Indeed, in the runoff water samples investigated here, the presence of triclosan was confirmed ($0.07 \mu\text{g l}^{-1}$). Sonochemical degradation in urban runoff was about twice as fast as that in deionised water and over 90% conversion was recorded in about 60 min of reaction. This can be explained in terms of dissolved solids facilitating nucleation which appears to be predominant in the case of urban runoff. Keck et al. [18] who investigated the sonochemical degradation of various aromatics in the presence and absence of inert quartz particles in the range 2–25 μm reported that performance was enhanced in the presence of solids and this was ascribed to solids altering the shape of bubbles from spherical to asymmetric, thus yielding larger surfaces available to react with more solute molecules. For the purpose of the present studies the experiment was also repeated with the runoff sample being centrifuged prior to triclosan contamination. As seen, there was no significant change in the rates of degradation which were in both cases faster than the one found in deionised water. How-

ever, when comparing the raw runoff sample with the centrifuged one, a slight decrease in rate ($\sim 12\%$) was observed when the sample was not centrifuged (raw) and it appears that although solid particles facilitated nucleation for this type of wastewater, a second and minor effect takes place whereby adsorption of solute molecules to particles is responsible for the small decrease in degradation rate. Zhang and Hua [19] studied the sonochemical degradation of bromobenzene, bromophenolate ion, and 2,4,5-trichlorobiphenyl in the presence of 10 nm and 15 μm silica particles and 35 μm organic resin (representing as the authors stated the “worst case”) with the latter two being separated from the solution by centrifugation. Overall, the authors found that the sonochemical decomposition rate constant for bromobenzene was not significantly impacted by very fine silica particles (10 nm) because their diameter was much smaller than the sound wavelength and as such could not impact the sound field. In the presence of the 15 μm silica particles, results were similar to the ones reported here and sonication rates decreased slightly ($<7\%$) due to partial adsorption of the solute molecules to the solid particles. As expected the effect was more dramatic when larger particles such as organic resin (35 μm) were present in the sonicated mixture [19]. Although larger particles may serve as nuclei for bubble formation, they can also sorb hydrophobic chemicals more effectively impeding thus their partitioning with the collapsing cavitation bubble [19,20]. This is in agreement with the results obtained here for the domestic wastewater sample where triclosan degradation was found to proceed at substantially lower rates than in any other sample tested. It is also possible that surfactants, typically present in domestic wastewater, accumulate in the interfacial region, thus reducing the number of sites available for triclosan degradation [16,21].

The analytical protocol used in this study was also capable of checking for the chlorinated by-products arising from triclosan degradation as these may actually be more toxic than triclosan itself as well as be dioxins precursors. Canosa et al. [2] developed a SPME-based method for detecting triclosan and its metabolites, namely methyl triclosan, 2,4-dichlorophenol and 2,3,4-trichlorophenol in aqueous samples (including influent and effluent wastewater samples of an urban sewage plant). The use of SPME also enabled monitoring the photochemical degradation of triclosan in water and wastewater when exposed to ultraviolet (UV) or sunlight irradiation [4,12,13]. These studies confirmed the triclosan to dioxin conversion and the formation of metabolites such as chlorinated phenols, chlorohydroxydiphenyl ethers, 2,8-dichlorodibenzo-*p*-dioxin and dichlorodibenzodioxin isomer or dichlorohydroxydibenzofuran in a variety of environmental matrices. It has also been reported [9] that the UV/TiO₂-induced photocatalytic decomposition of triclosan was accompanied by the formation of 2,4-dichlorophenol, a priority toxic pollutant which is known to be a dioxin precursor. In this work and under the present experimental conditions, none of the aforementioned metabolites was detected in any of the samples

tested. This is clearly demonstrated in Fig. 2 where different SPME/GC–ECD chromatograms obtained before (Fig. 2b) and after (Fig. 2c and d) sonication of the centrifuged urban runoff sample are shown. It should be mentioned here that similar chromatograms were obtained for the rest of the samples treated here. Comparison between the chromatogram corresponding to the original, unspiked sample (Fig. 2a) and the ones obtained after spiking with $5 \mu\text{g l}^{-1}$ triclosan (Fig. 2b) or even after sonication (Fig. 2c and d) reveals that the pattern of the extra peaks appearing in the original chromatogram remains practically unchanged. These extra peaks appearing in all chromatograms are due to the matrix and/or the use of SPME as a preconcentration method in which case the peaks are commonly referred to as

SPME contaminants. The assumption that triclosan sonochemical degradation is not accompanied by the formation of toxic by-products was also cross-checked and confirmed by means of SPME/GC–MS (SIM mode) analysis.

The absence of chlorinated by-products in the reaction mixture may be ascribed to the facts that (i) the hydrophobic triclosan (its solubility is about 1 mg l^{-1} at room temperature and the logarithm of the octanol–water partition coefficient is 4.8 [22]), may be localised near the cavitation bubble and undergo fast thermal degradation, thus minimising by-product formation and/or (ii) the rate of by-products formation is lower than the rate of their sonochemical degradation and, consequently, they do not accumulate in the reaction mixture.

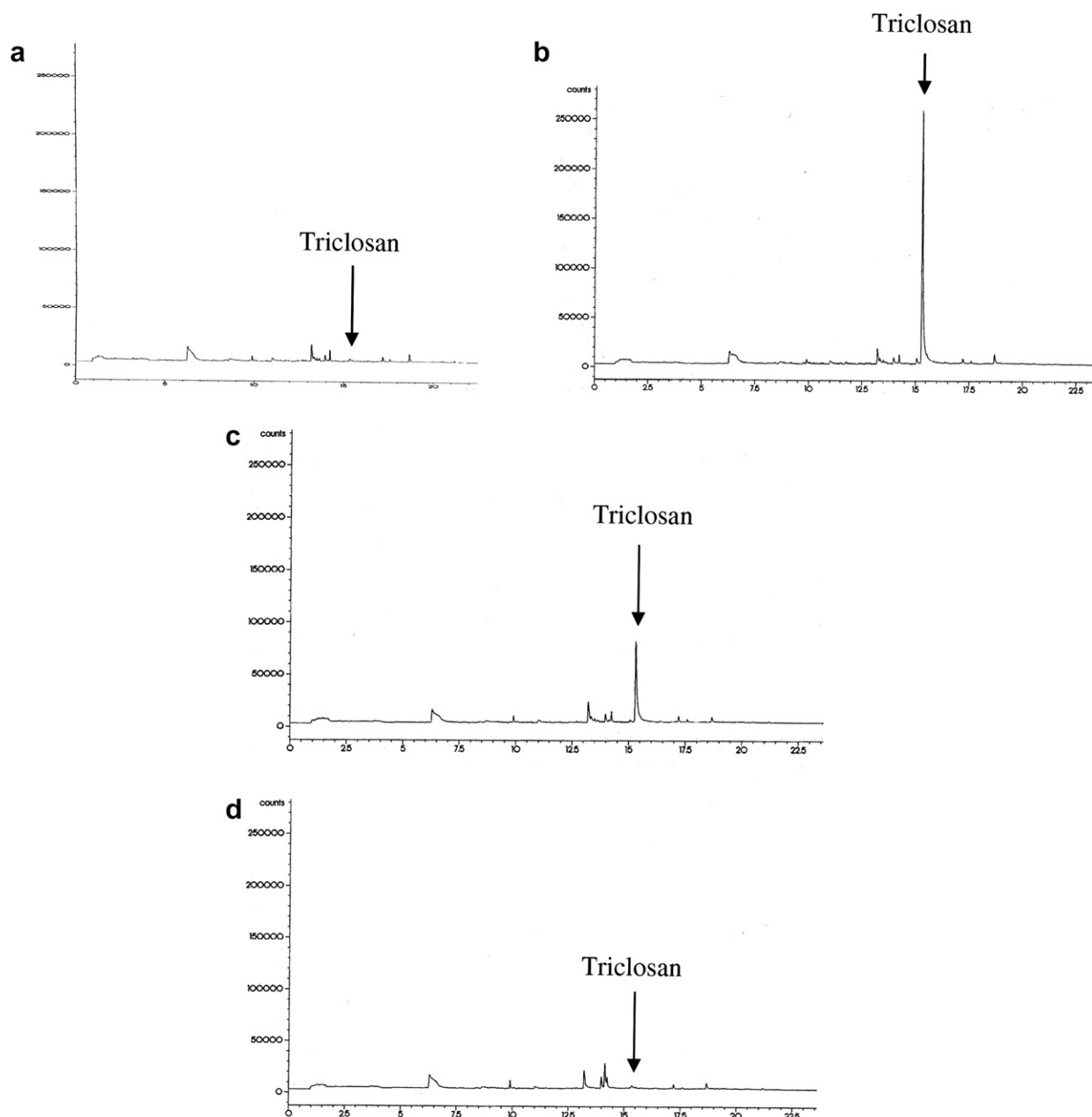


Fig. 2. SPME/GC–ECD chromatograms of the centrifuged urban runoff sample (a) before spiking; (b) after spiking with $5 \mu\text{g l}^{-1}$ triclosan and just before sonication; (c) after 15 min of sonication; (d) after 120 min of sonication.

4. Conclusions

The low frequency sonochemical degradation of triclosan in several model and actual samples of environmental importance has been investigated. In nearly all cases, complete conversion can be achieved at reasonable treatment times; however, the rate of degradation is evidently affected by the matrix components present in the various samples. The effect may be an increase or decrease depending on the behaviour of the matrix compound. Overall, degradation decreases in the order: seawater > 3.5% NaCl aqueous solution > centrifuged urban runoff ~ untreated urban runoff > deionised water > wastewater influent. At the experimental conditions in question, degradation was not accompanied by the formation of toxic metabolites which commonly appear as by-products of triclosan natural attenuation.

Acknowledgements

L.S.-P. and R.B. acknowledge the regional government Junta de Galicia for their doctoral and travel grants. The authors would like to thank V. Koukouraki for conducting TOC measurements.

References

- [1] K. Aranami, J.W. Readman, *Chemosphere* 66 (2007) 1052.
- [2] P. Canosa, I. Rodriguez, E. Rubí, R. Cela, *J. Chromatogr. A* 1072 (2005) 107.
- [3] D.E. Latch, J.L. Packer, B.L. Stender, J. VanOverbeke, W.A. Arnold, K. McNeill, *Environ. Toxicol. Chem.* 24 (2005) 517.
- [4] M. Lores, M. Llompарт, L. Sanchez-Prado, C. Garcia-Jares, R. Cela, *Anal. Bioanal. Chem.* 381 (2005) 1294.
- [5] M. Mezcuа, M.J. Gómez, I. Ferrer, A. Aguera, M.D. Hernando, A.R. Fernández-Alba, *Anal. Chim. Acta* 524 (2004) 241.
- [6] H. Singer, S. Müller, C. Tixier, L. Pillonel, *Environ. Sci. Technol.* 36 (2002) 4998.
- [7] Y.G. Adewuyi, *Ind. Eng. Chem. Res.* 40 (2001) 4681.
- [8] N.H. Ince, G. Tezcanli, R.K. Belen, I.G. Apikyan, *Appl. Catal. B: Environ.* 29 (2001) 167.
- [9] J.C. Yu, T.Y. Kwong, Q. Luo, Z. Cai, *Chemosphere* 65 (2006) 390.
- [10] S. Suarez, M.C. Dodd, F. Omil, U. von Gunten, *Water Res.* 41 (2007) 2481.
- [11] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, *Standard Methods for the Examination of Water and Wastewater*, 20th ed., APHA, AWWA, WEF, United Book Press Inc., Baltimore, Maryland, 1998.
- [12] L. Sanchez-Prado, M. Llompарт, M. Lores, M. Fernandez-Alvarez, C. Garcia-Jares, R. Cela, *Anal. Bioanal. Chem.* 384 (2006) 1548.
- [13] L. Sanchez-Prado, M. Llompарт, M. Lores, C. Garcia-Jares, J.M. Bayona, R. Cela, *Chemosphere* 65 (2006) 1338.
- [14] J.D. Seymour, R.B. Gupta, *Ind. Eng. Chem. Res.* 36 (1997) 3453.
- [15] N.N. Mahamuni, A.B. Pandit, *Ultrason. Sonochem.* 13 (2006) 165.
- [16] E. Manousaki, E. Psillakis, N. Kalogerakis, D. Mantzavinos, *Water Res.* 38 (2004) 3751.
- [17] O. Krüger, T.L. Schulze, D. Peters, *Ultrason. Sonochem.* 6 (1999) 123.
- [18] A. Keck, E. Gilbert, R. Köster, *Ultrasonics* 40 (2002) 661.
- [19] G. Zhang, I. Hua, *Chemosphere* 46 (2002) 59.
- [20] Z. Laughrey, E. Bear, R. Jones, M.A. Tarr, *Ultrason. Sonochem.* 8 (2001) 353.
- [21] B. Yim, H. Okuno, Y. Nagata, R. Nishimura, Y. Maeda, *Ultrason. Sonochem.* 9 (2002) 209.
- [22] M.S. Duan, N. Zhao, I.B. Össurardóttir, T. Thorsteinsson, T. Loftsson, *Int. J. Pharm.* 297 (2005) 213.