Chemosphere 78 (2010) 760–766

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Fate of triclosan in agricultural soils after biosolid applications

Nuria Lozano [a,b], Clifford P. Rice [b], Mark Ramirez [c], Alba Torrents [a,*]

[a] Department of Civil and Environmental Engineering, University of Maryland, College Park, MD 20742, USA
[b] Environmental Management and Byproduct Utilization Laboratory, ANRI, ARS/USDA, 10300 Baltimore Avenue, Beltsville, MD 20705, USA
[c] DCWASA, DC Water and Sewer Authority, 5000 Overlook Avenue, S.W., Washington, DC 20032, USA

ARTICLE INFO

Article history:
Received 22 July 2009
Received in revised form 29 September 2009
Accepted 5 October 2009
Available online 24 November 2009

Keywords:
Biosolid
Land-application
Soils
Triclosan

ABSTRACT

Triclosan (5-chloro-2-[2,4-dichloro-phenoxy]-phenol (TCS) is an antimicrobial compound that is added to a wide variety of household and personal care products. The consumer use of these products releases TCS into urban wastewater and this compound ends up in the environment when agricultural land is fertilized with wastewater biosolids. This study examines the occurrence of TCS in biosolids and its fate in biosolid-treated soils. TCS levels in biosolids generated from one repeatedly-sampled wastewater treatment plant averaged 15.6 ± 0.6 mg kg^{-1} dry wt. (mean ± standard error) with a slight increase from 2005 to 2007. Surface soil samples were collected from several farms in northern Virginia, US that had received no biosolids, one biosolid application or multiple biosolid applications since 1992. Farm soils that received one application presented TCS concentrations between 4.1 and 4.5 ng g^{-1} dry wt. when time since application was over 16 months and between 23.6 and 66.6 ng g^{-1} dry wt. for farms where sampling time after application was less than a year. Our results suggest that TCS content of biosolids are rapidly dissipated (estimated half-life of 107.4 d) when applied to agricultural fields. Statistical differences were found ($p < 0.05$) for residual build-up of TCS between multiple-application farms (at least 480 d after application) and controls suggesting that there was a slight build-up of TCS, although the concentrations for these farms were low (<10 ng g^{-1} dry wt.).

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Triclosan (5-chloro-2-[2,4-dichloro-phenoxy]-phenol (TCS)) is a bacteriostatic compound that is added to a wide variety of household and personal care products such as hand soap, toothpaste, deodorants and plastics in cutting boards and toys among other things (Daughton and Ternes, 1999). It has been used for more than 40 years and usage of antimicrobial and antibacterial products is steadily increasing both in the United States (US) and worldwide (Chalew and Halden, 2009). This compound is included in a group often defined as "Emerging Organic Pollutants" many of which are known endocrine-disrupting chemicals (EDC), and TCS could present a high potential to fall in this category since some studies have reported the EDC effects of TCS (Veldhoen et al., 2006; Crofton et al., 2007) and/or its metabolites (Ishibashi et al., 2004). However to date it is not clear if TCS is an EDC as studies are not conclusive. Furthermore, TCS blocks bacterial lipid biosynthesis which leads to concern for possible development of bacterial resistance to TCS (McMurry et al., 1998; Levy et al., 1999).

To date, several studies have reported the presence of TCS in water focusing on the removal of these chemicals through waste water treatment plants (WWTPs) (Lindstrom et al., 2002; McAvoy et al., 2002; Singer et al., 2002; Bester, 2003; Kanda et al., 2003; Sabaliunas et al., 2003; Bester, 2005; Nakada et al., 2006; Gomez et al., 2007; Heidler and Halden, 2007; Ying and Kookana, 2007). Despite its high removal rates in WWTPs, it is present in the effluent and has been detected in rivers and other receiving waters. Studies report concentrations of TCS in rivers between 11 and 98 ng L^{-1} (Lindstrom et al., 2002; Singer et al., 2002; Sabaliunas et al., 2003) and runoff from land receiving biosolid (Topp et al., 2008; Edwards et al., 2009; Sabourin et al., 2009). TCS is toxic to aquatic microorganism (Orvos et al., 2002; Samsøe-Petersen, 2003; Ishibashi et al., 2004) and is accumulated by algae (Coogan et al., 2007) and fish (Boehmer et al., 2004). Recently it has been shown that TCS may be accumulated by earthworms after land application of biosolids (Kinney et al., 2008).

Triclosan has been observed to biologically degrade under aerobic conditions in the laboratory in activated sludge systems (Federle et al., 2002; Stasinakis et al., 2007). In WWTPs using activated sludge as secondary treatment, generally higher than 90% removal is observed (McAvoy et al., 2002; Bester, 2003; Kanda et al., 2003; Sabaliunas et al., 2003; Heidler and Halden, 2007) yet it is not clear whether the main removal mechanism is degradation or sorption onto the biosolids. TCS presents low water solubility (12 mg L^{-1}) (Reiss et al., 2002), a high octanol–water partitioning

* Corresponding author. Tel.: +1 301 405 1979; fax: +1 301 405 2585.
E-mail address: alba@eng.umd.edu (A. Torrents).

0045-6535/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2009.10.043

coefficient (log K_{ow} = 4.8) (Halden and Paull, 2005) and high organic carbon–water partitioning coefficients (log K_{oc} = 3.8–4.0) (Lindstrom et al., 2002), thus it is accumulated onto biosolids (Singer et al., 2002; Bester, 2003; Morales et al., 2005; Heidler et al., 2006; Heidler and Halden, 2007). Land application of biosolids could represent a source of this compound to the environment.

In the United States, approximately 5.6 million dry tons of biosolids are produced annually and approximately 60% is land applied (NRC, 2002). Many questions remain with respect to the amounts and fate of organic pollutants released into the environment through land applied biosolids. Recent studies reported TCS soil half-life between 18 and 58 d (Ying et al., 2007; Wu et al., 2009) and between 2.5 and 35 d (unpublished data as in Reiss et al., 2009) under aerobic conditions while it was persistent under anaerobic conditions. Little is known about their fate in agricultural soils in a real-world, biosolids-treated-soils setting.

In this study, 26 commercial farms where selected and sampled. Most of these farms received biosolids from a WWTP in the Mid-Atlantic region (WWTP A). Fresh biosolids from this plant were sampled at 2-months intervals and monitored for TCS over two years to determine variations in TCS levels and assess trends. Our specific objectives were to (i) assess levels of TCS in biosolids and biosolid-treated agricultural soils and (ii) evaluate the disappearance of TCS in these agricultural top soils and assess the possible build-up of TCS upon multiple biosolid applications.

2. Materials and methods

2.1. Biosolid samples collection

Biosolids samples were collected every 2 months over 2 years (July 2005–October 2007) from a large wastewater treatment plant in the Mid-Atlantic region of the US (WWTP A). This plant consists of primary treatment, secondary treatment (activated sludge), nitrification–denitrification, effluent filtration, chloro-nitration/dechlorination and post aeration of the wastewater flow. It has a treatment capacity of 1.4 millions cubic meters per day. Collected biosolids were a combination of the solids from the primary, secondary and nitrification processes, which were dewatered and treated with lime to approximately 15% on a dry weight basis. Final biosolids were a Class B biosolid i.e. "biosolid treated to reduce pathogens to levels protective of human health and the environment, but not to undetectable levels" (USEPA, 1993). The samples analyzed were collected from the transfer lines leading to the storage tanks. Biosolid samples were placed in 250 mL amber, wide-mouth glass jars and kept frozen (−20 °C) until processing.

2.2. Soil samples collection

Field soil samples were collected between March 20 and April 01, 2006 from farms in northern Virginia. A total of 26 fields were targeted for sample collection. Table S1 presents the principle information about these farms. Three types of farm sites were selected: (A) Farms that had never received biosolids (zero application farms or control farms), (B) Farms that had received one biosolid application (all from WWTP-A), and (C) Farms that had received between 2 and 4 biosolid applications in the previous 3–13 years (mostly from WWTP A, but some came from other WWTPs in the same geographic area). All selected fields were pastures for grazing cattle, except two (field #2 of farm A and field #12 of farm H, Table S1) which were planted with corn. Sample collection points were recorded using a field GPS instrument (Trimble, Westminster, GeoExplorer Series). The sample collection sites that were located within each of these sampled areas were selected based on a spatial relationship that was related to the size and shape of each of the fields. Therefore in order to get representative sample coverage the size and shape of each field helped determine the number of samples to collect (column 6, Table S1) there were, in some cases, as few as 5 samples collected for a small field and as many as 14 samples were collected from one of the larger fields (e.g., field E-3, 18.82 ha, Table S1).

Surface soil samples were collected to a depth of approximately 10 cm. They were composites of three soil plugs that were each collected in a 30 cm diameter area around the collection focal point. Soil samples were transported on ice and finally kept in a freezer (−20 °C) until processing.

2.3. Standards and reagents

Triclosan (97%) was obtained from Aldrich (Aldrich Chemical Company, Inc, Milwaukee, WI, USA). Isotope-labeled $^{13}C_{12}$-TCS (⩾99%) was obtained from Wellington Lab. (Guelph, ON, Canada). All organic solvents were high purity, pesticide grade. Sand was obtained from JT Baker (Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA). Potassium phosphate monobasic (99.2%), potassium phosphate dibasic anhydrous (99.6%) and ammonium acetate (99%) were obtained from Fisher Scientific (Fisher Scientific, Fair Lawn, NJ, USA). Carbon-free deionized water (DI-water) was secured using a NANOpure system (Barnstead International, Dubuque, IA, USA). Glassware and sand were baked at 400 °C for 4 h in an industrial oven (Grieve, Round Lake, IL, USA) to drive off any organic materials.

2.4. Extraction and cleanup

TCS was extracted from soils and biosolids using an adaptation of a previously published method (Burkhardt et al., 2005). In brief, prior to extraction all samples were screened by passing them through a US standard #7 sieve (2.8 mm aperture size) to remove larger materials. Approximately 10 g and 0.2–0.3 g wet weight (wet wt.) were extracted respectively for soils and biosolids. All samples were spiked with $^{13}C_{12}$-TCS (100 ng ml^{-1}) internal standard before extraction to allow for isotope dilution quantitation to be performed. Extractions were performed by accelerated solvent extraction using an ASE model #200 apparatus (Dionex Corp. Sunnyvale, CA, USA) using water/isopropyl alcohol (IPA) (20:80, v/v). The extract were fractionated using solid phase Oasis®HLB cartridges (Waters Corporation, Milford, MA, USA). A dichloromethane (DCM)/diethyl ether (DEE) (80:20) solution was used to elute TCS from the cartridges. The solvent in the final extract was removed by nitrogen blowdown and the sample transferred with methanol to a final volume 1.5 ml (additional details are provided in Supplementary information, section 1).

2.5. Instrumental analysis

Extracts were analyzed by LC–MS. Chromatographic separation was performed on a reverse-phase liquid chromatographic column (Waters Xterra 5 μm MS C18 column – 150 × 2.1 mm) using a Waters 2695 XE LC instrument (Waters Corp., Milford, MA). Atmospheric pressure ionization-tandem mass spectrometry analysis was performed on a benchtop triple quadrupole mass spectrometer (Quattro LC from Micromass Ltd., Manchester, UK) operated using a negative electrospray ionization source (ESI-). Acquisitions were done in SIR (selected ion recording) mode with specificity being provided by the chlorine isotopes provided by the chlorines substituted on these compounds. Analyte concentrations were determined by isotope dilution methods using $^{13}C_{12}$-TCS as an internal standard to quantitate the unlabelled Triclosan. Peak integration and quantification was performed automatically using the MassLynx v4.0 software (Micromass Ltd., Machester, UK)

(additional details are provided in Supplementary information, section 2).

2.6. Quality assurance and quality control (QA/QC)

Method Detection Limits (MDLs) were determined using the procedure established by US EPA (USEPA, 1984). The Limit of Quantification (LOQ) was set at 2 times the MDL values. All samples were fortified with labeled $^{13}C_{12}$-TCS internal standard for analyte quantification and to correct for possible matrix interactions and any losses during sample extraction. At least seven standards at concentrations other than zero were run for each set of analyses and linearity correlations were required to yield *r*-squared values $\geqslant$0.99. Standards were injected every ten samples in order to verify stability of the instrument during the analyses. A laboratory blank, duplicate and spike were included in each batch that always included less than 15 samples.

3. Results and discussion

3.1. Method development

The Method Detection Limit (MDL) obtained for TCS was 1.00 ng g^{-1} wet wt; therefore the LOQ was 2.00 ng g^{-1} wet wt. Average Relative Standard Deviation (RSD) and recovery were 22.7% and 101.1%, respectively, for the non TCS-contaminated soils replicates ($n = 7$) used to calculate the MDL. Values below LOQ are not reported. Average percent recovery for all spiked TCS-contaminated soils samples analyzed in each batch was 86.8% and 85.5% for sludge samples.

3.2. Biosolids from WWTP-A

TCS biosolids concentrations at WWTP-A were between 12.1 and 18.8 mg kg^{-1} dry wt. ($n = 14$) with mean 15.6 ± 0.6 mg kg^{-1} dry wt. (mean ± SE; $n = 14$). The use of this bacteriostat seemed to be changing from 2005/06 to 2007 since the TCS concentrations were 14.4 ± 0.5 mg kg^{-1} (mean ± SE) for 2005/06 ($n = 8$) and 17.6 ± 0.8 mg kg^{-1} for 2007 ($n = 6$). Results indicated that the means were different ($p < 0.05$) suggesting that TCS usage might have increased; however, usage data over this time interval was not available to confirm this. Also some parameters in the WWTP may have changed between the two time periods in the study which could affect TCS removal favoring higher TCS concentrations in the biosolid for the later period. TCS concentrations found in this study are within the range found in other studies which varied from 0.09 to 66 mg kg^{-1} dry wt. (Table 1).

In this study, concentrations of TCS in the biosolids for fall-winter and spring–summer were 15.9 ± 0.1 and 15.3 ± 1.0 mg kg^{-1} dry wt. (mean ± SE) respectively. No significant differences were found ($p > 0.05$) suggesting that the concentrations present in the biosolids were not related to seasonal conditions like temperature for example. While higher summer TCS influent concentrations have been reported at other plants (Loraine and Pettigrove, 2006), there was insufficient data to check if we missed these differences in our collections by focusing only on biosolids.

3.3. Concentration in agricultural soil samples

The concentrations of TCS in soils from farms as a function of the number of biosolid applications (multiple-application farms ($n = 12$) and single-application farms ($n = 8$)) are presented in Fig. 1. Clearly application of TCS-laden biosolids causes elevated concentrations of TCS to occur in these soils but the concentrations are quite variable (Table S3 supporting information). Our data suggests that the two most important parameters controlling TCS top soil concentrations are the biosolids application rate and the time between application and sampling. For example, application rates in 2005 were significantly different between the multiple and single-application fields; rates for multiple-application fields were only 5.0, 5.6 and 0.9 tons ha^{-1} vs. 14.3 to 25 tons ha^{-1} for the six single-application fields. Thus concentrations were higher in the single-application fields. Furthermore in order to account for variations in concentrations within the single and multiple-application groups, it was possible to identify subgroups that showed this to be entirely due to time-dependent TCS dissipation. Therefore separating these according to the time since last biosolid application and viewing the concentrations in these subgroups supported the observation that the longer the time interval after the last application the lower the TCS concentrations.

In order to assess the fate and dissipation of TCS in agricultural top soil, measured concentrations were compared to predicted concentrations at selected sites that had received a single application from WWTP-A (Fig. 2). Initial Predicted Environmental Concentrations (PEC_{ini}) were determined using Eq. (1) (Jackson and Eduljee, 1994), where $C_{soil(0)}$ is the TCS concentration found in the soil before biosolid application (background levels determined in this study); $C_{biosolid}$ is the mean concentrations from our 2-year long survey of WWTP-A biosolids ($n = 14$) (mg kg^{-1}), AR_y is the application rate (kg ha^{-1}) as provided by commercial applicators and reported in Table S1; D is soil density which was considered constant (1.5×10^{-3} kg cm^{-3}); S_z is soil depth (10 cm) and CF is a conversion factor (cm^2 ha^{-1}).

$$PEC_{ini} = C_{soil(0)} + \frac{C_{biosolid} \times AR_y}{D \times S_z \times CF} \quad (1)$$

Fig. 2 shows mean predicted initial concentration (TCS–PEC_{ini}) compared to the mean concentrations found in the soils at different time intervals after application. As expected, dissipation increased as a function of time. TCS–PEC_{ini} initial concentrations in those farms where the time after applications were between 7–9 months was 206.6 ± 21.8 ng g^{-1} dry wt. and the concentration found in the soils after 7 to 9 months were 45.5 ± 6.8 ng g^{-1} dry wt., that represents 21.8% of their PEC_{ini}. In the farms with longer

Table 1
Summary of TCS concentrations reported in the sludge and biosolid samples.

Authors	Samples	Concentration (mg kg^{-1} dry wt.)
(McAvoy et al., 2002)	Primary, secondary and anaerobic digested sludge	0.5–15.6
(Bester, 2003)	Sewage sludge	0.40–8.8
(Morales et al., 2005)	Biological and disinfected sludge	0.42–5.4
(Chu and Metcalfe, 2007)	Activated sludge and biosolids	0.62–11.55
(Gatidou et al., 2007)	Sewage sludge	1.84
(Heidler and Halden, 2007)	Anaerobic digested sludge	30 ± 11
(Kinney et al., 2006)	Biosolids, variably treated	1.2–32.9 (median = 10.2)
(Ying and Kookana, 2007)	Biosolids	0.09–16.79
Present study	Biosolids	12.1–18.8 (mean = 15.6)

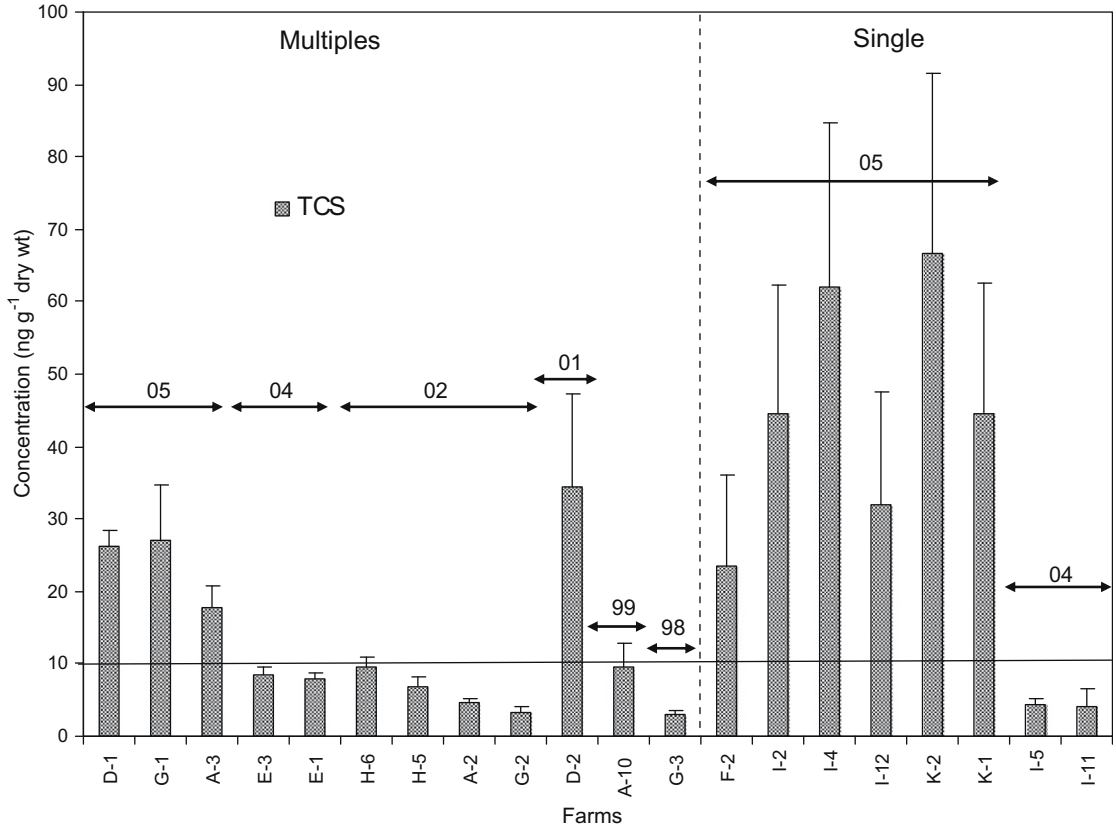

Fig. 1. TCS concentrations (mean ± SE) found in each field. The numbers 05, 04, 02, 01, 99 and 98 indicate the last two digits corresponding to the year of last biosolid application.

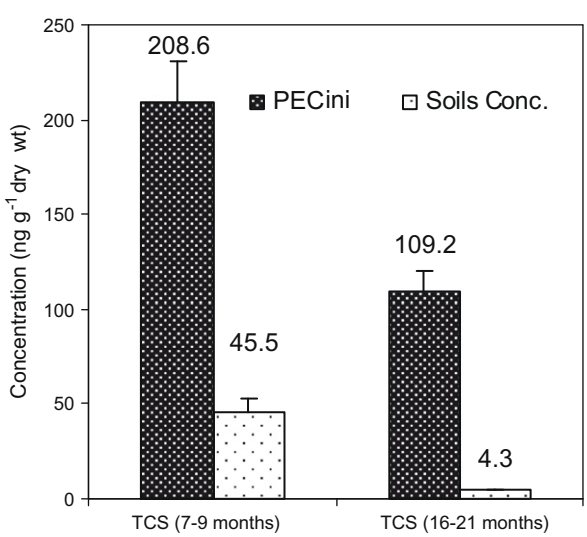

Fig. 2. Comparison of TCS concentrations observed (mean ± SE) and predicted (PEC_{ini}) in single-applications farms using the average TCS biosolid concentration and application rate. Time in months indicate the time after biosolid application. Please note that applications rates for the 7–9 month grouped data were significantly higher than the 16–21 month grouped data (see text).

times after biosolid application (16–21 months) the concentration found in the soils was 4.3 ± 6.8 ng g^{-1} dry wt. representing only 3.9% of the PEC_{ini} for these farms (109.2 ± 11.6 ng g^{-1} dry wt). Our results suggest a significant removal of TCS from the top soil of up to 96.1% after16 and 21 months of application and 78.2% after 7–9 months. When TCS-containing biosolids are associated with the soil more than 16 months all mean TCS concentrations were below 10 ng g^{-1} (Fig. 1 – both single and multiple applications) except for farm D-2 (Fig. 1). This farm received three applications with the last one in 2001 (around 5 years before the date of collection). TCS concentrations found in this soil was 34.6 ng g^{-1} dry wt. No explanation was found to justify this concentration. This farm was considered an outlier. However, when farms where no biosolids had been applied were compared with the rest of the farms where the time after last biosolid application was higher than 16 months only the multiple-application farms retain statistically ($p < 0.05$) higher levels. Therefore, the single-application farms TCS levels are similar ($p > 0.05$) in concentration to non-treated farms and their statistically lower concentration versus multiple-application farms suggests a slight build-up of TCS even though the total amount for all of them averaged only 2.2 times higher (mean, 6.6 ng g^{-1} dry wt.) than background levels.

Although there are a lot of factors affecting the dissipation of this kind of compound from topsoils, such as time since application, temperature, soil type, field management, variable soil microflora, etc., our data suggests that when time after application was long enough, concentrations in the soils were the same as background levels and only a slight build-up was observed when multiple biosolid applications were done.

While it is recognized that a large number of environmental and operational factors would determine TCS top soil concentrations, an effort was made to develop a preliminary mathematical model to predict top soils TCS concentrations as a function of application rate, number of applications, and time since last application. A dissipation half-life ($t_{0.5}$) was estimated using the single application data and Eq. (2) (Jackson and Eduljee, 1994) where $C_{soil(t)}$ is the mean concentration found in the soils in ng g^{-1} dry wt. at time t since last application; $C_{soil(0)}$ is the TCS concentration found in

the soil before biosolid application; PEC_{ini} is the concentration (ng g^{-1} dry wt.) at time zero of the biosolid application (Eq. (1)) and t is the time in days (d) between biosolid application day and the collection day.

$$C_{soil(t)} = (C_{soil(0)} + PEC_{ini}) \times e^{-\left(\frac{\ln 2}{t_{0.5}}\right)t} \quad (2)$$

As our data suggested that background levels are reached after 16 months, only single-applications farms where the time after application was between 7 and 9 months ($n = 6$) were used in Eq. (2) to calculate the mean half-life value of 107.4 d. This value was then used to determine the theoretical concentration in the soils after each biosolid application using Eq. (3), where background or residual concentrations was $C_{soil(0)}$ of 3 ng g^{-1} dry wt.; *PEC* was the predicted environmental concentrations at time zero, i.e. the day of biosolid application (Eq. (1)) (ng g^{-1} dry wt.); k was a dissipation rate constant of 0.00645 d^{-1} (ln 2/107.4 d, Eq. (2) above); t was the interval of time in d between applications or application date and sampling day for the last application. Maximum interval of time (t) in each application was the time from application until TCS reached the residual levels, C_0 for single application or $2.2 \times C_0$ for multiple applications; numbers 1, 2, 3, represented the number of applications; with a maximum of 4 for this study (additional details can be found in Supplementary information, section 3).

$$C_{soil(t)} = ((((PEC_1 + C_0)^{-k\times t_1} + PEC_2)^{-k\times t_2} + PEC_3)^{-k\times t_3} \cdots + PEC_n)^{-k\times t_n} \quad (3)$$

Fig. 3 shows the theoretical rate of dissipation applying the model (Eq. (3)) as an average (line) with PEC_{ini} (filled symbols) and concentrations measured in our study (open symbols). While average application rates and biosolid TCS initial concentrations where used in this exercise, Fig. 3 illustrates the capability of this time-dependent model to predict topsoil concentrations once application rate, initial biosolid concentration, and time since last application are known.

In a recent study in Midwestern USA, soil TCS concentrations were 160 ng g^{-1} dry wt. and 96 ng g^{-1} dry wt., 31 and 156 d after a single biosolid application (Kinney et al., 2008). In order to determine the predictive capabilities of our model under different experimental conditions, Eq. (3) was applied to the Kinney et al. study, using their application rates, TCS concentration in the biosolid, and days after biosolid application. Predicted TCS concentrations calculated using Eq. (3) were 106 ng g^{-1} dry wt. and 47 ng g^{-1} dry wt., 31 and 156 d respectively after biosolid application, which are close to values reported, indicating the capability of our model to predict TCS concentrations in these soils. However higher differences were found when our model was applied to a recent study in Michigan that received biosolids between 3 months and 3 years before collecting samples. TCS concentrations measured by the investigators in these soils for all cases were always lower than 1.02 ng g^{-1}, lower than our background concentrations (Cha and Cupples, 2009). Despite the lower applications rates and lower TCS biosolid concentrations that were used in these farms, our model would have led them to find higher TCS concentrations than the low concentration reported in their paper.

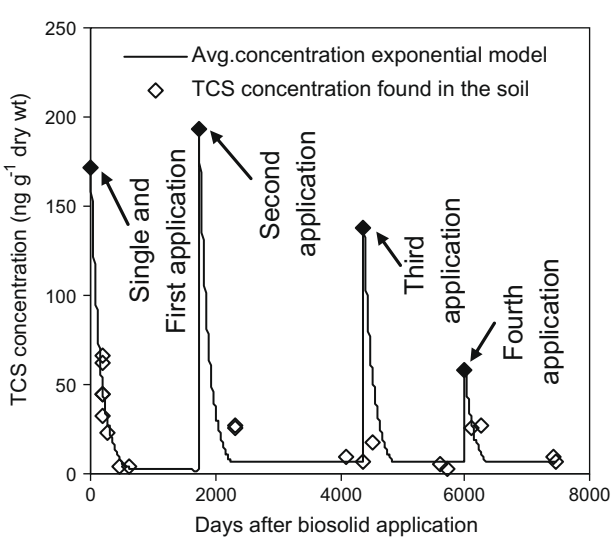

Fig. 3. Exponential model applied to single and multiple applications (solid line); PEC applied in each application (filled symbols) and the final concentrations measured in the soils (open symbols).

Today's literature presents some controversy about the TCS soils levels that could inhibit plant growth. Studies have reported that TCS affects rice and cucumber seed growth, soil respiration (Liu et al., 2009) and nitrogen cycle (Waller and Kookana, 2009) at concentrations around a microgram per grams of soil, and soil phosphatase activity at concentrations of 100 ng g^{-1}. Another study reported no negative effects on nitrification and soil respiration at concentrations as high as 2000 ng g^{-1} and TCS concentrations affecting plants were much higher than those found in our study (280 ng g^{-1}) (Reiss et al., 2009, both listed as unpublished data).

TCS concentrations as high as 100 ng g^{-1} were predicted using our model any time before 91 days after biosolid application, suggesting that TCS may affect phosphatase activity in these fields during the first three months after biosolid application. Considering these findings, even the maximum TCS concentration found in soils shouldnot present a high risk for soil toxicity. Therefore, to determine with any real certainty the true impact of TCS concentrations found on soils, further studies should be completed and possible build-up of degradation products should be determined.

TCS bioaccumulation onto earthworms has been suggested in soils 31 and 156 d after biosolid application (Kinney et al., 2008). Our results coupled with these recent studies suggest that TCS could accumulate in terrestrial organisms during the first few months (up to 16–21 months) after application while after this time TCS risks would be less since concentrations appear to fall to near background levels in soils.

Since TCS is a bacteriostat, there is a real potential that concentrations in soils resulting from biosolid applications might affect bacterial ecology of these systems. Especially since the ecological balance and competitive advantages of the multiple species inhabiting any soil environment are very complex and any small advantage one microbe might achieve due to exposure to these known bacteriostat could be amplified under these conditions. These studies might be enlightening and need to be conducted.

At this moment it is not clear what the precise removal processes are within the soil environment. Possible pathways are biological transformation, volatilization, photo-oxidation and leaching. Due to the low vapor pressures of this compound and the fact that sunlight only affects a thin layer of soil surface, the amount of losses of TCS due to volatilization or photo-oxidation are probably low. It is known that TCS can be degraded in soils under aerobic conditions (Ying et al., 2007; Wu et al., 2009) and that during bacterial degradation TCS is transformed to methyl triclosan (Hundt et al., 2000). Also there are some evidence that TCS can be biodegraded by soil bacteria (Meade et al., 2001) and fungi (Hundt et al., 2000; Cabana et al., 2007). Additional work should be conducted to assess biodegradation rates in the soil environment and determine of the fate of these biodegradation products.

4. Conclusions

TCS is present in biosolids at mean concentrations of 15.6 ± 0.6 mg kg^{-1} dry wt. (mean ± standard error) showing that it is removed from the waste water during biosolids collection. Concentrations ending up in biosolid do not seem to be related to seasonal or seasonally-linked temperature changes.

Varying concentrations of the TCS were measured in biosolids-treated agricultural soils after the biosolids had been applied and these concentrations were significant for short times after application and then went to low levels 16 months after application. However, for multiple-applications farms, residual concentrations found in the soils at times greater than 480 d after applications averaged two times higher than background level. A model for dissipation rates for TCS in soils receiving single and multiple applications of biosolids was developed and used to successfully describe values observed in this study. Finally the removal or dissipation processes for the TCS in soils appears to be mainly due to biological degradation.

Widespread land application of biosolids as a soil amendment and fertilizer source represents an important pathway for reentry of triclosan into the environment. Therefore more studies should be done with TCS especially if this compound has a high potential for endocrine disruption.

Acknowledgements

This study was supported by DC Water and Sewer Authority (DCWASA), Washington DC. The authors wish to thank the following people: Laura McConnell and Natasha Andrade for the overall design of the study and collecting samples, Jorge Loyo-Rosales for his encouragement and assistance with the analytical methods employed here and Krystyna Bialek for her technical support in the laboratory at USDA.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2009.10.043.

References

Bester, K., 2003. Triclosan in a sewage treatment process–balances and monitoring data. Water Res. 37, 3891–3896.

Bester, K., 2005. Fate of triclosan and triclosan-methyl in sewage treatment plants and surface waters. Arch. Environ. Contam. Toxicol. 49, 9–17.

Boehmer, W., Ruedel, H., Wenzel, A., Schroeter-Kermani, C., 2004. Retrospective monitoring of triclosan and methyl-triclosan in fish: results from the German environmental specimen bank. Organohalogen Compd. 66, 1516–1521.

Burkhardt, M.R., ReVello, R.C., Smith, S.G., Zaugg, S.D., 2005. Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for industrial and anthropogenic waste-indicator compounds in sediment. Anal. Chim. Acta 534, 89–100.

Cabana, H., Jiwan, J.L., Rozenberg, R., Elisashvili, V., Penninckx, M., Agathos, S.N., Jones, J.P., 2007. Elimination of endocrine disrupting chemicals nonylphenol and bisphenol A and personal care product ingredient triclosan using enzyme preparation from the white rot fungus *Coriolopsis polyzona*. Chemosphere 67, 770–778.

Cha, J., Cupples, A.M., 2009. Detection of the antimicrobials triclocarban and triclosan in agricultural soils following land application of municipal biosolids. Water Res. 43, 2522–2530.

Chalew, T.E.A., Halden, R.U., 2009. Environmental exposure of aquatic and terrestrial biota to triclosan and triclocarban. JAWRA J. Am. Water Res. Assoc. 45, 4–13.

Chu, S., Metcalfe, C.D., 2007. Simultaneous determination of triclocarban and triclosan in municipal biosolids by liquid chromatography tandem mass spectrometry. J. Chromatogr. A 1164, 212–218.

Coogan, M.A., Edziyie, R.E., La Point, T.W., Venables, B.J., 2007. Algal bioaccumulation of triclocarban, triclosan, and methyl-triclosan in a North Texas wastewater treatment plant receiving stream. Chemosphere 67, 1911–1918.

Crofton, K.M., Paul, K.B., DeVito, M.J., Hedge, J.M., 2007. Short-term in vivo exposure to the water contaminant triclosan: evidence for disruption of thyroxine. Environ. Toxicol. Pharmacol. 24, 194–197.

Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ. Health Perspect. 107 (Suppl. 6), 907–938.

Edwards, M., Topp, E., Metcalfe, C.D., Li, H., Gottschall, N., Bolton, P., Curnoe, W., Payne, M., Beck, A., Kleywegt, S., Lapen, D.R., 2009. Pharmaceutical and personal care products in tile drainage following surface spreading and injection of dewatered municipal biosolids to an agricultural field. Sci. Total Environ. 407, 4220–4230.

Federle, T.W., Kaiser, S.K., Nuck, B.A., 2002. Fate and effects of triclosan in activated sludge. Environ. Toxicol. Chem. 21, 1330–1337.

Gatidou, G., Thomaidis, N.S., Stasinakis, A.S., Lekkas, T.D., 2007. Simultaneous determination of the endocrine disrupting compounds nonylphenol, nonylphenol ethoxylates, triclosan and bisphenol A in wastewater and sewage sludge by gas chromatography-mass spectrometry. J. Chromatogr. A 1138, 32–41.

Gomez, M.J., Martinez Bueno, M.J., Lacorte, S., Fernandez-Alba, A.R., Aguera, A., 2007. Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast. Chemosphere 66, 993–1002.

Halden, R.U., Paull, D.H., 2005. Co-occurrence of triclocarban and triclosan in US water resources. Environ. Sci. Technol. 39, 1420–1426.

Heidler, J., Halden, R.U., 2007. Mass balance assessment of triclosan removal during conventional sewage treatment. Chemosphere 66, 362–369.

Heidler, J., Sapkota, A., Halden, R.U., 2006. Partitioning, persistence, and accumulation in digested sludge of the topical antiseptic triclocarban during wastewater treatment. Environ. Sci. Technol. 40, 3634–3639.

Hundt, K., Martin, D., Hammer, E., Jonas, U., Kindermann, M.K., Schauer, F., 2000. Transformation of triclosan by Trametes versicolor and Pycnoporus cinnabarinus. Appl. Environ. Microbiol. 66, 4157–4160.

Ishibashi, H., Matsumura, N., Hirano, M., Matsuoka, M., Shiratsuchi, H., Ishibashi, Y., Takao, Y., Arizono, K., 2004. Effects of triclosan on the early life stages and reproduction of medaka Oryzias latipes and induction of hepatic vitellogenin. Aquat. Toxicol. 67, 167–179.

Jackson, A.P., Eduljee, G.H., 1994. An assessment of the risks associated with PCDDs and PCDFs following the application of sewage sludge to agricultural land in the UK. Chemosphere 29, 2523–2543.

Kanda, R., Griffin, P., James, H.A., Fothergill, J., 2003. Pharmaceutical and personal care products in sewage treatment works. J. Environ. Monit. 5, 823–830.

Kinney, C.A., Furlong, E.T., Zaugg, S.D., Burkhard, M.R., Werner, S.L., Cahill, J.D., Jorgensen, G.R., 2006. Survey of organic wastewater contaminants in biosolids destined for land application. Environ. Sci. Technol. 40, 7207–7215.

Kinney, C.A., Furlong, E.T., Kolpin, D.W., Burkhardt, M.R., Zaugg, S.D., Werner, S.L., Bossio, J.P., Benotti, M.J., 2008. Bioaccumulation of pharmaceuticals and other anthropogenic waste indicators in earthworms from agricultural soil amended with biosolid or swine manure. Environ. Sci. Technol. 42, 1863–1870.

Levy, C.W., Roujeinikova, A., Sedelnikova, S., Baker, P.J., Stuitje, A.R., Slabas, A.R., Rice, D.W., Rafferty, J.B., 1999. Molecular basis of triclosan activity. Nature 398, 383–384.

Lindstrom, A., Buerge, I.J., Poiger, T., Bergqvist, P.A., Muller, M.D., Buser, H.R., 2002. Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. Environ. Sci. Technol. 36, 2322–2329.

Liu, F., Ying, G.G., Yang, L.H., Zhou, Q.X., 2009. Terrestrial ecotoxicological effects of the antimicrobial agent triclosan. Ecotoxicol. Environ. Saf. 72, 86–92.

Loraine, G.A., Pettigrove, M.E., 2006. Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in southern California. Environ. Sci. Technol. 40, 687–695.

McAvoy, D.C., Schatowitz, B., Jacob, M., Hauk, A., Eckhoff, W.S., 2002. Measurement of triclosan in wastewater treatment systems. Environ. Toxicol. Chem. 21, 1323–1329.

McMurry, L.M., Oethinger, M., Levy, S.B., 1998. Triclosan targets lipid synthesis. Nature 394, 531–532.

Meade, M.J., Waddell, R.L., Callahan, T.M., 2001. Soil bacteria *Pseudomonas putida* and *Alcaligenes xylosoxidans* subsp. Denitrificans inactivate triclosan in liquid and solid substrates. FEMS Microbiol. Lett. 204, 45–48.

Morales, S., Canosa, P., Rodriguez, I., Rubi, E., Cela, R., 2005. Microwave assisted extraction followed by gas chromatography with tandem mass spectrometry for the determination of triclosan and two related chlorophenols in sludge and sediments. J. Chromatogr. A 1082, 128–135.

Nakada, N., Tanishima, T., Shinohara, H., Kiri, K., Takada, H., 2006. Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Res. 40, 3297–3303.

NRC, 2002. Biosolids applied to land: advancing standards and practices. National Academy Press, Washington DC. pp. 1–368.

Orvos, D.R., Versteeg, D.J., Inauen, J., Capdevielle, M., Rothenstein, A., Cunningham, V., 2002. Aquatic toxicity of triclosan. Environ. Toxicol. Chem. 21, 1338–1349.

Reiss, R., Mackay, N., Habig, C., Griffin, J., 2002. An ecological risk assessment for triclosan in lotic systems following discharge from wastewater treatment plants in the United States. Environ. Toxicol. Chem. 21, 2483–2492.

Reiss, R., Lewis, G., Griffin, J., 2009. An ecological risk assessment for triclosan in the terrestrial environment. Environ. Toxicol. Chem. 28, 1546–1556.

Sabaliunas, D., Webb, S.F., Hauk, A., Jacob, M., Eckhoff, W.S., 2003. Environmental fate of triclosan in the river aire basin, UK. Water Res. 37, 3145–3154.
Sabourin, L., Beck, A., Duenk, P.W., Kleywegt, S., Lapen, D.R., Li, H., Metcalfe, C.D., Payne, M., Topp, E., 2009. Runoff of pharmaceuticals and personal care products following application of dewatered municipal biosolids to an agricultural field. Sci. Total Environ. 407, 4596–4604.
Samsøe-Petersen, L., M. Winther-Nielsen, and T. Madsen, 2003. Fate and Effects of Triclosan. Danish Environmental Protection Agency.
Singer, H., Muller, S., Tixier, C., Pillonel, L., 2002. Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments. Environ. Sci. Technol. 36, 4998–5004.
Stasinakis, A.S., Petalas, A.V., Mamais, D., Thomaidis, N.S., Gatidou, G., Lekkas, T.D., 2007. Investigation of triclosan fate and toxicity in continuous-flow activated sludge systems. Chemosphere 68, 375–381.
Topp, E., Monteiro, S.C., Beck, A., Coelho, B.B., Boxall, A.B., Duenk, P.W., Kleywegt, S., Lapen, D.R., Payne, M., Sabourin, L., Li, H., Metcalfe, C.D., 2008. Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field. Sci. Total Environ. 396, 52–59.
USEPA, 1984. Guidelines establishing test procedures for analysis of pollutants under the Clean Water Act; Final rule and interim final rule and proposed rule. 40 CFR Part 136, Appendix B. USEPA, Washington, DC.
USEPA, 1993. Standards for the use or disposal of sewage sludge. 40 CFR, Part 503. USEPA, Washington, DC.
Veldhoen, N., Skirrow, R.C., Osachoff, H., Wigmore, H., Clapson, D.J., Gunderson, M.P., Van Aggelen, G., Helbing, C.C., 2006. The bactericidal agent triclosan modulates thyroid hormone-associated gene expression and disrupts postembryonic anuran development. Aquat. Toxicol. 80, 217–227.
Waller, N.J., Kookana, R.S., 2009. Effect of triclosan on microbial activity in Australian soils. Environ. Toxicol. Chem. 28, 65–70.
Wu, C., Spongberg, A.L., Witter, J.D., 2009. Adsorption and degradation of triclosan and triclocarban in soils and biosolids-amended soils. J. Agric. Food Chem. 57, 4900–4905.
Ying, G.G., Kookana, R.S., 2007. Triclosan in wastewaters and biosolids from Australian wastewater treatment plants. Environ. Int. 33, 199–205.
Ying, G.G., Yu, X.Y., Kookana, R.S., 2007. Biological degradation of triclocarban and triclosan in a soil under aerobic and anaerobic conditions and comparison with environmental fate modelling. Environ. Pollut. 150, 300–305.