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Fate of Triclosan and Methyltriclosan in soil from biosolids application

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ABSTRACT

This study investigates the persistence of Triclosan (TCS), and its degradation product, Methyltriclosan (MeTCS), after land application of biosolids to an experimental agricultural plot under both till and no till. Surface soil samples ($n = 40$) were collected several times over a three years period and sieved to remove biosolids. Concentration of TCS in the soil gradually increased with maximum levels of 63.7 ± 14.1 ng g^{-1} dry wt., far below the predicted maximum concentration of 307.5 ng g^{-1} dry wt. TCS disappearance corresponded with MeTCS appearance, suggesting *in situ* formation. Our results suggest that soil incorporation and degradation processes are taking place simultaneously and that TCS background levels are achieved within two years. TCS half-life ($t_{0.5}$) was determined as 104 d and MeTCS $t_{0.5}$, which was more persistent than TCS, was estimated at 443 d.

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1. Introduction

Triclosan (5-chloro-2-[2,4-dichloro-phenoxy]-phenol (TCS)) is an antibacterial compound that is registered for different uses in hand soaps, toothpaste, deodorants, laundry detergent, antiseptics for wound care, and medical devices. As a material preservative, Triclosan is used in many products including adhesives, fabrics, vinyl, plastics, toys, toothbrushes, floor wax emulsions, textiles, etc. It is widespread in the environment and several studies have suggested endocrine disruptor properties of TCS (Crofton et al., 2007; Veldhoen et al., 2006). Triclosan is an hydrophobic compound (log $K_{ow} = 4.8$) (Halden and Paull, 2005) that is found at ppt, or even ppb levels, in wastewater influents (McAvoy et al., 2002) however, over 90% is removed by activated sludge in wastewater plants (Sabaliunas et al., 2003) where TCS accumulates in biosolids at concentrations from 0.09 (Ying and Kookana, 2007) to 133 (USEPA, 2009) μg g^{-1} dry wt. representing over 50% of the total TCS entering WWTPs (Heidler and Halden, 2007). It has been illustrated that TCS can transform to Methyltriclosan (5-chloro-2-(2,4-dichlorophenoxy)anisole (MeTCS)) through methylation of the hydroxyl group on the phenyl ring of Triclosan (Hundt et al., 2000). While several studies in WWTP suggest that this methylation is the result of a biological transformation (Bester, 2005; Boehmer et al., 2004; Lindstrom et al., 2002; McAvoy et al., 2002), no bacterial strains capable to methylate Triclosan have been isolated (Hay et al., 2001; Meade et al., 2001). Methyltriclosan is more liphophilic (log $K_{ow} = 5.0$) (Balmer et al., 2004) and believed to be more persistent in the environment than its parent TCS (Lindstrom et al., 2002). Reported MeTCS sludge concentrations range from 0.004 (Sánchez-Brunete et al., 2010) to 1.03 μg g^{-1} dry wt. (McAvoy et al., 2002) which are a two orders of magnitude lower than TCS sludge concentrations. TCS is toxic to aquatic organism (Orvos et al., 2002) and both, TCS and MeTCS, accumulate in algae (Coogan et al., 2007) and fish (Balmer et al., 2004; Boehmer et al., 2004). Both compounds have been detected in rivers, TCS at concentrations from 2.3 to 98 ng L^{-1} (Lindstrom et al., 2002; Singer et al., 2002) and MeTCS from 0.3 to 80 ng L^{-1} (Coogan et al., 2007; Kantiani et al., 2008). Also, a recent study has reported TCS bioaccumulation in terrestrial organisms like worms after biosolids land application (Kinney et al., 2008).

While studies suggest the presence of TCS and MeTCS in the environment, little is known about their fate after biosolids applications to agricultural fields. In the United States, approximately 7 million dry tons of biosolids are produced annually and approximately 55% is land applied (NEBRA, 2007). Recent studies reported TCS soil half-life between 18 (Ying et al., 2007) to 107 d (Lozano et al., 2010) under aerobic conditions while it was found persistent under anaerobic conditions. A recent aerobic laboratory study has reported values from 50 to 108 days for two different soils (Kwon et al., 2010). In lab experiments, when TCS is applied in the dissolved form, the rates for TCS losses were much higher (Ying et al., 2007) than the

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losses observed when the TCS source was through the application of biosolids to commercial farms (Lozano et al., 2010). None of the previous studies analyzed for the presence of MeTCS. The objective of this study was to conduct a controlled soil application of biosolids from a well-characterized source and determine TCS dissipation rates and the formation and subsequent degradation of MeTCS. The study was designed to determine the TCS soil dissipation rates under field conditions where the biosolids application was the only source of TCS and was intended to represent commercial practices and thus expected to be non-homogeneous (Hedley and McLaughlin, 2004). To address the heterogeneity of our system, 40 soils samples were periodically collected within a 0.24 ha plot. Sampling took place over 3 years with shorter intervals during the first eight months where the release-incorporation is expected to be more important. In order to focus on the truly soil-associated Triclosan, and not biosolids concentrations, samples were sieved through a 2.8 mm sieve, thus excluding the larger biosolid aggregates that were not broken down and incorporated in the soils at the collection time (Andrade et al., 2010).

2. Material and methods

2.1. Experimental design

A rectangular 0.24 ha area plot (Soil Series Sunnyside Fine Sandy Loam) on the experimental fields of the University of Maryland located in Beltsville, MD, received a single application of limed Class B biosolids on July 18, 2006 from a large wastewater treatment plant (WWTP-A) sited in the Mid-Atlantic region. Biosolids were applied at the rate of 72.3 wet tons per hectare following agronomic rates. A manure spreader pulled by a tractor was used to spread the biosolids on the soils utilizing commercial applications protocols. Plot design (Fig. S1) and soil characterization (Table S1) are provided in supporting information. The experimental plot was divided in 8 equally spaced columns, which were alternatively either tilled to a depth around 10 cm or left untilled (Fig. S1-B). Tilling was done the day after biosolids application. Soybeans were planted on July, 21st and harvested on December 12th. Each column was divided in 5 rows in order to section the field into 40 equally-sized sampling quadrants (quadrants dimensions: 7.6 m × 6.1 m).

2.2. Sampling

2.2.1. Biosolids samples

Three biosolids samples were randomly collected from the stockpile of biosolids material just prior to placing it in the manure spreader for application to the field plot. The samples were placed in 250 ml amber glass jars and kept frozen (−20 °C) until processing.

2.2.2. Soil samples

For each pre-established sampling time a total of 42 surface soil samples, 40 samples within the field and 2 control samples outside the field, (Fig. S1-A) were collected at pre-determined locations with the aid of a field GPS instrument. Each sample represented a composite of 3 surface core samples to a depth of approximately 10 cm. Sampling times included, before application (May 30, 2006), application day (July, 18, 2006), two weeks after application (August 1, 2006), two months after application (September 21, 2006), four months (November 14, 2006), 8 months (March 14, 2007), 1 year (July 18, 2007), 2 years (June 27, 2008) and 3 years (July 31, 2009) after biosolids application. While most of our sampling concentrated in the surface, some deep core samples were taken to assess downward movement. Eight deep core samples (6 from the field and 2 controls outside of the field) were collected to a depth of 80 cm one year after biosolids application (Fig. S1). Deep core samples were divided in three individual sub-samples, from 0 to 25 cm, 25–50 cm and 50–75 cm for analysis.

2.3. Standards and reagents

The standards for Triclosan (97%) and Methyltriclosan (99%) were obtained from Aldrich (Aldrich Chemical Company, Inc., Milwaukee, WI, USA). Isotope-labeled $^{13}C_{12}$-TCS (≥99%) and $^{13}C_{12}$-MeTCS (≥99%) were obtained from Wellington Lab. (Guelph, ON, Canada). All organic solvents were high purity, pesticide grade (Burdick and Jackson; Fisher Scientific and EMD Chemicals Inc.). 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. Samples extraction and analysis

TCS and MeTCS were extracted from soils and biosolids using an adaptation of previously published methods (Burkhardt et al., 2005; Lozano et al., 2010). 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. Deep core samples were divided in three horizons (each 25 cm deep) before sieving. Approximately 10 g (soil) and 0.2–0.3 g (biosolids) wet weight (wet wt.) were extracted. All samples were spiked to a final concentration of 100 ng ml^{-1} $^{13}C_{12}$-TCS and 100 ng ml^{-1} of $^{13}C_{12}$-MeTCS internal standards before extraction to allow for isotope dilution quantitation to be performed. Extractions were performed by accelerated solvent extraction employing an ASE model #200 apparatus (Dionex Corp. Sunnyvale, CA, USA) using water/isopropyl alcohol (IPA) (20:80, v/v). The extract were cleaned up 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 extracts were evaporated to dryness by nitrogen blowdown and then the samples were reconstituted in methanol to a final volume of 1.5 mL.

Extracts were analyzed by LC-MS to measure TCS. LC-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). After TCS was measured these methanol extracts were evaporated and transferred to 1 ml of hexane to analyze them for MeTCS. These hexane extracts were analyzed using an Agilent 6890 gas chromatograph (GC) coupled with an Agilent 5975 mass selective detector (MSD) operated in positive electron impact ionization mode. The analytes were separated using a (DB-5-MS) capillary column with a length of 15 m, diameter of 0.25 mm, and film thickness of 0.1 μm (J&W Scientific, Folsom, CA). LC-MS and GC-MS conditions and additional details including ions used for identification and quantification are provided in supplementary information and Table S2.

2.5. Quality control

Method Detection Limits (MDLs) were determined using the procedure established by 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 and $^{13}C_{12}$-MeTCS 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 ≥ 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 within each 15 sample batch. Statistical analysis was performed using GraphPad Prism 5.0 Software, Inc., San Diego, CA.

3. Results and discussion

3.1. Method performance

TCS method development was published elsewhere (Lozano et al., 2010). Briefly the TCS method detection limit (MDL) was 1.0 and 13.9 ng g^{-1} wet wt. for soils and biosolids respectively; therefore the limit of quantification (LOQ) was 2.0 and 27.8 ng g^{-1} wet wt. For duplicates, the relative standard deviations (RSD) were 22.7 and 7.0%, and recoveries were 101.0 ± 8.9 and 88.9 ± 2.9% for soils and biosolids respectively where 7 replicates were analyzed. The MeTCS MDL was 0.24 and 13.3 ng g^{-1} wet wt. for soils and biosolids respectively; therefore the LOQ was 0.48 and 26.6 ng g^{-1} wet wt. Relative standard deviations were 6.11 and 9.45%, and recoveries were 91.4 ± 1.8 and 94.8 ± 3.0% for MeTCS in soils and biosolids respectively with 7 replicates. TCS and MeTCS values that were below LOQ are not reported.

3.2. Biosolids and soil concentrations

The biosolids material that was applied had TCS and MeTCS concentrations of 19.1 ± 3.02 and 0.10 ± 0.01 μg g^{-1} dry wt. (mean ± SE; $n = 3$). This TCS concentration was typical for this plant

(Lozano et al., 2010). The MeTCS concentrations were in the lower end of reported values from 0.05 to 1.03 μg g^{-1} dry wt. (McAvoy et al., 2002). As illustrated in Fig. S1-A, 40 soil samples were taken within the field, sieved to remove any remaining biosolids and analyzed for TCS and MeTCS. Significant spatial variability was observed (Fig. S2) similar to the variability reported by others (Sort and Alcañiz, 2001) when studying the phosphorous released from biosolids. Statistical analysis was performed to assess variability trends, yet none was found to be statistically significant. Also, an analysis was performed to determine the effect of till versus no till and no significant difference in TCS concentrations existed between the two cohorts (Log transformed data. *t* student test; $p > 0.05$). This trend indicates that tillage of the field didn't appear to significantly affect the TCS soil incorporation and dissipation or MeTCS formation. Due to the nature of soil in general and the nature of biosolids application, the observed spatial variability strongly supports the need for a large number of samples to determine soil concentration of chemicals released upon biosolids applications. In this study, to discuss soil concentrations and dissipation rates, 40 sample arithmetic means were used (e.g. Fig. 1).

The average TCS and MeTCS concentrations found in the soils over the entire field at different times before and after application are shown in Fig. 1. Fig. 1A demonstrates that TCS background levels found in the soils before biosolids application (2.7 ± 0.7; mean ± SE; $n = 40$) clearly increased after biosolids application. TCS soil concentrations varied from 9.5 ± 1.5 ng g^{-1} dry wt. (mean ± SE; $n = 40$) on the day of application to 63.7 ± 14.1 ng g^{-1} dry wt. (mean ± SE; $n = 40$) two months after biosolids application. Mean TCS soil concentrations remained relatively constant from 2 months to eight months after application, yet TCS concentrations analyzed after one year (365 d) were lower and reached background levels 2 years after application (Fig. 1B). The TCS level found two and three years after biosolids application (9.9 ± 2.0 and 3.7 ± 0.6 ng g^{-1} dry wt., respectively) were considered background levels since there was no statistical difference between pre-application levels (Log transformed data. ANOVAs and Dunnett's multiple comparison post test; $p > 0.05$).

Detectable average TCS concentrations were found in the two-control soil samples collected on each of the collection dates. Control levels ranged from below the LOQ to 7.5 ng g^{-1} dry wt. ($n = 16$). These levels were similar to the average concentration analyzed in the soils before biosolids application that on an individual sample basis ranged from below the LOQ to 9.3 with a mean of 2.7 ng g^{-1} dry wt. ($n = 40$). Others have reported similar and even higher TCS background levels in soils that have never received biosolids (Lozano et al., 2010; Xia et al., 2010) or any other soil amendments. While it is not known the exact nature of other possible sources that may be causing these background concentrations, TCS has been found in indoor dust (Canosa et al., 2007; Geens et al., 2009) and since it has such widespread use, atmospheric deposition could be a source although TCS atmospheric concentrations have not been documented.

Fig. 1(A and B) also shows MeTCS concentrations found in the soils throughout the three year study. For the control soils, no MeTCS concentrations higher than the LOQ of 0.48 ng g^{-1} were found and none was in the soils samples collected prior to biosolids application (−49 d). Over the course of the study, MeTCS concentrations increased from 0.6 ± 0.1 ng g^{-1} dry wt. (mean ± SE; $n = 40$) on the application day to 34 ± 6.7 ng g^{-1} dry wt. one year after biosolids application suggesting that MeTCS is formed from the TCS in the biosolids. Similar to TCS, MeTCS levels decreased during the second and third years (Fig. 1B).

To test the hypothesis that TCS *in situ* biodegradation was responsible for the increases in MeTCS soil concentrations, we had to eliminate the contribution of MeTCS in the soil from MeTCS initially present in the biosolids. This was accomplished using Eq. (1) (Jackson and Eduljee, 1994) which provides an estimate for the maximum possible Initial Predicted Environmental Concentration (PEC_{ini}) of MeTCS in the soils assuming complete soil assimilation of the MeTCS present in the biosolids at the time of application. The values used in Eq. (1) were $C_{soil(0)}$, any background level of MeTCS in the soil before biosolids addition (-0- since none was found); $C_{biosolids}$, the mean concentration of MeTCS measured in the biosolids that were applied (0.10 μg g^{-1}, $n = 3$); AR_y, the biosolids application rate (2.33×10^4 dry kg ha^{-1}); D, the soil density, (1.4×10^{-3} kg cm^{-3}); S_z, the soil depth (10 cm) and CF, a conversion factor to change the units to cm^2 ha^{-1}.

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

The predicted maximum MeTCS PEC_{ini} was 1.7 ng g^{-1} dry wt. indicating that any MeTCS concentrations higher than this value had to occur as a result of *in situ* formation due to TCS biodegradation. Even 2 weeks after application, the measured MeTCS levels (5.2 ± 1.9 ng g^{-1} dry wt.) were higher than the predicted zero-time

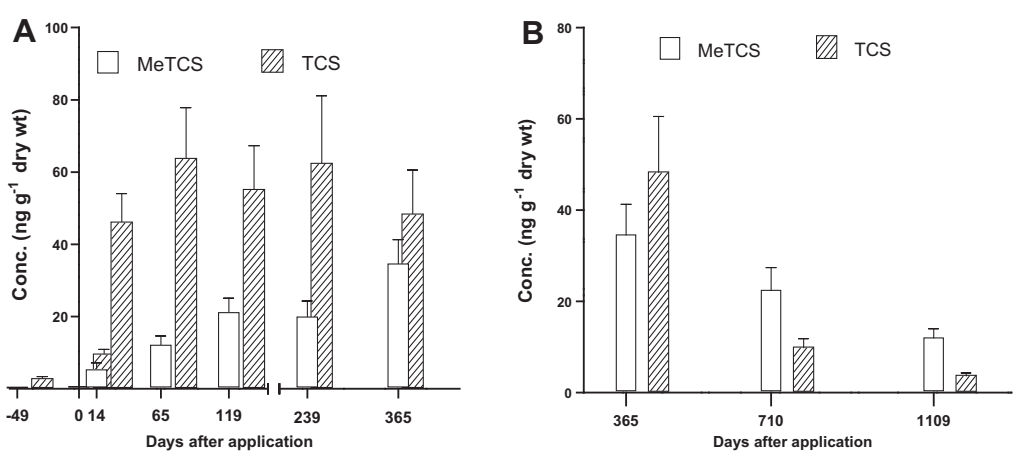

Fig. 1. TCS and MeTCS concentrations in ng g^{-1} dry wt. found in the soils per collection date (mean ± SE). Axes label represents the collection days for all study period. A. Represents the TCS and MeTCS concentrations found until one year after application where each bar represents 40 samples. −49 d was before application date; 0 d was application date; 14 d was two weeks after; 65 d was 2 months after; 119 d was four months after; 239 d was eight months after; 365 d was 1 year after. B. Represents the TCS and MeTCS concentrations found one year (365 d), 2 years (710 d) and three year (1109 d) after biosolids application. Each bar represents the mean of 40 samples.

PEC, thus it appears that TCS biodegradation started soon after biosolids application and it may have been taking place both within the biosolids and in the soil incorporated TCS. TCS degradation has been well documented within the WWTP (Bester, 2005; Heidler et al., 2006; Thompson et al., 2005; Ying and Kookana, 2007) thus bacteria that are present in the biosolids should be adapted to the TCS biodegradation and capable of degrading TCS within the biosolids.

Similar to MeTCS above, the maximum TCS PEC_{ini} was calculated using the Eq. (1), resulting in potential maximum soil concentration of 307.5 ng g^{-1} dry wt. for TCS in the surface 10 cm of the field. As expected, the measured TCS soil concentrations were always much lower than this PEC, clearly indicating that the biosolid-soil system takes some time to reach equilibrium and for the biosolid-bound TCS to become incorporated into the soil (Fig. 1A). Our results strongly suggest that at least two main processes are taking place simultaneously, release-assimilation of TCS from the biosolids to the soil coupled with *in situ* biodegradation of TCS both within the biosolid and in the soil. These observations also support the statement by Kwon et al. (2010) where addition of biosolids in their lab study slowed degradation of TCS.

There are other main processes that normally affect dissipation of organic compounds in soil; two important ones are leaching and runoff. Although no leaching or runoff samples were collected in this study since this was outside the scope of this project, deep core samples, down to 80 cm, were collected one year after biosolids application in order to test downward migration. TCS and MeTCS concentrations above the LOQ were only found in the first 25 cm of depth (Fig. S3). Furthermore, TCS and MeTCS concentrations in these samples were 2.8 and 2.7 times lower, respectively, than the TCS and MeTCS concentrations found at the surface. This showed that practically all TCS found one year after applications was still present in the first 10 cm of depth. Therefore TCS removal by leaching seemed to be insignificant during the first year where the highest TCS availability in the soil was observed. With respect to the runoff there are some studies that observed that only a 0.044% of the total TCS applied in the biosolids, is dissipated with runoff (Sabourin et al., 2009). Other processes like volatilization and photooxidation are also unlikely. Volatilization would be minimal because the vapor pressure coefficient is low (4×10^{-6} mm Hg at 20 °C) (Heidler and Halden, 2007) and photooxidation is minor because half of the field was tilled which would have facilitated biosolids incorporation into the first 10 cm of the soils which would reduce exposure to direct sunlight. While for the non tilled area (50% of the total plot) the possibility of photolysis would be mainly happening in the outer surface of biosolids chunks, which represents a minor percentage of the total TCS. Furthermore, photooxidation would only have been important right after application since the soils were planted, 3 days after biosolids application, with soybeans and their fast growth should have hampered the exposure of the TCS to the direct sunlight during the summer time where the photooxidation process would be more relevant. Others possible soil removal pathways could be the bioaccumulation in terrestrial organisms like worms (Kinney et al., 2008) and plant uptake, however, a recent study shown that even when TCS was accumulated in soybeans (root and leaf) after biosolids land application, the loss by plant uptake from the soils was negligible (Wu et al., 2010). More studies should be done to quantify all TCS removal pathways from the soil after biosolids application.

This study illustrates that soil concentrations of TCS upon land application of biosolids are influenced by two main processes; first where TCS is being released from the biosolids and incorporated into the soils (release-incorporation) and at the same time it is being biodegraded or dissipated. The soil incorporation stage appears to last from application day till 2 or 4 months (Days 65 and 119 data in Fig. 1A). Biodegradation/dissipation appears to be the main processes acting on the TCS and MeTCS in the soils 8 months (239 days) after biosolids application and it appears to lasts till TCS concentrations in the soils reach background levels, which occurred two years (710 days) after biosolids application.

Further analysis of the results presented in Fig. 1A, indicates that TCS soil concentrations reached a plateau at day 65, and this plateau included day 119 and lasted until day 239 (these samples represent a period from 2 months to 8 months after biosolids application). No statistical differences were found between the TCS concentrations measured on these collection dates (63.7 ± 14.1, 55.0 ± 12.3 and 62.3 ± 18.9 ng g^{-1} dry wt. for 2, 4 and 8 months respectively) (Log transformed data. ANOVAs and Dunnett's multiple comparison post test; $p > 0.05$). Yet higher and statistically different MeTCS concentrations were found between September (2 month post application) (12.1 ± 2.6 ng g^{-1} dry wt.) and November (4 months after application) (21.1 ± 3.9 ng g^{-1} dry wt.) indicating that continued TCS soil release-incorporation and degradation were still taking place over this time period. However, no statistical differences in MeTCS concentrations were observed between November (21.1 ± 3.9 ng g^{-1} dry wt.) and March (19.9 ± 4.4 ng g^{-1} dry wt.) (Log transformed data. ANOVAs and Newman–Keuls multiple comparison post test), suggesting that there may have been a slowing down, or cessation of TCS degradation (specifically the conversion of TCS to MeTCS) between November and March. This slower TCS biodegradation is likely linked to the low temperature in this period (winter time) which is known to affect microbial processes (Schwarzenbach et al., 2003; Thompson et al., 2005). Soil surface (~2 cm) temperature data that was collected at a weather station placed close to the field indicated that the temperature measured between September (2 months) and November (4 months) ranged from 3.7 to 19.8 °C while temperature registered between November to March ranged from 0.1 to 10.4 °C. Right after winter (from March to July that represents 239 and 365 days after application) the biodegradation process seemed be much more active since MeTCS levels increased significantly and this was also a period of warmer soil temperatures.

To test if possible soil aging during storage was contributing to a smaller sample recovery, a subset of year one samples were reanalyzed with year 3 samples (2 years after storage). The determined concentrations were not statistically different. Furthermore, results from PBDEs a more hydrophobic and persistent compound illustrates that onsite soil aging did not affect these soil concentrations within the time of this study (data not shown). Fig. 2 shows the TCS concentration analyzed in the soils at different times after biosolids application and the TCS concentration estimated per each collection date using Eq. (2) (Jackson and Eduljee, 1994) where PEC_{ini} was the predicted TCS estimated concentrations calculated as described above at the day of applications and then using a half-life for dissipation of 107.4 days to describe predicted losses from our previous work (Lozano et al., 2010). This model suggests that 8 months after biosolids application all of the TCS has been incorporated in the soil as the determined PEC at this time closely matches our results. However, insignificant changes were observed between 4 and 8 months (winter months) suggesting that the complete or total release from the biosolids and subsequent incorporation in the soils probably had actually been completed even earlier, between 2 and 4 months after biosolids application. These results strongly suggest that models such as Eq. (2) should only be used for relatively large time intervals unless one has temperature dependent half-lives.

Results from this study were further used to determine a TCS half-life ($t_{0.5}$) and compare it with what we reported earlier from commercial applications of biosolids in Virginia (Lozano et al., 2010). For this estimation the average soil concentrations of 62.3 ng g^{-1} (8 months after application) was used for the $C_{soil(t)}$

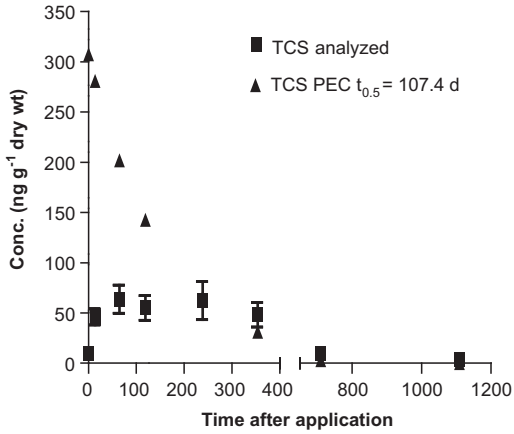

Fig. 2. Comparison of TCS concentration analyzed in the soils (■) at different times after biosolids applications and the TCS concentration estimated (▲) using a half-life of 107.4 days and an initial TCS concentration at time of applications (application day) of 307.5 ng g^{-1} dry wt. (TCS PEC calculated above).

value in Eq. (2); t is the time in days (239) corresponding to this 8 months period and PEC_{ini} is the predicted TCS concentration (307.5 ng g^{-1} dry wt.) at time zero when the biosolids were applied.

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

The TCS $t_{0.5}$ estimated using these values was 104 d. The accuracy of this $t_{0.5}$ was evaluated by using it to estimate TCS concentrations expected in our samples at 1 year and 2 years after application. The respective values were 26 and 4.5 ng g^{-1} dry wt., which were close to the observed values of 48.3 and 9.9 that were measured in this study. This supports the fact that these longer periods of time should be used to calculate the half-life of these organic compounds in soils after biosolids applications. Thus, these estimated half-life values appear to have properly addressed the main processes that were affecting the TCS dissipation in the field (release, degradation, temperature, weather, management of the field, etc.). Using Eq. (2) to calculate the half-life for TCS in this experimental plot, we obtained a $t_{0.5}$ of 104 d which is very close to the $t_{0.5}$ of 107.4 d found in a biosolids applications study on commercial farms during the same period (from Summer to Spring) and with similar temperature regime (Lozano et al., 2010). While our field determined value is very closed to the lab determined value of 108 days (Kwon et al., 2010), it is very different from the lab determined value of 20 days by Wu and associates (Wu et al., 2009).

The MeTCS concentration measured 1 year after application represented 12.7% of the total TCS dissipated during this period; while this percentage should be higher since MeTCS was also dissipating. In an attempt to determine an approximate MeTCS $t_{0.5}$, the soil MeTCS concentration after 2 years was used. By this time, TCS had reached background levels and all new formation of MeTCS was complete and removal would be the only factor causing further changes in the MeTCS concentrations from this point forward. Using this concentration, MeTCS $t_{0.5}$ was estimated using the Eq. (2). For this calculation, $C_{soil(t)}$ was the MeTCS concentration after 3 years (12.0 ng g^{-1} dry wt.); PEC_{ini} was the MeTCS concentrations found 2 years after biosolids applications (22.4 ng g^{-1} dry wt.) and t was the time elapsed between two and three year periods. Using these values our estimated MeTCS $t_{0.5}$ was 443 d which was 4.3 times longer than TCS $t_{0.5}$. While this represents a rough estimate, our work strongly supports the fact that MeTCS is much more persistent than TCS. Using this MeTCS $t_{0.5}$ value, we estimate that 4 years after application (which is a typical time between repeated biosolids applications in the study area; Andrade et al., 2010) MeTCS is still present at above background levels (7.1 ng g^{-1} dry wt.), hence MeTCS would present the ability to build up in the soils after multiple biosolids applications. Our estimates suggest that it would take 7.2 years for soil MeTCS to reach soil background levels, again confirming the higher MeTCS persistence in the environment as compared to TCS.

Although TCS can be accumulated in worms (Kinney et al., 2008), no prior studies have been published illustrating MeTCS persistence or accumulation. However, MeTCS has a lower solubility and higher sorption coefficients (log $K_{owMeTCS}$ of 5 and log $K_{ocMeTCS}$ of 4.6 L kg^{-1} (Lindstrom et al., 2002)) than its parent TCS (log K_{owTCS} of 4.8 (Halden and Paull, 2005) and log K_{ocTCS} of 3.8–4.0 L kg^{-1} (Lindstrom et al., 2002)). These facts might influence sorption processes that depend on the amount of organic carbon present in our soil samples. To determine if their concentrations were related with the organic content in the soils, three soil samples for each date of collection were analyzed for organic carbon (data not shown). Upon testing this relationship, no TCS and MeTCS correlation was found with the organic matter present in the soil (correlation coefficient, r^2 lower than 0.1 for TCS and lower than 0.2 for MeTCS).

This study clearly illustrates that soil incorporation/assimilation and biodegradation are two important mechanism concurrently involved in the fate of TCS when biosolids are applied to soil and that laboratory studies can rarely duplicate the complexity in a field. About 84% of TCS applied with the biosolids was removed from the soils one year after application, reaching soil background levels after 2 years. Meanwhile, increasing MeTCS levels were observed for the first year and then, decreasing MeTCS concentrations were observed over the second and third year, demonstrating that MeTCS formation in the soils is a byproduct of TCS removal. MeTCS soils concentrations never reach background levels during the 3 year study. TCS and MeTCS $t_{0.5}$ estimated were 104 and 443 d respectively, showing that MeTCS is dissipated too but that it is more persistent than its parent TCS. To our knowledge this is the first study that shows TCS removal in soils accompanied by MeTCS formation *in situ* after biosolids application. Also that MeTCS has a higher persistence in soils than its parent TCS.

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Appendix. Supporting information

Supplementary information associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2011.09.020.

References

Andrade, N.A., McConnell, L.L., Torrents, A., Ramirez, M., 2010. Persistence of polybrominated diphenyl ethers in agricultural soils after biosolids applications. Journal of Agricultural and Food Chemistry 58, 3077–3084.

Balmer, M.E., Poiger, T., Droz, C., Romanin, K., Bergqvist, P.A., Muller, M.D., Buser, H.R., 2004. Occurrence of methyl triclosan, a transformation product of the bactericide triclosan, in fish from various lakes in Switzerland. Environmental Science and Technology 38, 390–395.

Bester, K., 2005. Fate of triclosan and triclosan-methyl in sewage treatment plants and surface waters. Archives of Environmental Contamination and Toxicology 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 Compounds 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. Analytica Chimica Acta 534, 89–100.

Canosa, P., Rodriguez, I., Rubi, E., Cela, R., 2007. Determination of parabens and triclosan in indoor dust using matrix solid-phase dispersion and gas chromatography with tandem mass spectrometry. Analytical Chemistry 79, 1675–1681.

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. Environmental Toxicology and Pharmacology 24, 194–197.

Geens, T., Roosens, L., Neels, H., Covaci, A., 2009. Assessment of human exposure to Bisphenol-A, Triclosan and Tetrabromobisphenol-A through indoor dust intake in Belgium. Chemosphere 76, 755–760.

Halden, R.U., Paull, D.H., 2005. Co-occurrence of triclocarban and triclosan in U.S. water resources. Environmental Science and Technology 39, 1420–1426.

Hay, A.G., Dees, P.M., Sayler, G.S., 2001. Growth of a bacterial consortium on triclosan. FEMS Microbiology Ecology 36, 105–112.

Hedley, M.J., McLaughlin, M.J., 2004. Reactions of Phosphate Fertilisers and By-products in Soils, Phosphorus: Agriculture and the Environment. American Society of Agronomy/Crop Science Society of America/Soil Science Society of America, Madison, Wisconsin, pp. 181–252.

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. Environmental Science and Technology 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*. Applied and Environmental Microbiology 66, 4157–4160.

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.

Kantiani, L., Farré, M., Asperger, D., Rubio, F., González, S., López de Alda, M.J., Petrovic, M., Shelver, W.L., Barceló, D., 2008. Triclosan and methyl-triclosan monitoring study in the northeast of Spain using a magnetic particle enzyme immunoassay and confirmatory analysis by gas chromatography-mass spectrometry. Journal of Hydrology 361, 1–9.

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. Environmental Science and Technology 42, 1863–1870.

Kwon, J.W., Armbrust, K.L., Xia, K., 2010. Transformation of triclosan and triclocarban in soils and biosolids-applied soils. Journal of Environmental Quality 39, 1139–1144.

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. Environmental Science and Technology 36, 2322–2329.

Lozano, N., Rice, C.P., Ramirez, M., Torrents, A., 2010. Fate of triclosan in agricultural soils after biosolid applications. Chemosphere 78, 760–766.

McAvoy, D.C., Schatowitz, B., Jacob, M., Hauk, A., Eckhoff, W.S., 2002. Measurement of triclosan in wastewater treatment systems. Environmental Toxicology and Chemistry 21, 1323–1329.

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 Microbiology Letters 204, 45–48.

NEBRA, 2007. A National Biosolids Regulation, Quality, End Use and Disposal Survey Report, Final Report. North East Biosolids and Residuals Association (NEBRA), Tamworth, NH.

Orvos, D.R., Versteeg, D.J., Inauen, J., Capdevielle, M., Rothenstein, A., Cunningham, V., 2002. Aquatic toxicity of triclosan. Environmental Toxicology and Chemistry 21, 1338–1349.

Sabaliunas, D., Webb, S.F., Hauk, A., Jacob, M., Eckhoff, W.S., 2003. Environmental fate of triclosan in the River Aire Basin, UK. Water Research 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. Science of the Total Environment 407, 4596–4604.

Sánchez-Brunete, C., Miguel, E., Albero, B., Tadeo, J.L., 2010. Determination of triclosan and methyl triclosan in environmental solid samples by matrix solid-phase dispersion and gas chromatography-mass spectrometry. Journal of Separation Science 33, 2768–2775.

Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. Environmental Organic Chemistry, second ed. John Wiley & Sons, Hoboken, New Jersey.

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. Environmental Science and Technology 36, 4998–5004.

Sort, X., Alcañiz, J.M., 2001. Application of X-ray microanalysis to study the distribution of organic waste in soil. Geoderma 104, 1–15.

Thompson, A., Griffin, P., Stuetz, R., Cartmell, E., 2005. The fate and removal of triclosan during wastewater treatment. Water Environment Research 77, 63–67.

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, Code of Federal Register 600 Series Washington D.C.

USEPA, 2009. Targeted National Sewage Sludge Survey Statistical Analysis Report. Office of Water 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. Aquatic Toxicology 80, 217–227.

Wu, C., Spongberg, A.L., Witter, J.D., 2009. Adsorption and degradation of triclosan and triclocarban in soils and biosolids-amended soils. Journal of Agricultural and Food Chemistry 57, 4900–4905.

Wu, C., Spongberg, A.L., Witter, J.D., Fang, M., Czajkowski, K.P., 2010. Uptake of pharmaceutical and personal care products by soybean plants from soils applied with biosolids and irrigated with contaminated water. Environmental Science and Technology 44, 6157–6161.

Xia, K., Hundal, L.S., Kumar, K., Armbrust, K., Cox, A.E., Granato, T.C., 2010. Triclocarban, triclosan, polybrominated diphenyl ethers, and 4-nonylphenol in biosolids and in soil receiving 33-year biosolids application. Environmental Toxicology and Chemistry 29, 597–605.

Ying, G.G., Kookana, R.S., 2007. Triclosan in wastewaters and biosolids from Australian wastewater treatment plants. Environment International 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. Environmental Pollution 150, 300–305.