



Fate of triclosan in field soils receiving sewage sludge

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ABSTRACT

The anti-microbial substance triclosan can partition to sewage sludge during wastewater treatment and subsequently transfer to soil when applied to land. Here, we describe the fate of triclosan in a one-year plot experiment on three different soils receiving sludge. Triclosan and methyl-triclosan concentrations were measured in soil samples collected monthly from three depths. A large fraction of triclosan loss appeared to be explained by transformation to methyl-triclosan. After 12 months less than 20% of the initial triclosan was recovered from each soil. However, the majority was recovered as methyl-triclosan. Most of the chemical recovered at the end of the experiment (both triclosan and methyl-triclosan) was still in the top 10 cm layer, although there was translocation to lower soil horizons in all three soils. Between 16.5 and 50.6% of the applied triclosan was unaccounted for after 12 months either as a consequence of degradation or the formation of non-extractable residues.

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1. Introduction

Triclosan is a broad spectrum anti-microbial compound commonly used in personal-care products such as toothpaste and soaps. Analyses of biosolids for triclosan worldwide suggest that concentrations typically range between 0.5 and 55 mg kg⁻¹ (Bester, 2003; McAvoy et al., 2002; Heidler and Halden, 2007; McClellan and Halden, 2010), although the USEPA Targeted National Sewage Sludge Survey (TNSSS) (USEPA, 2009) found triclosan at concentrations of up to 133 mg kg⁻¹ dry weight, with mean concentrations of 12 ± 18 mg kg⁻¹ in U.S. sludge samples. It is notable that very few studies have reported triclosan concentrations in soil following sludge incorporation. Measured concentrations have been reported previously to range between 0.052 and 0.206 mg kg⁻¹ dry wt (Xia et al., 2010; Lozano et al., 2010), although these measurements were taken 7 and 12 months after application respectively. Modelled concentrations in soil have been estimated at 4.5 mg kg⁻¹ dry wt (Fuchsman et al., 2010). These concentrations compare with a soil microbial predicted no-effect concentration (PNEC) of 1 mg kg⁻¹ dry wt (Waller and Kookana, 2009), a crop PNEC of approximately 1 mg kg⁻¹ dry wt and an earthworm PNEC of 1026 mg kg⁻¹ dry wt (Wuethrich, 1990), suggesting that some effects may be possible if soils receive very high doses. Indeed, Butler et al. (2011) have shown that both microbial basal respiration and substrate induced

respiration can be inhibited by triclosan addition, although at much higher nominal concentrations than those expected in field soils. It is also important to obtain a thorough understanding of the fate and translocation of triclosan in agricultural soils receiving sludge in order to address concerns about its potential persistence, bio-accumulation and toxicity in the terrestrial environment and to assess potential transport to ground and surface waters.

Topp et al. (2008) reported that no triclosan could be detected in surface runoff when biosolids were injected into soil but when sludge was applied to the soil surface triclosan was detected in runoff up to 266 days after application. Triclosan has also been measured in soil drainage water via tile drain monitoring after sludge application (Edwards et al., 2009), suggesting that it has some potential for leaching. Lapen et al. (2008) have shown that triclosan leaching can be reduced by adding dewatered biosolids as opposed to liquid. In another study, Xia et al. (2010) measured triclosan in soils that had received biosolids annually for 33 years. They reported that between 49 and 64% of the extractable triclosan was located at depth (30–120 cm) indicating substantial translocation. Notwithstanding the clear potential for triclosan transport in or over soil, the loss of triclosan in runoff and leachate is usually a very small fraction of the mass applied (<<1%) suggesting that most of the chemical remains near the soil surface or is degraded (Sabourin et al., 2009).

Several studies have reported dissipation of triclosan in field soils. For example, Lozano et al. (2010) observed concentrations between 23.6 and 66.6 µg kg⁻¹ dry wt in U.S. soils one year after a single application of sludge. Concentrations decreased over time

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and were between 4.1 and 4.5 $\mu\text{g kg}^{-1}$ dry wt 16 months after application. Concentrations were slightly higher (ca. 10 $\mu\text{g kg}^{-1}$) in soil that had received repeated sludge applications. Cha and Cupples (2009) have also presented evidence for triclosan dissipation. Fields sampled between three months and four years after biosolids application contained lower triclosan concentrations than anticipated and when sampled a year later, concentrations had decreased further. A few studies have attempted to follow triclosan degradation explicitly and a range of degradation rates have been reported under different conditions. Ying et al. (2007), for example, reported a degradation half-life for triclosan of 18 days in a laboratory study in which triclosan was applied directly to a loam soil, although no degradation was observed in oxygen-deprived soils. Waria et al. (2011) reported degradation half-lives of 78 days for a silty clay loam and 421 days for a fine sand soil in a laboratory incubation study. Other reported half-lives include 13.1–32.5 days (Xu et al., 2009) and 107 days (Lozano et al., 2010) in the field and 13.5 days (Xu et al., 2008) and 2.5–35 days (Reiss et al., 2009) in the laboratory. Although different dissipation rates under different soil properties and environmental conditions should be expected, Cha and Cupples (2009) failed to correlate triclosan concentrations with soil characteristics. Mineralisation studies have shown that triclosan degradation can increase when applied with liquid biosolids compared to direct addition, particularly when compared with the addition of dewatered biosolids (Al-Rajab et al., 2009).

Methyl-triclosan (Me-TCS) is a known metabolite of triclosan. Although it does not possess antibacterial properties, it is more lipophilic and potentially more environmentally persistent than the parent compound (Chu and Metcalfe, 2007; Coogan et al., 2007) and has a high bioaccumulation potential in aquatic organisms (Ying and Kookana, 2007). Methyl-triclosan is formed by way of O-methylation when a methyl group is attached to the hydroxyl group on the triclosan molecule, increasing lipophilicity (Häggblom et al., 1988; Allard et al., 1987). In general, the anisole products of O-methylation also have a tendency to have increased toxicity (Goswami et al., 2007). It is produced exclusively by aerobic biodegradation of the parent compound (Chen et al., 2011) and has been reported in treated wastewater effluent (Bester, 2003) and river water (Coogan et al., 2007). Thus far, the only measured concentrations of Me-TCS in biosolids or soils receiving biosolids have been those reported by Waria et al. (2011), which reported a significant Me-TCS formation in laboratory-incubated soils.

In this study, the fate and translocation of triclosan and Me-TCS in agricultural soils receiving sewage sludge pellets under field conditions is reported. A primary objective was to better understand degradation and translocation processes by simultaneously monitoring the fate of the parent compound and a principal biotransformation metabolite.

2. Methods

2.1. Plot preparation

Three different soils (Silsoe farm in Bedfordshire, UK) with different textures and physico-chemical properties were selected (Table 1). All soils had not previously received sewage sludge and were in a similar arable rotation. Within each field, three replicate plots (3×3 m) were established. A control plot was also established in each field which received no sewage sludge. Sewage sludge was provided by a major UK water company in the form of heat-treated biosolid pellets from a commercial operation. The pellets were applied in September 2009, at rate of 50 tonnes dry mass ha^{-1} (5 kg m^{-2}) two days after the crop (Winter wheat: *Triticum aestivum*) had been drilled. The sludge was manually applied and manually incorporated into the top layer of the soil to a depth of 10 cm.

2.2. Sampling

Four weeks after sludge application and, thereafter, every month, five soil cores were collected in each plot at three depths (0–10 cm, 10–20 cm and 20–30 cm)

Table 1

Basic properties the three soils used in the experiments (EC – electrical conductivity, CEC – Cation exchange capacity, TOM – Total organic matter, TC – total carbon, WHC – water holding capacity).

Soil property	Loamy sand	Sandy clay loam	Clay
Soil series name	Bearsted	Evesham	Lawford
Grid reference	26°25'W, 52°25'N	25°56'W, 52°12'N	26°27'W, 52°33'N
pH	8.2	6.6	7.1
EC $\mu\text{S/cm}$	72.8	82.7	55.9
CEC cmol^+/kg	6.6	13.5	13
TOM %	3.95	5.94	7.625
Water content %	0.98	1.31	10.22
TOC	1.595	2.392	2.694
TC	1.714	2.348	2.778
Sand %	71.9	35.96	19.4
Silt %	16.4	30.12	24.16
Clay %	11.7	35.56	56.05
Bulk Density (kg/m^3)	1250	1300	1190
Total Nitrogen %	0.159	0.209	0.285
Max WHC (% m/m)	43.41	58.02	74.52
C/N ratio	10.8	11.2	9.7

Standard methods were employed (Soils were dried, sieved to <2 mm and stored following BS 7755 Section 2.6: 1994 and BS ISO 11464 2006). Soil pH was analysed following BS ISO 10390:2005; Total organic matter was obtained via loss on ignition (BS EN 13039: 2000); Total carbon and total nitrogen content was calculated after elemental analysis (BS 7755 section 3.8 and BS EN 13654-2 2001, respectively). Particle size distribution, electrical conductivity and cation exchange capacity were all obtained using BS 7755 (sections 5.4:1998, 5.5: 1999, 3.4: 1995 and 3.12: 1996 respectively).

using a 3 cm diameter tube auger. Sampling points were selected at the apices of a virtual “W” over the plot with a change in “W” orientation on each sampling occasion to attempt to account for spatial variability. Soil samples collected in each plot at each depth were bulked to form a single representative sample for the plot. All samples were air-dried, 2 mm sieved and tested for pH (BS ISO 10390:2005), gravimetric moisture content and organic matter content (BS EN 13039: 2000). In addition, monthly mean air temperature (T) was derived from daily air temperature data (MIDAS Land Surface Stations, UK Met Office). Volumetric water content (θ_v) was calculated from gravimetric moisture content (θ_m) by multiplying the bulk density.

2.3. Analytical method

Each bulked sample was extracted and analysed for triclosan and Me-TCS in triplicate. Accelerated solvent extraction (ASE) was used to initially remove the relevant compounds from the soil. 5 g of air dried soil was weighed into a 33 mL ASE cell and mixed with enough Ottawa sand (Fisher Scientific) to fill the cell. The sand is essential to allow solvent to flow through the cell without blocking the injector. Extraction was performed using 100% ethyl acetate at a pressure of 103 bars, and a temperature of 100 °C. Extractants were then cleaned up using solid phase extraction (SPE) using C18 cartridges (6 cm^3 , 1 g) under vacuum. Each cartridge was pre-conditioned with 5 mL methanol, 5 mL (10%) methanol and 10 mL water, the cartridges were then allowed to gently air dry by under vacuum for 10 min. The sample was then pulled through the cartridge at 10 mL min^{-1} with the rate controlled by adjusting the vacuum pressure. Each cartridge was allowed to dry for 1 min and washed with 2 mL methanol/water (25% v/v) to remove any polar co-extractives. The cartridge was then dried under full vacuum for 60 min. Elution was carried out using 2×2.5 mL aliquots of methanol followed by 2×2.5 mL aliquots dichloromethane. The eluents were combined and blown to dryness under a gentle nitrogen stream at 40 °C. Fifty μL of 1 ng L^{-1} ^{13}C labelled triclosan in nonane was used as an internal standard and added with 950 μL of hexane to reconstitute each extract which was then transferred to a GC sampling vial ready for analysis.

An Agilent 6890 GC was used, equipped with Chemstation software and a Zebtron ZB-5 HT, 30 m \times 0.25 mm \times 0.25 μm column. The Oven Temperature Program was as follows: 120 °C held for 1 min, followed by a temperature ramp of 10 °C min^{-1} to 310 °C, which was then held for 5 min. The MS was programmed to have a solvent delay of 4 min, with an interface temperature of 310 °C. The ionisation mode used was EI^+ electron impact and the method was run in full scan mode as well as Single Ion Monitoring (SIM). The ions used for identification and conformation were 218, 288 and 290 for triclosan; 300, 302 and 230 for Me-TCS and 254, 302 and 304 for the ^{13}C labelled triclosan internal standard. Recoveries in the range 89–101% of spiked triclosan at a concentration of 10 ng g^{-1} dry soil were obtained, with a mean recovery of 94.3%. The method limit of detection (LOD) was 1.4 ng g^{-1} and the limit of quantification (LOQ) was 4 ng g^{-1} . Sludge pellets were also extracted to check the homogeneity of the batch before applying to land. The LOD for extracting triclosan and Me-TCS from biosolids was found to be the same as from the

soils using this method of extraction. However, the recoveries were reduced to a mean of 82.6% in a spiked sample.

3. Results

3.1. Triclosan in the soil and sewage sludge

Triclosan and Me-TCS were not detected in any of the soil plots prior to sludge application or in control plot samples. The measured concentration ranges for triclosan and Me-TCS in the sludge pellets used ($n = 9$) were 11.22–28.22 mg kg⁻¹ for triclosan and 0.035–0.069 mg kg⁻¹ for Me-TCS (triclosan mean = 21.9, SD = 5.35 mg kg⁻¹; Me-TCS mean = 0.051, SD = 0.012 mg kg⁻¹). The measured concentrations of triclosan and Me-TCS in the top 10 cm layer of each soil type over the course of the experiment are shown in Fig. 1, along with key explanatory variables (pH, θ_v and T). The initial concentrations of triclosan (C_0) in this layer (Table 2) were in approximate agreement with the expected concentration (C_{ini} , mg kg⁻¹) derived from the mean measured concentration in sludge pellets, assuming zero background triclosan concentration in soil (e.g. Jackson and Eduljee, 1994):

$$C_{ini} = \frac{E \cdot C_{biosol}}{\rho \cdot z} \quad (1)$$

where C_{biosol} is the mean biosolid concentration (mg kg⁻¹), E is the application rate (kg m⁻²), ρ is the soil bulk density (kg m⁻³) and z is the mixing depth (m).

3.2. Triclosan and methyl-triclosan in the top 10 cm of soil

In all three soils, triclosan concentrations in the top 10 cm layer decreased relatively slowly in the first nine months after

Table 2

Predicted and measured concentrations of triclosan and methyl-triclosan applied to each plot ($n = 3$, standard deviation for each plot in parenthesis).

Soil	Predicted values (µg kg ⁻¹)		Measured values (µg kg ⁻¹)	
	TCS (SD)	Me-TCS (SD)	TCS (SD)	Me-TCS (SD)
Loamy sand	880 (33.3)	2.04 (0.52)	914.9 (83.9)	1.08 (0.08)
Sandy clay loam	846 (32)	1.96 (0.50)	773.5 (77.5)	2.19 (0.39)
Clay	924 (35)	2.14 (0.54)	948.6 (39.7)	2.17 (0.67)

sludge incorporation (October 2009). The rate of dissipation increased markedly in the summer months, after the June 2010 sampling. In the loamy sand soil 59% of the initial mass of triclosan was lost from the top 10 cm during the four month period between July and October. In contrast, the equivalent mass losses in the sandy clay loam and clay soils were 72 and 74% respectively over the same period. In parallel, there was a small but progressive increase in the concentration of Me-TCS to June 2010, followed by a more rapid increase in summer, suggesting that a significant fraction of the measured loss of triclosan was due to biotransformation of the parent compound to Me-TCS. The period of most rapid triclosan transformation coincided with a period of low soil moisture content (approaching the permanent wilting point of each soil) and increased air temperature (see Fig. 1). An apparent decrease in triclosan transformation was observed in October 2010. At this point all three soils were wetter and the temperature was lower (T was approximately 8 °C), suggesting that the rate of biodegradation may have been limited by abiotic factors. In the clay soil, the period of rapid triclosan dissipation appeared to occur slightly later (in August 2010) than in the other two soils, possibly due to a delay in soil drying (see Fig. 1).

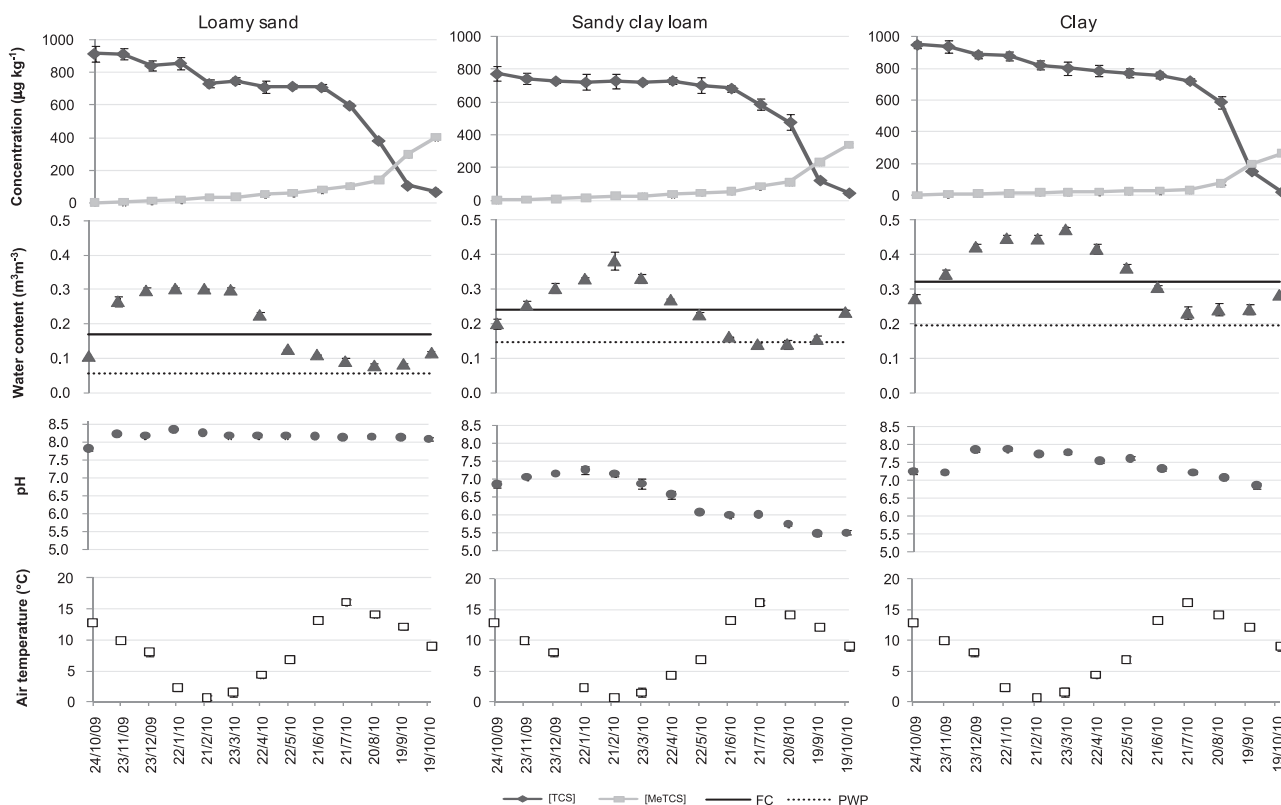


Fig. 1. The concentration of triclosan (TCS) and methyl-triclosan (Me-TCS) in the upper 10 cm of each soil plotted along side the water content showing field capacity (FC) and permanent wilting point (PWP), pH and air temperature.

3.3. Triclosan and methyl-triclosan in the lower horizons

All three soils showed similar triclosan and Me-TCS concentration trends in the lower horizons (Fig. 2). Triclosan concentrations in the 10–20 cm layer increased when the soil was wet (θ_v was greater than the respective field capacities in all three soils from November 2009 to April 2010) and soil temperatures were low to a peak in February 2010, suggesting translocation by leaching as the predominant process, driven by low soil moisture deficit and sustained rainfall and snow melt over the winter period. In the period after February 2010, triclosan concentrations decreased in this layer following an increase in soil moisture deficit as well as an increase in temperature. This decrease in triclosan concentration is coincident with an observed increase in Me-TCS concentrations, suggesting that a significant fraction of the loss in parent compound

during this period was due to biotransformation in situ. This is further supported by the rapid rise in Me-TCS concentrations between July and October 2010 in the 10–20 cm layer, which matches the temporal pattern reported above for the 0–10 cm layer, and which coincides with a substantial decrease in θ_v and an increase in T above 10 °C. It is pertinent to note that, in all three soils, concentrations of Me-TCS exceeded those of triclosan in the 10–20 cm layer by the late summer period. Overall triclosan concentrations and apparent dissipation rates were lower in the clay soil than in the other two soils.

In the 20–30 cm layer, increases in triclosan concentrations were delayed relative to those in the 10–20 cm layer (concentrations were >LOD from February 2010 onwards), which is consistent with the expected behaviour of a hydrophobic contaminant such as triclosan, in the absence of significant by-pass flow. Interestingly,

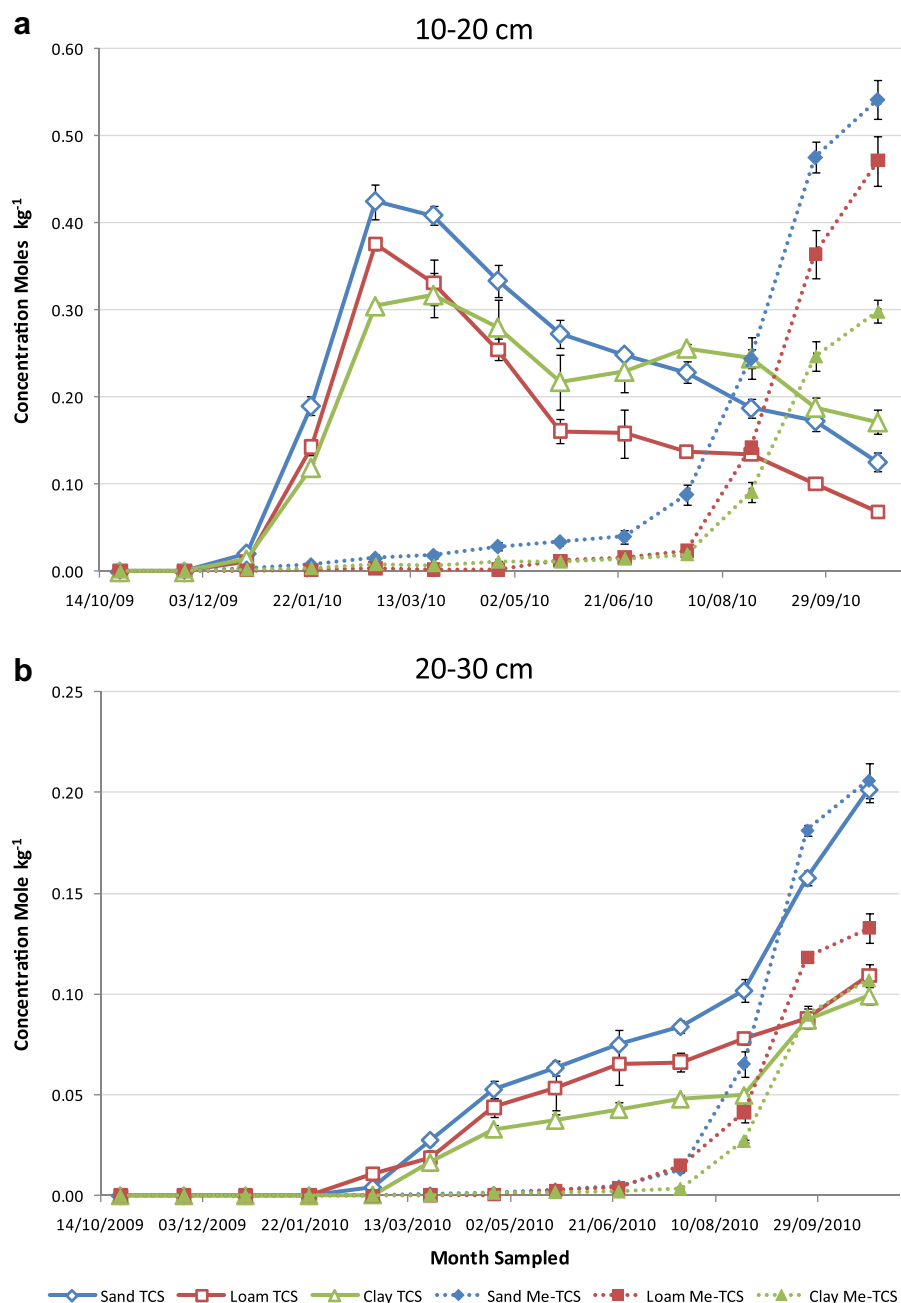


Fig. 2. The concentration of triclosan (TCS) and methyl-triclosan (Me-TCS) in the 10–20 cm and 20–30 cm soil layers in moles per kilogram. Note the different scale on each axis.

concentrations of triclosan continued to increase in this layer through to October 2010, when monitoring ceased, despite the fact that soil moisture contents in all three soils were relatively low (below field capacity) during much of the summer period, which would tend to limit inputs via leaching. However, it is possible that triclosan could also have been translocated due to processes such as bioturbation. It has been observed that earthworm activity increases in warmer and dryer soils, as they burrow deeper into the soil to find water (Perreault and Whalen, 2006). Concentrations of Me-TCS in the 20–30 cm layer were relatively low in all three soils until July 2010, when concentrations increased markedly. By September 2010, average Me-TCS concentrations in this layer exceeded those of the parent compound. Overall, concentrations of triclosan and Me-TCS in this layer were highest in the loamy sand and lowest in the clay soil, which reflects the expected relative propensity for leaching in these soils in terms of sorption (the sand and clay soils had the lowest and highest organic carbon contents, respectively) and in terms of drainage and solute transport processes.

3.4. Triclosan mass balance

It is possible to estimate the mass of chemical remaining in the soil relative to that which was initially added; assuming that one mole of Me-TCS is derived from one mole of triclosan. This is shown in Fig. 3. The mass remaining at the end of the experiment is shown in Table 3. The fraction of added chemical recovered as triclosan or Me-TCS after one year ranged from 49.4% in the clay soil to 83.6% in the loamy sand. Interestingly, the fraction of the final chemical mass recovered in triclosan form was similar for all three soils (18%, 12% and 10% for the sand, loam and clay soils respectively), suggesting a high degree of primary degradation. However, a high fraction of the triclosan initially applied (66%, 64% and 39% in the case the sand, loam and clay soils, respectively) was recovered as Me-TCS at the end of the study period in the top 30 cm, suggesting that ultimate biodegradation rates were much lower. It is also noteworthy that approximately 50% of the applied chemical mass was extracted from the top layer of the loamy sand and sandy clay loam soils, in either parent or metabolite form (mainly as Me-TCS). Since Me-TCS is much less mobile in the soil than the parent compound, this material is unlikely to leach further except, perhaps, in colloidal form.

The fraction of chemical mass which could not be recovered at the end of the one year experiment may have been mineralised, or may have formed non-extractable (or bound) residues. The formation of bound residues is a common phenomenon in chemical fate studies in soils and sediments (Mordaunt et al., 2005; Wanner et al., 2005; Boethling et al., 2009). They are operationally described as the chemical mass or radiolabel remaining in the soil at the end of a fate study after exhaustive sequential extractions (Gevao et al., 2005). The mechanism of retention is often uncertain but may include covalent bonding (Haider et al., 1992), incorporation (polymerisation) of the chemical in soil organic matter (see Boethling et al., 2009) or physical entrapment of the compound in the soil organic or mineral matrix (Pignatello and Xing, 1996; Fu et al., 1994) or the sludge pellets themselves (Hörsing et al., 2011). The use of radiolabelled compounds has also shown that a chemical can be incorporated into the soil biomass (Vyas et al., 1994; Federle et al., 2002). Bound residues are often assumed to be stable and biologically unavailable, at least in the short term and, thus, they will generally not be mobile (Semple, 2009), although it is possible that colloidal transport may translocate some bound material. It is also possible that some remobilisation could occur following substantial changes in soil moisture content, temperature or pH (Höllrigl-Rosta et al., 2003), or through microbially mediated residue release (Roberts and Standen, 1981; Khan and Behki, 1990).

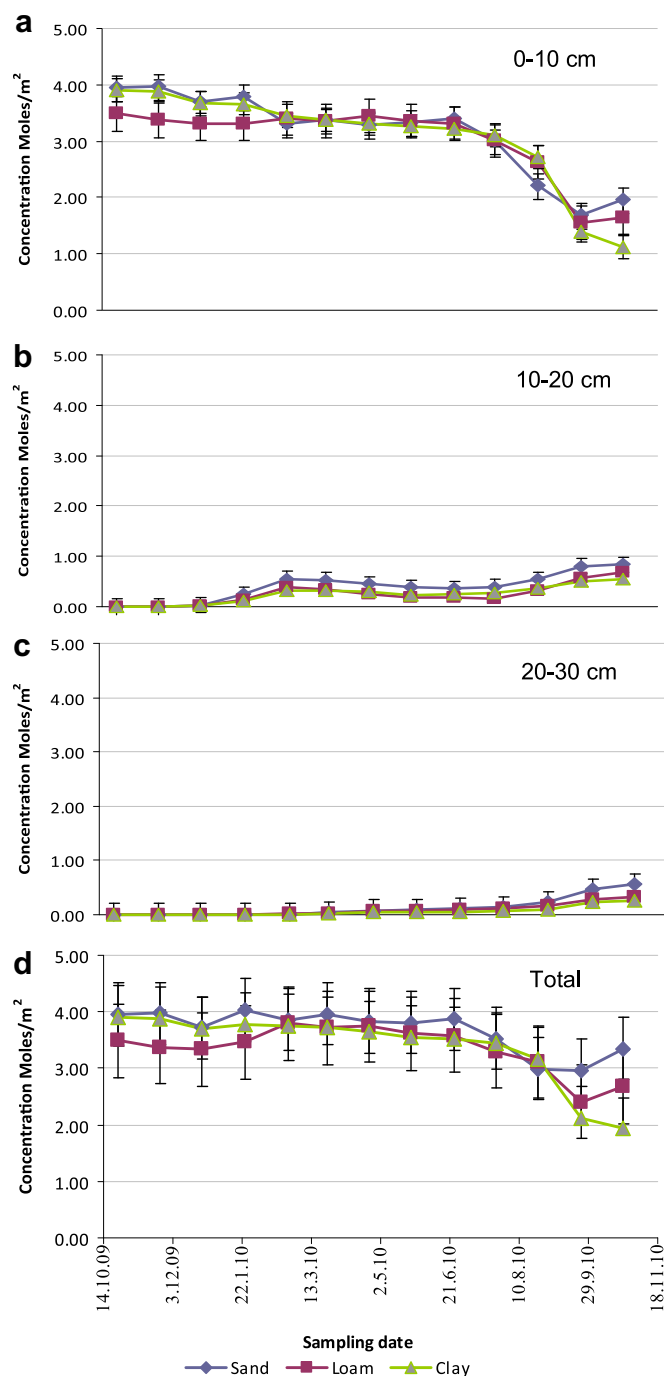


Fig. 3. The total amount (moles) of chemical recovered (triclosan and methyl-triclosan combined) for each soil in (a) 0–10 cm, (b) 10–20 cm, (c) 20–30 cm depth and (d) in all 3 layers.

4. Discussion

Although Me-TCS is just one of several potential metabolites resulting from the biodegradation of triclosan, the data presented here suggest that it is the most significant one in the agricultural soils receiving sludge. Microbially mediated degradation of triclosan is the only known source of Me-TCS (Lindström et al., 2002). In our study, between 59 and 73% of triclosan dissipation occurred between July and October in all soil types (Fig. 1). The close coincidence of declining triclosan concentration and increasing Me-TCS, particularly during the summer months provides convincing

Table 3
Mass balance calculations showing the amount of triclosan (TCS) and methyl-triclosan (Me-TCS) recovered in total in each soil layer in terms of mass and moles at the end of the experiment.

	Loamy sand soil			Sandy clay loam soil			Clay soil		
	Mass (μg)	Moles (mMol)	% of applied	Mass (μg)	Moles (mMol)	% of applied	Mass (μg)	Moles (mMol)	% of applied
TCS applied	914.9	3.164	100	773.5	2.679	100	948.6	3.284	100
TCS 0–10 cm	69.11	0.239	7.6	44.33	0.153	5.7	20.22	0.07	2.1
Me-TCS 0–10 cm	403.8	1.33	42.0	339.92	1.12	41.8	264.84	0.872	26.6
TCS 10–20 cm	36.39	0.126	4.0	19.78	0.068	2.5	49.69	0.172	5.2
Me-TCS 10–20 cm	164.38	0.541	17.1	143.09	0.471	17.6	90.62	0.299	9.1
TCS 20–30 cm	58.34	0.201	6.4	31.61	0.109	4.1	28.68	0.099	3.0
Me-TCS 20–30 cm	62.55	0.206	6.5	40.29	0.133	5.0	32.45	0.11	3.3
Total recovered (%)			83.6			76.7			49.4
Total TCS (%)			17.9			12.3			10.4
Total Me-TCS (%)			65.6			64.4			39.0

evidence for significant and seasonal biodegradation of triclosan. To some extent, this seasonality may account for some of the variation in triclosan half-lives reported in the literature (18–107 days: Ying et al., 2007; Lozano et al., 2010).

There are many factors that can affect the fate of organic chemicals in soil including abiotic factors (soil temperature, moisture content and land use), soil physical and chemical properties (e.g. texture, organic matter content, pH and porosity), chemical properties (molecular size and shape, degree of chlorination, pKa, aqueous solubility, hydrophobicity and vapour pressure) and the activities of soil biota and plants including adaptation of soil microorganisms to a particular chemical. Soil temperature can affect the rate of biodegradation by influencing soil microbial activity but will also affect partitioning. Neither triclosan nor Me-TCS are likely to be volatilised to any significant extent (the Henry's law constant for triclosan is $2.27 \times 10^{-3} \text{ Pa m}^3 \text{ mol}^{-1}$), although the methyl group on the Me-TCS will increase its volatility. Therefore the main fate processes are likely to be biodegradation, leaching, sorption to colloids – which can, themselves, be leached and sorption to the soil solid phase – which can be translocated via bioturbation (e.g. by earthworms).

The rate of triclosan degradation was relatively low during the winter period. This is likely to have been limited by high soil water content (which was above field capacity for much of the winter in all three soils), as well as by low temperatures. Triclosan degradation is known to be strictly an aerobic process (Ying et al., 2007). When soil moisture content is high, oxygen diffusion rates are limited and this can result in micro-aerobic or anaerobic conditions, particularly in aggregate centres (Arah and Smith, 1990), reducing overall microbial activity (Barros et al., 1995) and inhibiting aerobic degradation. Although soil microbial activity is often at its maximum at field capacity (Linn and Doran, 1984), it is interesting to note that rates of triclosan degradation appeared to be enhanced in our study (as evidenced by increased Me-TCS concentrations) at lower soil moisture contents from June onwards – even when approaching wilting point. This may have been promoted by increased soil temperatures during this period which may have increased microbial activity (Eash et al., 2008) and reduced sorption. For most organic pollutants, sorption to organic matter decreases with increasing temperature (ten Hulscher and Cornelissen, 1996; Schwarzenbach et al., 1993).

As expected, triclosan leaching, as evidenced by the appearance of triclosan in the 10–20 cm and 20–30 cm layers (Fig. 2), appears to have been most active during the winter period (November 2009 to February 2010), when the rate of soil water movement will be enhanced by high soil water content (increased hydraulic conductivity) and, in the study period, by heavy snow fall followed by thawing and heavy rainfall.

Soil pH can also affect the mobility of ionisable organic compounds, such as triclosan, in soil. Neutral triclosan tends to

dissociate to form a phenolate anion at high pH and this anion, will be repelled from negatively charged clay particles and from some organic colloids. Anionic triclosan, in addition to being more mobile, is photodegradable (Lyndall et al., 2010) – although this will be of limited relevance in soils. The ratio of anionic to neutral species can be calculated from

$$\log D = \log K_{OW} + \log \left[\frac{1}{1 + 10^{pH - pK_a}} \right] \quad (2)$$

where $\log D$ is the distribution coefficient (ratio of ionised to un-ionised compound) for a given pH and $\log K_{OW}$ is the octanol:–water partition coefficient (Thomas and Foster, 2005). The loamy sand soil studied here had an average pH of 8.2 which would result in 53.5% of the triclosan in anionic form at 25 °C. This compares with the sandy clay loam and clay soils which had average pH values of 6.6 and 7.1, respectively, resulting in respective ionised fractions of just 2% and 10%. This means that the mobility of both neutral triclosan and its phenolate ion in the loamy sand soil is likely to be much higher than in the other two soils due to a combination of relatively low organic matter content and relatively high pH. In addition to the loamy sand soil having an increased pH compared to the other soils, it also has a reduced CEC (6.6 cmol+/kg in the loamy sand, 13 cmol+/kg in the sandy loam and 13.5 cmol+/kg in the clay soil), which would reduce the ability of the soil to attract the triclosan, resulting in more movement. Biodegradation rates may also be enhanced because of the lower propensity of the anionic molecule to sorb to soil solids where it may be less accessible to microbes. The expectation of enhanced leaching is corroborated to some extent by the fact that concentrations of triclosan in the 10–20 cm layer of the loamy sand soil were higher than in the other two soils (Fig. 2) and by the fact that degradation rates (formation of Me-TCS) also appeared to be higher in this soil in all three layers. It is interesting to note that a marked decline in soil pH was observed in the sandy clay loam soil during the study. This could be due to the degradation of sludge which releases CO₂, to nitrification of mineralised N (which releases H⁺ ions) – again from the large volume of sludge applied or to the accumulation of organic acids generated during organic matter degradation (Veeresh et al., 2003), which can accumulate in small pores (Ngole, 2010). Dewatered sludge has been observed to significantly reduce soil pH due to the acidifying reactions of nitrogen and sulphur oxidation (Richards et al., 2000; Harrison et al., 1994). In any case, since the pH of this soil is already reasonably low (and, thus, the ionised fraction also low) such a pH change is unlikely to influence mobility or degradation rates.

Overall chemical recovery, triclosan or Me-TCS, was lowest in the clay soil (49% compared to 77% in the sandy clay loam and 84% in the loamy sand). This could be due to a higher rate of mineralisation in this soil, to the formation of undetermined metabolites or

to the higher organic matter content of this soil (Table 1) which will increase sorption (Agyin-Birikorang et al., 2010) and reduce both mobility (Behera et al., 2010) and degradation (as evidenced by a lower rate of Me-TCS formation). Fine textured soils generally have slower degradation rates than coarse sandy textured soils due to greater bioavailability in the coarser soils, especially at sub soil level (Rodríguez-Cruz et al., 2006). Higher organic matter content may also affect bound residue formation. Low recovery in the top 30 cm of the clay soil may also be a consequence of different leaching patterns in this soil. It is possible that triclosan advection in the clay matrix may have been limited by a higher fraction of immobile water (van Genuchten and Wierenga, 1977) in the smaller pores of this soil. On the other hand, preferential flow is a common feature of heavy soils, which are more likely to form cracks and macropores. It is, therefore, possible that some triclosan may have been leached beyond the top 30 cm of this soil.

Triclosan breakthrough occurred in December 2009 in the 10–20 cm layer and in February 2010 in the 20–30 cm layer in all three soils. Peak triclosan concentrations were observed in February 2010 (10–20 cm) – probably due to significant snow melt which occurred at this time in combination with heavy rainfall. As in the 0–10 cm layer, the rate of degradation of triclosan in the lower layers tended to increase, in all soils, when soil moisture content fell and temperatures increased. Although the data suggest that most Me-TCS in each layer was formed in situ, we cannot exclude the possibility that there may have been some translocation of Me-TCS from above, via leaching or bioturbation. Degradation rates of organic pollutants often decrease with depth (Soulas and Lagacherie, 2001). This can be attributed in part, to a decrease in organic matter content which will result in decreased microbial biomass implying that there may be less triclosan degradation in the lower depths compared to the top soil. Me-TCS formed in the upper layers of soil may rapidly become bound and unavailable for further degradation (Piutti et al., 2002).

The fact that the majority of the chemical extracted from all three soils at the end of the study was in Me-TCS form suggests that of the rate of primary degradation of triclosan was relatively high. This corroborates previous studies which have shown that triclosan can degrade rapidly (Ying et al., 2007; Lozano et al., 2010), although the formation of Me-TCS was not measured during these studies. The fact that most chemical was still in the upper 10 cm suggests that triclosan is not particularly mobile, again in broad agreement with previous work (e.g. Xu et al., 2009).

It is important to recognise that the concentrations of triclosan and Me-TCS reported here were extracted using a relatively harsh extraction process (ASE). Clearly not all of this extracted chemical will be bioavailable (Boethling et al., 2009). In addition, it is possible that some parent compound and metabolite was not extracted using the method employed, although the ASE is thought to be one of the most efficient extraction techniques available. In a previous laboratory incubation study using ^{14}C triclosan (Butler et al., 2010) we observed that only a small fraction of the radiolabelled sample applied to soil (ca. 1%) was extractable using CaCl_2 , which is considered to be the readily available fraction (Gevao et al., 2005) and a combined total of approximately 35% of the radiolabel was extractable using a mild solvent extraction system using methanol, representing the potentially available fraction (Mordaunt et al., 2005). This suggests that relatively little of the triclosan and Me-TCS measured in the field soils may be bioavailable.

There are no studies to the best of our knowledge showing the degradation of any chloroanisole compound under aerobic conditions. However previous work has shown that chloroanisoles can be degraded under anaerobic conditions in the presence of selected soil microbes such as *Desulfotobacterium frappieri* (Dennie et al., 1998). This could offer some explanation for the apparent

persistence of Me-TCS in the soils at the end of the field study. The majority of Me-TCS was formed at a time when the soil was aerobic. However, Me-TCS may be degraded under anaerobic conditions the following winter as observed with 2,4,6-trichloroanisole, which is first O-demethylated before being dehalogenated and ultimately mineralised (Goswami et al., 2007).

It is noteworthy that the sludge application rate used in the current study was over 5 times greater than the rate generally used operationally in the UK of 8–10 tonnes per hectare, although usage levels depend on the nutrient content of the soil and in the sewage sludge. An increase in the application rate could have the effect of altering the degradation kinetics in the soil by altering the soil physical and chemical properties (Weber et al., 2007) or by exerting toxic effects on soil microbes. However, the soil concentrations of triclosan observed here were clearly below any expected effect thresholds. Such high applications of biosolids would also have the affect of increasing the concentration of total nitrogen in the soil, which in turn would result in an increase in nitrifying bacteria. Certain nitrifiers have been observed to degrade triclosan, especially in the presence of enzymes produced by ammonia oxidising bacteria, which can function as a catalyst for triclosan degradation in the wastewater treatment facility (Roh et al., 2009). However, it is also possible that nitrifiers in the soil convert triclosan into Me-TCS as a defence mechanism against triclosan toxicity. This would need to be confirmed or refuted by further study.

5. Conclusions

Changes in the concentrations of triclosan and Me-TCS were observed at three different depths in three different agricultural soils over a one year period. Decreases in the concentration of triclosan were due to a combination of biodegradation, leaching, bioturbation and possibly the formation of non-extractable residues. Further work would need to be undertaken to determine whether triclosan or Me-TCS form non-extractable residues in field soils and whether their formation reduces toxicity due to being non-bioavailable to the soil microbes. All these processes have a strong seasonal component – being driven by changes in temperature, water content and drainage rates.

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