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Comparison of degradation between indigenous and spiked bisphenol A and triclosan in a biosolids amended soil

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HIGHLIGHTS

- Degradation of indigenous and spiked compounds from biosolids were compared.
- Differences were observed for both the rate and pattern of degradation.
- Spiked bisphenol A entirely degraded however the indigenous compound remained.
- TCS was detectable during the experiment however the degradation patterns varied.
- Spiking experiments may not be suitable to predict degradation of organic compounds.

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ABSTRACT

This study compared the degradation of indigenous bisphenol A (BPA) and triclosan (TCS) in a biosolids-amended soil, to the degradation of spiked labelled surrogates of the same compounds (BPA-d_{16} and TCS-$^{13}C_{12}$). The aim was to determine if spiking experiments accurately predict the degradation of compounds in biosolids-amended soils using two different types of biosolids, a centrifuge dried biosolids (CDB) and a lagoon dried biosolids (LDB). The rate of degradation of the compounds was examined and the results indicated that there were considerable differences between the indigenous and spiked compounds. These differences were more marked for BPA, for which the indigenous compound was detectable throughout the study, whereas the spiked compound decreased to below the detection limit prior to the study completion. The rate of degradation for the indigenous BPA was approximately 5-times slower than that of the spiked BPA-d_{16}. The indigenous and spiked TCS were both detectable throughout the study, however, the shape of the degradation curves varied considerably, particularly in the CDB treatment. These findings show that spiking experiments may not be suitable to predict the degradation and persistence of organic compounds following land application of biosolids.

1. Introduction

The release of the plasticizer bisphenol A (4,4′-(propane-2,2-diyl) diphenol) (BPA) and the antimicrobial agent triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) (TCS) into the environment through the application of biosolids to agricultural land has received increasing interest recently due to their high toxicity and/or their potential to cause endocrine disruption in exposed organisms (e.g. Orvos et al., 2002; Fukuhori et al., 2005; Veldhoen et al., 2006; Crofton et al., 2007; Waller and Kookana, 2009). These compounds are considered to be relatively hydrophobic, with log K_{ow} values of 3.32 and 4.76, respectively (Langdon et al., 2010); therefore, they are likely to have a high affinity to the solid phase in soils and biosolids, which in turn may influence their likelihood for degradation. Following the release of these compounds into the environment, an understanding of their potential to persist is required in order to assess the associated environmental risks.

The length of time required for BPA and TCS to degrade when added to soils has been assessed in several laboratory-based studies that have involved spiking elevated concentrations of compounds into soil samples and examining changes in concentration over time. Spiking experiments are commonly used to examine the degradation of organic compounds in soils because they enable control of the concentration levels of the compounds and ensure easy detection and interpretation of data. In general, BPA and TCS have been shown to degrade under aerobic conditions, with little or no degradation occurring under anaerobic conditions (McAvoy et al., 2002; Ying and

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Kookana, 2005; Press-Kristensen et al., 2008). Half-lives or DT50s (time taken for the concentration of the compound to decrease by 50%) of these compounds in spiking experiments have been reported for BPA to range from 1 to 7 days (Ying and Kookana, 2005; Xu et al., 2009) and for TCS to range from 13 to 58 days (Ying et al., 2007; Wu et al., 2009a; Xu et al., 2009).

The degradation of BPA and TCS in soils following the addition of biosolids was recently examined in laboratory incubation experiments by Langdon et al. (2011a). The study involved examining the degradation of the compounds that were indigenous to biosolids at the time of soil addition. The results obtained indicated that when BPA and TCS were indigenous to biosolids at the time of soil addition the DT50 values obtained were longer than those reported in previous research that had involved spiking the compounds into soil or biosolids-amended soil. Although variations in DT50 values were observed, it is difficult to draw direct comparisons between different studies due to varying soil types and experimental conditions. Therefore, a comparison of degradation rates between indigenous and spiked compounds, under the same experimental conditions is warranted.

The degradation data for indigenous BPA and TCS in the previous study (Langdon et al., 2011a) clearly showed a biphasic pattern with a readily degradable fraction and a recalcitrant fraction that remained through to the completion of the 224 day study. A schematic diagram of a biphasic degradation model is shown in Langdon et al. (2011a). There are several possible mechanisms that could explain the presence of recalcitrant fractions of compounds in biosolids (or similar matrices), including heterogeneous aggregates that contain anaerobic zones and the non-reversible sorption of compounds into the biosolids matrix resulting in decreased availability for microbial degradation (Hesselsoe et al., 2001; Sjöström et al., 2008; Wu et al., 2009b; Katayama et al., 2010). However, irrespective of the mechanisms responsible, if the degradation of the compounds is influenced by the biosolids matrix, it raises the question of whether conducting degradation experiments that involve using spiked compounds will yield the same results as experiments with compounds indigenous to biosolids. Therefore, the aim of the current study was to compare the degradation of BPA and TCS indigenous to biosolids at the time of soil addition to that of isotopically labelled surrogates of the same compounds that were spiked into a biosolids-amended soil. The use of isotopically labelled surrogates means that both the indigenous compounds and the spiked compounds can be identified within the same sample.

2. Materials and methods

2.1. Soil and biosolids

A bulk soil sample was collected from a field site at Mount Compass in South Australia (SA), Australia (35°21′44.95 S and 138°32′ 44.95 E), which is located approximately 70 km south of Adelaide, for use in this study. The site had no history of previous biosolids or sewage sludge applications. The soil had a pH of 4.4 (determined from a soil solution ratio of 1:5 in 0.01 M $CaCl_2$), an organic carbon content of 2.5% and consisted of 96% sand, 2.5% silt and 1.5% clay. The bulk sample was dried at 40 °C prior to being homogenised by grinding with a mortar and pestle and sieved to 2 mm. Three subsamples were removed from the dried homogenised soil for chemical analysis using the method outlined below to test for background concentrations of BPA or TCS prior to the commencement of experimental work.

Two biosolids were collected from a local wastewater treatment plant (WWTP) for use in this study. The WWTP serviced part of the city of Adelaide, therefore, the wastewater input was predominately from a residential source with some industrial inputs. Both biosolids had been treated by anaerobic digestion and thereafter one of the biosolids had been centrifuge dried (CDB) and the other had been solar dried in a lagoon system (LDB). The pH of the biosolids produced at the site is approximately 7.4 ($CaCl_2$) (Heemsbergen et al., 2009) and the total C was determined to be 13.6% and 8.1% for the CDB and LDB, respectively. The CDB was collected immediately following centrifugation, whereas the LDB was collected from a stockpile that had completed treatment less than one month prior to collection. At the time of collection the biosolids were thoroughly mixed. The moisture contents of the biosolids were 63% for the CDB and 52% for the LDB and for the experimental work undertaken in this study, the biosolids were used as collected (i.e., wet). Triplicate sub-samples were removed from each of the biosolids samples and freeze dried for analysis of the target compounds using the method outlined in Langdon et al. (2011b). The concentrations of the target compounds in the biosolids samples can be found in Langdon et al. (2011a).

2.2. Experimental design and setup

Individual 50 g samples were weighed from the dried bulk soil into glass jars and hydrated to 50% of their maximum water holding capacity (MWHC) with Milli Q (MQ) water (the method used to determine the MWHC is outlined in Jenkinson and Powlson, 1976). All samples were then placed in closed containers in the dark and pre-incubated at 22 °C for 14 days to rejuvenate and stabilise soil microbial communities. After the pre-incubation, either the CDB or LDB were added to the hydrated soil, at a rate equivalent to 50 dry t/ha (assuming a soil bulk density of 1.3 g/cm^3 and an incorporation depth of 10 cm) and mixed throughout the sample. All of the samples were then spiked with 200 μL of a stock solution containing the isotopically labelled compounds BPA-d_{16} and TCS-$^{13}C_{12}$ in methanol (at a concentration of 25 mg/L). The expected soil concentration in each of the samples was 96 μg/kg for both BPA-d_{16} and TCS-$^{13}C_{12}$. Immediately following spiking, five replicate samples from each of the biosolids treatments were freeze dried and stored in sample jars, in the dark until analysed as the initial sample (t_0). All the remaining sample jars were weighed, then placed on wet paper towel in containers with lids and kept in the dark at a constant temperature of 22 °C. The containers were opened to the air daily and the moisture content in the samples was maintained throughout the experiment by weight. At eight additional sampling times (3, 7, 14, 28, 56, 112, 168 and 224 days post biosolids addition and sample spiking), triplicate samples were removed from each of the biosolids treatments and freeze dried for immediate analysis of the target compounds. All decreases in the concentration of the compounds were assumed to be through degradation as a closed system was used, preventing the loss of the compounds through other processes of dissipation (e.g. leaching).

2.3. Sample extraction and gas chromatography–mass spectrometry analysis (GC–MS)

The method used for sample extraction and analysis in this study was based on that outlined in Langdon et al. (2011b), with the only variation being that in the current study a 10 g sample of biosolids-amended soil was extracted and analysed, as opposed to a 1 g sample. In brief, each freeze dried sample was extracted three times with a 1:1 mixture of methanol and acetone (15 mL) in an ultrasonic bath. For each sample the extracts were combined then diluted with MQ water and loaded onto an Oasis HLB® solid phase extraction (SPE) cartridge. Elution of the samples was conducted using 3 × 2.5 mL methanol, followed by 3 × 2.5 mL acetone, then 3 × 2.5 mL ethyl acetate and finally reconstituted in 4 mL of methanol. Each sample was then derivatized in 400 μL of pyridine and 100 μL of the silylation agent N,O-bis-(trimethylsilyl)-trifluorocetamide (BSTFA) + 1% trimethyl-chlorosilane (TMCS) (based on the method of Shareef et al. (2006)) and anthracene-d_{10} was added to each sample as an instrument internal standard (IS). Along with each batch of samples, a method blank was

run (i.e. a tube containing no biosolids) to detect any background contamination from any of the solvents or sample preparation steps. Samples were analysed using an Agilent 6890 Series GC system that was interfaced with an Agilent 5973 Network MS. The specific details of the GC–MS parameters, the typical retention times of each of the compounds and target and qualifier ions are reported in Langdon et al. (2011b). The concentrations of each of the compounds were determined from relative response factors based on the IS and then adjusted for extraction recoveries. The extraction recoveries were determined by spiking the labelled surrogates, BPA-d_{16} and TCS-$^{13}C_{12}$, into an additional set of samples at a known concentration one day prior to the commencement of extraction. The additional set of samples were extracted and analysed concurrently with the test samples to determine the extraction recoveries. The limit of detection (LOD) and limit of quantification (LOQ) for each of the compounds were determined as 3- and 10-times the signal to noise ratio and were 0.3 and 1.0 μg kg^{-1}, respectively, for BPA and BPA-d_{16}, and 0.8 and 2.7 μg kg^{-1}, respectively, for TCS and TCS-$^{13}C_{12}$.

2.4. Statistical analysis and interpretation

The statistical analyses conducted on the degradation data included a univariate analysis of variance (ANOVA) to determine if the concentrations of the compounds significantly changed over the 224 days of the experiment, using SPSS® Version 17. Nonlinear regressions were also conducted to determine the rate and pattern of degradation for each compound. There were two nonlinear regression models fitted to the degradation data of each compound based on first-order kinetics, using SigmaPlot®: a standard first order decay model and a biphasic degradation model. For the majority of cases, the degradation data was best explained by the biphasic model, therefore, only this data is presented. All of the statistical information relating to both the first order model and the biphasic model from this study can, however, be found in Supplementary information. The biphasic model that was used accounts for a degrading fraction and a recalcitrant fraction of the compounds and is defined by Eq. (1). The rate constant (k) from the biphasic model was used to calculate the time required for 50% of the degrading fraction to decompose ($DT50_{biphasic}$), and a y-intercept (x_0), which indicates the concentration of the recalcitrant fraction.

$$C_t = \left(C_0 e^{-kt}\right) + x_0 \quad (1)$$

3. Results

3.1. Data quality assurance and extraction recoveries

The average extraction recovery of BPA was 104% in the CDB treatment and 96% in the LDB treatment, with a relative standard deviation (RSD) of less than 25% across all the batches of samples analysed. For TCS, the average extraction recovery was 84% in the CDB treatment and 91% in the LDB treatment, with a RSD of less than 20%. The method blank samples that were analysed with each batch of samples showed concentrations of BPA and TCS that were below the LOD in all cases.

3.2. Degradation of bisphenol A and bisphenol A-d_{16}

At the commencement of the study, the initial t_0 samples in the CDB treatment showed concentrations of 6.4 μg/kg and 81 μg/kg for indigenous BPA and spiked BPA-d_{16}, respectively, whereas in the LDB treatment the t_0 concentrations were 11 μg/kg and 97 μg/kg, respectively (Table 1). In both treatments, the concentrations of BPA and BPA-d_{16} were found to significantly decrease during the study ($p<0.001$), however, the indigenous BPA remained above the LOD through to the completion of the study (Figs. 1 and 2). In contrast, the concentration of the spiked BPA-d_{16} decreased to below the LOD prior to the completion of the study (56 days post biosolids addition in the CDB treatment and 168 days post biosolids addition in the LDB treatment). The degradation data for the indigenous BPA and spiked BPA-d_{16} is shown in Figs. 1 and 2 and data is only presented for the duration of the study where the concentrations of the compounds were above the LOD.

The fit of the biphasic degradation model was significant for the indigenous and spiked BPA and BPA-d_{16} in both of the biosolids treatments (all p-values<0.001). In the CDB treatment, the rate of degradation, represented by the $DT50_{biphasic}$, was 5–5.6 days for the indigenous BPA, whereas for the spiked BPA-d_{16} it was 1–1.4 days (Table 2). This indicates that the rate of degradation of the spiked compounds was approximately 5-times faster than that of the indigenous compound. The recalcitrant concentration of the indigenous BPA was similar in both of the biosolids treatments and ranged from 2.2 to 2.5 μg/kg, which corresponded to 33% and 23% of the initial concentration (C_0, predicted by the regression model) in the CDB and LDB treatments, respectively (Table 2). In contrast, no recalcitrant fraction of the spiked BPA-d_{16} was present, due to the decrease in the concentration of this compound to below the LOD.

3.3. Degradation of triclosan and triclosan-$^{13}C_{12}$

In the initial t_0 samples, the concentrations of indigenous TCS were 213 μg/kg in the CDB treatment and 361 μg/kg in the LDB treatment, whereas the concentrations of the spiked TCS-$^{13}C_{12}$ were 88 and 80 μg/kg, respectively (Table 1). Over the duration of the study, the concentrations of both the indigenous and spiked compounds were found to decrease significantly ($p<0.001$); however, in all cases the concentrations remained above the compound LOD concentrations for the duration of the study (Figs. 3 and 4).

It is evident from Fig. 3 that the indigenous TCS showed a very different pattern of degradation to the spiked TCS-$^{13}C_{12}$ in the CDB treatment. The indigenous TCS showed a very rapid decrease in concentration of the degrading fraction with a $DT50_{biphasic}$ of <1 day and a recalcitrant fraction of 96 μg/kg (Table 2). This pattern is very similar to that observed in the previous laboratory-based degradation study (Langdon et al., 2011a). The spiked TCS-$^{13}C_{12}$ showed a slower decrease in concentration of the degrading fraction with a $DT50_{biphasic}$ of 27 days and a smaller recalcitrant concentration of 16 μg/kg. Although this recalcitrant concentration of the spiked compound was lower than the indigenous compound, it does indicate that there was some non-reversible sorption and development of a recalcitrant fraction of the spiked TCS-$^{13}C_{12}$, during this study. The large difference in the $DT50_{biphasic}$ values between the indigenous and spiked compounds may be due to a release of bound indigenous TCS at the commencement of the study, due to the change in pH (the biosolids pH was 7.4, whereas the soil pH was 4.4), resulting in it being more available for biodegradation.

In the LDB treatment there was little difference between the degradation of the indigenous and spiked TCS and TCS-$^{13}C_{12}$; however,

Table 1
The average and range of measured concentrations of bisphenol A (BPA), bisphenol A-d_{16} (BPA-d_{16}), triclosan (TCS) and triclosan-$^{13}C_{12}$ (TCS-$^{13}C_{12}$) for the initial (t_0) soil sample for the centrifuge dried biosolids (CDB) and lagoon dried biosolids (LDB) treatments.

Biosolids treatment	Initial compound concentration (μg/kg)			
	BPA	BPA-d_{16}	TCS	TCS-$^{13}C_{12}$
CDB	6.4 (5.0–7.8)	81 (72–92)	213 (166–263)	88 (77–101)
LDB	11 (4.1–21)	97 (78–123)	361 (149–572)	80 (52–108)

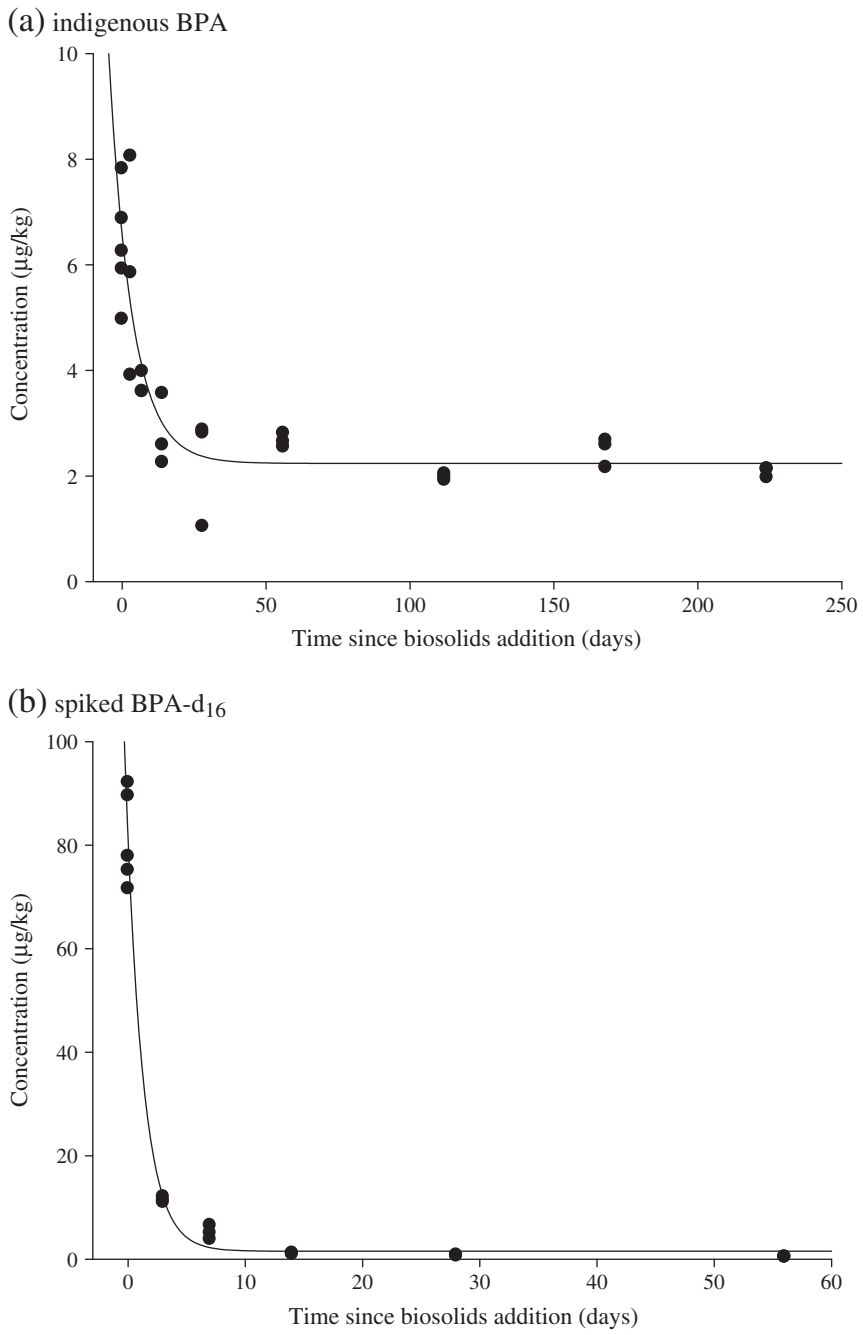

Fig. 1. Degradation of (a) indigenous BPA and (b) spiked BPA-d_{16} following the addition of centrifuge dried biosolids (CDB) to a soil, with the fit of a biphasic degradation model. Note that (b) only presents data for the duration of the experiment where the compound was above the limit of detection.

the $DT50_{biphasic}$ value was slightly longer for the indigenous compound (49 days) compared to the spiked compound (36 days; Table 2). Again, a recalcitrant fraction of the spiked TCS-$^{13}C_{12}$ developed over the duration of the study (12 µg/kg); however, similar to the CDB treatment this was considerably lower than the recalcitrant concentration of the indigenous compound in the same biosolids treatment (59 µg/kg) (Table 2).

4. Discussion

Overall, the degradation data obtained in this study showed that there were differences in the degradation of the compounds indigenous to biosolids compared to the same compounds (differentiated through isotopic labelling) spiked into a soil and biosolids matrix. These differences were very clear for BPA and BPA-d_{16} in both the biosolids treatments examined, where the concentration of the spiked compound decreased to below the LOD, in contrast to the indigenous compound which remained above the LOD. In addition, the rates of degradation of the indigenous and spiked BPA and BPA-d_{16}, as reflected in $DT50_{biphasic}$ values, were very different with the indigenous compound degrading approximately 5-times more slowly than the spiked compound.

The differences observed for TCS were not as clear as for BPA, however, some comparisons can still be made. In the CDB treatment, the parameters required to describe the degradation model were very different between the indigenous and spiked compounds. The rate of degradation of the degrading fraction was considerably faster for the indigenous compound (at least 27-times) and the recalcitrant fraction was much higher. In comparison, in the LDB treatment the

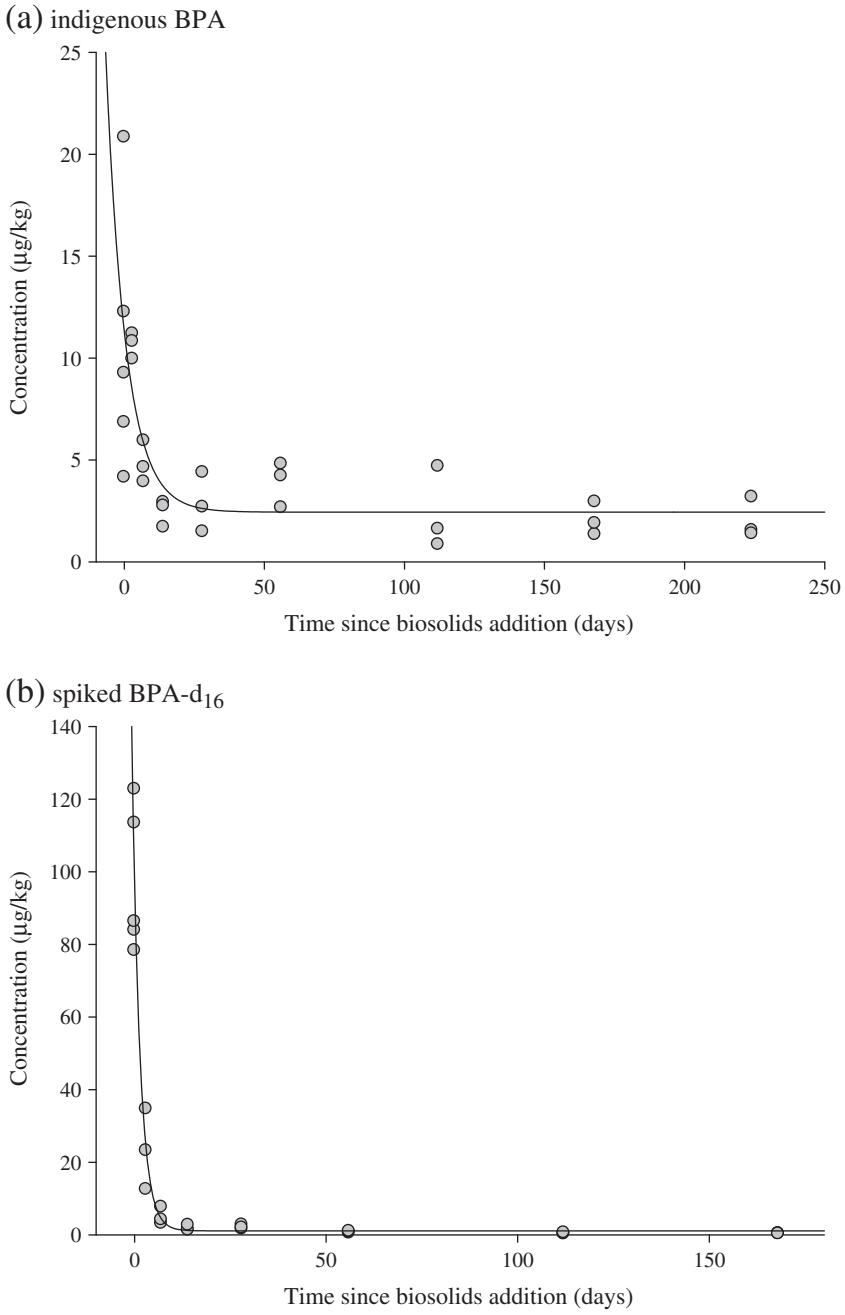

Fig. 2. Degradation of (a) indigenous BPA and (b) spiked BPA-d_{16} following the addition of lagoon dried biosolids (LDB) to a soil, with the fit of a biphasic degradation model. Note that (b) only presents data for the duration of the experiment where the compound was above the limit of detection.

Table 2
Summary of the degradation information from the biphasic model for the compounds bisphenol A (BPA), bisphenol A-d_{16} (BPA-d_{16}), triclosan (TCS) and triclosan-$^{13}C_{12}$ (TCS-$^{13}C_{12}$) for the centrifuge dried biosolids (CDB) and lagoon dried biosolids (LDB) treatments. The dissipation half lives ($DT50_{biphasic}$) are shown in days and the recalcitrant concentration is shown in µg/kg with the corresponding fraction of the predicted initial concentration (C_0) shown in brackets.

Measure	Centrifuge dried (CDB)		Lagoon dried (LDB)		Centrifuge dried (CDB)		Lagoon dried (LDB)	
	BPA	BPA-d_{16}	BPA	BPA-d_{16}	TCS	TCS-$^{13}C_{12}$	TCS	TCS-$^{13}C_{12}$
R^2	0.80	0.98	0.60	0.95	0.74	0.83	0.42	0.81
C_0 (µg/kg)	6.6	81	11	97	213	80	274	80
$DT50_{biphasic}$	5.6	1.0	5.0	1.4	<1	27	49	36
Recalcitrant concentration	2.2 (0.33)	<0.3	2.5 (0.23)	<0.3	96 (0.45)	16 (0.20)	59 (0.22)	12 (0.15)

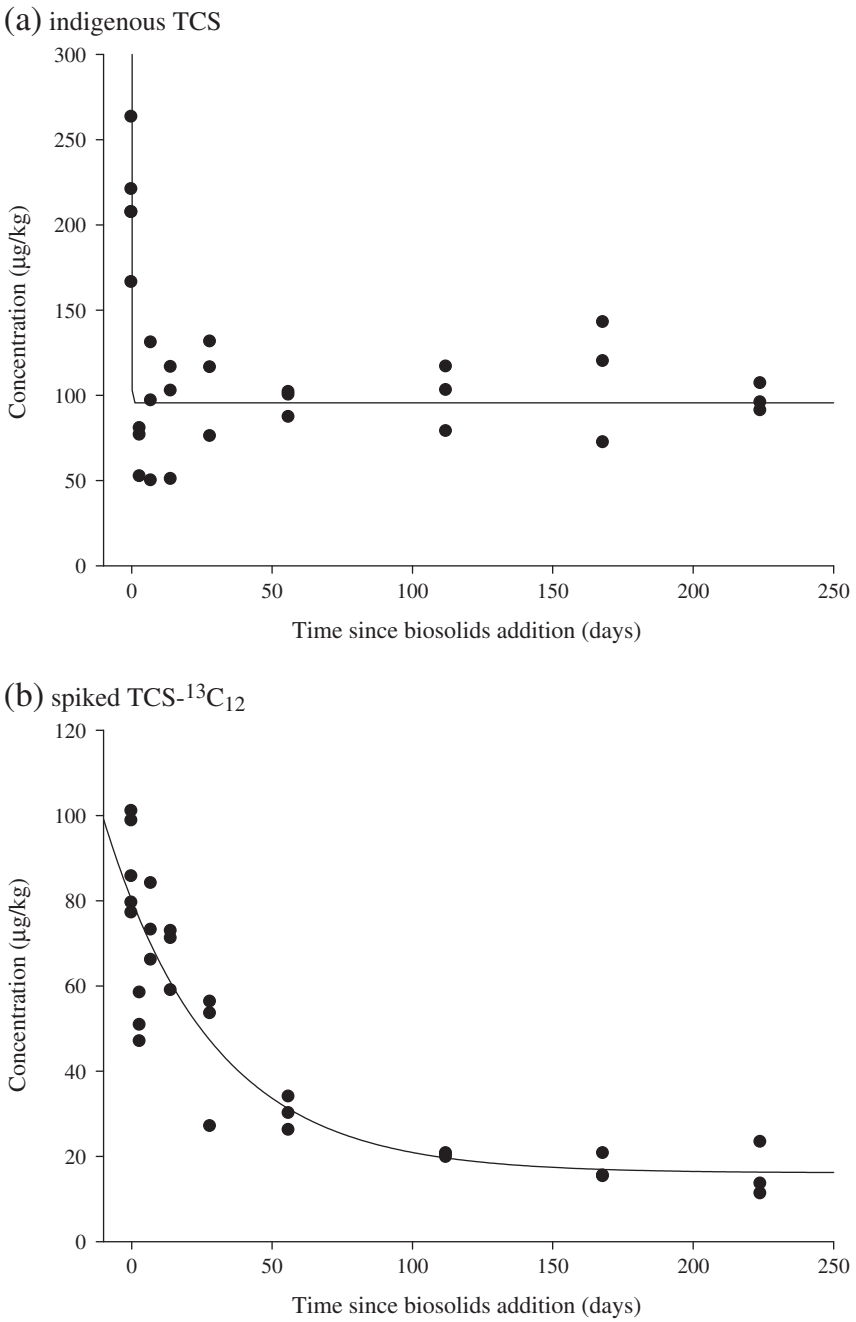

Fig. 3. Degradation of (a) indigenous TCS and (b) spiked TCS-$^{13}C_{12}$ following the addition of centrifuge dried biosolids (CDB) to a soil, with the fit of a biphasic degradation model.

differences between the indigenous and spiked compounds were not as marked and there were only small differences observed in the $DT50_{biphasic}$ values for the indigenous and spiked compounds, whereby the indigenous compound degraded at a rate only 1.6-times slower than that of the spiked compound. These differing results between the biosolids treatments for TCS show that there is some influence of the biosolids matrix on the degradation of the indigenous and spiked forms of TCS in the two biosolids treatments examined, which may be influenced in part by the variations in total C of the two biosolids (13.6% in the CDB and 8.1% in the LDB).

The differences observed in this study between the degradation of the indigenous and spiked compounds indicate that the use of spike degradation experiments may not provide an accurate assessment of the persistence of organic compounds following biosolids application to land. This finding may also apply to other organic soil amendments that are applied to agricultural land such as animal manures. In most cases, the rates of degradation were faster for the compounds that had been spiked into the samples compared to the indigenous compounds. In addition to this, it was clear that when BPA was added to a soil as an indigenous component of biosolids, there was a fraction that was recalcitrant, whereas when BPA was spiked into the soil–biosolids mix, there was no recalcitrant fraction. This indicates that the use of spiked degradation experiments may not account for the recalcitrant fraction that may be present for some compounds in biosolids-amended soils.

In other studies, recalcitrant fractions of compounds in biosolids or biosolids-amended soils have also been observed (e.g. Hesselsoe et al., 2001; Sjöström et al., 2008; Wu et al., 2009b). It is unclear what mechanism is responsible for this, however, there are several possibilities. The presence of anaerobic zones within the aggregates

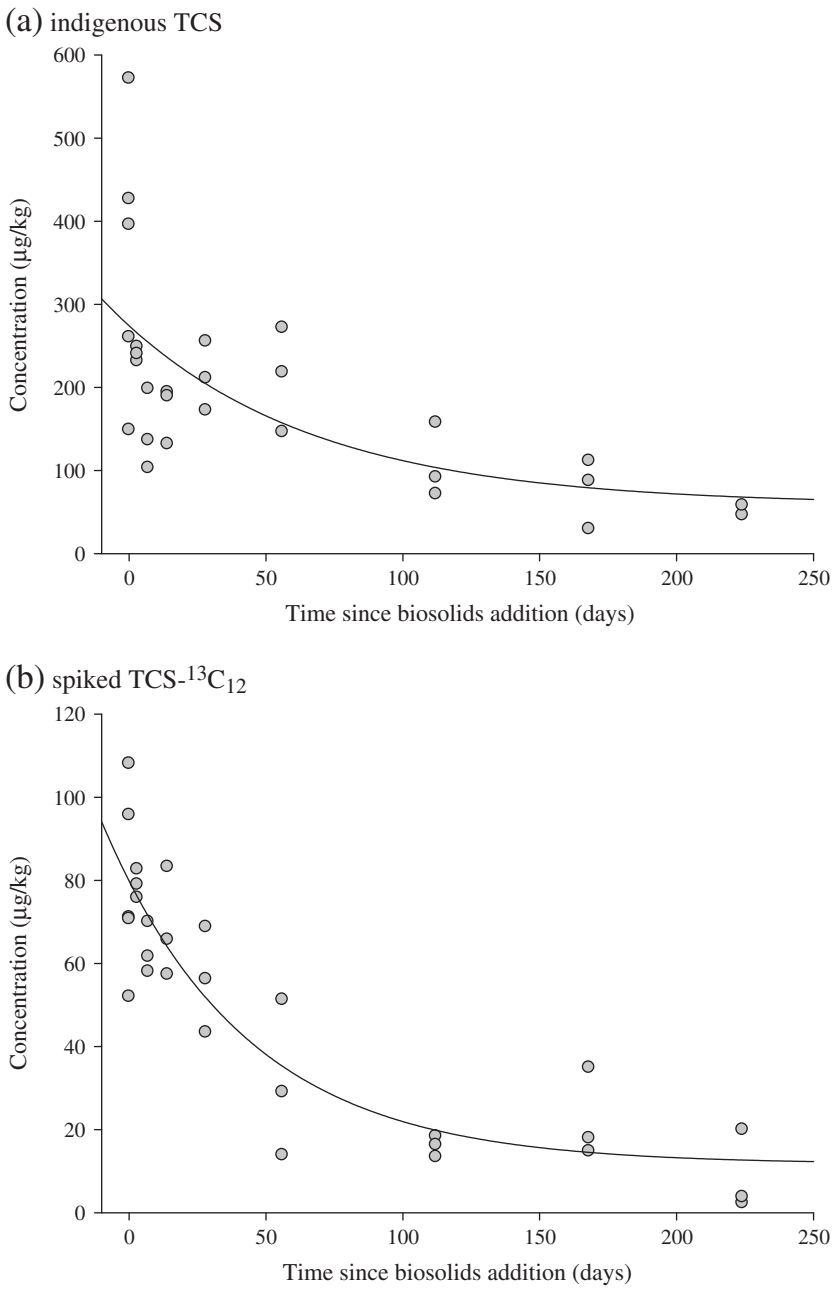

Fig. 4. Degradation of (a) indigenous TCS and (b) spiked TCS-$^{13}C_{12}$ following the addition of lagoon dried biosolids (CDB) to a soil, with the fit of a biphasic degradation model.

of biosolids (due to the propensity of biosolids to clump) may result in delayed degradation due to limited oxygen availability (Hesselsoe et al., 2001). Both of the compounds assessed in this study degrade solely under aerobic conditions (McAvoy et al., 2002; Ying and Kookana, 2005; Press-Kristensen et al., 2008), therefore limited oxygen availability is likely to influence the degradation rates of the compounds. A second possibility relates to non-reversible sorption of the compounds to the biosolids matrix (Wu et al., 2009b). It is possible that this non-reversible sorption, or ageing of the compounds within the matrix, results from the delayed degradation of these compounds that may occur during the anaerobic digestion process. As biosolids matrices can be particularly complex and contain various components, sorption may vary from one biosolids to another. Compounds that are spiked into biosolids or biosolids-amended soils are unlikely to sorb to the matrix in the same manner as compounds that become sorbed to biosolids through the treatment process. In addition, the distribution of a spiked compound within a biosolids aggregate is likely to differ to that of a compound that is indigenous to a biosolids sample. The spiked compound is likely to sorb to the outer portions of a biosolids aggregate and therefore be more available to microbes in the presence of oxygen, which will result in faster rates of degradation. It should be noted, however, that if the differences observed for the indigenous compounds are due to decreases in bioavailability, the indigenous compounds may be less likely to exert toxic effects on soil organisms than spiked compounds. Further studies examining the bioavailability of compounds indigenous to biosolids are therefore warranted. Although it is unclear what mechanism or combination of mechanisms are responsible for the differing degradation of the compounds assessed in this study, the results indicate that the use of spiking experiments to predict the degradation of compounds following addition of biosolids to land may provide inaccurate estimates of persistence. Although this study examined only two

compounds in two biosolids, the results are likely to be relevant for other organic compounds found in biosolids and potentially other organic amendments that are applied to land.

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References

Crofton KM, Paul KB, De Vito MJ, Hedge JM. Short-term in vivo exposure to the water contaminant triclosan: evidence for disruption of thyroxine. Environ Toxicol Pharm 2007;24:194–7.

Fukuhori N, Kitano M, Kimura H. Toxic effects of bisphenol A on sexual and asexual reproduction in *Hydra oligactis*. Arch Environ Contam Toxicol 2005;48:495–500.

Heemsbergen DA, Warne MStJ, Broos K, Bell M, Nash D, McLaughlin M, et al. Application of phytotoxicity data to a new Australian soil quality guideline framework for biosolids. Sci Total Environ 2009;407:2546–56.

Hesselsoe M, Jensen D, Skals K, Olesen T, Moldrup P, Roslev P, et al. Degradation of 4-nonylphenol in homogeneous and nonhomogeneous mixtures of soil and sewage sludge. Environ Sci Technol 2001;35:3695–700.

Jenkinson DS, Powlson DS. The effects of biocidal treatments on metabolism in soil — V. A method for measuring soil biomass. Soil Biol Biochem 1976;8:209–13.

Katayama A, Bhula R, Burns GR, Carazo E, Felsot A, Hamilton D, et al. Bioavailability of xenobiotics in the soil environment. Rev Environ Contam Toxicol 2010;203:1-86.

Langdon KA, Warne MStJ, Kookana RS. Aquatic hazard assessment for pharmaceuticals, personal care products and endocrine disrupting compounds from biosolids-amended land. Integr Environ Assess Manag 2010;6:663–76.

Langdon KA, Warne MStJ, Smernik RJ, Shareef A, Kookana RS. Degradation of 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan following biosolids addition to soil under laboratory conditions. Chemosphere 2011a;84:1556–62.

Langdon KA, Warne MStJ, Smernik RJ, Shareef A, Kookana RS. Selected personal care products and endocrine disruptors in biosolids: an Australia-wide survey. Sci Total Environ 2011b;409:1075–81.

McAvoy DC, Schatowitz B, Jacob M, Hauk A, Eckhoff WS. Measurement of triclosan in wastewater treatment systems. Environ Toxicol Chem 2002;21:1323–9.

Orvos DR, Versteeg DJ, Inauen J, Capdevielle M, Rothenstein A, Cunningham V. Aquatic toxicity of triclosan. Environ Toxicol Chem 2002;21:1338–49.

Press-Kristensen K, Lindblom E, Schmidt JE, Henze M. Examining the biodegradation of endocrine disrupting bisphenol A and nonylphenol in WWTPs. Water Sci Technol 2008;57:1253–6.

Shareef A, Angove MJ, Wells JD. Optimization of silylation using N-methyl-N-(trimethylsilyl)-trifluoroacetamide, N, O-bis-(trimethylsilyl)-trifluoroacetamide and N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide for the determination of the estrogens estrone and 17 alpha-ethinylestradiol by gas chromatography–mass spectrometry. J Chromatogr A 2006;1108:121–8.

Sjöström ÅE, Collins CD, Smith SR, Shaw G. Degradation and plant uptake of nonylphenol (NP) and nonylphenol-12-ethoxylate (NP12EO) in four contrasting agricultural soils. Environ Pollut 2008;156:1284–9.

Veldhoen N, Skirrow RC, Osachoff H, Wigmore H, Clapson DJ, Gunderson MP, et al. The bactericidal agent triclosan modulates thyroid hormone-associated gene expression and disrupts postembryonic anuran development. Aquat Toxicol 2006;80:217–27.

Waller NJ, Kookana RS. Effect of triclosan on microbial activity in Australian soils. Environ Toxicol Chem 2009;28:65–70.

Wu CX, Spongberg AL, Witter JD. Adsorption and degradation of triclosan and triclocarban in soils and biosolids-amended soils. J Agric Food Chem 2009a;57:4900–5.

Wu CX, Spongberg AL, Witter JD. Sorption and biodegradation of selected antibiotics in biosolids. J Environ Sci Health A 2009b;44:454–61.

Xu J, Wu LS, Chang AC. Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils. Chemosphere 2009;77:1299–305.

Ying GG, Kookana RS. Sorption and degradation of estrogen-like-endocrine disrupting chemicals in soil. Environ Toxicol Chem 2005;24:2640–5.

Ying GG, Yu XY, Kookana RS. Biological degradation of triclocarban and triclosan in a soil under aerobic and anaerobic conditions and comparison with environmental fate modeling. Environ Pollut 2007;150:300–5.