Chemosphere 86 (2012) 1050–1058

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Field dissipation of 4-nonylphenol, 4-t-octylphenol, triclosan and bisphenol A following land application of biosolids

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ARTICLE INFO

Article history:
Received 7 September 2011
Received in revised form 19 November 2011
Accepted 22 November 2011
Available online 21 December 2011

Keywords:
Biosolids
Field dissipation
4-nonylphenol
4-t-octylphenol
Bisphenol A
Triclosan

ABSTRACT

The persistence of contaminants entering the environment through land application of biosolids needs to be understood to assess the potential risks associated. This study used two biosolids treatments to examine the dissipation of four organic compounds: 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan, under field conditions in South Australia. The pattern of dissipation was assessed to determine if a first-order or a biphasic model better described the data. The field dissipation data was compared to previously obtained laboratory degradation data. The concentrations of 4-nonylphenol, 4-t-octylphenol and bisphenol A decreased during the field study, whereas the concentration of triclosan showed no marked decrease. The time taken for 50% of the initial concentration of the compounds in the two biosolids to dissipate (DT50), based on a first-order model, was 257 and 248 d for 4-nonylphenol, 231 and 75 d for 4-t-octylphenol and 289 and 43 d for bisphenol A. These field DT50 values were 10- to 20-times longer for 4-nonylphenol and 4-t-octylphenol and 2.5-times longer for bisphenol A than DT50 values determined in the laboratory. A DT50 value could not be determined for triclosan as this compound showed no marked decrease in concentration. The biphasic model provided a significantly improved fit to the 4-t-octylphenol data in both biosolids treatments, however, for 4-nonylphenol and bisphenol A it only improved the fit for one treatment. This study shows that the use of laboratory experiments to predict field persistence of compounds in biosolids amended soils may greatly overestimate degradation rates and inaccurately predict patterns of dissipation.

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1. Introduction

Land application of biosolids is a potential route of entry into the environment for numerous compounds that may pose a potential risk to organisms and ecosystems. Four organic compounds that have received considerable interest recently are the surfactant metabolites 4-nonylphenol and 4-t-octylphenol, the plasticiser bisphenol A and the antimicrobial agent triclosan. Most of the environmental concern surrounding 4-nonylphenol, 4-t-octylphenol and bisphenol A is that they have the ability to mimic natural estrogens by interacting with estrogen receptors (Jobling and Sumpter, 1993; Jobling et al., 1996; Fukuhori et al., 2005). Triclosan has also been shown to cause endocrine disruption in some organisms (e.g. Veldhoen et al., 2006; Crofton et al., 2007), furthermore, this compound can also exert a high level of toxicity, both in terrestrial (e.g. Waller and Kookana, 2009) and aquatic environments (e.g Orvos et al., 2002; Ishibashi et al., 2004).

The degradation of 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan in soils has been assessed in several studies. In some cases, results from these studies have been used to provide an indication of their expected persistence in the environment following land application of biosolids. In experiments that have involved spiking compounds into soil samples, degradation half lives have been reported of 1–17 d for 4-nonylphenol (Topp and Starratt, 2000; Roberts et al., 2006), approximately 5 d for 4-t-octylphenol (Ying and Kookana, 2005), 1–7 d for bisphenol A (Ying and Kookana, 2005; Xu et al., 2009) and 13–58 d for triclosan (Ying et al., 2007; Wu et al., 2009a; Xu et al., 2009). Slightly longer half lives of 16–23 d have been reported for 4-nonylphenol in a 45-d glasshouse trial, when the source of the contamination in the soil was solely through the addition of biosolids (Brown et al., 2009).

In a previous laboratory-based study conducted by Langdon et al. (2011a), the degradation of 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan was measured over 32 weeks when added to a soil via the addition of two different biosolids (i.e. a centrifuge dried biosolids and a lagoon dried biosolids). The

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doi:10.1016/j.chemosphere.2011.11.057

degradation rates, expressed as the time taken for 50% of the initial compound to dissipate (DT50), based on a first-order exponential decay model, ranged from 12 to 25 d for 4-nonylphenol, 10–14 d for 4-t-octylphenol, 18–102 d for bisphenol A and 73–301 d for triclosan. These degradation rates were found to be similar to or slightly longer than those reported in other research when the first-order model provided a good fit to the data. In the case of bisphenol A and triclosan, in one of the biosolids treatments, the first-order model was a poor fit to the data and the DT50 values obtained were considerably higher than that of the other treatment, at 102 d and 301 d, respectively. It was also determined that the degradation of 4-nonylphenol, bisphenol A and triclosan showed a biphasic pattern consisting of an exponentially degrading fraction and a non-degrading recalcitrant fraction, which remained until the completion of the 32 week study, in both biosolids treatments. This biphasic pattern was not observed for 4-t-octylphenol, which contained no recalcitrant fraction of this compound. In addition, in the previous laboratory study (Langdon et al., 2011a) both the rate and pattern of degradation was found to vary between the two biosolids treatments. The presence of a recalcitrant fraction of organic compounds following the addition of biosolids to soil indicates that there is an influence of the biosolids matrix on the degradation of the compounds. Non-degrading or recalcitrant fractions of organic compounds in soils have been reported in several studies and are suggested to be due to limited oxygen within the centre of biosolids aggregates (i.e. anaerobic zones) (Hesselsoe et al., 2001; Sjöström et al., 2008) and/or non-reversible sorption of the compounds to various components of the biosolids matrix (Wu et al., 2009b; Katayama et al., 2010).

When biosolids are applied to agricultural land, the field dissipation of compounds contained within the biosolids is likely to be strongly influenced by the environmental conditions as well as the biosolids matrix. Variations in temperature and available moisture are likely to play an important role in the dissipation of the compounds. This was evident in a laboratory to field comparison study which used ^{14}C-labelled triclosan (Al-Rajab et al., 2009). It was found that the mineralisation of the compound was more rapid in the laboratory study than in the field. As most degradation studies of compounds in biosolids have been conducted under laboratory or glasshouse conditions, field environmental conditions are rarely considered in the data interpretation.

The aims of this study were to (i) determine the rate of dissipation of 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan, following the addition of biosolids to agricultural land under field conditions in South Australia (SA), Australia; (ii) determine if the pattern of dissipation followed a first-order or a biphasic pattern; and (iii) compare the rate and pattern of dissipation of the compounds in the field to those observed in a preceding study conducted in the laboratory using the same soil and biosolids treatments (Langdon et al., 2011a).

2. Materials and methods

2.1. Field trial location, design and set up

The field site used in this study was located at Mount Compass, SA, Australia, which is approximately 70 km south of Adelaide (35°21′44.95S and 138°32′44.95E), had no history of previous biosolids or sewage sludge applications and historically has been used for pastures and cattle grazing. The soil had an average pH of 4.4, which was determined from a soil solution ratio of 1:5 in 0.01 M $CaCl_2$, an average organic carbon content of approximately 2.5%, and consisted of 96% sand, 2.5% silt and 1.5% clay. The climate at this location is Mediterranean, consisting of wet cold winters and dry hot summers. Weather conditions were monitored throughout the field study using a weather station at the site. The station measured ambient temperature and soil temperature (°C), rainfall (mm) and soil moisture (kilopascals, kPa).

The field trial used two different types of biosolids that were sourced from a wastewater treatment plant in SA. Both of the biosolids had been anaerobically digested. One had then been centrifuge dried (CDB) while the other had been solar dried in a lagoon system (LDB). The pH of the biosolids produced at this site is approximately 7.4 ($CaCl_2$) (Heemsbergen et al., 2009) and had a moisture content of approximately 40% and 50% in the CDB and LDB treatments, respectively. 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 field trial was established in May 2008, which is the start of the cereal cropping season in southern Australia. The trial consisted of three treatments, two locally produced biosolids and a control each conducted in triplicate. The overall plot design consisted of nine plots, each 2 m × 2 m, that were arranged in a latin square design. The biosolids were transported to the field site immediately following collection, for addition to the plots. The biosolids were applied to the surface of the required plots at a rate equivalent to 2-times the nitrogen limiting biosolids application rate (NLBAR). This rate is twice the permissible amount that can be added to agricultural soils under South Australian guidelines (SA EPA, 1997) and was equivalent to approximately 25 dry t ha^{-1} (where 1 ha is equal to 10 000 m^2) for the CDB treatment and 45 dry t ha^{-1} for the LDB treatment. The higher application rate was used to ensure the detection of the selected compounds in the soils. There was no addition of biosolids made to the three control plots. All of the plots (including the controls) were then cultivated with a rotary hoe to a depth of 10 cm to incorporate the biosolids, and in the case of the controls to replicate any effect from the rotary hoe. Wheat (*Triticum aestivum*) was then planted in each of the plots to simulate standard agricultural practice. Immediately following incorporation and planting, duplicate composite samples were taken from each of the plots. Each composite sample comprised of five randomised sub-samples that were taken from the top 10 cm of the soil profile with a soil core of 2 cm diameter. The samples were immediately returned to the laboratory for freeze drying and homogenisation for analysis to represent the initial (t_0) concentrations of the contaminants. Duplicate composite samples were then taken from each of the plots at intervals throughout a 336 d trial (i.e., 28, 56, 112, 168, 224, 280, 336 d post biosolids addition) to be freeze dried and homogenised for chemical analysis.

2.2. Sample extraction and gas chromatography–mass spectrometry (GCMS) analysis

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 the current study used a 10 g sample of biosolids amended soil for extraction and analysis. 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 Milli Q (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 and 3 × 2.5 mL ethyl acetate and 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 sample) 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 extracting and analysing a duplicate set of samples that had been spiked with known concentrations of the compounds 4-t-octylphenol, bisphenol A and triclosan. The difference in concentration between the spiked and the unspiked samples were then compared to the known spike concentration to calculate the recoveries as a percentage. For the compound 4-nonylphenol, the extraction recoveries were determined from the labelled surrogate 4-*n*-nonylphenol-d_8, which was spiked into the duplicate samples at a known concentration. The reason for the different method for extraction recovery determination for 4-nonylphenol was that the concentrations of this compound were relatively high within the samples, therefore by using a labelled surrogate, the spiked and unspiked compounds could be easily distinguished. 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 30 and 100 $\mu g\ kg^{-1}$, respectively, for 4-nonylphenol, 0.6 and 2.0 $\mu g\ kg^{-1}$, respectively, for 4-t-octylphenol, 0.3 and 1.0 $\mu g\ kg^{-1}$, respectively, for bisphenol A, and 0.8 and 2.7 $\mu g\ kg^{-1}$, respectively, for triclosan.

2.3. Statistical analysis and data interpretation

The method used for statistical analysis and data interpretation was the same as that used previously in Langdon et al. (2011a). Prior to all statistical analyses, the concentration data at each sampling time were converted to a ratio of the initial concentration (C_t/C_0). This normalised the data to an initial mean value of 1 and removed any variation at t_0 between the biosolids treatments and the compounds.

The statistical analyses conducted on the field dissipation data included a univariate analysis of variance (ANOVA) to determine if the compounds significantly decreased over the 336 d of the experiment, using SPSS® Version 17. Nonlinear regressions were also conducted to determine the dissipation patterns of each compound. There were two nonlinear regression models fitted to the dissipation data of each compound based on first-order kinetics, using SigmaPlot®. The first model was a standard first-order exponential decay model (i.e. with two fitting parameters) and the second model was a biphasic model (i.e. with three fitting parameters) that accounted for a dissipating fraction and a recalcitrant fraction of the compounds. The rate constant from the first-order model was used to determine the DT50. The rate constant from the biphasic model produced a $DT50_{biphasic}$, which indicated the degradation rate of the dissipating fraction, and a *y*-intercept (x_0), which indicated the magnitude of the recalcitrant fraction (expressed as a % of the initial concentration). The residual sums of squares were then used to statistically compare the two models and produce a probability value (*p*-value) to determine which model provided the best fit to the data. If the *p*-value from this comparison was less than 0.05 then the biphasic model was considered to provide a significantly better fit to the data. A detailed outline of the nonlinear regression models is provided in Langdon et al. (2011a).

It should be noted that the term dissipation is used throughout this paper to refer to overall decreases in concentrations of the compounds in the field trial. This is due to the field trials being an open system and processes other than degradation may be responsible for changes in concentration (e.g. leaching and volatilisation). However, due to the nature of the compounds examined, the processes of degradation are deemed to be the most significant mechanism for changes in concentration. In comparison, when referring to other research that has involved closed systems (e.g. laboratory incubations), the term degradation is used.

3. Results and discussion

3.1. Climatic conditions at the field site

The weather station data for the average maximum weekly ambient temperature, soil temperature and total weekly rainfall for the duration of the field trial is shown in Fig. 1, along with the timing of each soil sample collection. The winter months (June to August) and the summer months (December to February) have also been indicated. During weeks 41–43 of the field trial there was an error with the weather station and data could not be collected during this period (shown by the missing data in Fig. 1), only rainfall and ambient temperature could be recorded following this.

The majority of rainfall took place over the winter months of the field trial, which is typical of Mediterranean climates. The average weekly rainfall in this period was approximately 22 mm with a maximum of 67 mm in week 11. The maximum ambient temperature during this period ranged from approximately 11 to 20 °C. In comparison, during summer, with the exception of a small amount of rain at the start, the rainfall was generally zero, which also continued beyond the end of summer. During this period, the maximum ambient temperature ranged from 21 to 38 °C. Fig. 1 shows that over the duration of the trial, the soil temperature fluctuated consistently with the ambient temperature, however, as expected it generally remained slightly lower than the ambient temperature.

The soil moisture data obtained from the weather station showed that over the winter months when the majority of rainfall took place, the average matric potential in the soil was 9 pKa, indicating that the soil was essentially saturated during this period. The soil then dried for the period between winter and summer when the rainfall decreased, indicated by the matric potential ranging from 201 to 239 pKa for the period approximately 150–190 d post biosolids addition. This value decreased following the small amount of rain at the commencement of summer, however, then returned the values over 200 pKa until the completion of the study.

3.2. Data quality assurance and extraction recoveries

The method blanks run with each batch of samples were below detection for all of the compounds except for 4-nonylphenol. The concentrations of 4-nonylphenol in the method blanks varied from approximately 45 to 130 $\mu g\ L^{-1}$ in the final extract solution. The concentration of 4-nonylphenol in the method blank was subtracted from each of the samples within the same run prior to the concentrations being converted to $\mu g\ kg^{-1}$.

The extraction recoveries for each of the compounds averaged 80%, 98%, 104% and 120% for 4-t-octylphenol, 4-nonylphenol, bisphenol A and triclosan respectively. The average recovery for triclosan was higher than expected, however, this is likely to be due to the effect of the complex biosolids matrix on the GC–MS response of the analyte and the internal standard (anthracene-d_{10}) in the samples. The relative standard deviations (RSDs) for the recoveries of each compound were less than or equal to 30%. The recoveries for 4-nonylphenol and 4-t-octylphenol showed the least variation throughout the study with RSDs of 16% and 17%, respectively. In comparison, the recoveries for bisphenol A and triclosan showed higher variation throughout the study with RSDs of 23% and 30%, respectively.

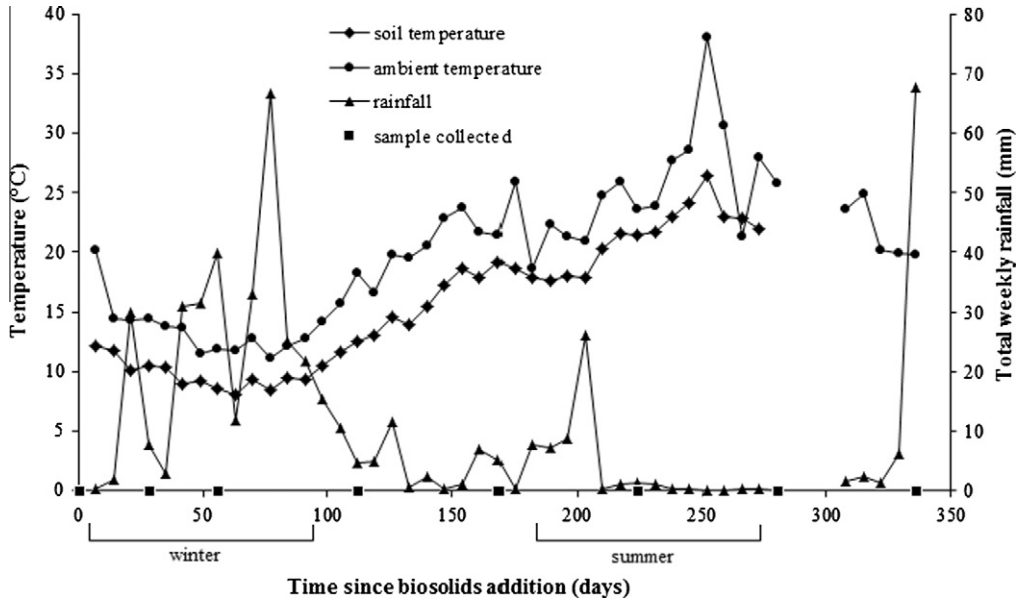

Fig. 1. Average maximum weekly temperature, soil temperature and total weekly rainfall for the 336 d duration of the field trial. Times at which samples of biosolids amended soil were taken for chemical analysis are also shown. The initial sample (t_0) was collected 26th May 2008 and winter months (June to August) and summer months (December to February) are indicated.

3.3. Control soil and preliminary biosolids analysis

Throughout the duration of the field trial, the controls were below the LOD for all four compounds tested in all samples. Therefore, there were no detectable background levels of the compounds at the field site.

The analysis of the two biosolids samples prior to their addition to the soil showed detectable levels of the four target compounds. In the CDB sample, the average concentrations of 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan were 79, 0.94, 0.22 and 5.2 mg kg^{-1}, respectively. In comparison, analysis of the LDB sample showed concentrations of 30, 1.6, 0.15 and 6.1 mg kg^{-1}, respectively.

3.4. Dissipation of 4-nonylphenol from biosolids amended soil

In the initial (t_0) soil samples, the average concentration of 4-nonylphenol in the CDB treatment was 887 μg kg^{-1} and in the LDB treatment it was 475 μg kg^{-1}. There was significant ($p < 0.0005$) dissipation of 4-nonylphenol following the addition of both biosolids treatments to the soil over the 336 d of the study (Fig. 2). In the two biosolids treatments, there was a significant ($p < 0.05$) decrease in the concentration of 4-nonylphenol 112 d post biosolids addition to the soil, however, following this there was no significant change ($p > 0.05$) in concentration through to the completion of the field trial.

The fit of the first-order model to the 4-nonylphenol dissipation data in this study was significant ($p < 0.05$), however the R^2 values derived were low at approximately 0.20 for both biosolids treatments (Table 1 and Fig. 2). The DT50 of 4-nonylphenol determined from the first-order model was 257 d in the CDB treatment and 248 d in the LDB treatment, indicating that there was little variation in the dissipation rate of 4-nonylphenol between the two biosolids treatments. These field DT50 values are up to 16-times longer when compared to those reported by Brown et al. (2009) in a glasshouse trial examining the degradation of 4-nonylphenol in biosolids amended soil. In addition, these values are approximately 10- and 20-times longer for the CDB and LDB treatments, respectively, than those obtained in a previous laboratory trial using the same soil and biosolids treatments (Langdon et al., 2011a).

The additional parameter in the biphasic model significantly ($p = 0.014$) improved the fit to the 4-nonylphenol dissipation data in the CDB treatment and increased the R^2 value to 0.30 (Table 1). This indicates that there was a non-degrading recalcitrant fraction of 4-nonylphenol in this treatment. The $DT50_{biphasic}$ for 4-nonylphenol from the CDB treatment was 41 d, with approximately 50% of the compound recalcitrant in the soil at the completion of the study ($x_0 = 0.47$) (Table 1) (which corresponded to 417 μg kg^{-1}). A biphasic pattern of degradation was also observed for this compound in the previous laboratory experiment (Langdon et al., 2011a), however, a considerably smaller recalcitrant fraction of approximately 20% was observed. In addition, the $DT50_{biphasic}$ in the laboratory was 5.8 d, (Langdon et al., 2011a) indicating that the rate of degradation in the laboratory was approximately 7-times faster than in the field (41 d). Other studies on the degradation of 4-nonylphenol following addition of sewage sludge to soils have also reported biphasic patterns of degradation. For example, Marcomini et al. (1988) reported a recalcitrant fraction of approximately 10% for 4-nonylphenol in a sewage sludge amended soil and Sjöström et al. (2008) reported recalcitrant fractions of 26–35% for nonylphenol following the addition of sewage sludge to soil.

In the LDB treated soil, the additional fitting parameter in the biphasic model did not significantly ($p = 0.092$) improve the fit of the data when compared to the first order model for this compound (Table 1). At the conclusion of the 336 d trial, however, there was 228 μg kg^{-1} of 4-nonylphenol remaining in the LDB treatment which corresponds to 48% of the initial concentration. This result is not consistent with the laboratory study conducted by Langdon et al. (2011a), which found this compound in this treatment showed a significant biphasic pattern of degradation. There are several suggestions for these differences between the laboratory- and field-based dissipation/degradation results. The variation in the dissipation data at each of the sampling events for this compound was considerably higher in the field than in the laboratory, which is common for field trials of this nature, mainly due to difficulties in obtaining a homogeneous sample. It

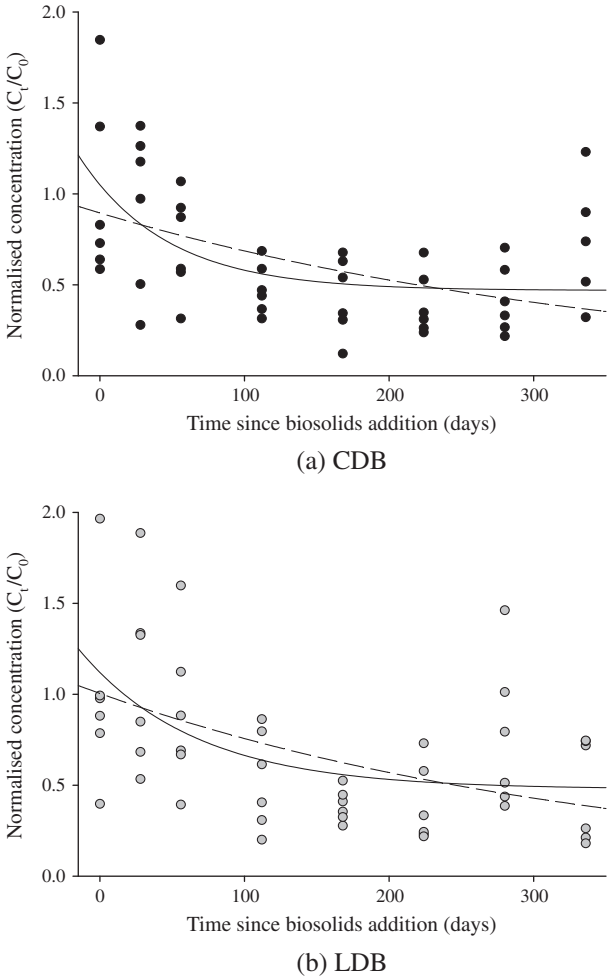

Fig. 2. Dissipation of 4-nonylphenol following the addition of (a) centrifuge dried biosolids (CDBs) and (b) lagoon dried biosolids (LDBs) to a soil. All concentration data are normalised as a ratio of the concentration at each sampling time to the initial concentration (C_t/C_0). The nonlinear regression fits for the first-order model and biphasic model are represented by the dashed line and the solid line, respectively.

is possible that this variation masked the overall pattern of the dissipation data for this compound in the LDB treatment. A further suggestion is that the portion of the dissipation curve that was obtained from this field trial only accounted for the initial exponential degrading phase and therefore the levelling off in concentration was not evident. This is possible due to the considerably slower dissipation rate that was observed in the field.

3.5. Dissipation of 4-t-octylphenol from biosolids amended soil

The initial (t_0) soil samples showed concentrations of 4-t-octylphenol in the CDB and LDB treatments of 7.0 and 27 μg kg^{-1}, respectively. There was significant ($p < 0.0005$) dissipation of the compound 4-t-octylphenol over the 336 d of this study (Fig. 3). In the two biosolids treatments, the 4-t-octylphenol concentration significantly ($p < 0.05$) decreased from the initial concentration 56 d post biosolids addition. From 224 d through till the end of the field trial at 336 d there was no significant ($p > 0.05$) change in the concentration of 4-t-octylphenol.

The fit of the first-order model to the dissipation data for 4-t-octylphenol was significant (both p-values $\leqslant 0.001$) and the R^2 values were 0.23 for the CDB treatment and 0.56 for the LDB treatment (Table 1). The DT50 values calculated from the first-order model were considerably different between the two treatments and were 231 d in the CDB treatment and 75 d in the LDB treatment (Table 1). This shows that the dissipation in the CDB treatment was substantially slower than in the LDB treatment, however, it is possibly also reflective of the poor fit of this model ($R^2 = 0.23$) to the CDB dissipation data. Laboratory based studies that have involved the spiking of 4-t-octylphenol into a soil have reported DT50 values of approximately 5 d under laboratory conditions (Ying and Kookana, 2005), which is approximately 46- and 15-times faster than the DT50 values obtained in this field trial. When the field DT50 results for this compound are compared to those obtained using the same soil and biosolids treatments in the laboratory, they are approximately 10- and 20-times longer for the CDB and LDB treatments, respectively (Langdon et al., 2011a).

The additional fitting parameter in the biphasic model significantly (both p-values $\leqslant 0.033$) improved the fit to the 4-t-octylphenol dissipation data in both biosolids treatments (Table 1). This indicates that for both biosolids treatments there was a recalcitrant fraction of 4-t-octylphenol over the 336 d of the field trial. The $DT50_{biphasic}$ values obtained from this model were 33 d for the CDB treatment and 41 d for the LDB treatment with the x_0 values indicating that 42% and 16% of the initial 4-t-octylphenol concentrations remained at the completion of the experiment in the CDB and LDB treatments, respectively (Table 1). These corresponded to concentrations of 2.94 μg kg^{-1} in the CDB treatment and 4.32 μg kg^{-1} in the LDB treatment.

The pattern of degradation of 4-t-octylphenol observed under laboratory conditions using the same soil and biosolids treatments (Langdon et al., 2011a) was not consistent with that observed in this field study. Under laboratory conditions, the degradation of 4-t-octylphenol followed a standard first-order decay model, showing continuous degradation with no statistically significant non-degrading fraction (i.e. the biphasic model did not significantly improve the fit of the degradation data in the laboratory). Therefore based on this comparison of results, it is possible that this compound will show further degradation in the field, under more favourable climatic conditions. As the weeks leading up to the completion of this trial had little or no rainfall, the soil, which consisted of 96% sand, contained little moisture. This lack of moisture may have resulted in the processes required for the degradation of this compound halting. Therefore, an additional seasonal cycle may lead to continued degradation of this compound.

3.6. Dissipation of bisphenol A from biosolids amended soil

At the commencement of the field trial, bisphenol A was detected in the soil treated with the CDB at a concentration of 2.1 μg kg^{-1} and the LDB at a concentration of 6.2 μg kg^{-1}. Through the 336 d of the trial, the concentrations of bisphenol A in both of the biosolids treatments decreased to concentrations below the LOQ of 1.0 μg kg^{-1} and in a small number of cases below the LOD of 0.3 μg kg^{-1}. For this reason, the normalised concentrations (C_t/C_0) that correspond to the LOD and LOQ for this compound are indicated in Fig. 4. For the ANOVA conducted on the data for this compound, all of the values, including those below the LOD and LOQ, were however used to avoid missing values. The concentrations of bisphenol A significantly ($p = 0.01$) decreased throughout the field trial in both of the biosolids treatments. The concentrations of bisphenol A were significantly ($p < 0.05$) lower than the initial concentration at 56 d post biosolids addition. After this there were no further significant changes in the bisphenol A concentration through to the completion of the trial at 336 d.

The fit of the first-order model to the dissipation data was only marginally significant for the CDB treatment ($p = 0.046$), however, it was highly significant for the LDB treatment ($p < 0.001$) and ex-

Table 1
Summary of the degradation information from the first-order and biphasic models for the compounds 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan for the centrifuge dried biosolids (CDB) and lagoon dried biosolids (LDB) treated soils. The dissipation half-lives determined using the first-order and biphasic models (DT50 and $DT50_{biphasic}$respectively) are shown in days and the *y*-intercept (x_0) values correspond to the C_t/C_0 values.

Model	Measure	4-Nonylphenol		4-t-Octylphenol		Bisphenol A		Triclosan	
		CDB	LDB	CDB	LDB	CDB	LDB	CDB	LDB
First order	R^2	0.20	0.21	0.23	0.56	0.09	0.37	–	–
	DT50	257	248	231	75	289	43	–	–
	p-value[a]	0.002	0.001	0.001	<0.001	0.046	<0.001	1.00	1.00
Biphasic	R^2	0.30	0.26	0.39	0.60	0.17	0.63	0.06	0.05
	$DT50_{biphasic}$	41	58	33	41	17	16	–	–
	x_0	0.47	0.48	0.42	0.16	0.45	0.23	–	–
	p-value[b]	0.014	0.092	0.002	0.033	0.056	<0.001	–	–
	Best fit	Biphasic	First order	Biphasic	Biphasic	First order	Biphasic	–	–

Values and parameters that could not be determined are indicated with a dash.
[a] Significance of the first-order model
[b] Significance of the biphasic model compared to the first-order model.

plained 9% and 37% of the variation in the data respectively (Table 1). The DT50 values determined from this fit were 289 d in the CDB treatment and 43 d in the LDB treatment. As the initial concentration of bisphenol A in the CDB treatment was low (2.1 μg kg^{-1}, Table 1) and the majority of the concentration data fell below the LOQ for this compound (Fig. 4), the DT50 calculated is considered unreliable. A smaller proportion of bisphenol A concentrations were below the LOQ in the LDB treatment, therefore, this data and the DT50 value calculated is likely to be more reliable. The field DT50 value of 43 d in the LDB treatment is at least 6-times longer than reported laboratory based DT50 values in soil spiking experiments (Ying and Kookana, 2005; Xu et al., 2009) and 2.5-times longer than that reported in Langdon et al. (2011a) when the same soil and biosolids treatments were assessed under laboratory conditions.

The additional fitting parameter in the biphasic model did not significantly improve the fit for the bisphenol A dissipation data in the CDB ($p = 0.056$) (Table 1), however, as discussed above it is difficult to draw reliable conclusions from the bisphenol A dataset in the CDB treatment due to the high proportion of data points that fell below the LOQ. In the LDB treatment however, the additional fitting parameter did provide a significant improvement ($p < 0.001$) to the fit of the model. Therefore, bisphenol A showed a biphasic pattern of dissipation in this treatment. This model explained 63% of the variation in the bisphenol A dissipation data and produced a $DT50_{biphasic}$ value of 16 d and a recalcitrant fraction of 23% of the initial concentration (Table 1). This corresponded to 1.4 μg kg^{-1} of the bisphenol A still remaining in the soil at the completion of the 336 d field trial. The degradation of bisphenol A under laboratory conditions, using the same soil and biosolids treatments, also showed a biphasic pattern with approximately the same proportion of the compound remaining in the soil (i.e. 24% remaining) (Langdon et al., 2011a). When the $DT50_{biphasic}$ values are compared between the laboratory and the field, the rate of degradation of the initial degrading fraction was twice as fast under laboratory conditions, with a $DT50_{biphasic}$ value of approximately 8 d.

3.7. Dissipation of triclosan from biosolids amended soil

The initial (t_0) soil samples showed concentrations of triclosan in the CDB and LDB treatments of 39 and 106 μg kg^{-1}, respectively. The ANOVA results indicated that the concentration of triclosan significantly ($p < 0.0005$) changed over the duration of the experiment. This significance is due to the concentrations within both of the biosolids treatments being slightly lower than the initial concentration at 28, 56 and 112 d post biosolids addition (see Fig. 5). However, the final four sampling times (i.e. 168, 224, 280 and 336) showed no significant ($p > 0.05$) difference in concentration when compared to the initial concentration. Therefore, there was no clear indication of dissipation over the period of the study.

This lack of dissipation was confirmed by the non-significant fit of the first-order model to the dissipation data for triclosan in both of the biosolids treatments (both *p*-values = 1.00) (Table 1, Fig. 5). In addition, the fit of the biphasic model was also non-significant (both *p*-values $\geqslant 0.26$). Therefore DT50 and $DT50_{biphasic}$ values were not determined. These results indicate that over the 48 week field trial there was no marked decrease in the soil concentration of triclosan. This outcome is markedly different from results that have been reported in other studies on the same compound. Laboratory based experiments that have involved spiking this compound into a soil to determine degradation have reported DT50 values ranging from 13 to 58 d (Ying et al., 2007; Wu et al., 2009a; Xu et al., 2009). In the previous laboratory experiment (Langdon et al., 2011a), using the same soil and biosolids treatments as that of the current field study, triclosan was found to significantly degrade. However in both treatments in the laboratory the pattern of degradation was found to be biphasic, indicating that there was a non-degrading fraction of this compound present. The field dissipation reported in the current study is also markedly different to that predicted by Lozano et al. (2010). That study used predicted initial concentrations and measured current concentrations to calculate a half life for triclosan of 107 d in agricultural soils following biosolids addition.

The degradation of triclosan following the addition of biosolids to soils has been compared between the laboratory and the field elsewhere using isotopically labelled triclosan (Al-Rajab et al., 2009). That study found that the laboratory results considerably under-estimated the persistence of triclosan, however, in contrast to the current field trial, Al-Rajab et al., 2009 did report some mineralisation of the ^{14}C-labelled compound, indicating that breakdown was occurring. These differences in results are likely to be related to the differing locations and climatic conditions of the field trials, as well as variations in the experimental design. For example, Al-Rajab et al. (2009) used labelled triclosan that had been spiked into the biosolids amended soils, whereas the current field trial examined the dissipation of triclosan that was indigenous to the biosolids at the time of soil application. The spiking of the compound into the matrix removes any influence that the aging of the compound in the biosolids matrix may have on the bioavailability and degradation of the compound.

The persistence of this compound beyond the completion of the current field trial is likely to be extensive as essentially a full

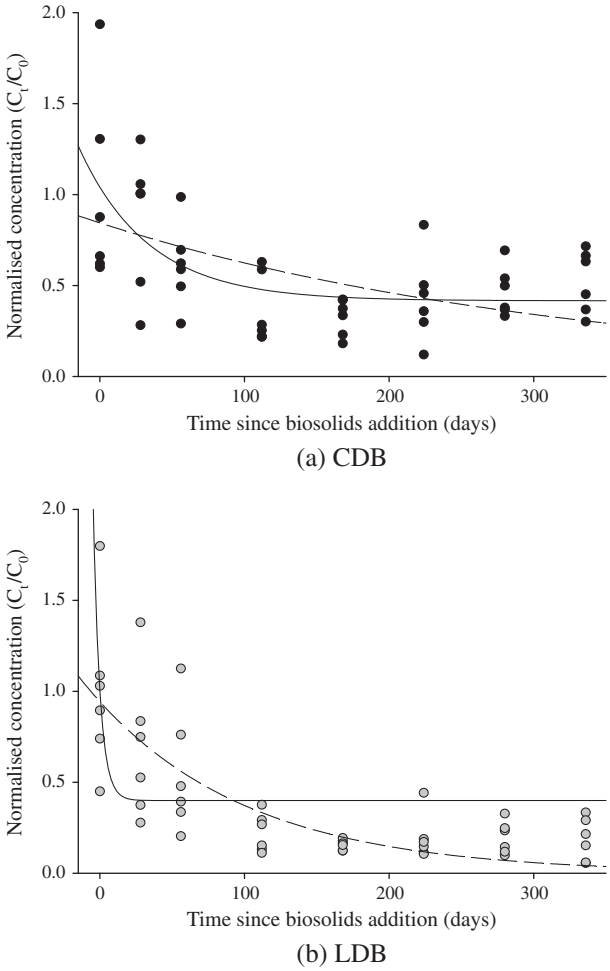

Fig. 3. Dissipation of 4-t-octylphenol following the addition of (a) centrifuge dried biosolids (CDBs) and (b) lagoon dried biosolids (LDBs) to a soil. All concentration data are normalised as a ratio of the concentration at each sampling time to the initial concentration (C_t/C_0). The nonlinear regression fits for the first-order model and biphasic model are represented by the dashed line and the solid line, respectively.

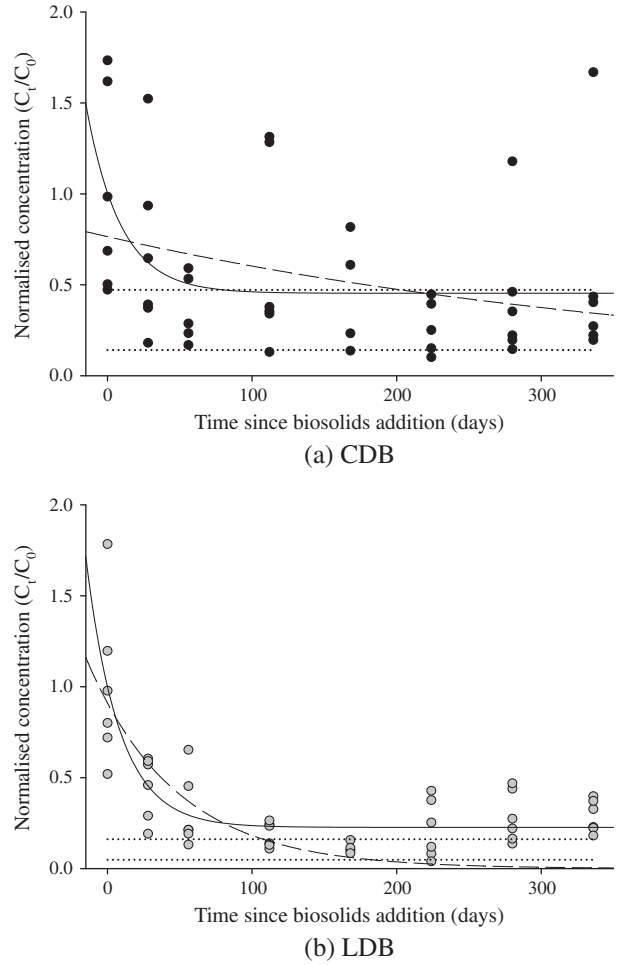

Fig. 4. Dissipation of bisphenol A following the addition of (a) centrifuge dried biosolids (CDBs) and (b) lagoon dried biosolids (LDBs) to a soil. All concentration data are normalised as a ratio of the concentration at each sampling time to the initial concentration (C_t/C_0). The nonlinear regression fits for the first-order model and biphasic model are represented by the dashed line and the solid line, respectively. The upper dotted line in the plots indicates the LOQ and the lower dotted line indicates the LOD for bisphenol A converted to the normalised concentration (C_t/C_0).

annual cycle was covered. This result therefore creates concern about the potential accumulation of triclosan in soils where biosolids have been applied to land in similar environmental and soil conditions. This is of particular concern if repeat applications of biosolids are used. Accumulation of this compound may lead to adverse effects on organisms in the surrounding soil environment (Waller and Kookana, 2009) or aquatic organisms due to runoff or leaching into adjacent waterways (Langdon et al., 2010).

3.8. Summary of laboratory to field comparison

As expected, replicate measurements of compound concentrations varied much more in the field study than in the laboratory study, and as a consequence, calculated dissipation rates of the compounds in the field are less precise. However, the large (several-fold) differences in dissipation rates between the laboratory and field studies for exactly the same combinations of biosolids and soil highlight the perils in using laboratory-derived values for modelling real-world behaviour of contaminants and the need to carry out some field studies, despite their greater intrinsic variability. Overall, this study clearly showed that the dissipation of the organic compounds, 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan following biosolids addition to soil was markedly different under field conditions than that observed in the laboratory. For 4-nonylphenol, 4-t-octylphenol and bisphenol A, the rates of dissipation were considerably slower in the field and in many cases the pattern of dissipation observed also differed. Triclosan showed the greatest difference between the field and the laboratory, whereby in the field no marked decrease in concentration was observed over the 48 weeks of the study. In addition, for the compounds that did degrade throughout the field trial (i.e. 4-nonylphenol, 4-t-octylphenol and bisphenol A) the concentrations that remained in the soil at the completion of the study were in all cases considerably higher than those that remained in the soil at the completion of the comparable laboratory experiment. The differences observed between the field and the laboratory are likely due to the less than optimal degradation conditions in the field. In general, the climate in South Australia is Mediterranean, with the majority of rainfall occurring in the winter months and little or no rainfall in the summer months (Fig. 1). In winter it is likely that degradation was limited by low temperatures, while in summer degradation was likely to have been limited by low water availability, especially given the sandy soil at the site. This would slow degradation of the compounds and also may have affected

the pattern of dissipation observed. In comparison, the laboratory experiment was conducted at more optimal conditions with a constant temperature of 20 °C and soil moisture at 50% of its maximum water holding capacity. It is possible that with another seasonal cycle in the field further dissipation may be observed, resulting in a continued decrease in the soil concentrations of these compounds. This is unlikely, however, for triclosan as over the 48 weeks of this field trial, which accounted for essentially an entire seasonal cycle, no marked change in soil concentration was observed.

Finally, it should be noted that the results reported in the study are site specific, in terms of both climate and soil type. The results overall do, however, show the dissipation rates of the compounds observed in the laboratory can grossly over-estimate the dissipation rates observed in the field following biosolids addition. This would in turn under-estimate the likely persistence of organic compounds in soils follow the application of biosolids. As a result, the extrapolation of laboratory based results, which do not take into account the variations in field conditions (i.e. temperature and soil moisture), should be used with caution when assessing the persistence of compounds and the potential environmental risks associated with the land application of biosolids.

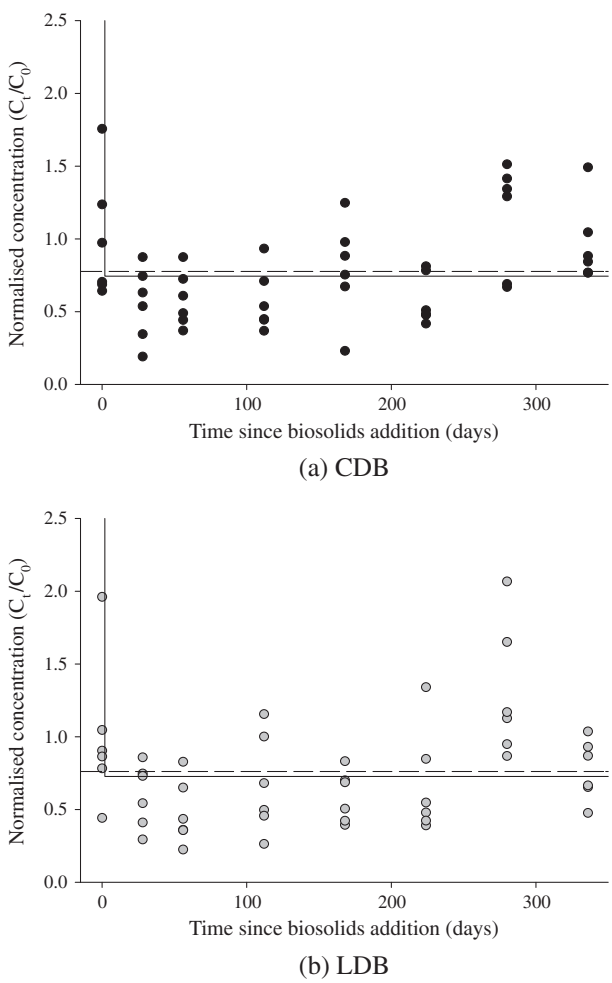

Fig. 5. Dissipation of triclosan following the addition of (a) centrifuge dried biosolids (CDBs) and (b) lagoon dried biosolids (LDBs) to a soil. All concentration data are normalised as a ratio of the concentration at each sampling time to the initial concentration (C_t/C_0). The nonlinear regression fits for the first-order model and biphasic model are represented by the dashed line and the solid line, respectively.

4. Conclusion

Following the addition of biosolids to soil under field conditions in South Australia with a Mediterranean climate, the compounds 4-nonylphenol, 4-t-octylphenol and bisphenol A were found to dissipate over a 336 d period, however, the compound triclosan did not show any dissipation. The time taken for 50% of the initial concentrations of the compounds to dissipate (DT50) were 257 and 248 d for 4-nonylphenol, 231 and 75 d for 4-t-octylphenol and 289 and 43 d for bisphenol A. Dissipation in the field took place approximately 10- to 20-times slower than in the laboratory for 4-nonylphenol and 4-t-octylphenol and approximately 2.5-times slower for bisphenol A. The use of a biphasic model significantly improved the fit to the 4-nonylphenol data in the CDB treatment but not in the LDB treatment. For 4-t-octylphenol, the biphasic model improved the fit in both biosolids treatments and for bisphenol A only in the LDB treatment. It is expected that with additional time, seasonal variation, and an additional rain event, the dissipation of 4-nonylphenol and 4-t-octylphenol would continue. The main factor that resulted in differences between the laboratory and the field was likely to be the unfavourable environmental conditions for degradation at the location of this field trial. The results reported in this study are site-specific, however, they show that the use of standard laboratory experiments that do not take into account variations in climatic conditions (e.g. temperature and moisture) may greatly overestimate dissipation rates and inaccurately predict dissipation patterns of compounds contained within biosolids.

Acknowledgements

The principle author (K.A.L.) wishes to acknowledge the financial support of Water Quality Research Australia (WQRA) (formally the Co-operative Research Centre for Water Quality and Treatment – CRCWQT), Western Australia Water Corporation, Victorian Department of Human Services and the Commonwealth Scientific and Industrial Research Organisation (CSIRO).

References

Al-Rajab, A.J., Sabourin, L., Scott, A., Lapen, D.R., Topp, E., 2009. Impact of biosolids on the persistence and dissipation pathways of triclosan and triclocarban in an agricultural soil. Sci. Total Environ. 407, 5978–5985.

Brown, S., Devin-Clarke, D., Doubrava, M., O'Connor, G., 2009. Fate of 4-nonylphenol in a biosolids amended soil. Chemosphere 75, 549–554.

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

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

Heemsbergen, D.A., Warne, M.St.J., Broos, K., Bell, M., Nash, D., McLaughlin, M., Whatmuff, M., Barry, G., Pritchard, D., Penney, N., 2009. Application of phytotoxicity data to a new Australian soil quality guideline framework for biosolids. Sci. Total Environ. 407, 2546–2556.

Hesselsoe, M., Jensen, D., Skals, K., Olesen, T., Moldrup, P., Roslev, P., Mortensen, G.K., Henriksen, K., 2001. Degradation of 4-nonylphenol in homogeneous and nonhomogeneous mixtures of soil and sewage sludge. Environ. Sci. Technol. 35, 3695–3700.

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

Jobling, S., Sumpter, J.P., 1993. Detergent components in sewage effluent are weakly estrogenic to fish – an in-vitro study using rainbow-trout (*Oncorhynchus mykiss*) hepatocytes. Aquat. Toxicol. 27, 361–372.

Jobling, S., Sheahan, D., Osborne, J.A., Matthiessen, P., Sumpter, J.P., 1996. Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. Environ. Toxicol. Chem. 15, 194–202.

Katayama, A., Bhula, R., Burns, G.R., Carazo, E., Felsot, A., Hamilton, D., Harris, C., Kim, Y.-H., Kleter, G., Koerdel, W., Linders, J., Peijnenburg, J.G.M.W., Sabljic, A., Stephenson, R.G., Racke, D.K., Rubin, B., Tanaka, K., Unsworth, J., Wauchope, R.D., 2010. Bioavailability of xenobiotics in the soil environment. Rev. Environ. Contam. Toxicol. 203, 1–86.

Langdon, K.A., Warne, M.St.J., Kookana, R.S., 2010. Aquatic hazard assessment for pharmaceuticals, personal care products and endocrine disrupting compounds from biosolids-amended land. Integrated Environ. Assess. Manage. 6, 663–676.
Langdon, K.A., Warne, M.St.J., Smernik, R.J., Shareef, A., Kookana, R.S., 2011a. Degradation of 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan following biosolids addition to soil under laboratory conditions. Chemosphere 84, 1556–1562.
Langdon, K.A., Warne, M.St.J., Smernik, R.J., Shareef, A., Kookana, R.S., 2011b. Selected personal care products and endocrine disruptors in biosolids: An Australia-wide survey. Sci. Total Environ. 409, 1075–1081.
Lozano, N., Rice, C.P., Ramirez, M., Torrents, A., 2010. Fate of triclosan in agricultural soils after biosolid applications. Chemosphere 78, 760–766.
Marcomini, A., Capel, P.D., Giger, W., Hani, H., 1988. Residues of detergent-derived organic pollutants and polychlorinated-biphenyls in sludge amended soil. Naturwissenschaften 75, 460–462.
Orvos, D.R., Versteeg, D.J., Inauen, J., Capdevielle, M., Rothenstein, A., Cunningham, V., 2002. Aquatic toxicity of triclosan. Environ. Toxicol. Chem. 21, 1338–1349.
Roberts, P., Roberts, J.P., Jones, D.L., 2006. Behaviour of the endocrine disrupting chemical nonylphenol in soil: assessing the risk associated with spreading contaminated waste to land. Soil Biol. Biochem. 38, 1812–1822.
SA EPA (South Australian Environment Protection Authority), 1997. South Australian biosolids guidelines. For the safe handling, reuse or disposal of biosolids. SA EPA, Adelaide.
Shareef, A., Angove, M.J., Wells, J.D., 2006. Optimization of silylation using N-methyl-N-(trimethylsilyl)-trifluoroacetamide, N, O-bis-(trimethyl.silyl)-trifluoroace tamide 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 1108, 121–128.
Sjöström, A.E., Collins, C.D., Smith, S.R., Shaw, G., 2008. Degradation and plant uptake of nonylphenol (NP) and nonylphenol-12-ethoxylate (NP12EO) in four contrasting agricultural soils. Environ. Pollut. 156, 1284–1289.
Topp, E., Starratt, A., 2000. Rapid mineralization of the endocrine-disrupting chemical 4-nonylphenol in soil. Environ. Toxicol. Chem. 19, 313–318.
Veldhoen, N., Skirrow, R.C., Osachoff, H., Wigmore, H., Clapson, D.J., Gunderson, M.P., Van Aggelen, G., Helbing, C.C., 2006. The bactericidal agent triclosan modulates thyroid hormone-associated gene expression and disrupts postembryonic anuran development. Aquat. Toxicol. 80, 217–227.
Waller, N.J., Kookana, R.S., 2009. Effect of triclosan on microbial activity in Australian soils. Environ. Toxicol. Chem. 28, 65–70.
Wu, C.X., Spongberg, A.L., Witter, J.D., 2009a. Adsorption and degradation of triclosan and triclocarban in soils and biosolids-amended soils. J. Agric. Food Chem. 57, 4900–4905.
Wu, C.X., Spongberg, A.L., Witter, J.D., 2009b. Sorption and biodegradation of selected antibiotics in biosolids. J. Environ. Sci. Heal. A 44, 454–461.
Xu, J., Wu, L.S., Chang, A.C., 2009. Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils. Chemosphere 77, 1299–1305.
Ying, G.G., Kookana, R.S., 2005. Sorption and degradation of estrogen-like-endocrine disrupting chemicals in soil. Environ. Toxicol. Chem. 24, 2640–2645.
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 modeling. Environ. Pollut. 150, 300–305.