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Degradation of 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan following biosolids addition to soil under laboratory conditions

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ABSTRACT

The reuse of biosolids through land application is common practice in many countries, however, there are some potential risks associated with the presence of contaminants within the biosolids. This study examined the degradation of four commonly found organic compounds, 4-nonylphenol (4NP), 4-t-octylphenol (4tOP), bisphenol A (BPA) and triclosan (TCS), in a soil following the separate addition of two biosolids over 32 weeks under laboratory conditions. The pattern of degradation was also assessed to determine if it followed a first-order decay model or if a biphasic model with a recalcitrant fraction better described the data. The time taken for the initial concentrations to decrease by 50% (DT50), based on a first-order model, was 12 to 25 days for 4NP, 10 to 14 days for 4tOP, 18 to 102 days for BPA and 73 to 301 days for TCS. For 4NP, BPA and TCS, a biphasic model fitted the degradation data better than the first-order model. After 32 weeks, the non-degraded recalcitrant fractions of these compounds were 17 to 21%, 24 to 42% and 30 to 51% of the initial concentrations, respectively. For 4tOP, the first-order model was sufficient in explaining the degradation, indicating that there was no recalcitrant fraction present. This study showed that the biosolids matrix may influence the rate and pattern of degradation of organic compounds in soils and that the use of standard first-order models may underestimate the persistence of some organic contaminants in biosolids amended soils.

Keywords: biosolids; soil degradation; 4-nonylphenol; 4-t-octylphenol; bisphenol A; triclosan

1. Introduction

Biosolids may contain a broad range of organic contaminants (e.g. Kinney et al., 2006; USEPA, 2009; Langdon et al., 2010), that can enter the environment when this product is applied to agricultural land as a replacement or supplement for inorganic fertilisers. Four specific organic compounds that have received increasing interest recently due to their potential adverse environmental effects, as a result of their toxicity and/or their ability to mimic natural hormones, are the surfactant metabolites, 4-nonylphenol (4NP) and 4-t-octylphenol (4tOP), the plasticiser bisphenol A (BPA) and the antimicrobial agent triclosan (TCS). These four compounds have been detected in biosolids at a range of concentrations, up to 438 000 µg/kg, 2400µg/kg, 4600 µg/kg (Kinney et al., 2006) and 133 000 µg/kg (USEPA, 2009), respectively. When assessing the potential risk that these compounds may pose to the environment following the application of biosolids to land, the time required for the compounds to degrade is an important factor that needs to be considered.

Soil degradation experiments conducted on the four target compounds (4NP, 4tOP, BPA and TCS) have reported half-lives or DT50 values (time taken for the initial concentration of the compound to decrease by half) ranging from 1 to 17 days (Topp & Starratt, 2000; Roberts et al., 2006), approximately 5 days (Ying & Kookana, 2005), 1 to 7 days (Ying & Kookana, 2005; Xu et al., 2009) and 13 to 58 days (Ying et al., 2007; Wu et al., 2009a; Xu et al., 2009), respectively. In addition to the above studies, the degradation of 4NP in soil following the addition of biosolids has been examined in more detail in several studies. For example, Marcomini et al. (1988) conducted a degradation experiment on several compounds, including 4NP, following sewage sludge application to soil and reported multiple phases of degradation for this compound. This consisted of an “initial” fast degradation phase, followed by a slower “transition” phase and then a final “persistent” phase. The average non-degraded residual concentration of 4NP at the completion of the experiment was 0.5 mg/kg (Marcomini et al.,

1988). In a more recent study, Brown et al. (2009), reported half-life values for 4NP in a biosolids amended soil of 16 to 23 days, however, found that 15 to 30% of the initial 4NP remained in the soil at the completion of the 45 day study.

It has been highlighted that the calculation of a single half-life or DT50 value for a compound in soil may be an oversimplification of a complex system, and the degradation is often more accurately described by models with multiple degradation phases (e.g. Hill & Schaalje, 1985; Marcomini et al., 1988; Ma, et al., 2004; Sarmah & Close, 2009), for example, biphasic degradation. Some research has shown that although a compound might show a small DT50 value in a soil (calculated from a standard first-order decay model), therefore predicting a fast degradation rate, accumulation over time can still be observed (Ciglasch et al., 2006). This indicates that the single DT50 value may not be appropriate in describing the degradation behaviour of some compounds. Biphasic degradation of organic compounds is often described using a two-compartment model where both fractions of a compound are degrading - one compartment degrading "fast" and the other compartment degrading "slow" (e.g. Hill & Schaalje, 1985; Ma, et al., 2004; Sarmah & Close, 2009). In several studies however, the slow degrading fraction has shown a rate constant of zero, indicating this fraction to be non-degrading or recalcitrant (e.g. Sjöström et al., 2008; Wu et al., 2009b).

The aim of this study was to examine the degradation of 4NP, 4tOP, TCS and BPA, following biosolids addition to a soil, under controlled laboratory conditions over a period of 32 weeks (i.e. 224 days). By conducting the study under controlled laboratory conditions, with constant temperature and moisture, any external influences caused by variations in climatic conditions were removed. The rate and pattern of degradation of the compounds was assessed to determine if it was consistent with a standard first-order degradation model or a biphasic model indicating the presence of a non-degrading or recalcitrant fraction was more appropriate.

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) (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. This soil had a pH of 4.4, which was determined from a soil solution ratio of 1:5 in 0.01M $CaCl_2$, 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 homogenized 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 ensure that there were no background concentrations of the target compounds (i.e. 4NP, 4tOP, TCS and BPA) prior to the commencement of all experimental work.

Two South Australian biosolids were collected and used in this study. Both biosolids had been treated by anaerobic digestion, but thereafter one of the biosolids had been centrifuge dried (CDB) and the other had been solar dried in a lagoon system (LDB). 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. 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. (2011).

2.2. Experimental design and set up

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 & 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 biosolids were added to the hydrated soil, in a randomised manner, 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. Five replicate samples from each biosolids treatment were then immediately freeze dried and homogenised by grinding and sieving to 2 mm before being stored 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 samples were opened to the air on a daily basis and the moisture content in the soil was maintained throughout the experiment by weight at 50% MWHC. At eight additional sampling intervals (3, 7, 14, 28, 56, 112, 168 and 224 days post biosolids addition), triplicate sample jars were removed from each of the biosolids treatments and freeze dried, ground and sieved for immediate analysis of the target compounds.

2.3. Sample extraction and gas chromatography-mass spectrometry analysis

The method used for sample extraction and analysis in this study was based on that outlined in Langdon et al. (2011), with the only variation being that the current study used a 10 g sample for extraction and analysis. In brief, each freeze dried sample was extracted three times with 1:1 methanol and acetone in an ultrasonic bath. For each sample the extracts were combined then diluted with MQ water and loaded onto Oasis HLB® solid phase extraction (SPE) cartridges. 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 biosolids) to detected any background contamination in 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 Mass Spectrometer (MS). The specific details of the GCMS parameters, the typical retention times of each of the compounds and target and qualifier ions are reported in Langdon et al. (2011). The concentrations of each of the compounds were determined from relative response factors based on the IS and then adjusted for extraction recoveries based on labelled surrogates (i.e. TCS-$^{13}C_{12}$, BPA-d_{16} and 4nNP-d_8) which were spiked into the samples one day prior to extraction. The recoveries of the labelled surrogates were used to determine the reproducibility of the method within each run and between different runs. 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 µg/kg respectively for 4NP, 0.6 and 2.0 µg/kg respectively for 4tOP, 0.3 and 1.0 µg/kg respectively for BPA, and 0.8 and 2.7 µg/kg respectively for TCS.

2.4. Statistical analysis and interpretation

Prior to all statistical analyses, the concentration data at each sampling interval 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 degradation data included a univariate analysis of variance (ANOVA) to determine if the compounds significantly decreased over the 224 days of the experiment, using PASW Statistics® 17. Nonlinear regressions were also conducted to determine the degradation patterns of each compound. There were two nonlinear regression

models fitted to the degradation data of each compound based on first-order kinetics, using SigmaPlot®. The first model was a standard first-order exponential decay model (with two fitting parameters) and the second model was a biphasic model (with three fitting parameters) that accounted for a degrading 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 degrading fraction, and a y-intercept (x_0), which indicated the recalcitrant fraction. The residual sums of squares were then used to statistically compare the two models to determine which provided the best fit to the data. A detailed outline of the nonlinear regression models is provided in the supplementary material.

3. Results

3.1. 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 4NP. The concentrations of 4NP in the method blanks varied from approximately 60 to 130 µg/L in the final solution. These background concentrations of 4NP were subtracted from each of the samples prior to the concentrations being converted to µg/kg.

The relative standard deviations (RSD) for the labelled surrogates within each run were in the majority of cases less than 25%, however, in few cases did vary up to 30%. This indicated that within each run the variation between the samples was relatively small. Comparison of the average recoveries of the labelled surrogates between each sampling interval was used to provide an indication of the variation in the method between each run. The overall average recovery for 4nNP-d_8 was 66% in the CDB treatment and 65% in the LDB treatment, for BPA-d_{16} it was 104% and 96%, respectively, and for TCS$^{13}C_{12}$ it was 84% and 91%, respectively. The RSD for these recovery averages, were below 20% for 4nNP-d_8 and TCS$^{13}C_{12}$ in each of the

193 treatments, whereas for BPA-d_{16} they were below 25%. This indicated that the method used for
194 extraction and analysis of the samples in this study was reproducible.
195
196 ***3.2. Preliminary field soil and biosolids analysis***
197 Analysis of the field soil prior to the commencement of the experiment showed that there were
198 no background concentrations of any of the target compounds, 4NP, 4tOP, BPA and TCS (i.e.
199 all compound concentrations < LOD). The analysis of the two biosolids samples prior to their
200 addition to the soil showed detectable levels of the four target compounds. In the CDB sample
201 the average concentrations of 4NP, 4tOP, BPA and TCS were 280 mg/kg, 2.3 mg/kg, 0.19
202 mg/kg and 3.1 mg/kg, respectively. There was minimal variation between the replicate sub-
203 samples of the CDB indicated by RSD values of less than 10% for each of the four compounds.
204 In comparison, analysis of the LDB sample showed concentrations of 43 mg/kg, 2.4 mg/kg, 0.17
205 mg/kg and 5.9 mg/kg, respectively. The LDB sample showed more variation between the
206 replicates when compared to the CDB, with RSD values of less than 20% for 4NP, 4tOP and
207 TCS and approximately 30% for BPA.
208
209 ***3.3. Degradation of 4-nonylphenol (4NP) from biosolids amended soil***
210 In the initial t_0 soil samples the average concentration of 4NP across the five replicates in the
211 CDB treatment was 11 800 µg/kg, whereas in the LDB treatment it was 1690 µg/kg (Table 1).
212 This large difference between the samples was expected due to the large variation in 4NP
213 concentration in the original biosolids samples. There was significant degradation of 4NP
214 following the addition of both biosolids treatments to the soil over the 224 days of the study ($p <$
215 0.0005) (Figure 1). For both biosolids treatments, from 28 days post biosolids addition, to the
216 completion of the experiment (i.e. 224 days) there was no significant change ($p > 0.05$) in
217 concentration of 4NP.
218

The fit of the first-order model for the 4NP degradation data to both biosolids treatments was significant (both p-values < 0.001) and had R^2 values of 0.62 and 0.68 for the CDB and LDB treatments respectively (Figure 1 and Table 2). The DT50 values for 4NP obtained from this model were 12 and 25 days for the CDB and LDB treatments, respectively. The statistical comparison of the two models (i.e. first-order and biphasic) to the 4NP degradation data showed that the biphasic model explained the data significantly better than the first-order model (both p-values ≤ 0.04, Table 2). The effect of adding the third parameter in the biphasic model on the fit to the data was more marked for the CDB treatment ($p < 0.001$) than for the LDB treatment ($p = 0.04$). The $DT50_{biphasic}$ values for 4NP were 5.8 days in the CDB treatment and 14 days in the LDB treatment (Table 2). The biphasic model fitted to the normalised degradation data produced x_0 values for the CDB and LDB treatments of 0.21 and 0.17 respectively, indicating 21% of the initial concentration of 4NP in the CDB treatment and 17% of the initial concentration of 4NP in the LDB treatments was persistent though to the completion of the experiment (i.e. after 224 days). These recalcitrant fractions corresponded to 4NP concentrations of 2500 µg/kg in the CDB treatment and 290 µg/kg in the LDB treatment at the completion of this study.

3.4. Degradation of 4-t-octylphenol (4tOP) from biosolids amended soil

The initial t_0 soil samples showed concentrations of 4tOP in the CDB and LDB treatments of 73 µg/kg and 129 µg/kg, respectively (Table 1). There was significant degradation of the compound 4tOP over the 224 days of this study ($p < 0.0005$) (Figure 2). The samples analysed from 28 days post biosolids addition to the completion of the experiment (i.e. 224 days), in both biosolids treatments, showed no significant changes in the concentration of 4tOP ($p > 0.05$).

The fit of the first-order model to the 4tOP normalised degradation data was significant for both the biosolids treatments (both p-values < 0.001) and also produced high R^2 values (0.81 for the CDB treatment and 0.79 for the LDB treatment) (Figure 2 and Table 2). The DT50 values

obtained for 4tOP from this model were 14 days for the CDB treated soil and 10 days for the LDB treated soil. The fit of the biphasic model to the 4tOP degradation data produced marginally higher R^2 values than the first-order model, however, it did not significantly improve the fit of the degradation data for 4tOP (p-values = 0.07 and 0.34 for the CDB and LDB treated soils respectively, Table 2).

3.5. Degradation of bisphenol A (BPA) from biosolids amended soil

At the commencement of the experiment, BPA was detected in the soil treated with the CDB at a concentration of 5.9 µg/kg and the LDB at a concentration of 9.8 µg/kg (Table 1). The concentrations of BPA in each of the biosolids treatments were found to significantly decrease over the 224 day study ($p < 0.0005$) (Figure 3). From 28 days post biosolids addition through to the completion of the experiment, there was no significant changes in BPA concentration ($p > 0.05$).

The fitting of the first-order model to the BPA degradation data was significant (both p-values ≤ 0.003) and produced R^2 values of 0.29 for the CDB treated and 0.55 for the LDB treated soils (Figure 3 and Table 2). The DT50 values that were obtained from the first-order model differed considerably between the two biosolids treatments, being 102 days for the CDB treated soils and 18 days for the LDB treated soils. The additional parameter in the biphasic model significantly improved the fit to the BPA degradation data for both the CDB and LDB treated soils (both p-values ≤ 0.003). The biphasic model accounted for 53% of the variation in the degradation data from the CDB treated soils and 68% of the variation from the LDB treated soils (Table 2). The $DT50_{biphasic}$ values calculated from this model were 8.7 days in the CDB treated soils and 7.7 days in the LDB treated soils (Table 2). The proportion of the initial BPA concentration than was predicted by the biphasic model to be recalcitrant at the completion of the experiment, was 42% in the CDB treated soils and 24% in the LDB treated soils (Table 2). These recalcitrant

fractions corresponded to virtually the same concentration in the two biosolids treatments at the end of the experiment, with values of 2.5 µg/kg and 2.4 µg/kg, respectively.

3.6. Degradation of triclosan (TCS) from biosolids amended soil

The initial t_0 soil samples showed concentrations of TCS in the CDB and LDB treatments of 184 µg/kg and 361 µg/kg, respectively (Table1). The concentrations of TCS significantly decreased throughout the duration of the experiment ($p < 0.0005$) (Figure 4). There was a rapid decrease in the concentration of TCS at the commencement of the experiment and this resulted in a significant decrease observed 3 days post biosolids addition for both biosolids treatments. The concentrations of TCS did not change significantly, however, from 14 days post biosolids addition until the completion of the experiment (i.e. 224 days) in both of the biosolids treatments.

The fit of the first-order model to the TCS degradation data was significant for both the CDB and LDB treated soils (both p-values ≤ 0.03), however, this model only accounted for 17% of the variation in the data for the CDB treatment, whereas, for the LDB treatment it accounted for 57% of the variation (Figure 4 and Table 2). The DT50 values calculated from the first-order model varied considerably between the two biosolids treatments and were 301 days and 73 days for the CDB and LDB treatments, respectively (Table 2). The fit of the biphasic model to the degradation data for TCS from both biosolids treatments showed higher R^2 values of 0.58 and 0.76 for the CDB and LDB treatments, respectively (Table 2), when compared to the first-order model. When the fits of the two models were compared statistically, the biphasic model significantly improved the explanation of variation in the data (both p-values < 0.001, Table 2). The $DT50_{biphasic}$ values obtained for TCS were 1.2 days in the CDB treatment and 6.3 days in the LDB treatment. The x_0 values obtained from the biphasic model for the TCS degradation data in the CDB and LDB treatments were 0.51 and 0.30, respectively, indicating that 51% and 30% of

297 the initial TCS remained in the soil. These recalcitrant fractions corresponded to 94 µg/kg and
298 108 µg/kg of TCS in the CDB and LDB treatments, respectively.
299
300 **4. Discussion**
301 When the DT50 values that were obtained in this study are compared to those that have been
302 reported in the literature, they are generally similar or only slightly higher when the majority of
303 the variation in the data is explained by the model. For example, Brown et al. (2009) reported
304 half life values for 4NP from a biosolids amended soil of 16 to 23 days, which is in the same
305 range as those reported in this study of 12 to 25 days. For 4tOP, in a study where the compound
306 was spiked into a soil, the average half life was reported to be 5 days (Ying & Kookana, 2005),
307 which is approximately 2- to 3-times smaller than those reported in this study of 10 to 14 days.
308 These small differences may be due to variations in experimental conditions and also from the
309 addition of the compound through spiking rather than in biosolids. For the two compounds BPA
310 and TCS, in the cases where the fit to the first-order model was reasonably good (i.e. $\geq$ 55%),
311 the DT50 values were only marginally larger than those reported in literature. In this study the
312 DT50 value for BPA in the LDB treatment was 18 days, whereas others have reported values
313 ranging from 1 to 7 days (Ying & Kookana, 2005; Xu et al., 2009). For TCS also in the LDB
314 treatment, the DT50 value in this study was 73 days, which is only slightly larger than the value
315 reported by Wu et al. (2009a) (i.e. 58 days), however it is approximately 4-times larger than that
316 reported by Ying et al. (2007). For BPA and TCS in the CDB treatment, where a low proportion
317 of the variation in the data was explained by the first-order model, the DT50 values are
318 considerably larger than those calculated for the LDB treatment and those in other studies. The
319 DT50 value for BPA in the CDB treatment was approximately 15-times larger than the highest
320 value reported in other studies (Ying & Kookana, 2005) and for TCS in the same biosolids
321 treatment, the value was approximately 5-times longer than the highest reported elsewhere (Wu
322 et al., 2009a). Due to the poor fit of the first-order model (i.e. two fitting parameter model) to the

degradation data for these two compounds in the CDB treatment, it is likely that the use of a DT50 value is not sufficient in explaining the degradation rate and pattern of these compounds and provides an unreliable prediction of their persistence.

When an additional parameter was used in the biphasic model, the fit to the data was significantly improved for 4NP, BPA and TCS. This was not the case for 4tOP, where the additional fitting parameter in the biphasic model provided no statistically significant improvement in explaining the variation in the data. This is likely to be due, in part, to the fit of the first-order model being quite good for this compound (R^2 = 0.79 and 0.81) and the fact that the normalised concentration values decrease more than the other compounds over the duration of the study (Table 2 and Figure 2). The results observed in this study for the compounds 4NP, BPA and TCS are consistent with other research. For example Marcomini et al. (1988) who reported a persistent fraction of approximately 10% for 4NP following sewage sludge addition to soil and Sjöström et al. (2008), who reported recalcitrant fractions of 26 – 35% for NP following the addition of sewage sludge to soil. There are several possible suggestions for the presence of a recalcitrant fraction of these compounds in a biosolids amended soil. It has been suggested that the presence of a recalcitrant fraction is due to the distribution of the compound throughout the heterogeneous aggregates of the biosolids (Hesselsoe et al., 2001; Sjöström et al., 2008). The formation of biosolids aggregates tends to produce aerobic zones in the outer areas and anaerobic zones in the centre of aggregates, which can result in persistent or recalcitrant concentrations of the compounds contained within the biosolids (Hesselsoe et al., 2001). As the compounds assessed in this study degrade predominately under aerobic conditions (e.g. McAvoy et al., 2002; Ying & Kookana, 2005; Press-Kristensen et al., 2008), the presence of anaerobic zones in the biosolids aggregates is likely to have resulted in the degradation slowing considerably or halting. A further hypothesis is that the recalcitrant fraction is due to sorption that is non-reversible which means that there is a sorbed fraction that is not available to

349 microorganisms and hence non-degradable (Wu et al., 2009b). In addition to these above
350 suggestions, it should be noted that generally a biosolids matrix is complex and may involve
351 many components. Various organic compounds may sorb more strongly to the matrix or to
352 different components of the matrix, resulting in the presence of recalcitrant fractions. This may
353 explain the differing proportions of each of the compounds in this study that were recalcitrant
354 using the same soil amended with different biosolids and the lack of a recalcitrant fraction
355 (statistically) for the compound 4tOP.
356
357 Overall, the results from this study raise concerns relating to the potential accumulation of
358 organic compounds in biosolids amended soils particularly if repeat applications are made. This
359 is particularly the case for the compounds BPA and TCS which had the highest recalcitrant
360 fractions (42% and 51% respectively). In addition, this study also showed that the use of a single
361 value, for example DT50, is insufficient in explaining the degradation of the four compounds
362 4NP, 4tOP, BPA and TCS. Although in most cases a large proportion of the data was explained
363 by the first-order model, this was significantly improved by the biphasic model. The use of the
364 most appropriate model is crucial when determining the risks associated with these compounds
365 following the addition of biosolids to land, as use of an incorrect model could lead to significant
366 underestimation of the persistence of organic compounds in biosolids amended soils.
367
368 **5. Conclusion**
369 The four compounds 4-nonylphenol (4NP), 4-t-octylphenol (4tOP), bisphenol A (BPA) and
370 triclosan (TCS) were found to degrade over time when added to a soil via two biosolids. The
371 time taken for the initial concentration to decrease by 50% (DT50), based on a standard first-
372 order decay model, were 12 to 25 days for 4NP, 10 to 14 days for 4tOP, 18 to 102 days for BPA
373 and 73 to 301 days for TCS. The use of the first-order model produced DT50 values that were
374 consistent with other research only when a considerable portion of the variation was explained

by the model. When the first-order model did not explain a considerable portion of the variation, the calculated DT50 values were markedly longer than those reported in the literature. For 4NP, BPA and TCS, a biphasic model, which accounts for a recalcitrant fraction, fitted the degradation data significantly better than the first-order model. The recalcitrant concentrations for these three compounds as predicted by the biphasic model were 297 – 2480 µg/kg for 4NP, 2.4 – 2.5 µg/kg for BPA and 94 – 108 µg/kg for TCS, which corresponded to 17 to 21%, 24 to 42% and 30 to 51% of the initial concentrations, respectively. In contrast, for 4tOP, the first-order model was sufficient for predicting its degradation thus indicating that there was no statistical evidence for a recalcitrant fraction of this compound. It appears that different biosolids matrices may influence the degradation of these compounds. The better fit of the biphasic model for some organic contaminants found in biosolids is possibly related to anaerobic conditions within biosolids aggregates and differential non-reversible sorption of compounds to the biosolids matrix. This study shows that the use of the most appropriate model for degradation is crucial when assessing the persistence of compounds in soils following the addition of biosolids.

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Table 1: The average and range of concentrations of the compounds 4-nonylphenol (4NP), 4-t-octylphenol (4tOP), bisphenol A (BPA) and triclosan (TCS) in the initial (t_0) sample for the centrifuge dried biosolids (CDB) and lagoon dried biosolids (LDB) treatments.

Biosolids treatment	**Initial compound concentration (µg/kg)**			
	4NP	**4tOP**	**BPA**	**TCS**
CDB	11800 (7780-16600)	73 (40-105)	5.9 (4.1-8.1)	184 (146-236)[a]
LDB	1690 (607-2480)	129 (53-193)	9.8 (5.0-15)	361 (238-503)

[a] The actual upper limit of this range was 462 µg/kg, however this value was removed as an outlier

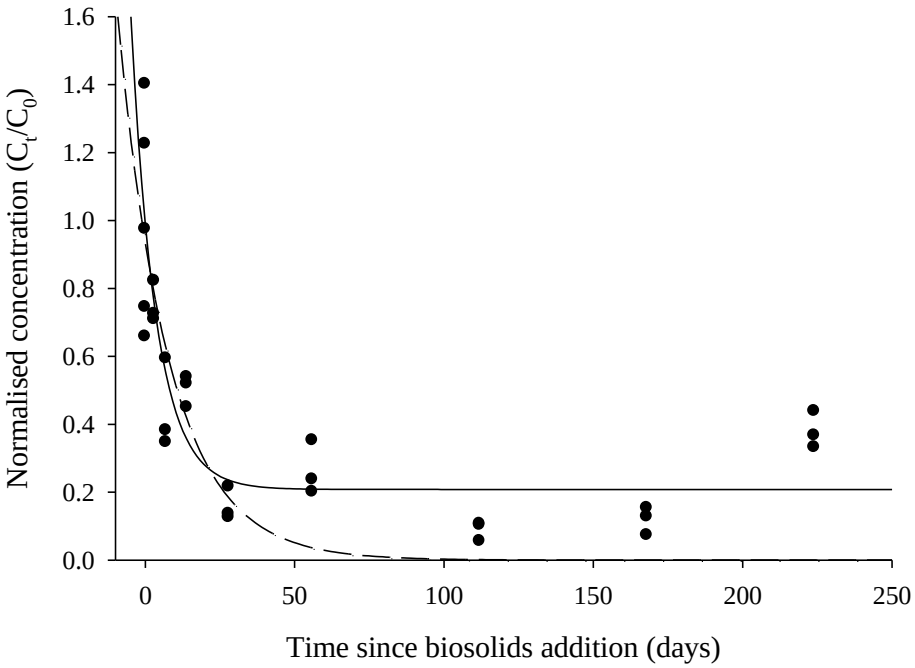
Table 2: Summary of the degradation information from the first-order and biphasic models for the compounds 4-nonylphenol (4NP), 4-t-octylphenol (4tOP), bisphenol A (BPA) and triclosan (TCS) for the centrifuge dried biosolids (CDB) and lagoon dried biosolids (LDB) treatments. The dissipation half lives determined using the first-order and biphasic models (DT50 and $DT50_{biphasic}$ respectively) are shown in days and the y-intercept (y_0) values correspond to the C_t/C_0 values. The significance values were calculated using equation 4-5.

Model	**Measure**	**4NP**		**4tOP**		**BPA**		**TCS**	
		CDB	**LDB**	**CDB**	**LDB**	**CDB**	**LDB**	**CDB**	**LDB**
first-order	**R^2**	0.62	0.68	0.81	0.79	0.29	0.55	0.17	0.57
	DT50	12	25	14	10	102	18	301	73
	p-value[a]	<0.001	<0.001	<0.001	<0.001	0.003	<0.001	0.03	<0.001
biphasic	**R^2**	0.78	0.73	0.83	0.80	0.53	0.68	0.58	0.76
	$DT50_{biphasic}$	5.8	14	9.9	8.7	8.7	7.7	1.2	6.3
	y_0	0.21	0.17	0.10	0.06	0.42	0.24	0.51	0.30
	p-value[b]	<0.001	0.04	0.07	0.34	0.001	0.003	<0.001	<0.001
	best fit	biphasic	biphasic	first order	first order	biphasic	biphasic	biphasic	biphasic

[a] significance of the first-order model; [b] significance of the biphasic model compared to the first-order model

Figure 1

(a) CDB



(b) LDB

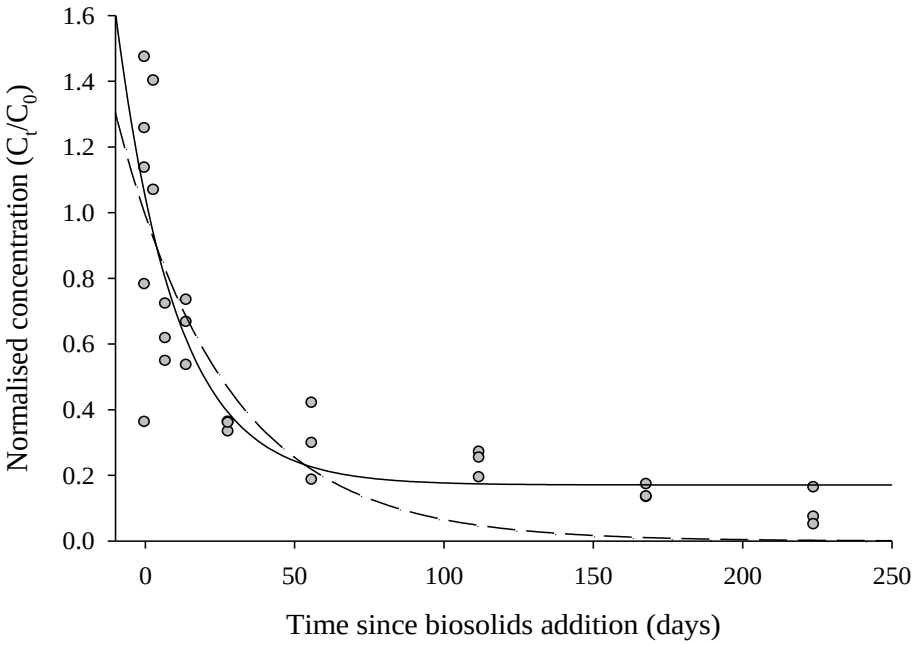
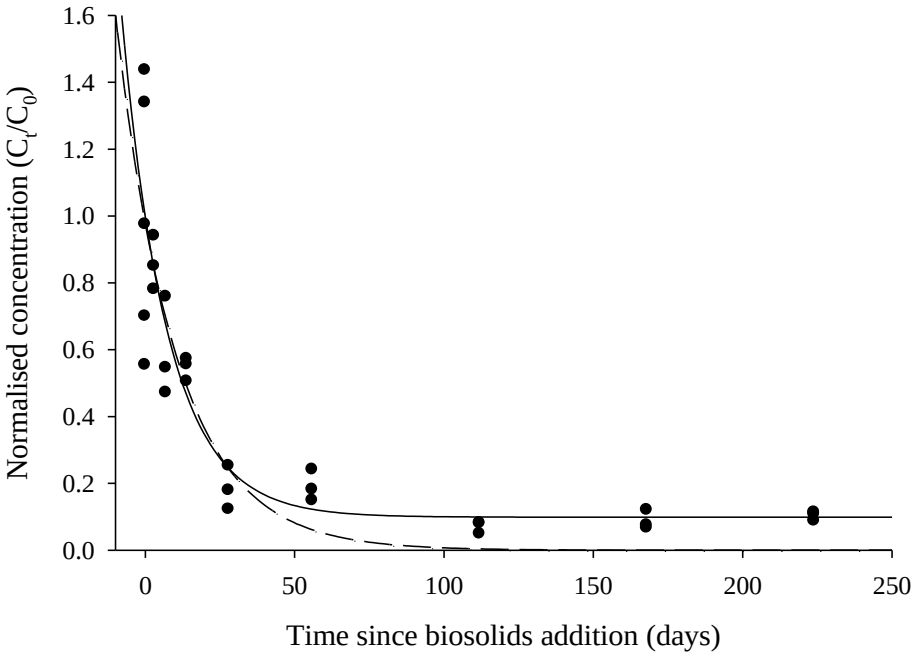


Figure 2

(a) CDB



(b) LDB

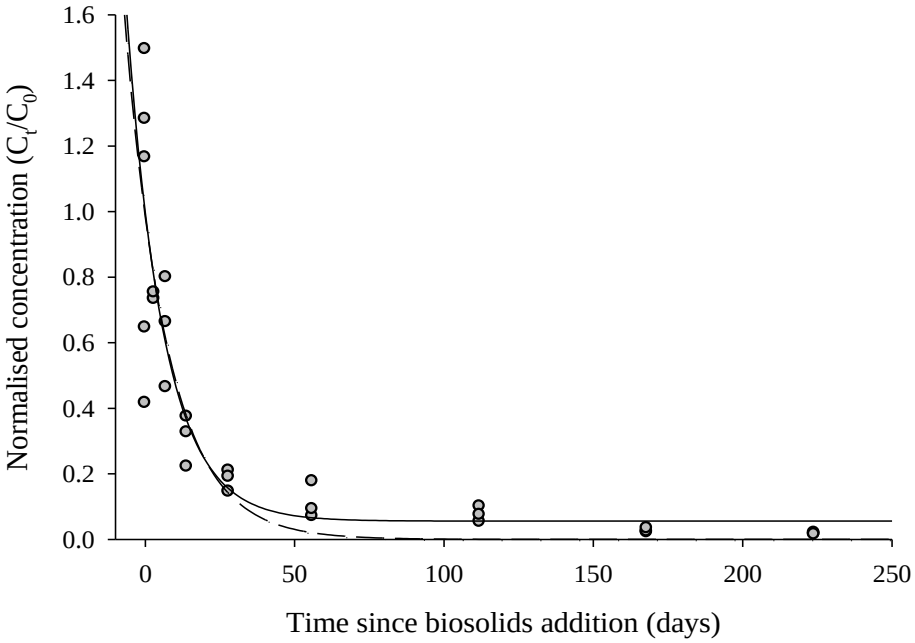
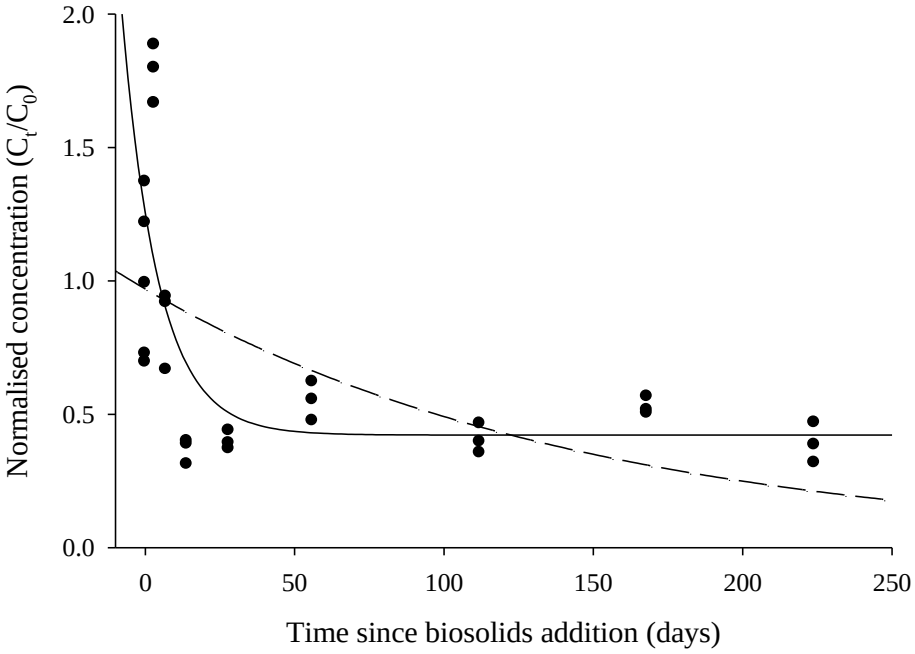


Figure 3

(a) CDB



(b) LDB

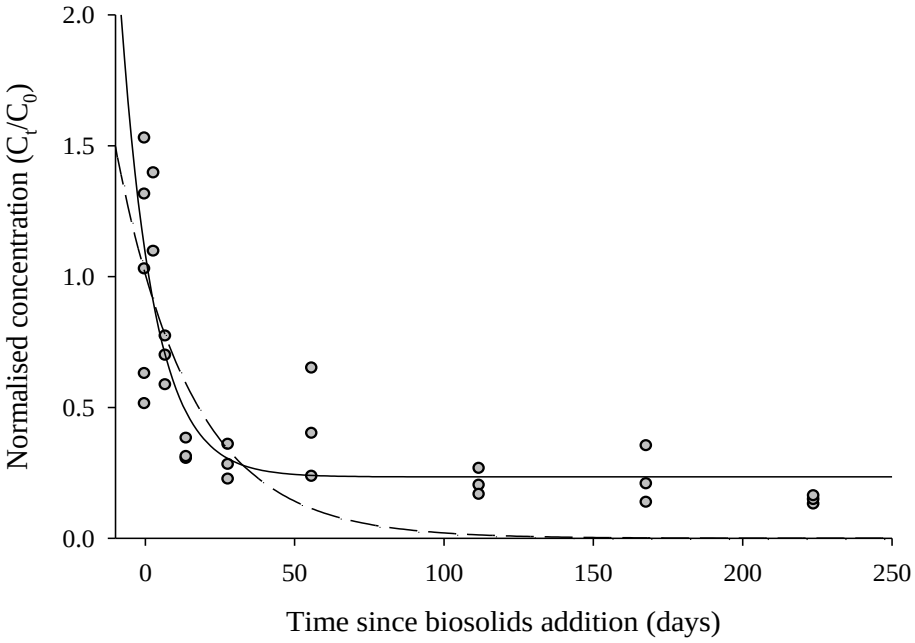
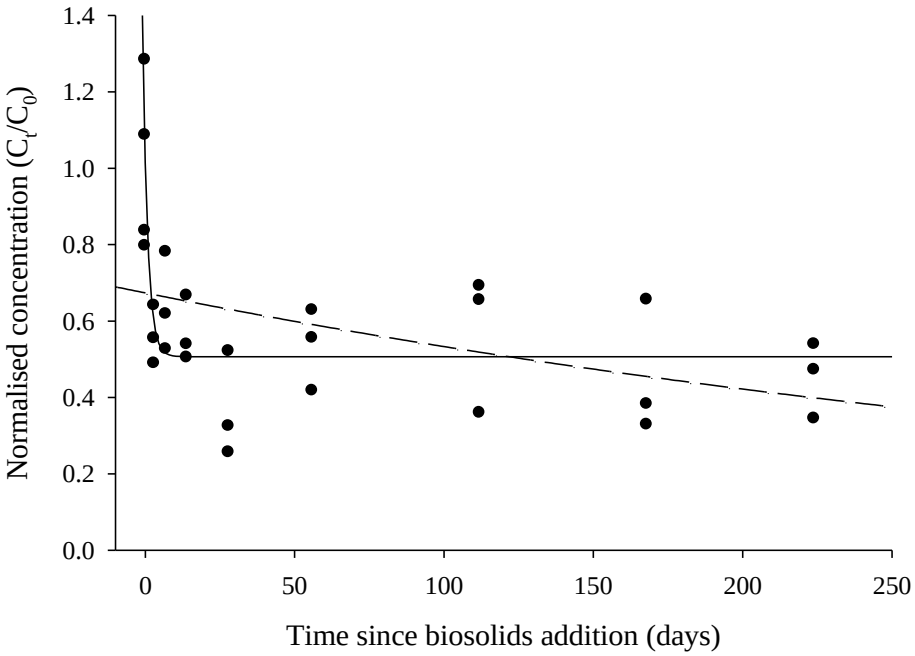


Figure 4

(a) CDB



(b) LDB