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

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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.

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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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