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Selected personal care products and endocrine disruptors in biosolids: An Australia-wide survey

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ABSTRACT

Personal care products (PCPs) and endocrine disrupting compounds (EDCs) are groups of organic contaminants that have been detected in biosolids around the world. There is a shortage of data on these types on compounds in Australian biosolids, making it difficult to gain an understanding of their potential risks in the environment following land application. In this study, 14 biosolids samples were collected from 13 Australian wastewater treatment plants (WWTPs) to determine concentrations of eight compounds that are PCPs and/or EDCs: 4-t-octylphenol (4tOP), 4-nonylphenol (4NP), triclosan (TCS), bisphenol A (BPA), estrone (E1), 17β-estradiol (E2), estriol (E3) and 17α-ethinylestradiol (EE2). Concentration data were evaluated to determine if there were any differences between samples that had undergone anaerobic or aerobic treatment. The concentration data were also compared to other Australian and international data. Only 4tOP, 4NP, TCS, and BPA were detected in all samples and E1 was detected in four of the 14 samples. Their concentrations ranged from 0.05 to 3.08 mg/kg, 0.35 to 513 mg/kg, <0.01 to 11.2 mg/kg, <0.01 to 1.47 mg/kg and <45 to 370 μg/kg, respectively. The samples that were obtained from WWTPs that used predominantly anaerobic treatment showed significantly higher concentrations of the compounds than those obtained from WWTPs that used aerobic treatment. Overall, 4NP, TCS and BPA concentrations in Australian biosolids were lower than global averages (by 42%, 12% and 62%, respectively) and 4tOP concentrations were higher (by 25%), however, of these differences only that for BPA was statistically significant. The European Union limit value for NP in biosolids is 50 mg/kg, which 4 of the 14 samples in this study exceeded.

1. Introduction

Personal care products (PCPs) and endocrine disrupting compounds (EDCs) are two groups of organic contaminants that have received interest recently due to their potential release into the environment following wastewater treatment and the potential for subsequent environmental risks. Environmental research into PCPs and EDCs has predominantly focussed on their removal from the aqueous phase during wastewater treatment (e.g. Zorita et al., 2009) and their potential deleterious effects to aquatic organisms when released in effluents (e.g. Batty and Lim, 1999; Castro et al., 2007). The removal of PCPs and EDCs from the aqueous phase occurs via degradation, as a result of treatment processes, or through sorption to the solid waste phase, referred to as biosolids. The levels of PCPs and EDCs that are found in biosolids may also be of environmental concern, as in many countries, including Australia, biosolids are applied to land as a supplement or replacement for inorganic fertilisers.

Numerous PCPs and EDCs have been identified in biosolids (Ternes et al., 2002; Braga et al., 2005; Kinney et al., 2006; Chu and Metcalfe, 2007), however, the potential environmental risks that these compounds pose vary. Eight PCPs and EDCs were selected for the current study because of environmental concerns, including their potential to cause adverse impacts to aquatic (Langdon et al., 2010) and/or terrestrial ecosystems (Waller and Kookana, 2009). The compounds selected were the EDCs 4-nonylphenol (4NP), 4-t-octylphenol (4tOP) and bisphenol A (BPA), the antimicrobial agent triclosan (TCS) and the natural and synthetic estrogenic compounds 17β-estradiol (E2), estrone (E1), estriol (E3) and 17α-ethinylestradiol (EE2).

The surfactant metabolites 4NP and 4tOP and the industrial chemical BPA are all compounds that have been found to mimic natural hormones and interfere with estrogen receptors in non-target organisms (Jobling and Sumpter, 1993; Jobling et al., 1996; Fukuhori et al., 2005). The compound 4NP tends to be very prevalent in biosolids at concentrations ranging from 600 to 438 000 μg/kg (Kinney et al., 2006). This finding is consistent with the widespread use of the parent alkylphenol ethoxylate compounds in many industrial and domestic surfactant products (Ying et al., 2002). In comparison, the parent compounds that ultimately degrade to 4tOP

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are used to a lesser extent in surfactant products, resulting in lower biosolids concentrations of this compound, with reported concentrations in the range from 167 to 2400 μg/kg (Kinney et al., 2006). The compound BPA, which is used in the production of polycarbonate plastics, epoxy resins and flame retardants (Staples et al., 1998), has been detected in biosolids at a similar range of concentration of 100–4600 μg/kg (Kinney et al., 2006).

Triclosan is a commonly used antimicrobial agent found in many domestic personal care products (e.g., soaps, detergents, surface cleaners, disinfectants, cosmetics and other topical personal care products, pharmaceuticals and oral hygiene products), with published concentrations in biosolids ranging from 90 μg/kg (Ying and Kookana, 2007) to 21 740 μg/kg (Campbell-Board, 2005). As TCS is used specifically for its antibacterial properties, its subsequent release into the environment may lead to toxicity to non-target organisms, with a specific risk to micro-organisms. In the recent Targeted National Sewage Sludge Survey (TNSSS), conducted by the United States Environmental Protection Agency (USEPA), TCS was detected in 94% of the samples at concentrations ranging from 0.43 to 133 mg/kg (USEPA, 2009).

The naturally occurring estrogen compound E2, its metabolites E1 and E3, and the synthetic estrogen compound EE2 (the active compound used in the female contraceptive pill) mainly enter the environment via WWTPs, following excretion from humans. These compounds have received considerable attention recently as they are highly potent compounds and can produce estrogenic responses in non-target organisms at trace concentrations, in the ng/L range (Mills and Chichester, 2005). In the TNSSS, the three naturally occurring estrogens, E1, E2 and E3, were detected in 71%, 13% and 21% of sludge samples, respectively, with the lowest overall concentrations being for E3 (7.6 to 232 μg/kg) and the highest being for E1 (26.7 to 965 μg/kg) (USEPA, 2009). Other published biosolids concentration values for E1 and E2 range from 12 to 150 μg/kg and 0.31 to 49 μg/kg, respectively (Ternes et al., 2002; Braga et al., 2005; Kinney et al., 2006). In comparison, EE2 has been detected in biosolids samples at considerably lower concentrations ranging from 0.42 to 17 μg/kg (Ternes et al., 2002; Braga et al., 2005), and in the TNSSS it was below the limit of detection (LOD) (i.e. <21 μg/kg) in all samples that were analysed.

The aim of this study was to conduct a survey of Australian biosolids to obtain data on concentrations of 4tOP, 4NP, TCS, BPA, E1, E2, E3 and EE2 and to determine if concentrations varied between WWTPs that used differing treatment processes (i.e. anaerobic or aerobic treatment). In addition, the aim was to compare the concentrations of the selected compounds to previous Australian and global concentration data, as well as threshold limits where available.

2. Materials and methods

2.1. Biosolids sample collection and preparation for analysis

Fourteen different biosolids samples, each collected as four replicates, were obtained between January and March 2009 from 13 WWTPs located in all six Australian states and the Northern Territory. Personnel at each WWTP collected the four replicates in pre-cleaned 250 mL glass jars with Teflon-lined lids. At the time of sampling, the personnel filled out an information sheet providing a description of the treatment processes used on the samples. After collection, all samples were placed in insulated containers with ice packs and sent by overnight courier to the laboratory where they were immediately placed in a freezer at −18 °C. All samples were then freeze dried, homogenised using a mortar and pestle and sieved to <2 mm.

2.2. Sample extraction and gas chromatography–mass spectrometry analysis

All replicates of the 14 different biosolids samples were extracted and prepared for analysis of the eight target compounds, 4tOP, 4NP, TCS, BPA, E1, E2, E3 and EE2. All glassware used for extraction and preparation of the samples had been pre-cleaned by solvent rinsing and baking at 350 °C. One day prior to sample extraction, 1 g of each biosolids sample was weighed into a glass tube (i.e. one tube for each replicate). For quality assurance, one of the replicates from each WWTP was duplicated and a method blank was run with each batch of samples. The method blank was an empty glass tube (i.e. containing no biosolids), which was run through the entire extraction and preparation concurrently with the biosolids samples. This was done to ensure that there was no contamination in any of the solvents or sample preparation steps. Two randomly selected samples from each batch were also spiked with labelled surrogates in methanol (i.e. 4nNP–d_8, TCS–$^{13}C_{12}$, BPA–d_{16}, E1–d_4, E2–d_4, EE2–$^{12}C_2$) that were used to determine recoveries (see Table 1 for details). Following surrogate spiking, samples were left overnight in the dark for extraction the following day. Each sample was extracted three times. Each extraction involved adding 10 mL of a 1:1 mixture of methanol and acetone to the sample and placing it in an ultrasonic bath for 10 min. After ultrasonication, the sample was centrifuged at 630 *g* for 20 min and the supernatant decanted into a 500 mL clean glass amber bottle. The subsequent two supernatants were added to the same amber bottle after extraction and centrifugation. The extracts were diluted to 500 mL with MilliQ (MQ) water and loaded onto Oasis HLB® solid phase extraction (SPE) cartridges which had been preconditioned

Table 1
Typical retention times for the internal standard, labelled surrogates and target compounds using gas chromatography–mass spectrometry (GC–MS) and the corresponding limit of detection (LOD) and limit of quantification (LOQ).

Compound type	Compound name	Retention time (min)	Quantitation ion (*m*/*z*)	Qualifier ion 1 (*m*/*z*)	Qualifier ion 2 (*m*/*z*)	Qualifier ion 3 (*m*/*z*)	LOD (μg/kg)	LOQ (μg/kg)
Internal standard	Anthracene d_{10}	12.31	188	158	94	–		
Labelled surrogates	4nNP–d_8	13.11	185	300	285	–		
	TCS–$^{13}C_{12}$	14.52	206	357	372	322		
	BPA–d_{16}	14.98	368	386	217	–		
	E1–d_4	17.43	346	220	261	246		
	E2–d_4	17.63	420	287	234	220		
	EE2–$^{13}C_2$	18.37	427	232	442	272		
Compounds	4tOP[a]	10.89	207	263	278	–	10	30
	4NP[a]	12.09	207	221	193	179	55	180
	TCS[b]	14.47	200	347	362	310	10	30
	BPA[c]	15.02	357	372	191	–	10	30
	E1[d]	17.43	342	257	244	218	45	150
	E2[e]	17.63	416	285	327	232	45	150
	EE2[f]	18.37	425	285	300	440	45	150
	E3[e]	18.97	311	345	504	386	45	150

Superscripts indicate for each analyte the labelled surrogate that was used to determine recoveries: [a]4nNP–d_8; [b]TCS–$^{113}C_{12}$; [c]BPA–d_{16}; [d]E1–d_4; [e]E2–d_4; [f]EE2–^{13}C.