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Polybrominated diphenyl ethers and polybrominated biphenyls in Australian sewage sludge

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ABSTRACT

This paper presents a brief review of the international scientific literature of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) in sewage sludge and a survey of these compounds in sewage sludge from 16 Australian wastewater treatment plants (WWTPs). The Σ PBDE mean concentration in the Australian study was $1137 \mu\text{g kg}^{-1}$ dry weight (d.w.) (s.d. 1116) and ranged between 5 and $4230 \mu\text{g kg}^{-1}$ d.w. The urban mean of $1308 \mu\text{g kg}^{-1}$ (s.d. 1320) and the rural mean of $911 \mu\text{g kg}^{-1}$ (s.d. 831) are not statistically different and are similar to levels in European sludges. Principal components analysis was performed on the data set and revealed that 76% of the data variation could be explained by two components that corresponded to overall concentration of the pentaBDE and the decaBDE commercial formulations. An analysis of variance was performed comparing PBDEs levels at three WWTPs over the years 2005 and 2006, finding differences between treatment plants (BDE-47) but no significant difference in PBDE levels in the years 2005 and 2006. Low levels of BB-153 were detected in all samples of this survey ($n=16$); mean $0.6 \mu\text{g kg}^{-1}$ d.w. (s.d. 0.5). This compound has rarely been reported in any other study of sewage sludges undertaken outside Australia. This work highlights the need for a risk assessment of PBDEs in sewage sludge when used for land application, taking into account typical levels found in Australian sludges and soils.

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1. Introduction

This paper presents a brief review of the international scientific literature of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) in sewage sludge and a survey of these compounds in sewage sludge from 16 Australian wastewater treatment plants (WWTPs). This research was undertaken because of concerns raised by the Australian waste water industry regarding organic contaminants in sewage sludge, in particular the brominated flame retardants (BRFs).

Due to the widespread use of polybrominated diphenyl ethers (PBDEs) as fire retardants in a wide range of products and as a result of their chemical properties, these compounds have now accumulated within many environmental compartments. This includes the accumulation of PBDEs within living organisms, resulting in the exponential increase in concentration in humans over the past

25 years (Norén and Meironyte, 2000). The scientific evidence overwhelmingly supports the argument that PBDEs are candidates for inclusion in United Nations Environment Programme's (UNEP) Stockholm Convention on Persistent Organic Pollutants (POPs), i.e., they are environmentally persistent (Law et al., 2006), capable of long-range atmospheric transport (Schmid et al., 2007), bioaccumulate (Harden et al., 2005) and are biologically active (McDonald, 2002). Therefore, it is crucial to know the levels and environmental fate of PBDEs. Sewage sludge is an important medium requiring monitoring for chemical pollution, as one of the responsibilities of wastewater treatment is to prevent the (re)release of chemical pollutants into the environment, and sewage sludge is an important sink for POPs. The analysis of sewage sludge for POPs provides valuable information about chemical pollution and the risk associated with the re-use of sewage sludge as biosolids for land application.

PBDEs are a class of BFR that have been manufactured in three commercial formulations, sold under the name of the prominent homologue, i.e., pentaBDE, octaBDE and decaBDE. These commercial formulations contain many BDE congeners (BSEF, 2005). In many nations, the use of PBDE fire retardants is being phased out – in particular, the pentaBDE and octaBDE formulations. Their use has been restricted in many parts of Europe, Japan, some states

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of the USA as well as in Australia (BSEF, 2005; NICNAS, 2007). The manufacture and use of PBBs was largely curbed in the 1970s as a result of a serious human contamination incident in Michigan, USA (IPCS, 1994). Similar to the PBDEs, PBBs were manufactured in three main commercial formulations that was sold under the name of the prominent homologue, i.e., hexaBB, octaBB and decaBB (IPCS, 1994). The production of PBBs has been phased out internationally with the last PBBs manufactured in France in 2000 (de Wit, 2002). However, the global demand for other BFRs continues to grow substantially with the increasing usage of organic polymer materials in construction, electronic and computer equipment. The global market for BFRs grew from 145000 tonnes in 1990 (Pettigrew, 1994), to over 310000 tonnes in 2000 (BSEF, 2005).

PBDEs first gained prominence as potential hazards in the late 1990s when the exponential increase of PBDE levels in Swedish mother's milk over a 25-year period, increasing from 0.07 ng g^{-1} lipid in 1972 to 4.02 ng g^{-1} lipid in 1997 (Meironyte et al., 1999). In general, the total PBDE concentrations in humans have increased by a factor of ~ 100 during the last 30 years (Hites, 2004). This accumulation of PBDEs in humans is causing concern among scientists and regulatory authorities (Harden et al., 2005; Schecter et al., 2006; Harrad and Porter, 2007; Schuhmacher et al., 2007; She et al., 2007). The Australian Government Department of Environment and Heritage commissioned a study measuring PBDE levels in human milk samples collected in 2002/2003. The mean concentration of PBDEs was 11 ng g^{-1} expressed on a lipid basis and ranged between 6.0 ng g^{-1} and 18 ng g^{-1} . On a worldwide basis, the levels of PBDE compounds detected in breast milk are higher than those levels observed in Europe and Japan but lower than those observed in North America and Canada (Harden et al., 2005).

Assessment of health risks associated with PBDE human accumulation and exposure is complicated and to date has not been adequately characterized. However the potential risks associated with exposure to the most bio-active congeners (tri- to octa-BDE) include thyroid hormone disruption, neuro-developmental defects and cancer (Darnerud et al., 2001; McDonald, 2002). Several studies have shown that PBDEs share the general property of organo-halogenated compounds in which *in vivo* exposure of rodents results in reduction of serum total and free thyroid hormone (thyroxine (T4)) levels (McDonald, 2002). The implications of altered thyroid hormone function, particularly during early development, are profound and have been hypothesized to lead to disrupted brain development and permanent neurological damage (Legler and Brouwer, 2003).

Currently there are no guidelines, either within Australia (NRMCC, 2004) or internationally (US EPA, 1999; European Commission, 2001), that regulate or propose permissible levels of PBDEs or PBBs in sewage sludge for land application. This article summarizes the scientific literature on PBDEs and PBBs levels in sewage sludge and presents results of an Australian sewage sludge survey conducted in 2006. All data reported are on dry weight (d.w.) basis unless otherwise stated.

2. Historical levels of PBDEs and PBBs in sewage sludge

There is a relatively small set of scientific literature that examines the issue of PBDEs and PBBs in sewage sludge. The data suggest that the use of PBBs has not resulted in the widespread distribution of PBBs in either the environment or in sewage sludge (de Wit, 2002). In contrast, the concentration of PBDEs in environmental matrices has increased dramatically since measurements were begun, and they are now found to be accumulating in most environmental compartments, including sewage sludge (de Wit, 2002). There have been comprehensive studies in Australia investigating PBDEs in environmental matrices (Toms et al., 2006); how-

ever, there have been no studies focusing specifically on sewage sludge. This review of the international body of work examining PBDEs in sewage sludge should aid understanding the typical levels of PBDEs in sludge, as well as the sources and environmental fate of these compounds. PBDEs and PBBs are assumed to circulate within the environment in much the same way as other persistent halogenated compounds.

2.1. Polybrominated diphenyl ethers

PBDEs were first detected in sewage sludge and other environmental samples in 1979 from samples collected near chemical manufacturing sites in the USA (de Carlo, 1979). It was not until 1992 that the concentration of PBDEs was first reported. The concentration of BDE-47 & -99, both components of the pentaBDE formulation, were measured in Swedish sludge ($n=2$, $15 \mu\text{g kg}^{-1}$ and $19 \mu\text{g kg}^{-1}$, respectively) (Nylund et al., 1992). These levels were similar to those reported from German sludges ($n=13$), with a mean Σ penta-BDE of $8.58 \mu\text{g kg}^{-1}$ and ranged from 0.22 to $17.13 \mu\text{g kg}^{-1}$ (Hagenmaier et al., 1992). The consistent presence of polybrominated dibenzofurans (PBDF) at relatively high concentrations (ranging from 0.21 to $3.05 \mu\text{g kg}^{-1}$ and a mean of $1.17 \mu\text{g kg}^{-1}$) was reported, which are similar to the concentrations of the chlorinated dioxins and furans (Rappe et al., 1998). They reported "a reasonably good correlation between the concentrations of PBDFs and PBDEs" and suggested that the PBDEs are the source of PBDFs observed in sludge. This is extremely important and requires more research, as PBDFs share the same level of toxicity as the chlorinated furans (IPCS, 1989, 1998).

The concentrations reported in those Swedish and German sludges in 1992 is low when compared to sludges analysed in the late nineties from various nations. For example, the sludge samples collected in Sweden in 1997–1998 ($n=3$) reflect concentrations of PBDEs in sludge more typical of those in contemporary sludges containing a mean concentration of BDE-47 of $65 \mu\text{g kg}^{-1}$ and BDE-209 of $220 \mu\text{g kg}^{-1}$ (Sellstrom et al., 1999; de Wit, 2002). These results show a higher burden of BDE-209 compared to the other congeners BDE-47 & -99, from the pentaBDE formulation. The dominance of BDE-209 was reported again in Swiss sludges ($n=8$) (Kohler et al., 2003). Also reported is the increase in concentration from an average BDE-209 concentration of $220 \mu\text{g kg}^{-1}$ in 1993 to $1100 \mu\text{g kg}^{-1}$ in 2002, an increase of 560%.

In 2001, the total concentration of penta-BDEs in USA biosolids ranged between 1100 and $2290 \mu\text{g kg}^{-1}$ and suggested that the input was consistently high, regardless of the region and irrespective of preliminary treatment. These levels are far higher than previously reported and exceeded those in European sludges by 10- to 100-fold. This was attributed to the much higher use of PBDEs, both the pentaBDE and the decaBDE formulations, within the USA. Unlike BDE-99, BDE-209 varied widely among the biosolids analysed ranging from 84.8 to $4890 \mu\text{g kg}^{-1}$. Further studies of PBDEs in USA sludges found a mean Σ PBDEs concentration of $1540 \mu\text{g kg}^{-1}$ in 2002 (Hale et al., 2002) and maximum concentration of Σ PBDE of $3955 \mu\text{g kg}^{-1}$ in 2004 (North, 2004).

BDE-209 was the dominant PBDE in Spanish sludges ($n=6$) collected in 2002, comprising $>95\%$ of the PBDE burden. (Fabrellas et al., 2004). An industrial sewage sludge sample from this Spanish study had a concentration of BDE-209 of $18032 \mu\text{g kg}^{-1}$ that is the highest reported to date. The total tri- to hexa-BDE levels are low relative to deca-BDE (5.3 and $177.3 \mu\text{g kg}^{-1}$, respectively), but are similar to concentrations reported in other studies. The concentration of PBDEs in Swedish sludges analysed by the Swedish EPA and reported by Law et al. (2006) again found that BDE-209 was the dominant species. The concentration was highly variable ranging from 5.6 to $1000 \mu\text{g kg}^{-1}$ (Law et al., 2006). Concentrations of the lower brominated PBDEs were fairly similar in all sewage sludge

Table 1

Concentration ($\mu\text{g kg}^{-1}$ dry weight) of PBDE-47, -99, -100 and -209 in sewage sludge from waste water treatment plants reported in the English-language peer reviewed scientific literature

Country	BDE-47	BDE-99	BDE-209	Reference
Sweden	15, 15	19, 19		Nylund et al. (1992)
Sweden	78, 80, 36	98, 100, 56	220, 270, 170	Sellstrom et al. (1999)
USA	498, 754, 359, 525, 518, 673, 536, 605, 421, 686, 674	743, 1157, 513, 584, 714, 815, 516, 572, 391, 648, 613	308, 1460, 553, 84.8, 1940, 4890, 368	Hale et al. (2001)
Netherlands	9.5, 11, 40	11, 14, 38	<180, 190, 8.6	de Boer et al. (2003)
Spain	83.6, 21.4, 28.3, 1.8, 49.8, 38.5	64.2, 23.4, 25.6, 37.6, 34.5,	5430, 756, 1203, 3591, 5837, 18632	Fabrellas et al. (2004)
Germany	25.2, 51.7, 35.2, 55.0, 26.7, 35.4, 88.0, 62.7	37, 72.2, 59.3, 76.9, 39.0, 54.2, 126.6, 94.2	217, 198, 639, 400, 177, 100, 268, 609	Hamm (2004)
USA	757 (mean)	944 (mean)	1183 (mean)	North (2004)
Sweden	49 (mean), 7.0 → 100	60 (mean), 8.1 → 150	120 (mean), 5.6 → 1000	Law et al. (2006)
Germany	20.3, 29.2, 37.6, 54.8, 54.8, 39.2, 36.2, 41.5, 39.8, 42.7, 92.3, 45.3, 28.1, 32.5, 41.0, 58.7, 95.2, 84.5, 115	23.6, 32.1, 37.9, 52.7, 60.5, 34.1, 40.4, 45.8, 48.2, 48.5, 95.3, 49.1, 29.9, 40.5, 42.4, 59.2, 118, 98.2, 124	133, 193, 247, 235, 270, 135, 354, 450, 411, 340, 302, 1141, 204, 605, 417, 393, 690, 556, 1339	Knoth et al. (2007)
China	5.0 (mean), 0.4 → 58.7	4.5 (mean), <3.4 → 69.7	68.5 (mean), <1 → 1108.7	Wang et al. (2007)

samples, indicating diffuse leaching of these from products into wastewater streams (Law et al., 2006).

Knoth measured the concentration of PBDEs in 39 sludge samples from different stages of the WWTP process from 11 municipal wastewater treatment plants in Germany, collected from March 2002 to June 2003. The concentration of lower brominated congeners was fairly consistent, while the BDE-209 concentration once again varied widely between 97 and 2217 $\mu\text{g kg}^{-1}$ (mean 256 $\mu\text{g kg}^{-1}$) and was again the most prevalent congener detected (Knoth et al., 2007). No change in the tri- to hepta-BDE congener profile ratios was observed (% of total BDE-28, -47, -99, -153, -154, -183 without -209) in sludge from different stages of the waste water treatment process (primary sludge, secondary excess sludge and dewatered digested sludge), which suggested that the degradation of BDE-209 and other higher brominated PBDEs to lower brominated congeners did not occur.

Sludge samples collected from 31 WWTPs in 26 cities in China report a low burden of PBDEs (Wang et al., 2007). These levels are about 10–100 times lower than those found in Europe and North America. PBDE levels in sludge were not found to depend on the location or treatment capacity of the WWTPs.

To summarize, the major congeners present in sewage sludge are BDE-47, -99 and -209 and the Σ PBDE concentrations are typically present in the $\mu\text{g kg}^{-1}$ to the low mg kg^{-1} range. These congeners represent the major commercial formulations of pentaBDE (BDE-47, -99) and decaBDE (BDE-209), which appear to be the original source. The reported concentrations of these congeners in the scientific literature is summarised in Table 1.

2.2. Polybrominated biphenyls (PBBs)

The concentration of PBBs in sewage sludge has received little attention, primarily because of the relatively low use of PBBs in manufacturing. All the studies, except one ($n=4$) that have investigated the levels of PBBs in sludge, showed PBBs to be below the detection limit (de Carlo, 1979; de Boer et al., 2000, 2003). In 2000, PBBs were not detected in WWTP influent or effluent or other environmental samples analysed (de Boer et al., 2000). In 2003, de Boer et al. again analysed environmental samples for PBBs. This time they analysed the samples of influents, effluents and suspended particulate matter from a wastewater treatment plant in the Netherlands for BBs-15, -49, -52, -101, -153, -169 and -209 but these were, once again, below the detection limit (de Boer et al., 2003). The detection limits for most PBBs were between <0.1 and <1 $\mu\text{g kg}^{-1}$, but for BB-209 the detection limits were generally between <1 and <10 $\mu\text{g kg}^{-1}$. This result is in agreement with the negligible PBB production in Europe over the past decades (de Boer et al., 2003).

BB-153, the main congener in the hexabromobiphenyl commercial formulation, was detected in Swedish sludges in 2002, but unfortunately the results are presented on a wet weight basis making comparison impossible (Oberg et al., 2002). It was reported that BB-153 co-eluted with BDE-154. Analytically, it has only been since the development of isotopically labelled standards, and the advent of facilities with ultra-trace capability, using high-resolution mass spectrometry that the detection of PBBs has been possible with a certain degree of certainty.

3. Sources of PBDEs in sewage sludge

Release of PBDEs into wastewater may occur during their synthesis, during incorporation into polymers or related finished products, during their use and disposal or recycling of these products, by cycling in the environment, or a combination of any of the above. As PBDEs are hydrophobic, resistant to degradation and widely used in products, it is logical to assume that some enter the wastewater treatment plant process and will subsequently be concentrated in high organic carbon-containing sewage sludges. However, evidence published by de Boer et al. (2003) and North (2004) have indicated that the common BDEs (-49, -99 and -209) are also present in the WWTP effluent, or more specifically, the suspended organic material.

Constituents of pentaBDE formulation were detected in eleven sludges collected from four different regions of the USA. (Hale et al., 2001). The concentrations (total of BDE-47, -99, -100, -153 and -154) were fairly consistent with concentrations ranging from 1100 to 2290 $\mu\text{g kg}^{-1}$ despite differences in facility location, industrial base and sludge stabilization process. This suggests that the source is domestic in origin as it is consistently present regardless of region. In contrast, levels of BDE-209 varied substantially between samples, ranging between 84.8 and 4 890 $\mu\text{g kg}^{-1}$, which suggests that the source of this compound is more random and derives from an industrial or other variable source. Another alternative explanation is that BDE-209's higher bio-degradability relative to other PBDEs (Bezares-Cruz et al., 2004) may cause the high variability in concentration observed. The trend of consistent pentaBDE formulation (BDE-47 & -99) concentrations and highly variable BDE-209 concentrations was observed in many other studies.

4. Methods

The aim of this research was to assess the typical PBDE burden within Australian sewage sludges. To achieve this, two studies were undertaken. The first is a survey of the concentration of PBDEs in sewage sludge samples taken from 16 Australian WWTPs

in 2006. The second is an analysis of PBDE levels in sewage sludge samples from three WWTPs over two successive years. PBDEs were quantified using isotope dilution internal standard high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Analysis was undertaken for the following PBDE congeners; BDE-17, -28&-33, -47, -49, -66, -77, -85, -99, -100, -119, -138&-166, -153, -154, -183, -184, -196, -197, -206, -207 and -209. The analyses were conducted at the National Measurement Institute (NMI), Sydney (Pymble), Australia.

4.1. Sampling methodology

4.1.1. Australian sewage sludge survey 2006

A survey of sewage sludge ($n = 16$) was conducted with samples collected from each State and the Northern Territory of Australia during 2006. Eight urban (population >1000000) and eight rural (population <300000) WWTPs were sampled. Table 2 describes the treatment process for each of the participating WWTPs. Sewage sludge samples were collected by on-site workers, who were provided with sample-kits containing pre-cleaned amber-glass jars with Teflon lined lids. Samples were sent via courier to NMI for analysis and freeze dried prior to sample treatment.

4.1.2. Comparison of PBDE levels over time

The concentration of PBDEs was measured in sludge samples from three WWTPs (U6, U7 and U8), collected in duplicate, during the years 2005 and 2006. Sample collection and analysis methods were the same as for the Australian Sewage Sludge Survey described above.

4.2. Sample treatment

Freeze dried sludge samples (20.0 g) were spiked with 10 μ l of mixed PBDE surrogate standards and were extracted into toluene using accelerated solvent extraction (Instrument Model Dionex ASE 100). The extracts were concentrated using a Buchi Syncore, which was used for concentrating samples throughout the extract cleanup process. The extract was transferred into hexane and then subsequently treated with concentrated sulfuric acid for destructive removal of organic material. The extract was then treated for inorganic and organic sulfur by activated copper and silver nitrate clean-up techniques, respectively. A commercial automated clean-

up procedure (PowerPrep™ by Fluid Management Systems, Waltham, MA, USA) that employs acid and base modified silica gels and basic alumina column chromatography was used to remove interferences from the sample extract. Extracts were concentrated to dryness under nitrogen and made up to 40 μ l with a PBDE internal standard. Analyses were undertaken for PBDEs and PBBs using isotope dilution high resolution gas chromatography – electron ionisation – high-resolution mass spectrometry, with monitoring of the following ions:

Tri, tetra, penta BDEs – M^+ , $[M+2]^+$, $[M+4]^+$, $[M+6]^+$; hexa, hepta, octa, deca BDEs – $[M+4-2Br]^+$, $[M+6-2Br]^+$, $[M+8-2Br]^+$; hexa BB – $[M+2-2Br]^+$, $[M+4-2Br]^+$.

The analytical procedure was based upon standard US EPA methodologies (US EPA, 2007).

4.3. Instrumental technique

Quantification was performed on an Agilent 6890 gas chromatograph that was coupled to a Thermo Finnigan MAT 95XL HRMS. The column used was a DB-5 column (J&W Scientific) 10 m \times 0.1 mm \times 0.1 μ m. One microlitre of sample extract was injected using the splitless method with an injector temp of 280 °C. The temperature program employed was an initial temperature of 120 °C held for 2 min, a ramp rate of 15 °C min⁻¹ from 120 to 230 °C followed by a 5 °C min⁻¹ increase from 230 °C to the final temperature of 320 °C that was held for 5 minutes. Helium was used as a carrier gas with constant flow mode of 0.4 ml min⁻¹. The transfer line was maintained at 280 °C. Electron ionisation (EI) mode was used with an electron energy of 70 eV, filament current of 0.7 mA, and ion source at 240 °C. The electron multiplier voltage was set to produce a gain of 10⁶.

4.4. Material, standards and reagents

Pesticide grade solvents were purchased from Merck and were tested for contamination prior to use. PowerPrep™ columns (acid and base modified silica gels and basic alumina) were purchased from Fluid Management Systems, Waltham, MA, USA.

Isotope dilution was performed using standard compounds purchased from Wellington Laboratories Inc., Guelph, Ontario, Canada. Surrogate Standard: BFR-LCS-STK; Calibration Standard: BFR-CVS; Recovery Standard: BFR-ISS-STK.

Table 2
Australian sewage sludge survey 2006 – type of treatment process and source of wastewater

WWTP	Population ^a	Treatment method	Source
U1	4297000	Anaerobically digested and freshly dewatered.	Services residential and industrial areas.
U2	1811000	Activated sludge, dewatered.	Composition industrial and domestic.
U3	1139000	Activated sludge. Dissolved air-flotation filtration.	Mixture of domestic and industrial and some groundwater runoff.
U4	1139000	Integrated fixed-film activated sludge.	Mixture of domestic and industrial and some groundwater runoff.
U5	3850000	Activated sludge plant. Anaerobically digested primary and secondary sludge. Dewatered in sludge drying pans. Stockpiled for >3 years.	Industrial and domestic
U6	1508000	Mesophilic anaerobic digestion, centrifuge dewatering, 110 ml day ⁻¹ .	Mainly domestic ~2% industrial input.
U7	1508000	Activated sludge. Mechanically dewatered. Chemically stabilized (lime). 60 ml day ⁻¹ .	Mainly domestic, ~5% industrial.
U8	1508000	Mesophilic anaerobic digestion, centrifuge dewatering, 120 ml day ⁻¹ .	Mainly domestic ~9% industrial input
R1	142000	Stored in a lagoon for 6 months. Dewatered by centrifuge and stockpiled for 4 months.	92% domestic 8% trade waste.
R2	106000	Lagoon. Dewatered by vacuum filtration.	Domestic and light industrial.
R3	27000	Activated sludge. Dewatered.	Domestic source.
R4	35000	Aerobic digestion. Dewatered.	Domestic and light industrial.
R5	202000	Chemically stabilized with lime.	Domestic and industrial
R6	52000	Dewatered and chemically stabilized (lime).	Mainly domestic.
R7	5000	Activated sludge and lagoon process. Land dried.	Domestic and abattoir
R8	14000	Oxidation treatment pond. Solar dried.	Domestic and Industrial

^a Population refers to the population of the town/city and not just the feeding population of the WWTP; U=urban (population >1000000), R=rural (population <300000).

4.5. Quality assurance/quality control

Internal standard isotope dilution quantification was undertaken within this study. This employs the use of $^{13}\text{C}_{12}$ labelled surrogates and internal standards. The $^{13}\text{C}_{12}$ surrogates ($^{13}\text{C}_{12}$ BDE-28, -47, -77, -99, -100, -126, -153, -183, -197, -205, -207, -209, BB-153) are added to the sample prior to extraction and are carried through all the laboratory operations. The internal standards ($^{13}\text{C}_{12}$ BDE-79, -139, 180, 206) were added just prior to analysis by HRGC-EI-HRMS. Both the recovery of the surrogate and internal standard response are then used in the quantification of the native BDEs.

Procedural blanks were performed in each batch of analyses. All glassware was placed in a furnace overnight at 450 °C and rinsed with solvent before use. Each batch of disposable equipment such as PowerPrep™ columns were checked prior to use for PBDE contamination. The limit of detection (LOD) was set as the limit of quantification (LOQ) and was determined as three times the blank amount.

The analysis of the higher brominated BDEs, particularly BDE-209, is recognised as being difficult because it can degrade during the analytical process (Covaci et al., 2003). Using a short thin-film capillary column, regularly changing the injection liner, and using a low source temperature minimized the potential for degradation of BDE-209.

The laboratory is accredited by the National Association of Testing Authorities (NATA) and has participated successfully in four international inter-laboratory studies.

4.6. Co-eluting congeners

Co-elution of congeners BDE-138 and -166 is a common problem (Korytar et al., 2005; US EPA, 2007). Therefore a precautionary approach was taken with BDE138/BDE166 and was reported as a co-elution.

It is also well known that there is co-elution on a DB-5 column between BB-153 and BDE-154 (Stapleton, 2006) Therefore the use of electron capture detector, negative-ion chemical ionisation and low-resolution mass spectrometry detectors can lead to an over estimation of either compound. The HRGC-EI-HRMS method used in this study overcomes these limitations by careful selection of the respective quantification and confirmatory ions for labelled surrogates and native compounds, as well as operating the mass spectrometer at high resolution ($R > 10000$), thereby ensuring accurate identification and quantification. The ions selected for the $^{13}\text{C}_{12}$ BB-153 surrogate and the native BDE-154 represent $[\text{M}+2-2\text{Br}]^+$ and $[\text{M}+6-2\text{Br}]^+$, respectively (Certificate of Analysis supplied by Wellington Laboratories). These ions are less abundant (<65%) than the $[\text{M}+4-2\text{Br}]^+$ ions but can be mass resolved from one another with an instrument resolution of >10000 . This approach has been validated by analysing certified standards, procedural blanks and samples containing high BB-153 and BDE-154 levels.

4.7. Statistical analysis

Principal components analysis (PCA) was performed to analyse the relationship among the PBDE congeners using the software package NTSYSpC version 2.20 (Exeter Software). The raw concentration data for each compound were standardised to a mean of zero and a standard deviation of one, and the PCA was conducted on the correlation matrix of the standardised data. Values below the detection limit were assumed to be zero for this analysis.

In the study of variation in PBDEs over time, analysis of variance (ANOVA) was used to test whether there were effects of year, WWTP or a year by WWTP interaction. WWTP effects were considered to be fixed while year and the interaction were considered as having random effects, so the significance of the WWTP effects

was tested against the interaction. A logarithm transformation was required to stabilise residual variance for some congeners.

5. Results and discussion

5.1. Australian sewage sludge survey 2006

5.1.1. Polybrominated diphenyl ethers

The concentration of PBDEs as measured in the 16 sewage sludge samples is supplied in Table 3. An estimate of the error associated with each analytical measurement has been calculated by the relative error of duplicate samples measured as part of the time study. BDE-47, -99 & -209 concentrations found in this survey are compared with international levels in Fig. 1a and b.

Examination of the correlation matrix revealed that there were three primary groups of compounds, with correlations high among congeners within groups and low between groups. The first two groups contained congeners that are representative of the pentaBDE and decaBDE formulations. The basis for group separation is that the individual congeners in each group are highly correlated with one another; they are the reported constituents of the commercial formulation and are present in similar ratios to those reported in the formulations. The ratio of the principal congeners of the pentaBDE formulation BDE 47:99 + 100:153 + 154 have a ratio of 41:51:8 which is similar to the reported ratio of 40:45:6 (Sjödin et al., 1998). The principal congeners of the decaBDE formulation BDE 209:206 + 207 + 208, reported to have a ratio of 97 – 98:0.3 – 3 were found in an overall ratio of 93:7 (Alaee et al., 2003).

The first two principal components explained 76% of the variation within the sample set. PCA1 was primarily representative of the average concentration of components in the pentaBDE formulation (BDE-47, -49, -66, -77, -85, -99, -100, -119, -139, -140, -153, -154) explaining 50% of sample variation and PCA2 corresponded to representative congeners of the decaBDE formulation (BDE-201, -203, -206, -207, -208 and -209), explaining an additional 26% of the sample variation. The third component explained 13% of the data variation; however, it was concluded that this component was not meaningful, as it corresponded mainly with variation in congeners that were at or below their detection limits (BDE-171, -180, -184 and -191). Given the high correlations within formulations, the concentration of PBDEs could be reasonably summarised by the concentration of three dominant congeners, BDE-47 and BDE-99 representing the pentaBDE formulation and BDE-209 representing the decaBDE formulation. A plot of PCA1 vs PCA2 (i.e. pentaBDE vs decaBDE formulations) does not reveal any obvious trends, such as associations with size of town (population) or industrialisation (Fig. 2).

If the PBDEs in sewage sludge were derived mainly from domestic products one would expect there would be consistency in the relative concentrations of PBDEs regardless of region. Using BDE-47 and BDE-99 as representatives of the pentaBDE formulation this proposal is confirmed; the mean of BDE-47 and BDE-99 is $136.5 \mu\text{g kg}^{-1}$ (s.d. $112 \mu\text{g kg}^{-1}$) and $138 \mu\text{g kg}^{-1}$ (s.d. 116), respectively. Therefore it is suggested that the primary source of the pentaBDE formulation in Australian sewage sludge is largely domestic. Concentration of the decaBDE formulation, on the other hand is highly variable (mean BDE-209 $715 \mu\text{g kg}^{-1}$, s.d. 981), consistent with previous reports in the scientific literature (Hale et al., 2001), suggesting a less uniform source than the domestic environment. Varied industrial applications could explain the variation observed.

Among the samples, two are quite unusual. These are urban WWTP U5 and rural WWTP R7. The urban WWTP U5 has an atypically high BDE-209 concentration. Sewage sludge may be stabilized for biosolids using a variety of methods and this elevated concentration may be a result of the method used at this WWTP, i.e., longer

Table 3
Concentration of PBDE congeners and PBB-153 $\mu\text{g kg}^{-1}$ dry weight in Australian sewage sludge survey conducted in 2006; U = Urban (Pop. > 1000000), R = Rural (Pop. < 300000)

	U1	U2	U3	U4	U5	U6 ^c	U7	U8 ^c	Urban Mean	Sd	R1	R2	R3	R4	R5	R6	R7	R8	Rural Mean	Sd	Overall Mean	Sd	Standard Error ^{a,b}
BDE 17	0.96	2.7	2.7	0.27	0.16	7.75	0.46	1.85	2.1	2.5	4.3	0.25	12	2.6	0.69	0.4	0.0065	3.6	3.2	4.5	2.6	3.4	0.3
BDE 28	2.0	3.1	25	1.1	<0.2	4.55	0.85	5.2	6.0	8.6	8.1	0.92	2.6	2.4	1.2	1.4	<0.06	11	3.7	4.1	5.0	6.9	0.4
+33																							
BDE 30	<0.04	<0.02	<0.06	<0.02	<0.03	<dl	<0.03	<dl	-	-	0.14	<0.006	0.012	<0.06	<0.05	<0.03	<0.008	<0.1	-	-	-	-	-
BDE 47	120	180	36	72	17	205	45	285	120	95	170	74	120	140	56	89	<0.4	410	160	140	140	110	19
BDE 49	3.8	5.6	2.3	2.3	1.9	7.95	1.5	8.45	4.2	2.8	16	1.9	6.4	5.6	2	3.1	0.035	23	6.7	8.3	5.3	5.7	1.1
BDE 66	3.3	6.1	1.4	2.9	0.59	7.15	1.5	7.7	3.8	2.8	8.4	1.9	4.2	4.8	1.7	2.8	0.017	14	4.6	4.9	4.2	3.7	2.1
BDE 71	<0.2	<2	<0.2	<0.3	<0.06	<dl	<0.2	<dl	-	-	1.6	0.17	8	1.9	<4	0.18	<0.009	1.4	2.9	3.5	-	-	-
BDE 77	0.049	0.055	0.0099	<0.01	<0.004	0.58	<0.03	0.092	0.2	0.2	0.1	0.027	0.06	0.069	<0.03	0.06	<0.004	0.16	0.09	0.05	0.13	0.17	0.6
BDE 85	4.8	6.7	11	3.1	1	8.8	1.8	11.5	4.9	3.9	5.1	5.8	3.9	5.8	1.8	4.2	0.013	14	5.0	4.9	4.9	4.1	2
BDE 99	130	190	31	84	22	230	48	315	131	106	210	120	130	170	51	130	0.37	400	150	140	140	120	49
BDE 100	26	39	8.6	16	4.4	47.5	9.6	63.5	27.0	21.0	41	21	24	32	11	21	<0.08	94	36	33	31	26	10
BDE 119	<0.9	<1	<0.1	<0.4	0.04	0.695	0.11	0.465	0.33	0.31	0.28	0.14	0.28	0.29	<0.6	0.21	<0.002	0.68	0.37	0.21	0.3	0.2	0.38
BDE 126	<3	<0.04	<0.5	<0.02	<0.5	0.805	<0.02	<dl	-	-	<0.1	<0.02	<0.02	<0.02	<0.03	<0.02	<0.01	<0.02	-	-	-	-	-
BDE 138 + 166						3.3	1.9	2.7	2.6	0.7	4.2	4.7	3.9	6.1	nd	4.2	11	11	6.3	3.3	4.7	3.1	1.4
BDE 139	1.5	2	0.49	0.82	0.31	2.8	0.42	3.15	1.4	1.1	1.6	1.9	1.1	1.5	0.4	1.3	<0.002	3.9	1.6	1.3	1.5	1.2	1.2
BDE 140	0.45	0.71	0.18	0.29	0.16	1.27	0.13	0.84	0.50	0.41	0.61	0.54	0.47	0.59	0.16	0.36	<0.01	1.1	0.54	0.35	0.5	0.4	0.4
BDE 153	13	20	4.8	8.2	4.9	23	4.4	28	13.3	9.3	23	14	13	17	4.6	13	0.064	35	13.8	12.1	13.5	10.1	2.0
BDE 154	10	16	4.3	6.1	3.2	19.5	3.9	24.5	10.9	8.1	19	9.8	12	15	3.8	8.4	0.04	33	12.0	11.6	11.4	9.4	3.0
BDE 156 + 169						4.8	<0.1	<dl	-	-	<0.09	<0.08	<0.06	<0.1	nd	<0.1	<0.09	<0.09	-	-	-	-	-
BDE 171	<0.09	<0.2	0.097	<0.4	0.41	3.87	0.099	0.375	0.97	1.63	0.38	0.11	0.17	0.27	0.13	0.2	<0.009	0.47	0.25	0.13	0.6	1.2	1.2
BDE 180	0.37	1.7	0.14	0.29	0.81	3.945	0.11	0.615	1.00	1.30	0.57	0.17	0.26	0.41	0.16	0.33	<0.003	0.67	0.37	0.19	0.8	1.0	1.0
BDE 183	9.6	19	3.9	5.1	15	13	1.9	10	9.7	5.9	13	3.3	3.7	11	3.3	7.3	0.083	11	6.1	4.5	8.1	5.4	3.0
BDE 184	0.16	0.39	0.094	0.11	0.2	2.23	0.064	0.41	0.46	0.73	0.67	0.098	0.2	0.47	0.075	0.19	<0.002	0.38	0.26	0.16	0.38	0.57	2.5
BDE 191	0.098	0.33	0.061	0.053	1.1	2.805	<0.04	<dl	-	-	0.2	0.047	0.14	0.092	0.053	0.082	<0.005	0.22	0.12	0.07	-	-	-
BDE 196	4.7	7.7	<0.2	<1	<2	7.4	1.6	4.2	5.1	2.5	6.4	2.2	4.7	4.2	3	4.3	<0.3	6.5	4.5	1.3	4.8	1.9	5.1
BDE 197	2.9	3.6	0.89	1.1	8.4	8.75	0.85	4.3	3.8	3.2	6.6	1.4	2.2	5.4	1.5	3	0.022	4.3	2.7	1.9	3.4	2.7	4.6
BDE 201	1.1	<4	<1	<0.7	14	4.85	0.38	1.3	4.3	5.7	2.8	0.44	1.8	1.2	0.59	1	0.015	2.7	1.2	0.9	2.6	4.0	4.0
BDE 203	<3	<3	<1	<2	40	8.35	1.3	5.1	13.7	17.8	7.8	2.4	5.7	4.5	2.3	3.7	<0.03	8.7	5.0	2.4	8.9	11.9	11.9
BDE 204	1.4	<3	0.64	0.97	<7	8.2	<0.1	<dl	-	-	<0.4	<0.6	<0.1	<0.4	<0.1	<0.2	<0.004	<0.3	-	-	-	-	-
BDE 205	<1	<0.7	<0.4	<0.6	<2	7.8	<0.2	<dl	-	-	<0.3	<0.2	<0.09	<0.2	<0.3	<0.2	<0.058	<0.3	-	-	-	-	-
BDE 206	32	9.7	3.1	4.5	98	30	6	27.5	26	31	28	7.6	31	8.5	8.2	7.9	0.093	31	14	13	21	25	15
BDE 207	13	12	5.7	6	110	19.5	6.3	12.5	23	35	21	5.9	20	8.7	7.4	9.9	0.094	19	11	7.5	18	27	14
BDE 208	7.9	6.5	2.7	2.8	97	15.7	3.7	7.95	18	32	14	3.4	10	4.4	3.9	5.7	0.064	14	6.3	4.9	13	25	25
BDE 209	1170	360	93	81	3780	530	130	910	880	1200	990	280	1210	260	250	180	3.4	1050	490	510	720	980	220
ΣPBDE ^a	1560	900	230	300	4230	1225	280	1735	1308	1300	1610	560	1630	710	420	500	4.5	2200	911	831	1137	1116	260
PBB-153	0.52	2.2	0.38	0.58	1	0.59	0.22	0.63	0.8	0.6	0.65	0.33	0.037	0.2	0.45	0.69	0.2	0.18	0.3	0.2	0.6	0.5	0.5

^a Does not include half detection limit.
^b The standard error associated with replicate sampling and analytical measurement calculated from five replicate samples as part of the time series study.
^c Mean concentration of replicate samples.

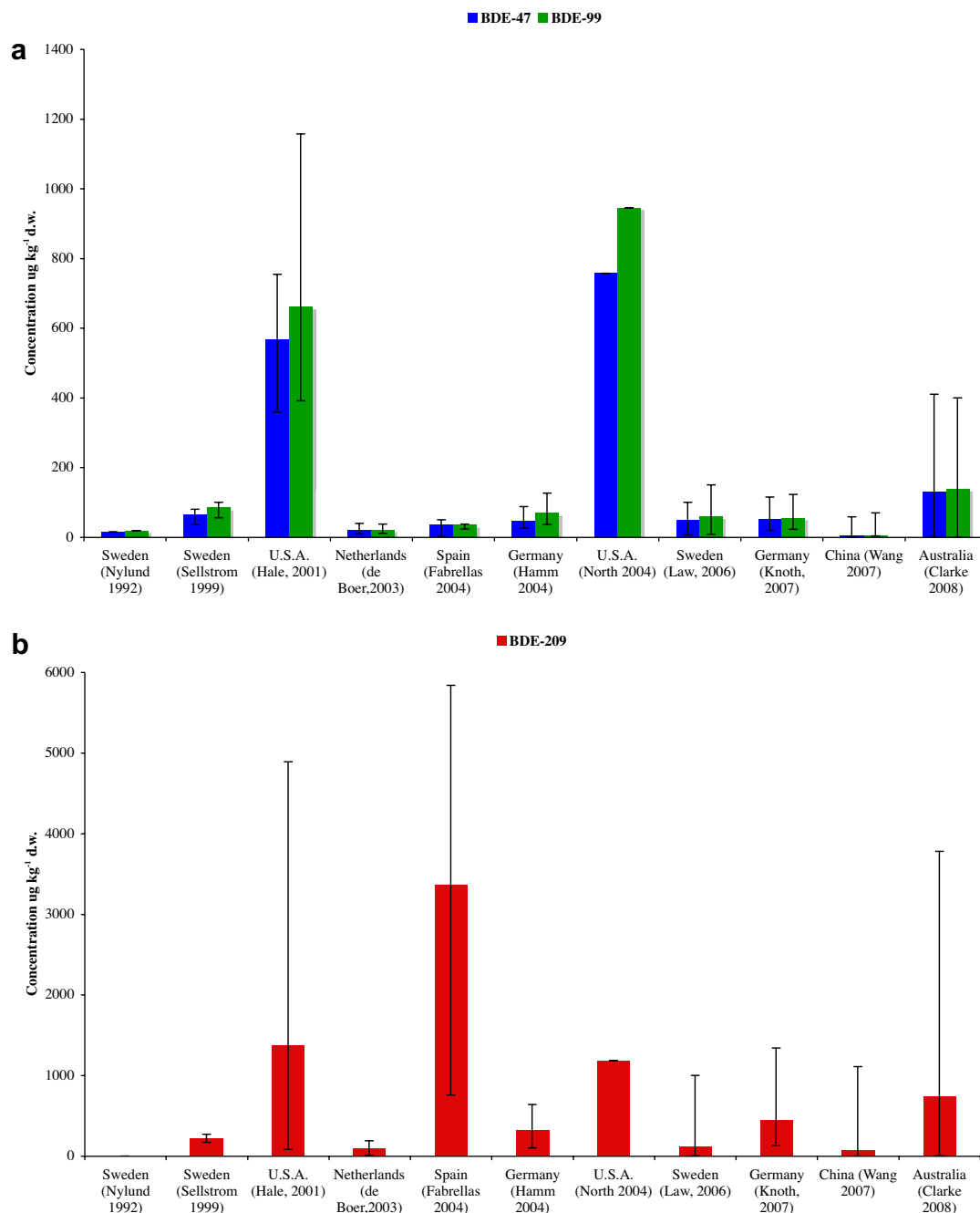


Fig. 1. A comparison of the major PBDE congeners $\mu\text{g kg}^{-1}$ dry weight (a) BDE-47, -99 and (b) BDE-209 from the Australian survey and the English peer reviewed scientific literature. The graphs represent the mean concentration and the error bars express the range reported. Note: the concentration of BDE-209 ($18\,632\ \mu\text{g kg}^{-1}$ d.w.) reported in one sludge from the Spanish survey 2004 was excluded from this presentation as it was considered an anomalous sample.

preparation time (three years). Over time there is a loss of organic material which may result in the concentration of the PBDEs on the remaining organic material, assuming no losses through biodegradation, physical breakdown or atmospheric losses. The other notable feature of the sample from U5 is the low burden of the pentaBDE formulation congeners, which suggests losses of these compounds due to above mechanisms leaving the BDE-209 to accumulate preferentially. Similarly, sludges from treatment plants R1 and R8, both lagoon processes that degrade organic material over time, have the second and fourth highest Σ PBDE concentrations in this study. Regardless of whether or not BDE-209 has been concentrated in the samples from U5, its continued elevated concentration in sewage sludge that has been aged for three years, contradicts lab-

oratory evidence of the faster degradation of BDE-209 compared to the other lower brominated congeners (Bezares-Cruz et al., 2004; Eriksson et al., 2004). This contradiction over the persistence of BDE-209 was found also in a 2005 Swedish field trial that found elevated levels of PBDEs, including BDE-209 ($2200\ \mu\text{g kg}^{-1}$ compared to the control of $0.75\ \mu\text{g kg}^{-1}$) twenty years after the last use of PBDEs at that site, and found no evidence of the photodebromination of BDE-209 in the soils studied (Sellstrom et al., 2005). Future analysis should also include total organic carbon measurements as well as dry weight measurements to enable the concentration of PBDEs to be standardised against total organic carbon.

Another unusual sample is rural WWTP R7, which has almost no PBDE burden. This is an anomaly both within the current

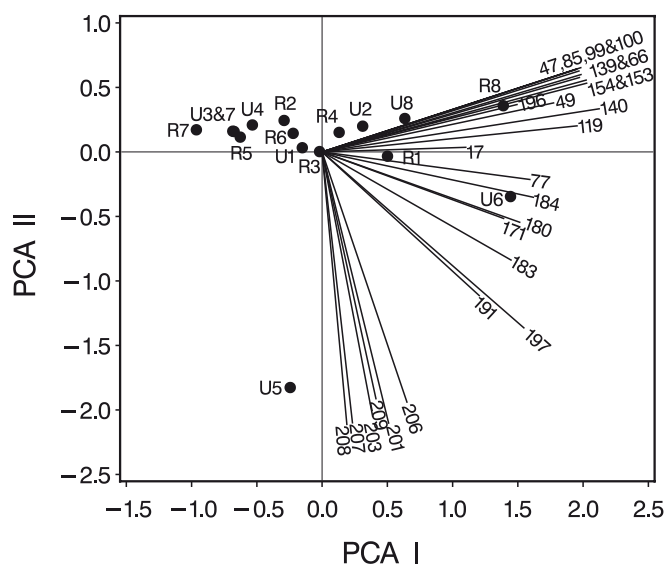


Fig. 2. Principal component analysis of PBDEs in Australian sewage sludge survey conducted in 2006. Plot of PCA1 vs PCA2, primarily representing pentaBDE and decaBDE commercial formulations, (A) score plot and (B) loading Plot.

sample set and the international literature. If the source of pentaBDE formulation congeners is domestic, one would expect there to be similar concentrations in all sludges regardless of region of wastewater treatment process. WWTP R7 is a small community that services an abattoir and it is possible that this treatment plant processes large volumes of animal waste, which may have lowered the PBDE concentration by dilution.

To provide a context in which to assess the magnitude of these PBDE burdens they have been compared to the contamination limits for the polychlorinated biphenyls (PCBs). In Australia, the National guidelines are contamination limit 1 of $200 \mu\text{g kg}^{-1}$ (restricted land application) and contamination limit 2 of $1000 \mu\text{g kg}^{-1}$ (unsuitable for land application) (NRMCC, 2004), which are similar to those in several European nations (European Commission, 2001). If it were appropriate to translate these guidelines directly from the PCB contamination limits to a PBDE contamination limit, then all samples,

except WWTP R7, would be unsuitable for unrestricted land application. Fifteen of the sixteen samples had a ΣPBDEs greater than $200 \mu\text{g kg}^{-1}$ and 7 of the 16 samples contained ΣPBDEs greater than $1000 \mu\text{g kg}^{-1}$. At this time no contaminant limits have been proposed for PBDEs and the practice of sewage sludge land application has not stopped in the USA and many other nations despite higher PBDE burdens than those observed in Australia. The PBDE levels found in Australian sludges are similar to those found in European sludge samples and ten to one hundred times greater than levels of PBDEs in European soils; ΣPBDEs $0.065\text{--}12 \mu\text{g kg}^{-1}$ (Hassanin et al., 2004). If the concentration of PBDEs in Australian soils are similar to European levels then it is likely that land application of sludge would increase the PBDE burden found in soils.

To summarise, the mean concentration of ΣPBDEs in this Australian survey was $1137 \mu\text{g kg}^{-1}$ (s.d. 1116). When comparing the urban mean of $1308 \mu\text{g kg}^{-1}$ (s.d. 1320) and the rural average of $911 \mu\text{g kg}^{-1}$ (s.d. 831) there is little variation and the difference is not significant at the 95% confidence level. The PBDE concentrations reported in this study are similar to those reported in the international scientific literature. Principal components analysis revealed that this data set could be reduced to two primary components reflecting the pentaBDE and decaBDE formulations and these two formulations can be suitably represented by the dominant congeners BDE-47, -99 and BDE-209, respectively.

5.2. Polybrominated biphenyls

The finding of BB-153 in all samples was unexpected (mean $0.6 \mu\text{g kg}^{-1}$, s.d. 0.5) and, as far as is known, there are no industries utilizing the hexabrominated biphenyl commercial (hexaBB) formulation in Australia. In terms of historical use, it is unclear whether this compound was ever used in Australia. The ubiquity of BB-153 strongly suggests that it was in a common product, such as automobiles or widely used domestic products. However, the use of hexaBB in Australia would be surprising considering it was banned from many Western nations in the 1970s following the Michigan contamination disaster. It is likely that BB-153 was imported in an unknown product, which was commonly used and widely distributed. A more concerning hypothesis is that this chemical is extremely persistent in the environment and has been subject to long-range atmospheric transport.

Table 4
Concentration of PBDEs $\mu\text{g kg}^{-1}$ dry weight in sewage sludge measured at three WWTPs (U6, U7 and U8) in the years 2005 and 2006

	U6		U7		U8						
	2005	2006	2005	2006	2005	2006					
BDE 17	3.5	3.9	7.7	7.8	1.1	1.1	0.46	1.6	1.5	1.8	1.9
BDE 28+33	4.6	4.6	4.6	4.5	2	1.7	0.85	4.3	4.7	5.1	5.3
BDE 47	230	210	200	210	71	64	45	230	240	290	280
BDE 49	8.4	8	7.7	8.2	2.4	2.5	1.5	6.9	8	8.9	8
BDE 66	9	6.9	7.4	6.9	2.3	2.4	1.5	6.8	8.4	8.4	7
BDE 77	0.13	0.1	1	0.16	0.024	0.025	<0.03	0.089	0.071	<0.1	0.092
BDE 85	12	13	9	8.6	3.6	3.6	1.8	11	13	12	11
BDE 99	250	300	220	240	110	79	48	260	270	330	300
BDE 100	50	62	47	48	23	16	9.6	54	56	64	63
BDE 119	0.54	0.47	0.96	0.43	0.15	0.15	0.11	0.45	0.48	0.46	0.47
BDE 138+166	3.3	2.8	4.2	2.4	0.81	0.8	1.9	3	3	2.9	2.5
BDE 153	28	29	23	23	8.8	8.6	4.4	27	29	27	29
BDE 154	27	25	18	21	7.3	7.6	3.9	24	24	26	23
BDE 183	16	16	15	11	3.5	3.4	1.9	11	13	10	10
BDE 184	0.5	0.46	4	0.46	0.14	0.14	0.064	0.41	0.41	0.47	0.35
BDE 196	5.3	4.6	11	3.8	1.2	1.2	1.6	3.5	3.5	4.5	3.9
BDE 197	9.5	9.3	12	5.5	1.9	1.9	0.85	6.2	6.1	4.6	4
BDE 206	36	34	40	20	6.6	7	6	20	25	29	26
BDE 207	50	42	28	11	7.8	6.6	6.3	23	16	14	11
BDE 209	810	830	500	560	260	160	130	480	760	950	870
ΣPBDE	1560	1600	1250	1200	510	370	280	1170	1480	1800	1670

5.3. Variation of PBDE levels over time

An ANOVA was performed on the concentration of the three components BDE-47, -99, -209 as well as Σ PBDEs at three WWTPs from the same city (U6, U7 and U8) over two years (2005 and 2006). From the correlation matrix (R) and principal components analysis previously performed, PBDE congeners were separated into groups that have been identified as the pentaBDE and decaBDE formulations. Given the high correlations within formulations, it is appropriate to conduct an analysis of variance on just the dominant congeners representative of each viz. BDE-47&-99 and BDE-209. Σ PBDEs was also analysed. Other congeners were measured and the raw data are provided in Table 4.

In all three cases there was a significant WWTP by year interaction indicating that differences in concentration existed between the WWTPs but the magnitudes of these differences varied depending on the year of measurement. There were also significant differences between WWTPs for BDE-47. The concentration of BDE-47 was significantly lower at U7 ($60 \mu\text{g kg}^{-1}$) than at the other two plants (U6 $213 \mu\text{g kg}^{-1}$, U8 $285 \mu\text{g kg}^{-1}$) and, while the differences in the concentrations of BDE-99, -209 and Σ PBDEs are not statistically significant they were also lower at U7, compared to U6 and U8 (Table 4). There were no overall significant differences between years or WWTPs for either BDE-209 or Σ PBDEs. The similar result for BDE-209 and Σ PBDEs is not surprising as BDE-209 is the most abundant congener. These findings demonstrate that WWTPs from the same city can have varying concentrations of PBDEs. A more comprehensive data set over a longer period of time would improve this analysis.

6. Conclusion

A survey of Australian sewage sludge in 2006 found the Σ PBDE mean concentration to be $1137 \mu\text{g kg}^{-1}$ d.w. (s.d. 116), with little difference between the urban (mean $1308 \mu\text{g kg}^{-1}$, s.d. 1320) and the rural (mean $911 \mu\text{g kg}^{-1}$, s.d. 831) samples. The PBDE levels in Australian sewage sludge reported in this study are similar to PBDE levels reported in the international scientific literature. Fifteen of the sixteen samples contained Σ PBDE greater than $200 \mu\text{g kg}^{-1}$ and seven were higher than $1000 \mu\text{g kg}^{-1}$. The PBDE burden found in Australian sludge is far higher than the levels reported in European soils. There are no published data available on PBDEs in Australian soils but if it is assumed that they have a similar PBDE burden to European soils, then sludge land application is likely to increase the PBDE levels in soil. A risk assessment of PBDEs in sewage sludge land application, taking into account typical PBDE concentration in Australian soils, should be undertaken.

Both the pentaBDE and decaBDE formulations appear to pass through the WWTP system unchanged. The concentration of pentaBDEs was found to be fairly consistent in concentration in the sludges surveyed, suggesting domestic sources, whereas the decaBDE formulation was found to be variable, which is best explained by different industrial inputs. Further research is suggested to clarify the sources of these compounds in WWTPs.

The finding of BB-153 in all samples analysed in this survey of sludges was unexpected as they are rarely analysed or detected in international research. The results demonstrate that PBBs are extremely environmentally persistent, capable of long-range atmospheric transport and are widely distributed within the Australian environment, albeit in low concentrations.

This is the first article to comprehensively focus on PBDEs and BB-153 in Australian sewage sludge and the first to provide a review of the international literature specifically on PBDEs and PBBs in sewage sludge. We have identified the issue of PBDEs in Australian sewage sludge as a potential problem for sewage sludge land application and the need for further research to ascer-

tain the risks to human health and the environment from this practice.

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