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POLYBROMINATED DIPHENYL ETHERS AND POLYBROMINATED BIPHENYLS IN AUSTRALIAN SEWAGE SLUDGE

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ABSTRACT

This paper presents a review of the international scientific literature of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) in sewage sludge and a survey of sewage sludge from sixteen Australian WWTPs. The ΣPBDE mean concentration was 1 137 μg kg^{-1} d.w. (s.d. 1 116) and ranged between 5 and 4 230 μg kg^{-1} d.w. The urban mean of 1 308 μg kg^{-1} (s.d. 1 320) and the rural mean of 911 μg kg^{-1} (s.d. 831) are not statistically different and are similar to international levels. 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 ANOVA 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 μg kg^{-1} d.w. (s.d. 0.5). This compound has rarely been reported in any other international study. 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.

1. INTRODUCTION

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 chemicals have now accumulated within many environmental compartments. This includes the accumulation of PBDEs within living organisms, resulting in an the exponential increase in concentration in humans over the past twenty-five years (Noren and Meironyte, 2000). The scientific evidence overwhelmingly supports the argument that PBDEs are in fact 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 understand 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 of POPs. The analysis of sewage sludge for POPs will provide valuable information about chemical pollution and the risk associated with the re-utilization of sewage sludge as biosolids for land application.

PBDEs are a class of brominated fire retardants (BFRs) that have been sold in three commercial formulations 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 of U.S.A. as well as in

Australia (BSEF, 2005; NICNAS, 2007). The manufacture and use of polybrominated biphenyls (PBBs) was largely curbed in the 1970s as a result of a serious human contamination incident in Michigan, U.S.A. (IPCS, 1994a). The production of PBBs has been phased out internationally with the last PBBs manufactured in France in 2000 (de Wit, 2002). However, in general, the global demand for 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 145,000 tonnes in 1990 (Pettigrew, 1994), to over 310,000 tonnes in 2000 (BSEF, 2005).

The toxicity of PBDEs is slowly becoming understood. PBDEs first gained prominence in the late 1990s when Norén *et al.* reported an exponential increase in PBDE levels in Swedish mothers' milk over a 25-year period (Noren and Meironyte, 1998). In general, the summed PBDE concentrations in people have increased by a factor of ~100 during the last 30 years - reaching as high as 190 ng/g lipid for breast milk from women in the USA in 2000 (Hites, 2004). There is concern among scientists and regulatory authorities due to the high levels of PBDEs in humans (Harden et al., 2005; Schecter et al., 2006; Harrad and Porter, 2007; Schuhmacher et al., 2007; She et al., 2007). In Australia the 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 expressed on a lipid basis and ranged between 6.0 ng/g and18 ng/g. 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).

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

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

102 2. CHEMICAL PROPERTIES

103 There are theoretically 209 PBDE and PBB congeners and they are numbered
104 according to the IUPAC system used for numbering PCBs based on the position of the
105 halogen atoms on the rings. The most common congeners are listed in Table 1.

106 2.1. Polybrominated Diphenyl Ethers

107 PBDEs have low vapour pressures and are very lipophilic, with log K_{OW}s in the range
108 5.9-6.2 for tetra-BDEs, 6.5-7.0 for penta-BDEs, 8.4-8.9 for octa-BDEs and 10 for

109 deca-BDE (IPCS, 1994b). High K_{OW}s (log K_{OW} > 4) indicate that these compounds
110 will partition strongly into organic material of sewage sludge and that they may
111 bioaccumulate.

112 The pentaBDE[1] formulation [Cas No: 32534-81-9] is a viscous liquid that contains
113 ~70% bromine by mass and is mainly used as an additive in polyurethane foam such
114 as furniture foams, and in the manufacture of some textiles. However, the pentaBDE
115 formulation was voluntarily withdrawn from the Japanese market and has been
116 banned in Europe since 2003, in some States of the U.S.A., and recently Australia in
117 2007 (Alaee et al., 2003; NICNAS, 2007). Most of the pentaBDE formulation still in
118 use (>97%) is used in North America (de Wit, 2002). The pentaBDE formulation
119 consists of 41-42% tetra-BDEs (mainly BDE-47), 44-45% penta-BDEs
120 (predominately BDE-99 and to a lesser extent BDE-100 (86:14)), and 6-7% hexa-
121 BDEs (BDE-153 and -154). The three congeners (BDE-47, -99, -100) are also the
122 predominant congeners found in biological matrices including human tissue (de Wit,
123 2002). In addition to the six main congeners listed, minor components have been
124 identified in the pentaBDE formulation, BDE-17, -28, -66, -85, -138, and -183 (Sjodin
125 et al., 1998).

126 The octaBDE formulation [32536-52-0] is a white powder that contains 79% bromine
127 by mass and is mainly used in the manufacture of acrylonitrile butadiene styrene
128 (ABS) resins, a common thermoplastic used to make light, rigid, moulded products
129 such as musical instruments (recorders) and children's building blocks. The EU

[1] A distinction is made between the PBDE homologues and the commercial formulation by the inclusion of a dash i.e. penta-BDE and pentaBDE respectively.

130 announced a ban on marketing of octaBDE in 2002 and Australia banned the use and
131 importation of octaBDE in 2007 (NICNAS, 2007).

132 The decaBDE formulation [1163-19-5] is a white powder containing 83% bromine
133 content by weight. The decaBDE formulation contains mainly deca-BDE (~97-98%)
134 but also contains a small amount of nona-BDE (~0.3 – 3%) (Alaee et al., 2003). The
135 decaBDE formulation is a general purpose flame retardant and can be used in
136 virtually any type of polymer including: polycarbonate, polyester resins, polyolefins,
137 ABS, polyamides, polyvinyl chloride and rubber. The decaBDE mix combined with
138 antimony oxide is used in processes that require high-temperatures such as in the
139 manufacture of high-impact polystyrene used in television and computer monitor
140 cabinets. Despite some debate as to the risks of the decaBDE formulation within the
141 European Parliament, there are currently no regulations regarding the the use of the
142 decaBDE formulation (BSEF, 2005). As of 2007, there are no regulations regarding
143 the use or importation of this product in Australia (NICNAS, 2007).

144 **2.2. Polybrominated Biphenyls (PBBs)**

145 Commercial PBB products are mixtures that are named after the dominant homologue
146 present; however, as with the PBDEs, they contain many other isomers. For example,
147 the commercial formulation commonly sold as “hexabromobiphenyl” (hexaBB) can
148 have hexa-BB concentrations ranging between 60 and 90% (IPCS, 1994a). There
149 have been 18 different compounds identified in one of these formulations, Fire-Master
150 BP-6 (IPCS, 1994a), with the major hexa-BB identified being 2,2′,4,4′,5,5′- or BB-
151 153 (Sundstrom et al., 1976). The decaBB formulation is reported to have a purity of
152 more than 98% with the remaining 2% being nona-BB (IPCS, 1994a).

In the USA and Canada, hexaBB (FireMaster™) was the principal PBB product. It was used as a fire retardant in three main commercial products: ABS plastics, coatings and lacquers, and polyurethane foam (IPCS, 1994a). The use of the hexaBB formulation as a flame retardant in thermoplastic resins was confined to products that do not come into contact with food or animal feed and are not used in fabrics to which humans are exposed (IPCS, 1994a). The use of hexaBB formulations was phased out following the Michigan contamination disaster in the early 1970s (IPCS, 1994a). HexaBB BFRs are banned in North America and in Europe (IPCS, 1994a; de Wit, 2002).

The decaBB formulation (Adine 0102™) was used as a flame retardant for thermoplastics and thermosets (e.g., in polyesters, epoxy resins, polystyrene, ABS, polyolefines, and PVC), for elastomers (e.g., in PU-elastomers and India rubber) and for cellulosics (e.g., chip-board). It is frequently used in association with antimony trioxide (Sb_2O_3) in a similar way to the decaBDE formulation. Its use in paints and varnishes has also been reported (IPCS, 1994a).

OctaBB and decaBB formulations were produced in the USA until 1979 (IPCS, 1994a). A mixture of highly brominated PBBs called Bromkal 80-9D was produced in Germany until mid 1980s (IPCS, 1994a). Technical grade decaBB (Adine 0102) was produced in France until the year 2000. Currently there are no known producers of PBBs internationally. It is unclear as to the use of PBBs in Australia, however there is no restrictions on the its manufacture, importation or use in Australia (NICNAS, 2001).

3. SEWAGE SLUDGE

There is a relatively small set of scientific literature that examines the issue of PBDEs and PBBs in sewage sludge. The use of PBBs has not resulted in the widespread distribution of PBBs in the environment or in sewage sludge, particularly when compared to the ubiquitous PBDEs (de Wit, 2002). The concentration of PBDEs in environmental matrices has increased dramatically since measurements were begun and 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, however, 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 in our understanding of the typical levels of PBDEs in sludge, as well as the source 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.

4. HISTORICAL LEVELS OF PBBS AND PBDES IN SEWAGE SLUDGE

4.1. 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 U.S.A. (de Carlo, 1979). However, it wasn't until 1992 that Nylund et al. first reported the concentration of two common PBDEs congeners found in sludge (2,2′,4,4′- tetra-BDE (BDE-47) and 2,2′,4,4′,5-penta-BDE (BDE-99) of 15 μg kg^{-1} and 19 μg kg^{-1} respectively), which are both components of the pentaBDE formulation (Nylund et al., 1992). These levels were similar those reported in a 1992 study by Hagenmaier et al. with ∑penta-BDE ranging from 0.22 and 17.13 μg kg^{-1} with an average of 8.58 μg

199 kg^{-1}, n=13 (Hagenmaier et al., 1992). Hagenmaier et al. also reported the consistent
200 presence of brominated furans (PBDF) at relatively high concentrations (ranging from
201 0.21 – 3.05 μg kg^{-1} and a mean of 1.17 μg kg^{-1}), which are similar to the
202 concentration of the chlorinated dioxins and furans (Rappe et al., 1998). Hagenmaier
203 stated "there is a reasonably good correlation between the concentrations of PBDFs
204 and PBDEs" and suggested that the PBDEs are the source of PBDFs observed in
205 sludge. This is extremely important and requires more research, as PBDFs share the
206 same level of toxicity as the chlorinated furans (IPCS, 1989, 1998).

207 The results reported by Nylund et al. (1992) and Hagenmaier et al. (1992) are
208 surprisingly low when compared to other modern literature. For example the sludge
209 samples collected in 1997-1998 from Stockholm, Sweden, reflect concentrations of
210 PBDEs in sludge more typical of those in contemporary sludges i.e. BDE-47 levels of
211 78, 80 and 36 μg kg^{-1}; BDE-209 levels of 220, 270 and 170 μg kg^{-1}. The
212 concentrations of BDE-47, -99, -100, and -209 were first presented by de Wit based
213 upon work of Sellstrom et al. and are presented in Table 3 (Sellstrom et al., 1999; de
214 Wit, 2002). These results show a higher burden of BDE-209 compared to the other
215 congeners from the pentaBDE formulation.

216 The dominance of BDE-209 was demonstrated again with findings by de Boer et al.
217 when concentrations of up to 920 μg kg^{-1} found in sludge samples from The
218 Netherlands (de Boer et al., 2000a). de Boer et al. also reported the concentration of
219 BDE-47, -99, -153 and -209 on suspended particulates in WWTP influent and
220 effluent, finding that BDE-47 and BDE-209 increased in concentration from an
221 average of 2.3 to 22 μg kg^{-1} and 24 to 350 μg kg^{-1} respectively in WWTP influents
222 and effluents (de Boer et al., 2000b). Unfortunately, the amount of suspended
223 material that was typical of these water samples was not provided, and should be

224 considerably lower in effluent than influent. It is not surprising that PBDEs are found
225 on suspended solids, since highly hydrophobic organic compounds will partition to
226 the sludge and suspended solids in preference to water through the WWTP process.
227 However, this finding may have consequences for the use of treated effluent, perhaps
228 requiring a higher level of treatment before effluent can be reused or discharged into
229 the environment. The presence of PBDEs in secondary treated effluent was also
230 reported by North in 2004. The congeners BDE-47, -99 and -209 were detected in
231 wastewater effluent at 10, 11 and 2 ng L^{-1} respectively (North, 2004). Again the
232 amount of suspended material was not reported. Hamm (2004) presented the PBDE
233 levels of eight German WWTP sewage sludges and suspended particulate matter from
234 their effluent. The total tri- to deca-BDE concentrations ranged from 231 to 982 μg
235 kg^{-1} (mean of 544 μg kg^{-1}) for sludges and from 71 to 353 μg kg^{-1} (mean of 209 μg
236 kg^{-1}) for the suspended particulate matter (Hamm, 2004).

237 In 2001, Hale et al. reported the total concentration of penta-BDEs in USA biosolids
238 as 1 100 to 2 290 μg kg^{-1} suggesting that input was consistently high, regardless of the
239 region and irrespective of preliminary treatment. These levels are far higher than
240 previously reported and exceeded those in European sludges by 10- to 100- fold. This
241 was attributed to the much higher use of PBDEs, both the pentaBDE and the
242 decaBDE formulations, within the U.S.A. Unlike BDE-99 and -100 (both part of
243 pentaBDE formulation), BDE-209 varied widely among the biosolids analyzed
244 ranging from 84.8 – 4 890 μg kg^{-1}. Incidentally, Hale et al. (2001) also reported that a
245 fish caught from a Virginia stream contained 47 900 ng g^{-1} (or 48 ppm) of total
246 PBDEs, one of the highest environmental burdens ever reported. In further work
247 investigating the levels of PBDEs in the U.S.A. in raw and treated sludges, Hale et al.
248 found an average total PBDEs of 1 540 μg kg^{-1} (Hale et al., 2002), while North

(2004a) found BDE-209 concentrations of 1 183 μg kg^{-1} and the ∑PBDE concentration up to 3 955 μg kg^{-1} (North, 2004).

In 2002, Oberg et al. reported the concentration of PBDEs and PBB-153 in 116 sewage sludge samples. Unfortunately the results were reported on a wet weight basis making it impossible to compare the levels determined with other international literature, as the water content of sewage sludge is highly variable. Oberg et al. does, however, report the detection of PBB-153 (Oberg et al., 2002).

Fabrellas et al. (2004) found that the major PBDE constituent of sludge (<95%) is BDE-209 with concentrations ranging between 786 and 5 837 μg kg^{-1}. In an industrial sewage sludge sample the concentration of BDE-209 was the highest ever reported at 18 032 μg kg^{-1}. Despite the relatively low concentrations of the total tri- to hexa-BDE levels (5.3 and 177.3 μg kg^{-1} respectively) relative to deca-BDE, these concentrations are still relatively high compared to other studies. The congener ratios resemble the pattern of the commercial pentaBDE formulation (Fabrellas et al., 2004).

In 2006, Law et al. reported the results of Swedish sludge analyzed for BDE-47, -99, -100, -153, -154, -209. Law et al. found that BDE-209 was the dominant species, with highly variable concentrations ranging from 5.6 to 1 000 μg kg^{-1} and an average concentration of 120 μg kg^{-1} (Law et al., 2006). Again the congener profile of BDE-47, -99, -100, -153 and -154 in all the Swedish sludges was similar to that of the pentaBDE technical product, which is probably the original source. Concentrations of the lower brominated PBDEs were fairly similar in all sewage sludge samples, indicating diffuse leaching of these from products into wastewater streams (Law et al., 2006).

272 Knoth et al. (2007) reported the concentration of PBDEs in 39 sludge samples from
273 different stages of the WWTP process from 11 municipal wastewater treatment plants
274 in Germany, which were collected from March 2002 to June 2003. The total tri- to
275 hepta-BDE concentrations (sum of BDE -28, -47, -99, -153, -154 and -183) ranged
276 from 12.5 to 288 (mean 108 μg kg^{-1}). The BDE-209 concentrations once again varied
277 widely between 97 to 2 217 μg kg^{-1} (mean 256 μg kg^{-1}) and was again the most
278 prevalent congener detected (Knoth et al., 2007). No change in the tri- to hepta-BDE
279 congener profile ratios was observed (% of total BDE -28, -47, -99, -153, -154, -183
280 without -209) in sludge from different stages of the waste water treatment process
281 (primary sludge, secondary excess sludge and dewatered digested sludge), which
282 suggested that the degradation of BDE-209 and other higher brominated PBDEs to
283 other lower brominated congeners did not occur.

284 Sludge samples collected from 31 WWTPs in 26 cities in China were analyzed for
285 PBDEs and organochlorine pesticides (OCPs) (Wang et al., 2007). The concentrations
286 of ∑PBDE (sum of congeners -17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154,
287 and -183) ranged from 6.2 to 57 μg kg^{-1}. The concentration of BDE-209 ranged from
288 below limit of detection (<1 μg kg^{-1}) to 1 109 μg kg^{-1} (with a median of 27 μg kg^{-1}),
289 and mean of 55% (median 69%) of the total PBDEs. These levels are about 10–100
290 times lower than those found in Europe and North America. PBDE levels in sludge
291 were not found to depend on the location or treatment capacity of the WWTPs.

292 To summarize, the major congeners present in sewage sludge are BDE-47, -99 and -
293 209 and the ΣPBDE concentrations are typically present in the μg kg^{-1} to the low mg
294 kg^{-1} range. These congeners represent the major commercial formulations of
295 pentaBDE (BDE-47, -99) and decaBDE (BDE-209), which appear to be the original
296 source.

297 **4.2. Polybrominated Biphenyls (PBBs)**

298 The concentration of PBBs in sewage sludge has received little attention, primarily
299 because of the relatively low use of PBBs in manufacturing. In general, the few
300 studies (n=3) that have investigated the levels of PBBs in sludge showed PBBs to be
301 below the detection limit (de Carlo, 1979, de Boer et al., 2003, de Boer et al., 2000).
302 In 2000, the presence of PBB was not detected in WWTP influent or effluent or other
303 environmental samples analysed (de Boer et al., 2000b). In 2003, de Boer again
304 analysed environmental samples for PBBs. This time they analysed the samples of
305 influents, effluents and suspended particulate matter from a Swedish wastewater
306 treatment plant for PBBs -15, -49, -52, -101, -153, -169 and -209 but they were, once
307 again, below the detection limit. (de Boer et al., 2003). The detection limits for most
308 PBBs were between < 0.1 and < 1 $\mu g\ kg^{-1}$, but for PBB-209 the detection limits were
309 generally between < 1 and < 10 $\mu g\ kg^{-1}$. This result is in agreement with the
310 negligible PBB production in Europe over the past decades (de Boer et al., 2003). It
311 is unclear as to whether these compounds have degraded or have been diluted to
312 undetectable levels or are seldom used within society. Analytically, it has only been
313 since the development of isotopically labelled standards, and the advent of facilities
314 with ultra-trace capability, using high-resolution mass spectrometry in the late 2007s,
315 that the detection of PBBs has been made possible with a certain degree of certainty.

316 **5. SOURCES OF PBDES IN SEWAGE SLUDGE**

317 Release of PBDEs into wastewater may occur during their synthesis, during
318 incorporation into polymers or related finished products, during their use and disposal
319 or recycling of these products, by cycling in the environment, or a combination of the
320 above. As PBDEs are hydrophobic, resistant to degradation and widely used in
321 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. In a study conducted by (Hale, 2001) examining 11 sludges collected from four different regions of the U.S.A., the constituents of pentaBDE formulation were detected in all 11 sludges analysed. The sludge had been stabilized in preparation for eventual land application. Concentrations (total of BDE-47, -99, -100, -153 and -154) were fairly consistent with concentrations ranging from 1 100 to 2 290 $\mu g\ kg^{-1}$ 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 to 4 890 $\mu g\ kg^{-1}$, which suggests that the source of this compound is more random and derives from an industrial source or other variable source. Another alternative 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.

6. METHODS

The results of two studies are reported. The first is a report on the concentration of PBDEs in sewage sludge samples taken from sixteen WWTPs from around Australia in 2006. The second is an analysis of PBDE levels in sewage sludge samples from three WWTPs over two successive years. The analyses were conducted at the National Measurement Institute (NMI), Sydney (Pymble), Australia. Sludge samples were extracted using accelerated solvent extraction (ASE) and the extracts were subsequently treated with concentrated sulfuric acid, treated for inorganic and organic sulfur by copper and silver nitrate clean-up techniques respectively, and then

chromatographically purified using a commercial automated clean-up procedure (PowerPrep™). Analyses were undertaken for chlorinated PBDEs and PBBs using isotope dilution capillary gas chromatography-electron impact high-resolution mass spectrometry with monitoring of either M^+, $[M+2]^+$ or $[M+4]^+$ ions. The analytical procedure was based upon standard U.S. EPA methodologies (U.S. EPA, 1994).

6.1. Instrumental Technique

Instrument: GC HP 6890 coupled to Finnigan MAT 95XL HRMS. **Column:** DB-5 column 10 m × 0.1 mm × 0.1 μm. **Inj. Temp:** 280 °C **Transfer line (DB-5):** 280 °C **Temperature program:** Initial temperature 120 °C hold 2 min, 120-230 °C at 15 °C/min, 230-320 °C at 5 °C/min 320 °C then hold 5 min **Carrier Gas:** Helium, constant flow mode (0.4 mL/min) **Injection volume:** 1 μl splitless **MS Parameters** Ionisation Mode: Electron Impact; Ion Source: 280 °C; Electron energy 70 eV; Filament Current: 0.7 mV; Electron Multiplier Voltage: Set to produce a gain of 10^6.

6.2. Australian Sewage Sludge Survey 2006

A national survey of sewage sludge (n = 16) was conducted, collecting samples from each state and the Northern Territory of Australia during 2006 by requesting samples from participating WWTPs. Sampling kits were provided to on-site workers who collected fresh sewage sludge samples, preferably at the last stage before land application and not taken from the top of the sludge pile. Samples were collected in pre-cleaned 250 mL amber glass jars with teflon lined lids and sent via courier to NMI for analysis. A variety of samples from urban (population > 1 000 000) and rural (population < 300 000) WWTPs were collected. Table 4 describes the treatment process for each of the participating WWTPs.

6.3. Comparison of PBDE Levels Over Time

The concentration of PBDEs was measured in sludge samples from three WWTP, collected in duplicate, during the years 2005 and 2006. Table 5 lists the WWTPs from which sewage sludge samples were collected. Sample collection and analysis methods were the same as for the Australian Sewage Sludge Survey.

6.4. Statistical Analysis

Principal components analysis 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 mean of zero and standard deviation of oneand the PCA conducted on the correlation matrix of the standardized 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 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.

7. RESULTS AND DISCUSSION

7.1. Analytical Discussion – Identification of BB-153

It is well known that there is co-elution on a DB-5 column between BB-153 and BDE-154. Therefore using any of the following techniques viz. GC-ECD, GC-NICI-MS and GC-EI-LRMS, can lead to an overestimation of either compound. The GC-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>10,000), thereby ensuring accurate identification and quantification. The ions selected for the $^{13}C_{12}$ BB-153 surrogate and the native BDE-154 represent $(M+-2Br)^{+2}$ and $(M+-2Br)^{+6}$, respectively. These ions are less abundant (<65%) compared to the M-2Br ions but can be mass resolved from one another with an instrument resolution of >10,000. This approach has been validated by analysing certified standards, procedural blanks and samples containing high BB-153 and BDE-154 levels and follows the recommended ions in the Certificate of Analysis supplied by Wellington Laboratories. The results presented here should therefore not be appreciably upwardly biased.

7.2. Australian Sewage Sludge Survey 2006

7.2.1. Polybrominated Diphenyl Ethers

The concentration of PBDEs as measured in the sixteen sewage sludge samples is supplied in Table 6. 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. A visual representation of BDE-47, -99, -209, as well as ΣPBDEs concentrations found in this survey are presented in Fig. 2 and a comparison with the results of this study and the international literature are presented in Fig. 3

Examination of the correlation matrix revealed that there were three primary groups of compounds; with correlations high among congeners within groups and low with congeners of other groups. The first two groups contained congeners that were 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

417 they are present in similar ratios to those reported in the formulations. The ratio of
418 the principal congeners of the pentaBDE formulation BDE 47:99+100:153+154 have
419 a ratio of 41:51:8 which is similar to the reported ratio of 40:45:6 (Sjodin et al., 1998).
420 The principal congeners of the decaBDE formulation BDE 209:206+207+208,
421 reported to have a ratio of 97-98:0.3-3 were found in an overall ratio of 93:7 (Alaee et
422 al., 2003).

423 The first two principal components explained 76% of the variation within the sample
424 set. PCA1 was primarily representative of the average concentration of components
425 in the pentaBDE formulation (BDE-47, -49, -66, -77, -85, -99, -100, -119, -139, -140,
426 -153, -154) explaining 50% of sample variation and PCA2 corresponded to
427 representative congeners of the decaBDE formulation (BDE-201, -203, -206, -207, -
428 208 and -209), explaining an additional 26% of the sample variation. The third
429 component explained 13% of the data variation, however it was concluded that this
430 component was not meaningful, as it corresponded mainly with variation in congeners
431 that were at or below their detection limits (BDE-171, -180, -184 and -191). Given
432 the high correlations within formulations, the concentration of PBDEs could be
433 reasonably summarised by the concentration of three dominant congeners, BDE-47
434 and BDE-99 and representing the pentaBDE formulation and BDE-209 representing
435 the decaBDE formulation. A plot of PCA1 vs PCA2 (i.e. pentaBDE vs decaBDE
436 formulations) does not reveal any obvious trends, such as associations with size of
437 town (population) or industrialisation (Fig. 4.)

438 If the PBDEs in sewage sludge were derived mainly from domestic products one
439 would expect there would be consistency in the relative concentrations of PBDEs
440 regardless of region. Using BDE-47 and BDE-99 as representatives of the pentaBDE
441 formulation this proposal is confirmed; the mean of BDE-47 and BDE-99 of 136.5 μg

442 kg^{-1} (s.d. 112 μg kg^{-1}) and 138 μg kg^{-1} (s.d. 116) respectively. Therefore it is
443 suggested that the primary source of the pentaBDE formulation in Australian sewage
444 sludge is largely from domestic sources. Concentration of the decaBDE formulation,
445 on the other hand is highly variable (mean BDE-209 715 μg kg^{-1}, s.d. 981), consistent
446 with previous reports in the scientific literature (Hale, 2001), suggesting a less
447 uniform source than the domestic environment. Varied industrial applications could
448 explain the variation observed. An alternative hypothesis is that the high variability
449 of BDE-209 is due to the higher degradation rate of this compound relative to the
450 lower substituted PBDEs (Bezares-Cruz et al., 2004).

451 Among the samples two are quite unusual. These are urban WWTP U5 and rural
452 WWTP R7. The urban WWTP U5 has an atypically high BDE-209 concentration.
453 Sewage sludge may be stabilized for biosolids using a variety of methods and this
454 elevated concentration may be a result of this method i.e. longer preparation time
455 (three years) and the subsequent loss of organic material compared to other sludges.
456 Similarly, treatment plants R1 and R8, both lagoon processes that degrade organic
457 material over time, have the second and forth highest ΣPBDE concentrations in this
458 study. Regardless of whether BDE-209 has been concentrated, its continued elevated
459 concentration in sewage sludge that is has been aged three years contradicts
460 laboratory evidence of the faster degradation of BDE-209 compared to the other lower
461 brominated congeners (Bezares-Cruz et al., 2004; Eriksson et al., 2004). This
462 contradiction over the persistence of BDE-209 was found also in a 2005 Swedish field
463 trial that found elevated levels of PBDEs, including BDE-209 (2 200 μg kg^{-1}
464 compared to the control of 0.75 μg kg^{-1}) twenty years after the last use of PBDEs at
465 that site, and found no evidence of the photodebromination of BDE-209 in the soils
466 studied (Sellstrom et al., 2005). Future analysis should also include total organic

467 carbon measurements as well as dry weight measurements to allow more accurate
468 comparison of the concentrations reported. The other notable feature of sample U5 is
469 the low burden of the pentaBDE formulation congeners. It is possible that this
470 treatment of sewage sludge (i.e. storage for three years) may have allowed the off-site
471 movement of these compounds by atmospheric transport.

472 The other unusual sample is rural WWTP R7, which has almost no PBDE burden.
473 This is quite an anomaly both within the current sample set and the international
474 literature. If the source of pentaBDE formulation congeners is domestic, one would
475 expect there to be similar concentrations in all sludges regardless of region of
476 wastewater treatment process. WWTP R7 is a small community that services an
477 abattoir and it is possible that this treatment plant processes large volumes of animal
478 waste, which may have lowered the PBDE burden by dilution.

479 To provide a context in which to assess the magnitude of these PBDE burdens they
480 have been compared to the contamination limits for the chemically similar
481 polychlorinated biphenyls (PCBs). In Australia, the National contamination limits
482 are Contamination Limit 1 of 200 $\mu g\ kg^{-1}$ (restricted land application) and
483 Contamination Limit 2 of 1 000 $\mu g\ kg^{-1}$ (unsuitable for land application) (NRMMC,
484 2004), which are similar to those in several European nations (European Commission,
485 2001). If it were appropriate to translate these guidelines directly from the PCB
486 contamination limits to a PBDE contamination limit, then all samples, except WWTP
487 R7, would be unsuitable for unrestricted land application. Fifteen of the sixteen
488 samples had a ΣPBDEs greater than 200 $\mu g\ kg^{-1}$ and seven of the sixteen samples
489 contained ΣPBDEs greater than 1 000 $\mu g\ kg^{-1}$. At this time no contaminant limits
490 have been proposed for PBDEs and the practice of sewage sludge land application has
491 not stopped in the U.S.A. and many other nations despite higher PBDE burdens than

492 those observed in Australia. However, the PBDE levels found in Australian sludges
493 are ten to one hundred times greater than levels of PBDEs in European soils; ΣPBDEs
494 0.065 – 12 μg kg^{-1} (Hassanin et al., 2004) and suggests that the land application of
495 sludge would increase the PBDE burden found in soils.

496 To summarise, the mean concentration of ΣPBDEs in this Australian survey was 1
497 137 μg kg^{-1} (s.d. 1 116). When comparing the urban mean of 1 308 μg kg^{-1} (s.d. 1
498 320) and the rural average of 911 μg kg^{-1} (s.d. 831) there is little variation and the
499 difference is not significant at the 95% confidence level. The PBDE concentrations
500 reported in this study are similar to those reported in the international scientific
501 literature (Fig. 3). Principal component analysis revealed that this data set could be
502 reduced into two primary components reflecting the pentaBDE and decaBDE
503 formulations and these two formulations can be suitably represented by the dominant
504 congeners BDE-47 , -99 and BDE-209 respectively.

505 **7.3. Polybrominated Biphenyls**

506 The finding of BB-153 in all samples is unexpected (mean 0.6 μg kg^{-1}, s.d. 0.5) and,
507 as far as is known, there are no industries utilizing the hexaBB formulation in
508 Australia. In terms of historical use, it is unclear whether this compound was ever
509 used in Australia. Despite this lack of knowledge, it is possible that the commercial
510 formulation of hexaBB was utilized in Australia. The ubiquity of BB-153 strongly
511 suggests that it was in a common product, such as automobiles or widely used
512 domestic products. However the use of hexaBB in Australia would be surprising
513 considering it was banned from many Western nations in the 1970s following the
514 Michigan contamination disaster. It is likely that BB-153 could was imported with an
515 unknown product, which was commonly used and widely distributed. A more

516 concerning hypothesis is that this chemical is extremely persistent in the environment
517 and has been subject to long-range atmospheric transport.

518 **7.4. Variation of PBDE Levels Over Time**

519 An analysis of variance was performed on the concentration of the three components
520 BDE-47, -99,-209 as well as ΣPBDEs at three Perth WWTPs (Beenyup, Subiaco and
521 Woodmans Point) over two years (2005, 2006). From the correlation matrix (R) and
522 principal component analysis previously performed, PBDE congeners were separated
523 into groups that have been identified as the pentaBDE and decaBDE formulations.
524 Given the high correlations within formulations, it is appropriate to conduct an
525 analysis of variance on just the dominant congeners representative of each viz. BDE-
526 47&-99 and BDE-209. Other congeners were measured and the raw data are provided
527 in Table 8.

528 In all three cases there was a significant WWTP by year interaction indicating that
529 differences in concentration existed between the WWTPs but the magnitudes of these
530 differences varied depending on the year of measurement. Despite the interaction
531 there were significant differences between WWTPs, but not between years, for BDE-
532 47. The concentration of BDE-47 was significantly lower at Subiaco (60 $\mu g\ kg^{-1}$)
533 than at the other two plants: Beenyup 213 $\mu g\ kg^{-1}$, Woodman Point 285 $\mu g\ kg^{-1}$. The
534 concentrations of BDE-99, -209 and ΣPBDEs were also lower, at Subiaco than at
535 Beenyup and Woodmans Point (Table 8). There were no overall differences between
536 years or WWTPs for either BDE-209 or ΣPBDEs. The similar result for BDE-209 and
537 ΣPBDEs is not surprising as BDE-209 is by for the most abundant congener.

8. CONCLUSION

A survey of Australian sewage sludge in 2006 found the ΣPBDE mean concentration to be 1 137 μg kg^{-1} d.w. (s.d. 1 116), with little difference between the urban (mean 1 308 μg kg^{-1}, s.d. 1 320) and the rural (mean 911 μg 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 ∑PBDE greater than 200 μg kg^{-1} and seven were higher than 1 000 μg kg^{-1} (Australian guidelines values for ΣPCBs in sewage sludge land application). The PBDE burden found in Australian sludge is far higher than the levels reported in European soils. If Australian soils have a similar PBDE burden to European soils, then sludge land application is likely to increase the PBDE levels in soil. The development of guidelines that estimate the risk of PBDEs in sewage sludge land application, taking into account typical PBDE concentration in Australian soils, should be developed.

Both the pentaBDE and decaBDE formulations appear to go 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 analyzed as part of this survey is unexpected. The results further demonstrate that PBBs are extremely environmentally persistent and that they are not only capable of long-range atmospheric transport, but are also now widely distributed within the Australian environment. The concentrations of PBBs in sewage sludge are not high, however, they are rarely analysed, detected or

563 reported in the international scientific literature due to a phasing out of these
564 compounds in 1970s.

565 This is the first article to comprehensively focus on PBDEs and BB-153 in Australian
566 sewage sludge and the first to provide a review of the international literature
567 specifically on PBDEs and PBBs in sewage sludge. We have identified the issue of
568 PBDEs in Australian sewage sludge as a potential problem for sewage sludge land
569 application and further research is required to ascertain the risks to human health and
570 the environment from this practice.

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Table 1

Names and congener numbers of prominent PBDEs and PBBs

Homologue	IUPAC No	Bromine Substitution
Tetra	47	2,2',4,4'
Penta	99	2,2',4,4',5
Penta	100	2,2',4,4',6
Hexa	153	2,2',4,4',5,5'
Hexa	154	2,2',4,4',5,6'
Hepta	183	2,2',3,4,4',5',6
Deca	209	2,2',3,3',4,4',5,5',6,6'

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Table 2

Major trade names and manufacturers of technical-grade PBBs and commercial PBB mixtures

PBB mixture	Trade Name	Manufacturer	CAS No.
HexaBBs	FireMaster(R) BP-6	Michigan Chemical Corp. (St. Louis, Mich.)	59536-65-1
	FireMaster(R) FF-1b	Michigan Chemical Corp. (St. Louis, Mich.)	67774-32-7
Octa/nonaBBs	Bromkal 80-9D	Chemische Fabrik Kalk (Cologne, Germany)	61288-13-9
	Technical octabromobiphenyl	White Chemical Corp. (Bayonne, New Jersey)	
	Octabromobiphenyl FR 250 13A	Dow Chemical Co. (Midland, Mich.)	
DecaBB	Adine 0102	Ugine Kuhlmann now Atochem (Paris, France)	13654-09-6
	Berkflam B 10	Berk (London, United Kingdom)	
	Flammex B-10	Berk (London, United Kingdom)	
	Technical decabromobiphenyl	White Chemical Corp. (Bayonne, New Jersey)	
	HFO 101	Hexcel (Basildon, United Kingdom)	

Reproduced from (IPCS, 1994a)

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Table 3

Concentration of PBDE -47, -99, -100 and -209 µg kg^{-1} d.w. in sewage sludge from waste water treatment plants reported in the English-language peer reviewed scientific literature.

Country	Reference	BDE-47	BDE-99	BDE-100	BDE-209
Sweden	Nylund, 1992	15, 15	19, 19		
Sweden	Sellstrom, 1999	78, 80, 36	98, 100, 56	24, 25, 13	220, 270, 170
U.S.A.	Hale, 2001	498, 754, 359, 525, 518, 673, 536, 605, 421, 686, 674	743, 1157, 513, 584, 714, 815, 516, 572, 391, 648, 613	106, 67, 88.5, 200, 115, 255, 112, 125, 113, 129, 176	308, 1460, 553, 84.8, 1940, 4890, 368
Spain	Fabrellas, 2004	83.6, 21.4, 28.3, 1.8, 49.8, 38.5	64.2, 23.4, 25.6, 37.6, 34.5,	14.0, 4.5, 5.7, 0.2, 8.0, 7.7	5430, 756, 1203, 3591, 5837, 18632
Germany	Hamm, 2004	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	5.9, 11.0, 7.0, 12.1, 6.1, 8.5, 19.0, 14.4	217, 198, 639, 400, 177, 100, 268, 609
U.S.A.	North, 2004	757 (mean)	944 (mean)	165 (mean)	1183 (mean)
China	Wang, 2007	5.0 (mean), 0.4 → 58.7	4.5 (mean), <3.4 → 69.7	1.0 (mean), <24.4 → 18.4	68.5 (mean), <1 → 1108.7

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Table 4

Australian Sewage Sludge Survey 2006 - Type of treatment process and source of wastewater; U = Urban, R = Rural

WWTP	Population[1]	Treatment Method	Source
U1	4,297,000	Anaerobically digested and freshly dewatered.	Services residential and industrial areas.
U2	1,811,000	Activated Sludge, Dewatered.	Composition industrial and domestic.
U3	1,139,000	Activated sludge. Dissolved air-flotation filtration.	Mixture of domestic and industrial and some groundwater runoff.
U4	1,139,000	Integrated fixed-film activated sludge.	Mixture of domestic and industrial and some groundwater runoff.
U5	3,850,000	Activated sludge plant. Anaerobically digested primary and secondary sludge. Dewatered in sludge drying pans. Stockpiled for >3 years.	Industrial and domestic
U6	1,508,000	Mesophilic anaerobic digestion, centrifuge dewatering,	Mainly domestic ~2% industrial input.
U7	1,508,000	Activated sludge. Mechanically dewatered. Chemically stabilized (lime).	Mainly domestic, ~5% industrial.
U8	1,508,000	Mesophilic anaerobic digestion, centrifuge dewatering,	Mainly domestic ~9% industrial input
R1	142,000	Stored in a lagoon for 6 months. Dewatered by centrifuge and stockpiled for 4 months.	92% domestic 8% trade waste.
R2	106,000	Lagoon. Dewatered by vacuum filtration	Domestic and light industrial.
R3	27,000	Activated sludge. Dewatered.	Domestic source.
R4	35,000	Aerobic digestion. Dewatered.	Domestic and light industrial.
R5	202,000	Chemically stabilized with lime.	Domestic and industrial
R6	52,000	Dewatered and chemically stabilized (lime).	Mainly domestic.
R7	5,000	Activated sludge and lagoon process. Land dried.	Domestic and abattoir
R8	14,000	Oxidation treatment pond. Solar dried.	Domestic and Industrial

[1]*Population refers to the population of the town/city and not just the feeding population of the WWTP*

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Table 5

Perth WWTPs that the sewage sludge concentration of PBDEs was measured in 2005 and 2006

Beenyup	110 ML/day, mesophilic anaerobic digestion, centrifuge dewatering, ~2% industrial input
Subiaco	60 ML/day dewatered and chemically stabilized. Mainly domestic. ~5% industrial input
Woodman Point	120 ML/day mesophilic anaerobic digestion, centrifuge dewatering, ~9% industrial input

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Table 6

Concentration of PBDE congeners and PBB-153 µg kg^{-1} d.w. detected in Australian Sewage Sludge Survey conducted in 2006; U = Urban (Pop. > 1,000,000), R = Rural (Pop. < 300,

	U1	U2	U3	U4	U5	U6[3]	U7	U8[3]	Urban Mean	Sd	R1	R2	R3	R4	R5	R6
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
BDE 28 + 33	2	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
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
BDE 47	120	180	36	72	17	205	45	285	120.0	95.4	170	74	120	140	56	89
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
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
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
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
BDE 85	4.8	6.7	1.1	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
BDE 99	130	190	31	84	22	230	48	315	131.0	106.0	210	120	130	170	51	130
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
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
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
BDE 138 + 166						3.3	1.9	2.7	2.6	0.7	4.2	4.7	3.9	6.1	nd	4.2
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
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
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

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
BDE 156 + 169						4.8	<0.1	<dl	-	-	<0.09	<0.08	<0.06	<0.1	nd	<0.1
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
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
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
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
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
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
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
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
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
BDE 204	1.4	<3	0.64	0.97	<7	8.2	<0.1	<dl	-	-	<0.4	<0.06	<0.1	<0.4	<0.1	<0.2
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
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
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
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
BDE 209	1170	360	93	81	3780	530	130	910	882	1237	990	280	1210	260	250	180
ΣPBDE[1]	1560	900	230	300	4230	1225	280	1735	1308	1320	1610	560	1630	710	420	500
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

[1]Does not include half detection limit

[2]The Standard Error associated with replicate sampling and analytical measurement calculated from five replicate samples as part of the time series study

[3]Reported is the average concentration of replicate samples

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Table 7

The first three principal components of PBDEs in Australian sewage sludge conducted in 2006

	PCA1	PCA2	PCA3
BDE 17	0.5030	0.0164	0.2822
BDE 47	0.8898	0.2918	-0.3169
BDE 49	0.8089	0.1733	-0.3736
BDE 66	0.8988	0.2629	-0.2819
BDE 77	0.7261	-0.0975	0.6562
BDE 85	0.8870	0.2923	-0.2483
BDE 99	0.9034	0.2976	-0.2914
BDE 100	0.8972	0.2858	-0.3137
BDE 119	0.8906	0.0920	0.0651
BDE 139	0.9042	0.2732	-0.1840
BDE 140	0.9676	0.1523	0.0951
BDE 153	0.9239	0.2427	-0.2628
BDE 154	0.9222	0.2536	-0.2825
BDE 171	0.6347	-0.2354	0.7016
BDE 180	0.6907	-0.2486	0.6147
BDE 183	0.6602	-0.3824	-0.1411
BDE 184	0.7384	-0.1603	0.6340
BDE 191	0.5491	-0.5078	0.6454
BDE 196	0.6814	0.1676	0.1891
BDE 197	0.7047	-0.6217	0.0754
BDE 201	0.2322	-0.9579	-0.1157
BDE 203	0.1765	-0.9340	-0.242
BDE 206	0.2963	-0.8839	-0.2892
BDE 207	0.1060	-0.9571	-0.2566
BDE 208	0.0864	-0.9627	-0.2376
BDE 209	0.1881	-0.8721	-0.3929

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Table 8

Concentration of PBDEs µg kg^{-1} d.w. at sewage sludge measured at three Perth WWTPs (Beenyup, Subiaco and Woodman Point) in the years 2005 and 2006.

	Beenyup				Subiaco			Woodman Point			
	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

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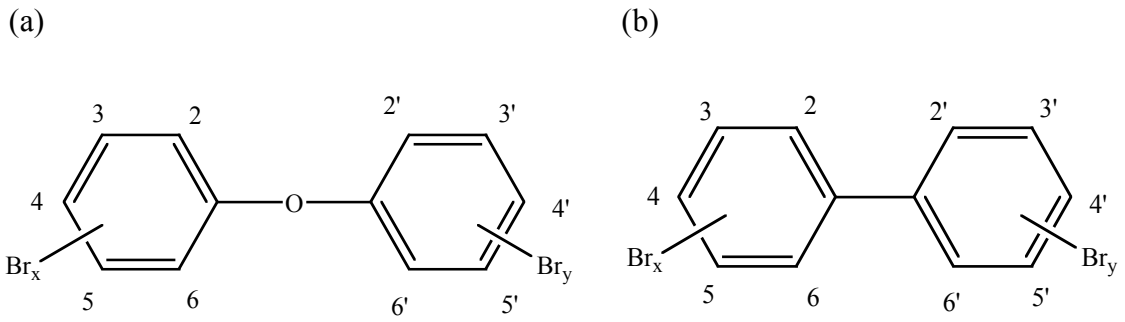

Fig 1. Chemical structure of four common brominated flame retardants (a) polybrominated diphenyl ether and (b) polybrominated biphenyls.

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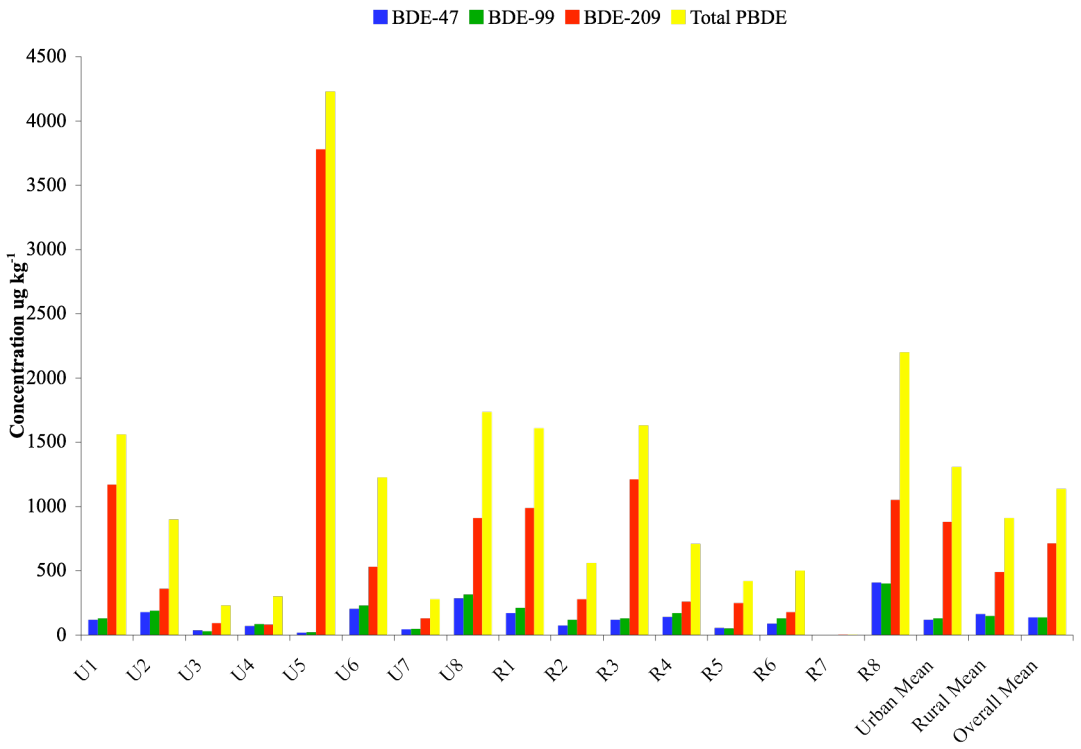

Fig. 2. Concentration of BDE-47, BDE-209 and ΣPBDE µg kg^{-1}) in Australian sewage sludge; U = Urban (Pop. > 1,000,000), R = Rural (Pop. < 300,000)

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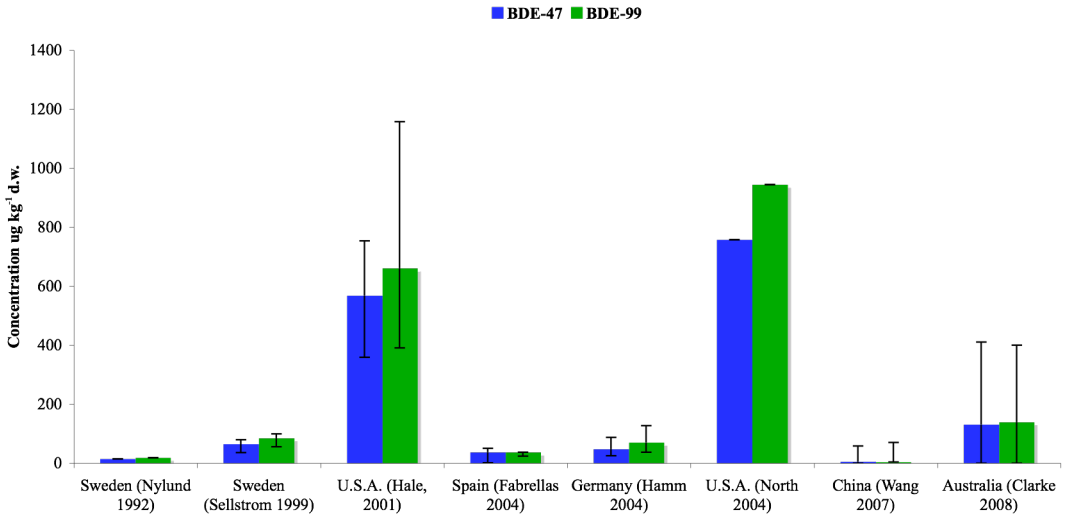
(A)



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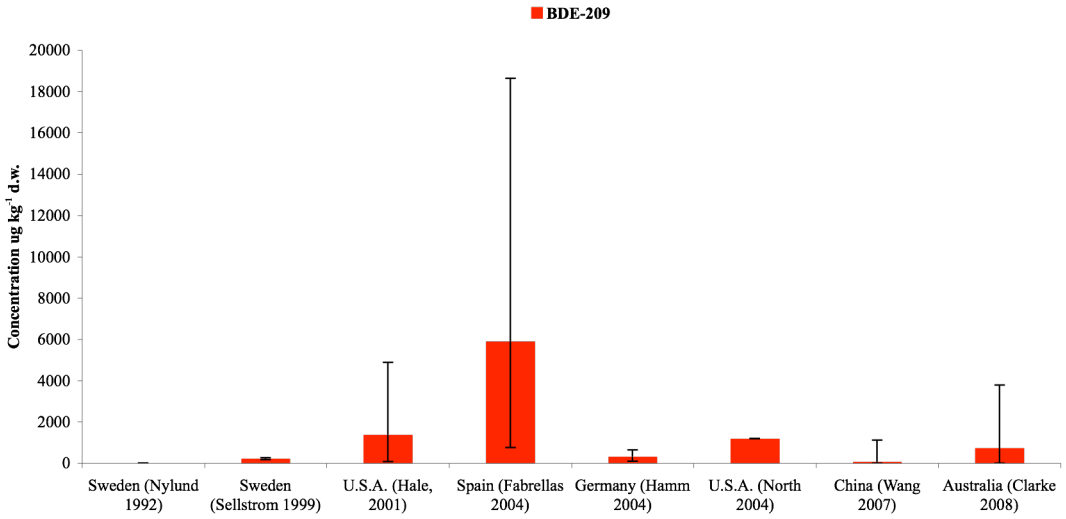

Fig. 3. A comparison of the major PBDE congeners µg kg^{-1} d.w. (a) BDE-47, -99 and (B) BDE-209 from the Australian survey and the English peer reviewed scientific literature. The graphs represent the mean concentration and the error bars express the range reported.

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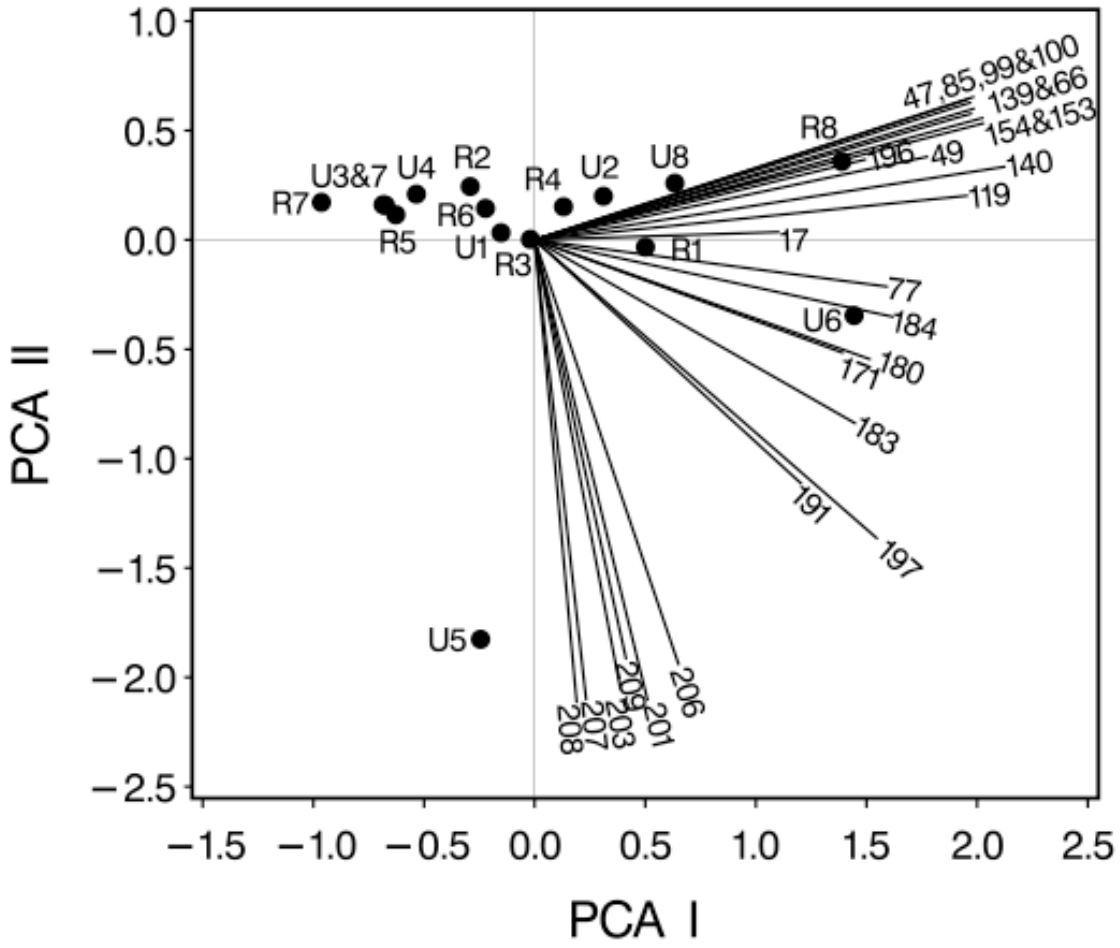

Fig. 4. Principal component analysis of PBDEs in Australian sewage sludge survey conducted in 2006. Plot of PCA1 vs PCA2, primarily representing pentaBDE and decaBDE commercial formulations (A) Score plot (B) Loading Plot.

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