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Investigating the distribution of polybrominated diphenyl ethers through an Australian wastewater treatment plant

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KEYWORDS

PBDEs, WWTP, sewage sludge, biosolids, treated effluent

ABSTRACT

The concentration of PBDE congeners was measured at various treatment stages of an Australian wastewater treatment plant (WWTP). This included four aqueous samples (raw, primary, secondary and tertiary effluent) and three sludges (primary, secondary and lime stabilised

biosolids). Semi-permeable membrane devices (SPMDs) were also installed for the duration of the experiment, the first time that SPMDs have been used to measure PBDEs in a WWTP. Over 99% of the PBDEs entering the WWTP were removed through the treatment process, principally by sedimentation. The main congeners detected were BDE 47, 99 and 209, which are characteristic of the two major commercial formulations viz pentaBDE, and decaBDE. All the PBDE congeners measured were highly correlated with each other, suggesting a similar origin. In this case, the PBDEs are thought to be from domestic sources since domestic wastewater is the main contribution to the inflow. The lower brominated PBDE congeners demonstrated a greater solubility than the higher ones, which reflects increasing K_{ow} with increasing bromination. The mean concentration of Σ PBDEs (defined as the sum of all targeted PBDEs) in chemically stabilized sewage sludge (biosolids) was $300 \mu\text{g kg}^{-1}$ dry weight, which is likely to be the minimum PBDE burden for all Australia sewage sludge. This corresponds to at least 110 kg of PBDEs contaminating Australian sewage sludge annually. It is estimated that 6.5 to 9.9 kg of PBDEs are disposed of each year with biosolids generated from Subiaco WWTP. Less than 10 g are released annually into the environment via ocean outfall and field irrigation and this level of contamination is unlikely to pose risk to humans or the environment. The release of treated effluent is not considered a large source of PBDE environmental emissions compared to biosolids or landfill.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are widespread environmental contaminants (Norén *et al.*, 1998, de Wit, 2002, Hites, 2004) and certain PBDEs have recently been included as United Nation's Persistent Organic Pollutants (POPs) in recognition of the threat that they pose to human health and the environment (UNEP, 2001, UNEP, 2009). This includes the penta-BDE and octa-BDE commercial formulations and they have largely been restricted for use in Europe and Australia (NICNAS, 2007). The deca-BDE formulation wasn't categorized as an UNEP POP and is still currently widely used internationally. Despite restriction on future uses, PBDEs are incorporated into many commonly used objects and are likely to cycle through the environment for some time to come. Investigations that quantify amounts of PBDEs entering the environment via wastewater treatment products (viz. effluents, sludges) are important and can aid efforts to minimize further environmental contamination.

PBDEs are routinely detected in sewage sludges in the low part-per-million range (Clarke *et al.*, 2008a). In sewage sludges, congeners representative of the pentaBDE (BDE47, 99, 100, 153, 154) formulations are often present at similar concentrations regardless of region, indicating domestic origins (Hale, 2001). BDE209, the primary congeners of the decaBDE formulation, is consistently the main PBDE congeners present in sewage sludge. In national sewage sludge surveys BDE 209 concentrations are highly variable, suggesting industrial and domestic sources (Fabrellas *et al.*, 2004, Clarke *et al.*, 2008b). Trace PBDE amounts (ng L^{-1}) have also been detected in treated effluent (de Boer *et al.*, 2000, Hamm, 2004, North, 2004, Knoth *et al.*, 2007) and recent studies have demonstrated this as a point source of environmental PBDE contamination (Toms *et al.*, 2006, Toms *et al.*, 2008). The contamination of sludges and effluents with PBDEs may have implications for disposal and beneficial reuse strategies. Also, given many

nations reliance on treated effluent for a range of purposes, including drinking water, understanding PBDE concentrations and fate in wastewater treatment is increasingly important.

A few studies have investigated the fate of PBDEs in WWTPs. A mass balance study of PBDEs in an USA WWTP found that 96% of PBDEs associated with the sludge during WWTP (North, 2004). On an annual basis the authors calculated that 22 kg were associated with sludge and 0.9 kg were released into the environment with treated effluent (North, 2004). A German study reported that no degradation of PBDE congeners was observed during wastewater treatment and estimated the annual environmental release of PBDEs associated with sewage sludge to be 500 kg year (Knoth *et al.*, 2007). The fate of many other organic pollutants in WWTPs has been studied and includes polychlorinated biphenyls (PCBs), organochlorinate pesticides, phthalates, nonphenyls and linear alkyl sulphonates (Choi *et al.*, 1974, Lawrence *et al.*, 1976, McIntyre *et al.*, 1981, Garcia Gutierrez *et al.*, 1984, Buisson *et al.*, 1986, Buisson *et al.*, 1988, Morris *et al.*, 1994).

PBDEs are expected to behave most similarly to PCBs in a WWTP. Of the identified WWTP organic pollutant removal mechanisms (degradation, air stripping, volatilization, effluent) only sedimentation in primary and secondary treatments is expected for PCBs and PBDEs. Volatilization losses are not high when chemicals are strongly bound to particles and normally only considered when the chemical is in the aqueous phase. The fraction that is sorbed to particulate matter or other solids phase is not directly available, under equilibrium conditions, for mass transfer across the water/air interface (Byrns, 2001). General principles of organic pollutant behavior in a WWTP are decreasing water solubility, as measured by the octanol-water partition coefficient (K_{ow}), the greater removal in primary sedimentation (Petrasek *et al.*, 1983, Buisson *et al.*, 1988, Morris *et al.*, 1994, Katsoyiannis *et al.*, 2006). However, there are contradictory experimental results with respect to the degradation of PCBs in a WWTP. Degradation of the

lower chlorinated PCBs (di-, tri-, tetra-) has been reported, while the higher chlorinated PCBs are generally resistant to degradation (Buisson *et al.*, 1986).

A number of studies have also successfully employed passive samplers for the measurement of a range of organic pollutants in the WWTP (Petty *et al.*, 2000, Stuer-Lauridsen *et al.*, 2000, Wang *et al.*, 2001, Yusa *et al.*, 2005, Bergqvist *et al.*, 2006, Katsoyiannis *et al.*, 2007). No other studies have reported measurements of PBDE concentrations in WWTP using passive sampling techniques.

The aim of this research is to measure the concentration of common PBDEs through an activated sludge WWTP process (using active and passive sampling techniques) and quantify the amount of PBDEs released into the environment via secondary effluent, tertiary effluent and sewage sludge.

METHOD

The experiment was conducted at an Australian WWTP, located in the city of Perth, Australia, which has a population of approximately one and a half million people. It is a conventional activated sludge treatment system that treats approximately 60 ML of water daily that derives primarily from domestic (~95%) sources, with a small contribution from industrial sources (~5%). Passive samplers were installed in the WWTP for 29 days and grab samples were collected on three occasions during this sampling period. 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; BDE17, 28+33, 47, 49, 66, 77, 85, 99, 100, 119, 138+166, 153, 154, 183, 184, 196, 197, 206, 207 and 209 and polybrominated biphenyl (PBB) congener 153. The analyses were conducted at the National Measurement Institute (NMI), Sydney (Pymble), Australia.

108 ***Sampling Methodology***

109 **Grab Samples**

110 Grab samples were collected from the various stages of the WWTP and measured for PBDE
111 congeners. Four aqueous samples (raw water, primary effluent, secondary effluent and tertiary
112 treated effluent) and three sludge samples (primary sludge, secondary sludge and lime stabilised
113 biosolids) collected on 12/11/07, 22/11/07 and 03/12/07 between 11am and 1pm which was peak
114 water in-flow. Inflow volumes were and volumes of water treated are listed in Table 1 (NOTE:
115 Volume of final effluent is greater than raw water due to the addition of flocculants). .

116 **Semi-Permeable Membrane Device Deployment**

117 Five semi-permeable membrane devices (SPMDs) were deployed for 29 days at the WWTP,
118 located in the raw water (PS1), primary effluent (PS2), secondary effluent (PS3) and tertiary
119 effluent (PS4a, PS4b) channels. They were regularly checked for interfering materials. A field
120 blank and laboratory blank were completed for quality control purposes.

121 ***Sample Treatment***

122 **Grab samples**

123 Freeze-dried sludge samples (20.0 g) were spiked with 10 µL of mixed $^{13}\text{C}_{12}$ PBDE surrogate
124 standards and were extracted into toluene using accelerated solvent extraction (Dionex Model
125 ASE 100). Effluents (1 L) were extracted into hexane using liquid-liquid extraction. The extracts
126 were concentrated using a BÜCHI Syncore® Analyst (BÜCHI Labortechnik AG, Flawil,
127 Switzerland), which was used for removing various solvents throughout the extract cleanup
128 process. The concentrated extract was solvent-exchanged into hexane and then subsequently
129 treated with concentrated sulfuric acid for destructive removal of organic material. The extract
130 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 and produce a cleaned up final extract. Extracts were concentrated to dryness under nitrogen and made up to 40 µL 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 U.S. EPA methodologies (US EPA, 2007).

Passive Samples - Semi-Permeable Membrane Devices (SPMDs) Preparation, Deployment & Extraction

SPMDs were prepared from lay-flat low-density polyethylene (LDPE) tubing (purchased from Brentwood Plastics, MO, USA) of size 105 cm long, 3.0 cm wide, wall thickness 0.003 cm. The tubing was pre-extracted two times by soaking overnight in hexane and then dried under nitrogen. 1 mL of triolein (Sigma Glyceryl Trioleate T7140 $\geq 99\%$) containing PAH performance reference compounds (Wellington Labs PAH-LCS-A deuterated surrogate) was added prior to the SPMD being heat-sealed. Air bubbles were removed with a short pasteur pipette and triolein spread along the tube, no further than 91.4 cm, where it was again sealed. Three SPMDs were looped into a cage for deployment.

After deployment, SPMDs were first wiped with a white Kimwipe™ and rinsed under a tap to remove surface material. The SPMDs were submerged in hexane for 30 s, followed by 1M HCl for 30 s, rinsed clean with milli-q water, acetone and 2-propanol. Once cleaned, the SPMDs were

extracted into 400 mL hexane for 8 to 18 h and then re-extracted in hexane for a further 6 h. The solvent was removed and exchanged with dichloromethane. The extract was passed through a 0.45 μm filter, followed by treatment with gel-permeation chromatography (GPC). 2mL of sample was eluted from a multi column GPC system (Waters Envirogel™ columns, 4.6mm x 30 mm guard – 19 mm x 150 mm – 19mm x 300 mm, 100 Å pore size, 10 μm nominal particle size) with dichloromethane at 5 mL min⁻¹. The concentrated extract was solvent-exchanged into hexane and then subsequently treated with concentrated sulfuric acid for destructive removal of organic material. 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 and produce a cleaned up final extract.

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 x 0.1 mm x 0.1 μm . A 1 μL 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 min. 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 maintaining the ion source at 240 °C. The electron multiplier voltage was set to produce a gain of 10⁶.

176 **Material, Standards and Reagents**

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

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

183 **Quality Assurance/Quality Control**

184 Internal standard isotope dilution quantification was undertaken within this study. This employs
185 the use of $^{13}\text{C}_{12}$ labeled surrogates and internal standards. The $^{13}\text{C}_{12}$ surrogates standards ($^{13}\text{C}_{12}$
186 BDE28, 47, 77, 99, 100, 126, 153, 183, 197, 205, 207, 209, BB153) are added to the sample prior
187 to extraction and are carried through all the laboratory operations. The recovery standards ($^{13}\text{C}_{12}$
188 BDE79, 139, 180, 206) were added just prior to analysis by HRGC-EI-HRMS. Both the recovery
189 of the surrogate and internal standard response are then used in the quantification of the native
190 BDEs.

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

196 The analysis of the higher brominated BDEs, particularly BDE-209, is recognized as being
197 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 BDE209.

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

Statistical Analysis

Statistical analysis was performed using Minitab 15.

RESULTS

Grab Samples

Measurement of PBDE congeners typical of commercial formulations was performed for aqueous and sludge samples collected from an Australian WWTP (Table 2). As expected PBDE congeners were greatly associated with the sludges with Σ PBDE ranging between 220 and 460 $\mu\text{g kg}^{-1}$ dw. The mean biosolids concentration was 300 $\mu\text{g kg}^{-1}$ dw and is lower than the national Australian mean of 1100 $\mu\text{g kg}^{-1}$ dw recently reported (Clarke *et al.*, 2008b). The low and consistent PBDE concentration in all sludges analysed suggests the primary source of PBDEs in raw water is the domestic environment. Similar to international studies BDE209 contributed the major portion of total PBDEs (>50%) and was found in the highest concentrations in primary sludges (217 $\mu\text{g kg}^{-1}$ dw), compared to the biosolids (163 $\mu\text{g kg}^{-1}$ dw) and secondary sludge (146 $\mu\text{g kg}^{-1}$ dw). PBDEs concentrations in the raw water and effluents were in the low ng L^{-1} range (0.058 – 100 ng L^{-1}). The concentration was significantly higher in the raw water (mean 70 ng L^{-1}) and primary effluent (mean 74 ng L^{-1}) compared to the secondary (mean 0.30 ng L^{-1}) and tertiary treated effluents (mean 0.34 ng L^{-1}). This indicates high PBDE removal rates through the WWTP, where PBDEs are likely to be associated with suspended solids (SS). Covariance

220 principal components analysis (PCA) performed on the raw data found that three congeners
221 (BDE47, 99 and 209) can explain >99% of the sample variation. Both the correlation PCA and
222 covariance PCA demonstrates that the concentration of PBDE congeners taken from the three
223 separate sampling events were consistent, with the highest variation found in the secondary
224 sludge samples. The returning activated sludge (RAS) process in wastewater treatment can
225 explain this observation.

226 In order to further examine the data the aqueous concentration data was manipulated from
227 mass/volume to mass/mass by dividing the effluent concentration ng L^{-1} by the SS concentration
228 (g L^{-1}). The assumption is that the majority of all PBDEs will be associated with the suspended
229 solids in the sample in preference to the aqueous phase based upon the high K_{OC} values of the
230 PBDE congeners.

231 On a mass/mass basis the concentrations of the PBDEs congeners (47, 99, 209 and Σ PBDEs)
232 were consistent throughout the WWTP (Figure 3). The concentrations of PBDEs were always
233 lower in the secondary and tertiary treated effluents compared to the raw water and primary
234 effluent. This may be because of the reduction in SS and also many congeners were not detected,
235 possibly because the limit of detection was inadequate. An analysis of variance was performed
236 (ANOVA) on each of the congeners to compare differences between the concentrations of PBDE
237 congeners in effluents (raw and primary only) and sludges. The concentration of BDE47 is
238 statistically significantly higher in the effluents compared to the sludges ($P=0.034$), which was
239 not observed for BDE99 ($P=0.118$) or BDE209 ($P=0.410$). The Σ PBDE concentration was also
240 found to have the highest concentration in the primary effluent, however there was no statistically
241 significant difference observed between effluents and sludges ($p = 0.608$). Covariance PCA again
242 showed that BDE47&99 and 209 explain >98% of the sample variation, 24% and 74%
243 respectively. Both the correlation PCA and covariance PCA demonstrates that there is a

similarity between the PBDE concentration patterns in all samples; with the exception of samples A2, C2 and C6 (Figure 2a). Also, PBDE congeners were largely correlated between the penta-BDE and deca-BDE formulations (Figure 2b).

The concentration of BDE47 is highest in the primary effluent which suggests that this compound is not only associated with the SS but is also dissolved in the aqueous phase to a small extent. This is in contrast to BDE209 that is preferentially partitioning to the SS and sludges with the highest mean concentration observed in the primary sludge. The ratio of BDE47:BDE99 found in the pentaBDE commercial formulation is reported to be 0.95:1 (Sjödin *et al.*, 1998). This is in contrast to the ratio that was found in the raw and primary effluent with BDE47 consistently higher in concentration than BDE99, with average ratios of 1.06:1 and 1.18:1 respectively. BDE47 is dissolved in the aqueous phase of the raw and primary effluent due to a lower K_{ow} ; perhaps due to the association with surfactant, the ratio of BDE47:BDE99 increases the relative concentrations in the primary treatment compared to the raw water. WWTP models employ the organic carbon-water partition coefficient (K_{oc}) to explain the partitioning of hydrophobic contaminants in wastewater treatment. Applying this technique the predicted concentration of BDE47 in the aqueous phase of the raw effluent theoretically will range between 0.1 to 0.4 ng L⁻¹ when the SS organic carbon content ranges between 60% to 10%. Assuming a high organic carbon content at this stage of the treatment process the concentration of BDE47 will be less than 0.15 ng L⁻¹ which can explain the observed increase of BDE47 relative to BDE99 found in the raw effluent samples.

Semipermeable membrane device

Substantial interference (bio-fouling) occurred on SPMDs located in the raw water and primary effluent. Therefore, recovery and quantification of the PRCs wasn't possible and hence,

quantification of PBDEs was also not possible. While not quantitative, SPMDs located in the raw water and primary effluents do provide qualitative information for dissolved PBDE levels. All PBDE congeners were detected in the dissolved fraction at these stages of the WWTP.

Recovery and quantification of the PFCs from SPMDs located in secondary and tertiary effluent channels was achieved and therefore, it was possible to quantify PBDEs concentrations. The flow-rate of the PBDE congeners, based upon the leaching of the PRCs, correlated to the linear uptake phase for PBDEs. The concentration of PBDEs in the aqueous phase was calculated according to $N(t) = R_s C_w t$ (where N = absorbed amount, R_s = water sampling rate, C_w = aqueous concentration, t = time) (Booij *et al.*, 2002). The major congeners detected in the SPMDs were 17, 47, 99 & 209. With the exception of BDE209, which was not detected in the secondary and tertiary effluents, these compounds are detected in all water sampled. The absence of BDE209 in the secondary and tertiary effluents indicates extremely high removal rates of BDE209 through the WWTP. The ratio of the congeners changed through the treatment process, with the ratio of BDE47:99 far higher in the secondary effluent than in the preliminary or primary effluent.

The concentrations of PBDEs in the aqueous phase of the effluent as determined by the SPMDs was higher (ranging between 1.4 and 2.2 ng L⁻¹) than that predicted simply based upon organic carbon-water partition coefficient; BDE47 predicted aqueous concentration ranges between 0.1 to 0.4 ng L⁻¹ and was determined by the SPMDs to be between 0.8 and 1.2 ng L⁻¹ in secondary and treated effluent.

Mass-balance equation

Quantities of PBDEs associated with each phase were calculated using the daily averages from the 2007; in-flow of 60.5 ML day⁻¹ with an average SS of 340 mg L⁻¹, biosolids of 22 000 kg dw, secondary outflow of 66.3 ML day⁻¹ and tertiary outflow of 1.82 ML day⁻¹ (C. Camplin - Process

Technical Officer 2008). Therefore, it has been calculated that 4.9 g Σ PBDEs enter the WWTP daily, or 1.8 kg annually. It is estimated that the total amount of PBDEs that are released into the ocean is 6.9 g per year (secondary effluent). This is significantly lower than the US reports of 900 g of Σ PBDE released per day into the surrounding ocean (North, 2004). There are a number of factors that may influence this discrepancy, such as the source of wastewater, the size of the WWTP and the efficiency of the WWTP process. The annual release of PBDEs was largely associated with biosolids (>99%) and it is estimated that 7.6 kg are disposed of in this manner, which is substantially higher than the calculated PBDEs in-flow (1.8 kg). This observation is unusual and it is possible that PBDEs are introduced during wastewater treatment (i.e. flocculation) or sewage sludge stabilization. It is estimated that Australia produces 3.6×10^8 kg of sewage sludge annually (Gale, 2007) and the average Σ PBDE concentration in biosolids observed will be used to estimate a minimum PBDEs burden associated with sewage sludge annually in Australia. Assuming that all sludge in Australia carry a similar burden of PBDEs equal to or greater than that observed (mean Σ PBDE sludge concentration of $300 \mu\text{g kg}^{-1} \text{ dw}$), then the amount of Σ PBDE associated with Australian sewage sludges annually is at least 110 kg, which is similar to the German annual estimate of 500 kg (Knoth *et al.*, 2007) on a population basis.

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313 **Figure Captions**

314 Figure 1 Flow diagram for the water treatment process with sampling points indicated by
315 numbers; PS indicates passive samplers.

316 Figure 2 Principal components analysis (correlation) performed on the mass standardized samples
317 collected from Subiaco WWTP from time periods A, B, C.; (A) Score plot of PCA2 vs PCA1 and
318 (B) loading plot.

319 Figure 3 Bar-chart of mean BDE47, 99, 209 & Σ PBDE concentration ($\mu\text{g kg}^{-1}$ dw) at the various
320 stages of the WWTP (Wastewaters: raw, secondary; Sludges: primary, secondary and biosolids.
321 Error bars represent the minimum and maximum concentrations.

322

Table 1 Volumes of water flowing into the experimental WWTP and released via secondary treated effluent and tertiary treated effluent (L)

Sample Label	Date	Inflow	Outflow	
			Secondary treated effluent	Tertiary treated effluent
A	Monday 12th November 2007	60.02×106	67.03	2.0
B	Thursday 22nd November 2007	64.43	65.75	1.27
C	Monday 3rd December 2007	61.37	66.22	2.2

323

324

325

Table 2 Concentration of polybrominated diphenyl ether congeners and polybrominated biphenyl 153 measured in grab samples (ef

	Monday 12th November 2007							Thursday 22nd November 2007				
	A1	A2	A3	A4	A5	A6	A7	B1	B2	B3	B4	B5
	Effluents ng L ⁻¹				Sludges µg kg ⁻¹ dw			Effluents ng L ⁻¹				Primary
	Raw	Primary	Secondary	Tertiary	Primary	Secondary	Biosolids	Raw	Primary	Secondary	Tertiary	Primary
SS mg/L	220	120	5	4				330	230	11	4	
BDE17	0.12	0.13	0.043	0.059	0.32	1.5	0.79	0.13	0.13	0.039	0.086	0.17
BDE28+33	<1	<1	<0.5	<0.5	1.3	1.5	0.98	<1	<1	<0.3	<1	0.95
BDE30	<0.04	<0.02	<0.02	<0.02	<0.04	<0.07	<0.02	<0.04	<0.03	<0.02	<0.04	<0.0
BDE47	17	21	<2	<2	48	39	51	20	15	<2	<4	31
BDE49	0.55	0.61	<0.05	<0.05	1.4	1.3	1.3	0.59	0.43	<0.04	0.089	0.82
BDE66	0.46	0.53	<0.03	<0.04	1.3	1	1.2	0.51	0.37	<0.04	0.057	0.86
BDE71	0.035	0.036	0.014	0.016	0.16	0.6	0.37	0.043	0.02	<0.007	0.025	0.06
BDE77	0.018	0.01	<0.005	<0.008	0.046	0.036	0.041	0.013	0.015	<0.005	0.0048	0.03
BDE85	0.53	0.77	<0.05	<0.04	1.9	1.7	1.7	0.73	0.51	<0.05	<0.08	1.1
BDE99	16	21	<1	<2	51	42	55	19	12	<1	<2	33
BDE100	3.1	3.9	<0.3	<0.3	9.4	8	9.6	3.9	2.6	<0.3	<0.5	6
BDE119	0.035	0.04	<0.02	<0.02	0.074	0.077	0.073	<0.3	<0.2	<0.02	<0.02	0.04
BDE126	0.0034	<0.02	<0.008	<0.01	0.0052	0.0053	0.0047	<0.01	<0.007	<0.008	<0.008	0.00
BDE138+166	0.14	0.19	<0.01	<0.04	0.46	0.45	0.5	0.19	0.13	<0.008	<0.007	0.35
BDE139	0.24	0.39	<0.01	<0.08	0.7	0.53	0.63	0.22	0.18	0.025	0.03	0.48
BDE140	0.061	0.081	<0.01	<0.07	0.2	0.15	0.21	0.05	0.052	<0.01	<0.008	0.11
BDE153	1.5	1.9	<0.1	<0.1	4.7	4	4.8	1.8	1.3	<0.1	<0.2	3.1
BDE154	1.1	1.4	<0.08	0.095	3.5	3.2	3.8	1.3	0.95	<0.09	<0.1	2.2
BDE156+169	<0.04	<0.06	<0.02	<0.07	<0.01	<0.02	<0.02	<0.08	<0.07	<0.02	<0.02	<0.0
BDE171	<0.06	<0.07	<0.06	<0.02	0.1	0.077	0.087	0.038	0.028	<0.01	<0.009	0.07
BDE180	<0.06	0.088	<0.03	<0.02	0.19	0.15	0.16	0.12	<0.04	<0.01	0.017	0.27
BDE183	0.59	0.71	<0.03	<0.04	1.9	1.3	1.6	1.3	0.62	<0.06	0.093	2.9

Table 2 Concentration of polybrominated diphenyl ether congeners and polybrominated biphenyl 153 measured in grab samples (ef

	Monday 12th November 2007							Thursday 22nd November 2007				
	A1	A2	A3	A4	A5	A6	A7	B1	B2	B3	B4	B5
	Effluents				Sludges			Effluents				
	ng L ⁻¹				µg kg ⁻¹ dw			ng L ⁻¹				
	Raw	Primary	Secondary	Tertiary	Primary	Secondary	Biosolids	Raw	Primary	Secondary	Tertiary	Primary
BDE184	0.024	<0.05	<0.004	<0.02	0.08	0.13	0.11	0.024	<0.008	<0.009	<0.009	0.04
BDE191	<0.03	<0.03	<0.03	<0.02	0.018	0.014	0.016	<0.02	<0.01	<0.01	<0.006	0.01
BDE196	<0.2	0.24	<0.2	<0.03	0.91	0.55	1	0.4	0.2	0.024	0.025	0.94
BDE197	0.35	0.35	<0.1	<0.02	1	0.88	1.1	0.62	0.29	0.026	0.049	1.5
BDE201	<0.1	<0.1	<0.09	<0.02	0.36	0.32	0.38	0.13	0.089	0.011	0.014	0.23
BDE203	<0.3	<0.3	<0.2	<0.04	0.95	0.63	0.71	0.44	0.31	0.03	0.031	0.91
BDE204	<0.01	<0.01	<0.1	<0.04	<0.04	<0.05	<0.03	<0.03	<0.01	<0.005	<0.008	<0.0
BDE205	<0.05	<0.2	<0.2	<0.03	0.024	0.016	0.01	0.015	<0.03	<0.02	<0.02	0.01
BDE206	<3	<2	<0.2	<0.08	11	5.2	6.5	2.5	1.5	<0.1	<0.2	6.7
BDE207	<2	<2	<0.1	<0.09	6.1	3.7	5.6	1.8	1.2	0.11	0.12	3.6
BDE208	<0.7	<1	<0.07	<0.04	3.2	1.7	2.4	0.71	0.51	0.06	0.068	1.4
BDE209	<60	<60	<3	<2	260	98	190	47	33	<2	<2	210
ΣPBDE	42	52	0.058	0.17	410	220	340	100	71	0.33	0.71	310
PBB153	<0.02	<0.04	<0.007	<0.02	0.25	0.16	0.19	0.11	<0.03	<0.02	0.036	0.23

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