1   **Investigating the distribution of polybrominated diphenyl ethers through an Australian**

2   **wastewater treatment plant**

3   Bradley O. Clarke [1,2], Nichola A. Porter[1,2,*], Robert K. Symons[3], Philip J. Marriott[1], Gavin J.

4   Stevenson[3] & Judy R. Blackbeard[2]

5   [1]School of Applied Sciences, RMIT University, Melbourne, Australia.

6   [2]Water Quality Research Australia, Adelaide, Australia

7   [3]National Measurement Institute, Sydney, Australia.

8   *Corresponding Author

9   RMIT University

10   School of Applied Science (Bld 3 Level 1)

11   Fax +61 9 9925 3747

12   Phone +61 9 9925 1787

13   brad.clarke.aus@gmail.com

14   **KEYWORDS**

15   PBDEs, WWTP, sewage sludge, biosolids, treated effluent

16   **ABSTRACT**

17   The concentration of PBDE congeners was measured at various treatment stages of an Australian

18   wastewater treatment plant (WWTP). This included four aqueous samples (raw, primary,

19   secondary and tertiary effluent) and three sludges (primary, secondary and lime stabilised

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20   biosolids). Semi-permeable membrane devices (SPMDs) were also installed for the duration of

21   the experiment, the first time that SPMDs have been used to measure PBDEs in a WWTP. Over

22   99% of the PBDEs entering the WWTP were removed through the treatment process, principally

23   by sedimentation. The main congeners detected were BDE 47, 99 and 209, which are

24   characteristic of the two major commercial formulations viz pentaBDE, and decaBDE. All the

25   PBDE congeners measured were highly correlated with each other, suggesting a similar origin. In

26   this case, the PBDEs are thought to be from domestic sources since domestic wastewater is the

27   main contribution to the inflow. The lower brominated PBDE congeners demonstrated a greater

28   solubility than the higher ones, which reflects increasing K_{OW} with increasing bromination. The

29   mean concentration of ΣPBDEs (defined as the sum of all targeted PBDEs) in chemically

30   stabilized sewage sludge (biosolids) was 300 µg kg^{-1} dry weight, which is likely to be the

31   minimum PBDE burden for all Australia sewage sludge. This corresponds to at least 110 kg of

32   PBDEs contaminating Australian sewage sludge annually. It is estimated that 6.5 to 9.9 kg of

33   PBDEs are disposed of each year with biosolids generated from Subiaco WWTP. Less than 10 g

34   are released annually into the environment via ocean outfall and field irrigation and this level of

35   contamination is unlikely to pose risk to humans or the environment. The release of treated

36   effluent is not considered a large source of PBDE environmental emissions compared to biosolids

37   or landfill.

38

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

62 nations reliance on treated effluent for a range of purposes, including drinking water,

63 understanding PBDE concentrations and fate in wastewater treatment is increasingly important.

64 A few studies have investigated the fate of PBDEs in WWTPs. A mass balance study of PBDEs

65 in an USA WWTP found that 96% of PBDEs associated with the sludge during WWTP (North,

66 2004). On an annual basis the authors calculated that 22 kg were associated with sludge and 0.9

67 kg were released into the environment with treated effluent (North, 2004). A German study

68 reported that no degradation of PBDE congeners was observed during wastewater treatment and

69 estimated the annual environmental release of PBDEs associated with sewage sludge to be 500 kg

70 year (Knoth et al., 2007). The fate of many other organic pollutants in WWTPs has been studied

71 and includes polychlorinated biphenyls (PCBs), organochlorinate pesticides, phthalates,

72 nonphenyls and linear alkyl sulphonates (Choi et al., 1974, Lawrence et al., 1976, McIntyre et al.,

73 1981, Garcia Gutierrez et al., 1984, Buisson et al., 1986, Buisson et al., 1988, Morris et al.,

74 1994).

75 PBDEs are expected to behave most similarly to PCBs in a WWTP. Of the identified WWTP

76 organic pollutant removal mechanisms (degradation, air stripping, volatilization, effluent) only

77 sedimentation in primary and secondary treatments is expected for PCBs and PBDEs.

78 Volatilization losses are not high when chemicals are strongly bound to particles and normally

79 only considered when the chemical is in the aqueous phase. The fraction that is sorbed to

80 particulate matter or other solids phase is not directly available, under equilibrium conditions, for

81 mass transfer across the water/air interface (Byrns, 2001). General principles of organic pollutant

82 behavior in a WWTP are decreasing water solubility, as measured by the octanol-water partition

83 coefficient (K_{OW}), the greater removal in primary sedimentation (Petrasek et al., 1983, Buisson et

84 al., 1988, Morris et al., 1994, Katsoyiannis et al., 2006). However, there are contradictory

85 experimental results with respect to the degradation of PCBs in a WWTP. Degradation of the

86   lower chlorinated PCBs (di-, tri-, tetra-) has been reported, while the higher chlorinated PCBs are

87   generally resistant to degradation (Buisson *et al*., 1986).

88   A number of studies have also successfully employed passive samplers for the measurement of a

89   range of organic pollutants in the WWTP (Petty *et al*., 2000, Stuer-Lauridsen *et al*., 2000, Wang

90   *et al*., 2001, Yusa *et al*., 2005, Bergqvist *et al*., 2006, Katsoyiannis *et al*., 2007). No other studies

91   have reported measurements of PBDE concentrations in WWTP using passive sampling

92   techniques.

93   The aim of this research is to measure the concentration of common PBDEs through an activated

94   sludge WWTP process (using active and passive sampling techniques) and quantify the amount of

95   PBDEs released into the environment via secondary effluent, tertiary effluent and sewage sludge.

96   **METHOD**

97   The experiment was conducted at an Australian WWTP, located in the city of Perth, Australia,

98   which has a population of approximately one and a half million people. It is a conventional

99   activated sludge treatment system that treats approximately 60 ML of water daily that derives

100 primarily from domestic (~95%) sources, with a small contribution from industrial sources

101 (~5%). Passive samplers were installed in the WWTP for 29 days and grab samples were

102 collected on three occasions during this sampling period. PBDEs were quantified using isotope

103 dilution internal standard high-resolution gas chromatography/high resolution mass spectrometry

104 (HRGC/HRMS). Analysis was undertaken for the following PBDE congeners; BDE17, 28+33,

105 47, 49, 66, 77, 85, 99, 100, 119, 138+166, 153, 154, 183, 184, 196, 197, 206, 207 and 209 and

106 polybrominated biphenyl (PBB) congener 153. The analyses were conducted at the National

107 Measurement Institute (NMI), Sydney (Pymble), Australia.

Sampling Methodology

Grab Samples

Grab samples were collected from the various stages of the WWTP and measured for PBDE

congeners. Four aqueous samples (raw water, primary effluent, secondary effluent and tertiary

treated effluent) and three sludge samples (primary sludge, secondary sludge and lime stabilised

biosolids) collected on 12/11/07, 22/11/07 and 03/12/07 between 11am and 1pm which was peak

water in-flow. Inflow volumes were and volumes of water treated are listed in Table 1 (NOTE:

Volume of final effluent is greater than raw water due to the addition of flocculants). .

Semi-Permeable Membrane Device Deployment

Five semi-permeable membrane devices (SPMDs) were deployed for 29 days at the WWTP,

located in the raw water (PS1), primary effluent (PS2), secondary effluent (PS3) and tertiary

effluent (PS4a, PS4b) channels. They were regularly checked for interfering materials. A field

blank and laboratory blank were completed for quality control purposes.

Sample Treatment

Grab samples

Freeze-dried sludge samples (20.0 g) were spiked with 10 μL of mixed $^{13}C_{12}$ PBDE surrogate

standards and were extracted into toluene using accelerated solvent extraction (Dionex Model

ASE 100). Effluents (1 L) were extracted into hexane using liquid-liquid extraction. The extracts

were concentrated using a BÜCHI Syncore® Analyst (BÜCHI Labortechnik AG, Flawil,

Switzerland), which was used for removing various solvents throughout the extract cleanup

process. The concentrated extract was solvent-exchanged 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

131 techniques, respectively. A commercial automated clean-up procedure (PowerPrep™ by Fluid

132 Management Systems, Waltham, MA, USA) that employs acid and base modified silica gels and

133 basic alumina column chromatography was used to remove interferences from the sample extract

134 and produce a cleaned up final extract. Extracts were concentrated to dryness under nitrogen and

135 made up to 40 μL with a PBDE internal standard. Analyses were undertaken for PBDEs and

136 PBBs using isotope dilution high-resolution gas chromatography – electron ionisation – high-

137 resolution mass spectrometry, with monitoring of the following ions:

138 Tri, Tetra, Penta BDEs - M^+, $[M+2]^+$, $[M+4]^+$, $[M+6]^+$; Hexa, Hepta, Octa, Deca BDEs - $[M+4-$

139 $2Br]^+$, $[M+6-2Br]^+$, $[M+8-2Br]^+$; Hexa BB - $[M+2-2Br]^+$, $[M+4-2Br]^+$.

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

141 **Passive Samples - Semi-Permeable Membrane Devices (SPMDs) Preparation, Deployment**
142 **& Extraction**
143 SPMDs were prepared from lay-flat low-density polyethylene (LDPE) tubing (purchased from

144 Brentwood Plastics, MO, USA) of size 105 cm long, 3.0 cm wide, wall thickness 0.003 cm. The

145 tubing was pre-extracted two times by soaking overnight in hexane and then dried under nitrogen.

146 1 mL of triolein (Sigma Glyceryl Trioleate T7140 ≥ 99%) containing PAH performance reference

147 compounds (Wellington Labs PAH-LCS-A deuterated surrogate) was added prior to the SPMD

148 being heat-sealed. Air bubbles were removed with a short pasteur pipette and triolein spread

149 along the tube, no further than 91.4 cm, where it was again sealed. Three SPMDs were looped

150 into a cage for deployment.

151 After deployment, SPMDs were first wiped with a white KimwipeTM and rinsed under a tap to

152 remove surface material. The SPMDs were submerged in hexane for 30 s, followed by 1M HCl

153 for 30 s, rinsed clean with milli-q water, acetone and 2-propanol. Once cleaned, the SPMDs were

154   extracted into 400 mL hexane for 8 to 18 h and then re-extracted in hexane for a further 6 h. The

155   solvent was removed and exchanged with dichloromethane. The extract was passed through a

156   0.45 μm filter, followed by treatment with gel-permeation chromatography (GPC). 2mL of

157   sample was eluted from a multi column GPC system (Waters Envirogel™ columns, 4.6mm x 30

158   mm guard – 19 mm x 150 mm – 19mm x 300 mm, 100 Å pore size, 10 μm nominal particle size)

159   with dichloromethane at 5 mL min^{-1}. The concentrated extract was solvent-exchanged into hexane

160   and then subsequently treated with concentrated sulfuric acid for destructive removal of organic

161   material. A commercial automated clean-up procedure (PowerPrep™ by Fluid Management

162   Systems, Waltham, MA, USA) that employs acid and base modified silica gels and basic alumina

163   column chromatography was used to remove interferences from the sample extract and produce a

164   cleaned up final extract.

165   *Instrumental Technique*

166   Quantification was performed on an Agilent 6890 gas chromatograph that was coupled to a

167   Thermo Finnigan MAT 95XL HRMS. The column used was a DB-5 column (J&W Scientific) 10

168   m × 0.1 mm × 0.1 μm. A 1 μL sample extract was injected using the splitless method with an

169   injector temp of 280 °C. The temperature program employed was an initial temperature of 120 °C

170   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

171   from 230 °C to the final temperature of 320 °C that was held for 5 min. Helium was used as a

172   carrier gas with constant flow mode of 0.4 mL min^{-1}. The transfer line was maintained at 280 °C.

173   Electron ionisation (EI) mode was used with an electron energy of 70 eV, filament current of 0.7

174   mA and maintaining the ion source at 240 °C.   The electron multiplier voltage was set to produce

175   a gain of 10^6.

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.

Quality Assurance/Quality Control

Internal standard isotope dilution quantification was undertaken within this study. This employs the use of $^{13}C_{12}$ labeled surrogates and internal standards. The $^{13}C_{12}$ surrogates standards ($^{13}C_{12}$ BDE28, 47, 77, 99, 100, 126, 153, 183, 197, 205, 207, 209, BB153) are added to the sample prior to extraction and are carried through all the laboratory operations. The recovery standards ($^{13}C_{12}$ BDE79, 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 was 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 response.

The analysis of the higher brominated BDEs, particularly BDE-209, is recognized as being difficult because it can degrade during the analytical process (Covaci *et al*., 2003). Using a short

198 thin-film capillary column, regularly changing the injection liner, and using a low source

199 temperature minimized the potential for degradation of BDE209.

200 The laboratory is National Association of Testing Authorities (NATA) accredited and has

201 participated successfully in four international inter-laboratory studies.

Statistical Analysis

203 Statistical analysis was performed using Minitab 15.

RESULTS

Grab Samples

206 Measurement of PBDE congeners typical of commercial formulations was performed for aqueous

207 and sludge samples collected from an Australian WWTP (Table 2). As expected PBDE

208 congeners were greatly associated with the sludges with ΣPBDE ranging between 220 and 460 μg

209 kg^{-1} dw. The mean biosolids concentration was 300 μg kg^{-1} dw and is lower than the national

210 Australian mean of 1100 μg kg^{-1} dw recently reported (Clarke *et al*., 2008b). The low and

211 consistent PBDE concentration in all sludges analysed suggests the primary source of PBDEs in

212 raw water is the domestic environment. Similar to international studies BDE209 contributed the

213 major portion of total PBDEs (>50%) and was found in the highest concentrations in primary

214 sludges (217 μg kg^{-1} dw), compared to the biosolids (163 μg kg^{-1} dw) and secondary sludge (146

215 μg kg^{-1} dw). PBDEs concentrations in the raw water and effluents were in the low ng L^{-1} range

216 (0.058 – 100 ng L^{-1}). The concentration was significantly higher in the raw water (mean 70 ng L^{-}

217 ^{1}) and primary effluent (mean 74 ng L^{-1}) compared to the secondary (mean 0.30 ng L^{-1}) and

218 tertiary treated effluents (mean 0.34 ng L^{-1}). This indicates high PBDE removal rates through the

219 WWTP, where PBDEs are likely to be associated with suspended solids (SS). Covariance

220   principal components analysis (PCA) preformed 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 ΣPBDEs)

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 ΣPBDE 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

244   similarity between the PBDE concentration patterns in all samples; with the exception of samples

245   A2, C2 and C6 (Figure 2a). Also, PBDE congeners were largely correlated between the penta-

246   BDE and deca-BDE formulations (Figure 2b).

247   The concentration of BDE47 is highest is the primary effluent which suggests that this compound

248   is not only associated with the SS but is also dissolved in the aqueous phase to a small extent.

249   This is in contrast to BDE209 that is preferentially partitioning to the SS and sludges with the

250   highest mean concentration observed in the primary sludge. The ratio of BDE47:BDE99 found in

251   the pentaBDE commercial formulation is reported to be 0.95:1 (Sjödin *et al.*, 1998).   This is in

252   contrast to the ratio that was found in the raw and primary effluent with BDE47 consistently

253   higher in concentration than BDE99, with average ratios of 1.06:1 and 1.18:1 respectively.

254   BDE47 is dissolved in the aqueous phase of the raw and primary effluent due to a lower K_{OW};

255   perhaps due to the association with surfactant, the ratio of BDE47:BDE99 increases the relative

256   concentrations in the primary treatment compared to the raw water. WWTP models employ the

257   organic carbon-water partition coefficient (K_{OC}) to explain the partitioning of hydrophobic

258   contaminants in wastewater treatment. Applying this technique the predicted concentration of

259   BDE47 in the aqueous phase of the raw effluent theoretically will range between 0.1 to 0.4 ng L^{-1}

260   when the SS organic carbon content ranges between of 60% to 10%. Assuming a high organic

261   carbon content at this stage of the treatment process the concentration of BDE47 will be less than

262   0.15 ng L^{-1} which can explain the observed increase of BDE47 relative to BDE99 found in the

263   raw effluent samples.

Semipermeable membrane device

265   Substantial interference (bio-fouling) occurred on SPMDs located in the raw water and primary

266   effluent. Therefore, recovery and quantification of the PRCs wasn't possible and hence,

267   quantification of PBDEs was also not possible. While not quantitative, SPMDs located in the raw

268   water and primary effluents do provide qualitative information for dissolved PBDE levels. All

269   PBDE congeners were detected in the dissolved fraction at these stages of the WWTP.

270   Recovery and quantification of the PFCs from SPMDs located in secondary and tertiary effluent

271   channels was achieved and therefore, it was possible to quantify PBDEs concentrations. The

272   flow-rate of the PBDE congeners, based upon the leaching of the PRCs, correlated to the linear

273   uptake phase for PBDEs. The concentration of PBDEs in the aqueous phase was calculated

274   according to $N(t) = R_S C_W t$ (where N = absorbed amount, R_S = water sampling rate, C_W = aqueous

275   concentration, t = time) (Booij *et al.*, 2002). The major congeners detected in the SPMDs were

276   17, 47, 99 & 209. With the exception of BDE209, which was not detected in the secondary and

277   tertiary effluents, these compounds are detected in all water sampled. The absence of BDE209 in

278   the secondary and tertiary effluents indicates extremely high removal rates of BDE209 through

279   the WTWP. The ratio of the congeners changed through the treatment process, with the ratio of

280   BDE47:99 far higher in the secondary effluent than in the preliminary or primary effluent.

281   The concentrations of PBDEs in the aqueous phase of the effluent as determined by the SPMDs

282   was higher (ranging between 1.4 and 2.2 ng L^{-1}) than that predicted simply based upon organic

283   carbon-water partition coefficient; BDE47 predicted aqueous concentration ranges between 0.1 to

284   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

285   treated effluent.

286   ### *Mass-balance equation*

287   Quantities of PBDEs associated with each phase were calculated using the daily averages from

288   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,

289   secondary outflow of 66.3 ML day^{-1} and tertiary outflow of 1.82 ML day^{-1} (C. Camplin - Process

290   Technical Officer 2008). Therefore, it has been calculated that 4.9 g ΣPBDEs enter the WWTP

291   daily, or 1.8 kg annually. It is estimated that the total amount of PBDEs that are released into the

292   ocean is 6.9 g per year (secondary effluent). This is significantly lower than the US reports of

293   900 g of ΣPBDE released per day into the surrounding ocean (North, 2004). There are a number

294   of factors that may influence this discrepancy, such as the source of wastewater, the size of the

295   WWTP and the efficiency of the WWTP process. The annual release of PBDEs was largely

296   associated with biosolids (>99%) and it is estimated that 7.6 kg are disposed of in this manner,

297   which is substantially higher than the calculated PBDEs in-flow (1.8 kg). This observation is

298   unusual and it is possible that PBDEs are introduced during wastewater treatment (i.e.

299   flocculation) or sewage sludge stabilization. It is estimated that Australia produces 3.6×10^8 kg

300   of sewage sludge annually (Gale, 2007) and the average ΣPBDE concentration in biosolids

301   observed will be used to estimated a minimum PBDEs burden associated with sewage sludge

302   annually in Australia. Assuming that all sludge in Australia carry a similar burden of PBDEs

303   equal to or greater than that observed (mean ΣPBDE sludge concentration of 300 µg kg^{-1} dw),

304   then the amount of ΣPBDE associated with Australian sewage sludges annually is at least 110 kg,

305   which is similar to the German annual estimate of 500 kg (Knoth *et al.*, 2007) on a population

306   basis.

307   **REFERENCES**

308   **ACKNOWLEDGMENTS**

Figure Captions

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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 & ΣPBDE concentration ($\mu g\ kg^{-1}$ 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.

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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	Outflow 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

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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}				
	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 ng L^{-1}				Sludges µg kg^{-1} dw			Effluents 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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