

Polybrominated diphenyl ethers (PBDEs) in English freshwater lakes, 2008-2012

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Submission of research article: “Polybrominated diphenyl ethers (PBDEs) in English freshwater lakes, 2008-2012” by Congqiao Yang, et al.

To whom it may concern

I hereby submit the above paper for consideration as a research article in *Chemosphere*. This is an original piece of work conducted by Congqiao Yang, Stuart Harrad, Mohamed Abou-Elwafa Abdallah, Jennifer Desborough, Neil L. Rose, Simon D. Turner, Thomas A. Davidson, and Ben Goldsmith (see below the details for all authors). The current study presents an investigation of the temporal/seasonal trends and spatial distribution of the concentrations of tri to hexa-BDEs in water from 9 freshwater lakes throughout England from April 2008 to February 2012. We believe that it warrants publication in *Chemosphere* as this study is only the second report – and the most comprehensive to date - of concentrations of PBDEs in European lake water, and is the first examination worldwide of seasonal trends in both concentrations and congener patterns.

I confirm that all co-authors have read and approve this version of the research paper, and care has been taken to ensure the integrity of the work.

The authors confirm that this is the original research work, and none piece of this manuscript has been published or is under consideration of publication elsewhere.

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I trust that I have submitted all the necessary information at the website, but if you require any further information, please don't hesitate to get in touch.

Thanks for your time and the authors appreciate your consideration of this manuscript!

Kind regards

Yours sincerely,
Congqiao Yang

HIGHLIGHTS

- PBDE concentrations are comparable to those in the Great Lakes
- Σ BDE concentrations in water samples showed TSS dependence
- Σ BDE concentrations showed seasonal trends: higher in colder than in warmer periods
- Generally higher BDE-47:99 ratios in warmer than colder months
- BDE-47:99 ratios decreased significantly with increasing TSS content of samples

18 **ABSTRACT**

19 Concentrations of tri-to-hexa-BDEs were determined in water samples taken from 9 English
20 lakes on 13 occasions between April 2008 and February 2012. Across all sites, concentrations
21 of Σ BDEs in individual samples ranged from 9.2 to 171.5 pg L^{-1} , with an average of 61.9 pg L^{-1} .
22 Notwithstanding the far greater use of the Penta-BDE commercial formulation in the USA,
23 concentrations in this study are comparable to the limited data available for the Great Lakes.
24 PBDE concentrations showed no evidence of a decline at any monitored location over the
25 study period. This may be because this study commenced 4 years after the introduction of
26 restrictions on the Penta- and Octa-BDE formulations. While concentrations normalised to
27 water volume at the different locations were statistically indistinguishable; significant spatial
28 variation was apparent when the data were normalised to total suspended solids (TSS) content.
29 However, this spatial variation was not correlated with factors such as population density and
30 lake catchment area, suggesting that concentrations of PBDEs in lake water in this study are a
31 complex integral of numerous factors. BDE-47:99 ratios and concentrations of Σ BDEs
32 respectively decreased and increased significantly with increasing TSS content. As TSS
33 content was elevated in colder compared with warmer periods, such seasonal variation in TSS
34 content appears a major contributor to the observed elevation of Σ BDE concentrations in
35 colder periods, and higher BDE-47:99 ratios in warmer periods.

36

37 **Keywords:** PBDEs; Lake Water; Temporal; Seasonal; Spatial; TSS

38

39 **1. Introduction**

40 Polybrominated diphenyl ethers (PBDEs) have been widely applied as brominated flame
41 retardant (BFR) additives for several decades in many commercial products including plastics,
42 rubbers, textiles, electronic components and building materials (Hale et al., 2006; Alaei et al.,
43 2003). They are of great concern because of their ubiquitous presence and persistence in
44 various environmental matrices, including biota, and their adverse effects in wildlife and
45 humans (Hallgren and Darnerud, 2002; Branchi et al., 2003; Hardy, 2002; McDonald, 2002).
46 Against this backdrop, the production and new use of the Penta-BDE and Octa-BDE
47 formulations was phased out in Europe and North America in 2004 (Hale et al., 2006), with
48 both listed in 2009 as Persistent Organic Pollutants (POPs) under the Stockholm Convention
49 (SCOP, 2009). The United Kingdom consumed larger quantities of the Penta-BDE mixture
50 than many other European countries (Kalantzi et al., 2004) and was the fourth largest PBDE
51 producer in the world, with an annual output of ~25,000 t (Alaei et al., 2003). This production
52 and use has had a demonstrable impact, exemplified by reports of the presence of PBDEs in
53 UK human milk, air, soil, and sediment (Kalantzi et al., 2004; Harrad and Hunter, 2006; Vane
54 et al., 2010).

55

56 Freshwater lakes provide important ecological, hydrological and societal services. However,
57 studies of contamination of PBDEs in lake water are relatively scarce. As part of the Open Air
58 Laboratories (OPAL) project, this study presents an investigation of the temporal/seasonal
59 trends and spatial distribution of the concentrations of tri to hexa-BDEs (i.e. those predominant
60 in the Penta-BDE formulation) in water from 9 freshwater lakes throughout England from
61 April 2008 to February 2012. We believe that this study is only the second report - and the most
62 comprehensive to date - of concentrations of PBDEs in European lake water, and is the first
63 examination worldwide of seasonal trends in both concentrations and congener patterns. It

64 complements our previous report on concentrations of hexabromocyclododecanes (HBCDs)
65 and tetrabromobisphenol-A (TBBP-A) in water, surficial sediment, and fish from the same
66 lakes (Harrad et al., 2009). This study focuses on tri- through hexa-brominated PBDEs that are
67 primarily found in the Penta-BDE commercial formulation. This reflects the fact that at the
68 outset of this study, reliable analytical methods for the determination of BDE-209 (the major
69 constituent of the Deca-BDE product) were not available in our laboratory.

70

71 The influence on PBDE concentrations and congener profiles of variables such as: total
72 suspended solids (TSS) in water samples, population density, and proximity to landfill sites are
73 examined, along with seasonal and temporal trends. As well as providing a valuable initial
74 baseline against which future contamination trends can be compared; our data are analyzed to
75 provide clues as to source attribution, and responses to recent restrictions on Penta-BDE use.
76 Moreover, while UK production and use of Penta-BDE was substantial, it was dwarfed by that
77 of the Americas which in 2001 (the most recent figures available) produced 7,100 t compared
78 to 150 t in Europe (BSEF, 2006). We therefore compare our findings with recent reports of
79 similar contamination in North America.

80

81 **2. Materials and methods**

82 *2.1. Sampling strategy and methods*

83 A map of the sampling locations is given as Figure 1, with more information about sampling
84 locations supplied as supporting information (Table S1). Sampling was conducted on 13
85 occasions from each of 9 English freshwater lakes; however one sample for THOP was missing
86 due to drought on one sampling occasion, and one sample was lost in analysis, making 115
87 samples in total. Between April 2008 to July 2010 inclusive, sampling frequency was quarterly,
88 switching to biannually thereafter until the last sampling event in February 2012. At each

89 location, a grab sample of 40 L of bulk water was collected from the profundal point of each
90 lake 50 cm below the surface in two x 20 L pre-cleaned HDPE containers. In November 2008,
91 a surficial sediment sample was also collected from each site via procedures reported
92 previously (Harrad et al., 2009).

93

94 2.2. Analytical protocols

95 2.2.1. Determination of PBDEs

96 Samples were filtered via gravity through a glass fibre filter (GFF, Whatman, UK, 12.5 cm
97 diameter, 1 μm pore size), followed by two pre-cleaned polyurethane foam (PUF) plugs (8 cm
98 diameter, 4 cm length, 0.03 g cm^{-3} each, PACS, Leicester, UK), with GFF and PUFs for each
99 sample combined prior to soxhlet extraction for 8 h with dichloromethane, as described
100 elsewhere (Harrad et al., 2009). For those samples taken in summer 2008, the filters and PUFs
101 were analysed separately to provide information on the operationally defined particulate phase
102 and dissolved phase. Freeze-dried surficial sediment samples (~1 g, accurately weighed) were
103 mixed with 2 g Cu powder for removal of sulfur prior to pressurised liquid extraction as
104 described previously (Harrad et al., 2009). Each sample was spiked prior to extraction with
105 appropriate quantities of the following internal standards: $^{13}\text{C}_{12}$ -labeled BDE-28, -47, -99, and
106 -153 (Greyhound Chromatography and Allied Chemicals, UK). Following extraction, crude
107 extracts were concentrated and then subjected to florisil column (1 g) clean up. Analytes were
108 eluted first with 15 mL hexane followed by 15 mL dichloromethane. The hexane and
109 dichloromethane elutes were combined and extracted with dimethyl sulfoxide (DMSO) (3 x 10
110 mL). The DMSO extracts were pooled, diluted with 35 mL deionised distilled water and
111 extracted sequentially with hexane (3 x 30 mL). The combined hexane extracts were then
112 evaporated to incipient dryness under a stream of nitrogen (Turbovap). Final sample extracts
113 were diluted in 50 μL hexane containing $^{13}\text{C}_{12}$ BDE-100 as a recovery determination standard

114 (RDS) and analysed for tri-hexa-BDEs via an Agilent 6850-5975 GC-MS operated in selective
115 ion monitoring (SIM) mode, as reported elsewhere (Harrad and Hunter, 2006). Briefly, 1 μL
116 sample was injected with an auto-injector in splitless mode at 280°C. BDEs-17, -28, -49, -47,
117 -66, -100, -99, -85, -154, and -153 were separated on a VF-5 ms capillary column (30 m x 0.25
118 mm x 0.25 μm). The initial column temperature was 140°C held for 2 mins, ramped to 200 °C
119 at 5 °C min^{-1} , then 300 °C at 2 °C min^{-1} held for 5 mins, and 2 °C min^{-1} to 310 °C. Ions
120 monitored were: m/z 405.8 for BDE-17 and -28; m/z 485.8 for BDE-49, -47, and -66; m/z
121 403.8 for BDE-100, -99, and -85; m/z 483.8 for BDE-154 and -153. For surrogate (internal)
122 standards, m/z 417.8, 497.8, 415.8, and 495.8 were monitored for ^{13}C -BDE-28, -47, -99, and
123 -153, respectively.

124

125 2.2.2. *Measurement of TSS*

126 To examine the relationship between PBDE concentrations and suspended particulate matter
127 loadings, TSS content was determined gravimetrically via gravity filtration through a GFF in
128 all samples using small aliquots of water (~1 L) collected from the same location at the same
129 time specifically for TSS determination only (see Table S2 for TSS data). Given the
130 uncertainty associated with TSS measurements acquired using these relatively small sample
131 volumes (the ratio of TSS mass to the mass of the GFF ranged from 0.6-16.4% w/w); TSS was
132 also determined gravimetrically before solvent extraction using the entire 40 L volume of the
133 samples collected in February 2011.

134

135 2.3. *Method validation and QA/QC*

136 Method validation and accuracy were assessed via replicate (n=3) analysis of NIST standard
137 reference material (SRM 2585), see Table S3 for details. These results reported RSD within 10%
138 for all the BDE congeners. Obtained results compared favourably with the certified values. For

139 each batch of 9 samples, 2 blanks (each containing 2 pre-cleaned PUFs and 1 piece of GFF)
140 were analysed. For the sediment samples, a sodium sulfate blank was analysed. PBDE
141 concentrations in these blanks were either below method detection limits (ranging from 0.2-1.4
142 pg L^{-1} for measured congeners), or revealed very trace and acceptable procedural
143 contamination (less than around 5% of that in water samples). More information on QA/QC
144 can be found in SI.

145

146 *2.4. Statistical analyses*

147 Statistical analyses were conducted using both Excel for descriptive statistics, with SPSS (IBM
148 SPSS Statistics 21) used for ANOVA, correlation, regression, and t-test analyses.

149

150 **3. Results**

151 Concentrations of Σ BDEs in this study ranged from 9.2 to 171.5 pg L^{-1} (see Table 1), with
152 concentrations normalised to TSS also reported. By comparison, Stapleton and Baker (2001)
153 reported that concentrations of PBDEs (BDE-47, -99, -100, -153, -154 and -183) in Lake
154 Michigan increased from a mean value of 31 pg L^{-1} in 1997 to 158 pg L^{-1} in 1999. A later study
155 reported that average concentrations of Σ BDEs (BDE-47, -66, -99, -100, -153 and -154; 2004)
156 in Lake Michigan were 18 pg L^{-1} and 3.1 pg L^{-1} for the dissolved phase and particulate phase,
157 respectively (Streets et al., 2006). Dissolved phase Σ BDE (BDE-47, -85, -99, -100, and -153)
158 concentrations in Lake Winnipeg, Canada had a mean value of 29.5 pg L^{-1} , with BDE-47 the
159 dominant congener (17.0 pg L^{-1} , n=6, 2004) (Law et al., 2006). By comparison, Σ BDE
160 (BDE-47, -99, and -153) concentrations in an urban estuary in Narragansett were $< 3 \text{ pg L}^{-1}$
161 (Sacks and Lohmann, 2012). Moreover, Σ BDE concentrations (same congeners as this study,
162 except BDE-49) were 0.2 pg L^{-1} to 299 pg L^{-1} in San Francisco Bay water samples collected in
163 July 2002, with BDE-47 dominant in most of the samples, followed by BDE-99 (Oros et al.,

164 2005). Oram et al. (2008) reported concentrations of BDE-47 in San Francisco Bay (2002-2006)
165 to range from 15.5 to 337 pg L^{-1} with a spatially unbiased mean value of 54.9 pg L^{-1} .

166

167 Outside North America, the Σ BDE (BDE-47, -99, and -153) concentration observed in a study
168 of the Scheldt Estuary and North Sea along the Dutch coast was around 1.6 pg L^{-1} (Booij et al.,
169 2002), an order of magnitude lower than that observed in this study. More comparable with this
170 study of freshwater lakes, mean concentrations of Σ BDE (BDE-28, -47, -99, -100, and -153) in
171 5 samples of water from Lake Thun in 2007, Switzerland were 36.4 pg L^{-1} ; the only other data
172 of which we are aware on PBDE concentrations in European lakes (Bogdal et al., 2010).
173 Further afield, in the Zhujiang River estuary in China, concentrations of Σ BDEs (BDE-28, -47,
174 -100, -99, -153, -154 and -183) were 26.1 to 94.6 pg L^{-1} and 71.4 to 156.9 pg L^{-1} in May and
175 October, respectively (Luo et al., 2008). In summary, the concentrations reported in our study
176 seem comparable and largely consistent with levels obtained elsewhere for various water
177 bodies, except where samples were taken in heavily source-impacted areas. For instance,
178 average Σ BDE concentrations (BDE-28, -47, -100, -99, -138, -153 and -154) in a reservoir at
179 an e-waste recycling area in China were 21.8 ng L^{-1} (Wu et al., 2008).

180

181 4. Discussion

182 4.1 PBDE concentrations: UK vs. USA

183 Interestingly, our data for English lakes is comparable with those reported for the USA (Streets
184 et al., 2006; Sacks and Lohmann, 2012) in spite of the far greater production of the Penta-BDE
185 product in the Americas than Europe. While this contrasts with the higher PBDE
186 concentrations observed in North American house dust compared to the UK (Harrad et al.,
187 2008), it is consistent with similar concentrations of PBDEs in outdoor air in the USA and the
188 UK (Harrad and Hunter., 2006). The cause(s) of these somewhat conflicting observations are

189 not clear at this time, but we note that the UK has a substantially higher population density than
190 the US, which means the Penta-BDE usage in the UK and the USA may actually be similar
191 when normalised to surface area.

192

193 *4.2. Partitioning of PBDEs between dissolved and particulate phase*

194 Table S4 reports the Σ BDE concentrations determined in the particulate and freely dissolved
195 phases separately in the July 2008 samples; the latter operationally defined as that passing
196 through a 1 μm pore size GFF, to provide information on relative abundances of the PBDE
197 concentrations in each phase. Across all sites, 62-77% of Σ BDE was found in the particulate
198 phase, with an average $\pm\sigma_n$ value of $68\pm 6\%$. Oros et al. (2005) reported the phase partitioning of
199 Σ BDEs (sum of 22 tri- through decabrominated congeners) in water samples ($n=3$) from the
200 San Francisco estuary, finding 78% to 93% of Σ BDEs present in the particulate phase using an
201 identical 1 μm cut-off to that used in this study. This is generally consistent with our findings,
202 particularly given the inclusion of BDE-209 in the San Francisco study.

203

204 *4.3. Factors influencing PBDE concentrations*

205 *4.3.1 Influence of TSS on PBDE concentrations*

206 The TSS content of samples collected from all sites in February 2011 was determined
207 gravimetrically after filtration of the entire 40 L sample. Values ranged from 0.32 mg L^{-1} at
208 HOLT to 46 mg L^{-1} at PFLE. As shown in Figure 2(a), the Σ BDE concentrations showed some
209 dependence on TSS ($r^2=0.2135$, blue line), that was enhanced significantly when the PFLE site
210 was excluded (green line, $r^2=0.7619$, $P<0.01$). Those strong correlations demonstrate clearly
211 the influence of TSS on PBDE contamination. Moreover, TSS contents determined for all
212 samples (using smaller volumes and likely subject to greater uncertainty) also showed positive
213 correlation with Σ BDE concentrations ($r^2=0.036$, $p<0.05$). With respect to the PFLE site,

214 although it exhibited PBDE concentrations at the higher end of those recorded in this study, the
215 concentrations recorded at this site were lower than expected given the high TSS content of
216 samples from PFLE. This site is known to occasionally to suffer episodes of cyanobacteria
217 (blue-green) algae in summer. Sugiura (1992) reported microbial degradation of PCBs on
218 suspended particulates in aquatic environments. Moreover, microbial transformation of
219 PBDEs in marine sediments was confirmed by Martin et al. (2004). While recognising that
220 more detailed study is required to verify this, we therefore hypothesise that the occasional
221 episodes of cyanobacteria at PFLE may have enhanced PBDE degradation, thereby reducing
222 the correlation between TSS and PBDE concentrations at this site. Inclusion of TSS data along
223 with season (warmer periods from March 21st to September 20th were defined as 1 while colder
224 periods from September 21st to March 20th were defined as 2) in linear regression analysis
225 revealed significant correlations between both parameters and Σ BDE.

226

227 Σ BDE=17.844 season + 0.53 TSS + 30.893; $r^2=0.133$, $p<0.05$; $\beta=0.313$ for season and $\beta=0.222$
228 for TSS (1)

229

230 This indicates that Σ BDE concentrations were higher in colder months and at higher TSS
231 values. Our findings are consistent with those of Oros et al. (2005), who reported a significant
232 positive relationship between Σ BDE concentrations and TSS in the San Francisco estuary.

233

234 4.3.2 Seasonal impacts on PBDE concentrations

235 As indicated by regression equation (1), PBDE concentrations at all sites were elevated in
236 colder compared to warmer periods (see Figure 3), with average water temperatures of 6.4 °C
237 and 16.4 °C across 9 lakes in the two periods, respectively. The higher β value for season
238 ($\beta=0.313$) than for TSS ($\beta=0.222$) suggests the former to exert a slightly stronger influence on

239 PBDE contamination levels. Data on PBDE seasonal trends in water bodies with which to
240 compare our data are extremely scarce. Luo et al. (2008) reported that PBDE concentrations in
241 water from the Zhujiang River Estuary varied seasonally being lower in May 2005 than
242 October of that year. However, in this instance, rather than water temperature, the cause was
243 attributed to the fact that in May brackish water was dominant in the estuary, as opposed to the
244 situation in October when fresh water from river runoff, which was indicated to be the major
245 contributor of PBDEs into the Estuary, was dominant. Moreover, there is conflicting
246 information about seasonal trends of PCB contamination in water bodies. Dissolved phase
247 concentrations of PCBs showed no seasonal trends in the Hudson River Estuary from
248 December 1999 to April 2001 (Yan et al., 2008), nor across Baltimore Harbour and the
249 Northern Chesapeake Bay in 1996-97 (Bamford et al., 2002). Consistent with our observations
250 however, maximum PCB concentrations associated with TSS in water from the Seine Estuary
251 were observed in winter over the period November 2002 to February 2005 (Cailleaud et al.,
252 2007).

253

254 In line with this study in the Seine for PCBs (but reported here for PBDEs for the first time), we
255 observed higher TSS contents in colder compared to warmer periods at CRAZ, EDGB, HOLT,
256 MARM, and THOP (by factors of 1.12, 1.83, 1.33, 1.41, and 2.27, respectively). Such winter
257 increments in TSS are likely attributable to greater re-suspension of sediment due to die-back
258 of aquatic plants and increased mixing of the water column due to higher precipitation and
259 wind speeds during colder periods. The increases in TSS corresponded with similar increments
260 in average Σ BDE concentrations at the same sites in colder compared to warmer periods
261 (factors of 1.14, 1.52, 1.08, 1.34, and 2.38, respectively). For these 5 sites therefore, the winter
262 increment in Σ BDE contamination appears at least partly attributable to seasonal variations in
263 TSS content. This is confirmed by the observation that while seasonal trends in

264 TSS-normalised PBDE concentrations were apparent; they were generally weaker than for the
265 un-normalised data with significantly higher concentrations in colder periods observed for only
266 6 out of 9 lakes (Fig. 4). In addition to seasonal variation in TSS content therefore, we
267 hypothesize that another likely explanation for our observed winter peak in Σ BDE
268 concentrations is that lower water temperatures will reduce the extent of PBDE volatilization.
269 Another possible contributory factor is that the rate of any PBDE degradation will be slower at
270 lower temperatures. Both of these factors favour higher PBDE concentrations when water
271 temperatures are lower.

272

273 *4.3.3 Temporal trends in PBDE concentrations*

274 There was no evidence for any significant temporal trend in PBDE concentrations (whether
275 water volume-based or TSS-normalised) at any of our 9 lakes over the 4 year monitoring period
276 of this study. This is in contrast with recent observations of declining atmospheric
277 concentrations. Specifically, European background airborne PBDE concentrations (BDEs -28,
278 -47, -49, -99, -100, -153, -154, and -183) were reported to have declined with a half-life of
279 2.2 ± 0.4 years between 2000 and 2008 (Schuster et al., 2010). Likewise, concentrations in air of
280 a similar range of PBDEs were reported to be declining during the 2000s at 3 out of 4 UK
281 monitoring locations with average half-lives between 2.0 and 3.5 years (Birgul et al., 2012).
282 Despite such evidence from the atmosphere of encouraging responses to the recent restrictions
283 on use of PBDEs in the EU; the absence of any decline on concentrations in lake water in our
284 study is not surprising given the four year duration of our study, the lack of any known direct
285 point sources of PBDEs to our lakes, and the comparatively long mixing times of freshwater
286 lakes in general that exceed those of the atmosphere. It is also possible that any decline in
287 PBDE concentrations at our lakes was rapid following the restrictions on PBDE manufacture
288 and use, and had thus occurred before our study commenced. We also note that no decline in

289 atmospheric PBDE concentrations was observed at one of the two UK rural sites monitored by
290 Birgul et al. (2012). Further longer-term monitoring is therefore required to elucidate the
291 impact on the lacustrine environment of restrictions on manufacture and use of PBDEs within
292 the EU.

293

294 *4.3.4 Spatial trends in PBDE concentrations*

295 As TSS content was shown above to influence PBDE concentrations; we also investigated
296 spatial trends in PBDE concentrations when normalised to TSS content. While no spatial
297 trends were apparent in PBDE concentrations expressed on a water volume basis; significant
298 inter-site variability was observed when PBDE concentrations were normalised for TSS
299 content (ANOVA, $p < 0.01$), with the highest and lowest concentrations at HOLT and PFLE,
300 respectively. This suggests that location does influence the PBDE concentrations observed in
301 our lakes. We investigated possible causes of this spatial variation via multi-linear regression
302 of TSS-normalised concentrations against factors such as: lake area, mean depth, lake
303 catchment area, lake catchment ratio (defined as the ratio of lake area to catchment area), lake
304 altitude, and the population density of both: (a) the local authority within which each site was
305 located; and (b) the local authorities within a 25 km radius of each site. No significant
306 relationships were detected, with the same lack of correlation observed also when
307 water-volume based PBDE concentrations were used as the dependent variable. These findings
308 likely reflect the fact that PBDE concentrations in water in the lakes in this study are a complex
309 integral of many influential factors.

310

311 *4.4 Congener profile of PBDEs*

312 The major congeners detected in all 115 samples were BDE-99 and BDE-47. BDE-99 was the
313 dominant congener at most sites with average BDE-47:99 ratios of 0.91, 0.66, 0.59, 0.92, 0.95

314 and 0.73 at CRAZ, EDGB, HOLT, PFLE, THOP and WAKE respectively. However average
315 BDE-47:99 ratios of 1.01, 1.02 and 1.08 were observed at CHAP, MARM and SLT,
316 respectively. The BDE-47:99 ratio in a given matrix is a complex integral of the ratio in the
317 initial source (~0.79-0.96 in Penta-BDE formulations; La et al., 2006), and the comparative
318 environmental fate of the two congeners following emission. The latter is governed by their
319 physicochemical properties, e.g. one would hypothesize greater partitioning to air for the more
320 volatile BDE-47, while BDE-99 would partition preferentially to soil and sediment due to its
321 higher K_{OA} and K_{OW} (Palm et al., 2002). This is consistent with previous studies reporting
322 BDE-47:99 ratios in soil at 10 UK locations of between 0.51 and 0.88, while in outdoor air
323 collected at the same 10 UK locations, BDE-47:99 ratios varied between 2.95 and 3.62 (Harrad
324 and Hunter, 2006). A paired t-test comparing average BDE-47:99 ratios in water samples for
325 each site over all 13 sampling events, with those determined in surficial sediment taken in
326 November 2008 at the same sites (see Table S5), showed BDE-47:99 ratios were significantly
327 higher ($p < 0.01$) in water (0.75 to 1.33 with average value of 1.09) than in surficial sediment
328 (0.29 to 1.16 with average value of 0.62). We hypothesise that the higher K_{OW} of BDE-99 leads
329 to greater partitioning to surficial sediment than water, and thus lower BDE-47:99 ratios in
330 sediment.

331

332 In comparison to our study, BDE-47 dominated most of the samples in San Francisco Bay,
333 followed by BDE-99 (Oros et al., 2005). The higher abundance of BDE-99 in our study may be
334 due to a number of factors. These include: differences in PBDE environmental fate and
335 behaviour between estuarine/marine waters and freshwaters, e.g. higher NaCl concentrations
336 in marine/estuarine water would “salt-out” the more lipophilic BDE-99 to surficial sediment;
337 possible international differences in the congener profile of the Penta-BDE formulation used;
338 varying transfer distances between source and sampling site which may alter the relative

339 abundance of different congeners, and/or greater environmental persistence of BDE-99 relative
340 to BDE-47 following recent restrictions on the manufacture and use of Penta-BDE. This latter
341 hypothesis is plausible given the fact that the Penta-BDE formulation was restricted earlier in
342 Europe than in the USA. Moreover, variations in the TSS content of the samples in different
343 studies may play a role. Further to our observations of the important influence of TSS on PBDE
344 concentrations, we also detected a decrease of BDE-47:99 ratios with increasing TSS content
345 in the February 2011 samples for which TSS measurements were made using the entire 40 L
346 sample, as shown in Figure 2(b). We believe this is a result of the stronger partitioning to
347 suspended sediment of BDE-99 relative to BDE-47, driven by its higher K_{OC} . To our
348 knowledge, this is the first report of a relationship between BDE-47:99 ratios and TSS in water
349 samples.

350

351 We also detected that at 7 of the 9 sampling sites, BDE-47:99 ratios displayed intra-site
352 fluctuation with generally higher ratios observed in samples taken in warmer sampling months
353 (July) than in colder months (January and February). To our knowledge, this is the first report
354 of such seasonal variation in congener patterns of PBDEs in freshwater lakes. The average
355 BDE-47:99 ratios in warmer periods exceed that in colder seasons by a factor of 1.48 across 13
356 sampling occasions. We examined the influence of season on our BDE-47:99 ratios further
357 using linear regression and again defining warmer periods as 1 and colder periods as 2. Defined
358 thus, season showed a statistically significant negative linear relationship with BDE-47:99
359 ratios across all 115 water samples.

360

$$361 \text{ BDE-47:99} = -0.414 \text{ season} + 1.689; (r^2=0.078, p<0.01) \quad (2)$$

362

363 In addition, BDE-47:99 ratios across all samples showed some dependence on water
364 temperature (see Table S6 for information) measured 50 cm below the surface at the time of
365 each sampling event with a regression linear equation of:

366

$$367 \text{ BDE-47:99} = 0.032 \text{ temperature} + 0.711; (r^2 = 0.068, p < 0.01) \quad (3)$$

368

369 Interestingly, when each site is examined individually, this seasonal trend in 47:99 ratios was
370 not significant in the first two years of monitoring, but was highly significant in the second half
371 of the monitoring period. Longer term monitoring is required to determine whether seasonal
372 variations in congener profiles are genuine. However, this seasonal variation is consistent with
373 the abovementioned inverse relationship between TSS and BDE-47:99 ratios and our
374 observation of higher TSS in colder periods. Additionally, we suggest that higher BDE-47:99
375 ratios in warmer than in colder periods may also be due to the fact that in warmer periods one
376 would expect preferential degassing from sediment of the more volatile BDE-47, and enhanced
377 temperature-driven partitioning of BDE-99 to sediment organic carbon in winter.

378

379 **5. Conclusions**

380 Based on the very limited data available, PBDE contamination levels in English freshwater
381 lakes were comparable to those in the Great Lakes. Despite being phased out in 2004, no
382 temporal trends were observed over the period 2008-2012. When normalised for TSS content,
383 PBDE concentrations showed significant inter-site variability, but no relationship was found
384 between this spatial variability and factors such as population density and catchment area.
385 Seasonal trends were observed, with higher PBDE concentrations in colder than in warmer
386 periods, and higher BDE-47:99 ratios in warmer months. These seasonal trends are in part
387 attributable to the increased TSS concentrations in colder compared to warmer months.

388

389 **Appendix: Supplementary materials**

390 Tables containing information on: sampling locations, TSS content and temperature of water
391 samples, QA/QC data, Σ BDE concentrations in operationally-defined particulate and dissolved
392 phases, as well as a comparison of BDE-47:99 ratios in water and surficial sediment samples.

393

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400

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Table 1: Concentrations of Σ BDEs^a in water expressed on both a water volume (pg L^{-1}) and TSS normalised basis (pg mg^{-1} , in parentheses)**in English lakes**

Location	Date	Apr/08	Jul/08	Nov/08	Jan/09	Apr/09	Jul/09	Oct/09	Jan/10	Apr/10	Jul/10	Feb/11	Jul/11	Feb/12	Average Concentration $\pm\sigma_n$
	Chapman's Pond (CHAP)		16.9 (2.0)	74.4 (7.1)	74.0 (10.9)	71.6 (19.9)	70.7 (8.8)	87.2 (6.4)	65.1 (4.7)	64.3 (11.6)	74.9 (5.5)	55.3 (5.4)	22.3 (2.5)	14.8 (1.1)	61.7 (33.3)
Crag Lough (CRAZ)		20.8 (7.4)	70.0 (21.5)	72.1 (10.2)	82.6 (23.6)	66.1 (73.4)	83.4 (22.5)	78.9 (56.3)	87.0 (67.0)	73.0 (36.5)	141.5 (11.0)	59.2 (4.4)	9.2 (1.9)	75.4 (30.8)	70.7 \pm 32 (28.2 \pm 23.8)
Edgbaston Pool (EDGB)		14.5 (19.3)	57.1 (14.1)	62.7 (9.5)	72.8 (16.8)	65.8 (7.2)	51.0 (25.5)	53.9 (39.9)	60.5 (11.1)	86.7 (31.5)	47.0 (14.9)	39.4 (5.1)	13.7 (4.3)	149.1 (10.8)	59.6 \pm 34 (16.2 \pm 10.6)
Holt Hall Lake (HOLT)		28.5 (49.1)	59.5 (99.1)	57.5 (34.8)	68.3 (30.8)	63.0 (45.0)	67.1 (40.6)	72.0 (35.1)	79.5 (45.4)	66.5 (57.9)	52.8 (36.4)	28.6 (26.0)	48.5 (19.0)	52.9 (27.9)	57.3 \pm 15 (42.1 \pm 20.0)
Marton Mere (MARM)		17.3 (15.1)	42.4 (10.9)	44.0 (14.9)	56.6 (24.1)	47.2 (17.8)	56.4 (40.3)	59.8 (37.4)	71.5 (13.5)	55.9 (27.3)	59.4 (10.0)	90.7 (10.5)	55.3 (42.6)	61.3 (42.3)	55.2 \pm 17 (23.6 \pm 12.9)
Fleet (PFLE)		16.0 (0.5)	61.0 (1.2)	72.9 (3.4)	88.8 (4.1)	79.3 (1.6)	88.8 (1.7)	69.6 (3.5)	86.6 (4.6)	110.1 (2.8)	71.6 (1.2)	83.5 (1.6)	48.3 (1.2)	72.9 (8.4)	73.0 \pm 23 (2.8 \pm 2.1)
Slapton (SLT)		41.9 (18.7)	60.2 (7.3)	56.2 (74.9)	64.9 (8.7)	56.5 (32.3)	69.1 (19.5)	132.7 (89.3)	90.7 (31.8)	85.2 (20.3)	85.4 (3.0)	31.1 (5.1)	24.4 (1.3)	90.3 (30.1)	68.4 \pm 29 (26.3 \pm 27.1)
Thoresby Lake (THOP)		15.0 (0.7)	44.2 (35.4)	49.7 (2.9)	56.8 (4.1)	56.0 (6.2)	60.9 (58.0)	-	122.2 (24.0)	-	73.3 (35.7)	171.5 (9.0)	21.3 (14.2)	136.0 (12.7)	73.3 \pm 49 (18.4 \pm 18.0)
Wake Valley Pond (WAKE)		33.0 (6.3)	45.0 (4.0)	41.6 (4.3)	45.9 (10.4)	40.3 (10.5)	46.5 (17.9)	53.4 (15.3)	59.2 (20.4)	52.4 (10.9)	38.0 (10.9)	17.7 (3.8)	13.8 (3.0)	52.7 (11.3)	41.5 \pm 13 (9.9 \pm 5.6)

^a Sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153



Fig. 1. Location of sampling sites

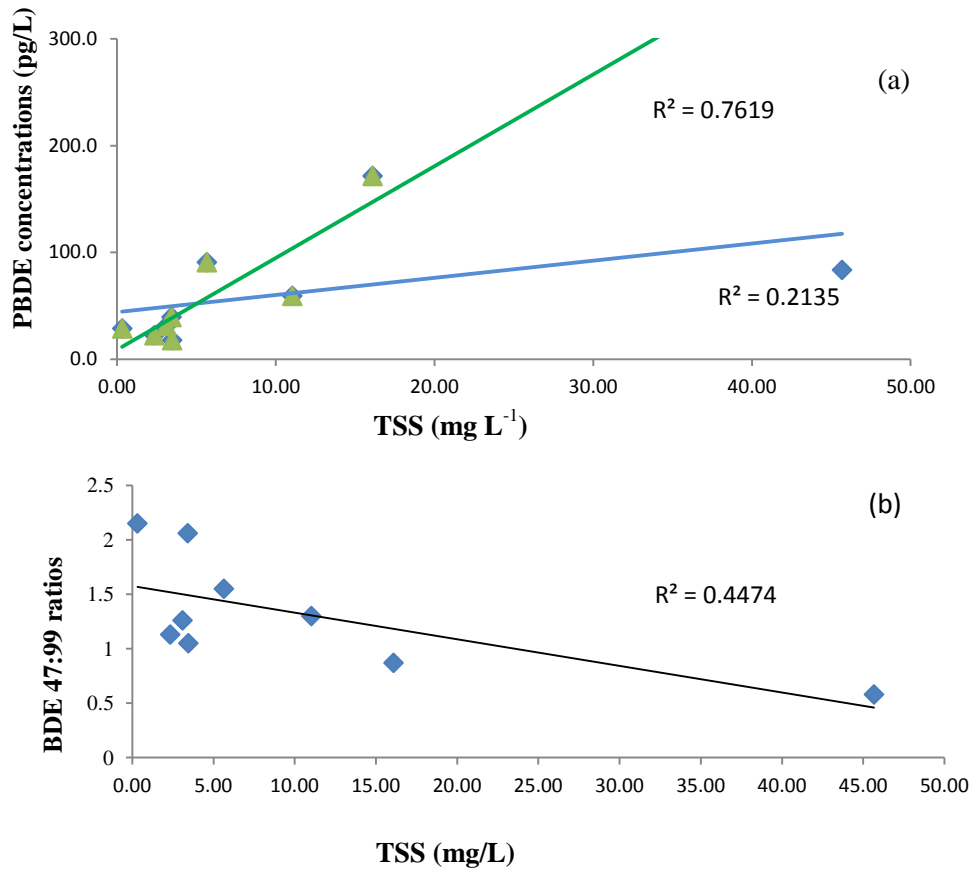


Fig. 2. Correlations between TSS content (measured for February 2011 samples only) and PBDE concentrations (a) (with and without PFLE sites, blue and green lines, respectively) and (b) BDE-47:99 ratios

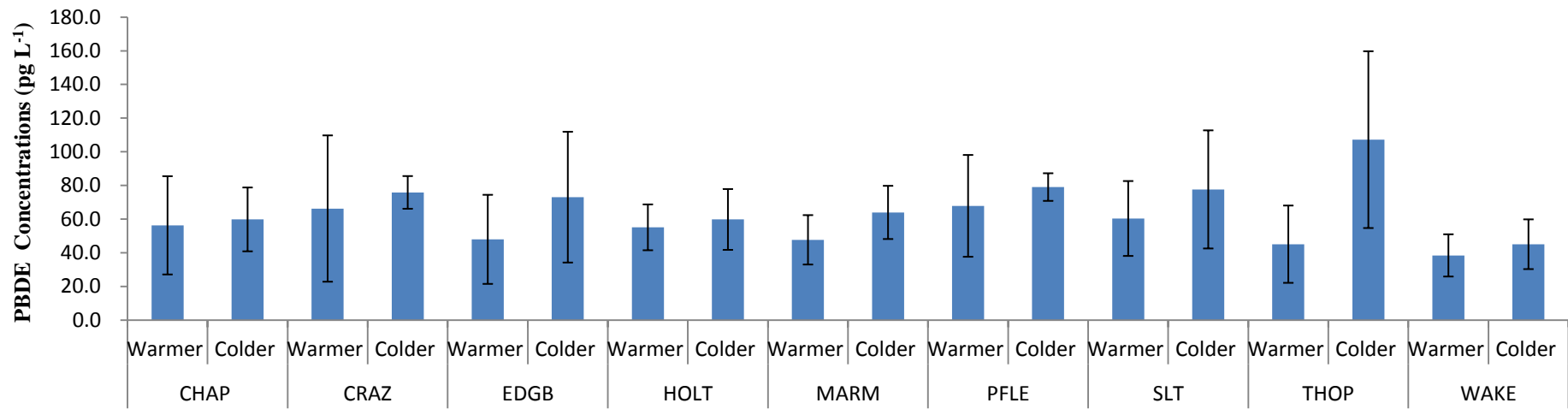


Fig. 3. Average PBDE concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012

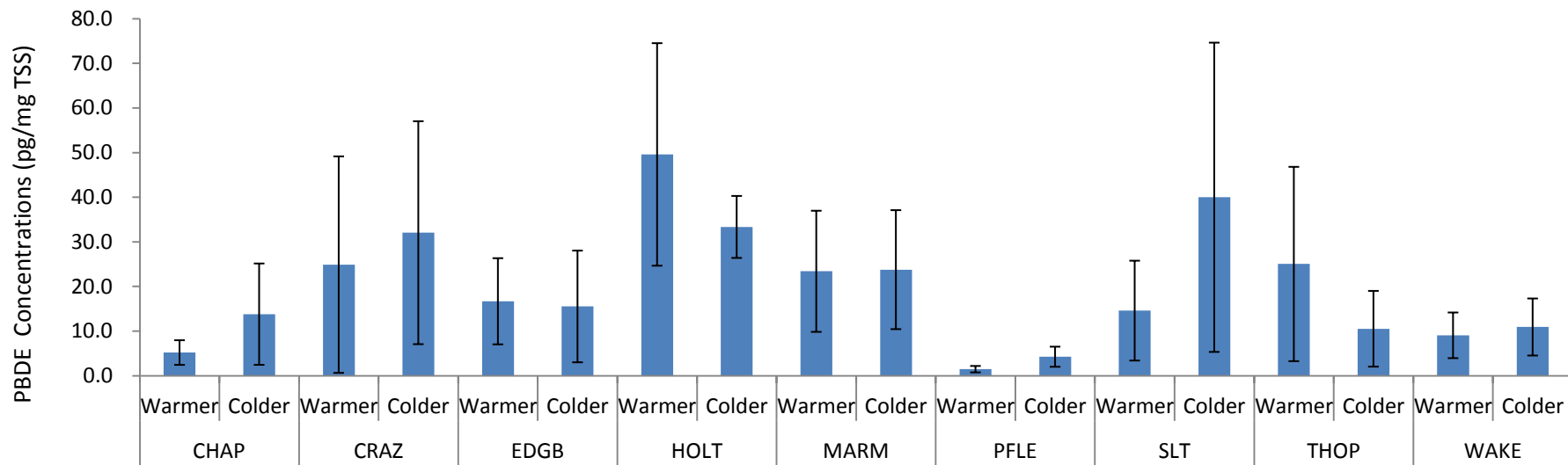


Fig. 4. Average TSS normalised PBDE concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012

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