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

Yang, Congqiao; Harrad, Stuart; Abdallah, Mohamed Abou-Elwafa; Desborough, Jennifer; Rose, Neil L; Turner, Simon D; Davidson, Thomas A; Goldsmith, Ben

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Corresponding Author: Dr. Congqiao Yang, PhD

Corresponding Author's Institution: University of Birmingham

First Author: Congqiao Yang, PhD

Order of Authors: Congqiao Yang, PhD; Stuart Harrad , Professor; Mohamed Abdallah , Assistant Lecturer; Jennifer Desborough, Doctor; Neil Rose , Professor; Simon Turner, Doctor; Thomas Davidson; Ben Goldsmith

Congqiao Yang

Environmental Chemistry
School of Geography, Earth & Environmental Sciences,
University of Birmingham,
Birmingham B15 2TT
UK
Tel +44 (0)121 414 5431
Fax +44 (0)121 414 3078
E-mail CXY083@bham.ac.uk

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.

The contact details of my co-authors are given below:

Stuart Harrad
Professor of Environmental Chemistry
School of Geography, Earth & Environmental Sciences
University of Birmingham
Birmingham B15 2TT
UK
Tel +44 (0)121 414 7298
Fax +44 (0)121 414 3078
E-mail S.J.Harrad@bham.ac.uk

Mohamed Abdel-Galil Abou-Elwafa Abdallah
Department of Pharmaceutical Analytical Chemistry
Faculty of Pharmacy
Assiut University
71526 Assiut
Egypt
Tel +2088241 1009
E-mail mae_abdallah@yahoo.co.uk

Jennifer Desborough
Environmental Chemistry
School of Geography, Earth & Environmental Sciences
University of Birmingham
Birmingham B15 2TT
UK
Tel +44 (0)121 414 5431
Fax +44 (0)121 414 3078
E-mail jennydesborough@yahoo.co.uk

Neil L. Rose
Environmental Change Research Centre
University College London
Gower Street
London WC1E 6BT
Tel +44 (0) 207 679 0543
Fax +44 (0) 207 679 0565
E-mail n.rose@ucl.ac.uk

Simon D. Turner
Environmental Change Research Centre
University College London
Gower Street
London WC1E 6BT
Tel 020 7679 2290
Fax 020 7679 0565
E-Mail: simon.turner@ucl.ac.uk

Thomas A. Davidson
Environmental Change Research Centre
University College London
Gower Street
London WC1E 6BT
Tel 020 7679 0515
Fax 020 7679 0565
E-Mail: thomas.davidson@ucl.ac.uk

Ben Goldsmith
Environmental Change Research Centre
University College London
Gower Street
London WC1E 6BT
Tel 07789 767 659
E-mail: b.goldsmith@ucl.ac.uk

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

Polybrominated diphenyl ethers (PBDEs) in English freshwater lakes, 2008-2012
C Yang et al

HIGHLIGHTS

- ➢ PBDE concentrations are comparable to those in the Great Lakes
- ➢ ΣBDE concentrations in water samples showed TSS dependence
- ➢ ΣBDE 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

1   **Polybrominated diphenyl ethers (PBDEs) in English freshwater lakes,**

2   **2008-2012**

3   Congqiao Yang [a,*], Stuart Harrad [a], Mohamed Abou-Elwafa Abdallah [b], Jennifer Desborough [a],

4   Neil L. Rose [c], Simon D. Turner [c], Thomas A. Davidson [c], Ben Goldsmith [c]

5   [a] Division of Environmental Health and Risk Management, School of Geography, Earth, and

6   Environmental Sciences, University of Birmingham, Birmingham, U.K

7   [b] Department of Analytical Chemistry, Faculty of Pharmacy, Assiut University, Assiut, Egypt

8   [c] Environmental Change Research Centre, Department of Geography, University College

9   London, London, U.K

10

11   *Author for correspondence

12   E-mail address: CXY083@bham.ac.uk

13   Postal address: Division of Environmental Health and Risk Management, School of

14   Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham

15   B15 2TT, UK

16   Tel. +44 121 414 5431

17   Fax +44 121 414 3078

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 ΣBDEs 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 ΣBDEs

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 ΣBDE 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

1. Introduction

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

Freshwater lakes provide important ecological, hydrological and societal services. However, studies of contamination of PBDEs in lake water are relatively scarce. As part of the Open Air Laboratories (OPAL) project, this study presents an investigation of the temporal/seasonal trends and spatial distribution of the concentrations of tri to hexa-BDEs (i.e. those predominant in the Penta-BDE formulation) in water from 9 freshwater lakes throughout England from April 2008 to February 2012. We believe that 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. 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: $^{13}C_{12}$-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 $^{13}C_{12}$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 ΣBDEs 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 ΣBDEs (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 ΣBDE (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, ΣBDE

160   (BDE-47, -99, and -153) concentrations in an urban estuary in Narragansett were < 3 pg L^{-1}

161   (Sacks and Lohmann, 2012). Moreover, ΣBDE 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 ΣBDE (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 ΣBDE (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 ΣBDEs (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 ΣBDE 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 ΣBDE 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 ΣBDE 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   ΣBDEs (sum of 22 tri- through decabrominated congeners) in water samples (n=3) from the

200   San Francisco estuary, finding 78% to 93% of ΣBDEs 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 ΣBDE 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 ΣBDE 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 ΣBDE.

226

227   ΣBDE=17.844 season + 0.53 TSS + 30.893; r^2=0.133, p<0.05; β=0.313 for season and β=0.222

228   for TSS   (1)

229

230   This indicates that ΣBDE 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 ΣBDE 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   (β=0.313) than for TSS (β=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 ΣBDE 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 ΣBDE 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 ΣBDE

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   BDE-47:99 = -0.414 season + 1.689; (r^2=0.078, p<0.01)   (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   BDE-47:99= 0.032 temperature+0.711; (r^2=0.068, p<0.01)   (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

Appendix: Supplementary materials

Tables containing information on: sampling locations, TSS content and temperature of water

samples, QA/QC data, ΣBDE concentrations in operationally-defined particulate and dissolved

phases, as well as a comparison of BDE-47:99 ratios in water and surficial sediment samples.

393

Acknowledgements

400

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Table 1: Concentrations of ΣBDEs[a] in water expressed on both a water volume (pg L^{-1}) and TSS normalised basis (pg mg^{-1}, in parentheses)

in English lakes

| Date / Location	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 ±σ_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)	57.9±24 (9.2±8.8)
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±32 (28.2±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±34 (16.2±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±15 (42.1±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±17 (23.6±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±23 (2.8±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±29 (26.3±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±49 (18.4±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±13 (9.9±5.6)

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

Figure
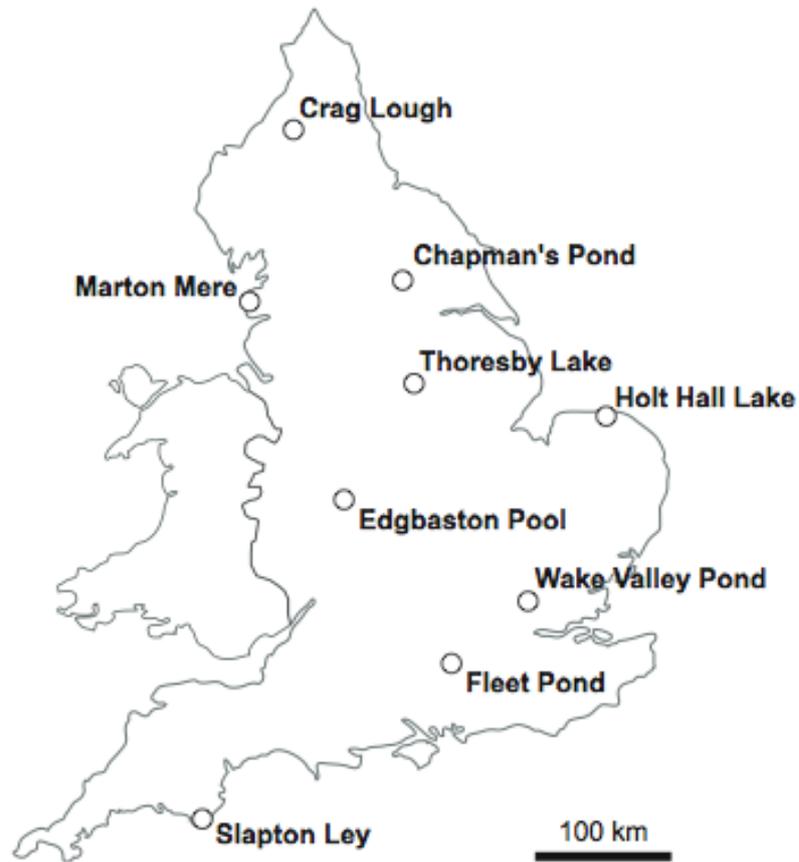
Fig. 1. Location of sampling sites
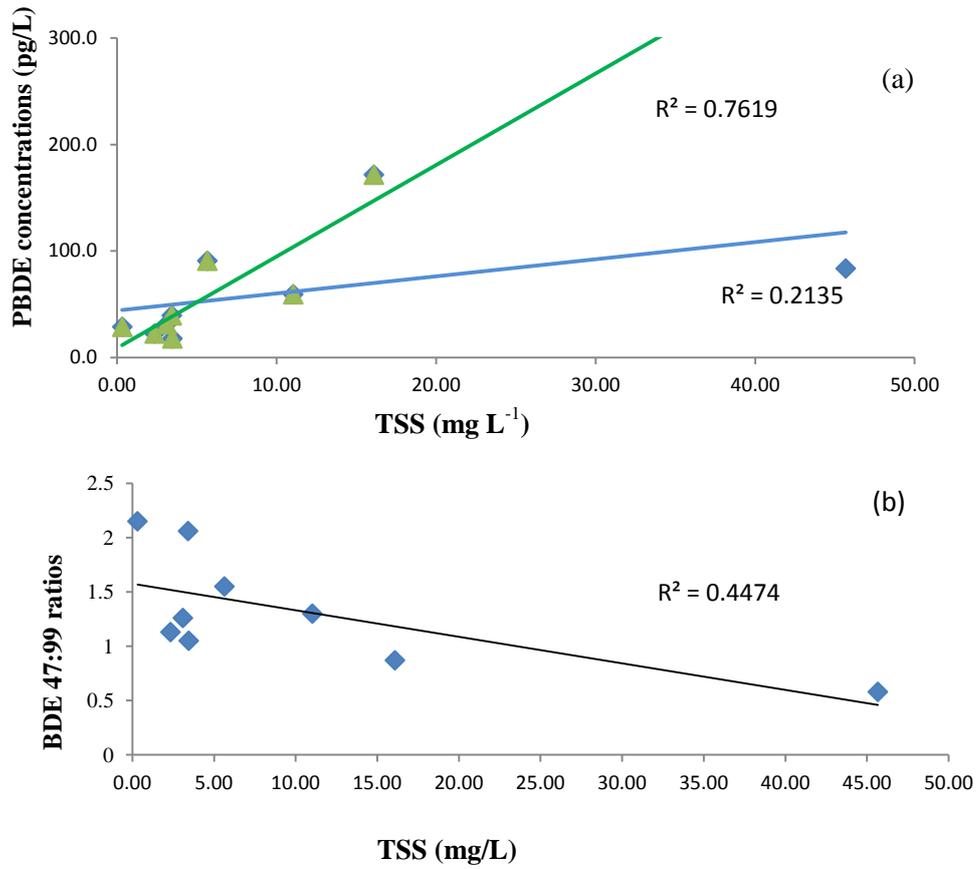
Fig. 2. Correlations between TSS content (measured for February 2011 samples only) and PBDE concentrations (a) (with and without PFLE sites, blue and green lines, respectively) and (b) BDE-47:99 ratios
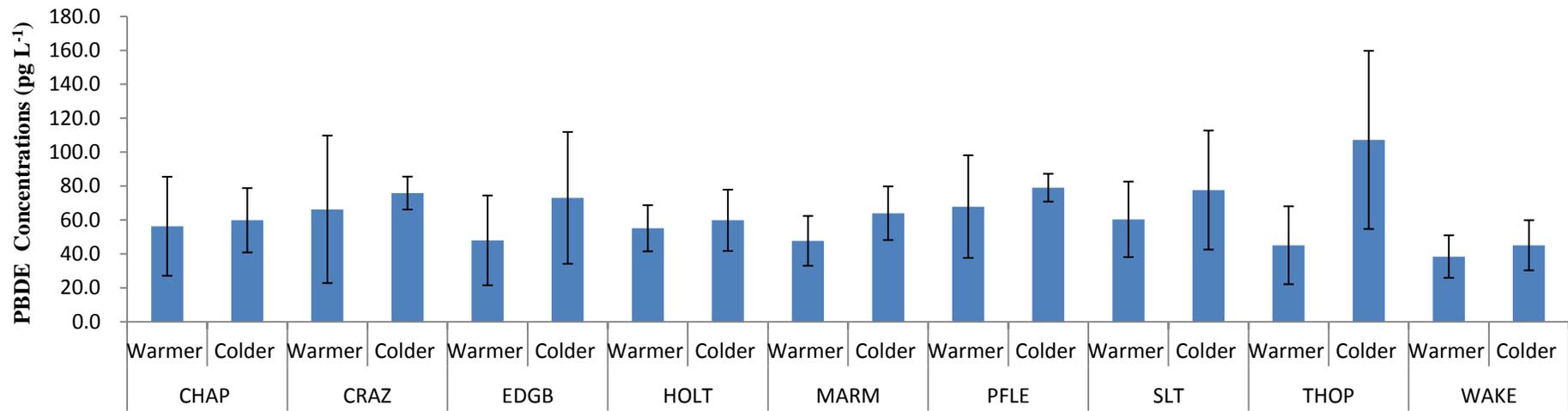
Fig. 3. Average PBDE concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012
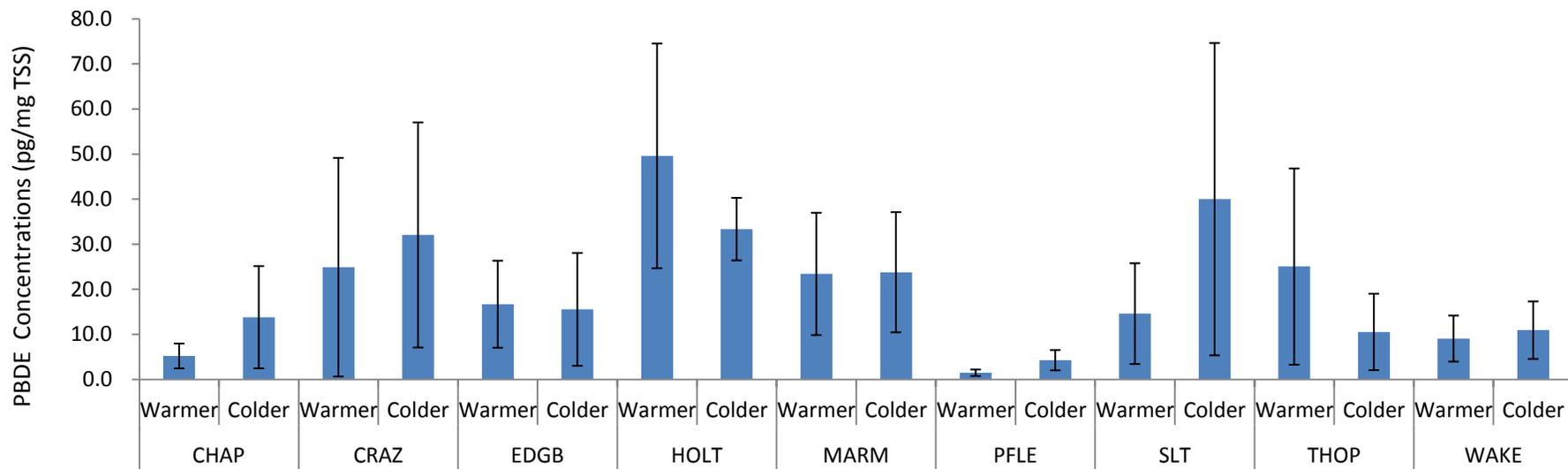
Fig. 4. Average TSS normalised PBDE concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012

Electronic Supplementary Material (online publication only)