

1                   **Legacy PBDEs and NBRs in Sediments of the Tidal River Thames Using Liquid**  
2 **Chromatography Coupled to a High Resolution Accurate Mass Orbitrap Mass Spectrometer**

3  
4                   Aristide P. Ganci<sup>1</sup>, Christopher H. Vane<sup>2</sup>, Mohamed A.-E. Abdallah<sup>1,4</sup>, Thomas Moehring<sup>3</sup>, Stuart Harrad<sup>1</sup>

5  
6                   <sup>1</sup> University of Birmingham, School of Geography, Earth and Environmental Sciences, Birmingham, B15 2TT, United Kingdom

7                   <sup>2</sup> British Geological Survey, Centre for Environmental Geochemistry, Keyworth, Nottingham, NG12 5GG, United Kingdom

8                   <sup>3</sup> Thermo Fisher Scientific (GmbH) Bremen, Hanna-Kunath-Str. 11, 28199 Bremen, Germany

9                   <sup>4</sup> Department of Analytical Chemistry, Faculty of Pharmacy, Assiut University, 71526 Assiut, Egypt

10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26

## 27 **Abstract**

28 Surface sediment samples (n=45) were collected along a 110 km transect of the river Thames  
29 in October 2011, starting from Teddington Lock out through the industrial area of London to  
30 the southern North Sea. Several legacy and novel brominated flame retardants (NBFRs) were  
31 analysed, including 13 polybrominated diphenylethers (PBDEs) (congeners 17, 28, 47, 99,  
32 100, 153, 154, 183, 196, 197, 206, 207 and 209), hexabromocyclododecane (HBCDDs),  
33 tetrabromobisphenol A (TBBPA), hexabromobenzene (HBB), 2,4,6-tribromophenol (TBP),  
34 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl) tetrabromophthalate  
35 (BEH-TEBP), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane  
36 (DBDPE), pentabromoethylbenzene (PBEB), anti/syn-dechlorane plus (a/s-DP),  
37 2,2',4,4',5,5'-hexabromobiphenyl (BB153) and  $\alpha$ -, $\beta$ -1,2-dibromo-4-(1,2-dibromoethyl)  
38 cyclohexane ( $\alpha$ -, $\beta$ -DBE-DBCH). A novel analysis method based on liquid chromatographic  
39 separation, followed by high resolution accurate mass detection using the Orbitrap platform  
40 was used for quantification. Results revealed that BDE-209 had the highest concentrations  
41 (<0.1 to 540  $\mu\text{g kg}^{-1}$  dw) and detection frequency, accounting for 95 % of all PBDE congeners  
42 measured. Indicative evidence of debromination of the PentaBDE technical mixture was  
43 observed through elevated relative abundance of BDE-28 in sediment compared to the  
44 Penta-BDE formulation. NBFRs were detected at comparable levels to PBDEs (excluding BDE-  
45 209), which indicates increasing use of the former. Spatial trend analysis showed that  
46 samples from industrial areas had significantly higher concentrations of  $\Sigma_{12}$ PBDEs,  $\Sigma$ HBCDDs,  
47 TBBPA, BEH-TEBP, BTBPE and TBP. Three locations showed high concentrations of HBCDDs  
48 with diastereomer patterns comparable to the technical mixture, which indicate recent input  
49 sources to the sediment.

50 **Keywords:** Brominated flame retardants, Spatial trends, Sources, Freshwater Environment

## 51 **1. Introduction**

52 In recent decades, a wide variety of brominated flame retardants (BFRs) have been added to  
53 consumer goods such as soft furnishings, building insulation foam, electronic and electrical  
54 goods. The most extensively used BFRs include: tetrabromobisphenol A (TBBPA),  
55 hexabromocyclododecane (HBCDD) and three commercial mixtures of polybrominated  
56 diphenyl ethers (PBDEs); namely pentabromodiphenyl ether (PentaBDE), octabromodiphenyl  
57 ether (OctaBDE) and decabromodiphenyl ether (DecaBDE)<sup>1</sup>. Within the European Union,  
58 manufacture and new use of the PentaBDE and OctaBDE formulations were prohibited in  
59 2004, and these formulations were listed under the UNEP Stockholm Convention on  
60 persistent organic pollutants (POPs) in 2009<sup>2</sup>. Restrictions on the manufacture and use of  
61 DecaBDE have followed, and it was listed in 2017 under Annex A of the Stockholm  
62 Convention. A key consideration with respect to the listing of DecaBDE under the Stockholm  
63 Convention is its potential to form lower BDEs by various debromination processes<sup>3</sup>.

64 Due to legislative restrictions on manufacture and use of these BFRs, several so-called novel  
65 BFRs (NBFRs) are likely finding wider use<sup>4</sup>. In general, increasing levels of NBFRs are being  
66 detected in various matrices relevant to environmental and human health<sup>5</sup>. The  
67 environmental impact of NBFRs is potentially similar to the restricted BFRs<sup>6</sup>. Animal studies  
68 have shown that exposure to BFRs can have endocrine, reproductive, and behavioural  
69 effects at doses comparable to human exposure<sup>7</sup>. Human epidemiological studies have  
70 reported association between exposure to BFRs and adverse neurodevelopmental and  
71 reproductive effects in humans<sup>8 9 10 11</sup>. Laboratory studies on NBFRs indicate genotoxicity in  
72 aquatic species<sup>12</sup>, as well as cytotoxic and anti-proliferation effects with a possible induction  
73 of apoptosis in human liver cancer cells<sup>13</sup>.

74 BFRs generally have limited biodegradability, are persistent and tend to accumulate in the  
75 environment<sup>14</sup>. Due to their chemical properties (i.e. low water solubility and high  $K_{ow}$   
76 values), NBFRs tend to partition to organic carbon rich matter and have been detected in  
77 sediment, dust and sewage sludge around the world<sup>4</sup>. We therefore hypothesize that  
78 sediments represent important sinks for NBFRs. Studies on BFRs in sediments in the UK have  
79 been conducted on samples from lakes<sup>15-17</sup>, rivers and estuaries<sup>18-21</sup>, coastal<sup>19, 22</sup> and marine  
80 regions<sup>19, 23</sup>. However, apart from one study in the UK<sup>19</sup>, which analysed a broad range of  
81 halogenated flame retardants in both marine and fresh water sediments, other studies in  
82 the UK have focused mainly on PBDEs and HBCDDs. Given this lack of information on the  
83 levels and profiles of NBFRs in freshwater sediments, the aim of this study is to compare  
84 concentrations of 13 PBDEs, HBCDDs, TBBPA and 10 selected NBFRs in surficial sediments  
85 taken at 45 locations along the tidal reaches of the River Thames in the UK. In addition, we  
86 examine spatial variations in PBDE and NBFR concentrations relative to the location of  
87 putative source activities such as sewage outfalls, in an effort to identify potential sources of  
88 these BFRs to the river. The Thames was chosen as it is one of the major rivers in Europe, has  
89 fairly complex sediment transport dynamics owing to its high tidal range, morphology and  
90 geology<sup>24</sup>. Its sediments are subject to regular capital and maintenance dredging which has  
91 the potential to mobilise and redistribute sediments or require disposal at sea or on-land.  
92 Recent evaluation of historical sediment profiles of mercury (Hg)<sup>25</sup> as well as surface  
93 distributions of phosphorus (P)<sup>26</sup> and natural tetraether lipids<sup>27</sup> confirm that contamination  
94 originates from both diffuse and point sources.

95

96 To the authors' knowledge, this is the most extensive comparison yet of levels, spatial  
97 trends, and potential sources of PBDEs and NBFRs in river sediments. Moreover, our study

98 exploits the potential of high resolution Orbitrap mass spectrometry for multi-residue  
99 analysis of a broad range of BFRs and NBRs in a single run with sensitive, rapid and reliable  
100 measurement of target analytes, as well as their potential degradation products.

101

## 102 **2. Materials and Methods**

### 103 **3.1. Study area**

104 The River Thames is one of the major rivers in Europe, with a total length of 354 km, a  
105 catchment area of 12,935 km<sup>2</sup> and an average discharge of 65.8 m<sup>3</sup>/s. It has a spring tidal  
106 range of between 5.2–6.6 m and extends 110 km from Teddington Lock through London and  
107 out to the southern North Sea (Figure 1). The Thames basin contains many major urban  
108 centres accommodating around a fifth of the UK population (ca. 12 million) of which > 10  
109 million live in Metropolitan London. London is intersected by 33 tributaries and about 60  
110 municipal and commercial discharge points. Numerous industries, ports, sewage treatment  
111 plants and power stations discharge into the tidal Thames<sup>27</sup>.

112

### 113 **3.2. Sample collection**

114 Sampling of sediments from the River Thames was carried out in October 2011 at the  
115 locations shown in Figure 1. All sites were accessed via a jet boat using predetermined GPS  
116 coordinates to accurately locate each position to  $\pm 3$  m<sup>25, 27</sup>. At each location, surface  
117 sediments (0-5 cm) were collected from four corners of a square of ca. 2 m<sup>2</sup> area, using  
118 either a stainless steel trowel or a polycarbonate tube fitted with a core catcher manually  
119 driven into the surface<sup>28</sup>. The four corner samples and one central sample were combined  
120 and transported to shore in a polyethylene zip lock bag. Sediments were immediately frozen  
121 at -18 °C in the dark to avoid post collection chemical changes and physical movement, then



141  $\gamma$ -HBCDDs, TBBPA /  $^{13}\text{C}$ -TBBPA and NFRs 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-  
142 TBB),  $^{13}\text{C}$ -EH-TBB, bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP),  $^{13}\text{C}$ -BEH-TEBP, 1,2-  
143 bis(2,4,6-tribromophenoxy)ethane (BTBPE),  $^{13}\text{C}$ -BTBPE, decabromodiphenyl ethane (DBDPE),  
144 pentabromoethylbenzene (PBEB), anti/syn-dechlorane plus (a/s-DP),  
145 2,2',4,4',5,5'-hexabromobiphenyl (BB153) and  $\alpha$ -, $\beta$ -1,2-dibromo-4-(1,2-  
146 dibromoethyl)cyclohexane ( $\alpha$ -, $\beta$ -DBE-DBCH) were all purchased from Wellington  
147 Laboratories Inc. (Guelph, Canada). Florisil HyperSep™ SPE cartridges (1 g, 60 cc),  
148 concentrated sulfuric acid, copper powder (particle size <100  $\mu\text{m}$ ) and anhydrous sodium  
149 sulfate (dried overnight at 120 °C) were acquired from Thermo Fisher Scientific  
150 (Loughborough, UK). The standard reference material (SRM 1944, “New York/New Jersey  
151 Waterway Sediment” certified for PCBs, PAHs and PBDEs) was obtained from the National  
152 Institute of Standards and Technology - NIST (Gaithersburg, MD, USA).

153

### 154 **3.5. Sample extraction/clean-up**

155 2 g of freeze-dried sediment were weighed into a pre-cleaned glass extraction tube and  
156 spiked with 20  $\mu\text{L}$  of the internal standard mixture ( $^{13}\text{C}$ -BDE-28, BDE-77, BDE-128,  $^{13}\text{C}$ -BDE-  
157 209,  $^{13}\text{C}$ -TBBPA,  $^{13}\text{C}$ - $\alpha$ -, $\beta$ -, and  $\gamma$ -HBCDDs,  $^{13}\text{C}$ -EH-TBB,  $^{13}\text{C}$ -BEH-TEBP and  $^{13}\text{C}$ -BTBPE), along  
158 with 2 g of copper for sulfur removal. Samples were then extracted using 4 mL of  
159 hexane:acetone (3:1 v/v), vortexing for 5 min, followed by ultrasonication (20 min) and  
160 centrifugation (5 min at 4000 rpm). This procedure was repeated twice. The combined  
161 extract was then evaporated to dryness under a gentle stream of  $\text{N}_2$  and reconstituted in 2  
162 mL of hexane. This was followed by a sulfuric acid wash of the extract, with the layers  
163 allowed to separate overnight. The organic phase was collected and the acid layer washed  
164 twice with 2 mL of hexane. The combined extracts were then reduced to  $\sim 1$  mL under a

165 gentle stream of N<sub>2</sub> and loaded onto a conditioned HyperSep™ 1 g Florisil SPE cartridge, on  
166 top of which 1 g of sodium sulfate was added. Subsequent elution was performed with  
167 20 mL of hexane:dichloromethane (1:1 v/v), with TBBPA eluted in a second fraction with 15  
168 mL of methanol. Both fractions were combined, concentrated to dryness under a N<sub>2</sub> flow in  
169 a Turbovap and reconstituted in methanol:toluene (1:1 v/v) containing 200 pg μL<sup>-1</sup> of  
170 <sup>13</sup>C-BDE-100 as a recovery determination standard.

171

### 172 3.6. Instrumental analysis

173 2 μL of each sample were analysed on a UPLC-Orbitrap-HRMS instrument (Thermo Fisher  
174 Scientific, Bremen, Germany) composed of an UltiMate® 3000 high performance liquid  
175 chromatography system equipped with a HPG-3400RS dual pump, a TCC-3000 column oven  
176 and a WPS-3000 auto sampler coupled to a Q-Exactive™ Plus Orbitrap mass spectrometer.  
177 Chromatographic separation was performed on a Thermo Scientific Accucore™ RP-MS  
178 column (100 x 2.1 mm, 2.6 μm) with water (mobile phase A) and methanol (mobile phase B).  
179 A gradient elution programme at a flow rate of 400-500 μL min<sup>-1</sup> was applied as shown in  
180 **Error! Reference source not found.** for a total run time of 17 min.

181 All parent BFRs were determined in negative atmospheric pressure chemical ionization  
182 (APCI) mode. The parameters of the Orbitrap were set as follows: (-) APCI full scan mode at  
183 70000 FWHM (full width at half maximum at 200 m/z), AGC target 1e<sup>6</sup>, maximum injection  
184 time 100 ms, scan range 250 to 1000 m/z, profile spectrum data type, sheath gas flow rate  
185 25 AU (arbitrary units), aux gas flow rate 5 AU, discharge current 30 μA, capillary  
186 temperature 250 °C, S-lens RF level 50 AU and aux gas heater temperature 320 °C. For  
187 screening identification of possible more polar degradation products and confirmation  
188 purposes, sediment extracts were also analyzed using the more universal, softer



189 electrospray ionisation (ESI) in negative mode, as described in the Supporting Information  
190 section. Both the HPLC gradient programme and ionisation values were optimized based on  
191 the measurement of reference standard solutions. Screening for brominated compounds  
192 was conducted using an All Ion Fragmentation Scan (AIF) in parallel to the Full Scan  
193 measurement and by monitoring the bromine mass trace in the final data raw files.  
194 Trace Finder™ version 3.3 software (Thermo Fisher Scientific, Bremen, Germany) was used  
195 to process raw data files, while quantification of the compounds of interest was conducted  
196 using Microsoft Excel 2010.

197

### 198 **3.7. QA/QC**

199 The standard reference material SRM 1944 (NIST) for sediment was used to evaluate the  
200 accuracy of the method for PBDEs and HBCDDs. One SRM sample was analysed for every 15  
201 sediment samples. Values obtained for the SRM 1944 were generally in good accordance  
202 with the certified levels (**Error! Reference source not found.**). In addition, non-certified  
203 compounds including BTBPE, BEH-TEBP, PBEB, TBP, BB153 and DP were detected in the SRM  
204 1944, although concentrations varied between replicates (9-65% RSD, Table SI 3).

205 Recoveries for internal standards were in the range of 90 to 120 % for all samples, except for  
206 <sup>13</sup>C-TBBPA, where recovery values were around 60 %. Limits of detection (LOD) and limits of  
207 quantification (LOQ) were estimated based on method described by Taylor <sup>30</sup> (**Error!**  
208 **Reference source not found.** and **Error! Reference source not found.**). Further QA/QC measures  
209 are described in the supporting information.

210

### 211 **3.8. Statistical analysis**

212 Statistical analysis of the data was performed using IBM SPSS statistics software version 23.  
213 A one-way ANOVA was used for testing significant differences between arithmetic means.  
214 For statistical purposes, “non-detect” values were replaced with zero, while “detect” values  
215 with a concentration below the LOQ were assigned a value of the LOQ/2 or in cases of a  
216 detection frequency below 50% the LOQ was multiplied by the detection frequency factor. P  
217 values < 0.05 were taken to indicate statistical significance.

## 218 **3. Results and Discussion**

### 219 **3.1. Levels and trends of PBDEs and NBFs in sediments**

220 Mean, median and concentration ranges of our target BFRs in surface sediments from the  
221 River Thames are summarised in Table 1, while concentrations of individual PBDE congeners  
222 are provided in **Error! Reference source not found.** To account for potential variability of  
223 concentrations due to organic carbon content, organic carbon normalisation was conducted  
224 on all sample concentrations using the measured total organic carbon (TOC) for each  
225 sample, as described in the supporting information. No correlation between BFR  
226 concentrations and TOC values was observed in the studied samples. This is likely explained  
227 by the fact that samples were taken from different locations with diverse source input  
228 strengths. If samples originate from the same location (such as sediment cores) with the  
229 same source input strength, a positive linear correlation between TOC and BFR dry weight  
230 concentration would be expected. Similarly, for the composition of the sediment, no  
231 correlation between the BFR concentration and its geological composition (clay, silt or sand  
232 content) was observed in this study.

233 **Table 1. Summary of the concentrations in both  $\mu\text{g kg}^{-1}$  dry weight and  $\mu\text{g kg}^{-1}$  organic carbon of selected BFRs in surficial sediments from the**  
 234 **River Thames**

Compound	DF (%)	Median	Average	Range	Median	Average	Range
		$\mu\text{g kg}^{-1}$ dry weight			$\mu\text{g kg}^{-1}$ organic carbon		
$\Sigma_{12}$ BDEs	16-100	3.8	5.9	n.d. – 29	182	228	n.d. – 672
BDE-28	27	<0.2	0.4	n.d. – 4.0	<0.2	12	n.d. – 116
BDE-47	53	<0.03	0.2	n.d. – 2.5	<0.03	6.7	n.d. – 48
BDE-99	71	0.5	0.8	n.d. – 4.4	15	28	n.d. – 130
BDE-153	16	<0.01	0.03	n.d. – 0.6	<0.01	1.2	n.d. – 33
BDE-183	71	0.05	0.1	n.d. – 0.7	0.4	3.3	n.d. – 23
BDE-206	96	2.6	3.3	n.d. – 11.7	115	135	n.d. – 389
BDE-209	100	148	174	0.03 - 535	6969	7673	0.03 - 20762
$\Sigma$ HBCDD	91	1.9	3.7	n.d. – 38	67	157	n.d. – 1357
TBBPA	98	0.6	0.6	n.d. – 2.6	21	34	n.d. – 476
EH-TBB	0		<0.03			<0.03	
BEH-TEBP	76	2.1	3.5	n.d. – 14	100	134	n.d. – 445
BTBPE	51	<0.02	0.4	n.d. – 3.8	0.7	15	n.d. – 142
TBP	69	0.1	0.1	n.d. – 0.4	3.5	4.6	n.d. – 34
anti-/syn-DP	11	<0.04	2.0	n.d. – 66	<0.04	51	n.d. – 1249
PBEB	7	<0.06	1.7	n.d. – 48	<0.06	53	n.d. – 1385
DBDPE	20	<0.45	1.3	n.d. – 24	<0.45	42	n.d. – 1154
$\alpha/\beta$ -DBE-DBCH	0		<1.1			<1.1	
HBB	0		<0.03			<0.03	
BB153	0		<0.01			<0.01	

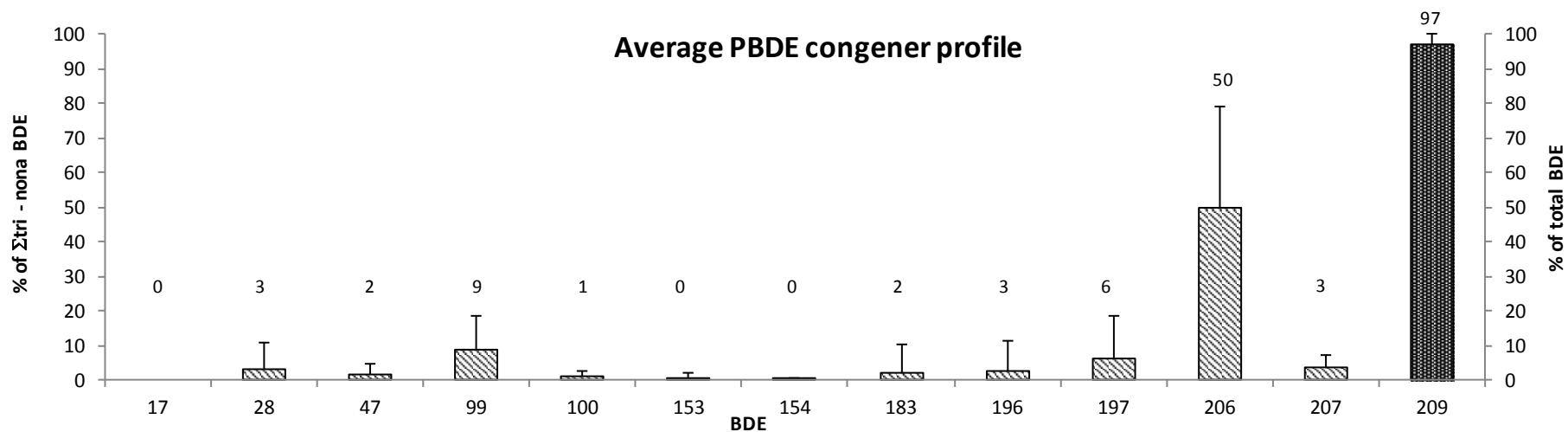
235 \*  $\Sigma_{12}$ BDEs does not include BDE-209

236 \* n.d. - not detected

237 \* < indicates the value of the LOD

238

239  
240  
241



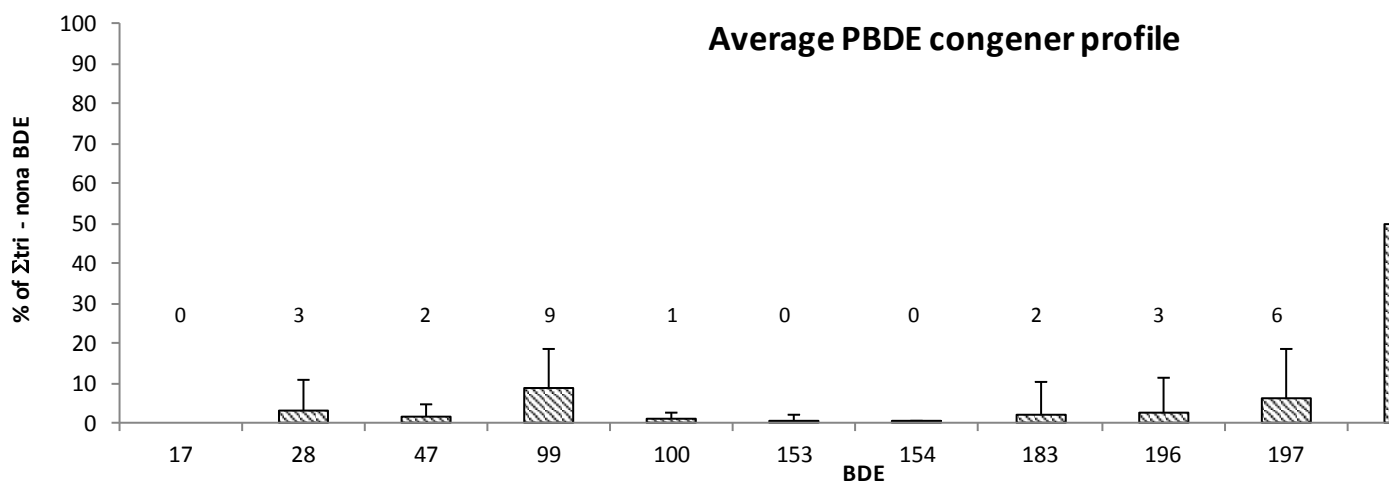
242

243 **Figure 2. Average PBDE congener profile in all sediment samples. BDE-209 is on a different scale. Average percent contributions are indicated**  
244 **above each congener with error bars representing the standard deviation.**

245

246 **3.2. PBDEs**

247 PBDE concentrations varied widely along the River Thames transect BDE-209 was the  
248 predominant congener in all sediments, accounting for ~ 95 % of total PBDEs detected (



249  
250 Figure 2). This is in agreement with Vane *et al.*, who reported BDE-209 to represent 80 % of  
251 total PBDEs in sediments collected from the Clyde Estuary around Glasgow, UK<sup>31</sup>. This  
252 indicates a higher proportion of the DecaBDE formulation in our samples, further supported  
253 by high concentrations of BDE-206. Similarly, other studies reported nona-brominated PBDE  
254 congeners as the second most abundant after BDE-209 in river sediment samples of the UK  
255 (inner Clyde estuary)<sup>31</sup> and China (industrial area of the Dongjiang river)<sup>32</sup>, possibly indicating  
256 degradation of BDE-209 to form lower brominated congeners. This finding is especially of  
257 interest with the recent listing of Deca-BDE under the Stockholm Convention. A comparison  
258 of our data to the technical Deca-BDE formulation will be discussed further on in this paper.

259 Concentrations of BDE-209 ranged from <0.1 to 540  $\mu\text{g kg}^{-1}$  dw (<0.1 to 20762  $\mu\text{g kg}^{-1}$  OC).  
260 Other PBDEs were detected at lower concentrations, with prominent congeners being BDE-  
261 206, followed by BDE-99 and BDE-28. Sediments from several UK lakes<sup>33</sup> contained BDE-209  
262 at concentrations ranging from 1.63 to 116  $\mu\text{g kg}^{-1}$  dw. Meanwhile, river and marine

263 sediments from various locations around the UK<sup>19</sup> were reported between 0.3 – 1333 µg  
264 kg<sup>-1</sup> dw, 1 – 2337 µg kg<sup>-1</sup> dw for sediments of the river Clyde<sup>31</sup> and 2 – 98125 µg kg<sup>-1</sup> dw for  
265 Scottish sediment cores<sup>34</sup>. This sets our study at the lower end of previously detected  
266 concentrations of BDE-209 in UK sediments.

267 Harrad recently reviewed the concentrations of legacy BFRs in UK environmental samples<sup>35</sup>.  
268 Where BFR levels in UK river and lake sediments were reported, BDE-209 was the prevailing  
269 congener, followed by BDE-99 and BDE-47. Interestingly in our study, levels for BDE-28 were  
270 higher than those found for BDE-47, suggesting a potential degradation of PentaBDE  
271 congeners to form BDE-28.

272

273 A recent study determined concentrations of PBDEs in sediments from the Thames estuary,  
274 reporting a concentration range for  $\Sigma_6$ BDEs (congeners 28, 47, 99, 100, 153 and 154) of  
275 <MDL to 14.4 µg kg<sup>-1</sup> dw<sup>21</sup>. This is in good accordance with our results, that reported  
276 concentrations for the same congeners ranging from n.d. to 12.8 µg kg<sup>-1</sup> dw. Barber *et al.*  
277 reported concentrations of  $\Sigma_{11}$ BDEs (i.e. excluding BDE-209) to fall between n.d. and 32.2 µg  
278 kg<sup>-1</sup> dw in river and marine sediments around the UK<sup>19</sup>, which is comparable to our range of  
279  $\Sigma_{12}$ BDEs of n.d. to 29 µg kg<sup>-1</sup> dw.

280

### 281 **3.3. HBCDDs and TBBPA**

282 HBCDDs (sum of  $\alpha$ -, $\beta$ -, and  $\gamma$  HBCDD) were detected in most samples (91 % detection  
283 frequency) at an average concentration of 3.7 µg kg<sup>-1</sup> dw, which is comparable to our  
284 average concentration of  $\Sigma_{12}$ BDEs (excluding BDE-209) of 5.9 µg kg<sup>-1</sup> dw. Concentrations of  
285  $\Sigma$ HBCDDs ranged from n.d. to 38 µg kg<sup>-1</sup> dw. A study on estuarine and marine sediments  
286 around the UK reported a comparable range from <MDL to 47.2 µg kg<sup>-1</sup> dw<sup>19</sup>. Values for lake

287 sediments in the UK ranged from 0.42 to 7.9  $\mu\text{g kg}^{-1} \text{dw}^{33}$ . Higher values were detected in the  
288 River Skerne in northeast England with concentrations from <2.4 up to 1680  $\mu\text{g kg}^{-1} \text{dw}^{20}$ ,  
289 likely originating from the vicinity of a former BFR manufacturing site. HBCDD concentrations  
290 in coastal marine sediments tend to be lower with maximum values up to 1.6 and 1.8  $\mu\text{g kg}^{-1}$   
291 dw reported for southern and northern UK respectively<sup>36</sup>.

292  
293 TBBPA was found in all but one Thames sediment, with a maximum concentration of 2.6  $\mu\text{g}$   
294  $\text{kg}^{-1} \text{dw}$  and an average of 0.6  $\mu\text{g kg}^{-1} \text{dw}$ , in which is an order of magnitude lower than found  
295 in this study for HBCDDs and  $\Sigma_{12}\text{BDEs}$ . Comparatively few studies have reported TBBPA  
296 concentrations in European sediment samples. Sediments from the southern and northern  
297 UK coast were reported to contain up to 6.4  $\mu\text{g kg}^{-1} \text{dw}$  for TBBPA and an average of 1.7 and  
298 2.7  $\mu\text{g kg}^{-1} \text{dw}$  respectively<sup>36</sup>. Interestingly however, TBBPA was the predominant compound  
299 with a detection frequency of 87 % in these coastal sediments. Morris *et al.*<sup>20</sup> analysed  
300 riverine and estuarine sediments from various rivers in the UK and found high average  
301 values of 451  $\mu\text{g kg}^{-1} \text{dw}$  and up to 9750  $\mu\text{g kg}^{-1} \text{dw}$  in the River Skerne. These elevated  
302 concentrations were attributed to the vicinity of sampling sites to a former BFR  
303 manufacturing site. TBBPA levels detected in our study are more comparable to those  
304 reported in sediment samples from rivers in The Netherlands and Germany with average  
305 values of 2.2  $\mu\text{g kg}^{-1} \text{dw}^{20}$  and 0.3  $\mu\text{g kg}^{-1} \text{dw}^{36}$  respectively.

306

### 307 **3.4. NFRs**

308 One or more NFRs were quantified in most samples at varying concentrations (Table 1) in  
309 the following order (detection frequency): BEH-TEBP (76 %) > TBP (69 %) > BTBPE (51 %),  
310 with DBDPE (20 %), DP (11 %) and PBEB (7 %) identified in fewer samples. Where detected,

311 concentrations of NBRs were comparable to those of PBDEs (excluding BDE-209). Target  
312 compounds like EH-TBB, HBB, BB-153 and  $\alpha/\beta$ -DBE-DBCH were not detected in any of the  
313 studied samples.

314 Consistent with our study, Barber *et al.*<sup>19</sup> did not detect HBB, BB-153 and DBE-DBCH in 42  
315 marine and river sediments samples from around the UK, while EH-TBB was detected in only  
316 one sample at a concentration of 0.29  $\mu\text{g kg}^{-1}$  dw. In addition, EH-TBB has been reported in  
317 sediment samples from UK lakes<sup>33</sup> and southern and northern coastal locations, with  
318 maximum concentrations of 1.35  $\mu\text{g kg}^{-1}$  dw and 26 % relative contribution in the  
319 investigated area<sup>36</sup>.

320 To our knowledge, this is the first study to detect BEH-TEBP in UK sediments (Table 1),  
321 although this FR has already been reported in sediments from South Africa<sup>37, 38</sup> and China<sup>39,</sup>  
322 <sup>40</sup>. We detected BEH-TEBP in 76 % of our samples with an average of 3.3  $\mu\text{g kg}^{-1}$  dw (134  $\mu\text{g}$   
323  $\text{kg}^{-1}$  OC) and maximum values of up to 14  $\mu\text{g kg}^{-1}$  dw (445  $\mu\text{g kg}^{-1}$  OC). This finding is  
324 comparable to values of La Guardia *et al.* in South Africa (average of 96  $\text{ng g}^{-1}$  OC, 60 %  
325 detection rate) and Zhu *et al.* in China (average of 1.01  $\text{ng g}^{-1}$  dw).

326 BEH-TEBP and EH-TBB are two of the main constituents of the technical flame retardant  
327 mixture Firemaster 550 (FM-550). In the present study, interestingly only BEH-TEBP was  
328 detected, possibly reflecting the infrequent use of FM-550 in the UK. The relative abundance  
329 of these two NBRs in the Thames estuary may thus be explained by applications other than  
330 FM-550. For example, BEH-TEBP is also used as a plasticiser, in contrast to EH-TBB for which  
331 the main application is as a flame retardant<sup>41</sup> and thus might explain our findings. Several  
332 studies in the UK have targeted both EH-TBB and BEH-TEBP in the indoor and outdoor  
333 environment. These studies focused on indoor dust<sup>42</sup>, indoor<sup>43</sup> and outdoor air<sup>44</sup>, food and



334 human milk<sup>45</sup>, as well as soil samples<sup>44</sup>. In general, where reported, BEH-TEBP was detected  
335 at concentrations 1-2 orders of magnitude higher than what was found for EH-TBB.  
336 Furthermore, EH-TBB was not detected in UK outdoor air or soil<sup>44</sup>, consistent with its  
337 absence here in Thames sediments.

338 Concentrations of BTBPE in our sediments reached up to 3.8  $\mu\text{g kg}^{-1}$  dw with a detection  
339 frequency of 51 %, which accords well with Barber *et al.*<sup>19</sup> who reported a maximum of 1.8  
340  $\mu\text{g kg}^{-1}$  dw and a detection frequency of 48 %. The presence of BTBPE was also reported in  
341 lake sediment in the UK<sup>33</sup>.

342 TBP was detected in 69 % of our sediments at relatively low concentrations up to 0.4  $\mu\text{g kg}^{-1}$   
343 dw. To our best knowledge, TBP has not been reported in UK sediments so far. DBDPE, DP  
344 and PBEB in our study were only detected in a small number of samples. DBDPE has been  
345 reported in sediments throughout Europe, including lake sediments in the UK (up to 6.4  $\mu\text{g}$   
346  $\text{kg}^{-1}$  TOC)<sup>33</sup> and Italy (up to 280  $\mu\text{g kg}^{-1}$  dw)<sup>46</sup>, as well as river sediments in the Netherlands<sup>47</sup>  
347 and Spain (both up to 24  $\mu\text{g kg}^{-1}$  dw)<sup>48</sup>. PBEB has been reported both in UK and German  
348 sediments<sup>19, 36</sup>, while the same goes for DP<sup>36, 49</sup>. HBB and BB-153 were not detected in this  
349 study, but their presence has been previously reported in surface and tributary sediments of  
350 Lake Ontario<sup>50</sup>, with HBB also detected in river sediments in Germany<sup>36</sup>. An extensive review  
351 on the presence of emerging brominated flame retardants in sediments around the world  
352 can be found elsewhere<sup>51</sup>.

353 The absence of DBE-DBCH from our sediments is perhaps surprising as DBE-DBCH has been  
354 reported to be the predominant NBRF in UK indoor air and dust<sup>43</sup>, outdoor air<sup>44</sup>, as well as  
355 UK human milk and diet samples<sup>45</sup>. This may be attributable to the physico-chemical  
356 properties of DBE-DBCH, namely its relatively high volatility and low  $K_{ow}$  compared to lower  
357 brominated BDEs. This is likely to minimise its partitioning to sediment. Benthic degradation

358 processes are a further possible cause and have been reported for DBE-DBCH in aerobic and  
359 anaerobic soil<sup>52</sup>. In European sediment it has been reported in German river sediments<sup>36</sup>.  
360 Outside Europe, DBE-DBCH was reported in sediments of the Great Lakes<sup>53</sup> for the first time  
361 in 2012, as well as in Chinese river and marine sediments<sup>39 40</sup>.

362

363

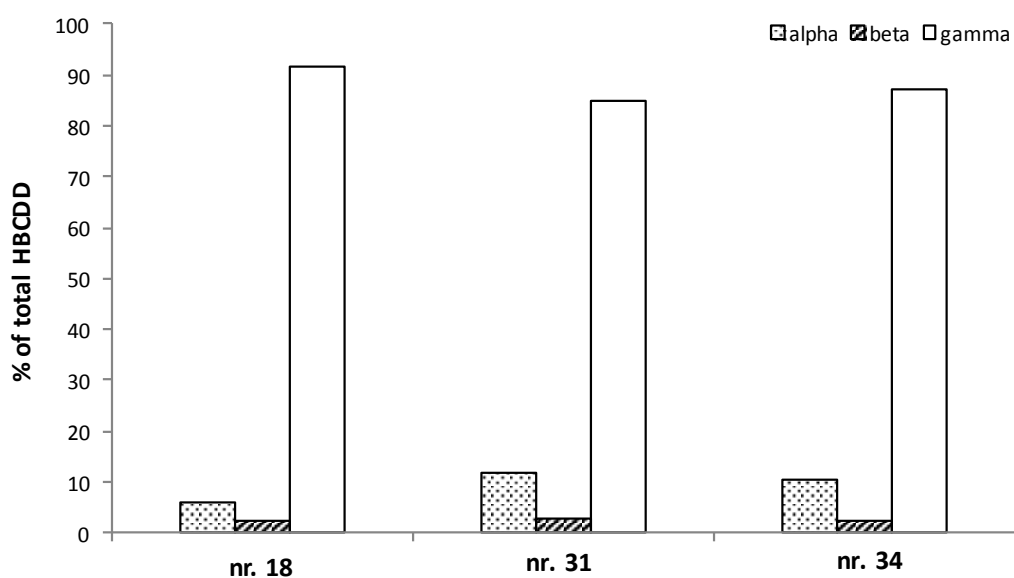
### 364 **3.5. Spatial trends in concentrations of PBDEs and NBFRs**

365 Spatial variation in BFR concentrations in sediments from the River Thames is shown in  
366 Figure 3 for  $\Sigma_{12}$ BDEs, HBCDDs and TBBPA (top), as well as  $\Sigma_{12}$ BDEs, BEH-TEBP, BTBPE and TBP  
367 (bottom). As shown, samples from the industrial area (numbers 13-34) showed substantially  
368 higher concentrations compared to both: (a) samples from the inner (numbers 1-12) and (b)  
369 outer (numbers 35-45) Thames. These differences were shown to be significant ( $p < 0.05$ ) via  
370 an ANOVA test of samples from the 3 groups. Inspection of the lower panel in Figure 5  
371 reveals that concentrations of  $\Sigma_{12}$ BDEs and BEH-TEBP show a similar concentration pattern  
372 along the river, possibly indicating the same source input. BTBPE and TBP on the other hand  
373 show only a few localised input hotspots.

374

375 HBCDDs in the industrial area showed three distinct locations with very high concentrations,  
376 around Gallions Reach (site nr. 18), St Clement's Reach (nr. 31) and Tilbury (nr. 34). A  
377 possible explanation could be the vicinity to sewage discharge locations, in close vicinity to  
378 site #s 30-33 (Long Reach STP) and 34-35 (Tilbury STP). Other sources impacting the  
379 sediments in this area could be discharges from activities utilising HBCDDs in their products,  
380 such as building and construction facilities, as well as textile manufacturers. Inspection of  
381 HBCDD diastereomer profiles at the three locations above, revealed the profile to resemble

382 that of the technical mixture, with  $\gamma$ -HBCDD predominant (85-92 %), followed by  $\alpha$ -HBCDD  
383 (6-12 %) and  $\beta$ -HBCDD (2-3 %) only present in small quantities (Figure 3). This could indicate  
384 fresh input sources at the locations of the analysed sediments, as the diastereomer profile in  
385 these samples differs markedly from that in other samples (Figure 4). On average, the  
386 diastereomer profile in samples from the industrial area contained mainly  $\gamma$ -HBCDD,  
387 followed by  $\alpha$ -HBCDD and only minor amounts of  $\beta$ -HBCDD, while in the non-industrial area  
388 the ratio between the three stereoisomers was more equal (Figure 4).  
389

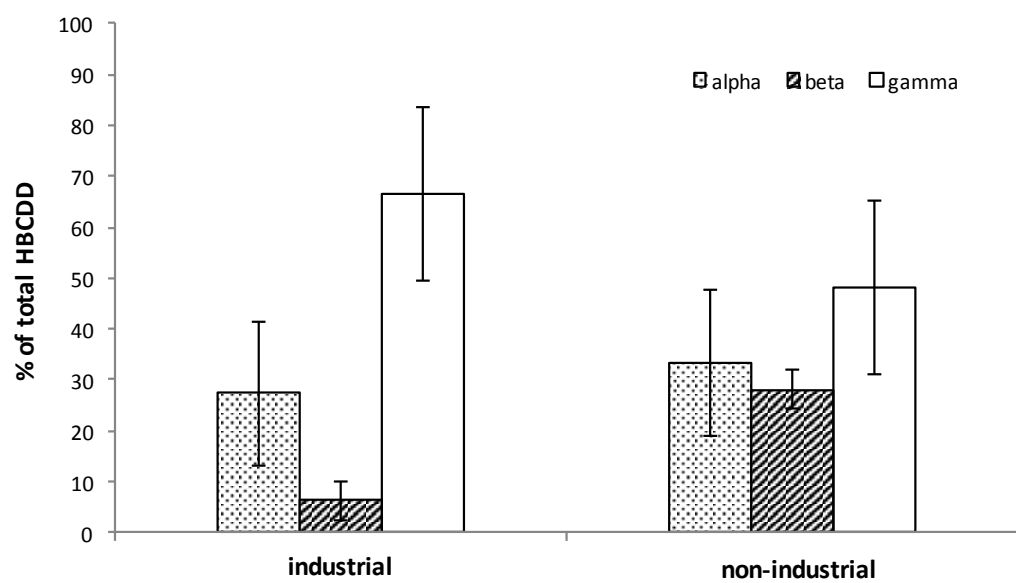


390

391 **Figure 3. HBCDD diastereomer profile in sediment from location #s 18, 31, and 34**

392

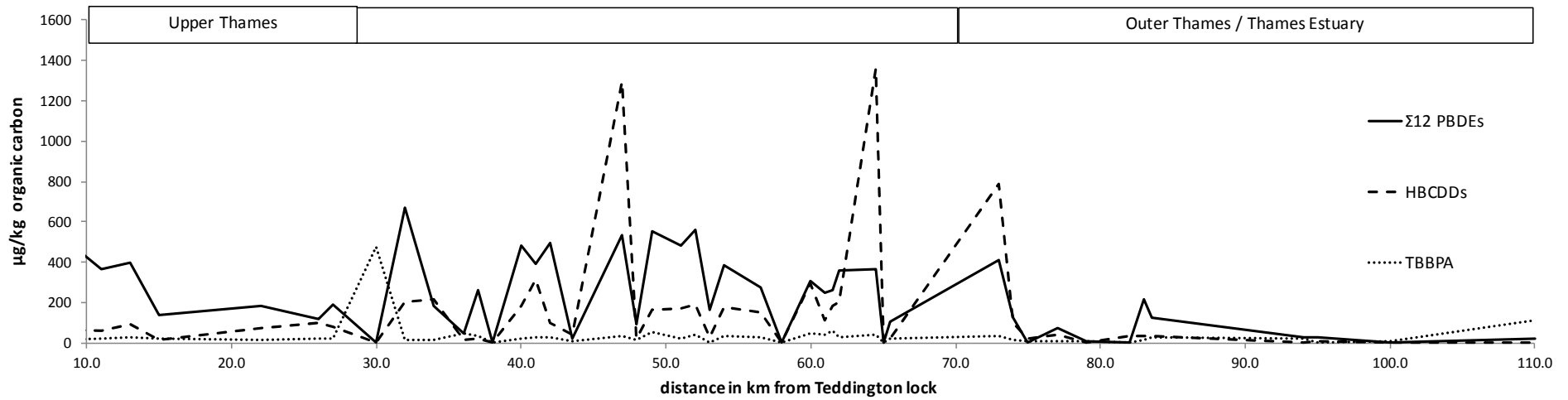
393



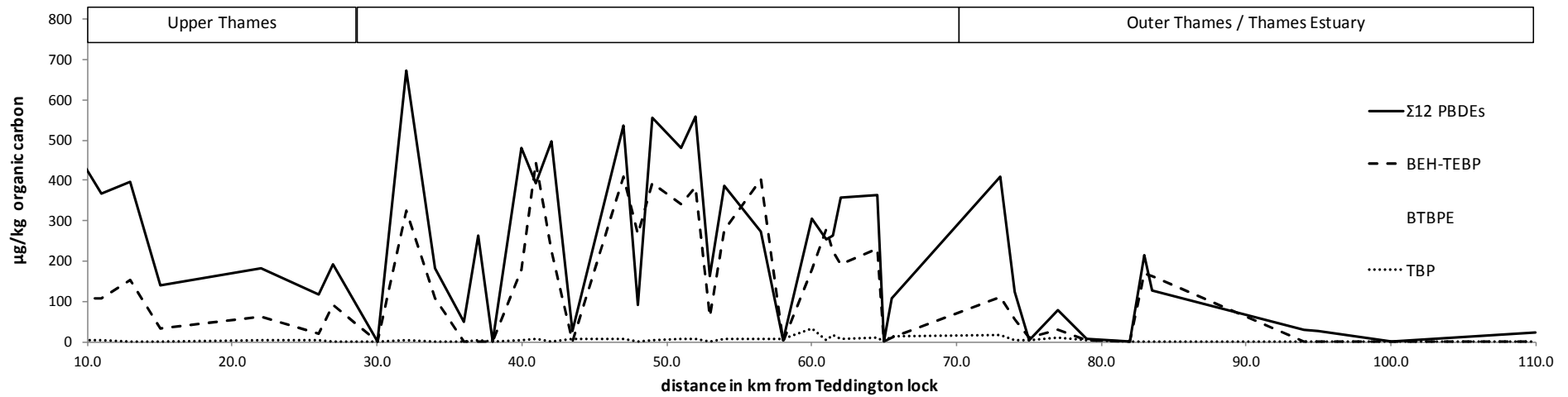
394

395 **Figure 4. Average HBCDD diastereomer profile in industrial and non-industrial area**

396



397



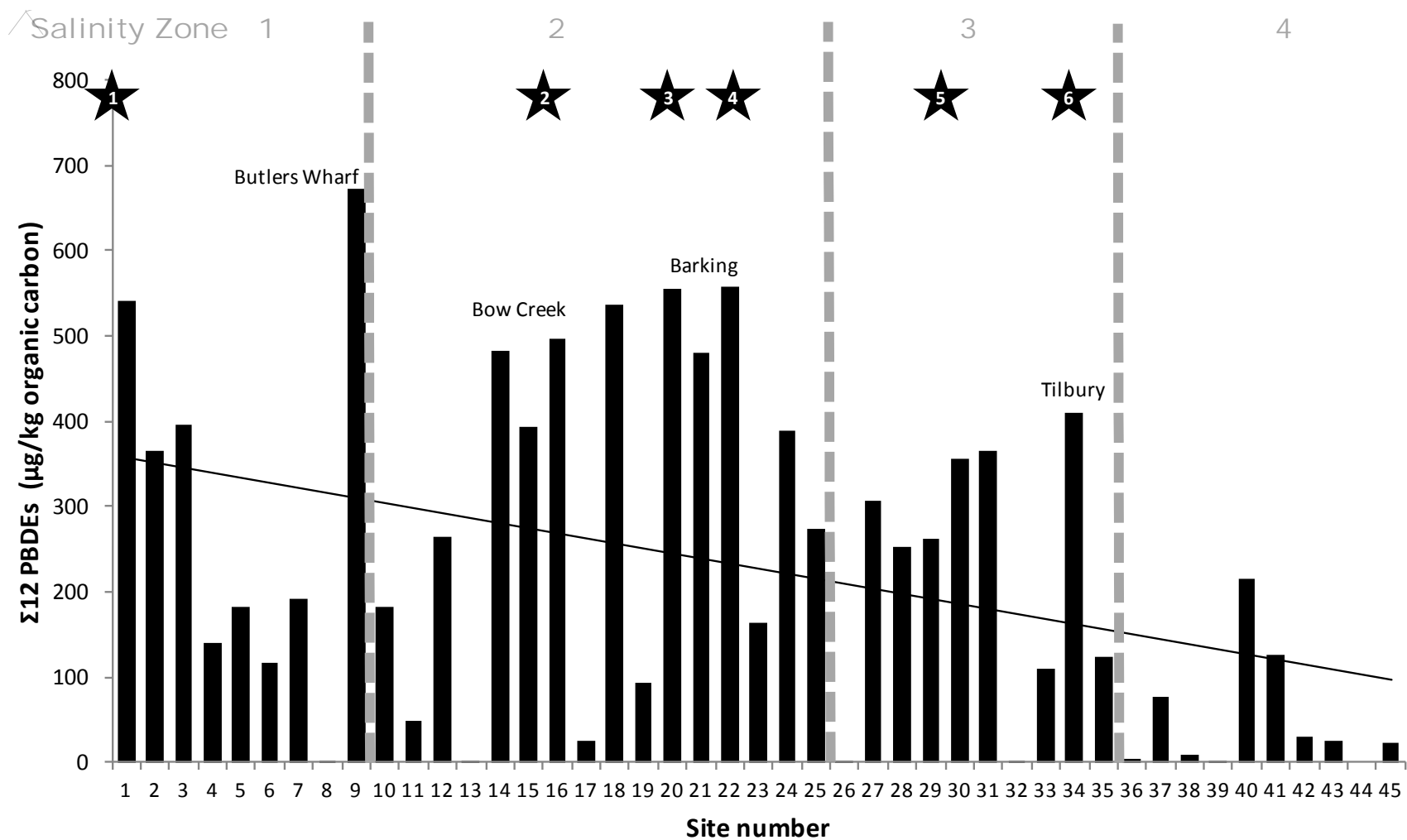
398

399 **Figure 3. Spatial trends for  $\Sigma_{12}$ BDEs, HBCDDs, and TBBPA (top) and  $\Sigma_{12}$ BDEs, BEH-TEBP, BTBPE, and TBP (bottom) measured (in  $\mu\text{g kg}^{-1}$**   
 400 **organic carbon) along the river Thames, with an approximate distance (km) from Teddington Lock.**  
 401

402 Figure 4 and Figure 5 illustrate the spatial variation in organic carbon-normalised  
403 concentrations of  $\Sigma_{12}$ BDEs and BDE-209 respectively. There is a general high-high-medium-  
404 low concentration profile from west to east for  $\Sigma_{12}$ BDEs (with average concentration values  
405 for the 4 zones of 290, 309, 219 and 51  $\mu\text{g kg}^{-1}$  OC), while for BDE-209 we observe a  
406 medium-high-high-low profile (7291, 9299, 9834 and 3255  $\mu\text{g kg}^{-1}$  OC), and a much less  
407 marked attenuation in concentrations on travelling west to east. This could be a possible  
408 indication for different sources of the two groups of compounds. The general decline from  
409 west to east for  $\Sigma_{12}$ BDEs is probably driven by increasing distance from London and  
410 associated urban sources, as well as flocculation-deposition of sediment controlled by  
411 salinity (salting-out) with increasing proximity to the coast. The four salinity zones indicated  
412 were adapted from the study of Pope *et al.*<sup>54</sup>. The observed variability in the PBDE transect  
413 data can be explained by the fact that suspended particles can travel up and down-stream by  
414 10 - 20 km on one tide.

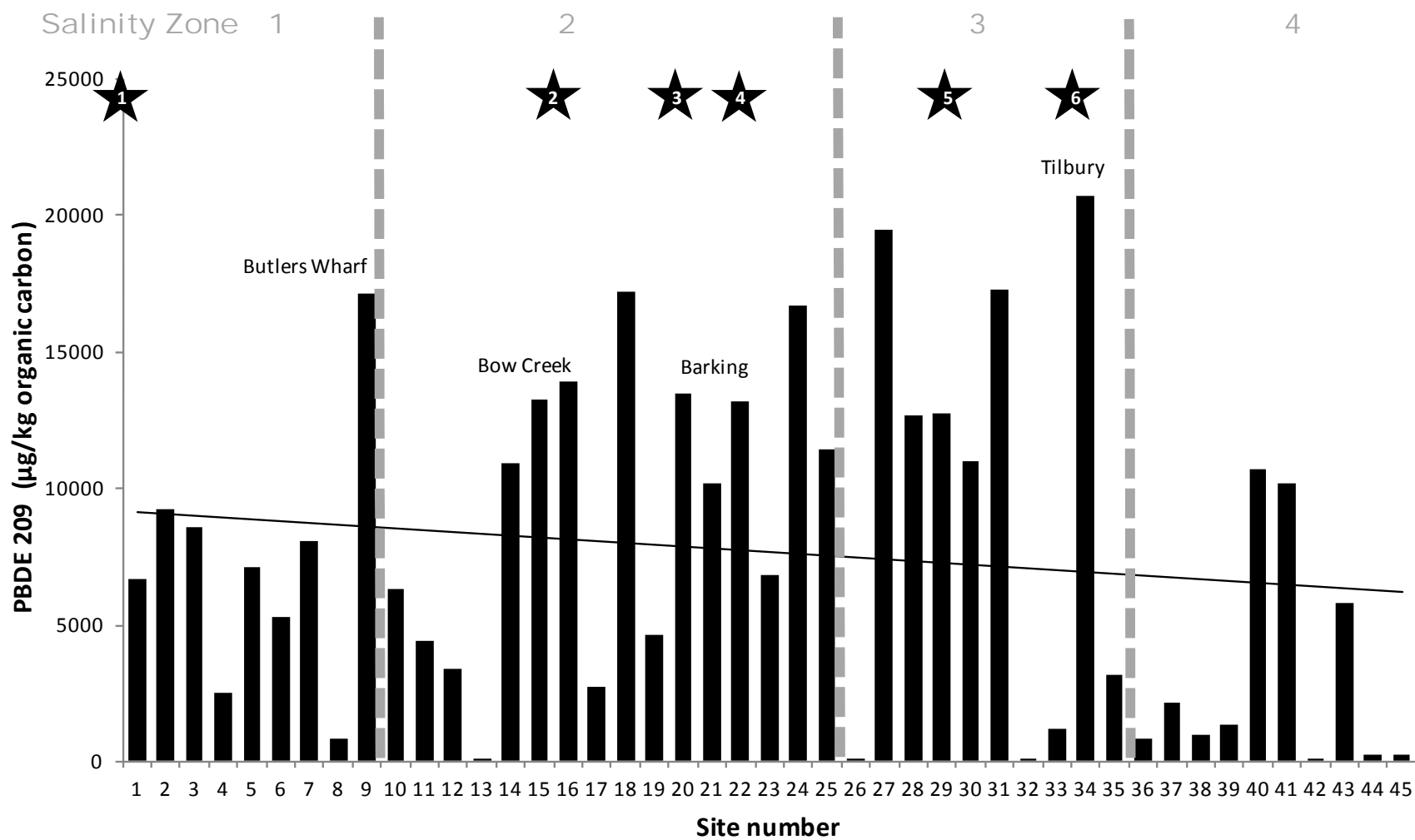
415

416 Sites like Bow Creek (site # 15) which receive contamination discharged from the Lea Valley  
417 due to industrial activity, Barking (# 21), a site situated close to a major sewage outfall  
418 Beckton from a sewage treatment plant (STP) and Tilbury (# 34) with its docks, power station  
419 and another STP show higher concentrations of  $\Sigma_{12}$ BDEs and BDE-209 related to the  
420 intensive land-river-use.



421

422 **Figure 4. Concentrations ( $\mu\text{g kg}^{-1}$  organic carbon) of  $\Sigma_{12}$  PBDEs in River Thames sediments at each sampling location. Stars represent the main**  
 423 **discharge locations of sewage effluents; 1. Mogden; 2. Abbey Mills; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP; 6. Tilbury STP.**  
 424 **Adapted from Lopes dos Santos and Vane <sup>27</sup>. STP – sewage treatment plants**



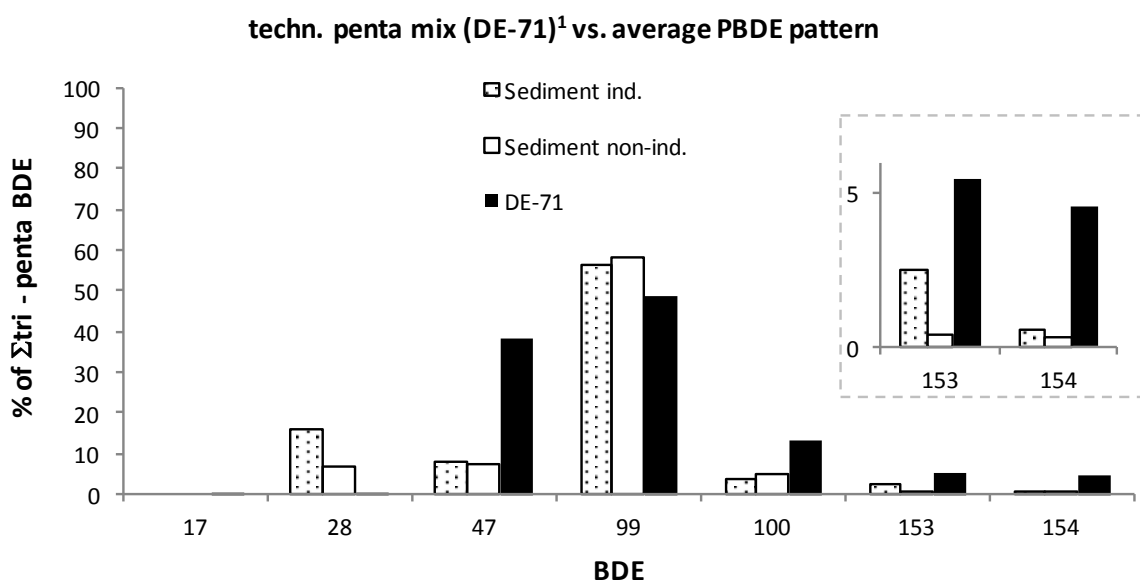
425

426 **Figure 5. Concentrations ( $\mu\text{g kg}^{-1}$  organic carbon) of BDE-209 in River Thames sediments at each sampling location. Stars represent the main**  
 427 **discharge locations of sewage effluents; 1. Mogden; 2. Abbey Mills; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP; 6. Tilbury STP.**  
 428 **Adapted from Lopes dos Santos and Vane <sup>27</sup>. STP – sewage treatment plants**

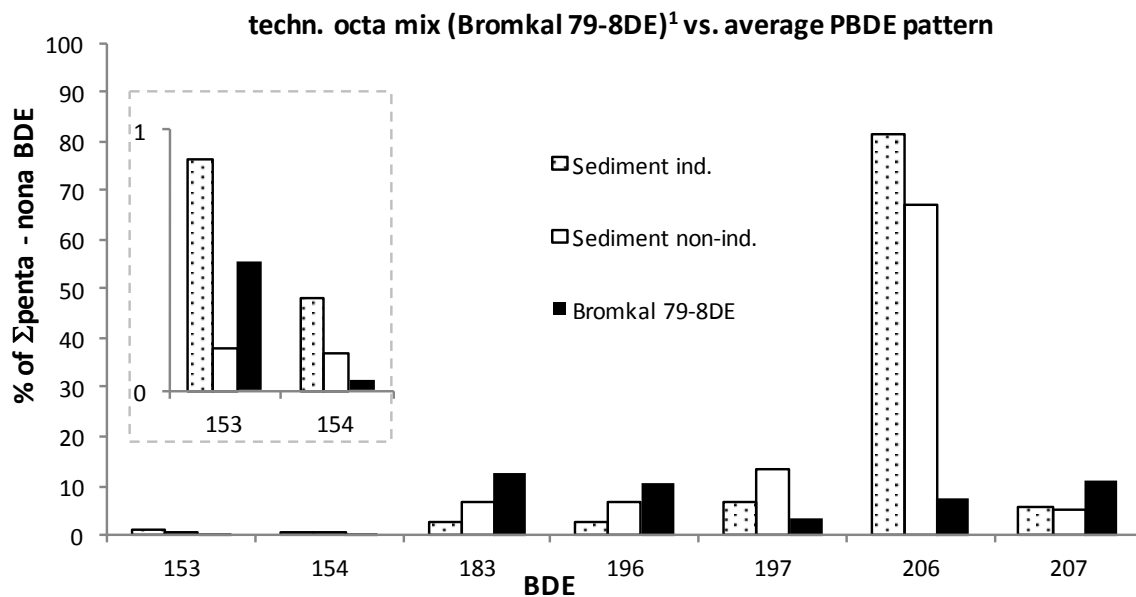


429 **3.6. PBDE/NBFR patterns**

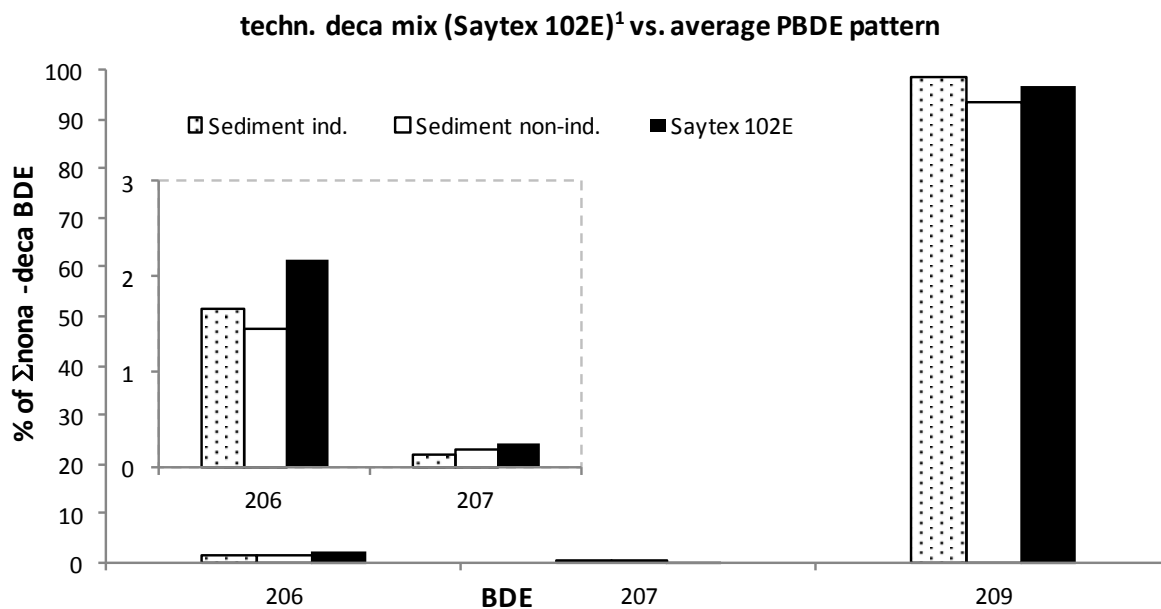
430 Figure 6 compares the average PBDE profile of the industrial area and the non-industrial one  
 431 against the Penta-, Octa-, and Deca- technical PBDE mixes. While caution must be exercised  
 432 when comparing congener profiles in environmental samples with those in the commercial  
 433 formulations, as congener-specific differences in physicochemical properties will modify the  
 434 congener profile between source and receptor; in general, no significant differences can be  
 435 observed between the pattern of PBDEs between the industrial and non-industrial area.  
 436 Compared to the technical Penta-BDE mixture, the PBDE profile pattern in our sediment is  
 437 shifted towards lower brominated congeners such as BDE-28, possibly indicating  
 438 debromination. In the Penta-BDE mixture, the ratio of BDE-47:99 is 0.79<sup>55</sup>, while in our  
 439 samples a shift towards BDE-99 is observable, most likely due the stronger tendency of BDE-  
 440 99 to partition to sediments. For the Octa-BDE technical mixture, the differences between  
 441 our sample and the technical mixture most likely relate to infrequent application and  
 442 emission of Octa-BDE in the UK. Technical Deca-BDE on the other hand, showed little  
 443 deviation from the pattern in our sediment, indicating widespread recent UK use and  
 444 application of this technical mixture.



445



446



447

448 **Figure 6. Comparison of an average PBDE profile in the industrial area (dotted) and outside**  
 449 **the industrial area (white) to a technical penta / octa / deca BDE mix (black) – <sup>1</sup> technical**  
 450 **mixture values adapted from La Guardia et al.<sup>55</sup>**

451

452 **3.7. Screening for degradation products and selected NBFRs**

453 The UPLC-HRMS used in this study proved to be an excellent platform for the identification  
 454 and quantification of PBDEs and NBFRs. Moreover, rapid HRMS analysis in full scan mode

455 allows post-acquisition data analysis for further identification of compounds/transformation  
456 products of interest (e.g. potential degradation products and NBRs).

457 To screen for further brominated compounds in the sample set, a Br trace ( $m/z = 78.918336$   
458 /  $80.916290$ ) was queried from the full scan - all ion fragmentation (AIF) acquisition using  
459 Xcalibur software. This revealed the presence of brominated compounds with shorter  
460 retention times than brominated PBDEs. Further investigation of the accurate mass, isotope  
461 patterns and comparison to the high resolution mass spectrum of hydroxylated PBDE (OH-  
462 BDE) standards revealed the identified peaks as OH-BDEs (further details are provided in the  
463 SI section). Unlike PBDEs, OH-BDEs have not been produced industrially and are not known  
464 by-products of technical brominated formulations<sup>56, 57</sup>. However, OH-BDEs have been  
465 reported in biotic and abiotic samples of the aquatic and marine environment, such as  
466 salmon<sup>56</sup>, mussels<sup>58</sup>, algae<sup>59</sup> as well as sediments<sup>60</sup>, surface waters<sup>61</sup> and sewage treatment  
467 plant effluents<sup>62</sup>. Studies suggest that they are natural products of marine environments, as  
468 well as a result of metabolic biotransformation from anthropogenic PBDEs<sup>59, 61</sup>. The position  
469 of the hydroxyl group (OH) has been postulated to be an indicator of whether OH-BDE  
470 congeners are formed through oxidation or metabolic reactions<sup>56, 58, 60</sup>. Possible sources and  
471 transformation found in the literature include microbial aerobic degradation<sup>63, 64</sup>,  
472 photochemical reactions of bromophenols<sup>65</sup> and PBDEs<sup>66</sup>, transformation of bromophenols  
473 by marine bacteria<sup>67</sup> and a red algae enzyme<sup>57</sup>, reactions of PBDEs with atmospheric OH  
474 radicals<sup>61</sup>, as well as in sewage treatment plants through oxidative reactions and excretion of  
475 human and animal metabolites<sup>61</sup>. Whether the OH-BDEs detected in the Thames sediments  
476 are of environmental and/or biological origin is beyond the scope of this paper. However,  
477 since OH-BDEs have been reported to exhibit similar or even enhanced toxic<sup>68</sup> and

478 estrogenic<sup>69</sup> effects on both human<sup>70</sup> and wildlife<sup>71, 72</sup> compared to PBDEs, their presence  
479 and relevance needs to be further investigated.

480 Barber *et al.*<sup>19</sup> reported on the presence of a wide range of NBRs in UK sediments.  
481 However, screening of our sediment samples for those such as: 2,3,5,6-tetrabromo-*p*-xylene  
482 (TBX), tris(2,3-dibromopropyl) phosphate (TDBPP), tetrabromo-bisphenoldiallylether  
483 (TBBPA-DAE), tetrabromobisphenol-bis(2,3-dibromopropylether) (TBBPA-DBPE),  
484 octabromotrimethyl-phenylindane (OBTMPI/OBIND), pentabromophenol (PBP) and  
485 pentabromobenzyl acrylate (PBB-Acr) did not reveal them to be present in our study.

486

487

#### 488 **4. Summary**

489 Brominated flame retardants have found wide application in consumer products and  
490 building materials. Densely populated areas such as London with its large industrial  
491 hinterland can thus act as emission sources of these chemicals. Since the river Thames  
492 passes through this area, it can act as an indicator of such emissions. Our data suggest that  
493 the input and presence of industrial activity and sewage treatment plants is a major source  
494 of BFRs to the river.

495

496 This is the first extensive study targeting several legacy BFRs and NBRs in sediments along  
497 the tidal River Thames. Results indicate that BDE-209 is the predominant congener in all  
498 samples, accounting for ~ 95 % of total PBDEs detected, with a concentration range of <0.1  
499 to 540  $\mu\text{g kg}^{-1}$  dw. This finding is of interest due to the recent listing of Deca-BDE under the  
500 Stockholm Convention, which underlines the current and future environmental concern over  
501 this BFR. Further, possible evidence of environmental debromination of Penta-BDE was

502 observed through the elevated relative abundance of BDE-28 in sediment compared to that  
503 in the Penta-BDE formulation. NFRs were detected in the following order (detection  
504 frequency): BEH-TEBP (76 %) > TBP (69 %) > BTBPE (51 %); with DBDPE (20 %), DP (11 %) and  
505 PBEB (7 %) identified only in a few samples. Concentrations of BEH-TEBP were found to be of  
506 a comparable range to those found for  $\Sigma_{12}$ BDEs in this study, as well as showing a similar  
507 concentration pattern along the river, possibly indicating a similar source input. Spatial  
508 variation analysis of the sediment samples further revealed that locations within the  
509 industrial area of London had significantly higher concentrations of  $\Sigma_{12}$ BDEs, HBCDDs, TBBPA,  
510 as well as BEH-TEBP, BTBPE and TBP. Analysis of HBCDD diastereomer patterns revealed  
511 samples from three locations within the industrial area possessed comparatively high  
512 concentrations and diastereomer profiles matching those of the technical mixture. This  
513 could possibly indicate fresh input sources at these locations.

514 The presence of hydroxylated PBDEs suggests the presence of transformation products in  
515 our sediments. Sources, formation reactions and impact on the environment and human  
516 health of these compounds have to be further investigated, along with the presence of other  
517 possible transformation products.

518

## 519 **5. Acknowledgements**

520 The research leading to these results has received funding from the Marie Curie Actions of  
521 the European Union's FP7 Programme under REA grant agreement # 606857 (ELUTE  
522 project). Thanks to Professor Adrian Covaci from the University of Antwerp for kindly  
523 providing the OH-PBDE standards. C.H. Vane publishes with permission of the Executive  
524 Director, British Geological Survey.

525

526 **References**

- 527 1. Shaw, S. D.; Blum, A.; Weber, R.; Kannan, K.; Rich, D.; Lucas, D.; Koshland, C. P.; Dobraca, D.;  
528 Hanson, S.; Birnbaum, L. S., Halogenated flame retardants Do the fire safety benefits justify the risks.  
529 *Organohalogen Compounds* **2010**, *73*, 2036-2039.
- 530 2. Barceló, D.; Eljarrat, E., *Brominated Flame Retardants*. 2011; Vol. 16.
- 531 3. Dirtu, A. C.; Ionas, A. C.; Malarvannan, G.; Covaci, A., Transformation Products of Brominated  
532 Flame Retardants (BFRs). In *Transformation Products of Emerging Contaminants in the Environment:  
533 Analysis, Processes, Occurrence, Effects and Risks*, Lambropoulou, D. A.; Nollet, L. M. L., Eds. John  
534 Wiley and Sons Ltd: Chichester, United Kingdom, 2014; pp 545-576.
- 535 4. Covaci, A.; Harrad, S.; Abdallah, M. A.; Ali, N.; Law, R. J.; Herzke, D.; de Wit, C. A., Novel  
536 brominated flame retardants: a review of their analysis, environmental fate and behaviour.  
537 *Environment International* **2011**, *37*, (2), 532-56.
- 538 5. de Wit, C. A.; Kierkegaard, A.; Ricklund, N.; Sellström, U., Emerging Brominated Flame  
539 Retardants in the Environment. In *Brominated Flame Retardants*, Eljarrat, E.; Barceló, D., Eds.  
540 Springer-Verlag: Berlin Heidelberg, 2011; Vol. 16, pp 241-286.
- 541 6. Ezechias, M.; Covino, S.; Cajthaml, T., Ecotoxicity and biodegradability of new brominated  
542 flame retardants: A review. *Ecotoxicology and Environmental Safety* **2014**, *110*, 153-167.
- 543 7. Lyche, J. L.; Rosseland, C.; Berge, G.; Polder, A., Human health risk associated with  
544 brominated flame-retardants (BFRs). *Environment International* **2015**, *74*, 170-80.
- 545 8. Hoffman, K.; Adgent, M.; Goldman, B. D.; Sjodin, A.; Daniels, J. L., Lactational Exposure to  
546 Polybrominated Diphenyl Ethers and Its Relation to Social and Emotional Development among  
547 Toddlers. *Environmental Health Perspective* **2012**, *120*, (10), 1438-1442.
- 548 9. Bradman, A.; Castorina, R.; Sjodin, A.; Fenster, L.; Jones, R. S.; Harley, K. G.; Chevrier, J.;  
549 Holland, N. T.; Eskenazi, B., Factors associated with serum polybrominated diphenyl ether (PBDE)  
550 levels among school-age children in the CHAMACOS cohort. *Environmental Science & Technology*  
551 **2012**, *46*, (13), 7373-81.
- 552 10. Berghuis, S. A.; Bos, A. F.; Sauer, P. J.; Roze, E., Developmental neurotoxicity of persistent  
553 organic pollutants: an update on childhood outcome. *Archives of Toxicology* **2015**, *89*, (5), 687-709.
- 554 11. Linares, V.; Belles, M.; Domingo, J. L., Human exposure to PBDE and critical evaluation of  
555 health hazards. *Archives of Toxicology* **2015**, *89*, (3), 335-56.
- 556 12. Berr, J. S.; Stapleton, H. M.; Mitchelmore, C. L., Accumulation and DNA damage in fathead  
557 minnows (*Pimephales promelas*) exposed to 2 brominated flame-retardant mixtures, Firemaster®  
558 550 and Firemaster® BZ-54. *Environmental toxicology and chemistry / SETAC* **2010**, *29*, (3), 722-729.
- 559 13. Sun, R. B.; Xi, Z. G.; Yan, J.; Yang, H. L., Cytotoxicity and apoptosis induction in human HepG2  
560 hepatoma cells by decabromodiphenyl ethane. *Biomedical and Environmental Sciences* **2012**, *25*, (5),  
561 495-501.
- 562 14. Segev, O.; Kushmaro, A.; Brenner, A., Environmental impact of flame retardants (persistence  
563 and biodegradability). *International Journal of Environmental Research and Public Health* **2009**, *6*, (2),  
564 478-91.
- 565 15. Yang, C.; Rose, N. L.; Turner, S. D.; Yang, H.; Goldsmith, B.; Losada, S.; Barber, J. L.; Harrad, S.,  
566 Hexabromocyclododecanes, polybrominated diphenyl ethers, and polychlorinated biphenyls in  
567 radiometrically dated sediment cores from English lakes, ~1950-present. *The Science of the total  
568 environment* **2016**, *541*, 721-728.
- 569 16. Harrad, S.; Abdallah, M. A.; Rose, N. L.; Turner, S. D.; Davidson, T. A., Current-Use Brominated  
570 Flame Retardants in Water, Sediment, and Fish from English Lakes. *Environmental Science &  
571 Technology* **2009**, *43*, 9077-9083.
- 572 17. Rippey, B.; Rose, N.; Yang, H.; Harrad, S.; Robson, M.; Travers, S., An assessment of toxicity in  
573 profundal lake sediment due to deposition of heavy metals and persistent organic pollutants from  
574 the atmosphere. *Environment International* **2008**, *34*, (3), 345-56.
- 575 18. Allchin, C. R.; Law, R. J.; Morris, S., Polybrominated diphenylethers in sediments and biota  
576 downstream of potential sources in the UK. *Environmental Pollution* **1999**, *105*, 197-207.

- 577 19. Barber, J. L.; Losada, S.; Bersuder, P.; Maes, T.; Bolam, S.; Lyons, B.; Law, R. J., Halogenated  
578 flame retardants in UK sediments. *Organohalogen Compounds* **2014**, *76*, (1348), 1348-1351.
- 579 20. Morris, S.; Allchin, C. R.; Zegers, B. N.; Haftka, J. J. H.; Boon, J. P.; Belpaire, C.; Leonards, P. E.;  
580 van Leeuwen, S. P. J.; de Boer, J., Distribution and Fate of HBCD and TBBPA Brominated Flame  
581 Retardants in North Sea Estuaries and Aquatic Food Webs. *Environmental Science & Technology*  
582 **2004**, *38*, 5497-5504.
- 583 21. Lu, Q.; Jürgens, M. D.; Johnson, A. C.; Crosse, J.; Whitehead, P., Persistent Organic Pollutants  
584 in sediment and fish in the River Thames Catchment (UK). *The Science of the total environment* **2017**,  
585 *576*, 78–84.
- 586 22. Webster, L.; Russell, M.; Walsham, P.; Phillips, L. A.; Hussy, I.; Packer, G.; Dalgarno, E. J.;  
587 Moffat, C. F., An assessment of persistent organic pollutants in Scottish coastal and offshore marine  
588 environments. *Journal of Environmental Monitoring* **2011**, *13*, (5), 1288-307.
- 589 23. Russell, M.; Robinson, C. D.; Walsham, P.; Webster, L.; Moffat, C. F., Persistent organic  
590 pollutants and trace metals in sediments close to Scottish marine fish farms. *Aquaculture* **2011**, *319*,  
591 (1-2), 262-271.
- 592 24. Littlewood, M.; Crossman, M. *Planning for Flood Risk Management in the Thames Estuary*; in  
593 Technical Scoping Report. Environment Agency: 2003.
- 594 25. Vane, C. H.; Beriro, D. J.; Turner, G. H., Rise and fall of mercury (Hg) pollution in sediment  
595 cores of the Thames Estuary, London, UK. *Earth and Environmental Science Transactions of the Royal*  
596 *Society of Edinburgh* **2015**, *105*, (04), 285-296.
- 597 26. Tye, A. M.; Rushton, J.; Vane, C. H., Distribution and speciation of phosphorus in foreshore  
598 sediments of the Thames estuary, UK. *Marine Pollution Bulletin* **2018**, *127*, 182-197.
- 599 27. Lopes dos Santos, R. A.; Vane, C. H., Signatures of tetraether lipids reveal anthropogenic  
600 overprinting of natural organic matter in sediments of the Thames Estuary, UK. *Organic*  
601 *Geochemistry* **2016**, *93*, 68-76.
- 602 28. Vane, C. H.; Harrison, I.; Kim, A. W., Polycyclic aromatic hydrocarbons (PAHs) and  
603 polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, U.K. *The Science of the total*  
604 *environment* **2007**, *374*, (1), 112-26.
- 605 29. Beriro, D. J.; Vane, C. H.; Cave, M. R.; Nathanail, C. P., Effects of drying and comminution type  
606 on the quantification of Polycyclic Aromatic Hydrocarbons (PAH) in a homogenised gasworks soil and  
607 the implications for human health risk assessment. *Chemosphere* **2014**, *111*, 396-404.
- 608 30. Taylor, J. K., *Quality Assurance of Chemical Measurements*. 1984.
- 609 31. Vane, C. H.; Ma, Y. J.; Chen, S. J.; Mai, B. X., Increasing polybrominated diphenyl ether (PBDE)  
610 contamination in sediment cores from the inner Clyde Estuary, UK. *Environmental Geochemistry and*  
611 *Health* **2010**, *32*, (1), 13-21.
- 612 32. Zhang, X. L.; Luo, X. J.; Chen, S. J.; Wu, J. P.; Mai, B. X., Spatial distribution and vertical profile  
613 of polybrominated diphenyl ethers, tetrabromobisphenol A, and decabromodiphenylethane in river  
614 sediment from an industrialized region of South China. *Environmental Pollution* **2009**, *157*, (6), 1917-  
615 23.
- 616 33. Yang, C. *Persistent Organic Pollutants in lacustrine environments*. University of Birmingham,  
617 Birmingham, 2014.
- 618 34. Webster, L.; Russell, M.; Adefehinti, F.; Dalgarno, E. J.; Moffat, C. F., Preliminary assessment  
619 of polybrominated diphenyl ethers (PBDEs) in the Scottish aquatic environment, including the Firth of  
620 Clyde. *Journal of Environmental Monitoring* **2008**, *10*, (4), 463-73.
- 621 35. Harrad, S., A meta-analysis of recent data on UK environmental levels of POP-BFRs in an  
622 international context: Temporal trends and an environmental budget. *Emerging Contaminants* **2015**,  
623 *1*, (1), 39-53.
- 624 36. Suhring, R.; Barber, J. L.; Wolschke, H.; Kotke, D.; Ebinghaus, R., Fingerprint analysis of  
625 brominated flame retardants and Dechloranes in North Sea sediments. *Environmental Research*  
626 **2015**, *140*, 569-78.
- 627 37. Olukunle, O. I.; Okonkwo, O. J., Concentration of novel brominated flame retardants and  
628 HBCD in leachates and sediments from selected municipal solid waste landfill sites in Gauteng  
629 Province, South Africa. *Waste Management* **2015**.

- 630 38. La Guardia, M. J.; Hale, R. C.; Newman, B., Brominated flame-retardants in Sub-Saharan  
631 Africa: burdens in inland and coastal sediments in the eThekweni metropolitan municipality, South  
632 Africa. *Environmental Science & Technology* **2013**, *47*, (17), 9643-50.
- 633 39. Lam, J. C. W.; Zhu, B. Z.; Xia, C. H.; Yang, S. Y.; Li, X. L.; Lam, P. K. S., Emerging halogenated  
634 flame retardants in coastal region of China. *Organohalogen Compounds* **2013**, *75*, 1269-1272.
- 635 40. Zhu, B.; Lam, J. C.; Yang, S.; Lam, P. K., Conventional and emerging halogenated flame  
636 retardants (HFRs) in sediment of Yangtze River Delta (YRD) region, East China. *Chemosphere* **2013**,  
637 *93*, (3), 555-60.
- 638 41. Knudsen, G. A.; Hughes, M. F.; Sanders, J. M.; Hall, S. M.; Birnbaum, L. S., Estimation of  
639 human percutaneous bioavailability for two novel brominated flame retardants, 2-ethylhexyl 2,3,4,5-  
640 tetrabromobenzoate (EH-TBB) and bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP). *Toxicology  
641 and Applied Pharmacology* **2016**, *311*, 117-127.
- 642 42. Al-Omran, L. S.; Harrad, S., Distribution pattern of legacy and "novel" brominated flame  
643 retardants in different particle size fractions of indoor dust in Birmingham, United Kingdom.  
644 *Chemosphere* **2016**, *157*, 124-131.
- 645 43. Tao, F.; Abdallah, M. A.; Harrad, S., Emerging and Legacy Flame Retardants in UK Indoor Air  
646 and Dust: Evidence for Replacement of PBDEs by Emerging Flame Retardants? *Environmental Science  
647 & Technology* **2016**, *50*, (23), 13052-13061.
- 648 44. Drage, D. S.; Newton, S.; de Wit, C. A.; Harrad, S., Concentrations of legacy and emerging  
649 flame retardants in air and soil on a transect in the UK West Midlands. *Chemosphere* **2016**, *148*, 195-  
650 203.
- 651 45. Tao, F.; Abou-Elwafa Abdallah, M.; Ashworth, D. C.; Douglas, P.; Toledano, M. B.; Harrad, S.,  
652 Emerging and legacy flame retardants in UK human milk and food suggest slow response to  
653 restrictions on use of PBDEs and HBCDD. *Environment International* **2017**, *105*, 95-104.
- 654 46. Poma, G.; Roscioli, C.; Guzzella, L., PBDE, HBCD, and novel brominated flame retardant  
655 contamination in sediments from Lake Maggiore (Northern Italy). *Environmental Monitoring and  
656 Assessment* **2014**, *186*, (11), 7683-92.
- 657 47. Kierkegaard, A.; Björklund, T.; Friden, U., Identification of the Flame Retardant  
658 Decabromodiphenyl Ethane in the Environment. *Environmental Science & Technology* **2004**, *38*,  
659 3247-3253.
- 660 48. Baron, E.; Eljarrat, E.; Barcelo, D., Gas chromatography/tandem mass spectrometry method  
661 for the simultaneous analysis of 19 brominated compounds in environmental and biological samples.  
662 *Analytical and bioanalytical chemistry* **2014**, *406*, (29), 7667-76.
- 663 49. Suhring, R.; Busch, F.; Fricke, N.; Kotke, D.; Wolschke, H.; Ebinghaus, R., Distribution of  
664 brominated flame retardants and dechloranes between sediments and benthic fish--A comparison of  
665 a freshwater and marine habitat. *The Science of the total environment* **2016**, *542*, (Pt A), 578-85.
- 666 50. Kolic, T. M.; Shen, L.; MacPherson, K.; Fayed, L.; Gobran, T.; Helm, P. A.; Marvin, C. H.;  
667 Arsenault, G.; Reiner, E. J., The Analysis of Halogenated Flame Retardants by GC-HRMS in the  
668 Environment. *Journal of Chromatographic Science* **2009**, *47*, 83-91.
- 669 51. Urs, J., Emerging Brominated Flame Retardants in Sediments and Soils: a Review. *Current  
670 Pollution Reports* **2016**, *2*, (4), 213-223.
- 671 52. Nyholm, J. R.; Lundberg, C.; Andersson, P. L., Biodegradation kinetics of selected brominated  
672 flame retardants in aerobic and anaerobic soil. *Environmental Pollution* **2010**, *158*, (6), 2235-40.
- 673 53. Yang, R.; Wei, H.; Guo, J.; Li, A., Emerging brominated flame retardants in the sediment of the  
674 Great Lakes. *Environmental Science & Technology* **2012**, *46*, (6), 3119-26.
- 675 54. Pope, N. D.; Langston, W. J., Sources, distribution and temporal variability of trace metals in  
676 the Thames Estuary. *Hydrobiologia* **2011**, *672*, (1), 49-68.
- 677 55. La Guardia, M. J.; Hale, R. C.; Harvey, E., Detailed PBDE Congener Composition of the Widely  
678 Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures. *Environmental Science &  
679 Technology* **2006**, *40*, 6247-6254.
- 680 56. Marsh, G.; Athanasiadou, M.; Bergman, A.; Asplund, L., Identification of Hydroxylated and  
681 Methoxylated Polybrominated Diphenyl Ethers in Baltic Sea Salmon (*Salmo salar*) Blood.  
682 *Environmental Science & Technology* **2004**, *38*, (1), 10-18.



- 683 57. Lin, K.; Yan, C.; Gan, J., Production of hydroxylated polybrominated diphenyl ethers (OH-  
684 PBDEs) from bromophenols by manganese dioxide. *Environmental Science & Technology* **2014**, *48*,  
685 (1), 263-71.
- 686 58. Malmvärn, A.; Marsh, G.; Kautsky, L.; Athanasiadou, M.; Bergman, A.; Asplund, L.,  
687 Hydroxylated and Methoxylated Brominated Diphenyl Ethers in the Red Algae *Ceramium tenuicorne*  
688 and Blue Mussels from the Baltic Sea. *Environmental Science & Technology* **2005**, *39*, (0), 2290-  
689 2997a.
- 690 59. Malmvärn, A.; Zebühr, Y.; Kautsky, L.; Bergman, A.; Asplund, L., Hydroxylated and  
691 methoxylated polybrominated diphenyl ethers and polybrominated dibenzo-p-dioxins in red alga and  
692 cyanobacteria living in the Baltic Sea. *Chemosphere* **2008**, *72*, 910-916.
- 693 60. Kerrigan, J. F.; Engstrom, D. R.; Yee, D.; Sueper, C.; Erickson, P. R.; Grandbois, M.; McNeill, K.;  
694 Arnold, W. A., Quantification of Hydroxylated Polybrominated Diphenyl Ethers (OH-BDEs), Triclosan,  
695 and Related Compounds in Freshwater and Coastal Systems. *Plos One* **2015**, *14*, 1-19.
- 696 61. Ueno, D.; Darling, C.; Alae, M.; Pacepavicius, G.; Teixeira, C.; Campbell, L.; Letcher, R. J.;  
697 Bergman, A.; Marsh, G.; Muir, D., Hydroxylated Polybrominated Diphenyl Ethers (OH-PBDEs) in the  
698 Abiotic Environment- Surface Water and Precipitation from Ontario, Canada. *Environmental Science*  
699 *& Technology* **2008**, *42*, 1657-1664.
- 700 62. Hua, W.; Bennett, E. R.; Letcher, R. J., Triclosan in waste and surface waters from the upper  
701 Detroit River by liquid chromatography-electrospray-tandem quadrupole mass spectrometry.  
702 *Environment International* **2005**, *31*, 621-630.
- 703 63. Robrock, K., Aerobic Biotransformation of Polybrominated Diphenyl Ethers (PBDEs) by  
704 Bacterial Isolates. *Environmental Science & Technology* **2009**, *43*, 5705-5711.
- 705 64. Xia, X., Microbial Degradation of Polybrominated Diphenyl Ethers- Current and Future.  
706 *Bioremediation and Biodegradation* **2013**, *4*, (1), 1-2.
- 707 65. Liu, H.; Zhao, H.; Quan, X.; Zhang, Y.; Chen, S.; Zhao, H., Formation of 2'-hydroxy-2,3',4,5' -  
708 tetrabromodiphenyl ether (2'-HO-BDE68) from 2,4-dibromophenol in aqueous solution under  
709 simulated sunlight irradiation. *Chemosphere* **2011**, *84*, 512-518.
- 710 66. Zhao, Q.; Zhao, H.; Quan, X.; Chen, S., Photochemical Formation of Hydroxylated  
711 Polybrominated Diphenyl Ethers (OH-PBDEs) from Polybrominated Diphenyl Ethers (PBDEs) in  
712 Aqueous Solution under Simulated Solar Light Irradiation. *Environmental Science & Technology* **2015**,  
713 *49*, 9092-9099.
- 714 67. Agarwal, V.; El Gamal, A. A.; Yamanaka, K.; Poth, D.; Kersten, R. D.; Schorn, M.; Allen, E. E.;  
715 Moore, B. S., Biosynthesis of polybrominated aromatic organic compounds by marine bacteria.  
716 *Nature Chemical Biology* **2014**, *10*, (8), 640-7.
- 717 68. Su, G.; Yu, H.; Lam, M. H.; Giesy, J. P.; Zhang, X., Mechanisms of toxicity of hydroxylated  
718 polybrominated diphenyl ethers (HO-PBDEs) determined by toxicogenomic analysis with a live cell  
719 array coupled with mutagenesis in *Escherichia coli*. *Environmental Science & Technology* **2014**, *48*,  
720 (10), 5929-37.
- 721 69. Meerts, I. A. T. M.; Letcher, R. J.; Hoving, S.; Marsh, G.; Bergman, A.; Lemmen, J. G.; van der  
722 Burg, B.; Brouwer, A., In Vitro Estrogenicity of Polybrominated Diphenyl Ethers, Hydroxylated PBDEs,  
723 and Polybrominated Bisphenol A Compounds. *Environmental Health Perspectives* **2001**, *109*, (4), 399-  
724 407.
- 725 70. Zota, A. R.; Park, J. S.; Wang, Y.; Petreas, M.; Zoeller, R. T.; Woodruff, T. J., Polybrominated  
726 diphenyl ethers, hydroxylated polybrominated diphenyl ethers, and measures of thyroid function in  
727 second trimester pregnant women in California. *Environmental Science & Technology* **2011**, *45*, (18),  
728 7896-905.
- 729 71. Van Boxtel, A. L.; Kamstra, J. H.; Cnijn, P. H.; Pieterse, B.; Wagner, M. J.; Antink, M.; Krab, K.;  
730 van der Burg, B.; Marsh, G.; Brouwer, A.; Legler, J., Microarray Analysis Reveals a Mechanism of  
731 Phenolic Polybrominated Diphenylether Toxicity in Zebrafish. *Environmental Science & Technology*  
732 **2008**, *42*, 1773-1779.
- 733 72. Legradi, J.; Dahlberg, A. K.; Cnijn, P.; Marsh, G.; Asplund, L.; Bergman, A.; Legler, J.,  
734 Disruption of oxidative phosphorylation (OXPHOS) by hydroxylated polybrominated diphenyl ethers

735 (OH-PBDEs) present in the marine environment. *Environmental Science & Technology* **2014**, *48*, (24),  
736 14703-11.

737