

Legacy PBDEs and NBRs in sediments of the tidal River Thames using liquid chromatography coupled to a high resolution accurate mass Orbitrap mass spectrometer

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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

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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 diphenyl ethers (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 or TBB), bis(2-ethylhexyl)
35 tetrabromophthalate (BEH-TEBP or TBPH), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE),
36 decabromodiphenyl ethane (DBDPE), pentabromoethylbenzene (PBEB), anti/syn-dechlorane
37 plus (a/s-DP), 2,2',4,4',5,5'-hexabromobiphenyl (BB153) and α -, β -1,2-dibromo-4-(1,2-
38 dibromoethyl) cyclohexane (α -, β -DBE-DBCH or TBECH). A novel analysis method based on
39 liquid chromatographic separation, followed by high resolution accurate mass detection
40 using the Orbitrap platform was used for quantification. Results revealed that BDE-209 had
41 the highest concentrations (<0.1 to $540 \mu\text{g kg}^{-1} \text{ dw}$) and detection frequency, accounting for
42 95 % of all PBDE congeners measured. Indicative evidence of debromination of the
43 PentaBDE technical mixture was observed through elevated relative abundance of BDE-28 in
44 sediment compared to the Penta-BDE formulation. NBFRs were detected at comparable
45 levels to PBDEs (excluding BDE-209), which indicates increasing use of the former. Spatial
46 trend analysis showed that samples from industrial areas had significantly higher
47 concentrations of Σ_{12} PBDEs, Σ HBCDDs, TBBPA, BEH-TEBP, BTBPE and TBP. Three locations
48 showed high concentrations of HBCDDs with diastereomer patterns comparable to the
49 technical mixture, which indicate recent input 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)¹. 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 2009². 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 processes³.

64 Due to legislative restrictions on manufacture and use of these BFRs, several so-called novel
65 BFRs (NBFRs) are likely finding wider use⁴. In general, increasing levels of NBFRs are being
66 detected in various matrices relevant to environmental and human health⁵. The
67 environmental impact of NBFRs is potentially similar to the restricted BFRs⁶. Animal studies
68 have shown that exposure to BFRs can have endocrine, reproductive, and behavioural
69 effects at doses comparable to human exposure⁷. Human epidemiological studies have
70 reported association between exposure to BFRs and adverse neurodevelopmental and
71 reproductive effects in humans^{8 9 10 11}. Laboratory studies on NBFRs indicate genotoxicity in
72 aquatic species¹², as well as cytotoxic and anti-proliferation effects with a possible induction
73 of apoptosis in HepG2 cells¹³.

74 BFRs generally have limited biodegradability, are persistent and tend to accumulate in the
75 environment¹⁴. 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 world⁴. 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 lakes¹⁵⁻¹⁷, rivers and estuaries¹⁸⁻²¹, coastal^{19, 22} and marine
80 regions^{19, 23}. However, apart from two UK studies^{19,24}, 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 geology²⁵. 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)²⁶ as well as surface
93 distributions of phosphorus (P)²⁷ and natural tetraether lipids²⁸ 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 **2.1 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 km² and an average discharge of 65.8 m³/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 Thames²⁸.

112

113 **2.2 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 ± 3 m^{26, 28}. At each location, surface
117 sediments (0-5 cm) were collected from four corners of a square of ca. 2 m² area, using
118 either a stainless steel trowel or a polycarbonate tube fitted with a core catcher manually
119 driven into the surface²⁹. 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 γ -HBCDDs, TBBPA / ^{13}C -TBBPA and NBFs 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-
142 TBB), ^{13}C -EH-TBB, bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP), ^{13}C -BEH-TEBP, 1,2-
143 bis(2,4,6-tribromophenoxy)ethane (BTBPE), ^{13}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 α -, β -1,2-dibromo-4-(1,2-
146 dibromoethyl)cyclohexane (α -, β -DBE-DBCH) were all purchased individually from Wellington
147 Laboratories Inc. (Guelph, Canada) and mixed as required. Internal standards were used for
148 the quantification of several native compounds as listed in Table SI 4. Florisil HyperSep™ SPE
149 cartridges (1 g, 60 cc), concentrated sulfuric acid, copper powder (particle size <100 μm) and
150 anhydrous sodium sulfate (dried overnight at 120 °C) were acquired from Thermo Fisher
151 Scientific (Loughborough, UK). The standard reference material (SRM 1944, "New York/New
152 Jersey Waterway Sediment" certified for PCBs, PAHs and PBDEs) was obtained from the
153 National Institute of Standards and Technology - NIST (Gaithersburg, MD, USA).

154

155 **2.5 Sample extraction/clean-up**

156 2 g of freeze-dried sediment were weighed into a pre-cleaned glass extraction tube and
157 spiked with 20 μL of the internal standard mixture (^{13}C -BDE-28, BDE-77, BDE-128, ^{13}C -BDE-
158 209, ^{13}C -TBBPA, ^{13}C - α -, β -, and γ -HBCDDs, ^{13}C -EH-TBB, ^{13}C -BEH-TEBP and ^{13}C -BTBPE), along
159 with 2 g of copper for sulfur removal. Samples were then extracted using 4 mL of
160 hexane:acetone (3:1 v/v), vortexing for 5 min, followed by ultrasonication (20 min) and
161 centrifugation (5 min at 4000 rpm). This procedure was repeated twice. The combined
162 extract was then evaporated to dryness under a gentle stream of N_2 and reconstituted in
163 2 mL of hexane. This was followed by a sulfuric acid wash of the extract, with the layers
164 allowed to separate overnight. The organic phase was collected and the acid layer washed

165 twice with 2 mL of hexane. The combined extracts were then reduced to ~1 mL under a
166 gentle stream of N₂ and loaded onto a conditioned HyperSep™ 1 g Florisil SPE cartridge, on
167 top of which 1 g of sodium sulfate was added. Subsequent elution was performed with
168 20 mL of hexane:dichloromethane (1:1 v/v), with TBBPA eluted in a second fraction with
169 15 mL of methanol. Both fractions were combined, concentrated to dryness under a N₂ flow
170 in a Turbovap and reconstituted in methanol:toluene (1:1 v/v) containing 200 pg μL⁻¹ of
171 ¹³C-BDE-100 as a recovery determination standard.

172

173 **2.6 Instrumental analysis**

174 2 μL of each sample were analysed on a UPLC-Orbitrap-HRMS instrument (Thermo Fisher
175 Scientific, Bremen, Germany) composed of an UltiMate® 3000 high performance liquid
176 chromatography system equipped with a HPG-3400RS dual pump, a TCC-3000 column oven
177 and a WPS-3000 auto sampler coupled to a Q-Exactive™ Plus Orbitrap mass spectrometer.
178 Chromatographic separation was performed on a Thermo Scientific Accucore™ RP-MS
179 column (100 x 2.1 mm, 2.6 μm) with water (mobile phase A) and methanol (mobile phase B).
180 A gradient elution programme at a flow rate of 400-500 μL min⁻¹ was applied as shown in
181 Table SI 2 for a total run time of 17 min.

182 All parent BFRs were determined in negative atmospheric pressure chemical ionization
183 (APCI) mode. The parameters of the Orbitrap were set as follows: (-) APCI full scan mode at
184 70000 FWHM (full width at half maximum at 200 m/z and scan rate of 3 Hz at 200 m/z), AGC
185 target 1e⁶, maximum injection time 100 ms, scan range 250 to 1000 m/z, profile spectrum
186 data type, sheath gas (nitrogen) flow rate 25 AU (arbitrary units), aux gas (nitrogen) flow rate
187 5 AU, discharge current 30 μA, capillary temperature 250 °C, S-lens RF level 50 AU and aux
188 gas heater temperature 320 °C. For screening identification of possible more polar

189 degradation products and confirmation purposes, sediment extracts were also analyzed
190 using the more universal, softer electrospray ionisation (ESI) in negative mode, as described
191 in the Supporting Information section. Both the HPLC gradient programme and ionisation
192 values were optimized based on the measurement of reference standard solutions.
193 Screening for brominated compounds was conducted using an All Ion Fragmentation Scan
194 (AIF) in parallel to the Full Scan measurement and by monitoring the bromine mass trace in
195 the final data raw files as an indicator for the presence of brominated compounds.
196 Subsequent identification of specific compounds was based on exact mass (Table SI-4) and
197 isotopic pattern.
198 Trace Finder™ version 3.3 software (Thermo Fisher Scientific, Bremen, Germany) was used
199 to process raw data files, while quantification of the compounds of interest was conducted
200 using Microsoft Excel 2010.

201

202 **2.7 QA/QC**

203 The standard reference material SRM 1944 (NIST) for sediment was used to evaluate the
204 accuracy of the method for PBDEs and HBCDDs. One SRM sample was analysed for every 15
205 sediment samples. Values obtained for the SRM 1944 were generally in good accordance
206 with the certified levels (Table SI 3). In addition, non-certified compounds including BTBPE,
207 BEH-TEBP, PBEB, TBP, BB153 and DP were detected in the SRM 1944, although
208 concentrations varied between replicates (9-65% RSD, Table SI 3).

209 Recoveries for internal standards were in the range of 90 to 120 % for all samples, except for
210 ¹³C-TBBPA, where recovery values were around 50 %, with detailed information in Table SI 4.

211 Limits of detection (LOD) and limits of quantification (LOQ) were estimated based on
212 method described by Taylor³¹ (Table SI 4). In brief, standards were analysed in replicates

213 (n=10). The standard deviation of each measured concentration was plotted versus the
214 specified concentration, giving a y-axis intercept of the resulting regression line corresponds
215 to s_0 . The LOD is then defined as $3 \times s_0$, while the LOQ is defined as $10 \times s_0$. LODs in sediment
216 matrix in general ranged from $0.0001 \mu\text{g}/\text{kg}$ (for HBCDDs) to $1.1 \mu\text{g}/\text{kg}$ (for DBE-DBCH), with
217 values for BDEs ranging from $0.001 \mu\text{g}/\text{kg}$ (for BDE-209) to $0.37 \mu\text{g}/\text{kg}$ (for BDE-17). To
218 minimise blank contamination, all glassware was cleaned by soaking in a detergent solution
219 overnight, before rinsing with deionised water. This was followed by washing with acetone,
220 hexane, toluene and dichloromethane and subsequent baking at $120 \text{ }^\circ\text{C}$ overnight. One
221 method blank (sodium sulfate replacing the sediment) was analyzed with every set of 6
222 samples. For some legacy BFRs (BDE-100, BDE-153, BDE-183, BDE-209 and HBCDDs)
223 concentrations in blanks were detected just above LODs up to $2.5 \pm 1.2 \text{ pg g}^{-1} \text{ dw}$ for
224 BDE-209. For NBFRs, only TBP and TBBPA were detected in blanks at average concentrations
225 of $106.2 \pm 30 \text{ pg g}^{-1} \text{ dw}$ and $186.2 \pm 43 \text{ pg g}^{-1} \text{ dw}$ respectively. Target analytes of the
226 associated batch were blank corrected by subtraction of average blank concentrations.
227 Concentrations in samples were therefore blank corrected by subtraction of average blank
228 concentrations.

229 **2.8 Statistical analysis**

230 Statistical analysis of the data was performed using IBM SPSS statistics software version 23.
231 A one-way ANOVA was used for testing significant differences between arithmetic means.
232 For statistical purposes, “non-detect” values were replaced with zero, while “detect” values
233 with a concentration below the LOQ were assigned a value of the $\text{LOQ}/2$ or in cases of a
234 detection frequency below 50% the LOQ was multiplied by the detection frequency factor.
235 P values < 0.05 were taken to indicate statistical significance.

236 **3 Results and Discussion**

237 **3.1 Levels and trends of PBDEs and NFRs in sediments**

238 Mean, median and concentration ranges of our target BFRs in surface sediments from the
239 River Thames are summarised in Table 1, while concentrations of individual PBDE congeners
240 are provided in Table SI 6. While individual HBCDD diastereomers were measured, they are
241 reported in Table 1 as Σ HBCDD only. By comparison, *anti*- and *syn*-DP as well as α - and β -
242 DBE-DBCH were reported as Σ DPs and Σ DBE-DBCH respectively owing to our inability to
243 chromatographically resolve the individual isomers. To account for potential variability of
244 concentrations due to organic carbon content, organic carbon normalisation was conducted
245 on all sample concentrations using the measured total organic carbon (TOC) for each
246 sample, as described in the supporting information. No correlation between BFR
247 concentrations and TOC values was observed in the studied samples. This is likely explained
248 by the fact that samples were taken from different locations with diverse source input
249 strengths. If samples originate from the same location (such as sediment cores) with the
250 same source input strength, a positive linear correlation between TOC and BFR dry weight
251 concentration would be expected. Similarly, for the composition of the sediment, no
252 correlation between the BFR concentration and its geological composition (clay, silt or sand
253 content) was observed in this study.

254 **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**
 255 **River Thames**

Compound	DF (%)	Median	Average	Range	Median	Average	Range
		$\mu\text{g kg}^{-1}$ dry weight			$\mu\text{g kg}^{-1}$ organic carbon		
Σ_{12} BDEs	16-100	3.8	5.9	n.d. – 29	182	228	n.d. – 672
BDE-28	27	<0.2	0.4	<0.2 – 4.0	n.d.	12	n.d. – 116
BDE-47	53	<0.03	0.2	<0.03 – 2.5	n.d.	6.7	n.d. – 48
BDE-99	71	0.5	0.8	<0.05 – 4.4	15	28	n.d. – 130
BDE-153	16	<0.01	0.03	<0.01 – 0.6	n.d.	1.2	n.d. – 33
BDE-183	71	0.05	0.1	<0.01 – 0.7	0.4	3.3	n.d. – 23
BDE-206	96	2.6	3.3	<0.1 – 11.7	115	135	n.d. – 389
BDE-209	100	148	174	0.03 - 535	6969	7673	0.03 - 20762
Σ HBCDD	91	1.9	3.7	<0.001 – 38	67	157	n.d. – 1357
TBBPA	98	0.6	0.6	<0.02 – 2.6	21	34	n.d. – 476
EH-TBB	0		<0.03			<0.03	
BEH-TEBP	76	2.1	3.5	<0.02 – 14	100	134	n.d. – 445
BTBPE	51	<0.02	0.4	<0.02 – 3.8	0.7	15	n.d. – 142
TBP	69	0.1	0.1	<0.01 – 0.4	3.5	4.6	n.d. – 34
anti-/syn-DP	11	<0.04	2.0	<0.04– 66	n.d.	51	n.d. – 1249
PBEB	7	<0.06	1.7	<0.06 – 48	n.d.	53	n.d. – 1385
DBDPE	20	<0.45	1.3	<0.45 – 24	n.d.	42	n.d. – 1154
α/β -DBE-DBCH	0		<1.1			n.d.	
HBB	0		<0.03			n.d.	
BB153	0		<0.01			n.d.	

256 * Σ_{12} BDEs does not include BDE-209

257 * n.d. - not detected – NB for organic carbon normalised data, detection limit differs for each sample due to varying TOC content

258 * DF (%) – detection frequency

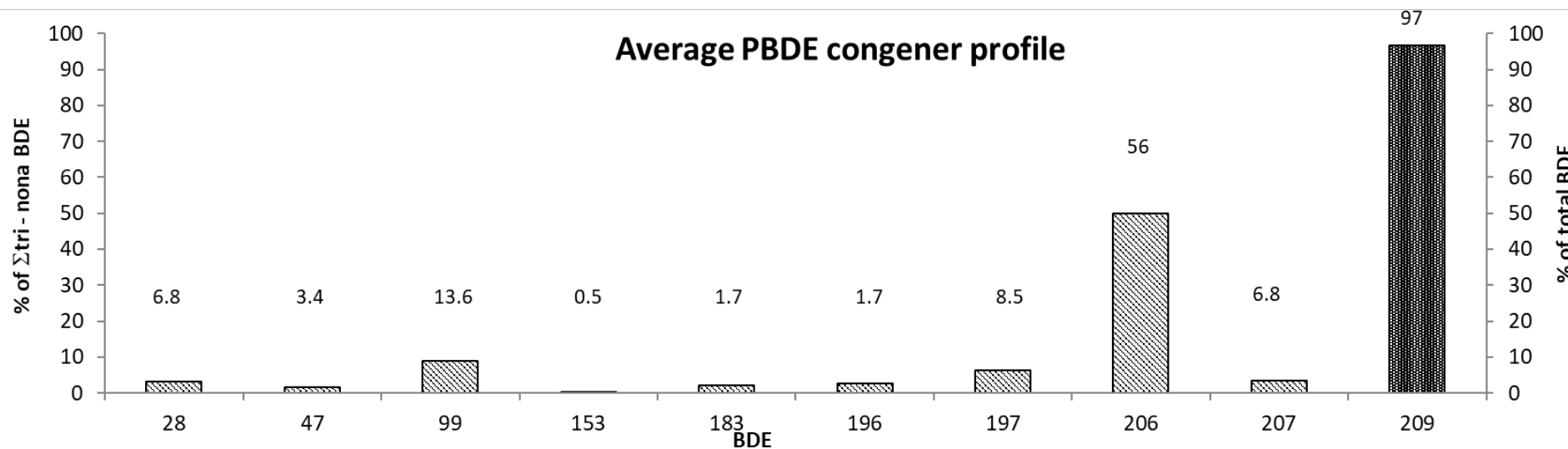
259 * < indicates the value of the LOD

260

261

262

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264

265 **Figure 2. Average PBDE congener profile in all sediment samples, expressed as %Σtri-nona-BDEs. BDE-209 is on a different scale, expressed as**
266 **%ΣBDEs. Average percent contributions are indicated above each congener.**

267 3.2 PBDEs

268 PBDE concentrations varied widely along the River Thames transect BDE-209 was the
269 predominant congener in all sediments, accounting for on average 96.7 % of total PBDEs
270 detected (Figure 2). This is in agreement with other studies, for example Vane *et al.*, who
271 reported BDE-209 to represent 80 % of total PBDEs in sediments collected from the Clyde
272 Estuary around Glasgow, UK³². This indicates a higher proportion of the DecaBDE
273 formulation in our samples, further supported by high concentrations of BDE-206. Similarly,
274 other studies reported nona-brominated PBDE congeners as the second most abundant
275 after BDE-209 in river sediment samples of the UK (inner Clyde estuary)³² and China
276 (industrial area of the Dongjiang river)³³, possibly indicating degradation of BDE-209 to form
277 lower brominated congeners. A comparison of our data to the technical Deca-BDE
278 formulation follows later.

279 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).
280 Other PBDEs were detected at lower concentrations, with prominent congeners being BDE-
281 206, followed by BDE-99 and BDE-28. Sediments from several UK lakes³⁴ contained BDE-209
282 at concentrations ranging from 1.63 to 116 $\mu\text{g kg}^{-1}$ dw. Meanwhile, river and marine
283 sediments from various locations around the UK¹⁹ were reported between 0.3 – 1333 μg
284 kg^{-1} dw, 1 – 2337 $\mu\text{g kg}^{-1}$ dw for sediments of the river Clyde³² and 2 – 98125 $\mu\text{g kg}^{-1}$ dw for
285 Scottish sediment cores³⁵. This sets our study at the lower end of previously detected
286 concentrations of BDE-209 in UK sediments.

287 Harrad recently reviewed the concentrations of legacy BFRs in UK environmental samples³⁶.
288 Where BFR levels in UK river and lake sediments were reported, BDE-209 was the prevailing
289 congener, followed by BDE-99 and BDE-47. Interestingly in our study, levels for BDE-28 were

290 higher than those found for BDE-47, suggesting a potential degradation of higher molecular
291 weight congeners to form BDE-28.

292
293 A recent study determined concentrations of PBDEs in sediments from the Thames estuary,
294 reporting a concentration range for Σ_6 BDEs (congeners 28, 47, 99, 100, 153 and 154) of
295 <MDL to $14.4 \mu\text{g kg}^{-1} \text{dw}^{21}$. This is in good accordance with our results, that reported
296 concentrations for the same congeners ranging from n.d. to $12.8 \mu\text{g kg}^{-1} \text{dw}$. Barber *et al.*
297 reported concentrations of Σ_{11} BDEs (i.e. excluding BDE-209) to fall between n.d. and $32.2 \mu\text{g}$
298 $\text{kg}^{-1} \text{dw}$ in river and marine sediments around the UK¹⁹, which is comparable to our range of
299 Σ_{12} BDEs of n.d. to $29 \mu\text{g kg}^{-1} \text{dw}$.

300

301 **3.3 HBCDDs and TBBPA**

302 HBCDDs (sum of α -, β -, and γ HBCDD) were detected in most samples (91 % detection
303 frequency) at an average concentration of $3.7 \mu\text{g kg}^{-1} \text{dw}$, which is comparable to our
304 average concentration of Σ_{12} BDEs (excluding BDE-209) of $5.9 \mu\text{g kg}^{-1} \text{dw}$. Concentrations of
305 Σ HBCDDs ranged from n.d. to $38 \mu\text{g kg}^{-1} \text{dw}$. A study on estuarine and marine sediments
306 around the UK reported a comparable range from <MDL to $47.2 \mu\text{g kg}^{-1} \text{dw}^{19}$. Values for lake
307 sediments in the UK ranged from 0.42 to $7.9 \mu\text{g kg}^{-1} \text{dw}^{34}$. Higher values were detected in the
308 River Skerne in northeast England with concentrations from <2.4 up to $1680 \mu\text{g kg}^{-1} \text{dw}^{20}$,
309 likely originating from the vicinity of a former BFR manufacturing site. HBCDD concentrations
310 in a study of coastal marine sediments were lower with maximum values up to 1.6 and 1.8
311 $\mu\text{g kg}^{-1} \text{dw}$ reported for southern and northern UK respectively²⁴.

312

313 TBBPA was found in all but one Thames sediment, with a maximum concentration of 2.6 μg
314 kg^{-1} dw and an average of 0.6 μg kg^{-1} dw, in which is an order of magnitude lower than found
315 in this study for HBCDDs and Σ_{12} BDEs. Comparatively few studies have reported TBBPA
316 concentrations in European sediment samples. Sediments from the southern and northern
317 UK coast were reported to contain up to 6.4 μg kg^{-1} dw for TBBPA and an average of 1.7 and
318 2.7 μg kg^{-1} dw respectively²⁴. Interestingly however, TBBPA was the predominant compound
319 with a detection frequency of 87 % in these coastal sediments. Morris *et al.*²⁰ analysed
320 riverine and estuarine sediments from various rivers in the UK and found high average
321 values of 451 μg kg^{-1} dw and up to 9750 μg kg^{-1} dw in the River Skerne. These elevated
322 concentrations were attributed to the vicinity of sampling sites to a former BFR
323 manufacturing site. TBBPA levels detected in our study are more comparable to those
324 reported in sediment samples from rivers in The Netherlands and Germany with average
325 values of 2.2 μg kg^{-1} dw²⁰ and 0.3 μg kg^{-1} dw²⁴ respectively.

326

327 **3.4 NBFRs**

328 One or more NBFRs were quantified in most samples at varying concentrations (Table 1) in
329 the following order (detection frequency): BEH-TEBP (76 %) > TBP (69 %) > BTBPE (51 %),
330 with DBDPE (20 %), DP (11 %) and PBEB (7 %) identified in fewer samples. Where detected,
331 concentrations of NBFRs were comparable to those of PBDEs (excluding BDE-209). Target
332 compounds like EH-TBB, HBB, BB-153 and α/β -DBE-DBCH were not detected in any of the
333 studied samples.

334 Consistent with our study, Barber *et al.*¹⁹ did not detect HBB, BB-153 and DBE-DBCH in 42
335 marine and river sediments samples from around the UK, while EH-TBB was detected in only
336 one sample at a concentration of 0.29 μg kg^{-1} dw. In addition, EH-TBB has been reported in

337 sediment samples from UK lakes³⁴ and southern and northern coastal locations, with
338 maximum concentrations of 1.35 $\mu\text{g kg}^{-1}$ dw and 26 % relative contribution in the
339 investigated area²⁴.

340 To our knowledge, this is the first study to detect BEH-TEBP in UK sediments (Table 1),
341 although this FR has already been reported in sediments from South Africa^{37, 38} and China^{39,}
342 ⁴⁰. We detected BEH-TEBP in 76 % of our samples with an average of 3.3 $\mu\text{g kg}^{-1}$ dw (134
343 $\mu\text{g kg}^{-1}$ OC) and maximum values of up to 14 $\mu\text{g kg}^{-1}$ dw (445 $\mu\text{g kg}^{-1}$ OC). This finding is
344 comparable to values of La Guardia *et al.* in South Africa (average of 96 ng g^{-1} OC, 60 %
345 detection rate) and Zhu *et al.* in China (average of 1.01 ng g^{-1} dw).

346 BEH-TEBP and EH-TBB are two of the main constituents of the technical flame retardant
347 mixture Firemaster 550 (FM-550). In the present study, interestingly only BEH-TEBP was
348 detected, possibly reflecting the infrequent use of FM-550 in the UK. The relative abundance
349 of these two NBRs in the Thames estuary may thus be explained by applications other than
350 FM-550. For example, BEH-TEBP is also used as a plasticiser, in contrast to EH-TBB for which
351 the main application is as a flame retardant⁴¹ and thus might explain our findings. Several
352 studies in the UK have targeted both EH-TBB and BEH-TEBP in the indoor and outdoor
353 environment. These studies focused on indoor dust⁴², indoor⁴³ and outdoor air⁴⁴, food and
354 human milk⁴⁵, as well as soil samples⁴⁴. In general, where reported, BEH-TEBP was detected
355 at concentrations 1-2 orders of magnitude higher than what was found for EH-TBB.

356 Furthermore, EH-TBB was not detected in UK outdoor air or soil⁴⁴, consistent with its
357 absence here in Thames sediments.

358 Concentrations of BTBPE in our sediments reached up to 3.8 $\mu\text{g kg}^{-1}$ dw with a detection
359 frequency of 51 %, which accords well with Barber *et al.*¹⁹ who reported a maximum of 1.8

360 $\mu\text{g kg}^{-1}$ dw and a detection frequency of 48 %. The presence of BTBPE was also reported in
361 lake sediment in the UK³⁴.

362 TBP was detected in 69 % of our sediments at relatively low concentrations up to $0.4 \mu\text{g kg}^{-1}$
363 dw. To our best knowledge, TBP has not been reported in UK sediments so far. DBDPE, DP
364 and PBEB in our study were only detected in a small number of samples. DBDPE has been
365 reported in sediments throughout Europe, including lake sediments in the UK (up to $6.4 \mu\text{g}$
366 kg^{-1} TOC)³⁴ and Italy (up to $280 \mu\text{g kg}^{-1}$ dw)⁴⁶, as well as river sediments in the Netherlands⁴⁷
367 and Spain (both up to $24 \mu\text{g kg}^{-1}$ dw)⁴⁸. PBEB has been reported both in UK and German
368 sediments^{19, 24}, while the same goes for DP^{24, 49}. HBB and BB-153 were not detected in this
369 study, but their presence has been previously reported in surface and tributary sediments of
370 Lake Ontario⁵⁰, with HBB also detected in river sediments in Germany²⁴. An extensive review
371 on the presence of emerging brominated flame retardants in sediments around the world
372 can be found elsewhere⁵¹.

373 The absence of DBE-DBCH from our sediments is perhaps surprising as DBE-DBCH has been
374 reported to be the predominant NBR in UK indoor air and dust⁴³, outdoor air⁴⁴, as well as
375 UK human milk and diet samples⁴⁵. This may be attributable to the physico-chemical
376 properties of DBE-DBCH, namely its relatively high volatility and low K_{ow} compared to lower
377 brominated BDEs. This is likely to minimise its partitioning to sediment. Benthic degradation
378 processes are a further possible cause and have been reported for DBE-DBCH in aerobic and
379 anaerobic soil⁵². In European sediment it has been reported in German river sediments²⁴.
380 Outside Europe, DBE-DBCH was reported in sediments of the Great Lakes⁵³ for the first time
381 in 2012, as well as in Chinese river and marine sediments^{39 40}.

382

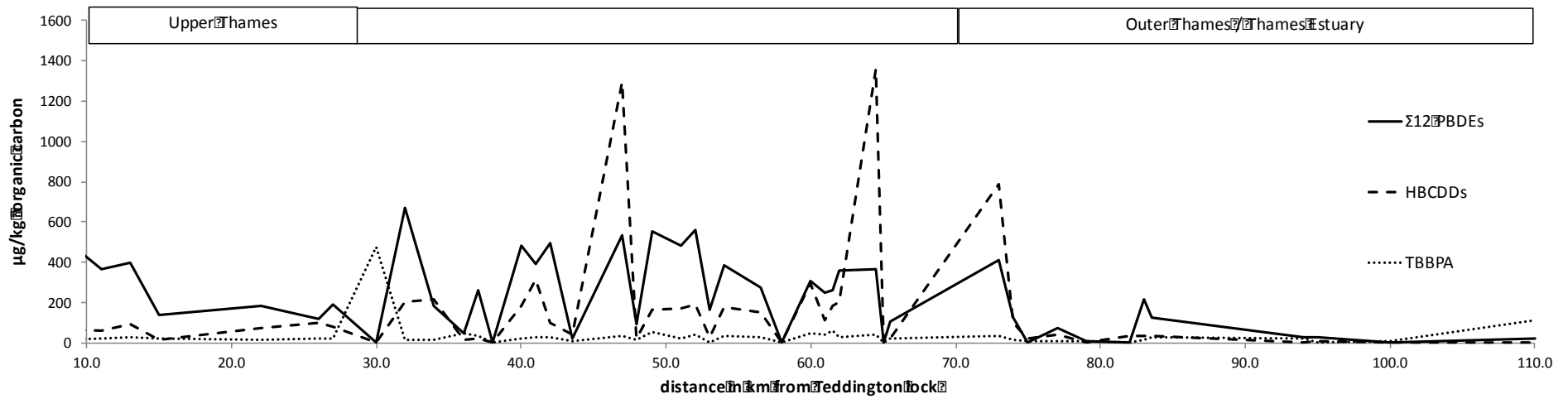
383

384 3.5 Spatial trends in concentrations of PBDEs and NFRs

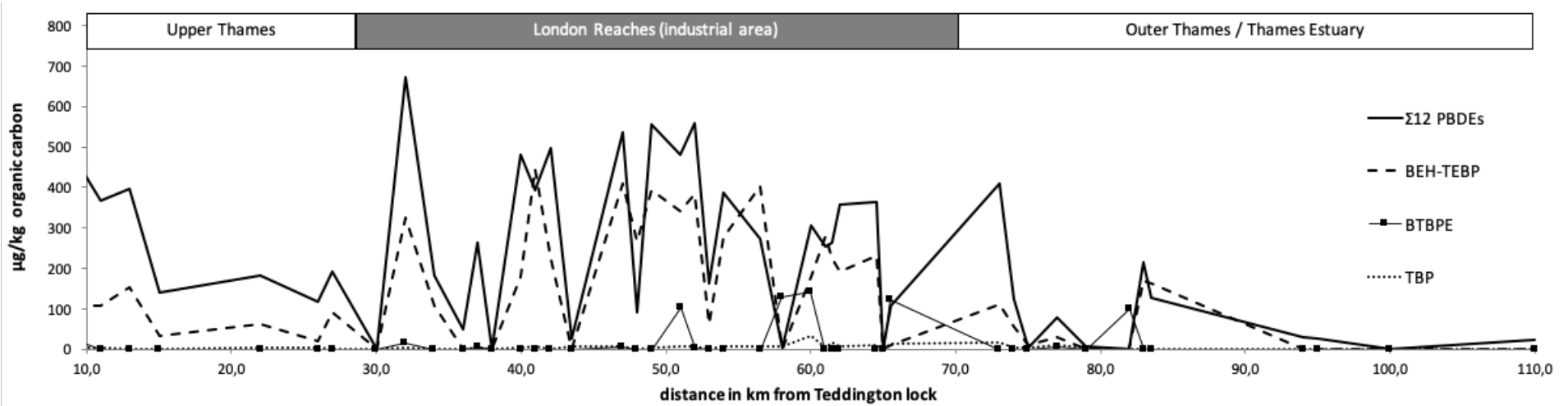
385 Spatial variation in BFR concentrations in sediments from the River Thames is shown in
386 Figure 3 for Σ_{12} BDEs, HBCDDs and TBBPA (top), as well as Σ_{12} BDEs, BEH-TEBP, BTBPE and TBP
387 (bottom). As shown, samples from the industrial area showed higher concentrations
388 compared to both: (a) samples from the upper and (b) outer Thames. Inspection of the lower
389 panel in Figure 3 reveals that concentrations of Σ_{12} BDEs and BEH-TEBP show a similar
390 concentration pattern along the river, possibly indicating the same source input. BTBPE and
391 TBP on the other hand show only a few localised input hotspots.

392

393 HBCDDs in the industrial area showed three distinct locations with elevated concentrations
394 compared to the median concentration of 1.9 $\mu\text{g}/\text{kg dw}$, around Gallions Reach (site nr. 18,
395 38 $\mu\text{g}/\text{kg dw}$), St Clement's Reach (nr. 31, 23 $\mu\text{g}/\text{kg dw}$) and Tilbury (nr. 34, 7.9 $\mu\text{g}/\text{kg dw}$). A
396 possible explanation could be the vicinity to sewage discharge locations, in close vicinity to
397 Abbey Mills STP (site 18), Long Reach STP (site 31), and Tilbury STP (site 34). Other sources
398 impacting the sediments in this area could be discharges from activities utilising HBCDDs in
399 their products, such as building and construction facilities, as well as textile manufacturers.
400 Inspection of HBCDD diastereomer profiles at the three locations above, revealed the profile
401 to resemble that of the technical mixture, with γ -HBCDD predominant (85-92 %), followed by
402 α -HBCDD (6-12 %) and β -HBCDD (2-3 %) only present in small quantities (Figure 4). This
403 could indicate fresh input sources at the locations of the analysed sediments, as the
404 diastereomer profile in these samples differs markedly from that in other samples (Figure 5).
405 On average, the diastereomer profile in samples from the industrial area contained mainly γ -
406 HBCDD, followed by α -HBCDD and only minor amounts of β -HBCDD, while in the non-
407 industrial area the ratio between the three stereoisomers was more equal (Figure 5).



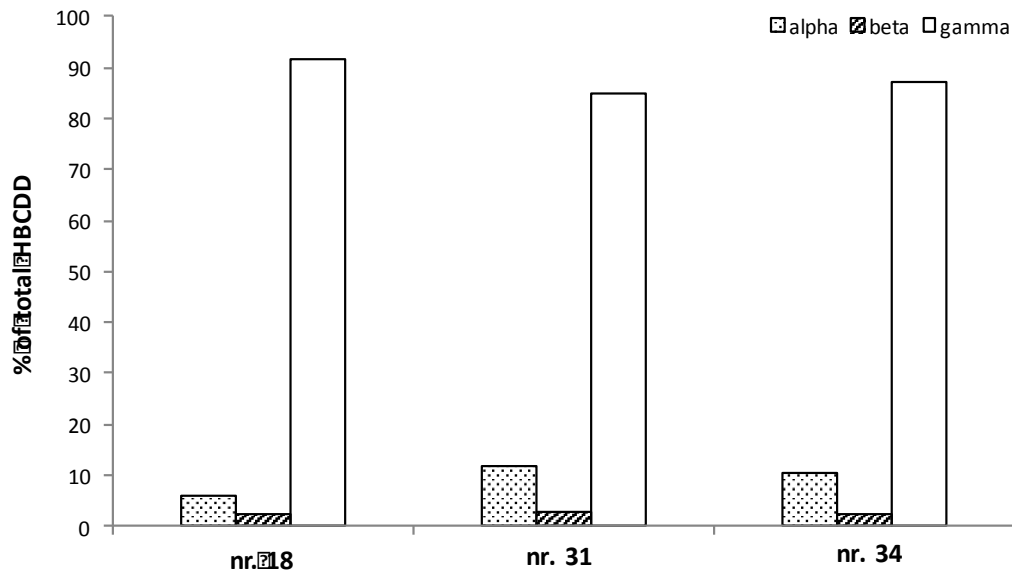
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409

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

412

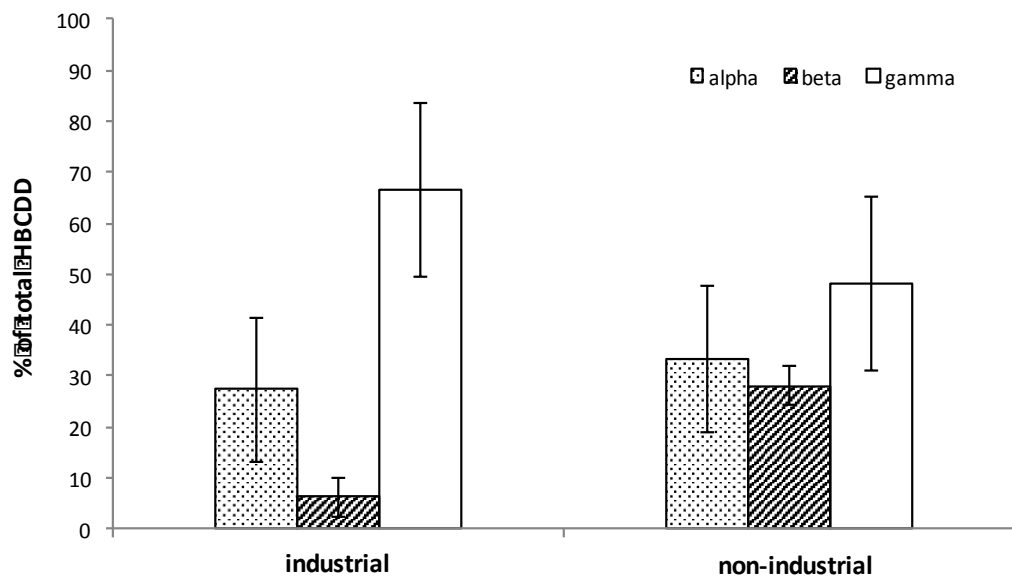


413

414 **Figure 4. HBCDD diastereomer profile in sediment from location #s 18, 31, and 34**

415

416



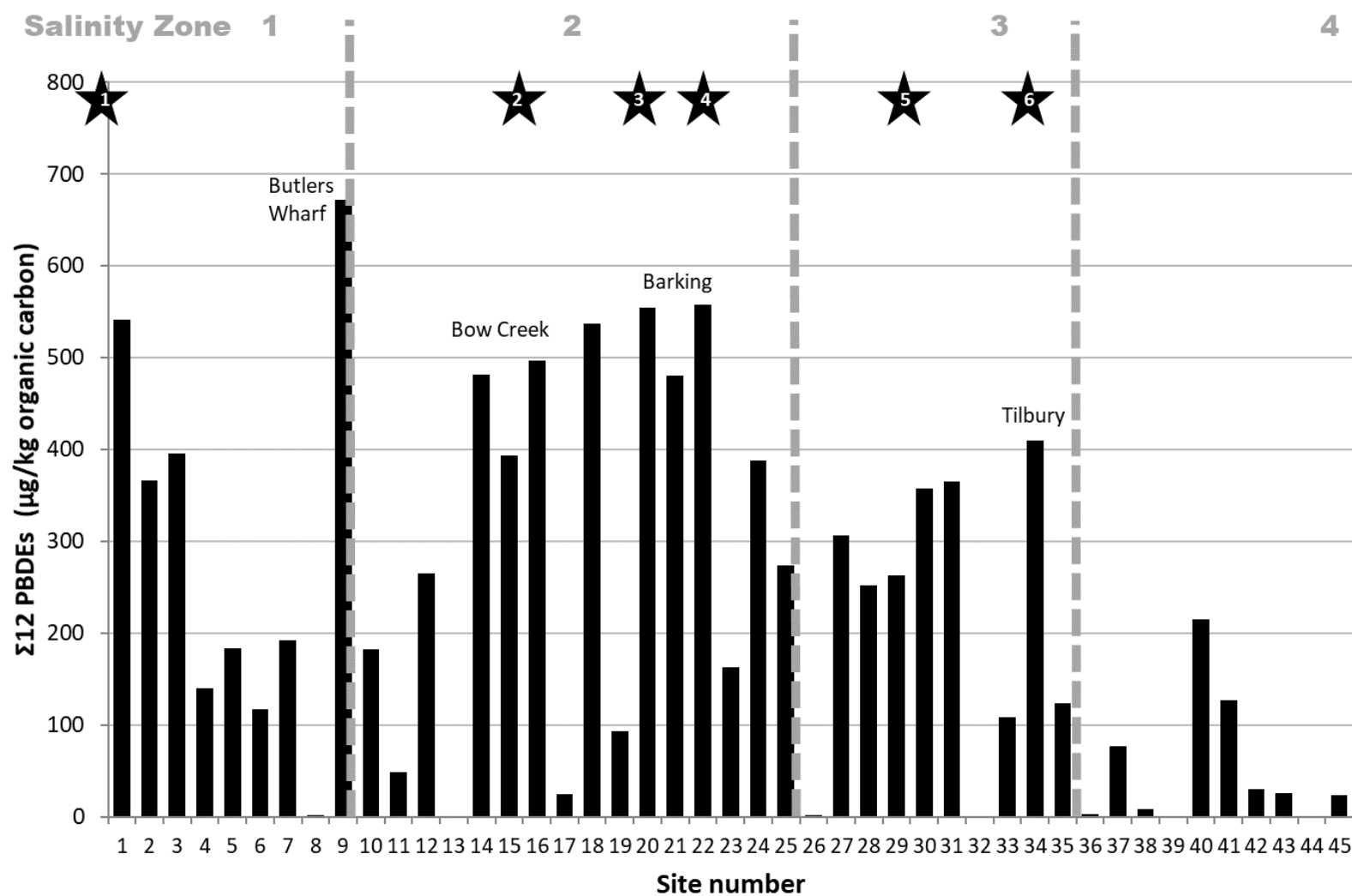
417

418 **Figure 5. Average HBCDD diastereomer profile in industrial and non-industrial area**

419

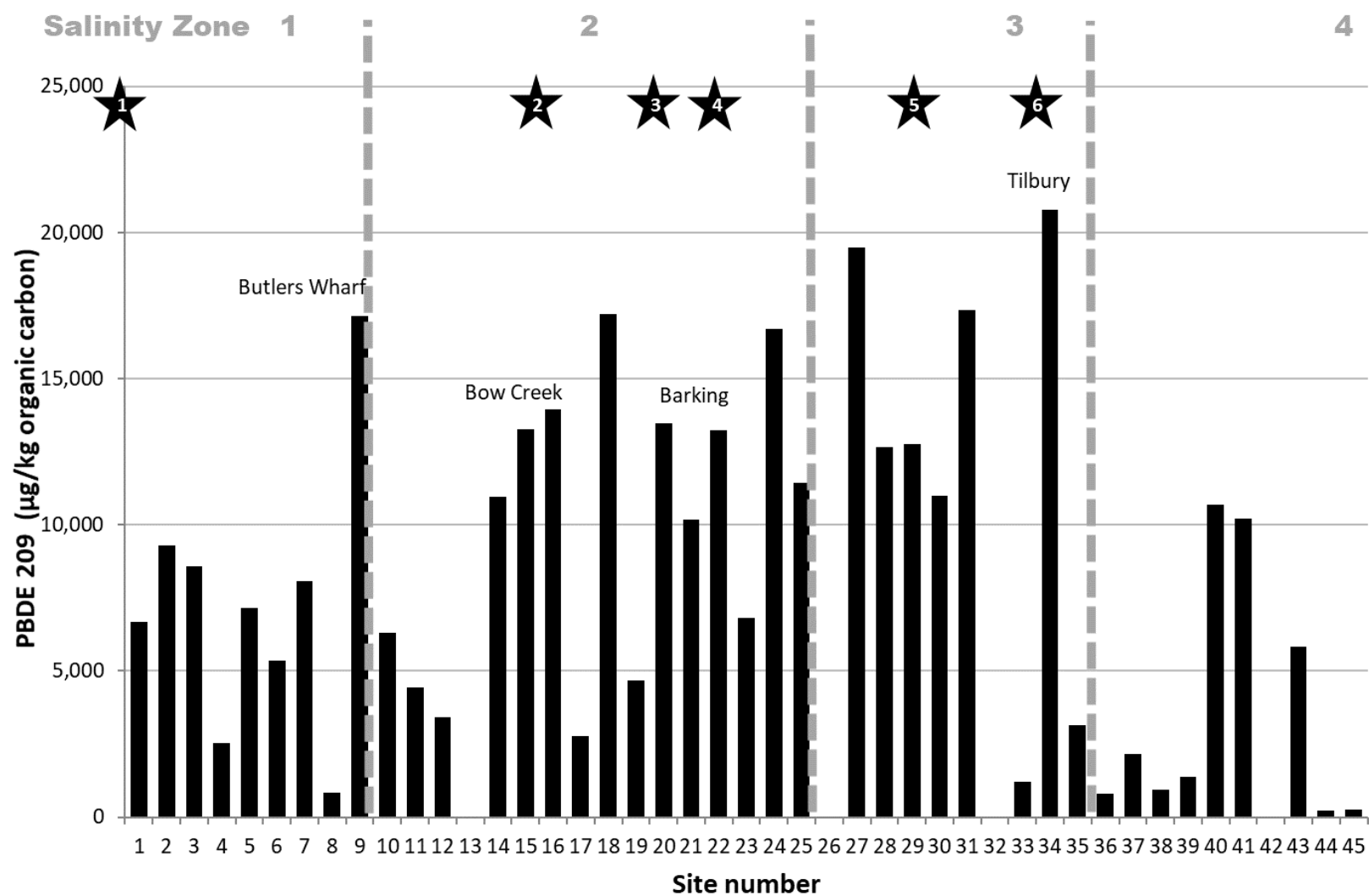
420 Figure 6 and Figure 7 illustrate the spatial variation in organic carbon-normalised
421 concentrations of Σ_{12} BDEs and BDE-209 respectively. There is a general high-high-medium-
422 low concentration profile from west to east for Σ_{12} BDEs (with average concentration values

423 for the 4 zones of 290, 309, 219 and 51 $\mu\text{g kg}^{-1}$ OC), while for BDE-209 we observe a
424 medium-high-high-low profile (7291, 9299, 9834 and 3255 $\mu\text{g kg}^{-1}$ OC), and a less marked
425 attenuation in concentrations on travelling west to east. This – coupled with an ANOVA test
426 that showed significantly ($p < 0.05$) higher SPBDE concentrations in the industrial area but no
427 such spatial difference for BDE-209 - could be a possible indication for different sources of
428 the two groups of compounds. The general decline from west to east for Σ_{12} BDEs is probably
429 driven by increasing distance from London and associated urban sources, as well as
430 flocculation-deposition of sediment controlled by salinity (salting-out) with increasing
431 proximity to the coast. The four salinity zones indicated were adapted from the study of
432 Pope *et al.*⁵⁴. The observed variability in the PBDE transect data can be explained by the fact
433 that suspended particles can travel up and down-stream by 10 - 20 km on one tide.



434

435 **Figure 6. Concentrations ($\mu\text{g kg}^{-1}$ organic carbon) of Σ_{12} PBDEs in River Thames sediments at each sampling location. Stars represent the main**
 436 **discharge locations of sewage treatment plants (STPs); 1. Mogden STP; 2. Abbey Mills STP; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP;**
 437 **6. Tilbury STP. Adapted from Lopes dos Santos and Vane²⁸**



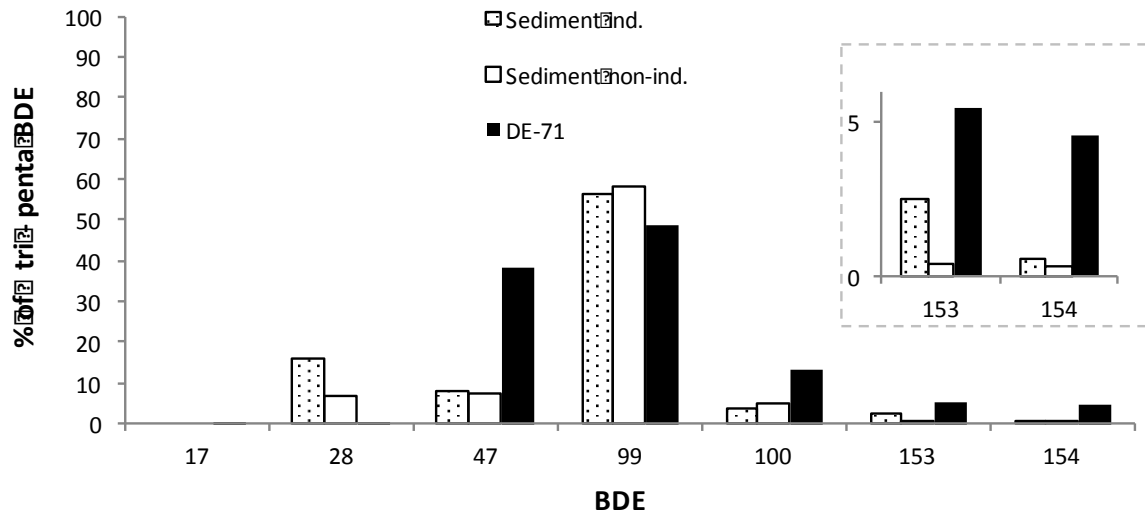
438

439 **Figure 7. Concentrations ($\mu\text{g kg}^{-1}$ organic carbon) of BDE-209 in River Thames sediments at each sampling location. Stars represent the main**
 440 **discharge locations of sewage treatment plants (STPs); 1. Mogden STP; 2. Abbey Mills STP; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP;**
 441 **6. Tilbury STP. Adapted from Lopes dos Santos and Vane²⁸**

442 3.6 PBDE/NBFR patterns

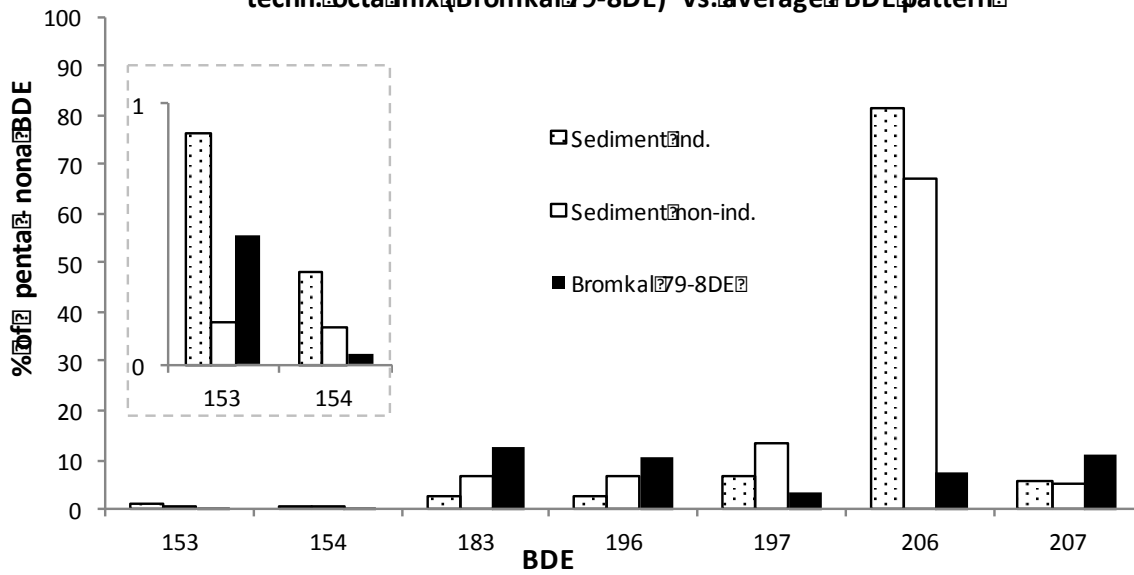
443 Figure 8 compares the average PBDE profile of the industrial area and the non-industrial one
444 against the Penta-, Octa-, and Deca- technical PBDE mixes. While caution must be exercised
445 when comparing congener profiles in environmental samples with those in the commercial
446 formulations, as congener-specific differences in physicochemical properties will modify the
447 congener profile between source and receptor; in general, no significant differences were
448 observed between the pattern of PBDEs between the industrial and non-industrial area.
449 Compared to the technical Penta-BDE mixture, the PBDE profile pattern in our sediment was
450 shifted towards lower brominated congeners such as BDE-28, possibly indicating
451 debromination. In the Penta-BDE mixture, the ratio of BDE-47:99 is 0.79⁵⁵, while in our
452 samples a shift towards BDE-99 was observable, most likely due the stronger tendency of
453 BDE-99 to partition to sediments, due to its higher K_{OW} and K_{OA} values⁵⁶. For the Octa-BDE
454 technical mixture, the differences between our sample and the technical mixture most likely
455 relate to infrequent application and emission of Octa-BDE in the UK, together with the
456 presence of minor proportions of hexa- through nona-BDEs in the Deca-BDE formulation
457 and/or environmental degradation of Deca-BDE congeners. Technical Deca-BDE on the other
458 hand, showed little deviation from the pattern in our sediment, indicating widespread recent
459 UK use and application of this technical mixture.

techn. penta mix (DE-71)¹ vs. Average PBDE pattern

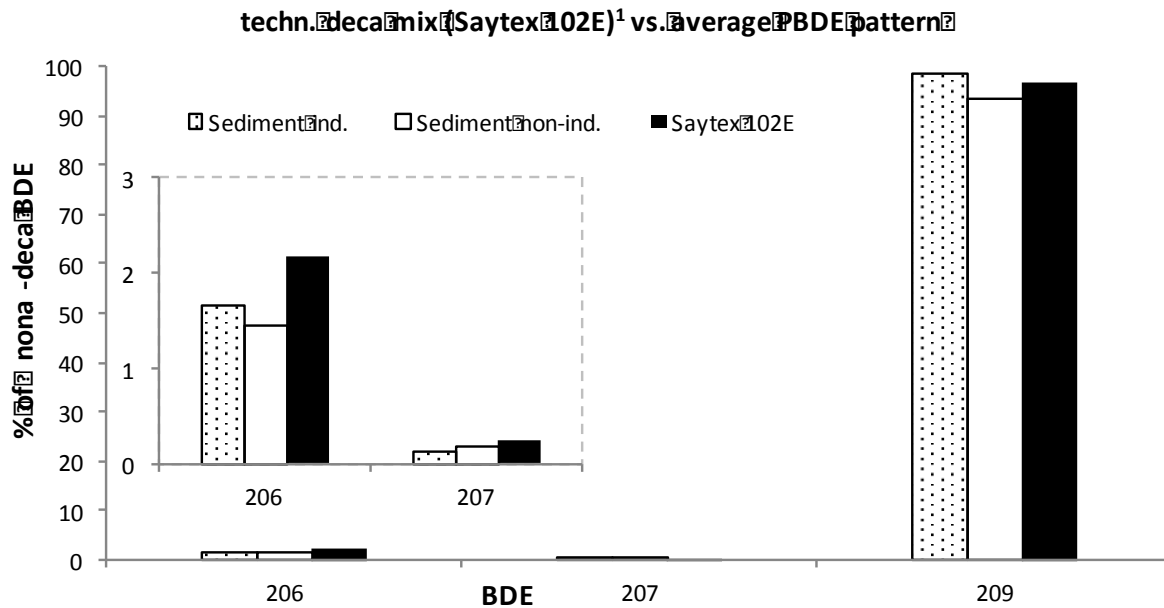


460

techn. octa mix (Bromkal 79-8DE)¹ vs. Average PBDE pattern



461



462

463 **Figure 8. Comparison of an average PBDE profile in the industrial area (dotted) and outside**
 464 **the industrial area (white) to a technical penta / octa / deca BDE mix (black) – technical**
 465 **mixture values adapted from La Guardia et al.⁵⁵**

466

467 3.7 Screening for degradation products and selected NBRs

468 The UPLC-HRMS used in this study proved to be an excellent platform for the identification
 469 and quantification of PBDEs and NBRs. Moreover, rapid HRMS analysis in full scan mode
 470 allows post-acquisition data analysis for further identification of compounds/transformation
 471 products of interest (e.g. potential degradation products and NBRs). A limitation here is the
 472 possible degradation of acid-labile compounds as a result of the acid wash step in our extract
 473 clean-up procedure.

474 To screen for further brominated compounds in the sample set, a Br trace ($m/z = 78.918336$
 475 / 80.916290) was queried from the full scan - all ion fragmentation (AIF) acquisition using
 476 Xcalibur software. This revealed the presence of brominated compounds with shorter
 477 retention times than brominated PBDEs. Further investigation of the accurate mass, isotope
 478 patterns and comparison to the high resolution mass spectrum of hydroxylated PBDE (OH-
 479 BDE) standards revealed the identified peaks as OH-BDEs (further details are provided in the

480 SI section). Unlike PBDEs, OH-BDEs have not been produced industrially and are not known
481 by-products of technical brominated formulations^{57, 58}. However, OH-BDEs have been
482 reported in biotic and abiotic samples of the aquatic and marine environment, such as
483 salmon⁵⁷, mussels⁵⁹, algae⁶⁰ as well as sediments⁶¹, surface waters⁶² and sewage treatment
484 plant effluents⁶³. Studies suggest that they are natural products of marine environments, as
485 well as a result of metabolic biotransformation from anthropogenic PBDEs^{60, 62}. The position
486 of the hydroxyl group (OH) has been postulated to be an indicator of whether OH-BDE
487 congeners are formed through oxidation or metabolic reactions^{57, 59, 61}. Possible sources and
488 transformation found in the literature include microbial aerobic degradation^{64, 65},
489 photochemical reactions of bromophenols⁶⁶ and PBDEs⁶⁷, transformation of bromophenols
490 by marine bacteria⁶⁸ and a red algae enzyme⁵⁸, reactions of PBDEs with atmospheric OH
491 radicals⁶², as well as in sewage treatment plants through oxidative reactions and excretion of
492 human and animal metabolites⁶². Whether the OH-BDEs detected in the Thames sediments
493 are of environmental and/or biological origin is beyond the scope of this paper. However,
494 since OH-BDEs have been reported to exhibit similar or even enhanced toxic⁶⁹ and
495 estrogenic⁷⁰ effects on both human⁷¹ and wildlife^{72, 73} compared to PBDEs, their presence
496 and relevance needs to be further investigated.

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

503

504 **4 Summary**

505 Brominated flame retardants have found wide application in consumer products and
506 building materials. Densely populated areas such as London with its large industrial
507 hinterland can thus act as emission sources of these chemicals. Since the river Thames
508 passes through this area, it can act as an indicator of such emissions.

509

510 This is the first extensive study targeting several legacy BFRs and NBFRs in sediments along
511 the tidal River Thames. Results indicate that BDE-209 is the predominant congener in all
512 samples, accounting for ~ 95 % of total PBDEs detected, with a concentration range of <0.1
513 to 540 $\mu\text{g kg}^{-1}$ dw. This finding is of interest due to the recent listing of Deca-BDE under the
514 Stockholm Convention, which underlines the current and future environmental concern over
515 this BFR. Further, possible evidence of environmental debromination of Penta-BDE was
516 observed through the elevated relative abundance of BDE-28 in sediment compared to that
517 in the Penta-BDE formulation. NBFRs were detected in the following order (detection
518 frequency): BEH-TEBP (76 %) > TBP (69 %) > BTBPE (51 %); with DBDPE (20 %), DP (11 %) and
519 PBEB (7 %) identified only in a few samples. Concentrations of BEH-TEBP were found to be of
520 a comparable range to those found for Σ_{12} BDEs in this study, as well as showing a similar
521 concentration pattern along the river, possibly indicating a similar source input. Spatial
522 variation analysis of the sediment samples further revealed that locations within the
523 industrial area of London had significantly higher concentrations of Σ_{12} BDEs, HBCDDs, TBBPA,
524 as well as BEH-TEBP, BTBPE and TBP. Analysis of HBCDD diastereomer patterns revealed
525 samples from three locations within the industrial area possessed comparatively high
526 concentrations and diastereomer profiles matching those of the technical mixture. This

527 could possibly indicate fresh input sources such as sewage treatment plants at these
528 locations.

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

533

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540

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