Legacy PBDEs and NBFRs 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 NBFRs in Sediments of the Tidal River Thames Using Liquid**

2 **Chromatography Coupled to a High Resolution Accurate Mass Orbitrap Mass Spectrometer**

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Abstract

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

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

1   Introduction

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

Due to legislative restrictions on manufacture and use of these BFRs, several so-called novel BFRs (NBFRs) are likely finding wider use[4]. In general, increasing levels of NBFRs are being detected in various matrices relevant to environmental and human health[5]. The environmental impact of NBFRs is potentially similar to the restricted BFRs[6]. Animal studies have shown that exposure to BFRs can have endocrine, reproductive, and behavioural effects at doses comparable to human exposure[7]. Human epidemiological studies have reported association between exposure to BFRs and adverse neurodevelopmental and reproductive effects in humans[8][9][10][11]. Laboratory studies on NBFRs indicate genotoxicity in aquatic species[12], as well as cytotoxic and anti-proliferation effects with a possible induction of apoptosis in HepG2 cells [13].

74   BFRs generally have limited biodegradability, are persistent and tend to accumulate in the

75   environment[14]. 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[4]. 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[15-17], rivers and estuaries[18-21], 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   geology[25]. 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 lipids[28] 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 NBFRs 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 km^2 and an average discharge of 65.8 m^3/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[28].

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 m^2 area, using

118 either a stainless steel trowel or a polycarbonate tube fitted with a core catcher manually

119 driven into the surface[29]. 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

122   transported frozen to the laboratory within 3 days. Each sample was freeze-dried, sieved to

123   pass a 2 mm brass mesh and ground to a fine powder using an agate ball-mill and stored in

124   sealed polyethylene bags in a desiccator in the dark[30].

125

126   **2.3   Study area**

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128   **Figure 1. Sampling locations (yellow diamonds) of surface sediments along the Thames**
129   **Estuary. Stars represent the main discharge locations of sewage effluents; 1. Mogden; 2.**
130   **Abbey Mills; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP; 6. Tilbury STP. Red**
131   **shaded area shows the main industrial discharge area on the Thames (samples 13-34). The**
132   **Teddington Lock on the left divides the river Thames into tidal and non-tidal sections.**
133   **Adapted from Lopes dos Santos and Vane[28]. STP – sewage treatment plants**

134

135   **2.4   Chemicals and Standards**

136   All solvents used were purchased from Fisher Scientific (Loughborough, UK) and were of

137   HPLC grade or higher. Native and labelled high purity standards for PBDEs (BDE-17, BDE-28,

138   ^{13}C-BDE28, BDE-47, BDE-77, BDE-99, BDE-100, ^{13}C-BDE100, BDE-128, BDE-153, BDE-154,

139   BDE-183,   BDE-196,   BDE-197,   BDE-206,   BDE-207,   BDE-209   and ^{13}C-BDE209),

140   hexabromobenzene (HBB), 2,4,6-tribromophenol (TBP), α-,β and γ-HBCDDs / ^{13}C-α-,β-, and

141   γ-HBCDDs, TBBPA / ^{13}C-TBBPA and NBFRs 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 N_2 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 N_2 flow

170 in a Turbovap and reconstituted in methanol:toluene (1:1 v/v) containing 200 pg μL^{-1} of

171 ^{13}C-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 1e^6, 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   ^{13}C-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 Taylor[31] (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 x s_0, while the LOQ is defined as 10 x s_0. LODs in sediment

216 matrix in general ranged from 0.0001 µg/kg (for HBCDDs) to 1.1 µg/kg (for DBE-DBCH), with

217 values for BDEs ranging from 0.001 µg/kg (for BDE-209) to 0.37 µg/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 °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 pg g^{-1} dw for

224 BDE-209. For NBFRs, only TBP and TBBPA were detected in blanks at average concentrations

225 of 106.2 $\pm$ 30 pg g^{-1} dw and 186.2 $\pm$ 43 pg g^{-1} 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 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.

3   Results and Discussion

3.1   Levels and trends of PBDEs and NBFRs in sediments

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

254 **Table 1. Summary of the concentrations in both µg kg^{-1} dry weight and µg kg^{-1} organic carbon of selected BFRs in surficial sediments from the**
255 **River Thames**

Compound	DF (%)	Median	Average	Range	Median	Average	Range
		µg kg^{-1} dry weight			µg 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
ΣHBCDD	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
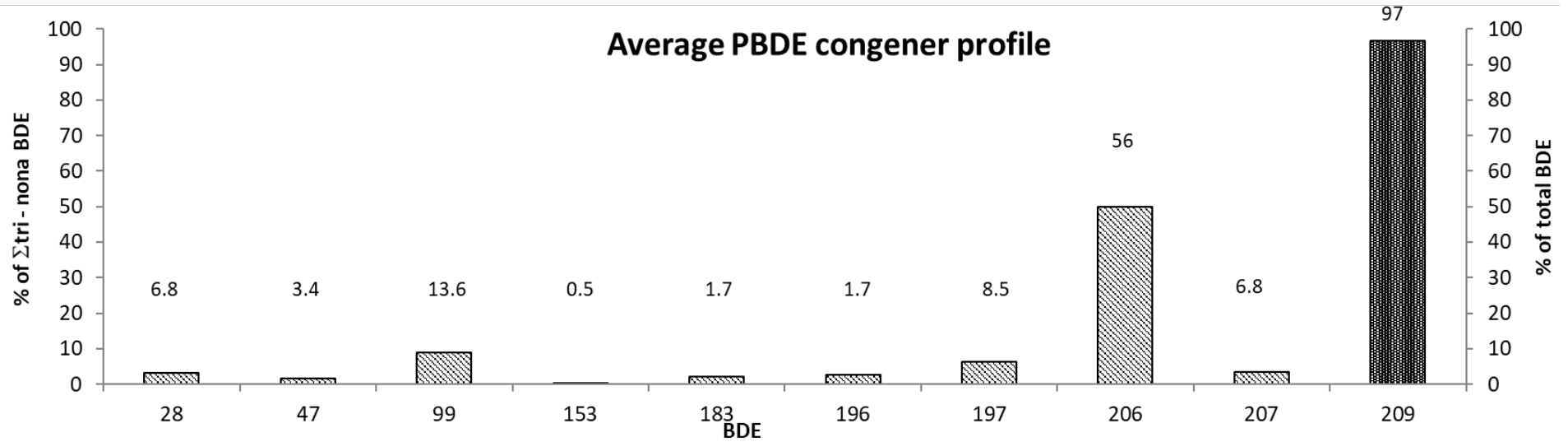258 * DF (%) – detection frequency
259 * < indicates the value of the LOD

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262
263

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

3.2 PBDEs

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

Concentrations of BDE-209 ranged from <0.1 to 540 µg kg^{-1} dw (<0.1 to 20762 µg kg^{-1} OC). Other PBDEs were detected at lower concentrations, with prominent congeners being BDE-206, followed by BDE-99 and BDE-28. Sediments from several UK lakes[34] contained BDE-209 at concentrations ranging from 1.63 to 116 µg kg^{-1} dw. Meanwhile, river and marine sediments from various locations around the UK[19] were reported between 0.3 – 1333 µg kg^{-1} dw, 1 – 2337 µg kg^{-1} dw for sediments of the river Clyde[32] and 2 – 98125 µg kg^{-1} dw for Scottish sediment cores[35]. This sets our study at the lower end of previously detected concentrations of BDE-209 in UK sediments.

Harrad recently reviewed the concentrations of legacy BFRs in UK environmental samples[36]. Where BFR levels in UK river and lake sediments were reported, BDE-209 was the prevailing 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_6BDEs (congeners 28, 47, 99, 100, 153 and 154) of

295   <MDL to 14.4 µg kg^{-1} 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 µg kg^{-1} dw. Barber *et al.*

297   reported concentrations of Σ_{11}BDEs (i.e. excluding BDE-209) to fall between n.d. and 32.2 µg

298   kg^{-1} dw in river and marine sediments around the UK[19], which is comparable to our range of

299   Σ_{12}BDEs of n.d. to 29 µg kg^{-1} 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 µg kg^{-1} dw, which is comparable to our

304   average concentration of Σ_{12}BDEs (excluding BDE-209) of 5.9 µg kg^{-1} dw. Concentrations of

305   ΣHBCDDs ranged from n.d. to 38 µg kg^{-1} dw. A study on estuarine and marine sediments

306   around the UK reported a comparable range from <MDL to 47.2 µg kg^{-1} dw[19]. Values for lake

307   sediments in the UK ranged from 0.42 to 7.9 µg kg^{-1} dw[34]. Higher values were detected in the

308   River Skerne in northeast England with concentrations from <2.4 up to 1680 µg kg^{-1} 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   µg kg^{-1} dw reported for southern and northern UK respectively[24].

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 respectively[24]. 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} dw[20] and 0.3 µg kg^{-1} dw[24] 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 lakes[34] and southern and northern coastal locations, with

338 maximum concentrations of 1.35 µg kg^{-1} dw and 26 % relative contribution in the

339 investigated area[24].

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 µg kg^{-1} dw (134

343 µg kg^{-1} OC) and maximum values of up to 14 µg kg^{-1} dw (445 µg 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 NBFRs 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 retardant[41] 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 dust[42], indoor[43] and outdoor air[44], food and

354 human milk[45], as well as soil samples[44]. 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 soil[44], consistent with its

357 absence here in Thames sediments.

358 Concentrations of BTBPE in our sediments reached up to 3.8 µg 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 μg kg^{-1} dw and a detection frequency of 48 %. The presence of BTBPE was also reported in

361 lake sediment in the UK[34].

362 TBP was detected in 69 % of our sediments at relatively low concentrations up to 0.4 μg 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 μg

366 kg^{-1} TOC)[34] and Italy (up to 280 μg kg^{-1} dw)[46], as well as river sediments in the Netherlands[47]

367 and Spain (both up to 24 μg 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 Ontario[50], with HBB also detected in river sediments in Germany[24]. An extensive review

371 on the presence of emerging brominated flame retardants in sediments around the world

372 can be found elsewhere[51].

373 The absence of DBE-DBCH from our sediments is perhaps surprising as DBE-DBCH has been

374 reported to be the predominant NBFR in UK indoor air and dust[43], outdoor air[44], as well as

375 UK human milk and diet samples[45]. 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 soil[52]. In European sediment it has been reported in German river sediments[24].

380 Outside Europe, DBE-DBCH was reported in sediments of the Great Lakes[53] for the first time

381 in 2012, as well as in Chinese river and marine sediments[39 40].

382

383

3.5 Spatial trends in concentrations of PBDEs and NBFRs

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

HBCDDs in the industrial area showed three distinct locations with elevated concentrations compared to the median concentration of 1.9 µg/kg dw, around Gallions Reach (site nr. 18, 38 µg/kg dw), St Clement's Reach (nr. 31, 23 µg/kg dw) and Tilbury (nr. 34, 7.9 µg/kg dw). A possible explanation could be the vicinity to sewage discharge locations, in close vicinity to Abbey Mills STP (site 18), Long Reach STP (site 31), and Tilbury STP (site 34). Other sources impacting the sediments in this area could be discharges from activities utilising HBCDDs in their products, such as building and construction facilities, as well as textile manufacturers. Inspection of HBCDD diastereomer profiles at the three locations above, revealed the profile to resemble that of the technical mixture, with γ-HBCDD predominant (85-92 %), followed by α–HBCDD (6-12 %) and β-HBCDD (2-3 %) only present in small quantities (Figure 4). This could indicate fresh input sources at the locations of the analysed sediments, as the diastereomer profile in these samples differs markedly from that in other samples (Figure 5). On average, the diastereomer profile in samples from the industrial area contained mainly γ-HBCDD, followed by α-HBCDD and only minor amounts of β-HBCDD, while in the non-industrial area the ratio between the three stereoisomers was more equal (Figure 5).
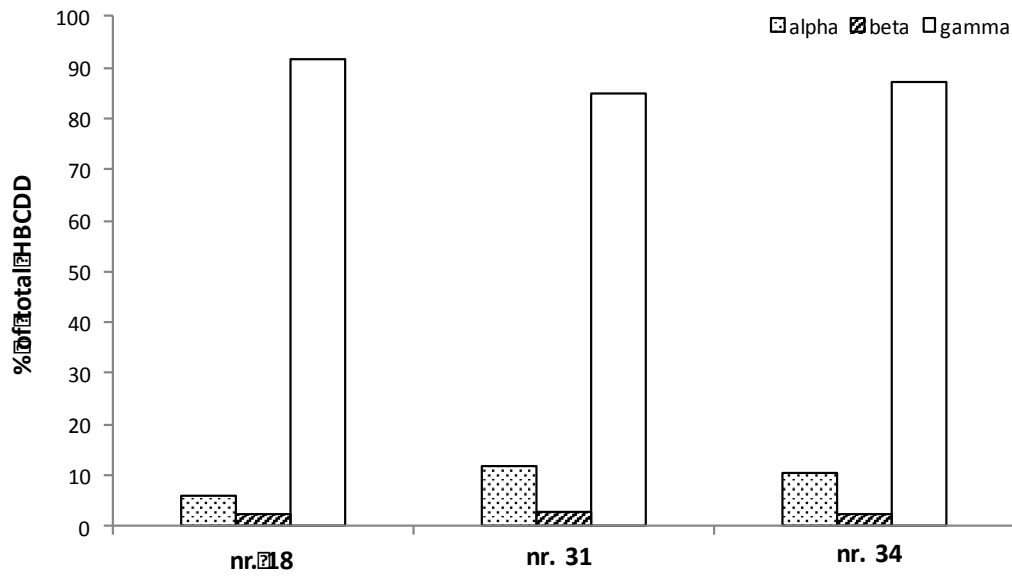
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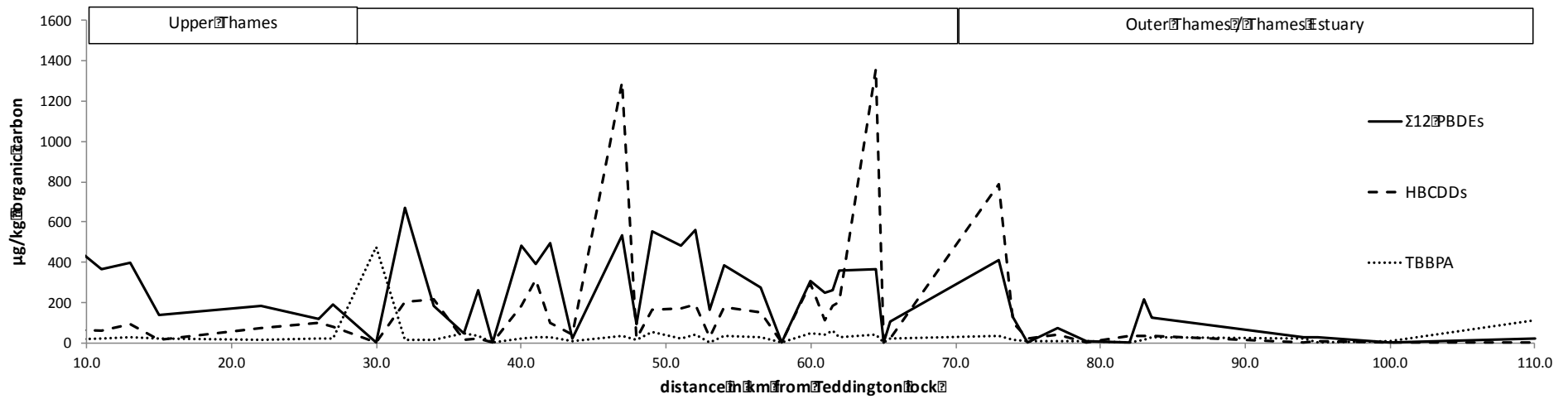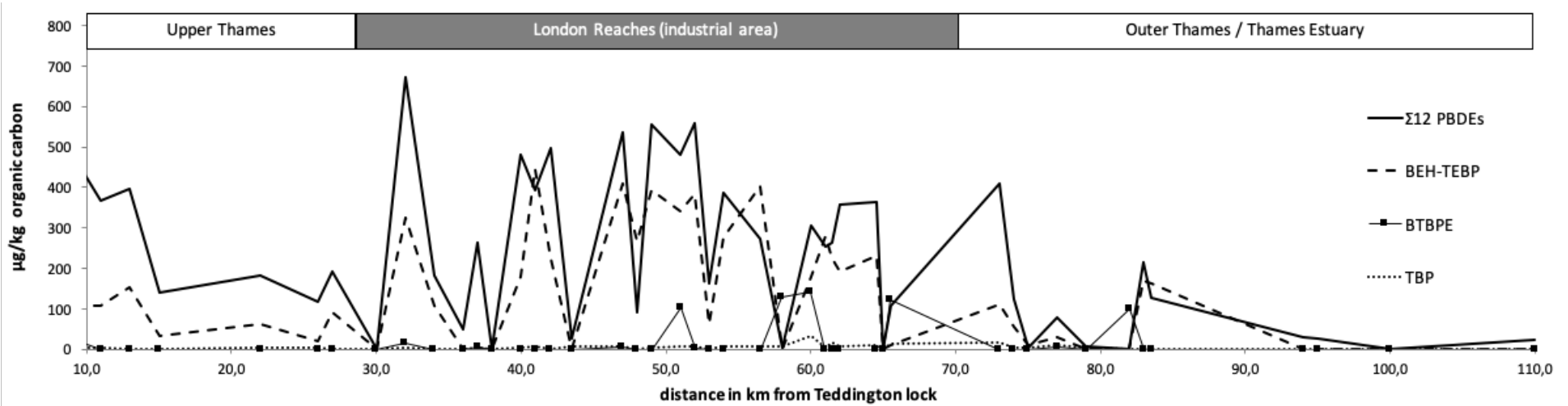
Figure 3. Spatial trends for Σ_{12}BDEs, HBCDDs, and TBBPA (top) and Σ_{12}BDEs, BEH-TEBP, BTBPE, and TBP (bottom) measured (in µg kg^{-1} organic carbon) along the river Thames, with an approximate distance (km) from Teddington Lock.
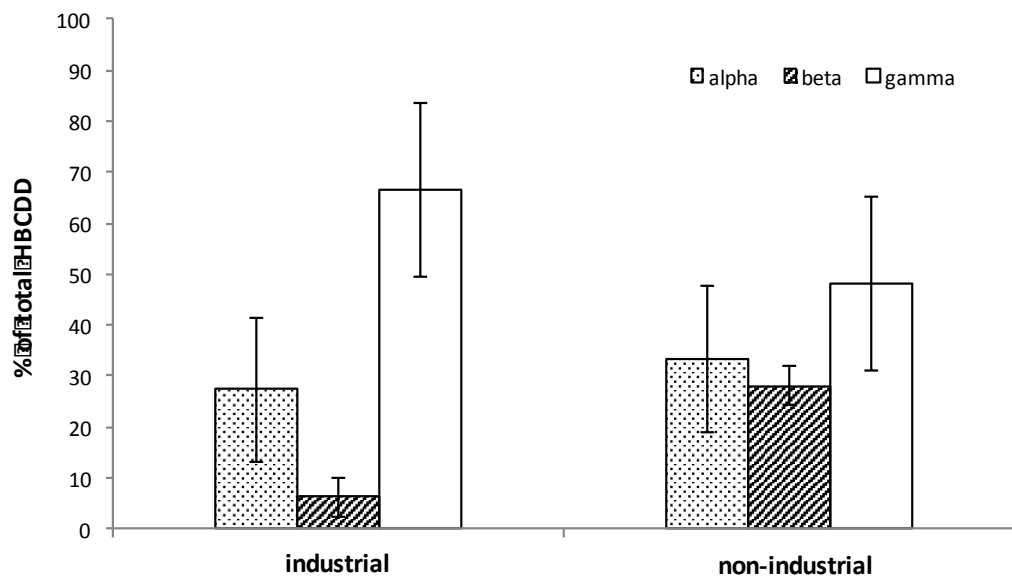
412

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

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

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

423 for the 4 zones of 290, 309, 219 and 51 μg kg^{-1} OC), while for BDE-209 we observe a

424 medium-high-high-low profile (7291, 9299, 9834 and 3255 μg 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 $\sum_{12}$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.
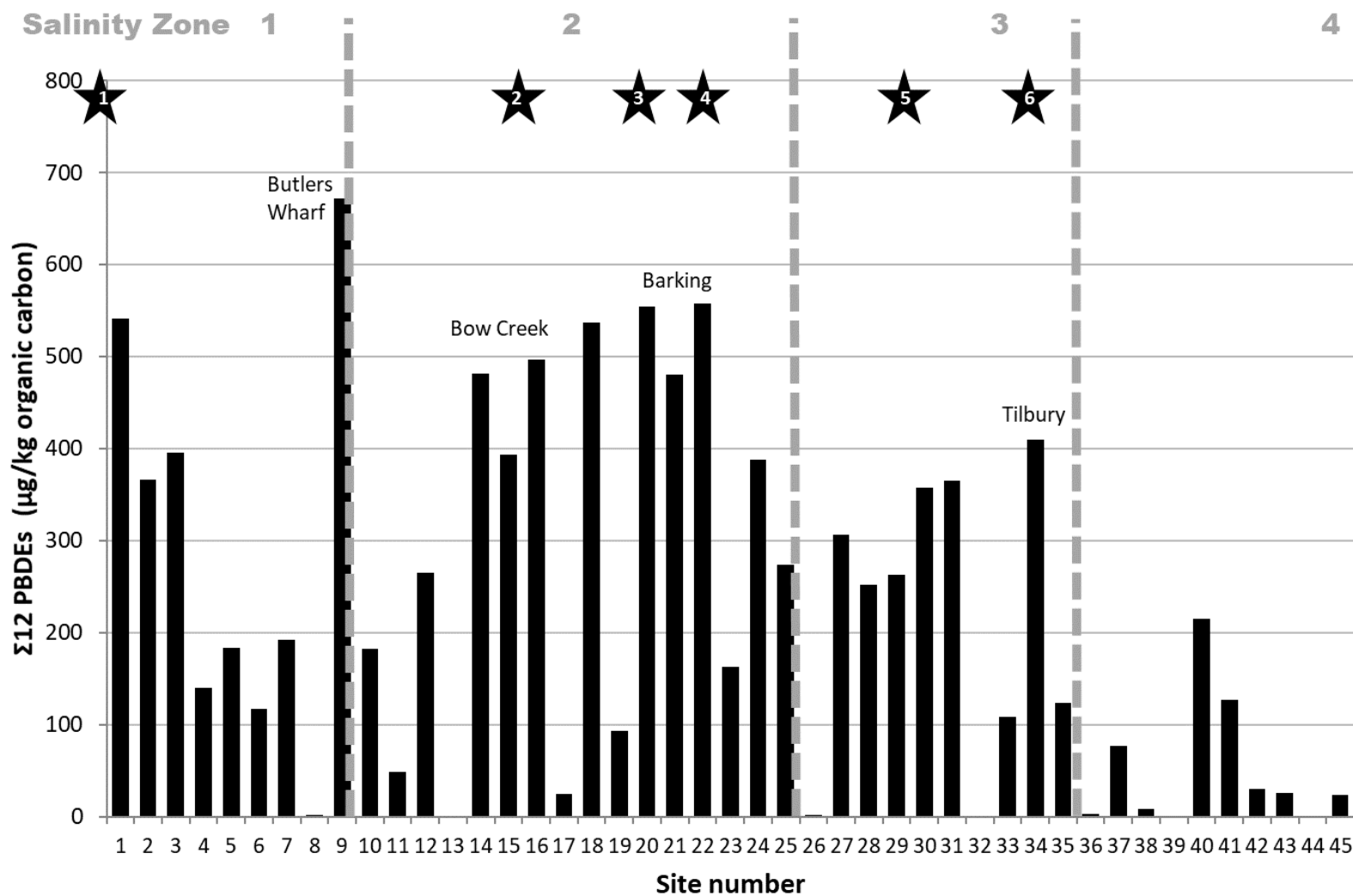
Figure 6. Concentrations (µg kg^{-1} organic carbon) of Σ_{12} PBDEs in River Thames sediments at each sampling location. Stars represent the main discharge locations of sewage treatment plants (STPs); 1. Mogden STP; 2. Abbey Mills STP; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP; 6. Tilbury STP. Adapted from Lopes dos Santos and Vane [28]
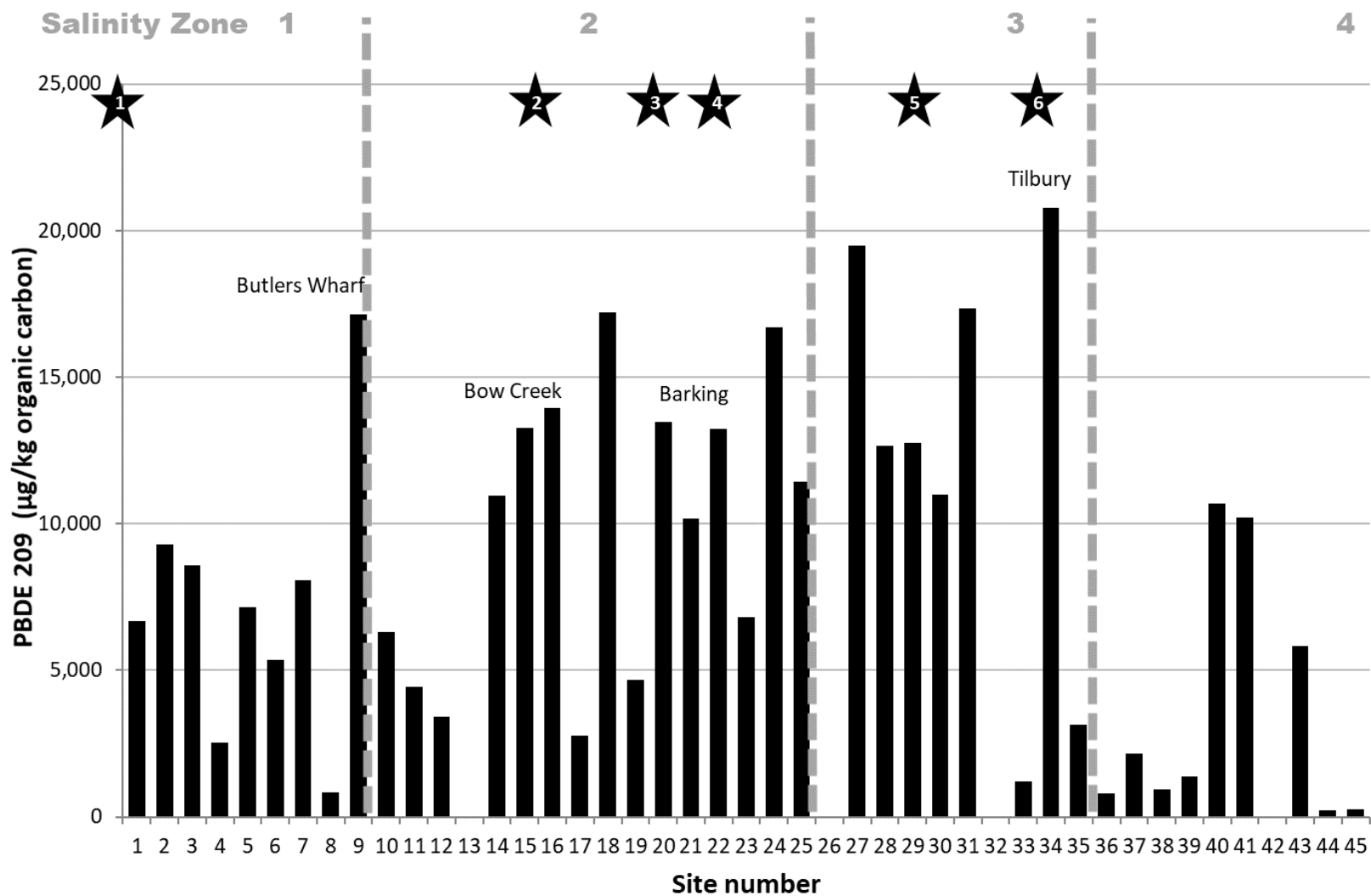
Figure 7. Concentrations (μg kg^{-1} organic carbon) of BDE-209 in River Thames sediments at each sampling location. Stars represent the main discharge locations of sewage treatment plants (STPs); 1. Mogden STP; 2. Abbey Mills STP; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP; 6. Tilbury STP. Adapted from Lopes dos Santos and Vane [28]

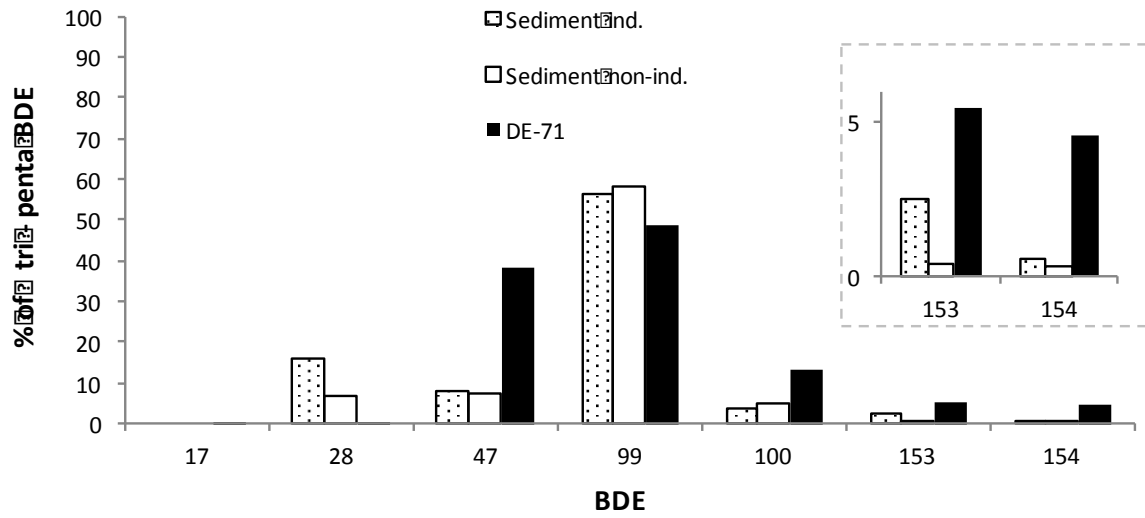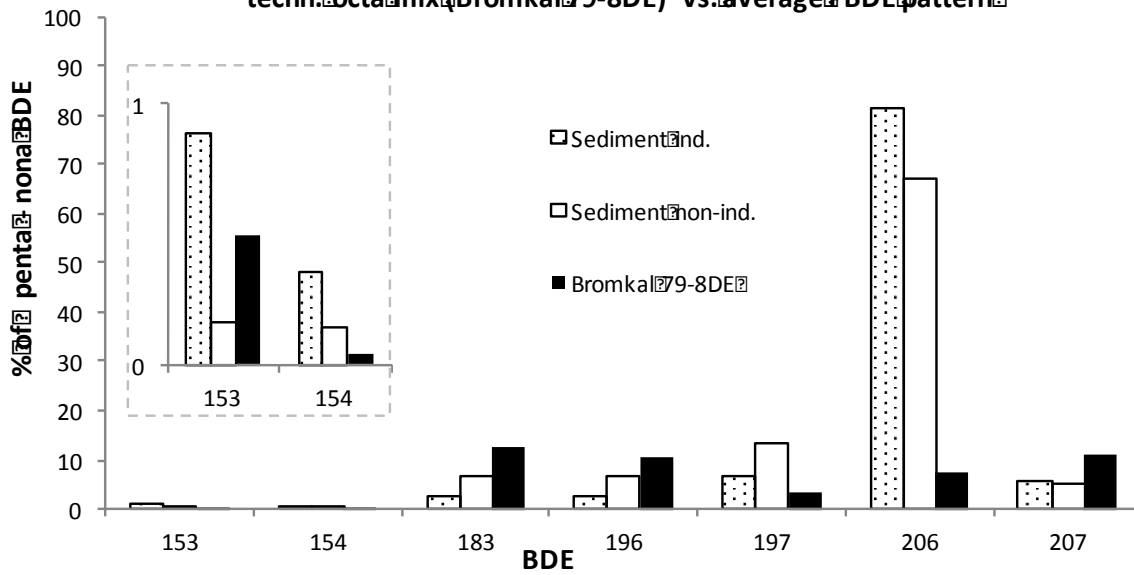## 3.6 PBDE/NBFR patterns

Figure 8 compares the average PBDE profile of the industrial area and the non-industrial one against the Penta-, Octa-, and Deca- technical PBDE mixes. While caution must be exercised when comparing congener profiles in environmental samples with those in the commercial formulations, as congener-specific differences in physicochemical properties will modify the congener profile between source and receptor; in general, no significant differences were observed between the pattern of PBDEs between the industrial and non-industrial area. Compared to the technical Penta-BDE mixture, the PBDE profile pattern in our sediment was shifted towards lower brominated congeners such as BDE-28, possibly indicating debromination. In the Penta-BDE mixture, the ratio of BDE-47:99 is 0.79[55], while in our samples a shift towards BDE-99 was observable, most likely due the stronger tendency of BDE-99 to partition to sediments, due to its higher K_{OW} and K_{OA} values[56]. For the Octa-BDE technical mixture, the differences between our sample and the technical mixture most likely relate to infrequent application and emission of Octa-BDE in the UK, together with the presence of minor proportions of hexa- through nona-BDEs in the Deca-BDE formulation and/or environmental degradation of Deca-BDE congeners. Technical Deca-BDE on the other hand, showed little deviation from the pattern in our sediment, indicating widespread recent UK use and application of this technical mixture.

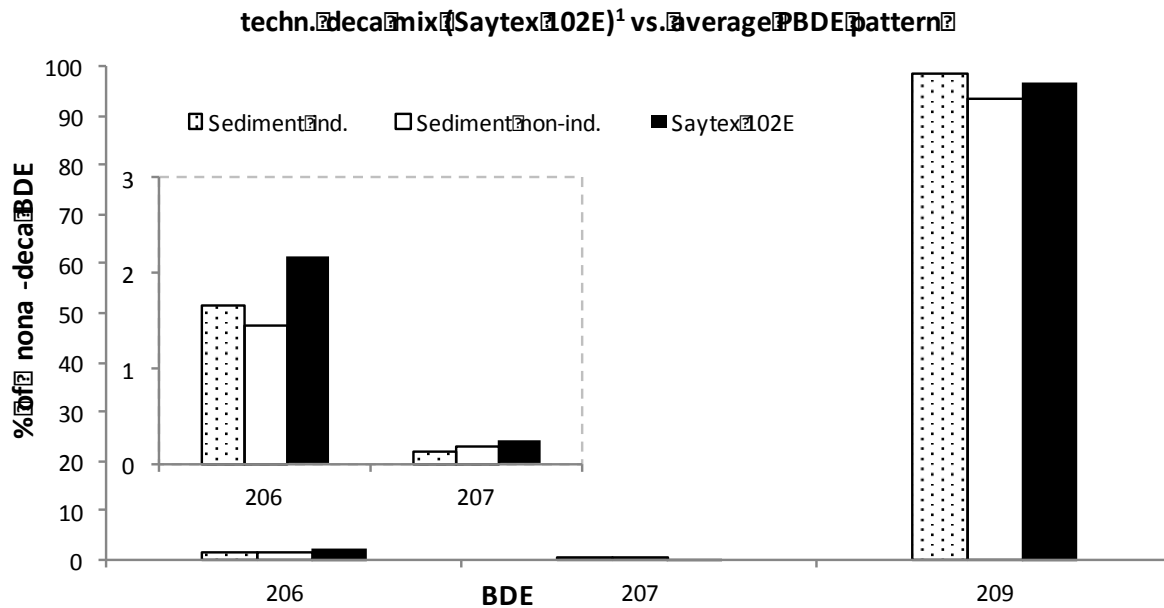## techn. penta mix (DE-71)[1] vs. average PBDE pattern

460

techn. octa mix (Bromkal 79-8DE)[1] vs. average PBDE pattern

461

techn. deca mix (Saytex 102E)[1] vs. average PBDE pattern

Figure legend: Sediment ind. | Sediment non-ind. | Saytex 102E

y-axis: % of nona -deca BDE

x-axis: BDE — 206, 207, 209

Inset chart (y-axis 0–3): 206, 207

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

3.7   Screening for degradation products and selected NBFRs

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

To screen for further brominated compounds in the sample set, a Br trace (m/z = 78.918336 / 80.916290) was queried from the full scan - all ion fragmentation (AIF) acquisition using Xcalibur software. This revealed the presence of brominated compounds with shorter retention times than brominated PBDEs. Further investigation of the accurate mass, isotope patterns and comparison to the high resolution mass spectrum of hydroxylated PBDE (OH-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   salmon[57], mussels[59], algae[60] as well as sediments[61], surface waters[62] and sewage treatment

484   plant effluents [63]. 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 bromophenols[66] and PBDEs[67], transformation of bromophenols

490   by marine bacteria[68] and a red algae enzyme[58], reactions of PBDEs with atmospheric OH

491   radicals[62], as well as in sewage treatment plants through oxidative reactions and excretion of

492   human and animal metabolites[62]. 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 toxic[69] and

495   estrogenic[70] effects on both human[71] 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 NBFRs 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 µg 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

534 **5   Acknowledgements**

540

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