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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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 diphenylethers (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), bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP), 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). 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 human liver cancer cells [13].

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

To the authors' knowledge, this is the most extensive comparison yet of levels, spatial trends, and potential sources of PBDEs and NBFRs in river sediments. Moreover, our study exploits the potential of high resolution Orbitrap mass spectrometry for multi-residue analysis of a broad range of BFRs and NBFRs in a single run with sensitive, rapid and reliable measurement of target analytes, as well as their potential degradation products.

2. Materials and Methods

3.1. Study area

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

3.2. Sample collection

Sampling of sediments from the River Thames was carried out in October 2011 at the locations shown in Figure 1. All sites were accessed via a jet boat using predetermined GPS coordinates to accurately locate each position to ±3 m[25, 27]. At each location, surface sediments (0-5 cm) were collected from four corners of a square of ca. 2 m^2 area, using either a stainless steel trowel or a polycarbonate tube fitted with a core catcher manually driven into the surface [28]. The four corner samples and one central sample were combined and transported to shore in a polyethylene zip lock bag. Sediments were immediately frozen at -18 °C in the dark to avoid post collection chemical changes and physical movement, then transported frozen to the laboratory within 3 days. Each sample was freeze-dried, sieved to pass a 2 mm brass mesh and ground to a fine powder using an agate ball-mill and stored in sealed polyethylene bags in a desiccator in the dark[29].

3.3. Study area

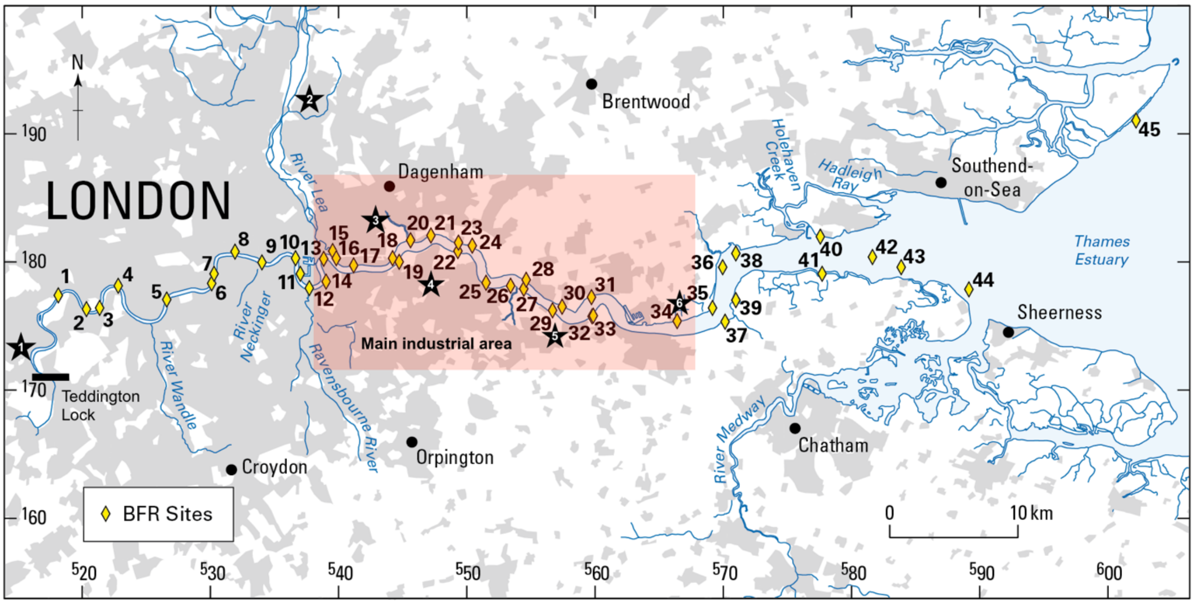


Figure 1. Sampling locations (yellow diamonds) of surface sediments along the Thames Estuary. Stars represent the main discharge locations of sewage effluents; 1. Mogden; 2. Abbey Mills; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP; 6. Tilbury STP. Red shaded area shows the main industrial discharge area on the Thames (samples 13-34). The Teddington Lock on the left divides the river Thames into tidal and non-tidal sections. Adapted from Lopes dos Santos and Vane[27]. STP – sewage treatment plants

3.4. Chemicals and Standards

All solvents used were purchased from Fisher Scientific (Loughborough, UK) and were of HPLC grade or higher. Native and labelled high purity standards for PBDEs (BDE-17, BDE-28, ^{13}C-BDE28, BDE-47, BDE-77, BDE-99, BDE-100, ^{13}C-BDE100, BDE-128, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-206, BDE-207, BDE-209 and ^{13}C-BDE209), hexabromobenzene (HBB), 2,4,6-tribromophenol (TBP), α-,β and γ-HBCDDs / ^{13}C-α-,β-, and γ-HBCDDs, TBBPA / ^{13}C-TBBPA and NBFRs 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), ^{13}C-EH-TBB, bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP), ^{13}C-BEH-TEBP, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), ^{13}C-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) were all purchased from Wellington Laboratories Inc. (Guelph, Canada). Florisil HyperSep™ SPE cartridges (1 g, 60 cc), concentrated sulfuric acid, copper powder (particle size <100 μm) and anhydrous sodium sulfate (dried overnight at 120 °C) were acquired from Thermo Fisher Scientific (Loughborough, UK). The standard reference material (SRM 1944, "New York/New Jersey Waterway Sediment" certified for PCBs, PAHs and PBDEs) was obtained from the National Institute of Standards and Technology - NIST (Gaithersburg, MD, USA).

3.5. Sample extraction/clean-up

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

gentle stream of N_2 and loaded onto a conditioned HyperSep™ 1 g Florisil SPE cartridge, on top of which 1 g of sodium sulfate was added. Subsequent elution was performed with 20 mL of hexane:dichloromethane (1:1 v/v), with TBBPA eluted in a second fraction with 15 mL of methanol. Both fractions were combined, concentrated to dryness under a N_2 flow in a Turbovap and reconstituted in methanol:toluene (1:1 v/v) containing 200 pg μL^{-1} of ^{13}C-BDE-100 as a recovery determination standard.

3.6. Instrumental analysis

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

All parent BFRs were determined in negative atmospheric pressure chemical ionization (APCI) mode. The parameters of the Orbitrap were set as follows: (-) APCI full scan mode at 70000 FWHM (full width at half maximum at 200 m/z), AGC target $1e^6$, maximum injection time 100 ms, scan range 250 to 1000 m/z, profile spectrum data type, sheath gas flow rate 25 AU (arbitrary units), aux gas flow rate 5 AU, discharge current 30 µA, capillary temperature 250 °C, S-lens RF level 50 AU and aux gas heater temperature 320 °C. For screening identification of possible more polar degradation products and confirmation purposes, sediment extracts were also analyzed using the more universal, softer electrospray ionisation (ESI) in negative mode, as described in the Supporting Information section. Both the HPLC gradient programme and ionisation values were optimized based on the measurement of reference standard solutions. Screening for brominated compounds was conducted using an All Ion Fragmentation Scan (AIF) in parallel to the Full Scan measurement and by monitoring the bromine mass trace in the final data raw files.

Trace Finder™ version 3.3 software (Thermo Fisher Scientific, Bremen, Germany) was used to process raw data files, while quantification of the compounds of interest was conducted using Microsoft Excel 2010.

3.7. QA/QC

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

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

3.8. Statistical analysis

Statistical analysis of the data was performed using IBM SPSS statistics software version 23. A one-way ANOVA was used for testing significant differences between arithmetic means. For statistical purposes, “non-detect” values were replaced with zero, while “detect” values with a concentration below the LOQ were assigned a value of the LOQ/2 or in cases of a detection frequency below 50% the LOQ was multiplied by the detection frequency factor. 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 **Error! Reference source not found.**. 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.

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 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	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
ΣHBCDD	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
α/β-DBE-DBCH	0		<1.1			<1.1	
HBB	0		<0.03			<0.03	
BB153	0		<0.01			<0.01	

* Σ_{12}BDEs does not include BDE-209

* n.d. - not detected

* < indicates the value of the LOD

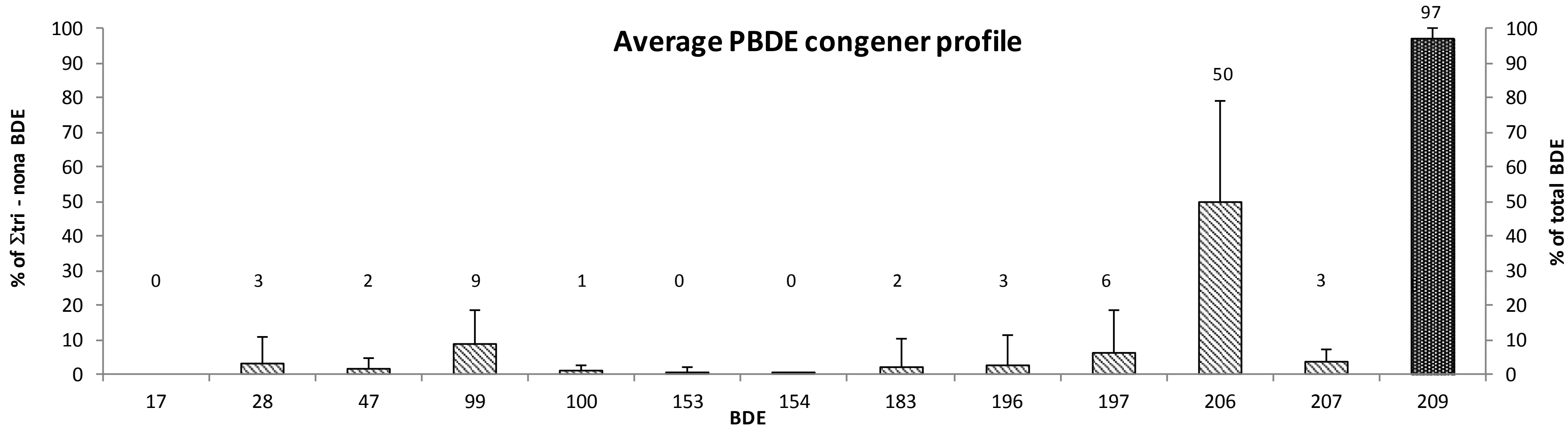


Figure 2. Average PBDE congener profile in all sediment samples. BDE-209 is on a different scale. Average percent contributions are indicated above each congener with error bars representing the standard deviation.

3.2. PBDEs

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

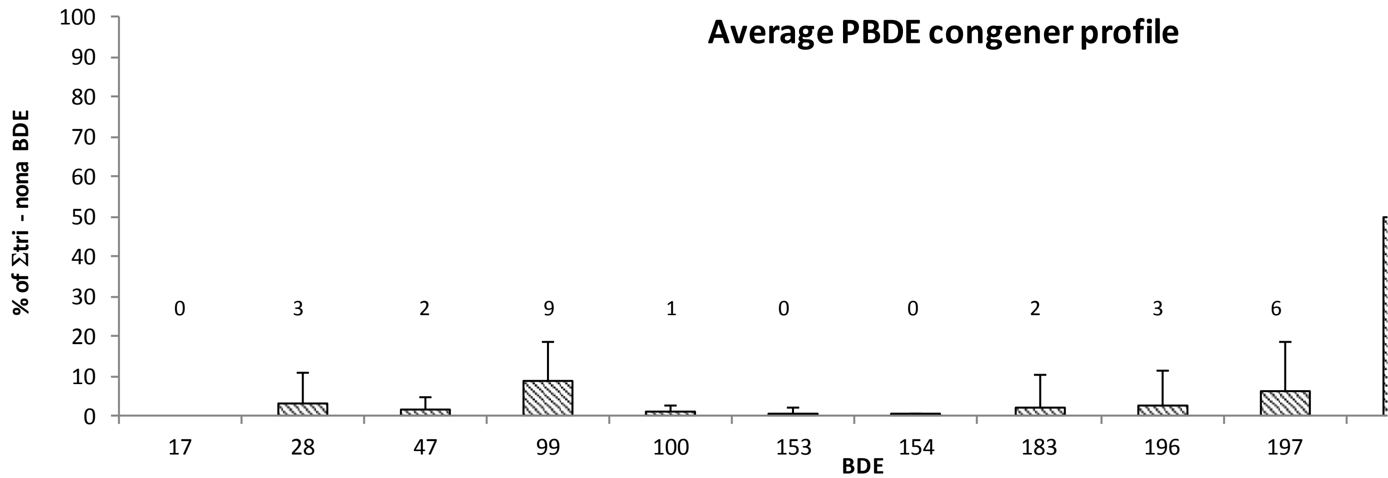


Figure 2). This is in agreement with Vane *et al.*, who reported BDE-209 to represent 80 % of total PBDEs in sediments collected from the Clyde Estuary around Glasgow, UK[31]. This indicates a higher proportion of the DecaBDE formulation in our samples, further supported by high concentrations of BDE-206. 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)[31] and China (industrial area of the Dongjiang river)[32], possibly indicating degradation of BDE-209 to form lower brominated congeners. This finding is especially of interest with the recent listing of Deca-BDE under the Stockholm Convention. A comparison of our data to the technical Deca-BDE formulation will be discussed further on in this paper.

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[33] 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[31] and 2 – 98125 µg kg^{-1} dw for Scottish sediment cores[34]. 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[35]. 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 higher than those found for BDE-47, suggesting a potential degradation of PentaBDE congeners to form BDE-28.

A recent study determined concentrations of PBDEs in sediments from the Thames estuary, reporting a concentration range for Σ_6BDEs (congeners 28, 47, 99, 100, 153 and 154) of <MDL to 14.4 µg kg^{-1} dw[21]. This is in good accordance with our results, that reported concentrations for the same congeners ranging from n.d. to 12.8 µg kg^{-1} dw. Barber *et al.* reported concentrations of Σ_{11}BDEs (i.e. excluding BDE-209) to fall between n.d. and 32.2 µg kg^{-1} dw in river and marine sediments around the UK[19], which is comparable to our range of Σ_{12}BDEs of n.d. to 29 µg kg^{-1} dw.

3.3. HBCDDs and TBBPA

HBCDDs (sum of α-,β-, and γ HBCDD) were detected in most samples (91 % detection frequency) at an average concentration of 3.7 µg kg^{-1} dw, which is comparable to our average concentration of Σ_{12}BDEs (excluding BDE-209) of 5.9 µg kg^{-1} dw. Concentrations of ΣHBCDDs ranged from n.d. to 38 µg kg^{-1} dw. A study on estuarine and marine sediments around the UK reported a comparable range from <MDL to 47.2 µg kg^{-1} dw[19]. Values for lake

sediments in the UK ranged from 0.42 to 7.9 µg kg^{-1} dw[33]. Higher values were detected in the River Skerne in northeast England with concentrations from <2.4 up to 1680 µg kg^{-1} dw[20], likely originating from the vicinity of a former BFR manufacturing site. HBCDD concentrations in coastal marine sediments tend to be lower with maximum values up to 1.6 and 1.8 µg kg^{-1} dw reported for southern and northern UK respectively[36].

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

3.4. NBFRs

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

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

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

BEH-TEBP and EH-TBB are two of the main constituents of the technical flame retardant mixture Firemaster 550 (FM-550). In the present study, interestingly only BEH-TEBP was detected, possibly reflecting the infrequent use of FM-550 in the UK. The relative abundance of these two NBFRs in the Thames estuary may thus be explained by applications other than FM-550. For example, BEH-TEBP is also used as a plasticiser, in contrast to EH-TBB for which the main application is as a flame retardant[41] and thus might explain our findings. Several studies in the UK have targeted both EH-TBB and BEH-TEBP in the indoor and outdoor environment. These studies focused on indoor dust[42], indoor[43] and outdoor air[44], food and human milk[45], as well as soil samples[44]. In general, where reported, BEH-TEBP was detected at concentrations 1-2 orders of magnitude higher than what was found for EH-TBB. Furthermore, EH-TBB was not detected in UK outdoor air or soil[44], consistent with its absence here in Thames sediments.

Concentrations of BTBPE in our sediments reached up to 3.8 µg kg^{-1} dw with a detection frequency of 51 %, which accords well with Barber *et al.*[19] who reported a maximum of 1.8 µg kg^{-1} dw and a detection frequency of 48 %. The presence of BTBPE was also reported in lake sediment in the UK[33].

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

The absence of DBE-DBCH from our sediments is perhaps surprising as DBE-DBCH has been reported to be the predominant NBFR in UK indoor air and dust[43], outdoor air[44], as well as UK human milk and diet samples[45]. This may be attributable to the physico-chemical properties of DBE-DBCH, namely its relatively high volatility and low K_{ow} compared to lower brominated BDEs. This is likely to minimise its partitioning to sediment. Benthic degradation processes are a further possible cause and have been reported for DBE-DBCH in aerobic and anaerobic soil[52]. In European sediment it has been reported in German river sediments[36]. Outside Europe, DBE-DBCH was reported in sediments of the Great Lakes[53] for the first time in 2012, as well as in Chinese river and marine sediments[39 40].

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 (numbers 13-34) showed substantially higher concentrations compared to both: (a) samples from the inner (numbers 1-12) and (b) outer (numbers 35-45) Thames. These differences were shown to be significant ($p<0.05$) via an ANOVA test of samples from the 3 groups. Inspection of the lower panel in Figure 5 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 very high concentrations, around Gallions Reach (site nr. 18), St Clement's Reach (nr. 31) and Tilbury (nr. 34). A possible explanation could be the vicinity to sewage discharge locations, in close vicinity to site #s 30-33 (Long Reach STP) and 34-35 (Tilbury STP). 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 3). 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 4). 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 4).

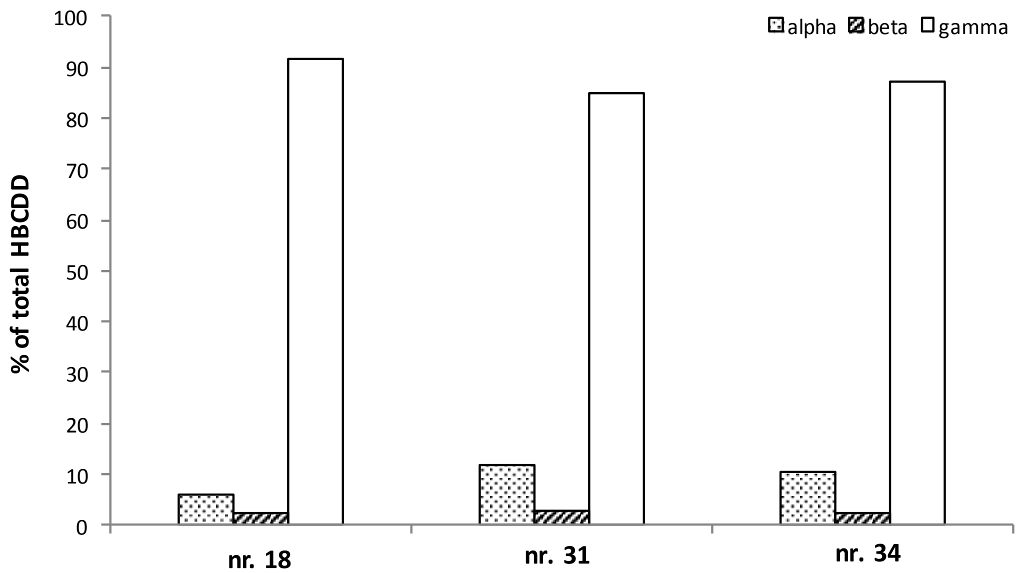


Figure 3. HBCDD diastereomer profile in sediment from location #s 18, 31, and 34

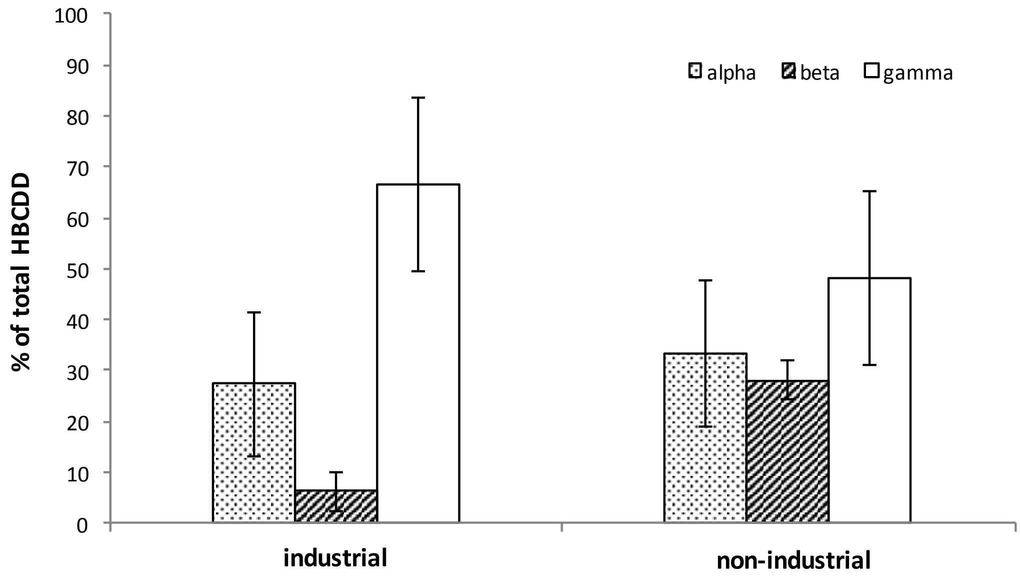
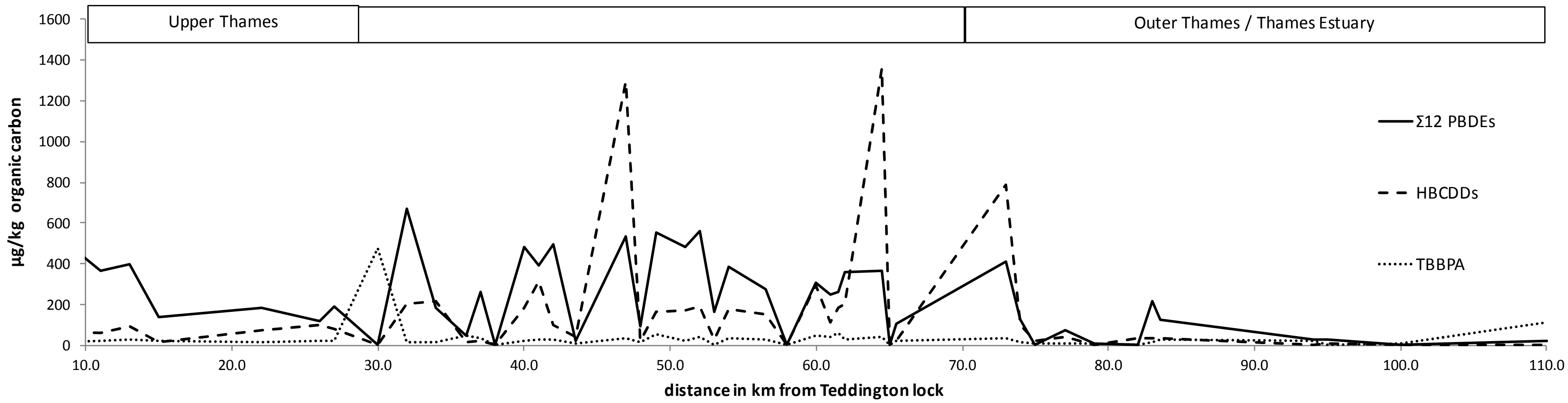


Figure 4. Average HBCDD diastereomer profile in industrial and non-industrial area



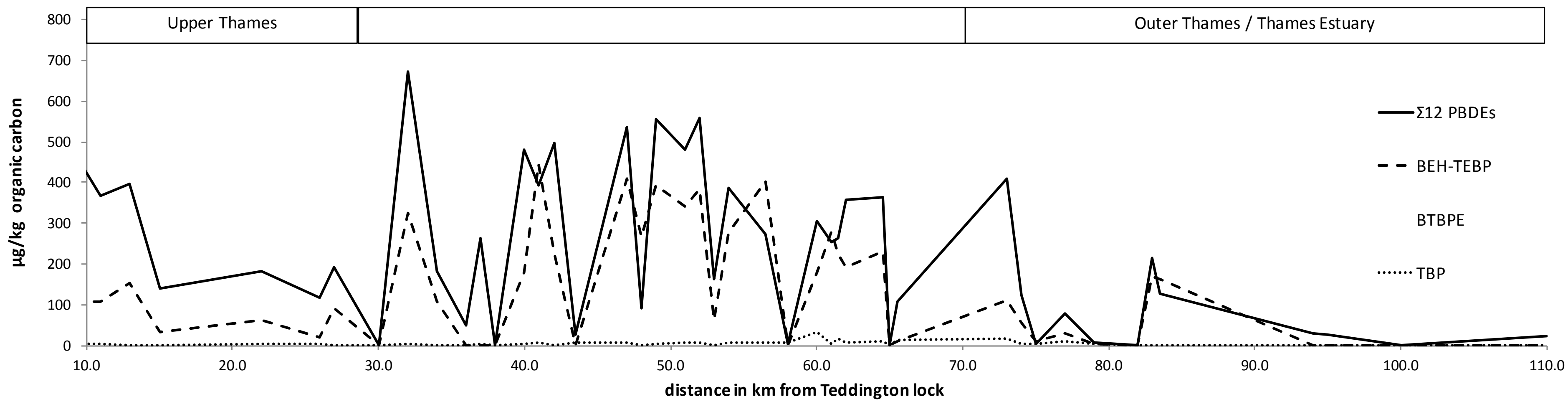


Figure 3. Spatial trends for Σ_{12}BDEs, HBCDDs, and TBBPA (top) and Σ_{12}BDEs, BEH-TEBP, BTBPE, and TBP (bottom) measured (in μg kg^{-1} organic carbon) along the river Thames, with an approximate distance (km) from Teddington Lock.

Figure 4 and Figure 5 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 for the 4 zones of 290, 309, 219 and 51 µg kg^{-1} OC), while for BDE-209 we observe a medium-high-high-low profile (7291, 9299, 9834 and 3255 µg kg^{-1} OC), and a much less marked attenuation in concentrations on travelling west to east. This could be a possible indication for different sources of the two groups of compounds. The general decline from west to east for $\sum_{12}$BDEs is probably driven by increasing distance from London and associated urban sources, as well as flocculation-deposition of sediment controlled by salinity (salting-out) with increasing proximity to the coast. The four salinity zones indicated were adapted from the study of Pope *et al.* [54]. The observed variability in the PBDE transect data can be explained by the fact that suspended particles can travel up and down-stream by 10 - 20 km on one tide.

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

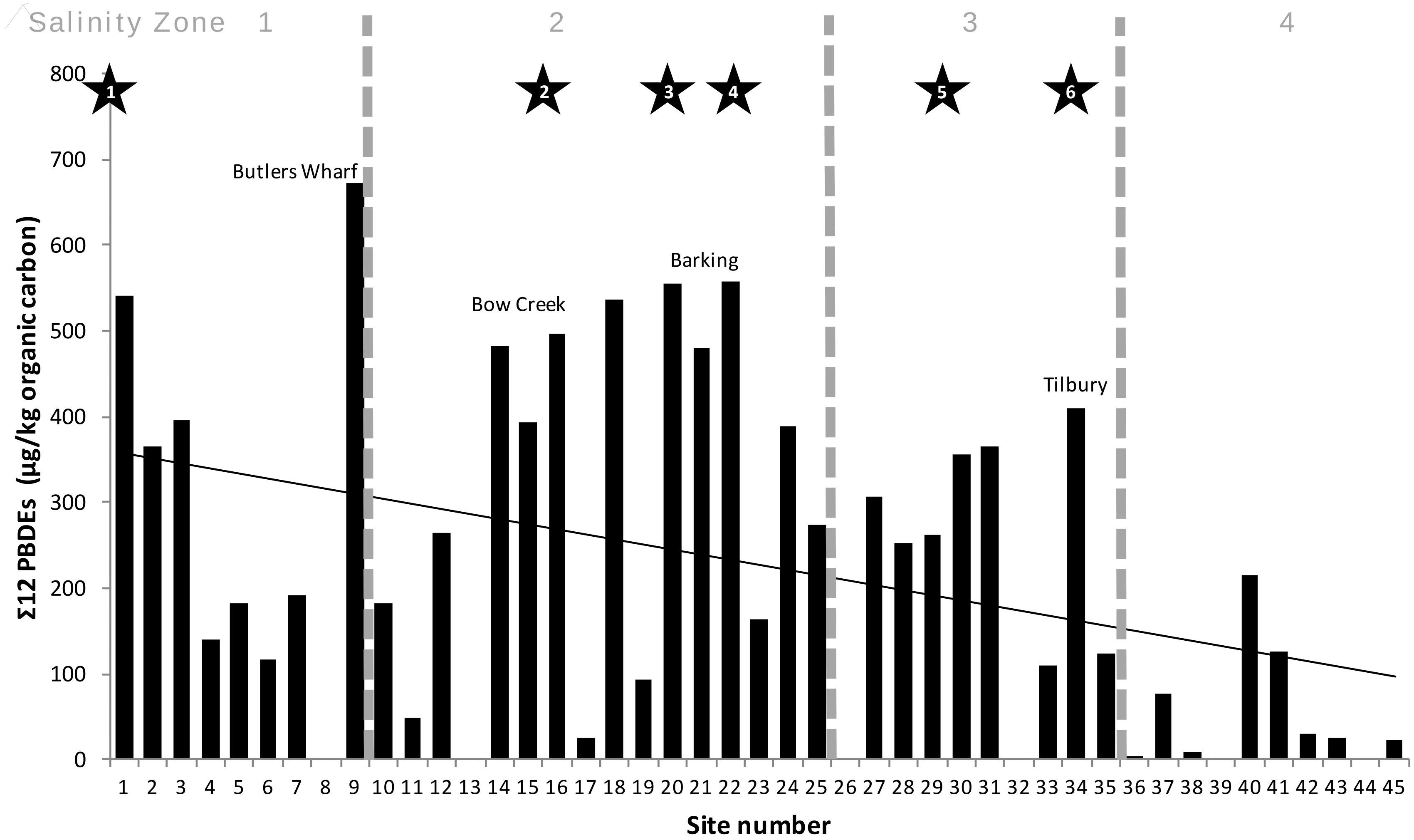


Figure 4. Concentrations ($\mu g\ kg^{-1}$ organic carbon) of $\sum_{12}$ PBDEs in River Thames sediments at each sampling location. Stars represent the main discharge locations of sewage effluents; 1. Mogden; 2. Abbey Mills; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP; 6. Tilbury STP. Adapted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

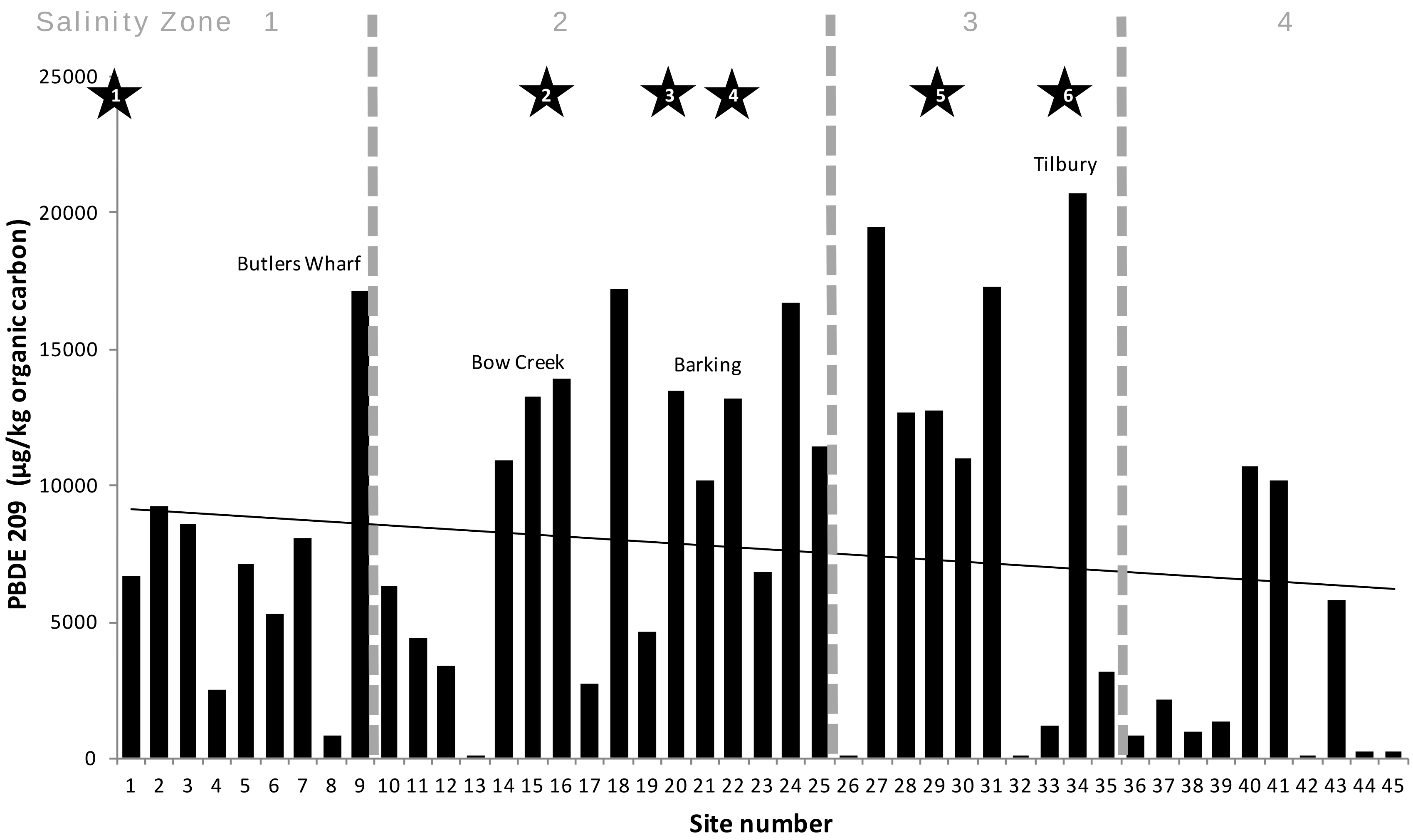
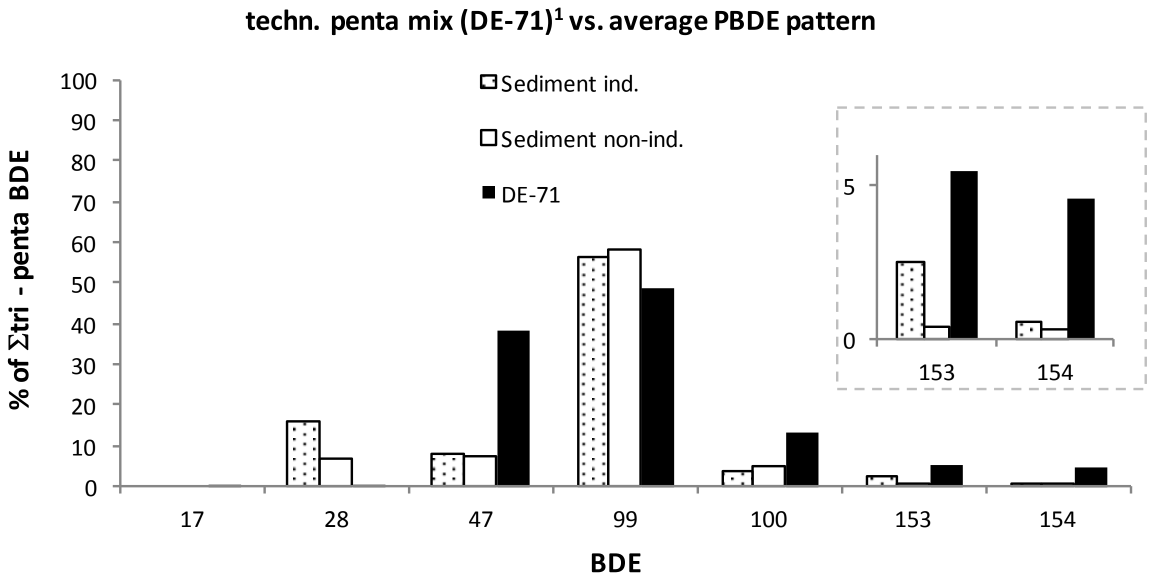
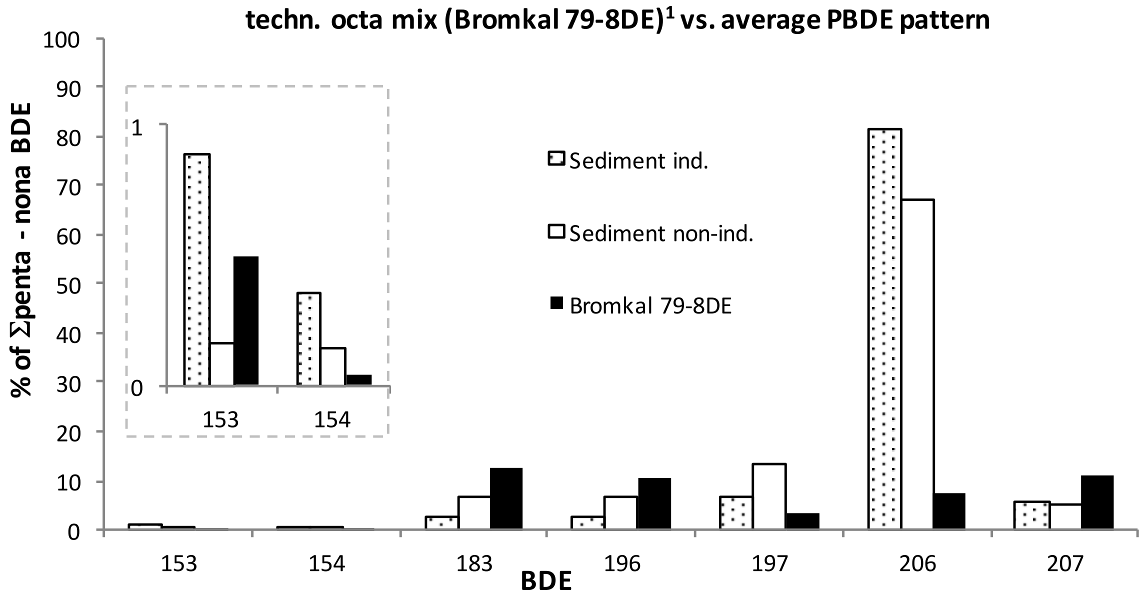


Figure 5. Concentrations (µg kg^{-1} organic carbon) of BDE-209 in River Thames sediments at each sampling location. Stars represent the main discharge locations of sewage effluents; 1. Mogden; 2. Abbey Mills; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP; 6. Tilbury STP. Adapted from Lopes dos Santos and Vane [27]. STP – sewage treatment plants

3.6. PBDE/NBFR patterns

Figure 6 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 can be 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 is 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 is observable, most likely due the stronger tendency of BDE-99 to partition to sediments. 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. 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.





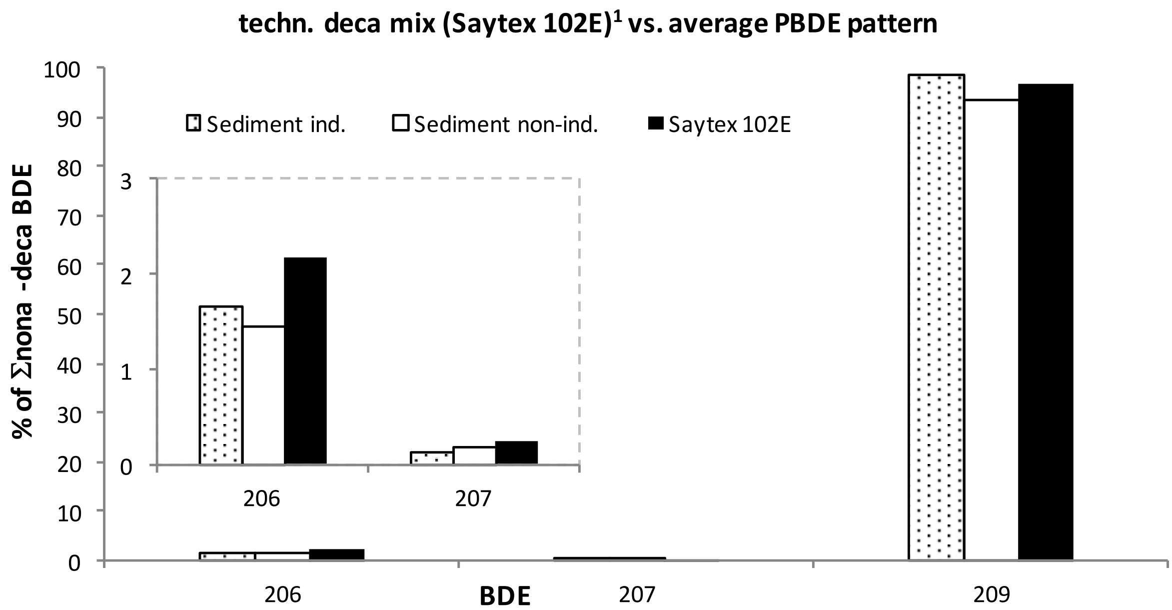


Figure 6. Comparison of an average PBDE profile in the industrial area (dotted) and outside the industrial area (white) to a technical penta / octa / deca BDE mix (black) – [1] technical mixture values adapted from La Guardia et al.[55]

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).

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 SI section). Unlike PBDEs, OH-BDEs have not been produced industrially and are not known by-products of technical brominated formulations[56, 57]. However, OH-BDEs have been reported in biotic and abiotic samples of the aquatic and marine environment, such as salmon[56], mussels[58], algae[59] as well as sediments[60], surface waters[61] and sewage treatment plant effluents [62]. Studies suggest that they are natural products of marine environments, as well as a result of metabolic biotransformation from anthropogenic PBDEs[59, 61]. The position of the hydroxyl group (OH) has been postulated to be an indicator of whether OH-BDE congeners are formed through oxidation or metabolic reactions[56, 58, 60]. Possible sources and transformation found in the literature include microbial aerobic degradation[63, 64], photochemical reactions of bromophenols[65] and PBDEs[66], transformation of bromophenols by marine bacteria[67] and a red algae enzyme[57], reactions of PBDEs with atmospheric OH radicals[61], as well as in sewage treatment plants through oxidative reactions and excretion of human and animal metabolites[61]. Whether the OH-BDEs detected in the Thames sediments are of environmental and/or biological origin is beyond the scope of this paper. However, since OH-BDEs have been reported to exhibit similar or even enhanced toxic[68] and estrogenic[69] effects on both human[70] and wildlife[71, 72] compared to PBDEs, their presence and relevance needs to be further investigated.

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

4. Summary

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

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

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

5. Acknowledgements

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