LEGACY PBDES AND NBFRS IN SEDIMENT SAMPLES OF THE RIVER THAMES USING LIQUID CHROMATOGRAPHY COUPLED TO A HIGH RESOLUTION ACCURATE MASS ORBITRAP MASS SPECTROMETER

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Introduction

Due to legislative restrictions on manufacture and use of some brominated flame retardants (BFRs), several new chemicals (NBFRs) have been developed. Due to their chemical properties, flame retardants in general have a tendency to accumulate on organic carbon rich matter and have been detected in samples of sediment, dust and sewage sludge around the world [1]. These matrices are of relevance to the environment and human health and levels and trends of both legacy BFRs and NBFRs have to be investigated and compared against each other. To explore the presence of these emerging pollutants in environmental matrices analytical methods for targeted analysis are required. Classically these compounds are determined by GC-based instrumental methods. In recent years, LC-based methods coupled to low resolution mass spectrometers have also been developed [2]. Advances in high resolution mass spectrometry facilitate accurate measurements and identification of target compounds and unknowns. In this work the potential of quadrupole Orbitrap benchtop technology will be exploited for targeted detection and quantification of selected PBDEs and NBFRs in sediment samples, along with the untargeted identification of possible degradation and transformation products. Since sediments are an important sink for environmental pollutants, they can provide information on the presence of emerging BFRs and how their levels compare to legacy BFRs. Further understanding the sources and spatial trend of such compounds can give us an insight on their environmental fate.

Materials and methods

Sampling. Sampling of Thames sediments 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 [3, 4]. At each location, surface sediments (0-5 cm) were collected from four corners of a square of ca. 2 m2 area, using either a stainless steel trowel or a polycarbonate tube fitted with a core catcher manually driven into the surface [5]. 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 then 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 [6].

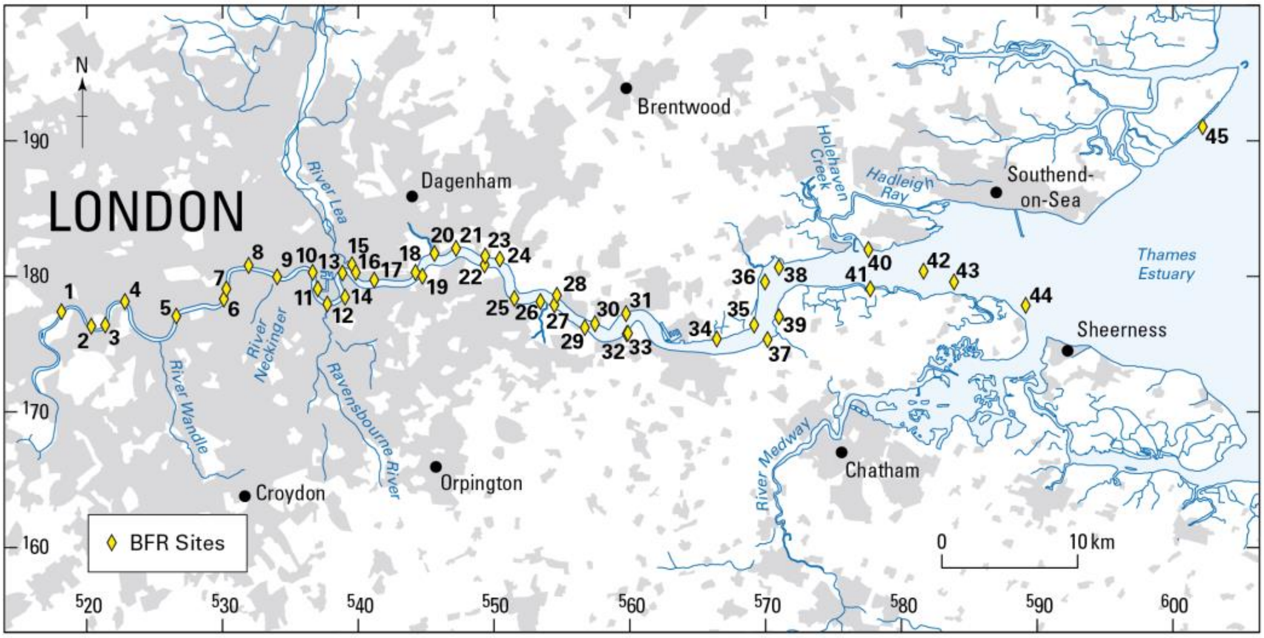

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Figure 1. Locations (yellow diamonds) of sampled and analyzed surface sediments from the Thames Estuary.

Extraction and clean-up. 2 g of freeze-dried sediment were weighed in to an extraction tube and spiked with a surrogate standard mixture (13C-BDE28, BDE77, BDE128, 13C-BDE209, 13C-EH-TBB, 13C-BEH-TEBP, 13C-BTBPE and 13C-α-,β-, and γ-HBCDDs). 2 g of copper was added for sulfur removal. The method was based on a ultrasonication-assisted extraction with hexane:acetone (3:1 v/v), vortex (5 min) followed by ultrasonication extraction (20 min) and centrifugation (5 min. at 4000 r.p.m.). This procedure was repeated twice. The combined extract was then evaporated to dryness under a gentle stream of N2 and reconstituted in 2 mL of hexane. This was followed by a sulfuric acid wash of the extract, with the layers allowed to separate over night. 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 N2 and loaded onto a conditioned HyperSep™ 1 g Florisil SPE cartridge. Subsequent elution was performed with 20 mL of hexane:dichloromethane (1:1 v/v). TBBPA was eluted in a second fraction with 15 mL of methanol. Finally both extracts were concentrated to dryness under a N2 flow in a Turbovap and reconstituted in methanol:toluene (1:1 v/v) containing 200 pg µl-1 of 13C-BDE100 as a recovery determination standard.

The reference material SRM 1944 (NIST) for sediment samples was used to evaluate the accuracy of the method for PBDEs and HBCDDs. An SRM sample was included for every 20 sediment sample, while method blanks (sodium sulfate replacing sediment) were analyzed every 5 samples.

UPLC-HRMS measurement. Final extracts were separated on a Thermo Scientific Accucore™ RP-MS 100x2.1 mm, 2.6 µm column on a Thermo Scientific UltiMate® 3000 HPLC system using a 17 min. gradient elution program with water (mobile phase A) and methanol (mobile phase B) at a flow rate of 400 µL min-1. The HPLC gradient elution program and APCI values were optimized based on the measurement of reference standard solutions. Samples were analyzed on a Q-Exactive™ Plus mass spectrometer with both an APCI and HESI source in negative ionization mode at a resolution of 70,000. Raw data files were processed using Thermo Scientific Trace Finder™ version 3.3 software.

Results and discussion

Initially, full scan experiments were conducted to obtain a general overview of the presence of compounds of interest in the samples. The use of high-resolution accurate mass (HRAM) instrumentation, together with powerful software tools like Trace Finder™, facilitates identification of targeted compounds by means of selectivity, elemental compositions and isotopic pattern scoring. Confirmation of compounds was also conducted using retention time of reference standards. For most compounds the pseudo-molecular ion $[M\text{-}Br+O]^-$ commonly formed in negative APCI mode was observed, for other compounds such as HBCDDs and TBBPA $[M\text{-}H]^-$ was monitored. Measurements in HESI were all based on the pseudo-molecular ion $[M\text{-}H]^-$. Quantification was based on the internal standard. MS/MS fragmentation experiments were performed on selected compounds, especially where no reference standard was available in order to obtain structural information. Recoveries for internal standards were in the range of 90 to 110 %. Values obtained for the SRM 1944 were generally in good accordance with the certified levels. In addition, non-certified compounds including 2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP), pentabromoethylbenzene (PBEB), 2,2',4,4',5,5'-Hexabromo-biphenyl (BB153) and dechlorane plus (DP) were detected in the SRM 1944.

An overview for the results of the analyzed sediment samples is shown in Table 1. Average results indicate that BDE209 is the prevalent congener and accounts for around 95% of total PBDEs detected, followed by BDE206 and BDE99. HBCDDs were detected in most samples at comparable concentrations to the Σ12BDEs (without BDE209). Also TBBPA was found in most samples but at an order of magnitude lower. The following NBFRs were quantified in most samples in the indicated concentration order: BEH-TEBP>BTBPE>TBP, while DBDPE, PBEB and DP were identified only in a few samples. Target compounds like EH-TBB, HBB, BB153 and α/β-DBE-DBCH were not detected in any of the sediments. Samples from the industrial area (number 13-34) showed significantly higher concentrations of Σ12BDEs, HBCDDS, TBBPA, BEH-TEBP, BTBPE and TBP compared to both the samples from the inner (number 1-12) and outer (number 35-45) Thames.

The HPLC-HRMS used in this study proved to be an adequate platform for the identification and quantification of PBDEs and NBFRs, with the possibility to screen for further compounds/transformation products of interest.

Table 1. Summary of the compounds analyzed in this study, their abbreviations, and their presence in the samples

Abbreviation	Compound name	Detection frequency	Concentration range (μg kg^{-1} dry weight)
Σ12BDEs	sum of BDEs 17, 28, 47, 99, 100, 153, 154, 183, 196, 197, 206 and 207	7-45/45	n.d. – 28.56
BDE209	decabromodiphenyl ether	45/45	0.03 - 534.90
ΣHBCDD	sum of α-, β- and γ- hexabromocyclododecanes	41/45	n.d. – 38.19
TBBPA	tetrabromobisphenol A	44/45	n.d. – 2.62
EH-TBB	2-ethylhexyl 2,3,4,5-tetrabromobenzoate	0/45	n.d.
BEH-TEBP	bis(2-ethylhexyl) tetrabromophthalate	34/45	n.d. – 13.74
BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane	23/45	n.d. – 3.84
TBP	2,4,6-tribromophenol	31/45	n.d. – 0.43
α/β-DBE-DBCH	1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	0/45	n.d.
HBB	hexabromobenzene	0/45	n.d.
BB153	2,2',4,4',5,5'-hexabromobiphenyl	0/45	n.d.

*n.d. – not detected

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