

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.

Material 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 m^2 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].

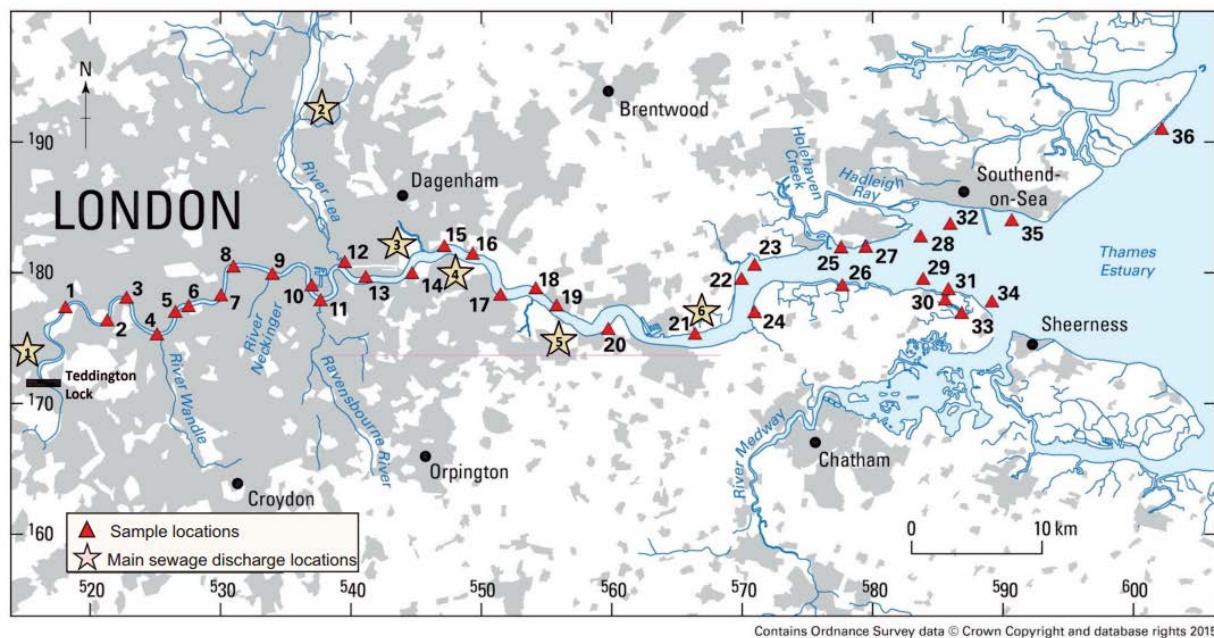


Figure 1. Locations (red triangle) of surface sediments from the Thames Estuary. Stars represent main discharge locations of sewage effluent.

Extraction and clean-up. 2 g of freeze-dried sediment were weighed in to an extraction tube and spiked with a surrogate standard mixture (^{13}C -BDE28, BDE77, BDE128, ^{13}C -BDE209, ^{13}C -EH-TBB, ^{13}C -BEH-TEBP, ^{13}C -BTBPE and ^{13}C - 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 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 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 \sim 1 mL under a gentle stream of N_2 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). Finally the extract was concentrated to dryness under a N_2 flow in a Turbovap and reconstituted in methanol:toluene (1:1 v/v) containing 200 $\text{pg } \mu\text{l}^{-1}$ of ^{13}C -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 100 x 2.1 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 $\mu\text{L min}^{-1}$. 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 an APCI source in negative ionization mode at a resolution of 35,000. 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 $[M-Br+O]^-$ commonly formed in negative APCI mode was observed and used for quantification (based on the internal standard). All ion fragmentation (AIF) was performed to obtain a Br ion trace, which aids in the identification of non-target bromine containing compounds. MS/MS fragmentation experiments were then performed on these compounds, especially where no reference standard was available in order to obtain structural information. Recoveries for internal standards were in the range of 70 to 99 %. Values obtained for the SRM 1944 were generally in good accordance with the certified levels as shown in Table 1. 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'-Hexabromobiphenyl (BB153) and dechlorane plus (DP) were detected in the SRM 1944.

Table 1. Comparison of UPLC-HRMS data for BFRs with NIST SRM 1944 certified values

Compound	UPLC-HRMS µg/kg (n=3)	Reference value SRM µg/kg
PBDE 47	1.80 ± 0.39	1.72 ± 0.28
PBDE 99	1.65 ± 0.30	1.98 ± 0.26
PBDE 100	0.48 ± 0.01	0.447 ± 0.027
PBDE 153	6.57 ± 0.83	6.44 ± 0.37
PBDE 154	1.05 ± 0.04	1.06 ± 0.08
PBDE 183	31.82 ± 0.21	31.8 ± 0.1
PBDE 206	6.96 ± 1.23	6.2 ± 1.0
PBDE 209	87.43 ± 5.3	93.5 ± 4.4
ΣHBCDDs	13.09	21.2

Preliminary results for the analyzed sediment samples indicate the presence of PBDEs (lower levels for BDEs-47, 99, 100, 153, 154, 183 and higher levels for BDE206 and 209), as well as HBCDDs and the occurrence of NBFRs like BEH-TEBP, BTBPE, but also 2,4,6-tribromophenol (TBP) and chlorinated DP.

Acknowledgements

This research has received funding from the Marie Curie Actions of the European Union's FP7 Programme under REA grant agreement n°606857. Freeze dried sediment samples were kindly provided by Dr Christopher Vane from the British Geological Survey.

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