

HALOGENATED FLAME RETARDANTS IN UK SEDIMENTS

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Introduction

Several studies have shown the widespread distribution, persistence and bioaccumulation capacity of the brominated flame retardants (BFRs) in the marine environment ¹. So far, studies have largely been focused on the groups of BFRs which have been the most used: the polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane and tetrabromobisphenol A. These results have led to increasing regulation and restrictions on the production and use of these compounds, and also to their substitution with other non-PBDE BFRs. The number of such chemicals is so large, that an effort has been made to unify their abbreviations to avoid confusion ². Some of the most commonly found of those chemicals are the 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB or EH-TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (TBPH or BEH-TEBP), hexachloro-cyclopentadienyl dibromocyclooctane (HCDBCO or DBHCTD), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB) and hexabromobenzene (HBB) and Dechlorane Plus (DPs or DDC-CO). Although there is not too much information about fate of these FRs, recent papers have shown the presence of some of these compounds in the environment ^{3,4} and also their bioaccumulation capacity ^{5,6}. Cefas has been analyzing sediment samples for flame retardants for >10 years ^{7,8}. Routine analysis of PBDEs for offshore monitoring programs for OSPAR has been going on since 2009 with hexabromocyclododecane (HBCDD) included since 2010. Also, monitoring of PBDEs in sediments in and around coastal dredge disposal sites has been carried out since 2005 in a varying sampling program focusing on different locations each year. On top of these regular programs, a number of *ad hoc* surveys have been conducted, which included in 2010 analyzing PBDEs and HBCDD from estuarine and river stations, and in 2012 analysing 40 marine and estuarine sediment samples collected in the UK over the period 2010-2012 (see Figure 1 for location of these alternative FR samples). The key findings of these surveys will be presented.

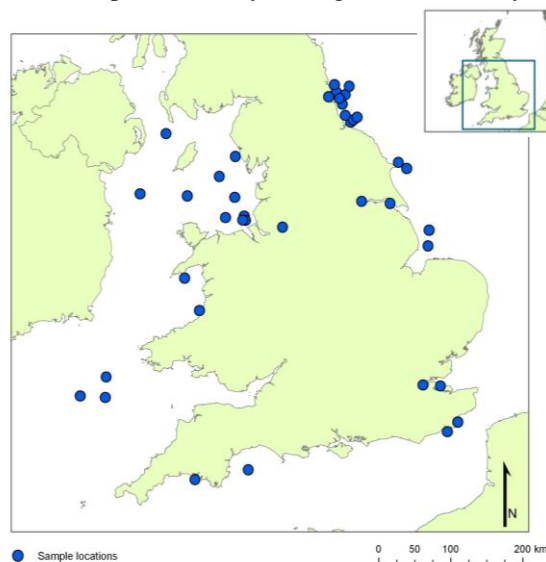


Figure 1: Map with the location of the marine and estuarine sediment samples analyzed for alternative FRs.

Materials and methods

Sediment samples for PBDE and HBCDD analysis were extracted with Soxhlet using hexane and acetone 1:1. Clean up for PBDE analysis was with alumina and silica columns, with subsequent instrumental analysis by gas chromatography-negative chemical ionization-mass spectrometry (GC-NCI-MS)⁹. Twelve BDE congeners were determined (BDE17, BDE28, BDE47, BDE66, BDE85, BDE99, BDE100, BDE138, BDE153, BDE154, BDE183 and BDE209). Quantification of BDE209 was carried out with a separate injection to the other PBDEs on a shorter 15m column. Clean up for HBCDD (α -, β - and γ -HBCDD, plus TBBP-A) analysis was with gel permeation chromatography (GPC) and solid phase extraction (SPE) using acid silica, with subsequent instrumental determination by ultra performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). The method for alternative FR analysis (>20 compounds as detailed in Table 1) employed pressurized liquid extraction, followed by double clean-up with gel GPC and SPE using Florisil, with subsequent instrumental determination by GC-MS/MS¹⁰. Samples were analysed alongside blank and reference materials (1 of each with every 10 samples) for QA/QC, with samples not meeting acceptance criteria being reanalyzed. All results are reported on a dry weight (dw) basis.

Results and discussion

In offshore marine sediments, flame retardants were detected in all but the most offshore stations. BDE209 was the most widespread distribution (quantifiable at 12/14 monitoring stations), with concentrations ranging from <0.1 to 25 $\mu\text{g}/\text{kg}$ dw. Highest concentrations were found in the Liverpool Bay area. BDE209 usually makes up >90% of ΣPBDE . BDE47 was the next most abundant congener (present at 9/14 stations), with concentrations ranging from <0.02-4 $\mu\text{g}/\text{kg}$ dw. Highest concentrations were found off the River Tees in the northeast of England. Additionally, BDE99 was present in 7 out of 14 stations, sometimes at higher concentrations than BDE47 in the northeast of England. Other BDEs such as 154, 153, 100 and 183 were also detected but only off the northeast of England. A tributary to the River Tees contained the only factory that manufactured penta-PBDEs in the UK, which probably accounts for this distribution. HBCDD was generally only detected in stations in the northeast of England, with γ -HBCDD the dominant isomer, mostly at concentrations < 1 $\mu\text{g}/\text{kg}$ dw. The exceptional value of 15 $\mu\text{g}/\text{kg}$ is again off the mouth of the River Tees, which also contained a factory manufacturing HBCDD.

In coastal sediments in and around dredge disposal sites, PBDEs were detected in all samples. BDE209 was again the dominant congener, usually making up >90% of ΣPBDE . In sites on the south coast of England, it was the only PBDE detected. At stations within disposal sites, especially in the northeast of England, which can be considered to be reflective of harbor sediments, BDE209 concentrations sometimes exceeded 100 $\mu\text{g}/\text{kg}$ dw. Outside of the disposal sites, concentrations were usually <20 $\mu\text{g}/\text{kg}$ dw. The exception to this is near the mouth of the River Mersey, where concentrations were >100 $\mu\text{g}/\text{kg}$ dw. BDE209 was not manufactured in the UK so these elevated levels come as a result of use rather than production. The sum of the other PBDEs, excluding BDE209, was <10 $\mu\text{g}/\text{kg}$ dw outside of disposal sites in the north east of England, and at or below LOQs in Liverpool Bay and the South. HBCDD was not analysed in these samples.

In samples from 6 rivers and estuaries (Humber, Medway, Thames, Alde, Tyne and Mersey) analysed in 2011, BDE209 was detected in all stations at concentrations ranging from 5-1000 $\mu\text{g}/\text{kg}$ dw, with Humber, Thames, Tyne and Mersey all in 100s of $\mu\text{g}/\text{kg}$ dw. BDE47 was detected in all but the Mersey at concentrations ranging from 1-7 $\mu\text{g}/\text{kg}$ dw. BDE99 was also detected in all but the Mersey at concentrations ranging from 0.1-10 $\mu\text{g}/\text{kg}$ dw. Many other PBDEs were detected. HBCDD was present in all stations, however in the Mersey and Alde, only γ -HBCDD was present at just above the LOQ (<0.1-0.5 $\mu\text{g}/\text{kg}$). In the other 4 locations, all 3 isomers were detected, with γ -HBCDD the dominant isomer at concentrations ranging from 1-40 $\mu\text{g}/\text{kg}$ dw, α -HBCDD ranging from 0.2-4 $\mu\text{g}/\text{kg}$ dw and β -HBCDD ranging from 0.1-3 $\mu\text{g}/\text{kg}$ dw. Highest concentrations for all flame retardants were in the Tyne followed by the Thames and then the Humber.

From the alternative FRs survey, which included a mix of offshore, coastal and estuarine samples, results show that some FRs such as BTBPE, PBEB, PBT and DDC-CO (DPs) are present in UK samples, currently at much lower concentrations than PBDEs (see Table 1). Over half of the non-BDE halogenated flame retardants analysed for were not detected in any samples. From this survey, it is not apparent which are the dominant flame retardants currently being used a replacement of PBDEs. Phosphate containing flame retardants were not included in these studies and could be more important than those that were.

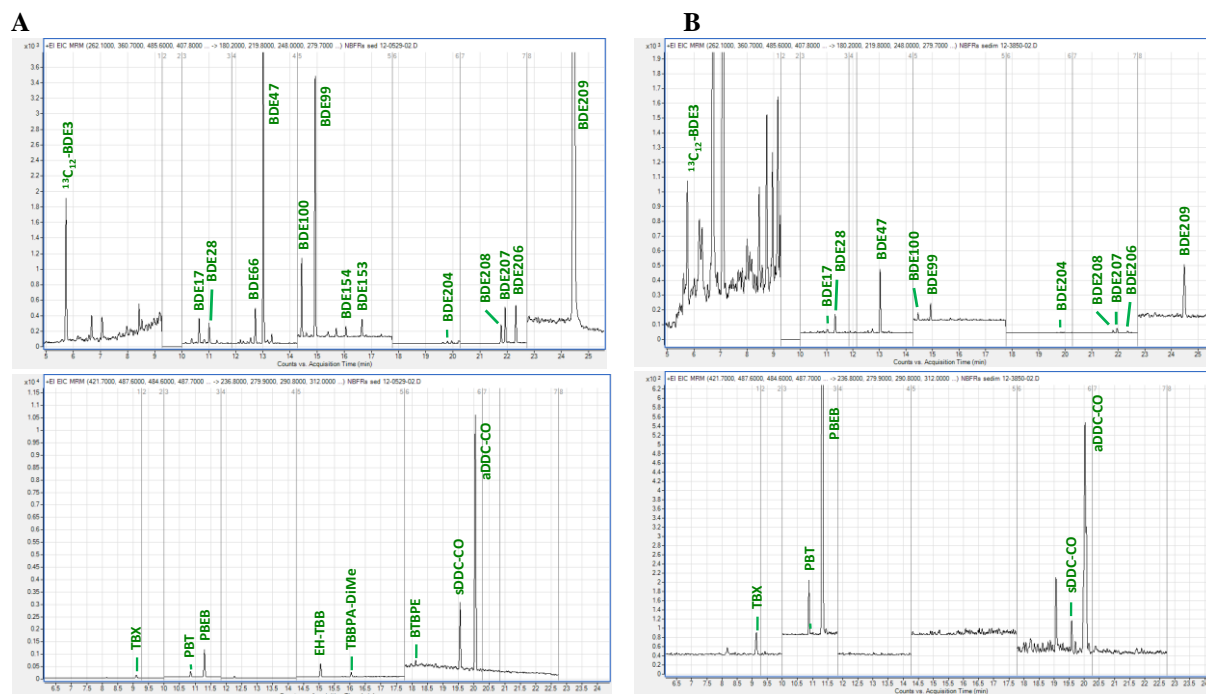
Table 1: Summary of the compounds analyzed in this study, their abbreviations, and their presence in the subset of samples analyzed for PBDEs, HBCDD and alternative FRs.

Revised abbreviation [2]	Previous abbreviation	Compound name	Frequency of detection	Concentration range ($\mu\text{g kg}^{-1}$ dry weight)
TBP-AE	ATE	2,4,6-tribromophenol allyl ether	0/42	n.d.
DiBTrCCH	DBTCC	Dibromotrichlorocyclohexane	0/42	n.d.
TeBDiCCH	TBDCC	Tetrabromodichlorocyclohexane	0/42	n.d.
a-DBE-DBCH	a-TBECH	α -1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane	0/42	n.d.
b-DBE-DBCH	b-TBECH	β -1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane	0/42	n.d.
d-DBE-DBCH	d-TBECH	δ -1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane	0/42	n.d.
g-DBE-DBCH	g-TBECH	γ -1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane	0/42	n.d.
BATE	BATE	2-bromoallyl 2,4,6-tribromophenyl ether	0/42	n.d.
TBX	pTBX	2,3,5,6,-tetrabromo- <i>p</i> -xylene	42/42	< 0.004* - 0.048
TrBTrCCH	TBTCC	Tribromotrichlorocyclohexane	34/42	n.d. - 0.275
b-TBCO	b-TBCO	β -1,2,5,6-tetrabromocyclooctane	0/42	n.d.
TBCT	TBoCT	Tetrabromo- <i>o</i> -chlorotoluene	0/42	n.d.
PeBCCH	PBCC	1,2,3,4,5-pentabromo-6-chlorocyclohexane	15/42	n.d. - 0.143
PBT	PBT	2,3,4,5,6-pentabromotoluene	42/42	< 0.004* - 0.041
PBEB	PBEB	Pentabromoethylbenzene	42/42	0.035 – 1.62
TBP-DBPE	DPTE	2,3-dibromopropyl-2,4,6-tribromophenyl ether	0/42	n.d.
PBBB	PBBB	Pentabromobenzylbromide	0/42	n.d.
HBB	HBB	Hexabromobenzene	0/42	n.d.
PBB-Acr	PBBA	2,3,4,5,6-pentabromobenzylacrylate	0/42	n.d.
DBHCTD	HCDBCO	Hexachlorocyclopentadienyldibromocyclooctane	0/42	n.d.
EH-TBB	EHTBB	2-ethylhexyl-2,3,4,5-tetrabromobenzoate	1/42	n.d. - 0.29
TBBPA-DiMe	diMeTBBPA	Dimethyl tetrabromobisphenol A	25/42	n.d. - 0.414
BB153	BB153	2,2',4,4',5,5'- hexabromobiphenyl	0/42	n.d.
BTBPE	BTBPE	1,2- <i>bis</i> (2,4,6-tribromophenoxy) ethane	20/42	n.d. – 1.80
BEH-TEBP	TBPH	<i>Bis</i> (2-ethylhexyl)-3,4,5,6-tetrabromophthalate	0/42	n.d.
<i>s</i> -DDC-CO	<i>s</i> -DP	<i>syn</i> -Dechlorane Plus	41/42	n.d. – 1.46
<i>a</i> -DDC-CO	<i>a</i> -DP	<i>anti</i> -Dechlorane Plus	41/42	n.d. – 8.89
OBTMPI	OBIND	Octabromotrimethylphenyl indane	0/42	n.d.
Σ BDES		Sum of BDEs 17, 28, 47, 66, 85, 99, 100, 138, 153, 154, 183	38/40	n.d. – 32.15
BDE209			42/42	0.304 -1333
Σ HBCDD		Sum of α -, β - and γ -HBCDD	14/32	n.d. – 47.2

n.d.: Not detected; *: Method quantification limit

From the results for concentrations in sediments, it can be seen that there is a clear gradient in concentrations with rivers>harbor>coastal>offshore (see Figure 2 for an example comparison chromatogram from the River Mersey and its receiving body, Liverpool Bay). Movement of sediments down river and remobilization by dredging will continue to bring flame retardants into the marine environment. The levels of alternative

brominated flame retardants in the UK's sediment are currently very low, but could increase as useage increases, and as contaminants migrate away from source areas in rivers and estuaries.



Figures 2A and 2B: Extracted MRM chromatograms showing NBFRs and PBDEs present in a Mersey river sediment (A) and an offshore sediment from outer Liverpool Bay (B).

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