

# Distribution and input of brominated flame retardants and Dechloranes in the German Bight

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## Introduction

Sediments are habitats to a variety of species and as such of vital importance to the integrity of aquatic ecosystems. They can also function as sinks for numerous organic contaminants, which tend to adsorb to particles, due to their physicochemical properties, e.g. low water solubility and high  $K_{OW}$ -values. For this study a GC-MS/MS method was developed to analyse brominated and chlorinated flame retardants (FR) in sediments from the German Bight. The focus was on the substitutes of the banned polybrominated diphenylethers (PBDEs), namely alternate BFRs and Dechloranes (Decs). The presented study is part of the “North Sea observation and assessment” (NOAH) Project. In NOAH six test fields were defined to represent different biogeochemical seafloor provinces in the German Bight. The results will be used to determine the decisive factors in the contamination pattern of the North Sea, assess the ecosystem services provided by the different sediment classes and create an atlas of the seafloor provinces.

## Materials and methods

Between August 2012 and August 2013 surface sediments were sampled from the German Bight (including the NOAH test fields), river Elbe and river Weser (Figure 1). The samples were taken during five sampling campaigns with the research vessels Heincke, Ludwig Prandtl and Storch respectively. Sediment samples were taken using a box corer. Only the first five centimeters of largely undisturbed cores were used for analysis. All samples were stored in acetone cleaned aluminium containers and stored at -20°C until extraction.

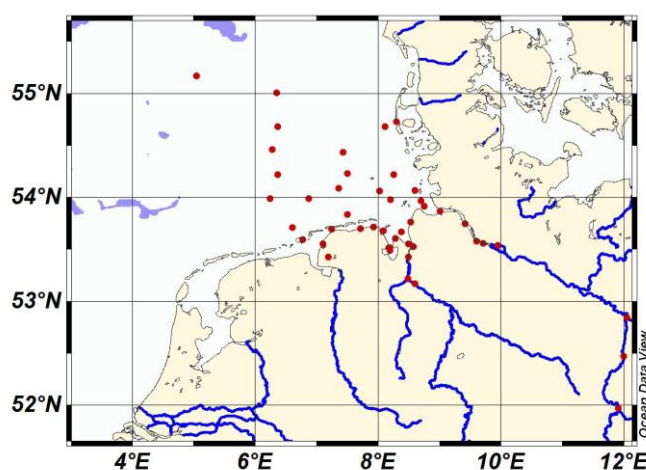


Figure 1: Sampling stations

The samples were homogenised with anhydrous Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) using an agate mortar. All samples were spiked with mass labelled surrogate standards 13C-BDE-28, 13C-BDE-47, 13C-BDE-99, 13C-BDE-153, 13C-BDE-183, 13C-MeOBDE-47, 13C-MeOBDE-100, 13C-HBB, 13C-synDP and 13C-PBBz.

Extraction and cleanup was performed using an online accelerated solvent extraction (DIONEX ASE-200) method. 33 mL stainless steel ASE cells were filled with 7 g 10% deactivated silica, 2 g Copper and 5 g dried sediment. The cells were extracted using the following method:

Dionex ASE-200 with Hexane as solvent, pressure (Nitrogen): 9 bar, temperature: 100°C, pressure: 120 bar, heat: 5 min., static (2x): 8 min., flush: 100%, purge: 60sec.

Extracts were reduced in volume to 150  $\mu\text{L}$  and each 500 pg (absolute) 13C-PCB-141 and 13C-PCB-208 was added as an injection standard to each sample.

Separate aliquots were dried to constant weight (at 105 °C) for the gravimetric determination of water content as well as the subsequent analysis of total organic carbon (TOC). TOC was measured using a LECO RC612 multiphase carbon/hydrogen/moisture determinator at 400°C.

In order to obtain maximum sensitivity as well as selectivity extracts were analysed by GC-MS in negative chemical ionisation mode (NCI) as well as GC-MS/MS in electron ionisation mode (EI).

For analysis in EI the instrument was fitted with a Restek 1614 column (15m x 0.25 mm i.d. x 0.10  $\mu\text{m}$  film thickness, Restek) and operated in multiple reactions monitoring mode (MRM). Samples were analysed for ten PBDEs, eight methoxylated PBDEs, twenty-four alternate BFRs and twelve Dechloranes.

NCI analysis was based on a method developed by Möller et al.<sup>1</sup>. The instrument operated in single ion monitoring mode (SIM) and fitted with a HP-5MS column (30m x 0.25mm i.d. x 0.25  $\mu\text{m}$  film thickness, J&W Scientific). In NCI sediments were analysed for 14 alternate BFRs, eight Dechloranes and three PBDE congeners.

Extraction and clean-up were conducted in a clean lab (class 10000). Materials containing FR were avoided during sample preparation and analysis.

Surrogate recoveries were determined for every sample. Mean recoveries were  $86 \pm 45\%$  for 13C-BDE-28,  $80 \pm 49\%$  for 13C-BDE-47,  $83 \pm 50\%$  for 13C-BDE-99,  $136 \pm 47\%$  for 13C-BDE-153,  $125 \pm 58\%$  for 13C-BDE-183,  $73 \pm 38\%$  for 13C-MeOBDE-47,  $139 \pm 24\%$  for 13C-MeOBDE-100,  $61 \pm 34\%$  for 13C-HBB,  $110 \pm 57\%$  for 13C-synDP and  $45 \pm 29\%$  for 13C-PBBz. All concentrations were recovery corrected.

A blank test, using  $\text{Na}_2\text{SO}_4$  treated similar to real samples, was conducted with every extraction batch (five samples). For all compounds, except TBP concentrations of FR in blanks were in the pg absolute scale, ranging from 6 pg absolute for DBE-DBCH to 220 pg absolute for BDE-28. The limit of detection (LOD) was calculated from a signal to noise ratio of three or by using the blank standard deviation method (where applicable). The limit of quantification (LOQ) was calculated from a signal-to-noise ratio of ten or using the blank standard deviation method (where applicable). In EI LODs ranged from 25 pg absolute for DDC-DBF to 420 pg absolute for BDE-28. The LOQ ranged from 85 pg for DDC-DBF to 880 pg for BDE-28. In NCI LODs ranged from 0.09 pg absolute for TBP-AE to 200 pg absolute for BDE-100 resulting in LOQs between 0.31 pg for TBP-AE and 500 pg for BDE-100.

## Results and discussion

Concentrations in general were low for all analysed compounds. With often less than 100 pg/g dw many compounds could only be discussed semi-quantitatively or qualitatively. The detection frequencies were highest for Dechloranes (100%) followed by alternate BFRs (88%) and PBDEs (56%). However, detection frequencies varied significantly with sampling sites. The low overall detection frequency of PBDEs may be explained by the higher blanks and resulting limits of detection for these compounds. However, concentration of alternate BFRs and Dechloranes were in a similar range as PBDEs, indicating that the substitutes are indeed replacing PBDEs as contaminants in sediments. BDE-209 was the only exception. Due to comparably high blanks it could only be quantified in 6% of the samples. Yet if it was detected the concentrations were at least one order of magnitude higher than all other found compounds. The high concentrations of BDE-209 (primary component of technical Deca-BDE)<sup>2</sup> were expected, due to the longer application and higher amounts of Deca-BDE in Europe, compared to technical Penta- and Octa-BDE, which were banned under the Stockholm Convention in the early 2000s<sup>3</sup>. Apart from BDE-209 primarily BDE congeners associated to the technical Penta-BDE mixture could be

detected. The abundances were almost identical to the composition of technical Penta-BDE with BDE-99 > BDE-47 > BDE-100 = BDE-85 > BDE-154, displaying the high persistence of technical Penta-BDE in sediments. In general PBDEs (mainly BDE-209) were predominant in sediments from the German Bight and, apart from the pesticide and flame retardant intermediate hexachloropolyphenylnorbornene (HCPN), East Frisian Islands, whereas alternate BFRs and Dechloranes were dominant in River Elbe and Weser. Due to the fact that flame retardants are largely applied in consumer products and building materials areas with large population or industry are potential emission hotspots<sup>4</sup>. Rivers, like Elbe and Weser, passing such potential emission hotspots can therefore be expected to represent recent emissions, such as the substitutes for PBDEs. The presence of banned PBDEs can largely be explained by their persistence in sediments<sup>5</sup>, as well as diffuse emissions from PBDE containing products and materials still in use. An exemption is the conspicuously high technical Penta-BDE concentration in Bremen/Bremerhaven harbour, indicating the presence of a point source in this area (Figure 2).

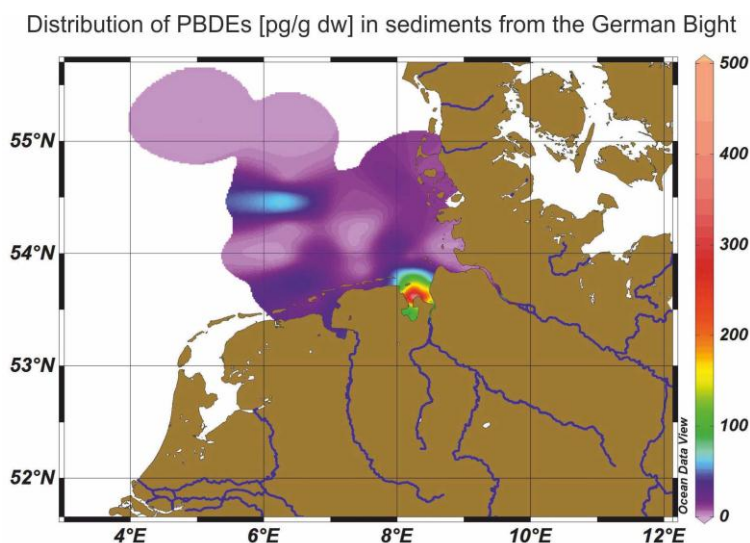


Figure 2: Distribution of sum PBDEs [pg/g dw] (without BDE-209) in sediments from the German Bight

The alternate flame retardant 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), a principal component in the PBDE substitute Firemaster 550, for example was the second most abundant and one of the highest concentrated flame retardant in river Elbe, while it could only be detected in a few isolated marine sediment samples.

Hexabrombenzene (HBB) had the highest overall detection frequencies of the alternate BFRs followed by TBP-DBPE > TBA > BATE > EH-TBB >  $\beta$ -DBE-DBCH > PBEB > TBP-AE. HBB is suspected to be a metabolite or transformation product of other brominated flame retardants such as PBDEs<sup>6</sup>, which could be an explanation for the high detection frequencies and concentrations. 1,3,5-tribromo- 2-(2,3-dibromopropoxy)- benzene (TBP-DBPE) was detected in about half of the analysed samples. The detection of TBP-DBPE in sediments indicates a high persistence in this matrix, as TBP-DBPE was only produced until the 1980s by one company in Germany<sup>7</sup>. The high abundance in sediments could be a reason for the continued detection of DPTE in various environmental matrices despite the lack of emissions. Other alternate BFRs detected in isolated samples throughout the sampling areas were Pentabromoethylbenzene (PBEB), Tribromoanisole (TBA), 1,3,5-tribromo-2-(2-propen-1-yloxy)- benzene (TBP-AE) and 2-bromoallyl-2,4,6-tribromophenyl ether (BATE). In case of PBEB the diffuse occurrence can be explained by its high persistence in sediments. TBA, TBP-AE and BATE on the other hand are suspected or proven transformation products of other brominated flame retardants such as TBP-DBPE<sup>7</sup>. TBA is additionally produced naturally in the marine environment<sup>8</sup>.

The alternate BFR DBE-DBCH could be almost exclusively detected in samples from the East Frisian Islands. A possible explanation could be that the water masses in this area are from the British Channel, whereas all other sampling areas were influenced by water masses from either river Weser or Elbe.

Dechloranes were unsuspectedly the most abundant compounds in the entire sampling area. A reason are probably the low average detection limit of these compounds, however the high abundance also displays the increasing relevance of Dechloranes as environmental contaminants. Dechlorane Plus (DP) was the most abundant Dechlorane (94%) followed by Dechlorane 602 (DDC-DBF), HCPN and Dibromoaldrin (DBALD). The high abundance of DP was expected, due to its frequent detection in previous studies from the North Sea<sup>9</sup>. Of the two isomers in the technical mixture (syn and anti) anti-DP was dominant in sediments, reflecting the composition of the technical product. DP therefore seems to not be subjected to significant biotransformation in sediments, or at least to no processes that change the isomer composition. DDC-DBF could be detected in 77% of the samples in low concentrations < 100 pg/g dw. The source remains unknown, because DDC-DBF is not reported as produced in or imported to the EU. However, DDC-DBF was previously detected in biota from Germany as well as Spain<sup>10,11</sup>. The detection of HCPN and DBALD were completely unexpected, as both have, to our knowledge, not been reported in any environmental matrices before. DBALD is a so called experimental mixed brominated, chlorinated flame retardant, which was first patented in the 1970s<sup>12</sup>. There is however no information available on current use or production. HCPN is an intermediate in the production of chlorinated flame retardants as well as heptane fungicides<sup>13</sup> and could potentially also be a biotransformation product or impurity in either of these compounds. Both compounds were found in highest concentrations around the East Frisian Islands. This could indicate an impact of the British Channel. However, the high concentrations of HCPN and the extensive agricultural use of the adjoining areas suggest, that at least the detection of HCPN might have been caused by the application of fungicides.

All analysed compound groups showed strong to very strong correlation with the total organic carbon (TOC) content of the analysed sediments with an average correlation coefficient of 0.82.

The results of this study show the increasing relevance of substitutes for PBDEs, especially Dechloranes in all seafloor provinces of the German Bight. More research is needed to identify sources and assess the potential negative environmental impacts of these compounds as well as their long-term fate in the marine environment.

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