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Fingerprint analysis of brominated flame retardants and Dechloranes in North Sea sediments

Roxana Sühling^{1,2*}, Jonathan L. Barber³, Hendrik Wolschke^{1,2}, Danijela Kötke¹,

Ralf Ebinghaus¹

¹Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute of Coastal Research, Department for Environmental Chemistry, 21502 Geesthacht, Germany;

²Leuphana University Lüneburg, Institute of Sustainable and Environmental Chemistry, 21335 Lüneburg, Germany

³Centre for Environment, Fisheries and Aquaculture Science (Cefas), Lowestoft, Suffolk NR33 0HT, United Kingdom

*Corresponding author: phone: +49 (0)4152 87-2353, fax: +49 (0)4152 87-2332,

Email: roxana.suehring@hzg.de

Abstract

53 brominated and chlorinated flame retardants were investigated in sediment samples from the German rivers Elbe and Weser, the German Bight, Jadebusen, East Frisian Coast as well as the UK east coast. The aim of the presented study was to investigate the prevalence of different halogenated flame retardant groups as contaminants in North Sea sediments, identify determining factors for the distribution and levels as well as to identify area specific fingerprints that could help identify sources.

In order to do that a fast and effective ASE extraction method with an on-line clean-up was developed as well as a GC-EI-MSMS and LC-ESI-MSMS method to analyse PBDEs, MeOBDEs,

alternate BFRs, Dechloranes as well as TBBPA and HBCDD. A fingerprinting method was adopted to identify representative area-specific patterns based on detection frequency as well as concentrations of individual compounds. Concentrations in general were low, with $< 1 \text{ ng g}^{-1} \text{ dw}$ for most compounds. Exceptions were the comparably high concentrations of BDE-209 with up to $7 \text{ ng g}^{-1} \text{ dw}$ in selected samples and TBBPA in UK samples with $2.7 \pm 1.5 \text{ ng g}^{-1} \text{ dw}$. Apart from BDE-209 and TBBPA, alternate BFRs and Dechloranes were predominant in all analysed samples, displaying the increasing relevance of these compounds as environmental contaminants.

1. Introduction

Sediments are habitats to a variety of species and are, as such, of vital importance to the integrity of aquatic ecosystems. They can function as sinks for numerous organic contaminants, which tend to adsorb to particles, due to their physicochemical properties, such as low water solubility and high K_{OW} -values. However, stored contaminants can also be released from sediments by e.g. remobilisation due to construction programmes or ingestion by benthic organisms. Sediments could therefore function as a long term and continual source for compounds with high persistence. Sediments from the coastal area of the German Bight represent a complex ecosystem with various habitats and ecosystem functions. Especially the mudflats of the North Sea, a world natural heritage site, are influenced by organic pollutants, which are discharged into the North Sea primarily through rivers.

Halogenated flame retardants have been applied in a variety of consumer products for the last decades. Some of them, such as the polybrominated diphenyl ethers (PBDEs) have, by now, been banned under the Stockholm convention due to their hazardous properties, including high persistence and bioaccumulation potential (Darnerud 2003). The ban of PBDEs has led to the application of a variety of halogenated substitutes with often very similar structures as PBDEs, resulting in potentially similar hazardous properties (Harju et al. 2009). As of today, there is little information available on the distribution of these emerging

halogenated flame retardants in the North Sea and even less on area specific patterns and the factors driving these patterns. Available data for PBDEs, HBCDD and TBBPA in European sediments mostly focus on contamination of river, rather than marine, sediments. Voorspoels et al. (2004) reported PBDEs in sediments from the Belgian North Sea as well as the Scheldt estuary and de la Cal et al. (2003) reported BDE congeners up to BDE-183 in marine sediments from north-east Spain. If analysed, highest concentrations were found for BDE-209 in all of the mentioned studies. For alternate BFRs and Dechloranes no data for marine sediments in Europe was found. In the Llobregat River basin Guerra et al. (2010) reported selected alternate BFRs with concentrations in the low ng g^{-1} dw range - similar to reported concentrations of PBDEs. López et al. (2008) detected concentrations in the low pg g^{-1} dw range of eight alternate BFRs in Dutch sediments. In Europe Dechloranes were reported in sediments from Kongsfjorden in Norway (Ma et al. 2015). Concerning marine sediments Peng et al. (2014) reported a variety of Dechloranes in a marine food web from North China.

For this study a GC-EI-MS/MS as well as a LC-ESI-MS/MS method with an on-line ASE extraction and clean up method were developed to analyse brominated and chlorinated flame retardants (FR) in sediments from the German part of the rivers Elbe and Weser, the German Bight, East Frisian Coast and UK east coast. The focus was on the substitutes of the banned polybrominated diphenylethers (PBDEs), namely alternate BFRs and Dechloranes (Decs). Furthermore the high production volume chemical Tetrabromobisphenol A (TBBPA) and the recently banned Hexabromocyclododecane (HBCDD) were included in the analysis.

The aim of this study was to identify determining factors for found contamination patterns and identify compounds of particular relevance. Representative and discernible contamination "fingerprints" were used to investigate relations and influences between the sampling areas as well as to identify potential driving factors for pollution, sources or source regions. Distance to the coast, riverine input, organic carbon content of the sediments as well as influence of currents transporting sediments e.g. from the English Channel were assessed as such potential driving factors for found contamination patterns. The presented

study is part of the “North Sea Observation and Assessment of Habitats” (NOAH) Project. The results of this study will be integrated with results of further NOAH studies to assess sea floor state and functions of the North Sea, ecosystem services provided by different sediment classes and create an atlas of representative seafloor provinces throughout the North Sea.

2. Materials and methods

2.1 Samples

Between August 2012 and August 2013 surface sediments were sampled from the UK east coast (n = 23), German Bight (n = 33), East Frisian Coast (n = 6), river Elbe (n = 9) and river Weser and Jadebusen (n = 12) (Figure 1). The samples from the German Bight and rivers were taken during five sampling campaigns with the research vessels Heincke, Ludwig Prandtl and Storch, respectively. Samples from the UK coast were collected on the research vessel Cefas Endeavour as part of the Clean Seas Environment Monitoring Program (CSEMP). Samples from the East Frisian Islands were provided by Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency (NLWKN). Sediment samples were taken using a box corer, except for those from the UK coast which were collected with a day grab. Only the first five centimetres of largely undisturbed cores were used for analysis. All samples were homogenized and stored in acetone cleaned aluminium containers at -20°C until extraction. For a full list of the analysed samples see supplement information table S1.

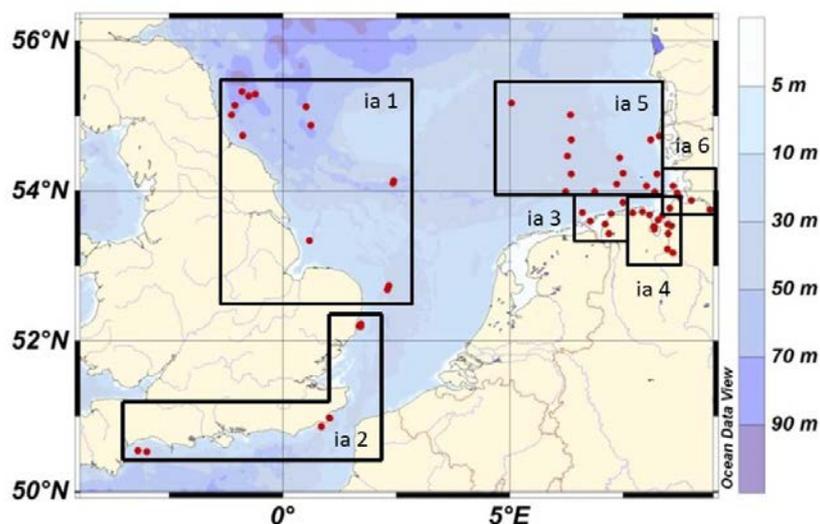


Figure 1: Sampling stations of the investigation areas (ia) 1-6; the investigation areas include the following sampling stations: ia 1: Northern UK Coast 1-17; ia 2: Southern UK Coast 1-6; ia 3: East Frisian Coast 1-6; ia 4: Jade/Weser 1-12; ia 5: North Sea 1-18 and ia 6: Elbe River 1-7

2.2 On-line ASE extraction and in-cell clean up

Larger pieces (> 2 mm) were removed from the sediment samples. The samples were homogenised with anhydrous Sodium sulfate (Na_2SO_4) using an agate mortar.

An in-cell clean-up and extraction method was developed using accelerated solvent extraction (Thermo Fisher ASE-200). 22 mL stainless steel ASE cells were filled with 7 g silica gel deactivated with 10% deionised water, 2 g copper activated with HCL and 5 g dried sediment. All samples were spiked with mass labelled surrogate standards ^{13}C -BDE-28, ^{13}C -BDE-47, ^{13}C -BDE-99, ^{13}C -BDE-153, ^{13}C -BDE-183, ^{13}C -MeOBDE-47, ^{13}C -MeOBDE-100, ^{13}C -HBB, ^{13}C -synDP and ^{13}C -PBBz.

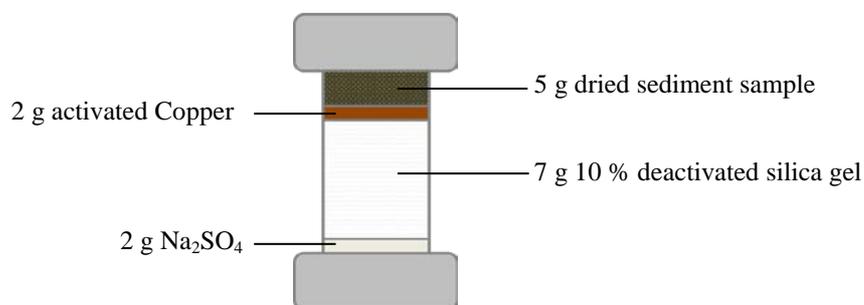


Figure 2: Schematic of the ASE in-cell clean up

The cells were extracted using the following method:

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

Extracts (2 x 100 % cell flush volume) were reduced in volume to 150 µL under a gentle stream of heated nitrogen (40°C) and 500 pg (absolute) ¹³C-PCB-141 and ¹³C-PCB-208 was added as an injection standard to each sample.

Cells were extracted a second time using the same ASE method but dichloromethane (DCM) as solvent. Extracts of the second fraction (20 mL) were transferred into methanol (MeOH) and reduced in volume to 150 µL. 30 % (v/v) H₂O was added as well as 500 pg ¹³C-PFNA and ¹³C-PFDA as injection standards. The first fraction was analysed using GC-ECNI-MS and GC-EI-MSMS. The second fraction was analysed using LC-ESI-MSMS.

By using the online extraction and clean up method work time as well as solvent use could be reduced drastically compared to classic Soxhlet and subsequent clean-up methods, to about 50 mL solvent per sample (including washing steps) and approx. 1 h work time (2 x 20 min extraction and approx. 20 min to reduce to final volume).

Separate sub samples 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 combustion method at 400 °C.

Recoveries of ¹³C-standards, extraction efficiency, blanks and reproducibility were tested in duplicates with and without matrix, during method validation (see section QA/QC). Acetone, hexane and dichloromethane (DCM) and methanol were pico grade and purchased from PromoChem.

Silica gel (0.063-0.200 mm) and granulated copper was purchased from Merck. Bio-Beads S-X3 (styrene divinylbenzene beads, 40 to 80µm bead size) were purchased from Bio-Rad Laboratories. Analytical standards were purchased from Wellington laboratories.

Average recoveries of ^{13}C -standards are presented in supplement information S5.

2.3 Instrumental analysis

In order to obtain maximum sensitivity as well as selectivity extracts were analysed by GC-MS in negative chemical ionisation mode (ECNI) as well as GC-MS/MS in electron ionisation mode (EI). The analysis was performed on Agilent 7000 B GC/MSMS System.

For analysis in EI the instrument was fitted with a Restek 1614 column (15 m x 0.25 mm i.d. x 0.10 μm film thickness, Restek) and operated in multiple reaction monitoring mode (MRM) at 70 eV. The programmable temperature vaporization injector (PTV) injector was operated in pulsed-splitless mode (injection pulse 25 psi for 2 min) with an inlet temperature program: 60 $^{\circ}\text{C}$ for 0.3 min, 300 $^{\circ}\text{C min}^{-1}$ until 280 $^{\circ}\text{C}$ and held for a final 10 min, with an injection volume of 2 μL . The GC oven program was as follows: initial 60 $^{\circ}\text{C}$ for 1 min, 10 $^{\circ}\text{C min}^{-1}$ until 280 $^{\circ}\text{C}$, held for 10 min, 40 $^{\circ}\text{C min}^{-1}$ until 300 $^{\circ}\text{C}$, held for another 2 min and a final 5 min backflush at 300 $^{\circ}\text{C}$ with a flow rate of 5.14 mL min^{-1} . The MS transfer line was held at 280 $^{\circ}\text{C}$. The ion source temperature was at 230 $^{\circ}\text{C}$ and quadrupole temperatures at 150 $^{\circ}\text{C}$.

Samples were analysed for eight PBDEs (BDE-28, -47, -66, -99, -100, -153, -154, -209), eight methoxylated PBDEs (5MeOBDE-47, 6MeOBDE-47, MeOBDE-49, -68, -99, -100, -101, -103), twenty three alternate BFRs (2,4,6-tribromophenol (2,4,6-TBP), 2,4,6-tribromophenyl allylether (TBP-AE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), Decabromodiphenylethane (DBDPE), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (TBP-DBPE), 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), Hexabromobenzene (HBB), Hexachlorocyclopentadiene (HCCPD), Hexachlorocyclopentadienyl-dibromocyclooctane (DBHCTD), Pentabromobenzyl acrylate (PBBA), Pentabromobenzylbromide, Pentabromobenzene (PBBz), Pentabromoethylbenzene (PBEB), Pentabromotoluene (PBT), Tetrabromo-p-xylene (TBX), 2,4,6-tribromoanisole (TBA), Tris-(2,3-dibromopropyl) isocyanurate (TBC), Tetrabromo-o-chlortoluene (TBCT), Bis(2-ethyl-1-hexyl)tetrabromophthalate (BEH-TEBPH), α/β -tetrabromoethylcyclohexane (α/β -DBE-DBCH), α/β -1,2,5,6-tetrabromocyclooctane (α/β -TBCO)), Dechlorane Plus (DP), the one- and

two-fold dechlorinated DP species (aCl11DP [-1Cl+1H], aCl10DP [-2Cl+2H]), 1,5-Dechlorane Plus monoadduct (DPMA), Dechlorane 601, 602 (DDC-DBF), 603 (DDC-Ant) and 604 (HCTBPH), Chlordene Plus (Cplus), Dibromochlordene (DBCD), Dibromoaldrin (DBALD), Hexachlorocyclopentadiene (HCCPD) and Hexachloro(phenyl)norbornene (HCPN).

ECNI analysis was based on a method developed by Möller et al. 2010 and adapted to a 15 min backflush at 300 °C and a flow rate of 5.14 mL min⁻¹. The instrument operated in selected ion monitoring mode (SIM) and fitted with a HP-5MS column (30 m x 0.25 mm i.d. x 0.25 µm film thickness, J&W Scientific). In ECNI sediments were analysed for 14 alternate BFRs (TBP-AE, PBB, TBCT, BATE, PBEB, PBT, HBB, TBP-DBPE, PBBA, DBHCTD, EH-TBB, BTBPE, TBC and BEH-TEBPH), syn- and anti-DP, aCl11DP, aCl10DP, 1,5-DPMA, DDC-DBF, DDC-Ant, HCTBPH, as well BDE-66, BDE-100 and BDE-154. Results for ECNI and EI analysis were indiscernible for all compounds detected with both methods, however, due to lower average detection limits achieved in ECNI analysis some low concentrated PBDE congeners could only be detected through this method. In case a compound was detected in EI as well as ECNI the average of all four (duplicates for each method) was used for quantification. In case a compound was only detected in EI or ECNI the average of the duplicate measurement was used for quantification.

HBCDD and TBBPA were analysed using liquid chromatography with tandem mass-spectrometry (Agilent LC 1290 / QQQ 6490), fitted with a Luna C18 column (Phenomenex Luna, 3 µm C18 100 Å, 150 x 2 mm) using electron spray ionisation in negative mode. Injection volume was 10 µL, mobile phases A and B MeOH/Water(H₂O) each with 10 mmol Ammonium acetate at a flow rate of 0.2 mL min⁻¹. The solvent gradient was as follows: initial 70:30 MeOH:H₂O for 4 min, 90:10 MeOH:H₂O for 7 min, 95:5 MeOH:H₂O for 3 min and 70:30 MeOH:H₂O for a final 4 min. The samples were provided in 70:30 MeOH:H₂O

A list of all target analytes with full compound name, abbreviation, CAS number and instrument parameters, including MRMs are presented in supplement information S2 – S3.

2.4 QA/QC

Extraction and clean-up were conducted in a cleanroom (class 10000; ISO 14644-1). Materials containing FR were avoided during sample preparation and analysis.

Isotopic labelled surrogate standards were used to control for variances during extraction and instrumental analysis. Individual recoveries were determined for every sample. Mean recoveries were $86 \pm 45\%$ for ^{13}C -BDE-28, $80 \pm 49\%$ for ^{13}C -BDE-47, $83 \pm 50\%$ for ^{13}C -BDE-99, $136 \pm 47\%$ for ^{13}C -BDE-153, $125 \pm 58\%$ for ^{13}C -BDE-183, $73 \pm 38\%$ for ^{13}C -MeOBDE-47, $139 \pm 24\%$ for ^{13}C -MeOBDE-100, $61 \pm 34\%$ for ^{13}C -HBB, $110 \pm 57\%$ for ^{13}C -synDP, $45 \pm 29\%$ for ^{13}C -PBBz, $51 \pm 40\%$ for D10-TBBPA and $74 \pm 44\%$ for ^{13}C - γ -HBCDD. During method validation recoveries of target analytes, extraction efficiency and reproducibility was tested with and without matrix. Average recoveries without matrix were $95 \pm 24\%$ and $75 \pm 24\%$ with matrix. Values for recoveries in spiked sediments ranged from $44 \pm 9\%$ for TBA to $124 \pm 32\%$ for BTBPE. Extraction efficiency was tested by extracting ASE cells twice into two separate vials. All target analytes were < limit of detection in the extract of the second extraction run. Reproducibility was high with a standard deviation (5 measurements) of < 10% for both GC-EI-MS/MS and LC-ESI-MS/MS.

A blank test, using Na_2SO_4 treated similarly to real samples, was conducted with every extraction batch (five samples). For most analytes concentrations of FR in blanks were in the one to two digit $\text{pg g}^{-1} \text{dw}$ scale, ranging from $0.25 \pm 0.5 \text{ pg g}^{-1} \text{dw}$ for HBB to $57 \pm 65 \text{ pg g}^{-1} \text{dw}$ for HCPN. Exemptions were the comparably high blanks of BEH-TEBP, BDE-209, PBB and TBP with $931 \pm 1613 \text{ pg g}^{-1} \text{dw}$, $4555 \pm 158 \text{ pg g}^{-1} \text{dw}$, $138 \pm 218 \text{ pg g}^{-1} \text{dw}$ and $362 \pm 423 \text{ pg g}^{-1} \text{dw}$, respectively. Average blank concentrations were subtracted from concentrations of target analytes of the associated batch. 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). Average LODs were below $1 \text{ ng g}^{-1} \text{dw}$ for most analytes, ranging from $1 \text{ pg g}^{-1} \text{dw}$ for PBEB to $794 \text{ pg g}^{-1} \text{dw}$ for PBB. Exemptions were high LODs for alpha DBE-DBCH, BEH-TEBP, BDE-209, TBCO and TBP

with LODs between 1266 and 5771 pg g^{-1} dw. The LOQ respectively ranged from 3 pg g^{-1} dw for PBEB to 17 ng g^{-1} dw for BEH-TEBP. In ECNI LODs ranged from 0.02 pg g^{-1} dw for TBP-AE to 50 pg g^{-1} dw for BDE-100 resulting in LOQs between 0.08 pg g^{-1} dw for TBP-AE and 125 pg g^{-1} dw for BDE-100. LC-ESI-MS/MS LODs were 83 pg g^{-1} dw for TBBPA, 57 pg g^{-1} dw for α -HBCDD, 29 pg g^{-1} dw for β -HBCDD and 70 pg g^{-1} dw for γ -HBCDD, resulting in LOQs of 185 pg g^{-1} dw for TBBPA, 171 pg g^{-1} dw for α -HBCDD, 77 pg g^{-1} dw for β -HBCDD and 175 pg g^{-1} dw for γ -HBCDD.

Blanks LODs and LOQs are presented in supplement information S4.

2.5 Data analysis

Peak areas of the obtained chromatograms were integrated using Agilent Technologies MassHunter Workstation Software Quantitative Analysis B.06.00. Further data analysis was performed with Microsoft Office Excel 2010. Statistical analysis, including normality test and Pearson correlation were performed using Origin Lab 9.1 Pro.

For the presentation of results analytes with detection frequencies over 50 % in the selected investigation area average concentrations \pm standard deviation were calculated. For compounds with a detection frequency < 50 % the range of detected concentrations are presented.

2.6 Fingerprint Method

To determine location specific patterns a method for the “Fingerprint Analysis of Contaminant Data” (Russell H. Plumb, Jr. 2004) by the United States Environmental Protection Agency (EPA) was adapted. The adaptations consisted of including the detection frequency of individual contaminants as weighing factor for the determination of investigation area specific fingerprint. For this the concentration [pg g^{-1} dw] of the analyte in each sample from the selected area was multiplied by the detection frequency [%], before determining the contribution to the sum contamination in the investigation area:

$$con_{xi}[\%] = \frac{c_{xi}[pg\ g^{-1}\ dw] * df_{xi}[\%]}{\sum_{i=1}^n c_{xi}[pg\ g^{-1}\ dw]}$$

With

$con_x[\%]$: Contribution in % of compound $X_{i=1-n}$ to the sum concentration in the investigation area

$c_{xi}[pg\ g^{-1}\ dw]$: Concentration of compound $X_{i=1-n}$ in $pg\ g^{-1}\ dw$

$df_{xi}[\%]$: Detection frequency in % of compound $X_{i=1-n}$

$\sum_{x=1}^n c_x [pg\ g^{-1}\ dw]$: Sum concentration of all compounds X in the investigation area in $pg\ g^{-1}\ dw$

The resulting contribution of individual substances to the contamination pattern in an investigated area was then used to create a “fingerprint” of the contamination patterns in that area. Only substances with a contribution of more than 10% were considered as part of the fingerprint.

To determine whether the resulting fingerprints were representative for the chosen investigation area contamination patterns from each sampling site in the investigation area were correlated. All sampling sites with a correlation to the other sampling sites of the investigation area of below 0.5 were excluded from that investigation area and further investigated. Patterns of these sampling sites were correlated with the remaining investigation areas as well as among each other to identify if an affiliation could be determined.

3. Concentrations and principal patterns of BFRs and Dechloranes in North Sea sediments

	Northern UK coast (ia 1)	Southern UK coast (ia 2)	East Frisian Coast (ia 3)	Weser/Jade (ia 4)	North Sea (ia 5)	Elbe River (ia 6)
Σ 5PBDEs	643 ± 532	< LOD - 1836	15 ± 13	155 ± 333	16 ± 12	< LOD - 77
BDE-209	< LOD - 4253	< LOD - 7211	< LOD	< LOD - 2427	< LOD - 5092	< LOD
MeOBDEs	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Total alternate BFRs	1237 ± 1870	619 ± 567	63 ± 34	129 ± 162	< LOD - 709	67 ± 57
Total Dechloranes	320 ± 265	176 ± 85	345 ± 202	356 ± 340	111 ± 260	100 ± 120
fsyn	0.55 ± 0.24	0.70 ± 0.28	0.40 ± 0.12	0.34 ± 0.18	0.47 ± 0.30	0.46 ± 0.26
TBBPA	2714 ± 1488	1686 ± 870	< LOD - 44	< LOD - 281	< LOD - 146	< LOD
Total HBCDD	< LOD - 1752	< LOD - 1574	175 ± 152	702 ± 1430	< LOD	< LOD - 469
TOC [%]	0.38 ± 0.21	0.43 ± 0.23	0.31 ± 0.21	0.78 ± 1.32	0.10 ± 0.11	0.33 ± 0.38
Sample type	muddy sand – black mud	muddy sand – black mud	sand – slightly muddy sand	sand - mud	sand – slightly muddy sand	sand – black mud

Table 1: Average concentrations in pg g^{-1} dw of the detected Σ 5PBDEs (BDE-47,-85,-99,-100,-154), BDE-209, MeOBDEs, total of detected alternate BFRs (TBP-AE, BATE, TBP-DBPE, EH-TBB, HBB, PBEB, TBA), total of detected Dechloranes (DBALD, DDC-DBF, syn-DP, anti-DP, HCPN), TBBPA, total HBCDD (α -, β -, γ -HBCDD) as well as fsyn (contribution of synDP to the total DP (syn- + antiDP) concentration), total organic carbon (TOC) [%] and sampling depth [m] in the investigation areas northern UK coast (ia1), southern UK coast (ia2), East Frisian Coast (ia3), Jade/Weser (ia4) German Bight (ia5) and river Elbe (ia6)

Concentrations in general were low for most analysed compounds. With often less than 100 pg g^{-1} dry weight (dw) (Figure 3, Table 1) many compounds could only be determined semi-quantitatively or qualitatively (see supplement information S6 –S9 for a detailed list of all results). An exemption was the comparably high concentrations of TBBPA at sampling sites from northern east-coast of England, that ranged between <LOD and 6.4 ng g^{-1} dw. Overall FR concentrations were higher in samples from the UK Coast than samples from Germany (Figure 3). This observation can be explained by the strict fire safety regulations in Britain (Guillaume et al. 2008). These lead to generally higher application and subsequent environmental concentrations of FRs compared to continental Europe (Trudel et al. 2011). The detection frequencies in general were highest for sum Dechloranes (100%) followed by

sum alternate BFRs (88%) and sum PBDEs (56%). However, detection frequencies of individual compounds 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. Yet, concentrations of alternate BFRs and Dechloranes were in a similar range as PBDEs, indicating that the substitutes are replacing PBDEs as contaminants in North Sea sediments. BDE-209 was the only exception. Due to comparably high blanks it could only be quantified in 9% of the samples. Yet if it was detected the concentrations were at least one order of magnitude higher than all other found compounds. These findings matched observations from marine sediments from north-east Spain, where BDE-209 was detected in concentrations of 3.0 – 132 ng g⁻¹ dry weight (dw), while Σ PBDEs (BDE47, BDE99, BDE100, BDE118, BDE153, BDE154, BDE183) were in the range of 0.86 – 2.34 ng g⁻¹ dw Cal et al. (2003). The high concentrations of BDE-209 (primary component of technical Deca-BDE) (Alaee et al. 2003) 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 (Stockholm Convention 2009).

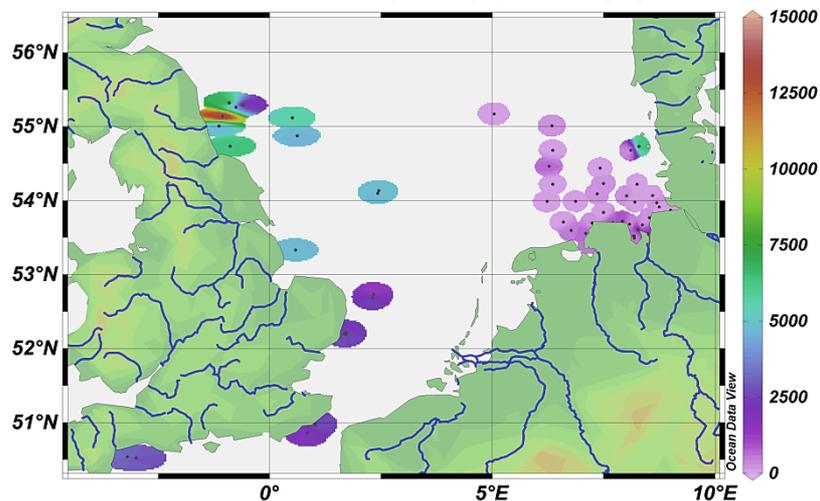


Figure 3: Total flame retardants [pg g⁻¹ dw] (PBDEs, alternate BFRs, Dechloranes, HBCDD and TBBPA) in sediments from all sampling stations

In the German Bight, apart from BDE-209, primarily BDE congeners associated with 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. Highest overall PBDE concentrations were found in samples from the UK coast with BDE-100 as main congener with up to 1.3 ng g⁻¹ dw followed by BDE-154, BDE-47 and BDE-99. This difference in congener patterns between the UK Coast and other sampling areas might have been caused by differences in LODs, since most detected BDE concentrations were close to the detectable or quantifiable limits. However, changes in the congener profiles could also be an indication for anaerobic degradation of BDE-209 in UK sediments. Huang et al. (2014) reported highest anaerobic debromination of PBDE congeners for BDE-209 followed by BDE-99. The subsequent degradation products they detected included BDE-100, which itself displayed very low further degradation rates. The difference in congener profiles between the UK coast and other investigation areas could therefore have been caused by anaerobic degradation of BDE-209 and BDE-99, resulting in the observed relative increase of BDE-100. Anaerobic conditions at the UK sampling sites rather than the remaining investigation areas can be explained by the differences in sediment types. Sediments from the UK sampling sites were primarily dark mud or muddy sand, whereas samples from the remaining sites were primarily sandy sediments (Table 1). Muddy sediments are often anaerobic below the first few centimetres, due to the high oxygen depletion by degradation of organic material and the small pore size. Sandy sediments, on the other hand, usually have a deeper aerobic zone, due to the larger pore size and less respiration/mineralisation processes in the sediment (Jorgensen et al. 1990). The presence of banned PBDEs, in general, can largely be explained by their persistence in sediments (Sacks and Lohmann 2012), as well as diffuse emissions from PBDE containing products and materials still in use. An exemption was the higher technical Penta-BDE concentration near the city of Bremen, indicating the presence of a point source in this area (Table 1). Due to the fact that flame retardants are largely applied in consumer products and building materials, areas with large population or industry (such as harbours) are potential emission

hotspots (Csiszar et al. 2013). Rivers, like Elbe and Weser, passing such potential emission hotspots can therefore be expected to represent recent emissions, such as the substitutes for PBDEs, or leachate from PBDE-containing products still in use.

TBBPA was unexpectedly the predominant compound in samples from the UK coast. It was detectable in 87% of the analysed samples with concentrations between 0.3 and 6.3 ng g⁻¹ dw. The detection frequency in all other sampling areas was 50% or less and detectable concentrations were at least one magnitude lower than in UK sediments with 0.01 - 0.3 ng g⁻¹ dw (Table 1). There is little information available on TBBPA concentrations in European sediments. Cefas (2006) reported levels of <0.1 – 6.9 µg kg⁻¹ dw in sediment samples from the Netherlands and up to 9750 µg kg⁻¹ dw in estuarine and riverine sediments from the English east coast. These high TBBPA concentrations in rivers and estuaries from the UK east coast, suggest that rivers are likely the primary sources for the comparably high concentrations of TBBPA in UK sediments close to river mouth found in this study.

HBCDD was the dominant BFR in river Weser as well as the East Frisian Coast. The stereoisomer contribution was similar to the technical product with over 70 – 90% (EFSA 2011) of the γ-HBCDD isomer. In sediments from the UK Coast (primarily southern UK Coast), however, the α-HBCDD isomer accounted for > 80% of sum HBCDD. A possible explanation for this conspicuous difference between isomer patterns at the UK and German coast could be the known abiotic transformation of γ-HBCDD to α-HBCDD (EFSA 2011). The degradation or transformation of γ-HBCDD seems to be enhanced in anaerobic conditions, comparable to the process reported for BDE-209 described earlier (EFSA 2011). This could suggest a less recent input of HBCDD at the UK coast compared to the German Bight, resulting in a predominance of transformation products.

Interestingly, HBCDD could only be detected at few sampling locations along the river Elbe in low concentrations and could not be detected at all in the German Bight, suggesting an input through localised sources around river Weser, East Frisian Coast and southern UK coast, rather than diffuse, widespread emissions around the North Sea.

Hexabromobenzene (HBB) had the highest overall detection frequencies of the alternate BFRs with 56% followed by TBP-DBPE > TBA > BATE > EH-TBB > β -DBE-DBCH > PBEB > TBP-AE (48%, 31%, 27%, 21%, 19%, 15%, 2%, respectively). HBB is suspected to be a metabolite or transformation product of other brominated flame retardants such as PBDEs (Yamaguchi et al. 1988), which could be an explanation for the high detection frequencies and concentrations. The alternate flame retardant 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), a principal component in the PBDE substitute Firemaster 550, 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 samples from other sampling stations in the German Bight, Weser or East Frisian Coast. In case of the UK coast EH-TBB could mostly be detected in samples close to the coast in the English Channel as well as the Humber estuary and the Tyne river mouth. Because of the use of EH-TBB as replacement for PBDEs in consumer products, emissions from major population areas through e.g. waste water treatment could be an explanation for the frequent detection of the compound in rivers and estuaries, rather than coastal or marine areas.

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 compartment, as TBP-DBPE was only produced until the 1980s by one company in Germany (von der Recke and Vetter 2007). The predicted half-life in sediments according to EPI suite (BIOWIN™ model) is 1600 days, which suggests, that TBP-DBPE is “very-persistent” according to the REACH legislation criteria (REACH online Annex XIII). However, TBP-DBPE has been reported to be transformed to tribromo- 2-(2-propen-1-yloxy)- benzene (TBP-AE) and 2-bromoallyl-2,4,6- tribromophenyl ether (BATE) in environmental samples (von der Recke and Vetter 2007). TBP-DBPE as well as its transformation products are known to be able to penetrate the brain-blood barrier and have endocrine disrupting properties (CECBP Report 2008, von der Recke and Vetter 2007). The high abundance in sediments could be a reason for the continued detection of TBP-DBPE in various environmental matrices such as water and fish (Möller et al. 2012, Sühning et al. 2014) despite the lack of emissions. Other

alternate BFRs detected in isolated samples throughout the sampling areas were Pentabromoethylbenzene (PBEB), Tribromoanisole (TBA), TBP-AE and BATE. In case of PBEB the diffuse occurrence could be explained by its persistence in the environment (Covaci et al. 2011). TBA, TBP-AE and BATE on the other hand are suspected or proven transformation products of other brominated flame retardants such as TBP-DBPE (von der Recke and Vetter 2007). TBA is additionally produced naturally by microorganism and fungi in the marine environment (Walter Vetter 2006).

The alternate BFR DBE-DBCH could be almost exclusively detected in samples from the East Frisian Coast as well as close to the harbours Bremerhaven and Wilhelmshaven, indicating point sources in these areas as input pathway for this chemical.

Dechloranes were unsuspectedly the most abundant compounds in the entire sampling area. A reason is probably the low average detection limit of these compounds, however the high abundance and similar concentrations to BFRs (Table 1) 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), Hexachloro(phenyl)norbornene (HCPN) and Dibromoaldrin (DBALD). The high abundance of DP was expected, due to its frequent detection in e.g. sea water reported in previous studies from the North Sea (Möller et al. 2012). 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 transformation 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 $< 100 \text{ pg g}^{-1} \text{ dw}$. 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 (Guerra et al. 2011, Sühring et al. 2013). The detection of DBALD was unexpected, as it has, 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 (Maul and Carlson 1976). There is however no information on current use or production. Another

“experimental flame retardant” detected in selected sediments was HCPN. HCPN is an intermediate in the production of chlorinated flame retardants as well as heptane fungicides (Santa Cruz Biotechnology) and could potentially also be a biotransformation product or impurity in either of these compounds. Both DBALD and HCPN were found in highest concentrations around the East Frisian Coast, indicating local sources. Concentrations of HCPN (average concentration from all sampling sites $106 \pm 113 \text{ pg g}^{-1} \text{ dw}$) were higher than concentrations found by Shen et al. (2014) in sediments from the Great Lakes ($5 - 41 \text{ pg g}^{-1} \text{ dw}$). The extensive agricultural use of the areas adjoining to the sampling stations with high HCPN concentrations in this study could be an indication that HCPN concentrations might have been caused by the application of fungicides.

4. Fingerprint analysis and determining factors for the observed contamination patterns

Considering the overall low concentrations and variability within sampling areas several factors had to be taken into consideration in order to assess potential factors for the measured contamination. Sediment transport, distance to coast as well as total organic carbon (TOC) were considered to be the main potential drivers for spatial distribution of contaminants. To identify area specific patterns, which would indicate, and potentially help determining, the main area specific driving factors and sources, a statistical fingerprinting method was applied. A first, general, observation was that all analysed compound groups showed strong to very strong correlation with the TOC content of the analysed sediments with an average Pearson correlation coefficient of $r = 0.82$, proving that TOC is an important factor for the distribution of halogenated flame retardants in the North Sea (Figure 4).

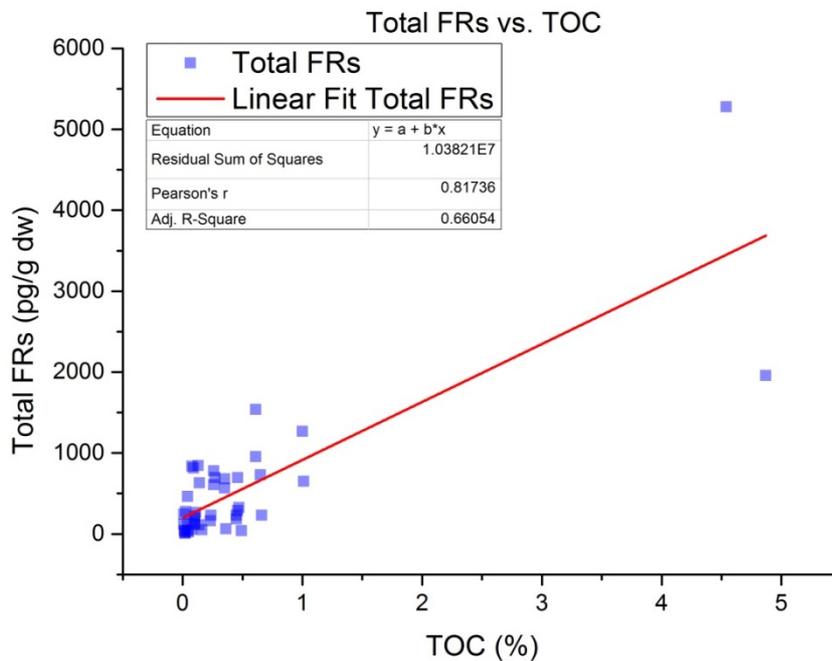


Figure 4: Correlation of TOC [%] and total FR concentration [$\mu\text{g g}^{-1} \text{ dw}$]

The strong correlation is interesting, as it could help to identify potential areas of concern, such as tidal creek "Hörnuntief" with a high TOC of 5% and corresponding high concentrations, compared to other sampling stations with similar distances to the shore. However, contamination patterns differed significantly (fingerprint analysis, t-test at level 0.05) between the analysed sampling areas, indicating different sources rather than just sedimentation and dilution effects. Six areas (investigation area) with distinct contaminant fingerprints were identified. Investigation areas were defined as the sum of regionally related sampling stations with a strongly correlated contamination pattern (Pearson correlation >0.5). All investigation areas were additionally inter-correlated to determine the degree of discernibility between the areas. The identified investigation areas were northern UK coast (ia1), southern UK coast (ia2), East Frisian Coast (ia3), Jade/Weser (ia4) German Bight (ia5) and river Elbe (ia6) (Figure 5).

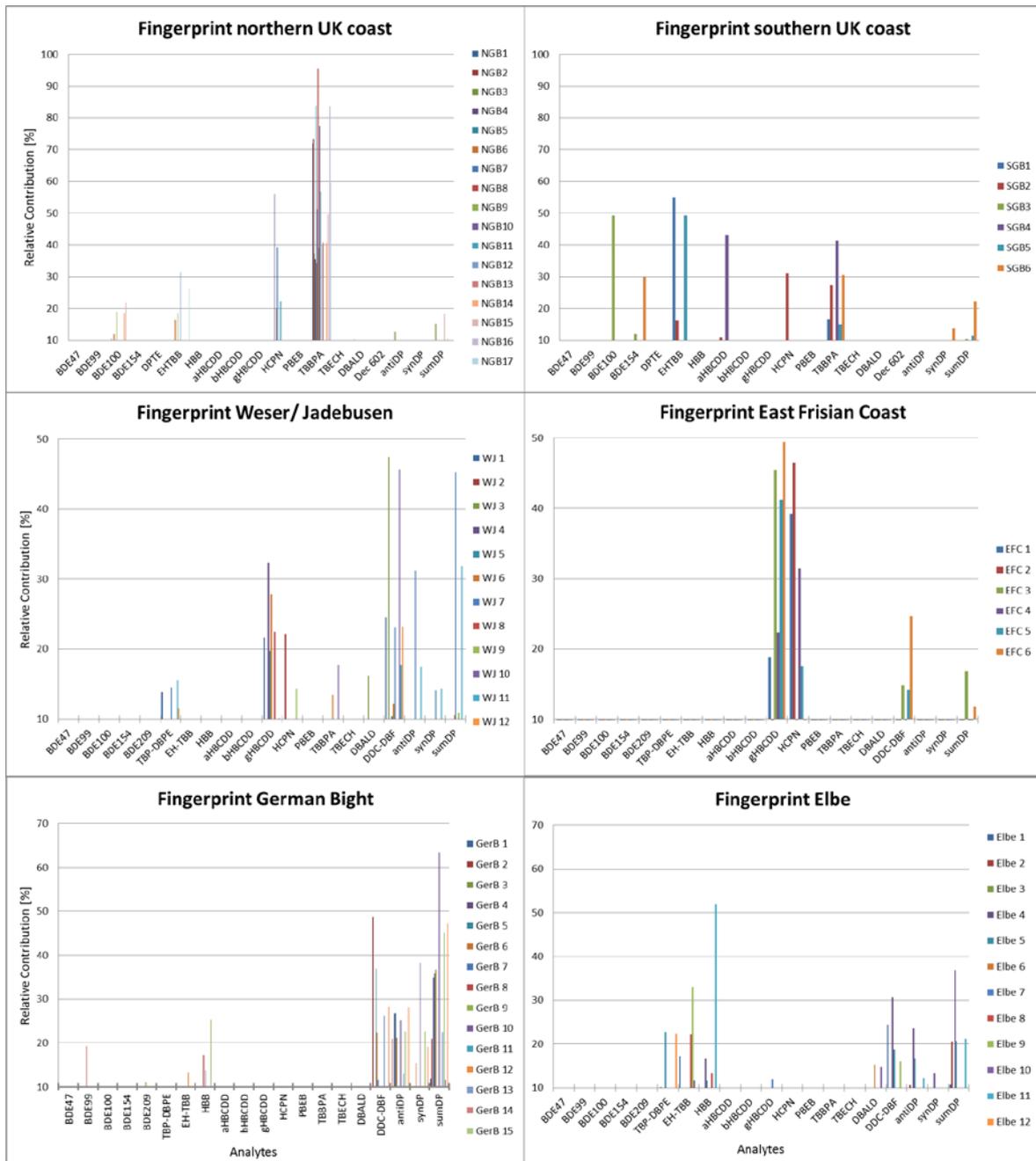


Figure 5: Fingerprint patterns in relative contribution [%] to total halogenated flame retardants in six investigation areas (ia) in the North Sea

The identified compounds contributing to the individual fingerprints were as follows:

Investigation Area	Compound	Relative contribution [%]
Ia 1 (Northern UK Coast)	TBBPA	56
	HCPN	11
Ia 2 (Southern UK Coast)	EH-TBB	26
	TBBPA	25
	α -HBCDD	13
Ia 3 (East Frisian Coast)	DP	10
	HCPN	34
	γ -HBCDD	30
Ia 4 (Jade/Weser)	DDC-DBF	12
	γ -HBCDD	18
	HCPN	14
Ia 5 (North Sea)	DP	12
	DDC-DBF	29
	HBB	19
Ia 6 (Elbe River)	HBB	10
	EH-TBB	15
	DP	14
	DDC-DBF	13
	DBALD	13
	HBB	11
TBP-DBPE	11	

Table 2: FRs with relevant ($\geq 10\%$) relative contribution to the fingerprint in the respective investigation area (ia)

The UK coast showed two distinct fingerprints; for the north-England and south-England east coast (Figure 5). The northern UK coast fingerprint (off the coast from Mablethorpe to the Scottish border) was dominated by TBBPA with 56% contribution followed by HCPN with

11% (Figure 5, Table 2). The southern UK coast fingerprint (Lowestoft and south) was, on the other hand, dominated by EH-TBB (26%) followed by TBBPA (25%), α -HBCDD (13%) and sumDP (10%) (Figure 5, Table 2). The difference in fingerprints between northern and southern UK sampling sites indicated different sources of contamination. TBBPA is used in a variety of consumer products. Therefore the presence in northern and southern sampling sites might be a result of diffuse emissions from consumer products and an input through e.g. waste water treatment facilities. The presence of HCPN could indicate agricultural sources in the north as well, whereas the dominance of PBDE replacements in the south indicated industrial sources or recent input. Interestingly, the sampling stations from within the English Channel did not correlate with either of the UK coast investigation areas (Pearson correlation of < 0.2) but instead with the fingerprint of the East Frisian Coast (Pearson correlation of 0.46 -0.70). An explanation for this relation are the oceanic currents along the east Frisian coast, which are primarily from a westerly direction (Laane et al. 2013), making the English Channel a potential source for contamination in this area. However, despite the overall strong correlation the English Channel did not seem to be the only contamination source for the East Frisian Coast. High contributions of HCPN (34%) and γ -HBCDD (20%) were identified at the East Frisian Coast (Table 2), that were not present in the English Channel sampling sites, suggesting, at least for HCPN, local sources in this area or potentially from the river Rhine (Figure 5). The presence of γ -HBCDD could potentially be explained by the transport of HBCDD from the English Channel with less transformation towards the α -isomer than in the English Channel due to aerobic sandy sediments sampled along the East Frisian Coast (as discussed above).

Contamination pattern of the German Bight seemed to be mostly driven by the patterns in the river Elbe with decreasing concentrations towards the open sea; which supported the hypothesis of rivers as contamination sources for the German Bight (Laane et al. 2013). Similar relations were found between the patterns in river Weser and the Jadebusen (Figure 5).

Exceptions were the sampling station at the tidal creek Hörnumtief as well as the sampling station near to the city of Bremen (Jade/Weser1), that both showed comparably high concentrations as well as a larger variety of compounds, due to the higher TOC and industrial sources in the area respectively. Interestingly the Bremen fingerprint correlated with the fingerprint from Wilhelmshaven harbour (Jade/Weser 9) and Jadebusen (Jade/Weser 10,11,12), indicating similar, potentially industrial sources (Table 3).

	J/W1	J/W 2	J/W 3	J/W 4	J/W 5	J/W 6	J/W 7	J/W 8	J/W 9	J/W10	J/W11	J/W12
Jade/Weser 1	1	0.02	0.05	0.04	0.03	0.08	0.11	0.02	0.75	0.77	0.56	0.38
Jade/Weser 2	0.02	1	0.29	0.61	0.92	0.94	0.95	0.60	0.40	0.55	0.39	0.69
Jade/Weser 3	0.05	0.29	1	0.72	0.49	0.34	0.44	0.71	0.47	0.14	0.49	0.58
Jade/Weser 4	0.04	0.61	0.72	1	0.74	0.53	0.63	0.79	0.39	0.28	0.34	0.82
Jade/Weser 5	0.03	0.92	0.49	0.74	1	0.91	0.97	0.63	0.46	0.51	0.43	0.75
Jade/Weser 6	0.08	0.94	0.34	0.53	0.91	1	0.96	0.61	0.50	0.62	0.43	0.66
Jade/Weser 7	0.11	0.95	0.44	0.63	0.97	0.96	1	0.63	0.54	0.61	0.50	0.72
Jade/Weser 8	0.02	0.60	0.71	0.79	0.63	0.61	0.63	1	0.48	0.32	0.37	0.67
Jade/Weser 9	0.75	0.40	0.47	0.39	0.46	0.50	0.54	0.48	1	0.88	0.90	0.72
Jade/Weser 10	0.77	0.55	0.14	0.28	0.51	0.62	0.61	0.32	0.88	1	0.79	0.71
Jade/Weser 11	0.56	0.39	0.49	0.34	0.43	0.43	0.50	0.37	0.90	0.79	1	0.72
Jade/Weser 12	0.38	0.69	0.58	0.82	0.75	0.66	0.72	0.67	0.72	0.71	0.72	1

Table 3: Correlation of fingerprints from individual sampling sites within the investigation area ia 4 Jade/Weser (J/W). Stations with a Pearson correlation below 0.2 were marked red, stations with a Pearson correlation below 0.5 were marked yellow

Despite its high concentrations, BDE-209 did not have the necessary 10% relative contribution in any sampling area to be considered in the fingerprint due to its low detection frequency. However, the low detection frequencies were mostly caused by the comparably high blanks – a result of the wide application and presence of the compound in indoor environments. Further research is needed to assess the potential contribution of BDE-209 to an area-specific FR fingerprint as well as the development of its contribution as environmental contaminant compared to novel and emerging FRs.

The results of this study provide a large dataset on the BFR and Dechlorane contamination of the German Bight, East Frisian Coast as well as the UK east coast, including discernible area specific fingerprints and information on the determining factors for found contamination patterns. The results show an increasing relevance of substitutes for PBDEs, especially Dechloranes in all seafloor provinces of the German Bight as well as the UK coast, with potential diffuse as well as point sources from industrial and agricultural applications as well as consumer products. The role of consumer products as sources for e.g. Dechloranes should be further investigated, especially considering, that the amounts in the products are not high enough to fall under the REACH legislation, but might accumulate in the environment to significant amounts. Further research is also needed to assess the potential negative environmental impacts of these compounds as well as their long-term fate in the marine environment.

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