Distribution of brominated flame retardants and dechloranes between sediments and benthic fish — A comparison of a freshwater and marine habitat

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HIGHLIGHTS

- Comparison between sediments and benthic fish in both freshwater and marine habitats
- Identification of a contamination hotspot for TBCO in the North Sea
- BSAFs for emerging halogenated flame retardants in marine benthic fish
- Strong correlations between TOC and flame retardant concentrations

GRAPHICAL ABSTRACT
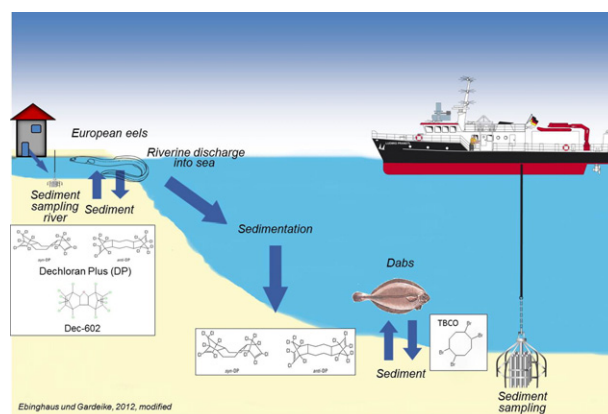
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ABSTRACT

A total of 53 halogenated flame retardants (HFRs) were analysed in sediments, European eels and dabs from both freshwater and marine sampling stations in the German Bight and the river Elbe.

Classic HFRs, such as polybrominated diphenylethers (PBDEs), were the highest concentrated HFRs in eels as well as in most dabs (apart from 1,2,5,6-tetrabromocyclooctane (TBCO)). In sediments, on the other hand, alternate BFRs and especially dechloranes dominated the contamination pattern. Dabs were still found to be statistically representative for the contamination patterns and relative magnitude in sediments from their respective habitats. Contamination patterns in eels seemed to be more driven by the contamination situation in the food chain or historical contamination of their habitat.

Unsuspectedly the alternate flame retardant TBCO was found in comparably high concentrations (up to 12 ng g^{-1} ww) in dabs from two sampling stations as well as in sediments from these stations (up to 1.2 ng g^{-1} dw). It could not be detected in any other analysed fish or sediment samples, indicating a localised contamination source in the area.

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Benthic fish
Sediments

This study provides information on HFR contamination patterns and behaviour in both marine and freshwater sediments and their potential role as contamination source for benthic fish.

1. Introduction

For several decades polybrominated diphenyl ethers (PBDEs) have been widely applied as halogenated flame retardants (HFRs). Due to their known adverse effects to humans and the environment PBDEs were banned for production and usage in the European Union (EU) (European Court of Justice, 2008) and voluntarily phased out in the US and other countries (US EPA, 2015). As a further regulation step technical Penta- and Octa- BDE mixtures were officially classified as Persistent Organic Pollutants (POPs) under the Stockholm Convention (SCOP, 2009) and Deca-BDE was proposed as POP candidate (SCOP, 2013).

However, the restriction of PBDEs has not lead to an overall reduction of the application of HFRs, but rather a shift towards the usage of alternate (non-PBDE) BFRs as well as chlorinated alternatives, such as dechloranes. There is limited data concerning POP potential of these substitutes yet many are suspected to at least partially fulfil the criteria (Harju et al., 2009).

Most HFRs currently in use are applied as additives, which means, that they are not chemically bound to the polymer they are used in and can therefore often easily migrate to the environment (Harju et al., 2009). Due to their lipophilic and often bioaccumulative properties, combined with a high persistence for most HFRs concentrations in water are usually very low. However, emitted HFRs can be stored and accumulated in sediments as well as fatty tissue of biota and subsequently the food-net. In order to assess the contamination status of a habitat with HFRs it is therefore important to assess the contamination status of sediments as well as the concentrations and potential exposure pathways of resident biota.

For this study HFR contamination in marine and freshwater sediments from the German Bight and the river Elbe investigated and compared to patterns found in dabs (Limanda limanda) and European eels (Anguilla anguilla) in their yellow eel life stage from the respective areas. Yellow eels and dabs were chosen due to their sedentary and benthic life style as well as their economic importance for the local fisheries in the German Bight (Belitz et al., 2012, Belpaire and Goemans, 2007a,b).

The aim of this study was to identify HFR contamination patterns and behaviour in both marine and freshwater sediments and their potential role as sources for benthic fish.

2. Material and methods

2.1. Samples

Muscle tissue of in total 24 dabs from three sampling areas in the North Sea was sampled during a sampling campaign with the research vessel Walther Herwig III in September 2013. Each sampling area consisted of one to three sampling stations at which up to five fish were caught (Table 1). Corresponding to the dab samples ten surface sediments from one to three sampling stations in the dab and eel sampling areas were sampled, using a box corer, during campaigns with the research vessels Heincke, Ludwig Prandtl and Storch from October 2012 to May 2013.

Contact with materials containing brominated flame retardants was avoided during sampling and sample processing.

In order to compare contamination patterns of benthic fish and sediments in freshwater habitats, obtained sediment data from river Elbe was compared to previously analysed yellow eels from the same areas (Sühring et al., 2013).

A detailed list of the analysed samples is presented in Supplement information Table S1.

2.2. Extraction and clean-up

The frozen dab samples were homogenised with anhydrous Na_2SO_4 (Merck) (2:1; w/w) for approximately 20 min. Using a stainless steel/glass 1 L laboratory blender (neoLab Rotorblender). All samples were spiked with mass labelled surrogate standards 4 ng (absolute) ^{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 (Wellington Laboratories, Cambridge Isotopes).

Extraction and clean-up of dab samples were performed in accordance with the method described in Sühring et al., 2013, using accelerated solvent extraction with subsequent gel permeation chromatography and silica gel clean-up. 500 pg (absolute) ^{13}C-PCB-141 and ^{13}C-PCB-208 were added as an injection standard to each sample. The lipid content of samples was determined gravimetrically from separate aliquots.

Sediment samples were homogenised with anhydrous Na_2SO_4 (Merck) (2:1; w/w). Extraction was performed using accelerated solvent extraction (ASE-200, Thermo fisher scientific GmbH) with an integrated clean up, as described in Sühring et al., 2015. 500 pg (absolute) ^{13}C-PCB-141 and ^{13}C-PCB-208 were added as an injection standard to each sample.

Separate aliquots were dried to constant weight (at 105 °C) for the gravimetrical 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.

2.3. Instrumental analysis

Samples were analysed for eight PBDEs (BDE-28, -47, -66, -99, -100, -153, -154, -183), 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), decabromdiphenylethane (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 + 1 H], aCl10DP [−2Cl + 2 H]), 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). To achieve maximum sensitivity as well as selectivity all samples were analysed using gas chromatography/mass spectrometry (Agilent QQQ 7000B) in negative ionisation mode (ECNI) with single MS (GC–MS) as well as electron ionisation mode (EI) with tandem-mass spectrometry GC–MS/MS.

For analysis in EI the instrument was fitted with a Restek 1614 column (15 m × 0.25 mm i.d. × 0.10 μm film thickness, Restek) with helium (purity 99,999%) as carrier gas and nitrogen as collision gas. The instrument was operated in a multiple reaction monitoring mode

(MRM) at 70 eV. ECNI analysis was based on a method developed by Möller et al. (2010). The method was extended to include further analytes and a backflush system. The instrument operated in selected ion monitoring mode (SIM) with methane as reactant gas. It was fitted with a HP-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific). In both EI and ECNI a restriction capillary (0.8 m × 0.1 mm i.d., deactivated) with a backflush system was used. In ECNI fourteen alternate BFRs, eight Dechloranes and three PBDE congeners could be analysed.

Peak areas of the obtained chromatograms were integrated using Agilent Technologies MassHunter Workstation Software Quantitative Analysis B.06.00. For quantification of target analytes detected in both EI and ECNI average concentrations of the four measurements (duplicate measurement in EI and ECNI) were used as final concentration. Further data analysis was performed with Microsoft Office Excel 2010. Statistical analysis, including normality test and t-test were performed using Origin Lab 9.1 Pro.

A list of all target analytes is presented in Supplement information S2.

2.4. QA/QC

Extraction and clean-up were conducted in a clean lab (class 10000). BFR containing material was avoided during sampling, sample preparation and analysis.

Recovery rates of IS 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 Na_2SO_4 treated similar 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 pg g^{-1} scale, ranging from 0.25 ± 0.5 pg g^{-1} for HBB to 57 ± 65 pg g^{-1} for HCPN. Exemptions were the comparably high blanks of BEH-TEBP, BDE-209, PBB and 2,4,6-TBP with 931 ± 1613 pg g^{-1}, 4555 ± 158 pg g^{-1}, 138 ± 218 pg g^{-1} and 362 ± 423 pg g^{-1}, 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 ng g^{-1} for most analytes, ranging from 0.75 pg g^{-1} for TBCT to 654 pg g^{-1} for PBB. Exemptions were high LODs for alpha DBE-DBCH, BEH-TEBP, BDE-209, TBCO and TBP with LODs between 1266 and 4839 pg g^{-1}. The LOQ respectively ranged from 2.5 pg g^{-1} for TBCT to 16.1 ng g^{-1} for BEH-TEBP.

A list of average blanks, LODs and LOQs and IS recoveries is presented in Supplement information S3 and S4.

3. Results and discussion

18 of the total 53 target analytes could be detected in sediment, dab or eel samples from the sampled locations. The detected compounds included eight PBDE congeners (BDE-28, -47, -66, -99, -100, -153, -154, -183), four alternate BFRs (TBP-DBPE, EH-TBB, HBB, PBEB, TBCO) and five dechloranes (DBALD, DDC-DBF, synDP, antiDP, aCl11DP). In the following section the occurrence of compounds in freshwater and marine sediments and fish is discussed individually.

3.1. Freshwater sediments vs. yellow eels from river Elbe

Data for yellow eels from river Elbe was previously published in Sühring et al. (2013).

The overall concentration and contamination pattern differed strongly between yellow eels and sediments from the same areas. Eels displayed wet weight concentrations up to two orders of magnitude higher than dry weight concentrations in sediments (Fig. 1). PBDEs were predominant in all eel samples, with total PBDEs of 8900 pg g^{-1} ww, whereas alternate BFRs and dechloranes only displayed concentrations of 211 pg g^{-1} ww and 130 pg g^{-1} ww respectively. These findings were congruent with previous reports of PBDEs in sediments and benthic biota from Belgium by Voorspoels et al. (2004), who reported significantly higher PBDE concentration in biota, as well as a relative increase of lower brominated BDE congeners such as BDE-47.

In sediments concentrations of alternate BFRs and dechloranes were similar to the ones found in eels (129 pg g^{-1} dw and 143 pg g^{-1} dw respectively), while PBDE concentrations were significantly lower with maximum total PBDE concentration of merely 56 pg g^{-1} dw. PBDE congener patterns differed as well between sediments and eels. More congeners were detected in eels with BDE-47 > BDE-100 > BDE-153 > BDE-99 > BDE-154 > BDE-183, whereas the congener distribution in sediments was BDE-99 > BDE-47 as well as high BDE-85 concentrations in one sample from Gorleben sampling site.

Patterns of alternate BFR differed significantly (t-test level 0.05) as well, despite the overall similar concentrations. In eels TBP-DBPE accounted for 92% of alternate BFR contamination, whereas EH-TBB was predominant in sediments (62% contribution to total alternate BFRs, TBP-DBPE: 26%). The predominance of "classic" BFRs such as PBDEs and TBP-DBPE in eels, in contrast to a predominance of PBDE substitutes, such as EH-TBB in sediments has several implications. On one hand it displays the persistence of PBDEs and associated compounds in biota, on the other hand it shows the increasing relevance of PBDE substitutes as environmental contaminants. The age of the sampled eels was between 10 and 14 years. They therefore had reached the European shore prior or around the time most technical BDE mixtures got banned by the Stockholm convention (SCOP, 2009). For years they were therefore likely exposed to primary PBDE and TBP-DBPE point sources as well as diffuse sources such as sediments. The low PBDE concentrations in sediments indicated that, at least at the sampling sites, sediments were likely not the major source of ongoing PBDE or TBP-DBPE exposure for eels. PBDE and TBP-DBPE concentrations must have therefore either been caused by uptake via e.g. the food chain or be the remainder of exposure in the early life stage of the eels, which would indicate a stability in the order of decades in the aquatic wildlife/food chain of the respective habitat. These findings were supported by the results of our previous study on HFR contamination of European and American eels throughout their life stages (Sühring et al., 2014). In this study we found that PBDE concentrations were significantly lower in juvenile European eels, than juvenile American eels, while adult eels from all sampling locations were predominantly contaminated with PBDEs. We concluded that the early restrictions in the EU compared to North America had caused this difference in contamination patterns, indicating historical contamination or uptake from stored chemicals (food chain or sediments) as sources for the PBDE contamination. The results from this study falsify the hypothesis of sediments as major source for PBDE contamination in adult eels, making historic contamination and uptake through the food chain the most likely sources.

The lack of EH-TBB in eel muscle tissue could either be an indication, that this compound is not readily taken up by the fish, quickly metabolised or that it is stored in other tissue types rather than muscle.

The second highest concentrated FR in freshwater sediments was unsuspectedly the aldrin related experimental flame retardant dibromoaldrin (DBALD) (Fig. 1). There is no information available on current use or production of DBALD even though it was already patented in 1976 (US patent 3941758) as a fire retardant additive for polymers (Maul et al., 1976). DBALD is structurally similar to the banned insecticide Aldrin, with two chlorine atoms substituted by bromine. Further research is necessary to identify potential sources of this contaminant. Interestingly, DBALD was not detected in any of the analysed fish
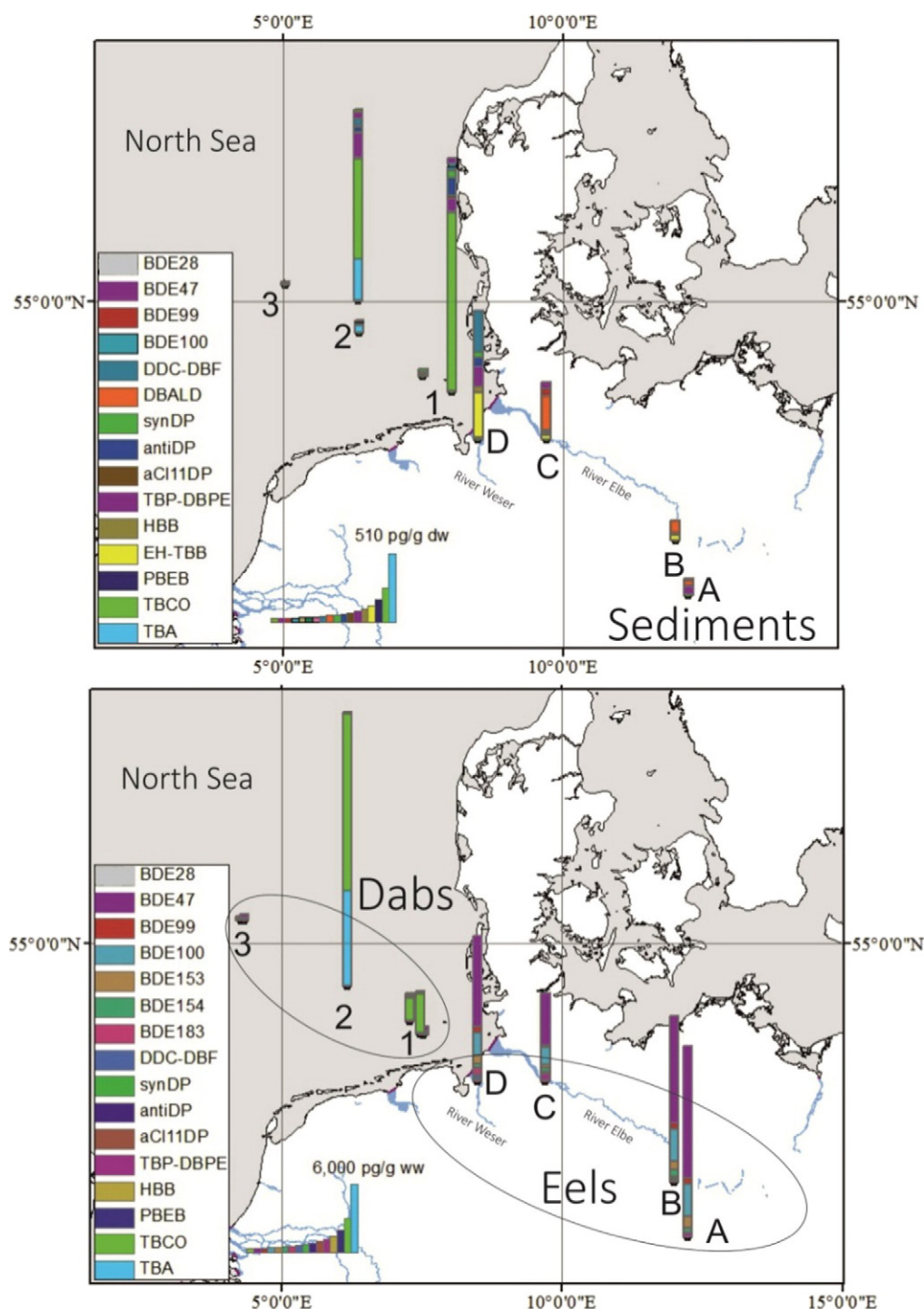
Fig. 1. Concentrations of detected BFRs and dechloranes in sediments [pg g^{-1} dw] (top) and the benthic fish eels and dabs [pg g^{-1} dw] (bottom) in the German Bight (sampling areas 1–3), river Elbe and river Weser (sampling areas A–D).

samples. This might indicate, that it is not readily uptaken, stored in tissues other than muscle or quickly excreted/transformed.

Contamination in eels and sediments did not differ significantly (t-test level 0.05) for the alternate BFR PBEB as well as sum Dechlorane Plus and the Dechlorane DDC-DBF, indicating, that sediments might be relevant sources of these contaminants in eels. The stereoisomer distribution of DP, however, was different for sediments and eels. While sediment concentrations represented more or less the technical DP mixture (57 ± 5% antiDP vs. 65–75% in the technical mixture) eels had significantly elevated contributions of the syn-isomer with 88 ± 17%. This

selective uptake or accumulation of synDP in fish had already been observed in previous studies (Sverko et al., 2011, Sühring et al., 2014).

A detailed list of all results is presented in Supplement information S5 and S6.

3.2. Marine sediments vs. dabs from the German Bight

PBDE in marine sediments from the German Bight were comparable to the concentrations in freshwater sediments with 62 ± 61 pg g^{-1} dw. PBDE concentrations in dabs, on the other hand, were very low

compared to concentrations found in eels with merely 146 ± 81 pg g^{-1} ww, indicating strong differences in contamination sources or uptake pathways. In both sediments and dabs BDE-47 accounted for over 60% of the total PBDE contamination, indicating the technical PentaBDE formulation as potential source. Further congeners detected were BDE-100 > BDE-28 > BDE-154 (in case of dabs).

Dechloranes were the most frequently detected contaminants group in both sediments and dabs with 169 ± 81 pg g^{-1} dw in sediments and 66 ± 35 pg g^{-1} dw in dabs. Similar to results reported for eels (Sühring et al., 2013) the highly bioaccumulative DDC-DBF (Shen et al., 2011a, b) was the highest concentrated Dechlorane in dabs (49 ± 33 pg g^{-1} ww), followed by the syn-isomer of DP (12 ± 3 pg g^{-1} ww) and the DP metabolite aCl11DP (5 ± 1 pg g^{-1} ww). In marine sediments, on the other hand, the anti-stereoisomer of DP was predominant (59 ± 58 pg g^{-1} dw), followed by syn-DP (47 ± 18 pg g^{-1} dw), DDC-DBF (<LOD - 111 pg g^{-1} ww) and aCl11DP (28 ± 16 pg g^{-1} ww). DDC-DBF was furthermore the least abundant of the detected Dechloranes in sediments, whereas it was detectable in every dab sample.

Alternate BFRs were only detectable in two sediment samples from known sedimentation areas with comparably high TOC (Table 1) and dabs from associated areas (Fig. 1). One exemption to this general pattern was the frequent detection of TBP-DBPE in dabs that was detectable in every dab sample with average concentrations of 60 ± 45 pg g^{-1} ww. TBP-DBPE is repeatedly reported as environmental contaminant in global biotic and abiotic matrices including air and water (Von der Recke and Vetter, 2007). The continued detection suggest ongoing emissions, even though there are no information on current production or use of TBP-DBPE and it has, officially, only been produced until the 1980s by one company in Germany (Von der Recke and Vetter, 2007). The low detection frequencies in sediments (only detectable in four samples) indicated that sediments might not be a relevant source for TBP-DBPE in the aquatic environment of the North Sea, further indicating the presence of current active sources, through e.g. ongoing application or emission from products.

Alternate BFR concentrations in general ranged from <LOD – 372 pg g^{-1} dw (excluding TBCO) in sediments and 65 ± 46 pg g^{-1} ww in dabs.

Unsuspectedly, comparably high concentrations of up to 1 ng g^{-1} dw in sediments and up to 12 ng g^{-1} ww in dabs of the alternate BFR 1,2,5,6-tetrabromocyclooctane (TBCO) was found in sediments from the two high-TOC sampling stations as well as in dabs from the area (Fig. 1, Table 1). These results were surprising, as TBCO could not be detected in any of the analysed river sediments or respective eel samples. This suggested the input via a localised source in the North Sea that has not yet been identified. Possible sources might be the introduction through ships (e.g. paint) or their cargo. Input through atmospheric deposition is unlikely, because of the low volatility of TBCO (<0.1 mm Hg (Cequier et al., 2014)), as well as the localised detection. As TBCO is used in consumer products diffuse emissions from urban areas seem to be a likely source. This would imply a high mobility of TBCO from rivers to North Sea sedimentation areas, since it could not be detected in any river sediments (Fig. 1).

TBCO is an additive flame retardant used in paint, plastics and textiles (Riddell et al., 2009). It has been reported in house dust from California with concentrations of up to 2 ng g^{-1} dust (Dodson et al., 2012), as well as in eggs of herring gulls from the Great Lakes (Gauthier et al., 2009). TBCO meets the criteria for potential aquatic hazardous substance as well as the very persistent and very bioaccumulative criteria of the REACH legislation (Fisk et al., 2003). There is however, limited information on production and use volumes. In Canada TBCO is listed in the non-domestic Substances List, with an approximate import of 10 tons per year (Riddell et al., 2009). The origin of the detected TBCO contamination in North Sea samples can only be speculated. Apart from TBCO, hexabromobenzene (HBB) could be detected at sediment sampling stations with comparably high TOC (Table 1) as well as in dabs from these areas. Concentrations were comparably low with a maximum of 14 pg g^{-1} ww in dabs and up to 38 pg g^{-1} dw in sediments. HBB is used in plastics, paper, woods, textiles and electronics. There is however, no reported current production or use in Europe (Dodson et al., 2012). The compound is therefore likely introduced through emissions from imported products, e.g. electronics. Sinkkonen et al. (2004) found HBB in all scrap samples collected at an aluminium recycling plant in southern Finland and Verreault et al. (2007) reported levels of HBB similar to those of the minor PBDEs (28, 116 and 155) in glaucous gulls from the Norwegian Arctic.

3.3. Comparison freshwater vs. marine habitat

A general observation for both freshwater and marine habitats were, that contamination patterns in sediments were close to the composition of the technical products, whereas patterns in fish differed significantly from technical formulations. The isomer distribution of DP, for example, was close to the technical product (65–75% antiDP) (Sverko et al., 2011) in both analysed marine and freshwater sediments, whereas synDP was predominant in eels as well as dabs (Table 1). This change indicates selective uptake or accumulation of the syn-isomer and had previously been reported by Sverko et al. (2011).

Table 1

Average concentrations of detectable total PBDEs (BDE-28, -47, -85, -99, -100, -153, -154, -183), TBCO, other detectable alternate BFRs (TBP-DBPE, EH-TBB, HBB, PBEB), total detectable dechloranes (DBALD, DDC-DBF, syn-, anti-DP, aCl11DP), fsyn (contribution of synDP to the total DP (syn- + antiDP) concentration), lipid content or total organic carbon (TOC) [%] and number of sampled individuals or sampling stations per area [n] for benthic fish (top) [pg g^{-1} ww] and sediments (bottom) [pg g^{-1} dw] from respective areas.

Fish (n) [pg/g ww]	Total PBDEs	TBCO	Other alternate BFRs	Total dechloranes	fsyn	Average lipid [%]
Dab 1 (n = 5)	58	11,951	25	44	1	2.0
Dab 2 (n = 10)	164	1352	115	106	1	0.50
Dab 3 (n = 9)	216	n.d.	56	48	1	0.78
Eel A (n = 5)	12,616	n.d.	240	42	1	27
Eel B (n = 5)	11,013	n.d.	66	105	0.74	27
Eel C (n = 5)	9436	n.d.	155	263	1	34
Eel D (n = 5)	5270	n.d.	490	154	0.66	26
Sediments (n) [pg/g dw]	**Total PBDEs**	**TBCO**	**OTHER alternate BFRs**	**Total dechloranes**	**f syn**	**Average TOC [%]**
Sediment 1 (n = 2)	122	1085	290	182	0.31	0.20
Sediment 2 (n = 3)	62	1223	117	219	0.31	0.17
Sediment 3 (n = 1)	n.d.	n.d.	n.d.	106	1	0.08
Sediment A (n = 1)	n.d.	n.d.	42	51	0.42	0.10
Sediment B (n = 1)	n.d.	n.d.	31	81	0.51	0.10
Sediment C (n = 1)	205	n.d.	421	329	0.37	0.61
Sediment D (n = 1)	77	n.d.	26	224	0.45	1.0

In case of PBDEs BDE-47 was the predominant congener in both eels and dabs. This could indicate exposure to technical PentaBDE, which contains up to 40% BDE-47 (Weinberg et al., 2010). Fish have also been reported to enzymatically debrominate BDE congeners with BDE-47 as metabolism endpoint (Eljarrat and Barceló, 2011). The high BDE-47 contribution could therefore also be an indication for metabolism processes.

In both freshwater sediments from river Elbe and marine sediments PBDEs were below the limit of detection (LOD) or quantification (LOQ) at most sampling sites (Fig. 1, Table 1). Where BDEs could be detected and quantified in Elbe river BDE-99 > BDE-47 were predominant, corresponding to the congener distribution of technical PentaBDE as potential source (Weinberg et al., 2010).

In marine sediments, on the other hand, the observed BDE congener profile was similar to PBDEs found in dabs, with mainly BDE-47, BDE-100 and BDE-28, suggesting technical PentaBDE mixture and subsequent debromination to BDE-47 as contamination source. The overall low concentrations of PBDEs in sediments were congruent with previous reports by Voorspoels et al., 2004 who measured PBDEs in freshwater sediments from Belgium. They reported detection of selected PBDE congeners in the pg g^{-1} dw to low ng g^{-1} dw range (apart from BDE-209). Other than BDE-209 they reported BDE-99, -47 and -100 as main congeners, similar to observations in this study Voorspoels et al. (2004).

The difference between BDE congener profiles in European eels versus sediments from associated sampling sites, while congener profiles of marine sediment samples and dabs matched was interesting. It implied differences in sources, uptake pathways or metabolism between the respective fish. This hypothesis was reinforced by the observed difference in the general contamination patterns between dabs, eels and their associated sediment samples. While eels were mainly contaminated with PBDEs (contribution 96%) and the associated sediments with merely 19% PBDEs, dabs displayed similar contributions of PBDEs (4%) as sediments (5% PBDEs). In general contaminant patterns between dabs and marine sediments matched well, whereas patterns between freshwater sediments and eels differed noticeably.

This again suggested a difference in the driving factors for contamination in freshwater sediments vs. marine sediments as well as in eels vs. dabs.

3.4. Determining factors for the observed contamination patterns

FR concentration in marine sediments displayed a strong correlation with organic carbon content (TOC) of the sediments with Pearson's r of 0.93 (Fig. 2).

In freshwater sediments from river Elbe the correlation of TOC and total FR concentration was noticeably lower with Pearson's r = 0.48. This difference was likely caused by a difference in contamination sources. Urban areas are a known source for chemicals, such as flame retardants, that are applied in consumer products (Csiszar et al., 2013). The found concentrations and patterns in the Elbe river are therefore, likely dominated by localised emission from urban areas along the river. The North Sea, on the other hand, seems to be mostly impacted by contaminants from diffuse sources, atmospheric deposition and river discharge. This leads to distribution patterns for organic contaminants coinciding with the distribution of high TOC sedimentation areas in the North Sea.

For dabs contamination patterns seemed to be driven by contaminants or sources present in their habitat as well as their lipid content in case of the very abundant or high concentrated compounds such as Dechloranes and TBA (r = 0.5–0.9). The impact of local sources was especially pronounced for the alternate BFRs TBCO and HBB, which could only be detected in dabs sampled close to sediment sampling stations that displayed high concentrations of these compounds. Magnitude of concentrations in dabs reflected known bioaccumulation potentials for different compounds, leading e.g. to an increase of the syn-isomer of DP in dabs as well as an increase of the highly bioaccumulative DDC-DBF.
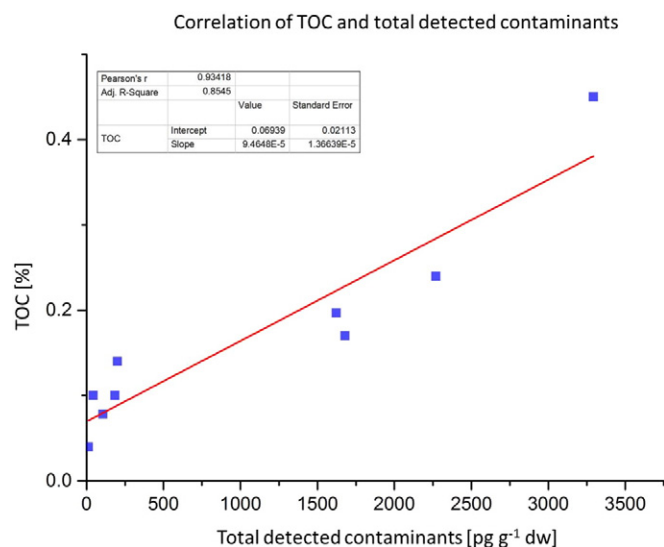

Fig. 2. Correlation of total detected contaminants in pg g^{-1} dw and TOC [%] in sediments.

Eels displayed a similar relation for DDC-DBF and dechloranes compared to sediments from the same sampling areas. The high PBDE concentrations however, indicated historic exposure or exposure through the food chain to PBDEs as driver for observed contamination patterns (Fig. 1). A high trophic magnification of PBDEs compared to dechloranes has already been reported in waterbirds from China (Zhang et al., 2011). This could also be an explanation for the high PBDE contributions in eels compared to dabs, which are at a similar trophic position (Gloyne and Shepherd, 1975) but have significantly lower lipid content and therefore lower bioaccumulation capacity for the highly lipophilic PBDEs (Shen et al., 2011a, b). Eels in their yellow eel life stage are known to strongly accumulate lipophilic contaminants such as BFRs, due to their high lipid content (Palstra et al., 2006). This characteristic, along with their longevity and sedentary life style during the yellow phase and wide distribution have proven to make eels suitable bioindicators for assessing the chemical status of river basin water bodies as defined in the European Water Framework Directive (WFP) (Belpaire and Goemans, 2007a). At the same time, the high accumulation through the food chain and storage within lipid rich muscle tissue seem to make eels unsuitable as indicator species for the contamination situation in sediments from their habitats — despite being sediment related, bottom dwelling fish.

3.5. BSAFs

Biota sediment accumulation factors (BSAFs) are used to describe the bioaccumulation of sediment-associated compounds into tissue of residential biota (Burkhard, 2009). BSAFs are especially useful for the prediction of residues of chemical contamination from sediments in fish, because the parameter was specifically developed for the description of non-equilibrium condition bioaccumulation of sediment contaminants in aquatic food webs (Burkhard, 2009). However, sedentary and benthic life-styles of the tested species are key criteria for the determination of meaningful BSAFs.

Due to the high differences between FR patterns in eels and their paired sediment samples, BSAF estimation was based on HFR results in the measured dabs. BSAFs were calculated using the following equation:

$$BSAF = \frac{C_d / f_l}{C_s / f_{OC}}$$

with C_d = analyte concentration in dab [pg g^{-1} ww], f_l = lipid content in the dab tissue per g ww, C_s = analyte concentration in paired

sediment sample [pg g^{-1} dw], and f_{OC} = TOC content in the sediment sample.

Average BSAFs ranged from 0.05 for BDE-28 to 3.8 for DDC-DBF (Table 2). In general calculated BSAFs were substantially lower than BSAFs reported in the literature (Table 2). However, determined BSAFs were in agreement with general patterns reported in literature, namely BSAF of DDC-DBF > BDE-47 > syn-DP > anti-DP (Table 2).

BSAFs, especially testing benthic fish, should always be interpreted with care. A variety of additional factors, such as biomagnification, maternal transfer or metabolism processes can have a significant impact on the accumulation patterns of contaminants in fish. However, BSAFs have proven useful to provide an overview of potentially accumulating compounds and the relevance of sediments as contamination source of the individual compounds for the tested species.

The results in this study would suggest the dechlorane DDC-DBF as well as the alternate BFR TBCO to be compounds of particular relevance with BASFs similar or higher than the known POPs BDE-47 and BDE-100.

4. Conclusions

The results for brominated and chlorinated flame retardants presented in this study indicate an increasing relevance of alternative BFRs and Dechloranes as contaminants in the marine and freshwater environment.

The distribution of HFRs in marine sediments seems to be driven by the biogeochemical properties of the sediments, namely TOC. In freshwater sediments, on the other hand, proximity to urban areas or point sources seems to be the driving factor for contamination pattern and magnitude.

Indications were found, that the magnitude of FR contamination in dabs are mainly driven by their lipid content. The found pattern for alternate BFRs and dechloranes matched FR patterns at related sediment sampling stations, indicating that dabs are suitable indicators for the contamination patterns of North Sea sediments with these compounds.

FR patterns in European eels, on the other hand, seemed to mostly represent historic use of PBDEs as well as their magnification through the food chain and did not represent contamination patterns in related sediment samples. It therefore has to be concluded, that European eels might be an indicator for the historic application of FRs in their habitat, as well as the contamination situation of the food chain. They are, however, not representative for contaminants stored in sediments and were therefore excluded for the calculation of BSAFs.

The calculated BSAFs provide an indication on accumulation of FRs in dabs. However, as sediments are not the only or primary source of FRs in dabs, further tests are needed to assess the impact of sediments as contaminant source for benthic fish in comparison to the impact of uptake via the food chain or water phase.

Table 2
Comparison of BSAFs calculated for this study and literature data.

Substance	BSAF this study	BSAF literature	Reference
BDE-28	0.05	5.89 (tubificid worm)	Tian et al. (2012)
BDE-47	3.4	5 (earthworm)	Sellström et al. (2005)
BDE-100	3.3	4.74 (tubificid worm)	Tian et al. (2012)
DDC-DBF	3.8	270 (lake trout)	Shen et al. (2011a),b
Anti-DP	n.d.	0.3 (lake trout)	Shen et al. (2011a),b
Syn-DP	0.2	0.8 (lake trout)	Shen et al. (2011a),b
aCl11DP	0.1	n.a.	n.a.
HBB	0.4	2.3–6.1 (earthworm)	Nyholm et al. (2010)
TBP-DBPE	0.8	n.a.	n.a.
TBCO	2.9	n.a.	n.a.

References

Belitz, H.D., Grosch, W., Schieberle, P., 2012. Lehrbuch der Lebensmittelchemie. 6. Springer.

Belpaire, C., Goemans, G., 2007a. Eels: contaminant cocktails pinpointing environmental contamination. ICES J. Mar. Sci. 64 (7), 1423–1436. http://dx.doi.org/10.1093/icesjms/fsm121.

Belpaire, C., Goemans, G., 2007b. The European eel *Anguilla anguilla*, a rapporteur of the chemical status for the water framework directive? Vie Milieu 57 (4), 235–252.

Burkhard, L. 2009. Estimation of Biota Sediment Accumulation Factor (BSAF) From Paired Observations of Chemical Concentrations in Biota and Sediment. U.S. Environmental Protection Agency, Ecological Risk Assessment Support Center, Cincinnati, OH. EPA/600/R-06/047.

Cequier, E., Ionas, A.C., Covaci, A., Marcé, R.M., Becher, G., Thomsen, C., 2014. Occurrence of a broad range of legacy and emerging flame retardants in indoor environments in Norway. Environ. Sci. Technol. 48, 6827–6835.

Csiszar, S.A., Daggupaty, S.M., Verkoeyen, S., Giang, A., Diamond, M.L., 2013. Somum: a coupled atmospheric transport and multimedia model used to predict intraurbanscale PCB and PBDE emissions and fate. Environ. Sci. Technol. 47, 436–445.

Dodson, R.E., Perovich, L.J., Covaci, A., Van den Eede, N., Ionas, A.C., Dirtu, A.C., Brody, J.G., Rudel, R.A., 2012. After the PBDE phase-out: a broad suite of flame retardants in repeat house dust samples from California. Environ. Sci. Technol. 46, 13056–13066. http://dx.doi.org/10.1021/es303879n.

Eljarrat, E., Barceló, D., 2011. The Handbook of Environmental Chemistry: Brominated Flame Retardants. 16th ed. Springer-Verlag, Berlin Heidelberg http://dx.doi.org/10.1007/978-3-642-19269-2.

European Court of Justice. 2008. "Court of Justice." Official Journal of the European Union: C 116/2–C 116/3.

Fisk, P., Girling, A.E., Wildey, R.J., 2003. Prioritisation of flame retardants for environmetal risk assessment. Environment http://www.environment-agency.gov.uk.

Gauthier, L.T., Potter, D., Hebert, C.E., Letcher, R.J., 2009. Temporal trends and spatial distribution of non-polybrominated diphenyl ether flame retardants in the eggs of colonial populations of Great Lakes Herring gulls. Environ. Sci. Technol. 43, 312–317.

Gloyne, A. R. and Shepherd, C. J., (1978), Marine Ecology and Fisheries: Cushing, D.H., Cambridge University Press, 1975; ISBN 0 521 20501 8, (184 pp.).

Harju, M., Heimstad, E.S., Herzke, D., Sandanger, T., Posner, S., Wania, F., 2009. Emerging "new" brominated flame retardants in flame retarded products and the environment. Norwegien Pollution Controll Authority Report 2462.

Maul, James J. (Grand Island, NY), Carlson, Richard D. (Grand Island, NY), (1976) for Hooker Chemicals & Plastics Corporation (Niagara Falls, NY). US patent 3941758.

Möller, A., Xie, Z., Sturm, R., Ebinghaus, R., 2010. Large-scale distribution of dechlorane plus in air and seawater from the Arctic to Antarctica. Environ. Sci. Technol. 44 (23), 8977–8982. http://dx.doi.org/10.1021/es103047n http://www.ncbi.nlm.nih.gov/pubmed/21047104.

Nyholm, J.R., Asamoah, R.K., van der Wal, L, Danielsson, C., Andersson, P.L., 2010. Accumulation of polybrominated diphenyl ethers, hexabromobenzene and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH) in earthworm (*Eisenia fetida*). Environ. Sci. Technol. 44, 9189–9194.

Palstra, A.P., van Ginneken, V.J.T., Murk, A.J., van den Thillart, G.E.E.J.M., 2006. Are dioxinlike contaminants responsible for the eel (*Anguilla Anguilla*) drama? Die Naturwissenschaften 93 (3), 145–148. http://dx.doi.org/10.1007/s00114-005-0080-z http://www.ncbi.nlm.nih.gov/pubmed/16508793.

Riddell, N., Arsenault, G., Klein, J., Lough, A., Marvin, C.H., McAlees, A., McCrindle, R., MacInnis, G., Sverko, E., Tittlemier, S., Tomy, G.T., 2009. Structural characterization and thermal stabilities of the isomers of the brominated flame retardant 1,2,5,6-tetrabromocyclooctane (TBCO). Chemosphere 74, 1538–1543.

SCOP. 2009. "Report of the Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants on the Work of Its Fourth Meeting; Stockholm Convention on Persistent Organic Pollutants: Geneva, 4 to 8 May 2009." World Trade (May 2009).

SCOP 2013. Persistent Organic Pollutants Review Committee. Proposal to list decabromodiphenyl ether (commercial mixture, cdecabde) in annexes a, b and/or c to the Stockholm convention on persistent organic pollutants. Report, 2013.

Sellström, U., de Wit, C.A., Lundgren, N., Tysklind, M., 2005. Effect of sewage–sludge application on concentrations of higher-brominated diphenyl ethers in soils and earthworms. Environ. Sci. Technol. 39, 9064–9070.

Shen, L., Reiner, E.J., MacPherson, K.A., Kolic, T.M., Richman, L.A., Marvin, C.H., Burniston, D.A., Hill, B., Brindle, I.D., McCrindle, R., Chittim, B.G., 2011a. Dechloranes 602, 603, 604, Dechlorane Plus, and Chlordene Plus, a newly detected analogue, in tributary sediments of the Laurentian Great Lakes. Environ. Sci. Technol. 45 (2), 693–699.

http://dx.doi.org/10.1021/es1027844http://www.ncbi.nlm.nih.gov/pubmed/21133428.

Shen, L., Reiner, E.J., Helm, P.A., Marvin, C.H., Hill, B., Zhang, X., MacPherson, K.A., Kolic, T.M., Tomy, G.T., Brindle, I.D., 2011b. Historic trends of dechloranes 602, 603, 604, dechlorane plus and other norbornene derivatives and their bioaccumulation potential in lake Ontario. Environ. Sci. Technol. 45 (8), 3333–3340. http://dx.doi.org/10.1021/es104328rhttp://www.ncbi.nlm.nih.gov/pubmed/21434636.

Sinkkonen, S., Paasivirta, J., Lahtipera, M., Vattulainen, A., 2004. Screening of halogenated aromatic compounds in some raw material lots for an aluminium recycling plant. Environ. Int. 30, 363–366.

Sühring, R., Möller, A., Freese, M., Pohlmann, J., Wolschke, H., Sturm, R., Xie, Z., Hanel, R., Ebinghaus, R., 2013. Brominated flame retardants and dechloranes in eels from German rivers. Chemosphere 90, 118–124. http://dx.doi.org/10.1016/j.chemosphere.2012.08.016.

Sühring, R., Byer, J., Freese, M., Pohlmann, J., Wolschke, H., Möller, A., Hodson, P.V., Alaee, M., Hanel, R., Ebinghaus, R., 2014. Brominated flame retardants and Dechloranes in European and American eels from glass to silver life stages. Chemosphere 116, 104–111. http://dx.doi.org/10.1016/j.chemosphere.2013.10.096.

Sühring, R., Barber, J.L., Wolschke, H., Kötke, D., Ebinghaus, R., 2015. Fingerprint analysis of brominated flame retardants and Dechloranes in North Sea sediments. Environ. Res. 2015, 569–578. http://dx.doi.org/10.1016/j.envres.2015.05.018.

Sverko, E., Tomy, G.T., Reiner, E.J., Li, Y., McCarry, B.E., Arnot, J.A., Law, R.J., Hites, R.A., 2011. Dechlorane Plus and related compounds in the environment: a review. Environ. Sci. Technol. 45 (12), 5088–5098. http://dx.doi.org/10.1021/es2003028http://www.ncbi.nlm.nih.gov/pubmed/21574656.

Tian, S., Zhu, L., Bian, J., Fang, S., 2012. Bioaccumulation and metabolism of polybrominated diphenyl ethers in carp (*Cyprinus carpio*) in a water/sediment microcosm: important role of particulate matter exposure. Environ. Sci. Technol. 46, 2951–2958.

United States Environmental Protection Agency (US EPA) 2015. DecaBDE Phase-Out Initiative. Announcement on the EPA website, accessed: 12.03.2015.

Verreault, J., Gebbink, W.A., Gauthier, L.T., Gabrielsen, G.W., Letcher, R.J., 2007. Brominated flame retardants in glaucous gulls from the Norwegian arctic: more than just an issue of polybrominated diphenyl ethers. Environ. Sci. Technol. 41, 4925–4931.

Von der Recke, R., Vetter, W., 2007. Synthesis and characterization of 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and structurally related compounds evidenced in seal blubber and brain. Environ. Sci. Technol. 41, 1590–1595.

Voorspoels, S, Covaci, A., Maervoet, J., Schepens, P. 2004. "PBDEs in marine and freshwater sediments from Belgium: levels, profiles and relations with biota" J. Environ. Monit., 6, 914–918.

Weinberg, I., Dreyer, A., Ebinghaus, R., 2010. Landfills as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air. Atmos. Environ. 45 (4), 935–941.

Zhang, X., Luo, X., Liu, H., Yu, L., Chen, S., Mai, B., 2011. Bioaccumulation of several brominated flame retardants and Dechlorane Plus in waterbirds from an e-waste recycling area in South China: associated with trophic level and diet source. Environ. Sci. Technol. 45 (2), 400–405. http://dx.doi.org/10.1021/es102251s.