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Chemicals of emerging concern in marine specimens of the German Environmental Specimen Bank

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Abstract

Background: Descriptor 8 of the Marine Strategy Framework Directive (MSFD) (Directive 2008/56/EC) addresses the good environmental status with regard to pollution of marine waters by chemical contaminants. Commission decision (EU) 2017/848 lays down the criteria and methodological standards on good environmental status of marine waters. Member States, in regional or subregional cooperation, shall establish lists of relevant contaminants beside those already covered by the Water Framework Directive (WFD). To provide information on emerging contaminants in marine biota, the German Environmental Specimen Bank (ESB) has compiled data of blue mussels and eelpouts from coastal sites in the North and Baltic Seas. Substances identified by the International Council for the Exploration of the Sea (ICES) as of emerging concern for the marine environment have been used as a starting point.

Results and conclusions: The study presents data of 19 emerging flame retardants and degradation products, 40 per- and polyfluoroalkyl substances (PFAS) and three cyclic volatile methylsiloxanes (cVMS). Among the emerging flame retardants, only Dec 602 was detected in all samples of 2015. Dec 604, Cl₁₀-antiDP, 1,5-DPMA, EH-TBB, PBEB, TBP-AE, BATE, BTBPE and HBBz were constantly < limit of quantification (LOQ). Time trends were barely detected. Legacy PBDE still dominates in most samples. PFAS concentrations were usually higher in samples from the North Sea sites compared to samples from the Baltic Sea. PFOS dominated in most samples. Increasing trends over time were detected for PFNA, PFDA and PFDoDA at the Baltic Sea site and for PFDA at one North Sea site. Concentrations of the cVMS D4, D5 and D6 were below the detection limit at the ESB sampling sites. Based on the results, it should be considered to include the emerging flame retardants DP and Dec 602 and the long-chain perfluoroalkyl substances PFNA, PFDA, PFUnDA and PFDoDA in a regular monitoring in the North and Baltic Seas.

Keywords: Chemicals of emerging concern, PFAS, Dechloranes, Alternative brominated flame retardants, Cyclic volatile methylsiloxanes, Eelpout, Blue mussel, Environmental Specimen Bank, OSPAR, HELCOM

Background

According to the Marine Strategy Framework Directive (MSFD) [1], monitoring for an integrative assessment of the good environmental status has to be established. In coastal waters, the scopes of the Water Framework Directive (WFD) [2] and the MSFD overlap. Thus, any

monitoring with regard to Descriptor 8 of the MSFD (“Concentrations of contaminants are at levels not giving rise to pollution effects”) should, where appropriate, comply with the requirements of the WFD [3]. Recommended substances for monitoring in marine environments are therefore initially those selected under the WFD [2, 4]. In addition, Member States are requested to establish in regional or subregional cooperation a list of other relevant contaminants, i.e., from offshore sources, that may lead to pollution in the marine region or subregion [5].

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Improvements in chemical analysis as well as screenings and research programs have led to the detection of new substances in the marine environment that give rise to concern because of problematic environmental properties like persistence, bioaccumulation and/or long-range transport [6, 7]. To cope with these upcoming substances, the Hazardous Substances and Eutrophication Committee (HASEC) of the Oslo-Paris-Commission (OSPAR; Convention for the Protection of the Marine Environment of the North-East Atlantic) requested advice from the International Council for the Exploration of the Sea (ICES) to identify chemicals of emerging concern (CEC), indicate information gaps and recommend what further work or information is needed to take action [8].

In response to the request, ICES in a first step identified eight substance groups with critical chemical properties (e.g., bioaccumulation potential, persistence, toxicity) that may be of emerging concern in the marine environment, i.e., Dechlorane Plus, alternative brominated flame retardants (aBFR), organo-phosphorous flame retardants (OPFR), antifoulants, per- and polyfluoroalkyl substances (PFAS) other than PFOS and PFOA, benzotriazoles, siloxanes, and anticorrosion agents (especially those applied in offshore windmill parks). The selection based on a review of published data and recent projects that include information on new and emerging chemicals. In a report issued by ICES in 2017, data were compiled on Dechlorane Plus and dechloranes 602 and 603, as well as 16 aBFR, 27 OPFR, 25 PFAS, and two types of corrosion agents used in offshore windmill parks, whereas new antifoulants, benzotriazole compounds, and methylsiloxanes were not considered [8].

The database of the German Environmental Specimen Bank (ESB) was used to gather additional data for these substance groups. Data were available for dechloranes (including Dechlorane Plus and its degradation products, and dechloranes Dec 602, 603 and 604), 10 aBFR, 40 PFAS, and 3 cyclic volatile methylsiloxanes (cVMS).

Dechloranes were developed as substitutes for the pesticide and flame retardant Mirex [9] that was banned worldwide under the Stockholm Convention [10]. Dechlorane Plus (DP) is used as a flame retardant for instance in plastics, electric and electronic devices, and building materials [9, 11]. It can be released to the environment during processing, use and disposal of products containing DP [11, 12]. The main entry to the marine environment is through rivers carrying contaminated wastewater and via atmospheric transport [13]. Under Regulation (EC) No 1907/2006 (REACH) [14], DP has been classified as a substance of very high concern (SVHC) because of its persistence and bioaccumulation potential. Similar properties are also assumed for the structurally related

1,5-Dechlorane Plus mono-adduct (DPMA) [15]. Little information on production and usage is available for Dechloranes 602, 603 and 604 [8].

Alternative brominated flame retardants are a heterogeneous group of brominated substances. Their market share grew as fire safety requirements increased and the use of legacy flame retardants like polybrominated diphenyl ethers (PBDE) was more and more regulated (e.g., [10, 16–18]). Commercial Penta- and Octa-BDE mixtures, for example, were restricted in the EU in 2004 [16] and several marker congeners of these mixtures were included in Annex A of the Stockholm Convention in 2009 [10]. Alternative BFR can enter the environment during production (of the commercial product as well as of products containing aBFRs), use (i.e., release from aBFR-containing products) and disposal. In rivers, waste water treatment plants are likely sources especially of aBFR used in consumer products [19]. Some aBFRs are found in the atmosphere and may be subject to long-range transport [6, 20]. Therefore, the main inputs to the marine environment are likely to be via rivers and atmospheric deposition. Many aBFR are persistent, bioaccumulative and/or toxic or potentially endocrine disruptive [6, 8].

PFAS are widely used substances, e.g., as stain repellents in papers and textiles, in non-stick cookware, fire-fighting foams, photographic and electronic devices, and industrial coatings [21]. They can enter the environment during manufacturing, usage and disposal whereby the main routes depend on the type of application [21, 22]. Main inputs into the marine environment are through rivers and atmospheric deposition [6, 22]. Many PFAS are persistent under environmental conditions. Their environmental behavior depends largely on their functional moiety and on the length of their carbon chain. Especially long-chain PFAS are bioaccumulative and can enrich in the food web, while short-chain PFAS tend to be mobile in sediments and waters (e.g., [23–29]). Moreover, some PFAS are toxic and/or endocrine disruptive [30, 31]. A number of long-chain PFAS (including PFOA, PFNA, PFDA, PFUnDA, PFDoDA and PFHxS) are classified as SVHC under the European REACH regulation [14]. PFOS and PFOA are regulated EU wide since 2006 and 2017, respectively [32, 33]. Under the Stockholm Convention [10], PFOS is listed in Annex B since 2009 and PFOA is listed in Annex A since 2019; PFHxS is proposed for listing.

Siloxanes comprise a large group of chemicals which have in common a backbone structure of silicone and oxygen atoms with side chains linked to the silicone atom. In case of the cVMS D4 (octamethylcyclotetrasiloxane), D5 (decamethylcyclopentasiloxane) and D6 (dodecamethylcyclohexasiloxane), the side chains consist of methyl groups. These siloxanes are used in biomedical

and cosmetic applications as well as in waxes and polishes. Substantial amounts are also used for the production of siloxane polymers. They can be emitted during industrial processes or the use of products and enter the environment mainly via air and waste water [34]. Under the European REACH regulation [14, 35], D4, D5 and D6 are classified as SVHC because of their environmental persistence, bioaccumulative properties, and in the case of D4, toxicity. Moreover, D4 is assumed to be endocrine disruptive [36]. From 2020 on, D4 and D5 will be regulated EU wide [35].

The aim of the present study is to show which of these CEC are detectable and may be of relevance in the German coastal environment. Data presented were elaborated in various projects of the German ESB and refer to concentrations in blue mussels (*Mytilus edulis* Complex) and eelpouts (*Zoarces viviparus*) from coastal sampling sites in the Lower Saxony Wadden Sea, the Schleswig–Holstein Wadden Sea, and the Baltic Sea Bodden National Park [37]. In some cases, available data cover time periods of up to 30 years. The focus, however, is on recent concentrations. Temporal trends are not discussed in detail but are used for the evaluation of potentially hazardous substances.

Materials and methods

Sampling sites

The ESB collects marine samples in coastal areas of the Central North Sea (FAO/ICES Division 27.4.b) and the Baltic Sea West of Bornholm (FAO/ICES Subdivision 27.3d.24). The locations of the sampling sites are shown in Fig. 1. For details, see [37].

The North Sea sites are located in the National Parks and Biosphere Reserves ‘Lower Saxony Wadden Sea’ (site NS 1) and ‘Schleswig–Holstein Wadden Sea’ (NS 2), the Baltic Sea sites (site BS) are situated in the ‘Bodden National Park of Western Pomerania’. More details including possible sources of contaminations at these sites are given in [38, 39].

Sampling and processing

Under the ESB program, blue mussels and eelpouts are sampled regularly.

Sampling and sample processing are highly standardized. The respective protocols are documented as Standard Operating Procedures (SOP) and are laid down in a basic concept [40].

Blue mussels are collected bimonthly at the North Sea sites and every 6 months (June and November) at the Baltic Sea site [41]. Eelpout is sampled once per year in May/June before the mating season [42].

Blue mussels and eelpout filets and livers are shock-frozen at $< -130\text{ }^{\circ}\text{C}$ immediately after sampling and biometrical characterization of the organisms. In the laboratory, the specimens (soft body of blue mussel, filets and liver of eelpout) are cryo-milled to a homogenous powder and annual composite samples are prepared for every site and specimen [43]. Aliquots of these composite samples are stored in the ESB archive at temperatures $< -130\text{ }^{\circ}\text{C}$ in an inert atmosphere above liquid nitrogen to minimize chemical alterations [38, 44].



Fig. 1 Coastal sampling sites of the German Environmental Specimen Bank. NS 1: North Sea—Lower Saxony Wadden Sea; NS 2: North Sea—Schleswig–Holstein Wadden Sea; BS: Baltic Sea—Bodden National Park. Sampled species: Lozenge: eelpout; Circle: blue mussel. Shading of symbols indicate that they belong to the same sampling areas, i.e., gray: NS 1; black: NS 2; white: BS

Target chemicals

The target chemicals are summarized in Table 1. The table includes the available data for the different ESB sampling sites. Time intervals differ between the matrices and sampling sites because the study relies on already existing data that were elaborated during different projects.

Besides the emerging FR identified by ICES [8], the structurally related compounds 1,5-DPMA, Dec 604 and the DP-degradation products Cl₁₀-antiDP and Cl₁₁-antiDP were analyzed. Furthermore, TBA—a fungal metabolite of the FR intermediate and fungicide 2,4,6-tribromophenol [45]—was included in the analysis. TBA has been reported in fish from various marine environments [46–50] and contributes to the overall burden of brominated compounds on organisms. For comparison, data on the WFD-relevant PBDE congeners BDE-28, -47, -99, -100, -153, and -154 were also included.

ICES [8] reviewed 23 PFAS that may be of emerging concern. For 13 of these substances, data were available in the ESB database (Table 1).

Time series for blue mussels ended in 2008 because PFAS concentrations were mostly below the limit of quantification (LOQ) of 0.5 µg kg⁻¹. For eelpout, data for liver and filet are available, albeit for different periods. PFAS preferably bind to serum proteins and are typically high in well-vascularized organs like liver, blood, and kidney [25, 26, 51]. Concentrations are especially high in liver tissue as the main organ of albumin synthesis. This was the reason why PFAS were initially analyzed in liver tissue. However, when compliance monitoring came into focus the PFAS analysis switched to filet because in Germany fish filet was recommended as the matrix to be investigated in the context of the WFD [52]. Time series for liver ended in 2008/2009 but additional liver data are available for 2015 from the sampling sites NS 2 and BS. PFAS data for eelpout filet are available for the years 2003–2017. The legacy substances PFOS and PFOA were included in the data compilation as benchmarks.

The ESB database also provides data on 25 other PFAS, including fluorotelomer sulfonic acids, poly-fluorinated/mixed halogenated sulfonic and phosphonic acids, perfluorooctane sulfonamides and derivatives as well as poly- and perfluoroalkyl phosphates. The data cover only 1 year (2015) and refer to eelpout livers from NS 2 and BS (Additional file 1: Table S11, S13). None of these additional 25 PFAS were detected in the samples. For the sake of clarity, they are not included in Table 1.

For the cVMS D4, D5 and D6, only data for eelpout filet from 2018 were available.

Chemical analysis

Chemical analysis and quality assurance/quality control are outlined in the Additional file 1 and in Neugebauer et al. [53] (FR), Rüdél et al. [54, 55] (PFAS) and Radermacher et al. [56] (cVMS).

In brief, for FR analyses samples of blue mussels and eelpout filet were extracted by accelerated solvent extraction (ASE) with dichloromethane: hexane followed by a multi-column clean-up and quantification based on API-GC-MS/MS in the case of emerging flame retardants and GC-MS/MS in the case of PBDE. The limits of quantification (LOQs) for all compounds were roughly in the range of 0.00004–0.139 µg kg⁻¹ wet weight (ww) depending on substance and matrix (Additional file 1: Table S1–S6, details also found in Neugebauer et al. [53]).

PFAS were analyzed in blue mussels and eelpout filet and liver by HPLC-MS/MS [54, 55]. Samples of blue mussels and liver tissue were extracted with methyl *tert.*-butyl ether and analyzed by HPLC-MS/MS with atmospheric pressure ionization in the negative ion electrospray mode. LOQs were set as 0.5 µg kg⁻¹ ww (Additional file 1: Table S9–S13). Eelpout filet samples were extracted using acetonitrile, *n*-hexane, and methanol and analyzed by HPLC-MS/MS. Depending on substance, the LOQs for all PFAS were in the range of 0.05–0.5 µg kg⁻¹ ww (Additional file 1: Table S9, S10, S12). PFAS concentrations given in the ESB database refer to a mixture of straight and branched isomers.

cVMS analysis in eelpout filet included extraction with ultrasonic treatment using acetonitrile/*n*-hexane and quantification by GC-ICP-MS/MS. Limits of detection (LODs) were 6.8 µg kg⁻¹ ww for D4, 3.1 µg kg⁻¹ ww for D5 and 8.3 µg kg⁻¹ ww for D6 (LOQs: D4: 20 µg kg⁻¹, D5: 9.2 µg kg⁻¹, D6: 25 µg kg⁻¹). For details refer to [56].

Data treatment

All concentrations presented in the current study refer to wet weight.

Temporal trend analysis, however, was based on lipid normalized concentrations in the case of (lipophilic) flame retardants and on dry weight-normalized concentrations in the case of (hydrophobic and lipophobic) PFAS for better comparison between years. Respective normalizations are recommended by the WFD Guidance Document No. 32 of biota monitoring [57] to enhance comparability between data. Trends were analyzed using the MS-EXCEL-based software tool “LOESS Trend (Version 1.1)” developed by J. Wellnitz (German Environment Agency). The tool fits a locally weighted scatterplot smoother (LOESS; fixed window width of seven years) through the annual contaminant data followed by tests for significance of linear and non-linear

Table 1 (continued)

		NS 1				NS 2				BS			
		BM	EP-f	EP-I	BM	BM	EP-f	EP-I	BM	BM	EP-f	EP-I	
		1988–2008	2003–2017	1994–2009	1993–2008	2003–2017	2003–2017	1993–2009+2015	1994–2008	2003–2017	1994–2008	2003–2017	1994–2008+2015
PFBA	Perfluorobutanoate	x		x	x		x		x		x		x
PFPeA	Perfluoropentanoate	x		x	x		x		x		x		x
PFHxA	Perfluorohexanoate	x	x	x	x	x	x		x	x	x		x
PFHpA	Perfluoroheptanoate	x	x	x	x	x	x		x	x	x		x
PFNA ^c	Perfluorononanoate	x	x	x	x	x	x		x	x	x		x
PFDA ^c	Perfluorodecanoate	x	x	x	x	x	x		x	x	x		x
PFUnDA ^c	Perfluoroundecanoate	x		x	x		x		x		x		x
PFDoDA ^c	Perfluorododecanoate	x	x	x	x	x	x		x	x	x		x
PFTriDA ^c	Perfluorotridecanoate	x		x	x		x		x		x		x
PFTeDA	Perfluorotetradecanoate												
PFBS	Perfluorobutane sulfonate		x				x (2015)		x (2015)		x (2015)		x (2015)
PFHXS ^c	Perfluorohexane sulfonate		x				x (2015)		x (2015)		x (2015)		x (2015)
PFHpS	Perfluoroheptane sulfonate												
PFDS	Perfluorodecane sulfonate		x				x		x		x		x
PFOSA	Perfluorooctane sulfonamide		x				x		x		x		x
PFOA ^c	Perfluorooctanoic acid		x				x		x		x		x
PFOS	Perfluorooctane sulfonic acid		x				x		x		x		x

Table 1 (continued)

Cyclic volatile methylsiloxanes	NS 1			NS 2			BS		
	BM	EP-f	EP-I	BM	EP-f	EP-I	BM	EP-f	EP-I
	2018			2018			2018		
D4 ^c		X			X			X	
Octamethylcy-clotetrasilox-ane	556-67-2								
D5 ^c		X			X			X	
Decamethylcy-clopentasilox-ane	541-02-6								
D6 ^c		X			X			X	
Dodecamethyl-cyclohexasi-loxane	540-97-6								

Italics: substances identified by ICES [8] as chemicals of emerging concern

^a Not included are 25 PFAS that were only analyzed in 1 year and were not detected in any sample (data shown in Additional file 1: Tables S11 and S13)

^b Alternative acronyms in brackets

^c Classified as SVHC under REACH

^d SVHC classification refers to the sum of syn- and antiDP (= DP, CAS-No. 13560-89-9); Sampling sites: NS 1: North Sea—Lower Saxony Wadden Sea; NS 2: North Sea—Schleswig—Holstein Wadden Sea; BS: Baltic Sea—Bodden National Park; specimens: BM: blue mussel; EP-f: eelpout filet; EP-i: eelpout liver

trend components by means of an Analysis of Variance (ANOVA) [58]. The tool has an integrated contrast test that allows to determine the difference between two time points (e.g., the first and the last years) based on the LOESS function and a *t* test, provided that the span between the time points is at least 7 years. In the present study, all data on trends (increase, decrease, significance) refer to linear trends based on lipid-, respectively dry weight-normalized concentrations (see above). The results of the contrast test (as %-change between the first and the last years) are included in the summary tables (Additional file 1: Table S14, S15).

Results and discussion

Flame retardants

Concentration ranges of FR during the entire study period are given in Additional file 1: Tables S1–S3 (dechloranes) and Additional file 1: Tables S4–S6 (aBFR + Σ 6 PBDE). The most recent concentrations are from 2015 and are illustrated in Fig. 2 and summarized in Table 2.

In 2015, Dec 602 was the only emerging FR detected in all samples. DP and Dec 603 were observed only in samples from the North Sea. In blue mussels from both North Sea sites, also low concentrations of the DP metabolite CL₁₁-antiDP were detectable (Table 2). DP, Dec 602 and Dec 603 are known to bioaccumulate and biomagnify in aquatic food webs [8, 9, 59, 60]. Our data confirm

their presence in organisms. For Dec 602 and DP, comparable concentrations have been reported for dabs from the German Bight [61].

BEH-TEBP was detected at all three sampling sites but only in one matrix at a time (i.e., in blue mussels at NS 2 and BS, and in eelpout filet at NS 1). Concentrations were in a similar range. The bioaccumulation potential for BEH-TEBP seems to be relatively low [62, 63] and there is no evidence of biomagnification [64]. Comparative data for marine biota are available only for the Arctic region, where concentrations in mussels were even lower than in the present study (no comparative data for fish filet) [13, 64].

PBT was found in all ESB samples in 2015. At present, little data on bioaccumulation or biomagnification for PBT are available [8]. Kurt-Karakus et al. [65] observed an enrichment in the freshwater food web of Lake Ontario but no trophic level-dependence of PBT accumulation.

TBP-DBPE was detected only in blue mussels from NS 2 and eelpout from BS in 2015. TBP-DBPE is assumed to be bioaccumulative [8, 65]. Concentrations are in the same range as those reported by Sühning et al. [61] for dabs from the German Bight.

DBDPE was found only in blue mussels from NS 2. It has to be noted, however, that the LOQ for DBPDE was relatively high (i.e., 0.04–0.14 $\mu\text{g kg}^{-1}$, depending on matrix and year, Additional file 1: Table S4–S6; LOQ for

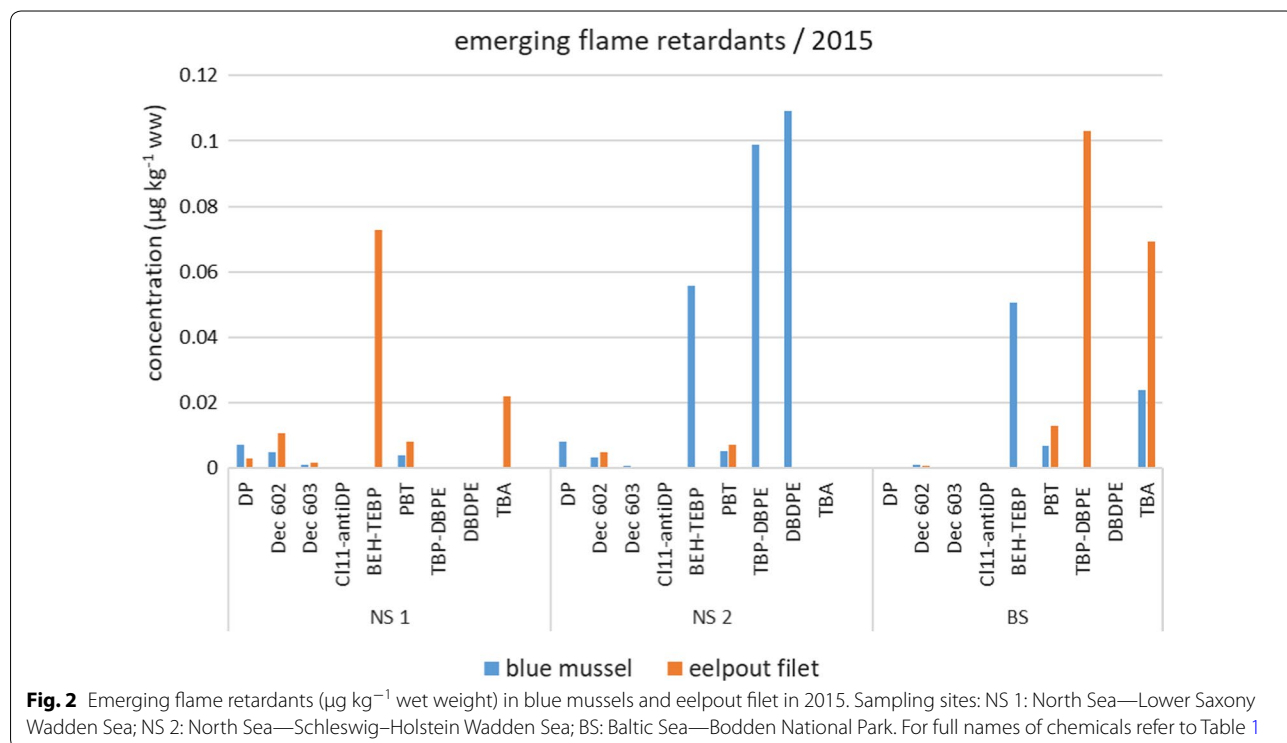


Table 2 Concentrations ($\mu\text{g kg}^{-1}$ wet weight) of flame retardants in blue mussels and eelpout filet in 2015 and long-term trends

Chemical	Blue mussel soft body					Eelpout filet		
	NS 1		NS 2	BS		NS 1	NS 2	BS
	Conc. ($\mu\text{g kg}^{-1}$)	Trend	Conc. ($\mu\text{g kg}^{-1}$)	Conc. ($\mu\text{g kg}^{-1}$)	Trend	Conc. ($\mu\text{g kg}^{-1}$)	Conc. ($\mu\text{g kg}^{-1}$)	Conc. ($\mu\text{g kg}^{-1}$)
DP	0.0073	o	0.0083	<LOQ ^a	–	0.0029	<LOQ ^a	<LOQ ^a
Dec 602	0.0048	–	0.0033	0.001	–	0.0107	0.0048	0.0009
Dec 603	0.001	–	0.0006	<0.0003		0.0018	0.0005	<0.0003
Dec 604	<0.0004		<0.0005	<0.0005		<0.0005	<0.0005	<0.0004
Cl ₁₀ -antiDP	<0.0002		<0.0002	<0.0002		<0.0002	<0.0002	<0.0002
Cl ₁₁ -antiDP	0.0001	–	0.0001	<0.0001		<0.0002	<0.0001	<0.0001
1,5-DPMA	<0.0001		<0.0002	<0.0001		<0.0002	<0.0001	<0.0002
EH-TBB	<0.0111		<0.0125	<0.0143		<0.0126	<0.0126	<0.0117
BEH-TEBP	<0.0384		0.0559	0.0506		0.0728	<0.0514	<0.0404
PBEB	<0.0003		<0.0003	<0.0003		<0.0003	<0.0003	<0.0003
PBT	0.004	+	0.0053	0.0067	o	0.0081	0.0072	0.013
TBP-AE	<0.0043		<0.0049	<0.0056		<0.0049	<0.0049	<0.0046
BATE	<0.0014		<0.0016	<0.0018		<0.0016	<0.0016	<0.0015
TBP-DBPE	<0.0269	–	0.0989	<0.0345	–	<0.0306	<0.0306	0.103
BTBPE	<0.0083		<0.0093	<0.0106		<0.0094	<0.0094	<0.0087
DBDPE	<0.0751		0.109	<0.0964		<0.0854	<0.0855	<0.0789
HBBz	<0.0008		<0.0009	<0.0011	o	<0.0009	<0.001	<0.001
TBA	<0.0142	o	<0.016	0.0239	o	0.0219	<0.0161	0.0694
∑ 6 PBDE	0.0208	–	0.363	0.0455	o	0.0762	0.0288	0.0371

Sampling sites: NS 1: North Sea—Lower Saxony Wadden Sea; NS 2: North Sea—Schleswig–Holstein Wadden Sea; BS: Baltic Sea—Bodden National Park

Italics: quantified substances; DP: sum of syn-DP and antiDP

Trends: o: no significant linear trend; +: increase; –: decrease; blank: insufficient data, no trend calculation possible. Time intervals for trend calculations: blue mussels: NS 1: 1985–2015 BS: 1992–2015. For NS 2 and for eelpout filet, data were only available for 2015. Trend calculation based on lipid normalized concentrations. For full names of chemicals refer to Table 1

^a LOQ for syn-DP: 0.002–0.0026 $\mu\text{g kg}^{-1}$, LOQ for antiDP: 0.00225–0.0029 $\mu\text{g kg}^{-1}$, depending on matrix (Additional file 1: Table S1–S6)

2015 in Table 2 or 0.085 $\mu\text{g kg}^{-1}$ for mussels from NS 2). DBDPE bioaccumulates and biomagnifies in aquatic ecosystems [8, 66]. The fact that DBDPE was detected only in blue mussels but not in eelpouts might reflect different exposures at the NS 2 sampling sites for blue mussels and eelpouts (Fig. 1).

TBA seems to be more relevant in the Baltic Sea. In 2015, it was detected in blue mussels and eelpout from BS with comparatively high concentrations in eelpout filet. By contrast, levels were <LOQ in blue mussels from both North Sea sites and in eelpout from NS 2; concentrations in eelpout from NS 1 were quite low. TBA has been frequently detected in marine invertebrates, fish and mammals [46, 48–50, 61].

Dec 604, Cl₁₀-antiDP, 1,5-DPMA, EH-TBB, PBEB, TBP-AE, BATE, BTBPE and HBBz were not quantified in any sample in 2015.

For comparison purposes, the concentrations of the WFD-relevant PBDE congeners BDE-28, -47, -99, -100, -153 and -154 (∑ 6 PBDE) were included in the

study. Concentrations of ∑ 6 PBDE in 2015 are shown in Table 2; the congener data are summarized in Additional file 1: Table S7.

Concentrations of ∑ 6 PBDE were mostly higher than those of emerging flame retardants. The only exceptions are BEH-TEHP, TBP-DBPE and TBA. For BEH-TEHP, concentrations in blue mussels from BS and in eelpout from NS 1 were similar to those of ∑ 6 PBDE. Levels of TBP-DBPE were higher than ∑ 6 PBDE concentrations in eelpout filet from NS 2. Concentrations similar to those of ∑ 6 PBDE were also observed for TBA in samples from BS.

In eelpout filet, some of the emerging FR were within the same concentration range as single BDE congeners (Additional file 1: Table S8): at the North Sea site NS 1, BEH-TEBP concentrations in eelpout filet were slightly higher than those of BDE-47, while Dec 602 was in the same range as BDE-99, -100 and -154. In eelpout from

NS 2, levels of PBT and BDE-154 as well as of Dec 602 and BDE-153 are within the same range.

The results demonstrate that some of the emerging flame retardants identified by ICES [8] (i.e., Dec 602, BEH-TEHP, TBP-DBPE, PBT, TBA) are present in marine biota from German coastal sites at concentrations that are similar to those of legacy PBDE.

Similar findings have been reported for freshwater fish from differently contaminated rivers in Spain, where Dec 602 levels were comparable to those of BDE-100 or BDE-47 or even to the sum PBDE congeners in whole fish [67]. Pena-Abaurrea et al. [50] found levels of TBA in muscle tissue of tuna from the Mediterranean Sea that were in the same range as BDE-154.

The data reflect the growing production and use of alternative FR in the past years that was triggered by the increasing regulation of the legacy FR [9, 18].

Looking at the long-term data, decreasing temporal trends ($p \leq 0.01$) are observed for Dec 602, Dec 603, Cl₁₁-antiDP and TBP-DBPE in blue mussels from NS 1, and for DP, Dec 602 and TBP-DBPE in blue mussels from BS (Table 2, Additional file 1: Table S14). None of these flame retardants are restricted in the EU to date. It can only be speculated that voluntary phase-outs and/or shifts to other less problematic FR are responsible for the observed decreases.

Increases over time ($p < 0.01$) were only observed for PBT in blue mussels from NS 1.

Concentrations of $\sum 6$ PBDE decreased more or less steadily in blue mussels and eelpout filet from NS 1 and in eelpout filets from NS 2 and BS (all $p < 0.01$). The blue mussel data show that $\sum 6$ PBDE already decreased before the commercial Penta- and Octa-BDE mixtures were regulated in the EU in 2004 [16] (no corresponding statement can be made for eelpouts, as the time series only begin in 2003). This possibly reflects the voluntary phase-out of commercial Penta-BDE by industrial users in Germany already in 1986 [68].

Per- and polyfluoroalkyl substances

The available data for PFAS are summarized in Additional file 1: Tables S9–S13. Figure 3 shows the concentrations of emerging PFAS in eelpout filet and liver in 2015. Table 3 summarizes the 2015 data and includes also PFOA and PFOS and the results of the trend analysis.

In 2015, concentrations in eelpout livers were mostly < LOQ ($0.3 \mu\text{g kg}^{-1}$) (Table 3). However, relatively high concentrations were observed for PFNA, PFDA and PFUnDA in liver samples from BS and for PFOSA in samples from NS 2 (Fig. 3). The liver concentrations were considerably higher than in the corresponding filet samples, which is attributable to the preferential binding of PFAS to serum proteins [25].

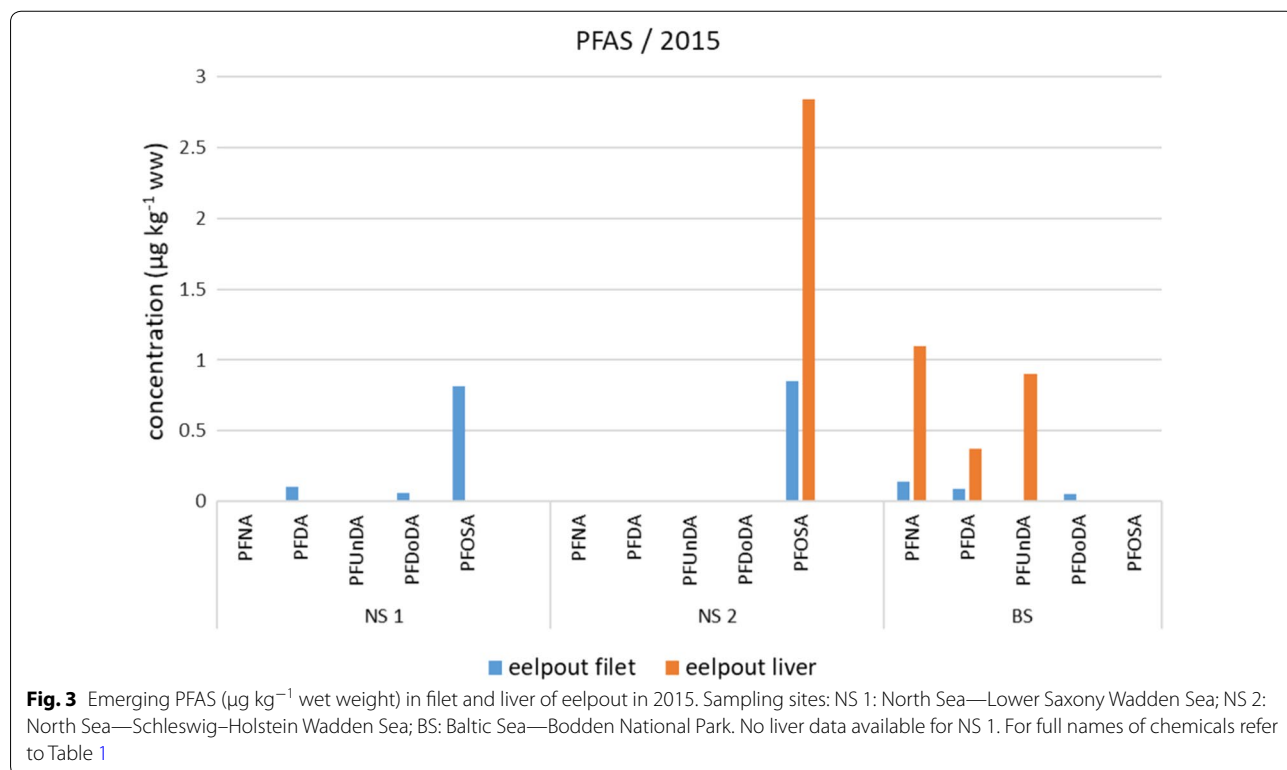


Fig. 3 Emerging PFAS ($\mu\text{g kg}^{-1}$ wet weight) in filet and liver of eelpout in 2015. Sampling sites: NS 1: North Sea—Lower Saxony Wadden Sea; NS 2: North Sea—Schleswig–Holstein Wadden Sea; BS: Baltic Sea—Bodden National Park. No liver data available for NS 1. For full names of chemicals refer to Table 1

Table 3 Concentrations ($\mu\text{g kg}^{-1}$ wet weight) of PFAS in eelpout in 2015 and long-term trends

Chemical	Eelpout filet						Eelpout liver	
	NS 1		NS 2		BS		NS 2	BS
	Conc. ($\mu\text{g kg}^{-1}$)	Trend	Conc. ($\mu\text{g kg}^{-1}$)	Trend	Conc. ($\mu\text{g kg}^{-1}$)	Trend	Conc. ($\mu\text{g kg}^{-1}$)	Conc. ($\mu\text{g kg}^{-1}$)
PFBA							<0.300	<0.300
PFPeA							<0.300	<0.300
PFHxA	<0.053		<0.058		<0.050		<0.300	<0.300
PFHpA	<0.053		<0.057		<0.050		<0.300	<0.300
PFNA	<0.053		<0.057		0.137	+	<0.300	1.1
PFDA	0.103	+	<0.057	o	0.089	+	<0.300	0.37
PFUnDA							<0.300	0.90
PFDoDA	0.056		<0.057		0.05	+	<0.300	<0.300
PFTriDA							<0.300	<0.300
PFTeDA							<0.300	<0.300
PFBS	<0.080		<0.085		<0.075		<0.300	<0.300
PFHxS	<0.080		<0.085		<0.075		<0.300	<0.300
PFHpS							<0.300	<0.300
PFDS	<0.080		<0.085		<0.075		<0.300	<0.300
PFOSA	0.814	-	0.853	-	<0.050		2.84	<0.300
PFOA	<0.053		<0.057		<0.050		<0.300	<0.300
PFOS	0.921	o	0.202	-	0.487	o	3.7	9.1

Sampling sites: NS 1: North Sea—Lower Saxony Wadden Sea; NS 2: North Sea—Schleswig—Holstein Wadden Sea; BS: Baltic Sea—Bodden National Park (Baltic Sea)
 Italics: quantified substances; blank: no data

Trends: o: no significant linear trend, +: increase, -: decrease; blank: insufficient data, no trend calculation possible. Time intervals for trend calculations: eelpout filet: 2003–2017; eelpout liver: NS 2: 1993–2009, BS: 1994–2008. For full names of chemicals refer to Table 1

The filet data at NS 2 and BS mirror the respective liver data. The only exceptions were PFUnDA and PFDoDA in fish from BS. For PFUnDA, no 2015 data in eelpout filet from BS are available. In the case of PFDoDA, however, the lower sensitivity of the analytical method applied to liver tissue may have led to the observed discrepancy (see Additional file 1: section ‘Chemical analysis’ and Tables S9–S13).

PFAS with carbon chain lengths < 8 carbon atoms were not detected in any sample. This reflects the lower bioaccumulation potential of short-chain PFAS compared to PFAS with long carbon chains [69, 70].

The legacy compound PFOS—included here as benchmark—was still detected in all samples in 2015 in mostly highest concentrations (Table 3). It dominated clearly in eelpout filet and liver from BS. At the North Sea sites, however, PFOS levels were in the same range as PFOSA in both eelpout filet and liver. By contrast, the concentration of the legacy compound PFOA in all samples was below the respective LOQ of 0.05–0.30 $\mu\text{g kg}^{-1}$.

Long-term data show significant decreasing trends for PFOSA in eelpout filet at both North Sea sites (both $p < 0.01$) and for PFOS in eelpout filet from NS 2 ($p = 0.01$). No respective trends were observed at the other sites (Table 3, Additional file 1: Table S15).

Increasing trends were detected for PFDA in eelpout filet at NS 1 and BS (both $p < 0.01$) and for PFNA ($p = 0.01$) and PFDoDA ($p = 0.02$) at BS (Table 3, Additional file 1: Table S15). At BS, the trends for PFNA and PFDA were not steady (Additional file 1: Fig. S1). The highest concentrations were detected around 2013. Whether the lower PFNA and PFDA concentrations toward the end of the study period actually indicate a decrease in exposure cannot be answered conclusively by the data. However, they may be related to the US EPA PFOA Stewardship Program that aimed at the global phasing out of PFOA, its precursors and related higher homolog chemicals by 2015 [22, 71].

Comparative published data for PFAS in liver samples from marine fish are available, e.g., for cod sampled in 2008 and 2009 at 15 sites around Norway [72]: PFOS was frequently detected in cod livers (in 144 of 200 samples), whereas PFHxS, PFOSA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA and PFTriDA were present in individual liver samples only. PFPeA, PFBA, PFHxA, PFHpA, PFTeDA, PFBS and PFDS were not detected at all. Reported concentrations were always higher than those detected at the ESB sites in the respective years. Danielsson et al. [73] report PFAS concentrations in livers of eelpout, herring and perch from differently polluted sites along

the Swedish coast in 2011. PFOS and PFDA concentrations in eelpout livers were slightly higher compared to the samples from the ESB site BS in the same year. For herring livers, decreasing trends since 2007/2008 were observed for PFOS, PFOSA, PFDA, PFUnDA and PFDoDA at many sites along the Swedish coast [74].

PFAS concentrations in eelpout filet from the Swedish coast were mostly in the same range as our data from BS [73, 75]. PFOS dominated in all samples. Concentrations of PFOA, PFNA and PFDA in Swedish eelpout samples were slightly lower than in eelpout samples from BS in the same year. As in eelpout filet from BS, PFHxA, PFHpA, PFBS, PFHxS and PFDS were not detected in any sample from Sweden. Similarly, PFBA and PFBS were not detected in perch and herring from Finnish coastal waters sampled between 2014 and 2016 [76].

Methylsiloxanes

The cVMS D4, D5 and D6 were not detected in any eelpout filet sample from 2018 (all < LOD, i.e., D4 < 6.8 µg kg⁻¹, D5 < 3.1 µg kg⁻¹ and D6 < 8.3 µg kg⁻¹).

Comparative wet weight concentrations of siloxanes in marine fish are, for instance, available from coastal waters of Norway and from the Baltic Sea. In whole fish samples of eelpout from the inner Oslo Fjord, Powell et al. [77] detected concentrations in the range of < 3.7–2.3 µg kg⁻¹ (D4), 14.4–72.8 µg kg⁻¹ (D5) and < 4.7–6.67 µg kg⁻¹ (D6). Filet concentrations are available for herring from the Baltic Sea (D4: < 4.4–0.5 µg kg⁻¹; D5: 10–21 µg kg⁻¹; D6: 2–5.4 µg kg⁻¹) [78]. The reported concentrations were partly lower than the LODs achieved here.

Comparison between the North Sea and the Baltic Sea sites

To determine whether there are fundamental differences in the type of contamination between the German coastal sites in the North Sea and the Baltic Sea, data of the sites NS 1 and NS 2 were compared to those of BS.

For FR, the most striking difference was the higher contribution of ∑ 6 PBDE to the total FR burdens of blue mussels and eelpout filets at the North Sea sites (Table 2). In 2015, the share of ∑ 6 PBDE in blue mussels was 55% at NS 1 and 56% at NS 2 compared to 36% at BS. In eelpout filet, the respective fractions were 39% at NS 1 and 70% at NS 2 compared to only 17% at BS.

These findings indicate that legacy PBDE still play a major role in the contamination of coastal sites in the North Sea, whereas this is less evident at the Baltic Sea site.

Clear concentration differences (factors of about 2–12) between the sampling sites in the North and the Baltic Seas were observed for DP, Dec 602 and Dec 603, all of which were higher in biota samples from the North Sea sites. Levels of PBT and TBA were higher in

blue mussels and eelpout filet from BS (factors of about 1.5–4) than in samples from the North Sea (Fig. 2, Table 2). For all other substances, differences between the North Sea sites and the Baltic Sea site were not consistent. There are, however, also differences between both North Sea sites indicating that the exposure differs also between the Lower Saxony Wadden Sea (NS 1) and the Schleswig–Holstein Wadden Sea (NS 2). In 2015, FR contamination of eelpout filet was higher at NS 1 compared to NS 2, whereas blue mussel contamination was higher at NS 2 (Fig. 2, Table 2). DBDPE and TBP-DBPE were detected only in samples from NS 2.

Patterns of emerging FR in 2015 are illustrated in Fig. 4. The concentrations of some FR especially in blue mussels were quite low and near the respective LOQ. They were nevertheless included in Fig. 4 to acknowledge their presence at the respective sampling site.

Particularly noticeable is the dominance of BEH-TEBP in blue mussels from BS and the high share of TBA, both of which are not reflected in mussels from the North Sea sites. In eelpout filet, the share of TBP-DBPE and TBA was higher at BS than at the North Sea sites, whereas the share of Dec 602 was lower.

When comparing the long-term trends of FR contamination at the different sampling sites, similar

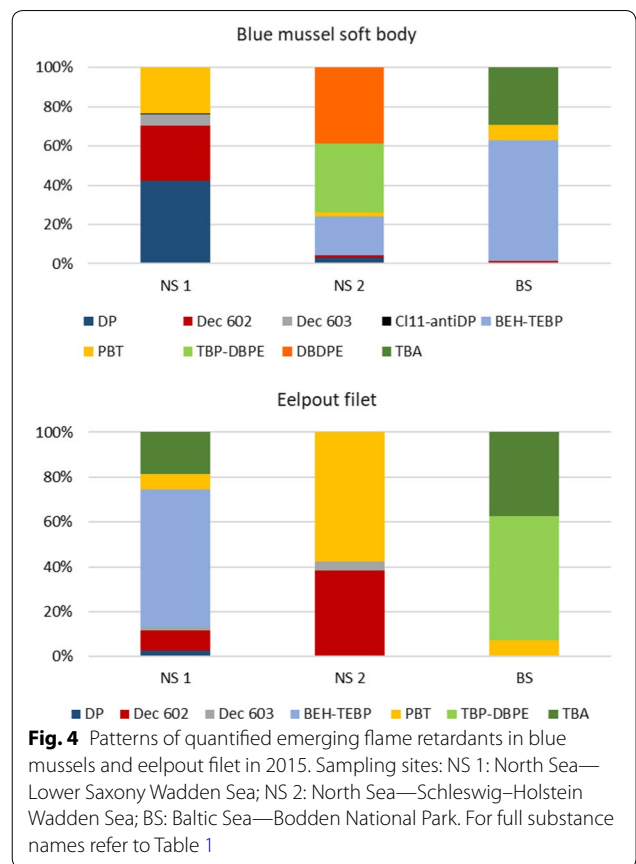


Fig. 4 Patterns of quantified emerging flame retardants in blue mussels and eelpout filet in 2015. Sampling sites: NS 1: North Sea—Lower Saxony Wadden Sea; NS 2: North Sea—Schleswig–Holstein Wadden Sea; BS: Baltic Sea—Bodden National Park. For full substance names refer to Table 1

(decreasing) trends can be observed for Dec 602 and TBP-DBPE in blue mussels from NS 1 and BS. Concentrations of Σ 6 PBDE decreased in eelpout filet from all three sites (Table 2, Additional file 1: Table S14).

Differences in long-term trends between the sites were observed for PBT (increase in blue mussels from NS 1 but no significant trends at BS), Dec 603 and CL₁₁-antiDP (both decreased in blue mussels from NS 1 but not at BS) and for DP (decrease at BS but no significant trend at NS 1).

Regarding PFAS, high concentrations of the legacy compound PFOS were still detected in both North Sea and Baltic Sea biota samples. In 2015, eelpout samples from BS were dominated by PFOS with shares of 64% in eelpout filet and 79% in eelpout liver. The respective fractions were smaller in eelpout samples from the North Sea sites (i.e., in eelpout filet 49% (NS 1) and 19% (NS 2), and in eelpout liver 57% (NS 2; no data for NS 1)).

A striking difference between eelpout samples from the North and the Baltic Sea sites is the higher share of PFOSA at the North Sea sites in 2015 (Fig. 5). By contrast, in eelpout from BS comparatively higher shares of PFNA, PFDA and PFUnDA (analyzed only in liver) were detected.

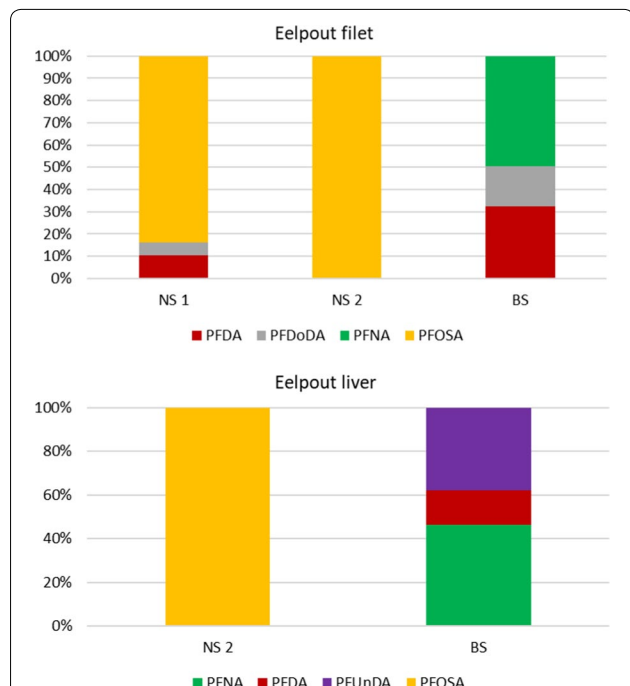


Fig. 5 Patterns of quantified emerging per- and polyfluoroalkyl substances in eelpout filet and liver in 2015. Sampling sites: NS 1: North Sea—Lower Saxony Wadden Sea; NS 2: North Sea—Schleswig-Holstein Wadden Sea; BS: Baltic Sea—Bodden National Park. For full substance names refer to Table 1

The concentrations of some PFAS detected in 2015 were quite low and close to the respective LOQ. They were nonetheless included in Fig. 5 to indicate their presence at the respective site.

Comparing the long-term trends of PFAS (Table 3, Additional file 1: Table S15) reveals that at both North Sea sites levels of PFOSA decreased in eelpout filet during the study periods, whereas no respective trends were observed at BS. On the other hand, an increasing trend for PFNA and PFDoDA could only be observed at the sampling site BS. PFDA increased significantly in eelpout filet from NS 1 and BS.

Summary and conclusions

The aim of the study was to provide data from the coastal sampling sites of the ESB for chemicals that may be of emerging concern for the marine environment. For reference purposes, also data of legacy compounds were included in the data analysis. The assessment of the potential hazards posed by the substances examined here is based on the concentrations and temporal trends of these chemicals in biota samples only. Relatively high concentrations that go hand in hand with increasing temporal trends are assumed to be particularly problematic.

Our data show that, despite being restricted worldwide since 2009 [79], the legacy compounds Σ 6 PBDE and PFOS still dominate in the majority of the samples. In 2015, it was only in blue mussels and eelpout filet from the Baltic Sea site and in eelpout filet from the North Sea site NS 1 that concentrations of some emerging flame retardants were within the same range or even higher than Σ 6 PBDE (i.e., BEH-TEBP in blue mussels and TBP-DBPE in eelpout filet from BS, and BEH-TEBP in eelpout filet from NS 1). For PFAS, only PFOSA was detected in concentration ranges comparable to those of PFOS in recent years (i.e., in eelpout filet from both North Sea sites).

Comparatively high concentrations in biota combined with increasing temporal trends were hardly observed. None of the emerging FR met these criteria. In 2015, concentrations of BEH-TEBP, TBP-DBPE and DBDPE were comparatively high but for none of these compounds, increasing trends over time were observed. By contrast, PBT concentrations increased at NS 1 but levels in 2015 were low.

However, even though concentrations were relatively low in 2015, DP may be of concern because of its classification as SVHC under the REACH regulation [14]. Furthermore, Dec 602 may be of relevance because it was present in all analyzed samples.

In the case of PFAS, relatively high concentrations combined with increasing trends were detected for

PFNA, PFDA and PFDoDA at the Baltic Sea site BS. Levels of PUnDA were quite high in eelpout livers in 2015 and indicate an increase over time (no trend analysis possible because of insufficient data; no 2015-data for PUnDA in file). PFDA and PFDoDA were also detected in eelpout file from NS 1 along with an increasing trend for PFDA.

Since PFNA, PFDA, PUnDA and PFDoDA are classified as SVHC under the REACH regulation [14], these chemicals may be of emerging concern at all investigated sites.

The cVMS D4, D5 and D6 seem to play only a minor role at the ESB sampling sites. Currently, the database for these substances in marine ESB samples is limited.

In summary, our results indicate that at least the emerging flame retardants DP and Dec 602 and the long-chain perfluoroalkyl substances PFNA, PFDA, PUnDA, and PFDoDA should be further considered for monitoring in the North and the Baltic Sea, e.g., when establishing lists of relevant contaminants through regional or subregional cooperation.

Supplementary information

Supplementary information accompanies this paper at <https://doi.org/10.1186/s12302-020-00312-x>.

Additional file 1. Details of chemical analysis and supplemental results.

Abbreviations

aBFR: Alternative brominated flame retardants; ASE: Accelerated solvent extraction; antiDP: Dechlorane Plus, anti-isomer; API-GC-MS/MS: Atmospheric pressure interface coupled to gas chromatography and tandem mass spectrometry; BATE: 2-Bromoallyl 2,4,6-tribromophenyl ether; BEH-TEBP: Bis(2-ethylhexyl)-tetrabromophthalate, also known as BEHTBP; BS: Baltic Sea; ESB sampling site in the Bodden National Park of Western Pomerania; BTBPE: 1,2-Bis(2,4,6-tribromophenoxy)ethane; CEC: Chemicals of emerging concern; Cl₁₀-antiDP: Decachloropentacyclooctadecadiene; Cl₁₁-antiDP: Undecachloropentacyclooctadecadiene; cVMS: Cyclic volatile methylsiloxanes; DBDPE: Decabromodiphenyl ethane; Dec: Dechlorane; DP: Dechlorane Plus; D4: Octamethylcyclotetrasiloxane; D5: Decamethylcyclopentasiloxane; D6: Dodecamethylcyclohexasiloxane; DPMA: 1,5-Dechlorane Plus mono-adduct, also known as 1,5-DPMA; EH-TBB: 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate, also known as EHTeBB; ESB: Environmental Specimen Bank; EU: European Union; FAO: Food and Agriculture Organization of the United Nations; FR: Flame retardant; HASEC: Hazardous Substances and Eutrophication Committee; HBBz: 1,2,3,4,5,6-Hexabromobenzene; HBCDD: Hexabromocyclododecane; HELCOM: Baltic Marine Environment Protection Commission; HPLC-MS-MS: High-performance liquid chromatography coupled to tandem mass spectrometry; ICES: International Council for the Exploration of the Sea; LOD: Limit of detection; LOESS: Locally weighted scatterplot smoother/trend tool; LOQ: Limit of quantification; MSFD: Marine Strategy Framework Directive; NS 1: North Sea 1: ESB sampling site in the Lower Saxony Wadden Sea; NS 2: North Sea 2: ESB sampling site in the Schleswig-Holstein Wadden Sea; OPFR: Organo-phosphorous flame retardants; OSPAR: Convention for the Protection of the Marine Environment of the North-East Atlantic; PBDE: Polybrominated diphenyl ethers, here: sum of BDE-28, -47, -99, -100, -153 and -154; PBEB: 2,3,4,5,6-Pentabromoethylbenzene; PBT: 2,3,4,5,6-Pentabromotoluene; PFAS: Per- and polyfluoroalkyl substances; PFBA: Perfluorobutanoate; PFPeA: Perfluoropentanoate; PFHxA: Perfluorohexanoate; PFHpA: Perfluoroheptanoate; PFNA: Perfluorononanoate; PFDA: Perfluorodecanoate; PUnDA:

Perfluoroundecanoate; PFDoDA: Perfluorododecanoate; PFTeDA: Perfluorotetradecanoate; PFTrDA: Perfluorotridecanoate; PFBS: Perfluorobutane sulfonate; PFHxS: Perfluorohexane sulfonate; PFDS: Perfluorodecane sulfonate; PFOSA: Perfluorooctane sulfonamide; PFOA: Perfluorooctanoic acid; PFOS: Perfluorooctane sulfonic acid; REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals (EU Regulation); SOP: Standard Operating Procedures; SVHC: Substance of very high concern; Syn-DP: Dechlorane Plus, syn-isomer; TBA: 2,4,6-Tribromoanisole; TBP-AE: 2,4,6-Tribromophenyl allyl ether, also known as ATE; TBP-DBPE: 2,4,6-Tribromophenyl-2,3-dibromopropyl ether, also known as DBPE; WDF: Water Framework Directive; ww: Wet weight.

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Authors' contributions

AF and HR are responsible for the data compilation, interpretation of the data and drafting of the manuscript. AD provided the data of emerging flame retardants and was significantly involved in revising the manuscript. JK and UP initiated the contribution, provided relevant background information and were involved in revising the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

Data are original data from the German Environmental Specimen Bank or are from the references given. The data on dechloranes, PBDE and PFAS are freely available on the website of the ESB (<http://www.umweltprobenbank.de/en>). Recent data of aBFR are given in Dreyer et al. (2019) Recent findings of halogenated flame retardants (HFR) in the German and Polar environment. *Environ Pollut* 253:850–863

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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