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Temporal trends of PBDD/Fs, PCDD/Fs, PBDEs and PCBs in ringed seals from the Baltic Sea (*Pusa hispida botnica*) between 1974 and 2015

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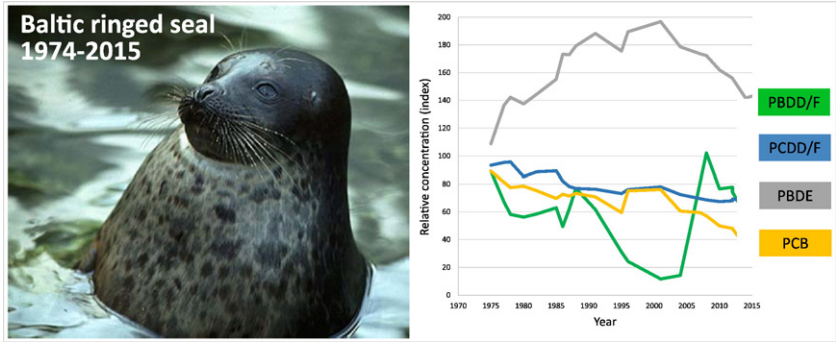
HIGHLIGHTS

- PBDD/Fs and other POPs were analysed in Baltic ringed seals during 1974–2015.
- HpBDF was the dominant PBDD/F congener, PBDD/F TEQ was 1% compared to total TEQ.
- PBDD/Fs showed no decreasing trend during 1974–2015.
- PBDEs showed increasing trend until end of 1990s, thereafter decreasing trends.
- PCDD/Fs and PCBs showed decreasing trends throughout the whole period.

GRAPHICAL ABSTRACT



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ABSTRACT

Temporal trends in exposure to persistent organic pollutants (POPs) were assessed in 22 pooled samples gathered from 69 individuals of Baltic ringed seal (*Pusa hispida botnica*) from 1974 to 2015. Samples were analysed for polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs). No previous study has reported on the occurrence of PBDD/Fs in marine mammals in the Baltic Sea. Concentrations of pollutants in Baltic ringed seal, a marine mammal and top predator, can be used as an indicator of pollutants concentrations in the Baltic region.

Visual inspection of data did not show any temporal trends for PBDD/Fs, while the PCDD/Fs and PCBs showed decreasing concentrations between 1974 and 2015. PBDEs increased until the end of the 1990s and then decreased until the end of the period. ∑PBDD/Fs ranged from 0.5–52.3 pg/g lipid weight (l.w.) (0.08–4.8 pg TEQ/g l.w.), with 1,2,3,4,6,7,8-HpBDF contributing on average 61% to ∑PBDD/Fs. ∑PCDD/Fs ranged from 103 to 1480 pg/g l.w. (39–784 pg TEQ/g l.w.), with 1,2,3,6,7,8-HxCDD, 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF showing the highest average concentrations. PBDD/F toxic equivalents (TEQ) contributed on average 1.1% to the total (PBDD/F + PCDD/F) TEQ. The ∑PBDEs concentration range was 18.7–503 ng/g l.w., with BDE #47 the predominant congener. The concentration range for ∑PCBs was 2.8–40.1 μg/g l.w., with #138 and #153 the most abundant congeners. Visual inspection of the data showed decreasing concentrations for all compound groups except PBDD/Fs. A slight increase in the PBDD/Fs concentrations was observed from 2004 onwards. This observation needs to be investigated further.

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1. Introduction

The Baltic Sea is considered to be the world's most contaminated brackish water area (Koistinen et al., 2008). The Baltic Sea has a large catchment area comprising a population of close to 100 million people and a multitude of pollutant sources, e.g. agricultural run-offs and industries (HELCOM, 2010). Pollutants that originate from anthropogenic sources enter the Baltic Sea through rivers, direct transfer from land or atmospheric transportation (Falandysz et al., 2000; Nfon and Cousins, 2006; Strandberg et al., 1998). Because the Baltic Sea is largely landlocked, water exchange between the North Sea and Atlantic is hampered, resulting in a residence time for water of approximately 25 to 35 years (Glasby and Szefer, 1998; Witt, 2002). These special conditions make the Baltic Sea vulnerable to anthropogenic input (Szlinder-Richert et al., 2009). As a result of the geographical and hydrological characteristics, concentrations of POPs in the Baltic Sea are in general higher compared to other marine areas (HELCOM, 2010).

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) are considered pollutants of concern (HELCOM, 2010). Owing to their toxic potential, PCDD/Fs have caused concerns regarding human and environmental health in the Baltic Sea region for many years (HELCOM, 2004). PCDD/Fs are unintentionally produced substances. Typical sources of emissions are metallurgical industries, pulp- and paper mills, combustion and mass production of numerous commercial chlorinated substances (Bergek et al., 1992). Chlorinated dioxins are considered one of the most toxic unintentional man-made substances (Birnbaum, 1994) and can cause several serious consequences, such as thymic atrophy, teratogenesis and reproductive effects (Birnbaum et al., 2003).

The chlorine atoms in the chlorinated dioxins and furans can also be substituted by bromine atoms to generate polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) (WHO, 1998). Brominated dioxins and furans show similar physiochemical and toxic properties to their chlorinated correspondents, i.e. PCDD/Fs (van den Berg et al., 2013; WHO, 1998). Compared to PCDD/Fs, the brominated dioxins and furans show lower resistance to photolytic reactions and consequently are less persistent in soil, sediment and biota (Buser, 1988). However, PBDD/Fs seems to be more persistent towards mammalian metabolism compared to PCDD/Fs (Birnbaum et al., 2003). Knowledge about how PBDD/Fs act in the food chain is so far limited, but owing to their similarities to PCDD/Fs, it is reasonable to assume that PBDD/Fs biomagnify in the food chain (Kannan et al., 2012). There are studies reporting findings of PBDD/Fs in different matrices, e.g. indoor dust, ambient air, flue gases, plastics, food samples, human milk, adipose tissue and blood from people with occupational exposure (Kannan et al., 2012). PBDD/Fs have also been found in the marine environment, including in pilot whales, fish, fish products and shellfish (Bjurlid et al., 2017; Fernandes et al., 2009; Kannan et al., 2012). To the best of our knowledge, no previous study of PBDD/Fs in ringed seal (*Pusa hispida botnica*) or any other marine mammal in the Baltic Sea has been carried out.

PBDD/Fs are usually unintentionally produced, and the major sources are polybrominated diphenyl ethers (PBDEs) or other brominated flame retardants (BFRs) (Ebert and Bahadir, 2003; Kannan et al., 2012). The most common formation of PBDD/Fs takes place during combustion of BFR-treated plastics, but it can also be formed in other ways, such as by photolysis of BFRs, production of BFRs and industrial processes (Ebert and Bahadir, 2003; Kannan et al., 2012). Atmospheric transport is the major transport pathway for PBDD/Fs (Kannan et al., 2012). Since PBDD/Fs have higher molecular weight and lower vapour pressure compared to analogous PCDD/Fs, they are probably less suitable for atmospheric transport than PCDD/Fs (Kannan et al., 2012). Studies in the Baltic Sea have indicated that some PBDD/F congeners have natural origin, and these congers are usually lower brominated PBDDs (mono-tetra) (Haglund et al., 2010; Malmvärn et al., 2008). In contrast, during combustion or other anthropogenically related processes, the PBDD/Fs formed are mostly furans and highly (tetra- to hepta-) substituted congeners (Arnoldsson, 2012).

In addition to being a major source for PBDD/Fs, PBDEs have their own issues. PBDEs are classified as POPs because they are toxic, persistent and can bioaccumulate and biomagnify (Burreau et al., 2006; Strandberg et al., 2001; Wania and Dugani, 2003; Wu et al., 2007). PBDEs may be emitted to the environment during the production, usage and disposal of PBDE-treated products (Shaw and Kannan, 2009). Several health disorders and abnormalities related to PBDEs have been shown in studies involving humans and animals (Darnerud, 2003; Domingo, 2012). Over the years, different PBDE mixtures have been used, e.g. penta-BDE (mostly tetra- (BDE #47), penta- (BDE #99, #100) and hexa- (BDE #153, #154) brominated congeners), octa-BDE (mainly hepta- (BDE #183) and some octa-brominated congeners) and deca-BDE (mostly the fully brominated BDE #209) (Darnerud et al., 2001; La Guardia et al., 2006). However, owing to their negative impact on human health and the environment, the penta-BDE and octa-BDE mixtures were banned or phased out from 2004 onwards (La Guardia et al., 2006; Ni et al., 2013), and several PBDEs are listed under the Stockholm Convention (Secretariat of the Stockholm Convention, 2009). PBDEs have been reported in the Baltic Sea in sediment and biological samples (HELCOM, 2010).

The concentration of POPs in aquatic ecosystems increases along the food chain and can reach high concentrations in a top predator such as seals (Nyman et al., 2002). However, the accumulation of POPs differs depending on the metabolism in different organisms and animals (Nyman et al., 2002). In general, marine mammals show high concentrations of lipophilic POPs not only due to their position in the food chain and lipid rich diet but also because of their late reproduction and long life (Hoydal et al., 2015; Kajiwara et al., 2006). In marine mammals, more than 90% of the total body load of lipophilic contaminants can be found in the blubber (Yordy et al., 2010).

The ringed seal (*Pusa hispida*) has shown dramatic population changes during the 1900s in the Baltic. At the beginning of the 1900s, there were approximately 200,000–300,000 ringed seals in the Baltic. However, the population declined dramatically such that by the 1980s, there were only around 5000 ringed seals remaining (Harding and Härkönen, 1999).

Initially, intensive hunting was the main cause for the decline in seal in seal population, but later on the population was affected by sterility, possibly caused by uterine occlusions associated to environmental contaminants, that further reduced the population (Harding and Härkönen, 1999; Helle et al., 1976). In particular, seals were seriously affected by high levels of polychlorinated biphenyls (PCBs) and pesticides in their food (Jensen et al., 1969). Ringed seals became protected in 1974 but it took about 15 years for the population to start to recover, and in 2013, the population was estimated to be approximately 10,000 (HELCOM, 2013).

The aim of this study was to investigate the occurrence of primarily PBDD/Fs but also PCDD/Fs, PBDEs and PCBs in Baltic ringed seal caught in the Swedish waters of the Baltic Sea from 1974 to 2015 in order to assess possible time trends. Concentrations of PBDD/Fs, PCDD/Fs and PBDEs were compared to investigate potential correlations. In addition to temporal trends, pollutant profiles were studied.

2. Materials and methods

2.1. Sampling and sample preparation

Ringed seals were collected from the Swedish waters of the Baltic Sea during the period 1974–2015. In total, 69 juvenile seals that were considered to be in good health were included in the study (see Table 1). The seals were collected from April to December. Ringed seals give birth around 1st of April in the Baltic Sea, and after 6 weeks they are weaned. They fast a shorter period before they start eating fish. One year old and older seals fast a short period during molting in the beginning of the summer. There were 43 females and 26 males in the sample set. The majority of the ringed seals in the study originated from the Bothnian Sea

Table 1
Sampling year, sampling area, number of seals per pool and weight of ringed seals included in the study.

Sampling year/sample ID	Seals/pool	Weight range (kg)	Sampling area
1974	2	23–28	Bothnian Sea, Bothnian Bay
1975	1	26	Bothnian Bay
1977	3	20–45	Bothnian Sea, Bothnian Bay
1978	2	25–48	Bothnian Bay, Sea of Åland
1980	1	35	Bothnian Bay
1982	1	20	Bothnian Bay
1985	4	36–45	Bothnian Sea, Bothnian Bay
1986	5	30–46	Bothnian Sea, Bothnian Bay, Sea of Åland
1987	4	32–48	Bothnian Sea, Bothnian Bay, Baltic Sea
1988	4	34–46	Bothnian Sea, Sea of Åland, Baltic Sea
1991	1	41	Baltic Sea
1995	2	29–34	Bothnian Bay, Baltic Sea
1996	1	31	Bothnian Bay
2001	5	26–35	Bothnian Sea, Bothnian Bay
2004	2	22	Bothnian Sea, Bothnian Bay
2007	5	28–40	Bothnian Sea, Bothnian Bay
2008	5	20–36	Bothnian Sea, Bothnian Bay
2010	2	34–39	Bothnian Sea, Bothnian Bay
2012A[a]	5	23–46	Bothnian Sea, Bothnian Bay
2012B[a]	5	20–26	Bothnian Sea, Bothnian Bay
2014	4	24–44	Bothnian Sea
2015	5	37–49	Bothnian Sea, Bothnian Bay

[a] Two different pools from 2012.

and Bothnian Bay, the northern part of the Baltic Sea. The seals' weights ranged from 20 to 49 kg, with an average weight of 33 kg. The blubber had a lipid content ranging from 87 to 98%, with an average of 92%. The vast majority of the seals were killed during fishing, eight were killed during hunting and for seven of the seals, information about the cause of death was lacking. The seals were not killed for scientific purposes. Their bodies were sent to the Swedish Museum of Natural History to be included in their biobank (see Table 1 for further information). The present study gives general information on the concentrations of POPs in Baltic ringed seals. However, owing to the study design, it does not take into account possible variations between catchment areas, gender, age and seasonal differences.

Blubber from the seals was sampled during necropsy. To avoid photolytical degradation the samples were packed in aluminium foil and stored at −25 °C in the Environmental Specimen Bank (ESB) at the Swedish Museum of Natural History (SMNH). Blubber samples were then collected from the ESB, semi thawed and subsampled into pooled samples of 5 g. The number of seals per pool varied from between 1 and 5 animals (see Table 1). The samples were freeze dried for at least 36 h at the MTM Research Centre, Örebro University before being homogenised in a mortar with anhydrous sodium sulphate (approximately 1:16). The homogenates were stored in a freezer (−20 °C) before sample extraction. Extraction, clean-up, analysis and data processing took place at MTM Research Centre.

2.2. Chemicals and materials

Anhydrous sodium sulphate from Sigma-Aldrich, Steinheim, Germany was used for homogenisation, and also in all open columns. The components of the multilayer silica were purchased from Sigma-Aldrich, Steinheim, Germany (silica gel, potassium hydroxide) and Merck, Darmstadt, Germany (sulphuric acid 95–97%). For the aluminium oxide (AlOx) column, Alumina B was purchased from EcoChrom MP Biomedicals, Eschwege, Germany. The active carbon column contained Carbopack C (80–100 mesh), Supelco Analytical, Bellefonte, USA and Celite 545, Sigma-Aldrich, Steinheim, Germany. Organic solvents were of pesticide grade and purchased from Fluka, Steinheim, Germany (dichloromethane and toluene), Scharlau, Sentmenat, Spain (ethanol); Sigma-Aldrich, Steinheim, Germany (tetradecane) and Merck, Darmstadt, Germany (*n*-hexane Suprasolv). PBDD/F standards (EDF-5408, EDF-5409, EDF-2046 A, ED-5356) were purchased from Cambridge Isotope Laboratories, Inc., Massachusetts, USA. PCDD/F standards (EN-1948ES, EN-1948IS, EPA-8290STN) were purchased from Wellington Laboratories Inc., Ontario, Canada. PBDE standards (MBDE-MXFS, MBDE-MXFR, BDE-MXF) were purchased from Wellington Laboratories Inc., Ontario Canada. PCB standards were purchased from Wellington Laboratories Inc., Ontario, Canada. OCP standards were purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany. A summary of all compounds included in the study is presented in Table S1.

2.3. Sample extraction and clean-up

Sample preparation for PBDEs and PCBs was as follow. The homogenates were spiked with ^{13}C–labelled internal standards (see Table S1) before the lipid fractions were extracted using a mixture of *n*-hexane:dichloromethane (1:1, approximately 150 ml). After evaporation of the solvents in a rotary evaporator the extracts were kept under a gentle stream of nitrogen until the constant weight of lipid fractions could be determined gravimetrically. The extracts were then treated with an open multilayer silica column containing KOH silica gel (3 cm), neutral activated silica gel (0.5 cm), 40% H_2SO_4 silica gel (3 cm), 20% H_2SO_4 silica gel (1.5 cm), neutral activated silica gel (1 cm) and Na_2SO_4 (1 cm). The extracts were eluted with 70 ml *n*-hexane and then evaporated before being transferred to GC vials. Addition of ^{13}C–labelled recovery standards was done prior to instrumental analysis, and extracts were kept in tetradecane. The extracts were stored in a freezer (−20 °C) before analysis.

For PBDD/Fs and PCDD/Fs, initial lipid extraction, lipid determination and composition of the multilayer column were as described above. After being passed through the multilayer column, the extracts were evaporated to approximately 2 ml before clean-up on an AlOx column. The AlOx column was used to separate aromatic and aliphatic compounds based on π-bonding interactions with two different solvent mixtures of *n*-hexane/dichloromethane. The first fraction was eluted with 70 ml of *n*-hexane/dichloromethane (49:1), and the second fraction containing PBDD/Fs and PCDD/Fs was eluted with 100 ml *n*-hexane/dichloromethane (1:1). Additional clean-up and fractionation of the dioxin fraction was performed using a column comprising active carbon dispersed in celite. The column was first eluted with 7 ml *n*-hexane to obtain a fraction of non-planar compounds, followed by elution with 90 ml toluene to retrieve a second fraction containing PBDD/Fs and PCDD/Fs. The carbon column was not eluted in the reversed direction. The extracts were evaporated and transferred to GC vials. Addition of ^{13}C–labelled recovery

standards was performed prior to instrumental analysis. The extracts were kept in toluene and stored in a freezer (−20 °C) before analysis.

2.4. Analysis

For PBDEs, gas chromatography/atmospheric pressure chemical ionisation/mass spectrometry was performed on a Xevo TQ-S tandem quadrupole mass spectrometer equipped with an APGC source (Waters Corporation, UK). Quantification was performed using the isotope dilution method. Splitless injections of 1 μl of the extract were applied to a 30 m (0.25 mm i.d., 0.25 μm) BPX5 GC column (SGE Analytical Science, Victoria, Aus). For further information regarding the analysis, see Geng et al. (2016) and Table S2.

PCBs were analysed using an Agilent 7890A GC connected to an Agilent 5975C MSD mass spectrometer equipped with an electron ionisation source (Agilent Technologies, USA). Source temperature was set to 230 °C and quadrupole temperature was set to 150 °C. Splitless injections of 1 μl of the extract were applied to a 30 m (0.25 mm i.d., 0.25 μm) DB-5MS GC column (J&W Scientific; Folsom, CA, USA). The GC oven program was as follows: 180 °C (2 min hold), 3.5 °C/min to 260 °C, 6.5 °C/min to 300 °C. It should be noted that use of such a short column may have carried the risk of co-elution and overestimation of some congeners.

For PBDD/Fs and PCDD/Fs, HRGC/HRMS analysis was performed on a Micromass Autospec Ultima operating at 10,000 resolution using electron ionisation at 35 eV. The source temperature was 250 °C, the trap current 500 μA, the detector voltage 450 V and the transfer line temperature 280 °C. All measurements were performed in the selective ion recording mode (SIR), monitoring the two most abundant ions of the molecular bromine or chlorine cluster. Quantification was performed using the isotope dilution method. For analyzing PCDD/Fs, splitless injection of 2 μl of the extract were applied to a 30 m (0.25 mm i.d., 0.25 μm) DB-5MS GC column (J&W Scientific; Folsom, CA, USA). The injector temperature was 275 °C. The oven temperature program was as follows: initial temperature of 180 °C (held for 2.0 min), then the oven temperature was increased by 3.5 °C/min to 230 °C, then by 15 °C/min to 300 °C with a final hold of 4.0 min. For PBDD/Fs, programmed temperature vaporiser (PTV) injection was used to apply 7 μl of the extract to a 15 m (0.25 mm i.d., 0.10 μm) DB-5MS GC column (J&W Scientific; Folsom, CA, USA). The oven temperature program was as follows: initial temperature of 100 °C (held for 1.25 min), followed by temperature increases of 13 °C/min to 170 °C, 35 °C/min to 240 °C, 10 °C/min to 300 °C and finally 20 °C/min to 325 °C, followed by holding at 325 °C for 4.20 min. The PTV settings were as follows: the initial temperature was 110 °C (held for 0.25 min) followed by a ramp with 700 °C/min to 325 °C (held for 5 min). By using columns with relatively short lengths, i.e. 30 and 15 m, there was a risk of co-elution and possibly overestimation of some congeners. However, in essentially all traces for all dioxin congeners monitored in this study, only analytes with matching retention times to the corresponding internal standards were detected. Therefore, the risk of overestimation due to co-elution was considered low. See Table S2 for information regarding molecular ions and transitions.

2.5. Quality assurance and quality control

Isotope ratios and retention times were used to confirm the identity of the analytes. For two ions of a molecular ion cluster, the isotope ratio was set to be within ±15% for positive identification. Ideally, the recovery of the internal standard should be within 50–120% range, but for a few congeners, this criterion was not met and concentrations for these congeners are highlighted with their corresponding recovery in the compiled data (Tables S4–S7). Method detection limits were calculated based on a signal-to-noise ratio of 3, and using the average lipid weight. Method quantification limits were calculated based on a signal-to- noise ratio of 10, and using the average lipid weight. See Table S3 for detailed information regarding method detection limits and method quantification limits. An extraction blank was prepared and analysed for every batch of 8 samples extracted. While analyzing, instrumental blanks of toluene were monitored. In the blanks, the concentrations of PCDD/Fs, PBDEs and PCBs were below 3% of the concentration in the samples, while no PBDD/Fs were detected in the blanks. Therefore, no consideration had to be taken of the content of the blanks. The MTM Research Centre regularly takes part in inter-laboratory comparison studies of PCDD/Fs, PCBS, PBDEs and OCPs in biological and environmental samples to ensure the quality of analysis. In the Interlaboratory Comparison Study UNEP 2016, MTM Research Centre obtained 81% satisfactory results for the 168 reported DL-POPs and 91% satisfactory results for the 32 reported PBDEs. For the UNEP 2016 test material, satisfactory results deviated ±25% from assigned values.

3. Results and discussion

3.1. Temporal trends in PBDD/Fs, PCDD/Fs, PBDEs and PCBs

Sums of lower and upper bound concentrations for all four compound groups and years are presented in Table 2. In the following text, all concentrations refer to lower bound concentrations. For more detailed information regarding concentrations, see Tables S4–S7 in the supplementary information and Sections 3.2–3.5 in the following text. One aspect that hampered firm conclusions regarding concentrations and temporal trends was that the different pools analysed consisted of different numbers of subsamples of seal blubber, in some cases from only one to two animals. Therefore, for pools consisting of samples from a few animals, any abnormal blubber concentrations had a large influence on the results, affecting interpretation of temporal trends. Another aspect was the low number of individuals included in the study: 69 seals covering a time range of 40 years may have been insufficient to determine accurately temporal trends. However, even though there were weaknesses in the study, using visual inspection of the data it was still possible to see trends in the concentrations of the studied compounds during the period 1974–2015. In Fig. 1, a comparative overview of the temporal

Table 2
Concentrations (lower and upper bound) of ∑PBDD/Fs, ∑PCDD/Fs, ∑PBDEs and ∑PCBs in blubber from Baltic ringed seals between 1974 and 2015.a, b, c

	∑PBDD/Fs LB/UB[a] (pg/g l.w.)	∑PCDD/Fs LB/UB[a] (pg/g l.w.)	∑PBDEs LB/UB[b] (ng/g l.w.)	∑PCBs LB/UB[b] (μg/g l.w.)
1974	34/34	1100/1100	19	40
1975	16/17	430/430	31	18
1977	7.7/13	1500/1500	95	–[c]
1978	8.4/20	460/460	44	17
1980	6.3/11	340/340	72	19
1982	9.8/16	740/740	66	13
1985	8.6/16	380/380	130	13
1986	3.8/12	260/260	190	17
1987	21/27	220/220	130	12
1988	11/16	220/220	270	19
1991	7.3/14	200/210	220	10
1995	1.2/12	140/140	130	8.4
1996	4.5/13	310/310	500	31
2001	0.5/6.2	180/180	200	9.1
2004	5.4/11	140/140	170	9.6
2007	52/55	120/122	150	8.4
2008	26/31	120/125	160	8.1
2010	8.6/16	100/104	81	4.9
2012A	28/35	130/130	110	7.1
2012B	6.7/12	120/130	80	4.8
2014	8.7/17	110/120	50	2.8
2015	34/35	110/110	90	5.2
Number of congeners	11	17	9	21

l.w. — lipid weight.
[a] LB — lower bound. For concentrations below the LOD, zero was used. UB — upper bound. For concentrations below the LOD, the LOD was used.
[b] LB and UB were the same, therefore only one concentration is shown.
[c] Not analysed owing to analytical mistakes.

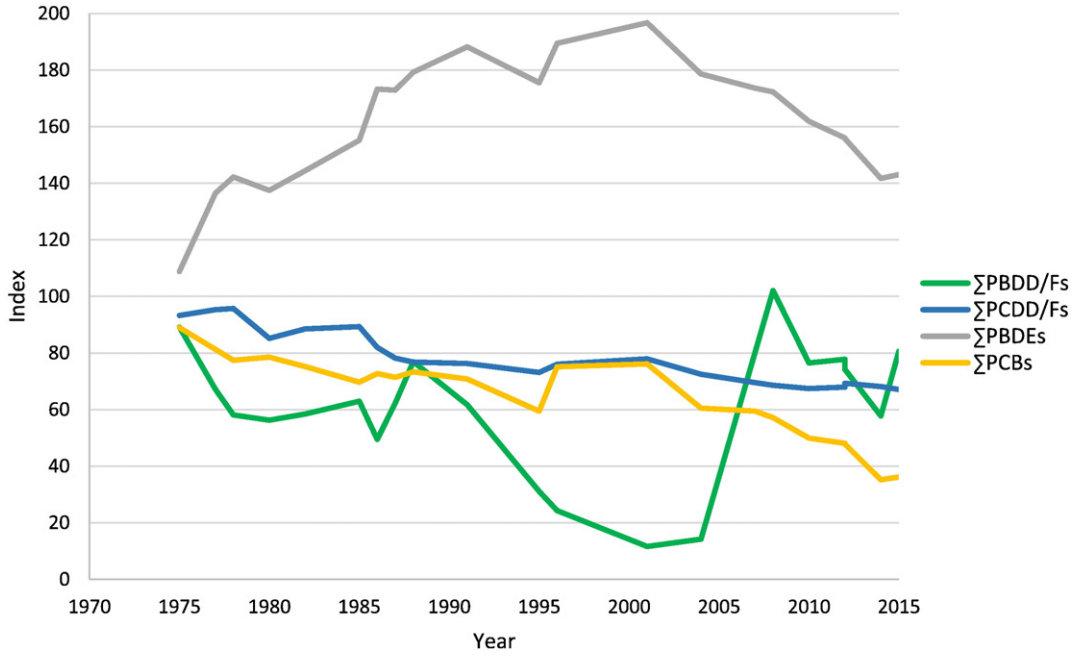

Fig. 1. Comparison of temporal trends of contaminants in blubber from Baltic ringed seals gathered between 1974 and 2015 presented as an index of changes in concentration over time. Concentrations of PBDD/Fs, PCDD/Fs, PBDEs and PCBs were logarithmized and the index calculated by setting 1974 as the start year with index 100.

trends for PBDD/Fs, PCDD/Fs, PBDEs and PCBs in the Baltic Sea during 1974–2015 is shown by using an index of changes in concentration over time: the lower bound concentrations of each compound group (Table 2) were logarithmized and the index calculated by assuming that 1974 was the starting year with index 100.

Using visual inspection of the data, temporal trends for PCDD/Fs and PCBs were similar and showed decreasing concentrations with some variations throughout the period 1974–2015. The correlation coefficient for PCDD/Fs and PCBs was $r^2 = 0.61$, and a reasonable explanation to correlation can probably be that PCDD/Fs are known by-products when producing PCBs and certain pesticides (Wikoff et al., 2012). Therefore, the phasing out of these chemicals has most probably contributed to the lower emissions of PCDD/Fs. However, incineration and combustion related processes are considered to be the main sources of emissions of PCDD/Fs. Thus, the introduction of efficient incineration processes as well as flue gas treatment has resulted in lower environmental levels of PCDD/Fs. The awareness actions to reduce PCDD/F emissions started during the same time period as restrictions on PCBs, which may explain the correlation between the compound groups (Olie et al., 1977).

Using visual inspection of the data, the trend in PBDD/Fs showed similarities, i.e. overall decrease, with PCDD/Fs and PCBs until around 2004, when the concentrations of PBDD/Fs started to increase while the other compound groups continued to decrease (see Table 2 and Fig. 1). However, since most of the concentrations of PBDD/Fs were close to their limit of detection (LOD), there was greater uncertainty in interpreting the temporal trend for this compound group. A probable explanation for the decrease between 1988 and 2004 is the introduction of optimised incineration processes, disfavouring dioxin formation and more efficient flue gas removal, whereas a possible explanation for the increase observed from 2004 to 2015 is related to the lifecycle of BFR treated materials. Since the increase of PBDD/Fs was probably caused by incineration of BFR treated materials or backyard burning, it is reasonable to assume that the amount of combusted BFR material has increased. A wide range of BRF treated materials, e.g. TVs and foam mattresses, may have a product life span of up to 20 years. This might mean that a TV produced in 1995 would emit PBDD/Fs if combusted in 2005. Tentatively, the results indicate that larger amounts of bromine containing waste may now be being incinerated, thereby elevating emissions of PBDD/Fs to the environment as discussed above. However, owing to the low concentrations detected, there is some uncertainty regarding the time trend. Despite this uncertainty, it is reasonable to conclude that concentrations of PBDD/Fs do not appear to have decreased during 1974–2015. On the contrary, the concentrations for the period 2007–2015 indicate that there may have been a slight increase of PBDD/Fs in the Baltic Sea, even though further studies are needed.

The trend for PBDEs differed clearly from all other compound groups. Using visual inspection of the data, the temporal trend for PBDEs showed an increase in concentration until around 2000, when the concentration started to decrease. A plausible explanation for the temporal decrease of PBDEs from around 2000 onwards was the ban and phasing out of BDE-mixtures that took place at the beginning of the 2000s (Darnerud et al., 2001; La Guardia et al., 2006; Ni et al., 2013).

Correlation coefficients were calculated between PBDD/Fs and PCDD/Fs or PBDEs. No correlation between PBDD/Fs-PCDD/Fs ($r^2 = 0.01$) or PBDD/Fs-PBDEs ($r^2 = 0.05$) was seen, which agrees with results from other studies on Baltic cod liver, pilot whales and shellfish (Bjurlid et al., 2017; Fernandes et al., 2009; Roszko et al., 2015). In Baltic salmon, a correlation was reported between individual PBDD/Fs and highly brominated PBDE congeners (Zacs et al., 2013). However, this was not seen in the present study. Although production of PBDEs is a major source for the formation of PBDD/Fs, more probably incineration related processes, such as municipal and hazardous waste incineration, are the main sources of environmental levels of PBDD/Fs. Even though tetra-, penta-, hexa-, hepta- and deca-BDEs are listed on the Stockholm Convention (Secretariat of the Stockholm Convention, 2009), there will still be a gap in time before all products containing PBDEs and other BFRs are incinerated. This might explain why the PBDD/Fs in seal blubber do not correlate with the trend for PBDEs as well as the slightly increasing trend seen for PBDD/Fs from 2004 onwards. Another possible explanation for the lack of correlation between PBDEs and PBDD/Fs in the Baltic ringed seals may be differences in exposure routes or metabolism for the two compound groups. Further details regarding each compound group is presented in the following sections.

3.2. Concentration and congener profiles of PBDD/Fs

In total, 22 pools were analysed for 11 (tetra- to hepta-BDD/F) congeners. PBDD/Fs were detected in all samples, with the total sum of all

congeners, ∑PBDD/Fs, ranging from 0.5 to 52 pg/g l.w. The 1,2,3,4,6,7,8-HpBDF congener contributed mainly to the ∑PBDD/Fs. The average ∑PBDD/Fs was 14 pg/g l.w. and the median was 8.6 pg/g l.w. Further details about concentrations and recoveries for all samples and congeners can be found in Table S2.

The most common congener was 1,2,3,4,6,7,8-HpBDF, detected in 19 of the 22 samples, followed by 2,3,7,8-TeBDF and 2,3,7,8-TeBDD, detected in 18 and 14 samples, respectively. The congeners that showed the highest concentrations were 1,2,3,4,6,7,8-HpBDF and 1,2,3,4,6,7,8-HpBDD. Among the detected congeners, the average contribution of 1,2,3,4,6,7,8-HpBDF to ∑PBDD/Fs was 61%, while 1,2,3,4,6,7,8-HpBDD showed the second highest contribution to ∑PBDD/Fs of 13% (concentrations below the LOD were calculated as zero). However, since 1,2,3,4,6,7,8-HpBDD was detected in only 9 samples, its abundance appeared to be sporadic, but when present, it was found in high concentrations. However, the LOD for 1,2,3,4,5,7,8-HpBDD was relatively high compared to the other congeners, which may explain why it was detected in only 9 out of 22 samples. Even though there were variations in the congener distribution in the samples (Fig. 2), there was no obvious trend during 1974–2015.

Current knowledge regarding the toxicity of PBDD/F in marine mammals is limited (van den Berg et al., 2013). For human risk assessment, it has been proposed that World Health Organization (WHO) 2005 toxic equivalency factors (TEF) can be used to calculate the PBDD/F TEQ, according to van den Berg et al. (2013). In our study, PBDD/F TEQ, ranged from 0.1 to 4.8 pg TEQ/g l.w., with an average of 0.7 TEQ/g l.w. and median of 1.0 pg TEQ/g l.w. It is worth noting that the congeners that showed the highest concentrations, 1,2,3,4,6,7,8-HpBDF and 1,2,3,4,6,7,8-HpBDD, have the lowest TEF values (0.01) (van den Berg et al., 2013) of all the detected PBDD/F congeners. The two congeners with the highest TEF values, 2,3,7,8-TeBDD and 1,2,3,7,8-PeBDD, showed the lowest average concentrations of all congeners.

Two studies from the Baltic Sea region have published results for the same congeners as the present study. Zacs et al. (2013) presented results from Baltic salmon. The most abundant congeners, i.e. 2,3,7,8-TeBDF, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF and 1,2,3,4,6,7,8-HpBDD, were detected in all 25 samples, while 1,2,3,4,6,7,8-HpBDF and 2,3,7,8-TeBDF were the two congeners with the highest concentrations. In Baltic cod liver, PBDD/Fs were detected and the most abundant congener was 1,2,3,7,8-PeBDF, while 2,3,4,7,8-PeBDF and 1,2,3,4,7,8-HxBDF were the congeners with the highest concentrations (Roszko et al., 2015).

To the best of our knowledge, there is only one previous study concerning PBDD/Fs in marine mammals. This study originated from our research group and concerned PBDD/Fs in pooled samples of blubber from pilot whales obtained from around the Faroe Islands (Bjurlid et al., 2017). The ∑PBDD/Fs range were comparable in the pilot whales study and present study, while the average ∑PBDD/Fs was twice as high in the Baltic ringed seal compared to the pilot whales, and the median was four times as high in the ringed seals compared to the pilot whales. A possible explanation for this difference is that the Baltic Sea is more polluted compared to the Atlantic. Another explanation is the age and size of the ringed seals and pilot whales differed. The pilot whales in Bjurlid et al. (2017) had a length range of 290–446 cm, which corresponded to ages of approximately 3–10 years. Therefore, the pilot whales were older and larger than the ringed seals in the present study, which might explain the difference in abundance and concentration of PBDD/Fs.

Brominated dioxins and furans have been detected in 14 species of fish and shellfish from six locations (Ashizuka et al., 2008; Fernandes et al., 2009; Food Standards Agency, 2006; Miyake et al., 2008; Rose et al., 2015; Skinner, 2011). Most of these studies reported that 1,2,3,4,6,7,8-HpBDF was the most abundant congener (Bjurlid et al., 2017; Rose et al., 2015; Skinner, 2011; Zacs et al., 2013), and several studies showed that furans were more abundant than dioxins (Bjurlid et al., 2017; Fernandes et al., 2008; Fernandes et al., 2009; Roszko et al., 2015). This is consistent with the results of the present study and probably indicates that the PBDD/Fs in the ringed seals originated from combustion and incineration related processes (Zhang et al., 2016).

3.3. Concentration and congener profiles of PCDD/Fs

The Baltic ringed seal samples from 1974 to 2015 were analysed for 17 (tetra- to octa) PCDD/F congeners. Chlorinated dioxins and furans were detected in all samples. The sum of all congeners, ∑PCDD/Fs, ranged from 103 to 1480 pg/g l.w., with an average of 338 pg/g l.w. and median of 211 pg/g l.w. (see Table S3 for further details regarding concentrations and recoveries). Several congeners were detected in all samples, i.e. 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD and 1,2,3,7,8,9-HxCDD, where 1,2,3,6,7,8-HxCDD, 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF showed the highest average concentrations. On average, the three congeners with the highest concentrations contributed 72% to ∑PCDD/Fs.

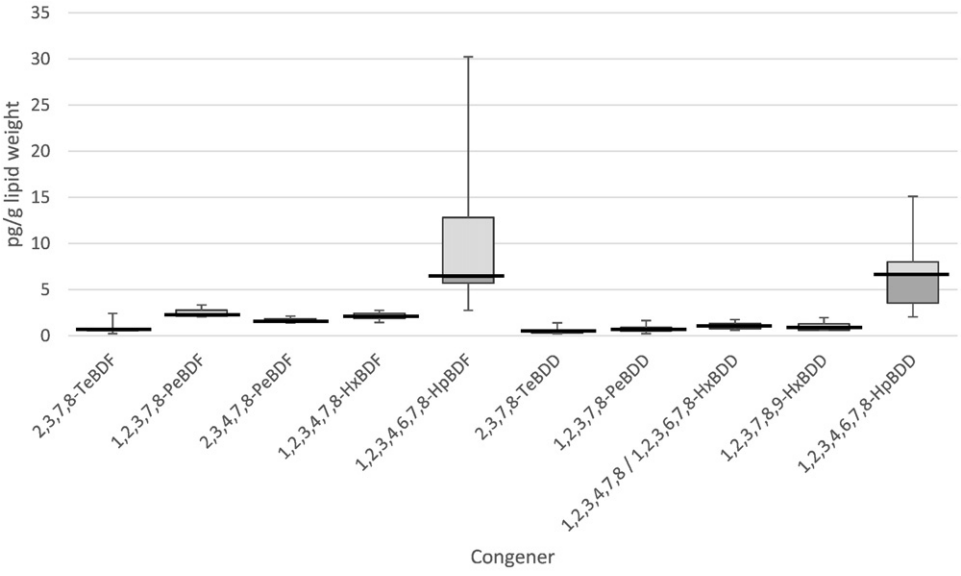

Fig. 2. Average congener distribution of PBDD/Fs shown as a box plot of the concentrations of detected congeners in blubber from Baltic ringed seal from 1974 to 2015. Solid black lines show median concentrations. Dark grey and light grey bars show lower and upper quartiles, respectively. Max and min values are shown by whiskers.

TEQ for the PCDD/Fs ranged from 39 to 784 pg TEQ/g l.w., with an average and median concentration of 166 and 98 pg TEQ/g l.w., respectively. Two of the chlorinated congeners with the highest concentrations are assigned the highest and second highest TEF values of 1 for 1,2,3,7,8-PeCDD and 0.3 for 2,3,4,7,8-PeCDF.

Fig. 3 shows the PCDD/F TEQ between 1974 and 2015, where the dotted line represents a moving average, where the average of two consecutive pools was calculated and plotted on the year for the latter pool. No major change in the congener distribution was detected during 1974–2015.

The congener profile of PCDD/Fs had a high impact on the total (PCDD/Fs + PBDD/Fs) TEQ. The contribution of PBDD/F TEQ to the total (PBDD/F + PCDD/F) TEQ ranged from 0.04–5.9%, with an average and median contribution of 1.1 and 0.6%, respectively. In blubber from pilot whales, the contribution of PBDD/F TEQ to the total TEQ was found to be 0–49%, and the average contribution of PBDD/F TEQ to the total TEQ was eight times as high as in the ringed seals (Bjurlid et al., 2017). The concentrations of PBDD/Fs were comparable in ringed seals to those in pilot whales, but because the concentrations of PCDD/Fs were higher in ringed seal, the PBDD/F TEQ contribution in ringed seal was lower. The ∑ PCDD/Fs range in ringed seals were up to 50 times as high compared to the pilot whales, and the average concentration in ringed seals were 20 times as high compared to the pilot whales (Bjurlid et al., 2017). In human adipose tissue samples, the contribution of PBDD/F TEQ to the total TEQ was shown to be on average 5% (Ericson Jogsten et al., 2010).

A number of studies have reported findings of PCDD/Fs in Baltic ringed seals. Roos and Haglund (2015) presented results for blubber samples from 40 juvenile ringed seals from 1978 to 2014 that were analysed individually. For the same time span, 1978–2014, the concentration range in the present study was similar. The congener distribution in the 40 ringed seals showed that 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD and 1,2,3,6,7,8-PeCDD were the congeners with the highest concentrations, in agreement with the results in the present study. Considering PCDD/F TEQ values, Roos and Haglund (2015) showed a decreasing trend from 1974 until around 2000, whereas no such trend was visible between 2002 and 2014. The decreases at around 1978 in Roos and Haglund (2015) and at the beginning of the present study might indicate that the concentrations in Baltic ringed seals were even higher during the 1960s. Overall, concentrations, congener distribution and temporal trends are comparable between Roos and Haglund (2015) and the present study.

In a study by Bergek et al. (1992), results were presented for 2,3,7,8-TeBDF, 2,3,7,8-TeBDD, 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD in blubber from 10 juvenile Baltic ringed seals collected during 1979–1990. Bignert et al. (1989) presented results for 2,3,7,8-TCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, and 1,2,3,7,8-PeCDD in blubber from Baltic ringed seals collected during 1986–1987. Koistinen et al. (1997) presented results for blubber from Baltic ringed seals collected during 1991–1992. All three studies showed comparable results to present study, although their datasets were too limited to show any temporal trends.

Baltic ringed seals shift between different food items, with herring being an important part of their diet (Sinisalo et al., 2007). Since Baltic herring is well studied, it is interesting to compare the congener profile and time trends of PCDD/Fs in herring to those in ringed seal. Miller et al. (2013) studied Baltic herring from 1979 to 2009 and (Airaksinen et al., 2014) studied Baltic herring from 1978 to 2009. The temporal trends in Miller et al. (2013) and Airaksinen et al. (2014), as well as congener distributions, are comparable to the trends detected in the present study.

3.4. Concentration and congener profiles of PBDEs

The samples were analysed for nine (#28, 47, 66, 100, 99, 85, 154, 153, 183) PBDE congeners, and PBDEs were detected in all samples during 1974–2015. The sum of all congeners, ∑ PBDEs, ranged from 19 to 500 ng/g l.w., with an average of 140 ng/g l.w. and median of 120 ng/g l.w. The recoveries varied from 53 to 108%, except for BDE #28, which showed recoveries from 24 to 46% for 1974–1996 (see Table S4 for further details regarding concentrations and recoveries).

Using visual inspection of the data, the temporal trend showed an increase of PBDEs from 1974 to 1996, followed by a decrease that started after 1996 and continued until the end of the present study. The congener distribution of PBDEs is shown in Fig. 4. The ∑ PBDEs during the final years of the present study were approximately three times higher compared to the initial years. BDE #28, 47, 66, 100, 99, 85, 154 and 153 were detected in all samples, with BDE #47 showing the highest concentrations followed by BDE#100 and BDE #99 (see Table S6). During 1974–2015, BDE #47 contributed on average 77% to ∑ PBDEs with a range of 70–82%. During 1974–2015, BDE #100 and BDE #99 contributed on average 11% and 9%, respectively, to ∑ PBDEs. However, a shift occurred during the 1980s when BDE #99 went from showing a slightly higher contribution to ∑ PBDEs than BDE #100 to showing the reverse relationship from the early 1990s until the end of the study. Even though the concentrations of BDE#154 and 153 were low in comparison to BDE #47, 100 and 99, the concentrations of BDE #154 and 153 and its contribution to ∑ PBDEs increased during 1974–2015. For BDE#154 and 153, the contribution to ∑ PBDEs increased from on average 0.5% in 1974 to on average 3.1% in 2015. Increases of BDE #154 and #153 were also detected between 1974 and 2015; for the sum of all PBDE congeners, the ratio between the concentrations in 1974 and 2015 was 1:5 (1974:2015), whereas the average ratio for BDE#153 and 154 was 1:39. Overall, this indicates that BDE #153 and 154 are making an increasingly important contribution to PBDEs in Baltic ringed seal, particularly as BDE #47 seems to be decreasing more rapidly than the other congeners. In this study, the Baltic ringed seal showed the highest concentration of PBDEs in 1996, which was subsequently followed by a downward trend. The penta-BDE mixture consisting mostly of BDE#47, 100, 99, 154 and 153 was banned in the EU and parts of the US in 2004 (Darnerud et al., 2001; La Guardia et al., 2006; Ni et al., 2013). It is likely

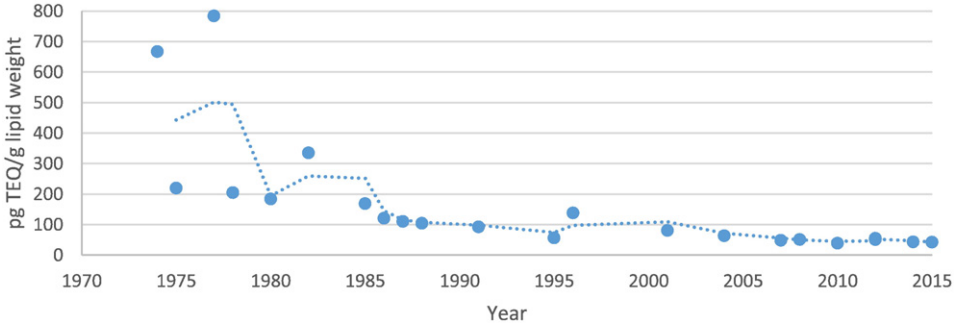

Fig. 3. Concentrations of PCDD/Fs expressed as toxic equivalents (pg TEQ/g l.w.) in blubber from Baltic ringed seal between 1974 and 2015. The dotted line represents a moving average, where the average of two consecutive pools was calculated and plotted on the year for the latter pool.

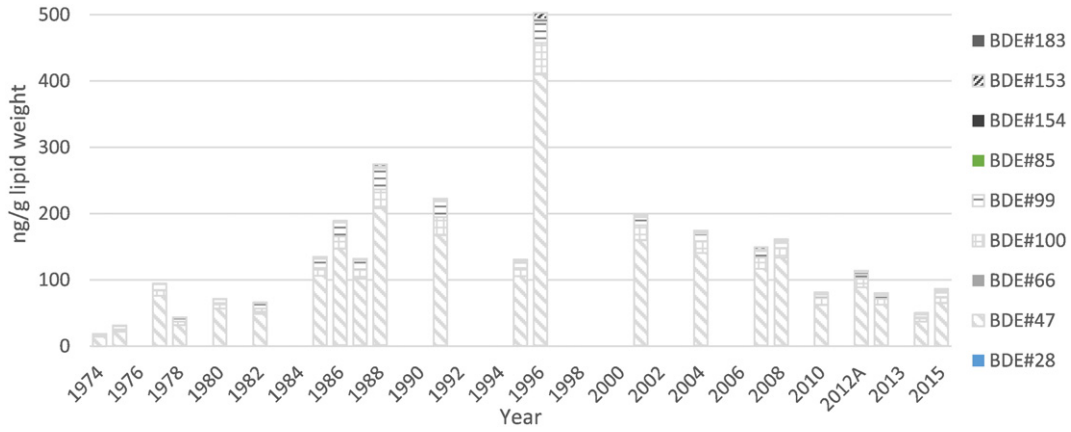

Fig. 4. Congener distribution of PBDEs in blubber from Baltic ringed seal during 1974–2015.

that phasing out of the penta-BDE mixture began before the ban took place, which might explain why no major reduction was observed in the component concentrations after 2004. Moreover, since the ringed seal is a top predator, it may take some time before any trends can be seen.

Andersson and Wartanian (1992) presented results for PBDEs in three pools of Baltic ringed seals collected during 1980–1988 (Andersson and Wartanian, 1992). These concentrations are comparable to those recorded in the present study for the same period (see Table S6). PBDEs was detected in liver from Baltic ringed seals collected during 2002–2007 (Routti et al., 2009), and the congener distribution was similar to that in the present study (BDE#47 was the predominant congener, followed by BDE#100/99 and BDE#154/153). However, owing to a lack of data, it was not possible to evaluate other potential temporal trends in Baltic ringed seal. However, Airaksinen et al. (2014) showed a similar temporal trend for PBDEs in Baltic herring during 1978–2009 as the temporal trend in ringed seal presented in this study. Moreover, the congener distributions in Airaksinen et al. (2014) and the present study were also similar.

3.5. Concentration and congener profiles of PCBs

Results of PCB analysis will only be presented here briefly because the main focus of this paper is PBDD/Fs. PCB data is presented solely for comparative purposes. The samples were analysed for 20 PCB congeners, and PCBs were detected in all pools for the study period 1974–2015. Detailed information regarding the concentrations of PCBs can be found in Table S5. Using visual inspection of the data, the temporal trend in PCB concentration was decreasing from 1974 to 2015 (Fig. 5).

The sum of the seven indicator PCBs (#28, 52, 101, 118, 105, 153, 138) ranged from 2.1 to 29 μg/g l.w., with an average of 9.8 μg/g l.w. and median of 7.5 μg/g l.w. All congeners were detected in all samples, with #138 and #153 showing the highest concentrations.

Several studies have reported findings on PCBs in Baltic ringed seal (Blomkvist et al., 1992; Helle et al., 1976; Karppanen and Henriksson, 1974; Koistinen et al., 1997; Nyman et al., 2002; Olsson et al., 1974; Perttilä et al., 1986; Routti et al., 2008). Both in terms of concentrations and congener distribution, there are similarities between the previous studies and the present study. Even though not showing identical time span as present study, two studies indicate decreasing temporal trends of PCBs in ringed seal (Nyman et al., 2002; Routti et al., 2008).

Publications reporting temporal trends of PCBs in Baltic herring (Airaksinen et al., 2014; Nyberg et al., 2015) have shown similar trends to those in the present study. Congener profiles in Baltic herring were also similar to the profiles in the present study (Airaksinen et al., 2014; Nyberg et al., 2015; Pikkarainen and Parmanne, 2006; Routti et al., 2005; Strandberg et al., 1998; Szlinder-Richert et al., 2008).

4. Conclusions

Ringed seals (*Pusa hispida*) were caught in the Baltic Sea during the period 1974–2015, and pools of blubber were analysed for primarily PBDD/Fs but also PCDD/Fs, PBDEs and PCBs. The concentrations of PBDD/Fs in Baltic ringed seals were generally low, i.e. most detected congeners had concentrations close to the detection limit, which hampered interpretation of temporal trends. Nonetheless, concentrations of PBDD/Fs varied over the studied time period and some trends differed compared to the other compound groups studied. Most noteworthy was the observation of a slight increase in PBDD/Fs concentrations from

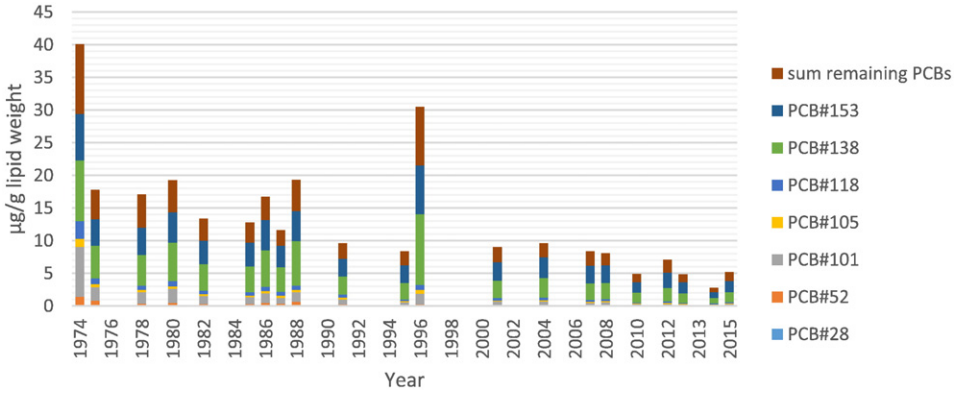

Fig. 5. PCBs in blubber from Baltic ringed seal (μg/g l.w.) between 1974 and 2015. The seven indicator PCBs are shown individually and the remaining 13 PCB congeners (i.e. PCB #66/70, 74, 110, 156, 157, 167, 170, 180, 187, 189, 194, 206, 209) are presented as a sum.

2004 onwards. This finding needs to be investigated further before any firm conclusions regarding increasing levels of PBDD/Fs in biota from the Baltic Sea region can be drawn. The predominant congener was 1,2,3,4,6,7,8-HpBDF followed by 1,2,3,4,6,7,8-HpBDD, which indicates that the PBDD/Fs in the ringed seals largely originated from incineration and combustion related processes. The average contribution of PBDD/F TEQ to the total (PBDD/F + PCDD/F) TEQ was 1.1%. Accordingly, the present concentrations of PBDD/Fs in Baltic ringed seals have a low impact, in comparison to PCDD/Fs, on the health of the studied seals.

The concentrations of PBDEs increased until the late 1990s, when they started to decrease. However, the concentrations in 2015 were still 4 times higher compared to those in 1974. No correlation was seen between concentrations of PBDD/Fs and PBDEs, which indicates differences in sources of exposure, routes of exposure and tentatively differences in metabolism of PBDEs and PBDD/Fs.

The temporal trends in PCDD/Fs and PCBs and showed decreasing concentrations, and correlations between the compound groups could be identified. Temporal trends differed between the chlorinated compounds (PCDD/Fs, PCBs) and PBDEs, where the chlorinated compounds showed a decreasing trend during the whole period. The different temporal trends reflect the timing of bans and actions taken to phase out the different compound groups.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.10.178.

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