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Bioaccumulation of polybrominated diphenyl ethers and hexabromocyclododecane in the northwest Atlantic marine food web

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ABSTRACT

Seven species of teleost fishes comprising major prey of northwest Atlantic harbor seals were analyzed for polybrominated diphenyl ethers (PBDEs). PBDE concentrations in whole fish samples (n=87) were compared with those measured previously in harbor seal blubber to evaluate the transfer of PBDEs from prey to predator. Hexabromocyclododecane (HBCD) concentrations were measured in three fish species to provide an initial estimation of HBCD contamination in this ecosystem. HBCD was detected in 87% of the fish samples at concentrations ranging from 2.4 to 38.1 ng/g, lw (overall mean 17.2 ± 10.2 ng/g, lw). ∑PBDE concentrations in fish ranged from 17.9 to 94 ng/g, lw (overall mean 62 ± 34 ng/g, lw). ∑PBDE concentrations in the harbor seals were two orders of magnitude higher than levels in the fish. Biomagnification factors (BMFs) from fish to seals averaged from 17 to 76, indicating that tetra- to hexa-BDEs are highly biomagnified in this marine food web. BDE-47 was the dominant congener in all samples, suggesting exposure to the penta-BDE mixture. The presence of higher brominated congeners including BDE-209 at measurable levels in fish and seal tissue, along with the very high biomagnification of BDE-153, as well as −155, and −154, suggests recent exposure to the octa- and deca-BDE formulations in this US coastal marine food web, as well as the additional contribution of BDE-209 debromination in fish to the loading of persistent PBDEs in the seals. This is the first study to report the occurrence of BDE-209 and other higher BDEs in commercially important marine fishes from the northwest Atlantic.

1. Introduction

The brominated flame retardants (BFRs) polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are synthetic organic compounds that are widely used as additives in a variety of household and commercial products to reduce their flammability. As a result of their environmental persistence and high production volume over the past 30 years, PBDEs and HBCD have become ubiquitous global contaminants, even in remote areas (de Wit, 2002; Hites, 2004). These are lipophilic compounds that bioaccumulate in marine food webs and have been found at high concentrations in top predators such as marine mammals (Hites, 2004; Covaci et al., 2006; Law et al., 2006b). Over the past three decades, North America has dominated the global market for the penta-BDE formulation, with annual usage estimated at 7100 metric tons (95%) in 2001 (BSEF, 2005). Restrictions have been imposed on the production and use of the penta- and octa-BDE formulations, while the third commercial product, deca-BDE (consisting of >97% BDE-209), represents 83% of the global market demand (BSEF, 2005) for use as an additive in high-impact polystyrene for television sets, computer casings, and electronic equipment (Alaee et al., 2003). Recently, some applications of deca-BDE were banned in Europe and in two US states (Betts, 2008), nevertheless, large amounts of deca-BDE have been released to the global environment and this chemical is still in high-volume use.

Recent attention has focused on the potential of highly brominated PBDEs, including BDE-209, to bioaccumulate in marine ecosystems. Metabolic debromination of BDE-209 has been demonstrated in freshwater fish, resulting in the formation of lower substituted BDEs (hexa- through nona-BDEs) that have the potential to be more persistent and bioaccumulative than the parent compound (Stapleton et al., 2004; Stapleton et al., 2006a; La Guardia et al., 2007). While direct exposure to commercial BDE mixtures is assumed to be the main source of PBDE uptake/accumulation in biota, it is plausible that BDE-209 debromination in fish may contribute to the loading of persistent BDEs in marine food webs (Stapleton et al., 2004; Law et al., 2006b; Stapleton et al., 2006a).

HBCDs are additive BFRs applied in extruded and high-impact polyurethane foams that are used as thermal insulation in buildings, in upholstery textiles, and to a lesser extent, in electrical equipment

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(Alaee et al., 2003). Few studies have reported on the occurrence of HBCD in marine ecosystems, and little information is available on the fate and environmental persistence of this compound. HBCD concentrations reported in marine fishes from Asia (Ueno et al., 2006), Arctic Canada (Tomy et al., 2008), and various areas of Europe (Morris et al., 2004; Janak et al., 2005; Covaci et al., 2006; Sørmo et al., 2006), vary significantly by region, species, and tissue examined. Little data exist on HBCD concentrations in marine fishes from US waters (Johnson-Restrepo et al., 2008). HBCD concentrations reported in cetaceans from the eastern US coast (Johnson-Restrepo et al., 2008; Peck et al., 2008) are one to two orders of magnitude lower than those detected in marine mammals from Europe (Law et al., 2003; Zegers et al., 2005; Covaci et al., 2006), where the market demand for this compound is two- to three-fold higher than in Asia or America, respectively (BSEF, 2005). Currently, there are no restrictions on the global production or use of HBCD.

Many BFRs including PBDEs and HBCDs have been shown to exert neurodevelopmental and endocrine-disrupting effects in animals (Birnbaum and Staskal 2004; Costa and Giordano, 2007). In view of the historical and ongoing dispersal of these compounds, there is a clear need for more information on the uptake/accumulation and biomagnification of PBDEs and HBCD in marine food webs.

The aim of the present study was to determine concentrations of PBDEs (mono- through deca-BDEs) in seven species of teleost fishes that are components of the harbor seal diet (Wood et al., 2001). PBDE concentrations and congener profiles in the fish were compared with those measured earlier in blubber samples of harbor seals (*Phoca vitulina concolor*) collected from the northwest Atlantic between 1991 and 2005 (Shaw et al., 2008) to examine the trophic transfer of PBDEs from prey to predator. HBCD concentrations were measured in three fish species to provide an initial estimation of HBCD contamination in this ecosystem. This is the first study to investigate the biomagnification of BFRs in the northwest Atlantic marine food web.

2. Materials and methods

2.1. Sampling

Eighty seven (87) prey-sized individual fish (<35 cm) were collected from the coast of Maine by staff of the State of Maine Department of Marine Resources during the May–June 2006 Gulf of Maine Trawl Survey of commercial groundfish stocks (Fig. S1-1). Species included silver hake (*Merluccius bilinearis*, $n=10$), white hake (*Urophycis tenuis*, $n=17$), Atlantic herring (*Clupea harengus*, $n=20$), American plaice (*Hippoglossides platessoides*, $n=10$), alewife (*Alosa pseudoharengus*, $n=10$), and winter flounder (*Pseudopleuronectes americanus*, $n=10$). Atlantic mackerel (*Scomber scombrus*, $n=10$) were caught by hook and line from the same area during June 2006. These species are all highly migratory and feed across an extended spatial range in the western Atlantic (from Newfoundland, Canada to South Carolina). Whole fish were directly placed on ice and transported to the laboratory where standard length and weight were recorded, then frozen and stored at −40° prior to shipment to the analytical laboratory. Details of the samples are given in Table SI-1.

2.2. Chemical analysis

The analytical method used for determination of PBDEs in fish has been described before (Päpke et al., 2004), with determination of total HBCD being integrated into the method described here. All analyses were performed following the isotope dilution method. Thirty-five native standards were obtained from Cambridge Isotope Laboratories (CIL) (Andover, MA,USA) and Wellington Laboratories (Guelph, Ontario, Canada). In total 13 internal ^{13}C-labelled standards were used. ^{13}C-labelled γ-HBCD was obtained from Wellington Laboratories and native α, β, γ isomers were obtained from CIL. Solvents were obtained from Merck, Darmstadt, Germany (n-pentane), Fluka, Buchs, Switzerland (diethyl ether), and Promochem, Wesel, Germany (ethanol, hexane, cyclohexane, dichloromethane and toluene). Silica gel, alumina oxide, sodium sulphate and potassium oxalate of the highest purity were obtained from Merck.

Due to the limited sample amounts of the various specimens and the necessity to reach adequate LODs (limit of detection), fish whole body samples were pooled and homogenized into 17 composites prior to analysis. In brief, fish composite samples were homogenized and analyzed for 35 PBDE congeners (mono- through deca-BDE) and HBCD using HRGC/HRMS. For extraction the fish sample (amount equal to approximately 1.5 g of lipids, ranging between 5 and 100 g fish tissue), was homogenized and mixed with 3 times the amount of sodium sulphate to result in an easy flowing powder. After addition of the internal PBDE standards, a mixture of cyclohexane and dichloromethane was applied to the column for extraction of PBDEs along with other lipophilic compounds and fat. Total amount of solvent used was between 150 and 600 ml. The extract was washed with water and dried over sodium sulphate. After solvent evaporation, gravimetric lipid determination was performed. Removal of all lipids was performed by acid treated and activated silica gel and on an aluminium trioxide column. The final extract was evaporated by a stream of nitrogen to a final volume of 50 µl containing C^{13} -labelled PBDE 139 (Wellington) as recovery standard. The measurements were performed by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) on a HP 5890 II GC coupled either with a Micromass AutoSpec or a Thermo Finnigan 95 XL mass spectrometer. A DB 5 column (30 m, ID=0.25 mm, film=0.1 µm) was used for gas chromatographic separation.

The HRMS was operated under EI conditions at $R=10{,}000$. The two most abundant ions were used for measurement (M^+ for tri- and tetra-BDE, and M-2Br$^+$ for penta- to deca-BDE). The identification of PBDEs and total HBCD was based on retention time and isotope ratio. Recoveries measured for the internal standards added normally ranged between 60 and 120%. Total (∑) PBDEs represent the sum of all the identified mono- to deca-BDE congeners. Data are presented on a lipid-weight basis. Wet weight PBDE data are provided in Supplementary material, Table SI-2.

2.3. Qa/qc

All analyses were conducted in accordance with the Eurofins ERGO accredited QA QC program. Regular participation in relevant international calibration tests, such as those of Quasimeme and Centre for Analysis of Residues in Traces, University of Liege, Belgium, for PBDE analysis; and Folkehelsa, Norwegian Institute of Public Healthfor HBCD analysis, are key components of this program. Performance characteristics were determined for each method, such as the detection and quantification limit, precision in series, precision from day to day (repeatability) within the scope of the introduction of a method. The quality management system was checked at regular intervals through independent experts in order to guarantee the continuation of the accreditation.

During each analysis series (approximately 10 samples), quality assurance pooled samples were examined. Within the scope of the analyses, blank samples were examined in parallel to the tissue samples in order to detect potential contamination of the analyzed samples by the chemicals and laboratory equipment. Analytical accuracy (trueness) was guaranteed through regular analyses of certified reference material (CRM). The gas-chromatographic system was examined regularly with respect to the required separation power. As regards the mass spectrometer, the required resolution and sensitivity were controlled. Calibration was implemented using multipoint calibration. The latter was verified within each measuring sequence by repeated injections of individual calibration points

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(recalibration). If the results diverged significantly, calibration was repeated, where required.

Within the scope of the analyses, various standards (13C-labeled internal and recovery standards) were applied. We consider the application of these standards to be an outstanding quality assurance measure, as the recovery rates of single components may be taken into account individually and per sample. The recovery rates were determined individually for each sample using 13C-labeled standards. All data met the QA QC specifications.

All analyzed data were checked with respect to their plausibility, taking into account the concentration ratios of the detected substances ("patterns"), possible information about the source of a contamination, and empirical values of comparable samples analyzed in the past. To test for plausibility (comparison of "patterns"), we have developed a software solution where the concentrations of all samples are normalized. Thus, "fingerprints" were laid on top of one another, showing distinctive features of individual samples. Where distinctive features were ascertained, the analysis data was internally rechecked carefully using all the raw data. Where required, the distinctive feature was pointed out in the test report.

2.4. Statistics

Statistical analyses were performed using SPSS 14.0. For concentrations below the level of detection, the result was treated as half the detection limit. To explore species differences in BDE congener profiles, the BDE profiles previously analyzed in harbor seal blubber samples were included with the profiles of whole fish composite samples in a principal components factor analysis (see discussion in Supplementary material, Fig. SI-1, SI-2).

3. Results and discussion

3.1. PBDE concentrations in teleost fishes

∑PBDE concentrations in fish ranged, on average, from 18.3 (in alewife) to 81.5 ng/g, lw (in Atlantic herring), with an overall mean of 62±34 ng/g, lw (Table 1). ∑PBDE levels comparable to those in this study were reported in muscle tissues of marine teleost fishes from a Florida coastal food web (mean range: 8–87.5, overall mean 43 ng/g, lw) (Johnson-Restrepo et al., 2005), in Atlantic cod (*Gadus morhua*) from the western and southern and Norwegian coast (Jenssen et al., 2007) (mean range 52–86 ng/g, lw), various fishes from the Belgian North Sea (range 16–103, mean 58 ng/g, lw) (Voorspoels et al., 2003) and the eastern (North Sea) coast of UK (range 49–69 ng/g, lw; mean 60 ng/g, lw) (Boon et al., 2002). ∑PBDE concentrations 3–15 times higher were reported in marine fishes from the California coast (mean 302 ng/g, lw) (Brown et al., 2006) and the Georgia coast (range 10–337 ng/g, lw) (Sajwan et al., 2008).

3.2. HBCD concentrations in teleost fishes

HBCD was detected in 87% of the fish samples (herring, alewife, and mackerel) at concentrations ranging from 2.4 to 38.1 ng/g, lw (overall mean 17.2±10.2 ng/g, lw) (Table 1). In this study, we did not measure the different HBCD stereoisomers in fish. Whereas commercial HBCD mixtures consist mainly of γ-HBCD (75–89%), α-HBCD (10–13%), and β-HBCD (1–12%) (Heeb et al., 2005), stereoisomeric profiles of HBCDs in marine biota are dominated by α-HBCD, and selective enrichment of this isomer is observed with increasing trophic level in the food web (Covaci et al., 2006). HBCD concentrations in our teleost fish samples were two- to four-fold lower than PBDE concentrations in the same samples and were also lower than HBCD levels reported in fish from Europe, reflecting the usage patterns of PBDEs and HBCD in the different countries (BSEF, 2005). Mean HBCD levels in muscle tissue of herring and salmon from Sweden collected in 2000 were 63 and 51 ng/g, lw, respectively (Remberger et al., 2004), while levels in muscle of plaice, bib, and whiting (silver hake) collected from the Scheldt Estuary, The Netherlands in 2001 were 40, 96, and 92 ng/g, lw, respectively (Janak et al., 2005). Comparable HBCD levels to those in our fish samples were reported in Atlantic cod from the Norwegian coast (mean range 18.7–25.6 ng/g, lw), polar cod from Bear Island (subarctic), Norway (mean 11.7 ng/g, lw) (Jenssen et al., 2007), and skipjack tuna from Asian waters (range 0.1–45 ng/g, lw) (Ueno et al., 2006). A recent study reported lower HBCD levels in blubber of bottlenose dolphins from the Florida coast (mean 7.38 ng/g, lw), whereas levels in muscle of Atlantic sharpnose shark (54.5 ng/g, lw) and bull shark (77.7 ng/g, lw) were three- to five- fold higher than those in our fish samples (Johnson-Restrepo et al., 2008).

Since the withdrawal of the penta-BDE and octa-BDE products, HBCD levels have been rising in fish and marine mammals from Europe and Asia, reflecting the increasing usage of HBCD as an alternative for PBDEs. In harbor porpoises from UK waters, a sharp increase in HBCD levels was observed from about 2001 onward (Law et al., 2006b). In Japan, HBCD concentrations in cetaceans appear to exceed those of PBDEs, (Tanabe et al., 2008). Stapleton et al. (2006b) reported that HBCD concentrations were increasing exponentially in California sea lions between 1993 and 2003, possibly indicating a shift toward greater usage of HBCD in the US.

3.3. PBDE concentrations in harbor seals

∑PBDE concentrations (mono-hexa-BDEs) in harbor seal blubber samples ranged from 80 to 25,720 ng/g, lw (overall mean 2403±5406 ng/g. lw; $n=42$) (Shaw et al., 2008). ∑PBDE levels in these harbor seals were an order of magnitude higher than those reported in seals from Europe, reflecting greater use of the penta-BDE product in the US. PBDE levels in the adult males (mean 1385 ng/g, lw) were four-to six-fold greater than those reported in adult male harbor seals

Table 1
Mean PBDE and HBCD concentrations (ng/g, lipid wt) in teleost fishes and in blubber of harbor seals from the northwest Atlantic

Species	N[a]	% lipid	28	47	49	66	75	99	100	153	154	155	181	183	197	203	207	209	∑PBDE	HBCD
Winter Flounder	10/1	0.6	0.56	35	1.5	0.67	0.14	2.5	6.4	0.78	2.0	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	52	n.a.
Atlantic Herring	20/6	1.1	0.55	40	13	0.87	0.92	6.9	6.8	0.45	1.4	0.61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	82	23
American Plaice	10/1	0.9	0.59	42	3.1	0.39	0.13	4.0	7.0	1.2	2.8	3.6	n.d.	0.13	n.d.	n.d.	n.d.	1.8	69	n.a.
White Hake	17/2	1.0	0.39	25	4.7	0.06	0.08	0.63	7.2	0.35	1.9	0.31	n.d.	n.d.	n.d.	n.d.	n.d.	0.91	42	n.a.
Alewife	10/2	10.2	0.44	8.3	1.6	0.33	0.19	3.6	1.7	0.30	0.72	0.19	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	18	7.6
Atlantic Mackerel	10/4	10.3	1.3	20	3.8	1.2	0.44	7.5	4.1	1.4	1.4	0.52	0.42	7.9	5.5	1.5	10	1.6	69	14
Silver Hake	10/1	2.2	0.83	18	4.5	0.35	0.09	6.3	4.0	0.31	2.2	0.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	38	n.a.
Harbor Seal[b]	7	63.4	1.8	904	1.5	0.05	0.05	134	49	210	31	45	n.d.	18	14	n.a.	n.a.	1.2	1385	n.a.

n.d. = not detected.
n.a. = not analyzed.
[a] *N* indicates number of whole fish sampled/number of resulting composites analyzed.
[b] For tri- to hexa-BDE congeners (BDEs-28, −47, −49, −66, −75, −99, −100, −153, −154, −155) values represent means of adult male harbor seals ($N=7$). For BDEs −181, −183, −197, −203, and −207, values represent means of harbor seals, all ages ($N=12$). For BDE-209, values represent means of harbor seals, all ages ($N=20$).

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collected from the North Sea during 1999–2004 (300 ng/g lw) (Weijs et al., 2007) and from the Dutch Wadden Sea (232 ng/g, lw) (Leonards et al., 2008). Higher PBDE levels were reported in adult male California sea lions (*Zalophus californianus*) collected during 1993–2003 (5778 ng/g lw) (Stapleton et al., 2006b) and in adult male harbor seals collected during 1997–1998 from San Francisco Bay (5135 ng/g, lw) (She et al., 2002), in accordance with the higher levels reported in coastal marine fishes from the same area (Brown et al., 2006).

3.4. PBDE congener profiles in fish and seals

Of 26 BDE congeners detected in teleost fishes, 10 tri- through hexa-BDEs (BDEs-28, −47, −49, −66, −75, −99, −100, −153, −154, and −155) accounted for 85–98% of the PBDE content. BDEs-47, −99, −100, −153 and −154, are generally dominant in biota worldwide and appear to have a higher potential for bioaccumulation (Watanabe et al., 2003). However, congener profiles among the fish species were variable (Fig. 1). Similar differences in congener profiles have been reported in freshwater and marine fish (Hale et al., 2001; Stapleton et al., 2004; Johnson-Restrepo et al., 2005; Anderson and MacRae, 2006; La Guardia et al., 2007; Xia et al., 2008) and reflect species-specific differences in uptake, and metabolism/ excretion of the individual BDE congeners. BDE 47 was the dominant congener in fish, accounting for 45–68% of the total PBDE content. Whereas BDE-99 constitutes 50% of the technical penta-BDE mixture, BDE-99 contributed much less to the total in the fish (≤20%), and large differences in BDE-99 abundance relative to BDE-47 were apparent between the species, including those belonging to the same family. In silver and white hake, BDE-47 contributed 46.3% and 58.8% to the total PBDE mass, respectively, while BDE-99 contributed 16.4% and 1.5%, respectively. Silver hake are voracious predators of other fish including other hake, while white hake are indiscriminate benthic feeders; thus, differences in dietary exposure as well as metabolic capacity may account for the variable BDE-99 accumulation in these species. In laboratory exposure studies, significant debromination of BDE-99 was observed in the intestinal tract of common carp (*Cyprinus carpio*), resulting in the conversion of BDE-99 to BDE-47 (Stapleton et al., 2004). In addition to debromination, preferential excretion of BDE-99 was suggested as a reason for lower accumulation of BDE-99, relative to BDE-47 in carnivorous marine fish (Isosaari et al., 2005). The penta-BDE-100 was relatively abundant in the fish, accounting for 7.5–17% of the total PBDE mass, while the tetra-BDE-49 was relatively abundant in five species (Atlantic herring, alewife, mackerel, white hake and silver hake), contributing 7.2–15.5% to the total. In all species, the hexa-BDEs −154 and −155 contributed more to the total than BDE-153, and in plaice, BDE-155 was the most abundant hexa-BDE.

In the adult male harbor seals, BDE-47 contributed 63% of the total PBDE content, followed by the hexa-BDE −153 (17%) and the penta-BDEs −99 (11.4%) and −100 (3.3%) (Fig. 1). Interestingly, BDE-155 was relatively more abundant in blubber than BDE-154. BDE-155 has rarely been reported in marine mammals (Stapleton et al., 2006b). This congener is present at only 0.2–0.7% in technical mixtures (La Guardia et al., 2006) and was identified, along with BDE-154, as a specific debromination product of BDE-209 in common carp (Stapleton et al., 2006a).

3.5. Differences in PBDE congener profiles

Overall, the fish contained a greater proportion of tri- and tetra-BDEs and the penta-BDE-100 in their tissues than were present in technical penta-BDE mixtures or in the seals. The tetra-BDEs −49, −66, and −75 were detected in every fish sample and accounted for 4–19% of the PBDE content, while these congeners never exceeded 2% of the total in the seals. BDE-49 accounts for only 0.4–0.7% of the technical penta-BDE mixture, but contributed 3–16% of the PBDE mass in fish tissues. In studies of the transfer of PBDEs from fish to marine mammals, BDE-49 has rarely been reported (Boon et al., 2002; Johnson-Restrepo et al., 2005; Sørmo et al., 2006; Jenssen et al., 2007). This congener is reportedly one of the breakdown products from anaerobic transformation of an octa-BDE technical mixture (Gaul et al., 2006), and may be indicative of reductive debromination of higher-brominated BDEs in fish.

3.6. Biomagnification of BFRs

This study clearly demonstrates that many PBDEs are able to bioaccumulate and biomagnify in this marine food web, as concentrations in harbor seal blubber were two orders of magnitude higher than those in teleost fishes. To estimate biomagnification factors (BMFs), we compared lipid-normalized concentrations of PBDEs in the seven species of teleost fishes with those in adult male harbor seals (Table 2). It should be noted that this analysis assumes that the species analyzed represent the sole source of the harbor seal diet. During the spring–summer season, harbor seal feed mainly on silver and white hake and Atlantic herring (species comprising ~70% of their diet), but they also consume a variety of schooling and demersal fishes (Wood et al., 2001). Hence, the seven species analyzed herein represent basic

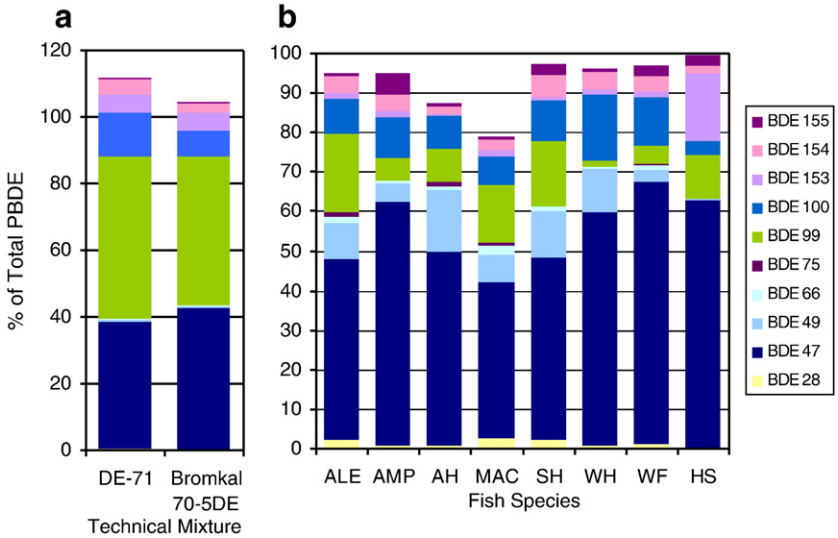

Fig. 1. PBDE congener profiles for two penta-BDE technical mixtures (La Guardia et al., 2006) (a) whole fish by species and adult male harbor seals (b). Species: ALE = alewife, AMP = American plaice, AH = Atlantic herring, MAC = mackerel, SH = silver hake, WH = white hake, WF = winter flounder, HS = harbor seals.

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Table 2
Biomagnification factors (BMFs) from marine fishes to harbor seals

Species	28	47	49	66	75	99	100	153	154	155	209[a]	∑PBDE
Winter Flounder	3.1	26.0	1.03	0.07	0.34	53.2	7.7	269	15.9	34.3	n.d.	26.6
Atlantic Herring	3.2	22.5	0.12	0.06	0.05	19.5	7.3	467	22.5	73.6	n.d.	17.1
American Plaice	3.0	21.4	0.48	0.13	0.45	33.9	7.0	174	11.3	12.4	0.67	20.3
White Hake	4.5	36.3	0.32	0.83	0.63	213	6.9	593	16.2	145	1.3	33.0
Alewife	4.0	109	0.93	0.15	0.26	37.2	29.8	700	447	236	n.d.	76.5
Atlantic Mackerel	1.4	45.7	0.40	0.04	0.11	17.9	12.1	148	21.9	86.3	0.75	20.1
Silver Hake	2.1	51.1	0.33	0.14	0.56	21.3	12.4	677	14.1	47.8	n.d.	36.4

Species: WF = winter flounder, AH = Atlantic herring, AMP = American plaice, WH = white hake, ALE = alewife, MAC = Atlantic mackerel, SH = silver hake (whiting).
[a] For BDE 209, BMF calculated with average of all harbor seals (N = 20). Other congeners, BMF calculated with average of adult males only (N = 7).

linkages in the seasonal food chain, but may not provide the complete picture of exposure to and bioaccumulation of PBDEs in the seals.

BMFs for ∑PBDEs between teleost fishes and harbor seals ranged, on average, from 17.1 to 76.5, indicating a high biomagnification potential. BMFs between the dominant prey species (silver hake, white hake, herring) and the seals averaged 36.4, 33, and 17.1, respectively. Comparable BMFs for ∑PBDEs were reported between predatory fishes and harbor seals in the North Sea (37.8, 29.5, and 26.7 for silver hake (whiting), herring, and Atlantic cod, respectively) (Boon et al., 2002), between polar cod and harbor seals (12.4) and ringed seals (36.9) in Svalbard, Norway (Sørmo et al., 2006; Jenssen et al., 2007), and between teleost fishes and bottlenose dolphins in a Florida marine food web (range 3–85) (Johnson-Restrepo et al., 2005).

The hexa-BDEs −153 and −155 were highly biomagnified in harbor seal blubber, with BMFs ranging from 148 to 677 and 12 to 236, respectively, reflecting the lack of metabolic capacity for these congeners in the seals. BDE-47 and BDE-99 were also biomagnified throughout this food web. BDE-99 was highly biomagnified from white hake to seals (BMF 213), whereas BMFs of BDE-99 were lower relative to BDE-47 from alewife, mackerel, and silver hake to seals. Since, BDE-99 is *meta-para*-substituted and may not be easily metabolized by seals (Boon et al., 1997), the higher biomagnification from white hake to seals suggests significant metabolic depletion of BDE-99 in this species. There was a lack of biomagnification of the tetra BDEs-49, −66, and −75, and very little biomagnification of the tri-BDE-28, suggesting that seals possess an efficient metabolism for these congeners.

Because HBCD was not measured in harbor seal blubber, we could not estimate the biomagnification potential for this compound. Elevated levels of HBCD reported in marine mammals are suggestive of biomagnification (Law et al., 2003; Morris et al., 2004; Zegers et al., 2005; Stapleton et al., 2006b; Johnson-Restrepo et al., 2008; Peck et al., 2008), but only a few studies have investigated the transfer of HBCD through the food chain (Covaci et al., 2006). Biomagnification of HBCD from forage fish to predator fishes was reported in a Lake Ontario (Tomy et al., 2004) and Lake Winnipeg food web (Law et al., 2006a), from fish to seals in a Norwegian Arctic food chain (Sørmo et al., 2006; Jenssen et al., 2007), and from fish to cetaceans in an eastern Canadian Arctic food web (Tomy et al., 2004; Tomy et al., 2008). In vitro studies using harbor seal liver microsomes suggest that α-HBCD is resistant to P450 metabolism (Zegers et al., 2005), whereas a recent study (Leonards et al., 2008) reported a lack of biomagnification of α-HBCD from fish to harbor seals, suggesting that seals can metabolize α-HBCD. In view of the increasing global use of this BFR compound, there is a need for more studies on the loading, kinetics, and biomagnification potential of HBCD in marine ecosystems.

3.7. Higher brominated congeners

Hepta- through nona-BDEs were detected in 26–39% of the teleost fish samples (Table 1). Hepta-BDE-183, considered a marker compound for the octa-BDE mixture, was detected in two species (plaice and mackerel). In the mackerel tissues, BDE-183 was detected at average concentrations of 7.9 ng/g, lw, while the octa-BDE 197 and nona-BDE-207 were detected at average concentrations of 5.5 and 9.9 ng/g, lw, respectively; BDEs-181 and 203 were also present at lower concentrations. In one mackerel sample, BDEs-183, −197, and −207 dominated the congener profile, accounting for 66% to the total PBDE content, whereas BDE-47 accounted for only 13% of the total. In the harbor seals, BDE-183 was detected in all samples analyzed (n = 12) at average concentrations of 17.6 ng/g, lw. This finding indicates that components of the octa-BDE mixture, which was principally used in molded parts of computers, televisions, car parts and other products, have contaminated this marine food web. In addition, octa-BDE 197 was detected in 58% of the seal samples (mean 24 ng/g, lw), along with several unidentified hepta- and octa-congeners. Thus, while the presence of tetra- to penta-BDEs in fish and seal tissue probably represents direct exposure to components of the penta-BDE mixture, the occurrence of hepta- through nona-BDEs suggests the additional contribution of metabolic processes and/or recent exposure to the octa- and deca-BDE mixtures, since a short half-life (months) is indicated for higher-BDE congeners (Thuresson et al., 2006).

Although BDE-209 is usually the dominant BDE detected in marine sediments (de Boer et al., 2003), it is often detected only at trace levels in marine mammals, and there are relatively few reports of the occurrence of BDE-209 in marine biota (Law et al., 2006b). High levels of BDE-209 have been reported in mussels from marine coastal waters off Korea (Moon et al., 2007). BDE-209 levels in the mussels were higher than the other BDE congeners, presumably because of their position as benthic feeders. In the present study, BDE-209 was detected in 35% of the fish samples (in plaice, mackerel, and white hake) and in 25% of the harbor seal blubber samples analyzed (n = 20), indicating that this congener is bioavailable in the marine food web. BDE 209 concentrations in teleost fishes (range 0.2 to 4 ng/g, lw) were similar to the levels found in harbor seal blubber (1.1 to 7.6 ng/g, lw) (Shaw et al., 2008), suggesting that BDE 209 can be accumulated at measurable levels in seals in the wild. A recent study (Thomas et al., 2005) demonstrated that gray seals (*Halichoerus grypus*) continuously exposed to deca-BDE-spiked food accumulated similar blubber concentrations of BDE-209 (2 to 8.2 ng/g, lw), suggesting that more or less continuous exposure to deca-BDE may be occurring through the marine food web.

Whereas fish are an important but not the sole source of PBDE exposure in humans (Schecter et al., 2005), prey fish consumption is the predominant exposure route for harbor seals. BDE-209 is strongly associated with sediment, thus, it is likely that marine fishes accumulate BDE-209 via ingestion of sediment-associated prey organisms such as zooplankton, benthic invertebrates, echinoderms, marine worms, and flatfishes (Bowman et al., 2000; Fishbase, 2008). Whereas the data in this study indicate that BDE-209 may be accumulated from fish to seals, the biomagnification potential was low, with BMFs ranging from <1 for plaice and mackerel to 1.3 for white hake. Whether the lack of biomagnification of BDE-209 is a

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result of a low assimilation rate for this large molecule into blubber or metabolic depletion in the fish is unclear. It is also possible that BDE-209 may be partitioning to tissues other than blubber in the harbor seal.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2009.02.018.

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