

LEVELS AND TEMPORAL TRENDS (1983–2003) OF POLYBROMINATED DIPHENYL ETHERS AND HEXABROMOCYCLODODECANES IN SEABIRD EGGS FROM NORTH NORWAY

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Abstract—The present study assessed temporal trends (1983–2003) of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) in eggs of herring gulls (*Larus argentatus*), Atlantic puffins (*Fratercula arctica*), and black-legged kittiwakes (*Rissa tridactyla*) in North Norway. Generally, PBDE concentrations increased between 1983 and 1993 and then leveled out, although species-specific trends were reported. Levels of α -HBCD increased in all species throughout the 20-year period. Levels of nona-BDEs and BDE 209 ranged from nondetectable to parts per billion. Nevertheless, highly variable procedural blanks were reported for the nona-BDEs and BDE 209, which clearly illustrates the importance of including blanks repeatedly during determination of these compounds.

Keywords—Polybrominated diphenyl ethers Hexabromocyclododecanes Norwegian Arctic Seabird eggs
Temporal trends

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) commonly are used to fireproof electrical and electronic equipment and textiles. These chemicals leak from products, and increasing concentrations have been reported in, for example, the Canadian Arctic in ivory gull (*Pagophila eburnea*) eggs during the period from 1976 to 2004 [1] and in ringed seals (*Pusa hispida*) during the period from 1981 to 2000 [2]. Although little is known about the effects of PBDEs on wildlife, results from laboratory experiments indicate estrogenic potencies in human cell lines [3], induction of developmental neurotoxic effects in adult mice [4], and activation of ethoxyresorufin-*O*-deethylase activity in human, rat, chick, and rainbow trout cells [5].

In the last few decades, penta-BDE, octa-BDE, and deca-BDE have been among the most extensively used technical BDE-mixtures (<http://www.epa.gov/oppt/pbde/pubs/proj-plan32906a.pdf>). Nevertheless, manufacture and use of penta-BDE and octa-BDE were banned within the European Union (EU) in 2004 [6]. Furthermore, production of penta-BDE and octa-BDE was discontinued voluntarily in the United States at the end of 2004 (<http://www.epa.gov/oppt/pbde/pubs/proj-plan32906a.pdf>), and in Japan, no use of commercial penta-BDE and octa-BDE has been permitted since 1991 and 2000, respectively [7]. The production of deca-BDE continued as a substitute for the banned penta-BDE and octa-BDE, with total production in 2006 exceeding 60,000 metric tons worldwide (<http://www.epa.state.il.us/reports/decabde-study/available-research-review.pdf>). However, the production and use of deca-BDE was banned and re-

stricted in some parts of the United States in 2007 and 2008 and, most recently, in the EU on July 1, 2008. Commercially manufactured deca-BDE is composed almost entirely of BDE 209, but it also contains low levels of nona-BDEs (BDEs 206, 207, and 208) [8]. In addition, hepta-, octa-, and nona-BDEs also may be formed during debromination/biotransformation of BDE 209 [9–12]. Few studies have assessed the levels of deca-BDE and isomer-specific levels of nona-BDEs in the environment and, in particular, in biota samples.

Hexabromocyclododecanes (HBCDs) are used mainly in thermoplastic polymers and textiles [13]. Hexabromocyclododecane is a technical product composed of different HBCD isomers (i.e., α -HBCD, β -HBCD, and γ -HBCD) [13]. Whereas γ -HBCD is the most dominant isomer in technical mixtures and sediments [14], α -HBCD is the primary isomer detected in most biota samples [14–16]. Hexabromocyclododecanes disrupt the thyroid hormone system, inhibit cytochrome P450 (CYP) 1A enzyme activity, and are associated with neurobehavioral alterations [13,17,18]. Nevertheless, little is known about the biological effects associated with HBCD exposure in free-ranging animals. Most studies so far have been conducted with laboratory animals using technical products of HBCD, in which the γ isomer dominates. Additionally, little is known about levels, isomer patterns, and temporal trends of HBCDs in seabirds.

In the present study, we addressed the information gap regarding temporal trends of PBDEs and HBCDs in wildlife by determining the levels of these compounds in eggs of herring gulls (*Larus argentatus*), Atlantic puffins (*Fratercula arctica*), and black-legged kittiwakes (*Rissa tridactyla*) collected in North Norway. Furthermore, the congener-specific

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accumulation of nona-BDEs and BDE 209 was assessed. The three species chosen for the present study commonly breed along the coast of Norway but represent different food niches. The Atlantic puffin and black-legged kittiwake both feed pelagically and mainly on small, shoaling fish, such as capelin (*Mallotus villosus*) and young herring (*Clupea harengus*), but sometimes also on zooplankton. Whereas the black-legged kittiwake feeds on the sea surface, the Atlantic puffin catches its food underwater, sometimes at depths of as much as 60 m but more commonly at shallower depths. The herring gull is a more coastal species and has a more varied and opportunistic diet, composed of fish offal and discards, human waste, and seabird chicks and eggs; hence, it is higher up the food chain than the black-legged kittiwake and Atlantic puffin [19].

The present study is part of an ongoing monitoring project that started in 1983 to evaluate contaminant burdens as well as spatial and temporal trends of a suite of halogenated organic contaminants and mercury in seabird eggs [20–22].

MATERIALS AND METHODS

Species studied and fieldwork

Eggs of herring gulls, Atlantic puffins, and black-legged kittiwakes were collected in 2003 at Røst (67°31'N, 12°07'E) and Hornøya (70°23'N, 31°09'E; both North Norway), but samples also were taken retrospectively from eggs of herring gulls, Atlantic puffins, and black-legged kittiwakes collected (and frozen) in 1983 and 1993 at Hornøya, Hekkingen (69°36'N, 17°50'E; Norway), and Røst to evaluate possible temporal trends. For all birds, $n = 10$ except for puffins in 1993, for which $n = 9$. After sampling, the individual eggs were homogenized, kept in the dark, and frozen (-20°C) until analysis to minimize the degradation. All eggs were analyzed in 2005/2006. The samples analyzed were kept frozen for greatly varying lengths of time (2–23 years), creating the potential for variations in degradation of the contaminants in question. It is, however, not possible to give any measure for the stability of the brominated flame retardants (BFRs) in biological samples, because the methods used to measure levels of BFRs are relatively new and were not available in 1983 or 1993. Thus, comparisons of old and new results from the same samples are not possible. This is a common problem for all studies assessing temporal trends of BFRs.

Determination of PBDEs and HBCDs

The determination of PBDEs (BDEs 28, 47, 99, 100, 153, 154, 206, 207, 208, and 209); α -, β -, and γ -HBCD; and total HBCDs (sum of α -, β -, and γ -HBCD) was performed at the Laboratory of Environmental Toxicology at the Norwegian School of Veterinary Science, Oslo, Norway. The content of the eggs were homogenized in a food blender. The egg homogenates (~ 3 g) were weighed in 80-ml centrifugation tubes and spiked with the internal standards of BDEs 77, 119, and 181 as well as [^{13}C]BDE 209 (Cambridge Isotope Laboratories). The lipids were extracted twice using cyclohexane and acetone (3:2) and an ultrasonic homogenizer (CPX750; Cole-Palmer Instruments). The supernatants of both extractions were merged and concentrated to approximately 1 ml using a Zymark® evaporation system (TurboWap II; Zymark Corporation) at 40°C with a gentle flow of nitrogen. The concentrated lipid extracts were quantitatively transferred to volumetric flasks and the volume adjusted to 5 ml with cyclohexane. The lipid levels were determined gravimetrically using a 1-ml aliquot

of the sample. For cleanup (i.e., removal of lipids), the remains of the lipid extracts were treated twice with ultraclean (purity, 96%), concentrated H_2SO_4 (Scanpure; Chemscan AS) and concentrated to approximately 0.3 ml using a gentle flow of nitrogen at 40°C . The sample concentrates were transferred to amber gas chromatography vials to minimize possible degradation by ultraviolet light.

For separation and determination of BDEs 28, 47, 99, 100, 153, and 154 as well as total HBCDs, aliquots (1 μl) of the egg concentrates were automatically injected (Agilent 7683 series auto sampler; Agilent Technologies) on a gas chromatograph (Agilent 6890 series)—mass spectrometer quadrupole detector (Agilent 5973 network, mass-selective detector) equipped with an injector operated in pulsed splitless mode (at 250°C) and a SPB-5 column (length, 60 m; inner diameter, 0.25 mm; film thickness, 0.25 μm ; Supelco). The temperature program was as follows: 90°C for 2 min, ramp to 190°C at $25^{\circ}\text{C}/\text{min}$, hold at 190°C for 1 min, ramp to 250°C at $5^{\circ}\text{C}/\text{min}$, hold at 250°C for 1 min, ramp to 320°C at $2.5^{\circ}\text{C}/\text{min}$, and hold at 320°C for 10 min. The PBDE congeners and total HBCDs were monitored using electron-capture negative ionization in selected-ion monitoring at m/z 79 and 81.

For separation and determination of BDEs 206, 207, 208, and 209, aliquotes (10 μl) were injected in a programmable-temperature vaporization injector (Agilent Technologies) coupled to a gas chromatograph—mass spectrometer (described earlier) and equipped with a DB-5MS column (length, 10 m; inner diameter, 0.25 mm; film thickness, 10 μm ; J&W Scientific, Agilent Technologies). The temperature program was as follows: 80°C for 2 min, ramp to 315°C at $25^{\circ}\text{C}/\text{min}$, and hold at 315°C for 10 min. The nona-BDEs and BDE 209 (in addition to [^{13}C]BDE 209) were monitored using electron-capture negative ionization in selected-ion monitoring at m/z 484.5 and 486.5 and at 494.5 and 498.5, respectively.

For separation and determination of the individual α -, β -, and γ -HBCD isomers, a liquid chromatograph connected to a mass spectrometer (API3000 LC/MS/MS System; Applied Biosystem) equipped with a Discovery C18 column (length, 15 cm; inner diameter, 2.1 mm; film thickness, 5 μm ; Supelco) was used. The mobile phase consisted of 1 mM ammonium acetate in water (30%) and 1 mM ammonium acetate in 99% acetonitrile and 1% water (70%) at 0.2 ml/min, which was gradually changed to 1 mM ammonium acetate in 99% acetonitrile and 1% water for 5 min and kept for 10 min. The tandem mass spectrometry analysis in negative electrospray ionization mode was performed in multiple-reactions monitoring mode at m/z 640.7 and 79.2.

For all components, five- to eight-point linear calibration curves were used, and calculations were done within the linear range for the components. Detection limits of individual compounds were determined as threefold the noise level and ranged from 0.01 to 0.17 ng/g wet weight.

Analytical quality

The laboratory used in the present study is accredited according to the requirements of the Norwegian Standard-English Standard International Organization for Standardization/International Electrochemical Commission (NS-EN ISO/IEC) 17025 (TEST 137). The laboratory's accredited analytical quality was found to be satisfactory in international relevant intercalibration tests (e.g., FIRE 2003, QUASIMEME 2003 [test 565: 33]).

Each sample series ($n = 15$ –20) contained two samples for

recovery (hen eggs spiked with recovery standards), one blind sample (hen egg), two of the laboratory internal reference samples (seal blubber), and three blanks (solvents). The mean relative recoveries of BDEs 28, 47, 99, 100, 153, 154, 206, 208, and 209 ranged from 91 to 111%, whereas the mean relative recoveries for BDE 207 and total HBCDs ranged from 124 to 144% and from 84 to 169%, respectively.

Results of the procedural blanks showed positive values for BDEs 153, 206, 207, 208, and 209. No contamination occurred in the procedural blanks of BDEs 28, 47, 99, 100, and 154 and of α -, β -, and γ -HBCD and total HBCDs. The blank values of BDE 153 were relatively constant and low. As a measurement, the quantification limit was increased for this congener. This method for correction could not be applied for the nona-BDEs and BDE 209, however, because these blank values showed variations that were too wide [23]. For BDEs 206, 207, 208, and 209, the blank values varied from less than 0.2 to 0.8 ng/ml, from less than 0.1 to 8.2 ng/ml, from less than 0.1 to 1.3 ng/ml, and from 0.03 to 2.6 ng/ml, respectively. As a result, these varying blank values could highly influence the results of PBDE concentrations in the seabird eggs. Consequently, the concentrations of nona-BDEs and BDE 209 in the seabird eggs are only reported if the concentrations were above the average blank level plus threefold the standard deviation. Values below the average blank level plus threefold the standard deviation are set to not detectable. The concentrations of nona-BDEs and BDE 209 were not included in Σ PBDEs (sum of BDEs 28, 47, 99, 100, 153, and 154). Because the results of the absolute concentrations of BDEs 206, 207, 208, and 209 in the eggs of the present study have high uncertainties, all concentrations are presented in a figure along with the average blank levels plus threefold the standard deviation (Fig. 1). The high variability among procedural blanks for nona-BDEs and for BDE 209 in the present study indicates contamination, most likely from the laboratory air. Significant concentrations of PBDEs (nona-BDEs were not determined) have been reported previously in laboratory air, with large differences in the degree of contamination with regards to sampling time and location [24]. This corresponds well with the highly variable blanks of the present study.

Data treatment

All inferential statistics were conducted using JMP® 6.0.0 2005 (SAS Institute). The pairwise Student's *t* test was used to test for statistical differences of PBDEs (natural logarithm [ln] ng/g lipid weight) except for BDEs 206, 207, 208, and 209 (because of many nondetectable values and background contribution of the analytes in the blanks) and α -HBCD concentrations in eggs of the three species from 1983, 1993, and 2003 ($\alpha = 0.05$). The overall temporal trends in seabird eggs were assessed first, followed by assessments of species-specific temporal trends. Because of the low sample size, the models did not correct for spatial trends.

RESULTS AND DISCUSSION

Levels of PBDEs and HBCDs

For details of the concentrations of the different congeners, see Table 1. The nona-BDEs and BDE 209 are reported in Figure 1 and are not included in Σ PBDEs because of the positive values found in the procedural blanks. Concentrations of BDEs 28, 47, 99, 100, 153, and 154 were detected in all the herring gull, Atlantic puffin, and black-legged kittiwake eggs.

The highest concentrations of Σ PBDEs generally were reported in eggs of herring gulls. This may be the result of their predatory habit of occasionally eating seabird eggs and chicks. Higher contaminant burdens in seabirds feeding primarily on seabirds and eggs, compared to those feeding mainly on fish, have been reported previously [25]. For all seabird eggs, BDE 47 was the most abundant PBDE congener, constituting from 35 to 80% of Σ PBDEs. Higher proportions of BDE 47 compared to other PBDE congeners also were found in eggs of common guillemots (*Uria aalge*) from the Baltic Sea [26], eggs of herring gulls from the Great Lakes (North America) [27], and eggs of goshawks (*Accipiter gentilis*), white-tailed eagles (*Haliaeetus albicilla*), and ospreys (*Pandion haliaetus*) from Norway [28]. A higher biomagnification factor for BDE 47, compared to those for the other congeners, could explain the observed patterns, as found previously in common guillemots, in which biomagnification factors decreased in the order BDE 47 > BDE 99 > BDE 100 [8]. Congener patterns in eggs of other birds of prey, such as merlins (*Falco columbarius*) [28] and peregrine falcons (*Falco peregrinus*) [29], differed through a predominance of BDE 153. Although habitat choice and migratory behavior may explain differences in PBDE patterns among birds, birds feeding in the terrestrial environment may be more highly exposed to higher-brominated PBDE congeners compared with marine species [30]. Other factors, such as metabolism, bioavailability and uptake efficiencies, also may influence the overall PBDE profiles.

The levels of nona-BDEs and BDE 209 generally were low in the present study, although some of the eggs contained concentrations well above the highest levels reported in the procedural blanks and most likely demonstrated the presence of nona-BDEs and BDE 209 in Arctic seabird eggs (Fig. 1). Concentrations of BDEs 206, 207, 208, and 209 above the average blank level plus threefold the standard deviation were found in 22, 14, 4, and 9, respectively, of the 96 analyzed eggs (Fig. 1). Concentrations above the procedural blanks for all three nona-BDE isomers and BDE 209 were only found in three eggs (Fig. 1). To our knowledge, the present study is the first to report levels of nona-BDEs in Arctic seabird eggs. In comparison, none of the eggs in a recent survey of nona-BDEs in peregrine falcon eggs in the United States showed a BDE 206 level above the sample quantification limit [31]. Although BDEs 207 and 208 was positively identified in the peregrine falcon eggs, the associated numerical values were approximate concentrations only [31]. Furthermore, BDE 209 could be confirmed and quantified in only 1 of 40 Belgian little owl (*Athene noctua*) eggs [32] and in only 4 of 32 previously analyzed glaucous gull (*Larus hyperboreus*) eggs from the Norwegian Arctic [33].

Detectable concentrations of the α -HBCD isomer were present in all samples of eggs from the three species studied (Table 1), whereas concentrations of the β -HBCD and γ -HBCD isomers were below the method detection limits in all samples. This corroborates previous reports of a strong prevalence of α -HBCD in seabirds [14]. Levels of α -HBCD were highest in the black-legged kittiwake eggs and decreased in the order herring gull eggs > Atlantic puffin eggs. The HBCD levels were in the same range as those reported in common guillemots from the Baltic Sea [26] and glaucous gull eggs from Bjørnøya [33]. Furthermore, the HBCD levels in the present study were somewhat lower than those reported in Swedish peregrine falcon eggs [34] and Belgium common tern (*Sterna hirundo*) eggs [14]. They were, however, higher than

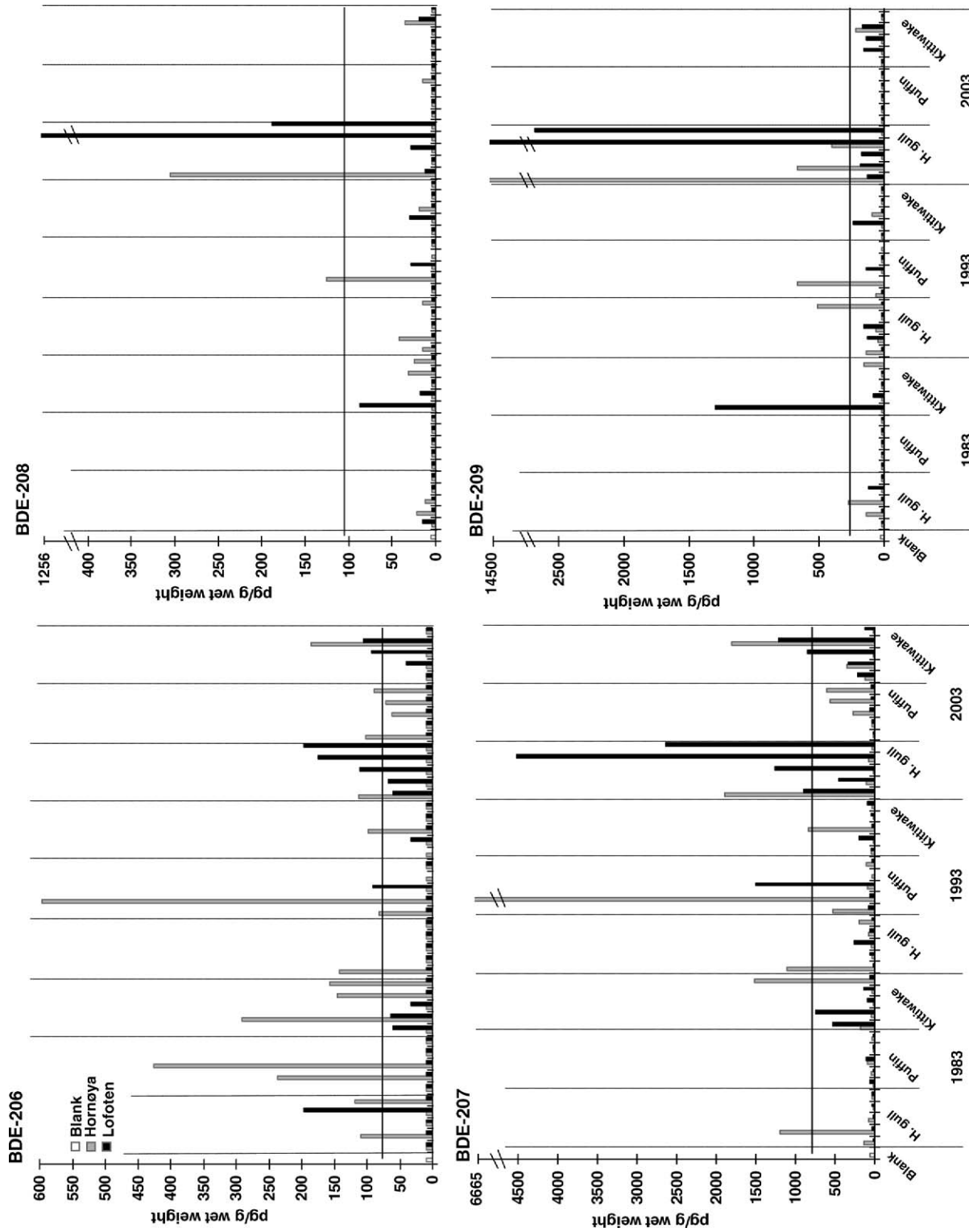


Fig. 1. Individual concentrations (pg/g wet wt) of nonabrominated diphenyl ethers (nona-BDEs; BDEs 206, 207, and 208) and deca-BDE (BDE 209) in eggs of herring gulls (*H. gull*; *Larus argentatus*; *n* = 30), black-legged kittiwakes (kittiwakes; *Rissa tridactyla*; *n* = 30), and Atlantic puffins (puffins; *Fratercula arctica*; *n* = 29) from Hornøya and Kjøst (North Norway) sampled in 1983, 1993, and 2003. Each column in the figure corresponds to an individual egg sample. Values below the detection limit were replaced by median blank concentrations. Average blank (white column) and average blank concentrations (pg/g wet wt) plus threefold the standard deviation (horizontal black line) of nona-BDEs and deca-BDE reported in blank samples also are presented.

Table 1. Concentrations (mean \pm standard deviation [SD]; ng/g lipid wt) of individual polybrominated diphenyl ethers (PBDEs), sum (Σ) PBDEs, and α -hexabromocyclododecane (α -HBCD) in eggs of herring gulls (*Larus argentatus*), black-legged kittiwakes (*Rissa tridactyla*), and Atlantic puffins (*Fratercula arctica*) from North Norway^a

	1983		1993		2003	
	Mean	SD	Mean	SD	Mean	SD
Herring gull						
BDE 28	8	5	19	9	7	3
BDE 47	350	215	497	294	412	191
BDE 100	51	34	77	50	71	25
BDE 99	35	21	133	167	45	30
BDE 154	5	4	15	9	16	6
BDE 153	7	6	18	15	19	16
Σ PBDEs	457	278	759	526	570	225
α -HBCD	16	9	31	15	108	48
Black-legged kittiwake						
BDE 28	7	3	11	10	7	4
BDE 47	97	45	183	172	141	69
BDE 100	12	6	25	25	16	8
BDE 99	18	8	61	78	16	9
BDE 154	5	7	7	6	7	3
BDE 153	6	4	21	33	10	5
Σ PBDEs	144	63	308	320	196	85
α -HBCD	30	34	57	26	142	91
Atlantic puffin						
BDE 28	5	2	13	4	4	1
BDE 47	48	21	95	30	41	17
BDE 100	13	4	23	5	11	4
BDE 99	28	9	58	10	21	8
BDE 154	5	2	12	2	9	4
BDE 153	4	1	16	10	6	2
Σ PBDEs	103	35	217	45	90	30
α -HBCD	12	4	32	15	58	20

^a For all species in all years, $n = 10$ except for Atlantic puffins in 1993, for which $n = 9$.

mean concentrations reported in peregrine falcon eggs from South Greenland (1986–2003) [29] and in little owl eggs from Belgium [32].

Temporal trends

In the overall assessment of temporal trends in seabird eggs (including eggs from all three species), Σ PBDEs increased from 1983 to 1993 and leveled out between 1993 and 2003 (Fig. 2 and Table 2). The species-specific temporal trends revealed slightly different results (Table 2). Levels of the higher-brominated PBDEs (BDEs 99, 153, and 154) were higher in 1993 than in 1983 for all species (Table 2). No temporal trends of the lower-brominated PBDEs (BDEs 28 and 47) were reported in the black-legged kittiwake eggs. In Atlantic puffin eggs, the levels of lower-brominated PBDEs peaked in 1993, then tended to drop until 2003. A similar trend was reported for BDE 28 in herring gull eggs, and the same tendency, though statistically insignificant, was observed for BDE 47 (Table 2). These results suggest that levels of the higher-brominated PBDEs (penta- and hexa-BDEs) generally increased from 1983 to 1993 and then leveled out between 1993 and 2003.

As a result of the increased use of deca-BDE during past years, an increasing time trend of BDE 209 and its debromination products in the seabird eggs could be expected. In the present study, we observed a greater frequency of high levels of BDEs 207, 208, and 209 in herring gull eggs from 2003 compared to those from 1983 and 1993; however, this

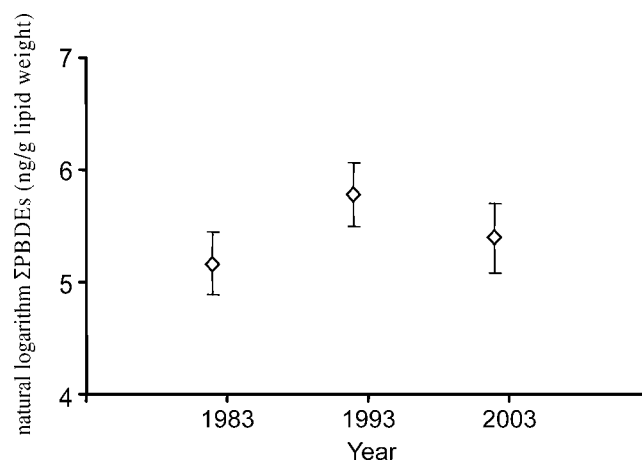


Fig. 2. Overall temporal trends (mean \pm confidence interval [natural logarithm]) of sum polybrominated diphenyl ethers (Σ PBDEs; pg/g lipid wt) in eggs of herring gulls (*Larus argentatus*), black-legged kittiwakes (*Rissa tridactyla*), and Atlantic puffins (*Fratercula arctica*) from North Norway. Levels of Σ PBDEs increased significantly from 1983 to 1993 ($p < 0.05$).

was not obvious for the other birds studied. The nona-BDEs in the studied seabird eggs might originate, in part, from debromination of deca-BDE in the eggs. The source from this might be from the mother bird or from the food ingested. Because of the low sample number, no conclusion could be made regarding the origin of the nona-BDEs in the studied bird eggs.

Reports of temporal trends of PBDEs in seabird eggs are scarce. The present results, however, corroborated a recent temporal trend study (1969–2001) of tetra- and penta-BDEs

Table 2. Overall and species-specific temporal trends (1983–2003) of polybrominated diphenyl ethers (PBDEs) in eggs of herring gulls (*Larus argentatus*), black-legged kittiwakes (*Rissa tridactyla*), and Atlantic puffins (*Fratercula arctica*) from North Norway^a

Species	Compound	1983–1993	1993–2003	1983–2003
Overall	BDE 28	↑↑	↓↓	—
	BDE 47	↑	—	—
	BDE 100	↑	—	—
	BDE 99	↑↑	↓↓	—
	BDE 153	↑↑	↓	↑
	BDE 154	↑↑	—	↑↑
Herring gull	BDE 28	↑	↓	—
	BDE 47	—	—	—
	BDE 100	—	—	—
	BDE 99	↑	—	—
	BDE 153	↑	—	↑
	BDE 154	↑	—	↑↑
Black-legged kittiwake	BDE 28	—	—	—
	BDE 47	—	—	—
	BDE 100	—	—	—
	BDE 99	↑	↓	—
	BDE 153	↑	—	—
	BDE 154	—	—	↑
Atlantic puffin	BDE 28	↑↑	↓↓	—
	BDE 47	↑	↓↓	—
	BDE 100	↑	↓↓	—
	BDE 99	↑↑	↓↓	↓
	BDE 153	↑↑	↓↓	↑
	BDE 154	↑↑	↓	↑

^a Two arrows indicate changes significant at $p < 0.0001$; one arrow indicates changes significant at $p < 0.05$. For all species in all years, $n = 10$ except for Atlantic puffins in 1993, for which $n = 9$.

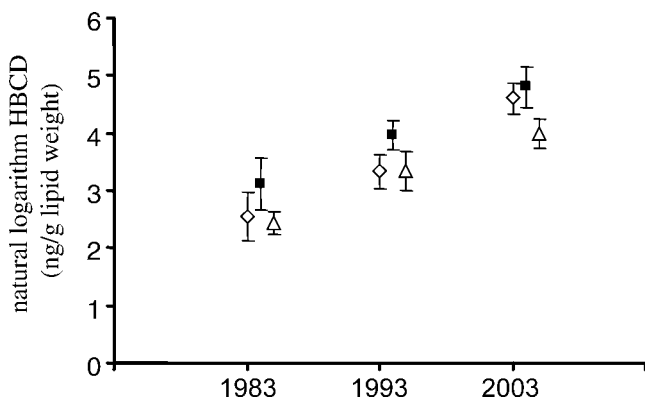


Fig. 3. Species-specific temporal trends (mean \pm confidence interval [natural logarithm]) of α -hexabromocyclododecane (α -HBCD) levels (pg/g lipid wt) in eggs of herring gulls (H. gull; *Larus argentatus*; \diamond), black-legged kittiwakes (Kittiwake; *Rissa tridactyla*; \blacksquare), and Atlantic puffins (Puffin; *Fratercula arctica*; \triangle) from North Norway. Levels of α -HBCD increased significantly from 1983 through 2003 in all species ($p < 0.0001$).

in eggs of common guillemots from the Baltic Sea [26]. That study reported increasing trends of PBDEs from the 1970s to the 1980s, with levels peaking around the mid to late 1980s and then dropping rapidly during the rest of the study period. The reports of decreasing/stable concentrations of PBDE in biota samples probably are explained by the phaseout in the production of penta-BDE and octa-BDE. In contrast to the reports mentioned above, studies in the Great Lakes and South Greenland documented increasing concentrations of PBDEs up until the turn of the century. For example, total levels of BDEs 99, 100, 153, and 209 in peregrine falcon eggs from South Greenland increased by 6 to 10% per year from 1986 to 2003 [29], whereas total concentrations of BDEs 28, 47, 99, 100, 153, 154, and 183 in herring gull eggs from the Great Lakes increased 20- to 75-fold from 1981 to 2000 [27].

Statistically significant increasing temporal trends were found for α -HBCD levels in herring gull, black-legged kitti-

wake, and Atlantic puffin eggs throughout the period of the present study (Fig. 3). This result is in contrast to findings in a similar study of total HBCDs in common guillemots from the Baltic [26]. In that study, peak concentrations were reported in the mid-1970s, followed by a decrease, by a second increase during the latter part of the 1980s, and finally, by no significant change from the 1990s to 2001 [26]. Furthermore, a temporal trend study (1986–2003) of HBCD levels in eggs of peregrine falcon from South Greenland revealed an insignificant decrease in concentrations of total HBCDs [29].

The percentage congener distribution of BFRs changed from 1983 to 2003. Generally, the proportion of BDE 47 to total BFRs (Σ BFRs) decreased from 1983 to 2003, whereas the proportion of α -HBCD relative to Σ BFRs increased during the same period (Fig. 4). An increase in α -HBCD concentrations and the proportion of α -HBCD relative to Σ BFRs from 1983 through 2003 probably is linked to the enhanced emission of this compound.

CONCLUSION

This is one of the first studies reporting nona-BDEs and BDE 209 in eggs of herring gulls, black-legged kittiwakes, and Atlantic puffins. Nevertheless, highly variable procedural blanks of BDEs 206, 207, 208, and 209 in the present study clearly illustrate the importance of repeatedly including blanks during the determination of these PBDE congeners.

We report a general increase in PBDE concentrations in Norwegian seabird eggs between 1983 and 1993, with a subsequent decrease/stabilization from 1993 to 2003. To date, few studies have assessed the temporal trends of PBDEs in seabird eggs; however, the results of the present study were corroborated by findings from a recent temporal trend study (1969–2001) of tetra- and penta-PBDEs in eggs of common guillemots in the Baltic Sea [26]. A reduction in emissions from European production could explain the decreasing concentrations of PBDEs in the present study. Nevertheless, concentration changes of PBDEs also might be associated with local use and emissions. Furthermore, large, species-specific dif-

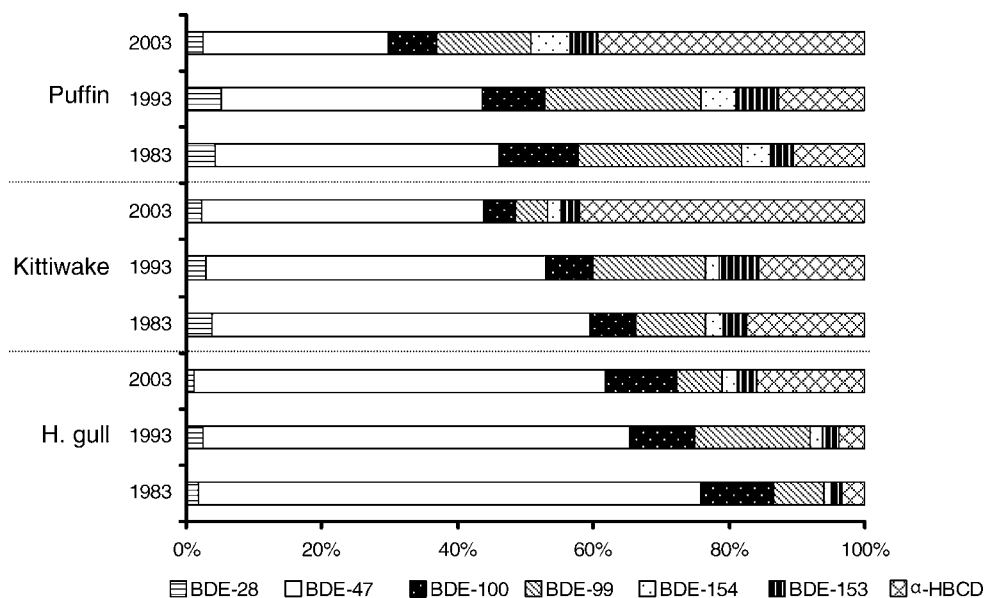


Fig. 4. Percentage congener distribution of brominated flame retardants in eggs of Atlantic puffins (puffins; *Fratercula arctica*; $n = 29$), black-legged kittiwakes (kittiwakes; *Rissa tridactyla*; $n = 30$), and herring gulls (H. gulls; *Larus argentatus*; $n = 30$) collected in 1983, 1993, and 2003.

ferences in temporal trends of contaminants were found, illustrating the differences in the ability of species to biotransform contaminants as well as in migration patterns and diet.

In concert with the decreasing/stabilizing concentrations of PBDEs in Norwegian seabird eggs, increasing temporal trends were found for α -HBCD throughout the study period. Furthermore, the percentage congener distribution of BFRs changed from 1983 to 2003, with an increase in the proportion of α -HBCDs relative to Σ BFRs. The increasing concentrations of HBCD most probably are explained by the enhanced emission of this compound. The present study shows that HBCD is present in the Norwegian environment and that levels are increasing in seabird eggs. More studies need to be conducted to assess if levels are approaching thresholds for biological effects.

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