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Brominated Flame Retardants in Polar Bears (*Ursus maritimus*) from Alaska, the Canadian Arctic, East Greenland, and Svalbard

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Polybrominated diphenyl ethers (PBDEs) were determined in adipose tissue of adult and subadult female polar bears sampled between 1999 and 2002 from sub-populations in Arctic Canada, eastern Greenland, and Svalbard, and in males and females collected from 1994 to 2002 in northwestern Alaska. Only 4 congeners (BDE47, 99, 100, and 153) were consistently identified in all samples. BDE47 was the major PBDE congener representing from 65% to 82% of the sum (Σ) PBDEs. Age was not a significant covariate for individual PBDEs or ΣPBDE. Higher proportions of BDE 99, 100, and 153 were generally found in samples from the Canadian Arctic than from Svalbard or the Bering-Chukchi Sea area of Alaska. Geometric mean ΣPBDE concentrations were highest for female polar bear fat samples collected from Svalbard (50 ng/g lipid weight (lw)) and East Greenland (70 ng/g lw). Significantly lower ΣPBDE concentrations were found in fat of bears from Canada and Alaska (means ranging from 7.6 to 22 ng/g lw). For the entire dataset, ΣPBDE concentrations were correlated with ΣPCBs. Higher total hexabromocyclododecane (HBCD) concentrations were found in fat of bears from Greenland and Svalbard than in those from Alaska. The geographical trends for PBDEs and HBCD parallel those for PCBs implying similar source regions for long range transport to the Arctic and bioaccumulation pathways in the arctic marine food web. All four major PBDE congeners were found to biomagnify from ringed seals to polar bears. BDE153 showed the greatest (71×) biomagnification factors (BMFs) and, on average, had a BMF that was 5.5-fold higher than for PCB congener 153 (13×) but similar to PCB congener 194 (73×), indicating that it is a highly bioaccumulative compound.

Introduction

The circumpolar distribution of the polar bear (*Ursus maritimus*), and its key role as apex predator in the marine environment, make it an important sentinel species for biomonitoring of spatial and temporal trends of contaminants (*1*−*4*). Feeding primarily on seals it is known to have some of the highest concentrations of organochlorine contaminants of any arctic species. Organochlorine pesticides (OCPs) and PCBs were first reported in polar bear tissues from Canada (*5*) and Greenland (*6*) nearly 30 years ago. Subsequently, PCBs, a wide range of OCPs and their metabolites (*7*), as well as PCB and PCB methyl sulfones (*8*), hydroxylated PCBs (*9*), chlorinated dioxin/furans (*10*), chlorinated naphthalenes (*11*), and perfluorinated acids (*12*, *13*), have been determined in polar bear populations.

Geographical trends of PCBs and OCPs have recently been examined in the Alaskan, Canadian, Greenland, and Svalbard populations by Verreault et al. (*14*) who followed up an earlier study by Norstrom et al. (*1*). Lie et al. (*15*) and Andersen et al. (*16*) studied selected PCBs and OCPs in polar bears in the Russian and Norwegian Arctic. To date, the highest degree of contamination among circumpolar polar bear populations has been reported from the western Russian Arctic, followed by the Svalbard area (*15*, *16*) and Eastern Greenland (*1*, *14*, *17*), whereas the lowest levels of PCBs and OCPs were reported from Alaska (Bering/Chukchi Sea) polar bear samples (*14*, *18*).

Brominated flame retardants have physical−chemical properties and use patterns somewhat similar to those of PCBs (*19*). There is, therefore, the potential for these compounds to be transported to the Arctic by the same pathways demonstrated to deliver PCBs to the Arctic. Using several global fate and transport models, Wania and Dugani (*19*) concluded that tetra- and penta- brominated PBDEs have arctic accumulation potential comparable to that of hexa−heptachloro biphenyls. Indeed, PBDEs have been detected in arctic air at low concentrations as well as in biota (*20*). PBDEs were first reported in arctic biota by Jansson et al. (*21*) who analyzed ringed seals (*Phoca hispida*) from Svalbard. Ikonomou et al. (*22*) showed that PBDEs had increased exponentially in ringed seals in the Canadian Arctic. Wolkers et al. (*23*) reported the detection of PBDE congener 47 (2,4,2′,4′-BDE) in polar bears along with other PBDE congeners (BDE 99, 100, 154) in polar cod (*Boreogadus saida*) and ringed seals from Svalbard. They concluded that polar bears were not the most suitable species for monitoring PBDEs because fewer congeners were detected in them than in seals or cod. However, detection limits in the study by

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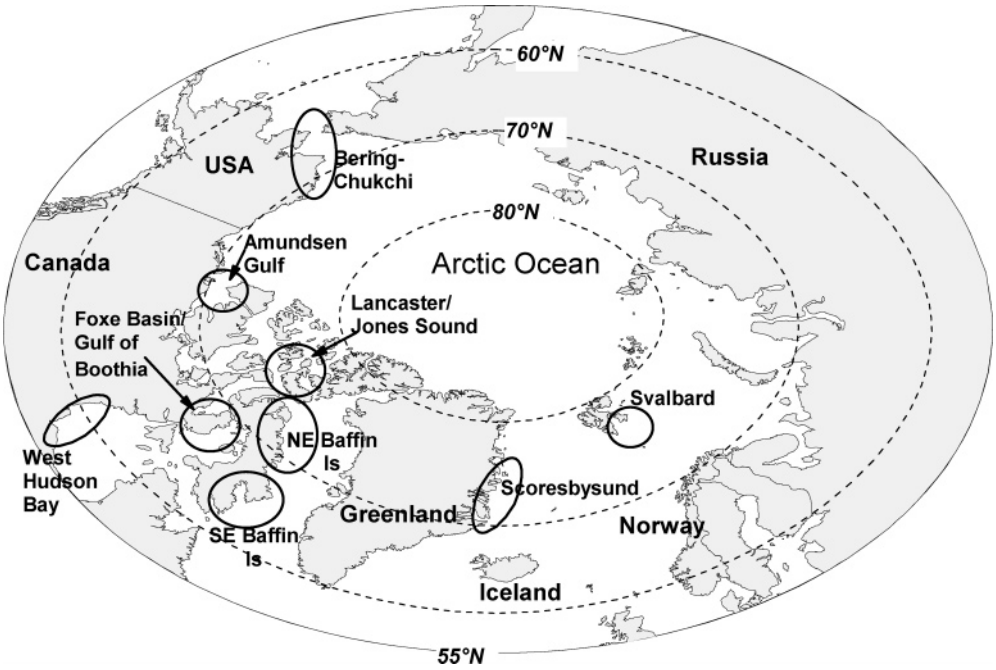

FIGURE 1. Map of arctic and subarctic regions showing the 9 sampling locations (circled areas) of polar bears: Bering-Chukchi Sea (Alaska), Amundsen Gulf, Western Hudson Bay, Foxe Basin/Gulf of Boothia, Lancaster Sound/Jones Sound, Northeastern Baffin Island, Southeastern Baffin Island (Canada), Scoresbysund (East Greenland), and Svalbard (Norway) area.

Wolkers et al. (*23*) were relatively high because of the use of mass spectrometry with electron ionization mode rather than the more widely used electron capture negative ionization mode. Verreault et al. (*24*) recently reported eleven BDE congeners, mainly comprised of BDE47 and with very low or nondetectable concentrations of BDE 209, in the plasma of female polar bears from Svalbard. Hexabromocyclododecanes (HBCDs), as represented by the α-HBCD isomer, were also detected in 14% of plasma samples of female Svalbard bears (*24*).

Spatial or geographic trends for PBDEs in the Arctic have not yet been determined in a systematic way although it is possible to infer from concentrations in ringed seal blubber reported by Wolkers et al. (*23*), Vorkamp et al. (*25*), and Ikonomou et al. (*22*) that PBDEs are higher in Svalbard and East Greenland than in the western Canadian Arctic.

Recently, a comprehensive study on the spatial trends of legacy, as well as $MeSO_2$-PCB/-*p*,*p*′-DDE metabolites, was carried out by Verreault et al. (*14*) in adipose tissue samples of polar bears from populations spanning Arctic regions of Canada, Alaska, East Greenland, and Svalbard based on samples collected mainly from 1999 to 2002. The study found geographic trends similar to those observed by Norstrom et al. (*1*) with highest levels in samples from East Greenland and Svalbard. Samples were also available from a detailed study of effects of age and sex on PCBs and OCPs in polar bears from Eastern Greenland (*17*). The objective of the present study was to determine PBDEs and HBCD in many of the same samples that had been analyzed for OCP/PCBs and to assess geographical trends as well as influence of sex and age. An additional objective was to examine biomagnification of PBDEs from seals to bears at multiple locations.

Materials and Methods

Sample Collection. Field sampling has been described in detail by Verreault et al. (*14*) and Dietz et al. (*17*, *26*) and was conducted under research licenses/permits from appropriate agencies in each country. Approximate sampling areas are shown in Figure 1 and latitude and longitude of the areas are given in the Supporting Information (Table S1). In the Canadian Arctic, Alaska, and Greenland, subcutaneous adipose tissue samples were collected from harvested bears as part of the Inuit subsistence hunt regulated by community quotas. Subcutaneous fat/fat biopsy samples were taken from the base of the tail (rump fat) within 12 h post mortem. In Svalbard, fat biopsy samples were collected from free-ranging bears tranquilized for research purposes by remote injection of a drug (Zoletil) in a dart fired from a helicopter. Samples were stored in individual polyethylene vials or small clear polyethylene (Whirlpak) bags. All samples were kept at −20 °C prior to sample preparation and extraction. Date, location of sampling, and sex were recorded for each individual, and a vestigial premolar tooth was extracted for age determination. The age of the individuals was determined by counting annual growth layers in the cementum of the tooth according to methods described elsewhere (*27*−*29*).

Contaminant Analyses. PBDEs and HBCD were analyzed in sample extracts and certified reference materials previously extracted for legacy PCB/OCPs. Details of the extraction and isolation procedures are given in Verreault et al. (*14*) and Dietz et al. (*26*, *30*). Samples from Canada and Greenland were extracted at the Great Lakes Environmental Research Institute (GLIER) at the University of Windsor and those from Alaska and Svalbard were extracted at the National Laboratory for Environmental Testing (NLET) at the National Water Research Institute. In brief, accurately weighed fat samples (0.5−1 g) were homogenized with anhydrous sodium sulfate (6:1 ratio by weight), and all were spiked with 1,3,5-tribromobenzene (TrBB) prior to extraction. Samples from AK and Svalbard were also spiked with 1,2,4,5-tetrabromobenzene (TeBB), δ-HCH, and PCBs 30 and 204. Samples were extracted using dichloromethane (DCM) and lipids and other biogenic materials were removed by gel permeation chromatography (GPC). The percent extractable lipid content (±0.1%) was determined gravimetrically by evaporating the first GPC fraction (130 mL). At GLIER the remaining GPC fraction (170 mL) was concentrated and eluted through a 33% KOH/silica gel (1.5 g) column with *n*-hexane/DCM (1:1), concentrated to 1 mL and applied to a Florisil column (8.0 g, 1.2% H_2O deactivated). The column was eluted with hexane followed by *n*-hexane:DCM (1:1) to separate PCBs from most PBDEs except BDE 47 which partially eluted in Fraction 1. The second

TABLE 1. Geometric Mean Concentrations and Ranges (ng/g Lipid Weight) of PBDEs, HBCD, and Total PCBs in Polar Bear Fat from 9 Arctic Locations (Figure 1)[a]

location		*N*	sex	% lipid	age (yrs)	BDE 47	BDE 99	BDE 100	BDE 153	ΣPBDE	PCB/PBDE ratio	HBCD[a]	ΣPCB[b]
Svalbard area	mean	15	F	91	12	40.6	2.30	0.87	3.18	49.8	73	44.4	5570
	min			71	5	23.7	0.14	0.14	0.15	27.0	66	18.2	2560
	max			100	25	86.7	13.71	4.73	9.73	114	80	109	14590
East Greenland	mean	44	F	90	7.9	50.9	3.85	1.47	11.8	69.6	95	44.5	6280
(Scoresbysund)	min			17	0.5	25.9	1.63	0.68	3.1	34.8	46	32.4	2310
	max			100	23	99.8	7.00	2.94	35.2	132	189	58.6	19760
NE Baffin Is	mean	9	F	96	6	12.9	2.39	0.65	1.66	18.5	34		2650
	min			84	4	3.0	1.14	0.06	0.05	4.4	8		1270
	max			94	11	27.7	5.69	1.63	10.5	43.1	54		4630
SE Baffin Is	mean	17	F	85	7	13.6	2.32	0.67	3.58	21.9	30		2670
	min			60	2	3.88	1.21	0.37	0.28	6.2	0		1170
	max			100	20	25.2	7.60	1.74	34.8	48.9	65		5090
Lancaster/	mean	6	F	89	10	8.85	2.29	0.50	0.69	13.2	21		1690
Jones Sound	min			89	4	5.41	1.76	0.27	0.05	8.1	5		1020
	max			81	19	30.9	3.17	0.93	4.51	39.1	64		2910
Foxe Basin/	mean	8	F	89	5	7.60	2.34	0.41	0.68	11.7	34		1010
Gulf of Boothia	min			17	2	4.10	1.04	0.06	0.27	5.8	4		449
	max			100	9	31.8	11.3	2.77	9.53	55.6	63		2720
West Hudson	mean	15	F	56	9	9.93	1.91	0.49	1.23	14.4	36		2610
Bay	min			23	3	2.63	1.02	0.06	0.24	4.3	9		1520
	max			81	14	27.1	6.62	2.00	7.76	45.5	60		8470
Amundsen	mean	10	F	95	6	11.0	2.46	0.68	1.50	16.1	37		2020
Gulf	min			85	2	3.78	0.85	0.25	0.29	5.3	31		865
	max			100	22	25.5	6.75	1.56	7.24	40.5	43		5190
Bering-	mean	8	F	60	8	4.93	0.78	0.20	0.11	6.71	480	0.40	2530
Chukchi Sea	min			36	4	3.49	0.51	0.12	<0.08	4.64	140	<0.01	1550
	max			90	14	7.28	1.42	0.31	0.68	11.3	770	35.1	5010
Bering-	mean	7	M	67	9	5.20	1.44	0.22	<0.08	6.84	380	<0.01	2380
Chukchi Sea	min			32	4	1.74	0.15	0.10	<0.08	2.91	220		1550
	max			100	14	12.7	3.00	0.96	0.26	16.6	670		4320

[a] Only females were analyzed except for bears from the Bering-Chukchi Sea area. [b] Sample numbers for HBCD were East Greenland,11; Svalbard, 15; Bering-Chukchi, 15. [c] PCB data results for individual samples analyzed by Verreault et al. (*14*) for which PBDE data were also available.

elution of 15% DCM/*n*-hexane contained the PBDEs except for BDE 209 which was not recovered efficiently from Florisil (*31*). Samples from Alaska and Svalbard were chromatographed on activated silica gel (8 g, 1.1 cm i.d. column), and eluted with hexane followed by *n*-hexane/DCM (1:1) to separate PCBs from most of the PBDEs. Again BDE 47 partially eluted in Fraction 1 and the bulk of the PBDEs eluted in Fraction 2. BDE 209 quantitatively eluted in the silica Fraction 1. The Florisil and silica gel elutions were concentrated to 1 mL by weight density (37 °C), and to the final volume of 100 μL in 2,2′,4-trimethylpentane (isooctane) under a gentle nitrogen flow.

Analyses of all PBDE/HBCD extracts were all carried out at NLET by gas chromatography−low resolution mass spectrometry (GC−MS) in electron capture negative ionization mode (GC-ECNIMS) on an Agilent 6890 GC-5973 MSD using HP5-MS capillary column (30 m × 0.25 mm × 0.25 um). Helium was used as carrier gas and separation was performed at a constant flow of 1.2 mL/min. Injection of 2 μL was performed in pulsed splitless mode at 172 kPa for 1.0 min at an injector temperature of 250 °C. The initial column temperature was 80 °C for 2 min, heated at 10 °C/min to 120 °C, and 3 °C/min to 285 °C, which was held for 15 min. The mass spectrometer was operated in the NCI mode with methane as the buffer gas. The temperatures were 106, 150, and 300 °C for the quadrupole, the ion source, and the interface, respectively. All PBDEs and HBCD were monitored at *m*/*z* 79/81. PBDEs and HBCD were quantified using an external standard consisting of 36 congeners (BDEs 7, 8, 10, 11, 12−13, 15, 30, 32, 28−33, 35, 37, 49, 47, 66, 71, 75, 77, 85, 99, 100, 105, 119, 116, 155−126, 138, 140, 153, 154, 166, 181, 183, 190, and 209). PCBs and OCPs were determined in the same extracts using GC-ECD as described in Verreault et al. (*14*) and Dietz et al. (*30*). BDE 209 was chromatographed using a 15-m DB5 column using the same GC conditions as for the lower brominated BDEs.

Quality Assurance. The certified reference material (SRM 1945, pilot whale blubber homogenate) from the National Institute of Standards and Technology (Gaithersburg, MD) was used in both analytical labs as a check of the accuracy and reproducibility of the entire analytical procedure. BDE47, 99, and 100 were within 15% of the consensus values in SRM 1945 reported by Kucklick et al. (*32*). In addition, 1 in 12 samples was extracted and analyzed in duplicate. Average deviation (relative to mean values; N = 8) was 9.0%, 19%, 19%, and 12%, respectively. The mean recoveries (±1 standard deviation (SD)) of 1,3,5-TrBB and 1,2,4,5-TeBB were 91±13 and113±21% (n = 82), respectively. Mean recoveries of PBDEs and HBCD spiked in triplicate at the Soxhlet extraction stage ranged from 81 to 129% (Table S2, Supporting Information). Reagent blanks that were run with each batch of 6 samples indicated minor background contribution from BDE47 representing from nil to 20% of the concentration of this congener in fat samples. Results were corrected by subtracting the blank on a batch by batch basis. Method detection limits (MDL) based on 3 × SD of the blanks after blank correction ranged from 0.01 ng/g lw for HBCD to 1.5 ng/g lw for BDE 47 (Table S2).

Data Analyses. Individual polar bears were grouped according to their location of capture or of harvest by Inuit hunters (Table 1 and Figure 1). Statistical analysis was conducted with Systat Ver 11 (Systat Software Inc.,Point Richmond, CA). Data for major PBDE congeners, sum PBDEs (ΣPBDE), and sum PCBs (ΣPCBs) were log10 transformed to reduce skewness and kurtosis. Shapiro−Wilk's tests indicated that log transformed data from each location were normally distributed. Analyses of covariance (ANCOVA) were performed to examine the effect of location and age on PBDE

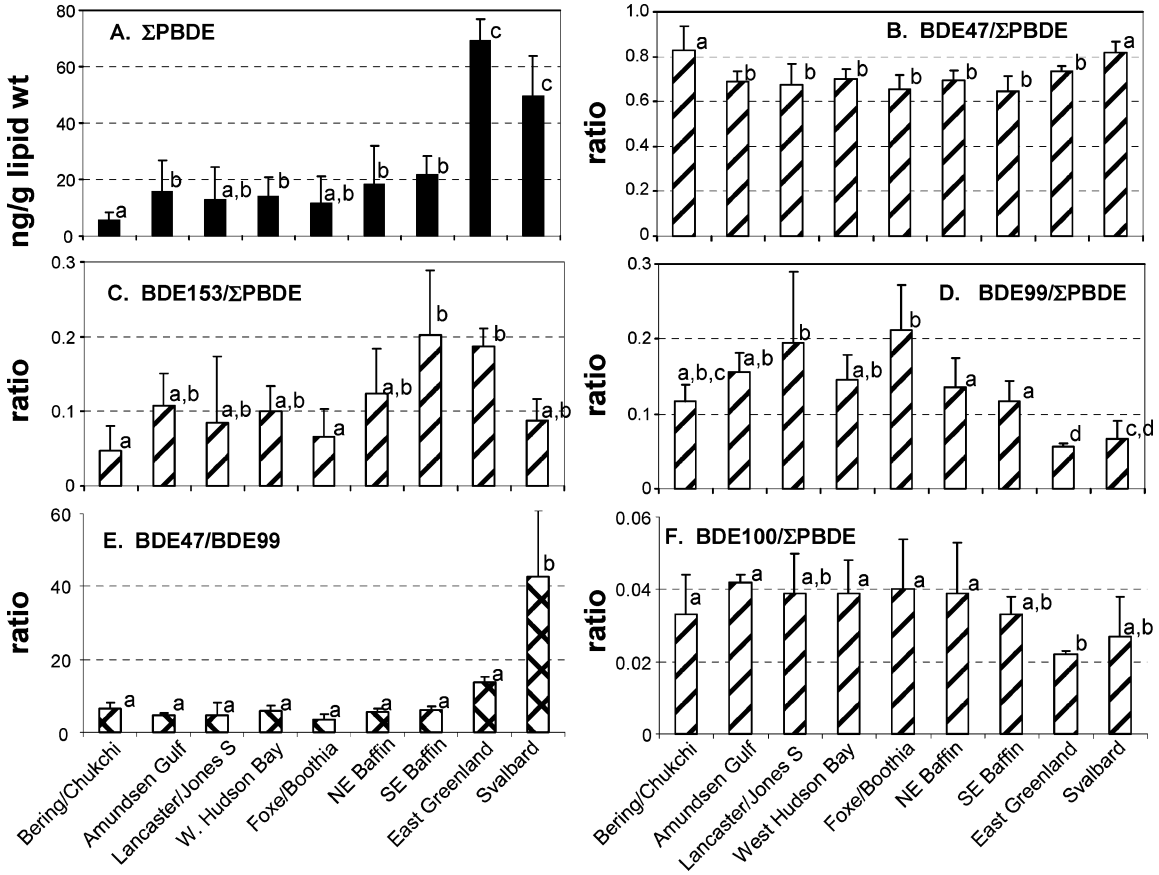

FIGURE 2. (A) Mean concentrations of ΣPBDEs (geometric means, lipid weight basis), (B−E) arthimetic mean PDE congener/ΣPBDE ratios, and (F) BDE47/BDE99 ratio, in female polar bears from 9 areas in the Arctic. Results are arranged longitudinally from west to east. Vertical lines are upper 95% confidence limits on the means. Means with the same letters are not significantly different (Tukey's test, $P > 0.05$).

concentrations, using the model [BDE congener] = location + age + (age × location). Because age × location was significant, while age was not significant, the model was reduced to [BDE congener] = location and a post hoc Tukey's test was performed to examine differences among locations ($P < 0.05$).

Results and Discussion

Identification of PBDEs and HBCD. Sample extracts from Canadian Arctic and East Greenland polar bears were screened for 33 PBDEs (dibromo- to heptabromo-BDEs) using low resolution GC-ECNIMS. However, only 4 PBDEs (47, 99, 100, and 153) were consistently identified. Chromatograms of a 33 congener standard and a sample from East Greenland are provided in the Supporting Information (Figure S1). BDE 17, 28−33, 66, 85, 154, 155−126 were identified in 1−8% of all samples. Samples from Svalbard and Bering-Chukchi were analyzed for the most common 13 PBDEs based on the low frequency of detection in the other samples. Higher frequencies of detection of congeners other than the major 4 were found in the Bering-Chukchi samples despite the lower numbers of congeners analyzed, e.g., BDE 17, 66, 155−126 (Supporting Information, Figure S2). These results point to possible regional differences in a broader array of congeners but further work using lower detection limits would be required to confirm this. Samples from Svalbard were screened for BDE 209 but it was not detected in any samples (<0.05 ng/g) (SI Figure S3). Therefore, the remaining discussion will focus on the 4 major PBDE congeners that were found in >65% of all samples.

Also identified was HBCD, which was present in 100% of the East Greenland samples (11 analyzed), 100% of Svalbard samples, and 13% of samples from the Bering-Chukchi. Chromatograms of the HBCD standard and a sample from East Greenland are provided in the SI (Figure S4). While HBCD is usually determined by LC−MS in order to separate individual congeners, we were able to chromatograph it successfully by GC. As discussed in Verreault et al. (*24*) any β- and γ-HBCD residues in the samples were most likely thermally isomerized to α-HBCD and/or degraded in the GC injection port, thus our results represent total HBCD.

Levels, Patterns, and Geographical Trends. The samples were collected from polar bear management zones or areas that have been identified as having distinct polar bear subpopulations (*1*). All samples were collected in the period 1999−2002 except for those from Alaska which were collected over the period 1994−2002. We restricted the analyses to female polar bears to reduce age (and age/reproductive) effects anticipated based on PCB and persistent OC pesticide trends with age in bears (*1*, *7*, *26*). Results of ANCOVA indicated that age was not a significant co-variate for individual PBDEs or ΣPBDE. Dietz et al. (*26*) also found no correlation of ΣPBDE with age of male and female polar bears from East Greenland. ΣPCB concentrations were not correlated with age of females in the same populations studied here. This was probably because reproductively active females excrete lipophilic contaminants via lactation (*1*).

Mean concentrations and ranges of major individual PBDEs, ΣPBDE, HBCD, and ΣPCB are presented in Table 1. Geometric mean concentrations of ΣPBDE ranged from 6.7 ng/g lipid weight (lw) in the Bering-Chukchi females to 69.6 ng/g lw in East Greenland (Figure 2A). Concentrations of ΣPBDE were significantly higher in bears from East Greenland and Svalbard than all other locations. BDE 47 was the most prominent individual congener with geometric means ranging from 4.93 ng/g lw in the Bering-Chukchi Sea group to

TABLE 2. Biomagnification Factors[a] for PBDE Congeners and CB 153 in Polar Bears Assuming Ringed Seal as the Prey Species

polar bear population	ringed seal location	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	CB153	CB180	CB194
Amundsen Gulf	Sachs Harbor[b]	3.3	3.4	5.8	130	1.5	13	33	81
Lancaster & Jones Sound	Grise Fiord/Resolute[b]	4.5	11	6.7	58	2.9	7.0	23	63
Southeast Baffin Is	Pangnirtung[b]	7.4	8.0	8.8	91	1.1	17	39	66
East Greenland[c]	Scoresbysund	1.8	1.0	0.6	8.8	0.2	12	33	82
Svalbard[d]	NE Svalbard	2.5	5.9	1.3			16		
,average BMF		3.9	5.8	4.7	71	1.8	13	32	73

[a] BMF = mean lipid wt concentration in bears divided by mean concentration in seal blubber. [b] Results for Sachs Harbor, Grise Fiord/Resolute, and Pangnirtung are from adult female ringed seal blubber collected in 2000−2003 (*43*). [c] Results for seals are from Vorkamp et al. (*25*). [d] Results for seals are from Wolkers et al. (*23*). BDE 153 was not reported and BDE 154 was not detected in seals this study.

50.9 ng/g lw in East Greenland females. Mean BDE47/ΣPBDE ratios varied from 0.65 to 0.82 among the 9 locations and were significantly higher in samples from the Bering/Chukchi Sea and at Svalbard (Figure 2B). BDE 153 was the next most prominent congener, except in the western North American Arctic, ranging from 0.11 ng/g in Bering-Chukchi animals to 11.8 ng/g lw in East Greenland bears. BDE153/ΣPBDE ratios were significantly higher in Southeast Baffin and East Greenland animals than all other locations while lowest fractions of BDE153 were found in animals from the Bering/Chukchi Sea (Figure 2C). BDE 99 was more prominent than BDE 153 in western North American Arctic bears (Amundsen Gulf and Bering-Chukchi Sea). BDE 99/ΣPBDE ratios were highest in samples from the Canadian Arctic and lowest in the Bering/Chukchi Sea, East Greenland, and Svalbard animals (Figure 2D). BDE47/BDE99 ratios were significantly higher at Svalbard compared to all other locations and otherwise did not differ significantly (Figure 2E). BDE 100 was generally present at lower concentrations than the other 3 congeners (Table 1) and BDE100/ΣPBDE ratios were significantly lower in East Greenland than in Bering-Chukchi and most Canadian locations (Figure 2F).

HBCD was determined only in a subsample of the Greenland bears ($N = 11$) and in all Bering-Chukchi and Svalbard bears. HBCD geometric mean concentrations were similar to those for BDE 47 in the Svalbard and East Greenland samples but much lower, on average, in Bering-Chukchi samples (Table 1). In the only previous report on HBCD in polar bears, concentrations were <0.03−0.85 ng/g ww in plasma and quantifiable in only 14% of samples of female polar bears from Svalbard (*24*), the same bears for which fat was analyzed in the present study. HBCD/BDE47 ratios were much lower in plasma (∼0.09) (*24*) compared with fat (1.1) indicating that HBCD is preferentially stored in fat relative to the PBDEs.

Mean concentrations and ranges of ΣPBDE in fat of female polar bears from Svalbard reported by Wolkers et al. (*23*) were almost identical to our observations (geomeans of 45 ng/g lw vs 50 ng/g lw). Wolkers et al. (*23*) detected only BDE47 in polar bears from Svalbard while this study found BDE47 represented about 82 ± 9% of ΣPBDE. The samples analyzed by Wolkers et al. were collected in 1999 whereas the ones from Svalbard used in this study were collected in 2002. Whether this 3 year difference had any effect is unknown because the time trends of PBDEs in Svalbard bears, and in polar bears in general, have not yet been studied.

Temporal trends of PBDEs in top predators from northern environments vary. Ikonomou et al. (*22*) found exponential increases of ΣPBDEs in ringed seals from the Amundsen Gulf region of the western Canadian Arctic from 1981 to 2000, however, more recent results from this group have shown a leveling off or decline from 2000 to 2003 (*33*). ΣPBDEs increased at about 10% per year between 1981 and 2003 in peregrine falcon (*Falco peregrinus*) in southern Greenland with no decline post-2000 (*34*). ΣPBDEs declined in fur seals (*Callorhinus ursinus*) from northern Japan during the 1990s following restrictions on PBDE use there (*35*) and have also declined in guillemot (*Uria algae*) eggs from the Baltic Sea (*36*). With the exception of samples from the Bering-Chukchi area, our samples were collected over a relatively narrow time window (1999−2002) such that changing PBDE concentrations in the polar bear food web probably have little impact. In the case of the Bering-Chukchi samples the wider time window (1994−2002) may have added to the variance of PBDE concentrations among samples although no consistent trend with sampling year was found for either females or males.

Concentrations of individual PBDE congeners were strongly correlated with each other ($P < 0.05$) at all locations but not with ΣPCB or CB153 concentrations in the same animals. The only exception was for samples from East Greenland where BDE47, BDE100, and BDE 153 were strongly correlated with CB153 and ΣPCB ($P < 0.01$). The larger sample size for this group ($N = 44$) may have helped in terms of statistical power. For the entire dataset, however, log ΣPBDE concentrations were significantly correlated with log ΣPCB ($R^2 = 0.41$, $P < 0.001$). ΣPCB/ΣPBDE ratios ranged from 21 in Lancaster Sound to 95 in East Greenland but were much higher (480) in female bears from the Bering-Chukchi area (Table 1). Mean ΣPCB/ΣPBDE ratios did not differ significantly in the Canadian Arctic bears nor between Svalbard and East Greenland. Thus, with the exception of the Alaskan bears, PBDEs appear to track PCBs implying common pathways in the marine food web. The exceptionally high ΣPCB/ΣPBDE ratios for the Bering-Chukchi animals imply much lower inputs of PBDEs to this region which, judging from past work on semi-volatile OCPs such as HCH isomers, is strongly influenced by Asian sources (*37*). The declining ΣPBDE concentrations in fur seals from Northern Japan during the 1990s suggests that eastern Asia was not a strong source region for Br_4−Br_6−PBDEs in the northern Bering Sea and Chukchi area. PBDEs (Br_4−Br_6) in skipjack tuna (*Katsuwonus pelamis*) from the central North Pacific were also much lower than in samples from the Japan Sea and the East China Sea (*38*).

The significantly higher BDE 99/ΣPBDE and BDE 100/ΣPBDE in Canadian Arctic animals compared to other locations (e.g., Bering-Chukchi and Svalbard) (Figure 2D and F) may be an indication of the influence of the use "penta" PBDE formulations in North America. About 95% of the global use of this brominated flame retardant product was in North America in 2001 (*39*) and, although it is now being phased out, there is a large amount in use. There is evidence for PBDEs in the arctic atmosphere from passive air sampling studies in the European Arctic (*40*) and northern Canada (*41*). The BDE 47/99 ratios in these studies were about 1 in air samples indicating that both congeners, which are major components of the "penta" product, are entering the arctic environment. In contrast, the PBDE pattern in polar bear fat is dominated by BDE47 presumably due to greater bioaccumulation of this isomer although debromination of BDE 99 (*42*) cannot be ruled out. The detection of BDE183 and

BDE209 in the plasma of female Svalbard bears (*24*) also suggests exposure of bears to BDE183 and BDE209 in the food web and this could be underestimated as a consequence of metabolic debromination. Ueno et al. (*38*) found higher ratios of BDE 47/99 in skipjack tuna with increasing latitude in the western North Pacific Ocean which they attributed to greater long-range transport of BDE47. Thus discrimination among isomers during long-range transport, as well as during bioaccumulation and metabolism, is influencing the congener pattern observed in polar bears and, as a result, source signatures could be lost.

Biomagnification. To investigate the influence of bioaccumulation within the polar bear marine food web on PBDE congener patterns we compared concentrations of PBDEs in ringed seal, the main prey species for polar bears, with those in bears from locations where data were available for both (Table 2). Results for ringed seals were available for Amundsen Gulf, Lancaster/Jones Sound, and Southeast Baffin Island polar bear populations using PBDE data from female ringed seals collected near the communities of Sachs Harbor, Grise Fiord, and Pangnirtung (*43*), East Greenland (*25*), and Svalbard (*23*). Biomagnification factors (BMFs) were, on average, >1 for BDE 47, 99, 100, 153, and 154 indicating overall accumulation from prey to predator. With the exception of BDE 153, the PDBEs had lower BMFs than CB153, CB180, and CB194 in the same locations. BDE 153 (2,2′,4,4′,5,5′-hexaBDE) has the same halogen substitution pattern as CB153 which may make it resistant to biodegradation and/or result in low efficiency of transfer via lactation. Boon et al. (*44*) observed BMFs of >10 between fish and harbor seal (*Phoca vitulina*) for BDE 47, 99, and 153 in the North Sea marine food web. Similar to the present study, BDE 100 and 154 had lower fish−seal BMFs than BDE 99 or BDE153, possibly due to their 2,2′,6 or 6′ (tri-ortho) substitution pattern which may make them susceptible to CYP450 oxidation or debromination. The BMF for BDE 153 ranged widely but was, on average, 5.5-fold higher than that for CB153 and similar to the BMF for the hepta- and octachlorobiphenyls, CB180 and CB194 (Table 2), indicating that it is a highly bioaccumulative compound. The polar bear−seal BMFs were relatively consistent despite the large distances among sites, e.g., between Amundsen Gulf in the western Canadian Arctic and Svalbard. The exceptions were the BMFs for BDE 99, 100, and 153 in East Greenland which were lower than those at all other sites (Table 2). This may imply differences in the transformation of PBDEs in the marine food web leading to polar bears or to food web differences. PCB BMFs showed much less variation among sites. Species differences in bioaccumulation and biotransformation of PBDEs have been noted for fishes (*42*, *44*) and this could lead to differences in congener patterns in fish-eating mammals and their predators.

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Supporting Information Available

Sampling dates and latitude/longitude of sampling areas, recoveries and MDLs of PBDEs, and sample chromatograms illustrating detection of PBDEs and HBCD. This material is available free of charge via the Internet at http://pubs.acs.org.

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