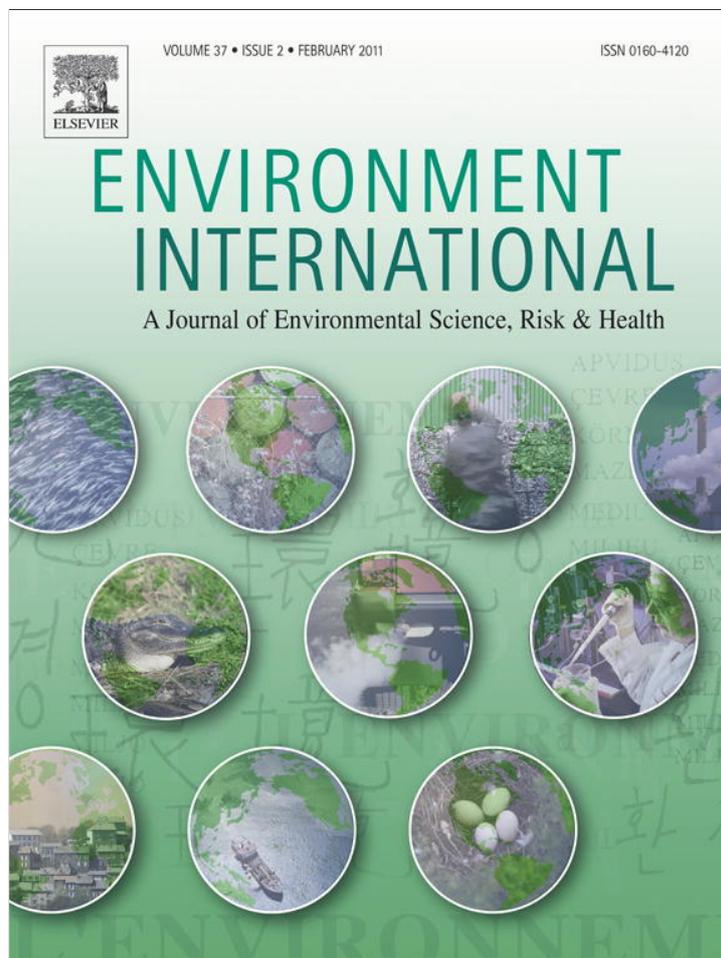


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Flame retardants and legacy contaminants in polar bears from Alaska, Canada, East Greenland and Svalbard, 2005–2008

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ABSTRACT

Flame retardants and legacy contaminants were analyzed in adipose tissue from 11 circumpolar polar bear (*Ursus maritimus*) subpopulations in 2005–2008 spanning Alaska east to Svalbard. Although 37 polybrominated diphenyl ethers (PBDEs), total-(α)-hexabromocyclododecane (HBCD), 2 polybrominated biphenyls (PBBs), pentabromotoluene, pentabromoethylbenzene, hexabromobenzene, 1,2-bis(2,4,6-tribromophenoxy)ethane and decabromodiphenyl ethane were screened, only 4 PBDEs, total-(α)-HBCD and BB153 were consistently found. Geometric mean \sum PBDE (4.6–78.4 ng/g lipid weight (lw)) and BB153 (2.5–81.1 ng/g lw) levels were highest in East Greenland (43.2 and 39.2 ng/g lipid weight (lw), respectively), Svalbard (44.4 and 20.9 ng/g lw) and western (38.6 and 30.1 ng/g lw) and southern Hudson Bay (78.4 and 81.1 ng/g lw). Total-(α)-HBCD levels (<0.3–41.1 ng/g lw) were lower than \sum PBDE levels in all subpopulations except in Svalbard, consistent with greater European HBCD use versus North American pentaBDE product use. \sum PCB levels were high relative to flame retardants as well as other legacy contaminants and increased from west to east (1797–10,537 ng/g lw). \sum CHL levels were highest among legacy organochlorine pesticides and relatively spatially uniform (765–3477 ng/g lw). \sum DDT levels were relatively low and spatially variable (31.5–206 ng/g lw). However, elevated proportions of *p,p'*-DDT to \sum DDT in Alaska and Beaufort Sea relative to other subpopulations suggested fresh inputs from vector control use in Asia and/or Africa. Comparing earlier circumpolar polar bear studies, \sum PBDE, total-(α)-HBCD, *p,p'*-DDE and \sum CHL levels consistently declined, whereas levels of other legacy contaminants did not. International regulations have clearly been effective in reducing levels of several legacy contaminants in polar bears relative to historical levels. However, slow or stalling declines of certain historic pollutants like PCBs and a complex mixture of “new” chemicals continue to be of concern to polar bear health and that of their arctic marine ecosystems.

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1. Introduction

Despite long distances from source regions, arctic environments and ecosystems are subject to contamination by a complex suite of industrial and agricultural chemicals and by-products known as

persistent organic pollutants (POPs) and collectively classified as organohalogen chemicals (Macdonald et al., 2000). Regarded as an environmental concern for approximately the last five decades, the original or “legacy” organohalogenes include the polychlorinated biphenyls (PCBs) and various organochlorine pesticides (OCPs). PCBs found use mainly as electrical insulators. In general, OCPs were applied as insecticides for agriculture and to control insect vectors of disease. Due to their characteristic persistence, potential for long-range transport, bioaccumulation and human and environmental health risks, these legacy POPs have been banned or severely restricted under national and international regulations. (e.g., Stockholm Convention on Persistent Organic Pollutants).

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Numerous recent- or current-use chemicals have also been released into the environment intentionally or by accidental leakage, some of which have accumulated in the Arctic and its biota. Examples include the current-use pesticide endosulfan as well as chemicals used in consumer products, such as those classified as poly- and perfluorinated compounds (PFCs) and brominated flame retardants (BFRs) (Butt et al., 2010; de Wit et al., 2010; Letcher et al., 2010; Weber et al., 2010). Recent- and current-use BFRs include but are not limited to polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) isomers, pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE). PBBs have not been used in North America since the 1970s; however, the DecaBB product was produced until 2000 in France (de Boer et al., 2000). The PBDE products, PentaBDE and OctaPBDE, have been phased out of use in the European Union and were voluntarily withdrawn from production in North America in 2004. In 2009, tetra-through hepta-brominated PBDEs, hexa-brominated PBBs, and several other chemicals were additionally listed under the Stockholm Convention (Stockholm Convention on Persistent Organic Pollutants, 2010). BTBPE has been marketed for use as a replacement for OctaBDE, and DPDPE is considered an alternative to DecaBDE (de Wit et al., 2010). DecaBDE is still produced, despite evidence that degradation of the primary component, BDE209, is a potential source of currently banned lower brominated congeners to the environment (Hakk and Letcher, 2003; Söderström et al., 2004). Phase-out of DecaBDE production in the United States is scheduled for 2012 (Bromine Science and Environment Forum, 2010). There are currently no restrictions on the production or use of HBCD, although it has been proposed for addition to the Stockholm Convention (de Wit et al., 2010). PBT, PBEB, HBB, BTBPE and DPDPE remain unregulated.

The polar bear (*Ursus maritimus*) is an ideal species for assessing the spatiotemporal trends of “emerging” BFRs and legacy POPs within arctic marine ecosystems (Norstrom et al., 1998). Polar bears are circumpolarly distributed, yet occur as regional subpopulations. Ongoing studies have secured samples from live handled bears or from individuals taken as part of annual quotas of subsistence hunted subpopulations. As top trophic feeding predators of arctic and subarctic marine food webs, polar bears accumulate high levels of, in particular, PCBs and chlordanes (CHLs). Given high contaminant biotransformation capacities, polar bears also have elevated tissue levels of persistent metabolites, including oxychlordanes and methyl-sulfone-(MeSO₂-) PCBs, relative to their prey (Letcher et al., 1998; Norstrom and Muir, 1994). Several studies have reported correlations between organohalogen levels and chemical biomarkers of endocrine, immune and reproductive function in particular polar bear subpopulations (Letcher et al., 2010; Skaare et al., 2000; Sonne, 2010). These potential health effects have been supported by controlled studies on model *Canoidea* species, specifically, Greenland sledge dog (*Canis familiaris*) and Norwegian Arctic fox (*Vulpes lagopus*) (Letcher et al., 2010; Sonne, 2010). Taken together, these studies indicate that polar bear contaminant burdens, in part, reflect the state of arctic marine ecosystem contamination and that this species may be a sensitive indicator of environmental health risks associated with such contamination. More specifically, continued monitoring of organohalogenes may provide information on polar bear health and on subpopulations which may be particularly vulnerable with respect to contaminant exposures.

The most comprehensive spatiotemporal trends studies of PCBs and OCPs to date on arctic biota have been on polar bears, with the exception of limited data on Russian subpopulations. In the first hemispheric-scale spatial comparison of selected chlorinated contaminants between subpopulations, adipose samples collected from 1989–1993 showed an increasing trend in \sum PCB, DDE, \sum MeSO₂-PCB and to a lesser extent \sum CHL levels from Alaska east to East

Greenland and Svalbard (Letcher et al., 1995; Norstrom et al., 1998). Elevated levels of POPs have also been observed in other high trophic level European Arctic biota relative to those from the North American Arctic (de Wit et al., 2004). Polar bears sampled in 1987–1995 from the western Russian Arctic (Franz Josef Land and Kara Sea) had higher \sum PCB levels than reported previously in other circumpolar subpopulations (Andersen et al., 2001). Samples collected in 1996–2002 again showed increasing trends in PCB and DDT levels from Alaska east to East Greenland and Svalbard, but a reversed gradient for hexachlorocyclohexanes (HCHs) (Verreault et al., 2005). For this 1996–2002 dataset, lower absolute levels but similar spatial patterns to PCBs were found for polybrominated diphenyl ethers (PBDEs) (Muir et al., 2006). However, to our knowledge there have been few or no geographic comparisons in any arctic biota for other “new” or replacement BFRs. New research building on previous studies can be used to address the emerging presence of recent-/current-use chemicals such as these BFRs, to assess the effectiveness of international controls on emissions of legacy POPs, and as well, to investigate possible climate change-related shifts in contaminant exposures due to, e.g., food web changes (e.g., McKinney et al., 2009).

Here, we assessed levels and patterns of several environmentally-relevant BFRs in polar bear adipose sampled from subarctic and arctic subpopulations spanning 189° in longitude from Alaska to Svalbard. This provided a large-scale picture of the current state of recent- and current-use BFR contamination in arctic marine ecosystems as represented by levels in this top predator. We also determined and compared this to current spatial trends in legacy contaminants and metabolites. Further, we made two- and three-point temporal comparisons with previous assessments to investigate how and why geographic variation in levels and patterns may be changing over time in arctic ecosystems.

2. Materials and methods

2.1. Sample details

Polar bears (total $n = 165$) were sampled from 2005–2008 in 11 subpopulations: Alaska–Chukchi/Bering Sea (AL), southern Beaufort Sea (SBS), northern Beaufort Sea (NBS), Gulf of Boothia (GB), Lancaster/Jones Sound (LJS), Baffin Bay (BB), Davis Strait (DS), western Hudson Bay (WHB), southern Hudson Bay (SHB), East Greenland (EG) and Svalbard (SV) (Table 1). Adipose samples were collected during native subsistence hunts, except in SV where fat biopsies were collected from live sampled polar bears. Collections occurred from October to mid-May. After sampling and during shipment, samples were kept frozen. At Environment Canada's National Wildlife Specimen Bank, samples were stored at -40°C until further processing. Ages were estimated by counting annual growth layer groups in the cementum of a vestigial premolar tooth or the lower right I3 using established methods (Calvert and Ramsay, 1998; Dietz et al., 2004). These methods are associated with greater uncertainty in age estimates for both young and old bears and for subpopulations that forage throughout the year, and additionally exhibit between-lab biases in age estimations (Christensen-Dalsgaard et al., 2010). Polar bears were considered subadults if ≤ 4 year old and adults otherwise (Norstrom et al., 1998).

2.2. Organohalogen contaminant analysis

All contaminant analysis was performed in the Letcher Organics Research Labs at the NWRC. (Ottawa, Canada). Contaminants were extracted from polar bear adipose tissue and analyzed on a 6890N gas chromatograph–5973N single quadrupole mass spectrometer (GC–MS) (Agilent Technologies, Palo Alto, CA, USA) as described previously (McKinney et al., 2009, 2010). Briefly, around 0.5 g samples were homogenized with sodium sulfate, spiked with internal standards

Table 1

Collection and biometric data for polar bears sampled in 2005–2008 from 11 subpopulations spanning Alaska east to Svalbard.

Subpopulation	n (AM:AF:S) ^c	Sampling year(s)	Collection date (range)	Capture coordinates	Median age (range)	Mean % lipid (\pm SE)
Alaska-Bering-Chukchi Sea (AL) [R2] ^a	12 (7:2:3)	2005–7	8Feb–19May	63–69 °N, 166–170 °W	6 (2–22)	68 \pm 4
S. Beaufort Sea (SBS) [R4-part] ^a	17 (8:4:5)	2006–7	9Dec–24May	69–70 °N, 120–138 °W	8 (2–20)	75 \pm 4
N. Beaufort Sea (NBS) [R4] ^a [Amundsen Gulf] ^b	29 (12:8:9)	2007	2Feb–13May	69–73 °N, 116–126 °W	6 (3–24)	78 \pm 2
Gulf of Boothia (GB) [R8] ^a	7 (3:1:3)	2007	30Mar–15May	69–70 °N, 90–92 °W	7 (3–24)	73 \pm 4
Lancaster/Jones Sound (LJS) [R7] ^a	13 (8:2:3)	2007–8	26Dec–18May	73–78 °N, 84–100 °W	6 (3–11)	82 \pm 2
Baffin Bay (BB) [R9,10] ^a [N. Baffin Island] ^b	14 (9:1:4)	2007–8	1Oct–6May	69–73 °N, 67–78 °W	5.5 (2–10)	81 \pm 3
Davis Strait (DS) [R14] ^a [S. Baffin Island] ^b	9 (6:0:3)	2008	26Jan–27Mar	62–63 °N, 66–70 °W	5 (3–15)	70 \pm 9
W. Hudson Bay (WHB) [R12] ^a	12 (6:1:5)	2007–8	1Nov–26May	60–62 °N, 91–95 °W	6 (3–29)	78 \pm 3
S. Hudson Bay (SHB) [R13] ^a	21 (15:4:2)	2007–8	25Feb–23Mar	55–57 °N, 78–80 °W	9 (3–28)	82 \pm 2
E. Greenland-Scoresby Sound (EG) [R15] ^a	20 (8:5:7)	2006	7Jan–16Mar	69–74 °N, 20–25 °W	6.5 (3–19)	82 \pm 2
Svalbard-Barents Sea (SV) [R16] ^a	9 (0:9:0)	2007	26Mar–11Apr	77–80 °N, 12–19 °E	9 (5–15)	78 \pm 5
All subpopulations	163	2005–8	1Oct–26May	55–80 °N, 170 °W–19 °E	7 (2–29)	78 \pm 1

^a Alternate name reported for comparable locations in Norstrom et al. (1998).^b Alternate name reported for comparable locations in Verreault et al. (2005).^c Age classifications were adult male and female (AM and AF > 4 year old) and subadult (S = 2–4 year old) (Norstrom et al., 1998).

(ISs; BDE30, ¹³C₆-ClBzs, ¹³C₁₂-PCBs, ¹³C₁₂-*p,p'*-DDE and 3-CH₃SO₂-2-CH₃-2,3',4',5,5'-pentaCB (MeSO₂-PCB IS)) and extracted by pressurized liquid extraction. Our lab has previously demonstrated that BDE30 is a suitable internal standard for BFRs of varying degrees of bromination (Gauthier et al., 2008). Following gel permeation chromatography to remove lipids and other bioorganics, samples were further separated into two fractions using silica solid phase extraction. The first fraction contained PCBs, OCPs and BFRs. The second fraction contained MeSO₂-PCBs. Samples were monitored for 8 non-PBDE BFRs (PBT, PBEB, HBB, BB101, BB153 (co-eluted with BDE154), total-(α -)HBCD, BTBPE and DBDPE), 37 PBDEs, 74 PCBs, 22 MeSO₂-PCBs, 3-MeSO₂-*p,p'*-DDE and 19 OCPs including chlorobenzenes (ClBzs), α -HCH, β -HCH, octachlorostyrene (OCS), CHLs, DDTs, dieldrin and mirex compounds. A complete list of all monitored compounds is provided in the Supplemental Information (Table S1). PCB and OCP standards were supplied by the Lab Services section of the Ecotoxicology and Wildlife Health Division at the NWRC (Ottawa, ON, Canada). Mass-labeled ¹³C-PCB internal standards (ISs) for PCB and OCP analysis were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). BFRs were purchased from Wellington Laboratories (Guelph, ON, Canada). MeSO₂-PCBs were kindly supplied by Dr. Å. Bergman (Stockholm University, Sweden). Standards were of >95% purity. A 30 m length \times 250 μ m i.d. fused silica DB-5 capillary column ((5% phenyl)-methylpolysiloxane, 0.25 μ m film thickness; J & W Scientific, Folsom, CA, USA) was used for GC separation of PCBs, OCPs and MeSO₂-PCBs/-DDE. For BFRs, a similar, but shorter (15 m) and thinner film thickness (0.10 μ m) column (DB5-HT) was used to minimize thermal decomposition and peak broadening of higher brominated BFRs (BDE209, DBDPE). To address the co-elution of BDE154 with BB153 with respect to analyte specific quantification, BDE154 was additionally monitored using [M-Br₂]⁻ anion isotopes, which were less abundant but allowed for mass spectral resolution, and thus separation from BB153. An Agilent 7683 series injector and autosampler were used. For PCB and OCP analyses, the MS detector was used in the electron impact (EI) ionization mode. For BFRs and MeSO₂-PCBs/-DDE, the MS detector was used in the electron capture negative ionization mode (ECNI).

2.3. Quality control for contaminant data

IS recoveries (from total $n = 165$ samples) were $88 \pm 10\%$, $59 \pm 18\%$, $89 \pm 14\%$, $88 \pm 15\%$, $105 \pm 25\%$ for BDE30, ¹³C₆-ClBzs, ¹³C₁₂-PCBs, ¹³C₁₂-*p,p'*-DDE and the MeSO₂-PCB IS, respectively. With each batch of 10 samples, a sodium sulfate blank and the NIST Pilot Whale blubber SRM1945 were also extracted. A small fraction of PCB (CBs 153, 138 and 180) and PBDE (BDEs 47 and 99) congeners were consistently detected at low levels in the blanks (<0.2 ng/g). Samples

were thus blank-subtracted on a batch-by-batch basis. However, BDE209 and DBDPE blank values were variable and sometimes similar to sample values. Unlike for other compounds wherein method limits of quantification (MLOQs) were based on a signal-to-noise ratio of 10, MLOQs for BDE209 and DBDPE were set to the blank average plus $3 \times$ SD. MLOQs ranged from around 0.05 ng/g lipid weight (lw) for most BFRs to 0.3 ng/g lw for total-(α -)HBCD and 1 ng/g for BDE209 and DBDPE. To determine BDE154 separately from BB153, we monitored [M-Br₂]⁻ that had a higher MLOQ of 0.4 ng/g lw. The MLOQs were around 0.1 ng/g lw for PCBs and OCPs and 0.5 to 0.9 ng/g lw for MeSO₂-PCBs and 3-MeSO₂-*p,p'*-DDE. In 19 repeated extractions and analyses of SRM1945, \sum PCB, \sum OCP and \sum PBDE levels were on average within $7 \pm 5\%$, $11 \pm 6\%$ and $16 \pm 11\%$ of the \sum -certified values, respectively. The majority of individual compounds/congeners were also in good agreement (<20% RSD) with the certified values. SRM1945 does not currently have certified values for MeSO₂-PCBs or any non-PBDE BFRs. Participation in annual Northern Contaminants Program (NCP; Indian and Northern Affairs Canada) QA/QC assessments for PCBs, OCPs and PBDEs in biological samples achieved <20% deviation from inter-laboratory mean concentrations. Duplicate polar bear sample %RSDs were on average 6%, 7%, 13% and 13% for \sum PCB, \sum OCP, \sum PBDE and \sum MeSO₂-PCB concentrations, respectively, and also showed <20% deviation for the majority of individual contaminants. There were originally 10 samples from DS and SV, but most major contaminants were below detection (related to very low lipid content) in one sample from each. These two bears were not included entirely in subsequent analyses to avoid leverage (undue influence of single samples) in the dataset.

2.4. Data analysis

Contaminant quantification methods have been detailed elsewhere (McKinney et al., 2010). Briefly, PCBs and OCPs were quantified by an external standard method, and ClBzs were also recovery corrected to account for volatility-related lower recoveries. MeSO₂-PCBs/-DDE and BFRs were quantified by an internal standard method based on the relative response factor of the analyte versus the appropriate internal standard, and thus concentrations were inherently recovery and performance corrected. Concentrations were calculated on a lipid weight basis.

Inferential statistical tests were performed using Statistica V6.0 (Statsoft, Tulsa, OK, U.S.A.). Individual or \sum -contaminants that were quantifiable in >70% of the bears and in >70% of the subpopulations were reported and subject to statistical analysis. Within this subset, concentrations <MLOQ were assigned a random value between zero and one-half the MLOQ for statistical analysis. Concentrations were log($x + 1$)-transformed to better approximate normal distribution

(Shapiro-Wilks *W* test) in each subpopulation. As BDE47, BDE99, BDE100 and BDE153 were the only consistently detected PBDEs in the samples, we focused on these 4 congeners to ensure reliability of spatial comparisons. For PCB and MeSO₂-PCB patterns, we focused on the 15 major congeners (or coeluting congeners; Fig. 2) which represented 88–99% and 92–98% of \sum PCB and \sum MeSO₂-PCB, respectively. All statistical tests were deemed significant at $p < 0.05$.

General linear models (GLM) with type III sum-of-squares analysis were used to determine the influence of sex, age and subpopulation on individual and/or \sum -contaminant levels (Table 2) using the initial model: $\log(\text{contaminant}) = \text{subpopulation} + \text{sex} + \text{age} + \text{age} \times \text{subpopulation} + \text{age} \times \text{sex}$. The $\text{sex} \times \text{subpopulation}$ term could not be tested as DS and SV comprised only males and only females, respectively. However, it was reasonable to assume that this term was negligible because this was the case in the 1989–1993 circumpolar study (Norstrom et al., 1998), and it was not significant in the model when DS and SV were excluded. Where age, sex, and interactions were not significant, a one-way ANOVA was used to test the reduced model, $\log(\text{contaminant}) = \text{subpopulation}$, followed by *post hoc* Tukey's HSD for unequal *n*. Given significant heteroscedasticity (Browne–Forsythe test) for dieldrin and OCS, non-parametric Kruskal–Wallis one-way ANOVA was performed followed by *post hoc* comparisons of mean ranks. Simple linear regression of individual or \sum -contaminant levels with average subpopulation latitudes and longitudes were also performed to further assess spatial trends.

Ages were not determined for 6.6% of bears (4 BB, 1 DS, 1 LJS, 2 NBS, 1 SBS and 2 SHB). These missing ages were estimated using sex-specific \sum CHL–age correlations generated from the entire dataset. Here and elsewhere (Norstrom et al., 1998; Verreault et al., 2005), \sum CHL levels have varied minimally across regions, such that the entire dataset could be used for imputation. Unlike other contaminants, \sum CHL levels have also shown consistent trends with age (Bernhoft et al., 1997). Although using the calculated values could artificially increase the correlations between \sum CHL and age, we found no inflation of *r*²-values (0.13 to 0.14 for males, 0.10 to 0.10 for females, respectively). To check that the age estimation procedure did

not bias the results, we re-analyzed the dataset excluding estimated-age bears. For initial GLMs on contaminants originally only significantly explained by subpopulation, only subpopulation was significant when run excluding the estimated-age bears. Therefore, age was not included in the reduced models, and there was no reason to exclude the estimated-age bears. For, contaminants originally explained by sex/age factors (and subpopulation, in most cases), namely β -HCH, \sum CHL, \sum MeSO₂-PCB (Section 3.1), their levels were also explained by these factors in the GLMs excluding the estimated-age bears. For these contaminants, we checked that the spatial results were not biased due to the presence of the estimated-age bears by re-calculating the spatial trends excluding these bears. The adjusted least-squares means were similar to the means including the estimated-age bears and the statistical results of between-population comparisons were identical.

Limited temporal comparisons were made between levels in the current 2005–2008 dataset and those reported across similar locations in 1989–1993 and 1996–2002 (Letcher et al., 1995; Muir et al., 2006; Norstrom et al., 1998; Verreault et al., 2005). The 1989–1993 study reported adult male and female data, given sex-differences in certain contaminant levels (Norstrom et al., 1998). However, only adult male samples were screened for MeSO₂-PCBs and 3-MeSO₂-*p,p'*-DDE in the 1989–1993 dataset (Letcher et al., 1995). The 1996–2002 study reported female data, both adult and subadult (Verreault et al., 2005). Age-adjusted female data were reported for a subset of contaminants to compare to the 1989–1993 study, but this adjustment resulted in only minor changes in mean levels. We compared the current 2005–2008 dataset to 1989–1993 adult females (except \sum MeSO₂-PCB and 3-MeSO₂-*p,p'*-DDE) and 1996–2002 age-unadjusted females to maximize the breadth of contaminant temporal data. However, comparisons of all available data, including 1989–1993 males and 1996–2002 age-adjusted females were additionally provided (Fig. S1). It is unlikely that quantitative temporal trends would be reliable given limited available time points, as well as inter-study biological and possible analytical variation (Henriksen et al.,

Table 2
Geometric means and 95% confidence intervals (ng/g lipid weight) of brominated and chlorinated contaminants and metabolites in adipose of polar bears from 11 subpopulations collected from 2005–2008.^a

	Alaska	S. Beaufort Sea	N. Beaufort Sea	Gulf of Boothia	Lancaster/Jones Sound	Baffin Bay	Davis Strait	W. Hudson Bay	S. Hudson Bay	E. Greenland	Svalbard
\sum PBDE	4.7 ^e 3.4–6.3	5.8 ^e 4.3–7.9	8.8 ^{de} 7.7–10.0	7.0 ^{de} 4.5–10.7	6.8 ^e 5.1–9.0	14.0 ^{cd} 11.4–17.0	27.1 ^{bc} 16.7–43.4	38.6 ^b 27.5–54.0	78.4 ^a 65.6–93.6	43.2 ^b 37.5–49.8	44.4 ^{ab} 32.5–60.6
BB153/BDE154	2.8 ^e 1.8–4.2	7.5 ^{de} 5.2–10.7	7.8 ^{de} 6.2–9.9	3.4 ^e 1.9–5.7	7.7 ^{de} 4.9–11.7	13.6 ^{cd} 8.3–21.8	28.8 ^{bc} 16.4–50.1	30.1 ^{bc} 15.9–56.0	81.1 ^a 63.7–103	39.2 ^b 31.5–48.8	20.9 ^{bcd} 12.9–33.6
total-(α -) HBCD	– –	1.4 ^d 0.9–2.1	1.8 ^{cd} 1.3–2.4	– –	0.9 ^d 0.5–1.3	1.6 ^{cd} 1.0–2.4	2.9 ^{bcd} 1.3–5.8	4.2 ^{bc} 2.4–6.9	5.2 ^b 4.2–6.3	21.9 ^a 16.6–28.8	41.1 ^a 26.9–62.7
\sum ClBz	178 ^a 128–247	145 ^a 106–197	237 ^a 199–282	304 ^a 231–400	234 ^a 194–283	266 ^a 205–344	255 ^a 149–435	221 ^a 174–279	171 ^a 150–194	189 ^a 141–253	166 ^a 115–240
α -HCH	21.9 ^{ef} 12.8–24.8	38.9 ^{cde} 28.4–53.1	63.5 ^{abc} 56.7–71.1	91.3 ^a 70.3–119	46.7 ^{abcd} 34.3–63.4	32.7 ^{de} 27.8–38.3	34.9 ^{bcdde} 23.4–51.9	48.9 ^{abcd} 38.1–62.8	65.7 ^{ab} 53.7–80.3	11.7 ^{fg} 9.7–14.0	8.5 ^g 6.8–10.6
β -HCH	367 ^a 267–504	249 ^{ab} 190–326	307 ^a 250–379	542 ^a 361–815	238 ^{ab} 174–324	137 ^{bc} 101–186	202 ^{abc} 139–294	141 ^{bcd} 102–196	113 ^{cd} 87–147	75.1 ^{de} 58.1–96.8	65.5 ^e 45.8–93.6
OCS	5.3 ^{ab} 3.8–7.4	6.5 ^{ab} 4.7–8.8	9.5 ^a 8.2–11.1	7.1 ^{ab} 5.1–9.7	5.2 ^b 4.4–6.2	6.1 ^{ab} 5.3–7.1	6.6 ^{ab} 3.6–11.4	8.9 ^{ab} 6.4–12.3	9.1 ^a 8.0–10.4	9.7 ^a 8.3–11.2	9.5 ^{ab} 6.3–14.2
\sum CHL	765 ^c 529–1106	1268 ^{bc} 926–1736	1982 ^{ab} 1555–2525	1824 ^{abc} 1135–2930	1130 ^{bc} 788–1619	2167 ^a 1523–3083	2135 ^{ab} 1383–3298	3477 ^a 2386–5068	2166 ^{ab} 1604–2924	1732 ^{ab} 1292–2321	1196 ^{abc} 793–1802
\sum DDT	77.2 ^{cdeg} 56.0–106	81.8 ^{efg} 60.5–110	93.7 ^{bcddef} 79.9–110	31.5 ^g 19.8–49.7	64.0 ^{fg} 44.1–92.7	179 ^{ab} 125–257	104 ^{abcdef} 60.0–181	88.1 ^{defg} 54.8–141	152 ^{abcde} 127–182	206 ^a 155–273	119 ^{abcdef} 75.0–187
dieldrin	69.1 ^b 41.7–114	126 ^{ab} 47.5–100	150 ^{ab} 104–153	115 ^{ab} 111–202	115 ^{ab} 90.8–146	197 ^a 161–241	183 ^{ab} 103–323	244 ^a 185–322	143 ^{ab} 111–185	156 ^{ab} 121–200	143 ^{ab} 107–190
\sum mirex	17.7 ^c 10.8–28.8	32.9 ^{abc} 24.0–44.8	50.0 ^a 42.4–59.0	22.6 ^{abc} 14.7–34.6	22.5 ^{bc} 18.3–27.6	33.1 ^{ab} 25.5–42.9	33.2 ^{abc} 17.9–61.1	50.4 ^a 34.5–73.5	51.7 ^a 41.7–64.0	51.6 ^a 42.6–62.4	43.1 ^{ab} 30.4–61.0
\sum PCB	1842 ^c 1115–3043	3688 ^{bc} 2600–5232	5541 ^{ab} 4518–6797	2445 ^{bc} 1599–3739	2598 ^{bc} 2005–3366	3211 ^b 2305–4472	4674 ^{abc} 2693–8114	4634 ^{ab} 3072–6992	5523 ^b 4617–6608	10537 ^a 8751–12,687	5137 ^{ab} 2854–9246
\sum MeSO ₂ -PCB	110 ^c 80–153	232 ^b 176–306	264 ^b 213–327	144 ^{bc} 94.7–219	184 ^{bc} 134–253	230 ^b 169–314	218 ^{bc} 149–320	206 ^{bc} 147–286	238 ^b 183–310	672 ^a 520–870	222 ^{bc} 155–319

^a GM and 95% CI were only calculated if > 70% of sample concentrations were above the MLOQ. For β -HCH, \sum CHL and \sum MeSO₂-PCB, GM and 95% CI were adjusted to a 7 year old female polar bear. Co-eluting BB153/BDE154 was on average 96% BB153. Subpopulations sharing the same superscript letter were not significantly different.

2001). Instead, we considered qualitative consistency in patterns of temporal comparisons across subpopulations (increases/decreases) and with longer-term studies in WHB from 1968–1999 and/or 1991–2007 (McKinney et al., 2010; Norstrom, 2001).

3. Results and discussion

3.1. Influence of biological factors on organohalogen levels

Age, sex, age × subpopulation and age × sex did not generally significantly explain contaminant levels. However, age and age × sex significantly explained β-HCH, Σ CHL and Σ MeSO₂-PCB levels. For these contaminants, the model was reduced to log(contaminant) = subpopulation + sex + age + sex × age. Weak but significant negative correlations of β-HCH and Σ MeSO₂-PCB levels with age occurred in female, but not male polar bears (Fig. 1). Σ CHL levels were weakly but significantly negatively correlated with age in male and female polar bears (Fig. 1). Therefore, we subsequently reported adjusted mean β-HCH, Σ CHL and Σ MeSO₂-PCB levels normalized to a female at 7 year old (median age) (Table 2).

Declining levels of certain contaminants with age in female polar bears are best explained by contaminant transfer to offspring through lactation. Specifically, the observation of declining β-HCH, Σ CHL and Σ MeSO₂-PCB levels with age in female polar bears may be due to preferential loss of these compounds from females through nursing relative to other contaminants. Polischuk et al. (2002) found elevated milk:adipose concentration ratios (>1) for Σ CIBz, Σ CHL and Σ HCH. Although not investigated in that study, similarly elevated lactational transfer of MeSO₂-PCBs to polar bear cubs was thus suggested from the current results. Previous studies have also reported declining male Σ CHL levels with age (e.g., Dietz et al., 2004; Norstrom et al., 1998). This finding is not well understood, but may be related to superior metabolism of CHLs in male polar bears and increasing (possibly exposure-induced) biotransformation capacity towards CHLs in males with age and/or to possible demographic differences in diets. It had been proposed based on earlier work that samples from adult female polar bears are preferable for use in contaminant monitoring studies due to a

lack of age effects in this demographic group (e.g., Verreault et al., 2005). Yet, decreasing levels of PCBs and several OCPs were recently found with age in female SBS polar bears, but only decreasing CHL levels with age in males (Bentzen et al., 2008) in closer agreement with the current study for certain contaminants.

It is unlikely that sample sizes (total n = 163) were too low to detect demographic variation for contaminants with relatively small demographic differences in levels (subpopulation contaminant concentrations listed by demographic group in Table S2). Norstrom et al. (1998) found with a larger dataset (n = 320 adults) that although Σ CHL levels showed clear sex/age effects, Σ PCB, p,p'-DDE and dieldrin levels did not. Nonetheless, that study found higher Σ PCB levels in adult males than females, which we and others (Bentzen et al., 2008; Dietz et al., 2004) did not observe. Previous reports of PBDEs in polar bears also did not find age or sex effects (Dietz et al., 2007; Muir et al., 2006). In addition to age and/or sex, other biological or ecological factors may have contributed to contaminant level variation. As sample collection was limited to just over half of the year, seasonal variation was likely reduced but not entirely eliminated. The influence of seasonal fasting may vary by demographic group (Dietz et al., 2004; Dietz et al., 2007; Polischuk et al., 2002) and also geographically, given spatial differences in year-round availability of sea ice on which polar bears hunt for marine mammals (Laidre et al., 2008). Habitat use variation may also have influenced contaminant levels within subpopulations (Olsen et al., 2003). Variation in diet or trophic level has been reported between subpopulations (Thiemann et al., 2008).

3.2. Spatial trends in BFR levels and patterns

Σ PBDE and BB153/BDE154 levels were highest among BFRs (Table 2). Yet, Σ PBDE and BB153/BDE154 levels were around 2–3 orders of magnitude lower than levels of the predominant legacy contaminant class, Σ PCB, consistent with earlier studies (Letcher et al., 2010). Significant variation in Σ PBDE levels between subpopulations showed higher levels in SHB followed by WHB, EG and SV, intermediate levels in the eastern Canadian Arctic, and lower levels in the western Canadian Arctic and AL. Subpopulation mean Σ PBDE levels hence decreased with increasing longitude (i.e., east to west; r = -0.70, p = 0.02). Given that the detected congeners mainly

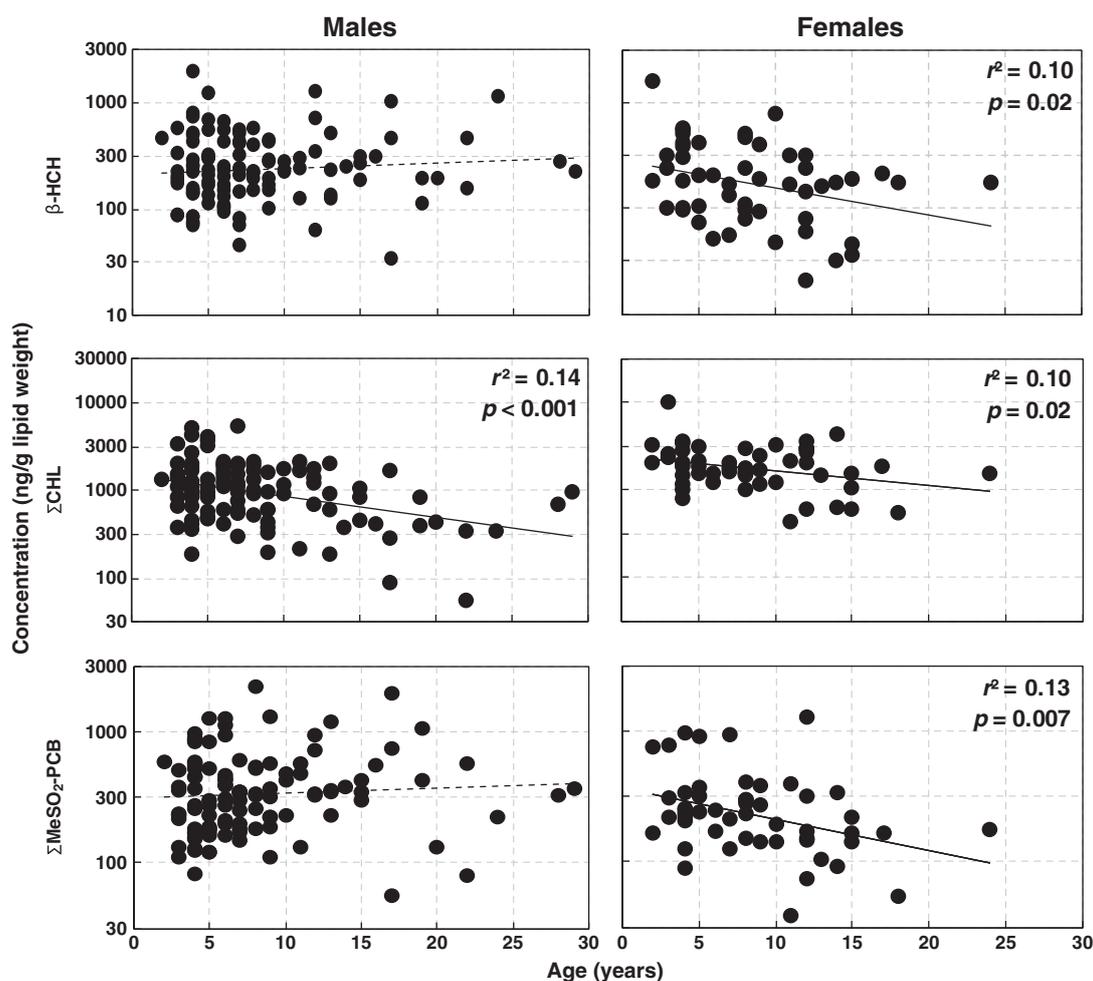


Fig. 1. Correlations of adipose concentrations of log(β-HCH), log(Σ CHL) and log(Σ MeSO₂-PCB) with age for male and female polar bears sampled in 11 subpopulations from 2005–2008. Solid trend lines indicate significant (p < 0.05) correlations. Dashed lines indicate non-significant correlations.

originated from pentaBDE products (de Wit et al., 2010), and that most pentaBDE use was in North America, higher levels in subarctic subpopulations (SHB, WHB) were likely related to closer proximity to North American source regions. Higher levels in EG and SV were consistent with PBDE trends reported in arctic marine mammals and seabirds and suggest atmospheric transport from major source regions of eastern North America and western Europe (as reviewed in de Wit et al., 2010).

Except for notably elevated SHB and WHB Σ PBDE levels, spatial variation was similar to the first geographic PBDE study on polar bears sampled in 1996–2002 (Muir et al., 2006). Similar to that study, BDE47 generally predominated, ranging from 46–76% of Σ PBDE (Fig. 2; Table S3). However, proportions of BDE153 (16–42%) approximately doubled and proportions of BDE99 fell by around half from the same regions in the 1996–2002 study. Like CB153, BDE153 may be a recalcitrant congener relative to other PBDEs such as BDE99. Increasing proportions of BDE153 could also be from environmental or metabolic debromination of BDE209 (e.g., Söderström et al., 2004). Further monitoring is necessary to confirm these temporal patterns, though; such a “weathered” or aged PBDE pattern shift was not identified in WHB polar bears sampled over 1991–2007 (McKinney et al., 2010). Mean BDE153 proportions were significantly negatively correlated with mean latitude ($r = -0.65, p = 0.03$), whereas BDE47 proportions were significantly positively correlated ($r = 0.64, p = 0.04$). For these two apparently more persistent congeners, proportions in polar bears reflect less discrimination of the more volatile BDE47 relative to BDE153 during long-range transport (Wania and Mackay, 1993). The reason for higher BDE153 proportions (and lower BDE47 proportions) in the higher latitude EG subpopulation was unclear.

Several non-PBDE BFRs were also screened, but only total-(α)-HBCD and BB153/BDE154 were consistently detected (Fig. 3). Total-(α)-HBCD was not quantifiable in >70% of AL and GB polar bears. Significant level differences were observed between remaining subpopulations (Table 2). Highest total-(α)-HBCD levels, comparable to Σ PBDE, were found in EG and SV. Mean total-(α)-HBCD levels in SV were 15- to 51-fold higher than in Canadian Arctic subpopulations implying large differences in source inputs between regions. These findings were consistent with much higher market demand for HBCD in Europe than in North America and Asia (de Wit et al., 2010). Total-

(α)-HBCD levels were higher in SHB and WHB than in central and western Canadian Arctic and AL subpopulations. However, this difference was not nearly as pronounced as for Σ PBDE. Subpopulation mean levels of total-(α)-HBCD were highly significantly negatively correlated with longitude ($r = -0.89, p = 0.001$).

Separate detection and quantification of BDE154 from BB153 using $[M-Br_2]^-$ anions was possible in 24% of samples wherein these anions were above the MLOQ. We estimated that BDE154 comprised on average only 4% (range: 0.5 to 13%) of the combined BB153/BDE154 concentration in these polar bear samples. Thus, BB153/BDE154 concentrations were on average a reasonable approximation of BB153 in polar bears, and implied that BB153 was at the highest concentration of any individual BFR across regions. This finding suggests that BB153 is highly persistent given that HexaBB production was much lower than that of PBDE products and that HexaBB production ceased in the 1970s (de Boer et al., 2000). Notable recalcitrance of BB153 has been observed in humans as well as in experimentally-dosed rats (Hakk and Letcher, 2003). Spatial patterns in mean BB153 levels were similar to Σ PBDE, significantly negatively correlated with longitude ($r = -0.60, p = 0.05$). Other BFRs were infrequently identified (<14% of all samples) including PBEB, BTBPE and DBDPE. HBB and BB101 were identified more frequently (50–60% of all samples), but at low levels (<3 ng/g lw) (Fig. 3). Similarly low and/or non-detectable levels of these BFRs were reported in Norwegian Arctic glaucous gull (*Larus hyperboreus*) plasma and eggs (Verreault et al., 2007). Overall, tetra- to hexa-PBDEs (and BB153) remained the main BFRs detected across subpopulations despite their phase-out and subsequent use of replacement BFRs.

3.3. Spatial trends in PCB and OCP levels and patterns

Across subpopulations, Σ PCB levels were highest among legacy contaminants (Table 2). Σ PCB levels were significantly different between subpopulations, with highest levels in EG and lowest levels in AL. Non-significantly lower Σ PCB levels were observed in GB, LJS and BB relative to SBS, NBS, WHB, SHB and SV. Consistent with previous studies (Verreault et al., 2005), mean Σ PCB levels were negatively correlated

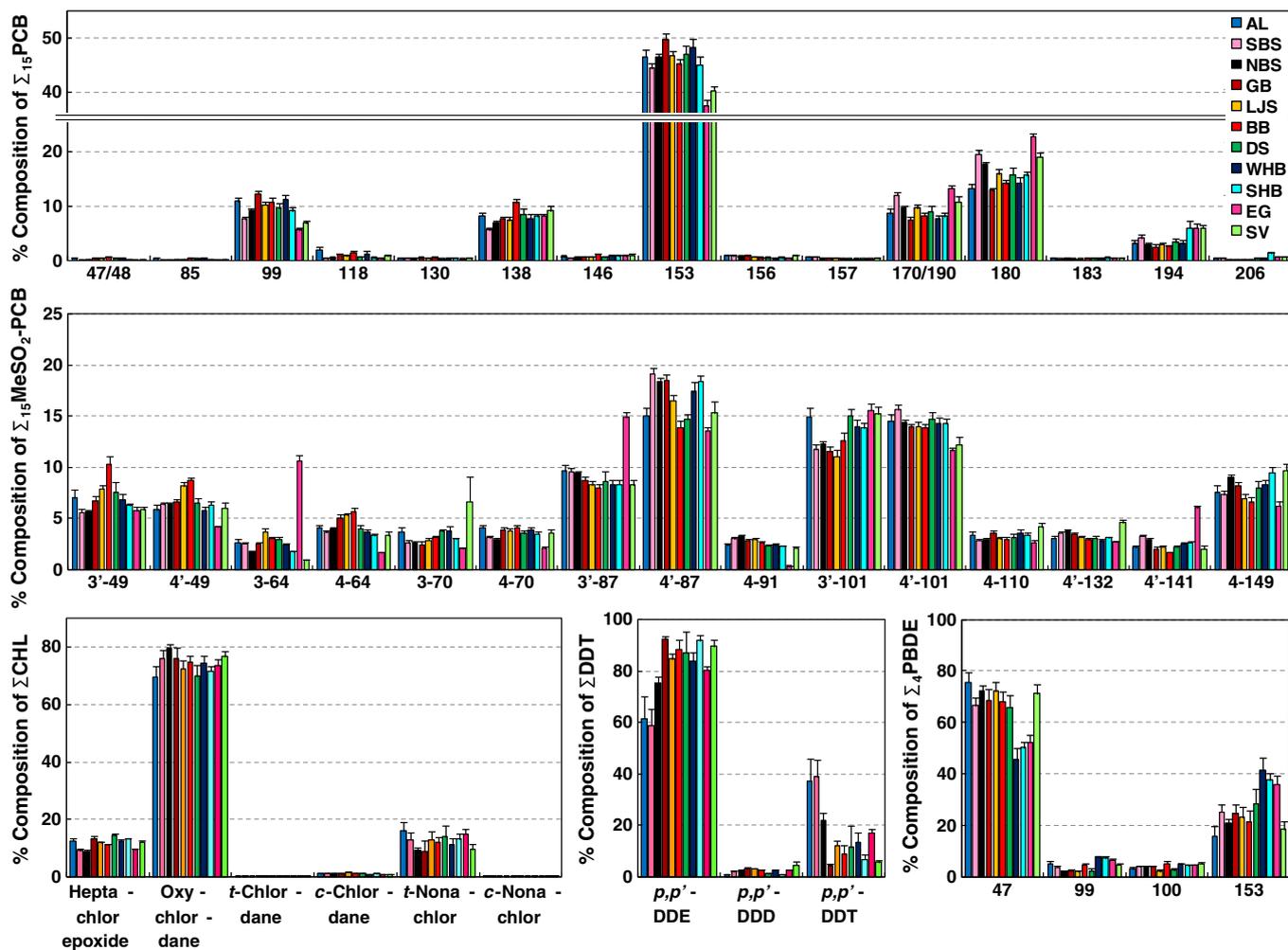


Fig. 2. Percent composition (+ SE) of individual contaminant concentrations to Σ -class for major contaminant classes determined in adipose from 11 polar bear subpopulations sampled in 2005–2008 (left to right): AL, SBS, NBS, GB, LJS, BB, DS, WHB, SHB, EG and SV. See Table 1 for key to subpopulation abbreviations.

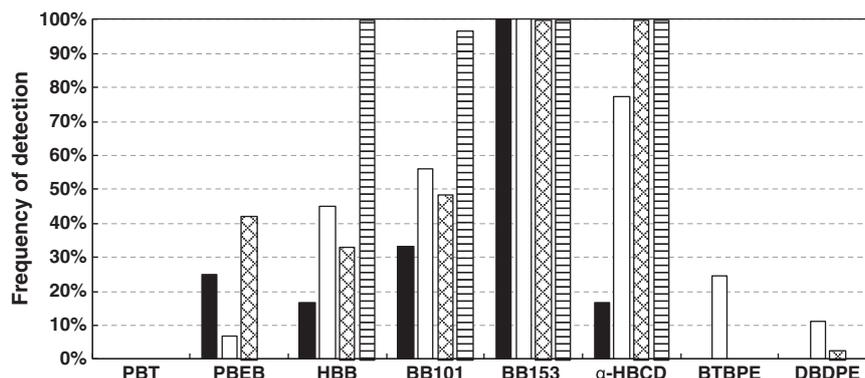


Fig. 3. Frequency of detection of non-PBDE BFRs in polar bear adipose in 2005–2008 from 4 regions (left to right): Alaska, the Canadian Arctic, Hudson Bay and the European Arctic. BB153 values are from detection of the coeluting BB153/BDE154, of which BB153 contributed on average 96%.

with longitude ($r = -0.62, p = 0.04$). As similar spatial differences were found for $\sum \text{MeSO}_2\text{-PCB}$ levels (longitudinal gradient: $r = -0.56, p = 0.07$), the remaining discussion focuses on PCBs. Besides east–west variation, other geographic variation in levels and patterns occurred. Elevated $\sum \text{PCB}$ in EG relative to all other subpopulations was in agreement with the 1989–1993 study (Norstrom et al., 1998), but not the 1996–2002 study (Verreault et al., 2005). This may be related to inter-year variation in availability of differentially-contaminated prey. For instance, within the adjacent SV subpopulation, seasonally preferential consumption of migratory and more contaminated harp seal (*Pagophilus groenlandicus*) versus ringed seal led to the hypothesis that harp seal are a vector of contaminant transport to this region (Kleivane et al., 2000). Breeding patches of harp and hooded seals (*Cystophora cristata*) are accessible to EG polar bears in March–April (R. Dietz, E. Born, personal observations). The use of chemical tracers of diets and food webs, such as stable isotopes and fatty acids, would serve to quantify the influence of this type of inter-year variation on comparisons of contaminant levels in biota between regions and over time (e.g., McKinney et al., 2009).

In all subpopulations, the congener contribution to $\sum \text{PCB}$ was $\text{CB153} > \text{CB180} > \text{CB99}$, CB138 , $\text{CB170/190} > \text{CB194}$, with lower to non-detectable levels of all remaining congeners (Fig. 2; Table S3). Higher proportions of highly chlorinated CB180 and CB170/190 and lower proportions of CB153 and CB99 in EG and to a lesser extent SV were possibly related to historic differences in PCB product use between lower latitude source regions (Andersen et al., 2001). Similarly elevated CB180 and CB170/190 proportions and $\sum \text{PCB}$ levels were observed in SBS and NBS relative to adjacent subpopulations. It was hypothesized that such PCB variation was related to a preponderance of more sympagic (ice-associated) versus pelagic phytoplankton and zooplankton in the lower food webs of this region (Norstrom et al., 1998). However, more recently it was shown that only levels of more water-associated contaminants like $\alpha\text{-HCH}$ and HCB were elevated in sympagic amphipods versus pelagic zooplankton (Borgá et al., 2002). Perhaps higher levels of PCBs (and proportions of highly chlorinated congeners) and other more particle-associated contaminants in Beaufort Sea subpopulations were more related to the large input of suspended particulate matter from the Mackenzie River (Macdonald et al., 2000). This

river flows northward from regions much further south and represents by far the largest riverine input to the Arctic Ocean within the Canadian Arctic (Macdonald et al., 2000).

Levels of $\sum \text{DDT}$ were relatively low in all subpopulations compared to $\sum \text{PCB}$ and $\sum \text{CHL}$ and showed no longitudinal gradient. Yet, mean p,p' -DDE levels decreased significantly with longitude ($r = -0.64, p = 0.04$; Table S3), similar to $\sum \text{PCB}$ and likely reflected historic geographic patterns in DDT use. Elevated proportions of p,p' -DDT in AL, SBS and to a lesser extent NBS (22–39% of $\sum \text{DDT}$; Fig. 2) were not consistent with the 1996–2002 study. The current DDT pattern in these western subpopulations appears to reflect a substantial contribution of fresh DDT inputs. To our knowledge, there is no published direct evidence for fresh DDT inputs to these regions. However, DDT was recently reintroduced for vector control in some Asian and African countries (6300 t produced in India alone in 2007) (van den Berg, 2008), which could explain elevated p,p' -DDT proportions in 2005–2007 western North American Arctic polar bears (Fig. 2). Nonetheless, $\sum \text{DDT}$ remained at similar or lower levels in AL, SBS and NBS than in the historically more polluted EG and SV subpopulations (Table 2). Further investigation of DDT emissions sources and transport pathways should be pursued to understand whether this permitted vector control exemption under the Stockholm Convention may be changing DDT patterns and possibly levels within these remote ecosystems.

Findings of relatively spatially uniform and higher $\sum \text{CHL}$ levels than all other OCPs were consistent with earlier studies (Verreault et al., 2005). Oxychlordanes predominated ($\geq 70\%$ in all subpopulations) even more so than in the 1996–2002 study (Verreault et al., 2005), suggesting continued weathering of CHL patterns (Fig. 2; Table S3). Unlike most contaminants and consistent with the 1996–2002 study, mean $\sum \text{HCH}$ and $\beta\text{-HCH}$ levels were both strongly positively correlated with longitude ($r = 0.81, p = 0.002$ and $r = 0.79, p = 0.004$, respectively). In AL, $\sum \text{HCH}$ levels approached those of $\sum \text{CHL}$. In all subpopulations, mean $\beta\text{-HCH}$ proportions to $\sum \text{HCH}$ were higher than $\alpha\text{-HCH}$, ranging from 66% to 77% in WHB and SHB to 94% in AL. Overall, these findings likely reflect greater use of technical HCH in Asia, increased $\alpha\text{-HCH}$ levels in air with latitude, and the importance of oceanic transport, particularly for $\beta\text{-HCH}$, from the North Pacific through the Bering Strait (Macdonald et al., 2000). $\sum \text{Cibz}$, OCS, dieldrin and $\sum \text{mirex}$ levels were relatively low and spatially uniform, consistent with the 1996–2002 study.

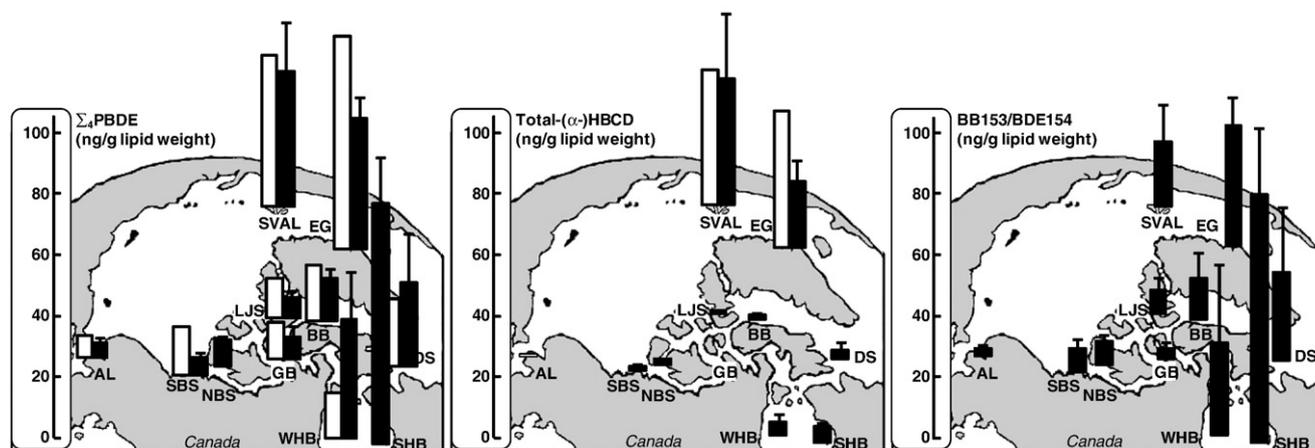


Fig. 4. Spatiotemporal patterns in geometric mean (+95% confidence interval) levels of major brominated flame retardants in adipose of polar bears from 11 subpopulations collected from 1996–2002 (□; from Muir et al., 2006) and from 2005–2008 (■; present study). The 1996–2002 study did not report BB153/BDE154, reported total-(α -)HBCD in AL, EG and SV only and did not report $\sum \text{PBDE}$ in SHB. The 1996–2002 SBS data shown was from NBS and SBS. Total-(α -)HBCD was below detection in 2005–2008 in the subpopulations AL and GB. See Table 1 for key to subpopulation abbreviations.

3.4. Temporal contaminant comparisons

BFRs were not assessed in the 1989–1993 study and only PBDEs were comprehensively determined in the 1996–2002 study (Muir et al., 2006). Σ PBDE levels were lower in 2005–2008 than in 1996–2002 for 7 of 9 subpopulations, but higher in WHB and similar in DS (Fig. 4). In SHB, 1996–2002 levels were unavailable. In a study on WHB polar bears from 1991–2007, Σ PBDE levels increased significantly, although levels in 2007 were lower than in 2003 (McKinney et al., 2010). Taken together, these findings suggest that Σ PBDE levels in polar bears, at the top trophic position of arctic marine ecosystems, may have recently started to reflect the circa 2004 pentaBDE and octaBDE phase-outs (de Wit et al., 2010). The 1989–1993 and 1996–2002 studies did not report BB153 levels. Given comparable 2005–2008 BB153 levels to Σ PBDE, lower production and earlier discontinuation of hexaBB (de Boer et al., 2000), BB153 levels have likely declined minimally. In agreement, BB153/BDE154 did not show declines in the study on WHB polar bears between 1991 and 2007 and in a study on ivory gulls (*Pagophila eburnea*) between 1976–2004 (Braune et al., 2007; McKinney et al., 2010). Total-(α)-HBCD levels were lower in 2005–2008 relative to 1996–2002 levels reported for AL, EG and SV. Although continued monitoring is required to confirm this temporal pattern, apparent HBCD decreases in polar bears may reflect decreased manufacture and/or improved controls on HBCD emissions recently implemented by the bromine industry (Law et al., 2008).

Regarding legacy contaminants, Σ CHL and *p,p'*-DDE levels decreased consecutively from 1989–1993 to 1996–2002 to 2005–2008 in most subpopulations. The 2005–2008 levels were lower relative to 1989–1993 levels in all subpopulations (Fig. 5). The only exception was Σ CHL levels in WHB. Non-declining Σ CHL levels in WHB was also reported in the longer-term studies, although levels may have peaked in the 1980s (McKinney et al., 2010; Norstrom, 2001). Concentrations may have leveled off in this region (Verreault et al., 2005); however, we observed a nearly 4-fold drop in Σ CHL levels in SHB in the current 2005–2008 study relative to the 1989–1993 study. One hypothesis is that relatively stable Σ CHL levels in WHB are more related to diet/food web changes within this region as indicated by stable carbon isotope ratio and fatty acid profile changes that have been correlated with sea ice changes in Hudson Bay (McKinney et al., 2009). In contrast, WHB *p,p'*-DDE levels substantially decreased compared to temporal patterns in most subpopulations and in agreement with the 1991–2007 Σ DDT (and *p,p'*-DDE) trends (McKinney et al., 2010). This may be related to a previous local source and contrasting ecological distribution of DDT in this region relative to other contaminants (McKinney et al., 2009). Although it was difficult to compare 3-MeSO₂-*p,p'*-DDE trends due to missing data for some subpopulations in earlier studies and the high number of non-detects, it appeared that levels generally decreased, consistent with *p,p'*-DDE trends.

Temporal patterns in Σ PCB levels varied among subpopulations and between studies. It was previously reported that mean Σ PCB levels decreased across

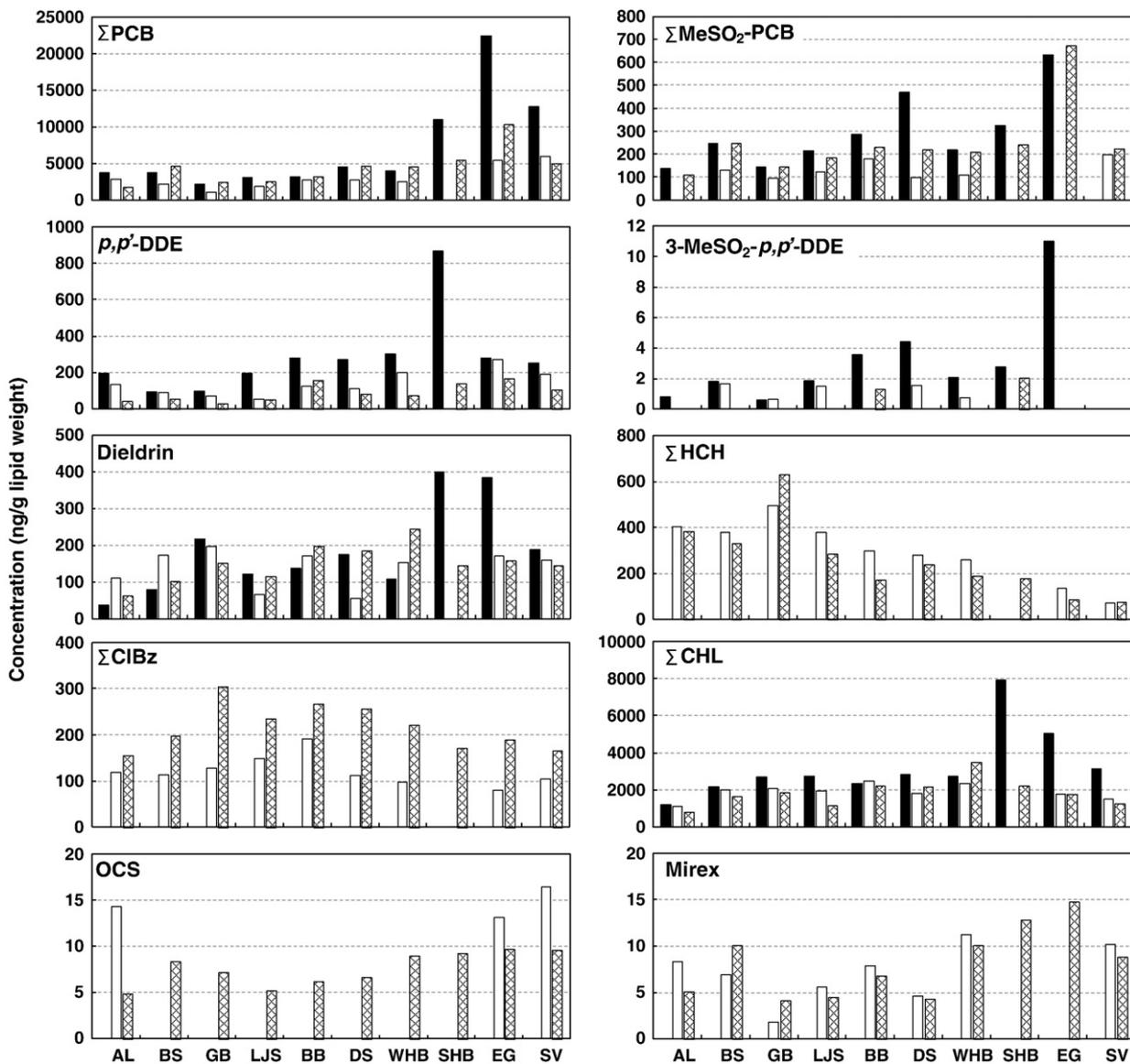


Fig. 5. Temporal comparisons of legacy contaminants in 10 polar bear subpopulations collected in 1989–1993 (black bars; from Letcher et al., 1995; Norstrom et al., 1998), 1996–2002 (white bars; from Verreault et al., 2005) and 2005–2008 (crosshatched bars; current study). Beaufort Sea (BS) samples were from SBS and NBS. Blank values indicated a contaminant that was not analyzed from the location/time point, with the following exceptions in which the contaminant was below the MLOQ for a majority of samples: OCS in 1996–2002 in BS, GB, LJS, BB, DS, WHB; mirex in 1996–2002 in EG; 3-MeSO₂-*p,p'*-DDE in 1996–2002 in BB, SV and in 2005–2008 in all except BB and SHB. See Table 1 for key to subpopulation abbreviations.

subpopulations from 1996–2002 in comparison to 1989–1993 (Verreault et al., 2005). Henriksen et al. (2001) reported decreasing CB153 levels throughout the 1990s in SV. Decreasing Σ PCB levels were also reported in the 1990s in WHB (Norstrom, 2001). However, when the current 2005–2008 data were compared to the 1996–2002 study, the decreasing pattern continued only in AL and SV. Similar non-declining patterns were observed for Σ MeSO₂-PCB. Σ PCB levels may have leveled off in the 2000s in most subpopulations, subsequent to the declines observed in the 1990s. In agreement, there was no detectable (declining) trend reported in the 1991–2007 WHB study (McKinney et al., 2010). Although many studies have found declining PCB trends in arctic biota, others have not (Rigét et al., 2010). Slow declines relative to OCPs and stalling declines of PCB trends were also reported between 1991–2005 in harbour porpoises (*Phocoena phocoena*) from various regions in the UK (Law et al., 2010). In agreement, PCB trends in arctic air have also not shown consistent declines (Hung et al., 2010). Temporal patterns of PCBs in the current study may also be related to inter-year variability effects on such short-term, limited comparisons, or possibly to changes in trends linked to climate and/or ecological changes (Carrie et al., 2010; Gaden et al., 2009; McKinney et al., 2009).

Dieldrin levels were variable and showed no declines, consistent with other temporal studies (Norstrom, 2001; Verreault et al., 2005). The only available comparisons for Σ HCH, Σ CIBz, OCS and mirex were between 2005–2008 and 1996–2002. Unfortunately, we previously found that analytical variation associated with recovery losses of relatively volatile α -HCH and CIBzs led to erroneously lower concentrations in earlier studies which would confound quantitative temporal comparisons between studies (McKinney et al., 2010). However, the 1991–2007 WHB study, wherein samples from all years were simultaneously analyzed and recovery corrected as necessary, showed decreasing α -HCH levels, increasing β -HCH levels and no change in Σ CIBz levels (McKinney et al., 2010). The finding of decreasing and increasing α -HCH and β -HCH levels, respectively, is best explained by greater partitioning of β -HCH into water resulting in the slower arrival to higher latitudes, as well as by greater metabolism and lower bioaccumulation of α -HCH in biota (Rigét et al., 2010). Lower OCS levels were found in 2005–2008 relative to 1996–2002 in AL, EG and SV. For other subpopulations, OCS was largely not detected in 1996–2002, whereas OCS was detected in all 2005–2008 samples, suggesting analytical variability between studies that may confound temporal comparisons. Mirex levels were lower in 6 of 9 subpopulations in 2005–2008 versus 1996–2002.

Some legacy contaminant levels appeared to decline in arctic marine ecosystems as inferred from polar bears, but this pattern was not universal. Slow or stalling declines in PCB levels relative to OCPs may be related to continued emissions from in-use materials and stored waste, despite previously declining environmental levels after product discontinuation in the 1970–1980s (Diamond et al., 2010). Another explanation for non-declining levels may be exemptions to international regulations including the use of DDT for vector control. In addition to continuing high levels of some historic pollutants, the increasingly complex mixture of “new” chemicals such as BFRs implies that these organohalogen pollution issues will remain an environmental concern in arctic ecosystems in years to come.

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Appendix A. Supplementary data

In this section can be found the complete list of monitored contaminants, subpopulation levels of individual compounds/con-

geners/metabolites and contaminant levels in adult males/females/subadults by subpopulation, and temporal comparisons for contaminants in 1989–1993, adult females/1989–1993 adult males/1996–2002 age-adjusted females/1996–2002 unadjusted females/current 2005–2008 bears. Supplementary data to this article can be found online at doi:10.1016/j.envint.2010.10.008.

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