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Legacy and new halogenated persistent organic pollutants in polar bears from a contamination hotspot in the Arctic, Hudson Bay Canada

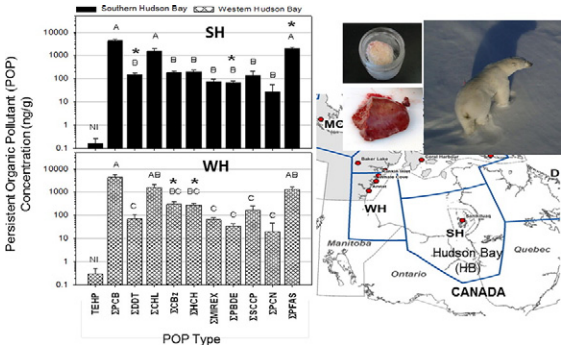
Letcher R.J. [a,b,*], Morris A.D. [a,b], Dyck M. [c], Sverko E. [d], Reiner E.J. [e], Blair D.A.D. [a], Chu S.G. [a], Shen L. [e]

[a] Ecotoxicology and Wildlife Health Division, Environment and Climate Change Canada, National Wildlife Research Centre, Carleton University, Ottawa, ON, Canada
[b] Department of Chemistry, Carleton University, Ottawa, ON, Canada
[c] Government of Nunavut, Igoolik, NU, Canada
[d] Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China
[e] Ontario Ministry of the Environment and Climate Change, 125 Resources Rd, Toronto, ON, Canada

HIGHLIGHTS

- 210 out of 295 legacy and new POPs were present in Hudson Bay (HB) polar bears.
- ΣPCBs, ΣCHLs and PFOS were the dominant POPs in fat or liver samples.
- Some POPs (e.g. ΣPFASs and ΣCHLs) were influenced by age, sex and/or subpopulation.
- Some new POP concentrations were comparable (ΣSCCPs) and some lower (ΣPCNs) to legacy POPs.

GRAPHICAL ABSTRACT



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ABSTRACT

A large and complex suite of 295 legacy and new halogenated persistent organic pollutants (POPs) were investigated in fat or liver tissue samples of polar bears collected in 2013–2014 from Southern (SHB) and Western (WHB) subpopulations of the Canadian Arctic contaminants hotspot of Hudson Bay. A total of 210 POPs were detected and/or quantifiable with some frequency in all fat or liver samples. POP profile and concentration differences were investigated both within (e.g. age and sex) and between the two subpopulations. Two time-point comparisons were made relative to POPs reported for Hudson Bay polar bears harvested in 2007–2008. ΣPolychlorinated biphenyl (PCB) concentrations at both time points were the most concentrated of the POP groups, and were spatially uniform with no detectable influence of sex or age, as were concentrations of the dominant congener CB153. ΣChlordanes (ΣCHLs, 74–79% oxychlordane) and the Σperfluoroalkyl substances (ΣPFASs, ≈60% perfluorooctane sulfonate (PFOS)) had the second greatest POP group concentrations in SHB and WHB respectively, with ΣPFASs and ΣCHLs being significantly influenced by age and/or sex. ΣCHLs were spatially uniform but ΣPFASs were greater in the SHB bears, as were e.g. some flame retardants, due to e.g. local contamination and/or changes in bear behavior and diet. Endosulfans and hexabromocyclododecane were detectable in samples from 2007–2008 but not from 2013–2014, which is consistent with their global POP regulations. ΣPolychlorinated naphthalenes (ΣPCNs) were consistently detected at relatively high concentrations compared to other arctic wildlife, however these concentrations were low relative to legacy POPs. ΣShort-chain chlorinated paraffins (ΣSCCPs) were major contributors to the overall POPs burden with concentrations comparable to other legacy POPs, though there was no significant difference between or within subpopulations

* Corresponding author at: Ecotoxicology and Wildlife Health Division, Environment and Climate Change Canada, National Wildlife Research Centre, Carleton University, Ottawa, ON, Canada.
E-mail address: robert.letcher@canada.ca (R.J. Letcher).

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for PCNs or SCCPs. Except for octachlorostyrene, POPs concentrations were generally lower in female and male bears from SHB in 2013–2014 relative to 2007–2008, however those of WHB males were greater over the same timeframe for almost all POPs.

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1. Introduction

Persistent organic pollutants (POPs) are contaminants of global interest, found in environmental matrices and wildlife from the Arctic to the Antarctic (Muir et al., 2013a; Nash, 2011). Contaminants are assessed for toxicity, persistence, long range transport (LRT), and bioaccumulation potential under the Stockholm Convention on POPs (SC-POPs) and are regulated by the 180 member parties if reclassified (United Nations Environment Programme, 2017). The initial 12 (legacy) POPs under the SC-POPs were all organochlorine compounds (OCs) that included the organochlorine pesticides (OCPs, 9 pesticides), polychlorinated biphenyls (PCBs) and industrial by-products (United Nations Environment Programme, 2017). Fourteen new and more structurally diverse POPs have been listed since 2009 including seven halogenated (Cl, Br or F) industrial compounds or flame retardants, and seven additional OCPs.

By definition POPs are capable of LRT through atmospheric or ocean currents, allowing them to reach the Arctic (Wania and Mackay, 1995). Once they are taken up into the food chain, the lipophilic properties of most POPs render them a concern for polar bears (*Ursus maritimus*) and other top predators in the complex arctic marine food web, which can biomagnify the levels of POPs in tissues hundreds of times as a result of their lipid-rich diets (Kelly et al., 2007, 2008; Norstrom et al., 1998; Letcher et al., 2009, 2010). Perfluoroalkyl substances (PFASs) are unique among POPs, as they have limited lipophilicity and bioaccumulate primarily in the liver, yet can still exhibit biomagnification (e.g. perfluorinated sulfonic acids (PFSAs) and perfluorinated carboxylic acids (PFCAs)) between consumers and their diets (Martin et al., 2004; Greaves et al., 2012). Some older and/or new POPs such as tetra- to heptabromodiphenyl ethers (PBDEs) and endosulfan bioaccumulate but remain at low (low to sub parts per billion) concentrations in marine mammals relative to legacy POPs (Kelly et al., 2008; Letcher et al., 2009, 2010; Morris et al., 2016). Other new or more recently emerged POPs such as flame retardants and perfluorooctane sulfonate (PFOS) and other PFASs biomagnify to greater extents, and can reach concentrations comparable to some recalcitrant PCB congeners in wildlife (Dietz et al., 2013a; Martin et al., 2004; Letcher et al., 2009, 2010, 2014a; Verreault et al., 2005a, 2005b).

Polar bears have been shown to bioaccumulate a broad array of POPs classified as organohalogen contaminants (OHCs) in their fat or liver, but also have a high capacity to metabolize OHCs. Metabolism can detoxify some contaminants and facilitate depuration but may also result in persistent and/or bioaccumulative and possibly toxic metabolites such as oxychlordane and *p,p′*-bis(4-chlorophenyl)-1,1-dichloroethylene (*p,p′*-DDE) (Letcher et al., 2009, 2010; McKinney et al., 2011a, 2011b). Polar bears from different Hudson Bay subpopulations have been reported, in some cases, to have significantly different concentrations and patterns of OHCs (McKinney et al., 2011b). For example, the sum (Σ) PCB concentrations were shown to be essentially constant in the Western Hudson Bay (WHB) or slowly decreasing in the Southern Hudson Bay (SHB) subpopulations, respectively, between 1989 and 2008 (McKinney et al., 2011b). In the same study the ΣOCP concentrations were variable as well; sum chlordanes (ΣCHL) followed the same trend as ΣPCBs, while *p,p′*-DDE decreased in both subpopulations. Increasing tissue residues of regulated OHCs are due to their persistence/recalcitrance, likely coupled with both seasonal and climate-related emissions from melting multiyear sea-ice and permafrost, as well as volatilization from land, seawater and lakes (among other potential effects) (Ma et al., 2011; Macdonald et al., 2005).

Relative to other circumpolar regions, Hudson Bay, East Greenland and Svalbard are hot spots in terms of POP exposure and levels in the tissues of polar bears from these subpopulations (Letcher et al., 2010). An objective of the present study was to investigate a broad suite of legacy and new OHCs in liver or fat tissues of polar bears that were recently collected in 2013–2014 from the SHB and WHB subpopulations, and included the screening and determination of new POP contaminants of interest. Thus, for the first time since 2007–2008, the profiles and levels of legacy, but also older, understudied and new OHCs, were investigated in polar bears from Hudson Bay and thus showing the increasing complexity of OHC exposure in these subpopulations (Letcher et al., 1995a; McKinney et al., 2011b; Muir et al., 2006). The suite included new POPs such as PFOS, PBDEs and polychlorinated naphthalenes (PCNs), candidate POPs such as short-chain chlorinated paraffins (SCCPs) and decabromodiphenyl ether (decaBDE/BDE209), and other relatively unregulated contaminants including organophosphate ester (OPE) flame retardants and plasticizers and alternative halogenated flame retardants (HFRs; including Dechlorane Plus (DDC-CO) isomers and the DDC-CO-like compounds Dec602 and Dec603) (regulatory status of these OHCs are summarized in Table S1). Reports of both SCCPs, PCNs, DDC-COs and DDC-CO-like compounds in top predators from the Canadian Arctic are relatively rare and few contemporary measurements exist, though they do meet the criteria for classification as POPs as a function of their environmental and physical-chemical properties, e.g. log*K*ow values and atmospheric half-lives (Bidleman et al., 2010; Helm et al., 2002; Strid et al., 2013; Tomy et al., 1999, 2000). Other study objectives were to better understand the sources/exposure pathways, temporal changes, age-sex differences, influence of climate change, etc., of legacy and new POPs in polar bears from Hudson Bay. Where possible, tissue concentrations of OHC classes in the present 2013–2014 bears were also compared to previously reported OHC data in Hudson Bay bear samples collected in 2007–2008.

2. Experimental section

2.1. Sample collection

Tissue samples (liver and subcutaneous fat) were collected in 2013–2014 from polar bears of different sexes and ages from the WHB ($n = 17$) and SHB ($n = 24$) subpopulations, where the harvests and sampling were carried out by participating local hunters and the Government of Nunavut (Igloolik, NU) (Fig. S1, Table S2) (Morris et al., Accepted for publication). Samples were excised, double-wrapped tightly in chemically rinsed (acetone and then hexanes) aluminum foil, and then placed inside a sterile Whirlpak bag and frozen to −20°C until subsampling and analysis at the Letcher Labs/Organic Contaminants Research Laboratory in the National Wildlife Research Centre [NWRC; Environment and Climate Change Canada (ECCC), Ottawa, ON]. When the samples were received at NWRC, they were completely frozen and with no indication of cross-contamination of the samples via contact with the Whirlpak bags. Furthermore, while the received fat samples were partially frozen, sub-samples of fat were taken from the inner core of the received fat samples, and thus from a section where no POP cross-contamination could have penetrated. After this sub-sampling step, remaining tissue aliquots were archived in ECCC's National Wildlife Specimen Bank located in the NWRC.

Growth layers of cementum on decalcified, stained sections of lower right incisors (I_3) were used to age the bears (Matson's Laboratory, Milltown, MT, USA) (Dietz et al., 2007; Matson et al., 1993). Nominal ages were not available for two animals from WHB (Table S2) so sex-specific regressions of the logarithm of *cis*-chlordane concentrations (ng g^{-1} wet weight) with age were tested to estimate these values (McKinney et al., 2011b). A significant model was found for male bears (Age = 14.4–8.25 * log[*cis*-chlordane] = 8.65 (≈9); $n = 28$, $F = 6.28$, $R^2 = 0.20$, $p = 0.019$), but not females [$n = 11$, $F = 2.27$, $R^2 = 0.20$, $p = 0.17$], therefore one WHB female bear was not assigned an age for analysis (and this WHB female was excluded from the general linear models (GLMs)).

2.2. POPs and analysis

A comprehensive and complex suite of 295 individual, legacy and new POPs were analyzed and/or determined according to the existing and published protocols; references and the details of the analytical methods used are fully described in the Supporting information. The following POPs were analyzed: PCBs (Gebbink et al., 2008a, 2008b): 74 single or co-eluting congeners (tri–decaCBs), OCPs (Ahn et al., 2006; Gebbink et al., 2008a, 2008b; Jorundsdottir et al., 2006): *p,p′*-bis(4-chlorophenyl)-1,1,1-trichloroethane (*p,p′*-DDT), *p,p′*-DDE, *p,p′*-bis(4-chlorophenyl)-1,1-dichloroethane (*p,p′*-DDD); chlorobenzenes (CBzs; 1,2,3,4-tetra-, 1,2,4,5-tetra-, penta-, hexachlorobenzene; TCB, PeCBz, HCB, respectively), α-HCH, β-HCH, γ-HCH, dieldrin, *cis*-/*trans*-chlordane and *cis*-/*trans*-nonachlor, Mirex, photo-Mirex, hexachlorobutadiene (HCBD), pentachlorophenol (PCP), pentachloroanisole (PCA), and *o, p′*- and *p,p′*-dicofol; PBDEs (McKinney et al., 2011a, 2011b): 25 single or co-eluting congeners (tri–decaBDEs); alternative HFRs and by-products (Ahn et al., 2006; Gauthier and Letcher, 2009; Jorundsdottir et al., 2006; McKinney et al., 2011a, 2011b; Norstrom et al., 2004): 24 HFRs (1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), pentabromoethyl benzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), decabromo-diphenyl ethane (DBDPE), 2,4,6-tribromophenyl allyl ether (TBP-AE), tetra-bromo-*o*-chlorotoluene (TBCT), pentabromotoluene (PBT), hexabromo-benzene (HBB), pentabromobenzyl acrylate (PBB-Acr), pentabromo-*p*-xylene (TBX), 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane (α-DBE-DBCH, β-DBE-DBCH), α-hexabromocyclododecane (α-HBCDD), octabromo-1,3,3-trimethyl-1-phenyl indane (OBTMPI), polybrominated biphenyls (BB-101, BB-153), pentabromophenyl allyl ether (PBP-AE), 5,6-Dibromo-1,10,11,12,13,13-hexachloro-11-tricyclo[8.2.1.02,9]tridecene (DBHCTD), 2,4,6-tribromophenyl-2,3-dibromopropyl ether (TBP-DPTE), 2,3-dibromopropyl pentabromophenyl ether (PBP-dbpe), bis(2-ethylhexyl)-tetrabromophthalate (BEH-TEBP), and Dechlorane Plus (*syn*-DDC-CO and *anti*-DDC-CO), Dec602, Dec603 and bis-(4-chlorophenyl) sulfone (BCPS); organophosphate esters (OPEs)) (Chu and Letcher, 2015): 17 compounds (tris(2-chloroethyl) phosphate (TCEP), tripropyl phosphate (TPrP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloropropyl) phosphate (TDCIPP), triphenyl phosphate (TPHP), tris(2,3-dibromopropyl) phosphate (TDBP), tri-*n*-butyl phosphate (TNBP), tris(4methylphenyl) phosphate (TMPP), 2-ethylhexyl diphenyl phosphate (EHDPP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-bromo-4-methylphenyl) phosphate (T2B4MP), tris(4-bromo-3-methylphenyl) phosphate (T4B3MP), tris(3-bromo-4-methylphenyl) phosphate (T3B4MP), tris(2-ethylhexyl) phosphate (TEHP), tris(tribromonentyl) phosphate (TTBNPP), triethyl phosphate (TEP) and 2,2-bis(chloromethyl_propane-1,3-diyl tetrakis(2-chloroethyl)bis(phosphate) (V6)); short-chain chlorinated paraffins (SCCPs) (Strid et al., 2013; Tomy et al., 1997): 24 congeners total, with the general formula $C_xH_{(2x-y+2)}Cl_y$, where $x = 10$–13 and $y = 5$–10 (penta- to decachlorinated, decanes to tridecanes); polychlorinated naphthalenes (PCNs): 68 congeners, mono- to octaCN (1–8 Cl; CN1-CN75); perfluoroalkyl substances (PFASs) (Houde et al., 2006; Greaves et al., 2012; Letcher et al., 2015): 13 (C_4–C_{16}) perfluorinated carboxylic acids (PFCAs) including perfluoro-*n*-nonanoic acid (PFNA) and perfluoro-*n*-octanoic acid (PFOA), 4 (C_4, C_6, C_8 and C_{10}) perfluorinated sulfonic acids (PFSAs) including perfluoro-1-hexanesulfonic acid (PFHxS) and perfluoro-1-octanesulfonic acid (PFOS), perfluoro-4-ethylcyclohexyl sulfonic acid (PFEtCHxS), and 4 fluorinated sulfonamides (FASAs) including perfluoro-1-octanesulfonamide (FOSA).

Sum (Σ) concentrations of quantifiable components were calculated for ΣPCB, ΣDDT, ΣCHL, ΣHCH, ΣCBz, ΣPBDE, ΣMirex, ΣPFAS, ΣSCCP, and ΣPCN (Tables S1 and S7); Five OPEs were quantifiable at sub-ppb levels in polar bear fat samples, but with variable and low detection frequencies (SHB/WHB), and were as follows, TEHP (71%/82%), TPHP (29%/24%), TCIPP (13%/6%), TBOEP (38%/35%) and TNBP (38%/29%).

2.3. Contaminant extraction and analysis

All details of POP sample extraction and analysis is based on published methods (as cited in Section 2.2) and can also be found in the Supporting information. Briefly, separate subsamples of liver (PFASs only) and fat (all other POPs) were extracted and the resulting chemical fraction were analyzed by either low resolution gas chromatography–mass spectrometry (LRGC–MS), high resolution GC-tandem mass spectrometry (HRGC-MS/MS), high resolution GC-high resolution mass spectrometry (HRGC-HRMS) or ultra-high performance liquid chromatography-MS/MS (UPLC-MS/MS). All LRGC–MS and UPLC-MS/MS based OHC analyses were performed at the OCRL-NWRC; SCCPs were analyzed by HRGC-HRMS (magnetic sector) and PCNs were analyzed by isotope dilution HRGC-HRMS at the National Laboratory for Environmental Testing (Environment and Climate Change Canada) and ALS Environmental, respectively (both in Burlington, ON, Canada). All available samples were analyzed for all OHCs with the exception of PCNs, which were analyzed in subset of fat samples ($n = 10$, $WHB_{Males} = 5$, $SHB_{Males} = 2$, $SHB_{Females} = 3$). HRGC-HRMS analyses of Dec602 and Dec603 were performed at Ontario Ministry of the Environment and Climate Change.

2.4. Quality analysis/quality control and data handling

Method limits of detection (MLODs) and method limits of quantification (MLOQs) for OHCs determined by LRGC–MS for bear fat sample fractions as the minimum amount of analyte that produced a peak with a signal-to-noise (S/N) ratio of 3 and 10, respectively (Table S6). The exception was for PCP, PCA and the dicofol isomers where the S/N ratios were 3 and 5 for the MLODs and MLOQs, respectively. UPLC-MS/MS-based MLODs were calculated in the same manner, but MLOQs were calculated using the student *t*-statistic and standard deviations of replicate injections of low concentration standards spiked into pork fat or liver (see Supporting information). When analyte levels approached the MLOQs and were detected in <50% of samples within a subpopulation, they were considered non-detects and were not included in any further calculations. When analyte detection frequencies were >50% but <100%, random values between zero and the MLOD were substituted into the dataset for statistical analysis (Antweiler and Taylor, 2008).

Native and isotopically enriched standards were spiked into fat tissue homogenates at the beginning of extraction to monitor recovery efficiencies and where applicable to quantify contaminants using internal standard based approaches (Table S3). A lab method blank and a standard reference material (SRMs = 1945c, pilot whale blubber, National Institute of Standards and Technology, Gaithersburg, MD, USA) or a spiked surrogate matrix (commercial pork fat or liver) were extracted with each batch of 10 samples (Tables S4 and S5). Data were inherently recovery corrected as internal standard based approaches were used for quantitation, and when warranted were blank corrected for any background contamination. After recovery correction, applicable blank correction, and MLOQ-based substitutions for non-detects,

the data were lipid normalized (concentrations of primary analytes tended to be correlated with lipid content) and were presented as ng g^{-1} lipid weight (lw); PFASs are presented as ng g^{-1} wet weight (ww) (lipid contents in Table 1). TEHP concentrations were lipid corrected for comparability despite not being correlated with lipid contents (see Table S7). Further details quality analysis, quality control and data handling are described in detail and discussed in the Supporting information.

2.5. Statistical analysis

The statistical analyses focused on the sum (Σ) concentrations for each subgroup of contaminants, along with contaminants of interest detected at high frequencies and concentrations (TEHP, CB153, cis-chlordane, oxychlordane, p,p′-DDE, dieldrin, HCB, β-HCH, BDE47, BB153, PFOS, PFOA). Statistical analyses were performed using Sigmaplot 11 or SYSTAT 13 (Systat Software Inc.).

Table 1
Geometric mean concentrations (ng g^{-1} lipid weight; except for PFASs, ng g^{-1} wet weight) and their respective 95% confidence intervals for sum (Σ) concentrations and selected contaminants (legacy or new POPs).[a,b] Amalgamated concentrations (not separated by age or sex) are available in Table S7.

	Southern Hudson Bay			Western Hudson Bay		
	Adult females	Adult males	Subadults (male + female)	Adult females	Adult males	Subadults (male + female)
n	5	10	9	1	12	4
Age	6 (5–7)	6.5 (5–18)	3 (2–4)	6	7 (5–13)	2 (1–4)
Lipid[c] (%)	82 ± 4.4	80 ± 6.0	80 ± 5.6	86	72 ± 16	77 ± 13
Lipid[d,e] (%)	84 ± 2.6	88 ± 5.0	85 ± 8.4	91	84 ± 8.7	85 ± 12
ng g^{-1}						
TEHP	0.109	0.154	0.218	0.132	0.292	0.448
95% CI	(0.0354–0.33)	(0.056–0.425)	(0.0855–0.557)	(–)	(0.136–0.628)	(0.230–0.871)
ΣPCB	4111	4276	4529	3090	4797	3357
95% CI	(2000–8453)	(3236–5649)	(3709–5531)	(–)	(3357–6855)	(2143–5260)
CB153	1489	1581	1879	1324	2037	1429
95% CI	(771–2877)	(1225–2042)	(1522–2321)	(–)	(1396–2972)	(904–2259)
ΣCHL	1905	979	2291	2529	1403	2223
95% CI	(1230–2951)	(711–1349)	(1738–3020)	(–)	(993–1982)	(1297–3811)
cis-Chlordane	10.9	7.94	15.0	12.7	11.5	13.8
95% CI	(7.21–16.6)	(5.61–11.2)	(10.1–22.4)	(–)	(8.18–16.1)	(7.18–26.4)
Oxychlordane	1581	738	1820	2183	1002	1694
95% CI	(1009–2477)	(505–1079)	(1384–2393)	(–)	(701–1432)	(887–3236)
ΣDDT	129	137	185	41.7	72.9	70.3
95% CI	(93.5–177)	(103–181)	(127–269)	(–)	(40.5–131.52)	(19.5–254)
p,p′-DDE	121	131	178	40.5	68.5	66.8
95% CI	(87.7–168)	(98.4–175)	(122–259)	(–)	(38.5–121.9)	(18.5–242)
ΣHCH	157	191	255	195	299	237
95% CI	(111 − 222)	(152–239)	(225–290)	(–)	(251–357)	(144–390)
α-HCH	49.2	43.0	74.3	47.4	45.4	32.4
95% CI	(34.9–69.3)	(30.8–59.8)	(62.2–88.7)	(–)	(34.2–60.3)	(12.4–84.5)
β-HCH	107	145	177	147	249	203
95% CI	(68.9–165)	(115–183)	(146–215)	(–)	(204–304)	(131–315)
ΣCBz	183	156	217	208	300	320
95% CI	(104–320)	(115–213)	(196–241)	(–)	(225–399)	(110–931)
Dieldrin	141	118	218	207	231	251
95% CI	(83.8–237)	(80.5–174)	(183–260)	(–)	(163–327)	(74.3–849)
ΣMirex	76.2	61.7	98.2	78.9	67	58.5
95% CI	(47.9–121.3)	(45.4–83.8)	(68.2–141.3)	(–)	(50.8–88.3)	(26.9–127.4)
Mirex	10.2	13.3	22.1	13	3.76	11.4
95% CI	(1.14–91)	(6.43–27.5)	(15.7–31)	(–)	(0.873–16.2)	(5.77–22.6)
Photomirex	59.7	45.1	75.9	65.9	55.7	47
95% CI	(43.3–82.4)	(32.4–62.7)	(52.2–110.2)		(42.5–73.1)	(21.0–105.2)
ΣPBDE	88.5	55.5	72.1	27.5	38.2	28.6
95% CI	(34.5–227)	(39.6–77.6)	(62.9–82.7)	(–)	(29.6–49.3)	(14.8–55.3)
BDE47	31.7	22.1	33.8	10.3	14.4	12.7
95% CI	(13.3–75.5)	(15.2–32.3)	(27.3–41.9)	(–)	(11–18.9)	(6.79–23.7)
BB153	39.2	41.8	30.8	21.1	26.7	18.3
95% CI	(24.5–62.5)	(29.3–59.6)	(23.2–40.9)	(–)	(16.6–43)	(10.4–32.1)
ΣSCCP	136	117.5	163	28.8	163	303
95% CI	(31–598)	(50.7–272)	(81.1–326)	(–)	(111–240)	(160–571)
ΣPCN	26.1	14.8	48.5	NM	20.2	NM
95% CI	(–)	(–)	(–)	(–)	(8.85–46.0)	(–)
ΣPFAS	2366	2427	1449	1888	1442	991
95% CI	(1710–3273)	(1942–3032)	(1223–1716)	(–)	(1183–1758)	(442–2223)
ΣPFCA	889	938	585	740	558	408
95% CI	(634–1247)	(785–1120)	(486–703)	(–)	(449–694)	(187–893)
PFOA	34.6	29.6	31.5	50.8	15.7	16.5
95% CI	(18–66.5)	(22.4–39.3)	(22.2–44.6)	(–)	(10.3–24.15)	(4.04–67.3)
PFOS	1459	1459	847	1135	863	566
95% CI	(1059–2009)	(1130–1884)	(716–1003)	(–)	(710–1049)	(243–1321)

[a] PFAS compounds were in ng g^{-1} wet weight (ww) in the liver, all others were lipid weight normalized (ng g^{-1} lw) in the fat.
[b] PCNs were measured in small numbers of samples in SHB (males = 2, subadults = 2, females = 1).
[c] WHB females were not tested statistically; errors could not be calculated when separated ($n = 1$).
[d] Lipid contents used for quantification of s, BCPS, dicofol isomers, PCP, and PCA.
[e] Lipid contents used for quantification of all other lipophilic compounds.

Statistical comparisons used logarithmically (log_{10}) transformed data which better approximated the normal distribution in a majority of cases; thus data are presented as geometric means and their 95% confidence intervals (Tables 1 and S7). Multivariate principle components analyses (PCA) were performed using the sum (Σ) of the individual concentrations of the major classes of organohalogen contaminants in polar bears from the Southern and Western Hudson Bay (Fig. 1). The data used for the PCA were not filtered by age or sex, and the PCA was performed to assess which contaminant concentrations varied by subpopulation. The PCNs were not included in the PCA due to their measurement in a reduced number of samples, and only TEHP was included as a single compound as it is representative of the ΣOPE concentrations (Table S7). An overall variance of 52.2% was explained by the first 2 PCs after the data were log_{10}-transformed to improve the left-skewing and range scaled (each variable is divided by its range) to make the features more comparable (standardization).

Multivariate General Linear Models (GLMs) were generated to assess effects of sex, subpopulation, age and the first-order interaction of sex × age on the log_{10}-transformed contaminant concentrations. The interaction of sex × subpopulation was not included in the models as SHB females were not included in the GLM (only one adult female was available), and age × subpopulation was not tested as it is not a relevant hypothesis that contaminants only vary with age in one of the adjacent Hudson Bay subpopulations but not the other. The models were tested using an automatic, backwards, step-wise sum of squares (Type III SS) procedure ($\alpha = 0.05$ for entry/exit) that built the final model using variables that resulted in the lowest corrected Akaike information criterion (AIC) score. Outliers identified automatically during the GLM procedures were sequentially excluded and the models were retested. In order to assess the differences in the covariate adjusted means between subpopulations, the percent difference/change (%) in SHB relative to the WHB was calculated by extracting the anti-log of the regression coefficient for significant relationships with subpopulation and multiplying by 100%. Partial η^2 values (measure of individual effect size relative to variance of the model) were calculated by Partial $\eta^2 = SS_{Effect}/(SS_{Effect} + SS_{Error})$ (McKinney et al., 2011b). The statistical analysis of PCNs and SCCPs were relatively limited overall due to the small sample size (PCNs) or quantification method (SCCPs; see Supporting information and in Strid et al., 2013 and Tomy et al., 1997), and only the ΣSCCP was included in the multivariate GLM analyses.

Pearson correlation analysis was also conducted on the log_{10}-transformed concentrations and to investigate the relationships between concentrations and age in specific groups of bears to compliment the results of the GLM.

3. Results and discussion

3.1. Overall trends of quantifiable contaminants

PCBs remain the most concentrated group of POP contaminants in polar bear fat, and in other environmental and biotic matrices in the Canadian Arctic (Letcher et al., 2010; Muir et al., 2013a). The geometric mean ΣPCB concentration was two to three fold greater than either the ΣCHL or ΣPFAS (largely PFOS) [ΣPCB (SHB = 4335 ng g^{-1} lw, WHB = 4295 ng g^{-1} lw); ΣCHL (SHB = 1549 ng g^{-1} lw, WHB = 1618 ng g^{-1} lw; and ΣPFASs (SHB = 1991 ng g^{-1} ww, WHB = 1343 ng g^{-1} ww) (Tables 1 and S7). The ΣPCB and ΣPFAS were greater than all other concentrations in both the SHB and WHB; with the ΣCHL concentration being greater relative to all other OCPs. The concentrations of ΣHCH and ΣCBz were greater in the WHB bears than those in the SHB (Tables 1 and S7). ΣOPE, Σdicofol and ΣPCP concentrations could not be calculated because of these low frequencies or complete lack of detection (Tables 1 and S7). Concentrations of TEHP, the only consistently detected OPE (detection frequency = 71–82%, geometric mean concentrations = 0.163–0.308 ng g^{-1} lw), were the lowest observed among all of the major contaminant groups. Sum-contaminant levels with intermediate concentrations (ΣDDT, ΣHCH, ΣCBz, ΣPBDE, ΣSCCP, ΣPCN, ΣMirex) were not markedly different from each other within the two subpopulations, particularly when their 95% confidence intervals are considered (SHB range = 26.6–204 ng g^{-1} lw, and WHB = 20.2–298 ng g^{-1} lw) (Tables 1 and S7).

The subpopulation groupings in the PCA score plot were reasonably well resolved and did separate, demonstrating both similarity among the contaminant patterns in bears from the same subpopulations and differentiation between them, though there was a relatively large overlap of their 95% confidence regions (Fig. 1a). The scores of the WHB versus SHB bears were significantly different across PC 2 (2-tailed *t*-test, $t = 6.51$, $p < 0.001$), but did not differ significantly across PC 1 (2-tailed *t*-test, $t = -0.939$, $p = 0.354$). The loadings plot shows that despite having the largest concentrations (with the exception of PFASs), the

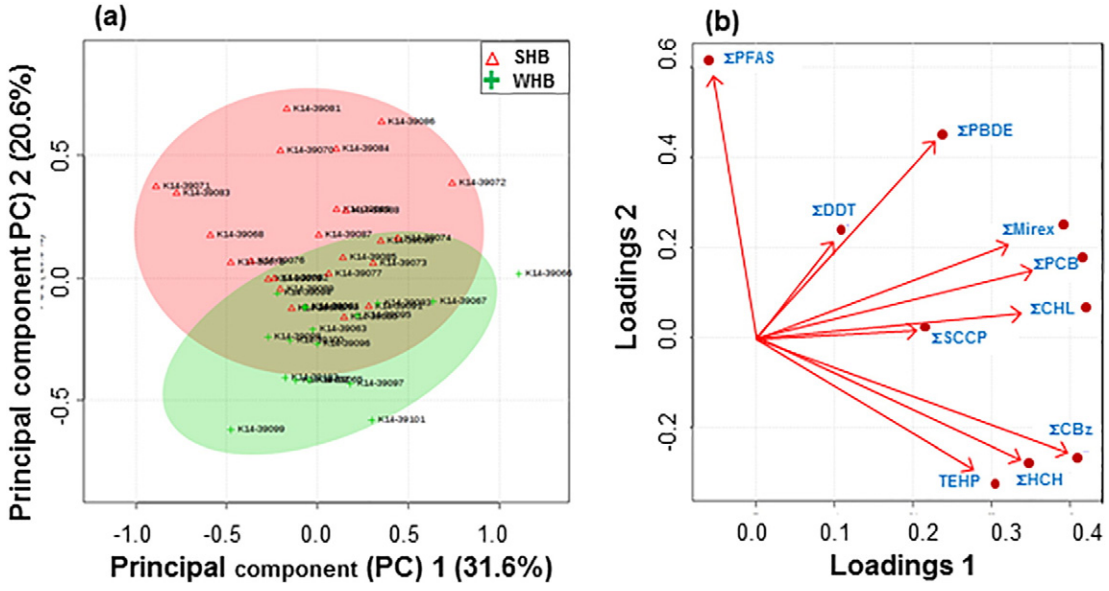

Fig. 1. Score plot (A) and factor loadings (B) from principle components analyses (PCA) of the sum (Σ) or individual concentrations (ng g^{-1} lipid weight; ΣPFASs ng g^{-1} wet weight) of major classes of organohalogen contaminants in polar bears from the Southern and Western Hudson Bay. The PCA is based on the same data as reported in Tables 1 and S7. An overall variance of 52.2% was explained by the first 2 PCs. The PCA data were log_{10}-transformed to improve the left-skewing and range scaled (each variable is divided by its range) to make the features more comparable (standardization).

loadings of ΣPCB and ΣCHL had little influence on the differentiation and clustering of the subpopulation scores (Fig. 1b). Indeed, these concentrations were very similar between the SHB and WHB when the bears were not separated by age or sex (Table S7). The ΣMirex and ΣSCCPs also had minimal impact on the separation of the scores of the bears. The primary drivers of the separation of the subpopulations across PC 2 were the loadings of ΣPFAS, ΣPBDE, and ΣDDT, concentrations which were greater in SHB bears over WHB bears, as well as ΣCBz, ΣHCH and TEHP, concentrations which were greater in WHB bears (Fig. 1, Table S7).

Large, spatially uniform concentrations have been previously reported for both PCBs and chlordanes in polar bears from these regions, and are due to their persistence and lack of direct emission sources (McKinney et al., 2011b; Verreault et al., 2005b). As stated, the influences of the ΣDDT, ΣPBDE and ΣPFAS concentrations were greater for the SHB bears, while ΣCBz and ΣHCH along with TEHP were greater in the WHB, corresponding to larger concentrations for these compounds in the respective subpopulations (Tables 1 and S7, Fig. 1). The CBz compounds are relatively volatile, while the HCHs are transported by different vectors (α-HCH is transported via atmospheric LRT, β-HCH primarily via ocean currents) (Li and MacDonald, 2005), which could skew their distribution across Hudson Bay, contaminating the marine food web to different degrees. The β-HCH isomer is also more bioaccumulative, so deviations in diet or food web structure can be an important confounding factor (McKinney et al., 2009).

Elevated concentrations of PBDEs and PFASs in the SHB may be due to their closer proximity to more southern and source urban centers (e.g., Great Lakes Regions) (Giesy et al., 2006; Ma et al., 2013). PBDEs and PFASs are also in many current-use products and could be in landfill leachate (Li et al., 2012), and/or be released from waste during burning in community landfills (A. Morris, *personal observation*). AM bears from the WHB are known to scavenge for food in town dumps (e.g. WHB bears in Churchill, MB, Canada) (Lunn and Stirling, 1985), although this is difficult to account for as a major influence on the overall diet of polar bears (Gormezano and Rockwell, 2013). Based on dietary or ecological tracers (e.g. stable carbon and nitrogen isotopes and fatty acid signatures) diet between and within populations have been shown to vary considerably (Derocher et al., 2002; McKinney et al., 2009, 2010), which can have substantial influence on polar bear contaminant exposures. As reported in McKinney et al. (2011a), we previously examined the geographic variation in polar bear diets including for bears from the SHB and WHB subpopulations (collected in 2007–2008), and using stable carbon and nitrogen and fatty acid signatures based on muscle and fat samples, respectively. Overall, WHB and SHB as well as eastern Arctic Davis Strait and East Greenland subpopulation bears had the most distinct ecological tracer signatures. The findings suggested that WHB and SHB bear diets are similar with more freshwater or terrestrially associated prey as compared to bears from other circumpolar subpopulations.

3.2. PCBs including two time-point comparisons

The GLM analyses indicated that none of the factors or interactions tested had a significant influence on the ($\log_{10}$) concentrations of ΣPCB or CB153. Table 1 shows the concentrations of the major analytes separated by age class and sex, and Table 2 summarizes significant results of the multivariate GLMs. As indicated in the previous section, the PCA also demonstrated limited/no influence of the ΣPCB on the separation of the scores of the bears from the SHB and WHB (Fig. 1), further supporting the results of the multivariate GLM (Table 2). These results were comparable to polar bear ΣPCB concentrations reported eight years earlier (2007–2008) from these subpopulations (McKinney et al., 2011b). Despite some observable differences in the concentrations between age classes, particularly in the WHB, the differences were not substantial enough to be detected by the GLM (note that WHB females were not included in the GLM as only one adult female was available). Therefore, the concentrations of the ΣPCB and CB153 can be viewed as relatively uniform across these subpopulations and groups.

Six of the most recalcitrant PCB congeners in the SHB and WHB polar bears comprised 86–88% of the ΣPCB (respectively) (Fig. S2). The concentrations of these congeners were of the order: CB153 > CB180 > CB99 ≈ CB170/190 > CB138/158 > CB194 (note that CB170/180 was slightly greater than CB99 in the SHB) (Table S7). These PCBs were also the most abundant when measured in polar bear populations in Canada, Greenland, Norway and Alaska (McKinney et al., 2011a, 2011b). The same congeners are consistently among the greatest concentrations in other Arctic wildlife; however different congeners have also been found to be abundant in other marine mammals (Kelly et al., 2007). The concentrations of these recalcitrant PCB congeners were similar between the subpopulations (Table S7). However, the less abundant congeners tended to be greater in the SHB bears which could be indicative of greater PCB weathering (differences in volatilization, partitioning properties, chemical and biological transformation, photodegradation, and bioaccumulation) (Letcher et al., 2010), and/or increased mobilization of PCB congeners due to climate change (Ma et al., 2011), which can alter the pattern of congeners in a given matrix from those dominated by Arochlor-related congeners (Letcher et al., 1998). Spatially, the concentrations of PCBs in the East Greenland polar bears in 2010 (Dietz et al., 2013b) were two to three-fold greater (median concentrations in East Greenland: subadults = 8935 ng g^{-1} lw; AFs = 6842 ng g^{-1} lw; AMs = 13,022 ng g^{-1} lw) than those presently observed (Tables 1 and S7), though the pattern of the highest level congeners was the same.

Two time-point comparisons were made using available data we have previously generated from sample analysis of 2007–2008 harvested bears (McKinney et al., 2011b). Relative to the 2007–2008 Hudson Bay bears, ΣPCB concentrations in the present 2013–2014 bears were 27% and 25% lower in SHB AMs and AFs (respectively), while the WHB males remained essentially unchanged (5.2% change) (Fig. 2). These declines are consistent with previous observations that demonstrated an approximately 50% decrease in ΣPCB concentrations over a 16 year period (1991–2007) in SHB females, while remaining temporally steady in WHB (McKinney et al., 2010, 2011b). Concentrations of PCBs were shown to be gradually decreasing in East Greenland polar bears over the period of 1983 to 2010, however the trends for AMs and AFs were not significant (Dietz et al., 2013b). PCB accumulation and toxicokinetics are also confounded by rapid metabolism (for all but the most recalcitrant PCB congeners) in polar bears (Letcher et al., 1998, 2010), changes in diet and food web structure (McKinney et al., 2009), as well as a number of ecological and physiological factors that can affect bioaccumulation, deposition and fate of all contaminants (weathering, revolatilization/mobilization, etc.) (Ma et al., 2011; Macdonald et al., 2005). Regardless, there appeared to be clear differences in trends for most of the contaminants in the present WHB males (Fig. 2). As was hypothesized by McKinney et al. (2009, 2010), dietary tracer results for WHB polar bears indicated increased proportional consumption of harbor and harp seals and a relative decrease in bearded seals. Bearded seals in other regions have been relatively less contaminated than other seals, and harp seals are migratory and may be a vector for transporting a more contaminated North Atlantic organohalogen signature to WHB polar bears.

3.3. Legacy OCPs and related compounds

The multivariate GLMs for the OCPs indicated variable influences of the covarying factors (Table 2). Among the chlordanes tested, ΣCHL and oxychlordane had significant effects of the sex of the bears on the log-concentrations (partial $\eta^2 = 0.31$ and 0.39 respectively, both $p < 0.001$). These models and *cis*-chlordane were also significantly influenced by age, but not subpopulation (partial $\eta^2 = 0.52–0.60$, $p < 0.001$). The ΣCHL concentrations were greater than for the other OCPs, and ΣCHL was dominated by the metabolites oxychlordane (74–79%)

Table 2
Summary of the results from general linear models (GLMs) generated to test the effects of sex, subpopulation, age and the interaction of sex × age on the concentrations (log_{10} transformed) of major contaminant groups and individual contaminants of interest. Partial η^2 were calculated using the adjusted Type III sum of squares from the final GLM models. The overall variance explained (R^2) is also given along with the sample sizes for each model (n).[a,b] Positive effects of subpopulation are associated with greater concentrations in the SHB.

Log [contaminant]	n	R^2		Sex	Sub-population	Age	Sex × age
TEHP	–	–	Coefficient (SE)	–	–	–	–
			F-ratio, *p*-value	–	–	–	–
			Partial η^2	–	–	–	–
ΣPCB	–	–	Coefficient (SE)	–	–	–	–
			F-ratio, *p*-value	–	–	–	–
			Partial η^2	–	–	–	–
CB153	–	–	Coefficient (SE)	–	–	–	–
			F-ratio, *p*-value	–	–	–	–
			Partial η^2	–	–	–	–
ΣDDT	37	0.27	Coefficient (SE)	–	0.098 (0.037)	−0.023 (0.011)	–
			F-ratio, *p*-value	–	6.90, 0.013	4.63, 0.039	–
			Partial η^2	–	0.17	0.12	–
p,p′-DDE	37	0.29	Coefficient (SE)	–	0.10 (0.037)	−0.023 (0.011)	–
			F-ratio, *p*-value	–	6.90, 0.009	4.63, 0.039	–
			Partial η^2	–	0.18	0.12	–
ΣCHL	36	0.71	Coefficient (SE)	0.096 (0.025)	–	−0.047 (0.007)	–
			F-ratio, *p*-value	15.0, <0.001	–	48.2, <0.001	–
			Partial η^2	0.31	–	0.59	–
cis-Chlordane	35	0.52	Coefficient (SE)	–	–	−0.042 (0.007)	–
			F-ratio, *p*-value	–	–	35.7, <0.001	–
			Partial η^2	–	–	0.52	–
Oxychlordane	36	0.74	Coefficient (SE)	0.19 (0.025)	–	−0.050 (0.007)	–
			F-ratio, *p*-value	21.5, <0.001	–	50.1, <0.001	–
			Partial η^2	0.39	–	0.60	–
ΣCBz	38	0.33	Coefficient (SE)	–	−0.13 (0.03)	–	–
			F-ratio, *p*-value	–	17.8, <0.001	–	–
			Partial η^2	–	0.33	–	–
ΣHCH	34	0.70	Coefficient (SE)	0.12 (0.037)	−0.029 (0.012)	−0.041 (0.007)	−0.037 (0.007)
			F-ratio, *p*-value	11.5, 0.002	5.34, 0.028	35.2, <0.001	28.3, <0.001
			Partial η^2	0.28	0.16	0.55	0.49
β-HCH	38	0.47	Coefficient (SE)	–	−0.094 (0.024)	–	−0.009 (0.004)
			F-ratio, *p*-value	–	14.7, 0.001	–	5.16, 0.029
			Partial η^2	–	0.30	–	0.13
Dieldrin	38	0.43	Coefficient (SE)	–	−0.12 (0.032)	−0.037 (0.010)	–
			F-ratio, *p*-value	–	14.6, 0.001	14.7, 0.001	–
			Partial η^2	–	0.29	0.30	–
ΣMirex	–	–	Coefficient (SE)	–	–	–	–
			F-ratio, *p*-value	–	–	–	–
			Partial η^2	–	–	–	–
ΣPBDE	37	0.33	Coefficient (SE)	–	0.12 (0.028)	–	–
			F-ratio, *p*-value	–	16.8, <0.001	–	–
			Partial η^2	–	0.32	–	–
BDE47	38	0.43	Coefficient (SE)	–	0.11 (0.034)	–	0.015 (0.006)
			F-ratio, *p*-value	–	9.88, 0.003	–	6.91, 0.013
			Partial η^2	–	0.22	–	0.16
BB153	37	0.40	Coefficient (SE)	–	0.12 (0.032)	0.030 (0.009)	–
			F-ratio, *p*-value	–	15.1, <0.001	10.6, 0.003	–
			Partial η^2	–	0.31	0.24	–
ΣSCCP	–	–	Coefficient (SE)	–	–	–	–
			F-ratio, *p*-value	–	–	–	–
			Partial η^2	–	–	–	–
ΣPFAS	38	0.46	Coefficient (SE)	–	0.096 (0.022)	0.026 (0.007)	–
			F-ratio, *p*-value	–	18.3, <0.001	15.3, <0.001	–
			Partial η^2	–	0.34	0.30	–
PFOA	37	0.32	Coefficient (SE)	–	0.14 (0.035)	–	–
			F-ratio, *p*-value	–	16.2, <0.001	–	–
			Partial η^2	–	0.32	–	–
PFOS	38	0.46	Coefficient (SE)	–	0.097 (0.024)	0.028 (0.007)	–
			F-ratio, *p*-value	–	17.1, <0.001	16.2, <0.001	–
			Partial η^2	–	0.33	0.32	–

[a] Sample sizes varied due to outlier detection and exclusion in each model.
[b] Concentrations were normalized to lipid weight (ng g^{-1} lw) except for PFAS which are presented as ng g^{-1} wet weight.

and heptachlor epoxide (10–12%), as well as *trans*-nonachlor (10–13%) (Fig. S2) as reported earlier for Hudson Bay bears (McKinney et al., 2011b). ΣCHL was not substantially different between subpopulations as indicated by the PCA (Fig. 1), but did vary within subpopulations as shown by the significant age and sex covariates in the GLM (Table 2). For example, the ΣCHL was greater in SHB subadults (2291 ng g^{-1} lw) and AFs (1905 ng g^{-1} lw) than AMs (979 ng g^{-1} lw) (oxychlordane and *cis*-chlordane mirrored this pattern). In WHB, the AFs (not included in the GLM) had the greatest concentration of ΣCHL (2529 ng g^{-1} lw) > subadults (2223 ng g^{-1} lw) > AMs (1403 ng g^{-1} lw) (Table 1).

The concentrations of ΣHCH were influenced by all of the variables tested in the GLM, including the sex × age interaction (Table 2). The effects of subpopulation were relatively weak but observable (partial $\eta^2 = 0.16$, $p = 0.028$), supporting the results from PCA (Fig. 1), while those of sex (partial $\eta^2 = 0.28$, $p = 0.002$) and age (partial $\eta^2 = 0.55$, $p < 0.001$) were more significant. The relationship with subpopulation

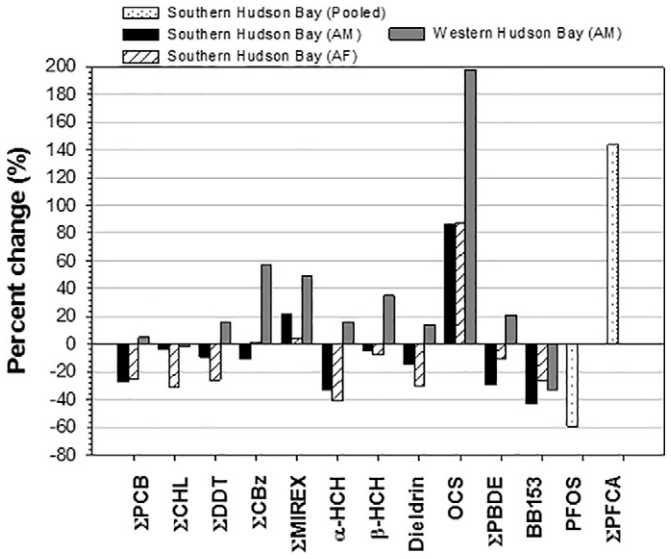

Fig. 2. Percent change of class groups and POPs of interest relative to those measured in 2007–2008 (lipophilic compounds) (McKinney et al., 2011b) or 2002 (PFASs) (Martin et al., 2004). Geometric means were compared for lipophilic contaminants, and mean concentrations of all SHB bears alone were compared for the PFASs (no WHB data were available). The ΣPFCA was selected to match that in Martin et al. (2004) (ΣPFCA = PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrA, PFTeDA, and PFPeDA). We did not measure PFPeDA, but it was below detection limited in 2002 and did not affect the comparison. AM = adult males, AF = adult females.

observed for ΣHCH was heavily influenced by β-HCH (subpopulation partial $\eta^2 = 0.30$, $p = 0.001$) as it was 72–84% of the ΣHCH in SHB and WHB, respectively (Tables 1, 2 and S7, Fig. S2).

Spatially, the concentrations of ΣHCH in the SHB bears were 94% (95% CI = 89–99%) of those in the WHB when considered as the covariate-adjusted concentrations from the GLM, while those of β-HCH were smaller (relative to the WHB) at 81% (72–90%). The concentrations of α-HCH did vary by subpopulation and demographics within subpopulations (Table 1), but they were a much smaller percentage of the ΣHCH than β-HCH (Fig. S2). Concentrations of HCHs within SHB were greatest in subadults; both ΣHCH and β-HCH were greater in subadults over AFs, and α-HCH was higher in subadults over AMs (Table 1). The adult males in both subpopulations had greater concentrations than females, though only the AMs from the WHB were greater than the subadults from the respective subpopulations. The variation of the HCHs with subpopulation, sex and age are likely indicative of different exposure routes or active metabolic pathways throughout the lifecycle. Both age (partial $\eta^2 = 0.30$, $p = 0.001$) and subpopulation (partial $\eta^2 = 0.29$, $p = 0.001$) were significant for Dieldrin (Table 2). Dieldrin was greater in the WHB when data were not filtered by age or sex (WHB = 234 ng g^{-1} lw, SHB = 155 ng g^{-1} lw) and in the AMs (Tables 1 and S7), with the GLM, covariate adjusted, mean concentrations in the SHB being 76% (66–88%) of those in the WHB. The concentrations in subadults (218 ng g^{-1} lw) were greater than those in the AMs (118 ng g^{-1} lw) and females (141 ng g^{-1} lw) in the SHB; with a similar pattern in the WHB, though the differences were less pronounced (Table 1).

Concentrations of ΣDDT and *p,p′*-DDE were relatively weakly affected by age (partial $\eta^2 = 0.12$, $p = 0.039$) and subpopulation (partial $\eta^2 = 0.17$–0.18, $p = 0.009$–0.013) with an essentially equal affect size (Table 2). The compounds were greater in SHB than WHB in overall concentrations (Table S7), and the adjusted means from the GLM indicated that the concentrations in the SHB were on average 25% (6.0–48%) and 26% (7.0–49%) greater than those in WHB for ΣDDT and *p,p′*-DDE, respectively. The effects of age were apparent in the results in SHB, as subadults had greater concentrations that AMs and AFs, though the WHB results for AMs and subadults were not consistent with SHB (Table 1). Declining concentrations of DDT in WHB bears over the period of 1991 to 2007 were shown to be associated with changes in diet and/or food web structure (McKinney et al., 2009), so the present differences between subpopulations could be due to the residual effects of decreases up to 2007 in the WHB bears (Fig. 2). The percent contributions of *p,p′*-DDT (to the ΣDDT concentrations) were small and similar between locations (≈3.4%). However, the actual concentrations of *p,p′*-DDT were greater in SHB (Tables 2 and S7) which could indicate more recent sources of DDT to that area of Hudson Bay, perhaps due in part to in-flows from the Churchill River (McKinney et al., 2009). The metabolite *p,p′*-DDE was 95–96% of the ΣDDT concentrations due to environmental weathering of DDTs and the well-known metabolism of *p,p′*-DDT to *p,p′*-DDE.

The ΣCBz concentrations were only influenced significantly by subpopulation (partial $\eta^2 = 0.33$, $p < 0.001$), with the adjusted mean concentrations in the SHB bears being 74% (65–85%) of those in the WHB. These data also support the results of the PCA which demonstrated that the loading of ΣCBz influenced the separation of the scores from SHB and WHB, favoring the WHB along PC 2 (Fig. 1). Concentrations of the ΣCBz, (SHB = 183 ng g^{-1} lw, WHB = 298 ng g^{-1} lw) and detectable components (HCB, PeCBz, 1,2,4,5-TCB) were all significantly greater in the WHB relative to SHB (Table S7). Percent contributions to ΣCBz were greatest for HCB (49–54%) > 1,2,4,5-TCB (33–39%) > PeCBz (12–13%) (Fig. S2), which was consistent with the CBz pattern reported in 2007–2008 bears (McKinney et al., 2011b). None of the variables included in the GLM had significant effects on ΣMirex (Table 2). Correspondingly, the ΣMirex and photo-Mirex did not differ by subpopulation; only Mirex was greater in the SHB over WHB bears (overall and in subadults) (Tables 1 and S7). Octachlorostyrene (OCS) is a by-product of the production, disposal and combustion of other OCs, and was never produced directly (Chu et al., 2003), yet was detected in 100% of the bear fat samples but with low and essentially identical concentrations in the SHB and WHB bears (19.9–21.4 ng g^{-1} lw).

When age was a significant variable in the GLMs of OCPs (ΣDDT, *p,p′*-DDE, ΣCHL, *cis*-chlordane, oxychlordane, ΣHCH, and dieldrin), the coefficients were uniformly negative, indicating an inverse relationship of the adjusted mean concentrations with age when the covariates are considered (Table 2). When the concentrations of the major OCPs were assessed independently using correlation analyses, only ΣCHL was correlated with age when all bears were used in the test (Pearson $r = -0.59$, $p < 0.001$, $n = 40$); the relationship remained significant in male but not female bears (Table S8). Contrasting with ΣCHL, ΣHCH was inversely related to age in female bears, but not males ($r = -0.62$, $p = 0.041$, $n = 11$), with β-HCH driving the negative relationship ($r = -0.68$, $p = 0.023$, $n = 11$). This is consistent with previous observations in a circumpolar study including bears from Alaskan, East Greenland and Svalbard subpopulations (McKinney et al., 2011b). In the same dataset, ΣCHL was found to decrease with age in both males and females, contrary to what we found here, however our sample size for females was also more limited ($n = 11$).

In Southern Beaufort Sea polar bears (Fig. S1) harvested in spring 2003, all of the OCs investigated were negatively correlated with age in females (including ΣPCB, ΣCHL, ΣDDT, *p,p′*-DDE, ΣHCH, β-HCH), and as observed here, only the ΣCHL was negatively correlated with age in males (Bentzen et al., 2008). This same study reported that for Southern Beaufort Sea male bears, e.g. CB153, ΣCHL and oxychlordane concentrations decreased with age, although these age-POP relationships have not been observed in previous studies across the Arctic (Muir et al., 2006; Verreault et al., 2005b). The negative relationship of ΣCHL concentration with age in male bears has been attributed to potential physiological adaptation to xenobiotic exposure (McKinney et al., 2011b). Dieldrin also exhibited inverse relationships with age in the overall dataset and in AM, but not AFs ($r = -0.37$–0.43, $p = 0.016$–0.019, $n = 29$–40), however, whether this relationship is driven by the same factors as that of chlordane is unknown at this time.

The greatest concentrations of OCPs tended to be in the subadults (Table 1) due to maternal contaminant offloading during both parturition and lactation (Polischuk et al., 2002), and potentially a lesser metabolic capacity than adult bears (McKinney et al., 2011b). Offloading should also reduce concentrations of some contaminants in females (HCHs, DDTs, CBzs), but PCBs and chlordanes have been shown not to be effectively offloaded (Polischuk et al., 2002), which is in general agreement with the present results (Table 1).

In the present 2013–2014 harvested bears there were distinct differences between the subpopulations, sexes and contaminants when two time-point comparisons were made with data from 2007 to 2008 collected bears (McKinney et al., 2011b) (Fig. 2). As with ΣPCB concentrations, the concentrations of ΣDDT, α-HCH, and Dieldrin in the present WHB males were greater than those in 2007–2008, while the remaining groups of bears had lower concentrations relative to that time-point. When there were greater concentrations between the two time-points for the present SHB males or SHB females, the increases in the WHB males exceeded them considerably (Fig. 2). OCS was the only contaminant to have increased in concentration in all groups (McKinney et al., 2011b), with present concentrations being between 86 and 198% greater than those measured in 2007–2008 (SHB AMs and WHB AMs, respectively) (Fig. 2). Conversely the ΣCHL was the only POP group to be relatively lower in all bears, with a larger decrease in the SHB females (31%) than males WHB or SHB (decreases of 1.7% and 3.5%, respectively). The ΣCBz and β-HCH were essentially unchanged in most groups except for the AM from WHB which were 57% and 35% greater, respectively. ΣMirex was one of the few contaminants (along with OCS) that increased in all groups investigated (4.2–49%), (McKinney et al., 2011b).

Bears from the 2007–2008 study were also previously shown to have increasing amounts of Dieldrin in WHB and decreasing amounts in the SHB bears relative to concentrations reported for bears in 1989 (McKinney et al., 2011b). Concentrations of ΣCBz in those bears also increased in the WHB (no data for SHB) relative to 1996 samples. Increasing β-HCH concentrations in the present WHB bears are consistent with previous results, which were hypothesized to be related to slower delivery via oceanic transport and the greater biomagnification potential of this isomer (McKinney et al., 2010). We also observed comparatively greater α-HCH in WHB males in 2013–2014 relative to 2007–2008, which contrasts with the previously observed decreases for this compound at that location (McKinney et al., 2011b). Why this α-HCH concentration trend was not consistent here was not clear. However, in general the decreasing trends of contaminants in the SHB were largely consistent with those in East Greenland (Dietz et al., 2013b). An exception was OCS, which increased in the present study, but decreased in previous studies in both East Greenland (−1.6 to −2.7% per year) and Hudson Bay (−1.5% per year) bears (Dietz et al., 2013b; McKinney et al., 2010).

The most likely explanation for the differences in the WHB males relative to the other bears are related to dietary and behavioral changes (in bears and/or through the food web), as was previously postulated (McKinney et al., 2009, 2010). AM bears from the WHB have been observed cannibalizing a polar bear (Dyck and Daley, 2002), are known to scavenge for food in town dumps (e.g. WHB bears in Churchill, MB, Canada) (Lunn and Stirling, 1985), and do feed on an increasing proportion of inland sources (plants, caribou) (Gormezano and Rockwell, 2013), which can alter POP exposure regimes. Fewer data are available on the changes in behavior and diet for the SHB bears, so comparative assessments with changes in WHB bears are currently not possible. The subpopulation effects of Dieldrin are more likely reflective of its historical use in the agriculturally active regions in e.g. Ontario and the Prairie provinces, although to our knowledge historical use records in Canada are scarce. The consistent increases of the more volatile contaminants in the WHB (e.g., α-HCH, CBz compounds, OCS) may be related to climate change effects including revolatilization and increased deposition from temperate/tropical regions (Ma et al., 2011; Macdonald et al., 2005). However, this was not consistent with results in the SHB, so other factors must also contribute to these increases that differentially affect the local populations of bears in the SHB and WHB. OCS is also released by combustion of OC-containing materials, as are CBzs, which could be significant due to the aforementioned landfill incineration, and mining/smelting around the Hudson Bay (Natural Resources Canada, 2015) (Fig. S3). However, specific information on the operational output or emissions from the mines or communities from 2007 to present could not be found, and thus this is highly speculative at this point.

In addition to the legacy OCPs, other pesticides and related compounds were measured in the bear fat samples. PCP and its degradation product PCA as well as HCBD are the most recent OCs to be listed under the SC-POPs (Annex A; United Nations Environment Programme, 2017) (Table S1), but were <MLODs in the fat of all bears under study (Table S7). PCP was reported to biomagnify in East Greenland polar bears from ringed seal diet using samples collected in 1999–2000 (Letcher et al., 2009), and was also reported in the plasma of Canadian (Resolute Bay) bears (Sandau et al., 2000), while PCA has only been reported in arctic marine fish and deep-sea invertebrates (Bidleman et al., 2013a; Vorkamp et al., 2004). HCBD was screened but was below detection limits in glaucous gull (*Larus hyperboreus*) eggs from Norway and in Alaskan polar bears; no other detections or reports in Arctic biota exist to our knowledge (Bentzen et al., 2008; Verreault et al., 2005a). These compounds appear to have limited bioaccumulation potential in Arctic biota (Vorkamp and Riget, 2014).

Endosulfan and related isomers were listed in 2009 under Annex A of the SC-POPs (United Nations Environment Programme, 2017). The present polar bear results are consistent with a report on α- and β-endosulfan isomers, which were variably quantified at low to sub ng g^{-1} lw concentrations in polar bears in high Arctic locations between 2007 and 2008 (Morris et al., 2016), but were below detection limits in the fat of the present bears (Tables S6 and S7). The present polar bear results are also consistent with Vorkamp et al. (2017) where for $n =$ 54 blubber samples of East Greenland ringed seals collected over the period of 1986 to 2012, β-endosulfan has 0% detection frequency and only 7 samples had concentrations of α-endosulfan above detection limits and with a maximum concentration of 0.26 ng g^{-1} lw. Given the metabolic lability of endosulfan, it is likely that polar bears rapidly metabolize accumulated endosulfan to concentrations below detection limits, particularly since it is no longer used (Deema et al., 1966; Dorough et al., 1977; United Nations Environment Programme, 2017).

A well-known pesticide and partly a substitute for DDT, dicofol (*p,p′*- and *o,p′*-isomers) is an in use OC miticide and acaricide in Europe, Asia, Africa and South America, and was recently proposed for listing under the SC-POP (United Nations Environment Programme, 2017). Only a few reports exist on the environmental occurrence and concentrations of dicofol isomers, and they have yet to be reported in circumpolar Arctic wildlife (Becker et al., 2012; Hoferkamp et al., 2010; Muir et al., 2013b, 2013c). The presence of dicofols in the Arctic has also been inferred in air by an abundance of *o,p′*-DDT, but it has not been observed in the Canadian Arctic (Becker et al., 2012; Hung et al., 2013) suggesting a limited distribution in Arctic media and wildlife. *p,p′*- and *o,p′*-dicofol were not detected in any of the present bear fat samples. Dicofol isomers have been shown to be metabolized to 4,4′-dichlorobenzophenone in laboratory rats (Hoferkamp et al., 2010), but was also not detected in the present Hudson Bay polar bear fat samples (R. Letcher, unpublished data), which further confirms that dicofol in not accumulated in Hudson Bay polar bears.

3.4. Polychlorinated naphthalenes

As was recently emphasized in Braune and Muir (2017), there are presently only a few studies on PCNs in Arctic biota. In the present study, PCNs were the second least concentrated contaminant group (ΣPCN = 20.2–26.6 ng g^{-1} lw; maximum concentrations for CN50 = 7.1–8.5 ng g^{-1} lw) in all Hudson Bay bears. It was not possible to

evaluate the influence of sex or age on PCN concentrations using a GLM due to limited sample sizes (Table 1), but the concentrations were quite comparable between subpopulations for total PCNs (when not filtered by age or sex), though there were inconsistent differences that could be observed for specific congeners (Table S7). The use of PCN mixtures was voluntarily limited around 1980, however PCNs were only recently regulated under (Annex A and C) the SC-POPs (United Nations Environment Programme, 2017). PCNs are primarily produced as secondary emissions from PCB/PCN-containing products during waste incineration as well as metal refining and processing (Helm and Bidleman, 2003). In the present bears, $\log_{10}$-transformed concentrations of ΣPCB and ΣPCN were weakly correlated (Pearson $r = 0.55$, $p = 0.10$, $n = 10$), however the p of 0.10 is not convincing evidence of strongly shared sources for these contaminants (Table S8).

The PCNs are known to have a relatively high biomagnification potential and are present in polar bear food sources (Bidleman et al., 2010; Helm et al., 2002). Concentrations reported in ringed seal (0.035–0.071 ng g^{-1} lw) and beluga (*Delphinapterus leucas*) (0.036–0.38 ng g^{-1} lw) from the eastern and southern coasts of Baffin Island (respectively), as well as in Alaskan and Greenland polar bears (3.2 ng g^{-1} lw in liver and 0.51 ng g^{-1} lw in fat, respectively), were substantially lower than those observed in the present bears (Bidleman et al., 2010; Corsolini et al., 2002; Helm et al., 2002). The only concentrations exceeding those reported in the present polar bear study and available in the literature were in plasma (62.8–74.0 ng g^{-1} lw) and eggs (49.0 ± 20.0 ng g^{-1} lw) of glaucous gulls from Norway (Verreault et al., 2005a). In a report of temporal trends in Canadian Arctic biota, PCNs were determined in eggs of thick-billed murre (*Uria lomvia*) collected from the Canadian high Arctic between 1975 and 2014 (Braune and Muir, 2017). Mean annual ΣPCN concentrations ranged from 364 ± 22.2 to 995 ± 52.8 pg g^{-1} (wet weight). If corrected for lipid weight the concentrations would be about ten times greater than reported, and thus the ΣPCN concentrations in the murre eggs were comparable to the present polar bear fat samples, which on average had mean ΣPCN concentrations > 10 ng g^{-1} (lw) (Tables 1 and S7).

Though the ΣPCN concentrations in the present Hudson Bay bears were greater, the pattern of PCN homologue groups (percent contributions to the ΣPCN) in liver of Alaskan bears (≈10% tetraCN, 89% pentaCN, and <1% hexaCN) was in good agreement with our findings in the present Hudson Bay polar bears (11–12% tetraCN, 85–86% pentaCN, 2–3% hexaCN) (Fig. 3) (Bidleman et al., 2010; Corsolini et al., 2002). The majority of the PCN burden in beluga was reported to be pentaCNs as well (33–57%), but with an abundance of hexa- and tetraCNs (22–45% and 13–24%, respectively). Ringed seal ΣPCN profiles were reported as primarily tetra- (58–83%), penta- (17–34%) and triCN (0–21%). These differences are likely due to different diets, locations and metabolic capacities of polar bears, pinnipeds and cetaceans (e.g., Letcher et al., 2010). Like the present polar bear fat samples, penta- and tetra-CN congeners (predominantly CN-52/60 and CN-42) were also reported to dominate the ΣPCN concentrations in the eggs of thick-billed murres from the Canadian Arctic (Braune and Muir, 2017).

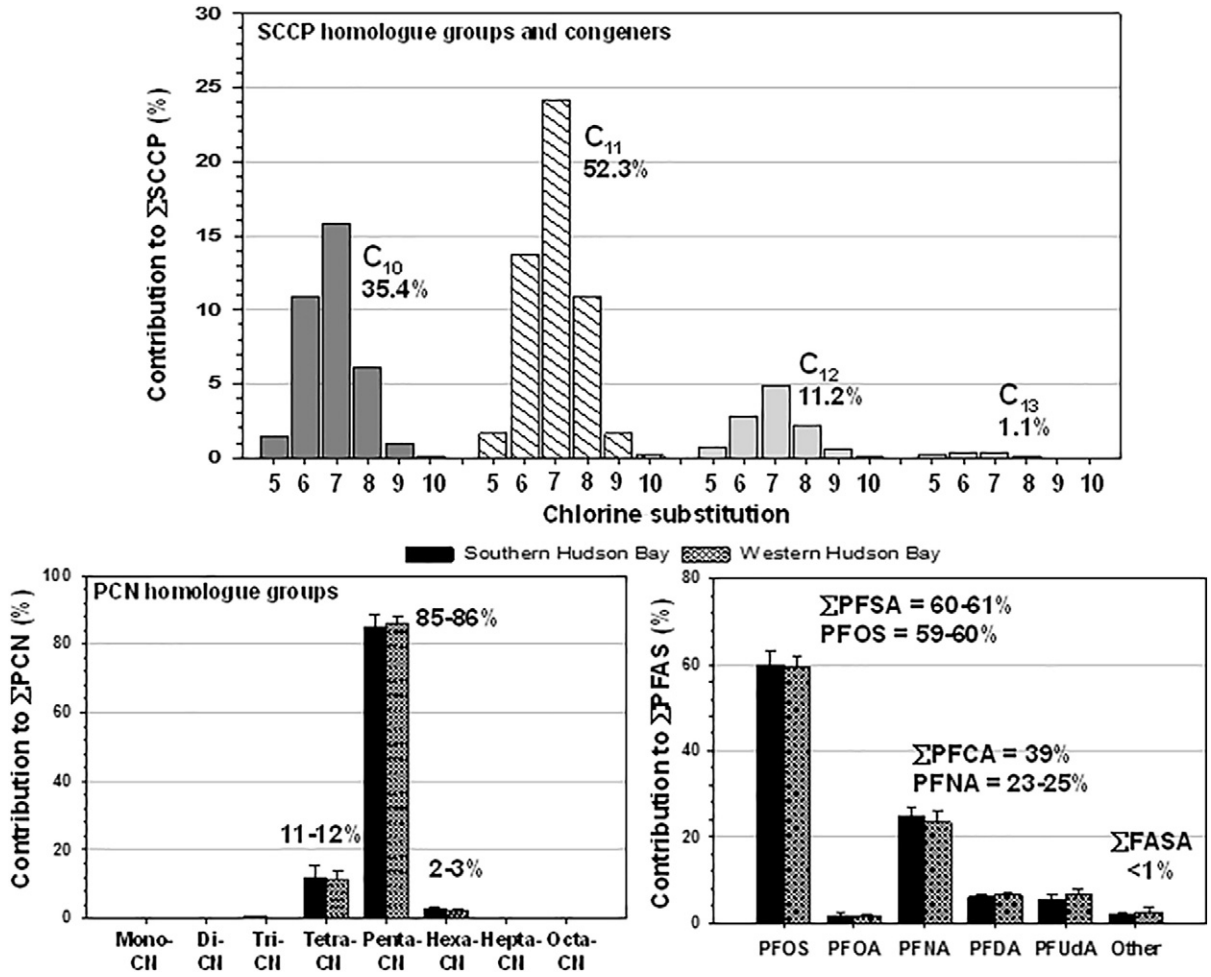

Fig. 3. Percent contributions of selected new and candidate POPs to the sum (Σ) concentrations (mean ± SD) in a given class of contaminants. Contaminants were measured in the fat and liver (PFASs) of polar bears from Southern and Western Hudson Bay (based on lipid weight concentrations, except PFASs, which are wet weight). The bars for the SCCPs represent their chlorine substitution number, and each group represents a carbon chain length (C_{10}, C_{11}, C_{12}, or C_{13}); the congener substitution pattern was calculated using the same values for all bears, so there was no variation between individual or subpopulations. Congener-specific contributions of PCNs and percent composition figures for other POPs are shown in Figs. S2 and S4.

Elevated concentrations of PCNs in Hudson Bay polar bears relative to marine mammals from other locations could be due shipping traffic, garbage incineration in communities (A. Morris, *personal observation*), or the mining and smelting rations surrounding Hudson Bay (Natural Resources Canada, 2015) (Fig. S3). Some PCN congeners previously reported as appropriate combustion indicators (CN52/60, -51, -54, and -66/67) were abundant in polar bears (CN52/60, -66/67 and particularly CN54) (Helm and Bidleman, 2003). However, several other congeners suggested to be more reliable indicators of combustion (CN26, -13, -44, and -29; in addition to CN54) were low in concentration or not measured, and the remaining congeners found at relatively high concentration in fat of polar bears are not associated with combustive sources and/or technical products (CN57, and -58) (Table S7, Fig. S4) (Helm and Bidleman, 2003). Metabolism or congener-specific biomagnification of PCNs were apparent for the present bears, as has been indicated in previous studies, as the pentaCNs are known to be more abundant in polar bears relative to technical products (<40%) or in air samples near combustion sources (<22%) (Bidleman et al., 2010; Helm and Bidleman, 2003).

3.5. Short chain chlorinated paraffins

As has been reported elsewhere (van Mourik et al., 2015), CP analysis has inherent analytical challenges including possible cross-contamination of samples in the field and in the lab. In the present study, two lab blank samples (one for the WHB samples and another for the SHB samples) were analyzed. Only 13 SCCPs were quantifiable (>MLOQ) and at very low average wet weight concentrations of 0.0161 to 0.0960 ng g^{-1} ww, and thus any lab cross-contamination of the bear (fat) samples was extremely low. These SCCP blank concentrations were also above but close to MLOQ values for the individual SCCPs which ranged from 0.0002 to 0.0036 ng g^{-1} ww (Table S6). As listed in Table S7, all SCCPs except one were quantifiable (>MLOQ) with 100% frequency in the present bear fat samples, and at concentrations at least 2 orders of magnitude greater than in the polar bear lab blanks.

SCCPs are currently under review for listing under the SC-POPs (United Nations Environment Programme, 2017). The ΣSCCP concentrations in the present bears were not different between or within the subpopulations and the loading of ΣSCCP appeared to have little effect on the scores in the PCA (Fig. 1, Tables 1 and S7). The GLM also did not detect any significant effects from the covariates for this sum (Table 2). SCCPs were detected in 100% of samples (except $C_{13}Cl_{10}$ which was a < MLOD), and concentrations were qualitatively greater in the WHB over SHB (Tables 1 and S7).

Of the homologue groups investigated, the undecanes (ΣC_{11}SCCPs) had the greatest concentrations (71.4–88.9 ng g^{-1} lw) > decanes (ΣC_{10}SCCPs = 48.4–60.3 ng g^{-1} lw) > dodecanes (ΣC_{12}SCCPs = 15.4–19.1 ng g^{-1} lw) > tridecanes (ΣC_{13}SCCPs = 1.52–1.89 ng g^{-1} lw). The heptachlorinated (Cl_7) decane and undecane congeners were the most abundant (SHB = 21.6 and 33.0 ng g^{-1} lw, WHB = 26.9 and 41.1 ng g^{-1} lw, respectively) (Table S7). The percent composition of the homologue groups was C_{10} = 35.4%, C_{11} = 52.3%, C_{12} = 11.2%, and C_{13} = 1.1% (Fig. 3). Beluga whales from the Mackenzie Delta (Western Canadian Arctic) also had profiles dominated by C_{10}SCCPs and C_{11}SCCPs, however the contributions of these homologue groups were reversed (contributing 52% and 39%, respectively) (Tomy et al., 2000). Ringed seals (*Pusa hispida*) were similar to beluga but they had greater contributions from C_{12}SCCPs (17% in seals and 9% in beluga), and lesser contributions from C_{10}SCCPs (43%) (Tomy et al., 2000). Norwegian Greenland shark (*Somniosus microcephalus*) SCCP profiles were also dominated by Cl_7 congeners in the C_{10} to C_{12} homologue groups, with 53% contributed by the ΣC_{11}SCCPs (≈equal to the present observations) (Strid et al., 2013). The main difference between sharks and bears was in the C_{10} (only 16% contribution in sharks) and C_{12} groups (29% in sharks), which indicates differences in the assimilation or processing/metabolism of these compounds. Little information regarding metabolism in Greenland sharks exists, but they are primarily benthic (McKinney et al., 2012), and have different dietary exposure regimes than that of bears.

Vorkamp et al. (2017) very recently reported on a suite of C_{10} to C_{13} SCCPs in the fat of polar bear collected in 2012 and 2014 from Scoresby Sound in East Greenland. The range of ΣSCCP concentrations was 1200–2700 ng g^{-1} ww for n = 5 2012 sampled bears and 370–1600 ng g^{-1} ww for n = 5 2014 sampled bears. The present Hudson Bay bears sampled in the same time period had much lower ΣSCCP concentration ranging from 75 to 207 ng g^{-1} ww (Table S9). Relative to the present bears, greater concentrations of SCCPs were found in beluga (210 ± 80 ng g^{-1} ww) and ringed seals (530 ± 200 ng g^{-1} ww) from Greenland and in Greenland sharks (430 ng g^{-1} lw) (Strid et al., 2013; Tomy et al., 2000). Vorkamp et al. (2017) also reported SCCPs in blubber of n = 10 ringed seals collected in 2012 and 2014 from Scoresby Sound and 710–1900 ng g^{-1} ww. The differences between species are likely to be related to local exposure, differences in their diets and lifecycles, and in metabolic capacities (Letcher et al., 2009, 2010; Strid et al., 2013; Tomy et al., 2000; Vorkamp et al., 2017). The Western Arctic (beluga) is also more susceptible to trans Pacific transport from Asian sources (Bailey et al., 2000), which is significant as Chinese production of SCCPs exceeded 1,000,000 t y^{-1} in 2011 (Chen et al., 2011). The prevalence of the more volatile C_{10}SCCPs and C_{11}SCCPs in Arctic marine mammals indicates atmospheric LRT over local sources (Tomy et al., 2000). SCCPs were detectable in 95% of plasma samples from 20 polar bears sampled in Svalbard, Norway during 2012, with mean concentrations of 3.99 ng/mL plasma (Norwegian Institute for Air Research (NILU), 2013). As mentioned, although there has been limited reporting of the analytical challenges (Sverko et al., 2012; van Mourik et al., 2015; Vorkamp et al., 2017).

3.6. Perfluoroalkyl substances

For polar bears from East Greenland, in liver samples collected in 2006, we previously reported that PFAS (and specifically PFOS and PFCA) concentrations were much greater in the liver followed by blood > brain > muscle ≈ adipose (Greaves et al., 2012). To our knowledge, the present study is the first report on PFASs in Canadian polar bears in over a decade (Smithwick et al., 2006). In the present study, ΣPFASs in liver were at concentrations approaching or exceeding that of ΣCHLs in fat, and the concentrations of PFOS (794–1191 ng g^{-1} ww) were within range of some of the most recalcitrant PCB congeners (e.g. CB180 = 766–820 ng g^{-1} lw) (Table S7). The composition of the ΣPFAS was essentially identical between subpopulations (ΣPFSA = 60–61%, ΣPFCA = 39%, ΣFASA < 1%), with PFOS and PFNA accounting for 60% and 25% of the ΣPFAS concentrations, respectively (Fig. 3). Despite the similarity in composition, analysis via GLMs showed consistent, strong, and significant effects of subpopulation on ΣPFAS, PFOS and PFOA (partial η^2 = 0.32–0.34, $p < 0.001$), as well as age for ΣPFAS and PFOS (partial η^2 = 0.30–0.32, $p < 0.001$) (Table 2). Unlike the significant effects with age observed for the OCPs, the adjusted mean concentrations from the GLM analysis increased with age for the PFAS compounds (Table 2).

Overall ΣPFAS concentrations were greater in the SHB relative to WHB, and the ΣPFAS loading also influenced the differentiation of the PCA scores between subpopulations in favor of the SHB (Fig. 1, Table S7). The covariate adjusted means from the GLMs for the ΣPFAS in the SHB bears were 25% (13–38%) greater than the adjusted concentrations in WHB bears, with very comparable results for PFOS [25% (12–39%)] and PFOA [38% (18–62%)]. Subpopulation influences are likely related to local sources (as previously mentioned), the transport and differential deposition of more volatile and water soluble precursors such as fluorotelomer alcohols (FTOHs) (Riget et al., 2013), and/or dietary differences. The concentrations in AMs and AFs from SHB were greater than those in subadults for both ΣPFAS and PFOS, and the ΣPFAS was positively correlated with age in all comparisons, which

corroborates the results from the GLMs ($r = 0.46$–0.73, $p = 0.0031$–0.012; Table 2). Though there is evidence of offloading of PFASs in utero and to young marine mammal calves via maternal transfer from milk (Reiner et al., 2011), this is presumably limited relative to OCs, or bioaccumulation in adults is rapid and extensive enough to maintain (liver) concentrations above those of subadults (Table 1).

The novel POP, PFEtCHxS, is a cyclic hydrocarbon analogue of PFOS, and is exclusively used in aircraft hydraulic fluids as an erosion inhibitor (de Silva et al., 2011). To our knowledge, this is the first report on PFEtCHxS in polar bears. PFEtCHxS was quantifiable at 96% and 88% frequency in liver samples from SHB and WHB bears, respectively (Table S7), although levels were very low and ranged from 0.406–1.45 and 0.090–0.296 ng g^{-1} ww, respectively. PFEtCHxS has also been detected at high frequencies but at among the lowest concentrations of PFSAs in herring gulls from the Great Lakes (Letcher et al., 2015). The low to non-detectable concentrations are presumably due to its use being limited to aircraft-related applications (de Silva et al., 2011). However, more data are required before conclusions can be reached as to the sources, transport and uptake of this compound in the Arctic given its relatively unique structure among PFASs.

FOSA was the only volatile FASA that was analyzed for and detected in any polar bear liver sample, and at 100% frequency, but at low concentrations (4.98–5.64 ng g^{-1} ww) (Table S7). FOSA can be formed from other volatile FASAs, including *N*-methyl-perfluoro-1-octanesulfonamide, which was presently measured but was not detected (Table S7) (Riget et al., 2013). Non-detectable FASAs could be forming FOSA, which in turn is metabolized to PFOS, which accumulates to high levels in tissues (particularly in the liver) as has been shown for East Greenland polar bears (Greaves et al., 2012). Letcher et al. (2014a) recently reported that polar bears can rapidly metabolize in vitro *N*-ethyl-perfluoro-1-octanesulfonamide to FOSA, and likely are able to easily metabolize FOSA to PFOS, which suggests that at least of portion of PFOS accumulating in bears likely comes from PFOS precursor metabolism by the bear. Furthermore, PFCA precursors such as FTOHs can be transported via atmospheric LRT and converted to PFCAs through biotransformation processes that increase the concentrations of perfluoroalkyl acids (PFAAs) as well as accumulating themselves (Martin et al., 2005). Taken together these processes suggest that the concentrations of the dominant PFASs in the fluorinated contaminant profiles of these bears (PFOS, PFNA, PFDA, PFUdA) are likely enhanced by biotransformation of PFAS precursors.

Spatially, PFASs have been detected throughout the Canadian Arctic, with some undergoing food web-wide biomagnification, and in some cases (e.g. PFOS) reaching concentrations at or exceeding legacy OCs in all trophic levels (Kelly et al., 2009). To our knowledge, the temporal trends of PFASs have not been reported in Canadian polar bears over the last 10 years. However, as of 2014 and compared to samples from SHB in 2002 (Martin et al., 2004) (arithmetic means of all SHB bears were compared), PFOS has decreased by 59% (Fig. 2). In the same two time-point comparison, concentrations of ΣPFCAs (selected to match (Martin et al., 2004)) in polar bear liver were 44% greater, with PFOA alone being 197% lower.

The decreases in PFOS concentrations over time presumably reflected regulations of this compound. The 3M Company voluntarily withdrew production of PFOS, perfluorooctanoic acid (PFOA) and related products between 2000 and 2002 (Houde et al., 2006; Jensen and Leffers, 2008), with global regulation via listing (Annex B) under the SC-POPs in 2009 (Table S1) (United Nations Environment Programme, 2017). Increases in the PFCAs are again related to increased production and use of the FTOHs (Letcher et al., 2015) and biotransformation once accumulated in the food web (Martin et al., 2005). This was a dramatic shift from the exponential increases in concentrations of PFOS observed in polar bears from 1972 to 2002 (Smithwick et al., 2006), though the PFCAs do continue to increase. Though temporal trend data are not available for Canadian bears, the results here agree well with recent trends from East Greenland bears, which showed exponential increases in PFOS up to 2006, followed by an approximate 64% total decrease by 2011 (Riget et al., 2013). However, concentrations of most long-chain PFCAs, including PFOA, were also declining significantly in Greenland animals (Riget et al., 2013), which is not the case for the present bears. Presumably this is a function of sources, as the Canadian Arctic and East Greenland are influenced by different air and water masses, and thus contaminant delivery via LRT is different between these locations.

3.7. PBDEs, PBBs and alternative HFRs

The majority of FR compounds, including many of the BDE congeners, were below their respective MLODs in all of polar bear fat samples (Tables S6 and S7). Concentrations of ΣPBDE and of BB153 were among the lowest sum concentrations for POPs (60–100 times lower than the ΣPCB; Tables 1 and S7). The similar range of their concentrations are not likely the result of common sources; BB153 was banned in North America by 1979 while PBDEs were regulated recently and are still present in a multitude of end use products (Abbasi et al., 2015; United Nations Environment Programme, 2017). The influence of subpopulation was apparent for ΣPBDE, BDE47 and BB153 ($\eta^2 = 0.22$–0.32, $p < 0.001$–0.003) (Table 2). The adjusted mean concentrations in the SHB bears were 32% (16–50%), 29% (10–50%) and 33% (15–53%) greater than in the WHB bears. Correspondingly, the concentrations of ΣPBDE, BDE47 and BB153 were greater in the SHB over the WHB in overall concentrations (Table S7) and those separated by sex and age (Table 1). Further supporting these results, the loading of ΣPBDE in the PCA exerted influence on the scores of the bears, contributing to the separation of the SHB and WHB animals across PC 2, as did the PFASs (Fig. 1).

Of these compounds, only BB153 also had a significant influence from age in the GLM analysis ($\eta^2 = 0.24$, $p = 0.003$), which was a positive effect like the PFASs and contrasting with the OCPs (Table 2). There were few substantial differences in the PBDE concentrations within the subpopulations when considered with their confidence intervals. As indicated by the GLM, these differences were more pronounced for concentrations of BB153, particularly when comparing adults and subadults—with greater concentrations observed for the older bears (Table 1).

The ΣPBDEs was composed of the four primary congeners from the commercial-pentaBDE mixture (BDE47, -99, -100, and -153), and were in the order of BDE153 (43–50%) > BDE47 (41–43%) > BDE99 (5–8%) > BDE100 (4–6%) (Fig. S4). These BDE congener patterns are almost identical to those reported for Hudson Bay bears harvested in 2007–2008 (McKinney et al., 2011b). Comparatively, the median ΣPBDE concentrations in East Greenland bears from 2006 to 2010 exceeded those in the WHB by approximately 2 times, but not those in the SHB (Dietz et al., 2013a). Like the PFASs, PBDEs are present in many broadly used synthetic materials and electronics (Abbasi et al., 2015; Kelly et al., 2008), and can be delivered via LRT, or from local sources (landfills), which could influence the spatial distribution of concentrations.

Like the OCs, relative to ΣPBDE concentrations in 2007–2008 bears (McKinney et al., 2011b), the concentrations in the present 2013–2014 bears were 11% to 29% lower, except AM from the WHB which increased by 21%; BB153 was one of the only contaminants that decreased in all three groups of bears (26% to 43%) (Fig. 2). The concentrations of BDE153 remained relatively unchanged between these two time points (compared among all bears), with the apparent decrease in the ΣPBDE in the SHB driven by BDE47 (McKinney et al., 2011b). These data support previous assertions that BDE153 is relatively recalcitrant or is formed via metabolic debromination of more brominated BDE congeners (e.g., from BDE209) (Hakk and Letcher, 2003; McKinney et al., 2011b; Muir et al., 2006).

Temporally decreasing concentrations were indicative of the effectiveness of regulation on these compounds in the 1970s (BB153) (banned in the USA in 1974, not manufactured in Canada), and in

2004 (PBDEs) (voluntarily withdrawn by US manufacturer, (Kelly et al., 2008)) followed by their listing under the SC-POPs in 2009 (Table S1) (United Nations Environment Programme, 2017). Previous measurements of BB153 may have had confounding co-elution of BDE154, so results should be interpreted cautiously, although it has been reported that BDE154 is very low as compared to any co-eluting BB153 (McKinney et al., 2011b). Concentrations of BDE153 and ΣPBDE, as well as that of HBCDD were reported to have temporally increased in East Greenland polar bears between 1983 and 2010, while concentrations of BB153 decreased over the same period (Dietz et al., 2013a). This seems to contradict the trends related to the regulatory action applied to the production and use of the PBDEs, however in the most recent time frames for polar bears from East Greenland, the ΣPBDE concentrations now also appear to be decreasing (Dietz et al., 2013a). The anomalous result for the present WHB males is likely due to differences in diet (and/or food web) and behavior (as hypothesized for the OCPs) (McKinney et al., 2010).

HBCDD is a recent (2014) addition to Annex A of the SC-POPs (Table S1), whereas decaBDE was added to Annex A in April 2017 (United Nations Environment Programme, 2017), and along with the other 19 HFRs screened in the present bears, these compounds were below detection limits (Table S7). Despite variable reports of BE209 in arctic predators (Tomy et al., 2008, 2009), decaBDE has not been detected in polar bears from Canadian subpopulations going back to samples collected in the early 2000s (McKinney et al., 2011b; Muir et al., 2006). Poor dietary assimilation and metabolic debromination are likely reasons that BDE209 was not detectable in the present bears as has been shown for American kestrels exposed via the diet to BDE209 (Letcher et al., 2014b). HBCDD was detected at low concentrations in SHB and WHB bears in 2007–2008 samples (4.2–5.2 ng g^{-1} lw) (McKinney et al., 2011b). Under continued annual monitoring programs, it was found that samples from 2009 to 2013 at SHB and WHB still had measurable amounts of HBCDD although there have been no detections in samples from 2014, 2015 or 2016 (R. Letcher, *unpublished data*). HBCDD production dropped from approximately 17,000 t y^{-1} to 3200 t y^{-1} in 2008 (Bidleman et al., 2013b), prior to its listing as a POP, so lack of detection in more recent bear samples is likely reflective of these regulations.

The flame retardant Dechlorane Plus (DDC-CO) was introduced in the mid-1960's as a replacement for Dechlorane (otherwise known as Mirex). DDC-CO is primarily used as an additive FR in thermoplastic materials like polyethylene, polyvinyl acetate, polypropylene, where it can be added at concentrations of 5–35% (by weight) (ECHA, 2007). In Arctic biota there is a dearth of information on DDC-CO isomers, and those that are available report levels as low or non-detectable. In Arctic marine mammals and fish, DDC-CO has been analyzed but not detected in e.g. ringed seal and beluga blubber from the Canadian Arctic and in liver of Greenland shark (*Somniosus microcephalus*) from around Iceland (Muir et al., 2013b; Shen et al., 2012; Strid et al., 2013). A 2012 survey of wildlife from East Greenland that included black guillemot eggs, glaucous gull liver, ringed seal blubber, and polar bear fat detected DDC-CO in >95% of the samples, but with none exceeding a concentration of 0.1 ng g^{-1} ww (Vorkamp et al., 2015). Results for the present Hudson Bay polar bears were consistent with these other Arctic findings where the DDC-CO *syn*- and *anti*-isomers were both below their respective MLODs (Table S6). In contrast, the structurally related analogues Mirex and photo-Mirex were measurable with >76% and 100% sample frequency, respectively. The range of Mirex and photo-Mirex concentrations were from <MLOD—14.6 ng g^{-1} lw and 43.4–71.2 ng g^{-1} lw, respectively (Table S7).

Two other "DDC-CO-like" norbornene derivatives, Dechlorane 602 (Dec602) and Dec603 were screened for in the fat fractions. Dec602 and Dec603 were measurable at 100% and 56% sample frequency, respectively, for all bears in both subpopulations. However, the range of Dec603 concentrations was very low and from <MLOD—1.1 ng g^{-1} lw. The concentration range for Dec602 was much greater and was 2.8–185 ng g^{-1} lw (Table S7). See Table S6 for MLOD and MLOQ concentrations. Dec602 concentrations were comparable to the HCH and DDT levels in bear fat (Table S7). Other Arctic reports on these DDC-CO analogues in Arctic wildlife are exceedingly rare. Vetter et al. (2015) identified Dec602 and a tentative metabolite in all samples studied in polar bears from East Greenland. In a small study of beluga whales sampled in 2000 and 2010 from Hendrickson Island in the Canadian Arctic, Dec602 and a monohydro-derivative of Dec602, were found in all eight blubber samples, whereas DDC-CO isomers and Dec603 were not detectable (Shen et al., 2012).

BCPS is used as a plasticizer and FR, and to our knowledge has not been previously reported in any Canadian Arctic biota, but was presently detected at a high frequency (94–96%), and showed spatial variability between the WHB and SHB (1.80 and 0.753 ng g^{-1} lw, respectively). These results agreed with those of TEHP (see section 3.8), but were not consistent with the finding for the other FRs (under study), which had greater concentrations in the SHB over WHB animals (Table S7). Over fifteen years ago, BCPS was reported in grey seals (*Halicoerus grypus*), fish and seabirds from Europe (Norstrom et al., 2004), and over 20 years ago in herring gull eggs from the Canadian portion of the Great Lakes basin (Letcher et al., 1995b). Concentrations in Swedish grey seals were also at least 27 fold greater than those observed in the present bears (Norstrom et al., 2004), but were themselves 2–3 orders of magnitude lower than CB153 (BCPS = 49–480 ng g^{-1} lw) (Table S7).

3.8. Organophosphate esters

The seventeen OPEs that were screened for in the present bear (fat) samples (Table S7), were the least important contaminant group in polar bears (Table S7). Recent OPE production estimates were 620,000 t y^{-1} in 2013, which exceeded brominated FRs (200,000 t y^{-1} in 2007) (Bergman et al., 2012; Suhring et al., 2016). Despite these high production volumes, the only OPE that was quantifiable in polar bear fat was TEHP, with concentrations of 0.163 ng g^{-1} lw and 0.308 ng g^{-1} lw in SHB and WHB, respectively. TEHP concentrations were spatially variable, however the GLM did not detect significant influences of subpopulation or any other covariate on this compound (Fig. 1; Tables 1, 2 and S7). Comparatively, the concentrations of BDE47 were approximately 44 to 170 fold greater, and those of the $C_{11}Cl_7$SCCP were approximately 130 to 200 fold greater than TEHP (Tables 1 and S7). Trace (detectable) amounts of TPHP, TCIPP, TBOEP and TNBP were found in the fat of the present bears but with <50% frequency of detection (Table S7). TEHP and the same detectable OPEs in bear fat were recently reported at concentrations of 1 to 1000 pg/m^3 in Canadian Arctic air samples (Suhring et al., 2016). This apparent contrast between OPEs in abiotic (air) and biotic (polar bear) Arctic media strongly suggests low biological persistence and (marine) food web accumulation due to either poor assimilation from the diet or rapid metabolism (Greaves et al., 2016). Extensive work on e.g. TPHP in birds, and specially herring gulls in vitro (in liver microsomal assays) from the Great Lakes, has shown that these birds can rapidly metabolize OPE to their OP diester metabolites (Greaves et al., 2016) or via other metabolic pathways such as hydroxylation, carboxylation and oxidative dehalogenation. Recently, using a polar bear liver microsomal assay, TDCIPP, TPHP, TNBP and TBOEP have been shown to be rapidly metabolized in vitro including to OP diesters (R. Letcher, *personal communication*).

4. Conclusions

The present study demonstrates that in 2013–2014 Hudson Bay polar bears are exposed an increasingly complex cocktail of OHC-POPs, with several identified and new POPs being quantifiable and with most at low part-per-billion levels. Of the investigated OHCs, concentrations of PCBs and CHLs remain the greatest in polar bears from the SHB and WHB subpopulations, however these concentrations do appear

to be decreasing slowly relative to those from 2007 to 2008 samples from the same subpopulations (McKinney et al., 2011b). PFOS and ΣPFAS are at concentrations that are comparable to legacy POPs, PCBs and oxychlordane, but relative to 10 years ago PFOS appears to be decreasing rapidly due to global regulation unlike the legacy OCs. ΣPFCAs in these Hudson Bay bears has increased greatly relative to 10 or more years ago, presumably due to continued production and atmospheric LRT of volatile precursors which are biotransformed to PFCAs (Martin et al., 2004, 2005).

PCNs were detected in polar bears here at the greatest concentrations reported in any biota from the Canadian Arctic (Bidleman et al., 2010), reaching concentrations that were within range of the ΣPBDEs, however, they remained among the lowest concentrations of the OHCs under study. Only a single OPE was quantifiable with any frequency (TEHP), although four other OPEs were detectable, suggesting limited dietary exposure, uptake and/or accumulation due to rapid metabolism in polar bears, despite very high global production and high levels in Arctic air (Suhring et al., 2016). Some new POPs detected years ago in polar bear fat (HBCDD and endosulfans) were below detection limits in the 2013–2014 samples. Similarly, the PBDEs and BB153 have decreased in most bears relative to reports in 2007–2008 (McKinney et al., 2011b), suggesting that bans and global regulations have been effective for these POPs. The very high production SCCPs were found in all bears at concentrations comparable to many legacy OCPs of concern. Further investigation of future and possibly retrospective trends and behavior with a focus on annual variations of e.g. SCCPs, PCNs, PBDEs, PFSAs, and PFCAs in polar bears are needed, given the dearth of recent data in the Arctic for these compounds. Considerations of ecological, atmospheric, and other environmental factors in connection to Arctic warming also need to be considered in the context of temporal trends and behavior of these OHCs. For example, contaminants in male bears from the WHB appear to be grossly different from the other bears, which is likely indicative of continued shifts in diet and behavior in these bears in connection to changes to the Arctic climate as has been suggested previously (McKinney et al., 2010).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.08.035.

References

Abbasi, G., Buser, A.M., Soehl, A., Murray, M.W., Diamond, M.L., 2015. Stocks and flows of PBDEs in products from use to waste in the U.S. and Canada from 1970 to 2020. Environ. Sci. Technol. 49, 1521–1528.

Ahn, Y.G., Seo, J., Shin, J.H., Khim, J., Hong, J., 2006. Development of new cleanup method of polychlorinated dibenzo-*p*-dioxins/dibenzofurans in fish by freezing-lipid filtration. Anal. Chim. Acta 576, 31–36.

Antweiler, R.C., Taylor, H.E., 2008. Evaluation of statistical treatments of left-censored environmental data using coincident uncensored data sets: I. Summary statistics. Environ. Sci. Technol. 42, 3732–3738.

Bailey, R., Barrie, L.A., Halsall, C.J., Fellin, P., Muir, D.C.G., 2000. Atmospheric organochlorine pesticides in the western Canadian Arctic: evidence of transpacific transport. J. Geophys. Res. 105, 11805–11811.

Becker, S., Halsall, C.J., Tych, W., Kallenborn, R., Schlabach, M., Mano, S., 2012. Changing sources and environmental factors reduce the rates of decline of organochlorine pesticides in the Arctic atmosphere. Atmos. Chem. Phys. 12, 4033–4044.

Bentzen, T.W., Follman, E.H., Amstrup, S.C., York, G.S., Wooller, M.J., Muir, D.C.G., O'Hara, T.M., 2008. Dietary biomagnification of organochlorine contaminants in Alaskan polar bears. Can. J. Zool. 86, 177–191.

Bergman, A., Ryden, A., Law, R.J., de Boer, J., Covaci, A., Alaee, M., Birnbaum, L., Petreas, M., Rose, M., Sakai, S., Van den Eede, N., van der Veen, I., 2012. A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals. Environ. Int. 49, 57–82.

Bidleman, T.F., Helm, P.A., Braune, B.M., Gabrielsen, G.W., 2010. Polychlorinated naphthalenes in polar environments—a review. Sci. Total Environ. 408, 2919–2935.

Bidleman, T.F., Kurt-Karakus, P., Li, Y.F., Hung, H., Ma, J., 2013a. Properties, sources, global fate and transport. In: Muir, D.C.G., Kurt-Karakus, P., Stow, J. (Eds.), Canadian Arctic Contaminants Assessment Report on Persistent Organic Pollutants—2013. Aboriginal Affairs and Northern Development Canada, Ottawa, ON, pp. 19–146.

Bidleman, T.F., Stern, G.A., Tomy, G.T., Hargrave, B.T., Jantunen, L.M., Macdonald, R.W., 2013b. Scavenging amphipods: sentinels for penetration of mercury and persistent organic chemicals into food webs of the deep Arctic Ocean. Environ. Sci. Technol. 47, 5553–5561.

Braune, B.M., Muir, D.C.G., 2017. Declining trends of polychlorinated naphthalenes in seabird eggs from the Canadian Arctic, 1975−2014. Environ. Sci. Technol. 51, 3802–3808.

Chen, M.Y., Luo, X.J., Zhang, X.L., He, M.J., Chen, S.J., Mai, B.X., 2011. Chlorinated paraffins in sediments from the Pearl River Delta, South China: spatial and temporal distributions and implication for processes. Environ. Sci. Technol. 45, 9936–9943.

Chu, S.G., Letcher, R.J., 2015. Determination of organophosphate flame retardants and plasticizers in lipid-rich matrices using dispersive solid-phase extraction and ultra performance liquid chromatography with atmospheric pressure chemical ionization mass spectrometry. Anal. Chim. Acta 885, 183–190.

Chu, S., Covaci, A., Voorspoels, S., Schepens, P., 2003. The distribution of octachlorostyrene (OCS) in environmental samples from Europe. J. Environ. Monit. 5, 619–625.

Corsolini, S., Kannan, K., Imagawa, T., Focardi, S., Giesy, J.P., 2002. Polychloronaphthalenes and other dioxin-like compounds in Arctic and Antarctic marine food webs. Environ. Sci. Technol. 36, 3490–3496.

de Silva, A.O., Spencer, C., Scott, B.F., Backus, S., Muir, D.C., 2011. Detection of a cyclic perfluorinated acid, perfluoroethylcyclohexane sulfonate, in the Great Lakes of North America. Environ. Sci. Technol. 45, 8060–8066.

Deema, P., Thompson, E., Ware, G.W., 1966. Metabolism, storage and excretion of C^{14}-endosulfan in the mouse. J. Econ. Entomol. 59, 546–550.

Derocher, A.E., Wiig, O., Andersen, M., 2002. Diet composition of polar bears in Svalbard and the western Barents Sea. Polar Biol. 25, 448–452.

Dietz, R., Riget, F.F., Sonne, C., Letcher, R.J., Backus, S., Born, E.W., Kirkegaard, M., Muir, D.C., 2007. Age and seasonal variability of polybrominated diphenyl ethers in free-ranging East Greenland polar bears (*Ursus maritimus*). Environ. Pollut. 146, 166–173.

Dietz, R., Riget, F.F., Sonne, C., Born, E.W., Bechshoft, T., McKinney, M.A., Drimmie, R.J., Muir, D.C., Letcher, R.J., 2013a. Three decades (1983–2010) of contaminant trends in East Greenland polar bears (*Ursus maritimus*). Part 2: brominated flame retardants. Environ. Int. 59, 494–500.

Dietz, R., Riget, F.F., Sonne, C., Born, E.W., Bechshoft, T., McKinney, M.A., Letcher, R.J., 2013b. Three decades (1983–2010) of contaminant trends in East Greenland polar bears (Ursus maritimus). Part 1: legacy organochlorine contaminants. Environ. Int. 59, 485–493.

Dorough, W.H., Huhtanen, K., Marshall, T.C., Bryant, H.E., 1977. Fate of endosulfan in rats and toxicological considerations of apolar metabolites. Pestic. Biochem. Physiol. 8, 241–252.

Dyck, M., Daley, K.J., 2002. Cannibalism of a yearling polar bear (*Ursus maritimus*) at Churchill, Manitoba. Arctic 55, 190–192.

ECHA, 2007. European Union Risk Assessment Report. Hexachlorocyclopentadiene, CAS No. 77-47-4. http://echa.europa.eu/documents/10162/8a93cd69-5a82-4c2f-b0bd-0bbe059074a2 European Union Risk Assessment Report, Ispra, Italy:p. 167.

Gauthier, L.T., Letcher, R.J., 2009. Isomers of Dechlorane Plus flame retardant in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes of North America: temporal changes and spatial distribution. Chemosphere 75, 115–120.

Gebbink, W.A., Sonne, C., Dietz, R., Kirkegaard, M., Born, E.W., Muir, D.C., Letcher, R.J., 2008a. Target tissue selectivity and burdens of diverse classes of brominated and chlorinated contaminants in polar bears (*Ursus maritimus*) from East Greenland. Environ. Sci. Technol. 42, 752–759.

Gebbink, W.A., Sonne, C., Dietz, R., Kirkegaard, M., Riget, F.F., Born, E.W., Muir, D.C., Letcher, R.J., 2008b. Tissue-specific congener composition of organohalogen and metabolite contaminants in East Greenland polar bears (*Ursus maritimus*). Environ. Pollut. 152, 621–629.

Giesy, J.P., Mabury, S.A., Martin, J.W., Kannan, K., Jones, P.D., Newsted, J.L., Coady, K., 2006. Perfluorinated compounds in the Great Lakes. In: Barceló, D., Kostianoy, A.G. (Eds.), Handbook of Environmental Chemistry. Springer-Verlag, Berlin Heidelberg, pp. 391–438.

Gormezano, L.J., Rockwell, R.F., 2013. What to eat now? Shifts in polar bear diet during the ice-free season in western Hudson Bay. Ecol. Evol. 3, 3509–3523.

Greaves, A.K., Letcher, R.J., Sonne, C., Dietz, R., Born, E.W., 2012. Tissue-specific concentrations and patterns of perfluoroalkyl carboxylates and sulfonates in East Greenland polar bears. Environ. Sci. Technol. 46, 11575–11583.

Greaves, A.K., Su, G., Letcher, R.J., 2016. Environmentally relevant organophosphate triester flame retardants in herring gulls: in vitro biotransformation and kinetics

and diester metabolite formation using a hepatic microsomal assay. Toxicol. Appl. Pharmacol. 308, 59–65.
Hakk, H., Letcher, R.J., 2003. Metabolism in the toxicokinetics and fate of brominated flame retardants—a review. Environ. Int. 29, 801–828.
Helm, P.A., Bidleman, T.F., 2003. Current combustion-related sources contribute to polychlorinated naphthalene and dioxin-like polychlorinated biphenyl levels and profiles in air in Toronto, Canada. Environ. Sci. Technol. 37, 1075–1082.
Helm, P.A., Bidleman, T.F., Stern, G.A., Koczanski, K., 2002. Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in beluga whale (*Delphinapterus leucas*) and ringed seal (*Phoca hispida*) from the eastern Canadian Arctic. Environ. Pollut. 119, 69–78.
Hoferkamp, L., Hermanson, M.H., Muir, D.C., 2010. Current use pesticides in Arctic media; 2000–2007. Sci. Total Environ. 408, 2985–2994.
Houde, M., Martin, J.W., Letcher, R.J., Solomon, K.R., Muir, D.C., 2006. Biological monitoring of polyfluoroalkyl substances: a review. Environ. Sci. Technol. 40, 3463–3473.
Hung, H.K.-K.P., Ahrens, L., Bidleman, T., Evans, M., Halsall, C., Harner, T., Jantunen, L., Lee, S.C., Muir, D., Shoeib, M., Stern, G., Sverko, E., Su, Y., Vlahos, P., Xiao, H., 2013. Occurrence and trends in the physical environment. In: Muir, D.C.G., Kurt-Karakus, P., Stow, J. (Eds.), Canadian Arctic Contaminants Assessment Report on Persistent Organic Pollutants—2013. Aboriginal Affairs and Northern Development Canada, Ottawa, ON, pp. 147–272.
Jensen, A.A., Leffers, H., 2008. Emerging endocrine disrupters: perfluoroalkylated substances. Int. J. Androl. 31, 161–169.
Jorundsdottir, H., Norstrom, K., Olsson, M., Pham-Tuan, H., Huhnerfuss, H., Bignert, A., Bergman, A., 2006. Temporal trend of bis(4-chlorophenyl) sulfone, methylsulfonyl-DDE and -PCBs in Baltic guillemot (*Uria aalge*) egg 1971–2001—a comparison to 4,4′-DDE and PCB trends. Environ. Pollut. 141, 226–237.
Kelly, B.C., Ikonomou, M.G., Blair, J.D., Morin, A.E., Gobas, F.A.P.C., 2007. Food web-specific biomagnification of persistent organic pollutants. Science 317, 236–239.
Kelly, B.C., Ikonomou, M.G., Blair, J.D., Gobas, F.A., 2008. Bioaccumulation behaviour of polybrominated diphenyl ethers (PBDEs) in a Canadian Arctic marine food web. Sci. Total Environ. 401, 60–72.
Kelly, B.C., Ikonomou, M.G., Blair, J.D., Surridge, B., Hoover, D., Grace, R., Gobas, F.A., 2009. Perfluoroalkyl contaminants in an Arctic marine food web: trophic magnification and wildlife exposure. Environ. Sci. Technol. 43, 4037–4043.
Letcher, R.J., Norstrom, R.J., Bergman, A., 1995a. Geographical distribution and identification of methyl sulphone PCB and DDE metabolites in pooled polar bear (*Ursus maritimus*) adipose tissue from western hemisphere arctic and subarctic regions. Sci. Total Environ. 160-161, 409–420.
Letcher, R.J., Norstrom, R.J., Bergman, A., 1995b. An integrated analytical method for determination of polychlorinated aryl methyl sulfone metabolites and polychlorinated hydrocarbon contaminants in biological matrices. Anal. Chem. 67, 4155–4163.
Letcher, R.J., Norstrom, R.J., Muir, D.C.G., 1998. Biotransformation versus bioaccumulation: sources of methyl sulfone PCB and 4,4′-DDE in the polar bear food chain. Environ. Sci. Technol. 32, 1656–1661.
Letcher, R.J., Gebbink, W.A., Sonne, C., Born, E.W., McKinney, M.A., Dietz, R., 2009. Bioaccumulation and biotransformation of brominated and chlorinated contaminants and their metabolites in ringed seals (*Pusa hispida*) and polar bears (*Ursus maritimus*) from East Greenland. Environ. Int. 35, 1118–1124.
Letcher, R.J., Bustnes, J.O., Dietz, R., Jenssen, B.M., Jorgensen, E.H., Sonne, C., Verreault, J., Vijayan, M.M., Gabrielsen, G.W., 2010. Exposure and effects assessment of persistent organohalogen contaminants in arctic wildlife and fish. Sci. Total Environ. 408, 2995–3043.
Letcher, R.J., Chu, S., McKinney, M.A., Tomy, G.T., Sonne, C., Dietz, R., 2014a. Comparative hepatic in vitro depletion and metabolite formation of major perfluorooctane sulfonate precursors in Arctic polar bear, beluga whale, and ringed seal. Chemosphere 112, 225–231.
Letcher, R.J., Marteinson, S.C., Fernie, K.J., 2014b. Dietary exposure of American kestrels (*Falco sparverius*) to decabromodiphenyl ether (BDE-209) flame retardant: uptake, distribution, debromination and cytochrome P450 enzyme induction. Environ. Int. 63, 182–190.
Letcher, R.J., Su, G., Moore, J.N., Williams, L.L., Martin, P.A., de Solla, S.R., Bowerman, W.W., 2015. Perfluorinated sulfonate and carboxylate compounds and precursors in herring gull eggs from across the Laurentian Great Lakes of North America: temporal and recent spatial comparisons and exposure implications. Sci. Total Environ. 538, 468–477.
Li, Y.F., MacDonald, R.W., 2005. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. Sci. Total Environ. 342, 87–106.
Li, B., Danon-Schaffer, M.N., Li, L.Y., Ikonomou, M.G., Grace, J.R., 2012. Occurrence of PFCs and PBDEs in landfill leachates from across Canada. Water Air Soil Pollut. 223, 3365–3372.
Lunn, N.J., Stirling, I., 1985. The significance of supplemental food to polar bears during the ice-free period in Hudson Bay. Can. J. Zool. 63, 2291–2297.
Ma, J., Hung, H., Tian, C., Kallenborn, R., 2011. Revolatilization of persistent organic pollutants in the Arctic induced by climate change. Nat. Clim. Chang. 1, 255–260.
Ma, Y., Salamova, A., Venier, M., Hites, R.A., 2013. Has the phase-out of PBDEs affected their atmospheric levels? Trends of PBDEs and their replacements in the Great Lakes atmosphere. Environ. Sci. Technol. 47, 11457–11464.
Macdonald, R.W., Harner, T., Fyfe, J., 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. Sci. Total Environ. 342, 5–86.
Martin, J.W., Smithwick, M.M., Braune, B.M., Hoekstra, P.F., Muir, D.C., Mabury, S.A., 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. Environ. Sci. Technol. 38, 373–380.
Martin, J.W., Mabury, S.A., O'Brien, P.J., 2005. Metabolic products and pathways of fluorotelomer alcohols in isolated rat hepatocytes. Chem. Biol. Interact. 155, 165–180.
Matson, G., Van Daele, L., Goodwin, E., Aumiller, L., Reynolds, H., Hristienko, H., 1993. A Laboratory Manual for Cementum Age Determination of Alaska Brown Bear First Premolar Teeth. Alaska Department of Fish and Game, Anchorage, AK.
McKinney, M.A., Peacock, E., Letcher, R.J., 2009. Sea ice-associated diet change increases the levels of chlorinated and brominated contaminants in polar bears. Environ. Sci. Technol. 43, 4334–4339.
McKinney, M.A., Stirling, I., Lunn, N.J., Peacock, E., Letcher, R.J., 2010. The role of diet on long-term concentration and pattern trends of brominated and chlorinated contaminants in western Hudson Bay polar bears, 1991–2007. Sci. Total Environ. 408, 6210–6222.
McKinney, M.A., Letcher, R.J., Aars, J., Born, E.W., Branigan, M., Dietz, R., Evans, T.J., Gabrielsen, G.W., Muir, D.C., Peacock, E., Sonne, C., 2011a. Regional contamination versus regional dietary differences: understanding geographic variation in brominated and chlorinated contaminant levels in polar bears. Environ. Sci. Technol. 45, 896–902.
McKinney, M.A., Letcher, R.J., Aars, J., Born, E.W., Branigan, M., Dietz, R., Evans, T.J., Gabrielsen, G.W., Peacock, E., Sonne, C., 2011b. Flame retardants and legacy contaminants in polar bears from Alaska, Canada, East Greenland and Svalbard, 2005–2008. Environ. Int. 37, 365–374.
McKinney, M.A., McMeans, B.C., Tomy, G.T., Rosenberg, B., Ferguson, S.H., Morris, A., Muir, D.C., Fisk, A.T., 2012. Trophic transfer of contaminants in a changing arctic marine food web: Cumberland Sound, Nunavut, Canada. Environ. Sci. Technol. 46, 9914–9922.
Morris, A.D., Muir, D., Solomon, K.R., Letcher, R.J., McKinney, M., Fisk, A.T., McMeans, B., Tomy, G.T., Teixeira, C., Wang, X., Duric, M., 2016. Current-use pesticides in seawater and their bioaccumulation in polar bear–ringed seal food chains of the Canadian Arctic. Environ. Toxicol. Chem. 35, 1695–1707.
Morris, A.D., Letcher, R.J., Dyck, M., Chandramouli, B., Fisk, A.T., Cosgrove, J., 2017. Multivariate statistical analysis and differentiation of metabolite profiles in the tissues of polar bears from Southern and Western Hudson Bay. Polar Biol. (Accepted for publication).
Muir, D.C., Backus, S., Derocher, A.E., Dietz, R., Evans, T.J., Gabrielsen, G.W., Nagy, J., Norstrom, R.J., Sonne, C., Stirling, I., Taylor, M.K., Letcher, R.J., 2006. Brominated flame retardants in polar bears (*Ursus maritimus*) from Alaska, the Canadian Arctic, East Greenland, and Svalbard. Environ. Sci. Technol. 40, 449–455.
Muir, D.C.G., Kurt-Karakus, P., Stow, J., 2013a. Canadian Arctic Contaminants Assessment Report on Persistent Organic Pollutants—2013. Aboriginal Affairs and Northern Development Canada, Ottawa, ON.
Muir, D.C.G., Kurt-Karakus, P., Stow, J., Blais, J., Braune, B., Choy, E., Evans, M., Kelly, B., Larter, N., Letcher, R., McKinney, M., Morris, A., Stern, G., Tomy, G., 2013b. In: Muir, D.C.G., Kurt-Karakas, P., Stow, J.E. (Eds.), Chapter 4: Occurrence and Trends in the Biological Environment. Canadian Arctic Contaminants Assessment Report on Persistent Organic Pollutants. Aboriginal Affairs and Northern Development Canada, Ottawa, ON, pp. 273–422.
Muir, D.C.G., Kurt-Karakus, P., Stow, J., Blais, J., Braune, B., Choy, E., Evans, M., Kelly, B., Larter, N., Letcher, R., McKinney, M., Morris, A., Stern, G., Tomy, G., 2013c. Occurrence and trends in the biological environment. In: Muir, D.C.G., Kurt-Karakus, P., Stow, J. (Eds.), Canadian Arctic Contaminants Assessment Report on Persistent Organic Pollutants—2013. Aboriginal Affairs and Northern Development Canada, Ottawa, ON, pp. 273–422.
Nash, S.B., 2011. Persistent organic pollutants in Antarctica: current and future research priorities. J. Environ. Monit. 13, 497–504.
Natural Resources Canada, 2015. Minerals and mining. In: Government of Canada (Ed.), The Atlas of Canada. Government of Canada, Ottawa, ON, Canada http://atlas.gc.ca/mins/en/index.html.
Norstrom, R.J., Belikov, S.E., Born, E.W., Garner, G.W., Malone, B., Olpinski, S., Ramsay, M.A., Schliebe, S., Stirling, I., Stishov, M.S., Taylor, M.K., Wiig, O., 1998. Chlorinated hydrocarbon contaminants in polar bears from eastern Russia, North America, Greenland, and Svalbard: biomonitoring of Arctic pollution. Arch. Environ. Contam. Toxicol. 35, 354–367.
Norstrom, K., Olsson, A., Olsson, M., Bergman, A., 2004. Bis(4-chlorophenyl) sulfone (BCPS) in Swedish marine and fresh water wildlife—a screening study. Environ. Int. 30, 667–674.
Norwegian Institute for Air Research (NILU), 2013. In: (NILU), N.I.f.A.R. (Ed.), Perfluorinated Alkylated Substances (PFAS), Brominated Flame Retardants (BFR) and Chlorinated Paraffins (CP) in the Norwegian Environment—Screening 2013. Norwegian Institute for Air Research (NILU), Oslo, Norway.
Polischuk, S.C., Norstrom, R.J., Ramsay, M.A., 2002. Body burdens and tissue concentrations of organochlorines in polar bears (*Ursus maritimus*) vary during seasonal fasts. Environ. Pollut. 118, 29–39.
Reiner, J.L., O'Connell, S.G., Moors, A.J., Kucklick, J.R., Becker, P.R., Keller, J.M., 2011. Spatial and temporal trends of perfluorinated compounds in beluga whales (*Delphinapterus leucas*) from Alaska. Environ. Sci. Technol. 45, 8129–8136.
Riget, F., Bossi, R., Sonne, C., Vorkamp, K., Dietz, R., 2013. Trends of perfluorochemicals in Greenland ringed seals and polar bears: indications of shifts to decreasing trends. Chemosphere 93, 1607–1614.
Sandau, C.D., Meerts, I.A.T.M., Letcher, R.J., Mcalees, A.J., Chittim, B., Brouwer, A., Norstrom, R.J., 2000. Identification of 4-hydroxyheptachlorostyrene in polar bear plasma and its binding affinity to transthyretin: a metabolite of octachlorostyrene. Environ. Sci. Technol. 34, 3871–3877.
Shen, L., Jobst, K.J., Helm, P.A., Reiner, E.J., McCrindle, R., Tomy, G.T., Backus, S., Brindle, I.D., Marvin, C.H., 2012. Identification and determination of the dechlorination products of Dechlorane 602 in Great Lakes fish and Arctic beluga whales by gas chromatography-high resolution mass spectrometry. Anal. Bioanal. Chem. 404, 2737–2748.
Smithwick, M., Norstrom, R.J., Mabury, S.A., Solomon, K., Evans, T.J., Stirling, I., Taylor, M.K., Muir, D.C., 2006. Temporal trends of perfluoroalkyl contaminants in polar bears

(*Ursus maritimus*) from two locations in the North American Arctic, 1972–2002. Environ. Sci. Technol. 40, 1139–1143.

Strid, A., Bruhn, C., Sverko, E., Svavarsson, J., Tomy, G., Bergman, A., 2013. Brominated and chlorinated flame retardants in liver of Greenland shark (*Somniosus microcephalus*). Chemosphere 91, 222–228.

Suhring, R., Diamond, M.L., Scheringer, M., Wong, F., Pucko, M., Stern, G., Burt, A., Hung, H., Fellin, P., Li, H., Jantunen, L.M., 2016. Organophosphate esters in Canadian Arctic air: occurrence, levels and trends. Environ. Sci. Technol. 50, 7409–7415.

Sverko, E., Tomy, G.T., Marvin, C.H., Muir, D.C., 2012. Improving the quality of environmental measurements on short chain chlorinated paraffins to support global regulatory efforts. Environ. Sci. Technol. 46, 4697–4698.

Tomy, G., S., G.A., Muir, D.C.G., Fisk, A.T., Cymbalisty, C.D., Westmore, J.B., 1997. Quantifying C_{10}–C_{13} polychloroalkanes in environmental samples by high-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry. Anal. Chem. 69, 2762–2771.

Tomy, G.T., Stern, G., Lockhart, W.L., Muir, D.C.G., 1999. Occurrence of $C_{10}-C_{13}$ polychlorinated *n*-alkanes in Canadian midlatitude and Arctic lake sediments. Environ. Sci. Technol. 33, 2858–2863.

Tomy, G., Muir, D.C.G., Stern, G., Westmore, J.B., 2000. Levels of $C_{10}-C_{13}$ polychloro-*n*-alkanes in marine mammals from the Arctic and the St. Lawrence River estuary. Environ. Sci. Technol. 34, 1615–1619.

Tomy, G.T., Pleskach, K., Oswald, T., Halldorson, T., Helm, P.A., MacInnis, G., Marvin, C.H., 2008. Enantioselective bioaccumulation of hexabromocyclododecane and congener-specific accumulation of brominated diphenyl ethers in an eastern Canadian Arctic marine food web. Environ. Sci. Technol. 42, 3634–3639.

Tomy, G.T., Pleskach, K., Ferguson, S.H., Hare, J., Stern, G., Macinnis, G., Marvin, C.H., Loseto, L., 2009. Trophodynamics of some PFCs and BFRs in a western Canadian Arctic marine food web. Environ. Sci. Technol. 43, 4076–4081.

United Nations Environment Programme, 2017. In: United Nations Environment Programme (Ed.), Stockholm Convention on Persistent Organic Pollutants. United Nations Environment Programme, Stockholm, Sweden http://chm.pops.int.

van Mourik, L.M., Leonards, P.E.G., Gaus, C., de Boer, J., 2015. Recent developments in capabilities for analysing chlorinated paraffins in environmental matrices: a review. Chemosphere 136, 259–272.

Verreault, J., Gabrielsen, G.W., Chu, S., Muir, D.C., Andersen, M., Hamaed, A., Letcher, R.J., 2005a. Flame retardants and methoxylated and hydroxylated polybrominated diphenyl ethers in two Norwegian Arctic top predators: glaucous gulls and polar bears. Environ. Sci. Technol. 39, 6021–6028.

Verreault, J., Muir, D.C., Norstrom, R.J., Stirling, I., Fisk, A.T., Gabrielsen, G.W., Derocher, A.E., Evans, T.J., Dietz, R., Sonne, C., Sandala, G.M., Gebbink, W., Riget, F.F., Born, E.W., Taylor, M.K., Nagy, J., Letcher, R.J., 2005b. Chlorinated hydrocarbon contaminants and metabolites in polar bears (*Ursus maritimus*) from Alaska, Canada, East Greenland, and Svalbard: 1996–2002. Sci. Total Environ. 351–352, 369–390.

Vetter, W., Gall, V., Skírnisson, K., 2015. Polyhalogenated compounds (PCBs, chlordanes, HCB and BFRs) in four polar bears (*Ursus maritimus*) that swam malnourished from East Greenland to Iceland. Sci. Total Environ. 533, 290–296.

Vorkamp, K., Riget, F.F., 2014. A review of new and current-use contaminants in the Arctic environment: evidence of long-range transport and indications of bioaccumulation. Chemosphere 111, 379–395.

Vorkamp, K., Pesceli, M., Rigét, F., Glasius, M., Lebeuf, M., Muir, D.C.G., 2004. Chlorobenzenes, chlorinated pesticides, coplanar CBs and other organochlorine compounds in Greenland biota. Sci. Total Environ. 331, 157–175.

Vorkamp, K., Bossi, R., Rigét, F.F., Skov, H., Sonne, C., Dietz, R., 2015. Novel brominated flame retardants and dechlorane plus in Greenland air and biota. Environ. Pollut. 196, 284–291.

Vorkamp, K., Rigét, F.F., Bossi, R., Sonne, C., Dietz, R., 2017. Endosulfan, short-chain chlorinated paraffins (SCCPs) and octachlorostyrene in wildlife from Greenland: levels, trends and methodological challenges. Arch. Environ. Contam. Toxicol. http://dx.doi.org/10.1007/s00244-017-0428-3 (in press June 17, 2017).

Wania, F., Mackay, D., 1995. A global distribution model for persistent organic chemicals. Sci. Total Environ. 160/161, 211–232.