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Blubber-depth distribution and bioaccumulation of PCBs and organochlorine pesticides in Arctic-invading killer whales

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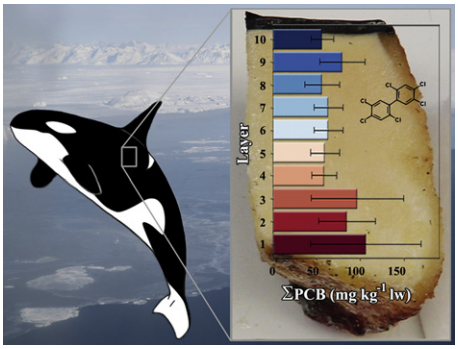
HIGHLIGHTS

- POP levels in Greenland orcas may be due to feeding both on fish and marine mammals.
- Levels of POPs decreased from sub-adults > adult males > adult females > fetuses.
- Limited variation found in lipid weight POP levels among full-depth blubber layers
- Biopsies may be a reasonable representation of POP levels in killer whale blubber.

GRAPHICAL ABSTRACT



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ABSTRACT

Sightings of killer whales (*Orcinus orca*) in Greenland have increased in recent years, coincident with sea ice loss. These killer whales are likely from fish-feeding North Atlantic populations, but may have access to marine mammal prey in Greenlandic waters, which could lead to increased exposures to biomagnifying contaminants. Most studies on polychlorinated biphenyl (PCB) and organochlorine (OC) contaminants in killer whales have used biopsies which may not be representative of contaminant concentrations through the entire blubber depth. Here, we measured PCB and OC concentrations in 10 equal-length blubber sections of 18 killer whales harvested in southeast Greenland (2012–2014), and 3 stranded in the Faroe Islands (2008) and Denmark (2005). Overall, very high concentrations of ΣPCB, Σchlordanes (ΣCHL), and Σdichlorodiphenyltrichloroethane (ΣDDT) were found in the southeast Greenland and Denmark individuals (means of ~40 to 70 mg kg^{-1} lipid weight). These concentrations were higher than in the Faroe Island individuals (means of ~2 to 5 mg kg^{-1} lipid weight) and above those previously reported for other fish-feeding killer whales in the North Atlantic, likely in part due to additional feeding on marine mammals. On a wet weight basis, concentrations of all contaminants were significantly lower in the outermost blubber layer (0.15–0.65 cm) compared to all other layers ($p < 0.01$), except for Σhexachlorocyclohexanes. However, after lipid correction, no variation was found for ΣCHL and Σchlorobenzene

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concentrations, while the outermost layer(s) still showed significantly lower ΣPCB, ΣDDT, Σmirex, Σendosulfan, and dieldrin concentrations than one or more of the inner layers. Yet, the magnitude of these differences was low (up to 2-fold) suggesting that a typical biopsy may be a reasonable representation of the PCB and OC concentrations reported in killer whales, at least on a lipid weight basis.

1. Introduction

Distribution of killer whales (*Orcinus orca*) into Arctic and sub-Arctic marine waters has historically been limited by sea ice cover (Reeves and Mitchell, 1988). However, with recent declines in sea ice extent, some killer whales appear to be expanding their ranges northward and/or extending the period of time spent within these environments, as documented in the eastern Canadian Arctic/sub-Arctic (Higdon et al., 2014, 2012), southeast Greenland (A. Rosing-Asvid, personal observation) and possibly the Chukchi Sea (Clarke et al., 2013). Yet, the movements and feeding ecology of killer whales within these waters and in North Atlantic regions are poorly known (Foote et al., 2010; Higdon et al., 2012). Observations of small killer whale groups (<10 individuals) attacking and feeding on diverse marine mammals suggest that these may be their main prey in the Canadian Arctic (Ferguson et al., 2012; Higdon et al., 2012; Reinhart et al., 2013). Such smaller foraging groups averaging five individuals are typical in the Northeast Pacific for the 'transient' ecotype that feeds primarily on marine mammals; in contrast, the fish-eating 'resident' ecotype in the Northeast Pacific forages in groups of up to 100 individuals (Herman et al., 2005; Higdon et al., 2012). Similarly, in the Northeast Atlantic, there appears to be smaller groups of marine-mammal specialists and larger groups that mainly forage on fish (Beck et al., 2012; Foote et al., 2010, 2009). Evidence suggests, however, that the Northeast Atlantic fish-feeders may be more generalist in nature, sometimes switching foraging strategy to hunt marine mammals (Beck et al., 2012; Foote et al., 2009; Vongraven and Bisther, 2013). It is thus possible that predation on marine mammals occurs during the open water season in the Arctic, after which killer whales migrate south to sub-Arctic and North Atlantic regions, where they might be feeding on other prey species, depending on availability (Lawson and Stevens, 2013; Matthews et al., 2011; Matthews and Ferguson, 2014). In fact, variation in nitrogen stable isotopes and relatively depleted carbon signatures suggests that some Canadian Arctic killer whales may forage consistently at lower latitudes, possibly indicating a different over-wintering range (Matthews and Ferguson, 2014). Further evaluation of their foraging ecology in apparently new Arctic habitats is warranted.

Killer whale predation on various Arctic marine mammal species (Ferguson et al., 2012; Reinhart et al., 2013) may represent a trophic ecological shift in the frequency with which killer whales feed on prey higher in the food web, and consequently lead to increases in their exposures to biomagnifying persistent organic pollutants (POPs). High body burdens of POPs, such as polychlorinated biphenyls (PCBs), are thought to be a major threat to certain killer whale populations, as documented in the Northeast Pacific and Northeast Atlantic (Jepson and Law, 2016; Jepson et al., 2016; Ross et al., 2000). POPs are synthetic organic compounds and industrial by-products, including the PCBs and organochlorine pesticides, such as DDT, some of which have been banned under national and international regulations (e.g., the Stockholm Convention; United Nations Environmental Programme, 2009). Yet, due to their persistence, tendency to bioaccumulate and biomagnify, and long-range transport potential, they continue to be present in the environment (Letcher et al., 2010). Dietary habits have been suggested to contribute to the particularly elevated contaminant concentrations in threatened killer whale populations. For instance, in the Northeast Pacific, blubber PCB levels measured in marine mammal-feeding transients were about five to 20 times higher than those in fish-feeding northern residents (Buckman et al., 2011; Ross et al., 2000).

Determination of POP concentrations in killer whales has nearly exclusively been based on blubber biopsies (Fossi et al., 2014; McHugh et al., 2007; Ross et al., 2000). Yet, biopsies generally consist of the top 2 cm of blubber tissue which, in killer whales, may represent a small fraction of the total blubber depth (Krahn et al., 2004). In cetaceans, blubber tissues exhibit stratification in lipid composition associated with diet and thermoregulation (Budge et al., 2006; Parry, 1949). For example, harbor porpoises (*Phocoena phocoena*) have up to four times higher concentrations of dietary fatty acids in more inner layers compared to outer layers, which are mostly comprised of more structural fatty acids (Budge et al., 2006). This stratification can potentially affect how lipophilic contaminants are distributed through the blubber depth (Krahn et al., 2004). Inconsistent variation of ΣPCB and ΣDDT concentrations among the inner, middle and outer blubber layers was previously reported for killer whales in the Northeast Pacific (Krahn et al., 2004), and between inner and outer layers of other cetaceans of different sexes and locations (Aguilar and Borrell, 1991; Krahn et al., 2004; Waugh et al., 2014). Yet, previous studies have used a very limited number of individuals (three killer whales in Krahn et al. (2004)) and rather coarse-scale analysis, i.e. three or fewer blubber subsections. A fine-scale analysis with a larger number of individuals is required to determine the efficacy of blubber biopsies in evaluating POPs exposures and potential health effects in killer whales.

In this study, full-depth blubber samples from 18 killer whales were opportunistically collected during incursions into sub-Arctic coastal waters off southeastern Greenland over the period of 2012–14, while a few other samples were collected in earlier years from Faroe Islands (2 in 2008) and Denmark (1 in 2005). The specimens provided a unique opportunity for the first fine-scale evaluation of blubber-depth (0.15 to 0.65 cm layers) profiles of PCB and OC pesticide concentrations in cetaceans. Given that the sample size obtained here was an order of magnitude larger than those of previous studies of blubber stratification in killer whales (Krahn et al., 2004), the influence of sex/age class (including two fetuses) and lipid content on blubber POPs profiles was also assessed. Considering that some of these individuals only had marine mammal remains in their stomachs, we tested our hypothesis that overall blubber POP concentrations are higher in these killer whales than in fish-feeding killer whales elsewhere due to marine mammal consumption. Second, based on the lipophilic properties of POPs and results from previous studies of whale blubber (Aguilar and Borrell, 1991; Waugh et al., 2014), we hypothesized that POP concentrations through the blubber depth vary with lipid content and sex/age class.

2. Material and methods

2.1. Sample collection

Twenty-one killer whales were sampled: one individual was stranded in Denmark in 2005, two in the Faroe Islands in 2008, and 16 were sampled opportunistically (two of which were pregnant, and the fetuses were also sampled) after being harvested for subsistence by local communities in southeast Greenland from 2012 to 2014 (Fig. 1). Aboriginal subsistence whaling in Greenland and elsewhere is permitted by the International Whaling Commission (see Supporting Information; Reeves (2002)). From the dorsal region of each individual, a full-

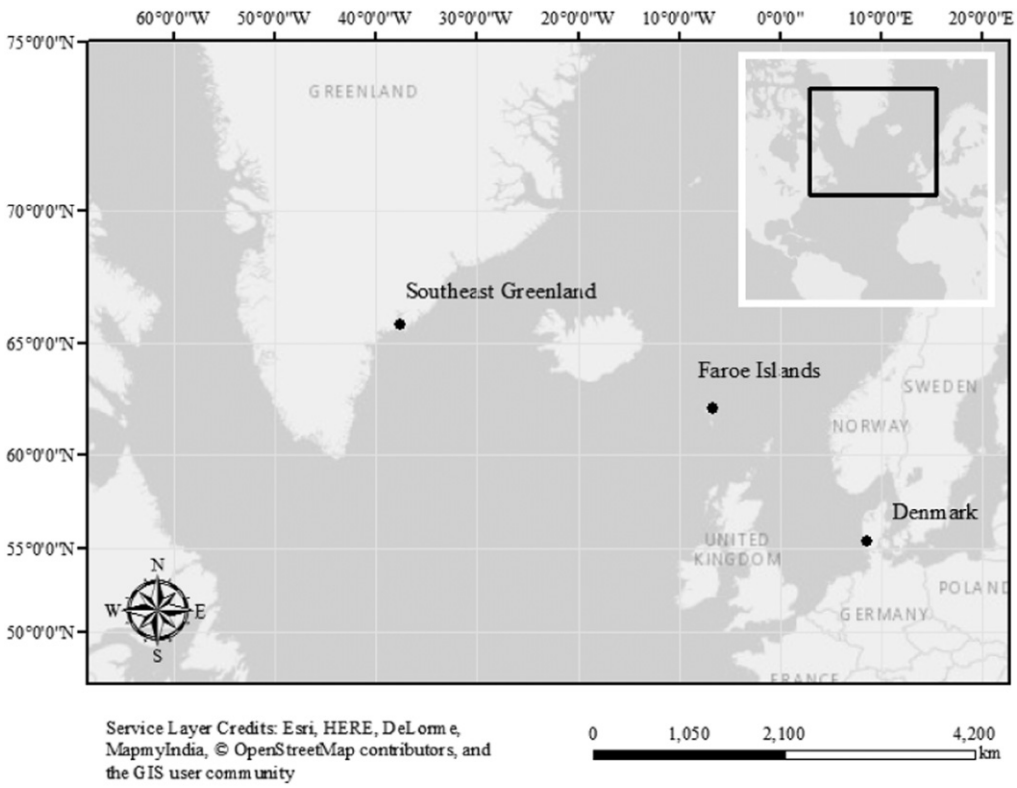

Fig. 1. Sampling locations for killer whales in this study: Denmark ($n = 1$, 2005, stranded), Faroe Islands ($n = 2$, 2008, stranded) and southeast Greenland ($n = 18$, 2012–2014, harvested).

Table 1
Sample collection and biological details for killer whales sampled in southeast Greenland ($n = 18$, 2012–2014), the Faroe Islands ($n = 2$, 2008) and Denmark ($n = 1$, 2005).

Sample ID	Sampling Location	GPS coordinates	Month/year	Sex	Age group	Killer whale length (cm)	Stomach contents	Blubber depth (cm)
48762	Esbjerg, Denmark	55°27 N 08°27E	01/2005	male	newborn	N.D.	N.D.	3.5
40888	Klarksvik, Faroe Islands	N.D.	04/2008	female	adult	574	N.D.	5.0
40889	Skalavik, Faroe Islands	N.D.	04/2008	female	sub-adult	395	N.D.	3.0
49341[a]	Tasiilaq, Greenland	65°37 N 37°57 W	08/2012	male	fetus	208	N.D.	3.0
48342[b]	Tasiilaq, Greenland	65°37 N 37°57 W	08/2012	female	fetus	166	N.D.	2.5
48339	Tasiilaq, Greenland	65°37 N 37°57 W	08/2012	male	sub-adult	460	N.D.	5.0
38340	Tasiilaq, Greenland	65°37 N 37°57 W	08/2012	male	sub-adult	400	Harp seal	4.0
48337	Tasiilaq, Greenland	65°37 N 37°57 W	08/2012	N.D.	sub-adult	350	N.D.	5.0
48335	Tasiilaq, Greenland	65°37 N 37°57 W	08/2012	female	adult	650	Harp and hooded seal	5.0
48336	Tasiilaq, Greenland	65°37 N 37°57 W	08/2012	probably female	adult	560	Harp seal	5.0
48338	Tasiilaq, Greenland	65°37 N 37°57 W	08/2012	female	adult	550	Harp seal	5.0
48735	Tasiilaq, Greenland	65°27 N 37°46 W	08/2013	female	sub-adult	353	Harp seal	3.7
48732	Tasiilaq, Greenland	65°20 N 37°10 W	09/2013	male	adult	N.D.	N.D.	3.0
48733	Kulusuq, Greenland	65°26 N 36°55 W	08/2013	female	adult	495	Harp seal	4.4
48736	Tasiilaq, Greenland	65°27 N 37°46 W	08/2013	female	adult	620	N.D.	6.5
35143	Kulusuq, Greenland	65°20 N 37°10 W	08/2013	female	adult	690	Harp seal, minke whale	4.6
51601	Tasiilaq, Greenland	N.D.	07/2014	male	sub-adult	N.D.	N.D.	4.2
51610	Tasiilaq, Greenland	N.D.	07/2014	male	sub-adult	600	N.D.	2.3
51613	Tasiilaq, Greenland	N.D.	07/2014	male	sub-adult	500–600	N.D.	3.8
51606	Tasiilaq, Greenland	N.D.	07/2014	N.D.	sub-adult	N.D.	N.D.	4.2
51607	Tasiilaq, Greenland	N.D.	07/2014	N.D.	sub-adult	N.D.	N.D.	1.5

Not determined data are indicated as N.D.
[a] Fetus of killer whale 48,335.
[b] Fetus of killer whale 48,338.

depth blubber sample was collected with skin attached (to determine directionality in the laboratory). Samples were stored at −20 °C to −80 °C until the time of analysis. Additional biological information was taken for some of these individuals, including sex/age class, body length, and stomach contents (Table 1). The sex of the individuals was determined visually by identifying the sexual organs and, for adult killer whales, by confirming the size of the dorsal fin (larger in males than females; Baird, 2001). Age class was determined based on sexual maturity and animal size, i.e., by examining the sexual organs at flensing/dissection and confirming with individual length (Duffield et al., 1995; Perrin, 1982). For some animals, age determination was based on local knowledge. The two pregnant Greenlandic killer whales (48,335 and 48,338) had fetuses at apparently different gestational stages, based on fetal length (Table 1) and blubber development. The fetus of 48,335 (49341) was at a more advanced gestational stage compared to that of 48,338 (48342), and possibly close to birth (length at birth reported 208–272 cm for killer whales; Perrin and Reilly, 1984).

2.2. Chemical analysis

We performed sample extractions and analysis at the Center for Environmental Science and Engineering, University of Connecticut. First, wet full blubber depth samples were divided into ten equal-length sections of ~0.3–0.4 g each, with the innermost section 1 being closest to the muscle and the outermost section 10 being closest to the skin (Fig. S1). Hence, the sections sampled varied from 0.15 to 0.65 cm dependent of the blubber thickness. We analyzed samples for ΣPCB (40 congeners including CB 18, 31/28, 44, 47/48/49/52, 66, 70/76, 74, 85, 87, 95, 99, 101/90, 105, 110, 118, 128, 130, 138, 146, 149, 151, 156, 157, 153, 170/190, 179, 180, 183, 184, 187, 195, 206, and 209) and OC pesticides including Σchlorobenzenes (ΣClBz: 1,2,4,5-tetraClBz, 1,2,3,4-tetraClBz, PeClBz and hexachlorobenzene (HCB)), Σhexachlorocyclohexanes (ΣHCH: α-, β-hexachlorocyclohexanes), Σchlordanes (ΣCHL: *cis*-nonachlor, *trans*-nonachlor, *cis*-chlordane, *trans*-chlordane, oxychlordane, heptachlor and heptachlor epoxide), aldrin, Σendosulfan (α-, β-endosulfan), ΣDDT (*p,p*-DDE, *p,p*-DDD, *p,p*-DDT), dieldrin, Σmirex (mirex, photomirex) and methoxychlor. We accurately weighed (four decimal places) and then extracted the samples using established procedures (McKinney et al., 2011). Briefly, each sample was homogenized with diatomaceous earth (Hydromatrix™), followed by spiking with the deuterated surrogates: 1,2,4,5-tetrachlorobenzene-d2, and 2,5-dichlorobiphenyl-d5, 2,3,4,5,6 pentachlorobiphenyl-d5, and 2,3,3′,4,4′,5 hexachlorobiphenyl-d3. Extraction proceeded using an accelerated solvent extraction (ASE) system with 1:1 dichloromethane:hexane for 3 cycles at 1500 psi and 100 °C. A 10% portion of the extract was used to determine lipid content gravimetrically. Extracts were filtered and purified by gel permeation chromatography and solid-phase extraction polar cartridges. We monitored concentrated extracts for PCBs and OCs using a gas chromatograph coupled with a Quattro Micro tandem mass spectrometer (GC-MS/MS) system on a Rxi-5Sil MS GC column (30 m length column of 0.25 mm I.D., 0.25 μm film thickness (Restek Corporation, PA, USA) (Provatas et al., 2014), and used Waters MassLynx™ software v. 4.1 (Milford, MA, USA) for data acquisition and processing. PCBs were monitored by multiple-reaction monitoring (MRM), while OCs were monitored by selected ion monitoring (SIM). Reagent blanks, recovery standards and calibration standards were run in the beginning and every 15 samples. The standard reference material NIST-1945 (whale blubber) was extracted with each batch of samples. We reported contaminant concentrations on a mg kg^{-1} lipid weight basis.

2.3. QA/QC results

Accuracies of ΣPCB and ΣOC, calculated as Relative Error, were within 20 ± 17% and 27 ± 11%, respectively, of the certified values for NIST-1945 ($n = 16$; Table S1). Surrogates spiked into samples showed recoveries of 77 ± 13% (1,2,4,5-tetraClBz) and 90 ± 20% (PCBs). The method limit of quantification was set to 10× the signal-to-noise ratio (McKinney et al., 2011) for each POP and ranged from 2.5 to 27 ng g^{-1} for PCBs and from 0.7 to 53 ng g^{-1} for OCs. Blanks were below the detection limit for PCBs and most OC compounds, although heptachlor and heptachlor epoxide were occasionally detected, and thus were blank subtracted on a batch-by-batch basis. We also found trace concentrations of *p,p′*-DDE, oxychlordane and *trans*-nonachlor in a few blanks. However, levels in blanks were more than ten times lower than the concentrations in our samples and thus blank subtraction was not performed for these analytes. Due to low recoveries for PCBs (67 ± 14%) and ClBz (70 ± 11%) in NIST-1945, concentrations of these contaminants but no other OCs, were recovery-corrected.

2.4. Statistical analysis

All contaminant groups were detected in >70% of all blubber samples. Prior to inferential statistical analysis, contaminant concentrations were log-transformed to meet normality requirements of linear models. All statistical analyses were performed using R software version 3.3.1 (R Core Team, 2015) and statistical significance was considered at $p < 0.05$.

Due to the sample size of just a few individuals in Denmark and the Faroe Islands, we only assessed the influence of sex/age class for killer whales sampled in southeast Greenland. Within this group, the sample sizes were sufficient to statistically compare adult females and sub-adults. For that, we used general linear models (one-way ANOVA) on lipid weight concentrations, followed by *post-hoc* Tukey's honestly significant difference tests. We additionally compared the proportions of individual contaminants within major contaminant groups, among adult females and sub-adults using the same statistical analysis on arcsine transformed data.

Differences in contaminant concentrations among blubber layers were assessed including individuals from all locations. However, we did not include fetuses because we observed a different color and/or texture in their blubber, possibly indicating incomplete development. To evaluate the influence of lipid content on contaminant distribution among blubber layers we used mixed effects models with repeated measures analysis of variance (repeated measures ANOVA) with the package *lme4* (Bates et al., 2014). We included each contaminant or sum (Σ) contaminant concentration as the dependent variable, *lipid percentage* as fixed effects and each *killer whale* individual as the random effects.

Because lipid content of blubber layers influenced wet weight contaminant concentrations ($p < 0.001$), we lipid corrected the data, i.e. reporting concentrations as mg kg^{-1} lipid weight, for further analyses. To evaluate differences among layers we used the same approach as for lipid content, but with *layer* as fixed effects instead, followed by *post-hoc* Tukey's honestly significant difference tests. To verify if *sex/age class* (i.e. adult females or sub-adults) influenced contaminant concentrations among layers, we added this variable and possible interactions, to the previous model as fixed effects.

Principal component analysis (PCA) of log transformed and standardized individual PCB and OC analytes on a lipid weight basis, was used to visualize the two-dimensional distribution of samples of southeast Greenland killer whales. We excluded killer whales from Denmark and the Faroe Islands from the PCA to facilitate visualization, since concentrations of contaminants in killer whales from these locations were distributed further from southeast Greenland in the PCA plot.

3. Results and discussion

3.1. PCB and OC concentrations in Northeast Atlantic killer whales

For all killer whales in this study, three contaminant classes dominated the blubber profiles at mean concentrations of ~40–60 mg kg^{-1} lipid weight (lw), specifically, ΣPCB, ΣDDT and ΣCHL (Table 2). Lower mean concentrations in the range of 1–10 mg kg^{-1} lw were found for

Table 2
Concentrations of polychlorinated biphenyls, organochlorine pesticides (mg kg^{-1} lipid weight) and lipid percentage (%) in killer whale blubber of individuals stranded in Denmark (2005) and the Faroe Islands (2008) and harvested in southeast Greenland (2012–2014). Results indicated as arithmetic mean (minimum-maximum).

	All individuals ($n = 21$)	Southeast Greenland ($n = 18$)				Faroe Islands	Denmark ($n = 1$)
Sex/age class		Adult male ($n = 1$)	Adult female ($n = 6$)	Sub-adult ($n = 9$)	Fetus ($n = 2$)	Adult ($n = 1$) and sub-adult ($n = 1$) females	Newborn male
Lipid %	57.1 (37.1–82.7)	67.7	57.2 (45.7–66.0)	54.7 (37.1–69.4)	45.2 (42.3–48.0)	61.3 (49.7–73.0)	83.7
ΣPCB	66.7 (9.01–356)	65.1	48.6 (19.6–65.5)	102 (9.01–356)	11.4 (9.47–13.4)	5.16 (2.75–7.57)	96.1
ΣClBz	1.64 (0.181–5.47)	1.01	0.842 (0.579–1.17)	2.66 (0.181–5.47)	0.701 (0.504–0.897)	0.306 (0.0262–0.350)	2.52
ΣHCH	0.0831 (0.0212–0.189)	0.100	0.0682 (0.0310–0.103)	0.109 (0.057–0.189)	0.0531 (0.0290–0.0771)	0.0322 (0.0210–0.0430)	0.0872
ΣCHL	39.6 (1.82–195)	40.2	19.3 (1.4–39.1)	65.9 (3.00–195)	10.2 (9.47–10.9)	2.23 (1.82–2.65)	57.5
Σendosulfan	2.80 (0.197–13.0)	2.81	1.44 (0.716–2.90)	4.28 (0.203–13.0)	0.740 (0.541–0.938)	0.240 (0.197–0.282)	6.78
ΣDDT	52.0 (3.67–235)	55.1	30.1 (16.1–50.2)	81.1 (4.35–235)	13.4 (7.89–18.9)	4.25 (3.67–4.82)	85.4
Dieldrin	4.61 (0.174–22.5)	3.44	1.50 (0.880–2.89)	6.66 (0.243–20.1)	0.624 (0.527–0.720)	0.362 (0.174–0.550)	22.5
Σmirex	7.66 (0.749–35.4)	7.26	5.68 (3.33–85.8)	12.2 (2.04–35.4)	1.87 (1.26–2.49)	0.836 (0.749–0.922)	4.54
ΣOC	108 (6.89–504)	110	59.7 (35.8–105)	173 (10.2–504)	27.6 (20.7–34.5)	8.25 (6.89–9.61)	179

Contaminants shown are Σpolychlorinated biphenyls (ΣPCB), Σchlorobenzenes (ΣClBz), Σhexachlorocyclohexanes (ΣHCH), Σchlordanes (ΣCHL) Σendosulfan, Σdichlorodiphenyltrichloroethanes (ΣDDT), dieldrin, Σmirex and Σorganochlorinated pesticides (ΣOC).

ΣClBz, Σendosulfan, dieldrin, and Σmirex, while the lowest concentrations were found for ΣHCH (<0.1 mg kg^{-1} lw). All individual contaminants were detected in each killer whale, with the exceptions of aldrin, methoxychlor and β-endosulfan not being detected in any individuals and 1,2,3,4-TeClBz, heptachlor and CBs18, 70/76, 110, 157, 184, 195, 206 and 209 being below the detection limit for >30% of the individuals.

Concentrations of PCBs and OCs in Greenland killer whales varied compared to those found in Denmark and the Faroe Islands, and in other North Atlantic regions. Among the three study locations, PCB and OC concentrations appeared to be higher in individuals sampled in Denmark and southeast Greenland relative to the two Faroe Islands individuals (Table 2). Although statistical comparisons were not possible due to low sample sizes for Denmark and the Faroe Islands, higher concentrations in Denmark are likely related to differences in age class. Newborns tend to have higher burdens of POPs than adults and sub-adults due to substantial transfer through mothers milk (Haraguchi et al., 2009; Krahn et al., 2009; Ylitalo et al., 2001). Comparing the Faroe Islands and Greenland, we found POP concentrations of more than an order of magnitude lower in Faroese whales compared to those of both the adult female and sub-adult killer whales sampled in southeast Greenland. Similarly, the southeast Greenland killer whales showed almost three times higher ΣPCB concentrations, and six times higher ΣCHL concentrations, than killer whales biopsied in Norway in 2002, with reported ΣPCB values of 27.0 mg kg^{-1} lw and ΣCHL of 6.70 mg kg^{-1} lw (Wolkers et al., 2007). Conversely, ΣPCB concentrations were three times higher in northeast Atlantic (177 mg kg^{-1} lw) and four times higher in the UK and Ireland adult females (225 mg kg^{-1} lw) sampled from 1990 to 2012 (Jepson et al., 2016), compared to southeast Greenland adult females.

The southeast Greenland killer whales showed variable levels of ΣPCB, ΣDDT, and ΣCHL relative to those previously reported for conspecifics outside the North Atlantic (Bachman et al., 2014; Krahn et al., 2009; McHugh et al., 2007). Higher ΣPCB and ΣCHL concentrations were found in Greenland killer whales (48.6–102 mg kg^{-1} lw and 10.2–65.9 mg kg^{-1} lw, respectively) compared to the southern resident ecotype in the northeast Pacific (37.3 mg kg^{-1} lw and 6.1 mg kg^{-1} lw, respectively) biopsied in 2007 (Krahn et al., 2009). In contrast, average ΣPCB concentrations (347 mg kg^{-1} lw) in the transient northeast Pacific ecotype killer whales biopsied from 2003 to 2007 (Buckman et al., 2011) were five times higher than in the southeast Greenland killer whales, while ΣDDT concentrations (2850 mg kg^{-1} lw) in two transient northeast Pacific killer whales stranded in 2002–2003 were nearly 55 times higher compared to southeast Greenland (Krahn et al., 2004).

Temporal and spatial variation in environmental concentrations of these contaminants may have contributed to the observed differences in PCB and OC concentrations among North Atlantic and northeast Pacific killer whales. Concentrations of several legacy organic pollutants such as DDTs, have been declining in Arctic marine species since restrictions to the mass production of these chemicals (Rigét et al., 2010) which would result in lower concentrations of these contaminants in killer whales sampled more recently. However, this is not consistent with higher concentrations found in southeast Greenland killer whales compared to other previous studies. Further, Jepson et al. (2016) found extremely high ΣPCB concentrations for killer whales sampled across the northeast Atlantic, irrespective of year of sampling, which they associated at least in part with proximity to highly industrialized areas. Thus, spatial variation in environmental concentrations of organic pollutants may explain the higher concentrations found in killer whales in European waters compared to those sampled in southeast Greenland.

Despite these factors, differences in diet seem to be a more likely explanation for the variation in contaminant concentrations among these killer whales. For example, the killer whale population in Norway is assumed to specialize on Norwegian spring-spawning herring (*Clupea harengus*), while evidence indicates that resident killer whales in the northeast Pacific feed largely on salmonid species, specifically Chinook salmon (*Oncorhynchus tshawytscha*; Similä et al., 1996; Ford et al., 1998; Ross et al., 2000). Northeast Pacific transients, conversely, specialize on marine mammals of various species (Ford et al., 1998; Ross et al., 2000). Hence, the marine mammal remains found in the stomachs of some killer whales in the current study (Table 1) and the observed contaminant concentrations intermediate between those of fish-eating killer whale populations and marine mammal-eaters, suggest that our killer whales may feed both on marine mammals and fish. However, we speculate that Greenland killer whales may feed more frequently on fish given the relatively larger difference in contaminant concentrations between resident and transient killer whales in the northeast Pacific (10 times lower in the resident fish-eaters) compared to the differences between Norway and Greenland killer whales (two to three times lower in the Norwegian fish-eaters). A seasonal change in diet to a larger proportion of marine mammals, possibly in Arctic and sub-Arctic waters, may explain the contaminant concentrations observed in southeast Greenland. These results are consistent with previous observations of killer whales switching hunting strategies to

predate both on seals and herring in Norwegian and Icelandic waters (Samarra et al., 2017; Vongraven and Bisther, 2013) and with reported varying stable isotope signatures found for killer whales across the North Atlantic (Foote et al., 2009; Samarra et al., 2017). In fact, based on variation in nitrogen stable isotope ratios, in addition to differences in body size and tooth wear, Foote et al. (2009) suggested two ecotypes of killer whales with distinct diets inhabiting the North Atlantic. Further work using fine-scale ecological tracers, such as fatty acid signatures, is now underway on the southeast Greenland killer whales to better understand their diet and consequent POP bioaccumulation in these apparently new habitats.

3.2. Potential health effects

Mean concentrations of ΣPCBs in southeast Greenland and Denmark killer whales were above the effects threshold of 9.0 mg kg^{-1} lw (used for ΣPCB by Jepson et al. (2016) based on Kannan et al. (2000) for *Aroclor 1254*) at which physiological effects, such as variation in thyroid hormone concentrations, were observed in experimental marine mammal studies. The PCB concentrations were also above the higher PCB threshold of 41.0 mg kg^{-1} lw (similarly calculated based on Helle et al. (1976) for *Clophen 50*) associated with reproductive impairment in ringed seals from the Baltic Sea. In fact, these contaminants have likely contributed to decreasing reproductive success of killer whale populations in industrialized areas, such as Gibraltar, Northwest Scotland and Western Ireland and to their disappearance from the Netherlands coast (Jepson et al., 2016). In addition, ΣPCB concentrations in southeast Greenland killer whales were above the effect thresholds associated with immunosuppression in beluga whales (*Delphinapterus leucas*) and bottlenose dolphins (*Tursiops truncatus*) tested using *in vitro* exposures (De Guise et al., 1998; Desforges et al., 2016; Mori et al., 2006), which may increase their susceptibility to infectious disease. Besides the effects on killer whale populations, highly biomagnifying organic contaminants are of concern to local communities harvesting the southeast Greenland killer whales for subsistence in the Arctic. Although the consequences of this exposure are not known, the harvesting and subsequent dietary exposure for humans is likely to increase in Greenland and other Arctic regions with the increasing presence of killer whales (Higdon et al., 2014, 2012).

3.3. PCB and OC patterns in Faroe Islands and southeast Greenland killer whales

Proportions of individual PCBs relative to ΣPCB and of individual CHLs relative to ΣCHL varied among sex/age classes of southeast Greenland killer whales (Fig. 2). Specifically, the proportion of tetra-PCBs was significantly higher in sub-adults ($n = 9$) compared to adult females ($n = 6$; $p = 0.04$). In addition, the proportions of heptachlor epoxide and oxychlordane were significantly higher in sub-adults ($p < 0.01$), while *trans*-nonachlor was significantly higher in adult females ($p = 0.01$). These differences are likely related to offload of contaminants by females during reproduction (Haraguchi et al., 2009; Ross et al., 2000; Ylitalo et al., 2001), discussed in sections 3.4 and 3.5. Nevertheless, the magnitude of the differences among sex/age classes was generally not large.

We found more substantial variation in the proportions of individual compounds relative to the sum-class, in southeast Greenland killer whales compared to the Faroese killer whales ($n = 2$; Fig. 2). Greenland killer whales had relatively higher proportions of hexa- and hepta-PCBs relative to ΣPCB, and lower proportions of tetra- and penta-PCBs, compared to Faroese whales. Proportions of oxychlordane and heptachlor epoxide relative to ΣCHL, and *p,p′*-DDE relative to ΣDDT, were higher in Greenland than in Faroe Islands killer whales. Although not statistically comparable, these patterns support the contaminant concentration data that suggest a diet richer in marine mammals for Greenland killer whales compared to the Faroe Islands. More highly chlorinated

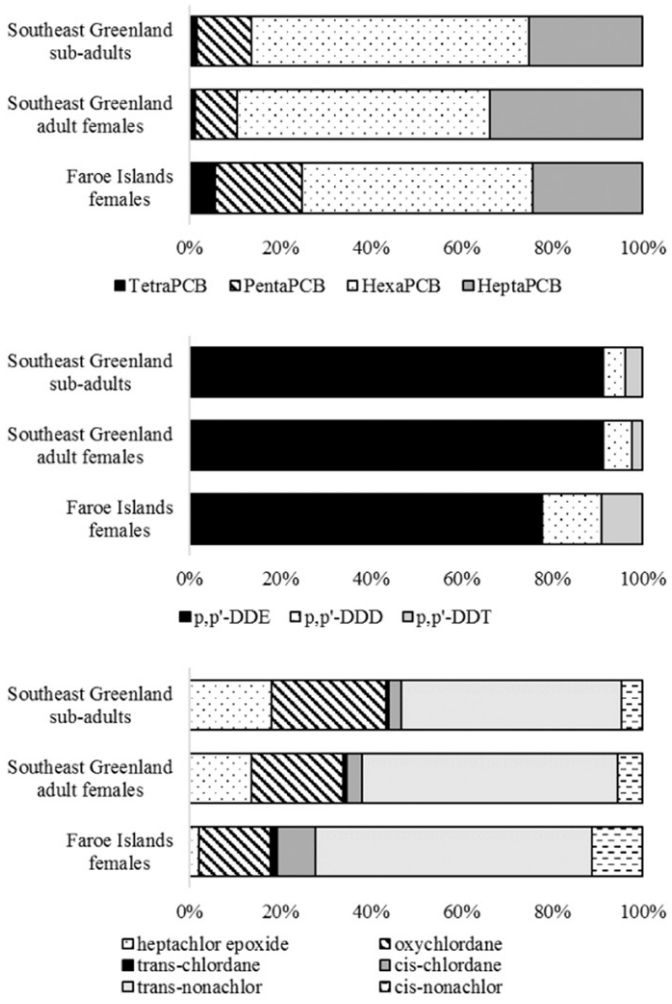

Fig. 2. Relative percent (%) of, from top to bottom: polychlorinated biphenyl (PCB) homologue groups to ΣPCB, dichlorodiphenyltrichloroethanes compounds to ΣDDT and chlordane compounds to ΣCHL in blubber of sub-adult ($n = 9$) and adult female killer whales ($n = 6$) harvested in southeast Greenland from 2012 to 2014, and sub-adult and adult females ($n = 2$) stranded in the Faroe Islands in 2008.

PCBs, such as CB-153, tend to be found in marine mammals relative to fish (Hoekstra et al., 2003; Sobek et al., 2010). In addition, higher proportions of metabolites compared to the parent OC are generally found for marine species at higher trophic levels, associated with biotransformation capacity of marine mammals relative to fish (Hoekstra et al., 2003; Krahn et al., 2007).

3.4. Influence of sex/age class on PCB and OC concentrations

In southeast Greenland, adult females showed significantly lower concentrations of PCBs and OCs relative to sub-adults (for each OC group: $p < 0.001$; and ΣPCB: $p = 0.02$; Fig. 3). However, one of the sub-adults (48339) had much higher ΣPCB concentrations (ΣPCB = 356 mg kg^{-1} lw) than other individuals and when removed from the analysis, differences in PCB concentrations were no longer significant between sub-adults and adult females ($p = 0.28$). For all other contaminants, removing 48,339 did not change the results between sex/age classes. These results indicate that individual variation can be substantial even within demographic groups, possibly related to diet, and should be considered carefully, especially with small datasets. Although statistical comparisons were not possible, the single adult male exhibited higher concentrations of all sum-contaminant classes relative to the mean of adult females. Previous studies have also found higher concentrations in sub-adult and adult male killer whales relative to adult

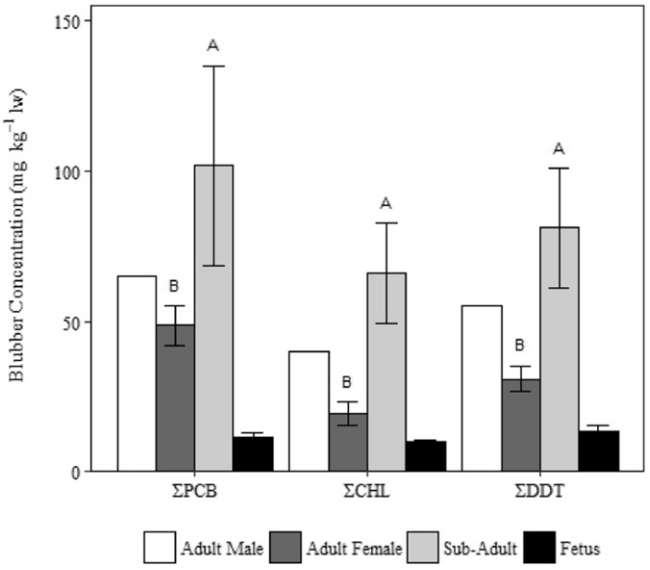

Fig. 3. Arithmetic mean concentrations (± SE in mg kg^{-1} lipid weight, lw) of Σpolychlorinated biphenyls (ΣPCB), Σchlordanes (ΣCHL) and Σdichlorodiphenyltrichloroethanes (ΣDDT) in full-depth blubber of killer whales sampled in southeast Greenland from 2012 to 2014, including one adult male ($n = 1$), adult females ($n = 6$), sub-adults ($n = 9$) and fetuses ($n = 2$). Significant differences for ΣPCB ($p = 0.02$), ΣCHL ($p < 0.001$) and ΣDDT ($p < 0.001$) concentrations between adult females and sub-adults are indicated by different letters.

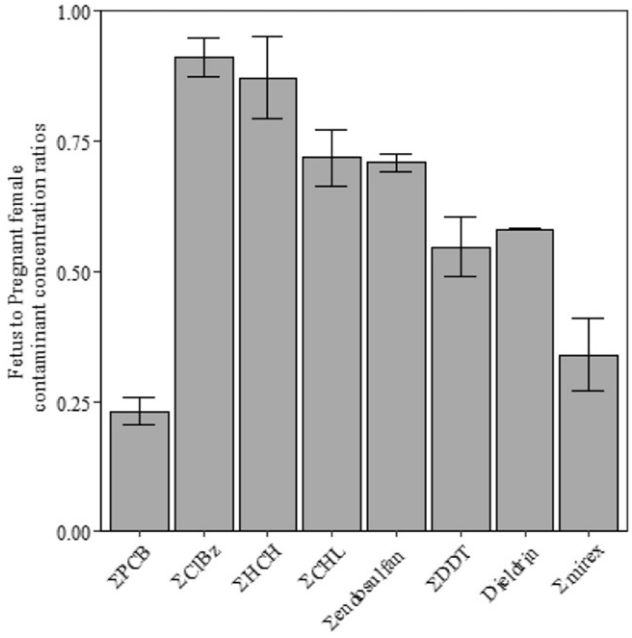

Fig. 4. Average ratios of concentrations of Σpolychlorinated biphenyls (ΣPCB), Σchlorobenzenes (ΣClBz), Σhexachlorocyclohexanes (ΣHCH), Σchlordanes (ΣCHL), Σendosulfan, Σdichlorodiphenyltrichloroethanes (ΣDDT), dieldrin and Σmirex in blubber of fetus relative to pregnant killer whale females harvested in southeast Greenland in 2012 ($n = 2$ pairs). The error bars represent the ranges of the ratios (minimum and maximum).

females (Ross et al., 2000; Ylitalo et al., 2001). Ross et al. (2000) reported increasing concentrations of PCBs in juvenile females, followed by a steep decrease once they reached reproductive age. At this time and onward, females transfer a substantial portion of their contaminant burden to their offspring during gestation and lactation explaining the consistent demographic variation seen in this and other studies (Haraguchi et al., 2009; Krahn et al., 2009; Ross et al., 2000; Ylitalo et al., 2001). However, some instances of adult females showing higher concentrations than adult males were previously found, possibly related to differences in the age composition of the two groups or impaired reproduction due to high exposure to PCBs (Buckman et al., 2011; Jepson et al., 2016).

3.5. Comparison between pregnant females and their fetuses

To our knowledge, this is the first study reporting POP concentrations in pregnant killer whales and their fetuses. We found that blubber from both pregnant females had similar or higher average concentrations of all sum-contaminant classes than those of their fetuses (Fig. 4). These results confirm that transplacental transfer of POPs occurs during gestation. Cetacean females can offload up to 60% of their POPs burden during reproduction, however, the bulk of it occurs during lactation (Borrell et al., 1995). Previous studies reported up to 18 times higher blubber concentrations of PCB, DDT and CHL in calves relative to lactating mothers (Haraguchi et al., 2009; Krahn et al., 2009; Ylitalo et al., 2001), which may be related to the large amount of lipid reserves and, consequently, lipophilic contaminants, mobilized from blubber to milk during its synthesis (Fowler et al., 2014; Oftedal, 1993). Nonetheless, even though fetus blubber concentrations were lower than those in their mothers, PCBs, CHLs, and DDT in particular were still elevated in both of the fetuses relative to various effect thresholds determined in adults of other marine mammal species (Desforges et al., 2016; Jepson et al., 2016). The consequences of fetal exposure to high concentrations of endocrine-disrupting chemicals during these early developmental stages are unclear, but likely to affect cell differentiation and tissue-organ development (Grandjean and Landrigan, 2006; Letcher et al., 2010; Sonne, 2010).

We found lower transplacental transfer for Σmirex and ΣPCB compared to other contaminants, which may be related to greater affinity of high log K_{ow} (above 6.5) contaminants for blubber versus blood and placental tissues (Desforges et al., 2012). Lower transplacental transfer was also previously found for higher molecular weight compounds, including mirex, relative to lower molecular weight and lower chlorinated POPs, such as HCHs and ClBz in ringed seals (*Pusa hispida*) from the Labrador coast (Brown et al., 2016). Additionally, limited transfer was found for highly chlorinated relative to less chlorinated PCBs from pregnant females to fetuses in beluga whales and from mother to calf in killer whales (Desforges et al., 2012; Haraguchi et al., 2009).

3.6. Variation in PCB and OC concentrations and patterns among blubber layers

Lipid content was a significant variable explaining differences in wet weight concentrations among blubber layers for all contaminant groups (ΣPCB: $F_{1,171} = 162$, $p < 0.001$; ΣClBz: $F_{1,172} = 264$, $p < 0.001$; ΣHCH: $F_{1,173} = 16.3$, $p < 0.001$; ΣCHL: $F_{1,172} = 231$, $p < 0.001$; Σendosulfan: $F_{1,171} = 256$, $p < 0.001$; ΣDDT: $F_{1,172} = 116$, $p < 0.001$; Dieldrin: $F_{1,171} = 207$, $p < 0.001$; Σmirex: $F_{1,172} = 177$, $p < 0.001$). On a wet weight basis, layer 10 (outer; closest to skin) showed significantly lower concentrations of ΣPCB, ΣClBz, ΣCHL, Σendosulfan, ΣDDT, dieldrin and Σmirex, ($p < 0.01$) compared to all other layers. Layer 9 also showed lower concentrations relative to some of the more inner layers for ΣClBz, Σendosulfan, ΣCHL, ΣDDT, dieldrin, and Σmirex ($p < 0.05$; Fig. S2). For ΣHCH, layer 10 only had significantly lower concentrations compared to layers 1, 4 and 8 ($p < 0.05$; Fig. S2).

Lipid normalization generally reduced variation in contaminant concentrations among blubber layers (ΣPCB: $F_{9,162} = 3.07$, $p < 0.01$; ΣClBz: $F_{9,162} = 2.18$, $p = 0.03$; ΣHCH: $F_{9,162} = 7.02$, $p < 0.001$; ΣCHL: $F_{9,162} = 1.97$, $p = 0.05$; Σendosulfan: $F_{9,162} = 2.53$, $p < 0.01$; ΣDDT: $F_{9,162} = 2.81$, $p < 0.01$; Dieldrin: $F_{9,162} = 2.83$, $p < 0.01$; Σmirex: $F_{9,162} = 3.88$, $p < 0.001$; lipid corrected concentrations per blubber layer in Table S2). No variation was found among layers for lipid weight concentrations of ΣClBz and ΣCHL. For Σendosulfan, dieldrin, and Σmirex, layer

10 only showed lower lipid weight concentrations relative to layers 1 and 2 ($p < 0.02$). Occasionally, lipid correction resulted in additional variation among other layers: concentrations of Σmirex in layers 5 and 8 were significantly lower than in layer 1 ($p < 0.02$), concentrations of ΣDDT were significantly lower in layer 5 compared to layers 1 and 2 ($p < 0.05$) and concentrations of ΣPCB were significantly lower in layer 8 compared to layers 1, 2 and 3 ($p < 0.05$). For ΣHCH, the opposite was found, with significantly higher concentrations in layer 10 compared to other layers ($p < 0.001$) except for layer 1, and significantly lower concentrations in layer 5 compared to layer 1 ($p = 0.02$; Fig. 5). Not surprisingly, the PCA plot of lipid corrected concentrations by blubber layer did not show any spatial segregation of layers 1 through 10 (Fig. S3). Krahn et al. (2004) found increases or no change in homogeneity after lipid correction among inner, middle and outer blubber layers for resident killer whales for ΣDDT and ΣPCB concentrations. However, the opposite occurred for heavily polluted transient killer whales i.e., increase in variation after lipid correction with higher concentrations in the inner layer compared to others. In the same study, two beluga whales sampled in Cook Inlet consistently had higher lipid-normalized ΣPCB and ΣDDT concentrations in the outer layer compared to the inner layer, although the reverse was found in one individual in Bristol Bay, Alaska (Krahn et al., 2004). A study of fin (*Balaenoptera borealis*) and male sei (*Balaenoptera physalus*) whales in the North Atlantic also showed inconsistent variation in lipid-normalized ΣPCB and ΣDDT concentrations in the outer compared to the inner blubber layers (Aguilar and Borrell, 1991). These inconsistencies could be related to the small sample sizes of these previous studies. Here, we show a significant influence of lipid content in PCB and OC variation with blubber depth,

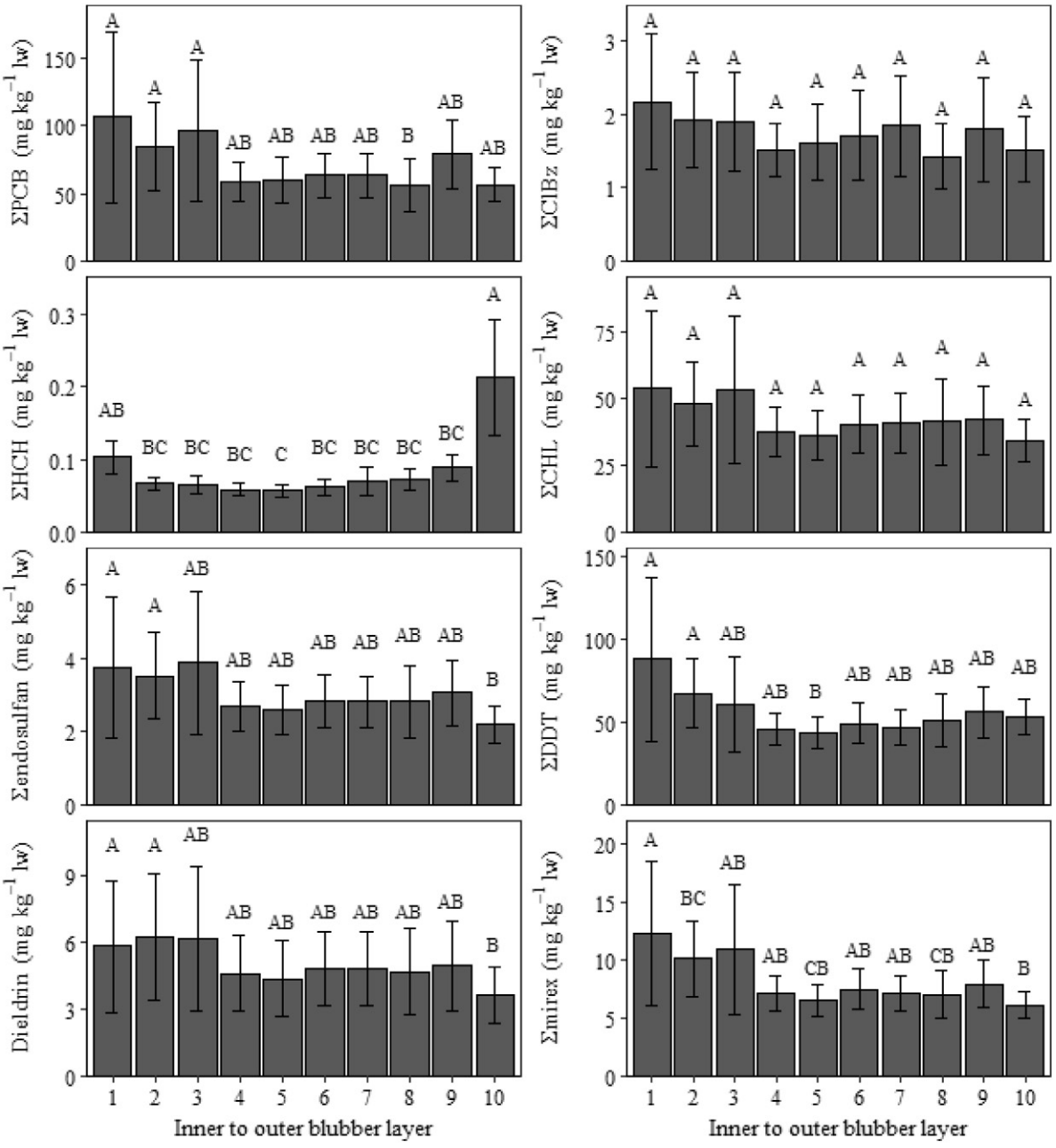

Fig. 5. Arithmetic mean of contaminants concentrations (± SE in *mg kg^{-1}* lipid weight, lw) among ten blubber layers for polychlorinated biphenyls (ΣPCB), Σchlorobenzenes (ΣClBz), Σhexachlorocyclohexanes (ΣHCH), Σchlordanes (ΣCHL), Σendosulfan, Σdichlorodiphenyltrichloroethane (ΣDDT), dieldrin and Σmirex of 19 North Atlantic killer whales. Layer 1 represents the innermost layer while layer 10 represents the outermost layer. Significant differences in contaminant concentrations among blubber layers are indicated by different letters above each bar (all $p < 0.05$). No differences were found among layers for ΣClBz and ΣCHL concentrations. Results include killer whales sampled in southeast Greenland ($n = 16$, 2012–2014), Faroe Islands ($n = 2$, 2008) and Denmark ($n = 1$, 2005), but not fetuses.

explaining 9–17% of the variation in wet weight concentrations, with the notable exception of HCH (2%). Results for HCH could in part be related to lower lipophilicity of HCHs relative to most other POPs (log K_{ow} ~ 3.8; Li et al., 2002), and thus weaker relationship to lipid content. Although there was still some variation among a few layers after lipid correction for Σendosulfan, dieldrin, Σmirex, ΣDDT, ΣPCB, concentrations were consistently higher among more inner layers (1, 2 and 3) compared to middle or more outer layers (5, 8 and 10).

The contaminant concentration results may to some extent be related to the structural composition of the blubber layers. Transient and resident killer whales showed a gradient of fatty acid composition from inner to outer layers, with higher proportion of triglycerides and lower of wax esters in inner compared to outer layers (Krahn et al., 2004). Among the three layers considered in this previous study, the outer layer (2 cm deep from the epidermis) was found to be the most different from all layers with respect to fatty acid composition. This could result in different affinity of certain contaminants and/or analytes to the different layers and the observed higher concentrations of some compounds in more inner layers compared to others. Positive correlations were previously found between ΣPCB concentrations and concentrations of triglycerides and free fatty acids in the blood of polar bears (*Ursus maritimus*; Knott et al., 2011). To verify this hypothesis, we further considered possible effects of fatty acid composition among killer whale blubber layers in POPs concentrations (fatty acid results from Bourque et al., unpublished data; including omega-6, omega-3, saturated, monounsaturated and polyunsaturated fatty acids). The distribution of omega-6 fatty acids had a significant positive relationship with the concentrations of all contaminants among blubber layers ($p < 0.05$), except for ΣHCH ($p = 0.61$). Nevertheless, lipid content explained 5 to 12 times more variation on a wet weight basis than omega-6.

Variation in contaminant concentrations among the layers could be related to different tissue turnover rates, and thus a chronological deposition of contaminants in blubber. If this was the case, we would expect to see higher PCB and legacy OC concentrations in the outer, lower turnover layers (representing a more historical signal). However, except for ΣHCH, we found lower Σendosulfan, dieldrin and Σmirex, ΣPCB, and ΣDDT concentrations in the outer layers relative to the more inner layers not supporting the chronological deposition hypothesis. Regardless, the observed differences in lipid-corrected concentrations among layers were only about two-fold or less for all contaminants. Further, a typical biopsy of 2 cm would represent full to half the blubber depth in most of the killer whales here (Table 1). Therefore, biopsies should give a reasonable representation of total concentrations, at least on a lipid weight basis.

3.7. Effects of sex/age class on contaminant deposition among layers

We did not find any variation in the deposition of contaminants among layers in adult female killer whales compared to sub-adults in southeast Greenland ($p > 0.12$). To account for possible confounding effects of reproduction, we examined data from the pregnant females more closely. There was no obvious trend through the layers for one of the pregnant females, but the other showed 4- to 16-times higher lipid-normalized concentrations of all contaminants in layer 1 compared to all other layers. Similar results were found in two lactating female humpback whales (*Megaptera novaeangliae*) from the Southern hemisphere (Waugh et al., 2014). The authors showed that, while there was no variation in lipid-normalized *p,p′*-DDE and HCB among layers for males, the two lactating females had higher lipid-normalized concentrations of *p,p′*-DDE in the inner layer compared to the outer layer, and one of the females also had higher HCB concentrations in the inner layer. The authors attributed this variation in contaminant concentrations with blubber depth to the lower lipid content in the inner layer, i.e. a higher turn-over of lipid reserves in the blubber tissue during the lactation period, which could similarly be associated with gestation in the pregnant female Greenland killer whale. Although biopsies may be considered a good estimate of contaminant concentrations in most groups within killer whale populations, this sampling approach may not reveal the extensive changes of contaminant concentrations in the innermost blubber layer of pregnant or adult lactating females.

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Appendix A. Supplementay data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.05.193.

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