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THE ARCTIC UNIVERSITY OF NORWAY

Faculty of Biosciences, Fisheries and Economics

Department of Arctic and Marine Biology

Temporal trends of persistent organic pollutants in Svalbard polar bears (*Ursus maritimus*) in relation to climate-associated changes in feeding habits

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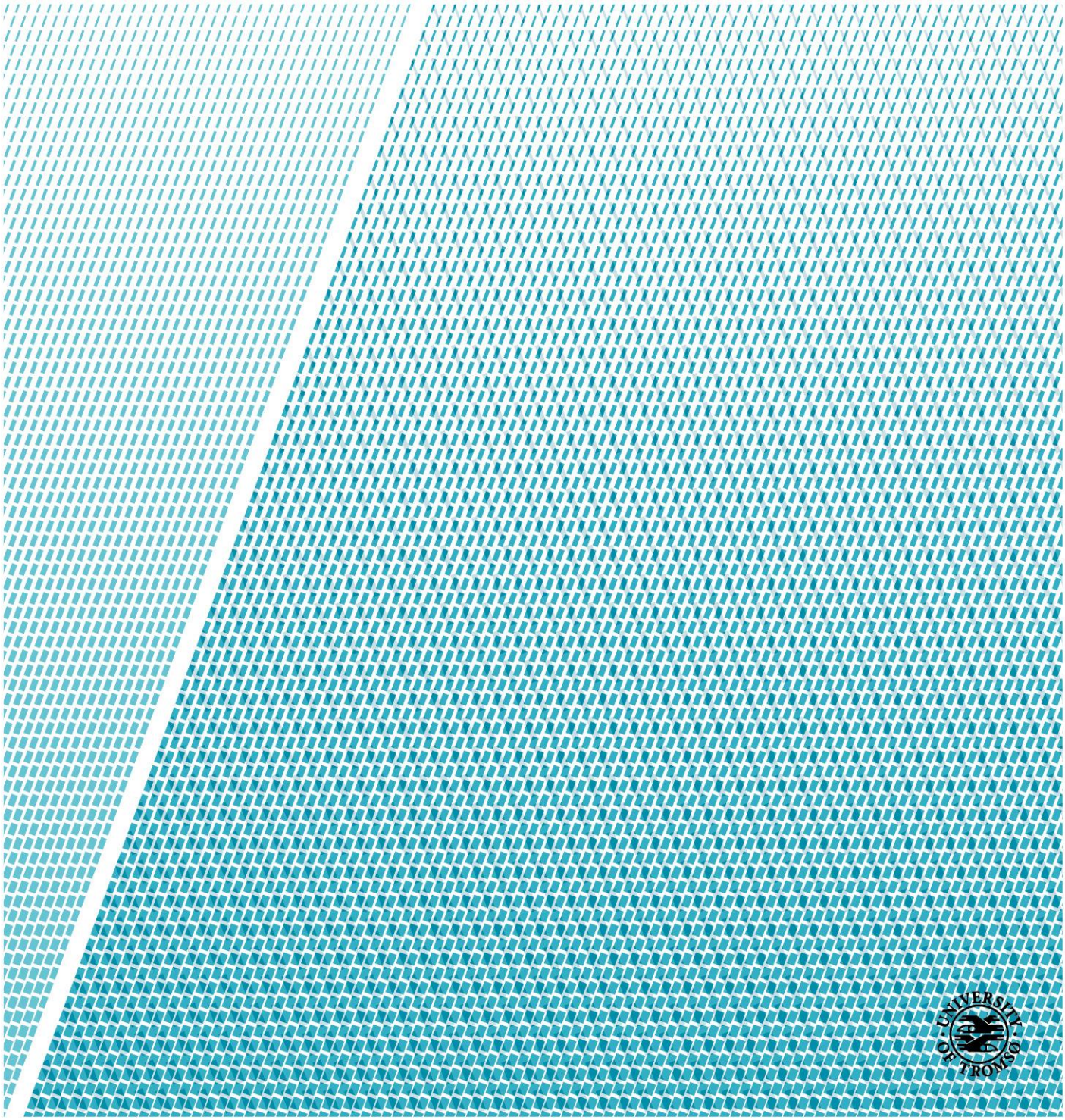
Anna Lippold

BIO-3950 Master thesis in Biology, May 2018



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IN COLLABORATION WITH

ABSTRACT

Persistent organic pollutants (POPs) reach the Arctic ecosystems from lower latitudes mostly via air and ocean currents. They biomagnify through Arctic food webs and reach considerably high concentrations in top predators such as polar bears (*Ursus maritimus*). Although many of these compounds have been banned or restricted for decades, concentrations of polychlorinated byphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) in Arctic biota still remain high. Temporal trend studies in Arctic biota help assess the effectivness of bans and restrictions. However, trends of POP concentrations in biota are affected by various factors, including dietary source and climate change. Because of retreating sea ice polar bears can be forced to feed at lower trophic levels or consider terrestrial food sources, potentially leading to a decreased uptake of contaminants.

We monitored plasma concentrations of 4 PCBs (CB-118, 138, 153, and 180), 4 OCPs (p,p'-DDE, HCB, β-HCH and oxychlordane), 2 PBDEs (BDE-47 and 153), and 5 OH-PCBs (OH-CB-107, 138, 146, 156, and 187) in female polar bears from Svalbard, Norway, over a 20 year time span (1997-2017). All 306 samples were collected in the spring (April). We examined temporal trends in relation to climate – associated changes in feeding habits by using stable isotope ratios of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) from red blood cells as feeding proxies representing polar bear winter diet. We found a significant decline of both $\delta^{13}C$ and $\delta^{15}N$ values over our study period, with a steeper trend for $\delta^{13}C$ after 2012, indicating an increasing intake of more terrestrial and lower trophic level prey. BDE-153 and β-HCH concentrations were stable over our study period, ΣPCB, ΣOH-PCB and BDE-47 showed a linear declining trend. For p,p'-DDE, HCB and oxychlordane however, trends only declined until 2010-12 and stalled thereafter. Interestingly, trends of all compounds changed in shape and/or rate when adjusted for changes in winter diet. ΣPCB, HCB, β-HCH and BDE-153 concentrations increased significantly after 2010-12 when adjusted for changes in winter diet. Our findings suggest that a climate – related diet shift leads to lower PCB, HCB, β-HCH, and BDE-153 exposure in the Svalbard polar bears, while p,p'-DDE, oxychlordane and BDE-47 exposure is mainly affected by emissions.

ACKNOWLEDGEMENT

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Anna Lippold

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1 INTRODUCTION

Although pristine and secluded, far away from most industries and inhabited by less than 1% of the World's population (research.uarctic.org), the Arctic contains considerably high levels of pollutants, in some arctic biota pollutant concentrations are as high as in people living in heavily industrialized areas (Bytingsvik et al. 2012; Fu et al. 2015). Persistent organic pollutants (POPs) are among the main chemicals present in the Arctic, and have a variety of properties that make them problematic for the environment, wildlife, and humans.

POPs persist in the environment for years or decades and are resistant to many forms of degradation (Jones and Voogt 1999; Sinkkonen and Paasivirta 2000). POPs reach the Arctic from distant sites of production and use via air and ocean currents, and river outflows (Macdonald et al. 2003). The so-called "cold condensation effect" in which compounds volatilized in warmer regions condensate in the cold Arctic, plays an important role in the long-range transport of POPs, especially the most volatile ones (Wania and Mackay 1996).

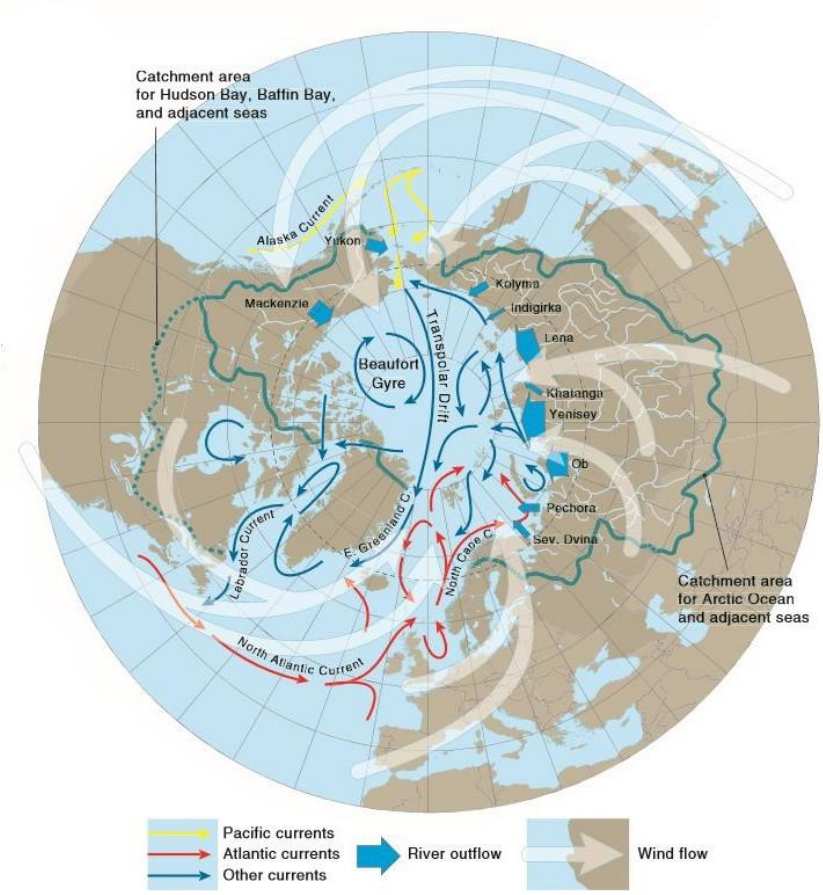


Figure 1: The major physical pathways that transport contaminants to the Arctic from lower latitudinal areas. (Macdonald et al. 2003)

From the abiotic environment, POPs are taken up by biota and biomagnify through the food web, leading to high concentrations in species at the top of the food web, such as polar bears (Hoekstra et al. 2003; Kelly et al. 2007; Muir et al. 1988; Sørmo et al. 2009). In polar bears lipophilic POPs such as PCBs, OCPs and PBDEs are quantitatively the most abundant compounds in adipose tissue, whereas per- and polyfluoroalkyl substances (PFAS) and

metabolized POPs such as hydroxylated PCBs (OH-PCBs) dominate in the blood circulation (Letcher et al. 2018; Tartu et al. 2017a; Tartu et al. 2017b). Hydroxylated POPs such as OH-PCBs accumulate in higher trophic level organisms via hydroxylation of ingested PCBs, ingestion of contaminated organisms, and ingestion of OH-PCBs produced by microorganisms in water and soil (Letcher et al. 2000; Tehrani and Aken 2014).

High concentrations of POPs have been associated with a number of adverse health effects in polar bears, such as effects on thyroid hormones (Bourgeon et al. 2017; Braathen et al. 2004; Skaare et al. 2001), vitamin A levels, (Skaare et al. 2001), testosterone levels (Oskam et al. 2003), the immune system (Bernhoft and Skaare 2000), bone density of skulls (Daugaard-Petersen et al. 2018; Sonne et al. 2004) and penile bones (Sonne et al. 2015). The effects of polybrominated diphenyl ethers (PBDEs), widely used as flame retardants, are unknown for polar bears, but laboratory animal studies have shown effects on neurobehavior (Branchi et al. 2002; Branchi et al. 2003; Eriksson et al. 2002), sex hormone levels and sexual development (Lilienthal et al. 2006), and thyroid hormone balance and levels (Hallgren et al. 2001; Zhou et al. 2001). OH-PCBs might be more toxic than their parent PCBs as they exert toxic effects like the inhibition of mitochondrial respiration, oxidative damage to the DNA, disruption of thyroid hormones and estrogenic activity at lower levels than PCBs (Navasimhan et al. 1991; Schuur et al. 1998; Srinivasan et al. 2001). Additionally the hydroxylation of PCBs increases their solubility and bioavailability (Camara et al. 2004)

Due to their adverse health effects on wildlife (for a review see (Letcher et al. 2010)) and humans (Kim et al. 2017; van den Berg et al. 2017), their persistence, capacity to travel long distances, bioaccumulate and biomagnify POPs are globally regulated. Regulations of PCBs and OCPs had already started in the 1970s with national bans (Li and Macdonald 2005). The United Nations Environment Program's (UNEP) Stockholm Convention (SC) on restriction or elimination of POPs was enacted in 2004. The first twelve compounds listed under the convention were PCBs, several OCPs, and a total of 28 compounds are currently listed including PBDEs (chm.pops.int). These regulations have led to generally decreasing trends in the Arctic since the 1990, both in the air and biota (AMAP 2015; Li and Macdonald 2005). However, concentrations of some compounds are only leveling off or even increasing (de Wit et al. 2010; Riget et al. 2016).

A number of chemical and biological factors, in addition to the emission, affect contaminant levels in biota, like physico-chemical properties of the compound, and sex, age, feeding ecology, migration and biotransformation capacities of the animal (Borgå et al. 2004). For instance, female polar bears rid themselves of a considerable amount of the contamination burden through lactation (Atkinson and Ramsay 1995). In contrast, contamination levels are generally higher (Norstrom et al. 1998), vary less seasonally and accumulate more with age in males than in females (Dietz et al. 2004). Seasonal variations in food availability and consequently body condition (Stirling and McEwan 1975) also affect contaminant concentration in polar bears, as body condition correlates negatively with contaminant levels (Tartu et al. 2017b). Contamination levels and patterns are ultimately defined by

species-specific biotransformation processes (Norstrom 2002). For example, polar bears are able to biotransform several PCBs, whereas DDT is also biotransformed at lower trophic levels (Letcher et al. 1998; Letcher et al. 2009).

Svalbard is particularly exposed to contaminants from both oceanic and atmospheric currents from Europe and North America (Hansen et al. 2015; Shindell et al. 2008), and shows some of the highest contaminant levels in the Arctic (McKinney et al. 2011; Muir et al. 2006). Furthermore the decline of Arctic sea ice, which is most pronounced within the Barents Sea area (Laidre et al. 2015), may lead to secondary emissions of POPs (Ma et al. 2011), as well as ecological changes in the marine food web (Antiqueira et al. 2018).

In some polar bear populations, climate driven decline in sea ice has already led to a shift towards more subarctic or terrestrial prey species, which influenced contaminant burden to some extent (McKinney et al. 2013; McKinney et al. 2009; Routti et al. 2017). Another study has shown a decline in mercury levels in West Hudson polar bears related to climate-associated diet changes (McKinney et al. 2017). Feeding habits and body condition, which are both related to sea-ice conditions, are strong predictors of lipophilic POPs in the Barents Sea polar bears (Tartu et al. 2016; Tartu et al. 2017b). Thus, we hypothesize that temporal trends of lipophilic POPs are related to both emission patterns as well as climate – related changes in feeding habits and body condition. To explore this hypothesis, we collected Svalbard polar bear plasma samples over 20 years and analyzed them for several PCBs, OCPs and 2 PBDEs. To determine diet trends we analyzed stable isotope values of carbon and nitrogen ($\delta^{13}C$ and $\delta^{15}N$) representing carbon source (marine vs. terrestrial) and trophic level, respectively. We compared non-diet-adjusted to diet-adjusted contaminant trends in order to understand if and how strongly climate-associated diet changes can affect contaminant levels in Svalbard polar bears from 2000-2017.

2 MATERIAL AND METHODS

2.1 FIELD SAMPLING

Adult female polar bears were opportunistically captured each year between 25th March and 5th May in the Svalbard area during the period 1997-2017 as part of a yearly polar bear monitoring program run by the Norwegian Polar Institute, Tromsø. Sampling time and sex of the bears were chosen to avoid seasonal and sex variation. The 306 samples represent 185 individuals, of which 54 were sampled 2 – 8 times. The bears were immobilized from a helicopter by remote injection of tiletamine hydrochloride and zolazepam hydrochloride (Zoletil Forte Vet®; Virbac, France). Blood samples were collected in heparinized tubes and kept cold and dark until centrifuged (3500 rpm, 10 min, within 10 h). Red blood cells and plasma were stored at -20 °C until analysis. A vestigial premolar tooth was used for age estimation (Christensen-Dalsgaard et al. 2009) for all bears captured for the first time. Body condition was determined by body condition index (BCI) based on body mass and length (Cattet et al. 2002). For bears not weighed in the field (n=75) body mass was estimated with 8% accuracy (Derocher and Wiig 2002).

The National Animal Research Authority (NARA), Norway, approved of all procedures.

2.2 PROXIES FOR FEEDING HABITS

Stable isotope values of nitrogen and carbon ($\delta^{15}N$ and $\delta^{13}C$, respectively) determined in red blood cells were used as proxies for feeding habits. Estimated half-lives of $\delta^{13}C$ and $\delta^{15}N$ in polar bear red blood cells are 1-2 and 3-4 months, respectively (Rode et al. 2016) and thus represent mostly the winter diet of the bears captured for this study.

Analytical procedures are described in supporting information (SI).

2.3 CHEMICAL ANALYSIS OF POPs

POP concentrations were monitored in polar bear blood plasma. The matrix was chosen due to good accessibility, and because PCBs show less variation in polar bear plasma than other matrices (Henriksen et al. 2001). A complete list of all targeted compounds, methods for clean-up, separation, quantification and quality assurance are explained in the SI.

2.4 DATA ANALYSIS

For the statistical analysis, the program R version 3.4.2 was used. Structurally similar and correlated compounds were summed. To analyse the effects of year, feeding habits, and additional biological variables on POP concentrations in polar bears, generalised additive mixed models (GAMM; R-package *mgvc*) were used. Nine candidate models were defined, with year as non-linear term, and $\delta^{15}N$ and $\delta^{13}C$ values in red blood cells, body condition, breeding status and age as fixed predictor variables (see Table S3 in SI). Highly correlated predictor variables (e.g. $\delta^{15}N$ and $\delta^{13}C$) were not included in the same models (Burnham et al. 2010). The recovery of spiked reference samples for analysis of β-HCH was inconsistent, thus β-HCH was additionally corrected for this variation.

We used model averaging based on Akaike Information Criterion (AIC; R-package *MuMIn* (Barton 2016)) to make inference from all candidate models and predictor variables. The models were ranked according to AIC, which was then used to calculate AIC weight ($e^{(0.5(AICmin-AICi))}$; relative likelihood divided by the sum of all likelihoods). AIC weights were used to calculate model averaged estimates for all predictor variables, and 95% confidence intervals to determine whether the parameters were significantly different from 0 at the 5% confidence level. Diagnostic plots were used to verify whether the distribution of the model residuals met the model assumptions.

Plots from the highest ranked GAMMs were used to illustrate what ecological and biological factors can affect temporal trends in concentration of POPs in polar bear blood. These models were then visually compared to plots from models using only year as predictor variable. Plots from the highest ranked GAMMs illustrate trends adjusted by their respective most influential predictor variable and reflect emission changes in the polar bear food web. Subsets of POP trends were obtained for each model by cutting at their relevant changing points, and estimates for each subset were derived from linear mixed models (LME, and LMER from the package *lme4*). For assessment of their significance, 95 % confidence intervals were used. Polar bear ID was included as a random factor in both GAMMs and LMEs. Temporal changes in feeding habits ($\delta^{15}N$ and $\delta^{13}C$) and BCI were also investigated by GAMMs with only year as non-linear term, and their yearly linear changes were obtained by using LMEs.

3 RESULTS AND DISCUSSION

3.1 POP CONCENTRATIONS IN FEMALE POLAR BEARS FROM SVALBARD 1997-2017

Table 1: Median (bold), min. and max. concentrations of persistent organic pollutants (POPs) in plasma samples from female polar bears collected on Svalbard between 1997 and 2017. All compounds are expressed in ng/g lipid weight except for ΣOH-PCB (ng/g wet weight). No samples were taken in 1999; n.a.: not analysed.

Year	Lipid %	ΣPCB	p,p'-DDE	HCB	β-HCH	Oxychld.	BDE-47	BDE-153	ΣOH-PCB
1997	**0.9**	**5661**	**42**	**203**	**42**	**1087**	**17**	**n.a.**	**n.a.**
	0.7; 1.1	3082; 8240	40; 45	201; 205	35; 49	727; 1447	14; 20		
1998	**1.1**	**3208**	**24**	**168**	**28**	**740**	**20**	**n.a.**	**n.a.**
	0.9; 1.3	2315; 10188	7; 44	62; 283	18; 45	545; 1589	11; 49		
2000	**1.1**	**3746**	**24**	**104**	**4**	**977**	**18**	**3.82**	**14576**
	0.6; 1.4	1736; 11199	6; 226	36; 346	2; 61	447; 1775	3.10; 42	0.66; 7.68	3601; 28158
2001	**1**	**5066**	**83**	**258**	**23**	**858**	**21**	**4.11**	**15681**
	0.6; 1.6	2700; 14453	5; 119	128; 451	2; 86	503; 3468	8.78; 28	0.74; 10	10556; 20072
2002	**1**	**5422**	**79**	**92**	**21**	**1259**	**17**	**3.65**	**13740**
	0.7; 1.5	2274; 22175	8; 143	40; 460	12; 56	716; 3039	8.03; 44	0.71; 12	6238; 21137
2003	**1.3**	**3333**	**35**	**84**	**n.a.**	**689**	**21**	**2.48**	**13741**
	1; 1.6	1654; 5930	8; 127	28; 292		345; 1034	14; 33	2.01; 8.65	9286; 25470
2004	**1**	**4185**	**58**	**126**	**24**	**1198**	**16**	**3.13**	**12157**
	0.5; 1.6	1500; 14461	6; 287	44; 219	10; 136	458; 3879	6.77; 37	0.59; 9.85	3383; 34437
2005	**1.2**	**3948**	**59**	**114**	**15**	**1513**	**13**	**3.78**	**12484**
	0.7; 1.4	2101; 14166	5; 130	35; 301	3; 51	343; 3621	6.25; 26	0.81; 8.58	6350; 18569
2006	**1.1**	**4564**	**52**	**111**	**30**	**1307**	**28**	**5.30**	**20345**
	0.8; 1.3	2141; 9267	8; 257	18; 233	11; 53	250; 2726	19; 42	0.88; 10	7156; 40211
2007	**1.5**	**1778**	**22**	**78**	**21**	**405**	**7.41**	**n.a.**	**6324**
	0.8; 2.1	914; 21535	4; 130	24; 229	7; 51	207; 1710	3.67; 18		2892; 13109
2008	**1.3**	**1887**	**21**	**73**	**14**	**514**	**11**	**n.a.**	**5264**
	0.8; 1.6	743; 9003	4; 228	33; 339	6; 42	172; 2155	1.30; 34		1354; 10720
2009	**1.2**	**2059**	**20**	**37**	**3**	**295**	**13**	**2.59**	**5896**
	0.8; 1.7	1060; 6760	5; 134	15; 109	2; 38	1; 956	6.47; 57	0.85; 7.06	3316; 10998
2010	**1.2**	**1924**	**7**	**56**	**13**	**432**	**9.11**	**1.82**	**6937**
	0.8; 1.5	777; 2855	4; 74	27; 204	3; 30	245; 794	6.32; 21	0.63; 3.12	2191; 13904
2011	**1.3**	**3461**	**20**	**123**	**n.a.**	**385**	**16**	**4.20**	**13401**
	0.9; 1.6	1539; 7978	7; 263	46; 324		282; 1552	6.73; 25	2.05; 11	4450; 21399
2012	**1.2**	**1426**	**14**	**59**	**18**	**351**	**10**	**2.19**	**6300**
	0.8; 1.7	513; 3910	0; 103	21; 206	4; 40	21; 953	2.73; 51	0.56; 9.09	1873; 14115
2013	**1.2**	**2239**	**25**	**111**	**26**	**467**	**12**	**3.91**	**5477**
	0.8; 2	930; 12068	0; 182	31; 603	11; 95	172; 1859	2.74; 31	0.56; 20	2130; 17270
2014	**1.2**	**2296**	**6**	**90**	**22**	**477**	**8.90**	**2.37**	**4454**
	0.5; 1.6	603; 12087	4; 474	21; 219	3; 91	101; 1232	1.25; 29	0.62; 18	927; 15003
2015	**1.3**	**2410**	**20**	**104**	**15**	**461**	**10**	**3.03**	**5151**
	0.9; 1.5	871; 9208	5; 80	24; 566	6; 54	173; 960	2.18; 55	0.33; 17	922; 13123
2016	**1.2**	**1394**	**17**	**87**	**13**	**313**	**8.03**	**3.68**	**3486**
	0.8; 1.6	558; 12772	1; 153	29; 352	4; 53	90; 1195	2.57; 29	0.74; 21	1962; 23092
2017	**1.3**	**1508**	**16**	**69**	**14**	**256**	**8.23**	**2.71**	**3870**
	1.1; 1.3	310; 9512	0; 85	19; 294	4; 75	42; 1394	1.24; 22	0.73; 13	460; 11586

Fifteen compounds were detected in all of the samples and are summarized in Table 1, additional concentrations are given in Table S5. PCB-153 showed the highest concentrations in polar bear plasma, followed by PCB-180 and oxychlordane (Table 1 and Table S5). This is in accordance with earlier studies on polar bears from Svalbard and other areas (Braathen et al. 2004; Dietz et al. 2013b; Kucklick et al. 2002). All PCB congeners we summed (PCB-118, 138, 153, 180) were highly correlated with each other ($r > 0.6$, $p < 0.0001$) except PCB-118, which correlated only with PCB-138 ($r = 0.28$, $p < 0.0001$). Similar correlations have been

reported before (Braathen et al. 2004). ΣPCB showed moderate or weak correlations (p>0.5) with the other compounds we detected, except for BDE-153 (r = 0.79, p<0.0001) and oxychlordane (r = 0.8, p<0.0001).

3.2 TRENDS OF BIOLOGICAL VARIABLES

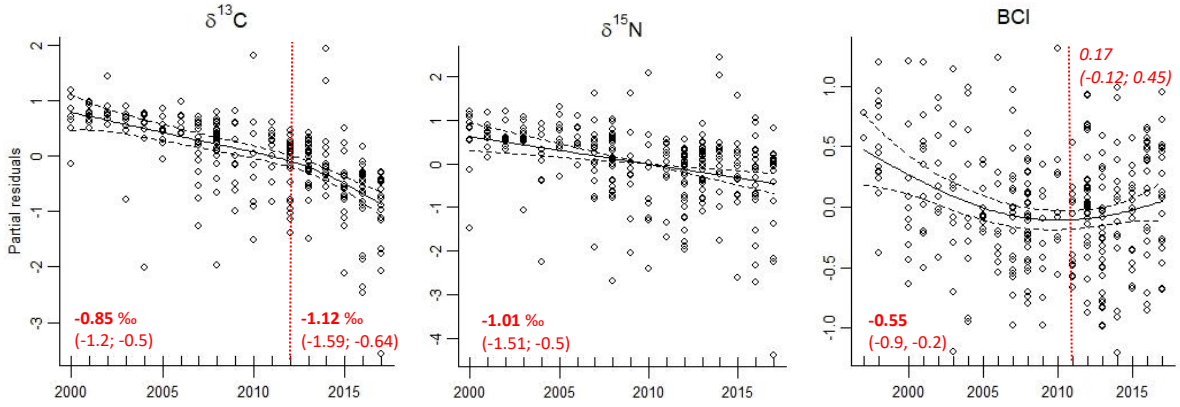


Figure 2: Trends of $\delta^{13}C$, $\delta^{15}N$ and body condition (BCI) of Svalbard polar bears from 1997 (2000) until 2017. $\delta^{13}C$ and $\delta^{15}N$ represent carbon source (high values: marine diet, low values: terrestrial diet), and trophic level, respectively, in polar bear winter diet. BCI shows the "fatness" of the bears (corrected for reproductive status; arbitrary scale without units). Trends are shown in ‰ for diet proxies and as scale units for BCI for the given time period, with 95% CI (derived from lme). Trends in italics are not significant. The trend estimates indicate change over the whole study period or time periods indicated by the red lines.

We observed a decrease of $\delta^{13}C$ and $\delta^{15}N$ over the study period, which is in accordance with a recently published trend of $\delta^{13}C$ and $\delta^{15}N$ partly based on the same polar bear individuals (Routti et al. 2017). The values for $\delta^{13}C$ decreased by 0.85 ‰ from 2000 to 2012 (95 % CIs: -1.2, -0.5; change per year: 0.077 ‰), and showed a steeper decrease of 1.12 ‰ after 2012 (95 % CIs: -1.59, -0.64; change per year: 0.279 ‰), whereas $\delta^{15}N$ decreased by 1.01 ‰ over the study period (95 % CIs: -1.51, -0.5; change per year: 0.063 ‰; Figure 2). As carbon isotopes ($\delta^{13}C$) indicate sources of primary productivity (Hobson et al. 1996), e.g. marine vs. terrestrial, our results suggest a larger proportion of terrestrial food items in polar bear diet over the study period, especially after 2012. The decline in $\delta^{15}N$ which fractionates and changes predictably between trophic levels (Hobson et al. 1996) and thereby reflects trophic position, indicates a shift of polar bear winter diet towards a lower trophic level. This is in accordance to the trend for $\delta^{13}C$ for polar bears, as terrestrial Arctic food chains are much shorter than Arctic marine food chains (Kelly et al. 2007). The shift in polar bear winter diet is likely related to the decline in sea ice in the Svalbard area. The number of days per year with optimal habitat for polar bears has decreased over time in Svalbard, as has the spatial overlap of polar bears and ringed seals (Hamilton et al. 2017; Lone et al. 2018). A shift towards a less marine and lower trophic level diet linked to sea ice decline has been reported for Svalbard polar bears (Tartu et al. 2018; Tartu et al. 2016). Some studies indicate that polar bears might be able to cover energy needs with land based prey (Gormezano et al. 2016; Gormezano and Rockwell 2015), but not all studies came to this conclusion (Dey et al. 2017; Rode et al. 2015). The "Suess effect", e.g. the gradual decrease of $\delta^{13}C$ in the

atmosphere due to combustion of fossil fuels leading to depleted $\delta^{13}C$ values, has likely very little influence on the observed $\delta^{13}C$ decrease in polar bears, as the $\delta^{13}C$ decrease in polar bears is over four times faster than the changes attributed to the Suess effect (Olsen et al. 2006; Routti et al. 2017).

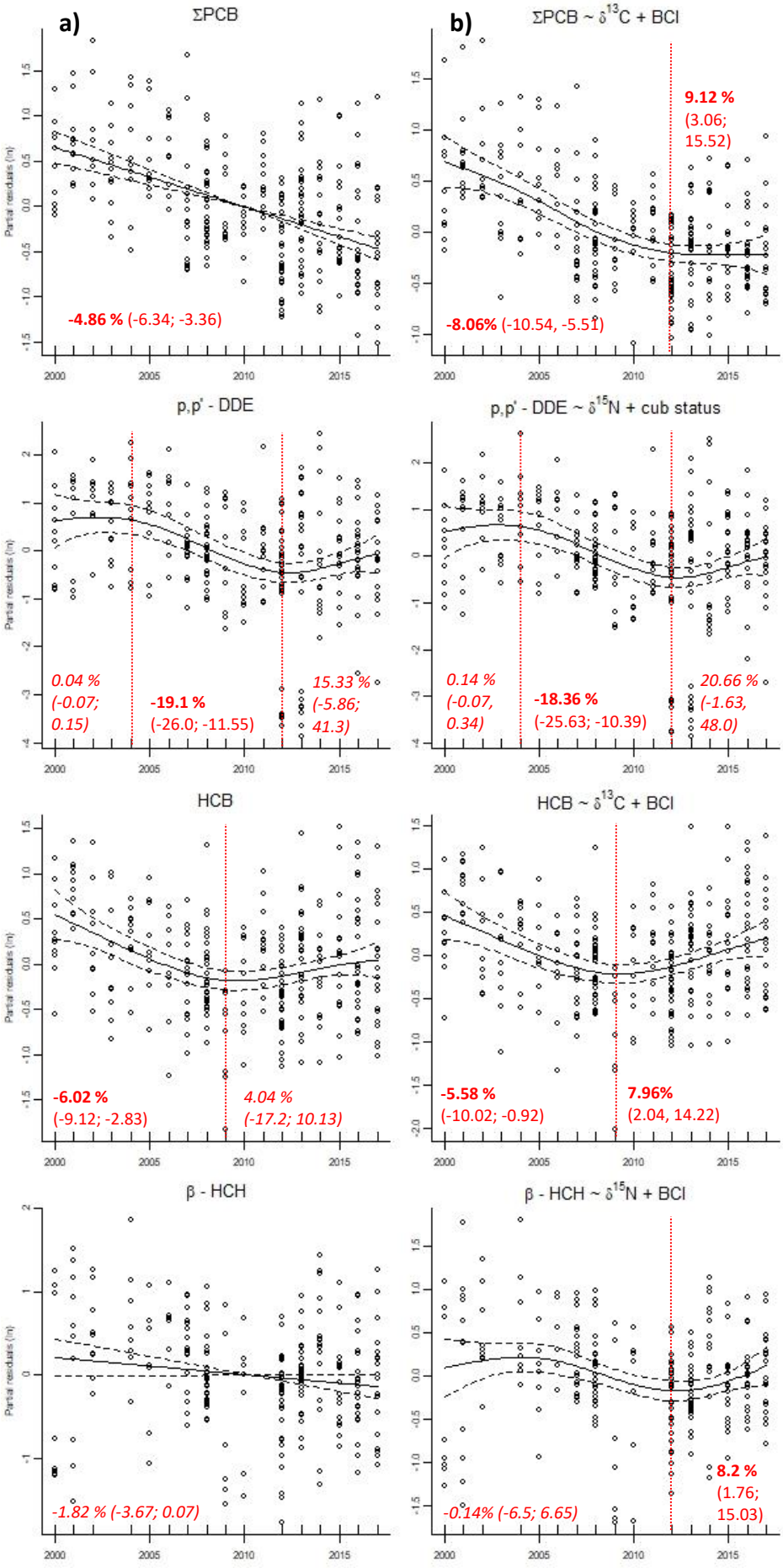
BCI values (corrected for reproductive status) declined slightly until 2011 (-0.55 BCI scale units; 95 % CIs: -0.9, -0.2; see Figure 1), which translates to a loss of 2.3 kg/year (95 % CIs: -3.5 kg, -1 kg) for a bear with average condition and length in the period from 1997 until 2011. This is likely related to sea ice decline, as e.g. observed for the southern Beaufort Sea polar bear subpopulation (Rode et al. 2010).

3.3 EFFECTS OF BIOLOGICAL VARIABLES ON POP CONCENTRATIONS

All the highest ranked GAMMs included diet proxies ($\delta^{13}C$ or $\delta^{15}N$) as predictors, which were positively related to all POPs (Table 2). Additionally, all the highest ranked models included either BCI or breeding status as predictor variables. BCI had a strong negative effect on all the compounds except p,p'-DDE (Table 2). Body condition had a slightly higher impact on POP concentration than diet, except for HCB and BDE-47, where the influence of $\delta^{13}C$ and $\delta^{15}N$ was higher than BCI (Table 2). These findings are consistent with a previous study on Svalbard polar bear females (partly the same females as in this study), which focused on seasonal and spatial differences of POPs (Tartu et al. 2017b). POP concentrations were positively affected by having cubs of the year ("breeding status C"; for GAMM estimates and significance see Table 2) for ΣPCB, BDE-153 and ΣOH-PCBs, while POP concentrations were mostly negatively affected when females had older offspring ("breeding status Y"; Table 2). Female polar bears nurse their cubs for more than two months (Amstrup 1993) entirely relying on their body fat, which transfers a part of the contaminant burden to the cubs with the milk, but also releases contaminants into the blood stream from the mobilized fat from the adipose tissue (Polischuk et al. 2002). After a year, the nursing females regain their previous body condition, which lessens contaminant concentrations (see Table 2) (Polischuk et al. 2002).

Table 2: Model-averaged estimates (bold) with 95 % confidence intervals (in brackets) derived from GAMM explaining the ln-transformed concentrations of POPs (ng/g lipid weight, and ln/g wet weight for ΣOH-PCBs) in female polar bears from Svalbard, Norway, by feeding habits ($\delta^{13}C$ and $\delta^{15}N$), body condition index (BCI), and breeding status (Y: with yearlings, C: with cubs of the year). The models also included age (years). Values for diet proxies and BCI have been standardized to ensure comparability. ΣPCB: CB-118, 138, 153, 180; ΣOH-PCB: OH-CB-107, 146, 138, 159, 187

response	(intercept)	$\delta^{15}N$ red blood cells	$\delta^{13}C$ red blood cells	BCI	breeding status Y	breeding status C	age
ln(ΣPCB)	**8.21**	**0.10**	**0.13**	**-0.29**	**-0.25**	**0.24**	**-0.02**
ln(p,p'-DDE)	**2.36**	**0.16**	**0.11**	**0.29**	**-0.01**	**-0.56**	**-0.01**
ln(HCB)	**6.78**	**0.08**	**0.14**	**-0.11**	**-0.15**	**0.07**	**-0.02**
ln(β-HCH)	**2.48**	**0.15**	**0.14**	**-0.24**	**-0.40**	**0.07**	**-0.04**
ln(Oxychlordane)	**4.90**	**0.13**	**0.12**	**-0.21**	**-0.32**	**0.05**	**-0.02**
ln(BDE-47)	**0.36**	**0.2**	**0.19**	**-0.09**	**-0.07**	**0.13**	**-0.01**
ln(BDE-153)	**-0.00**	**0.11**	**0.1**	**-0.31**	**-0.17**	**0.41**	**-0.01**
Ln(ΣOH-PCB)	**4.29**	**0.20**	**0.24**	**-0.04**	**-0.01**	**0.31**	**0.00**


a)
ΣPCB
-4.86 % (-6.34; -3.36)
b)
ΣPCB ~ δ13C + BCI
9.12 %
(3.06;
15.52)
-8.06% (-10.54, -5.51)
p,p' - DDE
0.04 %
(-0.07;
0.15)
-19.1 %
(-26.0; -11.55)
15.33 %
(-5.86;
41.3)
p,p' - DDE ~ δ15N + cub status
0.14 %
(-0.07,
0.34)
-18.36 %
(-25.63; -10.39)
20.66 %
(-1.63,
48.0)
HCB
-6.02 %
(-9.12; -2.83)
4.04 %
(-17.2; 10.13)
HCB ~ δ13C + BCI
-5.58 %
(-10.02; -0.92)
7.96%
(2.04, 14.22)
β - HCH
-1.82 % (-3.67; 0.07)
β - HCH ~ δ15N + BCI
8.2 %
(1.76;
15.03)
-0.14% (-6.5; 6.65)
Partial residuals (ln)
2000
2005
2010
2015

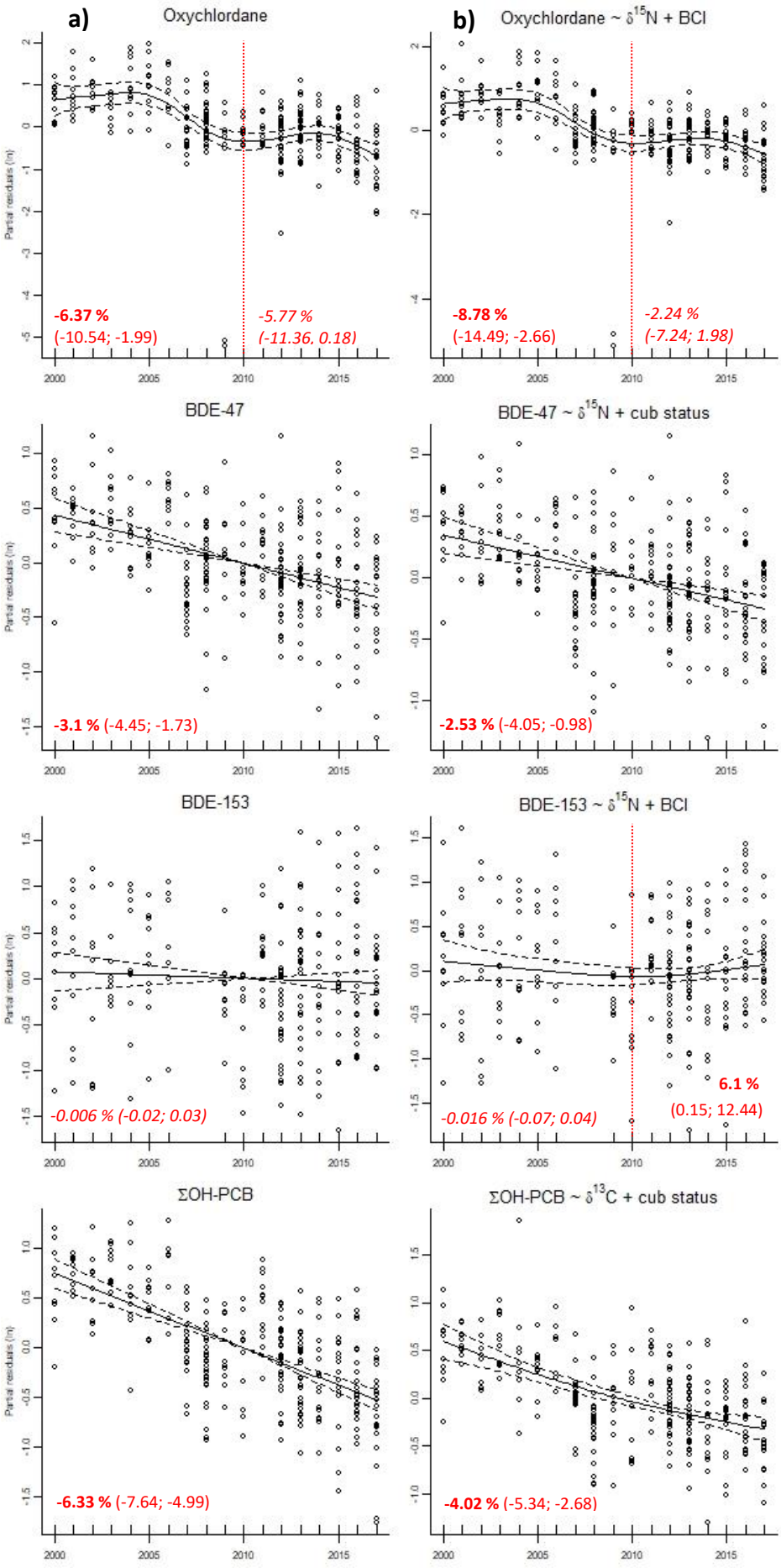


Figure 3a and b (contination from previous page): Temporal trends of ΣPCB, OCPs, PBDEs and ΣOH-PCBs in female polar bears from Svalbard, 1997(2000)-2017, a: non adjusted (left column), and b: adjusted for biol. variables (see headings, left column). The trend estimates (change per year) are derived from linear mixed models and given with 95% confidence intervals. The y-axes show partial residuals of the highest ranked GAMM (see table S3 in SI), e.g. the effects of year have been controlled for the variables included in the highest ranked model for the given compound. Trends in bold are significant, trends in italics are not.

3.4 TEMPORAL TRENDS OF POPs WITH AND WITHOUT THE EFFECTS OF BIOLOGICAL VARIABLES

Overall, all compounds declined in polar bear plasma from 1997 to 2017, except BDE-153 and β-HCH, which were stable over the study period. ΣPCB declined linearly by about 5% per year (see Figure 3 for LME trend estimates and 95% CI), p,p'-DDE declined nearly 20 % per year between 2004 and 12, and both HCB and oxychlordane 6% per year before 2009 and 2010, respectively. BDE-47 declined by 3% per year over the entire study period.

When the trends for each compound were corrected for predictors from their respective highest ranked model, the trends changed in shape for ΣPCB and β-HCH. The adjusted ΣPCB trend decreased almost twofold compared to the non-adjusted trend, but abruptly ceased to decrease in 2011 and thereafter increases significantly by 9% per year from 2011-17 (Table 2b). The non-adjusted trend for HCB was stable after 2009, but the concentrations increased by almost 8 % per year from 2009-17 when adjusted for $\delta^{13}C$ and BCI. The adjusted β-HCH concentrations were stable before 2012, but subsequently increased by about 8 % per year for the period 2012-17. All other compounds were only moderately affected by the biological variables we tested. The declining trend of organochlorine POPs we observed before 2010 is in accordance to numerous studies of Arctic biota (AMAP 2015; Andersen et al. 2015; Braune and Mallory 2017; Dietz et al. 2013b; McKinney et al. 2010). Trends for PBDEs in our study, however, are not decreasing comparably to organochlorine contaminants; the adjusted BDE-153 concentrations increased after 2010 and did not decrease before like PCBs and most OCPs, and BDE-47 is decreasing at a slower rate than most organochlorine contaminants. PBDEs have been used since the 1970, when e.g. PCBs were already phased out in many countries (Ask and Routti 2017; Li and Macdonald 2005). National and voluntary phase outs for PBDEs started in the early 2000 (EPA 2009), and they were added to the Stockholm convention in 2009 (pops.int). Overall, the later use and regulation of PBDEs compared to organochlorine contaminants could explain why BDE-47 linearly decreased over the study period, and BDE-153 did not show a significant trend in polar bear blood. This is, however, not in accordance to other studies: (Houde et al. 2017) described increasing trends of PBDEs in Canadian ringed seals before 2008, and a decline thereafter; and trends of PBDEs in East Greenland polar bears did not show a trend (McKinney et al. 2010) or increased for BDE-153, and BDE-47 did not show any significant trend (Dietz et al. 2013a).

Both adjusted and non-adjusted trends for OH-PCBs are declining linearly at a similar rate. Σ-OH-PCBs in our study do not show an increase for the last decade similar to their parent PCBs. In polar bears, OH-PCBs stem by a large degree from biotransformation as opposed to bioaccumulation (Letcher et al. 2009) and trends could be expected to be similar to PCBs, however, the OH-PCBs in this study could have many more parent PCBs than the four that were analysed.

A few recent studies are starting to report stalling declines of legacy POPs in the Arctic for the last decade (Riget et al. 2016), which is in accordance to our results. We found significant increases for diet adjusted trends of ΣPCB, HCB and BDE-153. All other compounds we analysed except for BDE-47 show no significant trend after ~ 2010, even though they significantly decreased before. These stagnating decreases or increases might be related to secondary emissions, i.e. the release of previously stored contaminants in ice, snow, or soil due to climate change (Ma et al. 2016; Macdonald et al. 2005). Similar stagnating contamination trends have also been reported for other Arctic species (Braune et al. 2015) or other contaminants (Routti et al. 2017). However, as discussed before, the climate change driven loss of sea ice also affects food web ecology, i.e. polar bears are forced to feed more on terrestrial and lower trophic level food items, which counters the effect of increasing contaminants in polar bears.

3.5 CONCLUSION AND FUTURE PERSPECTIVES

In the current study we present results for an extensive time series for legacy POPs in Svalbard polar bears. Our results show significant decreases until ~ 2010 of all POPs analysed, except β-HCH and BDE-153. Trends adjusted for diet showed significant increases after ~ 2010 for ΣPCB, HCB, β-HCH and BDE-153, while other trends did not significantly increase or decrease. The difference between adjusted and non-adjusted trends for most compounds in relation to the decline of both $\delta^{13}C$ and $\delta^{15}N$ indicates a shift in the diet of Svalbard polar bears that yields them from a certain amount of the contaminant exposure. However, the climate – induced shift in diet poses an additional stressor on Svalbard polar bears and needs to be investigated further. Our results and other studies referenced herein have shown the utmost importance to carefully account for ecological and biological factors in temporal trend studies of POPs. With ongoing climate change contaminant patterns and trends will become more difficult to estimate, as changes might be more far-reaching in respect to ecology (changes in e.g. food webs or migration patterns), biology (changes in e.g. body condition or reproduction), or the distribution in abiotic compartments (contaminant pathways, distribution or storage). All these need to be accounted for in future temporal trend studies to ensure precise estimations and accurate predictions.

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5 SUPPLEMENTARY INFORMATION

5.1 PROXIES FOR FEEDING HABITS

Stable isotopes were analysed according to previously published methods (Rogers et al. 2015; Routti et al. 2017; Tartu et al. 2016). Red blood cells were dried at 50 °C for three days and then homogenized using a bead-mill homogenizer (TissueLyzer, Qiagen GmbH, Hilden, Germany). The samples were weighed on a Sartorius ME5 microbalance (Sartorius AG, Göttingen, Germany) and transferred to 3.5 × 5 mm tin cups for further analysis. The samples were analysed using a Costech ECS 4010 elemental analyser (Costech, Valencia, CA) in line with a ThermoFinnigan DeltaPlus XP continuous-flow isotope ratio mass spectrometer (CF-IRMS, Thermo Scientific, Bremen, Germany) for $\delta^{13}C$ and $\delta^{15}N$, which was calibrated according to international reference standards from the International Atomic Energy Agency (IAEA-N1, IAEA-CH7, IAEA-C3, and IAEA-600) and the USGS (USGS-25, USGS-40, and USGS-41). Internal standards of purified methionine were included (Alfa Aesar, $\delta^{13}C$ = -34.58 ± 0.06 ‰, $\delta^{15}N$ = -0.94 ± 0.05 ‰; all data error are SD) as well as homogenized Chinook salmon muscle (UAA Stable Isotops Lab, $\delta^{13}C$ = -19.27 ± 0.05 ‰, $\delta^{15}N$ = 15.56 ± 0.13 ‰) with all samples as quality controls. SI values are reported in standard δ notation and referenced to Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}C$ and to air for $\delta^{15}N$. Long term rerecords of internal standards yield an analytical precision of 0.12 ‰ for $\delta^{15}N$ and 0.11 ‰ for $\delta^{13}C$. Replicates were analysed to determine intra-individual variability. The solids analyses were conducted at Jeffrey Welker's stable isotope laboratory at the Environment and Natural Resources Institute of University of Alaska, Anchorage (http://www.uaa.alaska.edu/enri/labs/sils).

5.1.1 QUALITY ASSURANCE

Long-term records of internal standards (BWBII keratin, freeze dried moose (*Alces alces*) blood, peach leaves and purified methionine) yield an analytical precision of 0.10 ‰ for $\delta^{15}N$ and 0.11‰ for $\delta^{13}C$.Measured values in reference materials are given in Table S1.

Table S 1: Measured $\delta^{13}C$ and $\delta^{15}N$ values for commercially available and in-house (University of Alaska, Anchorage, UAA) secondary isotopic reference materials analysed with polar bear samples

	Mean	SD	Difference from expected values	SD for difference
δ15N				
BWBII keratin (UAA)	14.38	0.06	-0.06	0.06
Purified methionine (Alfa Aesar)	-0.93	0.02	0.01	0.02
Freeze dried moose (*Alces alces*; UAA)	2.32	0.07	0.10	0.07
Peach Leaves (UAA)	2.11	0.18	0.13	0.13
δ13C				
BWBII keratin(UAA)	-18.51	0.04	-0.14	0.04
Purified methionine (Alfa Aesar)	-34.56	0.01	0.02	0.01
Freeze dried moose (*Alces alces*; UAA)	-28.27	0.11	-0.03	0.11
Peach Leaves (UAA)	-26.04	0.10	-0.06	0.07

5.2 CHEMICAL ANALYSES

Data for POP concentrations from 1997-2013 were provided by the accredited Laboratory of Environmental Toxicology at the Norwegian University of Life Science (NMBU) in Oslo, while the author personally analyzed samples from 2014-2017 in the same lab.

The obtained blood plasma was analysed for PCBs, OCPs and PBDEs according to the requirements of the NS-EN ISO/IEC 17025 (TEST 137) (Norwegian Standard-European Committee for Standardization, 2005). The laboratory is thereby accredited for the determination of PCBs, OCPs and PBDEs in biological matrices of animal and human origin.

The following contaminants were targeted in this study (* - detected in all years and discussed in this study):

PCBs:

- CB- 28, 52, 101, 118*, 138*, 153*, 180*

OCPs:

- dichlorodiphenyldichloroethylene (p,p'-DDE)*
- heptachlorobenzene (HCB)*
- hexachlorocyclohexane (HCH; α, β*, γ - isomers)
- oxychlordane*
- trans-nonachlor
- toxaphene[1]

PBDEs

- BDE-47*, 153*

OH-PCBs[1]:

- 4'-OH-CB106-108 (107*), 3'-OH-CB118, 4'-OH-CB130, 3'-OH-CB138*, 4'-OH-CB146*, 4'-OH-CB159*, 4'-OH-CB172, 3'-OH-CB180, 4'-OH-CB187*

The analytical standards were provided by Cambridge Isotope Laboratories, Inc., Andover, MA, USA for PCBs, OCPs, and BDEs; Ultra Scientific, Rhode Island, USA for PCBs; Supelco, Bellefonte, PA, USA for OCPs; LGC Promochem, Wesel, Germany for HCB.

5.2.1 EXTRACTION AND CLEAN UP

The extraction methods used were as described in (Brevik 1978) and later modified by (Polder et al. 2008). The method for the extraction of OH-metabolites is described in (Gabrielsen et al. 2011). This method is based on liquid/liquid extraction.

5.2.1.1 EXTRACTION

Approximately 2 g of polar bear plasma was weighed in 80 ml centrifuge glasses and internal standards were added. For the blind and recoveries 2 g cow blood (2009) was used, respectively, and for internal laboratory controls 0.25 g of harp seal blubber (*Pagophilus*

[1] The determination of these compounds is not accredited according to the above mentioned requirements, but performed following the accredited methods.

groenlandicus), 0.25 g of minke whale blubber (*Balaenoptera acutorostrata*) and 2.5 g blood from a male bearded seal (*Erignathus barbatus;* Barents sea). To all samples and controls 2 ml of NaCl solution, 10 ml 1 M sulphuric acid (H_2SO_4; Sigma Aldrich, St. Louis, Missouri, US; ≥ 97.5 %), 15 ml acetone, and 20 ml cyclohexane (CHX; VWR chemicals, UN1145) was added to solve fat and lipid soluble components in the polar solvents and OH-metabolites in 1 M H_2SO_4. The NaCl solution aids in separating the polar and unpolar phases. The samples were homogenized using an ultra sound sonicator (Cole Parmer Ultrasonic Processor CPX 750, Vernon Hills IL, USA) for 1 min and centrifuged (Beckmann Coulter Allegra® X-12R) for 10 min at 3000 rpm. The supernatant was transferred into Zymark® glasses and evaporated down to 1 ml at 40 °C and a gentle stream of N_2 (purity: 99.6 %; AGA AS, Oslo, Norway, pressure 0.6 ba) in a Zymark® Evaporator (TurboVap II, Zymark Corporation, Hopkinton, MA, USA). 5 ml acetone (VWR chemicals UN1090) and 10 ml CHX were added to the original sample glasses, homogenized for 30 sec. in the ultra sound sonicator and centrifuged for 10 min at 3000 rpm. The supernatant was added to the Zymark® glasses with the 1 ml of previous supernatant and evaporated in the same way to a total of approximately 1 ml per sample.

The internal laboratory controls (whale and seal blubber) were treated in the same way as described above, only 10 ml of water (purified Grade 1) were added to dilute the fat instead of 10 ml 1 M sulphuric acid. Whale and seal blubber extracts were transferred to volumetric flasks and filled with CHX to a total of 5 ml.

5.2.1.2 DETERMINATION OF FAT CONTENT

The fat content of the plasma samples and controls were determined gravimetrically. Due to the small sample size and the low amount of fat in blood, the whole sample was used for the determination of fat content. Glasses used for the determination of fat content were weighed when clean, dry and empty and the extracts were transferred completely to their respective weighed glasses. The Zymark® glass walls were rinsed 3 times with CHX. The extracts evaporated in a 40 °C sand bath with gentle N_2 blowing into the glasses through disposable glass Pasteur pipettes until only an inert, fatty residue was left in the glasses. The fat residues were weighed until a stable weight was obtained (+/- 0.002 g).

For the whale and seal blubber, an aliquot of 1 ml was used from the total extract size of 5 ml. This aliquot was evaporated overnight in a 40 °C sand bath and was weighed the next day after cooling down to room temperature. This process was repeated until stable weight.

The percentage of fat content was calculated by the following formula:

$$Lipid\% = \frac{glass\ with\ fat\ [g] - emty\ glass\ [g]}{inweight\ sample\ (plasma)\ [g]} * 100$$

For the fatty content calculation of whale and seal blubber, the formula had to be modified by multiplying the difference between empty and full glass with the total amount of the sample solution (5 ml).

After the determination of fat content, the fat extracts were solved in 1 ml CHX. The fat residue from the whale and seal aliquots were not further used.

5.2.1.3 ACID CLEAN UP

In order to get rid of fat and protein residues 4 ml concentrated H_2SO_4 (≥ 97.5 %) was added to all extracts, mixed (MS2 Minishaker, IKA® Works, INC.) for 10 sec. and then put 1 hour for incubation in a dark place to prevent the acid from breaking down in day light. The samples were centrifuged for 10 min at 3000 rpm and the supernatant was transferred into new clean glass test tubes. To ensure the supernatant was free of acid every pipette taken out was tested for acid with pH paper. Any extract residues remaining in the acid phase was solved in approximately 1 ml of CHX and taken out as supernatant after centrifugation of 10 min at 3000 rpm. Extracts and controls were taken further for the partitioning of the samples into chlorinated compounds and BFRs, and OH-metabolites.

The remaining whale and seal blubber solutions of 4 ml were divided into 2 glasses of 2 ml respectively and thereafter treated the same as the extracts.

After the acid clean up 150 µl of the clear seal blubber supernatant was put into a clear gas chromatography (GC) vial. From that vial 20 µl was put into another GC vial and filled up with 180 µl CHX (dilution 1:10).

5.2.1.4 SEPARATION OF OH-METABOLITES FROM OCPs, PCBs, AND PBDEs

5 ml 1 M potassium hydroxide (KOH) (Alfa Aesar, Pellets 85%, in 1:1 ethanol and purified Grade 1 water) was added to the clear extracts (cleaned with acid) to solve the polar OH-metabolites, whereas the other OCPs, PCBs, and PBDEs remained in the CHX. After homogenising on a Whirlimixer (VWR International, S/N: 200031637) and 5 min at 3000 rpm in the centrifuge the *infranatant* containing OH-metabolites was put into new test tubes. This procedure was repeated, leading to an amount of 10 ml KOH in the new test tubes.

5.2.1.5 EXTRACTION OF PCBs, OCPs, AND PBDEs

For OCPs, PCBs and PBDEs the former *supernatant* (CHX) was further processed. One Pasteur pipette of purified Grade 1 water was added to the extracts to collect the residues of KOH and the *supernatant* (CHX) was transferred to new test tubes calibrated with a 200 µl "Keeper" solution (2 % decane in CHX). Compounds remaining in the infranatant were disolved in 1 ml CHX and transferred to the same calibrated test tubes. The extracts were evaporated until the calibration mark in the 40 °C sand bath with a gentle N_2 stream blowing into the test tubes through Pasteur glass pipettes. The glass walls were rinsed with CHX in order to collect any remaining compounds sticking to the glass walls and evaporated down to the mark again. The extracts were adjusted with CHX to a final volume of 200 µl. The extracts were transferred to brown GC vials for analysis of chlorinated compounds and BRFs,

whereas the whale blubber was transferred into a clear GC vial for analysis of toxaphenes. The samples in GC vials were stored in the fridge (3.2 °C) until the GC analysis.

5.2.1.6 EXTRACTION OF OH-METABOLITES

For the extraction of OH-metabolites, the former *infranatant* was treated further. To re-protonate the OH-metabolites solved in the KOH phases about 30 drops of concentrated H_2SO_4 was added to the samples (pH about 1-2). Then 5 ml CHX was added to take up the compounds and this CHX supernatant was transferred into Zymark® glasses. This step was repeated again and the resulting 10 ml were evaporated down to 1 ml in the Zymark® evaporator (40 °C, 0.6 bar). The samples were then transferred from the Zymark® glasses into new test tubes calibrated to 1 ml with CHX, the Zymark® glass walls were rinsed twice with about 1 ml of CHX, which was also added to the sample in the calibrated test tubes. The samples were evaporated to the 1 ml calibration mark in a 40 °C sand bath and a gentle stream of N_2.

5.2.1.7 DERIVATIZATION

Polar compounds can lead to “peak tailing” in gas chromatography, therefore the polar OH-metabolites needed to be derivatized. In this process the H of the OH-group is substituted by an acetyl group, making the compound less polar. To achieve this 50 µl 1:1 solution of acidic anhydride and pyridine was added to all extracts, blind, recoveries, blanks and seal blood (whale and seal blubber were not analysed for OH-metabolites). The samples were mixed and placed into a heating cabinet (Termaks Type B8054, Bergen, Norway) at 60 °C for 30 min for incubation. 2 ml purified Grade 1 water was added to dissolve the remaining acid residues. The supernatant was transferred to new test tubes calibrated with 200 µl “Keeper” solution. The samples were evaporated, the inside of the test tubes rinsed once with CHX and evaporated again to the calibration mark and corrected with CHX to the end volume of 200 µl. Then the samples were transferred to brown GC vials and stored in the fridge until GC analysis.

5.2.2 GAS CHROMATOGRAPHIC ANALYSIS

The concentration of the chlorinated compounds as well as OH-metabolites was quantified with a high resolution GC (Hewlett Packard HP 6890 Series, USA) with NPD and ECD detectors (Agilent Technologies, 5975c inert XL EI/CI MSD triple axis detector, USA). PBDEs were quantified using a high resolution GC (Agilent 6890 Series GC system, USA) coupled with a mass spectrometer (Agilent 5973 Network Mass Selective Detector, USA). Details about the method can be found in (Polder et al. 2008) and (Gabrielsen et al. 2011). The carrier gas used for all GC methods was helium.

Table S 2: Limit of detection (LOD; ng/g) and recovery rate (%; "Recov.") of lipophilic pollutants and OH-PCBs in spiked reference material for polar bear plasma batches analyzed in 2007, 2009, 2011, 2014, 2015 and 2017. OH-PCBs and BDE-47 (all batches) and PCBs and OCPs (2007, 2009 and 2011) were measured by HRGC (Agilent 6890 Series with Agilent 7683 Series autosampler) connected to a quadrupole MS detector (Agilent 5973 Series). In 2014, PCBs and OCPs were measured using HRGC (Agilent 6890 Series with Agilent 7683 Series autosampler) connected two μ-ECD (Agilent 6890). In 2015 OCPs and PCBs were measured using HRGC (Agilent 6890 Series with Agilent 7683 Series autosampler) connected to a quadrupole MS detector (Agilent 5975 Series). In 2017 PCBs, OCPs and OH-PCBs were measured by HRGC (Hewlett Packard HP 6890 Series) with NPD and ECD detectors (Agilent Technologies, 5975c inert XL EI/CI MSD triple axis detector); and PBDEs by HRGC Agilent 5973 Network Mass Selective Detector coupled with a mass spectrometer (Agilent 5973). N.a. not analysed

	2007		2009		2011		2014		2015		2017	
	LOD	Recov	LOD	Recov	LOD	Recov	LOD	Recov	LOD	Recov	LOD	Recov
HCB	0.01	120	0.01	91	0.02	95	0.01	118	0.007	101	0.008	64
Oxychlordane	0.015	99	0.015	83	0.05	85	0.14	92	0.041	117	0.009	76
p,p'-DDE	0.025	107	0.025	100	0.03	97	0.07	105	0.126	123	0.015	106
PCB-118	0.01	104	0.04	99	0.06	102	0.015	95	0.015	97	0.005	105
PCB-138	0.02	90	0.03	103	0.06	111	0.02	97	0.011	119	0.005	106
PCB153	0.025	97	0.025	108	0.07	82	0.015	95	0.009	118	0.005	104
PCB-180	0.02	91	0.02	104	0.06	108	0.015	99	0.009	95	0.005	103
4 OH-CB-107	0.025	109	0.025	104	0.07	86	0.055	97	0.051	101	0.01	79
3'OH-CB-138	0.06	109	0.06	103	0.06	84	0.115	92	0.123	96	0.01	99
4 OH-CB-146	0.02	108	0.02	109	0.1	84	0.13	90	0.059	97	0.011	99
4'OH-CB-159	0.12	88	0.025	90	0.02	96	0.053	101	0.017	100	0.005	98
3'OH-CB 187	0.02	96	0.025	116	0.07	42	0.11	62	0.135	100	0.012	68
BDE-47	0.025	62	0.025	92	0.005	102	0.01	102	0.012	84	0.007	102

5.2.3 QUALITY CONTROL

To ensure quality control throughout the preparation and GC analysis of the samples both external and internal controls were included in all steps of all series. Each series of 15 – 17 samples included one blind, two recoveries, three blanks and the in-house controls seal and whale blubber and seal blood. The first two series also included the certified reference materials CRM 349 (series one; chlorobiphenyls in cod liver oil) and CRM 350 (series 2; chlorobiphenyls in mackerel oil), these are external European standards to ensure comparability to other laboratories. The internal controls contain known amounts of chemical compounds. Seal blubber was used for different chlorinated compounds and BFRs, whale blubber for toxaphenes and seal blood for OH-metabolites. Blind control and recoveries consisted of a similar matrix like the sample (cow blood) with an expected low concentration of pollutants. The three blanks consisted of only the solvents and added standards. Internal standards with known concentrations were added to all samples and controls to ensure control over the accuracy and sensitivity of both the extraction process and GC analysis. Standards for all chemicals analysed were used.

To ensure quality control in an international context the *Arctic Monitoring and Assessment Program (AMAP) Ring Test* was included with the last series of samples. AMAP instituted the Ring Test in 2001 for 32 compounds (including amongst others β-HCH, HCB, p,p'-DDE, PBDEs, PCBs, PFAS, toxaphene, and trans-nonachlor) in human serum and as in 2009, 28 labs participate in this quality control (AMAP 2009).

5.3 DATA ANALYSIS

1. YEAR
2. YEAR + $\delta^{13}C$
3. YEAR + $\delta^{15}N$
4. YEAR + $\delta^{13}C$ + Cub status
5. YEAR + $\delta^{15}N$ + Cub status
6. YEAR + $\delta^{13}C$ + BCI
7. YEAR + $\delta^{15}N$ + BCI
8. YEAR + $\delta^{13}C$ + Age
9. YEAR + $\delta^{15}N$ + Age

Table S 3: All candidate models used for GAMM analyses. Highly correlated predictor variables (e.g. $\delta^{15}N$ and $\delta^{13}C$) were not included in the same models (Burnham et al. 2010). For GAMM estimates (Table 2), all candidate models were averaged based on weight of AIC.

5.4 BIOLOGICAL INFORMATION

Table S 4: Biological information for polar bears sampled around Svalbard 1997-2017. Body condition index (BCI, arbitrary values), δ13C and δ15 in red blood cells, and age (years) are given as mean ± standard deviation. Solitary bears were alone or with a male, COY were together with cubs of the year, and YRL were with cubs aged between 1 and 2 years. The 306 samples collected represent 185 individual females. N.a.: not analysed. No samples were taken in 1999.

Year	BCI	Breeding status			$\delta^{13}C$	$\delta^{15}N$	Age
		Solitary	COY	YRL			Years
1997	-0.79 ± 0.07	0	1	1	n.a.	n.a.	8 ± 1
1998	-1.23 ± 0.61	0	13	0	n.a.	n.a.	13 ± 3
2000	-1.36 ± 0.78	5	3	2	-19.24 ± 0.64	16.82 ± 1.55	14 ± 4
2001	-1.06 ± 0.72	3	3	5	-19.11 ± 0.26	17.12 ± 0.51	13 ± 7
2002	-1.18 ± 0.49	3	4	2	-18.93 ± 0.29	17.00 ± 0.48	11 ± 4
2003	-1.45 ± 0.8	3	5	3	-19.33 ± 0.51	17.15 ± 0.84	10 ± 4
2004	-1.34 ± 0.92	6	4	0	-19.55 ± 1.47	16.44 ± 1.72	12 ± 6
2005	-1.37 ± 0.43	5	5	0	-19.29 ± 0.33	17.4 ± 0.48	13 ± 6
2006	-1.62 ± 0.72	4	6	0	-19.13 ± 0.35	17.19 ± 0.64	13 ± 5
2007	-1.51 ± 0.74	10	5	4	-19.78 ± 0.93	16.34 ± 1.36	11 ± 6
2008	-1.51 ± 0.58	17	11	3	-19.76 ± 0.90	16.24 ± 1.40	10 ± 5
2009	-1.83 ± 0.41	2	4	4	-20.08 ± 0.97	15.76 ± 1.45	13 ± 6
2010	-1.02 ± 0.81	9	0	1	-20.17 ± 1.24	15.5 ± 1.82	13 ± 6
2011	-1.79 ± 0.5	6	6	1	-19.59 ± 0.73	16.25 ± 1.32	12 ± 6
2012	-1.23 ± 0.65	18	9	6	-20.1 ± 0.83	15.7 ± 1.27	13 ± 6
2013	-1.72 ± 0.72	15	9	5	-19.98 ± 0.68	16.33 ± 0.97	12 ± 5
2014	-1.35 ± 0.86	13	2	1	-19.91 ± 0.65	16.39 ± 1.22	11 ± 5
2015	-1.69 ± 0.49	6	9	2	-20.51 ± 0.83	16.13 ± 1.3	14 ± 5
2016	-1.23 ± 0.69	12	7	4	-20.86 ± 1.15	15.52 ± 1.59	13 ± 4
2017	-1.23 ± 0.62	11	5	3	-20.92 ± 1.16	15.91 ± 1.91	12 ± 5

5.5 CONCENTRATIONS OF SINGLE PCB AND OH-PCB COMPOUNDS

Table S 5: Median (bold), min. and max. concentrations of PCB and OH-PCB compounds (summed in Table 1) in plasma samples from female polar bear collected on Svalbard 1997-2017. PCBs are given in ng/g lipid weight, and OH-PCBs in ng/g wet weight. No samples were taken in 1999; n.a.: not analysed.

	PCB-118	PCB-138	PCB-153	PCB180	OH-PCB 107	OH-PCB 138	OH-PCB 146	OH-PCB 156	OH-PCB 187
1997	**16**	**617**	**3230**	**1798**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
	12; 21	326; 907	1658; 4803	1077;					
1998	**32**	**365**	**1858**	**1107**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
	21; 49	276; 691	1351; 5225	566; 4366					
2000	**36**	**397**	**2276**	**701**	**8.07**	**1.05**	**50**	**0.40**	**72**
	4.32; 66	119; 1246	895; 7126	219; 3097	1.24, 44	0.06, 2.51	13, 67	0.13, 1.42	18, 200
2001	**26**	**480**	**3013**	**1446**	**8.29**	**0.9**	**52**	**0.40**	**87**
	15; 44	340; 1229	1621; 9300	595; 4007	4.02, 27	0.63, 1.54	34, 89	0.22, 0.87	49, 119
2002	**30**	**549**	**3446**	**1433**	**4.93**	**0.79**	**45**	**0.41**	**61**
	5.39; 52	176; 1369	1392;	685; 5926	1.56, 19	0.25, 1.90	23, 79	0.21, 0.89	39, 131
2003	**26**	**246**	**1836**	**1174**	**8.24**	**0.66**	**32**	**0.32**	**115**
	18; 68	137; 534	852; 3132	553; 2241	4.06, 14	0.48, 2.36	18, 64	0.19, 0.63	65, 213
2004	**31**	**413**	**2475**	**1272**	**7.20**	**0.91**	**40**	**0.32**	**67**
	12; 40	131; 1505	825; 9166	382; 3766	1.92, 24	0.06, 2.87	15, 81	0.12, 0.98	23, 139
2005	**33**	**491**	**2584**	**940**	**9.78**	**0.69**	**40**	**0.38**	**51**
	15; 60	179; 1327	1110; 9621	496; 3244	2.54, 51	0.06, 2.94	23, 73	0.01, 0.96	39, 135
2006	**25**	**555**	**2720**	**1240**	**9.80**	**1.07**	**67**	**0.4**	**129**
	14; 70	198; 1160	1166; 6907	413; 2277	2.68, 32	0.54, 1.36	22, 85	0.27, 0.52	40, 426
2007	**23**	**220**	**1009**	**568**	**8.72**	**1.18**	**31**	**0.28**	**57**
	11; 44	115; 396	486; 12626	250; 8545	1.83, 33	0.50, 2.57	15, 65	0.05, 0.72	18, 93
2008	**27**	**207**	**1164**	**650**	**3.71**	**0.57**	**27**	**0.25**	**38**
	11; 55	50; 757	403; 5057	275; 3179	0.72, 17	0.18, 1.54	6.19, 52	0.07, 3.11	7.98, 84
2009	**14**	**144**	**1084**	**809**	**4.00**	**0.54**	**25**	**0.28**	**32**
	0.32; 33	57; 757	580; 4166	388; 2273	2.10, 8.36	0.40, 1.38	9.70, 34	0.19, 1.52	14, 104
2010	**19**	**136**	**997**	**703**	**4.43**	**0.49**	**21**	**0.20**	**33**
	13; 34	61; 250	416; 1759	284; 941	2.54, 11	0.06, 0.94	10, 29	0.01, 0.35	13, 105
2011	**24**	**253**	**1962**	**1129**	**5.65**	**0.81**	**33**	**0.35**	**111**
	12; 80	74; 578	697; 3772	680; 3616	3.08, 16	0.30, 1.55	12, 56	0.20, 0.71	47, 235
2012	**16**	**101**	**793**	**547**	**4.29**	**0.51**	**18**	**0.16**	**48**
	2.25; 31	15; 487	285; 2138	153; 1870	1.33, 15	0.03, 1.18	7.28, 34	0.04, 0.41	18, 112
2013	**14**	**186**	**1189**	**886**	**4.90**	**0.72**	**21**	**0.15**	**38**
	0.68; 41	67; 673	423; 5803	335; 5614	2.56, 28	0.19, 2.55	9.32, 61	0.08, 0.57	15, 179
2014	**17**	**133**	**1291**	**818**	**3.43**	**0.27**	**18**	**0.19**	**27**
	3.36; 72	44; 490	293; 7256	191; 4400	0.43, 17	0.06, 2.18	2.61, 52	0.01, 0.88	5.62, 102
2015	**19**	**167**	**1386**	**841**	**4.01**	**0.5**	**25**	**0.19**	**32**
	6.47; 32	27; 628	484; 5130	297; 3432	1.59, 13	0.00, 4.97	4.75, 53	0.09, 0.76	5.38, 107
2016	**18**	**108**	**789**	**471**	**3.09**	**0.54**	**17**	**0.14**	**27**
	4.55; 52	34; 499	270; 6286	209; 5977	1.46, 28	0.24, 1.78	7.92, 74	0.00, 0.54	11, 81
2017	**16**	**122**	**829**	**527**	**4.01**	**0.46**	**20**	**0.16**	**23**
	5.91; 39	9; 961	162; 5961	132; 2575	0.63, 8.84	0.00, 0.98	2.08, 80	0.02, 0.63	3.45, 61