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Three decades (1983–2010) of contaminant trends in East Greenland polar bears (*Ursus maritimus*). Part 2: Brominated flame retardants

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A B S T R A C T

Brominated flame retardants were determined in adipose tissues from 294 polar bears (*Ursus maritimus*) sampled in East Greenland in 23 of the 28 years between 1983 and 2010. Significant linear increases were found for sum polybrominated diphenyl ether (ΣPBDE), BDE100, BDE153, and hexabromocyclododecane (HBCD). Average increases of 5.0% per year (range: 2.9–7.6%/year) were found for the subadult polar bears. BDE47 and BDE99 concentrations did not show a significant linear trend over time, but rather a significant non-linear trend peaking between 2000 and 2004. The average ΣPBDE concentrations increased 2.3 fold from 25.0 ng/g lw (95% C.I.: 15.3–34.7 ng/g lw) in 1983–1986 to 58.5 ng/g lw (95% C.I.: 43.6–73.4 ng/g lw) in 2006–2010. Similar but fewer statistically significant trends were found for adult females and adult males likely due to smaller sample size and years. Analyses of δ^{15}N and δ^{13}C stable isotopes in hair revealed no clear linear temporal trends in trophic level or carbon source, respectively, and non-linear trends differed among sex and age groups. These increasing concentrations of organobromine contaminants contribute to complex organohalogen mixture, already causing health effects to the East Greenland polar bears.

1. Introduction

Polar bears (*Ursus maritimus*) are considered a key species for identifying novel, often lipophilic organohalogen contaminants (OHCs), such as brominated flame retardants (BFRs), within arctic marine ecosystems due to their high-fat diet and top trophic position in Arctic food webs (Letcher et al., 2010; Norstrom et al., 1998). Polar bears feed primarily on marine mammals, mainly on ringed seal (*Phoca hispida*), with more minor dietary items including bearded seals (*Erignathus barbatus*), harp seals (*Phoca groenlandica*), hooded seals (*Crystophora cristata*), white whales (*Delphinapterus leucas*), narwhals (*Monodon monoceros*), and walrus (*Odobenus rosmarus*) (Derocher et al., 2004; Smith, 1980; Stirling and Archibald, 1977). The presence of novel or emerging OHCs in polar bears in these remote areas serves as an important indicator of their persistence, long-range transport and bioaccumulation potential.

Brominated flame retardants (BFRs), including polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are chemicals used in materials to make them more fire-resistant. Typical uses are in polyurethane foam, plastics used in electrics and electronic equipment including wire coating and printed circuit boards. BFRs are also used in expanded and extruded plastics as well as in various textiles including curtains, furniture coverings and carpets (de Wit et al., 2010). Many countries have legislated fire safety standards, leading to increased use of flame retardants (de Wit et al., 2010).

A large number of negative effects have been documented in polar bears primary from East Greenland and Svalbard where OHCs loads are highest (Letcher et al., 2010; Sonne, 2010). Potential toxic effects of certain PBDEs include neurotoxicity, as well as impacts on the thyroid hormone system and on sex hormones and reproduction. Likewise there are indications that HBCD exposure may affect the liver and thyroid hormone system, as well as cause neurobehavioral alterations (Letcher et al., 2010; Sonne, 2010). Given the growing body of evidence linking OHC exposures and biomarkers of deleterious effects, it is important to determine how OHC concentrations in polar bears are changing over time.

Global and regional conventions have been developed with the goal of reducing or even eliminating emissions of OHCs. The Stockholm Convention on Persistent Organic Pollutants (POPs) states

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that chemicals may qualify as POPs if they are found far from sources and thereby show evidence of long range transport (AMAP, 1998; de Wit et al., 2010). This has made the Arctic and the polar bear an important indicator for assessing persistence and bioaccumulation properties of these contaminants. Several BFRs have been deemed to have characteristics that qualify them as POPs according to the Stockholm Convention (AMAP, 1998; de Wit et al., 2010).

In a recent review, de Wit et al. (2010) documented that PBDEs and HBCD are ubiquitous in the Arctic, in both abiotic and biotic samples. This review also reported that PBDEs and HBCD spatial trends in marine mammals (and seabirds) are similar to those seen previously for polychlorinated biphenyls (PCBs), with highest concentrations found in East Greenland and Svalbard. These patterns made the authors conclude that western Europe and eastern North America constitute the main sources of these contaminants. De Wit et al. (2010) also reported the temporal trends of tetra- to hepta-brominated PBDEs and HBCD in the Arctic and found increasing concentrations or a tendency to leveling off depending on the matrix and location. However, despite a large number of studies reviewed no uniform picture emerged. Here, we examine longer-term and retrospective temporal trends of concentrations of brominated flame retardants (BFRs) in adipose tissue of 294 polar bears from the East Greenland subpopulation that were sampled between 1983 and 2010. A parallel study is presented in this issue on a large number of legacy OHCs from the same group of polar bears from East Greenland (Dietz et al., 2012). In the current study, we also examined stable isotopes (SI) of nitrogen and carbon to evaluate whether changes in diet and food web structure have occurred over this same time period, given that a number of studies have documented links between (SI) and contaminant loads (e.g. Dietz et al., 2009, 2011; McKinney et al., 2009, 2010). The present study together with the study by Dietz et al. (2008, 2011, 2012) represent the longest Arctic time series for contaminants to date, with 23 years of data sampled over a duration of 28 years.

2. Materials and methods

2.1. Sample details

A total of 294 polar bears were sampled from 1983 to 2010 in the Ittoqqortoormiit/Scoresby Sound region, East Greenland between ca. 69° to ca. 74° N (Supplemental Information Table S1). Adipose samples were collected during native subsistence hunts. After sampling and during shipment, samples were kept frozen. At the NERI Specimen Bank, samples were stored at −20 °C until further processing.

2.2. Age determination

Ages were determined by counting annual growth layer groups (GLGs) in the cementum of the lower right I3 using established methods (e.g. Dietz et al., 2004). Age classifications used were adult males ≥6 years of age and adult females ≥5 year; and the remaining were categorised as subadults following information from Rosing-Asvid et al. (2002). The subadults of both sexes were pooled for the statistical analyses of OHCs (Dietz et al., 2004).

2.3. Organohalogen contaminant analysis

Samples (n = 204) collected 1983–1996, 2003, 2004, 2006, 2007, 2008, 2009, and 2010 were analysed for PBDEs/BFRs based on methods previously described by Letcher et al. (2009) and McKinney et al. (2009, 2010, 2011a). Samples (n = 90) collected in 1999, 2000, and 2001 were analyzed for PBDEs/BFRs as reported in Muir et al. (2006). Details on preparation, chemical analysis, quality assurance and control are provided in the Supplemental Information.

2.4. Stable C and N isotope ratio analyses

All stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope determinations of polar bear hair samples were carried out in the Environmental Isotope Laboratory (EIL) at the University of Waterloo (Waterloo, ON, Canada). When enough hair material was available, stable isotope ratios (SIR) were analyzed to evaluate whether changes in trophic levels had occurred over time. Hair was available for 274 out of the 294 bears (subadult: n = 146; adult female: n = 61 and adult male: n = 67), covering the period from 1983 to 2010.

Samples for stable isotope analyses were prepared by first rinsing hair with 3:1 chloroform:methanol to remove lipid and water contamination. Grinding 20–40 mg of hair to a powder was performed according to Hobson and Sease (1998). Hair samples were run for $\delta^{15}N$ and $\delta^{13}C$ on a Delta Plus Continuous Flow Stable Isotope Ratio Mass Spectrometer (Thermo Finnigan/Bremen-Germany) coupled to a Carlo Erba Elemental Analyser (CHNS-O EA1108—Italy). Results were corrected using nitrogen standards IAEA-N1 and IAEA-N2 (both Ammonium Sulphate) and carbon standards IAEA-CH6 (sugar), EIL-72 (cellulose) and EIL-32 (graphite). Standards were placed throughout each run at a range of weights to allow for an additional linearity correction due to machine fluctuations or samples of varying signal peak areas, when necessary. The error for clean ball-milled standard material was ±0.2‰ for $\delta^{13}C$ and ±0.3‰ for $\delta^{15}N$.

2.5. Data analysis

For detailed data presentation, 7 of the most predominant flame retardants and their major congeners were selected among 14 BFRs (Table 1). Leaving out the more minor contaminants was justified by the observed significant autocorrelation between most of the analyzed groups of contaminants. The consecutive temporal trend analyses of these contaminants and SI followed the ICES (International Council for the Exploration of the Sea) temporal trend assessment procedure (Nicholson et al., 1998). In short, the log-median flame retardant concentration was used as annual contaminant index value. The total variation over time of the flame retardants and SIs was partitioned into a linear and a non-linear component. Linear regression analysis was applied to describe the linear component. A LOESS smoother (locally weighted scatter plot using a weighted quadratic least squares regression smoothing) with a window width of 7 years was applied to describe the non-linear component. The linear and non-linear components were tested by means of an analysis of variance (ANOVA). The theory behind the method is described in detail by Fryer and Nicholson (1999, 2002). Statistical analyses were performed using version 2.3.1 of the open source software R® (R development core team, 2010).

3. Results and discussion

Brominated flame retardants were analyzed in adipose tissue from 294 polar bears sampled in Central East Greenland between 1983 and 2010 (Supplemental Information Table S1). The majority of the samples (n = 156) were obtained from subadult bears during a 23 year period (1983–2010), whereas samples from 61 adult females were obtained in 19 years during a 27 year period (1984–2010) and 77 males in 16 years during a 22 year period (1989–2010; Supplemental Information Table S1).

3.1. Overall trend patterns

Significant linear increases were found for ΣPBDE, BDE100, BDE153 and HBCD, with average increases of 5.0%/year (range: 2.9 to 7.6%/year) among the subadult polar bears. Concentrations of BDE47, BDE99, and ΣPBDE also showed a significant non-linear

Table 1
Temporal trends of brominated flame retardant concentrations in three polar bear groups sampled in central East Greenland between 1983 and 2010. Significant trends are highlighted in bold.

Animal group	Subadult (1983–2010)				Adult female (1984–2010)				Adult male (1989–2010)			
	Annual change (%)	P (linear model)	P (non-linear model)	n (years)	Annual change (%)	P (linear model)	P (non-linear model)	n (years)	Annual change (%)	P (linear model)	P (non-linear model)	n (years)
Contaminants												
BB-153	−2.0	0.07	0.32	17	−2.2	0.30	0.91	12	−1.1	0.42	0.59	11
ΣPBDE	**3.1**	**<0.01**	**<0.01**	23	**2.0**	**0.05**	**<0.01**	19	**4.2**	**0.02**	**0.06**	16
BDE-47	1.6	0.14	**<0.01**	22	−1.2	0.45	**0.02**	19	2.1	0.57	**0.21**	16
BDE-100	**2.9**	**<0.01**	0.22	23	3.7	0.08	0.75	19	**6.4**	**<0.01**	0.90	15
BDE-99	1.5	0.16	**<0.01**	22	0.3	0.30	0.10	17	2.0	0.33	0.19	15
BDE-153	**6.2**	**<0.01**	0.12	23	**6.1**	**<0.01**	0.17	19	**5.2**	**<0.01**	0.41	16
HBCD	**7.6**	**<0.01**	0.27	13	**5.3**	**<0.01**	**<0.01**	13	**6.7**	**<0.01**	0.26	12
Mean significant trends	**5.0**	**4/7**	**3/7**		**4.5**	**3/7**	**3/7**		**5.6**	**4/7**	**2/7**	
Min significant trends	**2.9**				**2.0**				**4.2**			
Max significant trends	**7.6**				**6.1**				**6.7**			
δ-N15	−0.1	0.26	**0.01**	21	0.4	0.36	0.56	15	0.1	0.23	0.36	14
δ-C13	0.1	0.11	**0.03**	21	0.0	0.88	**0.03**	15	0.0	0.66	**0.03**	14

trend, indicating that their concentrations peaked during the years 2000–2004. Overall the average ∑PBDE concentrations increased 2.3 fold from 25.0 ng/g lw (95% C.I.: 15.3–34.7 ng/g lw) in 1983–1986 to 58.5 ng/g lw (95% C.I.: 43.6–73.4 ng/g lw) within the period 2006–2010 (Supplemental Information Table S2). Similar linear trends were found for adult females and adult males, though fewer significant trends were found in adult females and the fewest in adult males (Supplemental Information Table S2). Variation in the number of significant contaminant trends likely reflected differences in sample sizes and time periods represented for each group. In addition, it seems that the subadult bears are better indicators of the contaminant trends, perhaps because subadult bears have accumulated their contaminant burdens over a shorter time period relative to adults. In addition, adult bears may have a wider variation in their diet than younger bears. Overall these polar bears documented temporal trends which reflect the effect of international regulations and conventions on long range trans-boundary transport of legacy OHC contaminants and brominated flame retardants.

In a corresponding investigation of the same polar bear dataset, legacy OHCs were also analyzed (Dietz et al., 2012). Most legacy OHCs showed declining trends, in contrast to the BFRs. Nineteen legacy contaminant classes and major congeners underwent temporal trend analyses. Of these, 18 showed significant declines of on average −4.4% per year (range: −2.0 to −10.8 %/year) in subadult polar bears. This decline is an effect of banning of these legacy contaminants during the 1970s and the following two decades (AMAP, 1998).

3.2. Specific temporal trends

3.2.1. Brominated flame retardants (BFR)

3.2.1.1. BB-153. Decreasing trends for the BB153 ranged between −1.1 and −2.2%/year depending on age and sex group. The polybrominated biphenyl flame retardants, PBBs, consist primarily of hexa-, octa- and decabromo-biphenyls and have been used as additive flame retardants since the 1970s (de Wit et al., 2010). PBBs show a different time trend than the other BFRs, as hexaBB was banned earlier due to an accidental mixing of a hexaBB into cattle feed in Michigan, USA, in 1973. OctaBB and decaBB production continued in the US until 1979, but in France it was used until 2000 (Alaee et al., 2003). Few data are available in the literature on temporal trends of BB153. Except for a peak in 1987 (sampling years of only 1976, 1987 and 2004), concentrations of BDE154/BB153 in ivory gull eggs from Seymour Island in the Canadian Arctic showed no major changes between 1976 and 2004 (Braune et al., 2007).

3.2.1.2. ΣPBDE, PBDE congeners and HBCD. A significant temporal increase averaging +4.1%/year (range: +2.9 to +6.2%/year) was observed for ∑PBDE, BDE100 and BDE153 in subadult polar bears (Table 1; Fig.1a). The significant linear increasing trends were similar in adult female bears (mean: +4.1; range: +2.0 to +6.1%/year) and adult males (mean: +5.3; range: +4.2 to +6.4%/year). For subadult polar bears, ∑PBDE and BDE99 peaked in 2004, that is, increases of +7.4% and +7.7%/year occurred pre-2004 followed by dramatic declines of −18.0% ($p = 0.117$) and −30.5% ($p = 0.020$), respectively (Data not in table; Fig. 1b). For BDE47, a significant increase of +6.1%/year peaked in 2001, after which a non-significant decline of −12.8%/year ($p = 0.0987$) was observed in the subadult bears. This was one year after the world production of BDE47 peaked according to Alcock et al. (2003), indicating a surprisingly fast response of the bear concentrations to emissions changes. Concentrations of BDE100, BDE153 and HBCD showed no signs of decline during the period investigated. Only adult females showed comparable PBDE trends to those observed in the subadults. ∑PBDE in adult females showed significantly steeper increases than the overall increase, namely +8.0%/year. For BDE99, the increase of +10.6%/year in the adult females up to 2004 was not significant ($p = 0.065$). Declines in the adult female concentrations post-2004 were comparable to subadult bears, namely −16.9% ($p = 0.139$) and −42.6% ($p = 0.022$), respectively, for ∑PBDE and BDE99. For BDE47, a significant ($p < 0.001$) increase of +9.4%/year peaked in 2000, after which a significant decline of −19.5%/year ($p = 0.043$) was observed in the adult female bears.

BFR values have previously only been published from East Greenland covering the period 1999–2001, which did not allow for any temporal trend studies until now (Dietz et al., 2007). The temporal trend POP review by Rigét et al. (2010) did not include BFRs in polar bears or any other species either. Previous documented temporal trends in BFR concentrations varied among species, subpopulations and time periods investigated (de Wit et al., 2010). Due to low concentrations (<LOD), there was only data available on concetrations of two congeners (BDE47 and BDE99) for the East Greenland ringed seals dataset published by Vorkamp et al. (2011) versus the four PBDE congeners presented here for the polar bears. These ringed seals were monitored between 1986 and 2008 and showed a non-significant increase in BDE47 concentrations of +0.7%/year for subadults and declines of −2.5%/year for adults. For BDE99, linear trends were significant showing declines of −2.9%/year ($p < 0.01$) for subadults and −7.6%/year ($p = 0.02$) for adult seals (Vorkamp et al., 2011). Only the adult seals showed a significant decline for ΣPBDE of −3.1%/year ($p = 0.04$). The lack of significant increasing trends among the seals, as found for the polar bears, are probably linked to the few data points ($n = 1$ or 2) prior to 1999, whereas the period between 1999 and 2008 was strongly represented in 7 years of data (Vorkamp et al., 2011).

McKinney et al. (2010) was the first to report on the temporal changes in PBDE concentrations and patterns in polar bears, specifically for the western Hudson Bay population. In this longer-term study on western Hudson Bay polar bears (over the period of 1991–2007), increasing ΣPBDE levels (+13%/year) were found for BDE47, BDE99, BDE100 and BDE153. However, lower PBDE levels in 2007 relative to 2003 (except for BDE47) may have indicated recently stabilizing or declining trends (McKinney et al., 2010). This stabilization is likely related to the late-2004 North American phase-out of pentaBDE and octaBDE commercial formulations (de Wit et al., 2010). Furthermore, McKinney et al. (2011a) also concluded that ΣPBDE levels had declined in 2005–2008 relative to 1996–2002 (Muir et al., 2006) in polar bears from 7 of 9 subpopulations, including bears from East Greenland. The exception was for bears from western Hudson Bay and Davis Strait, where levels appeared to have increased in 2005–2008 relative to 1996–2002. As reported in McKinney et al. (2010), temporal change assessments were not possible for southern Hudson Bay bears as data was only available for the period from 2005 to 2008.

In a recent review article (AANDC, in press), an assessment of BFRs in Canadian Arctic ringed seals was presented. Levels of ΣPBDE continued to increase significantly in the southern Beaufort Sea at an annual rate of +9.2% between 1992 and 2010 and a very steep annual increase of +22% was found in East Baffin samples between 1999 and 2006. However, in Hudson Bay ΣPBDE declined in ringed seals (−7.0%/year; 2002–2010), though this trend was not significant.

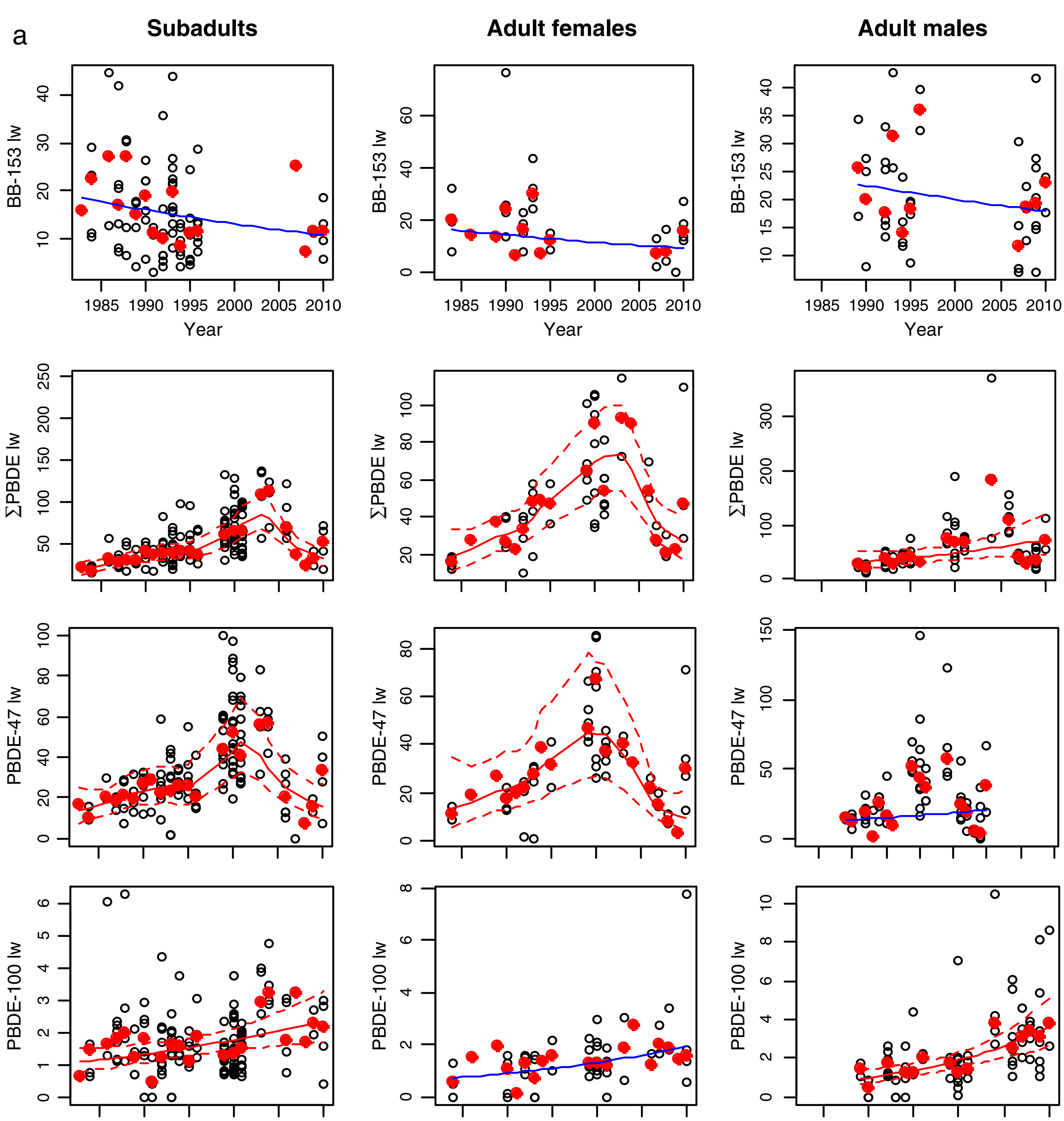

Fig. 1. Log-linear temporal trend of brominated flame retardants BB153, ΣPBDE, BDE47, BDE100, BDE99, BDE153 and HBCD in a retrospective time trend study on subadult, adult female and adult male polar bears from East Greenland. The filled red dots are median values. Red lines indicate significant trends and dotted line the 95% confidence intervals. Blue lines indicate non-significant trends. Trend and significance levels are provided in Table 1. All units of the graphs above are given in ng/g lw.

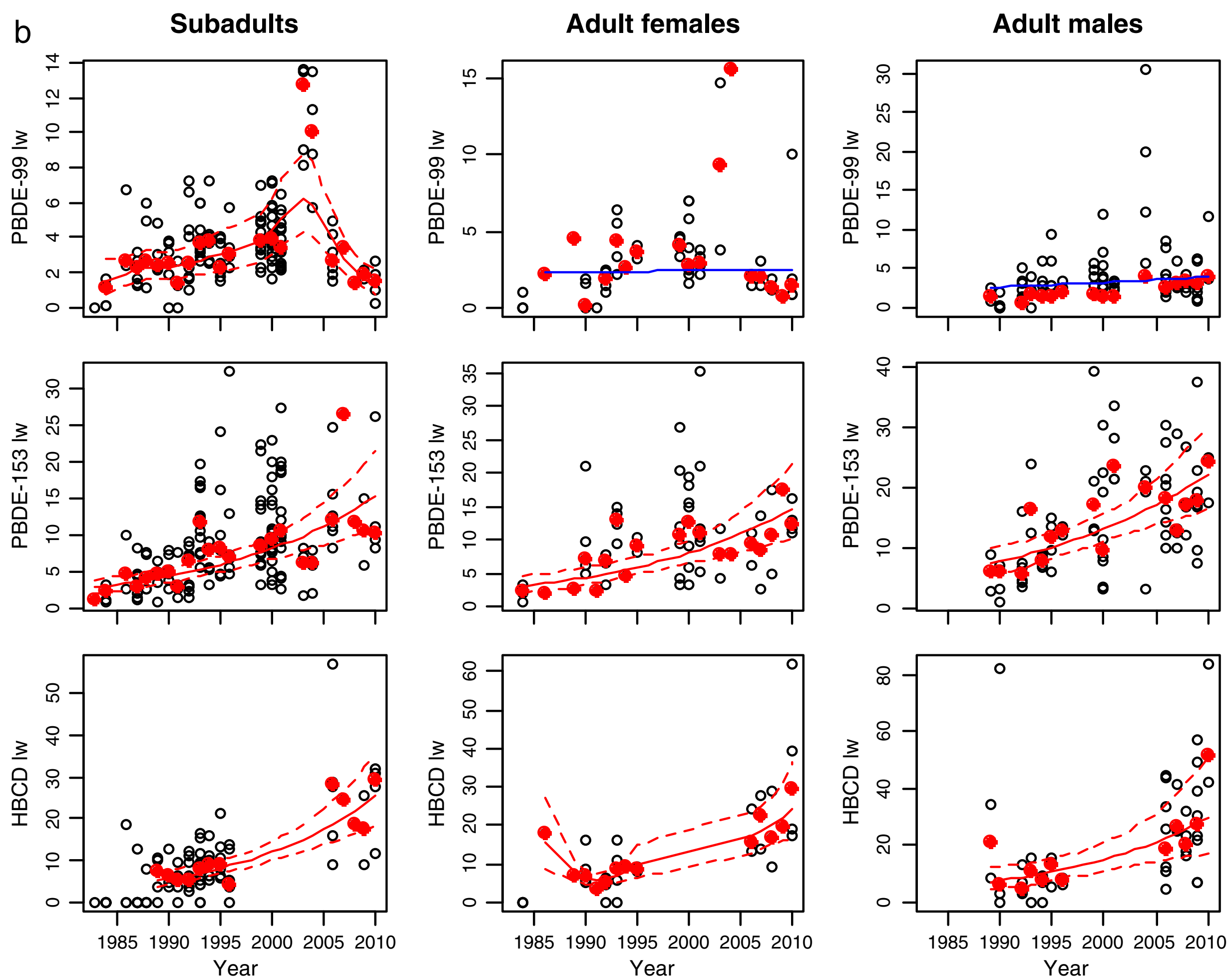

Fig. 1 (*continued*).

ΣPBDE appeared to reach maximum levels in 2005 and 2006 for the Lancaster Sound ringed seals, however, the overall trend from this area within the period 1972–2010 was a significant increase of +7.4%/year. Retrospective monitoring by Braune (2008) showed that concentrations of ΣPBDE in eggs of thick-billed murres and northern fulmars from Prince Leopold Island steadily increased from 1975 to 2003, after which levels started to decrease, driven largely by BDE47. These two Canadian time series with peaking BDE47 and ΣPBDE between 2003 and 2006 support our finding from polar bears in East Greenland of these PBDEs peaking between 2000 and 2004. Law et al. (2010) documented a highly statistically significant ($p<0.001$) decline in Σ_9PBDE concentrations in the blubber of 415 harbour porpoises (*Phocoena phocoena*) sampled in U.K. waters during the period 1992–2008. It was suggested from this data that the Σ_9PBDE concentration peaked around 1998, which declined overall by −67.6% as of 2008.

Significant temporally increasing HBCD trends were found for subadult, adult female and adult male polar bears with +7.6%, +5.3% and +6.7% increases per year respectively (Table 2). However, McKinney et al. (2011a) reported a decline in total-(α)-HBCD levels in polar bears (adipose tissue) collected in 2005–2008 compared to 1996–2002 (Muir et al., 2006) for East Greenland, Alaska, and Svalbard. Vorkamp et al. (2011) reported a significant ($p<0.01$) log-linear increase in HBCD levels of +6.1%/year for East Greenland subadult ringed seals up to 2008. In a recent update adding two more years of data this figure was updated to +6.4%/year for subadult ringed seals up to 2010 (Vorkamp et al., 2012). This trend was within the range of the 3 East Greenland polar bear age/sex groups investigated here. Our HBCD dataset does not show the resolution documented for UK harbour porpoises, where an increase was seen until 2004 followed by a decrease (Law et al., 2008).

3.2.1.3. Stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) as dietary tracers. It has been demonstrated that the abundances of naturally occurring stable isotopes of carbon ($^{13}C/^{12}C$) and particularly nitrogen ($^{15}N/^{14}N$) can provide food web and trophic level information. For instance, $\delta^{15}N$ exhibits a predictable step-wise enrichment between prey and consumer tissues (e.g., Hobson and Welch, 1992). A measure of quantitative diet and food web structure change is highly relevant to the interpretation of contaminant trends, e.g., for baseline concentrations as well as anthropogenic versus natural contributions (e.g. Dietz et al., 2009, 2011; McKinney et al., 2009, 2010). In the present study, $\delta^{15}N$ values showed only a significant non-linear temporal trend for subadult bears. Trophic level, as represented by $\delta^{15}N$, was declining prior to 1990, and subsequently exhibited a moderate increase (Table 1; Fig. 2). We decided not to correct the contaminant time trend data for $\delta^{15}N$ variation at this stage due to the lack of trends in the two adult groups and lack of pattern mirroring the contaminant trends. The $\delta^{13}C$ values on the other hand showed a significant ($p=0.03$) non-linear temporal trend for all three groups of analyzed polar bears. A decline (note the reversed y-axis-$\delta^{13}C$ in Fig. 2) of $\delta^{13}C$ prior to 1990–1991 was proceeded by a moderate increase, then a more or less stable period until 2010 for subadults and adult females. A more or less opposite pattern was observed for the adult males with a delay of about 5 years. Overall, the annual percent change was in the range of 0.0–0.1%/year. In contrast to $\delta^{15}N$, $\delta^{13}C$ values vary little along the food chain and are mainly used

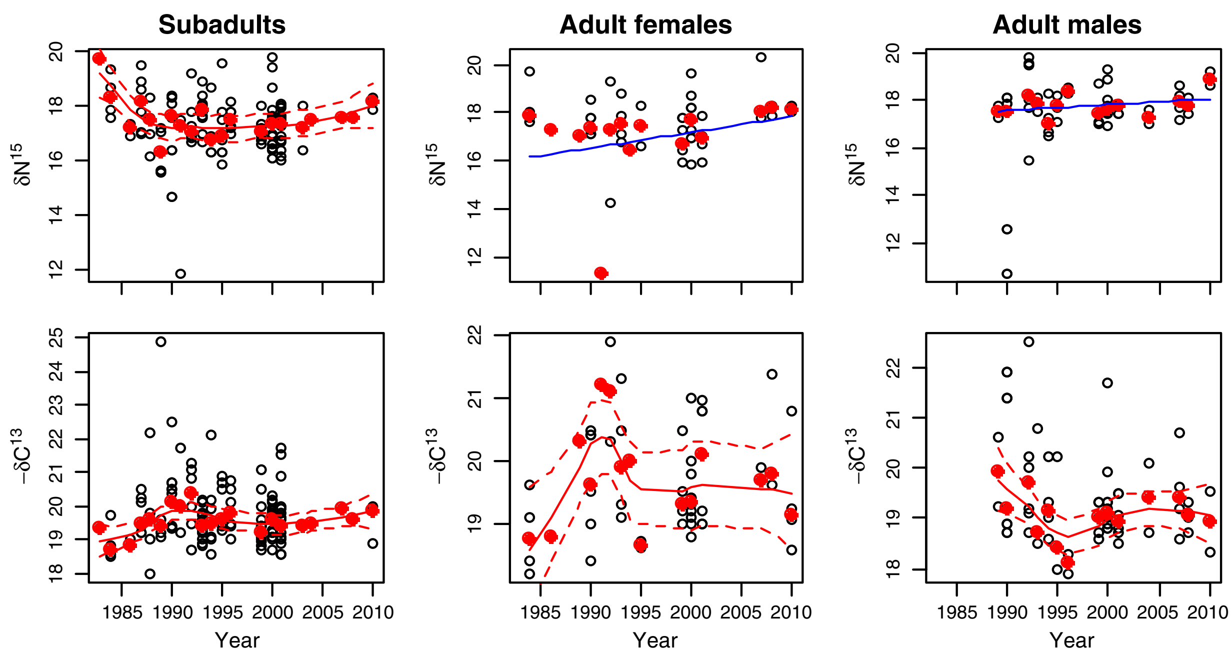

Fig. 2. Log-linear temporal trend of $\delta^{15}N$ and $\delta^{13}C$ in a retrospective time trend study on subadult, adult female and adult male polar bears from East Greenland. The filled dots are median values. Lines accompanied by dotted lines showing the 95% confidence intervals (CI) indicate significant trends ($p \leq 0.05$). Lines without CI indicate non-significant trends. Trend and significance levels are provided in Table 1.

to determine primary carbon sources in a trophic network (DeNiro and Epstein, 1978). In the marine environment, $\delta^{13}C$ values can also indicate inshore vs. offshore, or pelagic vs. benthic, contributions to food intake (France, 1995). Changes in $\delta^{13}C$ could hence reflect the spatial and temporal extent of ice along the East Greenland shore and hence the distribution of the polar bears proximity to land. To what extent the observed changes in $\delta^{13}C$ can be linked to climate change parameters remains to be elucidated. Yet, again the lack of trends mirroring the contaminant trends made us decide not to correct the contaminant time trend data for $\delta^{13}C$ in this study. We are currently analyzing fatty acids as an additional indicator of trophic ecology, and plan to investigate food web linkages to the contaminant trends in detail using a multiple tracer approach. This method has previously been conducted for geographical trends in polar bears (McKinney et al., 2011b).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.envint.2012.09.008.

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