Temporal trends of persistent organic pollutants in Arctic marine and freshwater biota

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Keywords: Environmental monitoring, POPs, temporal trends, Arctic, biota

Abstract

More than 1000 time-series of persistent organic pollutants (POPs) in Arctic biota from marine and freshwater ecosystems some extending back to the beginning of 1980s were analyzed using a robust statistical method. The Arctic area encompassed extended from Alaska, USA in the west to northern Scandinavian in the east, with data gaps for Arctic Russia and Arctic Finland. The aim was to investigate whether temporal trends for different animal groups and matrices were consistent across a larger geographical area. In general, legacy POPs showed decreasing concentrations over the last two to three decades, which were most pronounced for α-HCH and least pronounced for HCB and β-HCH. Few time-series of legacy POPs showed increasing trends and only at sites suspected to be influenced by local source. The brominated flame retardant congener BDE-47 showed a typical trend of increasing concentration up to approximately the mid-2000s followed by a decreasing concentration. A similar trend was found for perfluorooctane sulfonic acid (PFOS). These trends are likely related to the relatively

recent introduction of national and international controls of hexa- and hepta-BDE congeners and the voluntary phase-out of PFOS production in the USA in 2000. Hexabromocyclododecane (HBCDD) was the only compound in this study showing a consistent increasing trend. Only 12 % of the long-term time-series were able to detect a 5 % annual change with a statistical power of 80 % at $\alpha < 0.05$. The remaining 88 % of time-series need additional years of data collection before fulfilling these statistical requirements. In the case of the organochlorine long-term time-series, 45 % of these would require more than 20 years monitoring before this requirement would be fulfilled.

1. Introduction

Persistent organic pollutants (POPs) are chemicals that have a long lifetime in the environment and due to their physical-chemical properties, they are transported over long distances. POPs enter food-webs and accumulate, and in some cases biomagnify in wildlife and humans. Several global and regional conventions were developed with the goal of eliminating or reducing emissions of POPs. The Stockholm Convention on POPs initially addressed twelve priority POPs and since then these have been extended to 28 POPs as of 2017 (http://chm.pops.int). Despite the fact that several of these POPs were banned in the 1970's and 1980's and others have been restricted, they are still found in the environment at levels that may cause adverse effects to the health of top predators in Arctic food chains (Letcher et al., 2010). Humans living in the Arctic and consuming significant amounts of high trophic traditional food are exposed to legacy POPs, which may lead to adverse health effects (AMAP, 2009).

Temporal trend studies are an important means of assessing the fate of contaminants in ecosystems. They can provide a first warning that potentially harmful compounds may be increasing in the environment, e.g. in biota regarded as indicator organisms. Temporal trend studies may also indicate whether regulatory actions aimed at reducing harmful chemicals in the environment are proving successful, or whether environmental levels are approaching or exceeding threshold values for biological and possibly toxic effects. Several Arctic countries perform POP monitoring in biota, focussing on freshwater and marine ecosystems, resulting in time series of varying statistical power. Statistical power is an important consideration in relation to temporal trend monitoring. The power of a temporal trend represents the statistical probability of detecting a change of a given magnitude when this change actually occurs. It is desirable that monitoring data series have sufficient statistical power to minimise false negatives, i.e. the risk of incorrectly concluding that no change has occurred.

Rigét et al., (2010) assessed temporal trends of POPs in Arctic biota based on the time-series available up until 2008 and in the context of the Arctic Monitoring and Assessment Programme (AMAP). A large number of new time-series data has become available since then and additional years have been added to the time-series included in Rigét et al., (2010). Therefore, it was expected that this update would lead to a more robust assessment than the previous one. The objective of this study was to analyze trends for POPs in all time-series available from the Arctic, including an evaluation of their statistical power.

2. Datasets and statistical analyses

Time-series of POPs were available from seven Arctic countries for a total of 64 location-species-tissue combinations. Figure 1 shows the locations, together with the species or species group monitored. No series in biota are currently available for the Arctic areas of Russia and Finland. Time-series were available for marine mammals, seabirds, marine and freshwater fish and blue mussels.

Asmund et al. (2004) focused early on the quality assurance/quality control (QA/QC) of the Danish and Canadian laboratories, which were involved in the Greenlandic AMAP trend program. AMAP has worked towards harmonized programs with respect to methodologies and QA/QC in order to ensure the quality and credibility of AMAP assessments. For example, AMAP has established guidelines that cover all aspects of data generation from sample collection, handling and processing, to analysis, and data management, and that must be followed by the laboratories contributing to AMAP assessments. The laboratories responsible for the POP analyses included in this study participate in a number of QA/QC programs including the AMAP/NCP inter-laboratory studies (e.g. Tkatcheva et al. 2013), the QUASIMEME laboratory performance testing scheme (www.quasimeme.org), and equivalent QA/QC programs run by NOAA/NIST. All laboratories have established common internal QA/QC procedures and measures such as the use of internal and certified reference materials, analyses of blank and duplicates etc. Each individual time-series has been analysed by the same laboratory with the same method over several years.

Figure 1. Map of locations with long-term time-series. Symbols indicate animal group. Included are Air monitoring stations. From AMAP (2016).

Time-series were separated into long-term time-series starting before the year 2000 and short-term time-series starting in or after the year 2000. Several of the short-time time-series were derived by deleting data from years before 2000 of the long-term time-series. In total, 1074 long-term time-series and 735 short-term time-series were available covering the following POPs: Polychlorinated biphenyls

(PCBs) congeners, dichlorodiphenyltrichloroethane (DDT) and its transformation products, hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and pentachlorobenzene (PeCB), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and pentachlorobenzene (PeCB), chlordane-related pesticides (CHL) and heptachlor, dieldrin, mirex, octachlorostyrene (OCS), toxaphene, polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and perfluoroalkyl substances (PFASs). Octachlorostyrene (OCS) was included although not included in the Stockholm Convention because time-series were available and only few time-series study has been published. The distribution of available time-series by country, species group and time-series type are shown in Table 1.

Table 1. Number of long-term time-series (starting before year 2000) and short-term time-series (starting in or after year 2000) by country and species group.

Time series numbers by country:

Country	Long-term time-series	Short-time time-series
United States (Alaska)	186	17
Canada	323	200
Greenland	184	163
Faroe Islands	102	115
Iceland	109	137
Norway	155	89
Sweden	15	14
Total	1074	735

Time series numbers by species group:

Species group	Long-term time-series	Short-term time-series
Blue mussels	145	126
Freshwater fish	197	63
Marine fish	112	134
Seabirds	114	96
Marine mammals	506	316
Total	1074	735

Datasets were treated as in previous assessments of temporal trends of contaminants in Arctic biota (Rigét et al., 2010; AMAP, 2014; 2016). Only time-series with six or more years of data were included. Generally, time-series were considered inappropriate for trend analyses if three or more years had annual medians that were less than the reported detection limit. However, time-series were included if these years were concentrated in the end of the time-series, indicating a decreasing trend or in the beginning, indicating an increasing trend. In these cases, half of the detection limit was used to represent the actual annual medians.

A statistically robust method was applied to the time-series data. Covariates such as age, sex and lipid content were treated as recommended by data originators such as selecting a subset of similar characteristics e.g. sex and/or age. All time-series were treated with the same statistical method and therefore highly comparable results have been generated.

The statistical analyses were performed using the software package PIA (Plot and Image Analyses) (Bignert, 2013). Briefly, median concentrations were used as the annual index values to minimise the influence of outliers and values below detection limits. The method tests for the presence of a log-linear trend and/or non-linear trend by separating the total variance over time into a log-linear component and a non-linear component (Nicholson et al., 1998). The log-linear trend was tested by log-linear regression. A 3-point running smoother was applied to describe the non-linear trend component and

tested by mean of an analysis of variance (ANOVA). In general, $\alpha < 0.05$ was applied. The results of the trend analyses were classified into six classes as follows (AMAP, 2016):

- ***Increasing***, a statistically significant increasing log-linear trend.
- ***Increasing with non-linear trend component***, both an increasing log-linear and the non-linear trend components are statistically significant.
- ***Decreasing***, a statistically significant decreasing log-linear trend.
- ***Decreasing with non-linear trend component***, both a decreasing log-linear and the non-linear trend components are statistically significant.
- ***Non-linear component***, a statistically significant non-linear (fluctuating) trend with no significant increasing or decreasing trend.
- ***No trend***. The time-series did not exhibit a statistically significant trend.

Statistical power is defined as the probability of rejecting the null hypotheses in a case where a temporal trend exists, and thereby accepting the alternative hypotheses that a temporal trend exists (Cohen, 1977). For time-series, this describes the probability to detect a temporal trend, when the trend is in fact real.

The determination of statistical power of the time-series followed the method described by Fryer and Nicholson (1993). Two measures of power were estimated: 1) the number of years required to detect a log-linear trend of a 5 % annual change with 80 % power and a significance level $\alpha < 0.05$ with a one-sided test. 2) the minimum average annual percent change over a 10-year period that can be detected with 80 % power, $\alpha < 0.05$ and a one-sided test. The two measures are essentially the same but provide different information as the latter is not locked at a specific 5 % annual change.

3. Results

3.1 Polychlorinated biphenyls (PCBs)

PCBs are an industrial and by-product chemical that were produced in global total quantities of about 1.3 million tons (Breivik et al., 2007). They were listed in both Annex A (eliminate production and use) and Annex C (unintentional production) of the Stockholm Convention on POPs in 2004, but most industrial countries banned PCBs already back in the 1970s/1980s (AMAP, 1998). Nevertheless, there still are important sources of PCB emissions in the cities of Western Europe and North America due to legacy PCB use in closed systems such as electrical transformers (Diamond et al., 2010; Gasic et al., 2010).

A total of 347 long-term time-series were analyzed for concentrations of Σ_{10}PCB (CB-28, -31, -52, -101, -105, -118, -138, -153, -156 and -180) and individual congeners, mainly CB-153. Thirty-eight (38) % of Σ_{10}PCB and 34 % of CB-153 time-series showed a significant decreasing trend, and 13 % and 15 %, respectively, showed a significant decreasing trend together with a significant non-linear trend component (Figure 2). The mean annual decrease for all time-series was 3.7 % for Σ_{10}PCB and 3.8 % for CB-153. These time-series were spread over the entire Arctic area, for which data were available. Only one time-series (blue mussels, one location in Iceland) showed a significant increasing trend together

with a significant non-linear component for both Σ_{10}PCB and CB-153. However, this particular site is likely affected by a local pollution source and several other POPs (e.g. DDTs) likewise showed increasing trends (Sturludottir et al., 2013).

In seventeen long-term time-series covering all species groups (Table 1) and having analyzed eight of the same PCB congeners (CB-28, -52, -101, -105, -118, -138, -153 and -180), no significant difference was found between annual trends of individual congeners (ANOVA, p = 0.73).

For short-time time-series of Σ_{10}PCB and CB-153 fewer time series showed significant decreasing trends (20 % and 18 %, respectively) (Figure 2). The mean annual decrease was also lower (1.5 % and 2.5 %, respectively). Three time-series showed significant increasing trends of Σ_{10}PCB, one of these also for CB-153. These results indicate that the main decrease of PCBs occurred in earlier years and that the decrease has been less pronounced in recent years after 2000.

PCB time-series were available from five ringed seal (*Pusa hispida*) populations and one northern fur seal (*Callorhinus ursinus*) population covering the area from Alaska to East Greenland. The largest annual decrease of CB-153 was found in the eastern populations (East Greenland) and there was also a tendency to smaller annual decrease in the northern populations (Figure 3). However, no firm conclusion should be drawn as the length and the period covered by the time-series differed.

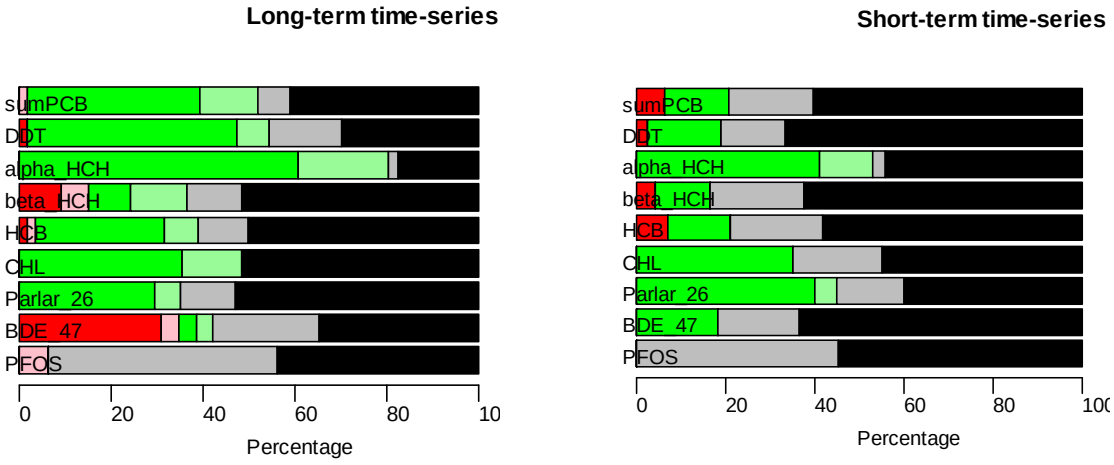
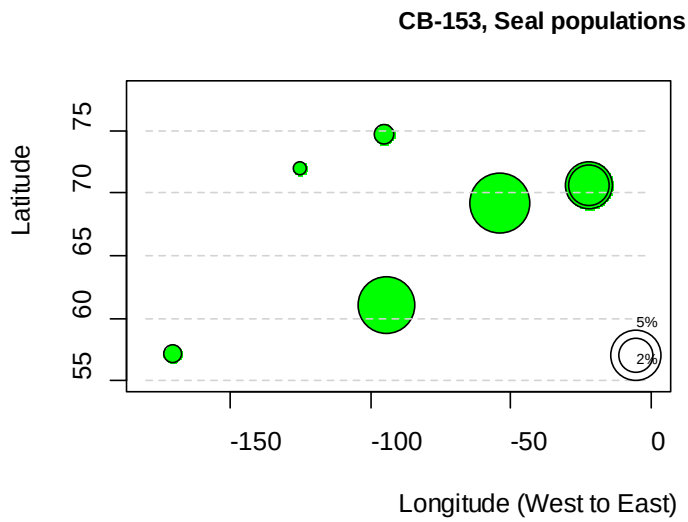


Figure 2. Overview of the trend results for POPs in long-term time-series (left) and short-term time-series (right). The colors represent the percentage of time-series with a given trend for each contaminant. Red = increasing trend, Pink = increasing with a non-linear trend. Green = decreasing trend, Light green = decreasing with a non-linear trend, Gray = non-linear trend, Black = no trend.



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206 **Figure 3.** The relative size of the annual decrease of CB-153 in seal populations across the Arctic from
207 Alaska to East Greenland. The double ring represents the juvenile (outer circle) and the adult seals (inner
208 circle) from the same location.

209 The mean annual decrease of Σ_{10}PCB in muscle tissue of freshwater fish was higher (-8.2 %) but not
210 significantly (t-test, p = 0.15) than in muscle tissue of marine fish (-5.3 %).

211 *3.2 Dichlorodiphenyltrichloroethane (DDT) and its transformation products*

212 DDT (insecticide) was listed in Annex B (restrict production and use) of the Stockholm Convention on
213 POPs in 2004, but like for PCBs most industrial countries banned DDT already back in the 1970s/1980s
214 (AMAP, 1998). In recent years, the global annual production was approximately 3300 metric tons and
215 used to control insects that spread diseases such as malaria primarily in tropical countries
216 (UNEP/POPS/COP.8/INF/6, 2017).

Time-series of ΣDDT (*pp'*-DDE, *pp'*-DDD, *pp'*-DDT) and individual *o,p'* and *p,p'* isomers were analyzed in a total of 165 time-series mostly of ΣDDT and *p,p'*-DDE (71 %). Several time-series of *p,p'*-DDD in blue mussels (*Mytilus edulis*) and some marine fish could not be evaluated due to several years with median values below the detection limit. Forty-six (46) six % of the long-term time-series of ΣDDT showed a significant decreasing trend, while only 32 % of the *p,p'*-DDE time-series showed a significant decrease. One ΣDDT time-series showed a significant increasing trend; this was the same time-series from Iceland that also showed an increasing trend for PCBs. The significant decreasing trends and those showing no significant trends were spread over the entire area from Alaska to northern Norway.

The mean annual decrease was 4.2 % for both ΣDDT and *p,p'*-DDE. For 55 species-tissue-location combinations having time-series of both ΣDDT and *p,p'*-DDE, no significant difference in annual change was found (paired t-test, $p = 0.64$). *p,p'*-DDE is the major metabolite of DDT (Kelce et al., 1995). The ratio between *p,p'*-DDE and Σ DDT may be a rough indicator of the age of DDT residues in the environment. Figure 4 shows the trends of this ratio in selected long-term time-series. In all four time-series the ratio *p,p'*-DDE/Σ DDT increased with time, and this increase was significant in polar bear (*Ursus maritimus*), ringed seal, and pilot whale (*Globicephala melas*) (log-linear regression of annual medians, $p < 0.01$ and $p = 0.03$, respectively), but was not significant in belugas (*Delphinapterus leucas*; $p = 0.12$). Therefore, no indication of a presence of 'fresh' sources of DDT to the Arctic environment were found. This is also supported by the twelve time-series of *p,p'*-DDT that have a mean annual decrease of 10.5 %, the largest mean decrease of all of the DDT isomers considered.

A total of seventeen long-term time-series of *o,p'*-DDE, *o,p'*-DDD, *o,p'*-DDT were available from pilot whales from the Faroe Islands and beluga and northern fur seal from the Alaska. None of these showed significant trends, except one (for female and juvenile beluga from East Chukchi/Bering Sea) where levels were relatively constant up to 1998 followed by a sharp decline giving a significant non-linear trend.

The proportion of short-term time-series showing significant decreasing trends was considerably lower than that of the long-term time-series (Figure 2). The mean annual decreases of the short-term time-series were 2.4 % and 3.6 % for ΣDDT and *p,p'*-DDE, respectively.

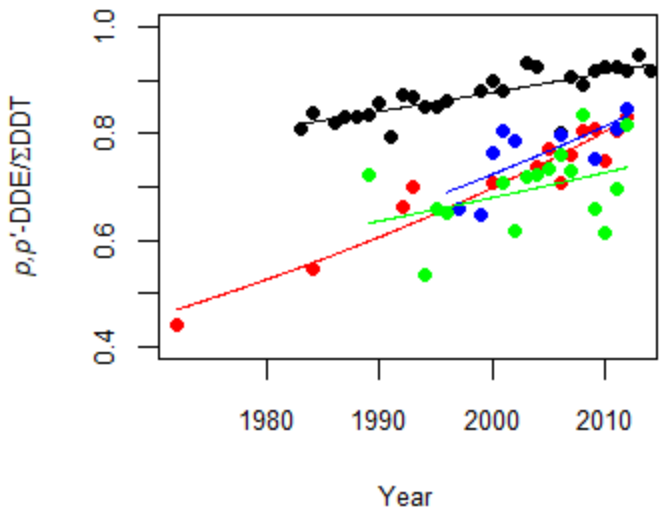

Figure 4. Trends of the ratio *p,p'*-DDE/ΣDDT in selected long-term time-series. Black – juvenile polar bears from East Greenland. Red – ringed seal from Resolute, Canada. Blue –pilot whale from Faroe Island. Green – beluga from Canada.

The mean annual decrease of ΣDDT in muscle tissue of freshwater fish was higher (-9.1 %) but not significantly (t-test, p = 0.18) than in muscle tissue of marine fish (-5.2 %).

3.3 Hexachlorocyclohexanes (HCHs)

Technical hexachlorocyclohexane (consisting of ca. 55-70 % α-HCH, 5-15 % β-HCH, 10-20 % γ-HCH (lindane) and small amounts of δ-HCH) was widely used as an insecticide prior to its phase out in a number of countries (including the USA, Canada and Nordic countries) in the late 1970s.(Li et al., 2005) There are only two lindane producing countries left (India and Romania) (Vijgen, 2006). α-, β-HCH and lindane were listed in Annex A of the Stockholm Convention in 2009, however, lindane had a specified exemption for cases where human health might be affected (http://chm.pops.int).

In total 110 long-term time-series of α-, β- and γ-HCH and 80 short-term time-series were available. However, several HCH time-series could not be evaluated because of more than three years with annual medians below detection limits. Thirty seven (80 %) of the long-term α-HCH time-series showed a significant decreasing trend or a significant decreasing trend together with a significant non-linear trend component (Figure 2). For the short-term time-series, the corresponding amount was 18 (53 %) (Figure

2). The mean annual decrease of the long-term time-series was 8.9 %, which was among the highest decrease of all the compounds (Figure 5). For the short-term time-series, the mean annual decrease was 9.9 %, showing that α-HCH has decreased after the year 2000 with a similar or higher rate than before 2000.

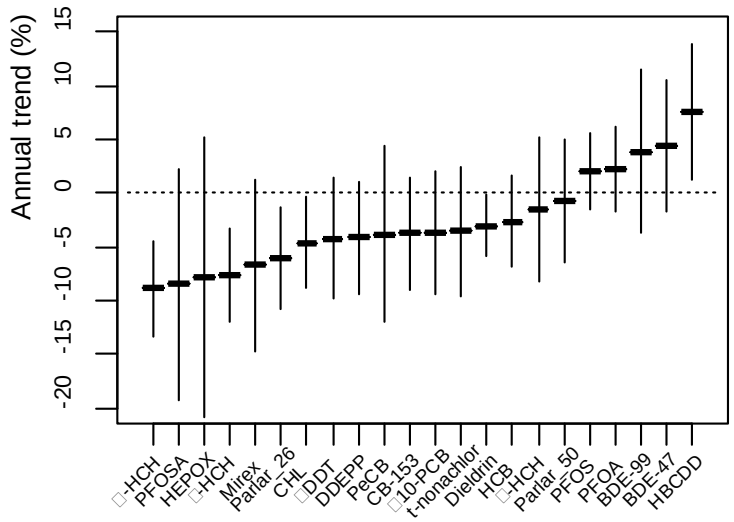

Figure 5. Mean of annual change (± SD) of POPs in the 1074 long-term Arctic time-series of compounds by increasing order.

The results for the time-series of β-HCH were quite different from those of α-HCH. More than half (64 %) of the β-HCH long-term time-series showed no significant trend or a significant non-linear trend, and both significant decreasing and increasing trends were found. In Canada, two seal populations showed significant increasing trends and time series for beluga and seabird eggs showed significant increasing trends together with a significant non-linear trend component. The mean annual decrease of 1.5 % for the long-term time-series is the lowest decrease among organochlorines, except the toxaphene congener Parlar_50 (Figure 5). Among the short-term time-series, 83 % showed no trend or a significant non-linear trend component.

The results of the γ-HCH time-series were closer to those of α-HCH than β-HCH with 70 % of the long-term time-series showing significant decreasing trend or significant decreasing trend together with a significant non-linear trend component. The corresponding percentage for the short-term time-series was 50 %. The mean annual decreases were 7.6 % and 6.2 % for long-term and short-term time-series, respectively, a somewhat smaller decrease than for α-HCH (Figure 5).

No general relationships between size of annual change in the long-term time-series and longitude were found for α, β and γ-HCH (linear regression, p = 0.30, p = 0.12 and p = 0.51, respectively). However, when considering only the seal populations, there appeared to be a tendency of lowest annual decrease of α-HCH in the two populations at highest latitude and in case of β-HCH an annual increase was found for these two populations (Figure 6).

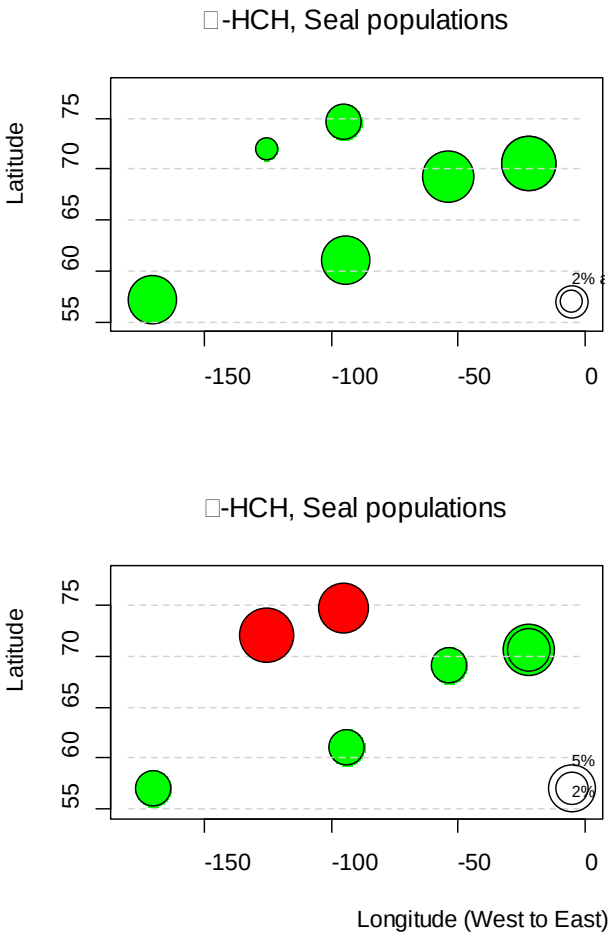

Figure 6. Annual decrease (green) and annual increase (red) in seal populations related to longitude and latitude. The size of circle represents the size of annual change. The double ring represents the juvenile (inner circle) and the adult seals (outer circle) from the same location.

3.4 Hexachlorobenzene (HCB) and pentachlorobenzene (PeCB)

HCB has had several uses in industry and agriculture (Becker et al., 2012). PeCB is not known to be manufactured for any commercial uses (Bailey et al., 2009). In the past, PeCB was one component of chlorobenzenes mixture (Bailey et al., 2009). HCB and PeCB have been listed in Annex A and Annex C of the Stockholm Convention (http://chm.pops.int). While HCB was among the initial POPs regulated in 2004, PeCB was added to the Stockholm Convention on POPs in 2009 (UNEP/POPS/POPRC.3/20/Add.2, 2007). (http://chm.pops.int).

Fifty-five (55) long-term time-series of HCB were available of which 36 % showed significant decreasing trends, some of these also with a significant non-linear trend component. Two time-series showed a significant increasing trend, one of them also with a significant non-linear component. The mean annual decrease for HCB time-series was 2.6 %, somewhat lower than for most other organochlorine compounds (Figure 5).

Six (6) out of 43 short-term time-series exhibited a significant decreasing trend and three (3); all from East Greenland show significant increasing trends. The remaining time-series showed no trend or with a significant non-linear trend component. The mean annual change for short-term time-series was close to 0 % indicating that no or limited change has occurred since 2000.

Despite the large proportion of declining trends of HCB observed across the North American and European Arctic over recent decades, the relative low mean rate of the declines compared to other organochlorines and the increasing trend at some sites after the year 2000 may indicate that HCB emissions (primary and secondary) and releases are still occurring.

Thirteen (13) long-term time-series of PeCB existed from Canada and the United States of which two (2) showed significant decreasing trend, one of them also with a significant non-linear trend component. The other time-series show either no trend (9) or a significant non-linear trend (2). The mean annual decrease change was 3.8 %.

3.5 Chlordane-related pesticides (CHL) and heptachlor

Complex mixtures of chlordane-related compounds were used as a broad-spectrum insecticide in seed dressing and have been banned or restricted for decades. Heptachlor is an insecticide used to control soil insects, termites and crop pests, and is also a constituent of technical chlordane. Heptachlor degrades in the environment to heptachlor epoxide, which is more persistent (Gannon and Bigger, 1958). Chlordane and heptachlor were listed in Annex A of the Stockholm Convention on POPs in 2004 (http://chm.pops.int) *Cis*- and *trans*-chlordane and *cis*- and *trans*-nonachlor, together with heptachlor are primary constituents of the more than 120 compounds in the technical chlordane mixture (Dearth and Hites, 1991).

There were 31 long-term time-series of ΣCHL (sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor and oxychlordane), 35 of *trans*-nonachlor and 20 of oxychlordane. Decreasing trends or decreases together with a non-linear trend component were found in 48%, 41% and 35% of the long-term time series for ΣCHL, *trans*-nonachlor and oxychlordane, respectively. Only one *trans*-nonachlor time-series showed an increasing trend, which was the same site also showing increasing trends of PCBs and DDTs influenced by local pollution sources. The mean annual decreases for ΣCHL, *trans*-nonachlor and oxychlordane were 4.6 %, 3.6 % and 3.0 %, respectively.

As for most organochlorines, the proportion of significantly decreasing trends in biota was smaller and the proportion of time-series showing no trend greater when considering the short-term time-series. The annual decrease since 2000 ranged between 0.6 % for *trans*-nonachlor and 4.3 % for ΣCHL.

Marine mammals and seabirds metabolize *cis*- and *trans*-chlordane (Fisk et al., 2001). Oxychlordane is the primary metabolite of *cis*- and *trans*-chlordane and is persistent in the environment (Tashiro and Matsumura, 1978; Bondy et al., 2000). The ratio between oxychlordane and ΣCHL may be a rough indicator of the age of chlordane residues in the environment. Figure 7 shows the temporal trends of the ratio between oxychlordane and ΣCHL in three long-term time-series. The general increasing levels of the ratio in the order beluga < ringed seal < polar bear express the relative metabolic potential among

these species. All three time-series show an increase in the ratio of oxychlordane/ΣCHL with time, however, only significantly in case of ringed seals (log linear regression, $p < 0.01$). This indicates that the metabolite oxychlordane increases relative to some of its precursors.

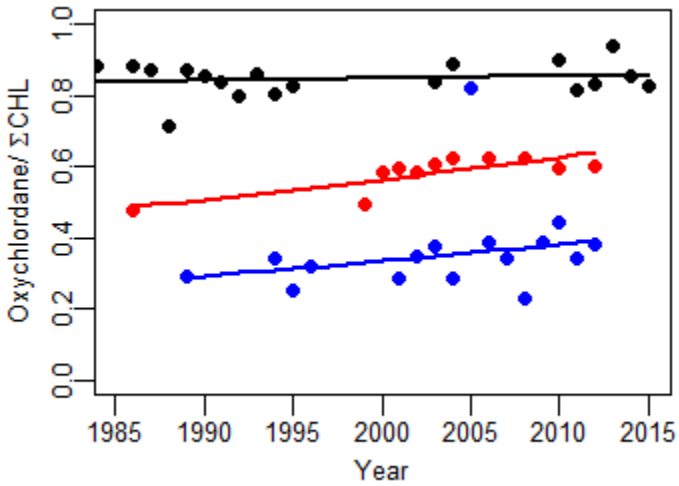

Figure 7. Trends of the ratio of oxychlordane/ΣCHL in juvenile polar bear (black) and ringed seal (red) both from East Greenland and beluga (blue) from northwest Canada.

Three time-series of heptachlor (seabirds and northern fur seals from Alaska) were available; however, in all years the annual medians were below detection limits. Twelve long-term time-series of heptachlor epoxide were evaluated; all from seabird eggs or marine mammal tissue. Of these, only two time-series showed significant decreasing trends or decreases together with a non-linear trend component; the other time-series showed no statistical trends. Heptachlor was one of the organochlorines with the highest annual decrease (Figure 5). None of the seven short-term time-series showed significant decreasing trends.

3.6 Dieldrin

Dieldrin is a pesticide used to control insect-borne diseases. It is also the degradation product of the pesticide aldrin (http://chm.pops.int). Both dieldrin and aldrin have been restricted or voluntarily withdrawn from use by most developed countries. Both pesticides were among the original compounds listed in Annex A of the Stockholm Convention on POPs in 2004 (http://chm.pops.int) .

Twenty-two (22) long-term time-series were available for dieldrin. Ten (10) of these (45 %) showed significant decreasing trends or decreases together with a non-linear trend component. The mean annual decrease was 3.0 %. Among the 13 short-term time-series only one showed a significant decreasing trend, and the mean annual decrease was close to zero indicating little if any change in levels since 2000. This indicates that dieldrin (and aldrin) contamination in the Arctic has slowly decreased following bans introduced in the period before the year 2000.

3.7 Mirex

Mirex is an insecticide primarily used in the 1960s and 1970s in the United States, but it was also used as a fire retardant (ATSDR, 1995). Mirex was among the original compounds listed in Annex A of the Stockholm Convention on POPs in 2004 (http://chm.pops.int).

Sixteen (16) long-term time-series for mirex were available originating from the Faroe Islands, Canada and USA (Alaska) and included marine mammals, seabirds and freshwater fish. Four (4) of these time-series showed significant decreasing trends, whereas the others showed either a non-linear trend or no trend. The mean annual decrease was 6.7 %. For short-term time-series, a total of ten (10) time-series existed, but only one showed a significant decreasing trend and the mean annual decrease was 1.9 %.

3.8 Octachlorostyrene (OCS)

Octachlorostyrene has never been used as a commercial product, but it may be produced during incineration and combustion process involving chlorinated compounds (Chu et al., 2003). Octachlorostyrene is not among the listed compounds in the Stockholm Convention on POPs (http://chm.pops.int).

Eleven (11) long-term time-series, all from Canada or Greenland, were available. Several marine fish and blue mussel time-series from northern Norway could not be evaluated because nearly all annual medians were below detection limits. Four (4) of the 11 time-series included in the evaluation showed significant decreasing trends, while the others showed non-linear or no trends. Considering the eleven (11) time-series from year 2000 and onwards, none showed a significant decreasing trend and the mean annual change was raised from a decrease of 4.5 % to an increase of 0.2 %.

3.9 Toxaphene

Toxaphene is an insecticide consisting of a complex mixture of polychlorobornanes and camphenes (De Geus et al., 1999). Toxaphene was among the initial 12 compounds listed by the Stockholm Convention on POPs in 2004.

Seventeen (17) long-term time-series of toxaphene congeners Parlar 26 and 50 were available including blue mussels, marine mammals, seabirds and freshwater fish. Of those six (6; 35 %) and five (5; 29 %) showed significant decreasing trends or decreasing together with a non-linear trend component for Parlar 26 and 50, respectively. No time-series showed significant increasing trends. The mean annual decrease was 6.0 % for Parlar 26 but was considerably lower for Parlar 50 (0.8 %).

Nine (9) out of 20 (45 %) and eight (8) out of 22 (36 %) short-time time-series of Parlar 26 and 50, respectively, showed significant decreasing trends one together with a significant non-linear trend component. The mean annual decrease was 5.9 % of Parlar 26 while Parlar 50 had a mean annual increase of 0.8 %.

3.10 Polybrominated diphenyl ethers (PBDEs)

PBDEs were used as flame retardants. Tetra-, penta-, hexa-, and hepta-BDE were added to Annex A of the Stockholm Convention in 2009, while deca-BDE was added in 2017 (UNEP/POPS/POPRC.10/10/2,

2014), with specified exemptions. There are still emissions of PBDEs to the environment because of the stock of in-use products (Abbasi et al., 2015). PBDEs can be subject to debromination and the products are lower brominated PBDE congeners (Söderström et al., 2004).

Most long-term time-series were available for the congeners BDE-47 (26) and BDE-99 (19) and only few for other congeners. BDE-47 was the compound with highest number (8) of time-series showing a significant increasing trend and in one case together with a non-linear trend component (35 %) (Figure 2). Only two time-series showed significant decreasing trends, one also having a significant non-linear trend component. Considering the short-term time-series of BDE-47, none showed an increasing trend and five (5) out of 23 (22 %) showed significant decreasing trends. The non-linear trend component was significant in 31 % of the long-term time-series of BDE-47 and a typical trend was an increase up until year 2005 followed by a decrease in recent years, which is quite different from the general trend of organochlorines (Figure 8). Only two (2) out of 19 (11 %) and one (1) out of 17 (5.9 %) long-term and short-term BDE-99 time-series, respectively, showed significant increasing trends. The mean annual change of long-term time-series of BDE-47 and BDE-99 were among the highest increase observed (Figure 5).

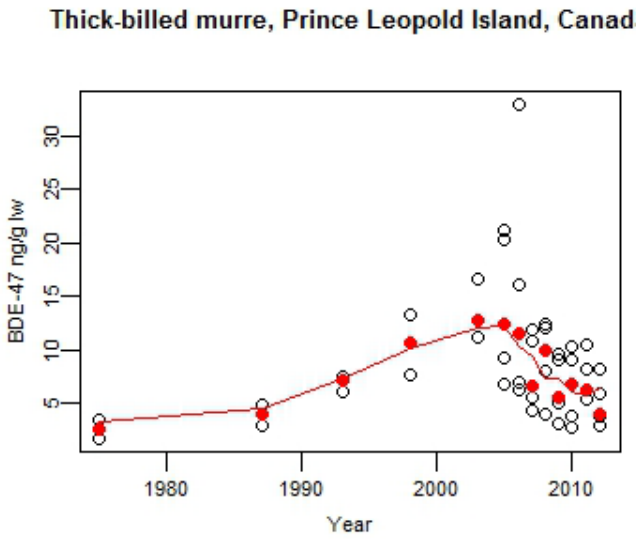

Figure 8. Pattern of change over time of BDE-47 in thick-billed murre from Prince Leopold Island in Canada (updated time-series published by Braune et al., (2015a). Red points = annual medians. Red-line = running three points average.

3.11 Hexabromocyclododecane (HBCDD)

HBCDD is used as an additive flame retardant and was listed in Annex A of the Stockholm Convention with specific exemptions in 2013 (UNEP/POPs/POPRC.6/13, 2010). Time-series were only available of the α-HBCDD diastereomer. All time-series deal with α-HBCDD in marine mammals or seabirds (one)

from Canada and Greenland; in total, seven (7) long-term time-series were available. Six (6; 86 %) of those showed significant increasing trends, one of them also with a significant non-linear trend component. HBCDD was the compound found with the highest annual mean increase (7.6 %).

3.12 Perfluoroalkyl substances (PFASs)

PFAS substances have had widely use in numerous industrial and commercial applications to make e.g. products more stain-resistant and waterproof (Buck et al., 2011). Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F) were added to Annex B (restriction) of the Stockholm Convention on POPs in 2009 (http://chm.pops.int). Other PFASs such as perfluorooctanoic acid (PFOA) and perfluorohexane sulfonic acid (PFHxS) are currently proposed for listing (http://chm.pops.int). Time-series of several PFAS substances were available, however only substances with more than ten (10) time-series are included here (PFOS, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnA). This restriction was made because the other PFAS compounds had several years with concentrations below limit of detection and were limited to cover only a few species.

Sixteen (16) long-term time-series of PFOS were available of which nine (9; 56 %) had a significant non-linear trend component. The others showed no trend except one also having a significant increasing trend (Figure 2). A common trend was a concentration increase until about the mid-2000s followed by decreasing concentrations (Figure 9). This trend is somewhat similar to the trend observed for BDE-47 and different from that of most organochlorine compounds. For the other compounds, about half of the time-series showed significant increasing trends or significant increasing trends together with a significant non-linear trend component (six (6) out of 11 (55%) PFNA, four (4) out of 10 (40 %) PFDA, six (6) out of 11 (55 %) PFUnA). None of these compounds showed a significant decreasing trend indicating that these compounds had not decreased as observed in several PFOS time-series.

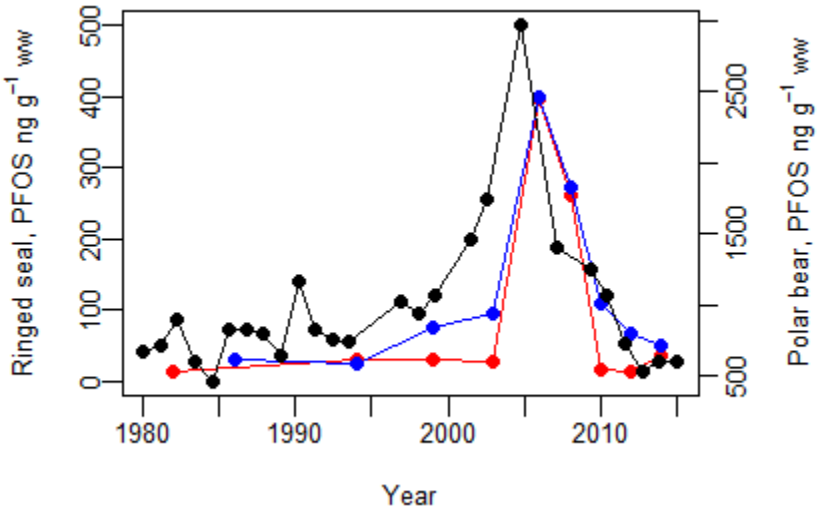

Figure 9. Patterns of change over time of PFOS in ringed seal from West Greenland (red) and ringed seal (blue) and polar bear (black) from East Greenland. Points represent annual medians. Updated time-series published by Rigét et al., (2013a).

For the short-term time-series of the selected PFAS compounds, none showed significant increasing or decreasing trends except two increasing trends of PFNA.

3.13 Statistical power

In order to compare the statistical power of different time-series it is necessary to apply or define statistical standard requirements. We use the requirements to be able to detect a 5 % annual change with a statistical power of 80 % at $\alpha < 0.05$ (AMAP, 2016). Only 12 % of the long-term time-series fulfilled these criteria and for the short-time time-series this number decreased to 4 % (not shown). Thirteen percent of the organochlorine (OC) long-term time-series had 80 % or more power to detect a 5 % annual change with $\alpha < 0.05$.

This also means that there was still a large part (88 %) of the long-term time-series not fulfilling these statistical requirements. The number of years in time-series with data is proportional to the power of the time-series. Figure 10 shows the frequencies of required number of years with data in cases of the long-term time-series of OC to being able to fulfill the set of statistical requirements. Forty-five percent (45 %) of the OC time-series need more than 20 years of data to fulfill this requirement.

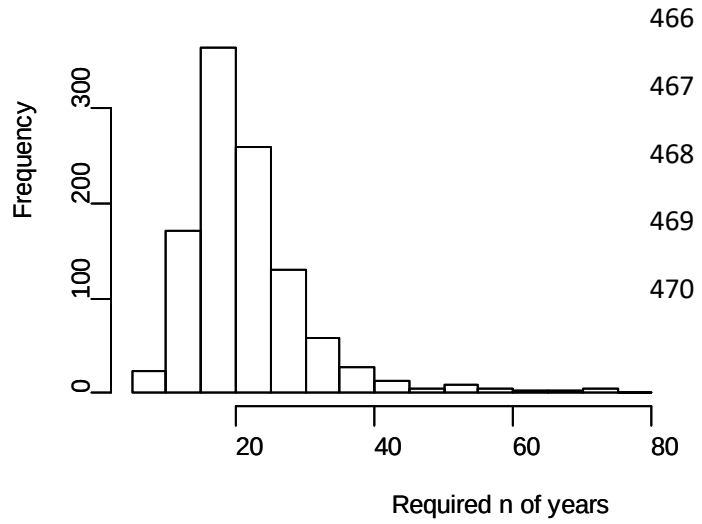

Figure 10. Histogram of the long-term OC time-series according to the number of years required to detect a 5 % annual change with 80 % power with $\alpha < 0.05$.

In order to compare the power of the long-term time-series among animal groups and tissues the power to detect a 5 % annual change with $\alpha < 0.05$ for a 10-year period was estimated together with the lowest detectable trend, which could be detected in a 10-year period with a power of 80 % (Table 2). The highest power and lowest detectable trend were seen for seabird eggs and marine mammal blubber and

the lowest power was found for fish liver and muscle. This may be related to the lower POP concentrations in fish where analytical uncertainties play a relatively larger role.

Table 2. Mean and CV of the statistical power of long-term time-series and lowest detectable trend (LDT) for a 10-year period for each media.

	Mean (CV %) power	Mean (CV %) LDT
Mussels, soft tissue	19.7 (94)	18.7 (43)
Freshwater fish	13.9 (69)	31.7(93)
Liver	12.7 (43)	24.1 (41)
Muscle	14.2 (74)	34.0 (97)
Marine fish	15.7 (69)	21.7 (45)
Liver	16.8 (76)	21.2 (45)
Muscle	14.0 (54)	22.6 (38)
Seabirds	30.5 (74)	20.9 (140)
Blood	16.8 (30)	17.9 (48)
Egg	32.0 (73)	21.1 (69)
Liver	7.9 (-)	34.3 (-)
Marine mammals	22.2 (83)	24.1 (118)
Adipose tissue	16.7 (53)	22.8 (89)
Blubber	23.9 (84)	23.3 (121)
Liver	13.8 (84)	54.2 (104)
Muscle	18.5 (38)	16.0 (36)

Discussion

The approach of analyzing a large number of time-series of POPs applying the same robust statistical methodologies consistently to all available time-series provides an overview of trends in POP developments across a large geographical Arctic area. On this basis a meta-analysis has been performed, addressing the direction and rates of the trends as well as the consistency among species and locations.

The time trend analyses of 1074 long-term time series (beginning before the year 2000) show that PCBs and organochlorine pesticides (OCs) have decreased in Arctic biota during the last 20 to 30 years. The same development of decreasing trends has been observed for most OCs in Arctic air (Hung et al., 2016).

However, for HCB and β-HCH, the decrease in Arctic biota has been rather slow or in some locations, the concentrations even increased. Emissions and releases of HCB may continue to a larger degree than those of most other OCs, associated with by-production of HCB in chemical processes (Barber et al., 2005). This is supported by the trend of HCB in Arctic air, for which Hung et al., (2016) reported increasing concentrations or a very slow decline at three Arctic monitoring stations over the last decade.

The trend of β-HCH is quite different from those of α-HCH and γ-HCH, although α- and β-HCH followed the same emission pattern, peaking in the early 1980s (Li and Macdonald, 2005). The large differences observed in the biota time trends are likely related to differences in chemical properties, more specifically the Henry's Law Constant, which means that α- and β-HCH partition differently between air and water, and the pathways to the Arctic are different (Li and Macdonald, 2005). The main pathway to the Arctic of β-HCH is by the ocean current while α-HCH is transported by air, causing a delay in the transport of β-HCH compared to α-HCH (Li et al., 2002). Furthermore, β-HCH is recalcitrant in most mammal species, while α-HCH and γ-HCH can be more readily metabolized (and so eliminated) (Moisey et al., 2001).

The relative few time-series of PCBs and OCs in Arctic biota extending back as far as the 1970s show that the downward trend of many of these compounds began decades before the Stockholm Convention on POPs entered into force. This is illustrated by the time-series of POPs in pike (*Esox lucius*) from a Swedish Arctic lake (Nyberg et al., 2014) and eggs of northern fulmar (*Fulmaris glacialis*) and thick-billed murre (*Uria lomvia*) from the Canadian Arctic (Braune et al., 2019). It also becomes evident when comparing the decrease rates in time-series starting after the year 2000 with those starting before the year 2000. The temporal trends of PCBs and OCs follow the schematic representation by Loganathan et al. (2016), where POP levels under national control and regulations in the 1980s and 1990s first decline relatively rapidly, followed by a long period with only slow declining concentrations. The global emissions of PCBs peaked in the mid-1970s, mainly related to the usage of PCB containing products (Breivik et al., 2002). This decrease in emissions is likely reflected in the first rapid decrease of PCBs in Arctic biota. The second phase of slow decrease might be related to secondary emissions e.g. volatilization from soil and vegetation (Ashraf, 2017) or from the ocean (as a results of sea-ice retreat and rising temperatures) (Ma et al., 2011) and potential releases by melting sea ice and glaciers (Bogdal et al., 2009). Furthermore, ongoing primary emissions exist from sources which are difficult to control (Diamond et al., 2010; Gasic et al., 2010), e.g. PCBs in building materials (Brown et al., 2016) and releases from e-waste (discarded electrical and electronic equipment) (Breivik et al., 2016). PCBs can also be formed unintentionally, e.g. in combustion processes (Ballschmiter et al., 1987), as reflected by their Annex C regulation in the Stockholm Convention. Despite these ongoing primary and secondary emissions the projected global atmospheric emissions in 2020 of 22 individual PCB congeners is predicted to be only ~2-5 % of the levels in 1970, when the emission peaked (Breivik et al., 2007). The time trend analysis indicates that current metabolisation and shedding (hair, feathers etc.) of most of the PCBs and OCs compounds in Arctic biota still exceeds these ongoing emissions, but that the rate of decrease today are minor.

The temporal trends of BDE-47 and PFOS were systematically different from those of many organochlorines as a period with increasing concentrations was followed by a period of a decreasing trend in many time series. For BDE-47, this is clearly seen in eggs of northern fulmar and thick-billed murre from the Canadian Arctic (Braune et al., 2015a): From 1975 to 2003, ΣPBDE concentrations increased exponentially followed by a rapid decrease to levels not significantly different from those from the early years. A similar trend was also found in ringed seals from East Baffin although the peak occurred later, i.e. in 2008 (Houde et al., 2017). Also in seabird eggs from the Pacific coast of Canada, the ΣPBDE concentrations peaked in the years around 2000 (Miller et al., 2014). The peak of the ΣPBDE

559 concentrations occurred at approximately the same time as the phase-out of the commercial Penta-BDE
560 and Octa-BDE mixtures in the EU and the U.S. (EU, 2003; Tullo, 2003) and prior to inclusion of PBDEs in
561 the Stockholm Convention in 2009. Abbasi et al. (2015) estimated the stocks of Penta- and Octa-BDE in
562 in-use products in the U.S. and Canada to have peaked in 2004. Therefore, it may be interpreted that at
563 least some Arctic animal populations responded rapidly to reduced production and/or use of PBDEs
564 despite the wide occurrence of PBDEs in consumer products with potential lifetimes of several years and
565 the persistency of PBDEs. In the review by de Wit et al., (2010) of PBDEs in the Arctic environment, a few
566 time-series showed signs of leveling off or decline. Today this appears to be even more pronounced.
567 Although the lag between national regulations and inclusion in the Stockholm Convention is much
568 shorter than for PCBs and OCs, the time trends of BDE-47 also indicate a rapid reaction to national
569 regulations. However, the decrease of PBDEs in biota was not yet observed in the Antarctic, indicating
570 the relevance of proximity to sources (Markham et al., 2018).
571
572 This observation of a rapid response to regulations is also valid for PFOS: The decline of PFOS
573 concentrations were connected to the phase-out of POSF-based chemicals by a large US company in
574 2000 (3M company, 2000). The decline in Arctic biota has been characterized as a rapid response to this
575 phase-out, as documented for Canadian ringed seals (Butt et al., 2007), Northern sea otters (*Enhydra*
576 *lutris*) (Hart et al., 2008) and Greenland ringed seals and polar bears(Rigét et al., 2013a). The trend of
577 PFOS in Arctic biota may be expected to further decrease in the coming years. Based on modelling
578 studies Zhang et al. (2017) estimated that in 2015 30 % of the cumulative PFOS discharges from North
579 America and Europe had entered the Arctic Ocean. The large-scale overturning of the North Atlantic
580 Ocean transports PFOS to deep waters of the oceans, which is the terminal PFOS sink. The surface
581 concentration was modeled to have decreased since year 2000, while the deep waters (> 1000 m)
582 concentrations was modeled to have increased since 2000.
583
584 Although fewer time-series were available, the long-chain perfluoroalkyl carboxylic acids (PFCA) PFNA,
585 PFDA and PFUnA did not show a similar decrease to that of PFOS, but rather a continuing increase.
586 Increasing trends of long-chain PFCAs in Arctic biota were reported in several cases (e.g. Rotander et al.,
587 2012; Braune and Letcher, 2013; Vorkamp et al., in press). Wang et al. (2014) estimated the global
588 emissions of C_4-C_{14} (PFCA) homologues to have increased in the period 1951-2002, followed by a
589 decrease and then another increase in the period 2002-2012. Since 2002, the production sites of long-
590 chain PFCAs and fluoropolymers has shifted from US, Japan and Western Europe to the continental Asia
591 (Wang et al., 2014), which likely will change the spatial and temporal trends in Arctic biota in the future.
592 Furthermore, PFOA, which was the main PFCAs in the emission inventories by Wang et al. (2014) has
593 been reviewed for inclusion in the Stockholm Convention. The Review Committee concluded that
594 inclusion in Annex A or B was recommended (UNEP/POPs/POPRC.13/7/Add.2, 2017).
595
596 The trend of α-HBCDD was different from those of PBDEs showing an increasing trend in five out of
597 seven time-series. Increasing trends of α-HBCDD have also been reported for two subpopulations of
598 beluga from Alaska (Hoguet et al., 2013) and in southwest Greenland peregrine falcon although not
599 significantly (Vorkamp et al., 2018). Houde et al., (2017) studying several ringed seals populations from
600 the Canadian Arctic found also increasing concentrations at several sites over the past decade. HBCDD

was listed for elimination in the Stockholm Convention in 2013, however, with specific exemptions that relate to its main use in expanded and extruded polystyrene (UNEP/POPs/POPRC.6/13, 2010). Furthermore, its presence in recycled polystyrene has been shown (Abdallah et al., 2018). These circumstances may still lead to primary emissions of HBCDD. However, time trends in Europe show decreasing concentrations of HBCDD (Esslinger et al., 2011), whereas HBCDD in fish increased, possible following the phase-out of PBDEs (Chen et al., 2011). It may therefore be expected that the increasing trend observed in Arctic biota will turn to more stable levels or even a decreasing trend in the coming years.

As discussed above, some trends in levels of POPs in Arctic biota seem to be a direct response to changes in emission levels. However, multiple factors can affect the accumulation of POPs in Arctic biota. For example, climate changes affecting sea ice coverage, animal migration patterns and distribution areas, and changes in feeding habits can substantially affect the POP concentrations in biota. There is growing evidence of the importance of the interactions between climate change and POPs and that climate change affects contaminant trends as reviewed by Ma et al. (2016). The number of studies showing that climate change or variability influence the temporal trend of POPs in Arctic biota is increasing (e.g. Bustnes et al., 2010; Rigét et al., 2013b; Braune at al., 2015b; Cabrerizo et al., 2018). Including climate variables in temporal trend analyses of individual time-series are therefore advisable in ongoing and future time trend studies. Ecological tracers such as stable isotope and/or fatty acids are also useful for reliable trend interpretation. Isotopic data are useful to control for variation in trophic level over time and are widely incorporated into contaminant-monitoring (Hebert and Popp, 2018). Fatty acids is another dietary tracer that can provide insights to changes of food web structure over time (McKinney et al., 2013; 2017).

But also in the absence of climate variables and/or ecological tracers in temporal trends established so far, a large number of time-series covering a large geographical area and including different matrices show consistency and agreement in the POP trends. These results provide indications of the effectiveness of national and global controls. This indication is particularly strong in the time series of PBDEs and PFOS for which voluntary measures and regulations (as well as closely following concentration maxima) occurred during the monitoring phase. In both cases, relatively rapid changes in the trends took place. For the organochlorines, most regulations occurred prior to the establishment of the time-series. The subsequent concentration decreases are less clearly visible in biota as most time-series were established later, as discussed above.

The statistical power analyses showed that only 12 % of the long-term time-series would be able to detect a 5 % annual change with a statistical power of 80 % at $\alpha < 0.05$, and also that many years (more than 10) with data are needed before any firm statistical conclusion can be drawn. This emphasizes that large efforts in terms of sampling and chemical analyses have to be invested in monitoring temporal trends, especially in remote areas such as the Arctic. However, it should be noted that often the annual changes are larger than 5 % - maybe closer to 10 %, and that the statistical power is higher to detect a

10 % annual change than a 5 % annual change. Other monitoring programmes, such as the AMAP mercury trend assessments, previously drew similar conclusions (Bignert et al., 2004; Rigét et al., 2011).

The chosen statistical requirements of the power analyses have a large impact on the outcome of a time trend. A more precautionary approach with regard to protection of the environment would be to use a significance level of 10 % in order to be able to give an early warning in a timely manner; i.e. in case of increasing trends of a contaminant. For the Greenlandic organochlorine time-series (in total 141), the number of time-series with 80 % power to detect a 5 % annual change would increase from 29 % to 43 % if the significance level was increased from 5 % to 10 %.

Sampling design, sample handling and analytical methods should be standardised as much as possible in temporal trend monitoring in order to avoid undesirable year-to-year variation. However, relatively long time-series are still needed because of the occurrence of a random year–to-year variance component beside a possible systematic trend component (Fryer and Nicholson, 1993). Random year-to-year variation in contaminant concentrations can arise from seasonal variations between years in e.g. prey item occurrence or climate variability.

In this study, bird eggs showed the highest statistical power of all animal tissues to detect trends. Using eggs in monitoring contaminants has several advantages over internal tissues (Furness and Greenwood, 2013 and references therein), which may add to the observed higher power. Eggs have a highly consistent composition, they can be sampled from the same location each year and there are no problems with confounding factors such as sex. The lowest power was found for fish liver and muscle and may be related to the rather low POP concentrations where analytical uncertainties play a relatively larger role.

Several time-series included in this study have a rather low power to detect temporal trends even if the number of years increase in the coming years. The objectives of individual trend monitoring should be stated based on sound statistical considerations and described in terms of quantitative measures, such as the number of years required to statistically detect a given rate of change, rather than the more general qualitative statements that are often employed. Furthermore, the trend study should be carefully designed and standardized as much as possible in order to be able to meet its objectives. This is especially important when working in the Arctic where sampling often is carried out in remote areas and is both costly and time consuming compared to working in temperate areas.

Acknowledgements

We would like to thank the national programs in the circumpolar countries for their funding and support of this work, as well as the community councils and hunters and trappers organizations in many circumpolar regions for their cooperation and active participation in the collection of biological samples. ICES in preparing data archived in the AMAP marine thematic data centre at ICES is also gratefully acknowledged

681 **References**

682 3M company, 2000. Phase-out plan for POSF-based products. US Environmental Protection Agency
683 Docket AR226-0588: USEPA, St. Paul, MN.

684 Abbasi, G., Buser, A.M., Soehl, A.,Murray, M.W.,Diamond, M.L. 2015. Stocks and Flows of PBDEs in
685 Products from Use to Waste in the U.S. and Canada from 1970 to 2020. Environ. Sci. Technol. 49(3):
686 1521-1528.

687 Abdallah, M.A-E., Sharkey, M., Berresheim, H., Harrad, S. 2018. Hexabromocyclododecane in
688 polystyrene packaging: A downside of recycling. Chemosphere 199: 612-616.

689 AMAP, 1998. AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment
690 Programme (AMAP), Oslo, Norway. xii+859 pp.

691 AMAP, 2009. AMAP Assessment 2009: Human Health in the Arctic. Arctic Monitoring and Assessment
692 Programme (AMAP), Oslo Norway. xiv+254 pp.

693 AMAP, 2014. Trends in Stockholm Convention Persistent Organic Pollutants (POPs) in Arctic Air, Human
694 media and Biota. By: S. Wilson, H. Hung, A. Katsoyiannis, D. Kong, J. van Oostdam, F. Riget, A. Bignert.
695 AMAP Technical Report No. 7 (2014). Arctic Monitoring and Asessment Programme (AMAP), Oslo. 54
696 pp.

697 AMAP, 2016. AMAP Assessment 2015: Temporal Trends in Persistent Organic Pollutants in the Arctic.
698 Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. vi+71pp

699 Ashraf, M.A. 2017. Persistent organic pollutants (POPs): a global issue, a global challenge. Environ. Sci.
700 Pollut. Res. 24:4223–4227.

701 Asmund, G., Vorkamp, K., Backus, S., Comba, M. 2004. An update on analytical methods, quality
702 assurance and quality control used in the Greenland AMAP programme: 1999-2002. Sci. Total
703 Environ. 331: 233-245.

704 ATSDR (Agency for Toxic Substances and Disease Registry), 1995. Toxicological profile for Mirex and
705 Chlordecone. Atlanta, GA: U.S. Department of Health and Human Services. Public Health Service.

706 Bailey, R.E., Wijk, D. van, Thomas, P.C. 2009. Sources and prevalence of pentachlorobenzene in the
707 environment. Chemosphere 75: 555-564.

708 Ballschmiter, K., Niemczyk, R., Schäfer, W., Zoller, W. 1987. Isomer-specific identification of
709 polychlorinated benzenes (PCBz) and –biphenyls (PCB) in effluents of municipal waste incineration.
710 Fresenius Z. Anal. Chem. 328: 583-587.

711 Barber, J.L., Sweetman, A.J., van Wijk, D., Jones, K.C. 2005. Hexachlorobenzene in the global
712 environment: emissions, levels, distribution, trends and processes. Sci. Tot. Environ. 349: 1-44.

713 Becker, S., Halsall, J.C., Tych, W., Kallenborn, R., Schlabach, M., Manø, S. 2012. Changing sources and
714 environmental factors reduce the rates of decline of organochlorine pesticides in the Arctic
715 atmosphere. Atmos. Chem. Phys. 12(9): 4033-4044.

716 Bignert, A., 2013. The PIA application for statistical analysis of time-series data.
717 [www.amap.no/documents/doc/pia-application-version-051113/1026]

718 Bignert, A., Riget, F., Braune, B., Outridge, P., Wilson, S. 2004. Recent temporal trend monitoring of
719 mercury in Arctic biota – how powerful are the existing data sets? J. Environ. Monit. 6: 351-355.

720 Bogdal, C., Schmid, P., Zennegg, M., Anselmetti, F.S., Scheringer, M., Hungerbühler, K. 2009. Blast from
721 the past: Melting glaciers as a relevant source for persistent organic pollutants. Environ. Sci. Technol.
722 43,21: 8173-8177.

723 Bondy, G.S., Newsome, W.H., Armstrong, C.I., Suzuki, C.A.M., Doucet, J., Fernie, S., Hierlihy, S.I., Feeley,
724 M.M., Barker, M.G. 2000. Trans-nonachlor and *cis*-nonachlor toxicity in Sprague-dawley rate:
725 comparisons with technical chlordane. Toxicol. Sci., 58:386-398.

726 Braune, B.M., Letcher, R.J. 2013. Perfluorinated sulfonate and carboxylate compounds in eggs of
727 seabirds breeding in the Canadian Arctic: Temporal trends (1975-2011) and interspecies comparison.
728 Environ. Sci. Technol. 47, 616-624.

729 Braune, B. M., Letcher, R. J., Gaston, A. J., Mallory, M. L. 2015a. Trends of polybrominated diphenyl
730 ethers and hexabromocyclododecane in eggs of Canadian Arctic seabirds reflect changing use
731 patterns. Environ. Res. 142: 651−661.

732 Braune, B.M., Gaston, A.J., Hobson, K.A., Gilchrist, H.G., Mallory, M.L. 2015b. Changes in trophic position
733 affect rates of contaminant decline at two seabird colonies in the Canadian Arctic. Ecotoxicol.
734 Environ. Saf. 115: 7-13.

735 Braune, B.M., Gaston, A.J., Mallory, M.L. 2019. Temporal trends of legacy organochlorines in eggs of
736 Canadian Arctic seabirds monitored over four decades. Sci. Total Environ, 646: 551-563.

737 Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C. 2002. Towards a global historical emission inventory
738 for selected PCB congeners – a mass balance approach: 2. Emissions. Sci. Total Environ. 290: 199-224

739 Breivik, K., Sweetman, A., Pacyna, J. M., Jones K. 2007. Towards a Global Historical Emission Inventory
740 for Selected PCB Congeners – a Mass Balance Approach. 3. An update. Sci. Total Environ., 377: 196–
741 198.

742 Breivik, K., Armitage, J.M., Wania, F., Sweetman, A.J., Jones, K.C. 2016. Tracking the global distribution of
743 persistent organic pollutants accounting for e-waste export to developing regions. Environ. Sci.
744 Technol 50: 798-805.

745 Brown, K.W., Minegishi, T., Cummiskey, C.C., Fragala, M.A., Hartman, R., MacIntosh, D.L. 2016, PCB
746 remediation in schools: a review. Environ. Sci. Pollut. Res. Int. 23(3):1986-1997.

747 Buck, R. C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., Voogt, P.D., Jensen, A.A., Kannan, K.,
748 Mabury, S.A., van Leeuwen, S.P.J. 2011. Perfluoroalkyl and polyfluoroalkyl substances in the
749 environment: Terminology, classification, and origins. IEAM 7(4): 513-541.

750 Bustnes, J.O., Gabrielsen, G.W., Verreault, J. 2010. Climate variability and temporal trends of persistent
751 organic pollutants in the arctic: a study of glaucous gulls. Environ. Sci. Technol. 15; 44(8): 3155-3161.

752 Butt, C.M., Muir, D.C., Stirling, I., Kwan, M., Mabury, S.A. 2007. Rapid response of arctic ringed seals to
753 changes in perfluoroalkyl production. Environ. Sci. Technol. 41(1): 42-49.

754 Cabrerizo, A., Muir, D.C.G., Köck, G., Iqaluk, D., Wang, X. 2018. Climatic influence on temporal trends of
755 polychlorinated biphenyls and organochlorine pesticides in landlocked char from lakes in the
756 Canadian high Arctic. Environ. Sci. Technol. DOI: 10.1021/acs.est.8b01860.

757 Chen, C., La Guardia, M.J., Luellen, D.R., Harvey, E., Mainor, T.M., Hale, R.C. 2011. Do temporal and
758 geographical patterns of HBCD and PBDE flame retardants in U.S. fish reflect evolving industrial
759 usage? Environ. Sci. Technol. 45: 8254-8261.

760 Chu, S., Covaci, A., Voorspoels, S., Schepens, P. 2003. The distribution of octachlorostyrene (OCS)
761 environmental samples from Europa. J. Exp. Med. 5: 619-625.

762 Cohen, J. 1977. Statistical power analysis for behavioural sciences. New York: Academic Press.

763 Dearth, M.A., Hites, R.A. 1991. Complete analysis of technical chlordane using negative ionization mass
764 spectrometry. Environ. Sci. Technol. 25: 245-54.

765 Diamond, M.L., Melymuk, L., Csiszar, SA., Robson, M. 2010. Estimation of PCB Stocks, Emissions, and
766 Urban Fate: Will our Policies Reduce Concentrations and Exposure? Environ. Sci. Technol. 44(8):
767 2777-2783.

768 de Geus, H.-J.; Besselink, H.; Brouwer, A.; Klungsøyr, J.; McHugh, B.; Nixon, E.; Rimkus, G.G.; Wester,
769 P.G.; de Boer, J. 1999. Environmental occurrence, analysis, and toxicology of toxaphene compounds.
770 Environ. Health Persp. 107, Suppl. 1, 115-144.

771 de Wit, C.A., Herzke, D., Vorkamp, K. 2010. Brominated flame retardants in the Arctic environment —
772 trends and new candidates. Sci. Total Environ. 408: 2885-2918.

773 Esslinger, S., Becker, R., Jung, C., Schröter-Kermani, C., Bremser, W., Nehls, I. 2011. Temporal trend
774 (1988-2008) of hexabromocyclododecane enantiomers in herring gull eggs from the German coastal
775 region. Chemosphere 83: 161-167.

776 EU, 2003. Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003
777 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing
778 and use of certain dangerous substances and preparations (pentabromodiphenyl ether,
779 octabromodiphenyl ether).

780 Fisk, A.T., Moisey, J., Hobson, K.A., Karnovsky, N.J., Nostrom, R.J. 2001. Chlordane components and
781 metabolites in seven species of Arctic seabirds from the Northwater Polynya relationships with stable
782 isotopes of nitrogen and enantiomeric fractions of chiral components. Environ. Pollut., 113: 225-238.

783 Fryer, R.J., Nicholson, M.D. 1993. The power of a contaminant monitoring programme to detect linear
784 trends and incidents. ICES J. mar. Sci. 50: 161-168.

785 Furness, R.W., Greenwood, J.J.D. 2013. Birds as Monitors of Environmental Change, Springer Science &
786 Business Media, 356 pp.

787 Gannon, N., Bigger, J.H. 1958. The conversion of Aldrin and heptachlor to their epoxides in soil. J. Econ.
788 Entomol. 51(1): 1-2.

789 Gasic, B., MacLeod, M., Klanova, L., Scheringer, M., Ilic, P., Lammel, G., Pajovic, A., Breivik, K., Holoubek,
790 I., Hungerbühler, K. 2010. Quantification of sources of PCBs to the atmosphere in urban areas: A
791 comparison of cities in North America, Western Europe and former Yugoslavia. Environ. Pollut.
792 158(10): 3230-3235.

793 Hart, K., Gill, V.A., Kannan, K. 2008. Temporal trends (1992-2007) of perfluorinated chemicals in
794 northern sea otters (*Enhydra lutris kenyoni*) from South-Central Alaska. Arch. Environ. Contam.
795 Toxicol. 56: 607-614.

796 Hebert, C.E. and Popp, B.N. 2018. Temporal trends in a biomagnifying contaminant: Application of
797 amino acid compound-specific stable nitrogen isotope analysis to the interpretation of bird mercury
798 levels. Environ. Toxicol. Chem. 37(5): 1458-1465.

799 Houde, M., Wang, X., Ferguson, SH., Gagnon, P., Brown, T.M., Tanebe, S., Kunito, T., Kwan, M., Muir,
800 D.C.G. 2017. Spatial and temporal trends of alternative flame retardants and polybrominated
801 diphenyl ethers in ringed seals (*Phoca hispida*) across the Canadian Arctic. Environ. Pollut., 223:266-
802 276.

803 Hoguet, J., Keller, J.M., Reiner, J.L., Kucklick, J.R., Bryan, C.E., Moors, A., Pugh, R.S., Becker, P.R. 2013.
804 Spatial and temporal trends of persistent organic pollutants and mercury in beluga whales
805 (*Delphinapterus leucas*). Sci. Total Environ. 449: 283-294.

806 Hung, H., Katsoyiannis, A.A., Brorström-Lundén, E., Olafsdottir, K., Aas, W., Breivik, K., Bohlin-Nizzetto,
807 P., Sigurdsson, A., Hakola, H., Bossi, R., Skov, H., Sverko, E., Barresi, E., Fellin, P., Wilson, S. 2016.
808 Temporal trends of persistent organic pollutants (POPs) in arctid air: 20 years of monitoring under
809 the Arctic Monitoring and Assessment programme (AMAP). Environ. Pollut.. 217:52-61.

810 Kelce. W.R., Stone, C.R., Laws, S.C., Gray, E., Kemppainen, J.A., Wilson, E.M. 1995. Persistent DDT
811 metabolite *p,p'*-DDE is a potent androgen antagonist. Nature, 375:581-585.

812 Letcher, R.J., Bustnes, J.O., Dietz, R., Jenssen, B.M., Jørgensen, E.H., Sonne, C., Vereault, J., Vijayan,
813 M.M., Gabrielsen, G.W. 2010. Exposure and effects assessment of persistent organohalogen
814 contaminants in arctic wildlife and fish. Sci. Total Environ. 408: 2995-3043.

815 Li, Y.-F., Macdonald, R.W.,Jantunen, L.M.M., Harner T., Bidleman, T.F., Strachan, W.M.J. 2002. The
816 transport of β-hexachlorocyclohexane to the western Arctic Ocean: a contrast to α-HCH. Sci. Total
817 Environ. 291: 229-246.

818 Li, Y. F., Venkatesh, S., Li, D. 2005. Modeling global emissions and residues of pesticides. Environ. Model.
819 Assess. 9(4): 237-243.

820 Li, Y., Macdonald R. 2005. Sources and pathways of selected organochlorine pesticides to the
821 Arctic and the effect of pathway divergence on HCH trends in biota: a review. Sci. Total Environ.
822 342(1): 87–106.

823 Loganathan, B.G., 2016. Persistent organic chemicals in the pacific basin countries: an overview. In:
824 Loganathan, B., Khim, J., Kodavanti, P., Masunaga, S. (Eds.), Persistent Organic Chemicals in the
825 Environment: Status and Trends in the Pacific Basin Countries I Contamination Status 1243. American
826 Chemical Society, pp. 1–15.

827 Ma, J., Hung, H., Tian, C., Kallenborn, R. 2011. Revolatilization of persistent organic pollutants in the
828 Arctic induced by climate change. Nat. Clim. Change 1: 255-260.

829 Markham, E., Brault, E.K., Khairy, M., Robuck, A.R. Goebel, M.E., Cantwell, M.G., Dickhut, R.M.,
830 Lohmann, R. 2018. Time trends of polybromninated diphenyl ethers (PBDEs) in Antarctic biota. ACS
831 Omega 3: 6595-6604.

832 McKinney, M.A., Iverson, S.J., Fisk, A.T., Sonne, C., Rigét, F.F., Letcher, R.J., Arts, M.T., Born, E.W.,
833 Rosing-Asvid, A., Diets, R. 2013. Global change effects on the long-term feeding ecology and
834 contaminants exposures of East Greenland polar bears. Global Change Biol., 19: 2360-2372.

835 McKinney, M.A., Atwood, T.C., Iverson, S.J., Peacock, E. 2017. Temporal complexity of southern
836 Beaufort Sea polar bear diets during a period of increasing land use. Ecosphere 8(1): e01633.
837 10.1002/ecs2.163.

838 Miller, A.,Elliott, J.E. Elliott, K.H., Guiguena, M.F., Wilson, L.K., Lee, S., Ldrissi, A. 2014. Spatial and
839 temporal trends in brominated flame retardants in seabirds from the Pacific coast of Canada.
840 Environ. Pollut. 195: 48-55.

841 Moisey, J., A.T. Fisk, K.A. Hobson and R.J. Norstrom, 2001. Hexachlorocyclohexane (HCH) isomers and
842 chiral signatures of α-HCH in the Arctic marine food web of the Northwater Polynya. Environ. Sci.
843 Technol. 35: 1920‑1927.
844
845

Nicholson, M.D., R. Fryer and J.R. Larsen, 1998. Temporal trend monitoring: Robust method for analysing contaminant trend monitoring data. ICES Techniques in Marine Environmental Sciences, 20. 22 pp.

Nyberg, E., Danielsson, S., Eriksson, U., Faxneld, S., Miller, A., Bignert, A. 2014. Spatio-temporal trends of PCBs in the Swedish freshwater environment 1981-2012, AMBIO 43: 45-57.

Rigét, F., Bignert, A., Braune, B., Stow, J., Wilson, S. 2010. Temporal trends of legacy POPs in Arctic biota, an update. Sci. Total Environ. 408: 2874-2884. [www.amap.no/documents/doc/amap-assessment-2009-persistent-organic-pollutants-pops-in-the-arctic/45]

Rigét, F., Braune, B., Bignert, A., Wilson, S., Aars, J., Born, E., Dam, M., Dietz, R., Evans, M., Evans, T., Gamberg, M., Gantner, N., Green, N., Gunnlaugdóttir, H., Kannan, K., Letcher, R, Muir, D., Roach, P., Sonne, C., Stern, G., Wiig, Ø. 2011. Temporal trends of Hg in Arctic biota, an update. Sci. Total Environ. 409:3520-3526.

Rigét, F., Bossi, R., Sonne, C., Vorkamp, K., Dietz, R. 2013a. Trends of perfluorochemicals in Greenland ringed seals and polar bears: Indications of shifts to decreasing trends. Chemosphere 93: 1607-1614.

Rigét, F., Vorkamp, K., Bossi, R., Hobson, K.A., Muir, D.C.G., Dietz, R. 2013b. Temporal trends of selected POPs and potential influence of climate variability in a Greenland ringed seal population. Environ. Sci. Process. Impact 15: 1706-1716.

Rotander, A., Kärrman, A., van Bavel, B., Polder, A., Rigét, F., Auðunsson, G.A., Vikingsson, G., Gabrielsen, G.W., Bloch, D., Dam, M. 2012. Increasing levels of long-chain perflurocarboxylic acids (PFCAs) in Arctic and North Atlantic marine mammals, 1984-2009. Chemosphere 86: 278-285.

Sturludottir, R., Gunnlaugsdottir, H., Jorrundsdottir H.O., Magnusdottir E.V., Olafsdottir K., Stefansson, G. 2013. Spatial and temporal trends of contaminants in mussel sampled around Icelandic coastline. Sci. Total Environ. 454-455: 500-509.

Söderström, G., Sellström, U., de Wit, C.A., Tysklind, M. 2004. Photolytic Debromination of Decabromodiphenyl Ether (BDE 209). Environ. Sci. Technol. 38(1): 127-132.

Tashiro, S., Matsumura, 1978. Metabolism of trans-nonachlor and related chlordane component in rat and man. Arch. Environ. Contam. Toxicol. 7:113-127.

Tkatcheva, V., B. Ali, E. Reiner, 2013. Northern Contaminants Interlaboratory Quality Assurance Program (NCP III – Phase 7). Northern Contaminants Program, Ottawa. [www.aadnc-aandc.gc.ca/eng/1100100035611/1100100035612]

Tullo, A. 2003. Great lakes to phase out flame retardants. Chem. Eng. News. 81(45), pp13.

UNEP/POPS/POPRC.3/20/Add.2. 2007. Stockholm Convention. Risk profile on pentachlorobenzene. http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs/tabid/2509/Default.aspx

879 UNEP/POPS/POPRC.6/13/Add.2. 2010. Stockholm Convention. Risk profile on
880 hexabromocyclododecane.
881 http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs/tabid/2509/Default.aspx.

882 UNEP/POPS/POPRC.10/10/Add.2. 2014. Stockholm Convention. Risk profile on decabromodiphenyl
883 ether (commercial mixture, c-decaBDE).
884 http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs/tabid/2509/Default.aspx.

885 UNEP/POPS/COP.8/INF/6. 2017. Stockholm Convention. DDT expert group and its report on the
886 assessment of scientific, technical, environmental and economic information on production and use
887 of DDT for disease vector control.
888 http://chm.pops.int/TheConvention/ConferenceofthePaties/Meetings/COP8/tabid/5309/Default.asp
889 x.

890 UNEP/POPS/POPRC.13/7/Add.2 2017. Stockholm Convention. Risk management evaluation on
891 pentadecafluorooctanoic acid (CAS No: 335-67-1, PFOA, perfluorooctanoic acid), its salts and PFOA-
892 related compounds.
893 http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC13/Overview/tabid/59
894 65/Default.aspx.

895 Vijgen J.2006. The Legacy of Lindane HCH Isomer Production and report annex, www.ihpa.info under
896 library.

897 Wang, Z., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbühler, K. 2014. Global emission inventories for
898 C_4-C_{14} perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030. PartI: production and
899 emissions from quantifiable sources. Environ. Int. 70: 62-75.

900 Vorkamp, K., Falk, K., Møller, S., Rigét, F.F., Sørensen, P.B. 2018. Regulated and unregulated halogenated
901 flame retardants in peregrine falcon eggs from Greenland. Environ. Sci. Technol. 52:474-483.

902 Vorkamp, K., Falk, K., Møller, S., Bossi, R., Rigét, F.F., Sørensen, P.B. (in press). Perfluorinated alkylated
903 substances (PFASs) and polychlorinated naphthalenes (PCNs) add to the chemical cocktail in
904 peregrine falcon eggs. Sci. Total Environ.

905 Zhang, X., Zhang, Y., Dassuncao, C., Lohmann, R., Sunderland, E.M. 2017. North Atlantic deep water
906 formation inhibits high Arctic contamination by continental perfluorooctane sulfonate discharges.
907 Global Biochemical. Cycles, 31: 1332-1343.

908