EXPERIENCES FROM 20 YEARS OF POP MONITORING IN GREENLAND MARINE BIOTA

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Introduction

Monitoring of contaminants in Greenland marine biota was initiated in 1994 and is still running. The aim of contaminant monitoring is to track temporal trends, which has been a valuable contribution to the effort of the Arctic Monitoring Assessment Programme (AMAP) to assess levels and trends in the circumpolar region. Over the years, AMAP output has been provided with important scientific information to the assessment under the Stockholm.Convention.[1] Temporal trends are useful in showing whether persistent organic pollutants (POPs) are accumulating in the Arctic, and are therefore candidates for control and in assessing the effectiveness of international agreements. Temporal trends of legacy POPs, and newer POPs such as polybrominated diphenyl ethers (PBDEs) and perfluorinated alkylated substances (PFASs) in Greenland marine biota will presently be summarized. The time-series derived with both retrospective samples and on-going sample collections are derived from samples in our tissue specimen bank. Statistical power is an important consideration in relation to temporal trend monitoring and experience from the AMAP assessment work is presented. There is increasing evidence for the warming climate in the Arctic to influence the temporal trends of POPs. In a temporal trend study of selected POP compounds in ringed seals from West Greenland, relationships were found with different climate indices (ice coverage, water salinity and temperature and Arctic Oscillation Index (AOI)) and an example is presented.

Materials and methods

Samples included in the regular Danish/Greenland monitoring programme of POPs are landlocked Arctic char, ringed seals, black guillemot eggs, polar bears and glaucous gulls for analysis of hexabromocyclododecane (HBCD). Samples were collected by local hunters; for Arctic char, gillnets were used. Compounds included are chlorinated “legacy” persistent organic pollutants (POPs), PBDEs, HBCD and PFASs. PBDEs, HBCD, PFASs were not included in the monitoring programme in the early years and parts of the time-series are results from retrospective studies based on samples in our specimen bank. Similarly, time-series of legacy POPs in ringed seals and polar bears have been extended backwards to the beginning of the 1980s. With regard to the chemical analyses detailed descriptions are found in case of legacy POPs[2,3,4], PBDEs[2,5], HBCD[6] and PFASs[7]. The temporal trend analysis is a robust regression-based method[8]. Annual median concentrations are used as the yearly contaminant index. The total variation over the time period is divided into a linear and a non-linear component. Log-linear regression is applied to describe the linear component and a 3-point running mean smoother to describe the non-linear component. The two components are tested by means of analysis of variance (ANOVA).

Results and discussion

In general, most of the legacy POPs showed significant ($p<0.05$) decreasing trends in the period from the beginning of the 1980s until today. The annual decreases are typically in the interval 3-10%. However, looking at the trends of the last 10-15 years no obvious decreases were found indicating that the main decrease in concentrations had happened before, probably in the 1970s.

Figure 1 shows the temporal trend of polychlorinated biphenyls (PCBs) in ringed seals from West and East Greenland with annual decreases of 5.9% and 4.1%, respectively. The general pattern with higher concentrations of most POPs in biota from East Greenland compared to West Greenland is also shown in the figure.

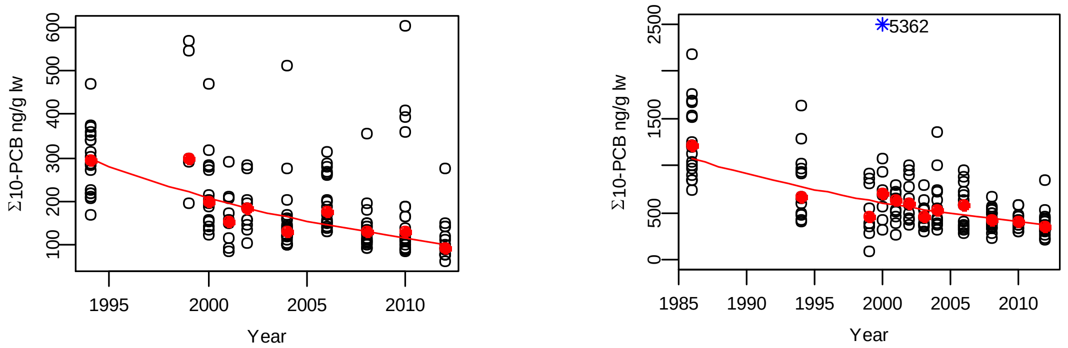

Figure 1. $\sum_{10}$-PCB in ringed seal blubber from West and East Greenland. Red points are annual medians, red lines are sigificant (p<0.05) regression lines. Blue star conciedwered as outlier (updated from [2,3])

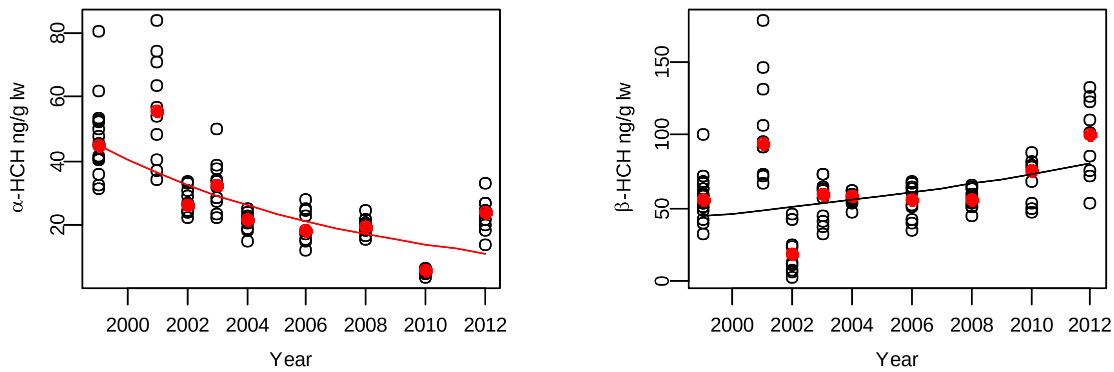

Figure 2. α- and β-HCH in black guillemot eggs from East Greenland. Red points are annual medians, red (significant (p<0.05) and black (not significant, p≥ 0.05) regression lines (unpublished)

The highest rate of decrease is seen for α-hexachlorocyclohexane (HCH) and was 8-10% in ringed seals from East and West Greenland (Figure 2). The trend of β-HCH was rather low and quite different from that of α-HCH as illustrated in Figure 2 for black guillemot eggs: α-HCH decreased significantly by 10.8% and β-HCH increased although not significantly by 4.6%. The pathways of the two isomers are different because of their different physical and chemical properties, e.g. higher volatility of α-HCH[9]. Hexachlorobenzene (HCB) is another compound which showed a rather low rate of annual decrease, typically 0-3% in ringed seal and polar bears.

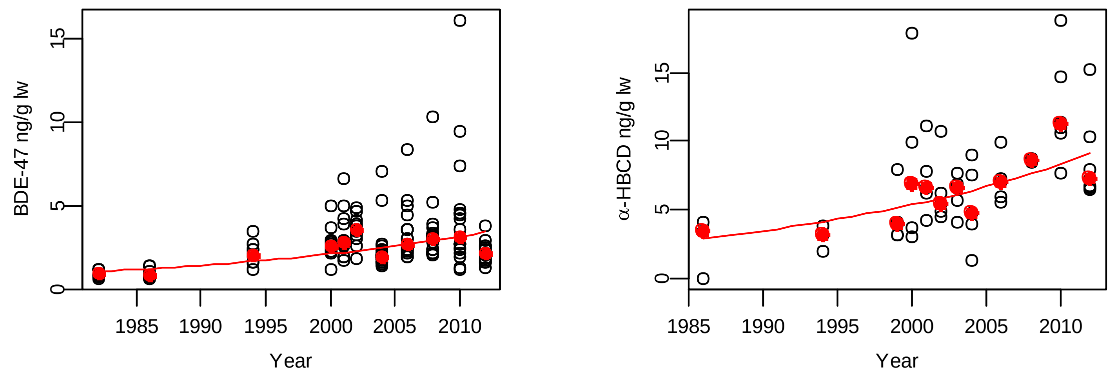

Figure 3. BDE-47 in ringed seal blubber from West Greenland and α-HBCD in ringed seal blubber from East Greenland. Red points are annual medians, red lines are sigificant ($p<0.05$) regression lines (updated from [2])

Ringed seal and polar bear PBDE time-series going back to the begining of the 1980s showed increasing trends or no significant trend. In case of polar bears ∑PBDE seemed to peak in the beginning of 2000s. Also α-HBCD showed a significantly increasing trend of 4.4% annually (Figure 3).

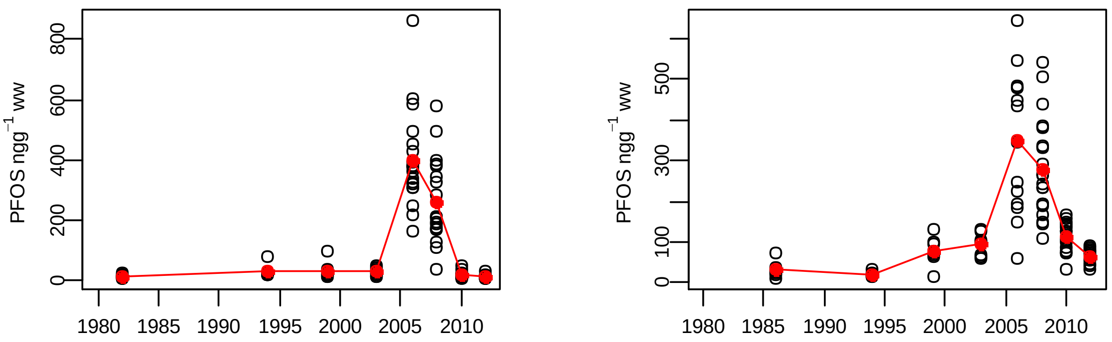

Figure 4. PFOS in ringed seal and polar bear livers from Central East Greenland. Red points are annual means. (updated from [7])

PFOS is an example of a compound which first increased in concentration and later decreased. PFOS seems to have peaked around 2006 in both ringed seals and polar bears from East Greenland as illustrated in Figure 4. Similar patterns are seen for other PFASs, whereas the trend of long-chain perfluorinated carboxylic acids (PFCAs) is less clear.

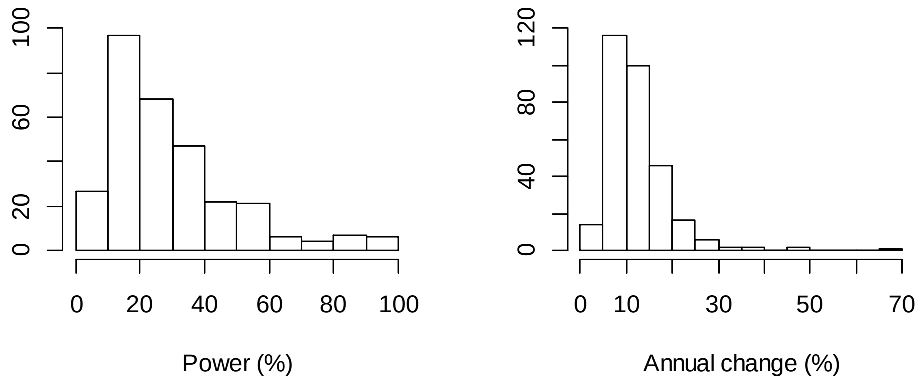

Figure 5. Based on the results of 316 legacy POP time-series.
Left: Frequency of the power (%) to detect a 5% annual change in a 10 years period with a sign. level of 5%.
Right: Frequency of lowest detectable trend in a 10 year period with a power of 80% and sign. level of 5%.
Redrawn from.[10]

An important consideration in temporal trend monitoring is statistical power, defined as the probability that the data set of interest is sufficiently sensitive to detect a trend of a specified magnitude. The power to detect a linear trend depends on: the magnitude of the trend, the number of years in the time-series, the number of samples per year, the residual variance, the significance level of the log-linear regression and whether the test is one- or two-tailed. In the most recent AMAP POP assessment of temporal trends of legacy POPs[10] the power of 316 time-series of POPs in Arctic biota from circumpolar countries showed that the power to detect a 5% annual change in a 10 year period with a significance level of 5% was rather low and also that the lowest detectable trend in a 10 year period with a power of 80% and a significance level of 5% was rather high (Figure 5). It was concluded that more than 10 years of data were required before sufficient power can be expected to be obtained.

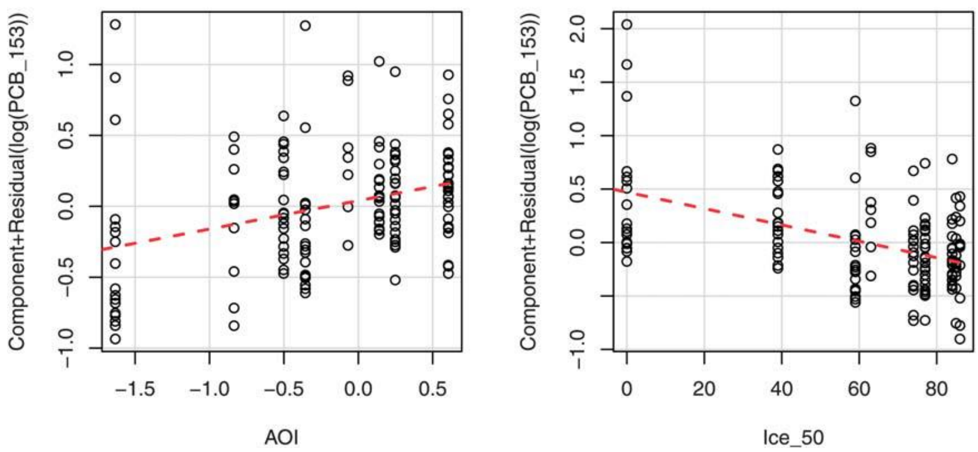

Figure 6. Component–residual plots show the relationships between PCB-153 concentrations in ringed seal blubber from central West Greenland and the winter Arctic Oscillation Index (AOI) (left) and number of days with ice coverage above 50% during winter (Ice_50) (right). Redrawn from. [3]

The influence of different climate indices on the temporal trends of selected POPs was studied in ringed seal from West Greenland[2]. A multiple regression model was applied and the Akaike's Information Criteria (AIC) were used as selection criteria to choose the most parsimonious model(s): Figure 6 shows an example of the results. In case of PCB-153 the two most important predictors besides the decreasing trend were winter AOI and ice coverage. The relationship with AOI is positive, which may be explained with enhanced transport of air masses from industrial regions of North America and Europe to the Arctic under high AO conditions. The negative relationship with ice coverage is unknown but may be explained by different food availability under different ice conditions.

Acknowledgments
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