Preliminary Results of Time Trend Studies of POPs in Marine Biota from Greenland

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Introduction

Monitoring of the temporal trends of contaminants is an essential component of any scientific and regulatory program, which is concerned with the possible effects of pollution on wildlife and human health. Time-series studies provide necessary information for contaminant risk assessments and also allow measurement of the success of any regulatory action to reduce contaminant emissions. Monitoring of POPs in biota from Greenland started in 1994 in connection with the upstart of the Arctic Monitoring and Assessment Programme (AMAP). The relatively short time-series was evaluated by Riget et al.[1]. Since then the time series have been extended and analyses of archived samples have been included. Furthermore, data on PCDD/Fs and non-ortho PCBs have become available from a retrospective study based on archived samples. The presented preliminary results from time trend studies are based on unpublished data on PCBs, DDTs, HCHs, HCB and *trans*-nonachlor, while data on PCDD/Fs and non-*ortho*PCBs have been presented by Riget et al[2].

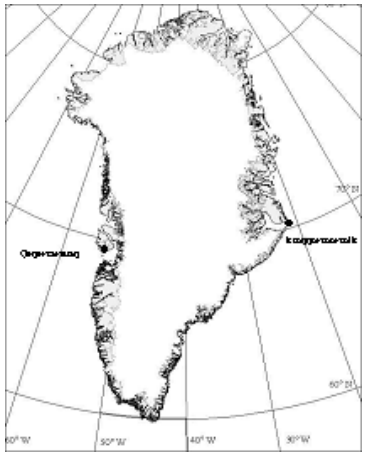


Figure 1. Map of locations

Materials and Methods

Sampling: The time trend studies of POPs includes ringed seals (*Phocahispida*) hunted by the Inuit population living in Ittoqqortoormiit, central East Greenland and in Qeqertarsuaq, central West Greenland (*Figure 1*). Furthermore, time trend studies have also been conducted on shorthorn sculpin (*Myoxocephalusscorpius*) from Ittoqqortoormiit. The temporal trend of PCDD/Fs and c-PCBs is based on ringed seals from Ittoqqortoormiit. The span of the time-series varied between compounds and locations. However, data were not available from each year in the time span period and the number of years with data varies between compounds and locations, with 4 as the lowest number of years and 7 as the highest. In case of ringed seal all compounds have been analysed in blubber tissue. In shorthorn sculpin the tissue analysed was the liver for all compounds.

Analysis: The compounds included in this overview of time trends are: polychlorinated biphenyls (PCBs): sum of CB28, CB31, CB52, CB101, CB105,CB118, CB138, CB153, CB156 and CB180, in the following called SPCB-10; DDT and its degradation products: sum of *p,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE, in the following called SDDT; hexachlorocyclohexane (HCHs): sum of α-, β- and γ-HCH, in the following called SHCH; hexachlorobenzene (HCB); *Trans*-nonachlor; dioxins (PCDDs): 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCCD,

1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD; furans (PCDFs): 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF and OCDF; non-*ortho* substituted PCB congeners (c-PCBs): CB77, CB126 and CB169.

PCBs and organochlorine compounds were analyzed with the following method: after homogenisation of the samples, the recovery standards CB-3, CB-40 and CB-198 were added and the samples were extracted in hexane/acetone (4:1) by soxhlet. The extract was then passed through a multi-layer column consisting of silica impregnated by sulphuric acid, pure silica and alumina. The samples were eluted with 250 ml *n*-hexane and concentrated to about 1 ml. After defined amounts of the internal standards CB-53 and CB-155 have been added, the samples were adjusted to a precise volume of 1 ml and analysed by dual column-gas chromatography (J&W Scientific DB-5 and DB-1701 capillary columns) with electron capture detection (model HP 5890). A detailed description of the analytical method is given by Cleemann et al.[3]. The quality assurance and control is described by Asmund et al.[4].

PCDD/Fs and c-PCBs were analyzed with the following method adapted from European standard EN-1948 2-3 for analysis of PCDD/F in flue-gas[5]: 5 g (wet weight) of homogenised blubber sample was spiked with $^{13}C_{12}$ labelled PCDD/F and c-PCB congeners and soxhlet extracted in toluene. The extract was stirred with SiO_2/H_2SO_4 for lipid destruction. Further clean up was performed with column chromatography on SiO_2/NaOH, SiO_2/H_2SO_4, acidic Al_2O_3 and carbon AX-21/Celite. The analysis of extracts was performed by GC-HRMS at 10000 resolution, using a 60 m Agilent J&W DB5-ms column, coupled to a Kratos Concept 1S mass spectrometer.

Analyses of temporal trends were performed by linear regression analyses of logarithmic transformed median concentrations. Median concentrations were chosen to represent yearly contaminant level in order to minimise influence of outliers and values below detection limit. The small number of years of data available in most cases (low degree of freedom) gives low power of the regression test.

Results and Discussion

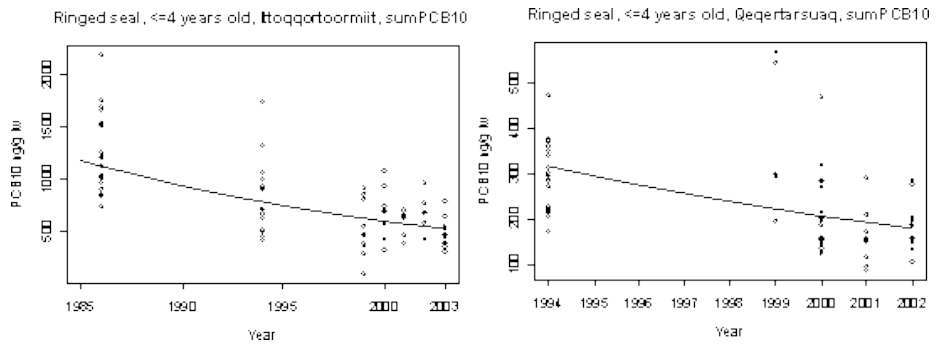
Figure 2 shows examples of time-series and Table 1 summarises the annual changes of compound concentrations estimated by regression analyses. ΣPCB-10, ΣDDT, ΣHCH concentrations all show a decreasing trend in both west and east Greenland with annual changes ranging between 3.8% and 10.1%. Among these compounds the annual decrease of ΣHCH appears to be the highest. HCB and *trans*-nonachlor concentrations also show decreasing trends except for shorthorn sculpin from Qeqertarsuaq, west Greenland.

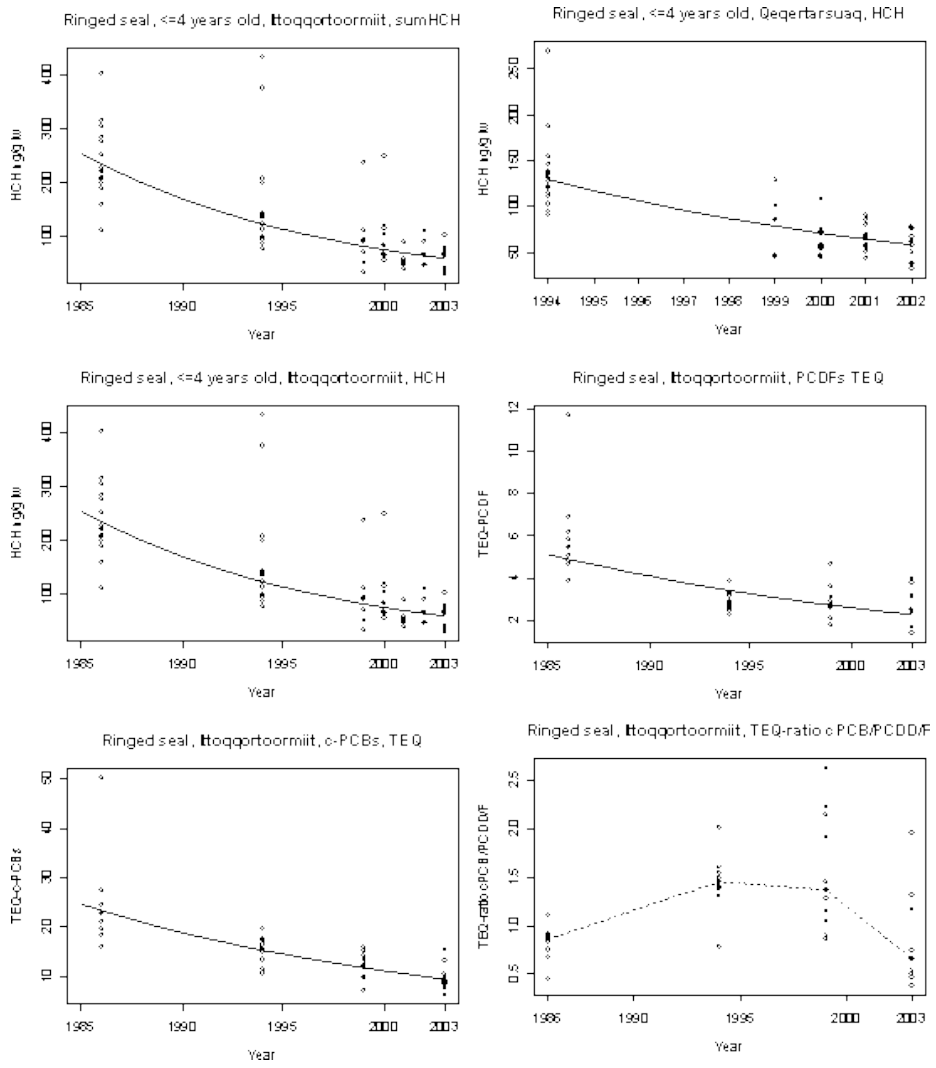
The PCDD WHO-TEQ concentration shows a 5.5% annual decrease in ringed seals from Ittoqqortoormiit, east Greenland since 1986. The PCDF WHO-TEQ concentration also shows a decreasing trend of 4.5%. c-PCBs concentrations decrease with an annual change of 4.5%. PCDDs and c-PCBs contribute almost equally to the WHO-TEQs, whereas the contribution from PCDF is minor. The total WHO-TEQ shows an annual decrease of 5.6%. Whereas c-PCBs show a continuously decreasing trend in the time period investigated, the trends for PCDD and PCDF have levelled off in the later years. An important question is the relative contribution to toxicity from c-PCBs and PCDD/F (Figure 2). The ratio rises from a value below 1 in 1986 to a maximum of about 1.5 in 1994-1999 and then decreases to low value in 2003. The curve reflects the transport of PCBs to the Arctic, which makes their level rise until PCBs were banned in many countries in the 1980ties. The decrease indicates that the ban takes effect, with a delay of a decade.

Table 1. Annual change (%) of concentrations estimated by log-linear regression analysis. Bold denotes significance at the 5% level. Values for PCDD/Fs and c-PCBs refer to changes in WHO-TEQ concentrations.

						trans-
ΣPCB-10	ΣDDT	ΣHCH	HCB	nonachlor		
						Qeqertarsuaq
Ringed seal, juvenile	-7.1	-9.1	**-10.1**	**-6.1**	-9.8	
1994,99,2000,01,02						
Ittoqqortoormiit						
Shorthorn sculpin						
1995,99,2000,01,02,03	**-4.9**	-3.1	**-11.0**	1.8	0.4	
Ringed seal, juvenile	**-4.5**	**-5.5**	**-8.0**	**-3.9**	**-6.9**	
1986,94,99,2000,01,02,03						
PCDDs	PCDFs	cPCBs	Total			
Ittoqqortoormiit						
Ringed seal	-5.5	-4.5	**-5.3**	-5.6		
1986,94,99,2003						

Figure 2. Temporal trend of selected compounds in ringed seal. Open circles are individual concentrations, solid circle is the median value. The solid line represents the result of linear regression analyses of logarithmic transformed median values and the broken line joints median values.





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