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Levels and temporal trends of PCDD/PCDFs and non-*ortho* PCBs in ringed seals from East Greenland

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Abstract

The levels and temporal trend of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) and non-*ortho* substituted PCBs (c-PCBs, i.e. CB77, CB126 and CB169) were determined in ringed seal blubber from central East Greenland collected in 1986, 1994, 1999 and 2003, respectively. Since 1986 the concentrations of PCDDs, PCDFs and c-PCBs all show a decreasing trend. The annual decreases were estimated to 5.2% and 5.3% for pg/g WHO-TEQ ww of PCDD/Fs and c-PCB, respectively. The annual median concentrations of PCDDs ranged from 5.4 to 24.4 pg/g WHO-TEQ ww and those of PCDFs from 2.5 to 5.1 pg/g WHO-TEQ ww. Compared to PCDD/Fs concentrations in ringed seals from other Arctic areas the levels of PCDD/Fs found in 1986 were the highest recorded. The annual median concentrations of c-PCBs decreased 24.2 to 9.1 pg/g WHO-TEQ ww. The levels of c-PCBs observed in 1986 are similar to levels found in ringed seals from Svalbard in 1990 and from eastern Hudson Bay in 1989–1992. The dominant and most TEQ-contributing PCDD congener was 1,2,3,7,8-PeCDD. CB126 was the dominating and most TEQ-contributing c-PCB congener. The concentrations of PCDDs, PCDFs and c-PCBs were highly significantly inter-correlated. Principal component analysis of the PCDD/PCDF congeners and c-PCBs was performed to analyse the pattern of compounds during time.

Keywords: Polychlorinated dibenzo-*p*-dioxins; Dibenzofurans; Coplanar PCB; Temporal trend; Ringed seal blubber; East Greenland

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) enter the environment as by-products of industrial processes mainly emitted to the atmosphere during combustion. The most significant local arctic sources are low-temperature, incomplete incineration of chlorine-containing materials such as PVC-plastics by open burning at garbage dumps (AMAP, 2004). PCDD/Fs are widely spread in the environment and have been detected in marine mammals from the Canadian and European part of the Arctic (Bignert et al., 1989; Norstrom, 1994; Oehme et al., 1990). However, there exist only few data on PCDD/Fs concentrations in marine biota from Greenland. Bruhn et al. (1999) reports on PCDD/Fs in harbour porpoises (*Phocoena phocoena*) from Southwest Greenland in 1995 and Oehme et al. (1995) reports on PCDD/Fs in harp seals (*Phoca groenlandica*) from the West Ice region of the Greenland Sea in 1991. Concentrations of non-*ortho* substituted PCB congeners (c-PCBs) in marine biota from Greenland are also scarce. Vorkamp et al. (2004) reports on c-PCBs (CB77, CB126 and CB169) in ringed seal, harp seal, beluga (*Delphinapterus leucas*) and narwhal (*Monodon monoceros*) from West Greenland.

In this study, we examine PCDD/Fs and c-PCBs concentrations in ringed seals (*Phoca hispida*) hunted by the Inuit population living in Ittoqqortoormiit (about 500 inhabitants), East Greenland far away from any known sources to these compounds. The occurrence of

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contaminants like PCDD/Fs and c-PCBs in seals from the area around Ittoqqortoormiit is therefore derive by long-range transport from lower latitudes, even if the process involved in the transport is not well understood. We selected samples from the years 1986, 1994, 1999 and 2003 in order to examine temporal trends.

Samples of ringed seals were available from Ittoqqortoormiit in central East Greenland (70°28′ N 21°95′ E) collected in the years 1986, 1994, 1999 and 2003. Ringed seal samples were obtained from local hunters mainly during May and June. The animals were either shot or caught in nets. Date, body length and circumference, weight and sex were routinely recorded. Blubber samples were taken for organochlorine analysis, muscle, liver and kidney samples for heavy metal analysis and the canines were collected for age determination. Samples were frozen and shipped to Denmark where they were kept frozen at −20 °C. In the laboratory, blubber samples were lightly thawed and before analysis the outer exposed tissue layer was cut away in order to minimise possible contamination due to handling and storage, and homogenised in liquid N_2 before being dividing into sub-samples and stored at −20 °C until analysed.

The age of the seals were estimated by counting annual layering in the cementum of the canine or premolar tooth after decalcification, thin sectioning (14 μm) and staining in toluidin blue as described by Dietz et al. (1991). The seals selected for this study were mainly juvenile. Number, sex and age of the analysed specimens are presented in Table 1.

The compounds analysed were the 2,3,7,8-substituted congeners of 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, and of the 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. Further, the non-*ortho* substituted PCB congeners (coplanar PCBs, c-PCBs): CB77, CB126 and CB169.

The analytical method for PCDD/Fs and c-PCBs is adapted from European standard EN-1948 2-3 for analysis of PCDD/F in flue-gas (CEN, 1996). To the homogenised blubber sub-sample, about 5 g ww, an extraction spike mixture is added, containing fourteen $^{13}C_{12}$-labelled PCDD/F congeners and three $^{13}C_{12}$-labelled c-PCB congeners. The sample is soxhlet extracted for 24 hours in 700 ml of toluene, vacuum concentrated, and cleaned-up by column chromatography on SiO_2/NaOH, SiO_2/H_2SO_4, acidic Al_2O_3, active carbon AX-21/Celite. The GC/MS analysis is performed using a Hewlett-Packard 5890 series II gas chromatograph fitted with an Agilent J&W Scientific DB-5MS capillary column 60 m × 0.25 mm i.∅, coupled to a Kratos Concept 1S mass spectrometer operating at resolution 10,000.

Table 1
Overview of ringed seal samples

Year	*N*	Mean age	Age range	M/F
1986	8	3.0	2–4	3/3[a]
1994	8	4.4	2–6	5/3
1999	10	3.5	1–6	6/4
2003	10	4.1	2–8	5/5

[a] Two seals were not sex determined.

For each analytical series, laboratory blanks were analysed. The blank results, ranging from 0.01–0.06 pg/g WHO-TEQ for PCDD/F and from 0.04 to 0.11 pg/g WHO-TEQ for c-PCB, constitute below 1% of the average results for the samples. The blanks were subtracted from the unknowns on an amount per sample basis. The extraction recoveries (mean ± sd all data) for PCDD/F 77 ± 28%, for c-PCB 39 ± 21%. The low recoveries for the c-PCBs must be caused by a matrix effect during the cleanup procedure, which was adapted from a method designed for milk. This does not, however, significantly influence the results, which are compensated for recoveries by the signal from ^{13}C-labelled extraction spikes.

The repeatability is estimated to 5–10%. The detection limits (medians all data) varied from 0.5–1 pg/g (TCDD-HpCDD), from 0.1–1 pg/g (TCDF-OCDF) and from 1–2 pg/g (CB126-CB77). Results below detection limit are treated as zero concentrations in the data analyses.

Toxic equivalent factors (TEF) have been developed to express concentrations of the different PCDD and PCDF congeners in terms of toxicity equivalents (TEQ). The congener having the highest toxicity, 2,3,7,8-TCDD, is taken as a reference, and its toxic equivalent factor is thus by definition set to 1. The structure of c-PCB congeners (and to a certain degree also mono-*ortho* PCB, mo-PCB) allows a coplanar configuration similar to that of PCDD and PCDF. Thus c-PCBs and mo-PCBs can exhibit a dioxin-like toxicity. The most toxic PCBs are the coplanar CB77, CB126 and CB169 (Daelemans et al., 1992). For those PCB-congeners WHO has devised a system, the WHO-TEF, which also comprises PCDD/F, used in this study. In addition to WHO-TEQs, this report are also use concentration sums: $\sum$PCDD = 2,3,7,8-TCDD + 1,2,3,7,8-PeCDD + ⋯ + OCDD. In the same way $\sum$PCDF and $\sum$c-PCB are defined analogously.

Two-way analyse of variance (ANOVA) was performed to test of differences between sexes in logarithmic transformed compound concentrations. Analyses of temporal trends were performed by linear regression analyses of logarithmic transformed median concentrations. Median concentrations were chosen in order to minimise influence of outliers and values below detection limit. Pearson's correlation analysis was performed