Polychlorinated compounds in Antarctic air and biota: Similarities and differences compared to the Arctic

<u>Michael Oehme</u>, John-Erik Haugen, Roland Kallenborn and Martin Schlabach Norwegian Institute for Air Research, P.O. Box 100, N-2007 Kjeller, Norway

1. Introduction

During the past 20 years numerous studies in the Arctic have shown that persistent organochlorines such as polychlorinated aromatics and pesticides are transported to this polar region and are highly accumulated in the Arctic food chain^{1,2)}. In seals and polar bears as well as inuits living from marine mammals very high levels of polychlorinated biphenyls have been found^{2,3)}. As a consequence circumpolar countries try now to identify source areas and to reduce emissions.

Based on the rather sparse data about level of organochlorines in Antarctic biota it has been concluded that this continent still belongs to the least polluted areas in the world. Much lower concentration than in the Arctic have been reported⁴⁻⁸). This has been explained by fewer industrial and agricultural areas in the Southern Hemisphere (only about 20% of all industrial regions are situated here). Furthermore, it was assumed that the cold water currents around Antarctic and the meteorological conditions are less favourable for long range transport compared to the situation in the Arctic. Unfortunately, many reports published so far about levels of organochlorines in Antarctic biota, suffer from the same problems as early studies in the Arctic: Concentrations of compound groups are not given isomer specifically, only a few non-systematic measurements were carried out and seasonal changes in the lipid production were not studied leading to different accumulation in the food chain. Furthermore, levels of organochlorines in Antarctic air were only measured episodically. Long-term ambient air measurements at 60-76°N have shown annual concentration variations of at least one order of magnitude due to long range transport episodes^{1,9}.

Based on selected published data and own measurements, the levels and relative concentration patterns of some organochlorines in ambient air and a few biota from the Antarctic will be compared with results from the Arctic. Similarities and differences between the two polar regions are discussed.

2. Methods

Sampling and analysis

48 h air samples of about 1000 m³ air (sampling speed, 20-25 m³/h) were collected at Terranova Bay (74°40'S, 164°10'E), Antarctica, from end of October to middle of

November 1993. Samples of 48 h were also taken weekly at Ny Ålesund, Spitsbergen, in 1993. The same high volume air sampling method and analytical techniques were used as described earlier^{1,9)}. Particles were collected on a glass fibre filter, and compounds in the vapour phase were adsorbed on polyurethane foam. Quantification was carried out by high resolution gas chromatography/mass spectrometry⁹⁾.

Seal blubber was collected from 11 female Antarctic fur seals (*Arctocephalus gazella*) at Bird Island, South Georgia (54°S, 38°W)¹⁰). Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) were quantified according to the method described in detail before¹⁰). All analyses were carried out under a comprehensive quality assurance protocol which fulfilled the requirements of the European Norm EN45'001^{9,10}).

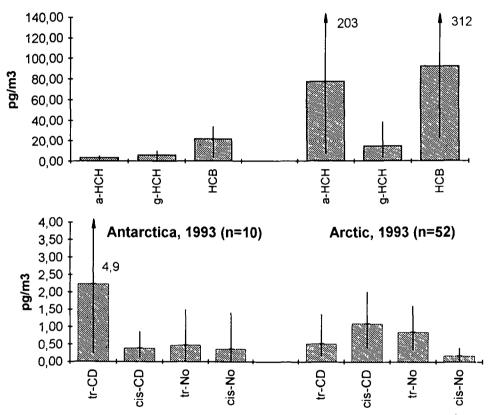


Figure 1: Average concentrations and standard deviations of selected polychlorinated pesticides in Arctic and Antarctic air.

3. Results and Discussion

Ambient air concentrations in the Arctic and Antarctica

Figure 1 compares the average concentrations of selected polychlorinated pesticides in ambient air at Ny-Ålesund (Arctic) and at Terranova Bay (Antarctica) in 1993. Though this preliminary Antarctic measuring campaign was very short, some significant differences could be found. Levels of hexachlorocyclohexanes (HCH) and hexachlorobenzene (HCB)

were lower in Antarctic air, and γ -HCH was the dominant HCH isomer. In Arctic air more α -HCH was detected, and the HCB level was about 5 times higher than in the Antarctic. This indicates that more pure γ -HCH has been applied in the Southern Hemisphere. In the Northern Hemisphere more technical HCH has been used with about 80-85% α -HCH. HCB is mainly emitted by industrial sources and combustion processes, and its long atmospheric half-life of about 1-2 years leads to a quite homogenous dispersion in the atmosphere of both hemispheres. Therefore, the lower levels found in Antarctica might reflect the smaller industrialised area in the Southern Hemisphere. Tanabe et al. found a comparable α -/ γ -HCH ratio in Antarctic air¹¹). Similar ratios between α -, γ -HCH and HCB have also been reported for Antarctic Weddell seal blubber (Lobodon carcinophagus)⁷).

The air concentrations of the four analysed chlordane compounds were comparable in both polar regions. However, the average trans/cis chlordane ratio in the Antarctic was about 4 and 0,5 in the Arctic. In earlier studies a seasonal variation between 0,4 to 1,4 could be observed in Arctic air¹) but never such a high ratio as in the Antarctic samples. Differences in the composition of the applied technical product can be the reason.

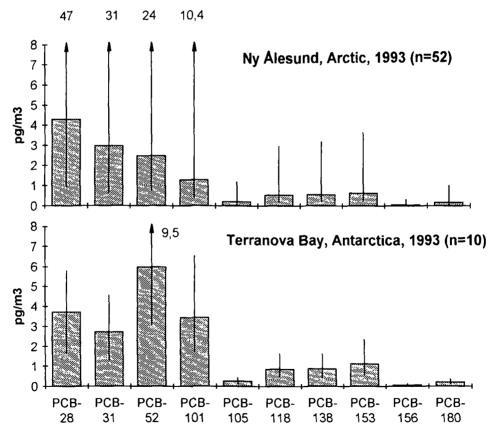


Figure 2: Average, minimum and maximum concentrations of selected polychlorinated biphenyl (PCB) congeners in ambient Arctic and Antarctic air in 1993.

ORGANOHALOGEN COMPOUNDS Vol. 20 (1994)

The average air concentration pattern of the 10 analysed PCB congeners (including the 6 compounds to be analysed according to IUPAC) is shown in Figure 2. The levels found in Arctic and Antarctic air were normally at least 5-10 times above the field blank. However, for PCB 156 and 180 the concentrations were not more than 3 times higher in a few Antarctic air samples. The concentrations of the higher chlorinated PCB in Antarctic air were comparable with those measured in the Arctic. However, the levels of PCB 28 and 31 were lower at Terranova Bay than the annual average at Spitsbergen in 1993. The planned Antarctic measuring campaign in 1995 will hopefully give some information if this observed deviation is caused by seasonal variations or a different source composition. Iwata et al. have also measured some of the analysed PCB congeners in ambiert air close to the Antarctic¹²). PCB 28 and 31 were much more dominant in these samples. The levels of the other PCB compounds were comparable with the presented data.

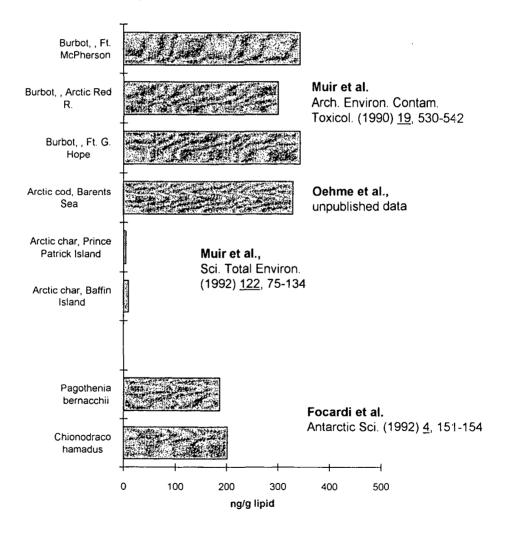


Figure 3: **DPCB** levels in fish liver from the Arctic and Antarctic

526

Table 1: Average, minimum, maximum and standard deviation of levels of 2,3,7,8-chlorine
substituted PCDD/PCDF and coplanar PCB congeners in 11 blubber samples from female
Antarctic fur seals

¹⁰⁰	Concentration, pg/g wet weight			
Congener	Average	± s _d	Minimum	Maximum
2,3,7,8-TCDD	0,35	0,07	0,22	0,46
1,2,3,7,8-PeCDD	1,32	0,44	0,73	1,86
1,2,3,4,7,8-HxCDD	0,33	0,11	<0,16	0,46
1,2,3,6,7,8-HxCDD	1,31	0,38	0,72	1,73
1,2,3,7,8,9-HxCDD	0,51	0,15	0,27	0,74
1,2,3,4,6,7,8-HpCDD	3,50	2,80	0,80	4,45
OCDD	19,2	18,1	7,0	71,0
2,3,7,8-TCDF	1,10	0,30	0,70	1,54
1,2,3,7,8-PeCDF ^a	0,45	0,24	0,23	1,13
2,3,4,7,8-PeCDF	0,95	0,31	0,56	1,42
1,2,3,4,7,8-HxCDF ^a	0,58	0,71	0,16	2,51
1,2,3,6,7,8-HxCDF	0,43	0,53	0,13	1,90
1,2,3,7,8,9-HxCDF	-	-	<0,04	<0,12
2,3,4,6,7,8-HxCDF	0,19	0,09	<0,10	0,39
1,2,3,4,6,7,8-HpCDF	0,78	0,49	0,23	1,97
1,2,3,4,7,8,9-HpCDF	0,34	0,25	<0,04	0,69
OCDF	2,25	1,66	0,77	6,88
TEQ (PCDD/PCDF) ^b	2,01	0,49	1,30	2,65
3,3',4,4'-TeCB	29,4	6,30	20,5	42,9
3,3',4,4',5,5'-PeCB	40,6	13,5	21,6	62,3
3,3,',4,4'5,5'-HxCB	8,50	2,61	4,64	12,1
TEQ (PCB) ^c	4,8	1,5	2,8	7,2

^a Not separated from 1,2,3,4,8-PeCDF or 1,2,3,4,7,9-HxCDF, respectively; ^b Nordic model; ^c see ref. 14.

PCB and PCDD/PCDF concentrations in Arctic and Antarctic marine biota

The comparison of PCB levels in Arctic and Antarctic biota is difficult. Sometimes concentrations are given on a wet weight basis without specifying the lipid content, sometimes on a lipid basis or even on a dry weight basis⁵). In addition, the species studied in the Arctic and Antarctic were different. So far, many publications have concluded that marine organisms from the Antarctic have a lower burden of organochlorines than biota from the Arctic⁴⁻⁸). This might be true, but a more systematic analysis of samples selected according to age, sex and geographic area is needed to draw a final conclusion. Selected data of the Σ PCB content in fish liver from the Arctic and Antarctic (see Figure 3), show that the levels in this organ might even be within the same range. This is more in accordance with the ambient air levels in both polar regions which are not significantly different.

Recently, the first systematic study has been finished concerning the presence of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in female Antarctic fur seals. PCDD/PCDF concentrations were determined in 11 seal blubber samples. The results clearly showed that PCDD/PCDF and coplanar PCB are also present in the

٤,

Antarctic environment (see Table 1). 2,3,7,8-chlorine substituted PCDD/PCDF were found at levels around 2 pg TEQ g⁻¹ blubber (Nordic model). Blank values were in general one order of magnitude lower or equal to the detection limit.

Compared to Arctic harp seals from the Greenland Sea¹³ (which also feed partially on crustacean) the concentrations were not more than 2-3 times lower in Antarctic fur seals. However, this difference can also partially be due to a different sex distribution (only female fur seals and male harp seals have been analysed). Levels in Arctic ring seals from Spitsbergen were about 5 times higher.

The PCDD/PCDF congener pattern in the Antarctic fur seal blubber was significantly different from that found in both Arctic ringed seals and harp seals which were very similar¹³). Reasons might be differences between the emission patterns of PCDD/PCDF in the Northern and Southern Hemisphere, different food habits or interspecies variations.

The congener pattern for CB-77, CB-126 and CB-169 in Antarctic fur seals v/ere quite similar to that found in Arctic seals. However, the levels expressed as TEQ¹⁴) v/ere about a factor of 5 lower than in Arctic harp seal. This is much less than the concentration differences reported earlier between Antarctic and Arctic seals for other PCB congeners. 1-2 orders of magnitude lower levels were found in Antarctic mammals^{6,7}).

5. References

- 1) Oehme M. (1991): Further evidence for long range air transport of polychlorinated aromates and pesticides: North America and Eurasia to the Arctic. Ambio 20: 293-297.
- 2) Muir D.C.G., R. Wageman, B.T. Hargrave, D.J. Thomas, D.B. Peakall and R.J. Norstrom (1992). Arctic marine ecosystem contamination. Sci. Total Environ. 122: 75-134.
- 3) Dewailly E., P. Ayotte, S. Bruneau, C. Laliberté, D.C.G. Muir, and R.J. Norstrom (1993): Inuit exposure to organochlorines through the aquatic food chain in Arctic Québec. Environ. Health Persp. 101, 618.
- Subramanian B.R., S. Tanabe, H. Hikada, and R. Tatsukawa (1983): DDTs and PCB isomers and congeners in Antarctic fish. Arch. Envrion. Contam. Toxicol. 12, 621-626.
- 5) Focardi S., L. Iari, and L. Marsili (1992): PCB congeners, DDTs and hexachlorobenzene in Antarctic fish from Terranova Bay (Ross Sea). Antarctic Science 4, 151-154.
- 6) Bacon C.E., W.M. Jarman, and D.P. Costa, Organochlorine and polychlorinated biphenyl levels in pinniped milk from the Arctic, the Antarctic, California and Australia. Chemosphere 24, 779-791.
- 7) Luckas B., W. Vetter, P. Fischer, G. Heidemann, and J. Plötz (1990): Characteristic chlorinated hydrocarbon patterns in the blubber of seals from different marine regions. Chemosphere, 21, 13-19.
- Norheim G., L. Sømme, and G. Holt (1982): Mercury and persistent chlorinated hydrocarbons in Antarctic birds from Bouvetøya and Dronning Maud Land. Environ. Pollut., 28A, 233-240.
- Oehme M., J.-E. Haugen, and M. Schlabach (1994): Ambient air levels of persistent organochlorines in spring 1992 at Spitsbergen and the Norwegian mainland. Comparison with 1984 results and quality control measures. Sci. Total Environ., in press.
- 10) Oehme M., M. Schlabach, and I. Boyd (1994): Polychlorinated dibenzo-p-dioxins, dibenzofurans and coplanar biphenyls are present in Antarctic fur seal blubber. Ambio, in press.
- Tanabe S, R. Tatsukawa, M. Kawano, and H. Hikada (1982): Global distribution and atmospheric transport of chlorinated hydrocarbons: HCH (BHC) isomers and DDT compounds in the Western Pacific, Eastern Indian and Antarctic Oceans. J. Oceanogr. Soc. Japan 38, 137-148.
- 12) Iwata H., S. Tanabe, N. Sakai, and R. Tatsukawa (1993): Distribution of persistent organochlorines in the Oceanic air and surface seawater and the role of ocean on their global transport and fate. Environ. Sci. Technol. 27, 1080-1098.
- 13) Oehme M., M. Schlabach, K. Hummert, B. Luckas, and E.S. Nordøy (1994): Determination of levels of polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls and pesticides in harp seals from the Greenland Sea, Sci Total Environ., submitted.
- 14) Safe S. (1990). Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and related compounds: Environmental and mechnistic considerations which support the development of toxicity equivalency factors (TEFs). Crit. Rev. Toxicol. 21, 51-88.