The Content of Polychlorinated Hydrocarbons in Arctic Mammals

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The use of chlorinated pesticides for more than 30 years and of polychlorinated biphenyls (PCB) for more than 40 years has caused a world-wide accumulation of these components in different ecosystems, ANDERSON et al. (1969), HOLDEN and MARSDEN (1967), HOLDEN and MARSDEN (1969), JENSEN et al. (1969), MADDOX (1972), MOORE and WALKER (1964), PRESTT et al. (1970), RISEBROUGH et al. (1968) and ULFSTRAND and SÖDERGREN (1972). Since no studies have been made on these components in Arctic ecosystems of Greenland, the present study was designed to elucidate this, especially concerning the concentrations of polychlorinated hydrocarbons (PCHC) in mammals. This is of interest since the Arctic sea mammals often migrate or eat migrating fish, thus being affected by PCHC from areas in which these components are used.

Materials and Methods

Material: Adipose tissue from mammals shot on the west coast of Greenland (from Narssarssuaq in South to Sukkertoppen in North) was taken mainly from the back, sealed in glass tubes and air mailed to Copenhagen for assay. Thus the present communication concerns assay of PCHC in fat tissue of two common porpoises (Phocaena phocaena), five bearded seals (Erignathus barbatus), five ringed seals (Phoca hispida), five hooded seals (Cystophora cristata), two Arctic foxes (Alopex lagopus), one polar bear (Ursus maritimus), and one sheep (Ovis aries).

Apparatus:

Gas chromatography: Model Perkin Elmer F 11 with a ^{63}Ni electron capture detector and a borosilicate glass column (2 mm, i.d. x 2 m), packed with a mixture of 5 % Dow 200 (125.000 cts) and 7 1/2 % QF_1 (10.000 cts) (1+1) on Chromosorb G. The column was conditioned at 250° for one week in order to avoid the QF_1 bleeding, and working conditions were as described DELVAUX (1971) with the exception of better separation at 180° column temperature than at 200° (injection temp. 220°, detector temp. 220°). Carrier gas: nitrogen at flow rate of 60-70 ml/min. detector supply 2/3 of maximal current. Sensitivity: 1 ng heptachloroepoxide gave 50 % of full scale. A Micro-Snyder evaporative concentrator was used and for thin layer chromatography (TLC) Desega Werke equipment (W. Germany) was used.

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Standards were as follows: Standards of PCHC: Heptachlor (1,4,5,6,7,8,8-heptachloro-3α,4,7,7α-tetrahydro-4,7-methanoindene) and heptachloroepoxide (Riedel, De Haën AG, Seelze-Hannover, W. Germany), lindane (1,2,3,4,5,6-hexachlorocyclohexane), op´DDT, pp´DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane) and pp´DDE (Ferrosan, Copenhagen, Denmark), Aldrin (1,2,3,4,10,10-hexachloro-1,4,4α,5,8,8α-hexahydro-endo,exo-1,4:5,8-dimethanonaphthalene) and Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4α,5,6,7,8,8α-octahydro-endo,exo-1,4:5,8-dimethano-naphthalene) (Shell Research Ldt., Sittinghourne, Kent, U.K.), Polychlorinated Biphenyls (PCB) (Aroclor 1254, 12 carbon atoms and 54 % chlorination) (Mosanto, St. Louis, Missouri, U.S.A.).

Reagents: n.hexane (b.p. 67-70°) distilled once or twice over NaOH pellets with a Vigreux column. Al_2O_3 (Brochmann activity II), were from BDH, Poole, Dorset, England. Acetone p.a. redistilled with 1 m Vigreux column, Na_2SO_4 anhydrous (p.a.) were all from Merck, Darmstadt, Germany. When concentrated 20 times, 10 µl of any solvent used did not reveal PCHC peaks when assayed in the gas-chromatograph. Glass wool and glasswares were rinsed in petrol-ether.

Extraction: About 400 mg adipose tissue was extracted two times, each with 7 ml n.hexane at 22° for 1 h and once overnight at 22°. Re-extraction with petrol-ether, chloroform + methanol (1:1), acetonitrile or acetone hexane 1:1 revealed remnants of PCHC to be less than 2 % of the original content.

Clean up: Raw extract was dried over Na_2SO_4 and concentrated below a stream of nitrogen at room temperature. The PCHC was weighed and dissolved in n-hexane to a concentration of about 100 mg/ml. 1 ml extract was separated from lipids by the single stage method (HOLDEN and MARSDEN, 1969). To a column of 2 g was added aluminia, activated to Al_2O_3 at 800° for 4 h, cooled and supplied with 5 % (v/w) water, then 100 mg lipid/1 ml hexane was added at the top. After 5 min. 1 ml hexane was applied and the column was eluted with a further 10 ml n-hexane. This eluate was reduced to 1 ml at 23° in a gentle stream of nitrogen. The column chromatography of this eluate was repeated. The final eluate, reduced to about 0.5 ml, was assayed in the gas chromatograph using 1.10 µl samples. By repeating the process in equipment without the sample, no PCHC peaks were found. Recovery was 80-100 % for lindane, heptachlor, heptachloroepoxide, aldrin, pp´DDE, dieldrin and pp´DDT. Lindane and aldrin were determined on the chromatogram obtained after the clean-up procedure. At this stage, raw pp´DDE (pp´DDE plus PCB) was also determined together with PCB, by combining the products obtained by multiplying the height of individual peaks with the corresponding retention time. This sum is divided by the product of peak height and the retention time of 1 ng pp´DDE (HOLDEN and MARSDEN, 1969). For identification purposes, spots of pesticides on the TLC (vide infra) were scraped off, eluted with 5 ml hexane and determined by GLC.

Thin-layer chromatography (TLC) was performed on 0.25 mm Aluminium oxide G (type E). 20 µl concentrated, de-lipidized PCHC extract from the aluminia column was applied on the TLC plates 1.5 cm from the lower edge and developed in an ascending system with 1 % (v/v) acetone in normal hexane for 15 min. The pattern of the standard markers on the TLC plates were sprayed with 0.10 g $AgNO_3$ dissolved in 1 ml water and 10 ml concentrated 2-phenoxyethanol (NOREN and WESTÖÖ, 1968). The solution was diluted to 200 ml with acetone and 5 drops 30 % hydrogen peroxide were added. The spots of markers localized the sample spots, (identified by their Rf-values). The sample spots were scraped off, eluted in hexane and re-chromatographed.

Statistical evaluation: Since the data presented below showed a non-Gaussian distribution the non-parametric, nominal Fisher test was used in order to evaluate the data obtained on the different species. The limit for comparison of data was chosen as arithmetic mean between the highest value in the species having lowest mean value, and the lowest value in the species showing the highest mean value. The level of significance was selected at the 1 % level.

Results

Table 1 shows the PCHC content in adipose tissue of some Arctic mammals killed in 1972 on the west coast of Greenland. Among the PCHC studied PCBs occurred in highest amounts. A peak value of 6.4 ppm PCB was found in the Common Porpoise(case 181).This species also showed the highest mean value of PCB (6.7 ppm).

Among all the species studied great variations in data occurred from animal to animal. With three individual exceptions, "raw" pp´DDE occurred in the second highest concentration among the PCHC assayed. Thus the polar bear contained the highest amount (mean value 1.3 ppm) followed by the bearded seal (mean value 0.47 ppm) and the common porpoise (mean value 0.32). The only exceptions to the rule that "raw" pp´DDE was found in the second highest amount among the PCHC studied was in the data on bearded seal (case 8), the sheep and the polar bear where aldrin in one case of the three species was found in amounts of 1.6, 0.41 and 3.1 ppm, respectively.

Lindane was found in all bearded seals (mean value 0.053 ppm) and in two cases of common porpoise studied, but only in 60 % of the ringed seals studied. Lindane was not found in the polar bear, and not in the hooded seal. Furthermore, heptachlor was rarely found, but small amounts of heptachlorepoxide were found in all but five samples.

TABLE 1

Content of Polychlorinated Hydrocarbons in Fat Tissue of Arctic Mammals.

Species	Sample No.	Lindane	Hepta-chlor	Aldrin	Hepta-chlor-epoxide	"raw" pp´DDE	PCB
Bearded seal (E-rignatus barbatus)	35	0.037	0.039	0.12	0.12	0.42	2.6
	29	0.64	n.d.	0.43	n.d.	0.67	0.6
	8	0.14	n.d.	1.60	n.d.	0.80	1.6
	8	0.019	0.017	0.042	0.045	0.24	3.0
	170	0.007	n.d.	0.029	0.022	0.20	1.2
Mean values		0.053	0.011	0.44	0.037	0.47	1.8
Ringed seal (Phoca hispida)	97	0.002	0.003	0.008	0.005	0.025	1.0
	96	0.005	n.d.	0.020	0.021	0.083	1.3
	30	0.025	n.d.	0.14	0.050	0.26	0.6
	158	n.d.	n.d.	0.025	0.025	0.20	0.7
	159	n.d.	n.d.	0.025	0.028	0.20	0.9
Mean values		0.006	0.001	0.044	0.026	0.15	0.9
Hooded seal (Cystophora cristata)	179	n.d.	n.d.	0.015	0.058	0.43	4.1
	180	0.017	n.d.	0.037	0.073	0.49	2.5
	183	n.d.	n.d.	0.029	0.062	0.31	1.9
	175	n.d.	n.d.	0.024	0.012	0.069	4.9
	178	n.d.	n.d.	0.035	n.d.	0.14	0.3
Mean values		0.003	n.d.	0.028	0.041	0.29	2.7
Common porpoise (Phocaena phocaena)	182	0.005	n.d.	0.043	n.d.	0.045	1.9
	181	0.018	n.d.	0.028	0.059	0.60	11.4
Mean values		0.012	n.d.	0.036	0.030	0.32	6.7
Polar bear (Ursus maritimus)		n.d.	n.d.	3.06	0.49	1.25	21.0
Arctic fox (Alopex lagopus)	91	0.019	n.d.	0.043	0.047	0.22	1.6
	95	n.d.	n.d.	0.032	0.080	0.052	3.9
Mean values		0.010	n.d.	0.038	0.064	0.14	2.8
Sheep (Ovis aries)	3	n.d.	n.d.	0.41	n.d.	0.19	1.2

The total content of all the components studied was found in the lowest amount in the sheep where only aldrin pp´DDE and PCB could be traced. Aldrin was however found in medium-size concentrations, when compared with the findings in the other animals under study.

The Fisher test revealed non-significant differences in the PCHC content among the animal species studied.

Only the PCB content of the ringed seal and the sheep was significantly lower than in the hooded seal ($p \leq 0.01$). No correlation between "raw" pp´DDE and the PCB content of the animals studied could be traced.

Discussion

Although HOLDEN (1968) found small amounts of dieldrin, DDE, TDE and DDT in one ringed seal shot on Baffin Island (Canada) little is known about the distribution of the PCHC components in the Arctic.

The PCB content in seals living in waters close to industrial areas (1.5 - 16 ppm/PCB (JENSEN et al., 1969) is similar to the PCB content in the Artic sea mammals found in the present communication (2.3-11.4 ppm). On the other hand "raw" pp´DDE occurs in lower amounts in the Arctic than in Swedish waters (JENSEN et al., 1969). However, within the species themselves there are great variations as regards PCHC content. The variation in seals HOLDEN 1968) and birds (PRESTT et al., 1970) has previously been described and is probably related to the age and amount of fat tissue of the animals.

The origin of PCHC in the Arctic seals may be from fish and indirectly from algae, absorbing PCHC from polluted Gulf Stream water.

Contrary to our findings in Arctic birds (BRÆSTRUP et al., 1973) a statistical evaluation of the correlation between the "raw" DDE content and the content of PCB in the individual mammals studied, excluded such a correlation between the content of these two components. This argues in favour of the idea that seals may be able, to a greater extent than birds, to metabolize some PCHC (vide infra).

Compared with our data collected among Arctic birds (BRÆSTRUP et al., 1973) the content of PCB is lower in the Arctic mammals, apart from the content found in the Polar Bear.
The content of PCB and "raw" pp´DDE is at least one order of magnitude lower in the Arctic mammals than in the sea birds concerned. As far as the seals are concerned this difference is difficult to explain since seals eat fish as do many Arctic sea

birds in which the PCHC content is dependent on the ecological level of the individual Arctic bird species (BRÆSTRUP et al., 1973). However, the reason may be that seals degrade and excrete more of the dietary PCHC than the sea birds do. The seals along the coastline of Greenland seem periodically to migrate as much as the sea birds, but the seals may to a lesser extent contact polluted sea-ways than sea birds do (BRÆSTRUP, 1949).

The present communication revealed the Arctic sheep to be low in PCHC content, explainable by its feeding solely on stuffs of plant origin. Contrary to that the Arctic fox being a scavenger contained high amounts of PCB and lindane but lower amounts of raw pp´DDE.

SUMMARY

17 fat tissue samples of four different Arctic seals species shot in Greenland, fat samples of one polar bear, two polar foxes and one sheep from south west Greenland were assayed for polychlorinated hydrocarbons (PCHC), aldrin, heptachlor, heptachlorepoxide, lindane, "raw" DDE and PCB.

"Raw" pp´DDE and PCB were found in all specimens in highest amount, peak values of pp´DDE were found in the polar bear and highest amount of PCB was found in a hooded seal.

Aldrin was also found in most samples, but only trace amounts of lindane, heptachlor and its epoxide were found variably. In PCHC content great variation from specimen to specimen was found in all species.

The data obtained are discussed in relationship to the possible sources of PCHC contamination of the Arctic.

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