DDE, PCB and Aldrin Levels in Arctic Birds of Greenland

by

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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 (1,7,9,10,12,13,18,19,20). 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 concentration of polychlorinated hydrocarbons (PCHC) in birds. This is of interest since these often migrate or eat migrating fish, thus being affected by areas in which PCHC are used.

Materials and Methods

Material: Adipose tissue from birds shot on the West Coast of Greenland (from Narssarssuaq in South to Sukkertoppen in North (4) was taken mainly from the neck, sealed in glass tubes and air mailed to Copenhagen for assay.

Apparatus:

Gas chromatograph: Model Perkin Elmer F 11 with a ^{63}Ni electron capture detector and a borosilicate glass column (3 mm, i.d. x 2 m), packed with a mixture of 5 % Dow 200 (125000 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 (6) 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. Reagents were as follows: Standards of PCHC: Heptachlor and Heptachloroepoxide (Riedel, De Haën AG, Seelze-Hannover, W. Germany), lindane, op´DDT, pp´DDT and pp´DDE (Ferrosan, Copenhagen, Denmark), Aldrin and Dieldrin (Shell Research Ltd., Sittingbourne, Kent, U.K.), Polychlorinated biphenyls (PCB) (Aroclor 1254, Monsanto, 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 coloumn, 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. Glass wool and glassware were rinsed in petrol-ether.

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Extraction: 400 lyophilized adipose tissue was extracted twice with n-hexane at 40° for 1 h and once overnight at 23°. 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 extract.

Clean up: Raw extract was dried over Na_2SO_4 and concentrated to 4 ml at room temperature under a gentle stream of nitrogen.

The PCHC in 1 ml extract were separated from lipid by the single stage method (9). To a column of 2 g Aluminia was added, activated to Al_2O_3 at 800° for 4 h, cooled and supplied with 5 % 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. The 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 with the product of peak height and the retention time of 1 ng pp´DDE (9). For identification purposes, spots of pesticide on the TLC (vide infra) were scraped off, eluted with 5 ml hexane and determined by TLC.

Thin-layer chromatography (TLC) was performed on 0.25 mm Aluminium oxide G (type E). 20 ul 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 standard marker of the TLC plates was sprayed with 0.10 g $AgNO_3$ dissolved in 1 ml water and 10 ml 2-phenoxyethanol (15). The solution was diluted to 200 ml with acetone and 5 drops 30% hydrogen peroxide were added. The spots of markers and of samples, identified by their Rf-values, were scraped off, eluted in hexane and re-chromatographed.

Results

Table 1 shows the PCHC content in adipose tissue of birds shot in 1972 on the West Coast of Greenland.

Among the birds showing the lowest mean concentration of "raw pp´DDE" were the king Eider (mean: 1.7 ppm), the Common Eider (0.8 ppm), the Harlequin Duck (1.1) and the Purple Sandpiper (1.1 ppm). However, the content was higher in Brünnich´s Guillemot (3.5 ppm) and the Ptarmigan (3.3 ppm), while the highest concentrations were found in the Cormorant (10.3 ppm) and the Raven (13.9 ppm). However, in these animals great individual variation occured.

Table 1

The content of chlorinated organic components in the fat tissue of arctic birds from Greenland.

Species	no.	ppm dry weight pp´DDE[+]	PCB	Lindane[+++]
King Eider (Somateria spectabilis)	166	1.1	1.1	n.d.[++]
	82	2.8	5.3	-
	119	1.3	3.5	0.02
Common Eider (Somateria mollissima)	68	0.8	2.0	0.12
Harlequin Duck (Histrionicus histrionicus)	79	1.1	2.2	n.d.
	110	1.9	3.2	0.08
	109	1.2	4.6	n.d.
	42	0.7	2.9	-
	41	1.2	4.8	-
Long tailed Duck (Clangula hyemalis)	84	1.3	4.1	
	51	1.0	6.0	0.06
	80	0.8	2.9	
Purple Sandpiper (Calidris maritima)	112	1.1	2.8	0.04
Brünnich´s Guillemot (Uria lomvia)	17	3.6	8.5	n.d.
	4	8.7	39.6	-
	3	2.4	6.3	-
	5	1.8	6.2	0.31
	18	1.2	3.9	-
Cormorant (Phalocrocorax carbo)	71	15.0	46.7	
	72	6.5	18.0	
	74	9.5	14.1	
Ptarmigan (Lagopus mutus)	121	3.6	9.1	n.d.
	120	4.0	11.1	0.11
	125	3.0	12.0	0.40
	126	1.9	2.9	n.d.
	124	3.9	15.8	0.18
Raven (Corvus corax)	101	16.4	34.6	0.18
	50	6.5	13.8	n.d.
	114	18.8	63.0	n.d.

+ pp´DDE represent the so-called "raw value" including some PCB
++ n.d. = not detectable
+++ identified as a fraction in CLC, which posesses an Rf-value of standard lindane.

In the case of PCB, the lowest concentration (mean values) was again found in the group of ducks, the figures ranging from 3.3 ppm for the King Eider, 2.0 ppm for the Common Eider, 1.2 ppm for the Harlequin Duck and 1.7 for the Long Tailed Duck. In this group, the Purple Sandpiper (2.8 ppm) may also be included. For the other species, the PCB concentration showed a higher concentration, the Ptarmigan containing 10.1 ppm, Brünnich's Guillemot 12.9 ppm, the Cormorant 26.3 ppm and lastly, the Raven 37.1 ppm, but great individual variation occurs.

pp'DDT and pp'DDD were not traced. Dieldrin was probably present in minor amounts, although no attempt was made in the present assay to determine the exact figure since the peak coexisted together with a PCB peak in the TLC-chromatogram. In about one third of the birds, trace amounts of lindane were found. Correlation analysis (Fig. 1) (Spearman Rank test) revealed a statistical significant correlation in the birds studied betwen the DDE content and the PCB content (coefficient of correlation 0.9, $p \leq 0.1$ %).

Discussion

Although Holden (8) 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 compounds in the Arctic. The present communication revealed some of these components and PCB to be present in most samples of sea birds located on the coastlines of South West Greenland.

The amounts of PCHC contained in each bird varies from one species to another. The reason for this would appear to be differences in age, dietary habits and possibly, winter migration to more heavily polluted areas of the world. Table 2 shows the dietary habits of the birds, the type of fish or vegetable matter consumed and the probable winter migratory quarters.

From the results of the present communication, it seems that the pesticide niveau is more influenced by the position of the bird in the food chain than by its migratory habits. This point is demonstrated by the fact that Brünnich's Guillemot, living from a diet of marine invertebrates and fish (11) and migrating to the Coast of New Foundland has, however, a mean concentration of raw pp'DDE which is only 3.5 ppm, while the Cormorant, preferably fish eating and non-migratory, has a mean content of raw pp'DDE which is 10.3 ppm.

The rather large concentration of pesticide found in the Ptarmigan is difficult to explain as the birds eat plant matter, berries and occasionally insects. They are non-migratory.

However, within the species itself, there is great variance as regards pesticide content (c.f. table 1). This variance has also previously been described in seals (8) and birds (18) and is probably related to the age and amount of fat tissue in the animals.

In the case of raw pp'DDE, the ducks, all with a diet of marine invertebrates, showed the lowest figures. The long Tailed Duck and the Common Eider are migratory birds. The greatest concentration was found in the Raven, a scavenger living off fish in the summer, supplemented by human refuse in the winter. This species is non-migratory.

The origin of PCHC found in the other Arctic sea birds may be from fish or from algae, absorbing PCHC from polluted Gulf Stream water. Finally, global air pollution cannot be ruled out, since many PCHC are rather volatile.

The biological impact on Arctic ecosystems of PCHC may be serious, since DDT not only decreases eggshell calcium (3), but also hampers temperature acclimatization of fishes (2, 16), ATP-ase-activity (21) and finally, alters the species composition of algae (14).

The DDE found may be formed in the Arctic animals or algae (17) or formed in ecosystems in higher temperature areas from pp´DDT.

The significant correlation found between the content of PCB and DDE in the fat tissue of the birds studied, may be explained by the high ecological level of the birds and the lipid solubilities of the two globally distributed PCHC under study and their metabolic inertness(5).

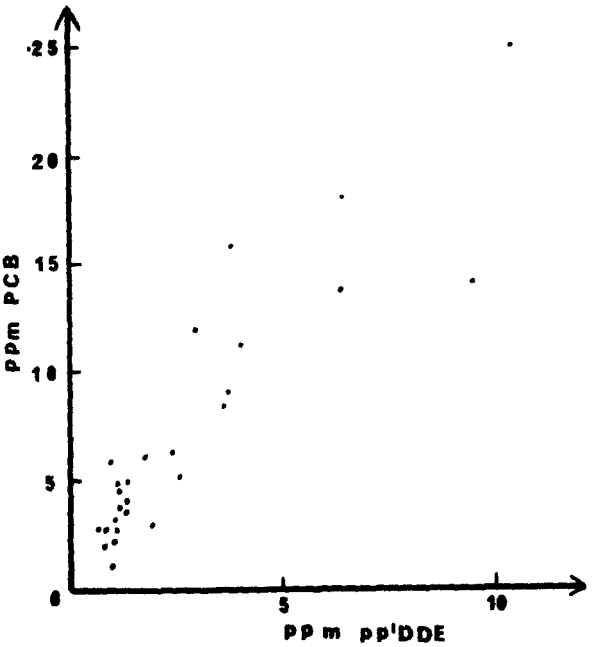

Fig. 1. Correlation between "raw pp´DDE" and PCB found in avian tissue.Coefficient of correlation α= 0.1 %.

Table 2

Dietary and Migratory habits of Arctic Birds.

Species	Dietary habits	Migratory habits
King Eider (Somateria spectabilis)	Marine invertibrates, berries and buds	North Atlantic Continent
Greenland Rock Ptarmigan (Lagopus mutus)	Tundra vegetation, berries, some incects	Non-migratory
Harlequin Duck (Histrionicus histrionicus)	Marine invertibrates	Non-migratory
Brünnich's Guillemot (Uria lomvia)	Fish, marine invertibrates	Migrates down coastline towards New-Foundland
Cormorant (Phalocrocorax carbo)	Fish	Costal bird
Purple Sandpiper (Calidris maritima)	Small crustaceans, insects	North West Europe
Raven (Corvus corax)	Scavenger (fish in winter garbage from humans)	Costal bird
Long tailed duck	Marine invertibrates	Western Europe

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