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Organochlorine compounds in cod from the
northern, central and southern part of
the North Sea and in hake of the Bay of
Biscay in 1974 - 1975.

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SUMMARY

Pesticides and PCB values were determined in 27 cod liver samples, 10 hake liver samples and 4 samples of mixed fish flesh derived from cod caught in three different parts of the North Sea and hake from the Bay of Biscay in 1974 and 1975.

The highest concentrations of organochlorine compounds were found in the southern part and the lowest in the northern part of the North Sea.

Mean values of PCB, Σ p,p'-DDT, dieldrin and HCB, on a fat base, were (ppm):

	north N.S.	central N.S.	south N.S.	Bay of Biscay
PCB	5	21	39	15
Σ p,p'-DDT	1,1	2,1	1,9	1,7
dieldrin	0,13	0,48	0,79	0,17
HCB	0,16	0,20	0,51	0,10

INTRODUCTION

In the autumn of 1974 and the spring of 1975 cod and hake were caught in the North Sea and the Bay of Biscay as much as possible in accordance with the requirements of the Working Group on Pollution Baseline and Monitoring studies in the Oslo Commission and ICNAF Areas.

The cod was coming from three different fishing grounds in the North Sea (northern, central, southern part) and the hake from the Bay of Biscay.

Four series of 7 or 10 liver samples from different individuals and one fish flesh sample, containing the flesh of all individuals together, were examined. A full description of the samples is given in table I.

METHOD

Extraction

All livers were analysed separately, whereas equal quantities fish flesh of 7 or 10 individuals from one fishing ground were combined for analysis.

After homogenization in a Waring blender, the sample (5 g liver; 40 g flesh) was ground with anhydrous sodium sulfate and extracted with n-pentane using a Soxhlet apparatus (3 hours).

Clean-up

Column chromatography was used to separate chlorinated hydrocarbons from lipids. Aluminiumoxide of zero activity (basic Merck No 1076) was deactivated with 10 % H₂O. The extracts were concentrated on a rotary film evaporator and transferred to a column (20 mm i.d.) of anhydrous sodium sulfate over 15 g deactivated Al₂O₃. The organochlorines were eluted with 200 ml n-pentane.

The eluate was concentrated to 2.0 ml after which separation of pesticides and polychlorinated biphenyls (PCB) took place. 2 g of activated silicagel (Merckosorb S I 60. No 10228; 2 hours at 210 °C) was slurried into a glass column (6 mm i.d.) with n-hexane and the solvent drained to the surface of the silicagel. The sample (2 ml) was transferred to the column, washed with 1,5 ml n-hexane and eluted first with 10 ml of hexane and then with 10 ml of hexane/ethylether mixture (85 : 15 % v/v). The first fraction contains HCB, PCB and most of the p,p'-DDE (70 %); the second fraction contains 30 % of the p,p'-DDE and the other pesticides.

Detection

The equipment used was a Packard-Becker gaschromatograph, type 419, provided with a ⁶³Ni Electron Capture Detector (305 °C). Glass columns of 1,5 m length and 2 mm i.d. were used, packed with two different stationary phases:

3 % NPGS at 215 °C (injection port 220 °C)
1,95 % QF-1/1,5 % OV-17 at 195 °C (injection port 200 °C)

The carrier gas was Ar/CH₄ at a flowrate of 30 ml/min.

Integrations and calculations were carried out by an Autolab computing integrator, System I.

Quantitative evaluation

The content of PCB has been calculated on the NPGS column by means of the peak having $t_r = 1,32$ relative to p,p' -DDE = 1.00. Aroclor 1254 was used as standard.

HCB, dieldrin, endrin, α -HCH, γ -HCH and p,p' -DDE were determined on the NPGS column and the other pesticides on the QF-1/OV-1 column.

p,p' -DDE in the first fraction was determined using the oxidation method described by Norén and Westöö (1). The p,p' -DDE/PCB peaks were measured before and after oxidation and the p,p' -DDE was calculated as the difference.

Some oxidation and dehydrohalogenation reactions were carried out with the second fraction for further identification of the pesticides.

RESULTS

The results are given in table II to V and summarized in table VI.

DISCUSSION

Considering the results it is obvious that the contamination of polychlorinated biphenyls is 5 to 10 times larger as the pesticide contamination. The most polluted area is the southern North Sea, followed by the central North Sea and the Bay of Biscay (figure 1).

A serious PCB contamination of the North Sea area by the north-western European countries must be concluded from this investigation.

The same can be concluded for HCB, dieldrin and p,p' -DDT, although the last group is more equally distributed. The PCB and pesticide concentrations in the flesh are 1 to 5 times higher than in the liver, with exception of p,p' -DDD occurring in a higher level in the liver.

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(1) G. Westöö, K. Norén

Acta Chem. Scand. 24, 1639-1644 (1970).

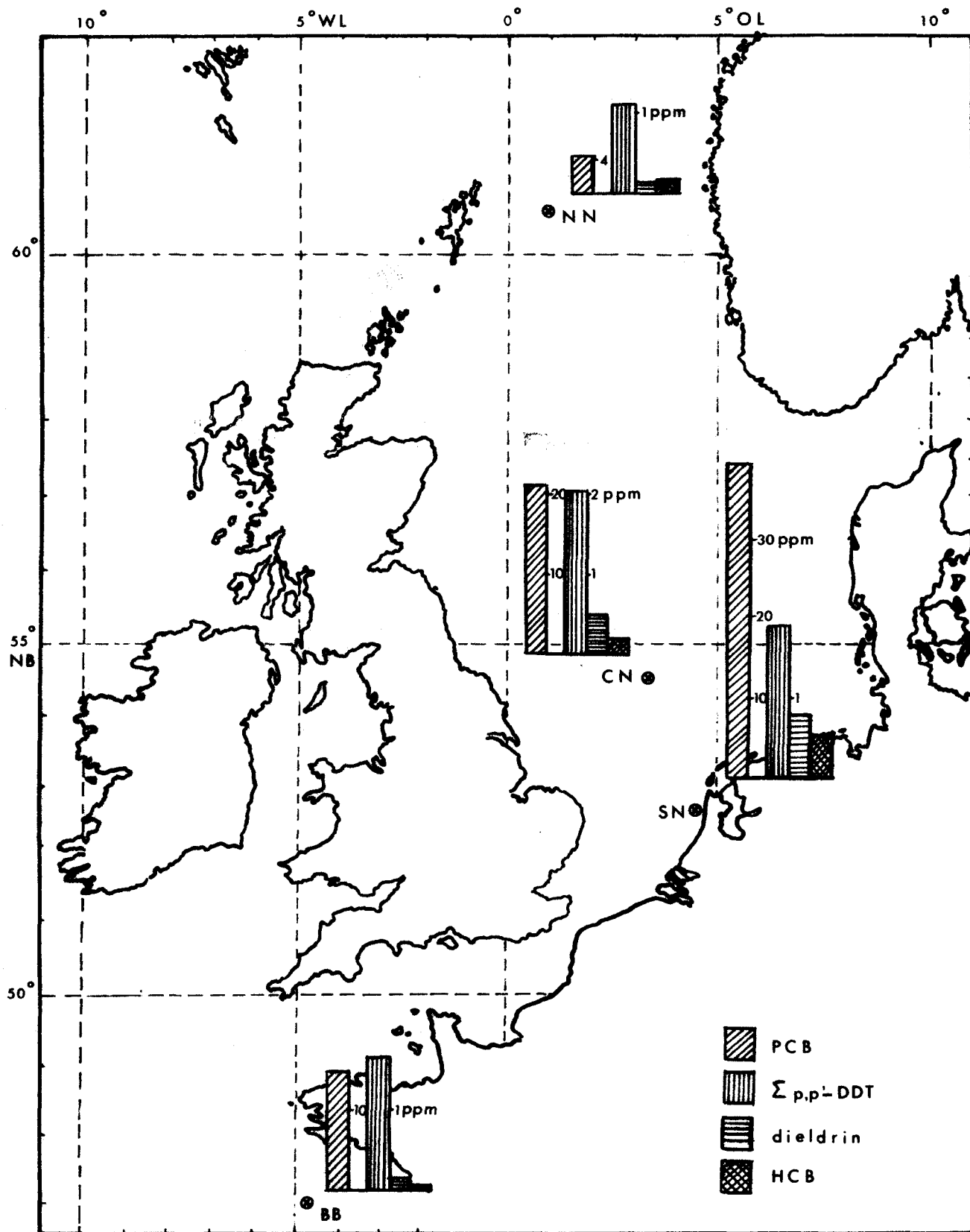


Fig.1. Mean values of PCB, $\Sigma p,p'$ -DDT, dieldrin and HCB in cod liver from the northern, central and southern part of the North Sea and in hake liver from the Bay of Biscay in 1974-1975 (expressed in mg/kg on a fat base)

TABLE I - Sample-data.

Fish	Fishing ground	Date	Number	Year class	Weight (g)	Length (cm)
Cod	northern North Sea 60°30'N 1°E (7504020202)	19- 2-1975	NN 1	1972	1620	54
			NN 2	1972	1340	52
			NN 3	1972	2000	58
			NN 4	1972	1910	57
			NN 5	1973	1440	51
			NN 6	1973	1190	47
			NN 7	1972	1970	57
			NN 8	1973	1360	49
			NN 9	1972	1840	55
			NN 10	1972	2030	61
Cod	central North Sea 54°30'N 3°20'E (7402020202)	14-10-1974	CN 1	1972	1500	56
			CN 2	1972	1430	55
			CN 3	1972	1860	59
			CN 4	1972	1660	57
			CN 5	1972	1420	54
			CN 6	1972	1450	54
			CN 7	1973	870	43
Cod	southern North Sea 52°40'N 4°30'E (7401020202)	27- 9-1974	SN 1	1972	3100	67
		28- 9-1974	SN 2	1972	2550	58
			SN 3	1972	1720	57
			SN 4	1972	3600	66
			SN 5	1972	1700	53
			SN 6	1972	1820	54
			SN 7	1972	2810	64
			SN 8	1972	3150	63
			SN 9	1972	2300	39
			SN 10	1972	1800	53
Hake	Bay of Biscay 46°56'N 4°47'W (7403030202)	23-10-1974	BB 1	1969	610	43
			BB 2	1970	430	39
			BB 3	1970	470	41
			BB 4	1970	490	40
			BB 5	1969	500	41
			BB 6	1972	390	40
			BB 7	1970	460	40
			BB 8	1969	340	37
			BB 9	1970	520	42
			BB 10	1969	480	41

TABLE II - Contents of pesticides and PCB's in cod liver (N.N. 1 - 10) and flesh from the northern North Sea (60°30'N, 1° E) expressed in mg/kg on a fat base.

Sample	NN 1	NN 2	NN 3	NN 4	NN 5	NN 6	NN 7	NN 8	NN 9	NN 10	Flesh
Fat (%)	50,0	46,7	40,7	38,5	41,1	44,5	38,2	30,8	40,0	33,1	0,10
HCB	0,16	0,13	0,16	0,15	0,13	0,12	0,15	0,17	0,22	0,16	0,43
α-HCH	0,22	0,08	0,07	0,04	0,06	0,07	0,08	0,06	0,04	0,07	0,24
β-HCH	-	-	-	-	-	-	-	-	-	-	-
γ-HCH	-	-	-	-	0,006	0,004	-	-	-	-	0,10
heptachlorepoxyde	0,02	0,02	-	0,03	0,03	0,02	0,03	0,03	0,05	0,05	0,08
dieldrin	0,08	0,08	0,04	0,09	0,13	0,05	0,11	0,14	0,28	0,30	0,17
p,p'-DDE	0,41	0,18	0,30	0,33	0,30	0,28	0,36	0,61	0,94	0,88	0,56
p,p'-DDD	0,28	0,23	0,26	0,41	0,17	0,20	0,30	0,27	0,54	0,71	0,25
p,p'-DDT	0,36	0,33	0,18	0,40	0,25	0,40	0,09	0,28	0,46	0,36	0,50
Σ p,p'-DDT	1,05	0,74	0,74	1,14	0,72	0,88	0,75	1,16	1,94	1,95	1,31
PCB	8,3	1,4	4,0	2,4	1,9	2,2	1,9	6,7	7,8	7,2	6,1

TABLE III - Contents of pesticides and PCB's in cod liver (CN 1 - 7) and flesh from the central North Sea (54°30'N, 3°20'E) expressed in mg/kg on a fat base.

Sample	CN 1	CN 2	CN 3	CN 4*	CN 5	CN 6	CN 7	Flesh
Fat (%)	32,0	40,1	44,3	5,6	34,7	46,3	45,4	0,06
HCB	0,15	0,34	0,32	0,30	0,15	0,14	0,12	0,46
α-HCH	0,15	0,17	0,16		0,13	0,22	0,24	0,34
β-HCH	-	-	-		-	-	-	-
γ-HCH	0,04	0,03	0,01		0,14	0,007	0,02	0,16
heptachlorepoxyde	0,07	0,06	0,08	0,02	0,06	0,05	0,05	0,12
dieldrin	0,48	0,63	0,76	1,38	0,38	0,30	0,33	0,34
p,p'-DDE	1,52	2,17	1,53	7,5	1,61	0,67	0,29	1,73
p,p'-DDD	0,80	0,84	0,75	6,7	0,60	0,18	0,31	0,49
p,p'-DDT	0,25	0,20	0,17	5,8	0,16	0,10	0,12	1,71
Σp,p'-DDT	2,57	3,21	2,45	20,0	2,37	0,95	0,72	3,93
PCB	18,0	45,0	38,0	279,7	15,7	6,9	3,3	48,6

* This cod was in a bad condition.

TABLE IV - Contents of pesticides and PCB's in cod liver (SN 1 - 10) and in flesh from the southern North Sea (52°41'N, 4°30'E) expressed in mg/kg on a fat base.

Sample	SN 1	SN 2	SN 3	SN 4	SN 5	SN 6	SN 7	SN 8	SN 9	SN10	Flesh
Fat (%)	48,3	51,3	40,6	53,0	55,4	49,9	62,5	60,9	43,8	61,1	0,05
HCB	0,71	0,41	0,68	0,47	0,46	0,48	0,47	0,65	0,38	0,42	0,90
α-HCH	0,09	0,09	0,11	0,08	0,10	0,10	0,12	0,13	0,10	0,15	0,29
β-HCH	-	-	-	-	-	-	-	-	-	-	-
γ-HCH	0,04	0,03	0,06	0,05	0,03	0,03	0,02	0,08	0,08	0,08	0,26
heptachlorepoxyde	0,22	0,15	0,08	0,06	0,23	0,05	0,05	0,13	0,10	0,08	0,40
dieldrin	1,36	0,53	1,11	0,76	0,74	0,84	0,70	0,88	0,42	0,53	1,07
p,p'-DDE	1,29	0,59	2,47	0,47	0,90	0,58	0,84	0,36	0,69	0,31	0,98
p,p'-DDD	0,79	0,23	1,07	0,32	0,68	0,47	0,48	0,32	0,40	0,21	0,22
p,p'-DDT	1,00	0,24	0,53	0,51	1,12	0,41	0,49	0,31	0,42	0,32	2,05
Σ p,p'-DDT	3,08	1,06	4,07	1,30	2,70	1,46	1,81	0,99	1,51	0,84	3,25
PCB	47,2	20,4	107,4	28,7	35,5	31,4	30,6	36,8	32,8	20,6	37,1

TABLE V - Contents of pesticides and PCB's in hake liver (BB 1-10) and in flesh from the Bay of Biscay (46°56'N, 4°47'W) expressed in mg/kg on a fat base.

Sample	BB 1*	BB 2	BB 3	BB 4	BB 5	BB 6	BB 7	BB 8	BB 9	BB 10	Flesh
Fat (%)	23,7	44,9	42,2	49,9	49,5	45,6	50,2	41,5	54,0	53,5	0,70
HCB	0,37	0,20	0,15	0,10	0,08	0,09	0,08	0,08	0,08	0,07	0,24
α-HCH	0,06	0,23	0,05	0,11	0,10	0,08	0,08	0,07	0,10	0,11	0,08
β-HCH	-	-	-	-	-	-	-	-	-	-	-
γ-HCH	0,06	0,05	0,04	0,06	0,05	0,03	0,03	0,04	0,04	0,04	0,05
heptachlorepoxyde	0,15	0,08	0,07	0,05	0,07	0,08	0,07	0,06	0,06	0,03	0,34
dieldrin	0,39	0,21	0,10	0,17	0,18	0,19	0,22	0,16	0,18	0,15	0,52
p,p'-DDE	3,40	2,40	1,80	0,80	0,42	0,39	0,32	0,27	0,40	0,18	4,02
p,p'-DDD	2,28	0,80	0,39	0,25	0,15	0,23	0,21	0,24	0,21	0,17	1,26
p,p'-DDT	1,69	2,06	0,38	0,56	0,63	0,32	0,40	0,35	0,38	0,19	3,16
Σp,p'-DDT	7,37	5,26	2,57	1,61	1,20	0,94	0,93	0,86	0,99	0,54	8,44
PCB	76,0	30,2	22,2	16,4	10,2	16,3	10,0	12,8	9,4	7,2	56,0

* This hake was in a bad condition.

TABLE VI - Minimum, maximum and mean values of pesticides and PCB's in cod liver from the North Sea and in hake liver from the Bay of Biscay in 1974 - 1975 (expressed in mg/kg on a fat base).

Fishery ground	Northern North Sea		Central North Sea		Southern North Sea		Bay of Biscay	
	range	mean	range	mean	range	mean	range	mean
Fat (%)	30,8 - 50,0	40,4	32,0 - 46,3	40,5	40,6 - 62,5	52,7	41,5 - 54,0	47,9
HCB	0,12 - 0,22	0,16	0,12 - 0,34	0,20	0,38 - 0,71	0,51	0,07 - 0,20	0,10
α-HCH	0,04 - 0,22	0,08	0,13 - 0,24	0,18	0,08 - 0,15	0,11	0,05 - 0,23	0,10
β-HCH	---	-	---	-	---	-	---	-
γ-HCH	0,00 - 0,006	0,001	0,007 - 0,14	0,04	0,02 - 0,08	0,05	0,03 - 0,06	0,04
heptachlorepoxyde	0,02 - 0,05	0,03	0,02 - 0,08	0,06	0,05 - 0,23	0,12	0,03 - 0,08	0,06
dieldrin	0,04 - 0,30	0,13	0,30 - 0,76	0,48	0,42 - 1,36	0,79	0,10 - 0,22	0,17
p,p'-DDE	0,18 - 0,94	0,41	0,29 - 2,17	1,30	0,31 - 2,47	0,85	0,18 - 2,40	0,78
p,p'-DDD	0,17 - 0,71	0,34	0,18 - 0,84	0,58	0,21 - 1,07	0,50	0,15 - 0,80	0,29
p,p'-DDT	0,09 - 0,46	0,31	0,10 - 0,25	0,17	0,24 - 1,12	0,54	0,19 - 2,06	0,59
Σ p,p'-DDT	0,72 - 1,95	1,1	0,72 - 3,21	2,1	0,84 - 4,07	1,9	0,54 - 5,3	1,7
PCB	1,4 - 8,3	5	3,3 - 45,0	21	20,4 - 107,4	39	7,2 - 30,2	15
Number of samples	10		6*		10		9*	

* Sample CN 4 is omitted in connection with the high values and the bad condition of the cod. Sample BB 1 the same.