# **Organochlorines including Polychlorinated Biphenyls in Muscle, Liver, and Ovaries of Cod,** *Gadus morhua*

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**Abstract.** Twenty-three specific organochlorine contaminants **and** polychlorinated biphenyls (PCBs), measured as three Aroclor<sup>®</sup> standards were analyzed in muscle, liver, and ovaries of cod, *Gadus morhua,* collected in the Northwest Atlantic. In general, contaminants were undetectable in muscle tissue, while concentrations were 10 times lower in ovaries than liver (wet weight). Comparison of results to other locations indicated a similarity between the ratio of the concentrations of *p,p'-*  DDE,  $p, p'$ -DDD and  $p, p'$ -DDT, in liver of cod from the northern North **Sea and** from the Northwest Atlantic, although with lower levels in the present study. The ratio of  $\alpha$ -HCH and ~/-HCH was between that of the **central and** northern North Sea. Similar ratios tend to indicate similar residence times in the atmosphere, from source to sampling area. Comparison of  $\Sigma$ PCB and  $\Sigma$ DDT in the liver of cod from various geographical locations showed the following **general trend** in concentrations: Arctic, Northwest Atlantic, West Atlantic, Norway < North Baltic, Nova Scotia, North Sea < South Baltic. It was observed that if the liver concentration of one compound was low (high), there was a tendency for all compounds to be low (high). Cluster analysis of organochlorines in liver pointed to the presence of four basic clusters, which could reflect similar physical chemical properties within a group. Concentrations of organochlorines in ovaries were below levels expected to affect egg **and** larval viability.

Chlorinated hydrocarbons are a series of ubiquitous contaminants in the marine environment. According to the group of experts on the scientific aspects of marine pollution (GESAMP 1990), organochlorine compounds can be subdivided into five groups. The three lower molecular weight groups include volatiles (up to three carbons), aliphatic and aromatic herbicides (up to six carbons), and long chain chlorinated paraffins. The other two groups comprise chlorinated insecticides, such as Mirex and Camphenes and chlorinated aromatics, such as the polychlorinated biphenyls (PCBs). Even though the direct production of many of these industrial contaminants has ceased in the

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US, Canada, and Europe, since the mid-1970s, a number of these compounds are chemically stable and can still be **detected**  in biota from around the world. A recent review by Barrie *et al.*  (1992) discusses the sources, occurrence, and use of organochlorines, especially in relation to the presence of contaminants in the Arctic.

The presence of organochlorines can affect reproductive success in animals (Addison 1989; Casillas *et al.* 1991; Elliott *et al.* 1988; Westernhagen *et al.* 1987), while in humans neurological diseases have been linked to pesticide exposure (Ecobichon and Joy 1982). Since, in the past, cod has represented a major target of commercial fisheries, the decline in the stocks has raised concern regarding the role played by pollutants. The level of contaminants in marine organisms inhabiting the waters around Newfoundland and Labrador, a major commercial fisheries area, has not been extensively investigated. Baseline levels of polycyclic aromatic hydrocarbons (PAH) and/or compounds (PAC) have been determined in marine mammals (Hellou *etal.* 1990, 1991), molluscs (Hellou *etal.* 1993a), and fish (Hellou *et al.* 1993b). The concentration of a large number of elements and heavy metals (Hellou *et al.* 1993c, 1993d) as well as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD and PCDF, Hellou *et al.* 1993e) have also been examined in fish, including cod. This study focuses on the level of a series of organochlorines, in cod, *Gadus morhua,* caught north of the island of Newfoundland. More than 23 chlorinated hydrocarbons were analyzed in muscle, liver, and ovaries of 10 female fish. These three tissues were chosen because muscle is important from a consumer perspective. The liver is rich in lipids, organochlorines are lipophilic and bioaccumulate to a larger extent in lipid rich tissues. As well, cod liver oil has been available as a health supplement product. Finally, the level of contaminants in ovaries would inform about possible effect on future larval hatchability. Results were compared to data published for cod inhabiting various geographical locations, to freshwater fish sampled across the United States, and to various species of marine mammals.

## **Materials and Methods**

Atlantic cod *(Gadus morhua)* were collected by trawling during a Department of Fisheries and Oceans (DFO) research vessel cruise in the North Atlantic Fisheries Organisation (NAFO) division 2J-3K, in November 1990. Trawling was carried out at a depth of 239-377 m, where the water temperature varied between 1.2 and 3.7°C. Fish were obtained from seven different sets (Hellou *et al.* 1993b) and frozen on board vessel at  $-40^{\circ}$ C, morphometrics and dissection were performed on land a few days later. Muscle tissue was removed from the caudal area of the fish, and liver from the thickest part of the organ, while ovary tissue was obtained from one lobe or the whole organ. Fish measured between 65 and 75 cm, weighed 2.4-4.7 kg, and were 7-9 years old. Only female fish were sampled and these were in the third or fourth stage of ovaries maturation, calculated according to the proce' dure outlined in Julshamn and Braekkan (1978).

Tissues were shipped on dry ice, to be analyzed by Axys Analytical Services, Sidney, British Columbia, Canada. Briefly, the method consisted of mixing tissue (10-20 g, wet weight) with powdered anhydrous sodium sulfate, allowing the mixture to stand until free-flowing, adding a surrogate labelled standard  $(^{13}C$ -labelled PCB 77, 126, and 169), loading onto a column and eluting with dichloromethane : hexane (1 : 1). Purification of extracts was carried out by column chromatography, using Biobeads SX-3 followed by deactivated Florisil. ® Fractionation yielded two fractions (F1 and F2) which were each spiked with a labelled recovery standard  $(^{13}C$ -labelled PCB 153). The FI fraction containing PCBs and less polar pesticides was analyzed by gas-chromatography-mass spectrometry (GC-MS), while the F2 fraction containing the polar pesticides was analyzed by GC equipped with an electron capture detector (ECD).

Blanks and duplicates were run with each set of 10 tissues. The three blanks had undetectable concentrations of the target compounds. Duplicate analyses gave results that varied by less than 10%, except for dieldrin that varied by  $30\%$  in one sample, while  $p, p$ -DDE varied by 50% in a different duplicate sample. Recoveries, as determined by the addition of internal labelled PCB standards were all high (>80%). Detection limits varied with each injection, they ranged from 0.1 to 2 ng/g, except for Aroclor® 1242, where detection limits varied between 6 and 28 ng/g.

The concentration of a series of organochlorines, including hexachlorobenzene (HCB), hexachlorocyclohexanes (HCH), dichlorodiphenyltrichloroethane (DDT) and its metabolites (DDE and DDD), various chlorinated cyclopentadiene derivatives, such as chlordanes, dieldrin, endrin, and polychlorinated biphenyls (PCB measured as Aroclor® standards) were determined in muscle, liver, and ovaries of cod, *Gadus morhua,* collected north of the island of Newfoundland.

The Wilcoxon matched-pairs signed rank test was used to compare the concentrations in liver and ovaries. Both Kendall's rank and the Pearson product-moment correlations were used to examine the degree of association among the concentrations of the compounds in liver. The former is more robust against departures from linearity and the magnitude of outliers. However, in the situation of levels failing below the detection limit (DL), as commonly occurred with concentrations in ovaries, it can be given a unique value only if no more than one concentration is below the DL, and this limit is, in turn, less than all other measured concentrations of the compound. However, if the usual assumptions underlying the Pearson product-moment correlation holds (bivarate normality), then the known DL can be used to obtain maximum likelihood estimates of the parameters, including the correlation coefficient (Warren, in preparation; E1 Shaarawi and Naderi 1991). In theory, the method can be applied when at least one concentration is known. The approach was used to extend the analysis for ovary concentrations beyond what was possible using solely rank correlation.

Because the sample size is small, statistical tests will have relatively low power, *i.e.,* a high probability of failing to detect real effects. Rather than base interpretations of the significance of individual test statistics at an arbitrary 5% level, our approach has been to take an overview of all tests to determine whether certain common patterns can be delineated. In this respect, cluster analysis can be helpful. The objective is to determine groups of compounds such that the pattern of behavior of compounds within a group is more similar than the pattern of behavior of compounds in different groups. Some trust can be placed in this, if, on the basis of chernistry, there appears to be a natural affinity between the organochlorines that form a group. Scott's (1972) method C2 was used for clustering. According to Scott, Joliffe (1970) found the method to perform well in comparison with the more sophisticated and time-consuming methods. In brief, the correlation between two groups is defined as the arithmethic mean of the correlation coefficients between the variables in one group and those in the other. At each stage, the two groups (which may contain only one variable) having the highest correlation were combined. Note that, unless otherwise stated, "significant" is taken to mean significant at the 5% level.

## **Results and Discussion**

In general, organochlorines were practically undetectable in the muscle (DL $\leq$ 2 ng/g, wet weight, except for Aroclor<sup>®</sup> 1242,  $DL < 6-28$  ng/g). Only HCB was present in all muscle samples, at concentrations similar to those observed in ovaries (Table 1). Eighteen of the 23 target compounds were detected in livers (considering PCB, measured in terms of Aroclor<sup>®</sup> standards, as "one" compound, rather than a mixture with possibly 209 isomers). Generally concentrations were 10 times more elevated than ovaries (Table 1), except for PCB (detected in terms of Aroclor<sup>®</sup> 1254), where concentrations were 30 times more elevated. If concentrations in liver and ovaries are compared using the Wilcoxon matched-pairs signed ranks test (for compounds where concentrations exceed the detection limit), the most extreme values possible are obtained. Therefore, differences must be regarded as highly significant.

#### *Comparison of Muscle Results*

A factor which affects comparison of results is time of sampiing. Time trends studies (Freeman *et al.* 1983; Andersson *et al.* 1988; Schmitt *et al.* 1990; Kannan *et al.* 1992) have demonstrated that since the production and most use of PCB and DDT ceased in the US, Canada, and Europe, in the mid-1970s, the concentration of organochlorines diminished in fish, including cod, until the early 1980s when it appeared to remain constant. The size of fish represents another variable affecting concentrations in tissues. Bigger cod have been shown to accumulate larger concentrations of ΣDDT and PCB (Falandysz 1984, 1986). There is a recognized trend for older fish to have larger concentrations of lipids associated with higher levels of organochlorines (Skinner 1991). Therefore, when available, results related to fish of the same size range as for the present cod, as well as those published for fish caught in the 1980s, are listed in Table 2.

The muscle results can be compared to three other studies (Table 2): the West Baltic, in 1977 (Schneider 1982), the Gulf of Finland, in 1978 (Miettinen *et al.* 1985), and the Baltic Sea, in 1983 (Falandysz 1986). The mean concentration of total HCH, DDT and PCB were lower (ND:  $\lt 0.2-2$  ng/g, wet weight) in fish from the Northwest Atlantic than at the other three locations. Although the mean concentration of HCB was more than three times higher than in the Baltic, ranges overlapped.

Very low levels of dieldrin were detected in three muscle samples. Dieldrin is a bacterial oxidation product of aldrin and





# Refers to the number of fish where organochlorines were detected

ND: not detected, only detectable concentrations were used to calculate means

Table 2. Comparison of muscle results (ng/g, wet weight)

Year	Location NW Atlantic 1991	Baltic <sup>a</sup> 1983	W Baltic <sup>b</sup> 1977	Finland <sup>c</sup> 1978
$\Sigma$ HCH	$< 0.02 - 2$	$13(5-48)$		
$\Sigma$ DDT	$< 0.02 - 2$	$10(2 - 58)$		$9(6-12)$
<b>HCB</b>	$2.2(0.5-3.9)$	$0.65$ (ND-2.7)		
<b>PCB</b>	$< 0.2 - 2$	$58(8-210)$	23	32
% lipids	0.33	0.34	0.73	0.46

<sup>a</sup>Falandysz (1986)

b Schneider (1982)

<sup>c</sup>Miettinen et al. (1985)

is perceived as one of the most potent organochlorine carcinogen (EPA 1981). Although its use has been restricted in Canada since 1971 and banned in the USA since 1975 (de Boer 1989; Elliott *et al.* 1988), dieldrin is still used as a termicide (Kannan *et al.* 1992). The authors are not aware of other data on dieldrin in muscle of cod, to allow comparison.

HCB was the only contaminant detected in all the muscle samples. In Canada, prior to 1970, HCB was used as a fungicide, since than it is only a byproduct of certain industrial combustion processes (Barrie *et al.* 1992). Long-range atmospheric transport and transport on particulates have been used to explain the concentration of HCB in animals collected in the open ocean. Given the present observations on HCB in fish from the Northwest Atlantic, it is also worth noting that HCB was the single chemical selected for monitoring in the North Sea Action Plan.

## *Comparison of Liver Results*

A large number of studies have been carried out on chlorinated hydrocarbons in the liver of cod (Table 3). In *Gadus morhua,*  this organ contains a large amount of lipids, and, as demonstrated in the case of marine mammals, organochlorines, which are relatively resistant to enzymatic transformations, preferentially concentrate in lipid rich tissues. Also, Ingebrigtsen and Solbakken (1985) have demonstrated that HCB, an organochlorine resistant to biodegradation, accumulates mainly in the liver of cod. In general, concentrations in fish from the Northwest Atlantic were at the lowest range of the values reported in the literature, for other geographical locations. This difference was more visible for the £DDT and for PCB, since comparisons can be made with seven other studies.

It should be noted that our PCB results are expressed in terms of three different PCB standards, namely, Aroclor® 1242, 1254, and 1260, which refer to mixtures containing 42, 54, and 62% chlorine. Since there are 209 possible PCB isomers, depending on the standard used, comparison of reported concentrations could appear higher or lower. However, regardless of the standards used in the other analyses, the PCB concentrations obtained in cod caught in Newfoundland waters were at the lowest end. Also, as demonstrated by Muir *et al.* (1988b),

(%)

Table 3. Comparison of liver results (mg/kg, wet weight)

<b>THOIC</b> Of COMPANYON OF HYG. TOGHIO (MICAG, WEL WEIGHT)											
Location	A <b>NWA</b>	В N. Bal.	C <b>NS</b>	D S Bal.	Е W At	F Norway	$G^a$ N Bal	$H^a$ Norway	N Sea	Ja N Fin	$K^b$ W Bal
Year Length	91 70	80 $23 - 35$	80	81 $61 - 70$	83 65	82	85 $31 - 35$	88	$77 - 87$ $36 - 112$	$85 - 89$	84
(cm)											
Lipid $(\%)$	58			47		31	57		$39 - 66$		
α-HCH	0.03		0.06	0.09		0.04			$0.01 - 0.11$		$0.02 - 0.19$
γ-HCH	0.01			0.08		0.01	0.02		$0.02 - 0.15$		$0.02 - 0.13$
$\Sigma$ chlor $^2$	0.17	0.02				0.09		0.08	$0.01 - 0.15$	0.06	

Heptachlor epoxide  $0.15$ <br>Dieldrin  $0.02$  0.06 Dieldrin 0.02 0.06 0.05-0.24 0.02-0.62  $\Sigma$ DDT 0.16 0.31 0.53 6.0 0.13 1.11 0.33 0.15 0.16–0.94 0.07 1.57 PCB 0.15 2.26 1.71 27 0.85 0.5 1.1 0.36 0.26 2.26

HCB 0.03 0.02 0.12 0.06 0.02 0.03 0.02 0.01-0.23 0.02 0.01-0.12  $\mu$ Heptachlor  $0.02$  0.05

<sup>a</sup>Concentrations in terms of lipid weight were transformed into wet weight values, by using an average of 50% lipids

 $b$ Different compounds were grouped under  $\Sigma$ chlordanes, while PCB refers to different standards or sum of congeners

A--More details in Table 1, for Northwest Atlantic

B--Wickstrom and Pyysalo (1981), North Baltic

C--Freeman *et al.* (1983), Nova Scotia

D-Falandysz (1984), South Baltic

E--Uthe *et al.* (1984), West Atlantic, on the Grand Banks

F Skare *et al.* (1985)

G--Haati and Pertilla (1988), North Baltic

H-Koistinen et al. (1989)

I-de Boer (1989), for the northern, central and southern North Sea

J-Paasivirta and Rantio (1991), north Finland

K-Staveland and Marthinsen (1989), southern Norway, reported 0.5-1.8 mg/kg of PCB in 2-3-year-old cod

results expressed in terms of the sum of PCB congeners are usually lower than those expressed in terms of Aroclor standards (example in Table 5).

Several interesting observations regarding liver concentrations came out of the present investigation. The ratio of  $\alpha$ -HCH to  $\gamma$ -HCH provides information about the time spent by the  $\gamma$ -HCH isomer (lindane) in the environment. Since the  $\alpha$ -HCH isomer derives from the  $\gamma$  counterpart (although in some cases, technical grade HCH contains the  $\alpha$  isomer), its predominance tends to indicate that the precursor,  $\gamma$ -HCH, was present for a long period in the atmosphere. The present ratio (3.3) can be compared to values obtained by de Boer (1989) for cod sampled in the northern North Sea (3.9), central (2.7), or southern North Sea (1.2). The Northwest Atlantic ratio would indicate similar long-range transport of HCH from point source to NAFO division 2J-3K, than from source to the northern-central North Sea (de Boer, 1989). Also, the concentrations observed for these two HCH isomers in liver samples from the Northwest Atlantic are similar to those obtained from the northern North Sea. The ratio of  $\alpha$  to  $\gamma$  isomers in the ovaries is 4.3 and is slightly different than in the liver, showing a different distribution in tissues.

*p,p'-DDE* is the primary degradation product of p,p'-DDT, while  $p, p'$ -DDD represents a second  $p, p'$ -DDT metabolite. The ratio of these three components provides information on the time spent by DDT in the environment, more metabolites indicating more weathering. The ratio of the mean values obtained in the present study, 4 : 2 : 3, for DDE : DDD : DDT, respectively, can be compared to those observed in the northern, 4.4 : 2 : 2.9, central, 2.7 • 1 : 2, and southern North Sea,

3.3 : 1.4 : 1.4. In all cases, DDE is the major detected component and comparison is closest with the northern North Sea. The actual concentrations for cod collected in NAFO division 2J-3K are in the lower range of concentrations observed in the North Sea, and similar to levels of  $\Sigma$ DDT for cod caught on the Grand Banks, in 1983, southwest of the present location, and lower than for fish from Norway, the Baltic, and Nova Scotia (Table 3). The ratio of these three compounds is of  $0:2:3$  in the ovaries, indicating that DDE is not transported to the ovaries at the same rate as DDD or DDT. These latter two isomers are present in the same relative ratio as in the liver, but at concentrations 10 times lower.

Examination of the data showed that if the liver concentration of an organochlorine was relatively high (low) in one fish, there was a tendency for all the other compounds to be high (low), in that fish. Cluster analysis of the 19 detected chlorinated hydrocarbons, showed four basic clusters (Figure 1):

la: *cis-chlordane, trans-chlordane,* p,p'-DDD, o,p'-DDD, HCB (weak), Aroclor<sup>®</sup> 1242 (weak)

lb: *trans-nonachlor, cis-nonachtor,* p,p'-DDE, p,p'-DDT, Aroclor<sup>®</sup> 1254 (weak)

2:  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, oxychlordane

3: endrin, dieldrin

Clusters la and lb are similar and could perhaps be regarded as forming a single cluster  $(\# 1)$ ; heptachlor epoxide could also fit in this group. Aroclor<sup>®</sup> 1260 did not link with any other of the 19 compounds analyzed and could, perhaps, be regarded as forming a separate "cluster." This clustering is interesting in view of the known relationship between some of these organo-



Fig. 1. Dendogram representing the results of cluster analyses performed on organochlorines in liver.  $S = n(n - 1)\Gamma/2$ , where  $\Gamma$  is Kendall's rank correlation and  $n = 10$ .

chlorines (for example, DDE and DDD are known to derive from DDT,  $\alpha$ -HCH from  $\gamma$ -HCH). This grouping could reflect similarities in physico-chemical properties determining their affinity for atmospheric transport. Information regarding seaair exchange of contaminants is scarce (Preston, 1992).

Positive correlations were observed between the concentrations of endrin and dieldrin in fish livers and the weight of the liver. All other organochlorines were negatively correlated with liver weight, with most being significant (Table 4). This result is surprising, since previous research has shown positive correlations between fish size and organochlorine concentrations (Falandysz 1983, 1986; Skinner 1991). However, Stronkhorst (1992) recently published data regarding PCB concentrations in livers of flounder. He observed that when concentrations were expressed in terms of wet weight, levels appeared to increase with fish length. When concentrations were expressed in terms of fat weight, they appeared to decrease with fish length. Stronkhorst (1992) also reported concentrations for liver of flounder collected between 1985 and 1990, where levels remained relatively constant. A similar observation of constant levels was reported by de Boer (1988), for cod collected between 1979 and 1987. The preliminary interpretation of our observation would point to increasing concentrations in the environment, during the last 2 years (at maximum), whereby younger fish accumulated more contaminants than older fish. In view of the known long half-life of organochlorines in fish (Niimi 1987) and the estimates of residence times for these contaminants in the North Atlantic (Bidleman *et al.* 1981), our explanation would appear reasonable. However, in view of the

Table 4. Rank correlation on liver concentration and liver weight

α-HCH $\beta$ -HCH $\gamma$ -HCH Oxychlordane <i>trans-Chlordane</i> cis-Chlordane Heptachlor epoxide	
	$-0.29$
	$-0.11$
	$-0.20$
	$-0.56$
	$-0.51$
	$-0.47$
	$-0.42$
<i>trans</i> -Nonachlor	$-0.51$
cis-Nonachlor	$-0.47$
$p, p'$ -DDE	$-0.56$
$o, p'$ -DDD	$-0.47$
$p, p'$ -DDD	$-0.38$
$p, p'$ -DDT	$-0.38$
<b>HCB</b>	$-0.60$
Diedrin	0.07
Endrin	0.24
Aroclor <sup>®</sup> 1242	$-0.56$
Aroclor <sup>®</sup> 1254	$-0.57$
Aroclor <sup>®</sup> 1260	$-0.29$

limited data set, this negative correlation needs further investigation. Naturally, a very high correlation was also present between liver and fish weight, as well as between the fish age and weight (0.5% level). There was a positive, but not formally significant correlation between liver weight and lipid content. However, the picture is virtually unaltered if partial correlations of liver concentration and liver weight, allowing for lipid content are considered.

Muir *et al.* (1988) noted that, in polar regions, the ratio of chlordanes, DDT, and PCB was nearly 1 : 1 : 1 in most animals (somewhat regardless of the specific compounds included when analyzing these groups of organochlorines). This ratio is unlike what is observed in mid-latitudes, where  $DDT >$  chlordanes  $>$ PCB. The ratio of chlordanes : DDT : PCB in liver was nearly **1 :** 1 : 1, for cod from the northwest Atlantic, similar to that observed by Muir *et al.* (1988), for Arctic specimens.

Concentrations of organochlorines in Arctic animals are relatively low compared to other locations (Muir *et al.* 1992). From data available regarding  $\Sigma PCB$ ,  $\Sigma DDT$ , and  $\Sigma$ chlordanes, Muir *et al.* (1992) concluded that levels of organochlorines in seals followed the general pattern of Atlantic, North Sea, Baltic  $>$ Northwest Pacific  $\geq$  Arctic  $\geq$  Antarctic. From studies of organochlorines in liver of cod, the following broad ranking can be made for mean DDT concentrations: Arctic < West and Northwest Atlantic, Norway  $(\times 2)$  < North Baltic, North Sea, Nova Scotia  $(\times 5-9)$  < South Baltic  $(\times 87)$ . Mean PCB concentrations follow a similar pattern: Northwest Atlantic, Arctic, Norway  $\lt$  West Atlantic, Nova Scotia, North Baltic ( $\times$ 4–8)  $\lt$ South Baltic  $(\times 135)$ . Mean HCB concentrations are relatively constant, around 0.02-0.06 mg/kg (Table 3). These levels indicate the following general trend for the more frequently studied organochlorines: Arctic, Northwest Atlantic, West Atlantic, Norway < North Baltic, Nova Scotia, North Sea < South Baltic.

The cyclopentadiene group contains some of the more toxic organochlorines, with the chlordanes as a subgroup. Technical chlordane is a pesticide containing more than 26 components and *trans-nonachlor,* the most persistent one, is generally in highest concentration (63 ng/g). Heptachlor epoxide, deriving from heptachlor and having a higher toxicity than the latter, is

Table 5. Comparison of relative organochlorine concentrations

Organochlorine (mg/g)	Freshwater <sup>a</sup> (whole fish)	NW Atlantic (liver)
$\gamma$ -HCH $\rightarrow \alpha$ -HCH	$\leq 10 \rightarrow \leq 10$	$9 - 30$
$cis$ -Chlordane $\rightarrow$ oxychlordane	$30 \rightarrow 10$	$42 - 26$
<i>trans</i> -Chlordane	20	12
<i>trans</i> -Nonachlor	30	63
cis-Nonachlor	20	-19
Heptachlor $\rightarrow$ heptachlor epoxide	$ND \rightarrow 10$	$ND \rightarrow 8$
<b>HCB</b>	< 10	33
$p, p'$ -DDT $\rightarrow p, p'$ -DDE, $p, p'$ -DDD	$30 \rightarrow 190, 60$	$54 - 72, 21$
PCB (1248 or 2, 1254, 1260)	60, 210, 150	26, 154, 87
Aldrin $\rightarrow$ dieldrin	$NA \rightarrow 40$	$ND\rightarrow 21$

<sup>a</sup>Schmitt et al (1990), NA: not analyzed, ND: not detected  $X \rightarrow Y$  indicated that Y derives from X

generally in lowest concentration within the subgroup. Oxychlordane, a metabolite of *cis-chlordane* was present in a lower concentration than the parent compound, which represents the most abundant component of technical chlordane. *Trans-chlor*dane, more persistent than the *cis* counterpart, was lower in concentration.

The general relative abundance of some of the chlordanes, as well as other organochlorines, is similar to that found in bottom-feeding and predator freshwater fish, sampled in the US, in 1984 (Schmitt *et al.* 1990). Although levels are within the same range of concentrations, the freshwater values are expressed in terms of whole fish rather than liver weight. Since liver represented on average 7% of the body weight of the cod, and this organ has by far the highest concentration of lipids (50%) and organochlorines (Table 1), we can conclude that the present results are at least 10-15 times lower than for the freshwater species (Table 5). This approximation neglects the lipid variable and the distribution of chemicals in tissues of the two different sets of fish. (For example, lipids represent 1.3% of the liver and 1.9% of whole small trout, while the weight of the liver represents 0.8% of the fish.)

Levels of organochlorines have also been investigated in marine mammals and a brief comparison is presented in Table 6. The concentrations in blubber (99% lipids) of various seals can be compared to the liver of cod (50% lipids), if expressed on a lipid weight basis. The sum of DDT and PCB (Aroclor  $1254^\circ$  for cod) is much lower in cod than in seals and whales from non-Arctic locations. Concentrations in Arctic seals are slightly more elevated than in cod from the Northwest Atlantic (Table 6). Liver concentrations in ringed seals have been shown to equal blubber concentrations, if expressed on a lipid weight basis (Muir *et al.* 1988), justifying the present comparison. The position of mammals versus fish in the food chain may explain the observed difference in contaminant levels.

# *Comparison of Ovaries Results*

Only two other studies have reported concentrations of organochlorines in ovaries of cod (Schneider 1982; Westernhagen *et al.* 1987). The mean PCB concentration of cod from the western Baltic (30-48 cm) was 3.0 mg/kg (lipid weight), compared to 0.18 mg/kg for cod (65-75 cm) from the Northwest Atlantic (Schneider, 1982). Concentrations reported by Westernhagen

*et al.* (1987) for Western Baltic cod, collected in 1984 were very close to those reported in Table 1, for  $\alpha$ -HCH,  $\gamma$ -HCH, HCB, heptachlor, heptachlor epoxide and dieldrin (2.5, 2.1, 0.02, 0.1, and 2.1 ng/g, wet weight, respectively). Levels of DDT, DDE, DDD, and PCB (7.9, 10, 6.2, and 41 ng/g, wet weight, respectively) were more elevated (at least three times) in Western Baltic cod.

Because of concentrations falling below DL, rank correlations were calculated for only 10 compounds, namely,  $\alpha$ -HCH, HCB, oxychlordane, *trans-chlordane, cis-nonahclor,* dieldrin, heptachlor epoxide,  $p, p'$ -DDE and Arochlor<sup>®</sup> 1254. These were dominantly positive. Three out of 45 correlations were non-significantly negative, while more than half the positive correlations were significant (5% level). Cluster analysis gave the following results (Figure 2):

1: *trans-chlordane, cis-nonachlor, trans-nonachlor,* Arochlor ® 1254, oxychlordane

lc:  $HCB$ ,  $p, p'$ - $DDE$ 

 $2: \alpha$ -HCH

3: dieldrin, heptachlor epoxide

The only notable differences between these and the clusters obtained with the liver concentrations are the shift of oxychlordane from cluster 2 to 1 and the linking of heptachlor epoxide to dieldrin. (The latter was also observed in liver when partial rather than simple rank correlations were used for clustering).

#### *Comparison of Liver to Ovaries*

This was done by product-moment correlations for the seven compounds, and rank correlations for the 10 compounds in ovaries and the 19 in liver where these could be calculated. By using the DL values, as indicated above, this was extended to 15 compounds in ovaries. The results summarized below were essentially the same, *i.e.,* structure that would be obtained by using the eight compounds in ovaries omitted when using the simple product-moment correlations must be very similar to those obtained with the product-moment correlations for the seven compounds:

- Members of clusters la and lb have positive or, at least, non-negative correlations, between concentrations in liver and ovaries.
- Members of cluster 1 in ovaries and clusters 2 and 3 in liver are, in general, negatively correlated.
- Members of cluster 1, with the possible exception of 1a in liver, and clusters 2 and 3 in ovaries are negatively correlated.
- Members of cluster 2 have substantial negative correlations between concentrations in ovaries and liver.
- Members of cluster 3 in ovaries and cluster 2 in liver have weaker negative correlations than above and would not normally be regarded as significant.

# *Significance of Results for Human and Animal Health*

The American consumer guidelines for chemical contaminants in fish are as follows: aldrin  $+$  dieldrin, 0.30 ppm; chlordane, 0.30 ppm; endrin, 0.30 ppm; heptachlor, heptachlor epoxide,

<b>Species</b>	Location (year)	<b>DDT</b>	PCB	
Grey seals <sup>a</sup>	Baltic (1976–78)	66	38	
Ringed seals <sup>a</sup>	Bothnia (1981)	65	75	
Ringed seals <sup>a</sup>	Spitzbergen (1980)	50	10	
Harp seals <sup>a</sup>	St. Lawrence (1982)	1.7	4.5	
Caspian seals <sup>a</sup>	Caspian Sea	38	1.9	
Ringed seals <sup>b</sup>	Arctic (1984)	F <sub>0.47</sub>	0.31	
		M 1.33	0.79	
White-Beaked dolphin <sup>c</sup>	Newfoundland (1982)	M 26.8-282	$3.23 - 28.3/32.0 - 282$	
		$F11.5-108$	1.32-9.79/8.05-104	
Pilot whale <sup>c</sup>	Newfoundland (1980)	$M$ 8.95-31.4	5.85-20.7/7.03-25.5	
		$F$ 1.27-22.2	$0.87 - 15.9/0.98 - 19.3$	
White-sided dolphin <sup>d</sup>	Faroe I (1987)	M 22.46	42.68	
		F 14.97	25.34	
Pilot whale <sup>d</sup>	Faroe I (1987)	M 31.39	48.81	
		F 13.40	26.27	
Cod (liver)	Northwest Atlantic	0.366	0.308	

**Table 6.** Comparison to blubber of marine mammals (mg/kg, lipid weight)

<sup>a</sup> Andersson *et al.* (1988), PCB compared to Clophen<sup>®</sup> A 50

<sup>b</sup>Muir *et al.* (1988), F: female and M: male seals, sum of 52 PCB congeners

<sup>c</sup> Muir *et al.* (1986), first PCB number refers to the sum of 49 congeners, followed by a 1:1 mixture of Aroclor<sup>®</sup> 1254:1260

<sup>d</sup> Borrell (1993). PCB refers to concentrations in terms of a 1:1 mixture of Aroclor® 1254:1260



**Fig.** 2. Dendogram representing the results of cluster analyses performed on organochlorines in ovaries.  $S = n(n - 1)\Gamma/2$ , where  $\Gamma$  is Kendall's rank correlation and  $n = 10$ .

0.30 ppm; total DDT, 0.50 ppm; total PCB, 2.0 ppm (wet weight). Similar tolerance levels exist in Canada and other countries. In the present study, the muscle of cod obtained from a major commercial fish stock was virtually free of organochlorine contamination. A notable exception was hexachlorobenzene, which was present in all muscle tissues, albeit at very low levels.

One of the primary concerns regarding organochlorines is their potential for affecting fish reproduction. Early studies with trout demonstrated that PCB or DDT concentrations in eggs or larvae in the ppm range impaired viability (Allison *et al.* 1964; Hogan and Brauhn 1975). A number of field studies have also suggested that egg and larval viability or larval fitness were affected when relatively high levels of organochlorines were present in ovary tissues (von Westernhagen *et al.* 1981; Hansen *et al.* 1985; Black *et al.* 1988; Spies and Rice 1988; Casillas *et al.* 1991; Nelson *et al.* 1990). On the basis of studies of a number of species in the North Sea, von Westernhagen *et al.* (1981) and Hansen *et al.* (1985) suggested a threshold

level for PCB in the 0.120 ppm range (wet weight). However, Collier *et al.* (1992) reported that fertilization success and larval abnormalities were not affected in English sole containing PCB levels up to 2.0 ppm (wet weight). Also, in the case of cod, von Westernhagen *et al.* (1987) found no effect on viable hatch in fish containing levels similar or higher than those found in this study. Extrapolating from laboratory studies with trout, field studies with a variety of marine species, and specific field studies with cod, it is difficult to make a case that the levels of organochlorine found in cod in the Northwest Atlantic are at sufficiently high levels to engender concern about effects on larval viability.

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