Polychlorinated Biphenyls and Organochlorine Pesticides in Some Freshwater and Marine Fishes

by V. Zitko

Fisheries Research Board of Canada
Biological Station, St. Andrews, N. B.

Polychlorinated biphenyls (PCB) were found in higher concentrations than organochlorine pesticides in all fish analysed. Concentrations of PCB in herring *(Clupea harengus)*, salmon *(Salmo salar)*, and mussel *(Mytilus edulis)* were higher than those reported by Jensen et al. for the same species from Swedish coastal waters (1). Concentrations of PCB in cod *(Gadus morhua)* were approximately the same in both cases. No comparative data for eel *(Anguilla rostrata)* and pickerel *(Esox niger)* are available. PCB concentrations in pike *(Esox lucius)* were reported from The Netherlands and Sweden (2).

Levels of DDT and metabolites are similar to those found by Jensen et al. (1) and lower than reported recently for Canadian Atlantic fishes (3). Highest levels of DDT and metabolites in salmon are reported from Sweden (1) and the lowest from Canada (3).

EXPERIMENTAL

Eel and pickerel were taken from several lakes and from the Saint John River system in New Brunswick, Canada, in summer 1970. Groundfish (cod *(Gadus morhua)*, hake *(Urophycis tenuis)*, plaice *(Hippoglossoides platessoides)*, and ocean perch *(Sebastes marinus)*) were taken on Nova Scotia banks in summer 1970. Mackerel *(Scomber scombrus)* and one sample of herring were taken in the Bay of Fundy in September and December 1970, respectively. Two samples of herring were taken in Chedabucto Bay, Nova Scotia, in January 1971; mussels were obtained from Miramichi Bay, New Brunswick, in October 1970. Salmon (grilse) were taken in the Northwest Miramichi River, New Brunswick, in June 1970. The samples were kept frozen until analysis. Whole fishes and mussels with shells were weighed before analysis. Whole herring, shucked mussels, the muscle of all other fishes, and samples of eel and pickerel liver were analysed. Two to ten specimens were usually combined and analysed in duplicate as one group.

Samples (5-6 g) were ground with anhydrous sodium sulfate and extracted with hexane in Soxhlet extractors for 1 h. The thimbles were pre-extracted with hexane. Volume of the extract was adjusted to 100 ml and an aliquot (5-25 ml) was evaporated in vacuum on a rotatory evaporator to approximately 1.5 ml and applied to

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a column (45 x 0.7 cm) containing 2 g of alumina (for chromatography, Fisher Scientific Co.), pretreated as described (4). The column was washed with hexane, the effluent (20 ml) was concentrated to 1.5 ml and applied to a column (45 x 0.7 cm), containing silicic acid (Mallinckrodt SILICAR®, 100-200 mesh), pretreated as described (5). The column was washed with hexane, collecting 10 ml (fraction I) and 20 ml (fraction II) of the effluent, and with 10 ml of 10% ether in hexane (fraction III). The fractions were evaporated just to dryness in a rotatory evaporator, dissolved in a known volume of hexane (0.2-1.0 ml) and analysed by gas chromatography (6).

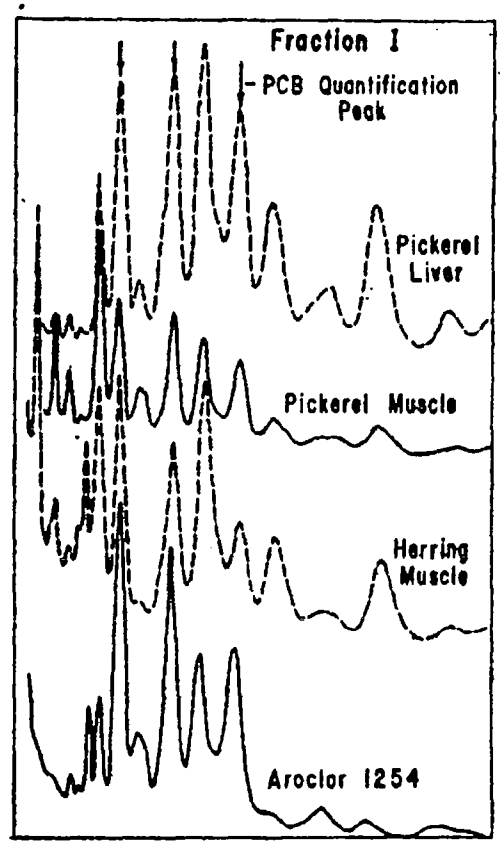

Figure 1. Gas chromatograms of fraction I.

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Untreated pesticide-grade hexane from Fisher Scientific Co. was used and benzene (5 ml/l) was added to Matheson Coleman & Bell pesticide-grade hexane, redistilled in glass, to obtain identical elution patterns (7).

To check the method, commercial corn oil was spiked with Aroclor® 1254 and organochlorine pesticides to contain PCB, hexachlorobenzene (C_6Cl_6), lindane, heptachlor, aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, p,p'-DDD, and p,p'-DDT in concentrations of 0.95, 0.29, 1.95, 1.95, 2.02, 3.81, 5.09, 2.72, 5.70, and 6.70 µg/g, respectively. The average percentage recovery (4 analyses) was 102 (99-105), 78 (77-78), 112 (107-117), 105 (96-115), 113 (112-113), 94 (93-95), 110 (107-113), 113 (110-117), 72 (70-74), and 109 (98-120), respectively.

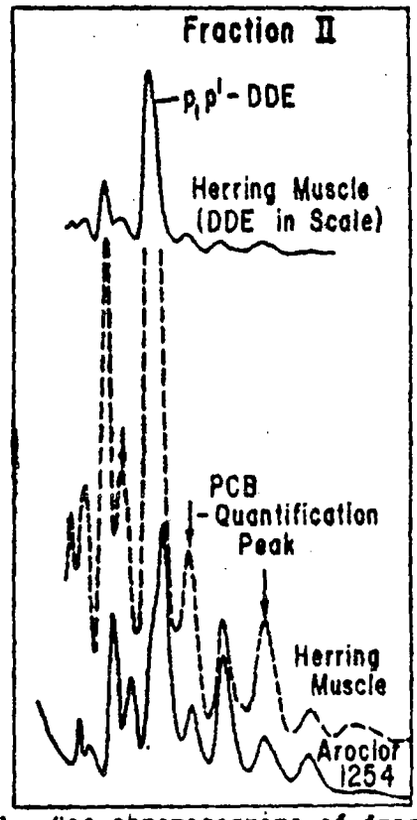

Figure 2. Gas chromatograms of fraction II.

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Three peaks, indicated in Figures 1 and 2 were used to calculate the concentration of PCB in terms of Aroclor® 1254, and the average concentration thus obtained is reported in Table 1. In some samples, containing a relatively high concentration of p,p'-DDE, the middle peak was not clearly separated from that of p,p'-DDE and only the 2 other peaks were used to quantify PCB.

RESULTS AND DISCUSSION

The method simultaneously cleans up the extract and fractionates PCB and organochlorine pesticides. Fraction I contains 70% of PCB, hexachlorobenzene, and some aldrin. Fraction II contains the rest of PCB, heptachlor, and p,p'-DDE, while lindane, heptachlor epoxide, dieldrin, p,p'-DDD, and p,p'-DDT are eluted in fraction III. The major difference between PCB in fractions I and II is the absence of peaks with relative retention times 0.97 and 1.04 (p,p'-DDE = 1.00) from fraction I. These peaks overlap with the peak of p,p'-DDE in fraction II. In most cases this interference is not significant and a correction of the p,p'-DDE quantification is not necessary.

It is impossible at the moment to quantify accurately PCB in terms of Aroclor® 1254 since the proportions of PCB peaks in the samples are not identical with those in Aroclor® 1254. For example, the total (fractions I and II) ratio of the areas under the first and third PCB quantification peak (Figs. 1 and 2) is 1.01 in Aroclor® 1254, while values of 1.35, 1.88, and 2.81 were found in eel, herring, and mussel, respectively. Error due to differences between commercial PCB and PCB found in the samples is difficult to estimate. It has been suggested that in some cases it may be as high as 100% (1). The precision of the results presented in Table 1, expressed as the difference between duplicate determinations, is 12.3% for eel, pickerel, salmon, herring and mackerel, and 14.6% for mussel. Standard deviation, calculated from all the analyses of eel, is 0.11. For p,p'-DDE the differences between duplicate determinations are 2, 4, 5, 15, 12, and 8% for eel, pickerel, salmon, herring, mackerel, and mussel, respectively. Standard deviations for all the analyses of eel are 0.03, 0.04, 0.16, and 0.004 for p,p'-DDE, p,p'-DDD, p,p'-DDT, and hexachlorobenzene, respectively.

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TABLE 1

PCB and organochlorine pesticides in freshwater and marine fishes.

Species	No. of specimens	No. of groups	Av. wt., g	µg/g, wet weight PCB	p,p'-DDE	p,p'-DDD	p,p'-DDT	C_5Cl_5
American eel (*Anguilla rostrata*)	13	4	380	0.71 0.36-1.01 0.57*	0.50 0.44-0.56 0.19*	0.19 0.00-0.37 -	0.20 0.18-0.56 -	0.012 0.006-0.019 0.010*
Chain pickerel (*Esox niger*)	2	1	492	0.33 4.93*	0.16 2.38*	0.03 0.14*	0.06 0.63*	0.003 0.016*
Atlantic salmon (*Salmo salar*)	4	1	1003	0.46	0.22	0.07	0.08	0.002
Herring (*Clupea harengus*)	10	2	222	0.54 0.38-0.73	0.24 0.13-0.30	0.04 0.00-0.08	0.15 0.09-0.23	0.006 0.005-0.006
	10	2	59	0.32 0.20-0.48	0.09 0.07-0.10	0.02 0.02-0.03	0.06 0.05-0.10	0.004 0.003-0.004
	10	2	10	0.34 0.19-0.54	0.06 0.01-0.06	0.01 0.00-0.04	0.05 0.01-0.08	0.003 0.002-0.004
Mackerel (*Scomber scombrus*)	4	1	310	0.35	0.07	0.02	0.07	0.001
Mussel (*Mytilus edulis*)	30	3	30	0.14 0.06-0.25	0.02 0.02-0.03	-	-	-
Cod (*Gadus morhua*)	3	1	1368	0.02	0.01	-	-	-
White hake (*Urophycis tenuis*)	1	1	1035	0.02	0.02	-	-	-
Plaice (*Hippoglossoides platessoides*)	2	1	686	0.03	0.01	-	-	-
Ocean perch (*Sebastes marinus*)	2	1	1267	traces	traces	-	-	-

*liver

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Some of the eels were taken from lakes receiving no industrial effluents or domestic sewage, both identified recently as a source of PCB (8). The levels of PCB found indicate a possibility of pollution by aerial fallout. The occurrence of higher PCB levels in the pelagic species (herring and mackerel) than in groundfish is consistent with this hypothesis. Higher levels of PCB and organochlorine pesticides in herring, average weight 222 g, than in herring, average weight 59 g, obtained from the same location, may indicate a weight-residue relationship similar to that observed for mercury residues in fish (9).

Several unidentified peaks, not corresponding to any found in Aroclor® 1242, 1254, and 1260, were observed in fractions I and II of some samples. A peak, relative retention time 2.85 (p,p'-DDE = 1.00, Fig. 1, pickerel liver, herring muscle), was found in many samples. A peak with the same retention time occurs in Aroclor® 1260.

Of the organochlorine pesticides, p,p'-DDE was present in highest concentrations, followed by p,p'-DDT and p,p'-DDD. A small peak with the retention time of dieldrin was found in pickerel liver. Most of the samples contained a small amount of hexachlorobenzene. It is likely that some of the recently reported levels of DDT and metabolites in Canadian Atlantic fishes (3) are too high due to interference of PCB.

In terms of acute toxicity, PCB are less toxic to fish than organochlorine pesticides (10). Little is known about the sublethal effects of PCB and it is not possible at the moment to make any conclusions about the toxicological significance of the levels of PCB found in fish. In view of the recently reported high levels of PCB in human milk and adipose tissue (11), and the identification of toxic chlorinated dibenzofurans in some commercial PCB preparations (12), more knowledge of the distribution and effects of PCB in the environment is needed.

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