Organochlorine Residues in Fish and Fishery Products from the Northwest Atlantic

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Abstract

The residues of polycholorinated biphenyls (PCBs) and DDT (p,p'-DDT and its metabolites) were determined in fish collected at various sites off the Atlantic Coast of Canada during 1971 and 1972. The results of analyses of 261 samples representing 29 species of crustacea, bivalves and finfish, indicated widespread distribution of these contaminants and preferential accumulation in lipid rich specimens. Only fatty specimens of pelagic finfish consistently contained more than 0.1 µg/g of PCB and DDT. Bluefin tuna was the only species with residues frequently in excess of 1 µg/g. No appreciable differences were observed in residue levels of specimens taken during different years or in specimens taken at different sampling sites. A total of 83 samples representing 7 selected tissues and fishery products were also analyzed for PCB and DDT. No residues of lindane, aldrin, heptachlor, heptachlor epoxide and methoxychlor, and only very low levels of dieldrin and hexachlorobenzene were present in the 104 samples examined for these residues.

Introduction

The work described in this paper was conducted in order to determine the extent of PCB and DDT contamination of various commercially important marine fish species from the Atlantic Provinces of Canada. A number of miscellaneous samples were also included in these analyses and a limited number of samples were examined for hexachlorobenzene, lindane, heptachlor, heptachlor epoxide, aldrin, dieldrin and methoxychlor.

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Materials and Methods

The samples for this work were collected at various sites off the Atlantic Coast of Canada from mid 1971 to late 1972. The 29 species sampled were: alewives *(Alosa pseudoharengus)*, capelin *(Mallotus villosus)*, catfish *(Anarhichas lupus)*, clams *(Mya arenaria)*, cod *(Gadus morhua)*, dogfish *(Squalus acanthias)*, eels *(Anguilla rostrata)*, grey sole *(Glyptocephalus cynoglossus)*, haddock *(Melanogrammus aeglefinus)*, halibut *(Hippoglossus hippoglossus)*, herring and sardines *(Clupea harengus harengus)*, lobster *(Homarus americanus)*, mackerel *(Scomber scombrus)*, mussels *(Mytilus edulis)*, oysters *(Crassostrea virginica)*, plaice *(Hippoglossoides platessoides)*, pollock *(Pollachius virens)*, queen crab *(Chionoecetes opilio)*, red crab *(Geryon quinquedens)*, rock crab *(Cancer irroratus)*, redfish *(Sebastes marinus)*, salmon *(Salmo salar)*, scallops *(Placopecten magellanicus)*, shrimp *(Pandalus borealis)*, smelt *(Osmerus mordax)*, striped bass *(Roccus saxatilis)*, swordfish *(Xiphias gladius)*, tuna *(Thunnus thynnus)* and yellowtail flounder *(Limanda ferruginea)*. These species were divided into 4 groups: Bivalves, Crustacea, Groundfish and Pelagic. The samples, unless otherwise indicated, were restricted to the edible portion only. For large specimens where the use of the entire edible portion was impractical, several cross-sections were homogenized together to obtain a representative sample. The clam, shrimp, mussel, scallop and oyster samples were prepared as composites of 1 lb of meat. The swordfish and bluefin tuna samples were taken from individual specimens and samples of the remaining species were prepared as composites from 6 or more specimens. The samples were collected from commercial catches from the Gulf of St. Lawrence, the Northumberland Strait, the Bay of Fundy, Coastal Nova Scotia and Coastal Newfoundland. The samples were wrapped in aluminum foil for shipment to the laboratory. Upon arrival at the laboratory the samples were homogenized, placed in solvent-washed glass jars fitted with foil-lined lids and immediately frozen at -29°C until taken for analysis. The analyses of selected tissues and fishery products were conducted on individual samples with the exception of the canned tuna samples which were prepared as composites.

For analyses, the samples were first thoroughly mixed with anhydrous sodium sulphate (from which any contaminants had been removed by extraction with hexane) at a 4:1 ratio of sodium sulphate to sample. The PCBs and pesticides were then extracted by high speed blending with two 100 ml aliquots of acetonitrile. The

sample size varied according to the lipid content with 20 g samples normally being used but 2-5 g samples were utilized for fatty samples such as cod livers. The acetonitrile extracts plus rinsings were combined, mixed with 500 ml of 5% sodium sulphate in glass distilled water and partitioned twice with 100 ml aliquots of petroleum ether. The petroleum ether extracts were combined, dried with granular sodium sulphate, flash evaporated to 2-3 ml and then applied to a 2.5 cm I.D. column containing 20 g of activated florisil for the simultaneous cleanup and separation of PCBs from p,p'-DDD and p,p'-DDT (REYNOLDS, 1969). This column was first eluted with 235 ml of glass distilled hexane (Fisher H-291). This eluate contained hexachlorobenzene, aldrin, heptachlor, o,p'-DDT, p,p'-DDE and PCB residues. It should be noted that (similar to the findings of ZITKO, 1971) several commercially available glass distilled and pesticide grade hexanes did not give as satisfactory separation as the above mentioned. The second elution consisted of 250 ml of 6% methylene chloride in hexane (prepared from pesticide grade solvents) and this eluate contained lindane, p,p'-DDD and p,p'-DDT. To recover heptachlor epoxide, dieldrin and methoxychlor, a third elution consisting of 250 ml of 25% ethyl ether in hexane (also prepared from pesticide grade solvents) was required. This third eluate was flash evaporated to 2-3 ml, diluted with hexane to 10 ml in a volumetric flask and a suitable aliquot (containing less than 0.1 g of fat) was eluted through 2 g of 5% deactivated alumina by 50 ml of hexane (HOLDEN and MARSDEN, 1969). The final eluates were flash evaporated to 2-3 ml, transferred quantitatively to graduated glass stoppered centrifuge tubes and the residues were estimated by electron capture gas chromatography. The instruments employed were a Hewlett Packard Model 5750 gas chromatograph equipped with a 200 millicurie tritium detector and a Varian Aerograph Model 1400 gas chromatograph equipped with a 250 millicurie tritium detector. The former instrument was fitted with a 6' x 1/4" glass column of 4% SE-30 plus 6% QF-1 on 80-100 mesh Chromosorb W, while the latter was fitted with a 6' x 1/4" glass column of 3% OV-1 on 80-100 mesh Chromosorb W.

PCB residues were estimated by comparison to a standard containing a 4:1 mixture of Aroclors 1254 and 1260. The PCB quantitation was effected using the sum of all peak heights for those peaks occurring after peak #7 (inclusive) of Aroclor 1254, using the numbering system of REYNOLDS (1969). Confirmation of the PCB residues was achieved by subjecting the PCB fraction to the KOH-ethanol digestion technique of HOLDEN and

MARSDEN (1967). This technique also served as confirmation for o,p'-DDT which would be present in the same fraction as the PCBs. The pesticide standards were prepared from chemicals obtained from Aldrich Chemical Company, using primary standard grade where available. Periodic confirmatory analyses for p,p'-DDD and p,p'-DDT were performed by the thin layer chromatographic method of MOATS (1969). All results were calculated as µg/g on a wet weight basis. Blanks carried through this entire procedure showed no chromatographic peaks that would interfere with the pesticides tested and generally no PCB trace was discernable. However, on occasion, a blank would exhibit PCB contamination which would correspond to as much as 0.003 µg/g if calculated on the basis of a 20 g sample. Recovery factors were established by analyzing standards which were taken through the entire procedure and by analyzing samples for which the background residues had been determined and to which known quantities of PCBs and pesticides had been subsequently added. With the exception of heptachlor, all recovery factors were in the range of 83-96% (±4-8%). The recovery of heptachlor was 61% (±7%). No recovery factors were incorporated into the residue calculations. This laboratory participated in the C.C.P.U.A. (Canadian Committee on Pesticide Use in Agriculture) pesticide check sample program and in the PCB check sample program coordinated by the Ontario Provincial Pesticide Residue Testing Laboratory (HOLDRINET, 1974).

Results and Discussion

The technique of REYNOLDS (1969) provided very satisfactory separation of p,p'-DDD and p,p'-DDT from the PCBs. Figure 1 shows the gas chromatogram of the PCB fraction (before confirmatory digestion by ethanol-KOH) of a tuna sample. This fraction contained the PCBs and p,p'-DDE but no p,p'-DDD or p,p'-DDT. Therefore quantitation of the PCB residue, using peaks occurring later than p,p'-DDE, could be effected with minimal interference. The PCB standard shown in this figure represents a mixture of Aroclors 1254 and 1260 at a 4:1 ratio. The pattern of peaks from this standard more closely resembled the pattern of peaks in the sample than any of several other mixtures of PCBs which were tested. All the samples in this work contained patterns of peaks in the PCB fraction which were very similar to the pattern observed in this tuna sample.

The PCB and ΣDDT results from the Bivalve, Crustacea, Groundfish and Pelagic species are given in Tables 1-4 respectively. The ΣDDT residue is the sum of the residues of p,p'-DDE, p,p'-DDD and p,p'-DDT. Residues of o,p'-DDT were not confirmed in any of these samples.

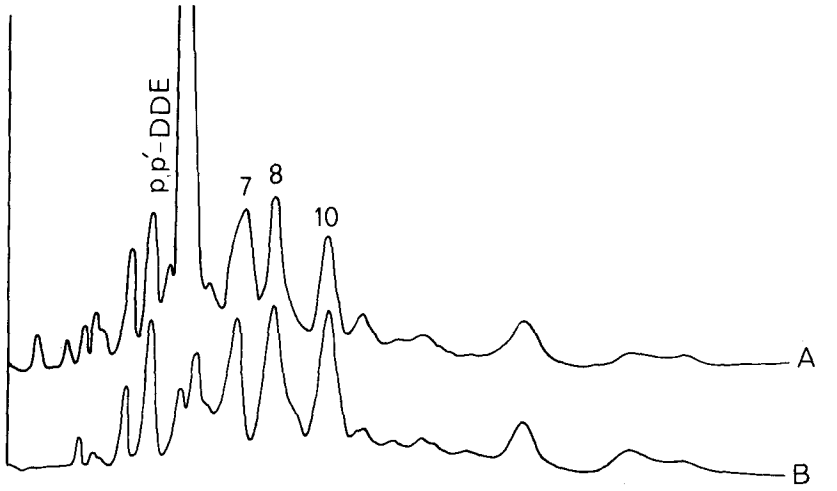

Figure 1. Gas chromatograms of (A) the PCB fraction from a tuna sample and of (B) a mixed standard containing 80% Aroclor 1254 and 20% Aroclor 1260.

TABLE 1

Residues (μg/g) of PCB and ΣDDT in bivalves from the Northwest Atlantic (1971-1972)

Species	#	Mean PCB (Range)	Mean ΣDDT (Range)
Clams	12	0.016(.003-.047)	0.007(.001-.021)
Mussels	8	0.023(.009-.047)	0.015(.011-.021)
Oysters	3	0.005(.002-.009)	0.003(N.D.-.006)
Scallops	11	0.018(.005-.051)	0.003(N.D.-.010)

TABLE 2

Residues (μg/g) of PCB and ΣDDT in crustacea from the Northwest Atlantic (1971-1972)

Species	#	Mean PCB (Range)	Mean ΣDDT (Range)
Lobster	27	0.098(.016-.70)	0.032(.005-.046)
Queen crab	7	0.027(.018-.037)	0.018(.006-.041)
Red crab	3	0.036(.015-.078)	0.061(.023-.13)
Rock crab	3	0.024(.021-.026)	0.024(.018-.028)
Shrimp	7	0.045(.014-.10)	0.003(N.D.-.015)

N.D. - None detected.

TABLE 3

Residues (μg/g) of PCB and ΣDDT in groundfish from the Northwest Atlantic (1971-1972)

Species	#	Mean PCB (Range)	Mean ΣDDT (Range)
Catfish	2	0.067(.033-.10)	0.066(.036-.095)
Cod	20	0.040(.012-.091)	0.024(.003-.075)
Grey Sole	2	0.011(.009-.012)	0.004(.004)
Haddock	17	0.016(.006-.034)	0.004(N.D.-.013)
Halibut	10	0.27 (.065-.60)	0.24 (.050-.72)
Plaice	3	0.030(.010-.065)	0.022(.008-.049)
Pollock	2	0.010(.009-.011)	0.007(.005-.010)
Redfish	17	0.071(.015-.17)	0.073(.024-.12)
Yellowtail	11	0.033(.012-.070)	0.020(.008-.045)

N.D. - None detected.

TABLE 4

Residues (μg/g) of PCB and ΣDDT in pelagic species from the Northwest Atlantic (1971-1972)

Species	#	Mean PCB (Range)	Mean ΣDDT (Range)
Alewives	11	0.39 (.21 -0.70)	0.22 (.13 -0.31)
Capelin	3	0.057(.046-0.074)	0.021(.013-0.032)
Dogfish	3	0.94 (.49 -1.4)	1.1 (.69 -1.5)
Eels	11	0.44 (.13 -1.2)	0.56 (.24 -1.1)
Herring	9	0.52 (.27 -0.74)	0.43 (.13 -0.77)
Mackerel	23	0.41 (.093-0.93)	0.26 (.080-0.64)
Salmon	8	0.11 (.069-0.19)	0.058(.035-0.092)
Sardines	1	0.12	0.077
Smelt	6	0.37 (.16 -0.75)	0.077(.047-0.099)
Striped bass	1	0.56	0.63
Swordfish	6	0.60 (.49 -0.79)	0.33 (.24 -0.48)
Tuna	14	3.9 (.62 -9.7)	3.1 (.60 -7.3)

With only one exception, the Bivalve, Crustacea and Groundfish species had mean PCB and ΣDDT residues of less than 0.1 μg/g. The exception was halibut (the fattiest of the groundfish tested) with mean residues of PCB and ΣDDT of 0.27 and 0.24 μg/g respectively. Almost all Pelagic species contained mean PCB and ΣDDT residues greater than 0.1 μg/g. The notable exception in this group was bluefin tuna with mean residues of 3.9 μg/g PCB and 3.1 μg/g ΣDDT. In the bluefin tuna samples, the residue levels increased with increasing specimen size. The 6 tuna weighing more than 600 lbs had mean PCB and ΣDDT residues of 5.4 and 4.2 μg/g respectively, as compared to mean residues of 2.8 and

2.3 µg/g in the 8 specimens weighing 600 lbs or less. An additional 4 samples of 500-600 lb bluefin tuna taken in July 1973 contained mean residues of PCB and ΣDDT of only 0.9 and 0.7 µg/g respectively.

As shown in Table 5, the proportions of p,p'-DDE, p,p'-DDD and p,p'-DDT contributing to the total DDT in the various species outline three categories, 1) Bivalves, where the principal metabolites were p,p'-DDE and p,p'-DDD with p,p'-DDT being the minor component, 2) Crustacea, where the residue was mainly p,p'-DDE while p,p'-DDD and p,p'-DDT were both very minor components and 3) Finfish, where p,p'-DDE and p,p'-DDT were the principal components with p,p'-DDD being the minor constituent. The bivalves and crustaceans appeared to maintain their particular proportions of metabolites regardless of the collection site and these proportions were very different from those in finfish taken from the same area.

TABLE 5

Mean proportions of ΣDDT occurring as p,p'-DDE, p,p'-DDD and p,p'-DDT

Group	p,p'-DDE	p,p'-DDD	p,p'-DDT
Bivalves	0.51(.41-.57)	0.36(.28-.48)	0.13(.11-.17)
Crustacea	0.84(.67-.92)	0.12(.04-.33)	0.04(0-.08)
Groundfish	0.45(.27-.70)	0.14(.05-.25)	0.41(.25-.59)
Pelagic	0.45(.29-.65)	0.17(.11-.24)	0.38(.19-.55)

A limited number of comparisons were made of the residue levels in species which were sampled at different places (the Gulf of St. Lawrence, Banquereau, Bay of Fundy, Brown's Bank, Northumberland Strait, George's Bank and Southwestern Nova Scotia). There were no appreciable differences in the residue levels in fish taken from these areas. Comparisons of residue levels in species sampled both in 1971 and 1972 also indicated no appreciable differences over these two years.

Table 6 shows the mean residues found in various selected tissues and fishery products. The two fatty tissues examined, cod liver and lobster hepatopancreas, contained high residues of both PCB and ΣDDT. Since the flesh of lobster and cod contained very low levels of these residues, the tendency for the lipid rich tissues to accumulate these residues is demonstrated. The processed materials all contained lower residues than would be suggested by the residues of their raw materials.

TABLE 6

Residues (µg/g) of PCB and ΣDDT in selected tissues and fishery products

Species	#	Mean PCB (Range)	Mean ΣDDT (Range)
Cod liver	11	5.1 (0.89 -19.3)	5.2 (0.50-23.3)
Cod liver oil	7	2.5 (1.6 - 2.9)	1.2 (0.97- 1.7)
Fish meal	40	0.15 (0.028- 0.74)	0.098(0.011-0.36)
Sea urchin roe	2	0.010(0.009-0.011)	0.004(0.004)
Tuna, canned	5	0.025(0.004-0.055)	0.013(0.003-0.026)
Tomalley, canned	7	0.37 (0.22 -0.52)	0.22 (0.14 -0.34)
Lobster hepatopancreas	11	5.3 (2.8 -12.7)	3.6 (1.1 -10.8)

Table 7 shows the mean hexachlorobenzene and dieldrin results from the 104 samples for which these residues were quantitated. The dieldrin and hexachlorobenzene residues were highest in the fatty samples, even though the levels in all samples tested were very low. No residues of aldrin, lindane, heptachlor, heptachlor epoxide or methoxychlor were confirmed in any of these samples.

TABLE 7

Residues (µg/g) of hexachlorobenzene (HCB) and dieldrin in fish and fishery products from the Northwest Atlantic

Species	#	HCB (Range)	Dieldrin (Range)
Alewives	6	0.006(.005-.007)	0.009(.004-.010)
Capelin	2	0.006(.006)	0.003(.003)
Clams	4	0.001(N.D.-.003)	N.D. (N.D.)
Cod	7	0.001(N.D.-.001)	N.D. (N.D.-.002)
Haddock	12	0.001(N.D.-.002)	N.D. (N.D.-.001)
Halibut	1	0.002	0.002
Herring	2	0.020(.016-.024)	0.014(.013-.014)
Lobster	13	N.D. (N.D.-.001)	0.002(N.D.-.004)
Mackerel	13	0.010(.002-.016)	0.014(.005-.026)
Mussels	3	0.003(.002-.004)	0.003(.001-.007)
Queen crab	4	N.D. (N.D.-.001)	0.001(N.D.-.001)
Redfish	10	0.003(.001-.006)	0.003(N.D.-.004)
Scallops	5	0.001(N.D.-.001)	N.D. (N.D.-.001)
Tuna	4	0.003(.002-.005)	0.004(.002-.006)
Yellowtail	4	0.002(.001-.002)	0.001(N.D.-.001)
Cod liver	1	0.039	0.035
Sea urchin roe	2	0.002(.001-.002)	N.D. (N.D.)
Lobster hepatopancreas	11	0.054(.022-.106)	0.017(.008-.028)

N.D. None detected.

Conclusions

Residues of DDT and PCBs were found at all sampling sites tested and in all species analyzed, but the magnitude of residues found was generally low. Of the 29 species sampled, only bluefin tuna (with mean residues of 3-4 μg/g) contained residues consistently greater than 1 μg/g. As various other workers have demonstrated, these residues were observed to accumulate preferentially in the fatty species. Thus the Pelagic species were found to contain almost ten times as much of these contaminants as the Groundfish, Crustacea and Bivalve species. The fishery products consistently contained lower residues than would be indicated by the raw material from which they were produced. No significant differences were found in the residue levels in fish sampled in 1971 as compared to those sampled in 1972 and no significant differences were observed in the levels of contamination at any of the sampling sites in this work. Although analyses were performed for seven other chlorinated pesticides, only minute quantities of two of these, dieldrin and hexachlorobenzene, were confirmed.

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