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A Report on an Intercomparison Study of the Determination of Chlorinated Biphenyl (PCB) Isomers in Fish Oil

by

J.F. Uthe, C.J. Musial
Fisheries and Environmental Sciences
Department of Fisheries and Oceans
Halifax Laboratory, Halifax, Nova Scotia
CANADA B3J 2S7

and

K.H. Palmork
Institute for Marine Research
5011 Bergen, NORWAY

Abstract

Five laboratories, employing capillary column gas chromatography, determined the levels of many chlorinated biphenyl isomers (PCB isomers) in Aroclor 1254 and in herring oil and the same oil spiked with Aroclor 1254. This study showed that the results were characterized by a large inter-laboratory variance, and that very few of the same isomers were being analyzed by all participants. The results also suggests that mis-identification of isomers may be occurring.

Resumé

Cinq laboratories, ou des colonnes capillaires sont utilisées pour la chromatographie en phase gazeuse, ont déterminé séparement les taux de plusiers isomeres du biphenyl chloruré (Isomeres PCB) dans l'Aroclor 1254, dans l'huile de hareng ainsi que dans un mélange composé d'huile de hareng et d'Aroclor 1254.

Cette étude a montré que les résultats des analyses sont caractérisés par une variance inter-laboratoire importante et que trés peu d'isomeres ont été analysés par tous le participants. Les résultats suggerent aussi la possibilité d'erreur dans l'identification des isomeres.

Since the early 1970's the International Council for the Exploration of the Sea (ICES) through activities designed to determine the extent of chemical contamination of the oceans has carried out intercalibration (intercomparison) exercises among the various participating national laboratories. (Uthe & Musial 1980; Holden 1980; Topping & Holden 1978). During the most recent organochlorine intercalibration study (Uthe & Musial, 1980) two of the participating laboratories reported the concentration of a number of individual chlorinated biphenyl isomers (PCB isomers) in the intercalibration oils. During the 1980 Statutory Meeting of the International Council for the Exploration of the Sea a number of papers presented to the Marine Environmental Quality committee discussed the determination of PCB isomers. Generally it was felt (Allchin 1980; Duinker et al. 1980; Tuinstra et al. 1980) that determination of PCB isomers by capillary gas chromatography rather than the more usual determinations by packed column gas chromatography with quantification based upon a selected industrial mixture of polychlorinated biphenyl (PCB) would contribute greatly in resolving many of the problems identified by the authors cited above. A number of intercalibration kits were still available from the fifth organochlorine intercalibration exercise and we decided to attempt an informal PCB isomer intercalibration study prior to the release of the report on the fifth organochlorine intercalibration at the Marine Chemistry Working Group Meeting in February, 1981. This report presents the results of this informal PCB isomer intercalibration study.

Material and Methods

The preparation of the intercalibration kits based on herring muscle oil and Aroclor 1254 has been described previously (Uthe & Musial, 1980). Participants were requested to analyze both the spiked and unspiked oils and Aroclor 1254 for as many PCB isomers as they could with no restrictions as to the methodology employed other than use of capillary gas chromatography. (Appendix I). The participating laboratories reporting for this study are listed in Table 1 along with an outline of each laboratory's analytical procedure.

Results and Discussion

Table 2 lists all PCB isomers which at least one laboratory identified and reported as well as the amount (µg/kg) of each PCB isomer reported by each participant. It is immediately obvious that individual laboratories are often determining different PCB isomers; generally each laboratory reports on from 15 to 22 of the combined total of 35 different PCB isomers reported. Of these 35 isomers 32 were reported to be present in the Aroclor 1254 supplied with the kits, with individual laboratories reporting on 15-22 PCB isomers in Aroclor 1254. The total amount of PCB isomers reported to be present in Aroclor 1254 represented from 52.2 to 88.1% by weight. Since the spiked oil contained 1 mg Aroclor 1254/g oil it is possible to calculate for each laboratory the overall recovery of the spike by utilizing the differences between the spiked and unspiked oils and the values reported for Aroclor 1254 itself. This has been done in Table 2 and these calculated Aroclor 1254 spike recoveries range from 61 to 125%.

Similarly we have calculated the recovery of each PCB isomer by subtracting the concentration of the isomer present in the unspiked oil from that of the spiked oil, dividing the resulting number by the amount of that isomer reported in Aroclor 1254. These recoveries ranged from 18-242%. It should be noted that in many of the PCB isomer amounts we are dealing with levels of less than 10 µg/kg. In our opinion these recoveries are acceptable considering that the coordinating laboratory spiked the oil while the others analyzed the oils at a much later date.

In order to easily and directly compare interlaboratory qualitative and quantitative results Tables 3, 4 and 5 tabulate all results from each participant for the spiked oil, unspiked oil and Aroclor 1254 respectively. Since these tables are for comparative purposes all results were rounded off to the nearest whole number. Out of the grand total of thirty-five PCB isomers for which one or more laboratories reported values only six isomers (IUPAC Nos. 44, 52, 87, 95, 97 and 153) were reported on by all five laboratories. Four out of five participants reported on four additional PCB isomers (IUPAC Nos 101, 138, 170 & 180). Out of the six isomers common to all laboratories, three of them (IUPAC Nos 52, 87 & 95) were reported by one or other of the participating laboratories as peaks which contained other isomers. Laboratory No. 4 reported that each of the pairs IUPAC 52 and 69 and 90 and 87 co-eluted from CP-Sil 5 and laboratory No. 5 reported that IUPAC Nos. 95 and 66 eluted at the same time from CP-Sil 7 (Table 2). Laboratory No. 1 also employed CP-Sil 7 coated capillary columns but did not report the same overlapping pairs, presumably due to lack of the appropriate PCB isomer. No interferring peaks were reported for the two remaining common isomers but that is not to say that this problem will not plague these and other isomers on certain capillary columns. This suggests that some limits will have to be placed upon selection of capillary columns as well as PCB isomers prior to coordinated studies of PCB isomers in marine biota.

Of the three remaining common isomers, a high degree of interlaboratory agreement was found only for IUPAC No. 44. The range of values reported for isomers Nos. 97 and 153 was considerably greater, the highest level being 3-4 times the lowest level reported.

The situation with respect to the isomers reported by four out of the five laboratories (IUPAC Nos. 101, 138, 170 & 180) is as follows. No interfering peaks were reported for any of these four peaks. The ranges of values reported for peaks 101 and 180 was similar to that reported above for peak 44 while the range of values reported for peaks 138 and 170 was approximately 3-4 fold.

A number of isomers were reported on by three or less participants, including one, 3,3',4,4'-tetrachlorobiphenyl (IUPAC No. 77) by one laboratory as being the major PCB isomer. The reported level of this PCB isomer is, however, significantly greater than the total percentage of tetrachlorobiphenyl isomers reported to be present in Aroclor 1254 (i.e. IUPAC Nos. 84, 110, 132, & 137). One must suspect that Table 5 and the

other tables contain a number of instances of misidentified PCB isomers since laboratories appear to be identifying most of the major peaks present on their chromatograms. Further evidence for this is suggested by the total of the average amount of each PCB isomer reported in Aroclor 1254 which was 1300 mg/g. Obviously there is an element of quantitative error included in this total. However the expected total is much less than the theoretical 1000 mg/g since analysts are not reporting on all isomers. The maximum total reported by any one laboratory (Table 2) was 881 mg/g. The occurrence of significant quantitative or qualitative errors such as shown in Table 5 indicates that there are substantial problems to be solved prior to successful interlaboratory studies of PCB-isomers in marine biota.

Two other laboratories (6 & 7) reported PCB concentrations in the oils based on the industrial Aroclor 1254 mixture rather than on individual isomers. Lab No. 6 used 2 prominent Aroclor 1254 peaks while No. 7 used 6 peaks. Their results for unspiked and spiked oils were 677 and 844, 1216 and 1708 (ng/g), respectively. These can be compared with the results (X_{excl}) of the Fifth ICES Intercalibration Study of PCBs in Biological Material (Tables 7 and 8) (X_{excl}) = 1.07 $\pm$ 0.33 g/g for unspiked oil and 1.93 $\pm$ 0.41 g/g for spiked oil. In this case it would appear that quantitation based on only 2 peaks would give misleading results. Lab No. 7 recovered 86.4% of the added PCB.

Participants were asked to state their choices of PCB isomers which should be studied in marine samples. Response ranged from a statement that routine analyses should be still based on technical mixtures through selected numbers of isomers to recommendations that all PCB isomers (or at least as many as investigators can obtain) be studied until problems have been identified and solved. Since the results of this study indicate that certain PCB isomers are co-eluted from some capillary columns we support the concept of studying all PCB isomers, especially those identified in industrial PCB preparations, to identify problems in their qualitative and quantitative determinations.

In conclusion it appears somewhat premature to recommend determination of PCB isomers in marine biota until inter-laboratory intercomparisons indicate satisfactory quantitative and qualitative performance. However, one must remember that intercomparison studies carried out with packed columns and industrial PCB mixtures as standards show very poor inter-laboratory performance (Holden & Topping 1978, Holden 1980, Uthe & Musial, 1980). In addition it has been shown (Duinker et al. 1980) that, even in the case where the chromatograms from packed column analyses of samples and standards (industrial PCB) are for all practical purposes identical, large differences become apparant with use of the capillary chromatograph and its much increased resolution. These differences were great enough to show that quantitative and qualitative column chromatography using industrial PCB as standards produce results which are in grave error.

The present study identified number of items as potential or actual problems associated with determining PCB isomers which will require resolution prior to use of PCB isomer analysis in coordinated monitoring and other interlaboratory studies.

These items are:

1. Availability of PCB isomers. Commercial suppliers are, as yet, unable to supply all needed PCB isomers. Some investigators are able to obtain some isomers from other researchers.

2. Purity of PCB isomers. It has been brought to our attention (Dr. V. Zitko, personal communication) that certain commercial PCB isomer preparations are impure.

3. Identity of PCB isomers. The results of this study suggest that some PCB isomers have been misidentified (by the suppliers ?).

4. Preparation of analytical standards. The amount of commercial PCB isomers offered for sale are generally from 5-10 mg. Preparation of quantitative standards from such small amounts of, often volatile, materials is difficult especially if duplicate weighed standards are to be prepared.

5. Different PCB isomers co-elute on certain capillary columns. Care will have to be exercised in selecting a column that will separate all isomers of interest. The electron capture detectors currently in use makes this extremely difficult since this detector is also sensitive to non-chlorinated compounds.

6. Clean-up and isolation procedures. The difference between adsorption chromatography and sulfuric acid clean-up shown by Holden (1980) must be investigated further as must the differences in Florisil and alumina results described by Uthe & Musial (1980).

References

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Table 1. Laboratories Participating in the PCB Isomer Intercalibration Study

Laboratory Number	Analytical Procedure	Laboratory
1	saponification, alumina clean-up CP-Sil 7	Rijks-Kwaliteitsinstitut voor Land-en tuinbouwprodukten, Wageningen, The Netherlands
2	H_2SO_4 clean-up SE-54	Institute of Marine Research Directorate of Fisheries Bergen, Norway
3	H_2SO_4 clean-up SE-54	Central Institute for Industrial Research, Royal Norwegian Council for Scientific and Industrial Research, Oslo, Norway
4	alumina clean-up silica split CP-Sil 5	Netherland Institute for Sea Research, Texel, The Netherlands
5	alumina clean-up silica split CP-Sil 7	Rijkinstituut voor Visserijonderzoek, IJmuiden, The Netherlands
6	H_2SO_4 clean-up SP-2100 measured as Aroclor 1254 based upon 2 peaks	Fiskeridirektoratet, Sentrallaboratoriet, Bergen, Norway
7	H_2SO_4 clean-up SE-52 measured as Aroclor 1254, based upon 5 or 6 peaks.	Centre National Pour L'Exploitation Des Océans, Centre Océanologique de Bretagne, Plouzané, France

Table 2. Concentrations of PCB Isomers in spiked and unspiked fish oils and Aroclor 1254 (μg/kg) and calculated recovery of isomers added by 1 mg/kg oil spike of Aroclor 1254 by coordinator.

Laboratory Number 1 (corrected for individual isomer recoveries)

PCB Isomer	IUPAC Number	Spiked Oil	Unspiked Oil	Arochlor 1254(mg/g)	Spiked - Unspiked (%) (1)
2,2'	4	75 (2)	70 (2)	-	-
2,2',3,5'	44	34	13	26	21(81)
2,2',4,5'	49	30	17	15	13(87)
2,2',5,5'	52	90	35	56	55(98)
2,3,4,4'	60	-	-	-	-
2,3,4,5	61	-	-	-	-
2,3',4',5	70	41	13	46	28(61)
2,3',5,5'	72	97	103	10	6(60)
3,3',4,4'	77	-	-	-	-
2,2',3,3',6	84	-	-	50	-
2,2',3,4,5'	87	61	17	52	44(85)
2,2',3,5',6	95	120	39	116	81(70)
2,2',3',4,5	97	46	11	27	35(130)
2,2',4,4',5	99	-	-	-	-
2,2',4,5,5'	101	165	68	94	97(103)
2,3,3',4,4'	105	-	-	-	-
2,3,3',4',6	110	-	-	-	-
2,3',4,4',5	118 +149 (4)	274	130	158	140(89)
2,2',3,3',4,4'	128	7	< 1	12	7(58)
2,2',3,3',4,5	129	-	-	3	-
2,2',3,3',4,6'	132	59	13	65	46(71)
2,2',3,3',6,6'	136	-	-	5	-
2,2',3,4,4',5	137	-	-	-	-
2,2',3,4,4',5'	138	88	39	71	49(69)
2,2',3,4,5,5'	141	20	10	14	10(71)
2,2',3,4',5',6	149	-	-	-	-
2,2',3,5,5',6	151	14	7	6	7(116)
2,2',4,4',5,5'	153	85	45	43	40(93)
2,2',4,4',6,6'	155	-	-	-	-
2,3,3',4,4',5	156	-	-	-	-
2,2',3,3',4,4',5	170	11	2	4	9(225)
2,2',3,4,4',5,5'	180	25	19	8	6(75)
2,2',3,4,5,5'6	187	13	11	< 1	2
2,2',3,3',4,4',5,5'	194	-	-	-	-
2,2',3,3',4',5,5'6	201	-	-	-	-
N	35	20	20	22	
Total ng/kg		1355	662	881 mg/g	693 (78%) (3)

(1) (Spiked-unspiked/Aroclor 1254) X 100
(2) Uncorrected
(3) from totals
(4) co-eluting isomer

Table 2. Concentrations of PCB Isomers in spiked and unspiked fish oils and Aroclor 1254 (μg/kg) and calculated recovery of isomers added by 1 mg/kg oil spike of Aroclor 1254 by coordinator.
Laboratory Number 2 (as reported by participant)

PCB Isomer	IUPAC Number	Spiked Oil	Unspiked Oil	Arochlor 1254(mg/g)	Spiked - Unspiked (%/) (1)
2,2'	4	-	-	-	-
2,2',3,5'	44	38.2	17.8	31	20.4(66)
2,2',4,5'	49	-	-	-	-
2,2',5,5'	52	74.0	38.2	61	35.8(59)
2,3,4,4'	60	-	-	-	-
2,3,4,5	61	-	-	-	-
2,3',4',5	70	-	-	-	-
2,3',5,5'	72	-	-	-	-
3,3',4,4'	77	-	-	-	-
2,2',3,3',6	84	-	-	-	-
2,2',3,4,5'	87	64.1	29.4	50	34.7(69)
2,2',3,5',6	95	112.3	57.1	89	55.2(62)
2,2',3',4,5	97	12.8	6.5	10	6.3(63)
2,2',4,4',5	99	128.0	109.0	39	19(49)
2,2',4,5,5'	101	123	62.5	90	60.5(67)
2,3,3',4,4'	105	58.3	26.7	44	31.6(72)
2,3,3',4',6	110	-	-	-	-
2,3',4,4',5	118	105	52.8	79	52.2(66)
2,2',3,3',4,4'	128	69.0	65.5	20	3.5(18)
2,2',3,3',4,5	129	-	-	-	-
2,2',3,3',4,6'	132	-	-	-	-
2,2',3,3',6,6'	136	-	-	-	-
2,2',3,4,4',5	137	-	-	-	-
2,2',3,4,4',5'	138	140	93.0	76	70(92)
2,2',3,4,5,5'	141	-	-	-	-
2,2',3,4',5',6	149	-	-	-	-
2,2',3,5,5',6	151	-	-	-	-
2,2',4,4',5,5'	153	103	74	49	29(69)
2,2',4,4',6,6'	155	-	-	-	-
2,3,3',4,4',5	156	-	-	-	-
2,2',3,3',4,4',5	170	15.7	10.5	8	5.2(65)
2,2',3,4,4',5,5'	180	51.9	43.7	18	8.2(46)
2,2',3,4,5,5,6	187	-	-	-	-
2,2',3,3',4,4',5,5'	194	3.1	3.7	1	-
2,2',3,3',4',5,5'6	201	-	-	-	-
N	35	15	15	15	
Total		1098	690	668 mg/g	408 (61%) (2)

(1) (Spiked-unspiked/Aroclor 1254) X 100
(2) From Totals

Table 2. Concentrations of PCB Isomers in spiked and unspiked fish oils and Aroclor 1254 (μg/kg) and calculated recovery of isomers added by 1 mg/kg oil spike of Aroclor 1254 by coordinator.

Laboratory Number 3 (as reported by participant)

PCB Isomer	IUPAC Number	Spiked Oil	Unspiked Oil	Arochlor 1254(mg/g)	Spiked - Unspiked (%) (1)
2,2'	4	-	-	-	-
2,2',3,5'	44	42	17	23	25(92)
2,2',4,5'	49	-	-	-	-
2,2',5,5'	52	122	43	56	79(141)
2,3,4,4'	60	-	-	-	-
2,3,4,5	61	-	-	-	-
2,3',4',5	70	-	-	-	-
2,3',5,5'	72	-	-	-	-
3,3',4,4'	77	-	-	-	-
2,2',3,3',6	84	-	-	-	-
2,2',3,4,5'	87	64	23	40	41(103)
2,2',3,5',6	95	116	41	61	75(123)
2,2',3',4,5	97	38	21	26	17(65)
2,2',4,4',5	99	61	33	30	28(93)
2,2',4,5,5'	101	144	53	71	91(128)
2,3,3',4,4'	105 + 132 (3)	92	44	51	48(94)
2,3,3',4',6	110	131	39	91	92(101)
2,3',4,4',5	118	117	52	59	65(91)
2,2',3,3',4,4'	128	26	9	16	17(94)
2,2',3,3',4,5	129	-	-	-	-
2,2',3,3',4,6'	132	-	-	-	-
2,2',3,3',6,6'	136	-	-	-	-
2,2',3,4,4',5	137	130	64	56	66(118)
2,2',3,4,4',5'	138	-	-	-	-
2,2',3,4,5,5'	141	-	-	-	-
2,2',3,4',5',6	149	100	58	42	42(100)
2,2',3,5,5',6	151	-	-	-	-
2,2',4,4',5,5'	153	130	86	41	44(107)
2,2',4,4',6,6'	155	-	-	-	-
2,3,3',4,4',5	156	-	-	-	-
2,2',3,3',4,4',5	170	12	8	6	4(67)
2,2',3,4,4',5,5'	180	38	32	8	6(75)
2,2',3,4,5,5',6	187	-	-	-	-
2,2',3,3',4,4',5,5'	194	2	1	1	-
2,2',3,3',4',5,5'6	201	-	-	-	-
N	35	17	17	17	
Total		1365	624	677 mg/kg	741(109%) (2)

(1) (Spiked-Unspiked/Aroclor 1254) X 100
(2) from totals
(3) co-eluting isomer

Table 2. Concentrations of PCB Isomers in spiked and unspiked fish oils and Aroclor 1254 (µg/kg) and calculated recovery of isomers added by 1 mg/kg oil spike of Aroclor 1254 by coordinator.
Laboratory Number 4 (Corrected for individual isomer recoveries)

PCB Isomer	IUPAC Number	Spiked Oil	Unspiked[1] Oil	Arochlor 1254(mg/g)	Spiked - Unspiked (%)[2]
2,2'	4				
2,2',3,5'	44	41.0	17.2	17.2	23.8(138)
2,2',4,5'	49	22.1	5.1	8.23	17.0(206)
2,2',5,5'	52+69[4]	46.6	20.1	12.6	26.5(210)
2,3,4,4'	60	25.6	20.6	2.90	5.0(172)
2,3,4,5	61	17.0	11.2	3.46	5.8(167)
2,3',4',5	70	62.8	27.5	24.3	35.3(145)
2,3',5,5'	72	13.9	8.7	3.2	-
3,3',4,4'	77	431	135	288	296(103)
2,2',3,3',6	84	-	-	-	-
2,2',3,4,5'	87 + 90[4]	8.6	5.5	12.5	13.1(105)
2,2',3,5',6	95	56.5	23.0	27.9	33.5(120)
2,2',3',4,5	97	13.6	5.3	7.31	8.2(112)
2,2',4,4',5	99	-	-	-	-
2,2',4,5,5'	101	-	-	-	-
2,3,3',4,4'	105	80.0	47.0	51.7	33(64)
2,3,3',4',6	110	-	-	-	-
2,3',4,4',5	118	-	-	-	-
2,2',3,3',4,4'	128	26.2	14.2	11.1	12(108)
2,2',3,3',4,5	129	-	-	-	-
2,2',3,3',4,6'	132	-	-	-	-
2,2',3,3',6,6'	136+p,p'DDE	122.1	122.5	4.4	-
2,2',3,4,4',5	137	-	-	-	-
2,2',3,4,4',5'	138	69.1	19.2	39.3	49.9(127)
2,2',3,4,5,5'	141	12.4	7.6	5.64	4.8(85)
2,2',3,4',5',6	149	-	-	-	-
2,2',3,5,5',6	151	-	-	-	-
2,2',4,4',5,5'	153	55.8	35.7	22.9	20.1(88)
2,2',4,4',6,6'	155	20.8	12.6	9.60	8.2(85)
2,3,3',4,4',5	156	12.6	-	5.79	?
2,2',3,3',4,4',5	170	-	-	-	-
2,2',3,4,4',5,5'	180	-	-	-	-
2,2',3,4,5,5',6	187	-	-	-	-
2,2',3,3',4,4',5,5'	194	12.4	12.6	-	-
2,2',3,3',4',5,5'6	201	-	-	-	-
N	35	20	19	19	
Total		1150 ng/kg	551 ng/kg	558 ng/kg	599(107%)[3]

(1) Also reported for unspiked oil. IUPAC No. 30; 1.5: 12+15+18; 5.2: 28+31+50; 6.25: 21+33+53; 2.9: 47+75; 10.1, pentachlorobenzene; 1.4 and hexachlorobenzene; 10.45 all uncorrected for recovery.
(2) (Spiked-Unspiked/Aroclor 1254) X 100
(3) from totals
(4) co-eluting isomer

Table 2. Concentrations of PCB Isomers in spiked and unspiked fish oils and Aroclor 1254 (μg/kg) and calculated recovery of isomers added by 1 mg/kg oil spike of Aroclor 1254 by coordinator.
Laboratory Number 5 (Corrected by participant for recovery)

PCB Isomer	IUPAC Number	Spiked Oil	Unspiked Oil [1]	Arochlor 1254(mg/g)	Spiked - Unspiked (%) [2]
2,2'	4	-	-	-	-
2,2',3,5'	44	42	16	24	26(108)
2,2',4,5'	49	25	11	12	14(117)
2,2',5,5'	52	84	35	44	49(111)
2,3,4,4'	60	-	-	-	-
2,3,4,5	61	-	-	-	-
2,3',4',5	70	-	-	-	-
2,3',5,5'	72	-	-	-	-
3,3',4,4'	77	176	58	N.R. [3]	118
2,2',3,3',6	84	-	-	-	-
2,2',3,4,5'	87	47	N.R. [3]	44	47(107)
2,2',3,5',6	95+66 [5]	144	56	84	88(105)
2,2',3',4,5	97	50	14	27	36(133)
2,2',4,4',5	99	-	-	-	-
2,2',4,5,5'	101	160	65	99	95(96)
2,3,3',4,4'	105	-	-	-	-
2,3,3',4',6	110	-	-	-	-
2,3',4,4',5	118	-	-	-	-
2,2',3,3',4,4'	128	30	13	7	17(242)
2,2',3,3',4,5	129	-	-	-	-
2,2',3,3',4,6'	132	-	-	-	-
2,2',3,3',6,6'	136	15	5	6	10(167)
2,2',3,4,4',5	137	-	-	-	-
2,2',3,4,4',5'	138	118	60	63	58(92)
2,2',3,4,5,5'	141	21	8	11	13(118)
2,2',3,4',5',6	149	84	47	39	37(95)
2,2',3,5,5',6	151	22	12	7	10(142)
2,2',4,4',5,5'	153	96	64	40	32(80)
2,2',4,4',6,6'	155	-	-	-	-
2,3,3',4,4',5	156	-	-	-	-
2,2',3,3',4,4',5	170	12	11	6	1(17)
2,2',3,4,4',5,5'	180	40	36	9	4(44)
2,2',3,4,5,5',6	187	18	20	N.R. [3]	-
2,2',3,3',4,4',5,5'	194	-	-	-	-
2,2',3,3',4',5,5'6	201	3	6	N.R. [3]	-
N	35	19	18	16	
Total		1187	537	522 mg/g	655(125%) [4]

(1) IUPAC 119, 121, 132, 140, 154, and 202 are not present
(2) (Spiked-unspiked/Aroclor 1254) X 100
(3) no report
(4) from totals
(5) co-eluting isomer

Table 3. Concentrations of PCB Isomers (μg/kg) in Spiked Oil

PCB Isomer	IUPAC Number	Laboratory Number 1	2	3	4	5
2,2'	4	75	-	-	-	-
2,2',3,5'	44	34	38	42	41	42
2,2',4,5'	49	30	-	-	22	25
2,2',5,5'	52	90	74	122	47 (1)	84
2,3,4,4'	60	-	-	-	26	-
2,3,4,5	61	-	-	-	17	-
2,3',4',5	70	41	-	-	63	-
2,3',5,5'	72	97	-	-	14	-
3,3',4,4'	77	-	-	-	431	176
2,2',3,3',6	84	-	-	-	-	-
2,2',3,4,5'	87	61	64	64	86	47
2,2',3,5',6	95	120	112	116	57	144
2,2',3',4,5	97	46	13	38	14	50
2,2',4,4',5	99	-	128	61	-	-
2,2',4,5,5'	101	165	123	144	-	160
2,3,3',4,4'	105	-	58	92	80	-
2,3,3',4',6	110	-	-	131	-	-
2,3',4,4',5	118	274	105	117	-	-
2,2',3,3',4,4'	128	7	69	26	26	30
2,2',3,3',4,5	129	-	-	-	-	-
2,2',3,3',4,6'	132	59	-	-	-	-
2,2',3,3',6,6'	136	-	-	-	122	15
2,2',3,4,4',5	137	-	-	130	-	-
2,2',3,4,4',5'	138	88	140	-	69	118
2,2',3,4,5,5'	141	20	-	-	12	21
2,2',3,4',5',6	149	-	-	100	-	84
2,2',3,5,5',6	151	14	-	-	-	22
2,2',4,4',5,5'	153	85	103	130	56	96
2,2',4,4',6,6'	155	-	-	-	21	-
2,3,3',4,4',5	156	-	-	-	13	-
2,2',3,3',4,4',5	170	11	16	12	-	12
2,2',3,4,4',5,5'	180	25	52	38	-	40
2,2',3,4,5,5',6	187	13	-	-	-	-
2,2',3,3',4,4',5,5'	194	-	3	2	12	-
2,2',3,3',4',5,5'6	201	-	-	-	-	3

1 - underlined values are for more than a single isomer - see Table 2.

Table 4. Concentrations of PCB Isomers (μg/kg) in Unspiked Oil

PCB Isomer	IUPAC Number	Laboratory Number 1	2	3	4	5
2,2'	4	70	-	-	-	-
2,2',3,5'	44	13	18	17	17	16
2,2',4,5'	49	17	-	-	5	11
2,2',5,5'	52	35	38	43	20	32
2,3,4,4'	60	-	-	-	21	-
2,3,4,5	61	-	-	-	11	-
2,3',4',5	70	13	-	-	28	-
2,3',5,5'	72	103	-	-	9	-
3,3',4,4'	77	-	-	-	135	58
2,2',3,3',6	84	-	-	-	-	-
2,2',3,4,5'	87	17	29	23	6	-
2,2',3,5',6	95	39	57	41	23	56
2,2',3',4,5	97	11	7	21	5	14
2,2',4,4',5	99	-	109	33	-	-
2,2',4,5,5'	101	68	63	53	-	65
2,3,3',4,4'	105	-	27	44	47	-
2,3,3',4',6	110	-	-	39	-	-
2,3',4,4',5	118	130	53	52	-	-
2,2',3,3',4,4'	128	< 1	66	9	14	13
2,2',3,3',4,5	129	-	-	-	-	-
2,2',3,3',4,6'	132	13	-	-	-	-
2,2',3,3',6,6'	136	-	-	-	123	5
2,2',3,4,4',5	137	-	-	64	-	-
2,2',3,4,4',5'	138	39	93	-	19	60
2,2',3,4,5,5'	141	10	-	-	8	8
2,2',3,4',5',6	149	-	-	58	-	47
2,2',3,5,5',6	151	7	-	-	-	12
2,2',4,4',5,5'	153	45	74	86	36	64
2,2',4,4',6,6'	155	-	-	-	13	-
2,3,3',4,4',5	156	-	-	-	-	-
2,2',3,3',4,4',5	170	2	11	8	-	11
2,2',3,4,4',5,5'	180	19	44	32	-	36
2,2',3,4,5,5',6	187	11	-	-	-	20
2,2',3,3',4,4',5,5'	194	-	4	1	13	-
2,2',3,3',4',5,5'6	201	-	-	-	-	6

1 - underlined values are for more than a single isomer - see Table 2.

Table 5. Concentrations of PCB Isomers (mg/kg) in Aroclor 1254

PCB Isomer	IUPAC Number	Laboratory Number 1	2	3	4	5
2,2'	4	-	-	-	-	-
2,2',3,5'	44	26	31	23	17	24
2,2',4,5'	49	15	-	-	8	12
2,2',5,5'	52	56	61	56	13	44
2,3,4,4'	60	-	-	-	3	-
2,3,4,5	61	-	-	-	4	-
2,3',4',5	70	46	-	-	24	-
2,3',5,5'	72	10	-	-	3	-
3,3',4,4'	77	-	-	-	288	-
2,2',3,3',6	84	50	-	-	-	-
2,2',3,4,5'	87	52	50	40	13	44
2,2',3,5',6	95	116	89	61	28	84
2,2',3',4,5	97	27	10	26	7	27
2,2',4,4',5	99	-	39	30	-	-
2,2',4,5,5'	101	94	90	71	-	99
2,3,3',4,4'	105	-	44	51	52	-
2,3,3',4',6	110	-	-	91	-	-
2,3',4,4',5	118	158	79	59	-	-
2,2',3,3',4,4'	128	12	20	16	11	7
2,2',3,3',4,5	129	3	-	-	-	-
2,2',3,3',4,6'	132	65	-	-	-	-
2,2',3,3',6,6'	136	5	-	-	4	6
2,2',3,4,4',5	137	-	-	56	-	-
2,2',3,4,4',5'	138	71	76	-	39	63
2,2',3,4,5,5'	141	14	-	-	6	-
2,2',3,4',5',6	149	-	-	42	-	39
2,2',3,5,5',6	151	6	-	-	-	7
2,2',4,4',5,5'	153	43	49	41	23	40
2,2',4,4',6,6'	155	-	-	-	10	-
2,3,3',4,4',5	156	-	-	-	6	-
2,2',3,3',4,4',5	170	4	8	6	-	6
2,2',3,4,4',5,5'	180	8	18	8	-	9
2,2',3,4,5,5',6	187	<1	-	-	-	-
2,2',3,3',4,4',5,5'	194	-	<1	1	-	-
2,2',3,3',4',5,5'6	201	-	-	-	-	-

1 - underlined values are for more than a single isomer - see Table 2.

APPENDIX I

Government of Canada / Gouvernement du Canada

Fisheries and Oceans / Pêches et Océans

Your file / Votre référence

Our file / Notre référence

PCB Individual Isomer Check Sample: Capillary GC

Dear Colleague:

Among the interesting results which issued from the ICES Organochlorine Intercalibration Studies No. 4 (CM1980/E:40) and No. 5 (CM1980/E:8) exercise was the variance among results obtained. In order to investigate this phenomenon a number of laboratories have indicated an interest in participating in a PCB isomeric check sample program using capillary gas chromatography. It is hoped that such a study would indicate if capillary chromatograph could reduce the wide variance in results found in previous intercalibration studies.

Therefore we have put together new test kits consisting of unspiked and spiked oil and a sample of the Aroclor 1254 used to spike the oil. We are requesting that you analyze all three samples (both oils and Aroclor 1254 itself) by capillary gas chromatography (after your usual cleanup procedure) by determining as many of the individual PCB isomers as your capability permits.

When reporting results please include the following information:

(1) Cleanup procedure (outline) if different than that used for OC Check sample 5.
(2) Type of gas chromatograph.
(3) Type of column (dimensions, coating, glass or fused silica, SCOT or WCOT, etc)
(4) Efficiency of the column; i.e. number of theoretical plates per meter (N/L), determined for an isomer which elutes at 60% (as closely as possible) of the run time for the Aroclor 1254 mixture. (Since not all labs have the same isomers, one isomer cannot be specified and we unfortunately do not have sufficient quantity of a suitable isomer to send to all the labs.) Please report which isomer was used in this calculation.
(5) Individual isomer names (identified by numbers on the chromatograms or by Ballschmiter and Zell numbers) and quantities (including estimates of variance) in µg(Kg (p.p.b.) of oil or of Aroclor 1254. Please also identify your source (supplier) of the isomers.

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6) Total PCB levels (sum of individual isomers) in the oils and 1254 in g/Kg.
7) % Recovery, and if the results have been corrected for recovery (using either an individual isomer correction value or an average correction value).
8) Samples of the chromatograms of the unspiked and spiked oils, Aroclor 1254, and your individual isomer analytical standard.
9) Method of standardization of chromatograph (internal or external).
10) Method of calculation (peak height or area, response factors or regression line).
11) Your recommendations as to which PCB isomers should be measured in marine biota.

If possible we would like to have your results before or during the February 1981 meeting of the Working Group on Pollution Baseline and Monitoring Studies in the North Atlantic so that a preliminary report might be prepared prior to future intercalibration studies, i.e. by the 1981 Statutory Meeting of ICES.

Your cooperation in this study is greatly appreciated.

Yours truly,

C.J. Musial, J.F. Uthe, K. Palmork

/dls

P.S. Please acknowledge receipt of the kit.