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CRITERIA DOCUMENT

PCBs

MONS 063322

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APPENDIX A. The Chemistry of PCBs (Hutzinger, Safe & Zitko).

APPENDIX B. The Toxicity of Polychlorinated Polycyclic Compounds and Related Chemicals (Kimbrough).

APPENDIX C. Review of PCB Levels in the Environment (U.S. EPA, Office of Toxic Substances, Draft report).

APPENDIX D. Review of Carcinogenic and Co-Carcinogenic Effects of PCBs.

APPENDIX E. Metabolism and Biodegradation.

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Errata
PCB Criteria Document

Sec. III.6.4 Effects on reproduction of birds

Line 3 should read - ppm of PCBs, corresponding to residues of only 1-2 ppm in whole eggs (150).

Sec. V. Criteria Formulation

Paragraph 1, line 5 should read - affected fish thyroid (73,95). At the 0.5 ppm dietary level PCBs caused enzyme induction in rats (219).

p. R-8

Reference 69: Pages cited should be 43-49 not 57-64

p. R-18

Reference 197: Pages cited should be 347-350 not 332-333

Appendices A and B are copyrighted materials and therefore have been omitted.

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I. INTRODUCTION

I.1 Principal sources of information

Comprehensive reviews of the occurrence of polychlorinated biphenyls (PCBs) in the environment and their potential hazards were published in 1972 by an Interdepartmental Task Force (ITF) (1) and by a Panel on Hazardous Trace Substances (PHTS) convened by the Office of Science and Technology (OST) and the National Institute for Environmental Health Sciences (NIEHS) (2). The latter report formed the basis for a draft Scientific and Technical Assessment Report (STAR) prepared by the Office of Research and Development (ORD) of the Environmental Protection Agency (EPA) in September 1974 (3). More specialised reviews of the chemistry and toxicology of PCBs were published in 1974 by Hutzinger, Safe and Zitko (4) and Kimbrough (5): these reviews are attached as Appendices A and B respectively to this document. A draft report (6) reviewing the occurrence and levels of PCBs in the environment has been prepared by EPA's Office of Toxic Substances (OTS) in January 1976 and is attached as Appendix C. A summary of industrial uses and environmental distribution of PCBs in the United States was prepared for OTS by Versar, Inc., in February 1976 (7). Important collections of scientific data are included in the proceedings of two conferences on PCBs, held in 1971 and 1975 (refs. 8 and 9).

I.2 Uses and releases of PCBs into the environment

Polychlorinated biphenyls (PCBs) are manufactured by the direct chlorination of biphenyl. Commercial products are complex mixtures of chlorobiphenyls and are marketed for various uses according to the percentage of chlorine in the mixture. The major producer of PCBs in the United States is the Monsanto Company, which now markets four mixtures (with 21%,

41%, 42% and 54% chlorine) for closed electrical system uses under the trademark 'Aroclor'. Prior to 1970 Monsento marketed a wider range of mixtures (containing up to 68% chlorine) and these were used in a number of other applications, including uses as plasticizers, heat transfer fluids, hydraulic fluids, fluids in vaccuum pumps and compressors, lubricants, wax extenders, etc. Following the discovery in the late 1960's that PCBs had become widespread environmental contaminants, Monsanto voluntarily limited its range of products and restricted sales to those for closed electrical system uses. However, because of the long life of many products containing PCBs, it is believed that a substantial fraction of the PCBs manufactured before 1971 remains in service (7). There is thus a potential for their discharge into the environment when the components containing them are scrapped or leak. Moreover, although imports of PCBs into the United States are small, comprising only 1-2% of domestic sales (7), much of the imported material appears to be sold for non-closed system uses (7). Thus, in evaluating the potential impact of PCBs released into the environment, it is necessary to consider not only the mixtures currently manufactured and sold by Monsanto, but also the other mixtures manufactured by Monsanto prior to 1970, and products manufactured overseas. Recent surveys have identified a number of sources of PCBs into the aquatic environment, including not only effluents from the manufacturing plant and the electrical industry, but also sewage treatment plants, urban run-off, steel and aluminum foundries, pulp and paper mills, automotive and metal finishing plants, hydraulic and heat transfer systems, investment casting operations, and shipping (10-12).

I.3 PCB mixtures and contaminants: the problem of evaluation

Evaluation of the potential environmental impact of the various commercial mixtures is complicated by the fact that the components of the mixtures differ greatly in their physical, chemical and biological properties. Accordingly the constitution of the mixtures often changes as the materials are transported through the environment, so that plants, animals, and humans are exposed to mixtures whose constitution differs from those whose toxicity has been tested in laboratory experiments. Although the environmental behavior and biological activity of a number of individual chlorobiphenyl isomers have been studied in recent years, it is still difficult to evaluate the potential toxicity of the complex mixtures found in the environment. In making this evaluation it is necessary to weigh carefully the results of studies of individual compounds, and to compare critically the environmental and toxicological properties of the commercial mixtures.

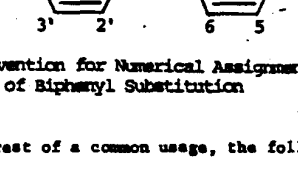
A further complication is that several commercial PCB mixtures have been reported to contain small quantities of highly toxic contaminants, polychlorinated dibenzofurans (PCDFs). Some of the toxic effects observed in animals and humans exposed to PCBs appear to be attributable to PCDFs, while others appear to be caused by PCBs themselves. There is also some evidance that small quantities of PCDFs may be formed from PCBs either in service or during metabolism by animals. Accordingly it is necessary to consider the potential effects of both classes of compounds when weighing the potential impact of PCBs released into the environment.

II. CHEMICAL AND PHYSICAL PROPERTIES

II.1 Nomenclature of chlorobiphenyls and isomers

Polychlorinated biphenyls consist of a mixture of chlorinated biphenyls with varying degrees of chlorination and isomeric constitution.

Some confusion has appeared in the literature because of the nomenclature that is used to describe the commercial preparations and the individual authenticated chlorobiphenyls. In order to clarify the nomenclature to be used herein, it is appropriate to digress briefly as follows. The biphenyl molecule has a total of ten (10) carbon-hydrogen bonds at which chlorine substitution can be accommodated. A schematic representation of the biphenyl molecule with the various positions at which substitution can be accomplished numbered in the American Chemical Society standard notation is presented below:



ACS Convention for Numerical Assignments of Biphenyl Substitution

In the interest of a common usage, the following rules will be followed in this report:

a. When referring to a mixture of different species, as occurs in the commercial products, the term polychlorinated biphenyls (abbreviation, PCBs) will be used.

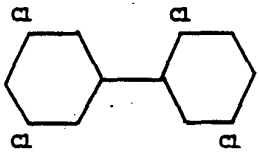
b. Those species of chlorinated compounds that arise from a specified number of chlorine substituents on the biphenyl

molecule will be referred to as chlorobiphenyls with a suitable numerical prefix to define the number of substituted chlorines; i.e., dichlorobiphenyl. Thus, there are a total of ten (10) chlorobiphenyls that might appear in the commercial mixtures.

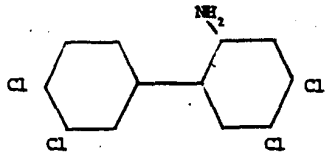
c. Those specific compounds that represent the class of compounds formed by a specific number of substituent chlorine atoms but differ in the locations at which substitution has taken place are referred to as isomers.

Thus, in terms of the above, the proper manner of referring to a commercial PCB mixture is as a "mixture of chlorobiphenyls containing various proportions of the isomers of each".

To illustrate the utility of the numbering system indicated previously, the correct names of the compounds shown below are:



2,3',5,5'-tetrachlorobiphenyl



3',4,4',5-tetrachloro-2-biphenylamine

In addition to biphenyl itself, which is found in some commercial mixtures, there are ten chlorobiphenyls comprising 209 possible isomers (Table II.1.1.)

In some sections of this report, chlorobiphenyls with 5 or more chlorine atoms will be referred to as "higher chlorobiphenyls" and those with 3 or fewer chlorine atoms will be referred to as "lower chlorobiphenyls". This distinction is made in recognition of the fact that the former group of compounds is much more persistent in the environment than the latter group, whereas tetrachlorobiphenyls are intermediate in persistence (Section IV.1 below).

II.2 Manufacture and nomenclature of commercial PCB mixtures

The world's principal manufacturers of PCBs are listed in Table II.2.1, with the trade names under which the products are sold. In the United States the sole manufacturer is the Monsanto Company which sells four mixtures under the tradename Aroclor(R). These four products, together with five mixtures whose manufacture has been discontinued since 1970, are listed in Table II.2.2 (from ref. 13). Except for Aroclor 1016, the last two digits in the Aroclor number specify the percentage of chlorine in the mixture. Aroclor 1016, introduced in 1971, is similar in constitution to Aroclor 1242 but is modified (by distillation) to include only about 1% of pentachlorobiphenyls (13).

II.3 Constitution of Aroclor mixtures

The commercial process by which the PCBs are made involved the chlorination of biphenyl with anhydrous chlorine in the presence of a catalyst which may be either iron filings or ferric chloride. The crude product is generally purified to remove color, traces of hydrogen chloride,

Table II.1.1

Empirical Formulation, Molecular Weights and Chlorine Percentage in PCBs

Empirical formula chlorobiphenyls	Molecular weight*	Percent chlorine*	No. of isomers
$C_{12}H_{10}$	154	0	1
$C_{12}H_9Cl$	188	18.6	3
$C_{12}H_8Cl_2$	222	31.5	12
$C_{12}H_7Cl_3$	256	41.0	24
$C_{12}H_6Cl_4$	290	48.3	42
$C_{12}H_5Cl_5$	324	54.0	46
$C_{12}H_4Cl_6$	358	58.7	42
$C_{12}H_3Cl_7$	392	62.5	24
$C_{12}H_2Cl_8$	426	65.7	12
$C_{12}HCl_9$	460	68.5	3
$C_{12}Cl_{10}$	494	79.9	1

*Based on Cl^{35}

Table II.2.1

The World's Major Producers of PCBs

Producer	Country	Tradename
Monsanto	U.S.A. and Great Britain	Aroclor(R)
Bayer	Germany	Clophen(R)
Prodelec	France	Phenoclor and Pyralene(R)
Caffaro	Italy	Fanclor
Kanegafuchi*	Japan	Kanechlor(R)
Mitsubishi-* Monsento	Japan	Santotherm(R)
Soval	U.S.S.R.	
Chemko	Czechoslovakia	

* Production discontinued for domestic use.

Table II.2.2

AROCLOR PRODUCTS MANUFACTURED IN THE U.S.

Current	Discontinued	Percent Chlorine
1221		21
	1232	32
1016		41
1242		42
	1248	48
1254		54
	1260	60
	1262	62
	1268	68
	1270	71

and the catalyst by treatment with alkali and subsequent distillation. The resulting product is then a more or less complex mixture of the chlorobiphenyls, the precise composition depending on the conditions under which chlorination was carried out.

II.3.1 Molecular composition

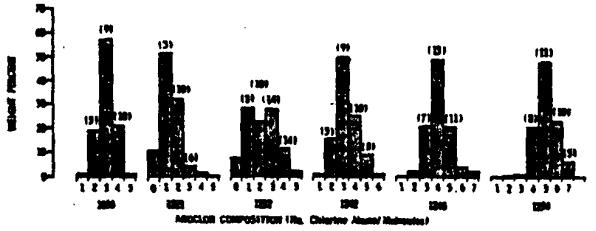
Table II.3.1 lists the distribution of the various chlorobiphenyls in six major Aroclor mixtures, as given by Monsanto (13), Webb and McCall (14), and Hirwe et al. (15). The differences between the results given for Aroclors 1242 and 1254 may reflect either differences in analytical methods or variations in constitution. These and other data are summarized in histogram form in Figure II.3.1 (16). No data appear to have been published on the molecular composition of the other Aroclor mixtures, but the data in Figure II.3.2 indicate that Aroclor 1262 consisted mostly of hexa- and heptachlorobiphenyls, and Aroclor 1268 mostly of octa- and nonachlorobiphenyls; Aroclor 1270 apparently consisted primarily of decachlorobiphenyl.

Figure II.3.2 presents high-resolution gas-liquid chromatograms of eight Aroclor mixtures (17). Each mixture contained a large number of components, including several isomers of each chlorobiphenyl; in most cases several major components are common to successive members of the Aroclor series.

Figure II.3.3 compares high-resolution gas-liquid chromatograms of Aroclors 1016 and 1242. The mixtures appear extremely similar except for the absence from Aroclor 1016 of a few minor constituents with relatively long retention times present in Aroclor 1242.

II.3.2 Isomeric constitution

A nearly complete identification of the chlorobiphenyl isomers present in Aroclors 1242, 1254, and 1260 was carried out by Sissons and



The congener composition of commercially available Aroclors based on the weight percent of biphenyls bearing different numbers of chlorine atoms/molecule. Data were obtained from reports by Webb and McCall (ref.20), Sissons and Welti (ref.18), and from information supplied by the Monsanto Industrial Chemicals Company.

Figure II.3.1 (from ref. 16)

Table II.3.1

Approximate molecular composition of Aroclors, from data in ref. 13 (M), ref. 14 (W), and ref. 15 (H).

Chlorobiphenyl	1221		1232	1016	1242			1248	1254			1260
	M	W	W	M	M	W	H	W	M	W	H	W
$C_{12}H_{10}$	11	7	6	Tr	Tr	-	-	-	Tr	-	-	-
$C_{12}H_9Cl_1$	51	51	26	1	1	1	Tr	-	Tr	-	-	-
$C_{12}H_8Cl_2$	32	38	29	20	16	17	4	1	0.5	-	-	-
$C_{12}H_7Cl_3$	4	3	24	57	49	40	39	23	1	-	0.5	-
$C_{12}H_6Cl_4$	2	-	15	21	25	32	42	50	21	16	36	-
$C_{12}H_5Cl_5$	0.5	-	0.5	1	8	10	14	20	48	60	45	12
$C_{12}H_4Cl_6$	-	-	-	Tr	1	0.5	-	1	23	23	18	46
$C_{12}H_3Cl_7$	-	-	-	-	Tr	-	-	-	6	1	1	35
$C_{12}H_2Cl_8$	-	-	-	-	-	-	-	-	-	-	-	6
$C_{12}H_1Cl_9$	-	-	-	-	-	-	-	-	-	-	-	-
$C_{12}Cl_{10}$	-	-	-	-	-	-	-	-	-	-	-	-

Tr - Trace (less than 0.1 percent)

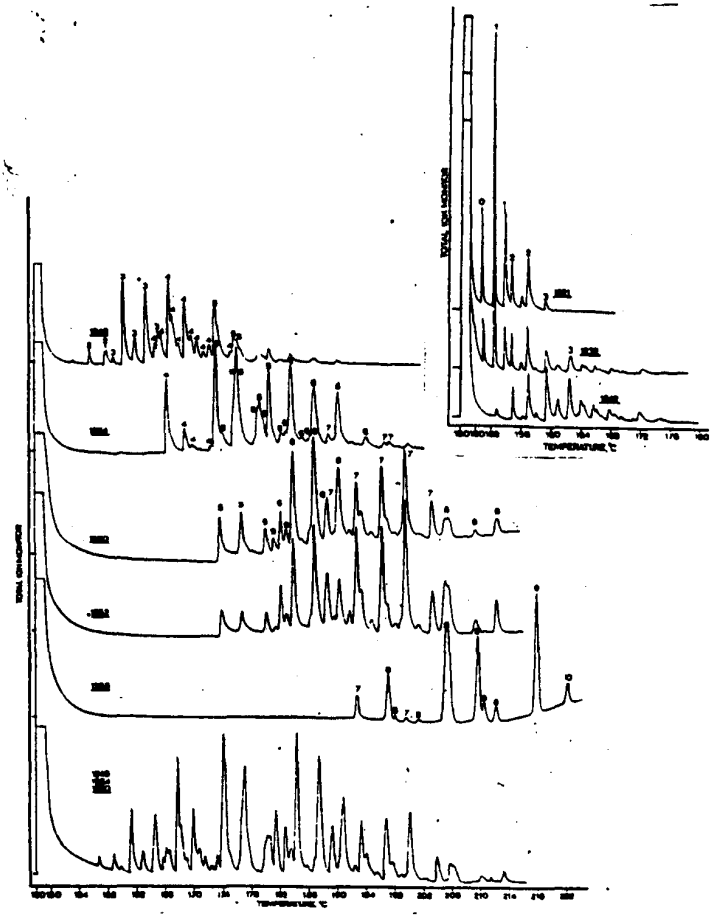


Figure II.3.2 Gas-liquid chromatograms of Aroclor mixtures (from ref. 17)

Underlined numbers designate the Aroclor formulation. Numbers above the peaks designate the number of chlorine atoms in the compound(s) determined from the mass spectrum; unnumbered peaks have the same number of chlorine atoms as marked peaks at the same temperature. Temperature program rate 2°C/minute, He 9 psig, 50 ft × 0.020 in. SE-30 SCOT column, PE-270 gic-MS.

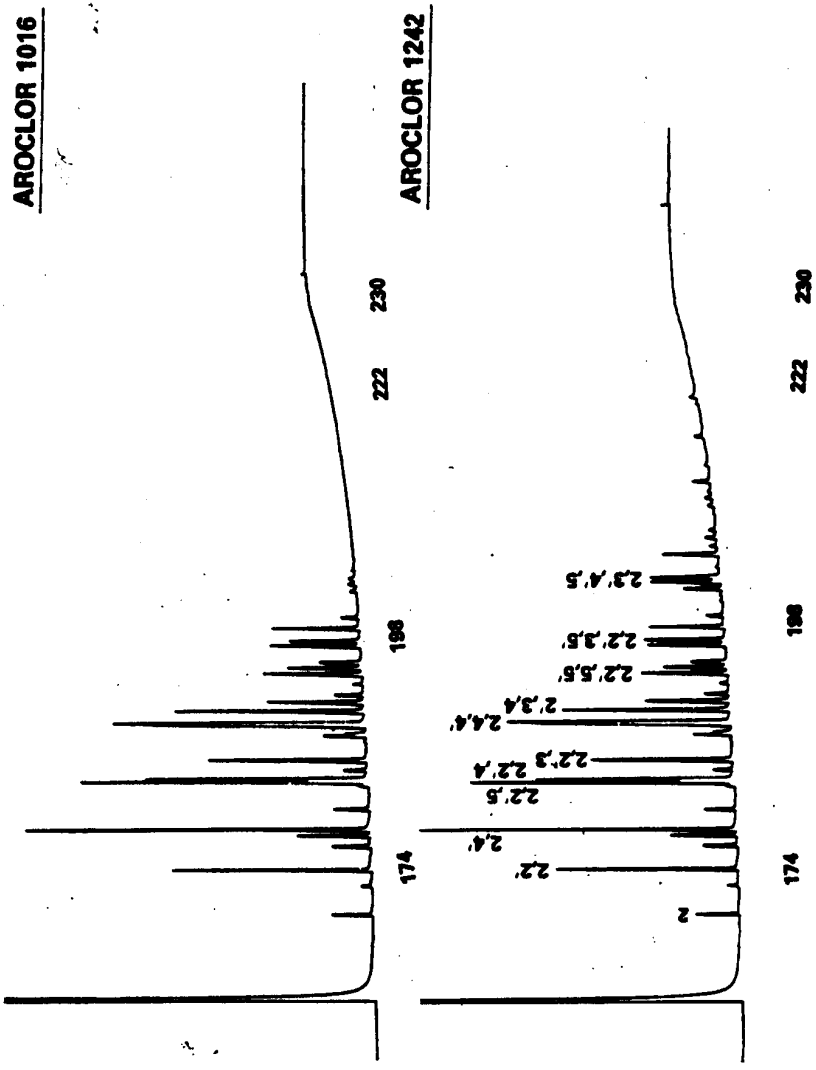


Figure II.3.3 High resolution capillary column chromatograms of Aroclors 1016 and 1242 (from ref. 13).

Welti (18) by use of a combination of gas-liquid chromatography, nuclear magnetic resonance (NMR) and mass spectroscopy (MS). The retention index (RI) system proposed by Kovats (19) was adopted in order to provide a characterization of the peak position in gas-liquid chromatography that is less sensitive to column conditions than retention time or relative retention time. Retention indices were used to identify minor constituents after the major constituents had been identified using NMR. The identifications of a number of the isomers have been confirmed independently (20).

Figure II.3.4 illustrates a gas-liquid chromatogram of Aroclor 1254 with the peaks numbered according to the scheme of Sissons and Welti (18). Table II.3.2 lists their identifications of the major constituents and Table II.3.3 lists the probable identities of the minor constituents. Figures II.3.5 and II.3.6 and Tables II.3.4 and II.3.5 give corresponding chromatograms and identification of the isomers present in Aroclors 1242 and 1260. Table II.3.6 gives the results of independent identification of the constituents of the major peaks in the chromatograms of Aroclors 1254 and 1260 (27): these agree closely with those in refs. 18 and 20.

II.4 Constitution of other commercial mixtures

Where data are available, the constitution of PCB mixtures manufactured in other countries appears to agree very closely with that of the corresponding Aroclor mixtures. Figure II.4.1, for example (from ref. 22) shows that gas-liquid chromatograms of Phenoclor DP6, Clophen A60, and Aroclor 1260 (all mixtures with 60% chlorine) are almost identical, except for a small difference in peak 3 in Clophen A60*. Jensen and Sundström (23) have identified and measured the relative quantities of most components of

* This peak corresponds to components 11, 14, and 15 listed for Clophen A60 in ref. 23, and to components 40 and 41 listed for Aroclor 1260 in ref. 18. The difference appears to be the presence of 2,3,6,2',3',6'-hexachlorobiphenyl in Clophen A60, but not in Aroclor 1260 (18, 23).

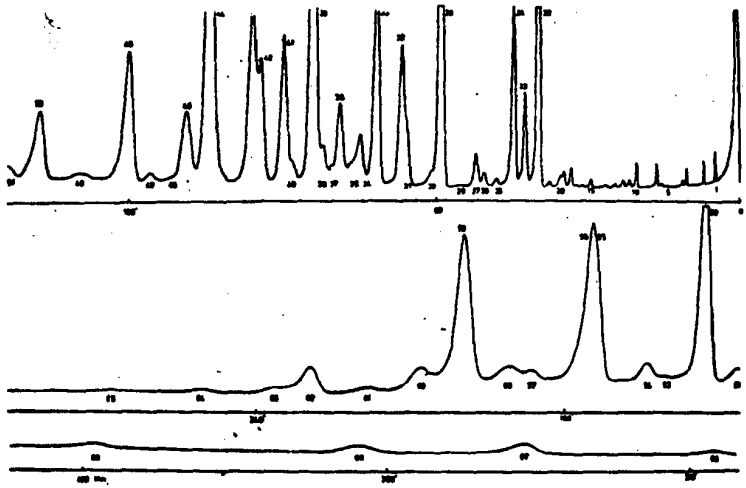


Figure II.3.4 Gas-liquid chromatogram of Aroclor 1254 (refs. 18, 21)

Table II.3.2 (from refs. 18, 21)

The retention indices, chlorine numbers and structures of the major PCB constituents in Aroclor 1254.

Peak No.	R.I.	Chlorine No.[a]	NMR determined structure	Alternative predictions	
				Structure	R.I.[b]
22	1994	4	2,5-2',5'	2-2',3',5'	1998
23	2010	4		2-2',4',5'	2012
				2,4-2',5'	2010
24	2023	4	2,3-2',5'	2-2',4',6'	2021
				2,4-2',4'	2027
		(5)		2,6-2',3',6'	2017
29	2089	5	2,5-2',3',6'	2,6-2',3',5'	2092
32	2119	5	2,3-2',3',6'		
33	2136	4	2,5-3',4'		
36	2159	5		2,5-2',3',5'	2159
39	2175	5	2,5-2',4',5'	2,4-2',3',5'	2175
				3,5-2',4',6'	2173
		(6)		2,6-2',3',4',6'	(2178)
				2,3,6-2',3',6'	2172
41	2191	5	2,4-2',4',5'	2,3-2',3',5'	2189
42	2203	5	2,3-2',4',5'		
43	2207	5	2,5-2',3',4'		
44	2228	5	3,4-2',3',6'	2,4-2',3',4'	2226
45	2238	—		2,5-2',3',4'	2240
				2,6-3',4',5'	2240
				3,4-3',5'	2238
				2,3,5-2',4',6'	2240
48	2264	6	2,3,6-2',4',5'	2,4-2',3',4',6'	(2263)
50	2299	6	2,3,4-2',3',6'		
53	2321	5	3,4-2',4',5'		
55	2346	5	3,4-2',3',4'		
56	2356	6	2,4,5-2',4',5'	2,5-2',3',4',5'	(2360)
				3,5-2',3',4',5'	(2367)
59	2390	6	2,3,4-2',4',5'	2,3-2',3',4',5'	(2391)
				2,4,6-3',4',5'	2386
		(7)		2,3,5-2',3',5',6'	(2390)

[a] Cl No. between brackets: Chlorine number of minor constituent not associated with accurate R.I.
[b] R.I. between brackets: Predicted R.I. using Table VIII of Ref.18

MCNS 063343

Table II.3.3 (from ref. 18)

THE RETENTION INDICES, CHLORINE NUMBERS AND PREDICTED STRUCTURES OF THE MINOR PEAKS IN AROCLOR 1254

Peak No.	*R.I.*	*Chlorine No.*	*Structure*	*Predicted R.I.*[a]
1	1490	0	Biphenyl	1491[b]
2	1579	1	2-	1577[b]
3	1672	2	2-2'	1669[b]
4	1688	1	4-	1687[b]
5	1750	2	2-5'	1754
6	1758	—	2,4-	1756[b]
7	1763	2	2-5'	1770
8	1774	3	2-2',6'	1765
9	1782	2	2-4'	1782[b]
10	1833	3	2-2',5'	1831
11	1849	3	2-2',4'	1848
12	1865	3	2-2',3'	1864
			3-3',6'	1866
13	1870	3	4-3',6'	1878
14	1896	—	4-4'	1894[b]
15	1922	4	2-2',4',6'	1924[b]
16	1935	—	2-3',5'	1932
			2-2',3',6'	1932
			3-3',5'	1932
17	1943	—	4-3',5'	1944
18	1952	3	3-3',4'	1949
19	1963	3	3-3',3'	1963
			4-3',4'	1962[b]
20	1966	3	3-3',5'	1963
			4-3',4'	1962[b]
21	1980	3	2-3',4'	1975
22	2040	4	4-3',5',6'	2041
			2,3-3',4'	2041
26	2051	4	2-3',3',4'	2047
			2,3-3',3'	2055
27	2058	4	2,3-3',3'	2055
28	2071	4	2,6-3',4'	2071
30	2097	—	3-3',5',5'	2097
			2,4-3',4',6'	2097
			2,3-3',5'	2094
			2,6-3',5',5'	2092
31	2113	5	2,3-3',5',6'	2120
			2,3-3',4',6'	2112
34	2146	4	2-3',4',5'	2144
			3-3',3',4'	2148
35	2152	— (not 6)	3-3',3',4'	2148
			2,4-3',4'	2134
37	2164	—	2,3-3',4'	2168
			2,3,6-3',4',6'	2160
38	2169	—	2,3-3',4'	2168
			2,3,6-3',5',6'	2173
40	2186	—	2,3-3',5',5'	2183
			3,5-3',5',6'	2185
46	2246	—	3-3',4',5'	2245
			2,4-3',5',6'	(2241)
			2,5-3',4',6'	(2247)
			2,3,5-3',5',6'	2238
47	2254	—	4-3',4',5'	2257
			2,3-3',5',6'	(2256)
			3,5-3',5',5'	2259
			2,4,5-3',4',6'	2256

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Table II.3.3 (continued)

Peak No.	R.I.	Chloride No.	Structure	Predicted R.I.[a]
49	2283	—	2,3-2',3',4',6'	(2278)
			2,6-2',3',4',5'	(2283)
			3,4-3',4'	2282[b]
51	2310	5	2,5-3',4',5'	2307
			3,5-3',3',4'	2310
		(7)[c]	2,3,6-2',3',5',6'	2303
53	2335	5	2,3-3',4',5'	2338
		(7)[c]	2,3,6-2',3',4',6'	(2329)
54	2340	6	3,5-3',3',5',6'	(2335)
			2,3,5-2',4',5'	2340[b]
57	2372	—	2,4-2',3',4',5'	(2376)
			2,3,4-2',3',5'	2374
58	2376	6	2,4-2',3',4',5'	(2376)
			3,4-3',3',5',6'	(2379)
			2,3,4-2',3',5'	2374
60	2400	6	3,4-2',3',4',6'	(2401)
			3,4,5-2',3',6'	2396
61	2413	7	2,3,5-2',3',4',6'	(2412)
62	2425	6	2,3,4-2',3',4'	NMR
63	2433	7	2,3,6-2',3',4',5'	(2439)
			2,4,5-2',3',4',6'	(2428)
			2,4,6-2',3',4',5'	(2430)
64	2451	7	2,3,4-2',3',5',6'	(2450)
65	2466	7	2,3,4-2',3',4',6'	(2462)
66	2489	6	2,4,5-3',4',5'	2488[b]
67	2519	6	3,4-3',3',4',5'	NMR
68	2543	7	2,4,5-2',3',4',5'	(2541)
			3,4,5-2',3',5',6'	(2548)
69	2577	7	2,3,4-2',3',4',5'	NMR

[a] Smaller peaks eluted earlier than major parts of peaks 51 and 53, respectively.
[b] R.I. of synthesised compound.
[c] R.I. between brackets: Predicted R.I. using Table VIII.

Table II.3.4 (from ref. 18)

THE RETENTION INDICES, CHLORINE NUMBERS AND PREDICTED STRUCTURES OF AROCLOR 1242 PEAKS

Peak No.	R.I.	Chlorine No.[a]	Structure	Predicted R.I.[a]
3	1672	2	2-2'	1669[b]
6	1765	2	2-3'	1770
8	1781	2	2-4'	1782[b]
9	1833	3	2-2',5'	1831
10	1849	3	2-2',4'	1848
11	1863	3	2-2',3'	1864
			3-3',6'	1866
12	1879	3	4-3',6'	1878
13	1896	2	4-4'	1894[b]
15	1935	3	2-3',3'	1932
			3-3',5'	1932
17	1951	3	3-3',4'	1949
18	1961	3	3-3',3'	1963
			4-3',4'	1962[b]
19	1966	3	3-3',3'	1963
			4-3',4'	1962[b]
20	1980	3	2-3',4'	1975
21	1996	4	2-3',3',5'	1998
			2,5-2',5'[b]	1994[b]
22	2011	4	2-2',4',5'	2013
			2,4-2',5'	2010
24	2024	4	3-3',3',6'	2029
			3-3',4',6'	2011
31	2092	3	4-3',4'	2088
		4	2,5-3',5'	2094
		(5)	2,4-2',4',6'	2097
			2,5-2',3',6'[b]	2089
34	2138	4	2,5-3',4'[b]	2138
35	2148	4	2-3',4',5'	2144
			3-2',3',4'	2148

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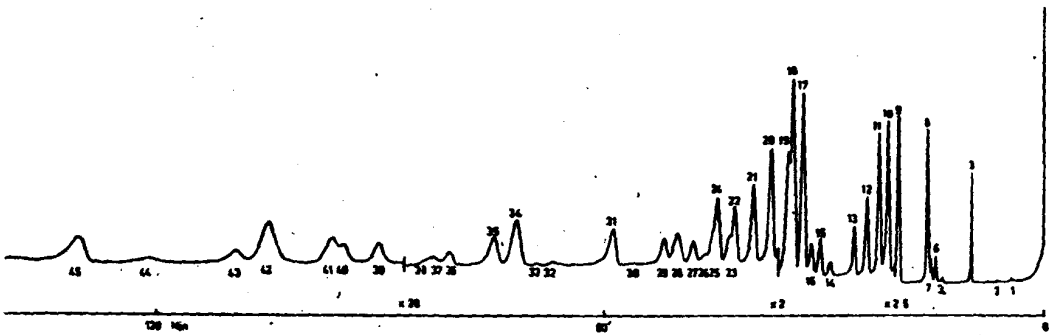
Table II.3.4 (continued): minor peaks in Aroclor 1242

Peak No.	R.I.	Chlorine No.[d]	Structure	Predicted R.I.[c]
1	1490	0	Biphenyl	1491[b]
2	1580	—	2-	1577[b]
4	1750	2	2,5-	1744
5	1758	—	2,4-	1736[b]
7	1774	3	2-2',6'	1765
14	1983	4	2-2',4',6'	1924[b]
			2,5-2',6'	1927
16	1944	3	4-3',5'	1944
23	2015	4	2-2',4',5'	2012
25	2028	4	3-2',4',6'	2029
			2,3-2',5'	2025
			2,4-2',4'	2027[b]
			2,6-3',5'	2028
26	2037	4	4-2',4',6'	2033[c]
27	2041	4	4-2',3',6'	2041
28	2058	4	2,3-2',4'	2041
			2-2',3',4'	2047
			2,3-2',3'	2055
29	2061	—		
30	2080	3	3-3',4'	2076
32	2121	4	2,3-3',5'	2125
			4-2',4',5'	2125
33	2129	4	2,3-3',5'	2125
			4-2',4',5'	2125
36	2167	4	4-2',3',4'	2160
37	2174	4	2,3-3',4'	2168
38	2178	—	2,4-2',3',5'	2173
			2,5-2',4',5'[a]	2175[b]
			2,6-2',3',4',6'	(2175)
			3,3-2',3',6'	2183
			3,5-2',4',6'	2173
39	2195	3	2,4-2',4',5'[a]	2191
40	2207	5	2,3-2',4',5'	2206[b]
			2,5-2',3',4'[a]	2210
41	2212	5	2,5-2',3',4'[a]	2210
42	2232	5	2,4-2',3',4'	2226
			3,4-2',3',6'[a]	2228
43	2242	6	2,4-2',3',5',6'	(2241)
			2,5-2',3',4',6'	(2247)
			2,3,5-2',4',6'	2240
44	2268	—	2,4-2',3',4',6'	(2263)
			2,3,6-2',4',5'[a]	2264[b]
45	2287	—	2,6-2',3',4',5'	(2283)
			3,4-3',4'	2283[b]
			2,3,4-2',4',6'	2291

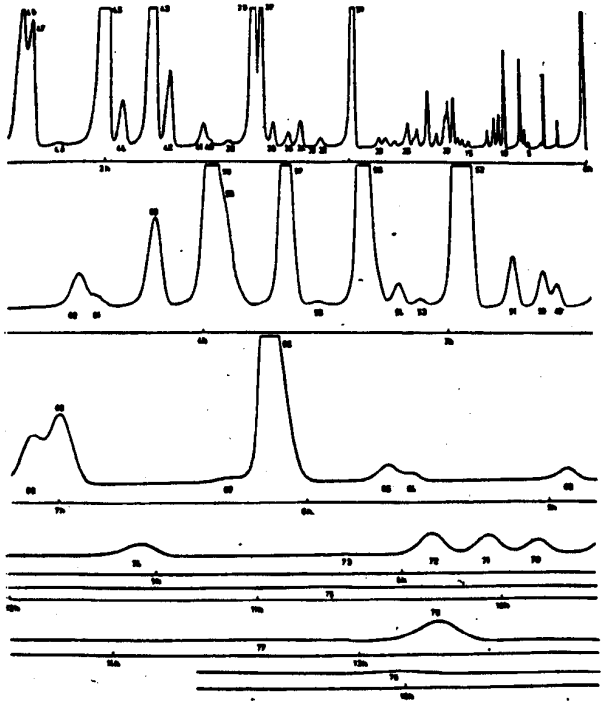
[a] Structures found in Aroclor 1254 by NMR determinations.
[b] R.I. of synthesized compound or NMR standard.
[c] R.I. between brackets: Predicted R.I. using Table VIII.
[d] Cl No. between brackets: Chlorine number of minor constituent not associated with accurate R.I.



0.2 μl of 1% Aroclor 1242 solution chromatographed on an Apiezon L SCOT column at 205°. Initial attenuation setting of 5 × 10^2 reduced as indicated; flame ionization detector.

Figure II.3.5 (from ref. 18)

MONS 063347



1 0.25 µl 10% Aroclor 1260 solution chromatographed on an Apiezon L SCOT column at 205°. Attenuation setting maintained at 1 x 10^2; flame ionization detector.

Figure II.3.6 (from ref. 18)

Table II.3.5 (from ref. 18)

THE RETENTION INDICES, CHLORINE NUMBERS AND PREDICTED STRUCTURES OF AROCLOR 1260 PEAKS

Peak No.	*R.I.*	*Chlorine No.*[a]	*Structure*	*Predicted R.I.*[b]
31	2086	5	2,3-2',3',6'[c]	2089
			2,3-2',4',6'	2081
37	2168	6	2,3,6-2',3',6'	2173
38	2174	5	2,4-2',3',5'	2175
			2,5-2',4',5'[c]	2173[c]
			3,5-2',4',6'	2175
43	2239	6	2,4-2',3',5',6'	(2241)
			2,3,5-2',4',6'	2240
45	2264	6	2,4-2',3',4',6'	(2263)
			2,3,6-2',4',5'[c]	2264[c]
47	2296	6	2,3,4-2',3',6'[c]	2299
48	2300	7	2,3,6-2',3',5',6'	(2303)
			2,4,6-2',3',5',6'	(2295)
52	2358	6	2,5-2',3',4',5'	(2360)
			3,5-2',3',4',6'	(2357)
			2,4,5-2',4',5'[c]	2356[c]
55	2390	6	2,3-2',3',4',5'	(2391)
			2,3,4-2',4',5'[c]	2392[c]
			3,4,5-2',4',6'	2388
		(7)	2,3,5-2',3',5',6'	(2390)
57	2411	7	2,3,5-2',3',4',6'	(2412)
			2,4,5-2',3',5',6'	(2406)
58	2428	6	2,3,4-2',3',4'[c]	2425[c]
59	2432	7	2,4,5-2',3',4',6'	(2428)
			2,4,5-2',3',4',6'	(2428)
			2,4,6-2',3',4',5'	(2430)
		8	2,3,5,6-2',5',3',6'	2438[c]
60	2445	7	2,3,4-2',3',5',6'	(2440)
			2,3,6-2',3',4',5'	(2430)
66	2542	7	2,4,5-2',3',4',5'	(2542)
68	2575	7	2,3,4-2',5',4',5'[c]	(2575)
			3,4,5-2',3',4',6'	(2570)
76	2724	8	2,3,4,5-2',3',4',5'	(2726)

Peaks 2--21 in Aroclor 1254 chromatogram were also present in Aroclor 1260.

22	1994	4	2-2',3',5'	1996
			2,5-2',5'[c]	1994[c]
23	2009	4	2-2',4',5'	2012
			2,4-2',5'	2010
24	2013	—	2-2',4',5'	2012
			2,4-2',5'	2010
25	2022	4	3-2',4',6'	2021
26	2024		2,3-2',5'	2025
			2,4-2',4'	2027[c]
27	2030	—	3-2',5'	2033
			3-2',3',6'	2029
			4-2',4',6'	2033[c]
			2,4-2',4'	2027[c]
			2,6-3',5'	2028
28	2040	4	4-2',3',6'	2041
			2,3-2',4'	2041
29	2050	4	2-2',3',4'	2047
			2,3-2',5'	2055
30	2058	4	2,3-2',3'	2053
32	2117	—	3-2',4',5'	2114
			2,3-2',3',6'	2114

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Table II.3.5 (continued): minor peaks in Aroclor 1260

Peak No.	R.I.	Chlorine No.[a]	Structure	Predicted R.I.[b]
33	2125	—	4-2',4',5'	2123
			2,3-3',5'	2125
34	2135	4	2,5-3',4'[a]	2138
35	2146	4	2-3',4',5'	2144
			3-2',3',4'	2148
36	2158	5	2,5-2',3',5'	2159
39	2192	—	2,3-2',3',5'	2189
			2,4-2',4',5'[a]	2191
40	2205	5	2,3-2',4',5'	2206[c]
41	2209		2,5-2',3',4'[a]	2210
42	2229	5	2,4-2',3',4'	2226
			3,4-2',3',6'[a]	2228
44	2254	6	2,3-2',3',5',6'	(2256)
			2,4,5-2',4',6'	2256
46	2283	—	2,3-2',3',4',6'	(2278)
			2,6-2',3',4',5'	(2283)
			3,4-3',4'	2282[c]
49	2321	5	2,4-3',4',5'	2323
			3,4-2',4',5'[a]	2319
50	2326	7	2,3,6-2',3',4',6'	(2329)
			2,4,6-2',3',4',6'	(2321)
51	2340	6	2,5-2',3',5',6'	(2335)
			2,3,5-2',4',5'	2340[c]
53	2372	—	2,4-2',3',4',5'	(2376)
			2,3,4-2',3',5'	2374
54	2379	—	2,4-2',3',4',5'	(2376)
			3,4-2',3',5',6'	(2379)
			2,3,4-2',3',5'	2374
55	2402	6	3,4-2',3',4',6'	(2401)
61	2460	7	2,3,4-2',3',4',6'	(2462)
62	2463	8	2,3,4,6-2',3',5',6'	(2464)
63	2486	8	2,3,6-2',3',4',5',6'	(2489)
			2,4,6-2',3',4',5',6'	(2481)
			2,3,4,6-2',3',4',6'	2490[c]
		6	2,4,5-3',4',5'	2488[c]
64	2518	6	3,4-2',3',4',5'[a]	(2516)
65	2522	7	2,3,5-2',3',4',5'	(2523)
67	2530	—	3,4,5-2',3',5',6'	(2548)
69	2578	8	2,3,5-2',3',4',5',6'	(2577)
			2,3,4,5-2',3',5',6'	(2581)
70	2587	8	2,3,4,5-2',3',5',6'	(2581)
71	2597	8	2,4,5-2',3',4',5',6'	(2593)
72	2605	8	2,3,4,5-2',3',4',6'	(2603)
73	2618	9	2,3,5,6-2',3',4',5',6'	(2624)
74	2640	8	2,3,4-2',3',4',5',6'	(2627)
[d]	—	9	2,3,4,6-2',3',4',5',6'	(2650)
75	2682	—	3,4,5-2',3',4',5'	(2682)
77	2738	—	3,4,5-2',3',4',5',6'	(2738)
78	2770	9	2,3,4,5-2',3',4',5',6'	(2768)
[d]	—	10	2,3,4,5,6-2',3',4',5',6'	2810[c]

[a] Structures found in Aroclor 1254 by NMR determinations.
[b] R.I. between brackets: Predicted R.I.'s using Table VIII.
[c] Cl No. between brackets: Chlorine number of minor constituent not associated with accurate R.I.
[d] Peaks observed on mass spectrometer oscilloscope, but not on GLC.
[e] R.I. of synthesised compound.

MONS 063350

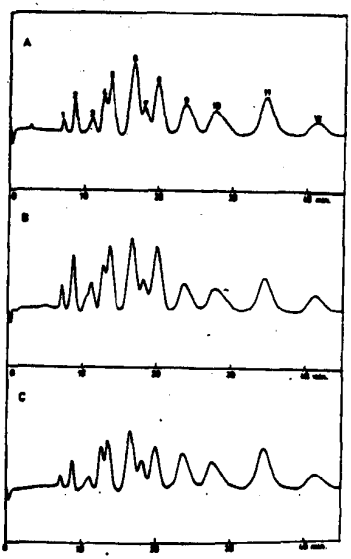
Table II.3.6 (from ref. 27)

TABLE 3. Structural identity of the major PCBs in the gas chromatographic peaks of Aroclors 1254 and 1260

Aroclor 1254 peak No.	Aroclor 1260 peak No.	Predicted chlorine substitutions		Retention time (min)			
				Column 1		Column 2	
		From peak matching	From Table 2	From Fig. 1B,D	Predicted from Table 2	From Fig. 1A,C	Predicted from Table 2
1		[a]2,5,2',5'		3.35	[e]3.35	2.38	[e]2.38
2		[a]2,5,2',3'		3.78	3.79	2.90	2.90
3			[b]2,4,2',3'	4.10	3.88	3.13	2.94
4	1	[a]2,5,2',3',6'	[c,d][2,5,3',4']	5.01	4.91 (4.97)	3.91	3.84 (3.87)
5	2	[a]2,5,2',4',5'		5.90	5.89	4.43	4.42
6		[a]2,4,2',4',5'		—	6.03	4.80	4.48
7a		[a]2,3,2',4',5'		—	6.68	5.40	5.38
7b			[c,d][2,5,2',3',4'	6.90	6.91	5.70	5.75
8		[a]3,4,2',3',6'		7.35	7.28	6.17	6.25
	3	[a]2,3,6,2',3',6'	[b]3,4,3',4')	7.35	[e]7.20 [e](7.35)	6.38	[e]6.20 [e](6.30)
	4		[b]2,4,2',3',4',6'	8.23	8.17		6.31
9a	5	[c,d][2,4,5,2',3',6'		8.79	8.64	7.15	7.13
9b		[a]3,4,2',4',5'			8.73		7.19
10	6	[c,d][2,4,5,2',4',5'					
11		[a]2,3,4,2',3',6'	[c,d][3,4,2',3',4')	10.37	10.14 (10.24)	9.30	9.28 (9.36)
	7		[b]2,5,2',3',4',5'	11.27	11.21	9.35	9.33
12	8	[a]2,4,5,2',3',4'		12.26	[e]12.16	10.68	[e]10.68
	9		[b]2,4,5,2',3',4',6'	14.12	14.07	11.58	11.56
15			[c,d][2,3,4,2',3',4'	14.30	[e]14.27	13.93	[e]13.90
	10	[a]2,3,6,2',3',4',5'		16.28	16.43	14.58	15.06
16				17.15	—	15.93	—
17	11	[a]2,4,5,2',3',4',5'		[f]19.73	—	[f]17.22	—
18	12	[a]2,3,4,2',3',4',5'		23.31	23.13	22:94	22.55

[a]Matched to a peak in Webb and McCall (1972).
[b]Matched to a peak in Tas and Kleipool (1971) or Tas and de Vos (1972).
[c]Indicated to be present by Sissons and Welti (1971).
[d]Substitution giving the closest predicted retention time.
[e]Retention time of standard compound.
[f]Retention time used to calculate $\delta_{x,y,z}$.
Note: Peak numbering and chromatographic conditions are given under Fig. 1 and in the Materials and Methods section.

MONS 063351



Gas chromatograms of *A*: Phenochlor DP 6 (Prodelec, Fr), *B*: Clophen (Bayer, Ger.), *C*: Aroclor 1260 (Monsanto, U.S.)

Column: glass, 1.9 meters × 3 mm i.d. packed with 3% OV-1 on gas-chrom Q, 80–100 mesh, temp. 180 °C, flow 60 ml N_2/min. Detection: electron capture

Figure II.4.1 (from ref. 22)

Clophen A60 and Clophen A50: these are listed in Table II.4.1 and show good agreement with those for Aroclors 1260 and 1254 respectively (Tables II.3.3, II.3.5).

Six major constituents of Phenochlor DP6 have also been identified (22, 24) as shown in Table II.4.2. These identifications agree with those of the corresponding constituents in Clophen A60 (compounds 11, 19, 29, 32, 38, 49 and 50 in ref. 23). No details appear to have been published of the constitution of the Phenochlor with 42% chlorine which is being imported into the United States (7, p. 210).

Table II.4.3 lists the reported constitution of three commercial Kanechlor mixtures (from refs. 25, 26). Gas-liquid chromatography suggests that the constitution of KC-400 was very similar to that of Aroclor 1248 (Figure II.4.3)*, but the reported correspondence of Kanechlors KC-300 and KC-500 to Aroclors 1242 and 1254 appears to have been less close.

Fenclor DK, now being imported into the United States from Italy at a rate of about 180,000 kg/year (7, p.210), consists of decachlorobiphenyl (ibid.).

II.5 Occurrence of certain substitution patterns in PCB mixtures

The data summarized in Tables II.3.2, II.3.3, II.3.4, II.4.1 and II.4.2 indicate that certain patterns of chlorine substitution are much more frequent than others in commercial mixtures. Figure II.5.1 illustrates the most common substitution patterns on each of the phenyl rings in the biphenyl molecule. By contrast, chlorobiphenyls with substitutions in the 3-; 3,5-; 3,4,5-; and, especially, the 2,4,6- positions are more unusual (18, 23).

Certain substitution patterns are believed to influence the biological activity of chlorobiphenyls (see Section IV below) and it is useful to review the frequency of these substitution patterns in the commercial Aroclor mixtures.

* See Table II.4.4 for 5 isomers identified in KC-400 (ref. 395).

Table II.4.1 (from ref. 23)

Relative retention times on two GLC columns and amounts of polychlorinated biphenyls in Clophen A 50, A 60 and in human adipose tissue.

Compound No.	Structure[a]	No. of ortho-chlorines	Relative retention time		Percentage in Clophen		Human tissue
			Apiezon L	SF 96	A 50	A 60	
1	2,5-2',5'	2	0.25	0.30	5.0		
2	2,4-2',5'	2	0.26	0.30	1.4		
3	2,3-2',5'	2	0.27	0.33	1.9		1.1
4	(2,-2',3',4')	2	0.30	0.43	1.2		0.66
5	(4-2',3',6')	2	0.32	0.43	2.1		0.56
6	2,5-2',3',6'	3	0.35	0.43	4.4[b]	2.9	1.2
7	2,3-2',3',6'	3	0.38	0.49	2.5[b]	0.28	0.48
8	3,4-2',5'	1	0.41	0.42	3.9		1.5
9		1 or 2	0.42		2.2[c]		2.0[c]
10	2,5-2',3',5'	2	0.45	0.49	2.2	1.1	1.2
11	2,3,6-2',3',6'	4	0.47	0.61	0.50	1.0[d]	
12	2,5-2',4',5'	2	0.48	0.50	7.0[b]	5.6	4.2
13	2,4-2',4',5'	2	0.51	0.51	1.8[b]		1.9
14	2,3-2',4',5'	2	0.53	0.57	1.4[b]		
15	2,5-2',3',4'	2	0.53	0.58	5.4	1.4	2.3
16	2,3-2',3',4'	2	0.55	0.66	1.0		
17	3,4-2',3',6'	2	0.56	0.62	7.6[b]	2.9	4.7
18	2,3,5-2',3',6'	3	0.60	0.70	1.2	4.2	1.0
19	2,4,5-2',3',6'	3	0.64	0.71	2.0[b]	6.5[d]	0.13
20	2,5-2',3',5',6'	3	0.65	0.68	1.3	3.3	0.43
21	2,3-2',3',5',6'	3	0.70	0.74	0.5		0.05
22	2,3,4-2',3',6'	3	0.72	0.83	1.8	3.2	0.15
23		1 or 2	0.76		0.6[c]		
24	2,3,6-2',5',5',6'	4	0.77	0.91	0.09	0.96	
25	3,4-2',4',5'	1	0.79	0.74	5.0[b]	1.6	5.4
26	2,3,6-2',3',4',6'	4	0.84	0.95	0.05	0.37	
27	2,3,5-2',4',5'	2	0.85	0.86	0.90	2.9	2.7
28	3,4-2',3',4'	1	0.87	0.86	3.6		1.9
29	2,4,5-2',4',5'	2	0.90	0.86	4.2[b]	12.9[d]	21.5
30	2,3,4-2',3',5'	2	0.94	0.97	1.1	1.5	
31		1 or 2	0.96	0.93			
32	2,3,4-2',4',5'	2	1.00	1.00	5.1	11.3[d]	14.0
33	2,3,5-2',3',5',6'	3	1.01	1.06	0.04	0.49	0.90
34		4	1.02		0.05[c]		
35		1 or 2	1.04	1.10	1.1[c]	2.0[c]	1.5[c]
36	2,4,5-2',3',5',6'	3	1.08	1.13	0.39	3.3	3.5
37	2,3,4-2',3',4'	2	1.11	1.16	1.3	2.0	0.81
38	2,3,6-2',3',4',5'	3	1.13	1.29	0.33	3.7[d]	
39	2,4,5-2',3',4',6'	3	1.14	1.16	0.17	1.8	2.5
40	2,3,4-2',3',5',6'	3	1.15	1.32	0.27	2.1	1.3
41	2,3,5,6-2',3',5',6'	4	1.23	1.34	0.005	0.07	
42	2,3,4-2',5',4',6'	3	1.28	1.40	0.13	1.3	0.57
43	2,3,4,6-2',3',5',6'	4	1.34	1.44	0.007	0.08	
44	2,4,5-3',4',5'	1	1.41	1.19	0.47	1.0	0.49
45	2,3,6-2',3',4',5',6'	4	1.45	1.59	0.008	0.09	
46	2,3,4,6-2',3',4',6'	4	1.46	1.51		0.03	
47	3,4-2',3',4',5'	1	1.55	1.37	0.81	1.5	2.0
48	2,3,5-2',3',4',5'	2	1.59	1.49	0.23	0.90	1.2

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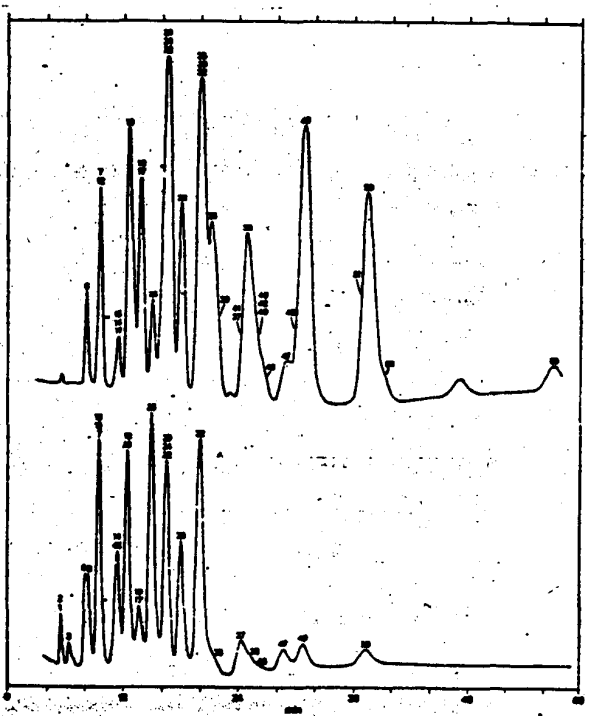
Table II.4.1 (continued)

Compound No.	Structure[a]	No. of ortho-chlorines	Relative retention time Aroclor L	Relative retention time SF 96	Percentage in Clophen A 50	Clophen A 60	Human tissue
49	2,4,5-2',3',4',5'	2	1.71	1.56	0.98	7.6[d]	7.7
50	2,3,4-2',3',4',5'	2	1.88	1.82	0.72	4.1[d]	3.9
51	2,3,4,5-2',3',5',6'	3	1.94	1.99	0.08	0.76	0.77
52		1 or 2	2.02	1.96	0.23[e]	1.0[e]	[e]
53	2,3,4,5-2',3',4',6'	3	2.07	2.05	0.06	0.44	0.94
54	2,4,5-2',3',4',5',6'	3	2.15	2.04	0.01	0.28	0.46
55	(2,3,5,6-2',3',4',5',6')	4	2.23				[e]
56	2,3,4-2',3',4',5',6'	3	2.40	2.20	0.01	0.17	0.31
57	2,3,4,6-2',3',4',5',6'	4	2.45	2.56		[e]	[e]
58	3,4,5-2',3',4',5'	1	2.74	2.41	[e]	[e]	
59	2,3,4,5-2',3',4',5'	2	3.18	2.81	0.35	0.67	1.7
60	2,3,4,5,6-2',3',4',5',6'	4	4.12				0.62
					86.7	99.4	100.0 percent
	p,p'-DDE		0.52	0.58			
	p,p'-DDD		0.71	0.73			
	p,p'-DDT		0.90	0.97			

[a] Tentative structures are given in brackets.
[b] Component found present in Aroclor 1254 by Webb and McCall (20)
[c] Figures calculated using responses of chlorobiphenyls with similar retention times in the same fraction from the charcoal column.
[d] Component found present in Phenoiclor DP 6 by Tas *et al* (22, 24)
[e] Present in trace amounts only.



Chromatograms of Clophen A 60 (upper trace) and Clophen A 50 (lower trace) on mixed OF 1/SF 96 1.5 m column (2/3 OF 1, 10 percent and 1/3 SF 96, 6 percent) at 200°C.

Only a limited number of figures are shown due to lack of space

Figure II.4.2 Gas-liquid chromatograms of Clophen A60 and Clophen A50, showing numbering of components listed in Table II.4.1.

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Table II.4.2 Six constituents identified in Phenochlor DP6 (22, 24)

Peak no. in Figure II.4.1	Identification
3	2,3,6,2',3',6'- hexachlorobiphenyl
5	2,3,6,2',4',5'-hexachlorobiphenyl
6	2,4,5,2',4',5'- hexachlorobiphenyl
8	2,3,4,2',4',5'- hexachlorobiphenyl
10	2,3,4,5,2',3',6'- heptachlorobiphenyl
11	2,3,4,5,2',4',5'- heptachlorobiphenyl
12	2,3,4,5,2',3',4'- heptachlorobiphenyl

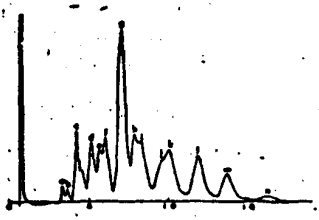

Fig. 1. Kanechlor 400

Table II.4.3 Reported constitution of Kanechlor mixtures

	Kanechlor				
	KC-200	KC-300	KC-400	KC-500	KC-600
Corresponding Aroclor (from ref. 25)	1232	1242	1248	1254	1260
Constitution (from ref. 26)					
2-Cl		17%	3%	-	
3-Cl		60%	33%	5%	
4-Cl		23%	44%	27%	
5-Cl		0.6%	16%	55%	
6-Cl		-	5%	13%	

Table II.4.4. Five constituents identified in Kanechlor KC-400 (ref. 395)

Constituent	Peak no.
2,4,3',4'- tetrachlorobiphenyl	g1
2,5,3',4'- tetrachlorobiphenyl	g2
2,3,4,4' - tetrachlorobiphenyl	h
3,4,3',4'- tetrachlorobiphenyl	k
2,3,4,3',4'- pentachlorobiphenyl	m

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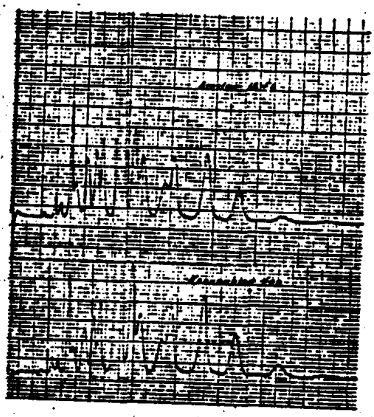
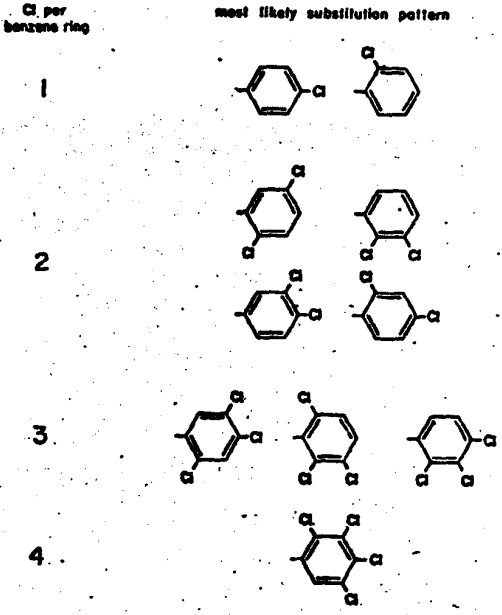


Comparison of gas chromatograms of Kanechlor 600 (Japan) and Aroclor 1248 (USA).

Figure II.4.3 (from ref. 21)

Figure II.5.1
Moieties from Which Principal
Chlorobiphenyl Isomers are Formed



The most common substitution patterns for the chlorobiphenyls found in PCB preparations. Only one phenyl-ring is shown. The most abundant tetrachlorobiphenyls, for example, are those from the dichlorophenyl-moieties shown. One di- and one trichlorophenyl- would give most abundant penta-chlorobiphenyls, etc.

II.5.1 Adjacent unsubstituted positions

The presence of two adjacent carbon atoms without chlorine substitution in one or both rings is believed to facilitate metabolism, because it permits the formation of arene oxide intermediates (28). Essentially all chlorobiphenyls with 5 or fewer chlorine atoms have at least one pair of adjacent unsubstituted carbon atoms, because of the rarity of 3,5- substitution in the natural mixtures (see above). Hence virtually 100 percent of the constituents of Aroclors 1016, 1242 and 1248 fall into this category (Table II.3.1 above). From the data in Table II.4.1 it can be determined that about 92% of the constituents of Clophen A50 and about 66% of the constituents of Clophan A60 have at least one pair of adjacent unsubstituted carbon atoms. The corresponding Aroclors (1254 and 1260) would presumably share these properties.

II.5.2 Number of ortho-chlorines

Jensen and Sundström (23) presented evidence that chlorobiphenyls with three or four chlorine atoms in the ortho-positions (2- and 6- positions) are more easily metabolized than those with only one or two ortho-chlorines. Table II.5.1 shows that compounds with three or four chlorines in the ortho-position are virtually absent from Aroclor 1242 (and from Aroclor 1016), but are fairly well represented in Clophens A50 and A60 (which correspond to Aroclors 1254 and 1260).

II.5.3 4,4'-substitution

McKinney (29) has suggested that chlorobiphenyl isomers with chlorine substitution in both the 4- and 4'- positions tend to be biologically active and well retained in tissues. Table II.5.2 shows that the number and proportion of these isomers increases with increasing chlorination of the mixture.

Table II.5.1 Frequency of compounds with various numbers of ortho-chlorine substitutions and with 4-4' substitution in selected PCB mixtures.

	Aroclor 1242 (from Table II.3.4)		Clophen A50 (from ref. 23)		Clophen A60 (from ref. 23)	
	percent of total	no. of compounds	percent of total	no. of compounds	percent of total	no. of compounds
4- ortho-chlorines	0	0	0.7	8	2.6	9
3 ortho-chlorines	< 1	4	15.2	17	34.7	16
2 or 1 ortho-chlorines	99	45	69.8	32	62.0	20
4-4' substitution	10-15	8	25.0	18	47.7	18
3-4 substitution						
on one ring	ca.20	17	35.4	21	38.2	19
on both rings	< 1	1	23.0	17	49.6	18

Note: information for Aroclor 1242 is less complete and precise because the compounds in this mixture were not all identified unequivocally (18).

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II.5.4. 3,4 - substitution

McKinney et al. (30) have also shown an association between biological activity and substitutions in the 3,4-, 4,5-, or 3,4,5- substitutions on one or both rings. 3,4- and 4,5- substitutions are frequently found in PCB mixtures, but 3,4,5- is usually found only as part of a 3,4,5,6- substitution pattern (Figure II.3.1). Table II.5.1 shows that chlorobiphenyl isomers with 3,4- or 4,5- substitutions are frequent in PCB mixtures and constitute more than half of the components in the more chlorinated mixtures. However, 3,4,5,3',4',5'- hexachlorobiphenyl, an exceptionally toxic isomer (30), has not been detected in commercial mixtures. The nearest equivalent, 3,4,5,2',3',4',5'- heptachlorobiphenyl, is present only in trace quantities (Tables II.3.5, II.4.1), and 2,3,4,5,2',3',4',5'- octachlorobiphenyl is only a minor constituent (ibid.). 3,4,3',4'- tetrachlorobiphenyl, which has an analogous structure, is probably a minor constituent of Aroclor 1242, but may be absent from Aroclor 1016 (Table II.3.4., Figure II.3.3)*.

II.5.5 Toxic contaminants in commercial PCB mixtures

Vos et al. (31) isolated a highly toxic fraction from samples of Clophen A60 and Phenoclor DP-6 and tentatively identified in it small quantities of polychlorinated dibenzofurans (PCDFs). This identification has been confirmed by Bowes et al. (32), who found several chlorodibenzofurans (CDFs) with 4-6 chlorine atoms per molecule in the same mixtures. The total quantity of PCDFs in Clophen A-60 and Phenoclor DP-6 was estimated to be 8.4 and 13.6 ppm respectively (Table II.6.1). PCDFs were also detected in American-manufactured Aroclors 1248, 1254 and 1260, at total concentrations varying from 0.8 ppm (Aroclor 1260) to 2.0 ppm (Aroclor 1248) (Table II.5.2). PCDFs were not detected in a single sample of Aroclor 1016 (32).

* This isomer is a major constituent of KC-400 (Table II.4.4).

Table II.3.2 (from ref. 32)

Chlorinated dibenzofuran concentrations[a] in Aroclor, Clophen and Phenoclor

PCB	4-Cl	5-Cl	6-Cl	Total
Aroclor 1248 (1969)	0.5 (25)	1.2 (60)	0.3 (15)	2.0
Aroclor 1254 (1969)	0.1 (6)	0.2 (12)	1.4 (82)	1.7
Aroclor 1254 (1970)	0.2 (13)	0.4 (27)	0.9 (60)	1.5
Aroclor 1260 (1969)	0.1 (10)	0.4 (40)	0.5 (50)	1.0
Aroclor 1260 (lot. AK3)	0.2 (25)	0.3 (38)	0.3 (38)	0.8
Aroclor 1016 (1972)	ND	ND	ND	—
Clophen A-60	1.4 (17)	5.0 (59)	2.2 (26)	8.4
Phenoclor DP-6	0.7 (5)	10.0 (74)	2.9 (21)	13.6

[a]Expressed as $\mu g\ g^{-1}$ PCB. Values in parentheses represent quantity as percentage total dibenzofuran.
ND, not detected ($<0.001\ \mu g\ g^{-1}$).

Amounts of PCB ranging from 1.0 to 2.0 g were dissolved in 400 ml hexane, placed on a Florisil column (180 g, internal diameter 31.5 mm), and eluted with: an additional 1,600 ml hexane, and successive 800 ml volumes each of 5% diethyl-ether–hexane, 25% diethyl-ether–hexane and acetone, at a rate of approximately 7 ml min^{-1}. The major portion of the PCB was eluted in the hexane fraction, which was discarded. On addition of the 5% mixture, the eluates were collected in six successive 400 ml volumes. To eliminate the polar solvents, each eluate was evaporated twice just to dryness and taken up each time in a minimal amount of hexane. Each fraction, in 1 ml hexane, was placed on a microalumina column[34] and eluted with 10 ml each of 1% and 20% methylene chloride in hexane. These were also taken twice just to dryness and made to up a volume of 1 ml in hexane to eliminate the methylene chloride before gas chromatographic analysis. Aliquots of all fractions obtained before and after partitioning on alumina were injected into a six foot glass column containing 3% OV1 on 100–120 mesh Supelcoport in Tracor MT220 and Hewlett–Packard 3700 gas chromatographs equipped with ^{63}Ni electron-capture detectors. PCBs were found to be present in each fraction eluted from the Florisil column in amounts sufficient to interfere with the detection of trace contaminants. Partitioning on the alumina columns separated most of the PCB interference into the 1% methylene chloride fractions. On removal of this interference, different peak patterns appeared in the chromatograms of the 20% methylene chloride fractions. Compounds eluting in the 20% methylene chloride fraction were collected for mass spectrometric analysis using a 20:1 effluent splitter, and a trap consisting of a capillary tube (1 mm internal diameter, 100 mm long) bent to a U shape, immersed in a liquid nitrogen bath. Methylene chloride (20%; 4 μl) in hexane was injected into the capillary as a rinse, removed with a 1.0 μl micropipette, and placed directly on the mass spectrometer probe. The probe was inserted into a GEC AEI MS902 high resolution mass spectrometer and the solvent removed by the force pump. The probe was rapidly inserted into the ion source and multiple scans were recorded in the on-line high resolution mode[35].

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PCDFs have also been detected in several Japanese-made PCBs at concentrations of 1-33 ppm (33-35), with the highest concentration in a sample of KC-400 (35) (Table II.5.3).

The CDFs present in commercial PCB mixtures range from dichloro- to heptachlorodibenzofurans (33, 34), but most of those detected have been tetrachloro-, pentachloro- and hexachloro-dibenzofurans (32-34). At least 11 CDFs were detected in the European and American products (32) and at least 15 in KC-400 (35). The only isomers that have been precisely identified to date are 2,3,7,8- tetrachlorodibenzofuran and 2,3,4,7,8- pentachlorodibenzofuran (36). (There are 119 structurally different CDF isomers.)

Polychlorinated napthalenes (PCNs) have also been identified in small quantities in Clophen A60, Phenoclor DP-6, Aroclor 1254 and KC-400 (31-33).

Despite occasional statements that commercial PCBs may contain polychlorinated dibenzo-p-dioxins (PCDDs), there appear to be no authenticated reports of their presence (32). The structure of PCDFs and PCDDs is shown in Figure II.5.2.

II.6 Physical properties of chlorobiphenyls and PCB mixtures.

II.6.1 General properties

The general physical properties of some representative chlorobiphenyls are summarised in Table II.6.1; those of the Aroclor mixtures, including Aroclor 1016 and Aroclor 1270 (decachlorobiphenyl), are summarised in Table II.6.2. Although most chlorobiphenyls are solids at room temperature, lower chlorinated mixtures (e.g., Aroclors 1221, 1232, 1242, and 1248) are mobile oils and increasing chlorine content results in mixtures taking on the consistency of viscous liquids (Aroclor 1254) or sticky resins (Aroclor 1260

Table II.5.3 (from ref. 34)

Concentration of chlorinated dibenzofurans in Kanechlors and "Yusho oil".

Samples		Chlorodibenzofurans						Concentration (ppm)	
		Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	a	b
Kanechlors	300			+	+			1	1.5
	400	+++	++++	++++	+++			18	17
	500				+	+++	+	4	2.5
	600			+	+	++	++	5	3
"Yusho oil"	A		+	++	+++	+		5	4.5
	B		+	++	++	+		4	5
	C		+	++	+++	+		5	5

a: Calculated from peak heights, b: Calculated by perchlorination method.

Figure II.5.2.

Skeletal structures of: *a*, chlorinated biphenyl, $x+y = 1$–10; *b*, chlorinated dibenzofurans, $x+y = 1$–8; *c*, chlorinated dibenzodioxins, $x+y = 1$–8.

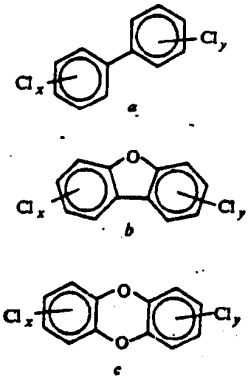


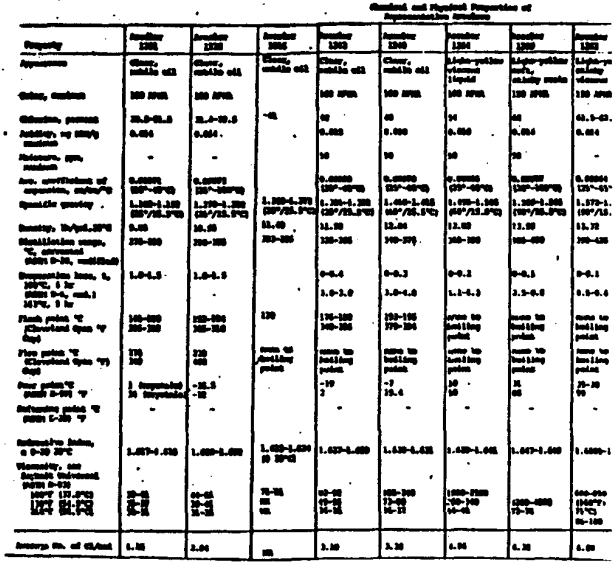
Table II.6.1 (from ref. 21)

PHYSICAL PROPERTIES OF CHLOROBIPHENYLS (Hubbard, 1964; Cook, 1972)

Compound	Melting point, °C	Boiling point, °C (mm Hg)
*2-chloro-	34	267–268; 154(12)
3-chloro-	89	284–285
*4-chloro-	76	125(14)
*2,2'-dichloro-	61	
3,3'-dichloro-	29	322–324; 320–326
*4,4'-dichloro-	148	315–319
3,5-dichloro-	36	166(10)
2,5-dichloro-		171(15); 192(30)
3,4-dichloro-	49	195–200(15)
2,3-dichloro-		172(30)
*2,4'-dichloro-	44	
3,4,3',4'-tetrachloro-	172	220(50)
3,4,2',5'-tetrachloro-	103	
2,6,2',6'-tetrachloro-	198	
*2,5,3',5'-tetrachloro-	162	
2,4,2',4'-tetrachloro-	83	
*2,5,2',5'-tetrachloro-	85	
2,4,5,3',4'-pentachloro-	179	195–220(10)
2,3,4,5,2',4',5'-heptachloro-		240–280(20)

* Present in commercial mixtures.

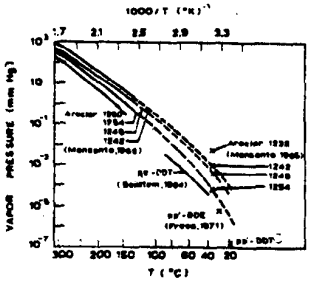
Table II.6.2 (from ref. 7)



and 1262). This results from the mutual depression of melting points of the components. Resinous Aroclors retain their strictly resinous state permanently; they do not "dry" even when exposed to air in thin films. With the exception of Aroclor 1221 and 1268, PCBs and Aroclors do not crystallize upon heating or cooling but at a specific temperature, defined as a "pour point", change into a resinous state.

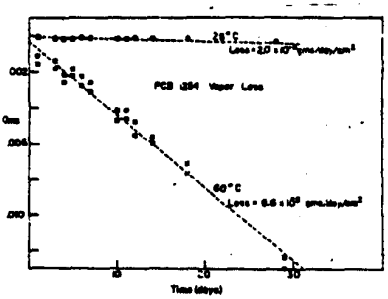
II.6.2 Vapor pressure and volatilization

Figure II.6.1 summarizes the vapor pressures of four Aroclor mixtures as functions of temperature (2). Figure II.6.2 displays the results of measurements of the vapor loss of Aroclor 1254 from its own surface at two temperatures (37). Table II.6.3 compares the vaporization rates of a range of Aroclor mixtures from their own surfaces at the same temperature (4). Both vapor pressure and vaporization rate are much higher in the less chlorinated mixtures; this indicates that the lower chlorinated chlorobiphenyls are much more volatile than the higher chlorobiphenyls. A consequence of this difference in volatility is that the mixtures are differentiated on vaporization. Figure II.6.3. shows chromatograms of Aroclor 1016 and of vapors volatilizing from it (13): the components with shortest retention times (dichlorobiphenyls -- see Figure II.3.3) are much more prominent in the vapor than in the standard, whereas the trichlorobiphenyls are much less volatile and the tetrachlorobiphenyls are hardly represented at all in the vapors. Similar differentiation of the chlorobiphenyls with 4-7 chlorine atoms is illustrated in Figure II.6.4, which shows measurements of vapor loss of components of Aroclor 1254 from dry sand and cycled sand (alternately moistened with water and dried) (37).



Vapor pressures of selected Aroclors, p,p'-DDT, and p,p'-DDE.

Figure II.6.1 (from ref. 2)



Loss of Aroclor 1254 from itself as a function of time

Figure II.6.2 (from ref. 37)

Table II.6.3 (from ref. 4)

VAPORIZATION RATES OF AROCLORS

Aroclor (surface area: 12.28 cm^2)	Wt. loss (g)	Exposure at 100°C (hr)	Vaporisation rate ($g/cm^2/hr$)
1221	0.5125	24	0.00174
1232	0.2572	24	0.000874
1242	0.0995	24	0.000338
1248	0.0448	24	0.000152
1254	0.0156	24	0.000053
1262	0.0039	24	0.000013
1260	0.0026	24	0.000009
4465	0.0064	72	0.000007
5442	0.0039	72	0.000004
5460	0.0032	72	0.000004

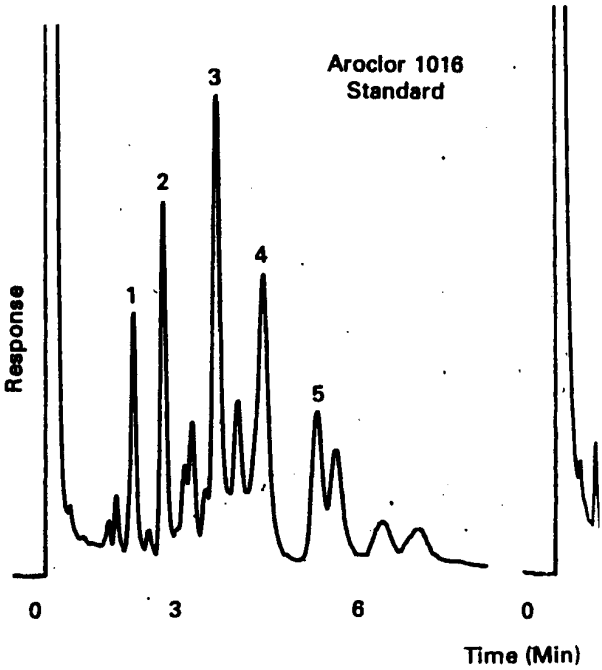
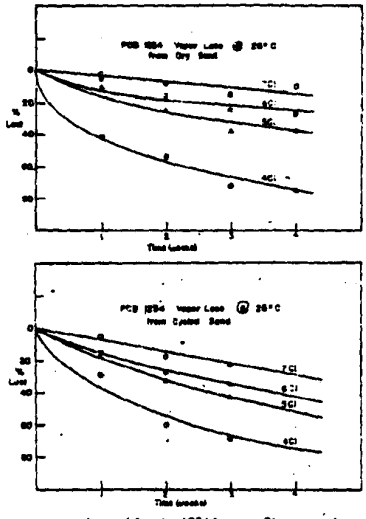


Figure II.6.3. Gas-liquid chromatograms illustrating components of Aroclor 1016 (13).



Loss of Aroclor 1254 from an Ottawa sand

Figure II.6.4 (from ref. 37)

II.6.2.1 Factors affecting the rate of volatilization

Figure II.6.4 shows that the rate of evaporation of the higher chlorobiphenyls (7, 6 and 5 chlorine atoms) from sand was markedly increased by cycling with water, but that the volatilization of tetrachlorobiphenyls was not affected much. In other words, the periodic evaporation of water from the sand enhanced the total volatilisation of PCBs, but reduced the degree of differentiation of the chlorobiphenyls. When heated at 100°C in water solution (conditions of co-distillation), however, the total volatilization of PCBs was reduced, and the degree of differentiation was increased (Table II.6.4) (4, 38). It is known from studies of pesticides that soil moisture and evaporation of water have a strong influence on the rate of volatilization of chlorinated hydrocarbons from soils and sand.

MacKay and Wolkoff (39) calculated theoretical evaporation rates for various Aroclors from water, assuming that they are in true solution, that the solution is well mixed, and that the vapor formed is in equilibrium with the liquid at the interface. Because of the very high activity coefficients of chlorobiphenyls in water, this analysis predicted very rapid volatilization rates (Table II.6.5). In fact, under laboratory conditions, PCBs appear to volatilize fairly rapidly from water in aquaria (40) and even from flasks plugged with glass wool (41). In the latter experiment, the time required for half of a 25 µg/l solution of Aroclor 1260 to disappear was of the order of 6-12 weeks; only a small fraction was recovered from the glass wool. However, in the same conditions volatilization was markedly reduced in the presence of sediments (42), and there was then little or no volatilization between 6 and 12 weeks. Hence, in natural waters, it seems likely that adsorption to sediments (see below) would limit the rate of vapor loss to the atmosphere.

Table II.6.4 (from ref. 32)

PERCENT LOSS IN AREA OF SEVEN CHROMATOGRAM PEAKS OF AROCLOR AFTER HEATING

Aroclor 1254 peak	% Peak Remaining After Heating with water 25 min	with water 60 min	without water 10 min
1	34	17	13
2	59	26	15
3	78	27	20
4	60	46	20
5	86	49	27
6	100	85	28
7	100	67	16

Table II.6.5 (from ref. 39)

Solubility, Vapor Presure and Halflife for Vaporization from Water of Selected Aroclors at 25°C

PCB Type	Solubility (mg/l)	Vapor Pressure (mm Hg)	Theoretical halflife for vaporization from 1 m. water column
Aroclor 1242	0.24	4.06×10^{-4}	5.96 hr.
Aroclor 1248	5.4×10^{-2}	4.94×10^{-4}	58.3 min.
Aroclor 1254	1.2×10^{-2}	7.71×10^{-5}	1.2 min.
Aroclor 1260	2.7×10^{-3}	4.05×10^{-5}	28.8 min.

II.6.3 Solubility in water

Table II.6.6 summarizes two sets of measurements of the solubility of individual chlorobiphenyls in water (43, 44). For the four chlorobiphenyls studied in both experiments, the results of Haque and Schmedding (44) indicate much lower solubilities than those of ref. 43. Metcalf et al. (45) give still lower values for the water solubilities of two of the same chlorobiphenyl isomers (0.016 ppm for 2,5,2'- trichlorobiphenyl and 0.016 ppm 2,5,2',5'- tetrachlorobiphenyl). Haque and Schmedding (44) attributed the discrepancy to the long period required to achieve equilibrium between the chlorobiphenyls and water: they allowed more than one month to achieve equilibrium, whereas Wollnöfer et al. (43) allowed only two hours. However, Schoor (46), in a very detailed study, has given evidence that "solutions" of chlorobiphenyls in water are in fact stable emulsions of chlorobiphenyl aggregates. A "conservatively high" estimate based on ultracentrifugation experiments indicated that the average solubility of the constituents of Aroclor 1254 is less than 0.1 µg/l (0.1 parts per billion) in fresh water and less than 0.04 µg/l in salt water (46).

Although the physical nature of the "solutions" of chlorobiphenyls and their absolute solubilities in water are thus in serious question, there is no doubt that the equilibrium concentrations of the "solutions" are much higher for the lower chlorinated biphenyls (Table II.6.6). This is reflected in the reported "solubilities" of the commercial mixtures: over 200 ppb for Aroclor 1221, 225-250 ppb for Aroclor 1016, 200 ppb for Aroclor 1242, 48-100 ppb for Aroclor 1248, 40 ppb for Aroclor 1254, and 25 ppb for Aroclor 1260 (2, 4, 13, 47). It is also reflected in differential uptake of the various components of the mixtures into "solution". Figure II.6.5, for

Table II.6.6. Solubility in water of various chlorobiphenyl isomers as reported by two groups of authors (43, 44)

Compound	Solubility (ppm) (Wallpöfer et al., 1973)	(Haque and Schmedding, 1975)
Monochlorobiphenyls		
2-	5.9	
3-	3.5	
4-	1.19	
Dichlorobiphenyls		
2,4-	1.40	
2,2'-	1.50	
2,4'-	1.88	0.637 ± 0.004
4,4'-	0.08	
Trichlorobiphenyls		
2,4,4'-	0.085	
2',3,4-	0.078	
2,2',5-	—	0.248 ± 0.004
Tetrachlorobiphenyls		
2,2',5,5'-	0.046	0.0265 ± 0.008
2,2',3,3'-	0.034	
2,2',3,5'-	0.170	
2,2',4,4'-	0.068	
2,3',4,4'-	0.058	
2,3',4',5-	0.041	
3,3',4,4'-	0.175	
Pentachlorobiphenyls		
2,2',3,4,5'-	0.022	
2,2',4,5,5'-	0.031	
Hexachlorobiphenyl		
2,2',4,4',5,5'-	0.0088	0.000953 ± 0.00001
Octachlorobiphenyl		
2,2',3,3',4,4',5,5'-	0.0070	
Decachlorobiphenyl	0.015	

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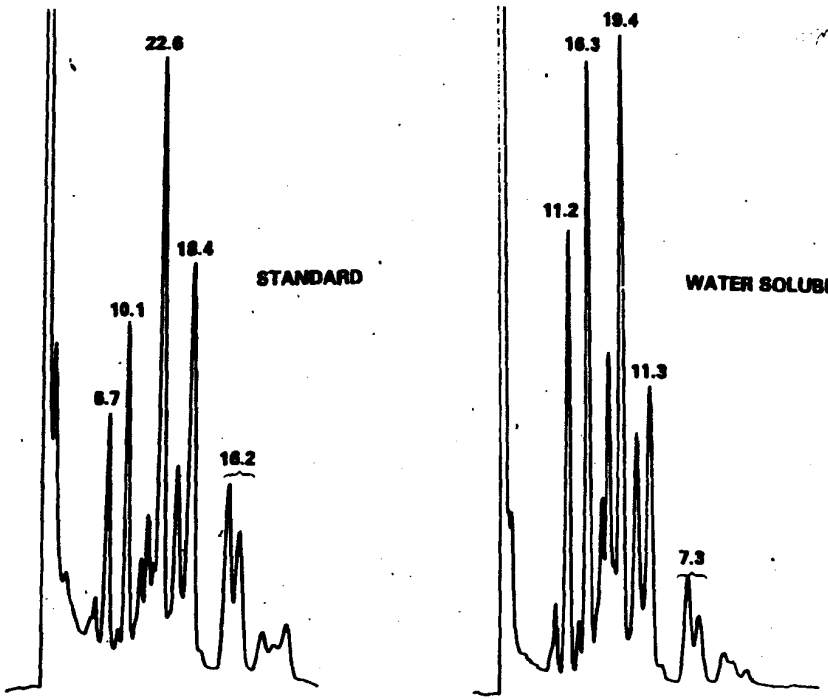

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Figure II.6.5 (from ref. 13)

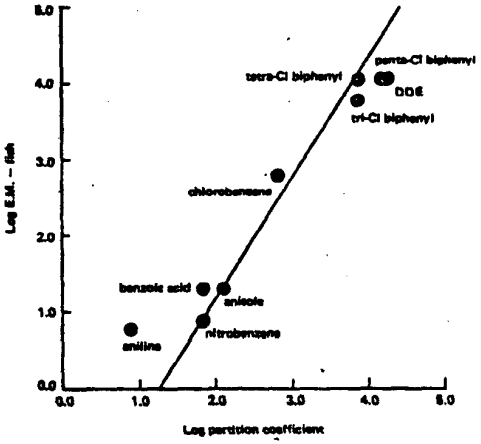
example, compares a gas-liquid chromatogram of Aroclor 1016 with that of an extract from a water "solution": it shows that the dichlorobiphenyls are much better dispersed in water than the tri- and tetra-chlorobiphenyls. Similar differentiation of the components of Aroclor 1254 on dispersal into water has been demonstrated (2, 4, 37, 38).

II.6.4 Solubility in organic solvents and partitioning into lipids

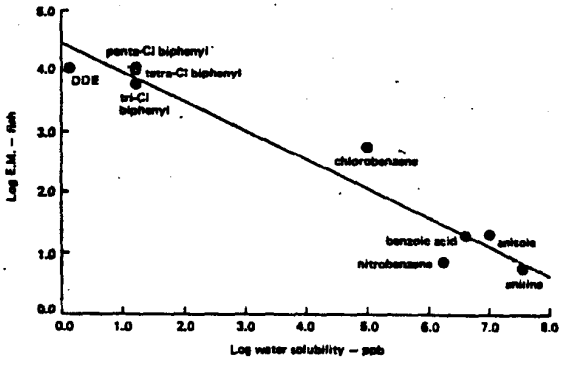
Chlorobiphenyls are freely soluble in many organic solvents (4, Table 4). As a consequence of their very low solubilities in water (Table II.6.6) they are very strongly partitioned into organic solvents, including lipids in biological systems (2, 45). Metcalf et al. (45) give figures in the range 10-20,000 for the partition coefficients between octanol and water of representative tri-, tetra-, and pentachlorobiphenyls. Partition coefficients between these two solvents have been found to correlate well with ecological magnification factors in aquatic organisms (45 - see Figure II.6.6).

II.6.5 Adsorption to soils, sediments, and particulates

PCBs are strongly adsorbed from water onto solid surfaces, including glass and metal surfaces in laboratory apparatus (46) and soils, sediments and particulates in the environment (37, 42, 48-51). Figure II.6.7 illustrates the adsorption of Aroclor 1254 from a water solution onto a variety of particulate materials (37). Adsorption was much more efficient onto Woodburn soil (with a high organic content) and clays than onto sand or silica gel. Another study (47) showed that Aroclor 1016 was extremely strongly adsorbed to a silty clay loam soil (36% clay, 6% organic carbon) and could only be leached with difficulty from sandy and silty loams. Even from the silty loam, less than 0.05% of the total quantity of Aroclor 1016 added

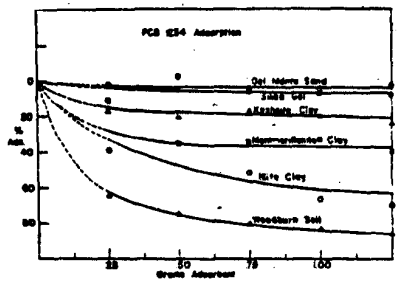


Plot of log E.M. (ecological magnification) for fish *vs.* log octanol/water partition coefficient.



Plot of log E.M. (ecological magnification) for fish *vs.* log water solubility (ppb).

Figure II.6.6 (from ref. 45)



Percent decrease in the concentration of Aroclor 1254 by the addition of increasing amounts of adsorbent. Original concentration of Aroclor 1254, 56 ppb

Figure II.6.7 (from ref. 37)

to the soil was leached in a four-month period. It was also observed in this experiment that the material leached from the soil consisted mainly of mono- and dichlorobiphenyls: the tetrachlorobiphenyls were apparently retained completely by the soil particles (Figure II.6.8).

In aquatic environments, PCBs are strongly associated with sediments and are usually found at much higher concentrations in sediments than in water in contact with them (12, 48, 49). Munson et al. (50) have found that PCBs (and other chlorinated hydrocarbons) in Chesapeake Bay are strongly associated with suspended sediments (Figure II.6.9): the PCBs are believed to be transported into the Bay from rivers and harbors and to move around the Bay in association with the suspended sediments (50). As with other chlorinated hydrocarbons (51), PCBs are probably associated particularly strongly with micro-particulates (down to 0.15 μm in diameter or less).*

There has been some debate whether PCBs carried in the air are in the vapor phase or are attached to airborne particulates. Recent measurements of PCBs in air over the North Atlantic Ocean (52, 53) have suggested that most of the PCBs there are in the vapor phase. However, PCBs have been detected on airborne particulates in urban areas (2) and on particulate matter in dry fallout (12, 54). It seems likely that there is some differentiation of the chlorobiphenyls, because the PCBs detected as vapors over the North Atlantic were reported as matching Aroclors 1242 and 1248 (tri- and tetrachlorobiphenyls) while those on dry fallout were reported as matching Aroclor 1254 and Clophen A50 (penta- and higher chlorobiphenyls) (12, 53, 54). However, the measurements are not definitive, because some of the differen-

* In the study reported in ref. 51, the chlorinated hydrocarbons extracted from the micro-particulate fraction of suspended sediments in water from Lake Erie were identified as various pesticides, including aldrin and endrin. However, this study took place before the recognition of PCBs as widespread contaminants in the aquatic environment, and it is likely that at least some of the residues in fact consisted of PCBs.

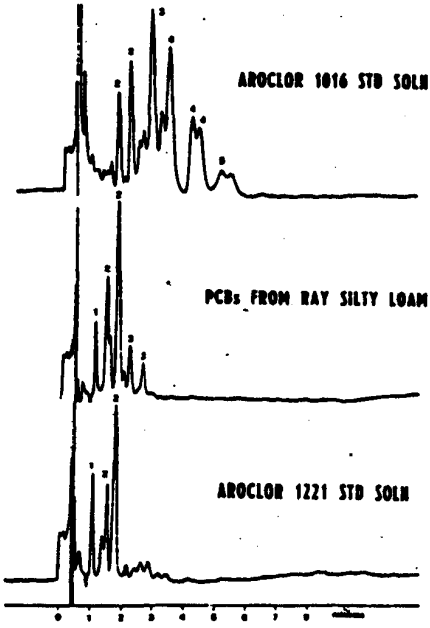
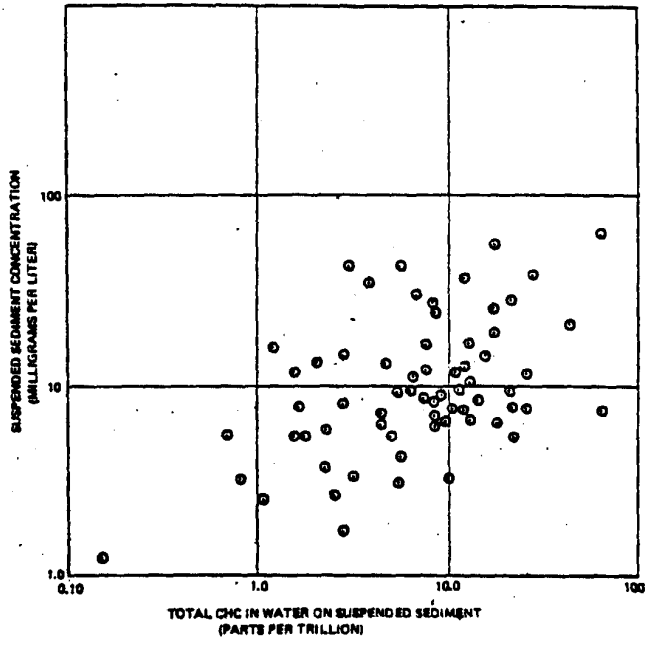


Figure II.6.8 (from ref. 47). Gas chromatograms illustrating differential leaching of components of Aroclor 1016 from soil.



A plot of the log of the suspended sediment concentration in the water (milligrams per liter) versus the log of the total CHC concentration in the water associated with the suspended sediment (parts per trillion).

Figure II.6.9 (from ref. 50)

tiation may take place during the process of collection -- i.e., the more volatile lower chlorobiphenyls may evaporate from the particulates as they are trapped on the collectors.*

II.6.6 Concentration at the air-water interface

Two recent studies have indicated that PCBs, like other chlorinated hydrocarbons, are strongly concentrated into the surface microlayers of ocean and estuarine waters, especially in surface slicks of natural lipids or mineral oils. Table II.6.7 summarizes two sets of measurements made in Narragansett Bay, Rhode Island (55). Sample 1 was from a heavy slick and Sample 2 from a less visible slick. Table II.6.8 summarizes a series of measurements in the Sargasso Sea (52). In each case the surface waters that were sampled contained concentrations of PCBs 3-50 times higher than the sub-surface waters. Since, for practical reasons, the surface microlayer itself could not be sampled, it is likely that the enrichment factor in the microlayer is often very much higher than this.

There appears to be some differentiation of chlorobiphenyls at the air-water interface, since Bidleman and Olney (52) reported that airborne PCBs resembled Aroclors 1242 or 1248 while those in the surface waters resembled Aroclors 1254 or 1260. However, it is not clear whether this differentiation results from differential volatility, differential fallout, or some other mechanism. Indeed, there are several mechanisms by which PCBs can be transferred across the air-water interface, and it is not yet clear for either inland waters or the oceans whether the net transfer is upwards or downwards (56).

* Thomas has recently detected PCBs in both gaseous and particulate fractions of ambient air, in a ratio of about 5:1 (396). Similar results have been reported by Tsou (402).

Table II.6.7 (from ref. 55)

CONCENTRATION AND ENRICHMENT FACTORS OF POLYCHLORINATED BIPHENYLS (AS AROCLOR 1254) IN SURFACE MICROLAYER SAMPLES FROM NARRAGANSETT BAY, RHODE ISLAND

Sample 1			Sample 2		
Concentration (μg/liter)		Enrichment factor	Concentration (μg/liter)		Enrichment factor
Surface	Subsurface		Surface	Subsurface	
4.2 1	0.15 ± 0.04	28±10	0.45 ± 0.11	≤0.05	≥9

Table II.6.8 (from ref. 52)

POLYCHLORINATED BIPHENYLS (AS AROCLOR 1260) IN SARGASSO SURFACE MICROLAYER (SM) AND SUBSURFACE WATER (SS)

Collection date (1973)	Location	Sample	PCB* (ng/liter)	Enrichment factor
4/9	29°56'N,64°40'W	SM	11.2	3.1
		SS	3.6	
4/10	30°45'N,66°50'W	SM	4.9	5.4
		SS	<0.9	
4/10	30°34'N,66°59'W	SM	8.3	8.3
		SS	1.0	
4/11	28°53'N,65°07'W	SM	42.6**, 19.3	47.3
		SS	<0.9**, <0.9	21.4
4/12	29°56'N,63°00'W	SM	3.8	4.2
		SS	<0.9	
4/13	30°00'N,64°30'W	SM	5.6	3.5
		SS	1.6	
4/16	31°34'N,63°49'W	SM	5.0	2.8
		SS	1.8	
4/17	31°38'N,63°57'W	SM	8.4	9.3
		SS	<0.9	

*Blank value was 0.9 and was subtracted in calculating the above results.
**Sample taken in a Sargassum windrow.

II.7 Physical properties of chlorinated dibenzofurans

No measurements appear to have been published of the physical properties of CDFs that would be required to predict their environmental behavior. Tetra- and pentachlorodibenzofurans are more polar than the corresponding chlorobiphenyls (31), but their retention times in gas-liquid chromatography are similar (36).

II.8 Chemical properties of chlorobiphenyls and commercial mixtures

II.8.1 General chemical stability

As a general rule, PCBs are considered to be inert to almost all of the typical chemical reactions. PCBs do not undergo oxidation, reduction, addition, elimination, or electrophilic substitution reactions except under extreme conditions. For example, whereas many compounds undergo oxidation with oxidizing reagents as mild as iodine and household hydrogen peroxide, mono-, di-, and trichlorobiphenyls require boiling nitric acid (4). Chlorines can be replaced by reductive dechlorination with any metal hydride such as lithium aluminum hydride while high temperature (245°) treatment with alkali in an autoclave can result in chlorine displacement by hydroxide.

II.8.2 Photochemical reactions

The reactions of paramount environmental importance are the few that PCBs appear to undergo readily. These are alkali- and photochemically-catalized nucleophilic substitutions and photochemical free radical substitutions, all of which occur with alkali and water.

Photolysis generally has been found to give three types of products depending on conditions (4, 57-61). Chlorine is replaced by hydrogen (reductive dechlorination) in non-aqueous, non-polar solvents and by alkoxy groups in non-aqueous, polar solvents. Chlorine is replaced by hydroxy groups in

aqueous systems and in thin films on glass interfacing with aqueous systems. Studies in non-aqueous solvents do not appear to be environmentally significant in spite of the presence of analogous hydrogen donors in nature unless the PCB product with one less chlorine is found to be more toxic than the PCB reactant. Nevertheless, some useful information can be obtained on approximate rate of decomposition and site of chlorine loss from non-aqueous studies. In hexane, the most prominent reactions of 2,5,2',5'-tetrachlorobiphenyl were the progressive reductive dechlorination and formation of polymeric materials. Photolysis in hexane also showed 33 percent decomposition of the PCB in 24 hours. Ruso et al. (57-59) have performed the most extensive and thorough studies of the photochemical decomposition of PCBs. They observed the reactions of the tetrachlorobiphenyls shown in Table II.8.1. It was found that 90 to 95 percent of the starting materials reacted in methanol solution. Products consisted predominantly of dechlorinated PCB with minor but detectable amounts of methanol substitution (methoxylated) products. In all cases, the amount of methoxylated products did not exceed five percent of the total amount of dechlorination products formed, with trichloromethoxybiphenyls being the main components. Methanol substitution occurred at the same site from which a chlorine was lost. The methoxylated product of 2,4,2',4'-tetrachlorobiphenyl was identified as 2,4,4'-trichloro-2' methoxybiphenyl by comparison of GC retention time and mass spectra with those of authentic samples prepared in the laboratory. Each of the tetrachlorobiphenyls which contained chlorines in the ortho position lost them upon irradiation. Similarly, those tetrachlorobiphenyls containing only meta- and para-chlorines upon irradiation lost the meta-chlorines preferentially. This behavior was also observed in the formation of the secondary products, dichlorobiphenyls, resulting in loss of ortho- or meta- but not

Table II.8.1 (from ref. 58)

Tetrachlorobiphenyls	--PHOTOPRODUCTS IN HEXANE AND IN METHANOL		
	Dechlorinated products	Time, sec	Methoxylated products
I: 2,5,2',5'-	2,3',5-Trichlorobiphenyl	167	Trichloromethoxybiphenyl
	3,3'-Dichlorobiphenyl	128	Dichlorodimethoxybiphenyl*
	3-Chlorobiphenyl*		
II: 2,4,2',4'-	2,4,4'-Trichlorobiphenyl	190	Trichloromethoxybiphenyl
	4,4'-Dichlorobiphenyl	148	Dichlorodimethoxybiphenyl*
	4-Chlorobiphenyl*		
III: 2,3,2',3'-	2,3,3'-Trichlorobiphenyl	182	Trichloromethoxybiphenyl
	3,3'-Dichlorobiphenyl	129	Dichlorodimethoxybiphenyl*
IV: 3,4,3',4'-**	3,4,4'-Trichlorobiphenyl	192	Trichloromethoxybiphenyl
	4,4'-Dichlorobiphenyl	147	
V: 3,5,3',5'-	3,3',5-Trichlorobiphenyl*	181	
VI: 2,6,2',6'-	2,2',6-Trichlorobiphenyl*	158	Trichloromethoxybiphenyl*
	2,2'-Dichlorobiphenyl*	69	

*Represented less than 1% of total product formation.
**3,3',4-Tetrachlorobiphenyl was observed in <2%.

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para-chlorines. The tertiary products, monochlorobiphenyls, were only formed in one percent yield or not at all. This occurred either because of insufficient energy absorption by dichlorobiphenyls at the wavelengths employed or by decreased reactivity of meta- and para-chlorines relative to those on the ortho position.

The rate of photolysis reaction for all PCBs studied was found to be zero order (independent of the amount of each PCB) in both hexane and methanol (Table II.8.2 -- ref. 58). A marked increase in rate was observed, however, when solutions were degassed prior to irradiation. Oxygen is known to act as a triplet (free radical) quencher by accepting or sponging up excess electronic energy from free radicals before any chemical change occurs. Thus, an increase in rate upon removal of oxygen implies that a free radical process is occurring. In the environment, this implies that photochemical transformation will be enhanced under anaerobic conditions.

The two pathways operating to give replacement of chlorine by hydrogen and methoxyl group and the probable intermediates, inferring the corresponding mechanism, are shown in Figure II.8.1.

The photochemical behavior of higher chlorobiphenyls appears similar to that of the tetrachlorobiphenyls (60-61). 2,4,5,2',4',5'-hexachlorobiphenyl undergoes reductive dechlorination when irradiated in degassed methanol, losing one or both ortho-chlorines (61). Irradiation of Aroclor 1254 in aqueous solution gave rise to dechlorinated and hydroxylated products (60). Hexa- and octachlorobiphenyls are more photochemically reactive than tetrachlorobiphenyls (60), so that under irradiation the higher components of Aroclor 1254 are selectively degraded (60, 61 -- Table II.8.3).

Table II.8.2 Photolysis rates of tetrachlorobiphenyls (from ref. 58)

Tetrachlorobiphenyl	$k_h \times 10^8$ M sec^{-1} (degassed)*	$k_h \times 10^8$ M sec^{-1} (O_2)	$k_m \times 10^8$ M sec^{-1} (degassed)	$k_m \times 10^8$ M sec^{-1} (O_2)
2,4,2',4'-	15.0	2.8	18.0	4.2
2,3,2',3'-	2.4	1.0	4.0	1.5
2,5,2',5'-	2.2	0.5	4.8	0.7
3,4,3',4'-	1.4	0.8	3.5	2.2
2,6,2',6'-	0.4	0.2	0.5	0.2
3,5,3',5'-	<0.1		<0.1	

* Rate of reaction in hexane solution.

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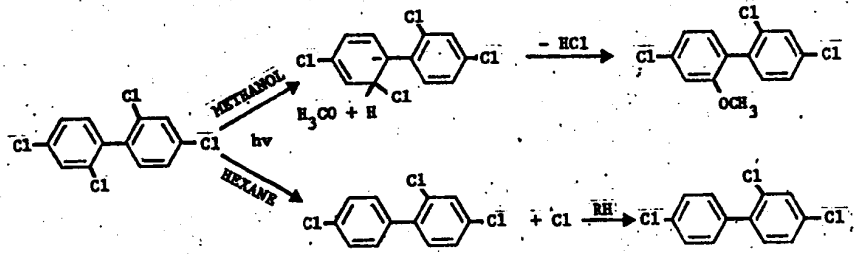

UV-irradiation of 2,2';4,4'-tetrachlorobiphenyl in methanol and hexane, products formed and probable mechanism.

Figure II.8.1 (from data in ref. 58)

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TABLE II.8.3 (from ref. 61)

Sunlight Irradiation of Aroclor 1254.

Initial Concentration of Aroclor 1254 in Hexane

	1 ppm			10 ppm			100 ppm		
	% remaining after			% remaining after			% remaining after		
Peak No.	1 week	2 weeks	3 weeks	1 week	2 weeks	3 weeks	1 week	2 weeks	3 weeks
1	97	109	143	65	104	104	85	131	139
2	111	137	161	111	140	180	114	164	184
3	74	76	79	113	94	88	110	110	101
4	83	104	109	127	108	143	92	99	120
5	103	89	87	98	96	94	118	70	63
6	181	211	196	210	206	241	157	205	218
7	58	51	36	68	58	40	68	58	42
8	84	89	75	111	98	90	105	96	80
9	66	47	30	53	44	44	80	56	47
10	62	47	41	49	50	59	80	64	54

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II.8.3 Photochemical production and degredation of chlorinated dibenzofurans

The creation of free radicals by sunlight allows the environmental replacement of chlorines by hydroxy groups from water without the intervention of alkali. When this occurs at the ortho position (found to be the most preferred for chlorine loss) the resulting 2-hydroxychlorobiphenyl is perfectly positioned to allow oxygen to bond to an ortho position of the other ring. This results in the creation of potentially the most important class of contaminant in PCBs or commercial mixtures, the chlorodibenzofurans (CDFs).

Studies in aqueous solvents have continuously established the hydroxylation of mixtures of PCBs, although at times the location has not been established. Thus, irradiation of Aroclor 1254 in hydroxylic solvents at pH 9 yields compounds corresponding to the addition of water to the PCB molecules and a more polar carboxylic acid fraction. The same sample irradiated as a thin film does not yield the water-addition products, but mass spectrometry of 2,5,2',5'-tetrachlorobiphenyl reveals the presence of new hydroxylated species and a polar "carboxylic" fraction. No attempt was made to determine whether the polar carboxylic acid fractions in these studies were the same but it was generally concluded from a number of different irradiations of 2,5,2',5'-tetrachlorobiphenyl that dechlorination, formation of polymers, and carboxylic products, as well as hydroxylation, does occur (60).

Activating the ring will make it more capable of hydroxylation. Many means can be used to activate the ring, such as the intermediacy of a copper complex (the Ullmann reaction). In the presence of powdered copper or copper salts, a few hours at 160° converts normally unreactive o-chlorophenols to chlorinated dibenzo-p-dioxins, contaminants of 2,4-D and 2,4,5-T production

with very similar chemical, physical and, probably, toxicological properties to CDFs (62, 63). Thus, in the environment either heat, light, or metals and metal salts in water could theoretically accelerate the transformation of PCBs into PCDFs.

The ultraviolet component of sunlight is sufficiently energetic to generate free radicals from both phenols and PCBs. The energies required to break the Ar-Cl bond to form hydroxy-PCBs and the ArO-H bond to form CDFs correspond to wavelengths near 360 and 320 nm, respectively -- clearly within the sunlight region. Analogous free-radical mechanisms have been proposed to explain reactions of polychlorophenol (PCP) and other chlorophenols in sunlight (62).

The alternate photonucleophilic formation of phenols from PCBs was demonstrated to afford hydroxy PCBs both with simple models and with highly complex Aroclors. Contrary to previous results (57), irradiation of an aqueous suspension of 4,4'-dichlorobiphenyl provided 4-chloro-4'-hydroxybiphenyl and 4-chlorobiphenyl (62, 63). Irradiation experiments with five pure 2-chlorinated biphenyls as 5 mg/l aqueous suspensions, showed that traces of 2-chlorodibenzofuran were detectable although only the 2,5-dichloro- and 2,5,2',5'-tetrachlorobiphenyls provided identifiable amounts (a roughly steady 0.2 percent yield during a seven-day irradiation) (62, 63). The environmental significance of this is threefold: (1) ortho-chlorobiphenyls can be hydroxylated by radiation similar to sunlight when they are suspended in aqueous media; (2) the product(s) are converted to CDFs; (3) rates of CDF formation by this process are approximately the same as their rates of degradation, leading to an approximately steady concentration. Hutzinger also has speculated that chlorodibenzofurans may be formed from chlorobiphenyls under photochemical conditions which lead to oxygenated products (60).

Although no chlorodibenzofurans were detected in a number of chlorobiphenyl samples which had been exposed to sunlight for over two months, preliminary results indicated the formation of chlorodibenzofurans from 2,4,6,2',5',6'-hexachlorobiphenyl in model experiments (irradiation in methanol) (Anderseon et al., cited in ref. 64).

Before any knowledge on accumulation of CDFs can be obtained, relative rates of their formation and decomposition must be determined. Unfortunately, only a few rates of decomposition have been determined, such as those of 2,8-di- and octachlorodibenzofuran, as shown in Figure II.8.2 (64). Decomposition is faster in methanol than in hexane. In contrast to the chlorinated dibenzo-p-dioxins, where the degradation of the octachloro derivative on irradiation in methanol solution is much slower than that of the 2,7-dibenzo-p-dioxin, the di- and octachlorodibenzofurans show similar rates of decomposition.

Rutzinger et al. (64) observed that photolysis of 2,8-di- and octachlorodibenzofuran in methanol and hexane solutions results in rapid dechlorination and accumulation of unidentified resinous polymeric products. Dechlorination is also observed to a certain extent when thin films of these compounds were exposed to sunlight. This is similar to the non-aqueous behavior of PCBs from which these CDFs arose. This suggests that CDFs in the environment, like PCBs, will only reductively dechlorinate when in organic media or thin films. Crosby and Moilanen (63) found that irradiation of 2,8-dichlorodibenzofuran resulted in a slow dehalogenation in hexane, explaining the previous appearance of 2-chloro-dibenzofuran. Irradiation in methanol substantiated the rapid disappearance of the dichlorodibenzofuran (64). Decomposition in aqueous suspension was found to be slow (63).

Unfortunately, these preliminary data do not allow direct comparison of environmental dibenzofuran degradation rates with rates of their photo-

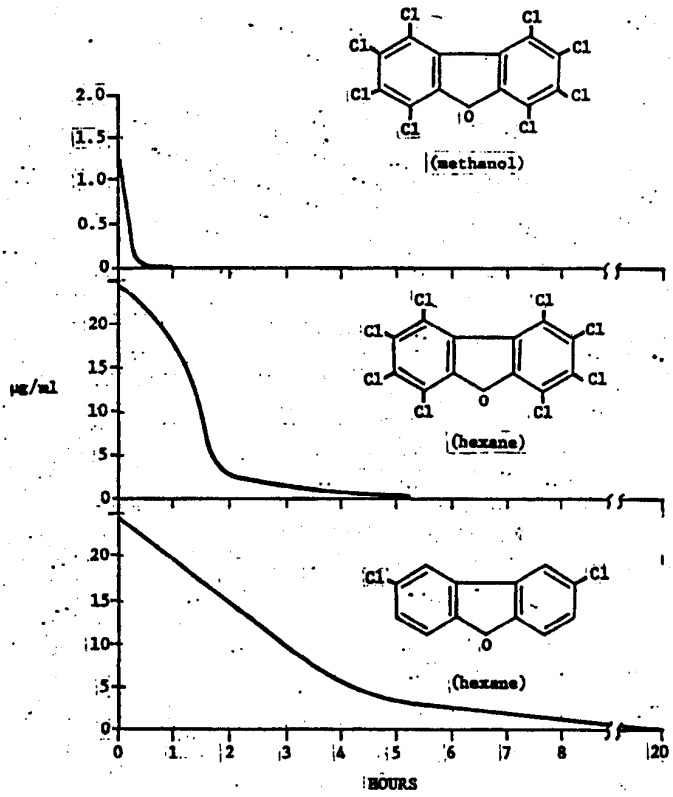

Figure II.8.2 (from ref. 64)

Photochemical degradation of chlorodibenzofurans in solution. Irradiation wavelength 310 nm.

chemical formation from corresponding chlorobiphenyls. In view of the photochemical lability observed for some chlorodibenzofurans, however, it seems reasonable that most isomers will not accumulate excessively in the environment with the possible exception of 2-CDF. Since accumulation is relative when a wide range of toxicity is considered, the steady state conversion of two-tenths percent of some PCBs to PCDFs is very important and potentially very significant. A further environmental complication is that other investigators have been unsuccessful in detecting the conversion of PCBs to PCDFs in light, perhaps due to the aforementioned rapid decomposition for most isomers under energetic (254 nm) irradiation conditions or the presence of sensitizers. The addition of the photosensitizer 4,4'-dichlorobenzophenone to a methanol solution of 2,8-dichlorodibenzofuran during irradiation resulted in a sharp increase in the decomposition rate of that CDF (63). Both natural and synthetic photosensitizers have been shown to affect other xenobiotics, and the environmental sensitization of degradative photolysis of CDFs seems quite plausible.

II.8.4 Probable formation of PCDFs from PCBs in service.

In the "Yusho" incident in Japan in 1968, large numbers of persons were poisoned by consuming rice-oil contaminated with PCBs (Kanechlor KC-400) from a leaking heat-exchanger (35; see Section III.15 below). Recent studies have shown that although the original Kanechlor KC-400 contained only about 20 ppm of PCDFs, the toxic rice-oil contained relatively much larger quantities of PCDFs (PCB/PCDF ratio 84-200 in the rice-oil, versus 50,000 in KC-400) (34; 35, Table 5). Further, the PCDFs in the Yusho oil contained substantial quantities of hexachlorodibenzofurans, which have not been detected in KC-400 (33-35). This suggests that most of the PCDFs in the Yusho oil had been formed in service, probably in the heat-exchanger. According to Kuratsune, elevated levels of PCDFs have been discovered in PCBs in other heat-exchangers in Japan.*

In a parallel incident in the United States in 1971, fish meal being processed for poultry food was contaminated with Aroclor 1242 and proved highly toxic to broiler chickens (65). Subsequent tests with the contaminated feed, which contained 148 ppm of PCBs, showed it to be much more toxic to chicks than feed containing 200 or even 400 ppm of Aroclor 1242, and the symptoms of poisoning were different (2, 65: see Section III.6.2 below). This again suggests that a more toxic agent had been formed in service. This situation is complicated by the report that the contaminated feed also included 8.8 ppm of "BHC" (presumably an isomer of HCH, hexachlorocyclohexane) (65). However, the identification of this compound is questionable, because HCH is rarely found in marine fish or in other components of poultry feeds at more than trace levels.

* This information was presented by Kuratsune at the PCB conference in November 1975 (9) but documentation is not yet available.

Hence the component reported as HHC in the contaminated fish meal may in fact have been a breakdown product of PCBs.

According to Broadhurst (66), a general disadvantage of PCBs in many of their applications (including capacitor and transformer uses as well as heat transfer uses) is their tendency to decompose under the action of heat or electrical arcing to form corrosive HCl. Hence the evidence summarized above, that PCDFs or other toxic breakdown products may be formed in service in heat-exchangers, needs to be followed up by investigation of the composition and toxicity of PCBs after service in electrical equipment also (2).