The Sources of the Coplanar PCBs

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The term "coplanar PCB" (cPCB) is currently used to denote the non-*ortho* substituted PCB congeners, such as No. 77 (34-34 tetrachlorobiphenyl), No. 126 (345-34 pentachlorobiphenyl), and No. 169 (345-345 hexachlorobiphenyl). These congeners generally constitute less than 0.1% of the total PCBs present in man or wildlife, yet are believed to contribute much or most of their potential for dioxin-like (*AhR*-mediated) toxic effects. The origin of the cPCBs has been considered uncertain, and was recommended as a subject for future research in a recent widely publicized, but uncitable, draft risk assessment document.

We examine here data relating to three alternative hypotheses as to the source of the environmental cPCBs, namely, (a) releases of the commercial PCB products, e.g., Aroclors, (b) solar photolysis of the higher PCB congeners, and (c) emissions from combustion processes.

Table 1 presents a comparison of the reported environmental levels of the cPCBs with those of congeners sufficiently persistent in biota to serve as internal references. The referenced congener used was either 153, 156, or 118, in that order of preference, according to data availability. Congeners 153, 156, and 169 are highly persistent in man and most other species because of their very low metabolic rates, while Nos. 118 and 126 are metabolized slowly and 77 quite rapidly (1). However, the mono-*ortho* substituted congeners 156 and 118 are less persistent in some marine mammals, which have a P4501A-like metabolic activity (1).

Comparison with the cPCB levels in total Aroclor production as calculated in Table 2 shows that the levels of 77 in biota are about 4- to 3,000-fold lower than in the Aroclors, as expected from its ready metabolizability; those of 169 are 20- to 200-fold higher; and those of 126 range between 0.2 and 16 times the Aroclor value, but would presumably be much higher if no metabolism had occurred. The levels of congeners 189, 205, and 209, which constituted respectively 0.02, 0.007, and 0.008% of 1957-77 Aroclor production, have been less frequently reported in the literature. However, available data compilations (2,3) indicate that their levels are also one to two orders of magnitude higher in man and wildlife relative to those of other difficultly metabolized Aroclor components, such as congeners 153, 180, and 194. Accordingly, we conclude that environmental PCB congeners 126, 169, 189, 205, and 209 must be derived largely from non-Aroclor sources.

To characterize the conceivable cPCB formation by photodechlorination in organic microenvironments, we examined the changes in congener levels that occurred after exposing hexane solutions of various Aroclors to direct summer sunlight. We found that conversions of 156 to 126, or of 189 to 169, could indeed occur. However, the kinetics (Table 3) showed that any appreciable formation of 169 by this route would be accompanied by extensive losses of 74 and 156 in photic zone biota such as periphyton, phytoplankton, and filter-feeding molluscs. Such biota often do show reduced bioaccumulation of PCB 156 and other high K_{OW} congeners, but not any clear depressions in the levels of the highly photolabile PCB 74 relative to those of other mono-*ortho* tetrachlorobiphenyls such as Nos. 66 and 70 (4). Presumably, the penetration of short wavelength solar ultraviolet into natural waters is insufficient to effect appreciable PCB dechlorination. In addition, of course, solar dechlorination could not explain the increased environmental levels of PCBs 189, 205, and 209.

It is known that trace levels of dioxins, PCDFs, chlorobenzenes, PCBs, and other chlorinated organic compounds can be formed whenever carbonaceous materials containing chlorine in any form are burned (5-7). However, their distributions vary widely. Under some conditions of combustion (5) the PCBs formed are mainly the lower congeners, along with large amounts of the cPCBs (5,6), as shown in Table 1. This indicates that emissions from such systems could be the source of the observed environmental excesses of congeners 126 and 169. Under other conditions (7) the PCBs formed are mainly the nona- and decachlorobiphenyls (PCB Nos. 206 and 209) along with considerable 156, 189, and 205, and some 169. Hence, combustion processes of this type could be the source of the elevated environmental levels of congeners 189, 205, and 209, as well as 169.

In summary, we conclude from the available PCB congener distribution data that combustion processes, rather than Aroclor releases or Aroclor photolyses, are the most likely source of most environmental cPCBs.

References

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Table 1. Levels of PCB Congeners 77, 126, and 169 in Aroclors, Man, Piscivores, Fish, and Incinerator Emissions Relative to Those of (Parenthesized) Congener 153, 156, or 118

Specimen Type	Data Source	PCB Congener No. 77	126	169	153	156	118
TOTAL 1957-77 AROCLOR	TABLE 2	96.	0.95	0.01	(1000)	127	891
Human adipose, Japan	Tanabe '89	2.22	2.10	0.58	NR	(127)	578
Human serum, Sweden	Patterson '89	0.70	0.27	0.22	(1000)	NR	530
Human milk, Sweden	Noren '90	0.18	0.65	0.31	(1000)	95	168
Human milk, Norway	Johansen '94	0.40	1.36	1.68	(1000)	101	229
Blood, USA, Michigan	Schecter '93	1.96	2.61	1.14	(1000)	149	405
Blood, Netherlands	Koopman-Esseboom '94	0.08	0.78	0.46	(1000)	115	187
Blood, German adults	Wurthe '94	0.09	0.25	0.42	(1000)	120	126
Blood, German children	Wurthe '94	<0.3	0.66	0.47	(1000)	116	149
Milk, Quebec, Inuit	Dewailley '94	0.06	0.53	0.56	(1000)	NR	149
Milk, Quebec, urban	Dewailley '94	0.22	2.15	0.87	(1000)	NR	405
Killer whale, W. Pacific	Tanabe '89	3.21	0.24	0.51	NR	(127)	735
Dall's porpoise, W. Pacific	Tanabe '89	26.6	1.85	1.27	NR	(127)	3200
Harbor porpoise, N. Sea	DeBoer '93	0.67	0.22	0.62	(1000)	1	46
W.B. Dolphin, N. Sea	DeBoer '93	0.85	0.73	1.85	(1000)	11	55
Harp seal, N. Atlantic	Oehme '94	0.61	0.73	0.65	(1000)	11	89
Sole, N. Sea	DeBoer '93	5.5	1.2	0.7	(1000)	38	410
Oysters, E. Schelde	DeBoer '93	13.0	2.6	0.5	(1000)	<20	300
Shrimp, Dutch coast	DeBoer '93	24.0	8.2	1.1	(1000)	35	460
Forster's tern, L. Michigan	Kubiak '89	0.51	3.48	0.96	NR	(127)	1000
Chinook, L. Michigan	Williams '92	22.0	8.0	NR	NR	(127)	600
Bald eagle, L. Huron	Schwartz '93	5.7	16.0	1.85	NR	(127)	577
Yellow eel, Netherlands	DeBoer '93	0.3	0.6	0.21	(1000)	50	300
Pike-perch, Netherlands	DeBoer '93	8.0	1.2	0.17	(1000)	37	350
Incinerator emissions	Sakai '93	170.0	59.0	33.0	NR	(127)	800
Incinerator emissions	Sakai '94	950.0	630.0	143.0	NR	(127)	63
Scrap metal burner	Strandell '94	NR	89.0	NR	NR	NR	(891)

Table 2. Weight Fractions of PCB Congeners in Commercial Aroclors and in Total 1957-1977 USA Production

Aroclor	% of Total Production[d]	Coplanars, µg/g[a]			Non-coplanar PCBs, wt. %[b]					
		77	126	169	105	118	138	153	156	189
1242	51.76	3610	22	0.1?	0.56	1.00	0.27	0.42	0.06	0.00
1248	6.76	4630	67	0.3	1.35	2.38	0.63	0.61	0.16	0.00
1254	15.73	380	38	0.6	3.66	8.43	4.12	4.52	1.16	0.03
1260	10.61	180	4	0.16	0.06	0.85	5.83	12.34	0.70	0.11
Others[c]	15.14[c]	---	---	---	---	---	---	---	---	---
Total	100.00	2260	22	0.2	0.96	2.10	1.48	2.35	0.30	0.02

a) Average of values from Huckins `80; Kannan `87, `88; Tanabe `87; Pruell `88; Schwartz `93; DeBoer `93.
b) Average of values from Schulz, Petrick, Duinker `88, `89; Schwartz `93; DeBoer `93; Wagner (in preparation); Frame (in preparation).
c) Mainly Aroclors 1221 and 1016, which lack the listed congeners. Contributions from the minor Aroclors 1232, 1262, and 1268 not listed but included in the totals.
d) Calculated from reported sales data, Monsanto `80.

Table 3. Disappearance Rates of Photolabile PCB Congeners from Hexane Solutions of Aroclors 1242, 1254, or 1260, or PCBs 138, 153, or 180 in Quartz Tubes Exposed to Direct Sunlight of 43° N, 19 July to 12 October 1993

Congener	No.	k (da.-1)	Congener	No.	k (da.-1)
Mono-orthos			25-4	31	0.005
245-4	74	0.3	25-34	70	~0.0001
2345-34	156	0.3	*Di-orthos*		
245-34	118	0.18	2346-34	158	0.04
234-34	105	0.11	234-245	138	0.02
245-345	167	0.08	2346-345	191	0.008
2345-345	189	0.08	234-234	128	0.006
24-34	66	0.06	2345-234	170	0.006
23-34, 234-4	56, 60	0.03	2345-245	180	0.004
24-4	28	0.015	245-245	153	0.0008