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Non-*O,O*'-Chlorine Substituted Congeners in Commercial Polychlorinated Biphenyl (PCB) Mixtures of the World

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Polychlorinated biphenyls (PCBs) are well known environmental contaminants with persistence, bioacumulation and human health problems (Safe 1994). Most important dioxin-like biological effects of PCBs are correlated well with non-*ortho* Cl substituted congeners such as 33'44-tetra (IUPAC#77), 344'5-tetra (81), 33'44'5-penta (126) and 33'44'55'-hexa (169) (Kannan 2000) and three out of these four congeners were measured, for the first time, in commercial mixtures by Kannan et al. (1987). Though most other reports (Safe 1987; Schulz et al. 1989; Boonyathumanondh et al. 1995; Frame et al. 1996) claimed a complete characterization of commercial PCBs, these congeners, were not quantitated in their analysis due to restrictions in the detection range. The analytical chemistry of non-*ortho* Cl CBs started as early as in 1979 (Kamops et al. 1979). However, the earlier studies were not systematic and focused only on Aroclor mixtures. Among the Aroclors 1242, 1248 and 1254 were the best studied till date. Among the four co-planar congeners 77 was well studied. Among the various global studies it was only two groups that carried out systematic analytical work with most sensitive determination (Kannan et al. 1987; 2005).

MATERIALS AND METHODS

Thus, 22 commercial PCB mixtures from various countries have been analyzed for the content of non-*ortho* chlorine substituted co-planar PCBs. American mixtures such as Aroclor 1016, 1221, 1242, 1248, 1254 and 1260 have been covered in this study. Three different lots of Aroclor 1254 were analyzed as well, considering its wide use in toxicological experiments and environmental studies. Among the German PCB mixtures (Clophen) A30, A40, A50 and A60 were analyzed. Among the French PCB mixtures (Phenoclor) DP30, DP40, DP50 and DP60 were analyzed. Similarly, among the Japanese mixtures (Kanechlor) KC-300, KC-400, KC-500 and KC-600 were analyzed. In addition we analyzed one Russian (Sovol) and one Polish PCB (Chlorfen) mixture as well. This was achieved using a combination of electron donor-acceptor (EDA) high-performance liquid chromatography (HPLC) using high resolution PYE [2-(1-pyrenyl) ethyldimethyl silylated silica gel] column and multidimensional gas chromatography – electron capture detection (MDGC-ECD) (Kannan et al. 2005).

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RESULTS AND DISCUSSION

Among the four co-planar congeners, 3,3',4,4'-T_4CB (#77) was determined the highest followed by 344'5-T_4CB (81), 33'44'5-P_5CB (126) and 33'44'55'-H_6CB (169). One unusual observation was the enrichment of all these congeners in lot # 6024 of Aroclor 1254. The content was almost five times higher than Aroclor 1242 and 1248 and several fold higher than other lots of Aroclor 1254 such as CAS 11097-69-1 and 124-191. The enrichment was 285 times for #77; 17 times for #81 and 56 times for #126. The content of #169 was similar. All the three lots were obtained from USEPA but in different times (Table 1). Apart from the enrichment of toxic co-planar congeners, these two lots contained elevated levels of other toxic congeners such as #105, 110, 118, 132, 138, 149 and 151 as well (Fig.1).

Table 1. Non-*O,O'*-chlorine congeners (μg/g) in commercial PCB mixtures.

Aroclor	77	81	126	169
AR 1016	37	11	18	29
AR 1221	25	9.9	13	20
AR 1242	5550	250	75	51
AR 1248	2840	38	20	7.2
AR 1254(1)	84	22	61	24
AR 1254(2)	24000	370	3400	20
AR 1254(3)	15	11	167	13
AR 1260	69	16	76	12
Clophen				
A30	10600	280	52	84
A40	6500	67	170	64
A50	60	25	25	15
A60	29	10	27	7,9
Phenoclor				
DP 30	690	42	9.4	11
DP 40	6040	67	260	86
DP 50	1.7	2.9	14	1.9
DP 60	194	17	47	35
Kanechlor				
KC 300	370	39	18	11
KC 400	1304	180	16	33
KC 500	330	8,4	39	11
KC 600	320	11	9.8	3,1
Sovol	3970	18	690	12
Chlorofen	55	57	71	127

1. lot # 11097-69-1; 2. lot # 6024; 3. lot # 124-191

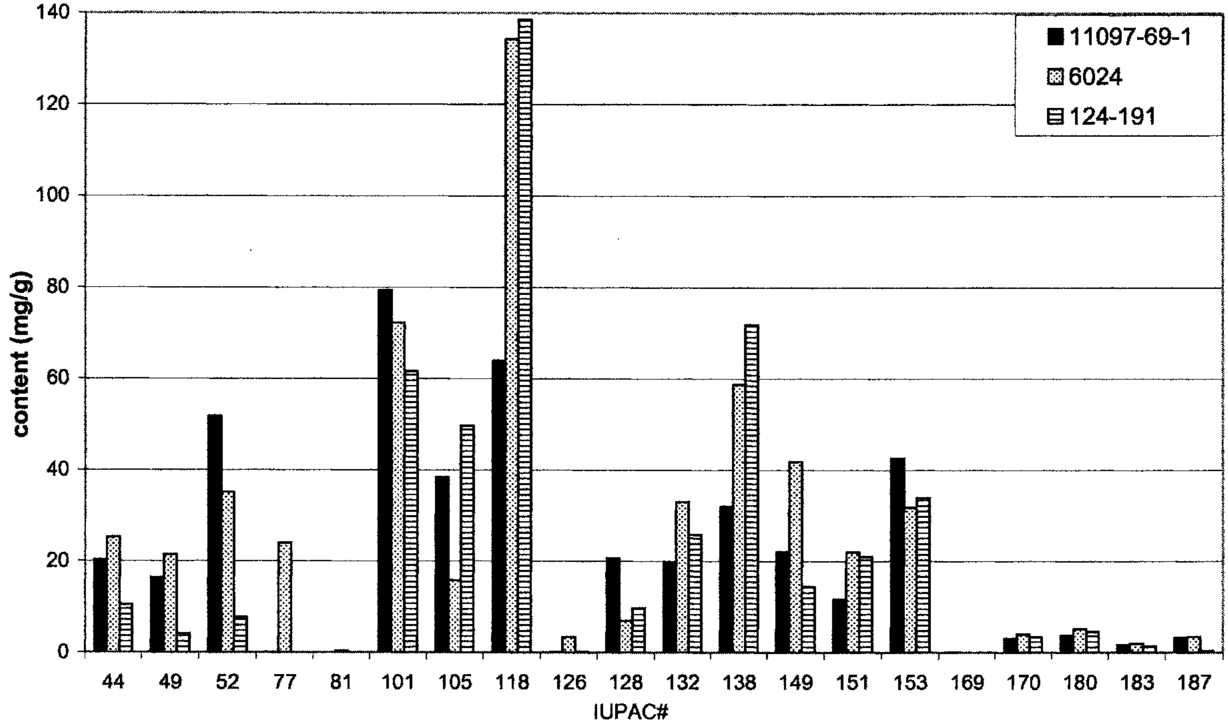

Figure 1. PCB composition in Aroclor 1254 lots, including non-*O,O'*-Cl congeners.

The German (Clophen) and French (Phenoclor) mixtures did not show any peculiar patterns and the congener ratio between the 4 non-*ortho* Cl PCBs was similar i.e. #77>81>126>169. The mixtures with 30% and 40% chlorination contained the highest content of #77 and 81 as expected. However, it was not the penta mixture (50% Cl) that contained the highest content of #126, instead the tetra (40% Cl) mixture.

Japanese (Kanechlor), Russian (Sovol) and Polish (Chlorfen) mixtures showed some peculiarities in the PCB composition. For example, Sovol contained the highest concentration (690 μg/g) of the most toxic 33'44'5-P_5CB among the mixtures we tested. On the other hand, Chlorfen contained the highest concentration (127 μg/g) of 33'44'55'-H_6CB. Though Kanechlor's co-planar PCB composition is similar to that of European and American mixtures, they contained several non-PCB impurities and found to have several PCB congeners enriched.

USEPA has provided 2378-TCDD toxic equivalent factors (TEFs) online (http://www.epa.gov/toxteam/pcbid/tefs.htm) for a set of 4 non-*ortho* Cl PCBs and a set of 8 mono-*ortho* Cl PCBs. Our present study enabled us to calculate TEQs for all the four non-*ortho* Cl congeners in commercial mixtures (Table 2). Among all the test mixtures, lot no. 6024 of Aroclor 1254 showed the highest TEQs. This is, for example, 10 times higher than lot no.124-191. Burgin et al. (2001) have demonstrated in an elegant experiment whether the difference in the TEQs of the these lots explained the different *in vivo* responses seen on a weight basis in male Long-Evans rats. They treated the animals orally with a single dose of 0-1,000 mg/kg of each lot. Hepatic ethoxy-, methoxy-, and pentoxyresorufin *O*-deethylase (EROD, MROD, and PROD, respectively) activities as well as serum thyroxine (T4) concentrations and measures of oxidative stress were determined 4 days after treatment. Results, on a weight basis, indicated that lot 6024 led to a greater induction of EROD, MROD, and PROD. Thus it was demonstrated that lot to lot variation in PCB composition possible and they affect biological activity accordingly. Sovol showed the next highest toxic potential. The French and German mixtures, especially at 40% chlorination level, showed considerable toxic potential as well. In comparison, the Kanechlor mixtures (Japanese) and Chlorfen (Polish) showed low TEQs.

Thus it is concluded that all the 22 different PCB commercial mixtures showed the presence of potentially toxic non-*ortho* Cl substituted PCB congeners. When reporting toxicity data it is important to show the detailed composition of PCB mixtures, as lot to lot variation in co-planar PCBs exists.

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Table 2. TEQs of non-*ortho* chlorine congeners in commercial PCB mixtures.

Sample	77	81	126	169	Sum
AR1016	3.70x10-6	1.10x10-6	1.80x10-3	2.90x10-4	2.09x10-3
AR1221	2.50x10-6	9.90x10-7	1.30x10-3	2.00x10-4	1.50x10-3
AR1242	5.55x10-4	2.50x10-5	7.50x10-3	5.10x10-4	8.59x10-3
AR1248	2.84x10-4	3.80x10-6	2.00x10-3	7.20x10-5	2.36x10-3
AR1254-1	8.40x10-6	2.20x10-6	6.10x10-3	2.40x10-4	6.35x10-3
AR1254-2	2.40x10-3	3.70x10-5	3.40x10-1	2.00x10-4	3.43x10-1
AR1254-3	1.50x10-6	1.10x10-6	1.67x10-2	1.30x10-4	1.68x10-2
AR1260	6.90x10-6	1.60x10-6	7.60x10-3	1.20x10-4	7.73x10-3
A30	1.06x10-3	2.80x10-5	5.20x10-3	8.40x10-4	7.13x10-3
A40	6.50x10-4	6.70x10-6	1.70x10-2	6.40x10-4	1.83x10-2
A50	6.00x10-6	2.50x10-6	2.50x10-3	1.50x10-4	2.66x10-3
A60	2.90x10-6	1.00x10-6	2.70x10-3	7.90x10-5	2.78x10-3
DP30	6.90x10-5	4.20x10-6	9.40x10-4	1.10x10-4	1.12x10-3
DP40	6.04x10-4	6.70x10-6	2.60x10-2	8.60x10-4	2.75x10-2
DP50	1.70x10-7	2.90x10-7	1.40x10-3	1.90x10-5	1.42x10-3
DP60	1.94x10-5	1.70x10-6	4.70x10-3	3.50x10-4	5.07x10-3
KC300	3.70x10-5	3.90x10-6	1.80x10-3	1.10x10-4	1.95x10-3
KC400	1.30x10-4	1.80x10-5	1.60x10-3	3.30x10-4	2.08x10-3
KC500	3.30x10-5	8.40x10-7	3.90x10-3	1.10x10-4	4.04x10-3
KC600	3.20x10-5	1.10x10-6	9.80x10-4	3.10x10-5	1.04x10-3
Sovol	3.97x10-4	1.80x10-6	6.90x10-2	1.20x10-4	6.95x10-2
Chlorofen	5.50x10-6	5.70x10-6	7.10x10-3	1.27x10-3	8.38x10-3

1254-1 (CAS 11097-69-1); 1254-2 (Lot No. 6024); 1254-3 (Lot No. 124-191)

REFERENCES

Boonyathumanondh R, Watanabe S, Laovakul W, Tabucanon M (1995) Development of a quantification methodology for polychlorinated biphenyls by using Kanechlor products as the secondary reference standard. Fresenius J Anal Chem 352:261-267

Burgin DE, Diliberto JJ, Derr-Yellin EC, Kannan N, Kodavanti PRS, Birnbaum LS (2001) Differential Effects of two lots of Aroclor 1254: Congener-specific analysis and neurochemical end points. Environ Hlth Perspect 109: 1163-1168

Frame GM, Wagner RE, Carnahan JC, Brown Jr. JF, May RJ, Smullen LA, Bedard DL (1996) Comprehensive, quantitative, congener-specific analyses of eight aroclors. Chemosphere 33: 603-623

Kamops LR, Trotter WJ, Young SJ, Smith AC, Roach JAG, Page SW (1979) Separation and quantitation of 3,3',4,4'-tetrachlorobiphenyl and 3,3',4,4',5,5'-hexachlorobiphenyl in Aroclors using Florisil column chromatography and gas liquid chromatography. Bull Environ Contam Toxicol 23:51-56

Kannan N, Tanabe S, Wakimoto T, Tatsukawa R (1987) Coplanar PCBs in Aroclors and Kanechlor mixtures. J Assoc Off Anal Chem, 70:451-454
Kannan N (2000) Non- and mono-*ortho* chlorinated biphenyls. In: J.Paasivirta (ed) The Handbook of Environmental Chemistry, vol 3. Springer-Verlag, Berlin, p 127
Kannan N, Yim UH, Hong SH, Shim WJ, Li DH, Oh JR (2005) PYE [2-(1-pyrenyl)ethyldimethysilylated silica] column HPLC and HR-GC- (micro) ECD in the accurate determination of toxic co-planar PCBs and Polybrominated diphenyl ethers (PBDEs). Bull Korean Chem Soc 26:529-536
Safe S (1987) Polychlorinated Biphenyls (PCBs). In: Safe S, Hutzinger O (Ed) Mammalian and Environmental Toxicology, vol 1, Springer-Verlag, Berlin, p 133
Safe S (1994) Polychlorinated-biphenyls (PCBs) - Environmental-Impact, Biochemical and Toxic Responses, and Implications for Risk Assessment. Crit Rev Toxicol 24:87-149
Schulz DE, Petrick G, Duinker JC. (1989) Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. Environ Sci Technol 23:852-859