AN INVESTIGATION OF AROCLOR MIXTURES AND THEIR DIOXIN-LIKE PCB (DLPCB) CONGENER CONTRIBUTIONS

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Introduction:

Characteristics such as stability, good insulating properties and low flammability, initially made PCBs commercially popular and valuable and resulted in their mass production. From 1929 until 1978 (in North America and Western Europe) and the early 1990s (in Eastern Europe & Russia), PCBs were produced as technical mixtures for use in transformers, capacitors, and electrical equipment etc. [1,2]. Furthermore, PCBs were also found to inadvertently be produced as by-products in a wide variety of chemical processes containing chlorine and hydrocarbon sources such as in the manufacturing of chlorobenzenes, vinyl chloride, various pigments and adhesives. However, these particular PCB by-products typically do not resemble the technical mixtures and therefore cannot be identified correctly using Aroclor matching techniques[1]. PCBs consist of a total of 209 isomers and congeners and are often classified and quantified based on the commercial product (e.g. Aroclors) that they most resemble. Due to the complexity in resolving all 209 PCBs, some countries have congener lists for regulatory evaluation based on occurrence of specific representative congeners that are based on their higher relative concentrations in the technical mixtures, ability to bio-accumulate and levels in the environment [3]. Over the last 2-3 decades, environmentalists have raised concerns regarding PCBs, especially since they have been found to be quite persistent, ubiquitous, extremely stable and toxic. PCBs are known to bio-accumulate in adipose tissue and have been identified with different toxicological endpoints including dioxin-like and non-dioxin-like [4]. It is the dioxin-like behaviour (a planar molecule with dimensions of ≅ 3 x 10 Δ) that sets the criteria for Dioxin-like toxicity of PCBs [4,5]. PCBs belong to a group of halogenated aromatic hydrocarbons (HAHs), including 2,3,7,8-TCDD and other similar structures, all of which are known to invoke a response through the aryl hydrocarbon receptor (AhR). The degree of response (i.e. ability to interact and activate the Ah receptor) is proportional to the Toxic Equivalency Factor (TEF) [4]. The WHO (World Health Organization) has identified 12 of the 209 congeners as having dioxin-like activity and assigned TEF values to these congeners relative to the 2,3,7,8 -tetrachlorodibenzo-p-dioxin (TEF=1). The 12 dioxin-like PCBs (DLPCBs) consist of 4 coplanar (BZ#: 77, 81,126,169) and 8 mono-ortho substituted congeners (BZ#: 105,114,118,123,156,157,167 and 189) [6]. The dioxin-like behaviour of these 12 permit TEQs (Toxic Equivalent Quantity = Σ (TEFs x Concentration)) to be calculated, resulting in a more clearly defined and reproducible endpoint than with Arolcor matching quantification. The following is an investigation of various Aroclor mixtures; 1016,1221,1242,1248, 1254, and 1260 using PCB 118 as an indicating marker. Eleven of the 12 DLPCBs were identified and quantified in the above list of Aroclor mixtures. The composition of 10 DLPCBs were normalized relative to PCB 118, which has the largest contribution in all cases.

Experimental

Standards

The DLPCBs in the various Aroclor mixtures were quantified by isotope dilution with $^{13}C_{12}$ labelled standards. DLPCB standards were purchased from Wellington Laboratories Inc. (Guelph, Canada) and the Aroclor mixtures were purchased Monsanto (USA).

Sample Preparation

The concentration of DLPCBs in Aroclor mixtures being investigated were determined from 300 ng/mL solutions in iso-octane. Exactly, 1.0mL of each Aroclor solution was fortified with 12 $^{13}C_{12}$ –Labelled –DLPCB surrogates prior to chromatographic cleanup. The 4 coplanar DLPCBs were isolated from the mono-ortho DLPCBs using a 3 stage column cleanup (silica/alumina/carbon). Complete details of cleanup methodology and analysis are listed in MOE Method E3418 [7].

Instrumentation

All analyses were performed using HRGC/HRMS. An HP6890 Plus gas chromatograph (GC) was interfaced to a VG Autospec High Resolution mass spectrometer. An Rtx-5 column; 60m X 0.25mm X 0.25 μm (Restek Corp. USA) was used for chromatographic separation and the GC-HRMS system was tuned to 10,000+RP (10%valley definition). The coplanar PCBs were analyzed using the PCDD/F GC/MS experiment and the mono-ortho PCB fraction was analyzed separately using a different GC/MS experiment as described in Table I. The two fractions are analyzed separately to avoid any interferents and minimize possible coelutions. In MOE Method E3418, the coplanar PCBs are analyzed with the PCDD/Fs fraction to reduce or eliminate coelution from other congeners which occur on a 5% phenyl GC column (see below).

PCDD/F & Coplanar Fraction (Coplanar PCBs)	Mono-Ortho PCB Fraction Co-eluting Congener (s)
77	110
81	87
126	129, 178

The majority of the coeluting congeners end up in the mono-ortho fraction allowing more accurate quantification.

Table I HP6890 Plus GC Run Conditions MOE Method 3418

Oven Temperature Program	PCB_PCDD GC Experiment (For PCDD/F and Coplanar PCBs)	PCB_MOE GC Experiment (For DLPCBs Only)
Initial Conditions	100°C hold 1 minute	150°C hold 1 minute
1st Ramp Rate	100°C to 200°C at 40°C/ minute	150°C to 200°C at 5°C/ minute
2nd Ramp Rate	200°C to 235°C at 3°C / minute	200°C to 235°C at 3°C / minute
Hold Time	235°C hold 10 minutes	235°C hold 10 minutes
3rd Ramp Rate	235°C to 300°C at 6°C / minute	235°C to 300°C at 12°C / minute
Hold Time	300°C hold until 2 minutes after OCDD elutes	Hold 1 minute

Results and Discussion

Concentrations for the DLPCBs detected in each of the Aroclor mixtures are reported as (µg/g) in Table II. Results for the non-detected congeners are indicated by a value of less than (<) detection limit. A TEQ value is given for DLPCB contribution in each of the Aroclor mixtures.

From Table III, the TEQ range for the Aroclors are as follows; 1016<1221<1242<1260<1248<1254. The results listed below indicate that Aroclor 1254, containing mostly Cl_4 through to Cl_8 congeners, has the highest TEQ value of the six technical mixtures. 1254's high TEQ is attributed to elevated contributions from PCB 126 (Cl_5) and PCB 189 (Cl_7), both of which have a substantial TEF value significantly contributing to the overall TEQ. None of these 6 Aroclor mixtures were found to contain PCB 169 at the reported detection limits. Aroclor 1016 was found to have the lowest TEQ value and can be attributed to the fact that Aroclor 1016 contains very few Cl_5 through to Cl_8 substituted congeners.

Table IV lists the DLPCBs contributions based on percentage relative to PCB 118. The following is a summary of the general characteristics of each Aroclor mixture with respect to PCB 118. The comparison of indicating congeners (**in bold**) relative to 118 is presented below in Table II. These congeners are examined due to their differing but distinct contributions in each of the technical mixtures.

Table II

Aroclor	Relative Ratios
Aroclor 1016	118 > 105 > 156 > 77 > 167 ≅ 114
Aroclor 1221	118 > 105 > 156 >**123**>**167** > **77** >114>189
Aroclor 1242	118 > 105 > 77 > 114 >156 ≅123>189
Aroclor 1248	118 > 105 > 77 > 114 >123 >156 >189
Aroclor 1254	118 > 105 > **156** >**167** >123 >189>77
Aroclor 1260	118 > **156** > 105 > 123 >167 ≅ **189** >77

Aroclor 1260 is distinctive from the other 5 mixtures in that it has a highest relative value of PCB 156 and 189 and that PCB 156 is higher in concentration than 105 by a factor of 2½. Similarities exist between Aroclor 1242 and 1248. Both have similar relative concentration ratios for both PCB 114 and 123, however they differ in that PCB 77 in Arolcor 1242 is higher relative to 1248 by a factor of 2. Aroclors 1016, 1221, and 1254 are similar in that 118>105>156>77. Aroclor 1254 is distinct from the other two in that it has a higher relative concentration of PCB 156 and 167. It is also notably different in that it has very little of PCB 77 and 189 (<1%) which is due in part to1254 having greater levels of congeners with higher degrees of chlorination, Cl_4 through to Cl_7 than 1242 and 1248. Aroclors 1016 and 1221 have similar contributions of 105 and 156 relative to 118. However, 1221 has almost double the contribution of PCB 77 & 167 relative to Aroclor 1016. Aroclor 1221 contains PCB 123 whereas in 1016 it was not detected.

Conclusion:

Aroclor mixtures contain considerable levels of DLPCBs. Particular patterns of these congeners can be identified and attributed as being characteristic of a specific Aroclor.

TABLE III DLPCB LEVELS (µg/g) FOUND IN AROCLORS

PCB Congener	TEF (WHO)	Aroclor 1016	Aroclor 1221	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
PCB 81	0.0001	<7	<3	43	80	11	<2
PCB 77	0.0001	9.3	47	1300	3000	200	63
PCB 123	0.0001	<7	100	150	730	2500	2300
PCB 118	0.0001	160	500	4000	21000	100000	6300
PCB 114	0.0005	8.3	13	210	1100	2400	87
PCB 105	0.0001	83	190	2600	14000	43000	1500
PCB 126	0.1	<10	<7	14	73	57	<10
PCB 167	0.0001	8.7	53	50	230	6000	1200
PCB 156	0.0005	16	67	130	500	14000	4000
PCB 157	0.0005	<10	3.7	18	100	2800	280
PCB 169	0.01	<3	<3	<7	<3	<3	<7
PCB 189	0.001	<3	8.0	3.7	12	400	1100
TEQ (µg/g)		0.038	0.14	2.4	12	31	4.4

TABLE IV ***DLPCB Composition Based on Percentage Relative to PCB 118***

PCB Congener	Aroclor 1016	Aroclor 1221	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
PCB 81	<4	<0.6	1.1	0.38	0.011	<0.03
PCB 77	5.8	9.4	33	14	0.20	1.00
PCB 123	<4	20	3.8	3.5	2.5	37
PCB 118	100	100	100	100	100	100
PCB 114	5.2	2.6	5.3	5.2	2.4	1.4
PCB 105	52	38	65	67	43	24
PCB 126	<6	<1	0.35	0.35	0.057	<0.2
PCB 167	5.4	11	1.3	1.1	6.0	19
PCB 156	10	13	3.3	2.4	14	63
PCB 157	<6	0.74	0.45	0.48	2.8	4.4
PCB 169	<2	<0.6	<0.2	<0.01	<0.01	<0.1
PCB 189	<2	1.6	0.093	0.057	0.40	17

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