

PCB CONGENERS IN USED TRANSFORMER FLUIDS; A COMPARISON OF AROCLOR TEQS FROM THREE STUDIES.

Blye D^{1*}, Goodman N², Hart J³, Michell M¹, Tondeur Y³, Tordini A¹, Vining B³

¹Environmental Standards, Inc., PO Box 810, Valley Forge, PA, USA; ²Electric Power Research Institute, 3420 Hillview Avenue, Palo Alto, CA, USA; ³SGS Environmental Services, 5500 Business Drive, Wilmington, NC, USA

Introduction

Polychlorinated biphenyls (PCBs) were used extensively in North America and Europe as dielectric and thermal insulating fluids in electrical equipment from about 1929 until the mid- to late-1970s. After this period, further production was banned by most governments on both continents due to concerns about the toxicity and bioaccumulative properties of the chemicals. PCBs were manufactured and sold as a wide range of commercial formulations, of which the most common were the Aroclors (Monsanto trade name). A number of Aroclor products were manufactured, each having different dielectric, physical, chemical, and toxicological properties controlled by the distribution of the individual PCB molecules (congeners) present in each. There are 209 possible PCB congeners, containing from one to 10 chlorines on the biphenyl molecule. New uses of PCBs are banned in the United States; however, PCB-containing fluids are still present in in-use electrical equipment such as transformers, although levels have declined over time.

The World Health Organization (WHO) has identified 12 PCB congeners (WHO PCBs) with toxicity characteristics similar to those of polychlorinated dibenzo-*p*-dioxins (PCDDs) and assigned each a “toxicity equivalence factor” (TEF) that relates its toxicity to that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD)¹. These dioxin-like PCBs (DLPCBs) are non-ortho-substituted, “coplanar” PCBs. In a pure Aroclor, summing the TEFs for all of the WHO PCBs in the material would provide a toxic equivalent (TEQ), relating the overall toxicity of the Aroclor to 2,3,7,8-TCDD.

Two previous data sets of DLPCBs in Aroclors (EPA 2003 and Rushneck 2004) reported low levels of two of them (PCB-126 and PCB-169) in some Aroclors, but the amounts and resulting TEQs differ substantially^{2,3}. The EPA 2003 data set represents a compilation of PCB congener data from previous studies, whereas the Rushneck 2004 data set was based on analysis of Aroclor reference standards. The objective of this study was to measure the concentrations of PCB congeners in used PCB transformer fluids, to better understand the toxicity of the materials as represented by their TEQs. The study was designed to permit a direct comparison of TEQs for Aroclor 1242, Aroclor 1254 and Aroclor 1260 to TEQs for the same Aroclors based on the data sets from EPA 2003 and Rushneck 2004. Since the EPRI study used samples of used transformer oil while the other studies provide data on pure Aroclor standard material, this study also provides information about whether the TEQ of an Aroclor increases or decreases with normal transformer fluid use. Finally, the study was intended to provide a better understanding of the congener distribution of Aroclor mixtures, which may allow future determination of risk associated with PCB-containing materials using less expensive analytical methods.

Materials and methods

Fifteen archived transformer fluid samples from a previous EPRI study that used high-resolution gas chromatography/low-resolution mass spectrometry (HRGC/LRMS) were reanalyzed by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The samples consisted of nine fluid (likely chlorinated benzenes, although the matrix was not determined) and six mineral insulating oil (oil) samples encompassing the range of Aroclor formulations and concentrations in the previous study.

Each of the samples was prepared by a dilution technique and analyzed using modified EPA Method 1668C for determination of PCB congeners by HRGC/HRMS⁴. The analyses were conducted by SGS Environmental Services, located in Wilmington, NC, USA. To quantify DLPCBs in the presence of much higher levels of non-DLPCB congeners, two separate GC/MS analyses were initially planned for every sample. An analysis for the full 209 PCB congeners (including the 12 WHO PCBs) was performed using an SPB-Octyl GC column. Oil samples underwent a cleanup using a strong anion exchange sorbent to remove mineral oil prior to this analysis. An analysis for the 12 WHO PCBs was performed using a DB-1 GC column after passing the sample through

the method-specified carbon fractionation column to separate the DLPCBs from the rest of the PCB congeners. However, it was discovered that this separation was not complete, even after a second pass through the fractionation column: the data showed clear indications of non-DLPCB congeners remaining after separation. As a result, a third analysis for the 12 WHO PCBs was performed on the SPB-Octyl column using the sample extract that underwent carbon fractionation.

One other modification to EPA Method 1668C was made for this project. For some samples, a set of alternate mass ions with lower responses were used for select congeners to provide a wider dynamic range. This allowed high concentration and low concentration congeners to be measured in the same run while avoiding quantitation errors associated with saturating the MS detector.

Results and discussion

Based on the congener distribution in the samples, three samples were identified as Aroclor 1242, four samples were identified as Aroclor 1254, and seven samples were identified as Aroclor 1260. One sample appeared to be a mixture of approximately 60:40 of Aroclors 1254 and 1260. For 10 of the 15 samples, the total PCBs measured in this study were similar or slightly lower than the concentrations reported in the previous EPRI study (based on HRGC/LRMS). Four fluid samples had significantly lower PCBs than previously reported and one oil sample had significantly higher PCBs. The reason for this discrepancy is not known, but may be due to sample preparation, analytical procedures or sample heterogeneity.

TEQs were calculated for each sample (Table 1). The TEQs for the fluid samples ranged from 0.04 µg/g (with zero used for not-detected results) or 0.1 µg/g (with the estimated detection limit [EDL] used for not-detected results) up to a maximum of 10 µg/g. The TEQs for oil samples were lower (0.0003 [not-detected = 0] or 0.0008 [not-detected = EDL] to 0.01 µg/g), which is consistent with the fact that concentrations of both total PCB and WHO PCBs were higher in the fluid samples. The concentration of PCB-126 in the study samples was the primary driver for determining TEQ.

Table 1 – TEQ Comparisons of Study Samples to Published Aroclor Data Sets (TEQs calculated using 2005 WHO TEFs)

EPRI ID	Matrix	Aroclor	TEQ, ND=0 (µg/g)	TEQ, ND=EDL (µg/g)	Rushneck ¹ TEQ, ND=0 (µg/g) ³	Rushneck TEQ, ND=EDL (µg/g) ³	EPA ² TEQ, ND=0 (µg/g) ^{3,4}
318237	Fluid	1254/1260	3	3	2	2	70
6001755	Fluid	1260	0.5	0.5	0.2	0.3	70
6535943	Fluid	1260	0.04	0.2	0.07	0.07	20
6537275	Fluid	1260	0.04	0.2	0.06	0.06	20
73D1699	Fluid	1242	5	5	4	4	5
B983498	Fluid	1260	0.1	0.1	0.04	0.04	10
F-958020	Fluid	1242	2	2	2	2	3
G-855504	Fluid	1254	10	10	4	4	50
YDR-76131	Fluid	1254	2	2	2	2	30
4151019	Oil	1260	0.006	0.006	0.006	0.006	2
4925883	Oil	1254	0.006	0.006	0.009	0.009	0.1
4925886	Oil	1254	0.004	0.004	0.01	0.01	0.2
6625586	Oil	1260	0.0009	0.005	0.003	0.004	1
77V2535	Oil	1242	0.01	0.01	0.007	0.007	0.01
F591300-66P	Oil	1260	0.0003	0.005	0.0009	0.001	0.3

¹ Rushneck (2004); ² EPA (2003); ³ TEQs are concentration –corrected based on total PCB in the individual samples; ⁴ EDL Values not available for EPA study.

TEQs for each Aroclor identified in the samples were compared to concentration-corrected TEQs calculated from the data sets from EPA 2003 and Rushneck 2004. Concentration correction was necessary since EPA 2003 and Rushneck 2004 studied “pure” Aroclor standards while the samples for this study are often diluted with oil or other fluids. The adjusted DLPCB congener concentrations were then multiplied by the 2005 WHO TEFs and summed to obtain the concentration-corrected TEQ for that Aroclor. TEQ comparisons were conducted with not-detected concentrations set to zero and to the EDL. Figures 1 and 2 present the TEQ comparisons for the fluid samples and oil samples, respectively, with the not-detected concentrations set to zero. The EPRI analyses are labeled in these figures as the SGS Study.

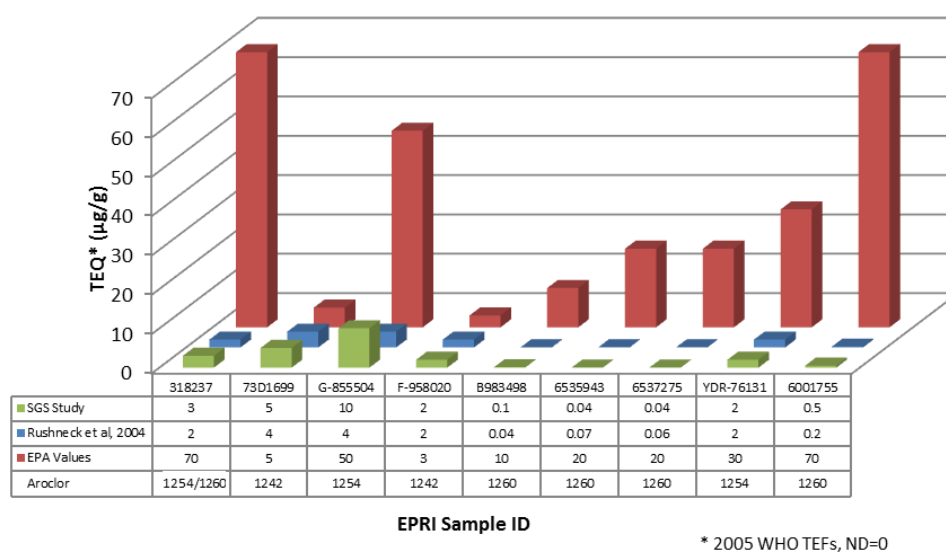


Figure 1 - Comparison of TEQs by sample - fluid samples, concentration-corrected; SGS, Rushneck (2004) and EPA, (2003) values, ND=0

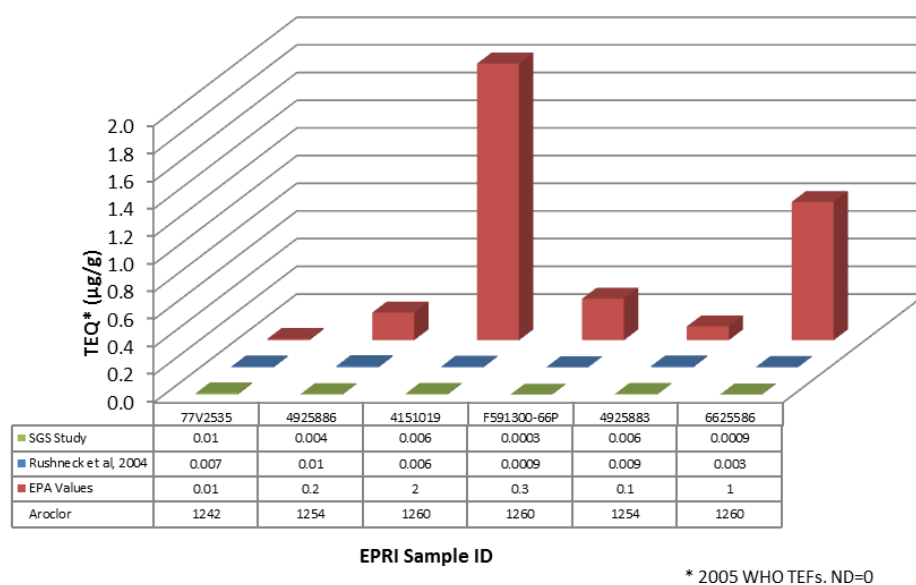


Figure 2 - Comparison of TEQs by sample - oil samples, concentration-corrected; SGS, Rushneck (2004) and EPA, (2003) values, ND=0

The data presented in Figures 1 and 2 clearly indicate:

- For Aroclor 1242, TEQs compared well across all three data sets.
- For Aroclors 1254 and 1260, the EPA 2003 data set TEQs are significantly higher than the Rushneck 2004 and current study TEQs.
- The current study TEQs for Aroclors 1254 and 1260 are comparable to the Rushneck 2004 TEQs, but are higher for 6 of the 15 samples (not-detected = zero).

Comparisons of TEQs by sample with the not-detect values set to the EDL show similar results to the not-detect values set to ND. A statistical comparison of the TEQs for the study data set to the Rushneck 2004 and EPA 2003 data was performed for each Aroclor type. Prior to the statistical evaluation, the study data were normalized to represent TEQs as pure Aroclors, for direct comparison to the two reference data sets. Statistical comparisons were conducted with not-detected concentrations set to zero and to the EDL. The results of these statistical comparisons also show good comparison of the three data set TEQs for Aroclor 1242 and again show TEQs for EPA 2003 to be high relative to this study data and Rushneck 2004. The statistical comparisons show comparability between the Aroclor 1254 and Aroclor 1260 TEQs for this study data and Rushneck 2004.

The explanation for the extremely high TEQ in the EPA 2003 data set is that the concentration of PCB-126 is extremely high in that data set relative to the concentrations observed in the current study and Rushneck 2004.

The EPA 2003 TEQs for Aroclor 1254 and 1260 greatly exceed the TEQs from Rushneck 2004 as well as the upper bound 95% confidence interval and interquartile range TEQ for the EPRI study data. Based on the results of this study and the Rushneck 2004 data set, the EPA 2003 congener data overestimate the dioxin-like toxicity of Aroclors 1254 and 1260.

When normalized for the total Aroclor concentration in each sample, the EPRI TEQs are similar, on average, to the Rushneck 2004 TEQs, which were calculated using pure Aroclor standards. This supports a conclusion that the TEQs for transformer fluids do not change with use compared to the original Aroclor, i.e., there is no consistent increase in the most toxic congeners in terms of weight percent of the Aroclor mixture.

When normalized for the total Aroclor content in each sample, the three data sets produce similar TEQs for Aroclor 1242, due to the absence of the most toxic DLPCB congeners in that mixture.

The finding that the EPA Method 1668C recommended procedure for separating DLPCBs from non-DLPCBs is inadequate when applied to samples of the type analyzed in this project is significant. The implication is that concentrations of some of the DLPCB congeners (including those contributing most to the TEQ of Aroclors 1254 and 1260) could potentially be biased high. Mass fragments that result from the loss of one or two chlorines from higher-chlorinated PCB congeners can interfere with the response of a co-eluting or closely-eluting PCB congener that has one or two fewer chlorines. It is possible that historical studies of PCB-containing fluids containing these Aroclors were also impacted by the identified interferences, and that data from previous studies that used the separation column are potentially biased (likely a high bias). The magnitude of the bias due to interference from non-DLPCBs was not determined in our study, but should be investigated further.

Acknowledgements

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References:

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