POLYCHLORINATED BIPHENYLS AND PCDD/DFs IN KANECHLOR TECHNICAL PCB FORMULATION FROM JAPAN BY ISOTOPE DILUTION METHOD USING HRGC-HRMS

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Introduction

Polychlorinatedbiphenyls (PCBs), are persistent compounds with high thermal stability, chemical stabilities and excellent dielectric properties. Because of these physical and chemical properties, PCB preparations have been used for diverse technical appliances, particularly as dielectric fluids in industrial operations, heat transfer applications and plasticizers. There exists a wide range of technical PCB formulations under different trade names such as Kanechlor and Santotherm (in Japan), Clophen (in Germany), Aroclor, Pyranol, Interteen, Chloretol, Dyknol, Noflamol, and Hyvol (in United States), Sovol (in Russia), Chlorofen (in Poland), Phenoclor and Pyralene (in France), Fenoclor and Apirolio (in Italy), Delor (in Czechoslovakia). Few studies have put forward the levels of PCBs and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/DFs) in some technical mixtures and estimated the toxic equivalent quantity contributed by these compounds[1-5].

In the present investigation, a new standard material that contains mono- through deca-chlorinated biphenyls was proposed by our team[5] and synthesized in Wellington Laboratories, Canada were analyzed in order to determine PCBs by isotope dilution technique using high-resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS). Earlier we reported contamination profiles of PCBs in transformer oil from Japan and various technical PCB formulations from Japan, Germany, USA, Russia and Poland with particular reference to mono- through decachlorobiphenyls for the first time[5]. There were limited number of samples, however, for the analyses of Kanechlor, which was supposed to be deviation of congener composition according to the production lots. In the present study, we analyzed more samples of Kanechlor technical formulations for PCBs, PCDD/DFs and their TEQs and compared their levels to our earlier attempt. The isomer/congener-specific analysis, levels of dioxin-like PCBs also calculated and discussed.

Materials and Methods

Kanechlor Mixture and Standard Materials: In general, commercial PCB standards were not mixed and available individually and or mixture of only few congeners. Only recently, commercially available native and isotope labeled individual PCB standard mixtures (from mono- through deca- chlorobiphenyls) was developed by us and synthesized in Wellington Laboratories at Canada[5]. These standard solution mixtures contain predominant PCB congener in each chlorine degree in commercial PCBs and co-planar PCBs. Briefly, the native standard solutions with IUPAC number and its corresponding internal standard and its concentrations will be reported elsewhere. The commercial PCB such as Kanechlor was obtained from different laboratories with original conditions (without opening of seal or mix up with any solvents) due to the strict PCB regulation in Japan. Each six or seven number of Kanechlor (except KC-200 and KC-1000 that is maximum of 2 each) was obtained in different laboratory. Individual analyses were performed from 1 gram of the Kanechlor samples. The Kanechlor formulation was initially dissolved in *n*-hexane containing 10% toluene. The solutions were diluted with n-hexane for further analysis. The 22 $^{13}C_{12}$-labeled PCB standards were spiked prior to the major PCB analysis along with co-planar PCB analysis from the aliquot of the diluted solution. Major component PCB congener analysis was conducted directly from the diluted solutions. In addition, from aliquot of the same solution, 19 $^{13}C_{12}$-labeled PCDD/DFs and 14 co-planar PCBs standards were spiked in and then subjected in to sequence of alumina and carbon column cleans up. In this fractions both PCDD/DFs and non-ortho PCBs were analyzed after inclusion of syringe spikes accordingly.

HRGC/HRMS Analysis: For quantification and identification, HRGC (HP6890, Hewlett Pacakard)/ -HRMS (Autospec Ultima, Micromass) fitted with DB-5MS column (60 m, 0.32 mm i.d., 0.25 um film thickness, J&W Scientific) was used. The temperature was programmed with the following order; 150°C for 1-min. (20°C/min.) to 185°C, (2°C/min.) to 245°C, hold for 3-min., (6°C/min.) to 290°C. The interface temperature was programmed as 5-10°C higher than the maximum value of each temperature program. The MS was operated in SIM mode for each congener group at the electron impact ionization energy was 35-40eV. The MS was operated at a resolution >12,000 in an attempt to reduce the interference of fragment ions from higher chlorinated PCBs with lower chlorinated congeners. Two ions were monitored for each congener group. Individual congeners were identified by comparison to reference standard solutions and published data.

Results and Discussion

The homologue pattern of Kanechlor obtained were about 90% (Figure 1). Remaining 10% of PCBs might be loosed during dilutions of the Kanechlor mixture and also the predominant standard solution used might have further impact.

The lower levels of KC-1000 suggest the inclusion of trichlorobenzene and pentachlorobiphenyls. The homologue profiles revealed the domination of TrCBs in KC-200 and 300, TeCBs in KC-400, PeCBs and HxCBs in KC-500, HxCBs and HpCBs in KC-600. The MoCBs have considerable contribution in KC-200.

The PCB levels in these Kanechlor mixtures varied with different samples although the technical grade is same. This implied the lot (production) difference of PCBs.

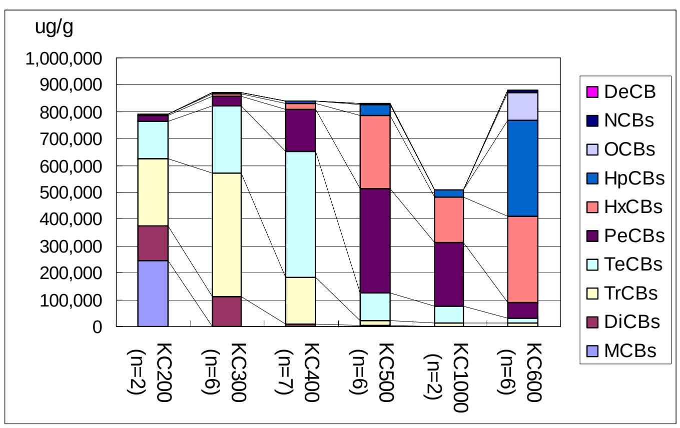

Figure 1. Homologue composition of Kanechlor technical PCB.

It is worth indicating that among 27 major PCB congeners their contribution found to be 50% to the total PCBs concentrations in Kanechlor standards (Figure 2). When calibration standard mixtures results in-corporated all the major PCB congeners were found in Kanechlor standard formulations with considerable confidence.

The averaged concentrations of PCDDs and PCDFs in Kanechlor samples were shown in Figure 3. When compare to the PCBs concentrations, the levels of PCDDs and PCDFs were 90-fold lesser with minimum of about 3 ppm and maximum of about 31 ppm. The TeCDFs were more than 60% contribution in KC-200, 300 and 400. The PeCDFs + TeCDFs were equivalently contributed (40%), and HxCDFs were 40% in KC-500 and KC-1000. The HxCDFs, HpCDFs, OCDF was prevalent (>75%) PCDF congeners in KC- 600. The contribution of PCDDs was very low with the presence of only TeCDD in KC-500 and 600 samples. Again the concentrations of PCDD/DFs varied between lot numbers. Composition of PCDD/DFs in between the same KC numbers was also considerably varied.

The concentrations of co-planar PCBs comprised with 1% to 10% (Figure 4). The 1-% levels were noticed in KC-200 while KC-500 showed maximum. The greater levels in KC-600 probably due to the inclusion of two di-ortho PCBs and thus without these two PCBs the concentrations levels of WHO co-planar PCBs would have been about less than 2%. It is prominent that PeCB-118, PeCB-105, HxCB-156 and TeCB-77 were prevalent co-planar PCBs in all Kanechlor samples. The congener pattern of co-planar PCBs was predominated by TeCB-77/PeCB-105 and 118 in KC-200 through KC-400.

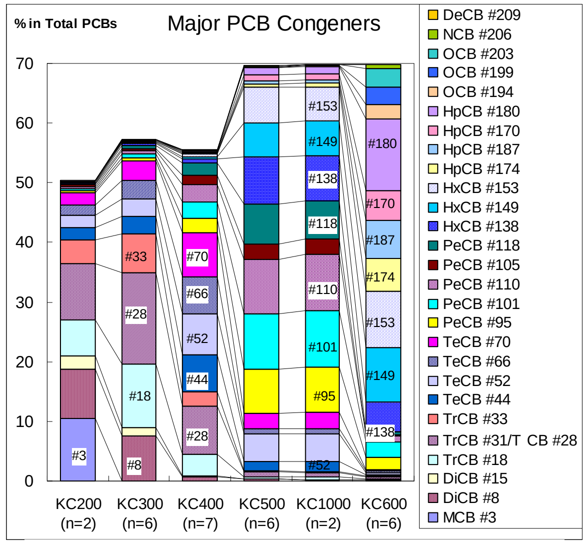

Figure 2. Major PCB congeners profile in Kanechlor technical PCB

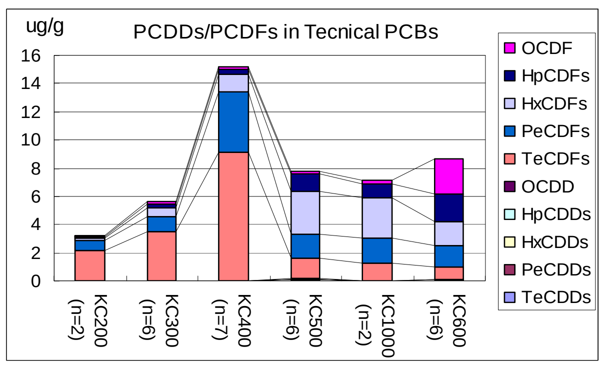

Figure 3. PCDD/DFs homologue profile in Kanechlor technical PCB

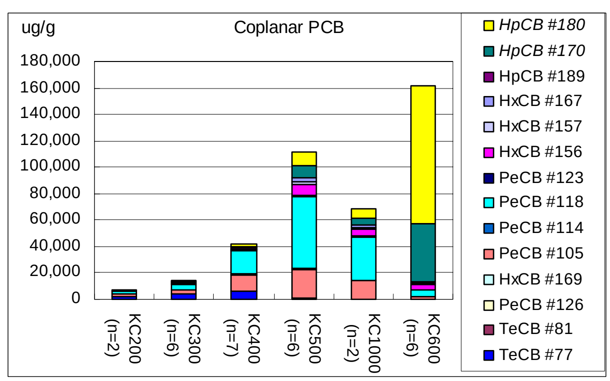

Figure 4. co-planar PCB composition in Kanechlor technical PCB. (including di-ortho PCBs)

In KC-500, 600 and 1000 the HxCB-156 replaced TeCB-77. The influence of di-ortho PCBs in KC-600 was predominated with contribution of HpCB-180 and 170. Other than these two di-ortho PCBs, the PeCB-118 seems to predominant co-planar PCB in KC-600 mixtures.

The TEQ concentrations of PCDDs, PCDFs, non-ortho PCBs and mono-ortho PCBs have shown in Table 1. The TEQ levels varied from 1.5 to 18 ppm(ug-TEQ/g) with non-ortho PCBs predominated (60-70% to the total TEQ) in KC-200, 300 and 400. Particularly PeCB-126 contributed more than 50% of the TEQ. Mono-ortho PCBs were major accumulants (85%) in KC-500, 600 and KC-1000. Especially PeCB-118 and HxCB-156 contributed more than 60%. Apart from the PCB, the TEQ concentration levels of PCDFs varied from 0.029 to 0.63 ppm(ug-TEQ/g) and the TEQ contribution of PCDFs were low. The 2378-TeCDF, 23478-PeCDF, 123478-HxCDF and 234678-HxCDF also contributed to the TEQ with less than 8 % in all the samples. Particularly PCDDs noticed ND to 2 ppb(ng-TEQ/g) in any of Kanechlor samples as TEQ contributor and their influence in this regard could negligible.

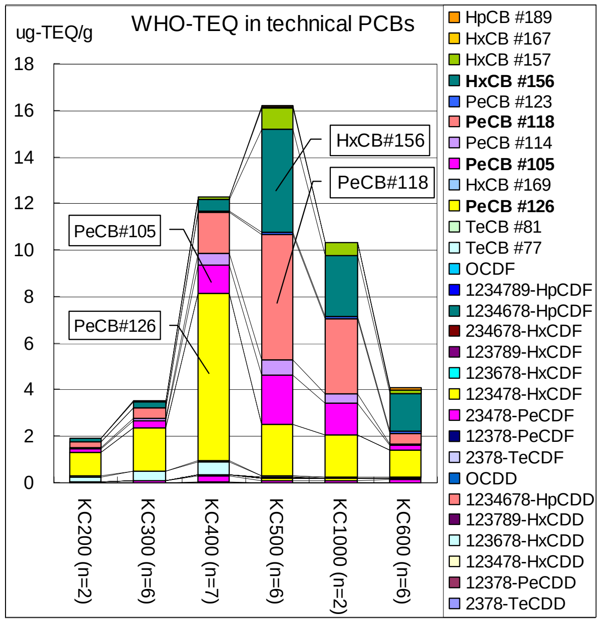

Figure 4. TEQ concentrations of PCDD/DFs, Co-planar PCBs in Kanechlor technical PCB.

The variation of TEQ found to be different at 3-times maximum. This is the first report of toxic PCBs and PCDD/DFs in several Kanechlor technical PCB formulations from Japan by isotope dilution technique using HRGC-HRMS.

Table1. WHO-TEQ in technical PCBs (averaged data and range) (unit ng-TEQ/g)

	KC200	**KC300**	**KC400**	**KC500**	**KC600**	**KC1000**
Total PCDD TEQ	0	0	0.0076 (0-0.052)	0.60 (0-2.0)	0.11 (0-0.46)	0.01 (0-0.2)
Total PCDF TEQ	67 (65-69)	110 (29-150)	350 (62-630)	230 (100-370)	220 (150-270)	220 (210-240)
Non-ortho PCBs TEQ	1,200 (1,100-1,400	2,300 (1,100-2,900)	7,800 (3,300-9,300)	2,300 (1,800-3,000)	1200 (260-4,400)	1,900 (1,800-1,900)
Mono-ortho PCBs TEQ	600 (570-630)	1200 (370-1,500)	4,100 (2,100-5,200)	14,000 (12,000-15,000)	2,700 (1,800-3,200)	8,200 (7,600-8,900)
Total TEQ	**1,900 (1,700-2,100)**	**3,500 (1,500-4,500)**	**12,000 (5,500-15,000)**	**16,000 (15,000-18,000)**	**4,100 (3,100-7,700)**	**10,000 (9,600-11,000)**

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