COMPOSITION AND CONTENT OF CBs, CDFs AND CNs OF CLOPHEN A60

Sachi Taniyasu[1], Jerzy Falandysz[2], Agnieszka Świętojańska[2], Magdalena Flisak[2], Yuichi Horii[1], Nobuyasu Hanari[1], Nobuyoshi Yamashita[1], Gert Petrick[3]

[1]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba
[2]Department of Environmental Chemistry & Ecotoxicology, University of Gdańsk, Gdańsk
[3]Institute for Marine Research, University of Kiel, Kiel

Introduction

Chlorobiphenyls (CBs; polychlorinated biphenyls, PCBs) starting from the year 1929 periodically become increasingly important and highly welcomed industrial compounds but further claimed as globally diffused environmental, food and human body contaminants. Those compounds, when contained in any man-derived product at concentration exceeding 50 mg/kg nowadays are considered as hazardous waste which should be safely disposed world-wide. Chlorobiphenyls form very complex mixtures with tens of congeners which are found and quantified as principal constituents in an original technical CB formulations manufactured. The technical CB mixtures such as Aroclor, Kanechlor or Delor series usually contain by-side trace constituents and including dioxin-like highly toxic substances such as chlorodibenzofurans (CDFs; polychlorinated dibenzofurans, PCDFs) and chloronaphthalenes (CNs; polychlorinated naphthalenes, PCNs), while no chlorodibenzo-p-dioxins (CDDs; polychlorinated dibenzo-p-dioxins, PCDDs) could be detected. An introduced concept "to take a short cut" in analysis and assessment of the total CBs content of the sample includes measurement of selected "indicator" congeners, i.e. IUPAC Nos. 28, 52, 138, 153 and 180. The state-of-art approach when related to CBs environmental issues is to know and understand composition, absolute concentrations, environmental and body distribution, and elimination rates of all congeners constituting or contaminating the sample.

Clophen A60 is one of the several technical chlorobiphenyl formulations of the Clophen family manufactured in the past by the Bayer AG (former I.G. Farben) in Germany [1]. Congener-specific data on CB composition of Clophen A60 as well as of Clophen A30, A40, A50, and T64 have been a subject of several earlier investigations [2-12]. In this report qualitative and quantitative data are presented on chlorobiphenyl constituents of technical Clophen A60 and on it's some by-side impurities such as highly toxic CDDs, CDFs and CNs after HRGC-LRMS, 2D-HPLC and HRGC-HRMS separation, detection, identification and quantification. 101 peaks representing 116 CB congeners were quantified in Clophen A60, and most contributing were CBs nos. 138, 153, 134/144/149 and 180 with 15.4, 12.3, 8.2 and 6.5 %, respectively. Amongst of CN homologue

groups the profile in descending order followed by hepta-, hexa-, octa- and penta-CNs with 56, 26, 16 and 2 %, respectively.

Materials and Methods

A sample of the technical Clophen A60 formulation (gift from Dr. U. Bauer, Germany) was dissolved in *n*-hexane. Detection and quantification of chloronaphthalene, chlorodibenzofuran and chlorodibenzo-*p*-dioxin constituents as well as of non-*ortho*-coplanar chlorobiphenyls in Clophen A60 was accomplished after two-dimensional high performance liquid chromatography (2D-HPLC) separation from a bulk of *ortho*-substituted chlorobiphenyls using a porous graphitic carbon and pyrenyl silica columns. The liquid chromatograph used was a high pressure liquid chromatograph model LC-10AD (Shimadzu Corporation, Kyoto, Japan), and liquid chromatograph pump employed to deliver solvents was model LC-10 AD also of Shimadzu.

The gas chromatographic separation, detection and quantification of planar CBs, tri- to octa-CN, hepta-CDD/Fs and octa-CDD/F was achieved using a capillary column (0.25 mm i.d. and 30 m in length) coated at 0.25 μm film thickness with (DB-17) liquid phase (J&W Scientific, Folsom, CA, USA). The column head pressure was kept at 120 kPa. The GC oven temperature was programmed from 70 °C (1 min) to 200 °C at a rate of 15 °C/min, and then to 270 °C at 4 °C/min, with a final hold time of 15 min. The gas chromatograph used was the model Hewlett-Packard 6890 GC, which was interfaced with a JEOL JMS-7000 model high-resolution mass spectrometer and operated in an electron impact (EI) mode (38 eV energy and 500 μA ion current), with selective ion monitoring (SIM) at a resolution above 10,000 amu (10 % valley). The ion source temperature was at 270 °C, interface temperature was at 270 °C, and trap current was 500 μA. An internal isotopically labelled ($^{13}C_{12}$ labelled) standards of non-, mono-, and di-*ortho* CBs, CDFs and CDDs as well as external native standards of all groups of compounds analysed have been employed to assure high analytical quality of the data. Di-through octa-CB congeners in Clophen A60 were identified and quantified using a mixture composed of equivalent amount of technical PCB formulations of the Kanechlor series (Kanechlor 300, 400, 500 and 600 added at 1:1:1:1 ratio; Equi-Kanechlor) of known chlorobiphenyl composition and content. Nona- and deca-CB were not quantified in Clophen A60 in this study. Composition and content of CB congeners in Equi-Kanechlor mixture have been reported elsewhere [13].

Results and Discussion

Di- (0.03 %), tri- (0.03 %), tetra- (0.32 %), penta- (9.9 %), hexa- (52.7 %), hepta- (32.1 %) and octa-CB (4.9 %) homologue groups were quantified in Clophen A60 (Fig. 1), while mono-, nona- and deca-CB were not determined. In some earlier studies on the chlorobiphenyl composition of the Clophen A60 apart from di- to octaCBs also nona-CBs (from 0.185 to 0.81 %) and deca-CB (from 0.0 up to 0.2 %) were found [4,7].

In study by Takasuga et al. (1996) after HRGC-HRMS analysis was found that CB homologue group profile of an another lot of technical Clophen A60 was dominated by hexa-CBs (~54 %), and followed by hepta- (~28 %), penta- (~16 %) and tetra-CBs (<2 %), what is somewhat different when compared to the data obtained in this study [12].

The tetra- to octa-CDFs quantified in Clophen A60 in this study were found in the total concentration of 12 μg/g. The profile of tetra- to octa-CDF homologue groups in Clophen A60 is

dominated by penta-CDFs (46 %) and in descending order followed by tetra-CDFs (27 %) hexa- and hepta-CDFs, while octaCDF remained undetected (Fig. 2). A noted composition of CDF homologue groups in Clophen A60 is a somewhat different to that earlier reported for the mixtures of technical CBs belonging to the family of Delors, Aroclors and Kanechlors.[14, 16]. It was suggested, that a mentioned specific profile of CDF homologue groups with prevalence of tetra-CDFs and in descending order followed by penta-, hexa-, hepta and octa-CDF, irrespectively of the chlorination pattern of the technical CB mixtures, could be due to CDFs formation from the precursor molecules but not because of the conditions of synthesis [14].

A by-side tetra- to octaCDF quantified in Clophen A60 were separated into 72 peaks representing 62 single resolved constituents, while 16 congeners co-eluted in pairs, 3 in triplicate and 4 in quartet. Amongst of chlorodibenzofuran congeners quantified a most potent as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) analogue with net 425 ng TEQ/g contribution was highly toxic 2,3,4,7,8-PeCDF, while the total CDFs TCDD TEQ of this formulation was assessed for 594.5 ng/g .

As reviewed by Falandysz (1999), a several reports where published in the 1970s and 1980s and which notified on co-occurence of highly toxic CDFs but also CNs quantified in technical CB formulations of the Kanechlor, Aroclor, Clophen and Phenoclor series [1]. In those studies, when relatively less sophisticated analytical methods and instrumentation was used CDFs content varied between 80 and 33000 μg/g for fresh CB mixtures, while between 20000 and 510000 μg/g in some used formulations. In more recent papers tetra- to octaCDF content of several Aroclor and Kanechlor mixtures was between 0.598 and 26 μg/g [15] In another study tetra- to octaCDF content of Delor 103, 104, 105 and 106 was <0.1, 68, 18 and 38 μg/g, respectively [14]. Additionally, as reported in other study of two Chinese CB formulations, the CDFs contaminated the mixtures at concentration from 6.2 to 7.9 μg/g (220-420 ng TCDD TEQs/g), while for CDDs were below the method limit of quantification of < 4 and up to 120 ng/g [17] .

The total CNs concentration of Clophen A60 was 41.27 μg/g. Two other CB formulations of the Clophen series, *i.e.* Clophen A40 and T64 contained a by-side CNs in concentration of 102.6 and 86.4 μg/g, respectively [16]. A by-side CNs were also found as contaminants in all types of the technical CB formulations of the Aroclor, Kanechlor, Phenoclor and Delor series examined, while concentrations ranged between 5.2-67, 32-160, 150-460 and 82-450 μg/g, respectively [14, 16].

The percentage composition of by-side CN homologue groups of the technical CB formulations of Aroclor, Kanechlor, Phenoclor and Delor series increased with increase of the degree of chlorination of the parent mixture [14, 16]. Hence, presence of naphthalene as impurity in technical biphenyl and its subsequent chlorination during CBs synthesis leads to by-side formation of CNs, while yield seems to be largely dependent on the purity or other words naphthalene content of technical biphenyl.

In this study heptaCNs (56 %) followed by hexa- (26 %) and octaCN (15 %) highly dominated in CN homologue groups profile of Clophen A60 (Fig. 3). All congeners of the tri- to octaCN homologue groups were quantified as by-side impurities of Clophen A60. Nevertheless, after pre-separation using the Hypercarb-HPLC but without of the pyrenyl(PYE)silica-HPLC step, and further applying DB-17 liquid phase for capillary column - mass spectrometry (GC-MS) separation and quantification a several congeners of tetra-, penta- and hexa-CN still co-eluted., while 1,2,4-/1,3,7-/1,4,6-TeCNs (nos. 14/21/24) and 1,3,8-/1,4,5-TrCNs (nos. 22/23) could not be pre-separated.

The total TCDD TEQ of planar dioxin analogues quantified in Clophen A60 was 5908 ng/g with a greatest contribution of 89, 10 and 1 % from CBs, CDFs and CNs, respectively.

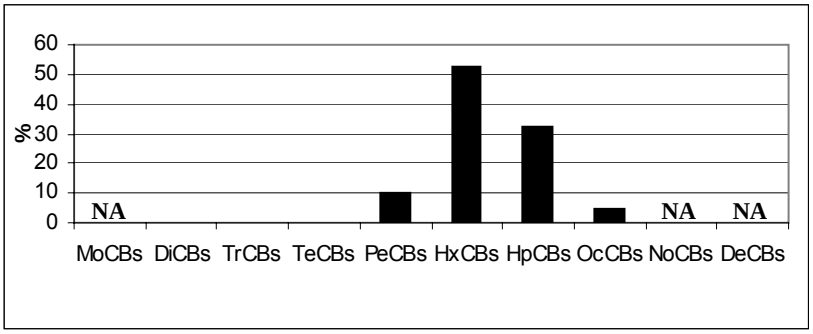

Fig. 1. Profile (%) of CB homologue groups in Clophen A60 (NA; not analyzed).

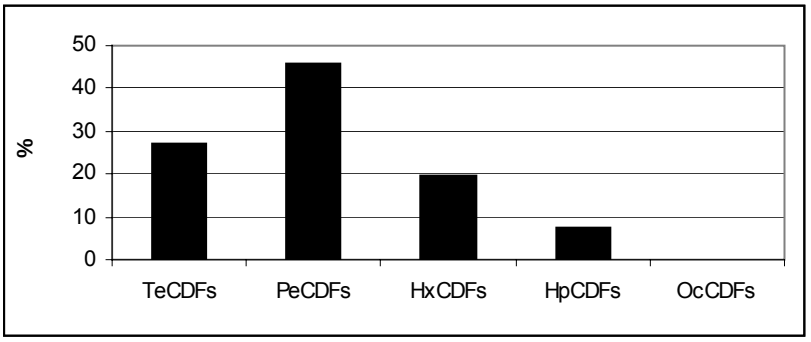

Fig. 2. Profile (%) of tetra- to octaCDF homologue groups in Clophen A60.

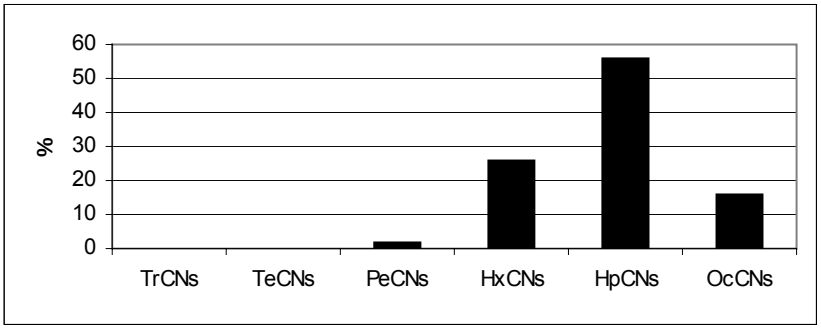

Fig. 3. Profile (%) of tri- to octaCN homologue groups in Clophen A60.

References

1. Falandysz, J. Polychlorinated biphenyls (PCBs) in the environment: chemistry, analysis, toxicity, concentrations and risk assessment (*in Polish*). Fundacja Rozwoju Uniwersytetu Gdańskiego, Gdańsk, ISBN83-86230-52-5, 1999.
2. Frame, G..M., (1997) Fresenius Z. Anal. Chem. , 357, 714.
3. Cochran, J.W.; Frame, G.F., (1999) J. Chromatogr. A., 843, 323.
4. Jensen, S.; Sundström, G.., (1974) Ambio, 3, 70.
5. Schulte, E.; Mallisch, R., (1983) Fresenius Z. Anal. Chem., 314, 545.
6. Schulte, E.; Mallisch, R., (1984) Fresenius Z. Anal. Chem., 319, 54.
7. Duinker, J.C.; Hillebrand, M.T.J., (1983) Environ. Sci. Technol., 17, 449.
8. Duinker, J.C.; Schulz, D.E.; Petrick, G.., (1988) Anal. Chem., 60, 478.
9. Ballschmiter, K.; Schafer, W.; Buchert, H., (1987) Fresenius. Z. Anal. Chem., 326, 253.
10. Schulz, D.E.; Petrick, G..; Duinker, J.C., (1989) Environ. Sci. Technol., 23, 852.
11. Budzinski, H.; Hermange, Y.; Pierard, C.; Garrigues, P.; Bellocq, J., (1992) Analusis, 20, 155.
12. Takasuga, T.; Inoue, T.; Ishida, T.; Ireland, Ph.., (1996) Organohalogen Compounds, 27, 391.
13. Tanabe, S.; Tatsukawa, R.; Phillips, D.J.H., (1987) Environ. Pollut., 47, 41.
14. Taniyasu, S.; Kannan, K.; Holoubek, I.; Ansorgova, A.; Horii, Y.; Hanari, N.; Yamashita, N.; Aldous, K.M. , (2003) 126, 169.
15. Wakimoto, T.; Kannan, N.; Ono, M.; Tatsukawa, R.; Masuda, Y., (1988) Chemosphere, 1988, 743.
16. Yamashita, N.; Kannan, K.; Imagawa, T.; Miyazaki, A.; Giesy, J.P., (2000) Environ. Sci. Technol., 34, 4236.
17. Ke, J.; Lingjun, L.; Yudong, C.; Jun, J., (1997) Chemosphere, 34, 941.