CHLOROBIPHENYLS AND BY-SIDE IMPURITIES CONTENT AND COMPOSITION OF CHLOROFEN

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

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

Introduction

The technical chlorobiphenyl (CB; polychlorinated biphenyl, PCB) formulations are complex mixtures of many chlorobiphenyl congeners with dioxin- and non-dioxin-type of effects and can contain also some highly toxic impurities such as chloronaphthalenes (CNs), chlorodibenzofurans (CDFs) and less chlorodibenzo-*p*-dioxins (CDDs) [1-5].

Chlorofen is trade name for technical CB formulation produced in Poland in 1966-1970 by the Zakłady Chemiczne (Chemical Company) in the town of Ząbkowice Śląskie. Chlorofen is highly chlorinated type of technical CB mixture and has an appearance of a light-to-dark-brown sticky and viscous resin, which was used as lubricant in mining industry in Poland [6,7].

The technical CB formulations manufactured become further a diffuse type source of the environmental pollution both with a parent compounds and by-side contaminants [11-21]. Hence, a detailed knowledge of the composition and content of toxic and persistent constituents in technical CB mixtures is helpful to understand environmental fate, effects, hazardous waste inventory and identification of point sources of emission of those compounds. In this communication are given congener-specific data on CBs, CNs, CDFs and CDDs content and composition of Chlorofen.

Materials and Methods

A sample of Chlorofen obtained was a kindly gift from the Department of Pharmacology and Toxicology of the National Veterinary Institute in Puławy, Poland. In brief, the analytical method used to quantify planar non-*ortho* substituted CBs as well as CDFs, CDDs and CNs included a several steps. An enrichment and fractionation of the analyte was achieved using two HPLC systems consisting of a porous graphitic carbon (Hypercarb, Hypersil, USA) and pyrenyl silica column (PYE, Nacalai Tesque, Japan). The HPLC system used was a model LC-10AD (Shimadzu Corporation, Kyoto, Japan). The HRGC-HRMS quantification of planar CBs, 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 gas chromatograph used was the model Hewlett-Packard 6890 GC, which was interfaced with the JEOL JMS-7000 model high-resolution mass spectrometer. The column head pressure was

kept at 120 kPa and 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 [9].

For GC separation, detection, idntification and quantification of tetra- through hexa-CDD/Fs the capillary column used was of 60 m in length and 0.25 mm i.d. coated with SP2331 at 0.25 μm film thickness (Supelco, Bellefonte, PA, USA). The comumn was installed in the GC model Hewlett Packard 6890 Series II interfaced with the HRMS model Micromass Autospec-Ultima. The GC oven temperature was programmed from 100 °C (1 min) to 200 °C at a rate of 20 °C/min, and then to 260 °C at 2 °C/min with a final hold time of 35 min. The mass spectrometer was operated in an electron impact (EI) mode (34 eV energy and 500 μA ion current), with selective ion monitoring (SIM) at a resolution above 10 000 amu (10 % valley). Quantification was based on an external standard containing tetra- to octa-CDD/Fs (Wellington Laboratories).

Results and Discussion

Profile (%) of di- to octa-CBs in Chlorofen is presented at Fig. 1. Amongst of highly toxic four non-*ortho* and eight mono-*ortho* CB congeners quantified in Chlorofen only a few were found, *i.e.* 3,3′,4,4′-TeCB (no. 77), 2,3′,3,4,4′,5-HxCB (no. 156), 2,3,3′,4,4′,5′-HxCB (no. 157) and 2,3′,4,4′,5,5′-HxCB (no. 167). A most abundant of planar CBs in Chlorofen with 4.484 mg/g is 2,3,3′,4,4′,5′-HxCB (no. 157).

Chlorodibenzo-*p*-dioxins as well as tetra-, penta- and hexa-CDFs were absent in Chlorofen in concentration above the method limit of quantification (0.01 μg/g). The compositional profile (%) of CDF homologue groups of Chlorofen is highly dominated by OcCDF (Fig. 2). Hepta-CDF concentrations ranged from 0.2 to 4.9 μg/g, and for octa-CDF was 347.3 μg/g. In terms of dioxin-like toxicity contribution from CDFs in Chlorofen was 44.7 ng/g of TEQ (2,3,7,8-T4CDD Toxicity Equivalent Quantity) .

An absolute concentration value of CNs in Chlorofen is 353 μg/g The compositional profile of CNs in Chlorofen is highly dominated by octachloronaphthalene (Fig. 3) occupying 97 %, while the total TEQ of CNs with 731 ng/g is an order of magnitude greater when compared to contribution by CDFs. Apart from the technical Chlorofen these fully chlorinated congener was also a dominating constituent of the by-side CNs quantified in some another highly chlorinated technical CB formulations such as Aroclor 1260 (~ 80 %), Aroclor 1262 (~ 75 %), Kanechlor 600 (~ 85 %) and Phenochlor 6 (~ 60 %) [3]. Nevertheless, no data are available on the content and compositional profile of CNs in a such highly chlorinated CB mixtures like Aroclor 1268, Aroclor 1270, Fenchlor 70 or technical decachlorobiphenyl Fenchlor DK formulations. The three different lots of Aroclor 1254 till now examined varied largely in abundance of OcCN in the total load of a by-side CNs in this mixture and it's relative content was between 4.6 and 10 % [3].

The technical CB formulations are an important source of environmental pollution with CNs [9-10]. Based on the total amount of 1000 tones of Chlorofen manufactured the amount of by-side CNs is 352 kg, while 343 kg is from OcCN alone. Further, the amount of TEQ due to manufacture of Chlorofen is estimated for 3097.8 g, and 2300 g was from CBs, 44.7 g from CDFs and 731 g from CNs.

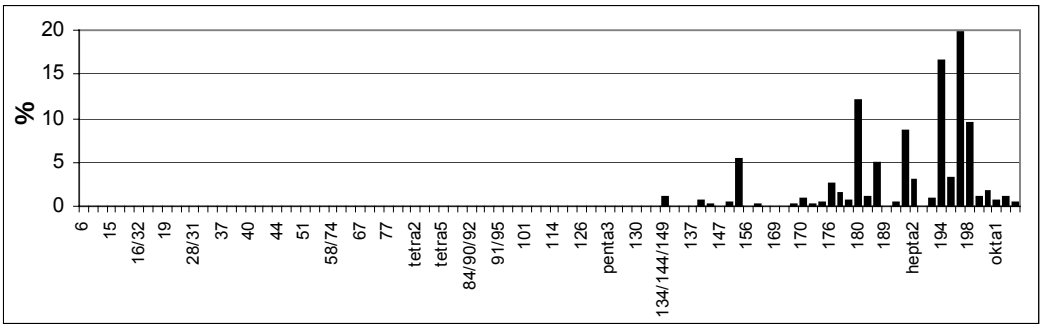

Fig. 1. Profile (%) of chlorobiphenyl congeners in Chlorofen (mono-, nona- and decaCB not quantified).

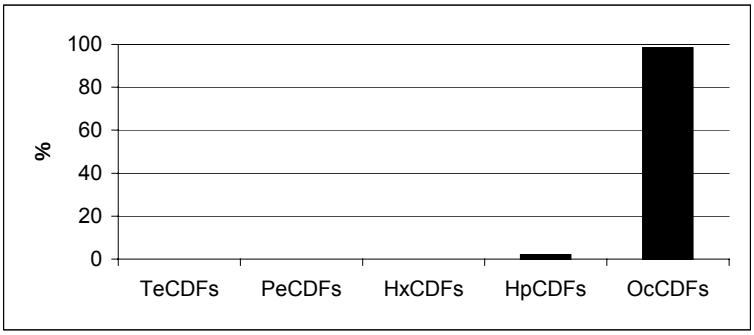

Fig. 2. Profile (%) of CDF homologue groups in Chlorofen.

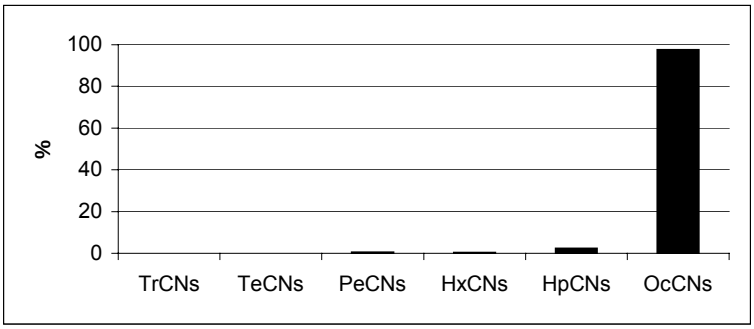

Fig. 3. Profile (%) of CN homologue groups in Chlorofen.

References

1. Wakimoto, T.; Kannan, N.; Ono, M.; Tatsukawa, R.; Masuda, Y., 1988) Chemosphere, 1988, 743.
2. PCBs Recent Advances in Environmental Toxicology and Health Effects. L.W. Robertson, L.G. Hansen (eds.). The University Press of Kentucky, ISBN 0-8131-2226-0, 2001.
3. Yamashita, N.; Kannan, K.; Imagawa, T.; Miyazaki, A.; Giesy, J.P., (2000) Environ. Sci. Technol., 34, 4236.
4. Taniyasu, S.; Kannan, K.; Holoubek, I.; Ansorgova, A.; Horii, Y.; Hanari, N.; Yamashita, N.; Aldous, K.M., (2003) Environ. Pollut., 126, 169.
5. Ke, J.; Lingjun, L.; Yudong, C.; Jun, J., (1997) Chemosphere, 34, 941.
6. Falandysz, J.; Yamashita, N.; Tanabe, S.; Tatsukawa, R., (1992) Intern. J. Environ. Anal. Chem., 47, 129.
7. Falandysz, J.; Szymczyk, K., (2001) Pol. J. Environ. Stud., 10, 189.
8. Falandysz, J.; Puzyn, T., (2004) J. Environ. Sci. Health., 39A, 1505.
9. Falandysz, J., (1998) Environ. Pollut.,10, 77.
10. Falandysz, J., (2003) Food Addit. Contam., 21, 995.
11. Gevao, B.; Harner, T.; Jones, K.C., (2000) Environ. Sci. Technol., 34, 33.