Analysis of PCBs in emission samples: non ortho, mono-ortho and homolog totals by level of chlorination

Werner Tirler[1], Giulio Voto[1], Massimo Donegà[1], Gerhard Kahr[2]

[1]Eco-Research, Via Negrelli 13, 39100 Bolzano, Italy
[2] Monitoring Systems, Schloss 2, Kottingbrunn, Austria

Introduction

Polychlorinated biphenyls (PCBs) are one of the most widespread persistent organic pollutants, identified in every component of the global ecosystem. A production of approximately 2 * 10 [9] Kg technical PCB occurred form 1930 to the late 1970 [1] and the total amount released into the environment is estimated in 370. 000 [2] tonnes. Twelve of the possible 209 PCBs are non- and mono-ortho substituted chlorinated biphenyls. They resemble 2,3,7,8-tetrachloro dibenzo-p-dioxin (TCDD) in their biological action, bio accumulating through the food chain and causing immuno-, reproductive and dermal toxicities. Therefore in 1997 the Word Health Organisation (WHO) extended the concept of toxic equivalency (TEQs) [3] also to these group of "dioxinlike" PCBs.
At the moment a fraction of the produced PCBs is collected with the household waste and burned in incinerators. PCBs are evaporated during waste incineration and are partially destroyed during the incineration process, dependent on residence time/temperature. Catalytic dioxin destruction shall additionally reduce the emissions of PCBs. Anyway all PCBs left in the flue gas are emitted in the environment. Some publications present this as an additional source of PCBs [2,4,5,6].
This work aims to investigate the congeners and homologous group distribution of PCBs in emission samples of municipal solid waste incinerators and to calculate the WHO-TEQ_{PCB} in relation to the WHO-$TEQ_{PCDD/F}$.

Materials and Methods

The evaluation was conducted on emissions of a municipal solid waste (MSW) incinerator with a total net capacity of 270 t/day, using roller type combustion grate and energy recovery (electricity and district heating). Flue gas cleaning is performed by a fabric filter and a wet scrubber, in line with a final SCR (Selective Catalytic Reduction) unit for NOx and PCDD/F conversion.
Directly on the stack an automatic sampling system wasis installed , capable to perform isokinetic sampling of ~~.~~ PCDD/F for periods from 6 hours to 6 Weeks. This DioxinMonitoringSystem is using the dilution method which is described in the EN-1948 Part 1 [7] and permits to collect the PCDD/F as well as PCB on a cartridge containing a dust filter and two dry poly urethane foams [8]. At the end of sampling the cartridge was transferred to the lab. There the sample was extracted, cleaned and evaluated using the EN 1948 part 2 and 3. After soxhlet-extraction with toluene the sample extract was split in two parts:~~.~~ One for PCDD/F and the other for PCB determination. After sulphuric acid (98%) pre-treatment an automatic multicolumn system (Dioxin PowerPrep, FMS) clean up has beenwas used for Dioxins and for PCBs. For PCB analysis carbon $^{13}C_{12}$ labelled Standards (labeled "dioxinlike" congeners as well as labeled first and last eluting congener of each chlorination level) were added according EPA 1668A [9] after sampling. The HRGC- HRMS analysis has beenwas conducted on a Agilent 6890 gaschromatograph coupled on a Thermofinnigan MAT 95 XP operating at resolution 10.000. A HT-8 PCB 60 m, 0,25 mm column from SGE was used for PCB analysis.

Fig. 1: Chromatogram of a Mixture containing all possible 209 PCB congeneres

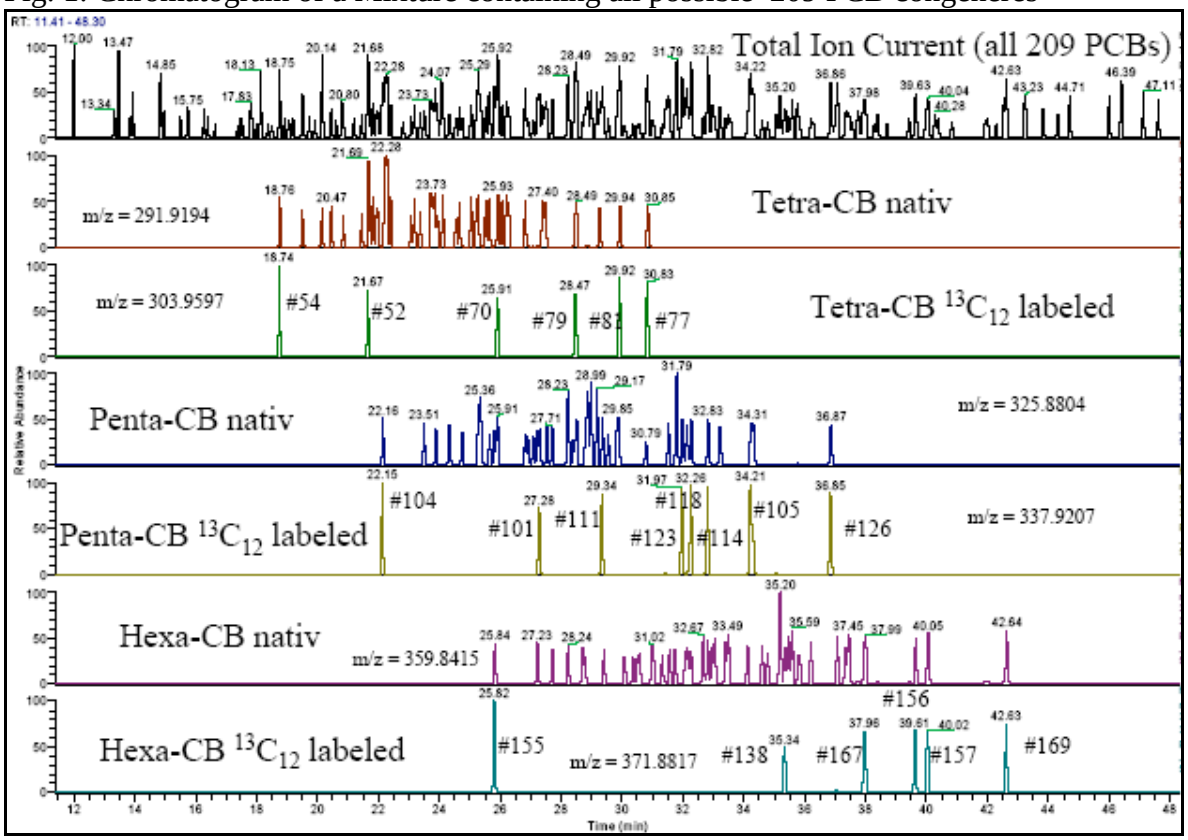


Fig. 2: Chromatogram of mono, di and trichloro CB in the emission sample

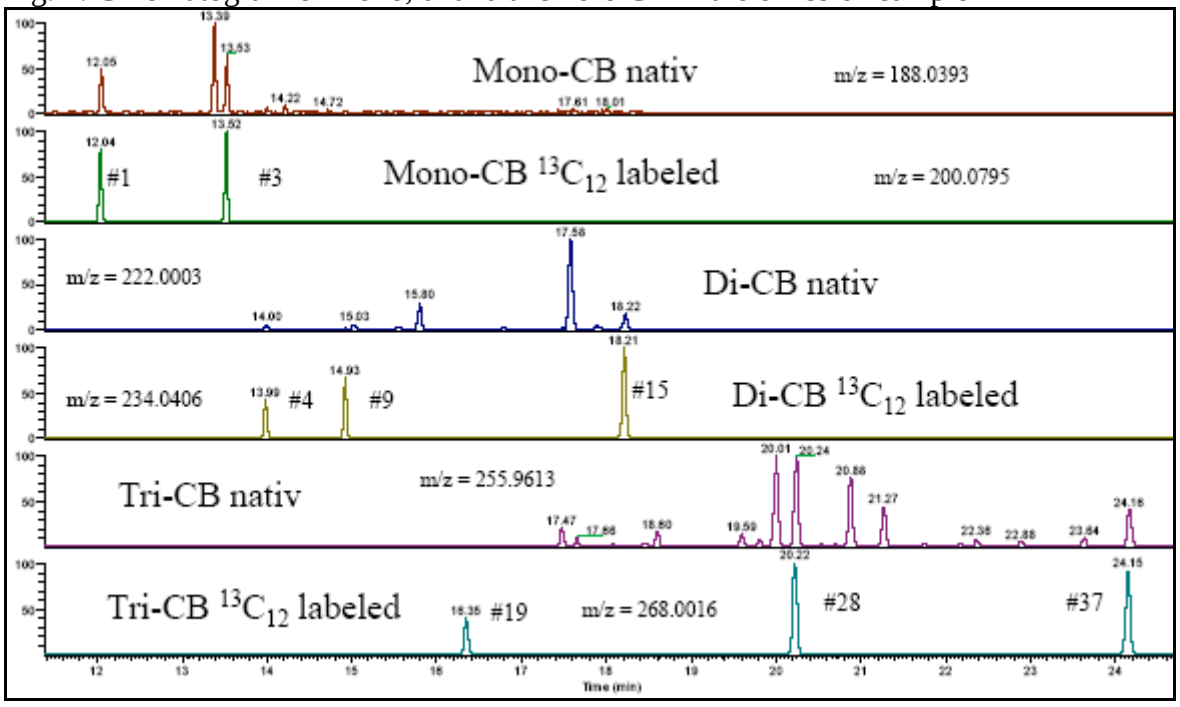


Fig. 3: Chromatogram of tetra, penta and hexa CB in the emission sample

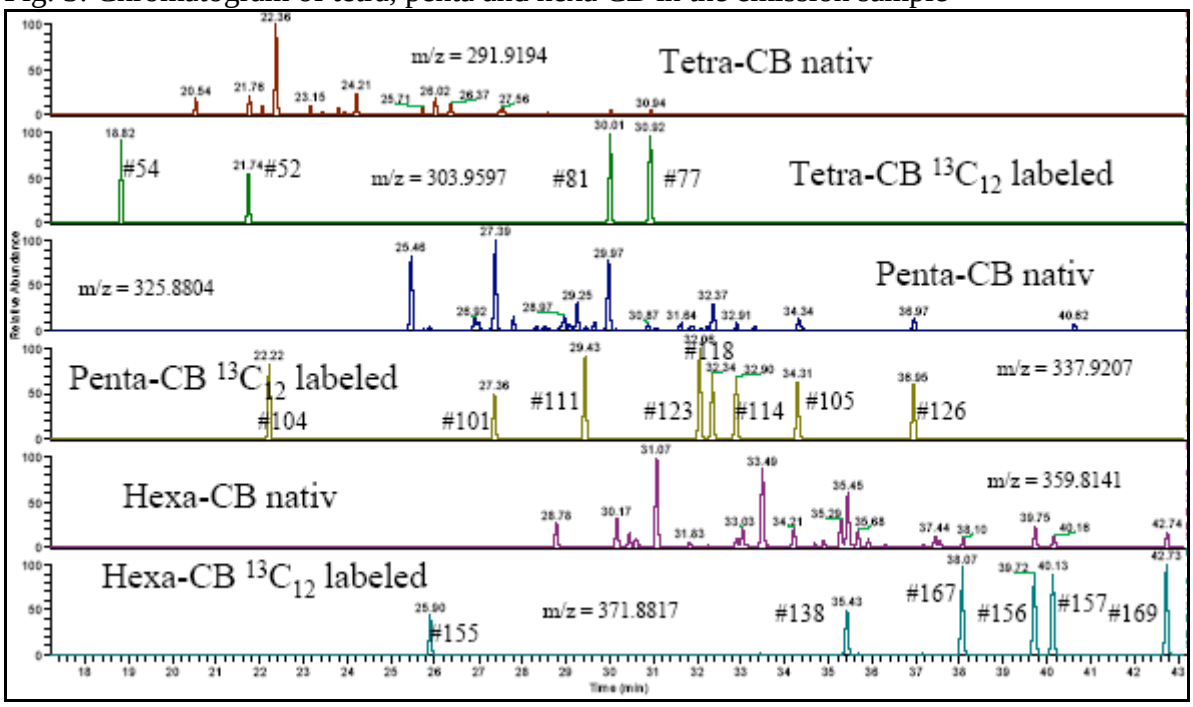
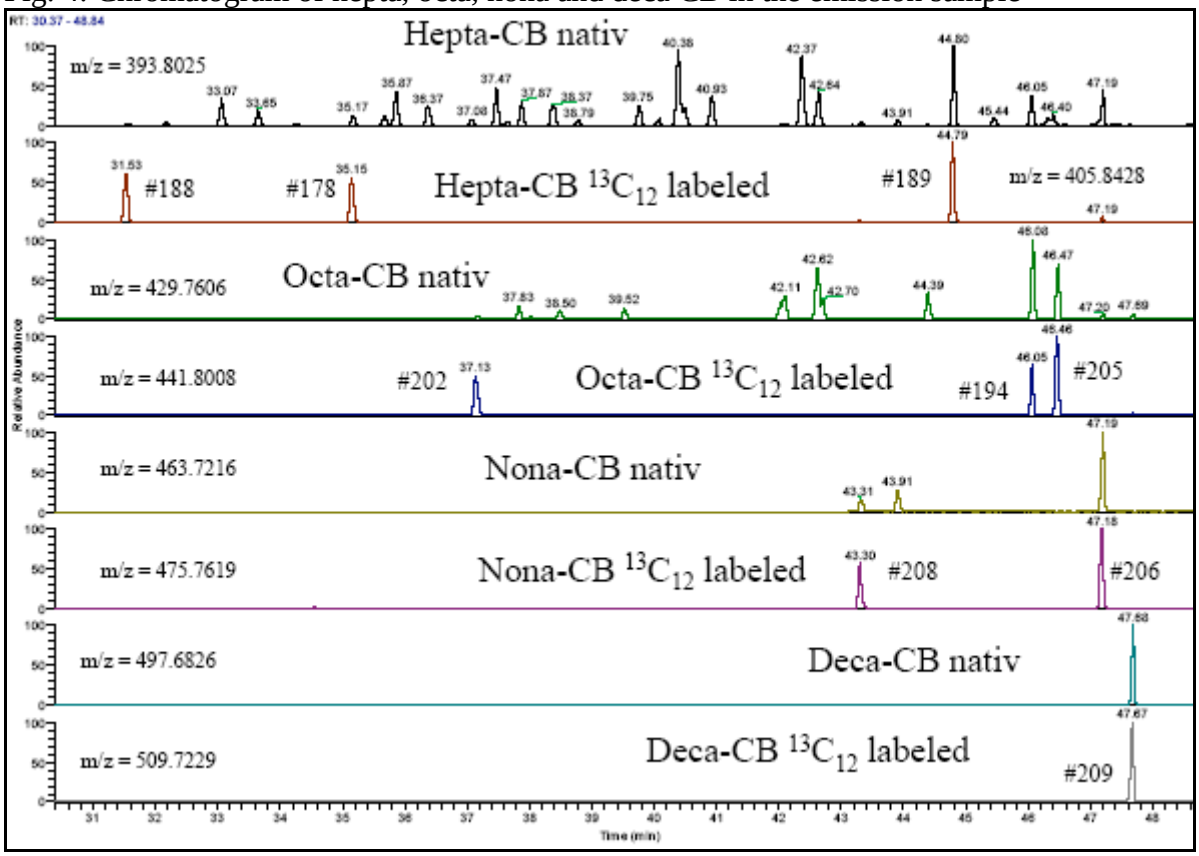


Fig. 4: Chromatogram of hepta, octa, nona and deca CB in the emission sample



Results and Discussion

The chromatogram of a mixture of all possible 209 PCB congeners is shown in Fig1. Especially for the tetra-, penta- and hexachlorinated biphenyl homologous group quite complex chromatograms are obtained. Fig. 1 shows, that PCB#126 and PCB#169 are well resolved by the described method, without interferences.

The chromatograms obtained by the emission sample (Fig. 2, 3 and 4) presents only few of the possible congeners of each chlorination level at significant concentrations. As table 1 shows especially PCB#126 (I-TEF = 0,1) and PCB#169 (I-TEF = 0,01) represents 98% of the calculated WHO-TEQ_{PCB}.

Table 1: Concentration of PCBs in an emission sample of a MSW incinerator

	ng/Nm^3 (dry at 11% O_2)		Ng/Nm^3 (dry at 11% O_2)
PCB #77	0,010	Mono-CB tot	0,01
PCB #126	0,014	Di-CB tot	0,04
PCB #169	0,013	Tri-CB tot	0,11
PCB #81	0,008	Tetra-CB Tot	0,53
PCB #105	0,016	Penta-CB tot	0,23
PCB #114	0,009	Esa-CB tot	0,60
PCB #118	0,025	Epta-CB tot	0,36
PCB #123	0,002	Octa-CB tot	0,15
PCB #156	0,018	Nona-CB tot	0,26
PCB #157	0,010	Deca-CB	0,23
PCB #167	0,009		
PCB #189	0,035		
WHO-TEQ_{PCB}	**0,0016**		

The WHO-$TEQ_{PCDD/F}$ was measured with 0,053 ng /Nm_3 (dry at 11% O_2). The contribution of the WHO-TEQ_{PCB} to the total toxicity is 3 %.

References

1. Lindström G., Wingfors H., and Van Bavel B. *Organohalogen Compounds*, 1999, 40, 181
2. Kannan N. (2000) in: The Handbook of Environmental Chemistry Vol. 3 Part K New Types of Persistent Halogenated Compounds, ISBN 3-540-65838-6
3. Van den Berg M., Birnbaum L., Bosveld B.T.C., Brunström B., Cook P., Feely M., Giesy J., Hanberg A., Hasegawa R., Kennedy S.W., Kubiak T., Larsen J.C., van Leeuwen F.X.R., Liem A.K.D., Nolt C., Peterson R.E., Poellinger L., Safe S., Schrenk D., Tillit D., Tysklind M., Younes M., Waern F. and Zacharewsky R. (1998): Environm. Health Persp. 106, 775
4. Erickson M. D. (1997) Analytical Chemistry of PCBs, ISBN 0-87371-923-9
5. Miyata H., Aozasa O., Mase Y., Otha S., Khono S., Asada S., *Chemosphere*, 1994, 27:233
6. Thanner G., Moche W.: Monographien, 153 (2002) ISBN 3-85457-625-0
7. CEN, Stationary source emissions – determination of the mass concentration of PCDD/Fs, report EN 1948-1,2,3, CEN 1996
8. Tirler W., Donegà M., Voto G., Kahr G. *Organohalogen Compounds*, 2003, 60, 509
9. EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue By HRCG-HRMS, (1994), EPA 821-R-00-002 Office of Water