FORM

LEVELS OF COPLANAR PCBs IN FLUE GASES OF HIGH TEMPERATURE PROCESSES AND THEIR OCCURRENCE IN ENVIRONMENTAL SAMPLES

J.P. Boers^A, E.W.B. de Leer^A, L. Gramberg^B and J. de Koning^C

- A TNO Institute of Environmental Sciences, P.O. Box 6011, 2600 JA Delft, Schoemakerstraat 97, The Netherlands
- ^B TNO Nutrition and Food Research, P.O. Box 360, 3700 AJ Zeist, Utrechtseweg 48, The Netherlands
- C TNO Institute of Environmental and Energy Technology,
 P.O. Box 342, 7300 AH Apeldoorn, Laan van Westenenk 501,
 The Netherlands

Introduction

There is little information available about the occurrence and quantitative analysis of the non-ortho substituted (coplanar) PCBs (IUPAC nr. 77, 126 and 169) in flue gases of municipal¹/chemical waste incinerators and other high temperature processes and their occurrence in environmental samples, such as soils and sediments.

The objective of this study is to obtain more information about the levels and significance of the non-ortho PCBs in relation to the PCDDs/PCDFs. With this aim, we subjected different incineration/high temperature processes and environmental samples to the analysis of 2,3,7,8-substituted PCDDs/PCDFs and non-ortho PCBs.

Materials and methods

The flue gases were sampled using the Ströhlein/PUF dilution method. This entails isokinetically extracting a part of the flue gas using an electrically heated sampling probe in accordance with the Dutch Practical Guideline NPR 2788. Part of the flue gas is rapidly cooled to a temperature below 40 degrees centigrade using dried filtered air.

Soil sample 1 was taken from an industrialized area in the vicinity of a Municipal and Chemical waste incinerator (refers to CWI and MSWI-1 in Table 1). The soil sample was taken from the top layer (0-5 cm) using a core sampler. Soil sample 2 was col-

FORM

lected from an area with cable burning and metal shredder activities and should be regarded as highly contaminated. Both soil samples were a composite of different sub-samples taken from a well defined area. Harbour surface sediment was collected from the harbour of Duisburg (Germany). All soil, sediment and filter cake samples were dried and homogenized before analysis.

Prior to Soxhlet extraction with toluene, ¹³C-labeled PCBs (77, 126 and 169) and 13 or 16 ¹³C-labeled PCDD/Fs were added. After matrix isolation the extracts were submitted to a clean-up involving active carbon (AMOCO PX-21 or NORIT A Supra), multilayer silicagel and activated aluminum oxide. ¹³C 1234-T4CDD was used as an injection standard. The extracts were analyzed with high-resolution gas chromatography in combination with high-resolution mass spectrometry (HRGC-HRMS) using a non polar DB-5 column for the PCB-analysis and a polar column (SP2331) for the PCDDs/PCDFs analysis, operating the HRMS (Finnigan MAT-95) at a resolution of 8000-10000 (10% valley definition). The two most abundant ions for the native and corresponding labeled compounds were monitored. A complete description of the analytical methodology will be published elsewere². TCDD-equivalents are calculated according to the I-TEF proposed by Safe³.

Results

Flue gas cleaning	CWI* none	MSWI-1* ESP	MSWI-2** ESP/dry scrubber/ fabric filter	MSWI-3* ESP	Sinter plant** wet scrubber			
	ng/Nm ³ at 11% O ₂							
PCB-77	3.18	1.57	0.54	6.02	19.12			
PCB-126	2.37	1.55	0.25	8.62	3.87			
PCB-169	0.82	0.74	0.087	4.09	0.78			
Σ I-TEQ copi-PCBs	0.31	0.21	0.034	1.13	0.62			
Σ I-TEQ PCDD/Fs	6.1	7.0	1.0	21.4	5.3			
Σ I-TEQ (copl-PCBs + PCDD/Fs)	6.41	7.21	1.034	22.53	5.92			
%copl-PCB	4.8	2.9	3.3	5.0	10.4			

 Table 1
 Levels of the non-ortho
 PCB 77, 126, 169 and
 PCDDs/PCDFs in flue gases of high tem - perature processes.

 These sources have additional flue gas cleaning installed and do not represent the emissions to the air

** emissions to the air

- CWI = Chemical Waste Incinerator
- ESP = ElectroStatic Precipitator

MSWI = Municipal Solid Waste Incinerator MSWI-3 = RDF (Refuse Derived Fuel) The results of the analysis of the flue gases for the non-ortho PCBs (IUPAC nr. 77, 126 and 169) are given in Table 1. The flue gases were sampled after the flue gas purification system(s) mentioned in Table 1. Only samples from MSWI-2 and the sinter plant represent the emissions to the air. The other incinerators have additional flue gas cleaning installed.

Levels of the non-ortho PCBs in harbour sediment, soil and by-products of high temperature processes are given in Table 2. The results in Table 2 are the mean values of three independent analyses. Figure 1 illustrates coplanar PCB patterns of environmental samples and by-products of high temperature processes.

Table 2Levels of the non-ortho PCBs 77, 126, 169 and PCDDs/PCDFs in harbour sediment, soil
and by-products of high temperature processes.

	harbour sediment		soli sampie 1		soli sample 2		filter dust from a metal recia- mation plant		filter cake MSWI		
	ng/kg DW (mean ± sd); n=3										
РСВ-77 РСВ-126 РСВ-169	1979±211 85±8 24±3	(89) (82) (82)	29.1±7.4 8.2±2.4 2.9±0.8	(65) (78) (75)	96367±221 4650±286 1252±48	3(12) (36) (77)	3556±34 5323±8 3176±92	(79) (94) (105)	633±144 538±14 288±16	(51) (77) (88)	
Σ I-TEQ COPI-PCBS Σ I-TEQ PCDD/FS Σ I-TEQ (COPI-PCBS + PCDD/FS)	29.5 111 141		1.26 ND -		1491 3767 5259		727 7698 8425		75 2808 2882		
% PCB TEQ	21.0] -		28.4		8.6		2.6		

ND = not determined

() = average recoveries (n=3)





FORM

Conclusions

We found evidence for the occurrence of the non-ortho PCBs in flue gases of chemical and municipal waste incineration plants. The coplanar PCBs can account for up to 10% of the total toxic equivalents (PCBs + PCDDs/PCDFs). We believe that the nonortho PCBs are formed by "*de novo*" synthesis mechanism, similar to the formation of PCDD/Fs.

Metal reclamation and sinter processes could be an important source for non-ortho-PCBs.

Sediment and with PCDD/F contaminated soils contain coplanar PCBs with a different congener distribution pattern in comparison to the emissions of high temperature processes. PCB 77 occurs in the highest concentrations, followed by PCB 126 and PCB 169. The non-ortho PCBs in harbour sediment and with PCDD/F contaminated soil can account for up to 21 and 28% of the I-TEQ respectively. Further research is necessary to find other sources that can explain the high levels of coplanar PCBs found.

References

- 1 Sakai S., Hiraoka M., Takeda N., Shiozaki K. Coplanar PCBs and PCDDs/PCDFs in Municipal Waste Incineration, Dioxin '92, Vol. 9, 215-218, Tampere, Finland, August 1992.
- 2 Boers J.P., Leer E.W.B. de, Gramberg L. Analysis of non-ortho-PCBs and PCDD/Fs in flue gases of incineration processes and environmental samples, In preparation.
- 3 Safe S. Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). Crit Rev Toxicol 1990; 21: 51-88.