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Total TEQ emissions (PCDD/F and PCB) from industrial sources

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1. Introduction

Since the latest evaluation of the toxicity of organochlorine compounds by the WHO, emissions from industrial sources are more and more rated with respect to *total TEQ* values considering both, polychlorinated dibenzodioxins (PCDD) and furans (Fs) as well as polychlorinated biphenyls (PCBs) (van den Berg et al., 1998). Meanwhile it was several times reported about total TEQ emissions from industrial sources. However, there are only few data available which corresponding to the latest WHO toxicity equivalent factors and considering all 12 WHO-PCBs (Alcock et al., 1998; Pernin et al., 1998).

In the present work some selected results from emission measurements carried out in the years 1998–2000 at different industrial plants and crematories are given. This work is aiming to show which part of the total TEQ value is caused by the dioxin/furan emission and which part can be assigned to the PCB emission. Furthermore it was investigated which congeners from both substance classes are substantially responsible for the total TEQ value. Additionally in order to give an estimation of the thermodynamic force to form the different WHO-PCB congeners heats of formation (HoF) were calculated via semiempirical molecular orbital methods using the MOPAC program package (WinMOPAC).

2. Materials and methods

Flue gas samplings reported in this work were carried out at eight different plants given in Table 1. At five plants 6-h-samplings according to European standard EN 1948 were performed (CEN, 1996). At three plants the long-term sampling system AMESA was used for 14- and 30-day-samplings respectively (Funcke et al., 1993; Mayer et al., 2000). PCDD/Fs and PCBs were collected together within the same sample.

Extraction of the samples was carried out with toluene in a separation funnel (condensate) and in a Soxhlet extractor (particle filter and XAD resin) respectively. The clean-up was carried out via liquid chromatography using silica and alumina columns. All analyses were performed by HRGC/HRMS on HP 5890A/VG AutoSpec systems.

3. Results and discussion

Total TEQ emissions of the eight plants are shown in Fig. 1. The highest TEQ values were found at crematory 2, the sintering plants and at the municipal waste incinerator with older technology. TEQ emissions below the 0.1 ng/m^3 limit were found at the modern municipal waste incinerator, the hazardous waste incinerator and at the cement kiln. Proportional and absolute amounts of TEQ values related to PCDD/Fs and PCBs are given in Fig. 2. Shares of PCB-TEQs were found between 0% and 16%.

In Fig. 3 the proportional contribution of the 17 individual PCDD/Fs to the PCDD/F-TEQ is shown. As can be seen from this figure the highest parts are contributed by 23478-pentaCDF and 12378-pentaCDD in most of the samples. The two samples from the sintering plants are characterized by lower parts of pentaCDD but higher parts of pentaCDF. Other tetra- through hepta-chlorinated compounds are relevant as well in the range up to 20%. Contributions of octaCDF and octaCDD to the PCDD/F-TEQ are negligible.

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Table 1
Industrial emission sources

Plant	Description	APC[a] technology	Sampling	Year of sampling
MWI 1	Municipal waste incinerator	Older technology (ESP, WS)	AMESA	1998
MWI 2	Municipal waste incinerator	BAT (BF, 2 stage WS, ACR, SCR)	AMESA	2000
HWI	Hazardous waste incinerator	BAT (ESP, 2 stage WS, ACR, SCR)	AMESA	1999
SINT 1	Sintering plant	(ESP, primary measures)	EN 1948	2000
SINT 2	Sintering plant	(ESP, primary measures)	EN 1948	1999
CEM	Cement kiln	Updated technology (ESP)	EN 1948	1999
CREM 1	Crematory	Elder technology (ESP)	EN 1948	1998
CREM 2	Crematory	Elder technology (Cyclone, BF)	EN 1948	1998

[a] APC: Air pollution control (ESP—electrostatic precipitator; WS—wet scrubber; BF—bag filter; ACR—activated coke reactor; SCR—selective catalytic reactor; BAT—best available technology).

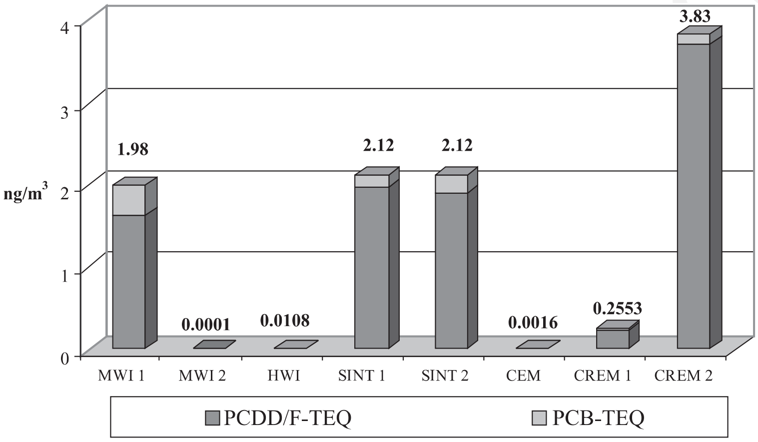

Fig. 1. Total TEQ emissions of industrial sources.

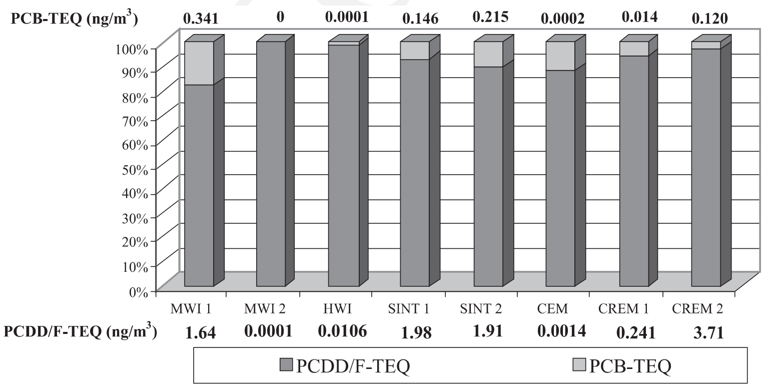

Fig. 2. Proportional TEQ emissions and absolute parts of PCDD/F- and PCB-TEQs.

On the other hand, as can be seen from Fig. 4, the PCB-TEQ in the eight emission samples investigated is mostly influenced by the PCB-126. With exception of the cement kiln the share of PCB-126 is more than 90% of the PCB-TEQ. The cement kiln is the only source which shows significant TEQ contribution from PCB-118 and PCB-156. PCB-169 is present in most samples and contributes up to 6% of the PCB-TEQ. In the emissions from the municipal waste incinerator 2 with best available technology and a very low total TEQ value of 0.0001 ng/m^3 PCBs could not be detected at detection limits of 0.0001 to 0.0009 ng/m^3.

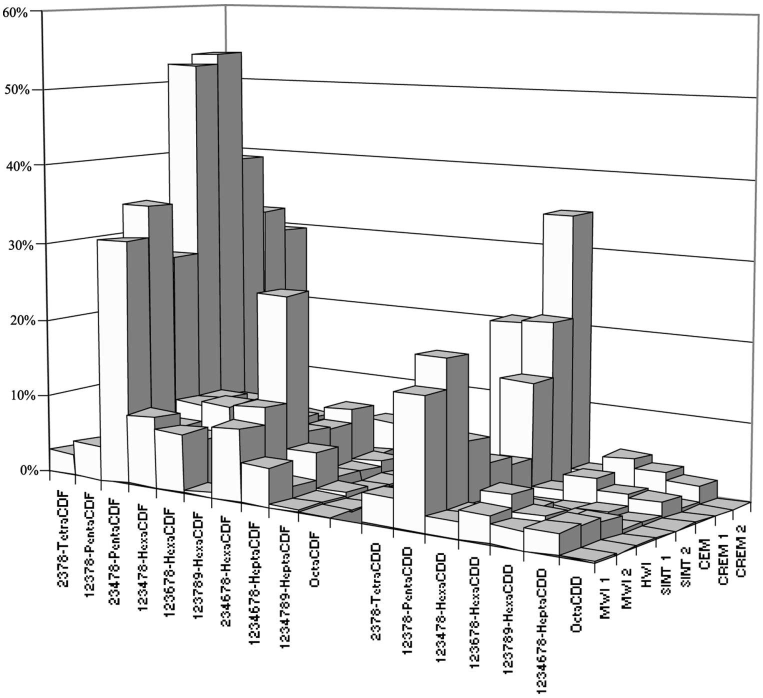

Fig. 3. Proportional contribution of individual PCDD/Fs to the PCDD/F-TEQ.

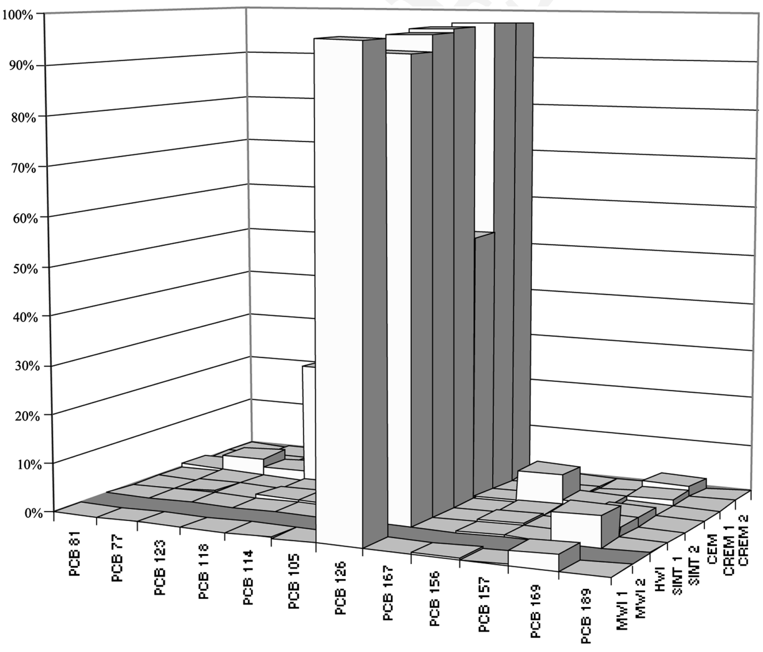

Fig. 4. Proportional contribution of individual PCBs to the PCB-TEQ.

The results of the semiempirical calculations are listed in Table 2. Therefore the PCB-189 is thermodynamically more stable than any other PCB congener of the WHO group. The energy differences are pointed out in Table 2 as ΔHoF in kJ/mol respectively in % (every single energy difference divided by the sum of the energy differences).

Table 2
Physicochemical data of the WHO-PCB congeners according to the MOPAC calculations

PCB no.	Cl substitution	HoF (kJ/mol)	ΔHoF* (kJ/mol)	ΔHoF (%)	Dipole moment (Debye)
81	344′5	91.7	0.0	0	1.512
77	33′44′	89.2	2.5	1	1.921
123	2′344′5	69.7	22.0	9	2.575
118	23′44′5	69.0	22.7	9	1.989
114	2344′5	84.5	7.2	3	1.380
105	233′44′	80.1	11.6	5	3.037
126	33′44′5	73.2	18.5	7	1.567
167	23′44′55′	53.4	38.3	15	1.400
156	233′44′5	65.2	25.5	10	1.721
157	233′44′5′	63.4	27.3	11	2.786
169	33′44′55′	58.3	33.4	13	0.029
189	233′44′55′	50.0	41.7	17	1.256
		Sum	250.7	100	

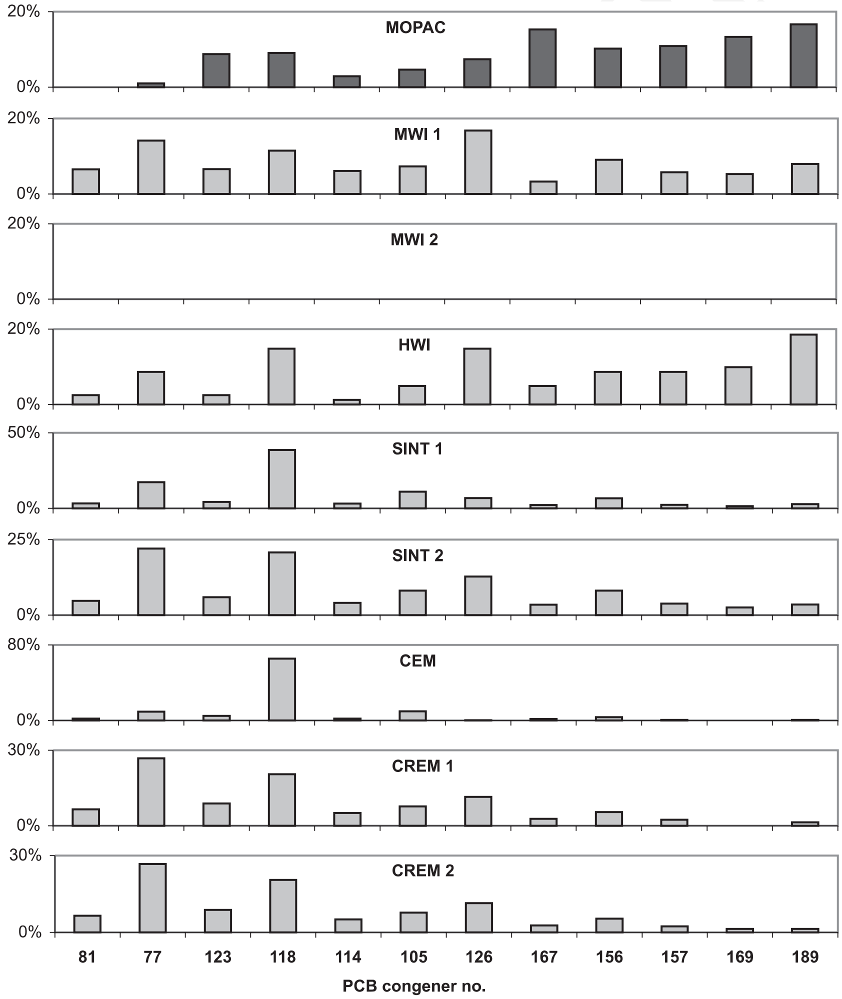

Fig. 5. Proportional contribution of the single PCB congeners to the sum of the PCB congeners in comparison with the thermodynamical preferences according to the MOPAC calculations (see line MOPAC resp. ΔHoF in %, Table 2).

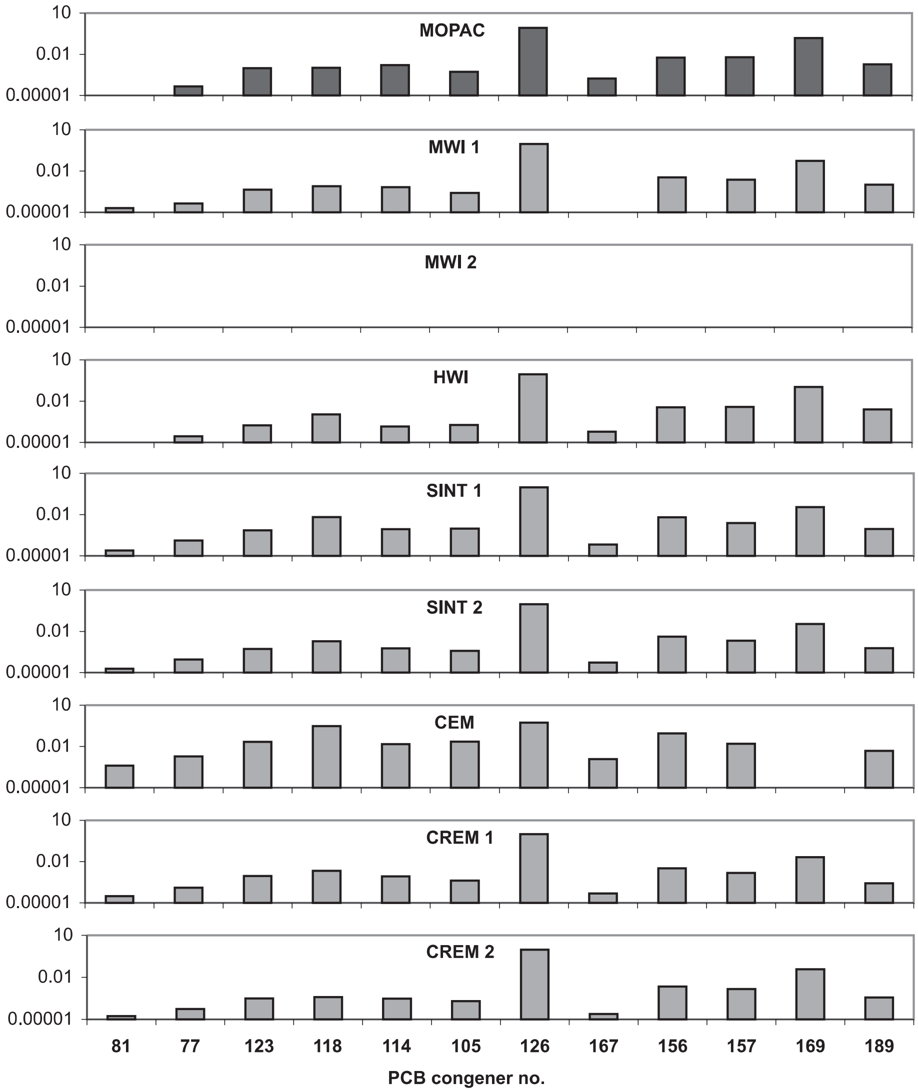

Fig. 6. Proportional contribution of individual PCBs to the PCB-TEQ in comparison with MOPAC calculations (ΔHoF × TEQ).

As it can be seen from Fig. 5 there is a tendential correspondence between fact and theory. Fig. 5 shows the MOPAC calculation results in comparison with the real percentage proportion of the single PCB congeners (Luthardt and Schulte, 2000) with respect to the sum of the WHO-PCB congeners concentration.

Therefore from a "thermodynamical point of view" the more stable PCBs 123 and 118 would be predicted as more likely to be formed in the combustion process. This tendency is followed by a slight decrease for PCB 114 and again an increase for the PCBs 105–126.

The correspondence seems to be not very good for the PCBs 167–189, although the municipal and hazardous waste incinerators show some similarity with the MOPAC predictions for PCB 156–189.

Taking the WHO-TEQ factors into consideration the MOPAC profile looks quite similar to the PCB-TEQ contribution patterns, surely based on the impact of the big differences between the single congeners "personal" TEQ factors (see Fig. 6).

4. Conclusions

Within this work it was found that the contribution of PCBs to the total TEQ of different industrial sources does not exceed 16%. PCB-TEQ in emission samples is mainly set by the part of PCB-126. Other PCB congeners are mostly insignificant with respect to total TEQ emissions.

By means of semiempirical calculations the PCB-189 was found to be the thermodynamical most stable congener of the WHO list. The TEQ ruling PCB-126 is only midranged considering the thermodynamic preference in the combustion process.

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