Dioxin-like PCB in indoor air contaminated with different sources

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Introduction

Polychlorinated biphenyls (PCB) have been used in public building constructions for various purposes in the 1960s and 1970s, mainly as an additive to concrete, caulking, grout, paints, as a major constitutent of permanent elastic Thiokol rubber sealants[1, 2] and flame retardant coatings of acoustic ceiling tiles[3]. Offgazing of semivolatile PCB from building materials can nowadays still result in considerable house-dust contamination[4] and in indoor air concentrations exceeding 10,000 ng/m³ [5, 6]. In Germany, PCB levels in indoor air in non-occupational settings have been regulated with a tolerable total PCB concentration of 300 ng /m³ and an intervention level of 3000 ng/m³ [7]. Lower re-entry criteria have been proposed by Michaud et al.[8].

Technical mixtures of PCB contain dioxin-like non- and mono-ortho substituted PCB congeners and are contaminated with trace amounts of polychlorinated dibenzodioxins (PCDD) and mainly dibenzofurans (PCDF), sharing overlapping toxic effects and physicochemical properties. We report here on levels of dioxin-like PCB measured in buildings with various PCB sources and correlations among PCDD/PCDF and dioxin-like PCB and di-ortho PCB.

Materials and Methods

Data on concentrations of non-dioxinlike di-ortho PCB, dioxinlike PCB and PCDD/PCDF were obtained by sampling of indoor air in eight rooms in four different buildings. One building was contaminated due to PCB containing Thiokol sealants and the others due to PCB containing flame retardants. These buildings were selected because total PCB concentrations in indoor air had been found between 1000 and 3000 ng/m³ indicating the need for remediation.

Eight hours before sampling the air of each room was exchanged by opening the windows, then windows and doors were kept closed overnight and air sampling started the next morning. In buildings no. 3 and 4 (results in last two rows of table 1), sampling started in the late afternoon after typical use (seminar room and office, respectively) and performed overnight while doors and windows were kept closed. Air samples were taken on polyurethane foam by a high volume sampler (building no. 4: low volume sampler) according to the German technical guideline VDI 3498 part 1. After addition of corresponding $^{13}C_{12}$-labelled PCB and PCDD/F standards, soxhlet extraction of PU foams was performed with toluene. The clean up included separation of PCDD/F from PCB and of non-ortho PCB from ortho-substituted PCB. Analysis was performed by well-proven methods of HRGC/HRMS (high resolution gas chromatography/ high resolution mass spectometry) by accredited and quality ensured laboratories (ERGO Hamburg, LfU Augsburg[9]). TEQ levels were calculated using TEF values according to recent WHO recommendations[10]. According to the German regulation[7], total PCB in indoor air were calculated as the sum of 6 indicator PCB (PCB 28, 52, 101, 138, 153, 180) multiplied by factor 5. Results for levels of indicator PCB and TEQ were correlated using Spearman rank correlation coefficients and linear regression analysis (SPSS 11.5).

Results and Discussion

Results for indoor air concentrations of PCB and TEQs for PCDD/PCDF, mono-ortho and non-ortho PCB for the four different buildings are presented in Table 1. Total PCB concentrations ranged from 720 to 2300 ng/m³ and total TEQs from 0.4 to 5.9 pg/m³. PCB congeners 126, 118 and 156 contribute an average share of 70 - 80% and PCDD/F of 10% to the total TEQ (PCB + PCDD/F). Figure 1 depicts the distribution of the 6 indicator di-ortho PCB congeners. The pattern of the Thiokol case resembles a Clophen A30/A40 mixture and the flame retardant pattern is similar to a Clophen A50 pattern.

Table 1: Results of indoor air measurements in four buildings with different PCB sources (Thiokol sealants and flame retardant)

Source	Σ PCB (Σ6 x 5) [ng/m³]	TEQ PCDD/F [pg/m³]	TEQ PCB non-ortho [pg/m³]	TEQ PCB mono-ortho [pg/m³]	Σ TEQ PCDD/F+PCB [pg/m³]	ratio Σ TEQ/Σ PCB pg/µg
Thiokol sealant	715	0.041	0.122	0.224	0.387	0.5
	1298	0.046	0.273	0.436	0.755	0.6
	2253	0.044	0.212	0.444	0.701	0.3
flame retardant	1007	0.121	0.397	1.29	1.81	1.8
	1077	0.121	0.482	1.65	2.25	2.1
	1674	0.375	1.16	3.04	4.56	2.7
flame retardant	1257	0.972	1.47	3.41	5.85	4.7
flame retardant	1377	0.745	0.722	3.24	4.71	3.4

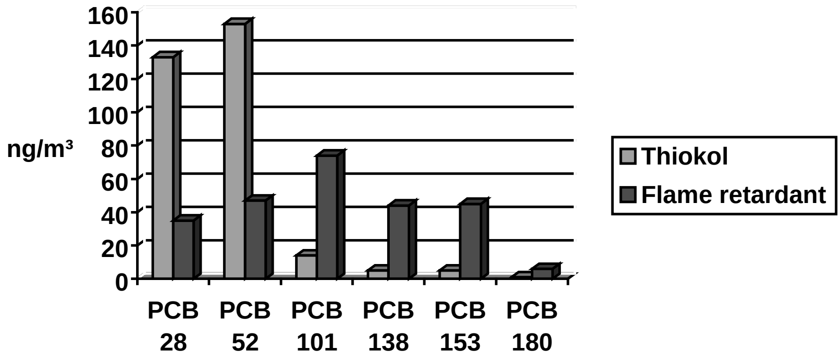

Figure 1: Histogram of mean PCB congener pattern in indoor air in rooms with different PCB sources (Thiokol sealant source; flame retardant source)

Analysis of normal PCB is feasible by GC-ECD or GC-MS, whereas PCDD, PCDF and dioxin-like PCB require a more extensive clean-up procedure and a more sophisticated instrumental method (GC-HRMS). It may be possible for indoor air that contamination of technical PCB mixtures with PCDD/PCDF and dioxin-like PCB and similar physicochemical properties will lead to correlation of classical di-ortho PCB with PCDD, PCDF and dioxin-like PCB expressed as toxic equivalents (TEQ). Such a correlation might allow to estimate TEQ by extrapolation from the results of less sophisticated analytical methods. However, the last column in table 1 shows that rooms with a flame retardant source had a 3 to 15 times higher TEQ-contamination of indoor air compared to the Thiokol source at the same level of total PCB. In the rooms contaminated with Thiokol sealants, a total PCB concentration of 1000 ng/m³ corresponds to a TEQ level of 0.3 – 0.6 pg/m³. A similar correlation of 0.3 - 1.2 pg TEQ/m³ per 1000 ng/m³ of total PCB was demonstrated recently by Kohler et al.[11] in five buildings where the pattern of individual PCB congeners in indoor air indicated Clophen A30/A40 as the source of PCB contamination.

From the results of the present study this relationship is only applicable if a congener pattern of lower chlorinated PCB is prevailing. If however the pattern is shifted towards higher chlorinated congeners (figure 1) a ratio of 1.8 – 4.7 pg

TEQ/m³ corresponding to 1000 ng total PCB/m³ must be considered (table 1). Hence direct extrapolation from total PCB might be misleading and underestimating TEQ exposure.

Intercorrelation of PCB revealed a negative correlation of the tri- and tetra-chlorinated PCB congeners 28 and 52 with dioxin-like PCB and TEQ. Figure 2 presents the curve fit of a linear regression analysis between the sum of PCB 101, 138, 153 and 180 and PCB TEQs. We recommend to use algorithms to calculate the expected PCB TEQ in indoor air in cases where the indoor air is contaminated with PCB, thus enabling a more precise risk assessment.
Rather than estimating TEQ from total PCB calculated as the sum of 6 di-ortho congeners, a congener-specific approach might yield a more precise estimate of the concomitantly occurring contamination.

Since the sum of PCB congeners 101, 138, 153 and 180 showed highest correlation these indicators are proposed for calculation of PCB TEQ according to the regression formula:

PCB TEQ [pg/m³] = 0.018 x (PCB 101 + 138 + 153 + 180) + 0.034 [ng/m³]

Based on these congeners another algorithm could be derived for total TEQ (PCDD/F + PCB) as:

Total TEQ [pg/m³] = 0.021 x (PCB 101 + 138 + 153 + 180) – 0.042 [ng/m³]

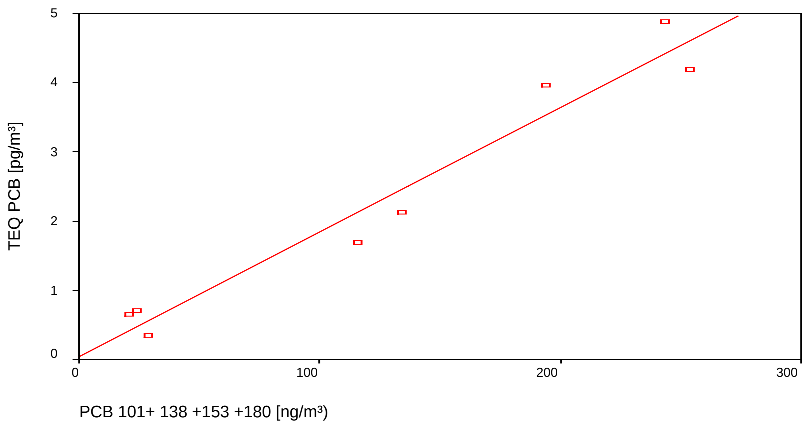

Figure 2: Regression of sum of PCB 101, 138, 153 and 180 and sum of dioxin-like PCB (TEQ):
PCB TEQ [pg/m³] = 0.018 x (Σ PCB 101, 138, 153, 180) + 0.034 [ng/m³]

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