

CONCENTRATIONS OF 209 PCB CONGENERS IN HUMAN BLOOD SAMPLES FROM INDIVIDUALS EXPOSED TO PCB VIA INDOOR AIR

Kraft M¹, Sievering S¹, Lohmann N², Rauchfuss K^{1*}

¹ North Rhine-Westphalia State Agency for Nature, Environment and Consumer Protection, Leibnizstr. 10, D-45659 Recklinghausen, Germany; ² Eurofins GfA Lab Service GmbH, Neuländer Kamp 1a, D-21079 Hamburg, Germany

Introduction

Polychlorinated Biphenyls (PCBs) are persistent synthetic organochlorines. The variation of possible positions of chlorine atoms on their benzene rings leads to 209 different possible PCB congeners. Due to the diverse commercial PCB mixtures, that have been developed and used throughout the decades, and because of the variation of environmental half-lives among the different congeners, the ambient concentrations vary from one congener to the other.

Usually only a small number of indicator congeners are analyzed in environmental samples. To estimate the total PCB content in a certain medium these indicator congeners are usually multiplied by a specific factor, depending on the assumed relative share of the indicator congeners from total PCB in the analyzed matrix.

Due to its lipophilicity PCB accumulates in the food chain and in human lipid tissue and can cause a variety of dose-dependent adverse health effects in different tissues and organs.

For Human Biomonitoring regularly PCB 138, PCB 153 and PCB 180 are analyzed as indicator congeners in blood samples. According to the German "Human Biomonitoring Commission" at the Federal Environment Agency the sum of these indicator congeners represents about 50 % of the total PCB body burden, so that it has to be multiplied by factor two to calculate the total amount.¹ The data, which formed the base of this convention, was taken from different exposure studies with participants mainly exposed to PCB by dietary intake. The number of congeners examined in these studies varies from 19 to 51.^{2,3}

Although their prohibition in the early 1980ies PCB can still be detected in higher concentrations in elder buildings in particular in those constructed during the 1960ies and 1970ies. People living or working inside these edifices can be exposed to elevated levels of PCB through indoor air. Some studies showed, that due to the different pattern of congeners, the exposure to lower chlorinated PCBs - specifically to PCB 52 and PCB 28 - is relatively higher via indoor air than through dietary intake.^{4,5}

With our study we examined, whether the three indicator congeners PCB 138, PCB 153 and PCB 180 would represent 50 % of the body burden also in a study group which was specifically exposed to PCB by indoor air, and if the convention of multiplying this sum by factor two could lead to precise results even in the case of estimating the PCB body burden after indoor air exposure. To investigate the distribution of the different congeners in human blood samples all 209 congeners needed to be analyzed.

Materials and methods

We collected blood samples from adults working in different public buildings, where they had been exposed to elevated concentrations of PCB in indoor air. The participants were recruited from a university, a school and a town hall. The selection of the participants has been carried out by using data from previous indoor air measurements. The exposure concentrations of PCB in 36 rooms have been reassessed to verify the elevated exposure levels. In questionnaires we asked for other possible exposure sources, such as dietary habits, for the type of buildings where the participants used to live, some social determinants and the time budgets spent at their working places.

In total, 44 whole blood samples were analysed for PCBs at Eurofins GfA Lab Service GmbH in Hamburg. For the collection, storage and transport of whole blood pre-cleaned 100 ml glass containers (Schott/Duran) equipped with Teflon-lined caps were used. To avoid any break down of the samples, heparin as anticoagulant was added to the glass containers before collection. All samples were stored below -20°C until start of the analysis.

30 g of whole blood were spiked with a mixture of 35 ¹³C₁₂-quantification standards (Mono- to DecaCB). The sample was diluted with 20 ml water and 5ml ethanol were added. Liquid/liquid partitioning was performed

three times with 20 ml hexane each and once with hexane/iso-propanol (3:2). The combined extract was washed with water and dried over sodium sulfate. After solvent evaporation, gravimetric lipid determination was performed. The lipid fraction was diluted with hexane. Clean up was performed by column chromatography using a combination of sulfuric acid treated silica and activated alumina. The cleaned extract was reduced to a final volume of 50 to 100 μ l containing additional 7 $^{13}\text{C}_{12}$ -labelled PCBs (Di- to NonaCBs, except HeptaCBs) as recovery standards.

The following HRGC separation was performed on an HT8-PCB 60m x 0.25 mm x 0.25 μ m GC-column using Thermo DFS and Waters Autospec high resolution mass spectrometers at mass resolution $R \geq 10.000$. With the chosen setup, a maximum separation of about 180 signals is possible. Quantification was narrowed down to 170 separations for reasons of constant data quality. Quantification was performed using the isotope dilution method resulting in the quantification of 141 individually separated PCB-congeners, 27 co-eluting pairs of PCB-congeners and two data sets each for three resp. four co-eluting PCBs.

QA/QC measures consisted e.g. in monitoring the quantification standard recovery rates (acceptance 40-120%), as well as batch blanks and control samples. The limit of quantification was established based on an approach according to EN1948-4 using the average laboratory blank level plus 5-fold standard deviation. Calibration was established preparing an initial multipoint calibration curve for reference purposes, and daily single-point calibrations checked against the multipoint curve. This was performed individually for all reported congeners/groups. Further details of the method and quality criteria are described elsewhere.⁶ Statistical evaluation has been carried out by using "SPSS Statistics" (Version 19).

Results and discussion

Our monitoring of indoor air detected PCB concentrations between 92 and 2797 ng/m^3 (Median: 477 ng/m^3 ; 95th Percentile: 2266 ng/m^3), so most of the participants have been exposed to elevated PCB levels. The dominant congeners which could be detected in indoor air were lower tri- and tetra-chlorinated PCBs such as PCB 18, PCB 28, PCB 31 and PCB 52.

63 congeners could be quantified in each of the 44 blood samples, another 96 congeners in at least one blood sample. The following 50 congeners could not be quantified in any of the samples: PCB 2, PCB 10, PCB 11, PCB 14, PCB 21, PCB 23, PCB 24, PCB 29, PCB 30, PCB 34, PCB 35, PCB 36, PCB 38, PCB 39, PCB 50, PCB 54, PCB 57, PCB 58, PCB 61, PCB 62, PCB 67, PCB 73, PCB 76/80, PCB 78, PCB 79, PCB 88, PCB 94, PCB 96, PCB 100, PCB 104, PCB 106, PCB 116/125, PCB 122, PCB 129, PCB 140, PCB 143, PCB 145, PCB 150, PCB 152, PCB 155, PCB 168, PCB 173, PCB 176, PCB 185, PCB 186, PCB 188, PCB 192, PCB 199 und PCB 204.

Total PCB lipid weight concentrations in the 44 blood samples (Σ 209 PCB congeners) ranged from 99 to 2152 $\text{ng PCB}/\text{g lipid}$ (Median: 454 ng/g ; 95th Percentile: 1404 ng/g). PCB 153 and the co-eluted congeners PCB 189/193 and PCB 138/160 were the most relevant congeners in the blood samples. To 14 other congeners relevant shares $> 1\%$ could be attributed (see Figure 1).

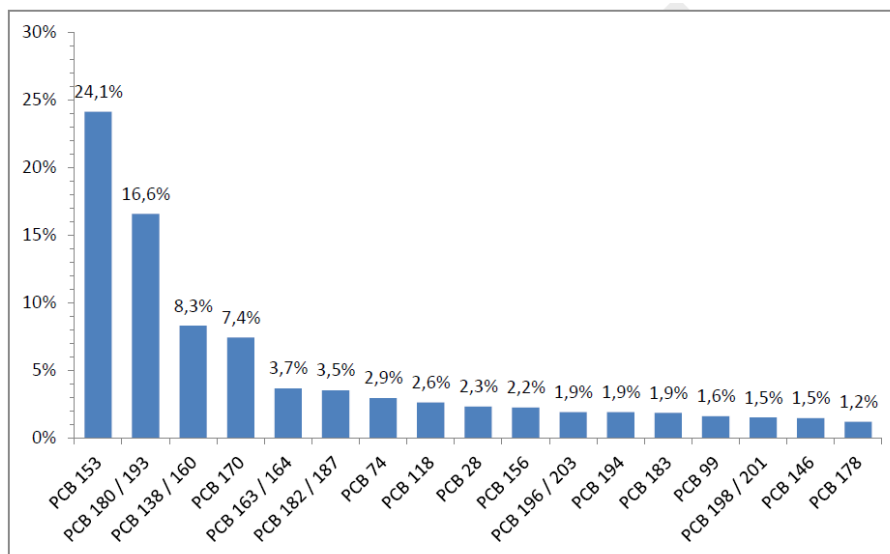


Figure 1: Relevant relative share of single congeners (> 1%) to the total body burden in 44 blood samples (Median).

Over all the median relative contribution of the three indicator congeners (Σ PCB 138, 153 and 180) was 49 %, but the relative share of these congeners varied over the 44 different samples (24% to 61%). If a regular variation of ± 5 % is taken into account, the majority of the samples (32 of 44) showed a relative contribution of the indicator congeners of about 50% (between 45% and 55%). Four samples showed higher percentages than 55% and in eight samples the indicator PCBs shared less than 45% of the body burden.

When we calculated the total body burden for each sample by the convention Σ PCB 138, 153 and 180 multiplied by the factor 2, and then compared these results to the sum of all the 209 measured congeners for each sample, a strong and highly significant correlation between both results could be found. Figure 2 shows the highly significant correlation ($p < 0.001$).

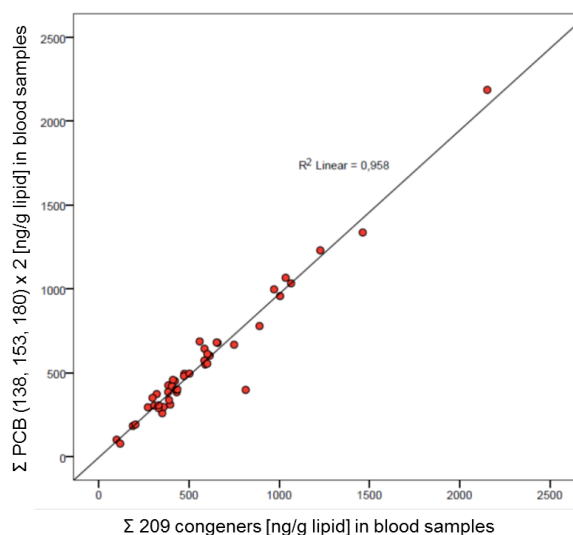


Figure 2: Correlation between calculated and measured PCB body burden in 44 human blood samples (three indicator congeners)

We further investigated, whether an alternative calculation could lead to an even stronger correlation between calculation and measurement. Therefore we chose six indicator congeners, which further take into account the lower chlorinated congeners (PCB 28, PCB 52, PCB 101 and again the three higher chlorinated congeners PCB 138, PCB 153 and PCB 180), multiplied the sum of these six indicator congeners by the factor two as well, and

compared the result to the measured body burden (Σ 209 congeners). The results of the correlation analysis are shown in figure 3.

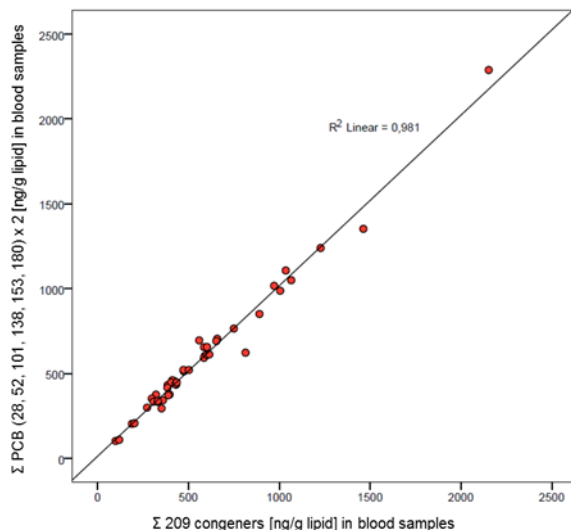


Figure 3: Correlation between calculated and measured PCB body burden in 44 human blood samples (six indicator congeners)

The calculation with six indicator congeners is slightly stronger correlated (r : 0,990) to the determination of the body burden by measuring all 209 PCB congeners, than the conventional calculation of using only three indicator congeners (r : 0,979).

Although the convention issued by the German “Human Biomonitoring Commission” - to calculate the total PCB body burden by measuring three indicator congeners and multiplying their sum by factor 2 - leads to quite good results, even in groups exposed mainly by indoor air, the inclusion of the three lower chlorinated congeners into the calculation could further improve the convention and enhance the results of estimating PCB body burden based on indicator congeners.

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