

## Indoor contamination in a former PCB-manufacturing region of Slovakia

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### Introduction

In Eastern Europe, a major manufacturer of polychlorinated biphenyls (PCBs) was the Chemko Stražské company, located in the area of Michalovce, Slovakia. From 1959 to 1984, Chemoko Stražské produced 21482 tonnes of PCB formulations.<sup>1</sup> The legacy of PCB manufacturing in this region left high levels of environmental contamination in soil, water, sediment, air and biota, including concentrations of PCBs in outdoor air up to 1700 ng/m<sup>3</sup>.<sup>1</sup>

In 2002, a human cohort study was established in the region surrounding the Chemko Stražské factory, with a focus on PCB exposure and possible links to health effects. The cohort consists of >1000 mother-child pairs, with an original focus on PCB exposure and developmental and endocrine-related effects in children.<sup>2</sup> Geographic analysis of PCB serum levels suggested an exponential decrease in serum concentration with increasing distance of residence from the former factory.<sup>3</sup> This suggests that the contaminated environment is leading to higher human exposure to PCBs, but the exposure pathway is not clear.

In 2015, indoor air and dust samples were collected from the homes of a subset of children in conjunction with the ongoing cohort, with the following objectives: (1) screen levels of indoor persistent organic pollutants (POPs) and emerging contaminants in residences in Eastern Slovakia and compare with other regions; (2) evaluate whether proximity to the PCB manufacturing site leads to elevated indoor levels of PCBs; (3) identify the major toxicity risk factors in indoor air and dust; and (4) compare indoor levels of PCBs with blood serum levels of PCBs to evaluate a possible link between indoor levels and human exposure.

### Materials and methods

Indoor samples were collected in 60 homes in Eastern Slovakia, with 30 from homes of highly exposed children (i.e., those with high levels of PCBs in blood serum) and 30 from homes with average/low exposure children. Air samples were collected by polyurethane foam passive air sampler (PUF-PAS), deployed with a single-bowl configuration for 1 month periods. Dust samples were collected in single-use polyester sampling socks inserted in the front end of a household vacuum cleaner, by vacuuming exposed floor surfaces in the homes. Collection protocols were as described in Venier et al.<sup>4</sup> Samples were collected in the main living area of the home between March and May 2015. Additionally, window and furniture wipes were collected as complementary sources of information.

All samples were analyzed for a broad suite of legacy POPs and emerging chemicals. The target compounds were 9 PCB congeners, 10 polybrominated diphenyl ethers (PBDEs), 12 organochlorine pesticides/isomers/metabolites (OCPs), 26 polycyclic aromatic hydrocarbons (PAHs), 18 organophosphate esters (OPEs), 22 novel halogenated flame retardants (NFRs), hexabromocyclododecane (HBCDD) – 4 isomers, and 6 polycyclic musks (PCMs). This suite of compounds covers a broad range of sources, regulatory status and use/emission levels to allow comparison between the PCBs, with known nearby contamination vs.

compounds with typical indoor sources (e.g., flame retardants) vs. those with typical outdoor sources (e.g., OCPs, PAHs).

Air and wipe samples were extracted using automated warm Soxhlet extraction (40 minutes warm Soxhlet followed by 20 minutes of solvent rinsing) with dichloromethane (DCM) in a B-811 extraction unit (Büchi, Switzerland), and dust samples were extracted by repeated (3x) sonication in 1:1 hexane:acetone. Samples were split 30:70, with PAHs, PCMs, NFRs, and OPEs analyzed in the 30% aliquot, and PCBs, OCPs, PBDEs and HBCDD in the 70% aliquot. The 70% fraction was cleaned-up on an H<sub>2</sub>SO<sub>4</sub> modified silica column, eluted with DCM/n-hexane (1:1), while the 30% fraction was fractionated on a silica column with 5 g of activated silica and 1 g Na<sub>2</sub>SO<sub>4</sub>. The first was eluted with 5 mL n-hexane followed by 50 mL DCM (for PAH, PCM, NFR analysis) while the second fraction was eluted by 20 mL of acetone/DCM (70:30) (OPE analysis).

Samples were analyzed by gas-chromatography/mass spectrometry (GC-MS), excepting HBCDD, which was quantified by liquid chromatography-tandem mass spectrometry (LC-MS/MS) on an Agilent 1100 series HPLC system with a Phenomenex LUNA C-18 column (100 × 2 mm, 3 μm particles size) and Phenomenex SecureGuard C18 pre-column. PAHs and PCMs were analyzed on a 7890A GC (Agilent, USA) equipped with a 60 m x 0.25 mm x 0.25 210 μm Rxi-5Sil MS column (Restek, USA) coupled to a 7000B MS (Agilent, USA). PBDEs were analysed by high resolution GCMS (HRGC/HRMS) with a 7890A GC equipped with a 15 m x 0.25 mm x 0.10 μm RTX-1614 column (Restek, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). PCBs and OCPs were analysed by GC-MS/MS with a 7890A GC equipped with a 60 m x 0.25 mm x 0.25 μm HT8 column (SGE, USA) coupled to a 7000B MS (Agilent, USA) operated in EI+ MRM. NFRs were analysed by high resolution GCMS (GC/HRMS) using a 7890A GC equipped with a 15 m x 0.25 mm x 0.10 μm RTX-1614 column (Restek, USA) coupled to an AutoSpec Premier MS. OPEs were analysed by GC-MS/MS with a 6890A GC (Agilent, USA) equipped with a 60 m x 0.25 mm x 0.25 μm Rxi 5Sil MS column (Restek, USA) coupled to a Quattro Micro GC MS (Waters Micromass, UK) operated in EI+ MRM.

Sample masses were adjusted for analytical recoveries, and methods were validated based on analysis of reference materials, in particular NIST SRM 2585 (house dust). Field blanks were collected during sampling, and samples were adjusted for blank levels based on the average of the field blank. Samples with masses less than the average of the field blanks plus 3x the standard deviation of the field blank were reported as below the method detection limit.

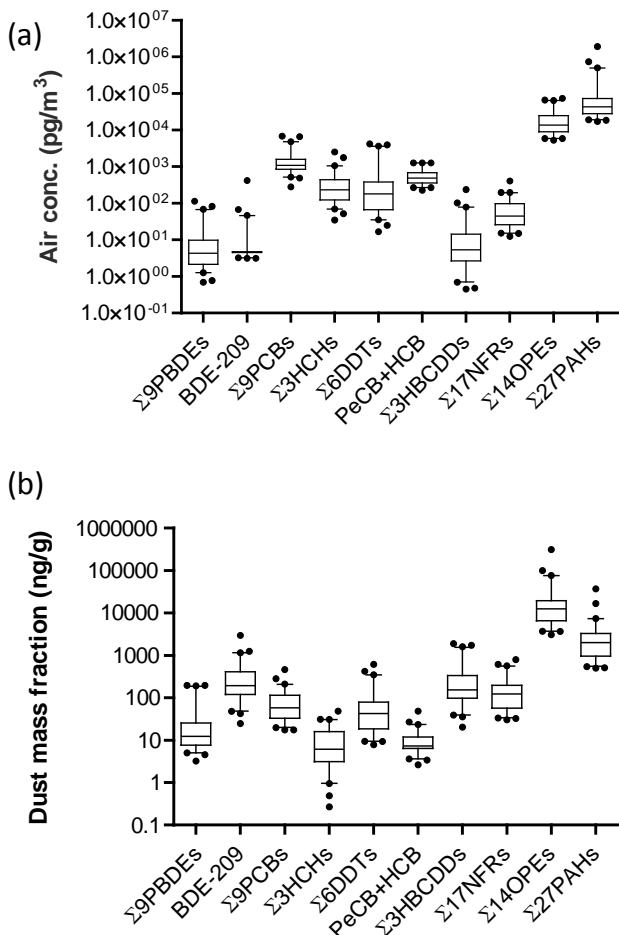
## Results and discussion

The dominant compound class in air was PAHs, with median concentrations of  $\sum_{27}$ PAHs of 113 ng/m<sup>3</sup>, followed by OPEs (median: 19.7 ng/m<sup>3</sup>). Other compound groups were orders of magnitude lower (Fig 1a). The dominant compound class in dust was OPEs (median 22.2 μg/g), and similarly to indoor air, there were order of magnitude differences between compound groups (Fig. 1b). While there was a great deal of individual variability among residences, the typical profile of indoor dust was dominated by three OPEs: TPhP, TBEP and TDCIPP, while the typical profile of indoor air was dominated by three PAHs: phenanthrene, acenaphthene and acenaphthylene (Fig. 2). The major flame retardants in air were TiBP and TnBP, each comprising ~4% of the total contaminant loading.

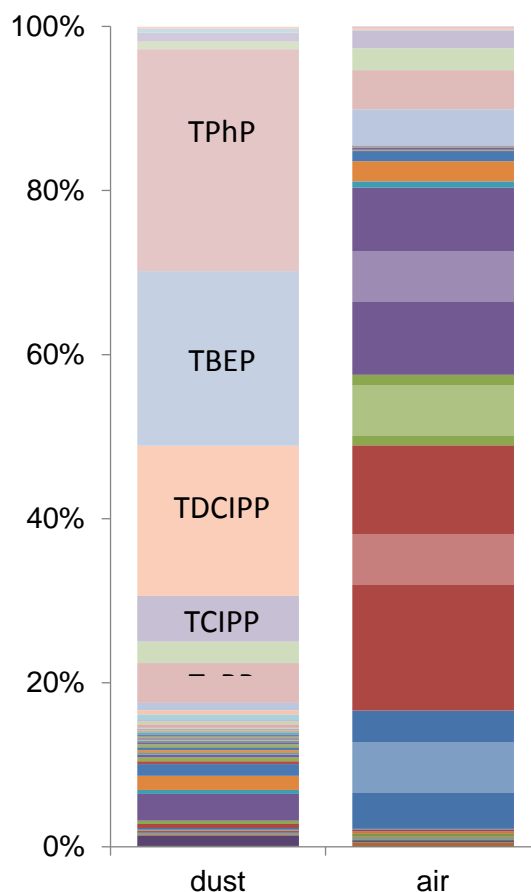
Concentrations of certain compounds were strongly correlated with other compounds, which may indicate similar sources. For example, in air, concentrations of OCPs (HCHs, DDTs) were all strongly correlated, with Spearman r of 0.72. Additionally, PBDEs, HBCDDs and OPEs were correlated (Spearman r of 0.36-0.38), but NFRs were not correlated. In dust, all flame retardant groups (PBDEs, NFRs, and OPEs) were correlated with each other, with the exception of HBCDD, which was not correlated with any other compound group. This suggests a difference source profile for HBCDD than for the other flame retardants, such as specifically insulation as an

HBCDD source<sup>5</sup>, while general consumer and household products as a source for other FRs.

Air and dust concentrations for individual compounds were also compared using Spearman  $r$ . The more volatile compounds (PCBs, OCPs, tetra-hexa-BDEs) had a significant correlation between concentrations in air and dust, while the less volatile compounds (high molecular weight PAHs, many OPEs and NFRs) did not. This discrepancy has previously been noted in comparisons of air and dust (e.g., Venier et al.<sup>4</sup>) and suggests that higher molecular weight compounds with current active sources do not reach equilibrium between air and dust. Despite the hypothesized high concentrations of PCBs, the concentrations of PCBs in indoor air and dust were within the range of what has been measured for other similar areas. The concentrations of PCBs in air ranged from 0.282 to 6.92 ng/m<sup>3</sup>, with a median of 1.09 ng/m<sup>3</sup>. This is within the range measured in homes in Canada,



**Fig. 1:** Comparison of ranges and means of compound groups in Slovak residences in (a) air and (b) dust.



**Fig. 2:** Profiles of median compound distribution in dust and air from all residences. Major contributing compounds are identified.

Czechia and USA.<sup>6</sup> Similarly, PCBs in dust, with a range of 17.4 to 465 ng/g (median: 58.0 ng/g) were also within the range measured in Canada, Czechia, UK and USA.<sup>6,7</sup> Thus, this suggests that the elevated levels of PCBs in human serum measured in residents are not due to indoor levels of PCBs, and rather most likely caused by an alternate exposure pathway, such as diet, through ingestion of locally grown food. This fits with the paradigm of PCBs as a legacy chemical, where the primary exposure pathway has shifted from environmental to dietary.<sup>8</sup>

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