POLYBROMINATED DIPHENYL ETHERS IN THE INDOOR ENVIRONMENT – PRELIMINARY RESULTS FROM AN EXPOSURE STUDY IN DENMARK

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of high volume chemicals applied as flame retardants in a variety of products, such as electronic equipment, upholstery, textiles, building materials and plastic products. Two of the main technical mixtures, Penta-BDE and Octa-BDE, have been banned by the European Union and most states of the USA, while the fully brominated Deca-BDE remains unregulated at present. However, discussions on its ban in electronic equipment are currently taking place in the European Union. The intensive industrial and commercial use of PBDEs has led to a ubiquitous presence and to increasing concentrations in the environment over the past 40 years [1]. Being chemically similar to polychlorinated biphenyls (PCBs), they are assumed to exhibit similar toxicological effects, such as reproductive and developmental deficiencies, due to endocrine-modulating effects, immunosuppression and carcinogenity [2]. Their fate in the environment was also found to be similar to PCBs, for instance with regard to geographic trends in the Arctic [3], so it seemed obvious also to expect the same routes of exposure to humans. As a consequence of bioaccumulation and biomagnification, PCBs and PBDEs accumulate in lipid-rich tissue of high trophic level animals, thus leading to uptake by humans with e.g. fatty fish. [4]. In addition to this well-described distal exposure, however, sources in the home, i.e. proximal exposure, have been shown to contribute significantly to the human exposure to PBDEs: Due to their presence in a number of products of every-day use, they have been detected in indoor air and, most significantly, in house dust [5]. Only by including these pathways in the description of human exposure, it has been possible to explain the differences in PBDE levels generally found between Europeans and North Americans [5]. In this project, we have worked with a cohort of 43 pregnant women from the Copenhagen area to study relations between external exposure in their homes, lifestyle factors and eventually, the pre-and neo-natal exposure of the child, via placenta and breast milk. This paper presents preliminary results on PBDEs in the indoor environment, with focus on particles and dust.

Materials and Methods

Recruiting

The 43 participants in this study were recruited through the maternity ward of the University Hospital of Copenhagen and the Institute of Public Health, University of Copenhagen. They agreed to having samples of air and particles collected in their homes, over a period of five days immediately prior to Caesarean section, to logging their activities during this period and to providing the contents of their vacuum cleaner bags for analysis. A second set of dust samples was collected approximately three months after child birth. The participants filled in an extensive questionnaire on their lifestyle and potential contact with PBDEs. Additional samples to assess internal exposure included blood plasma, placenta, umbilical cord blood plasma and breast milk, however, these are not covered in this short paper.

Sampling

Quartz filters (Supelco) heated to 450°C overnight and polyurethane foam (PUF) cylinders (22 mm diameter, 30 mm length, 0.022 g/cm^3 density, Supelco) cleaned by overnight extraction with dichloromethane were placed into a glass holder connected to the pump. The sampler was deployed in the living rooms of the participants' homes for approximately five days. Air was pumped through the filter and PUF at a rate of 5 L min^{-1}. Following dismantling, the filters and PUFs were stored at -20°C in aluminium foil and pre-cleaned glass containers, respectively. The dust samples originated from the participants' private vacuum cleaners. The contents were

sieved several times, down to a size fraction of < 75 µm, which was stored at -20°C in aluminium containers until analysis.

Chemical analysis

Approximately 0.5 g of dust and whole filters were extracted by pressurized liquid extraction (ASE 200, Dionex) at 125°C using dichloromethane:hexane (1:1). For clean-up of the extracts, 1 g of silica was added to each cell. Prior to extraction, the samples had been spiked with ^{13}C-BDE-209 and BDE-77. Recoveries between 80-120% based on BDE-77 concentrations were found acceptable. The extracts were evaporated and adjusted to a precise volume of 1 ml, following addition of BDE-116 as a syringe standard. The samples were analysed by gas chromatographic separation (model HP 6890) with mass spectrometric detection (MS, model HP 5973), using electron capture negative ionisation (ECNI). The capillary column was a 60 m J&W Scientific DB-5 capillary column, while BDE-209 was analysed on a 15m J&W Scientific DB-1 column. Samples were analysed in batches of up to 11 individual samples. At least one dust sample per batch was extracted in duplicate. Two blanks were included, in the beginning and at the end of the extraction sequence, respectively, as well as a duplicate sample of the certified reference material NIST SRM® 2585: Organic contaminants in house dust. The following congeners were included in the analysis: BDEs 17, 28, 47, 49, 71, 85, 99, 100, 153, 154, 183 and 209.

Results and Discussion

The results presented in this short paper are preliminary, as analyses and data treatment are not complete. At present, results on BDE-209 are available for all filter and dust samples (Figure 1), and a subset of 10 and 14 samples have been analysed for the remaining BDE congeners in dust and air particles, respectively (Figure 2). For privacy protection, residence identification is based on random numbers. PUFs have not been analysed yet as the method development indicated differences in recoveries and blanks between pressurized liquid extraction and Soxhlet extraction. None of the dust samples, but four filter extracts had recoveries below 80% for BDE-77 (Figure 2). Since the analyses could not be repeated, the BDE concentrations (except BDE-209) were corrected for recovery for these four samples.

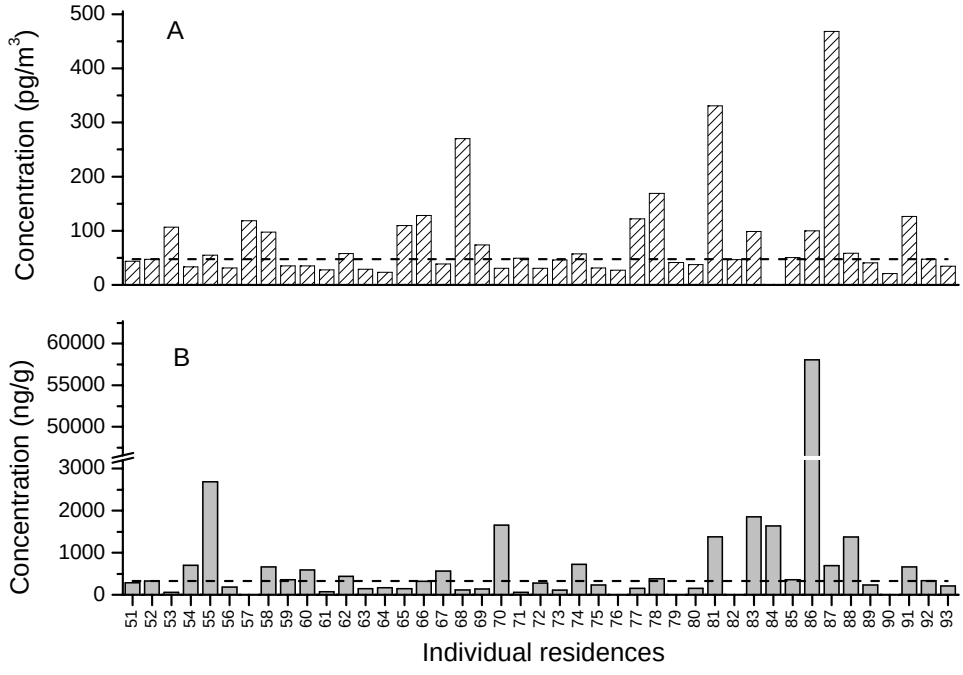

Figure 1: Concentrations of BDE-209 in air particles (A) and dust (B), collected at 43 individual residences in the Copenhagen area. The dashed lines indicate the median values. 76: No dust sample available. 84: No filter sample available. 57, 79, 82 and 90: Analyses of dust samples not complete.

The BDE-209 concentrations in dust covered a range of three orders of magnitude, from 55 to 58000 ng/g. Sample 86 was analysed twice to confirm the exceptionally high concentration. The median value of all dust samples was 332 ng/g. This level is similar to previous findings from Denmark and Sweden, while results from Germany were closer to the minimum value of this study [6,7,8]. BDE-209 in dust from the USA was generally an order of magnitude higher than European values, except for a concentration of 7100 ng/g detected in British samples [6,7].
BDE-209 in particle samples varied by a factor of 22, from 21 to 468 pg/m^3. The median value was 47 pg/m^3. Information on particle-bound PBDEs is sparse, as most studies add the PBDE concentrations on particles and those in air; however, BDE-209 is mainly detected in the particulate phase [9]. Results from the USA showed a considerable increase of BDE-209 from room air (94 pg/m^3) to personal air (174 pg/m^3), collected within the breathing zone of the participant. This might be related to activity patterns, including re-suspension of dust and thus, higher particle concentrations in personal air [9]
Interestingly, there was no correlation between BDE-209 concentrations in particles and dusts. Correlation analysis was performed on ln-transformed data and Spearman's correlation coefficient was found to be 0.197, i.e. not statistically significant at a 5% significance level. This result is somewhat surprising, as re-suspension of dust might be an important contribution to particle levels [9].

The remaining BDE congeners have been determined in a subset of 10 dust and 14 filter samples (Figure 2). In the sum calculation of "Other PBDEs", values below the limits of detection were treated as zero. This mainly applied to the filter samples where only BDEs 47 and 99 were above the limit of detection in all samples. BDEs 17, 28, 66, 85, 154 and 183 were not detected in any of the filter samples. With very few exceptions, all congeners were found in the dust samples. Similarly to the filter samples, the main congeners in dust were BDEs 47, 99 and 71.
The concentration of the other PBDEs varied by a factor of > 200 within this small set of samples, while there was a factor of 4 between the lowest and the highest filter sample. Thus, ΣPBDE (incl. BDE-209) in dust ranged between 184 and 4513 ng/g, with a median value of 650 ng/g. This is also similar to previous results from Denmark and Sweden [6,8] and less than half of some concentrations reported from North America [10]. However, bearing in mind the large range of BDE-209 concentrations (Figure 1), these results are subject to change as more data become available.
ΣPBDE (incl. BDE-209) in filter samples ranged from 57 to 532 pg/m^3, with a median value of 120 pg/m^3. This is approximately 4 and 6 times below particle + air concentrations reported for room air and personal air, respectively, from the USA [9]. With the exception of residence 54, Figure 2 showed higher proportions of BDE-209 to ΣPBDE in dust than in airborne particles. In the dust samples, BDE-209 accounted for 86% of ΣPBDE (median value), while the proportion of BDE-209 was only 44% in filter samples (median value). However, as Figure 2 illustrates, the inter-homes variation can be very large.
Given the small dataset, the power of statistical analyses is low. However, correlation analyses on ln-transformed data indicated that BDE-209 behaved differently from the other BDEs: No significant correlation was found between BDE-209 and "Other PBDEs" in the same samples, neither for ΣPBDE (incl. BDE-209) in dust and filter samples. However, a correlation coefficient of 0.577 was found between "Other PBDEs" in dust and filters, which was not significant at a 5% significant level, but indicated some relation between non-BDE-209 congeners.

The next steps in this study will focus on the finalisation of the chemical analyses of filter, dust and PUF samples. Questionnaires and activity-logs have been received and are presently checked for completeness. Analyses of human samples have been commenced, as presented in another paper of this issue [11]. Thus, a large dataset will be obtained, subject to multivariate analyses to analyse sources of exposure and to study pre- and neo-natal exposure.

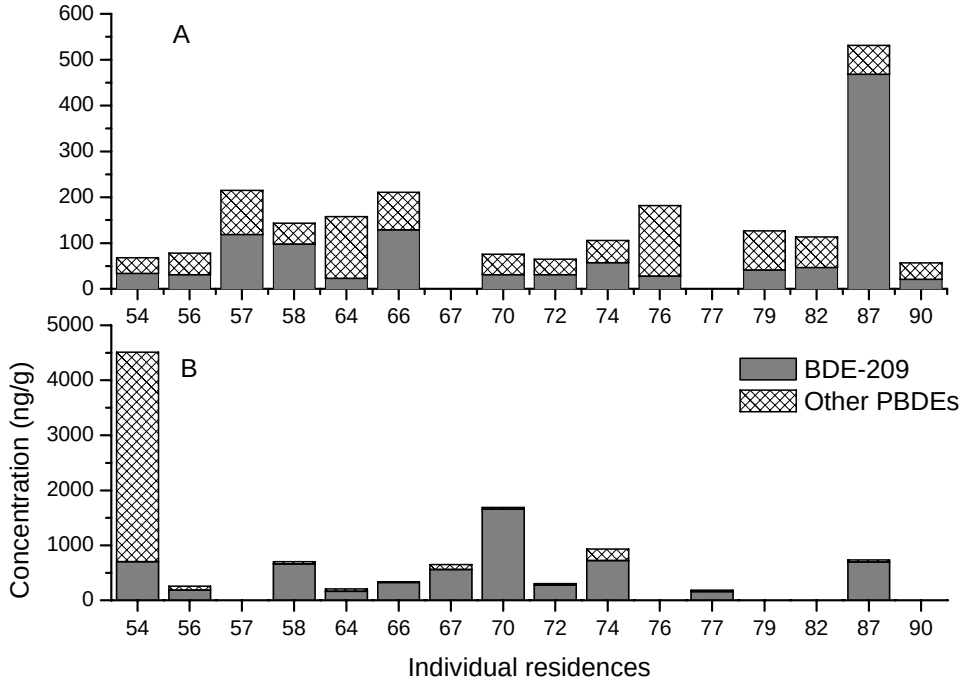

Figure 2: Concentrations of BDE-209 and summed concentrations of other BDEs in airborne particles (A) and dust (B), in a subset of the 43 samples. "Other PBDEs" were corrected for recovery in the filter samples 54, 56, 57 and 64. Gaps in the figure indicate that the analyses are not completed at present, with the exception of residence 76 (no dust sample available).

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