Implications of Passive Sampling Derived Concentrations of Airborne PCBs and PBDEs in Urban Indoor Microenvironments

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Introduction

Polychlorinated biphenyls (PCBs) and polybrominated diethyl ethers (PBDEs) are ubiquitous environmental contaminants that are a cause of major environmental concern because of their persistence, ability to bioaccumulate and their potential impact on human health. Although most studies consider that the vast majority of human exposure to PCBs and PBDEs occurs via the dietary pathway; application of these compounds in building materials and products employed in indoors (i.e. furniture, electronic and electrical equipment) along with elevated indoor air concentrations [1-4] and the high proportion of time spent in such environments (i.e. typically more than 90%), implies that inhalation exposures may be significant for some people. Given the relative lack of data on airborne concentrations of PCBs and PBDEs in a wide range of indoor microenvironments, this study monitors these compounds in a series of domestic and workplace indoor microenvironments frequented by the UK population using Polyurethane Foam (PUF) disks as passive samplers.

Experimental Procedures

Passive air samplers as described by other authors[5] were located at 23 different indoor microenvironments within the Birmingham and West Midlands area of the UK, including 12 homes, 10 offices, and one private car for sampling periods of between 4 and 6 weeks. To examine both seasonal trends and within-building variations in concentrations, sampling was conducted in two separate rooms within the same home/office (two homes and one office building) for 12 months. Previously described extract purification procedures were used with slight modifications for both PCBs and PBDEs[1,2]. GC/MS analysis and instrument specifications for PCBs and PBDEs were set up as described elsewhere[1,2]. The analytical method was assessed based on recoveries of surrogate/internal standards. As part of our ongoing quality control measures, the repeatability of our passive sampling and analytical procedures combined was evaluated by simultaneously deploying 5 samplers in the same domestic microenvironment. The low relative standard deviations observed for ∑PCB (7%) & ∑PBDE (18%) concentrations in this exercise demonstrate good repeatability for our sampling and analytical method. Generally, concentrations of PCBs and PBDEs in the 2 field blanks and 8 method blanks analysed were less than 5% of concentrations in samples and therefore sample data are uncorrected for blank levels. PUF disk sampling rates (R) for our target compounds were derived from our own calibration experiments (not reported here due to space restrictions). To estimate PBDE concentrations individual congener-based sampling rates were applied (1.1-1.9 m^3/day). However for PCBs, the average R values for each homologue group (Tri-CB=0.72, Tetra-CB=0.70, Penta-CB=0.9, Hexa-CB=0.99 and hepta-CB=1.27 m^3/day) were used due to the minimal variability of R values for individual isomers within each homologue group.

Results and discussion

Indoor air concentrations: The sampling locations and PCB & PBDE concentrations in indoor microenvironments along with outdoor air data from other studies are presented in Table 1. In the indoor environments studied, ∑PCB levels (sum of 63 congeners) ranged from 0.41 to 54.5 ng/m^3 (mean = 5.2 and median = 2.55 ng/m^3) and ∑PBDE levels (sum of congeners; 28, 47, 49, 66, 85, 99, 100, 153, and 154) varied from 5.1 to 1418 pg/m^3 (mean = 148.2 and median = 38.4 pg/m^3). To our knowledge, this is the first report on passive sampler-derived indoor air concentrations of PCBs. A previous study focused on highly contaminated indoor environments, reported levels of PCBs ranging from <100 to >6000 ng/m^3 (mean = 790 ng/m^3)[4]. However, our findings are in good agreement with the most spatially relevant study available for comparison, in which PCB levels between 1.1 and 69 ng/m^3 (mean =

9.0 and median =3.9 ng/m^3) were reported for 14 different indoor microenvironments from the West Midlands[2]. Importantly, t-test analysis revealed no statistically significant differences in ∑PCB concentrations between our data and those of the earlier study[2] (P>0.34), suggesting that there has been no obvious decline in the contamination of indoor air with PCBs in the West Midlands over the last ca. 7 years.

PBDE concentrations in this study are lower than those reported by Shoeib et al[6] ranging from76.3 to 2088 pg/m^3 and Harrad and co-workers[1] (60-15509 pg/m^3, mean=1855 pg/m^3 and median =762 pg/m^3). The reasons for these obvious variations are unclear but might be related to: differences in air sampling methods; unlike HiVols,[1, 6] passive air samplers are not specifically designed to capture PBDEs present on particulate matter; the fact that the passive samplers provide concentrations that are time-weighted averages over 4-6 weeks under normal room-use conditions, rather than temporally brief snapshots recorded under more artificial conditions (e.g. no occupants due to sampler noise, and windows closed); as well as variations in concentrations between the different microenvironments sampled in different campaigns. This study's data are comparable to but still lower than recently reported passive sampling results for ∑PBDEs in Canadian residential homes that reported a range between 2 and 3600 pg/m^3 (mean = 260 and median = 100pg/m^3).[3] The differences between the two studies may be a reflection of the high profile of PBDE usage pattern in North America relative to Europe. Even though an appreciable proportion of ∑PBDEs are present in the particulate phase[1]; we compared our data with previously recorded data on concentrations of PCBs and PBDEs in West Midlands outdoor air using HiVol samplers[1,7]. The high indoor-outdoor gradients found in this study (on average 21 and 7 for PCBs and PBDEs, respectively) are in line with previous reports.[1-3] These findings, along with the racemicchiral signatures of some PCB congeners in outdoor air [8],suggest that the ventilation of PCB and PBDE-contaminated indoor air provides a significant source of these compounds to outdoor air in the West Midlands conurbation.

Within-building and seasonal variation: The average concentrations of ∑PCB and ∑PBDE in two different rooms of two homes (H1 & H2) and one office building (O) over identical monitoring periods are shown in Figure 1. In H1 - an apartment - and the office building the monitored rooms were located in the same floor. However in H2 – a 2 storey house - they were located on two different floors. Paired t-test analysis revealed statistically significant differences in ∑PCB (p= 0.0139) and ∑PBDE concentrations (P=0.0002) in the two different microenvironments of H2. Similar differences were observed for ∑PBDE concentrations in the office building (p=0.0047) which is in line with our previous data[1]. These variations may be due to differences in usage patterns (e.g. of computer usage, and room ventilation) of each microenvironment, and the presence of different source types and numbers in each microenvironment. Even though there were no statistically significant differences in concentrations of target pollutants in H1 (P>0.24), the last pair of samples which – unlike previous sample pairs taken in H1 - were taken with all doors and windows closed, showed ∑PCB and ∑PBDE concentrations in H1A to be 1.8 and 2.4 times higher than H1B, respectively. An indication of the influence of room contents on PBDE contamination is that in OB, ∑PBDE levels showed a sharp decline (>75%) after replacing a PC constructed in 1998 was replaced with a new one.

The average concentrations of PCBs and PBDEs in different seasons (2-3 samples are averaged for each season) are summarized in Table 2. One-way variance analysis showed statistically significant differences in concentrations of PCBs only in OA (highest in summer) and PBDEs only in H2B (highest in summer) and OB (where differences were due to the above-mentioned change of PC). For the other monitoring locations, differences in pollutant levels were not statistically significant but the ratio of the maximum to minimum concentration over the whole monitoring period varied from 1.5 to 2.1 for PCBs and from 1.6 to 7.8 for PBDEs. This finding, along with the intra-building variability in PCB and PBDE concentrations has significant implications for the accuracy of estimations of inhalation exposure that are based on short term samples that do not take into account potential seasonal variations.

***Human exposure via inhalation*:** To estimate human inhalation exposure to PCBs and PBDEs (assuming 100% absorption of intakes), the following algorithm was used:

$$\sum Exposure = [(C_H F_H) + (C_O F_O) + (C_C F_C) + (C_{OA} F_{OA})]\, R_R$$

Where ∑Exposure is the daily adult human exposure via inhalation (ng of ∑PCB and ∑PBDE person^{-1} day^{-1}); $C_{H/O/C/OA}$ is the ∑PCB and ∑PBDE levels in homes/offices/cars/outdoor air, respectively (ng/m^3); $F_{H/O/C/OA}$ is the respective fraction of time spent in each environment. We used an adult respiration value of 20 m^3 per day[2], and

assumed that people spend 67.9%, 23.8%, 2.9% and 5.4% of their time at home, in the workplace, on public transport and in private cars, and outdoors, respectively – based on previously reported data[2] and our own survey based on activity diaries of 40 individuals. The human inhalation exposure estimates derived from our data showed a mean daily intake of 85.0 and 4.3 ng day $^{-1}$ for SPCBs and SPBDEs, respectively. Median intakes found in this study (∑PCBs=55.7 ng and ∑PBDEs= 3.1 ng person^{-1} day^{-1}) are comparable with but lower than previous estimates that reported daily inhalation exposures of 110 (average) and 6.9 (median) ng person^{-1} day^{-1} for ∑PCB and ∑PBDE, respectively[1, 2]. However, the wide variability of concentrations between the indoor microenvironments studied here and the observed seasonal variation in each microenvironment, means that exposures could be much higher for some people, a fact that is consistent with the observation that in Sweden, while most people appear to be similarly contaminated, about 5% of the population have significantly elevated body burdens of PBDEs (as evidenced by concentrations in blood) that cannot be explained by their dietary intake[9].

Acknowledgment:

The authors gratefully acknowledge the provision of scholarship to Sadegh Hazrati from Iranian Ministry of Health and Medical Education.

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Table 1.PCBs and PBDEs Concentrations in different indoor environments

Locations	Number of samples	∑PCBs (ng/m^3) Mean (concentration range)	Median	SD	∑PBDEs (pg/m^3) Mean (concentration range)	Median	SD
Home	12	2.81 (0.6-9.9)	2.3	2.6	49.6 (5.1-168.2)	17.3	59.1
Office	10	8.7 (1.3-54.5)	4	16.2	207.5 (9.7-1418.2)	54.4	431.2
Car	1	0.4	0.4	[a]NA	409.6	NA	NA
Mean indoors		5.2 (0.4-54.5)	2.5	10.8	148.2 (5.1-1418.2)	38.4	297.7
Outdoor air		0.252 [7]	NA	156	21 (10-33) [1]	18	8.7

[a] = not available

Figure 1.Within-building variation of ∑PCB and ∑PBDE concentrations in indoor microenvironments

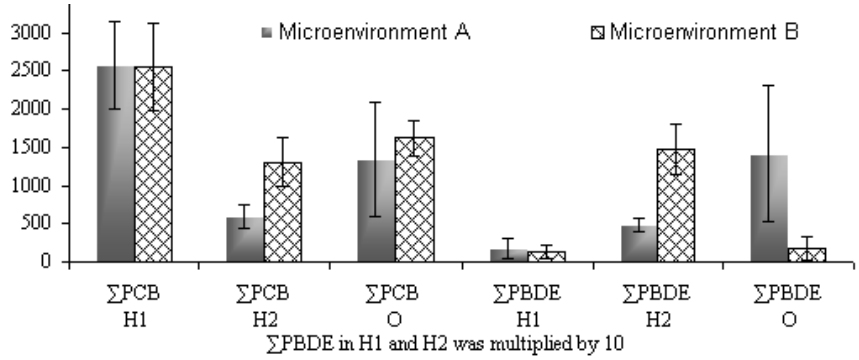

Table 2.Seasonal variation in concentrations of ∑PCB and ∑PBDE

	∑PCB					∑PBDE				
	Spring	Summer	Autumn	Winter	P-value	Spring	Summer	Autumn	Winter	P- value
H1A	2936	2832	1855	2653	NS	20.8	29	8.3	11.1	NS
H1B	2740	2341	NA	2645	NS	20	14.4	NA	6	NS
H2A	636	644	436	678	NS	53.8	53.3	50.3	36.7	NS
H2B	1387	1061	NA	1464	NS	151.1	180.9	NA	110	0.04
OA	1191	2617	902	918	0.008	1368.1	2400.7	876.3	1174.7	NS
OB	1734	1780	1470	1448	NS	83.2	83.2	423.9	167.1	0.004

H=Home, O=Office, A/B=Indoor microenvironment number within the same building, NS=not significant