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Passive Sampling Survey of Polybrominated Diphenyl Ether Flame Retardants in Indoor and Outdoor Air in Ottawa, Canada: Implications for Sources and Exposure

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The polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in plastics of soft furnishings, TV sets and computers, and insulation in the indoor environment. The penta-BDEs—now banned in most parts of Europe but still used in North America—are additive flame retardants that may be released to the indoor environment via volatilization or as dusts. In this study, to investigate general population PBDE exposure, air was sampled in 74 randomly selected homes in Ottawa, Canada and at seven outdoor sites during the winter of 2002–3, using polyurethane foam (PUF) disk passive air samplers. The passive sampling rate ($2.5 \text{ m}^3 \text{ day}^{-1}$) was determined through a pilot study employing active and passive samplers side-by-side at selected indoor locations. Indoor air concentrations of PBDEs were log-normally distributed with a geometric mean of 120 pg m^{-3} and a median of 100 pg m^{-3} , approximately 50 times higher than the range of outdoor air concentrations ($<0.1\text{--}4.4 \text{ pg m}^{-3}$). The maximum daily human exposure via the inhalation pathway based on median PBDE levels found in this survey was estimated to be 1.9 ng day^{-1} (female) and 2.0 ng day^{-1} (male), representing 4.1% (f) and 4.4% (m) of overall daily intake.

Introduction

The polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants in many everyday products, including soft furnishings, cars, textiles, insulation, and electronic equipment (1). The global demand for PBDEs has been substantial—an estimated 70 000 tons in 1999, for example, were manufactured and used as three main technical mixtures, the penta, octa, and deca products (2). These formulations are named after the average level of

bromination of the complex mixture of PBDE congeners from several homologue groups. The penta-BDE mix constituted a relatively minor part of the market share for PBDEs ($<13\%$); nonetheless, its principal congeners, BDE-47 (a tetra-BDE) and -99, are detected in the highest levels in all ambient environmental compartments but sediment (3). There is therefore considerable interest in how they escape from sources, enter environmental compartments, and reach biota, including humans. Their main uses are indoors—in homes, workplaces, and vehicle interiors. Possible pathways of release include volatilization (4) or formation of dusts (5) during the use of treated products. Other entry routes into the environment include emissions during their manufacture and disposal (6–8). PBDEs make up 5–30% by mass of a flame-retarded material (1). Treated products therefore represent significant reservoirs of the penta-BDE mix (9), so they are the focus of attention for emission estimates (4, 10).

The penta-BDE mix is currently being considered as a potential/candidate persistent organic pollutant (POP) under the 1998 United Nations Economic Commission for Europe (UNECE) POPs convention. Some penta-BDE mix congeners appear to have properties that trigger concerns about their potential long-range atmospheric transport (LRAT), environmental persistence, tendency to bioaccumulate, and potential toxicity (11, 12). In contrast to the decreasing levels of most POPs over the last 20 years, PBDE levels in the environment are increasing (3). Legislation has been passed to prohibit the marketing and use of the penta-BDE mix in the European Union (13). Leading up to this decision, European manufacturers avoided usage of the penta-BDE mix in their products (2). However, globally the penta-BDE mix is used predominantly (98%) in North America (2) to flame retard polyurethane foam, in furniture, vehicles (e.g., car seating), and bedding. PBDE levels in the North American population appear to be $\sim 15\text{--}20$ times higher than in European studies (3). Regulatory action has been slower in North America, although California has recently announced a plan to ban both the penta- and the octa-formulations by 2008 (14). Recently, the main U.S. producer of penta- and octa-BDE mixes announced that it would discontinue these products as part of a voluntary agreement with the U.S. EPA (15).

On average, North Americans spend approximately 90% of their time indoors, most of this being at home (16, 17). In Canada, this figure increases to 96–98% during winter months (17). Exposure to elevated indoor levels may therefore represent an important pathway of human exposure to PBDEs (9). In this study, passive air samplers were used to simultaneously and noninvasively sample PBDEs in 74 randomly selected homes in Ottawa, Canada and seven outdoor sites across the city. The objectives were to (1) establish the range of indoor air concentrations; (2) assess the indoor–outdoor gradient of PBDE concentrations; and (3) consider the implications for human exposure via indoor air. For most traditional POPs, dietary intake dominates human exposure (18); however, this study provides data to help examine the potential significance of the inhalation pathway.

Theory of Passive Samplers. Passive air samplers (PAS) operate without the aid of a pump and consist of an accumulating/sorbing medium with a high retention capacity for the target analytes. PAS facilitate multiple concurrent time-integrated sampling in locations where active samplers would not be practical over such periods (e.g., in homes), due to excessive noise, cost, and equipment size. One such design, which has been thoroughly evaluated for other POPs

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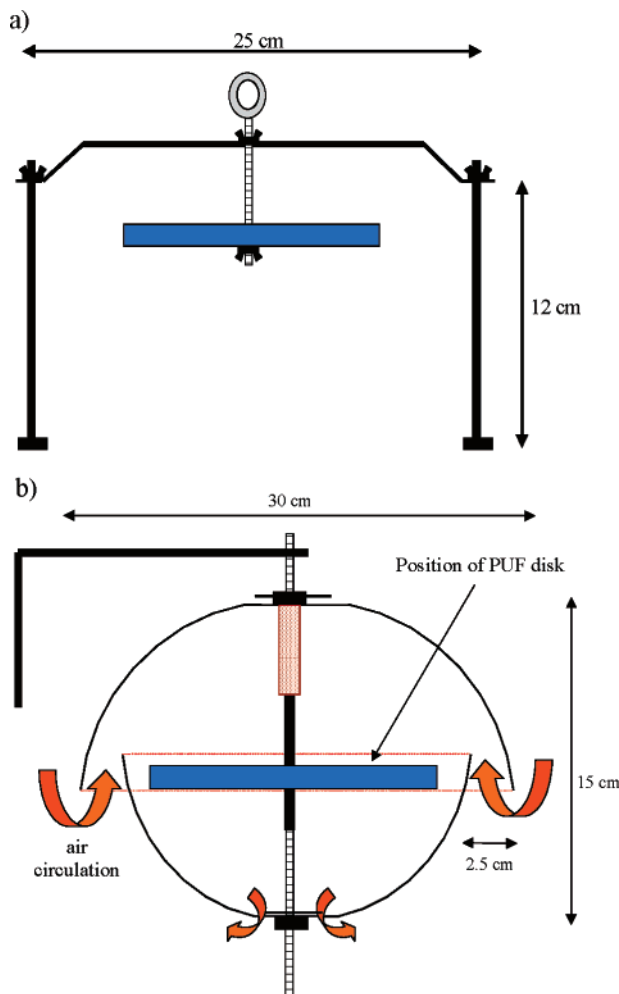


FIGURE 1. Indoor (a) and outdoor (b) passive air samplers used in this study.

and deployed in field studies, utilizes polyurethane foam (PUF) disks to retain POPs from the atmosphere (19). The maximum amount of chemical that may be taken up by the PUF disk is defined by the PUF–air partition coefficient, $K_{\text{PUF-A}}$. Previous work has shown that $K_{\text{PUF-A}}$ is well-correlated to K_{OA} , and the time required for a chemical to reach saturation is inversely proportional to $K_{\text{PUF-A}}$ (19). For chemicals with K_{OA} values greater than $10^{8.5}$, such as PBDEs, the sampling rate remains linear over the first 100 days at a few $\text{m}^3 \text{ day}^{-1}$ (20), and uptake is controlled by the air concentration of the POP. The uptake rate is a weak positive function of temperature (19) but is strongly related to wind speed, with faster uptake at higher air flows. However, wind speed dependence is minimal at the very low flow rates (21) typical of indoor air. During outdoor deployment, a low-wind environment is preserved by housing samplers in protective chambers.

Materials and Methods

Design and Deployment of the Samplers. Figure 1 shows the deployment conditions used in this study. The shelter for the indoor air samplers consisted of a tripod support, open to the air at all sides, to minimize restriction of the generally low indoor air flows, while preventing gravitational deposition of coarse particles. The outdoor chamber design dampens the wind speed effect on uptake and protects the sampling medium from precipitation, coarse aerosols, and ultraviolet radiation, which may degrade the target compounds (22).

Study Location. The study was conducted in Ottawa, Canada (population 780 000). A two-stage stratified sampling process was used to select a representative sample of residences. First, the city was divided into three geographical areas based on level of urbanization, using 2001 Canada Census data provided by Statistics Canada. A total of 1024 urban core Dissemination Areas (DAs), 124 urban fringe DAs, and 79 rural fringe DAs are defined for the city. Stratified random sampling was used to select 31 DAs to be sampled in the urban core, four in the urban fringe, and three in the rural fringe, to obtain satisfactory precision in the overall estimate of the mean level for the city. A simple random sample selection was carried out to select DAs from each geographical area. In the second stage, the number and type of dwellings (houses and apartments) were recorded by drive-through in the selected DAs, using 2001 Census maps, and homes to be sampled were selected by stratified random sampling. PAS were deployed for approximately 3 weeks in each home between December 2002 and March 2003, in a place within the home with little disturbance, such as on top of a piece of furniture. A questionnaire was completed in each home on house characteristics, residents' lifestyle, etc. to attempt to identify factors affecting chemical loadings, and dust samples were collected that will form the basis of a further study. Passive samplers were also deployed at seven outdoor locations around the city for a 3 month period. These were located in the backyards of houses and were mounted on a tree or fence about 1.5 m above the ground.

Precleaning Method. All solvents used were OmniSolv, chromatographic grade. All glass pipets, glass wool, and sodium sulfate used were baked overnight at 450°C and stored in sealed containers until use. Samplers and lab equipment were solvent rinsed before use. Nonflame retarded PUF disks (14 cm diameter \times 1.35 cm thick; surface area 365 cm^2 ; density 0.0213 g cm^{-3} ; from Pacwill Environmental, Stoney Creek, ON, Canada) were pierced in the center using a cork borer. They were rinsed with water and Soxhlet extracted overnight with acetone. The solvent was changed to petroleum ether (PE), and two further overnight preextractions were carried out. The final solvent extract was concentrated and analyzed by GC/ECD to verify cleanliness. PUF disks were dried under vacuum in a desiccator and then stored in solvent-rinsed amber glass jars. Disks were spiked prior to exposure with a mixture of depuration compounds of differing K_{OA} (BDE-3, d_6 - γ -HCH, PCB-107, and PCB-198) not naturally present in the environment: the requisite volume of standard solution was mixed with $\sim 25 \text{ mL}$ of PE. PUF disks were placed on solvent-rinsed foil, evenly soaked with the spike solution, and allowed to air-dry for a few minutes on each side, being turned with solvent-rinsed tongs, and then returned to their jars and stored until use. If necessary, further solvent evaporation was performed using a stream of pure nitrogen. PUF disks were placed in the samplers at the time of deployment. The deployment time of each sampler was noted. After retrieval, the PUF disks were returned to their glass jars, sealed externally with Teflon tape, and dispatched to the laboratory for analysis. PUF disks were stored at room temperature and analyzed within 2 weeks.

Determination of Passive Sampler Uptake Rate. PAS and low-volume active air samplers were set up simultaneously for 17–20 days during eight indoor tests in various lab and office locations. The sampling rate of the active samplers was adjusted to approx $3 \text{ m}^3 \text{ day}^{-1}$ (2 L min^{-1}) based on previous estimated uptake rates of PUF disk samplers (19). The active samplers were BGI-400-4 Personal Air Sampling Pumps (from BGI Incorporated, Waltham, MA). One PUF plug (22 mm o.d. \times 76 mm), followed by a half PUF plug (22 mm o.d. \times 38 mm) was fitted in the sampler-head glass tube (ORBO-1000, i.d. 22 mm, from Supelco). No glass fiber filter

was used in order to reproduce the sampling performance of the PUF disks. All passive and active PUF were analyzed for PBDEs as described next.

Sample Preparation and Analysis. PBDE-2 and -35 were added as surrogate standards to the harvested active and passive samples prior to extraction. All samples were Soxhlet extracted for 21 h in PE, concentrated to 0.5 mL and transferred to iso-octane by rotary evaporation and nitrogen blow-down. Any samples visibly containing particulates were filtered through a pipet packed with glass wool. Samples visibly containing water were passed through a similar setup containing anhydrous sodium sulfate on top of the glass wool. Mirex was added as an internal standard (10 μL of 10 ng μL^{-1}) for volume correction and to adjust for variations in instrument response. Outdoor samples were acid cleaned by making the sample volume up to ~ 3 mL with 1:1 iso-octane/PE and shaking with ~ 2 mL of concentrated sulfuric acid for at least 1 min using a vortex mixer. The sample was centrifuged, and the sulfuric acid layer was removed by pipet. A second acid rinse was performed, and then a final rinse of ~ 4 mL deionized water was performed. Samples were placed in the freezer (-20°C) overnight, any remaining water was removed by pipet, and the samples were concentrated to 200 μL for analysis by GC/MS. The mirex internal standard is stable to acid treatment and therefore corrects for any volume loss during the acid cleanup.

Extracts were analyzed by GC/MS on a Hewlett-Packard 6890 GC fitted with a DB-5 60 m column (J&W Scientific, Rancho Cordova, CA), i.d. 0.25 mm, film thickness 0.25 μm , and operated with helium as the carrier gas. This was coupled to a Hewlett-Packard 5973 mass selective detector MS in NCI (negative chemical ionisation) mode with methane as reagent gas. The injector temperature was 250°C ; transfer line 300°C ; source 230°C ; quadrupole 106°C . Sample injection volume was 2 μL in splitless mode. Masses 79, 81 (PBDEs), 261, 263 (d_6 - γ -HCH), 326, 328 (PCB-107), 404 (Mirex) 430, and 423 (PCB-198) were monitored. Compounds were identified and quantified by comparison with a series of standard solutions of known concentration (from Cambridge Isotope Laboratories, Andover, MA). Peaks were quantified only if $S/N > 3$, and the ratio of the ion to its qualifier ion was within 15% of the standard value.

QA/QC. Throughout the sampling period, clean PUF disks ($n = 7$) prepared as for sampling were transported and stored with the samples but not deployed. These travel blanks were analyzed to evaluate various sources of contamination. A solvent blank was analyzed to check for contamination from the laboratory and equipment, and levels were found to be lower than those in the travel blanks. The method detection limit for each congener was calculated by linear extrapolation from the lowest standard in the calibration, to the point where signal/noise = 3. Detection limits typically increased with level of bromination and were between 1.2 and 18 pg m^{-3} for indoor samples and 0.11–3.9 pg m^{-3} for outdoor samples. For analytes found in travel blanks, the detection limit was raised to the mean of the travel blank levels + 3 SD. Seven sets of indoor samples and three sets of outdoor samples were deployed as duplicates, to evaluate reproducibility. Differences between duplicate samples were typically $< 20\%$. The analytical method was assessed based on recoveries of surrogate compounds (PBDE-2 and -35) as well as the higher molecular weight depuration compounds (PCB-107 and -198), which should experience no detectable loss over the deployment period. Recoveries for BDE-2 were highly variable due to chromatographic interferences; therefore, only recoveries for BDE-35 are reported. These had a mean of $116 \pm 16\%$. Recoveries for PCB-107 and -198 were 110 ± 25 and $89 \pm 11\%$, respectively. Sample values were not therefore recovery corrected. The other depuration compounds (BDE-3, d_6 - γ -HCH) had not sufficiently volatilized to allow back-

calculation of the air volume sampled; levels had not reduced below 80% of the initial amount added, after recovery correction, and losses were therefore not considered significant.

Results and Discussion

Sampler Uptake Rates. A sampling rate of $2.5 \text{ m}^3 \text{ day}^{-1}$ was determined from the indoor calibration studies, based on the average slope of the best-fit regression lines between the passive (pg day^{-1}) and active (pg m^{-3}) data for each congener found (BDE-17, -28, -47, -99, -100). The average r^2 value of the best-fit lines was 0.97, with a standard deviation of 0.2 and relative standard deviation of 7.4% on the sampling rate between these congeners. This rate therefore applied to all congeners, irrespective of bromination level. This is slightly lower than the $3\text{--}4 \text{ m}^3 \text{ day}^{-1}$ derived by Shoeib and Harner (19) for the outdoor sampler. Air volumes of $\sim 50 \text{ m}^3$ were therefore sampled during the 21 day indoor deployments. Longer exposure (72 days) and higher uptake rates outdoors yielded air volumes of $\sim 250 \text{ m}^3$.

General Comments on the Levels. Table 1 summarizes the levels found indoors and outdoors. PBDEs were detected in all indoor samples, where levels varied over more than 3 orders of magnitude, from 2 to 3600 pg m^{-3} , with a geometric mean of 120 pg m^{-3} . In contrast, several of the outdoor samples were below the limit of detection. Detectable values ranged between 1.5 and 4.4 pg m^{-3} , about 50 times lower than the average indoor concentration. Figure 2 presents a summary of the data from this study and compares results with other previously reported values. There are still relatively few studies on indoor air levels of PBDEs. The most relevant comparison is with a small study by Shoeib et al. (23), involving only four homes in/near Toronto, for which the data are highlighted in Figure 2. The range of levels found in Ottawa homes is in good agreement with those found in this previous study. Sjödin et al. (8) report on values in a range of working environments in Sweden, including a recycling facility (see Figure 2). This latter location gave extremely high values (28–110 ng m^{-3}), over an order of magnitude higher than the scale used in Figure 2. PBDE levels from this study are therefore similar to those of many work environments. The limited outdoor data from this study ($< 0.1\text{--}4.4 \text{ pg m}^{-3}$) are lower than other reported urban values (22, 25, 27, 29), which are typically in the range of 4.8–52 pg m^{-3} . This is probably because sampling was during the winter when low temperatures, and hence higher K_{OA} values, result in a smaller proportion of PBDEs in the gas phase. In summary, it is clear that indoor air from homes in Ottawa is relatively contaminated with PBDEs as compared to outdoor air, with a marked indoor–outdoor gradient. Home ventilation is therefore likely to be a source to the outdoors, which may explain why urban areas, with high concentrations of homes, have relatively high PBDE levels (22, 25, 29).

Further Comments on the Range of Indoor Air Concentrations. As often observed with such data, the indoor air concentrations were log-normally distributed, as shown in Figure 3. While the geometric mean is 120 pg m^{-3} , 8.2% of the samples exceeded 600 pg m^{-3} , with the highest sample extending up to 3600 pg m^{-3} .

The data were evaluated with respect to the questionnaire data, compiled for each of the homes, to assess possible causes for the range in values. The house containing the highest levels had recently been paint stripped using a heat gun and insulated. The second and third highest levels were recorded in homes where the windows had recently been upgraded, while one had new carpets, and the other had recently purchased electronic equipment. However, no correlations were obtained between indoor air levels of PBDEs and house age, or percentage of the home carpeted, when the whole dataset was evaluated statistically. This is perhaps

TABLE 1. Summary of PBDE Levels Found in Ottawa Homes (a) and Outdoors (b) (pg m^{-3})^a

(a)	mean	median	range	percentile 5	percentile 95	SD	<i>n</i> > dl
BDE-17	12	6.1	<dl to 160	<dl	52	22	66
BDE-28	24	11	<dl to 310	2.3	110	45	70
BDE-71	11	3.1	<dl to 240	<dl	39	30	60
BDE-47	160	66	<dl to 1600	11	860	290	72
BDE-66	2.9	<dl	<dl to 98	<dl	17	12	21
BDE-100	10	4.2	<dl to 160	<dl	57	24	55
BDE-99	42	15	<dl to 890	<dl	200	110	60
BDE-85	0.72	<dl	<dl to 32	<dl	4.2	3.9	6
BDE-154	1.9	<dl	<dl to 57	<dl	9.6	7.3	13
BDE-153	1.6	<dl	<dl - to 74	<dl	6.3	8.7	10
Σ PBDE	260	100	2.0–3600	18	1100	520	73

(b)	mean	median	range	SD	<i>n</i> > dl
BDE-17	0.017	<dl	<dl to 0.06	0.029	2
BDE-28	0.095	0.16	<dl to 0.17	0.089	4
BDE-47	0.87	0.88	<dl to 1.9	0.87	4
BDE-100	0.11	<dl	<dl to 0.38	0.15	3
BDE-99	1.1	1.4	<dl to 1.9	0.78	5
Σ PBDE	2.2	2.6	<dl to 4.4	1.7	5

^a Only congeners found above the detection limit are shown. <dl = below detection limit, *n* > dl = number of samples above detection limit.

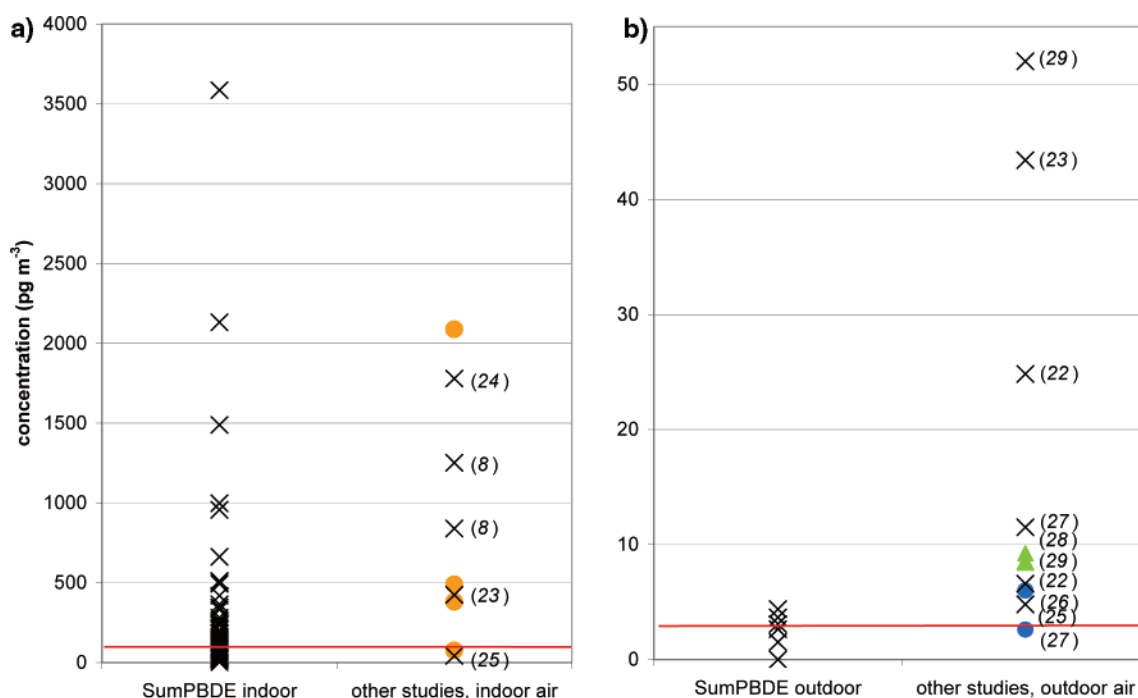


FIGURE 2. Levels found in this study (solid red line marks median level) as compared to mean values from previous studies. (a) Indoor levels. Orange circle indicates a residential sample (23); all other indoor comparison points are from occupational settings (8, 23, 24, 25). (b) Outdoor levels. Blue circles indicate European air levels (26, 27), and green triangles mark rural samples from North America (28, 29). All others are urban/mixed samples from North America (22, 23, 25, 29).

not surprising; the concentrations measured in any particular home will be affected by many different sources, complicated by additional factors such as ventilation rate, proximity of the sampler to potential sources, age of those sources, and so on.

Gas versus Particle Phase Sampling. The design of the indoor passive samplers protects the PUF disk from deposition of coarse dust particles from above; however, fine suspended particulates may deposit on the sampler. It is therefore useful to investigate whether these samplers were sampling the gas phase, the particulate phase, or both. The average congener profile composition is compared to the gas and particle phase profiles from another indoor air study (23) (see Figure 4). This indicates that the indoor passive

samplers are sampling mainly the gas phase with only a small contribution from particulates.

Comments on the Congener Composition. The average and range of indoor air congener profiles is compared to that of Bromkal 70-5DE (30), a penta-BDE commercial mixture, in Figure 5. It is clear that there is high variability in the congener profile of the indoor samples, presumably reflecting the range of sources and commercial mixtures used in treated products. The average indoor air profile differs from that of the penta-mix. As the last section shows, volatilization from indoor sources appears to be the main mechanism accounting for the occurrence of PBDEs in indoor air; therefore, air would be expected to be relatively enriched in the lower brominated, more volatile congeners. The

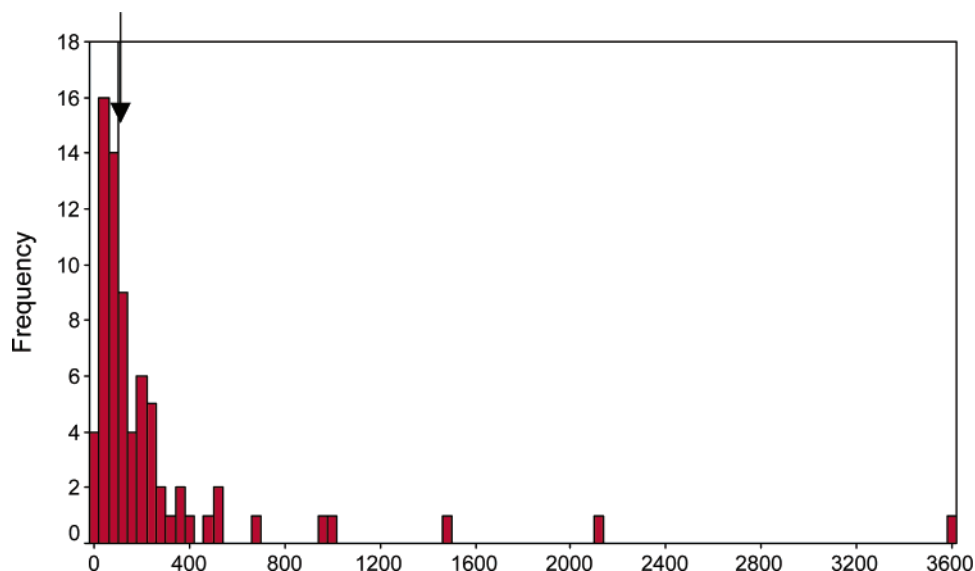


FIGURE 3. Histogram showing the distribution of Σ PBDE indoor air concentrations (pg m^{-3}). Arrow marks the median of 100 pg m^{-3} .

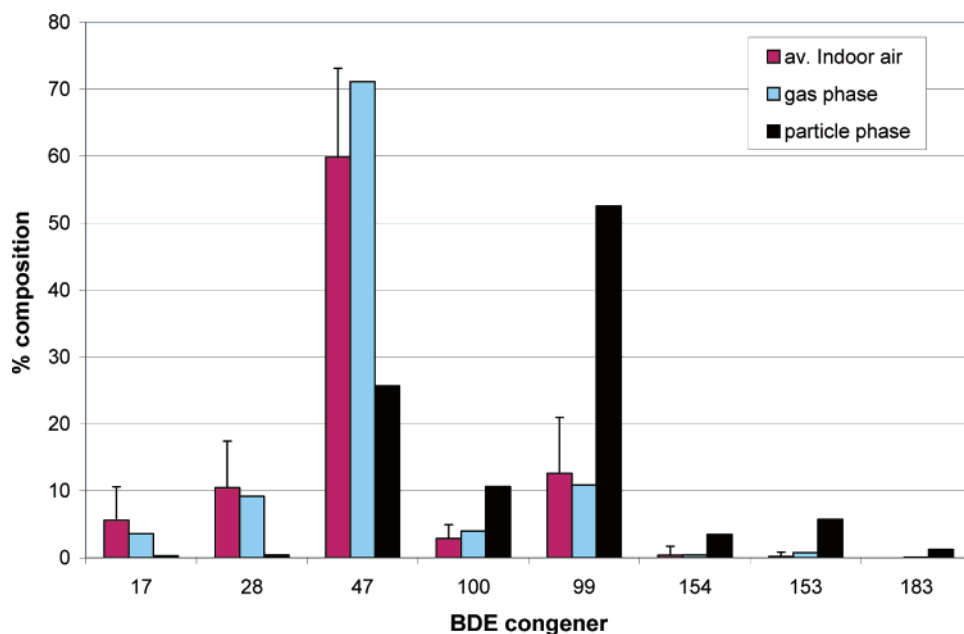


FIGURE 4. Comparison of the average indoor air congener profile from this study with gas and particulate phase profiles from Shoeib et al. (23) measured in indoor air using conventional high-volume air samplers.

proportion of a congener in air above this commercial mixture was calculated by applying its K_{OA} value (20) to the proportion present in the commercial mix. The resulting K_{OA} -corrected congener profile is plotted for comparison, which appears to be more similar to the indoor air congener profile observed.

This is highlighted in Figure 6, where principal components analysis is used to compare the relative congener composition of samples. Congeners that were detected in $>70\%$ of samples (i.e., BDE-17, -28, -47, -99, and -100) were used for the plot, which shows that the technical formulations are relatively enriched in the heavier congeners (BDE-99 and -100), while indoor air is enriched in the more volatile constituents. Houses with the highest ten PBDE levels are marked with a solid green square, and many of these cluster around the calculated K_{OA} -corrected congener profiles of the commercial mixtures (30, 31), suggesting direct volatilization from a PBDE source within the home.

The outdoor air profile is closer to that of the Bromkal 70-5DE commercial mix in Figure 5. As previously mentioned, this is probably due to the much colder sampling temper-

atures that tend to drive PBDEs out of the gas phase and onto particulates. It is possible that the small particle fraction sampled, discussed in the previous section, enriched in the higher molecular weight PBDEs, now significantly contributes to Σ PBDE and results in a profile more similar to the commercial mixture. Because of the very different sampling conditions, and this confounding factor preventing the use of simple temperature correction, this will not be discussed further.

Human Exposure. Given that on average people spend 90% of their time in indoor environments (16, 17) it is useful to estimate the daily PBDE intake by the inhalation pathway from concentrations found in this study. As discussed previously, the PAS is also likely to sample the suspended ultrafine/inhalable dust fraction. It is therefore assumed that sampled values represent a best estimate of inhaled PBDE levels. Because of lack of absorption efficiency data for PBDEs, 100% absorption of inhaled PBDE was assumed, representing an upper limit for uptake. Resting inhalation rates of 7.5 and 6 L min^{-1} for males (m) and females (f), respectively, were

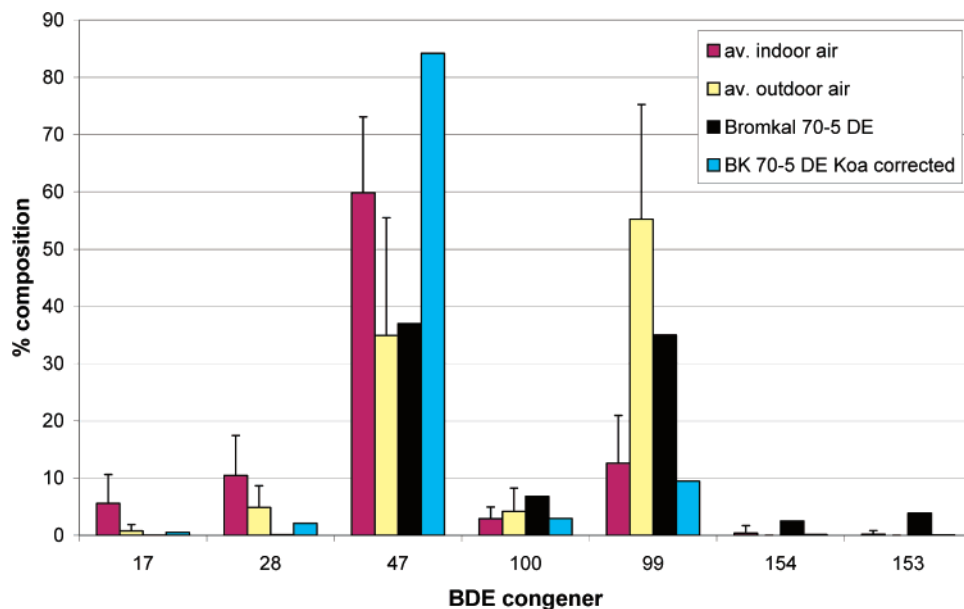


FIGURE 5. Average PBDE congener profile of indoor air as compared to the commercial penta-BDE mixture Bromkal 70-5 DE (30). The composition of this mix was corrected for volatility by applying the K_{OA} of each congener (20). Error bars mark the standard deviations about the mean for the indoor and outdoor air samples.

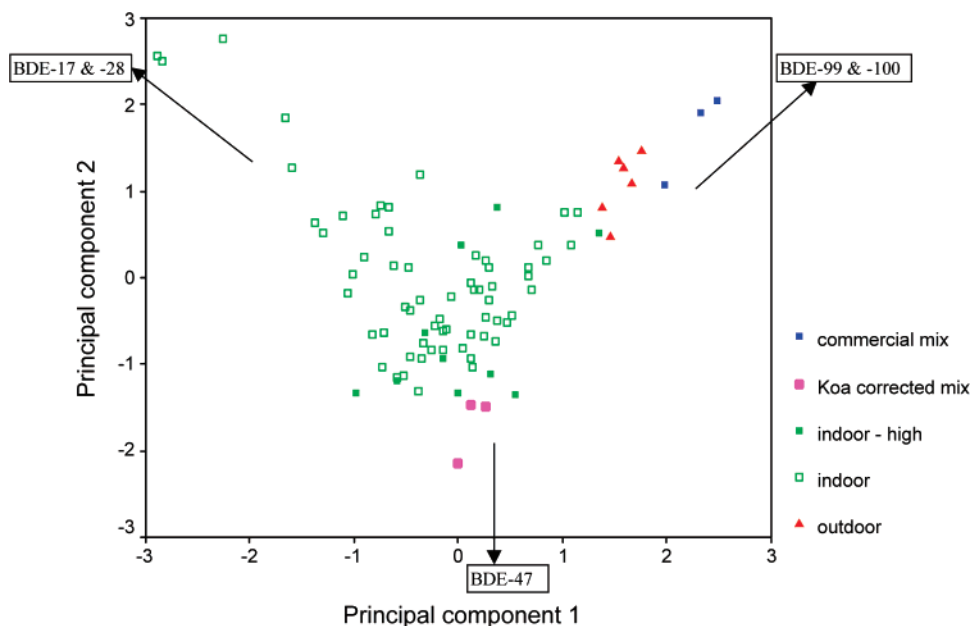


FIGURE 6. Scatter plot of the principal component factors for each sample congener profile. For comparison, the commercial penta-mix profiles are also shown (30, 31) as are the K_{OA} -corrected (20) profiles. Arrows display separation of the congeners by the PCA.

used in these calculations, and light activity inhalation rates of 20 L min^{-1} (m) and 19 L min^{-1} (f) (32) were used. It was assumed that the 10% of time spent outdoors was during waking hours, and that 8 h per day were spent resting, with the remaining 16 h being light activity. Since outdoor levels were low as compared to the indoor levels, these were considered insignificant and not included in the calculations.

Table 2 shows the four exposure levels calculated: a low level using the fifth percentile levels, a median level, a high exposure using 95th percentile levels, and a maximum level. These intakes were compared to the estimated mean dietary intake of 44 ng day^{-1} for Canada (33). At median levels, we estimate that the maximum daily human exposure via the inhalation pathway based on PBDE levels found in this survey would be 1.9 ng day^{-1} (female) and 2.0 ng day^{-1} (male), representing 4.1% (f) and 4.4% (m) of overall daily intake (ODI—the sum of both dietary and inhalation intakes).

TABLE 2. Human Exposure to Σ PBDE by Inhalation of Indoor Air Levels from This Study^a

daily intake		fifth percentile	median	95th percentile	max
ng d^{-1}	male	0.37	2.0	23	71
	female	0.34	1.9	21	66
% ODI	male	0.8	4.4	34	62
	female	0.8	4.1	32	60

^a % ODI was calculated taking into account the estimated mean dietary intake of 44 ng d^{-1} for Canada (33).

However, there is 50-fold variation between the fifth and 95th percentiles, representing a range of 0.8–32% (f) and 0.8–34% (m) of ODI. For residents of the house experiencing the highest levels found, the intake through inhalation was

calculated to be 66 (f) and 71 (m) ng day⁻¹, representing 60% (f) and 62% (m) of the ODI. This may help to explain why 5–10% of people in previous studies had elevated levels of PBDEs (34). Variability in inhalation intake is very large and needs to be taken into account, as well as the known variability in dietary intake in explaining the range of levels found in humans.

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