Environmental Science & Technology

ARTICLE

pubs.acs.org/est

Sources, Emissions, and Fate of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls Indoors in Toronto, Canada

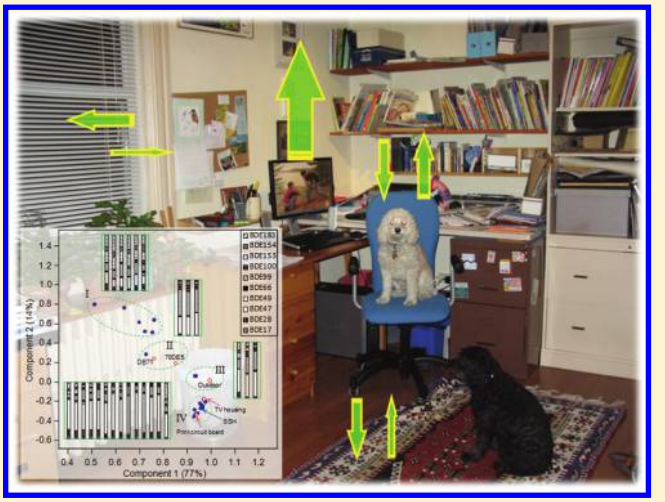
Xianming Zhang,[†] Miriam L. Diamond,*[,†] Matthew Robson,[†] and Stuart Harrad[‡]

[†]Department of Geography, University of Toronto, Toronto, Ontario M5S 3G3, Canada

[‡]Division of Environmental Health and Risk Management, Public Health Building, School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, United Kingdom

Supporting Information

ABSTRACT: Indoor air concentrations of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) measured in 20 locations in Toronto ranged 0.008−16 ng·m^{-3} (median 0.071 ng·m^{-3}) and 0.8−130.5 ng·m^{-3} (median 8.5 ng·m^{-3}), respectively. PBDE and PCB air concentrations in homes tended to be lower than that in offices. Principal component analysis of congener profiles suggested that electrical equipment was the main source of PBDEs in locations with higher concentrations, whereas PUF furniture and carpets were likely sources to locations with lower concentrations. PCB profiles in indoor air were similar to Aroclors 1248, 1232, and 1242 and some exterior building sealant profiles. Individual PBDE and PCB congener concentrations in air were positively correlated with colocated dust concentrations, but total PBDE and total PCB concentrations in these two media were not correlated. Equilibrium partitioning between air and dust was further examined using log-transformed dust/air concentration ratios for which lower brominated PBDEs and all PCBs were correlated with K_{OA}. This was not the case for higher brominated BDEs for which the measured ratios fell below those based on K_{OA} suggesting the air-dust partitioning process could be kinetically limited. Total emissions of PBDEs and PCBs to one intensively studied office were estimated at 87−550 ng·h^{-1} and 280−5870 ng·h^{-1}, respectively, using the Multimedia Indoor Model of Zhang et al. Depending on the air exchange rate, up to 90% of total losses from the office could be to outdoors by means of ventilation. These results support the hypotheses that dominant sources of PBDEs differ according to location and that indoor concentrations and hence emissions contribute to outdoor concentrations due to higher indoor than outdoor concentrations along with estimates of losses via ventilation.



INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) continue to raise concerns because of widespread exposure in the general population and links to adverse health effects.[1−5] As additive flame retardants, PBDE commercial formulations, namely Penta-, Octa-, and Deca-BDE, were manufactured and used in various products containing flexible and rigid plastics (Table S1),[1] from which they are released over a product's lifetime.[2] In response to increasing levels in the environment and health concerns, North America and Europe negotiated and then legislated a ban of the production of Penta and Octa and their uses in new products[1] and in 2009 these two mixtures were listed as POPs under the Stockholm Convention.[3] Canada has banned the production of Deca and the European Union has restricted its use.[4] Despite these regulations, existing stocks of PBDEs remain in use in furniture and electrical and electronic products in homes, offices, and commercial enterprises where the products can still act as a source of these compounds to the indoor environment and then outdoors.[5,6]

Although the production of PCBs was banned in many countries in the 1970s, stocks remain in use and in storage in, primarily, transformers and capacitors and flexible building sealants.[7−9] Similarly to PBDEs, these uses of PCBs, in addition to newly created PCBs in paint pigments,[10,11] act as sources to the indoor environment.

Higher concentrations of PBDEs and PCBs measured indoors than outdoors[12,13] imply that the indoor environment is an important exposure route of these compounds.[5,14] We are vulnerable to exposure indoors because of low, but significant

Received: August 12, 2010
Accepted: February 23, 2011
Revised: February 8, 2011
Published: March 17, 2011

emissions over time from products and materials containing PBDEs and PCBs. As well, minimal removal rates in the indoor environment such as restricted air exchange rates, contribute to elevated indoor concentrations.[15] Our vulnerability to elevated indoor concentrations is exacerbated because of the time we spend indoors. For example, on average, North Americans spend 90% of their time indoors and in Canada, this increases to 96−98% during winter[16] where energy saving measures have made our indoor environments more airtight. Thus, the importance of the indoor environment to exposure augers for a better understanding of emissions and the main emission sources that give rise to indoor concentrations. In addition, where food is the dominant exposure route,[17,18] we have hypothesized that sources of PBDEs and PCBs in foods can be ultimately related back to elevated indoor levels.[6,19,20]

This paper presents results to examine two hypotheses: (1) dominant emission sources of PBDEs differ among indoor environments and (2) the indoor environment is a source of PBDEs and PCBs to the outdoor environment. The results presented are concentrations of PBDEs and PCBs in air and dust from a 20 indoor locations that lend support to the first hypothesis. The Multimedia Indoor Model of Zhang et al.[15] is used to estimate total emissions and fate of PBDEs and PCBs, including export to outdoors, which provides evidence for the second hypothesis. The modeling effort is supported by a detailed multimedia sampling campaign conducted in one location.

METHODS

Indoor Air Sampling. Indoor air and dust samples were collected from 20 indoor locations including offices, homes, and laboratories in Toronto, Canada in August−September 2006. PBDE and PCB dust concentrations of 10 samples were previously reported.[5,14] Details of the sampling locations are listed in Table S2.

The passive air sampling strategy used in this study has been described previously.[21] Briefly, the polyurethane foam (PUF) disks used in the passive samplers[22] were precleaned by Soxhlet extraction with dichloromethane (DCM, HPLC grade, Caledon Lab Ltd.) for 16 h prior to sampling. The stainless steel shelters for the PUF disks were rinsed sequentially with tap water, distilled water, and DCM. The cleaned PUF disks were stored in a precleaned foil in airtight bags before deploying. After a sampling period of 27−38 days, the PUF disks were removed from their shelters, placed in precleaned airtight glass jars, and stored at −18 °C until extraction 8−10 months later. Chemical concentrations in air (assumed to be primarily gas phase) were derived from the mass of chemicals detected in the PUF disks using the passive sampling rates of Hazrati and Harrad.[22]

Multiple Indoor Phases Sampling. From August to October 2007, we intensively studied an additional location which was a university office (referred as SSH hereafter) of dimensions 13.56 $m^2 \times 2.69$ m. We sampled indoor gas- and particle-phases of air using passive PUF disks and GFF filters housed in a low volume air sampler and surface films on the interior side of a window and glass beads (diameter 3 mm, Figure S1). The sampling approaches followed Diamond et al.[23] and Wu et al.[24] and are described in the SI.

Sample Analysis. Samples were Soxhlet extracted for 16 h with DCM and then cleaned up with concentrated H_2SO_4 and alumina chromatography (further details presented in the SI). The samples were analyzed on an Agilent 6890N gas chromatograph coupled to an Agilent 5975 mass selective detector operated in EI^+ and SIM mode. The detailed information on the instrumental analysis of PCBs and PBDEs is also described in the SI.

Quality Control. Two field blanks for the passive air sampling campaign were taken by transporting precleaned PUF disks to the field, installing the PUF disks in the shelters and then immediately removing and storing the disks. Storage and analysis were the same as for the samples. For the active air sampling, GFFs and PUF plugs were put into the sampling cartridge for the same length of time as the samples but without activating the pump. Surface film blanks were acquired by exposing the precleaned Kimwipes to indoor air at SSH until the solvent on the Kimwipes dried. Blank concentrations were either nondetect or less than 5% of those detected in the samples for all PBDE and PCB congeners except BDE-183, PCB-27, -53, -193, and -191, for which maximum blank/sample ratios were 0.27, 0.077, 0.17, 0.073, and 0.16, respectively. The reported concentrations were not blank corrected. Recoveries of surrogate standards ranged from 59% to 73% for PBDE homologue groups (2Br-7Br) and 69% to 76% for PCB homologue groups (3Cl-7Cl). Detailed recoveries for PBDEs and PCBs are shown in Figure S2.

Instrument detection limits (IDL) and method detection limits (MDL) were determined by analyzing the calibration standards using the same method as sample analysis. Melymuk (2007)[25] details the methods used to calculate IDL and MDL which were listed in Table S3. Six samples of standard reference material (SRM 1944-New York/New Jersey Waterway Sediment) were analyzed using the same method to assess the accuracy and precision of the analysis. The root-mean-square error between the concentrations we measured and the certificated values was 1.4 $ng \cdot g^{-1}$ (Figure S3).

Data Analysis. Commonly reported congeners were selected for comparison with other studies. For congeners not detected, one-half of the MDLs were assigned for statistical analysis (SPSS 11.0, using a significance level α=0.05). Principal component analysis (PCA) was performed on relative congener concentrations of the indoor air samples. PBDE commercial products,[1] outdoor air[26] and emissions from TV housing and printed circuit board,[27] and Aroclor mixtures of PCBs [28] and PCBs in building sealant samples[29] were included in the PCAs for PBDEs and PCBs, respectively. For congener profiles in condensed phases such as technical mixtures and building sealants, the concentrations were multiplied by their respective vapor pressures[14] to reflect the corresponding air concentration.

Modeling of PBDE and PCB Emissions and Fate Indoors. The multimedia indoor fugacity model developed by Zhang et al.[15] was used to estimate emission rates and to estimate the fate of PBDEs and PCBs in SSH. Only the predominant congeners (i.e., PBDE-28, -47, -66, -99, -100, -153, -154 and PCB-28, -31, -44, -52, -110, -138, -153, -180) were selected for modeling. The previous version of the model [15] treated PUF and carpet as potential sources of PBDEs using a pseudosteady-state formulation parametrized with measured PBDE concentrations. Lacking measured concentrations of PBDEs in the PUF-containing furniture and carpet in the office, we used lower (2×10^3 $ng \cdot g^{-1}$) and upper bound (10^6 $ng \cdot g^{-1}$) concentrations in PUF, again using a pseudosteady-state formulation.[15,30] Since to our knowledge PCBs were not intentionally added to PUF or carpet during production, these materials were not assigned a concentration and we assumed steady-state conditions. Considering the importance of air exchange rate (AER), we ran the model with a lower (0.19 h^{-1}) and upper bound (8.69 h^{-1}) reported for nonresidential building.[31]

Table 1. Total PBDE and PCB Concentration in the Air Measured in This Study and Comparison with Other Studies

		ΣBDE				ΣPCB			
		this study	Harrad (2006)	Wilford (2004)	Gevao (2006)	this study	Harrad (2006)	Kohler (2005)	Menichini (2007)[a]
location		Toronto, Canada	Birmingham, UK	Ottawa, Canada	Kuwait	Toronto, Canada	Birmingham, UK	Switzerland	Rome, Italy
sampling method		PAS (PUF)[b]	PAS (PUF)	PAS (PUF)	PAS (PUF)	PAS (PUF)	PAS (PUF)	Low-Vol[c]	Low-Vol
sampling rate ($m^3 \cdot d^{-1}$)		1.1−1.9	1.1−1.9	2.5	2.5	0.70−1.27	0.70−1.27	n/a[d]	36
sampling period (d)		∼30	∼30	∼20	∼40	∼30	∼30	n/a[d]	1
air concentration	min	0.008	0.004	0.002	0.002	0.8	0.5	<100	9.5
($ng \cdot m^{-3}$)	median	0.071	0.047	0.100	0.008	8.5	3.5	410	n/a
	mean	0.930	0.110	0.260	0.24	15.3	10.7	790	n/a
	max	16.463	1.416	3.600	0.385	130.5	101.7	>6000	41.5

[a] ΣPCB calculated as five times the sum of six indicator concentrations as handled by Kohler 2005. [b] PAS (PUF): Passive Air Sampler (PUF disk as the sampling medium). [c] Low-Vol: Low-volume air sampler. [d] Total sampling volume of 0.18 m^3.

RESULTS AND DISCUSSION

PBDE and PCB Concentrations in Indoor Air. Concentrations of ΣBDE in the 20 indoor air samples ranged between 0.008 and 16 $ng \cdot m^{-3}$ with a geometric mean of 0.072 $ng \cdot m^{-3}$ and a median of 0.061 $ng \cdot m^{-3}$ (descriptive statistics for individual congeners and ΣBDE are supplied in Table S4). PBDE concentrations at the 20 locations followed a log-normal distribution (determined using a Kolmogorov−Smirnov test) and varied by up to $\sim 10^5$-fold, which was consistent with previous studies.[5,12,21] As seen in Table 1, the air concentrations reported here were comparable to the median concentration of 0.047 $ng \cdot m^{-3}$ measured in Birmingham UK using the same methods and passive sampling rates (1.1−1.9 $m^3 \cdot d^{-1}$)[21] and 0.100 $ng \cdot m^{-3}$ measured in 94 homes of Ottawa using passive air samplers with a slightly different design and a sampling rate of 2.5 $m^3 \cdot d^{-1}$,[32] but slightly higher than that measured 0.008 $ng \cdot m^{-3}$ in Kuwait using similar PUF passive samplers with a sampling rate of 2.5 $m^3 \cdot d^{-1}$.[33] The range of the indoor-to-outdoor concentration ratio (I/O) calculated from the geometric means of this study and the reported outdoor concentrations in Toronto (0.003−0.030 $ng \cdot m^{-3}$)[26] was 2.4−24, which was consistent with the I/O range determined in other studies[12,21] and is consistent with the hypothesis that indoor environments are a source of PBDEs to the outdoor environment as a result of building ventilation.[6,15]

Among the 20 locations studied here, concentrations in offices ($n = 5$) of 0.79 $ng \cdot m^{-3}$ was higher than that of homes ($n = 10$) of 0.49 $ng \cdot m^{-3}$ (means were not significantly different). This pattern of concentrations was similar to that found by Harrad et al. (2006) who reported that indoor air concentrations of PBDEs in UK offices were statistically higher than those in homes.[21]

As with other studies, correlations between PBDE air concentrations and potential PBDE sources in the 20 indoor environments (e.g., numbers of PUF furniture items and numbers of computers and other electrical devices which are compiled in Table S2) were weak or nonexistent.[12,30,34,35] Zhang et al.[15] postulated that this lack of correlation is consistent with the modulation of indoor emission rates, chemical fate and concentrations by indoor materials, notably PUF furniture that can act as either a source or sink, and/or by differences in indoor environmental characteristics such as air exchange rate and/or temperature.

Total PCB air concentrations (ΣPCB) ranged from 0.8 to 130.5 $ng \cdot m^{-3}$ for the 20 indoor locations. Concentrations of individual congeners and the descriptive statistics are summarized in Table S5. ΣPCB in the air of the 20 indoor environments followed a log-normal distribution (Kolmogorov−Smirnov test) with a geometric mean and median of 6.5 $ng \cdot m^{-3}$ and 8.5 $ng \cdot m^{-3}$ respectively. For homes, offices, and other types of environments, the geometric means (and median) of ΣPCB were 5.9 (8.0), 12.5 (14.0), and 6.2 (10.0) $ng \cdot m^{-3}$, respectively.

The concentration range of ΣPCB measured in this study was comparable to that of Birmingham, UK (0.5−100 $ng \cdot m^{-3}$) measured using the same method.[21] For the six indicator PCB congeners (PCB-28, 52, 101, 153, 138, 180), total concentrations reported here (0.2−39.7 $ng \cdot m^{-3}$) were not different ($p = 0.10$) from concentrations measured in four buildings in Rome (1.9−8.3 $ng \cdot m^{-3}$; active sampling at 1.5 $m^3 \cdot h^{-1}$)[13] but were lower ($p < 0.001$) than the measured concentrations (3.3−374 $ng \cdot m^{-3}$; active sampling at 3 $m^3 \cdot h^{-1}$) in German indoor air where PCBs were attributable to permanently elastic sealants.[36]

We also compared PCB-31/28, 52, 49, 44, 95, 101, 110, 149, 118, 153, 138, and 180 in the indoor air reported here with those measured at six outdoor sites in downtown Toronto during summer.[37] The outdoor concentrations ranged from 0.072 to 0.55 $ng \cdot m^{-3}$ with a geometric mean of 0.18 $ng \cdot m^{-3}$, which was lower than the geometric mean of the indoor measurement of 0.65 $ng \cdot m^{-3}$. The I/O calculated from the geometric means was 3.6, which falls on the lower end of the 2−50 I/O range based on five studies in Europe and US.[13]

Sources of PBDEs and PCBs in Indoor Air: Analysis of Congener Profiles. All the reported congeners present in Penta-BDE mixtures (BDE-17, 28, 47, 49, 66, 99, 100, 153, 154) were significantly correlated with each other ($r = 0.48-0.99$, $p \leq 0.033$). BDE-183, a marker for Octa-BDE mixture, was not significantly correlated with the congeners in the Penta-BDE mixture, which is consistent with different sources of these mixtures.[38]

PCA on the congener profiles of PBDEs was used to further investigate the hypothesis that emission sources differ among the 20 locations plus SSH. Principal component 1 (PC1) and 2 (PC2) accounted for 77% and 14% of the variance within the data set, respectively. We distinguished four clusters in the PCA plot (Figure 1).

Cluster I (CAN01, CAN03, CAN09, CAN10, CAN14, CAN15), which included four homes, an office, and a power plant, had greater

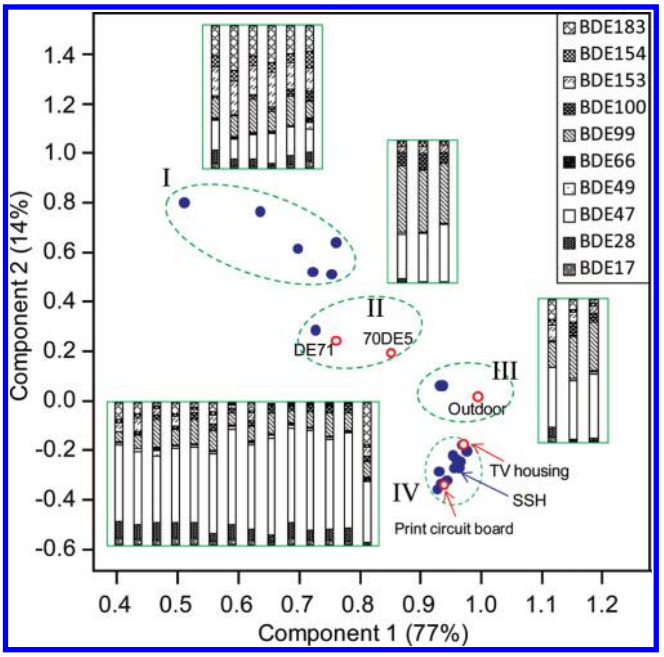


Figure 1. Principal component analysis and congener profiles of PBDEs in the indoor air samples (blue solid dots). PBDEs in outdoor air,[26] commercial Penta-BDE formulation,[1] and an emission profile from a printed circuit board and TV housing[27] were included as references (orange hollow dots) for source identification. The PBDE concentration profiles of the indoor air are separated into four clusters. Cluster I includes CAN01, 03, 09, 14, and 15; Cluster II includes CAN12; Cluster III includes CAN11 and 17; Cluster IV includes CAN02, 04, 05, 06, 07, 08, 13, 16, 18, 19, 20, and SSH.

portions of heavier congeners such as BDE-153 and -183 than BDE-47 and -99. The geometric mean of PBDE in air was 0.020 ng·m^{-3}, which was lowest of all the clusters. These locations did not have computers and had fewer electrical devices than other locations (Table S2). All of these locations except CAN03 (power plant) were carpeted.

Cluster II included two Penta-BDE commercial products and CAN12, which is a gymnasium containing a very large volume of PUF. The air concentration in CAN12 was ~100 fold higher than that of other locations in this study. We hypothesize that the PUF acted as the major PBDE source at this location.

Cluster III contained two research chemistry laboratories (CAN11 and CAN17) together with the outdoor air profile.[26] This clustering is consistent with the high ventilation rates in the research laboratories bringing in outdoor air, although it is puzzling that the mean concentration of 0.73 ng·m^{-3} was higher than that of the homes and >10 times higher than outdoor air concentrations.

Cluster IV included the remaining locations and emissions from a printed circuit board and a TV housing.[27] From this we surmise that the main PBDE sources for this cluster were electrical devices: this supposition is consistent with information on room contents obtained at all the sites (Table S2). Air concentrations at Cluster IV locations were relatively high in BDE-28 and -47 which originate from the Penta-mixture for which the vapor pressures increase more as a function of increasing temperature than the more highly brominated congeners.[39] Thus, we hypothesize that electrical equipment that heats up during operation was the dominant source of PBDEs in these indoor locations compared with PUF furniture and carpet backing that appeared to dominate the sources in Cluster I with its lower average air concentration. This is in line with the results of Hazrati and Harrad (2006) who showed a decrease in PBDE concentration in air by 80% after an old computer was replaced with a new one.[40] This also agrees with the results of Allen et al. (2008) who found that bromine was more frequently detected in electronics at higher concentrations than in furniture.[30]

PCB congener profiles also suggested a potential source of emissions. Tri- and tetra-PCBs accounted for over 75% of ΣPCB in indoor air. PCB-18/17, 31/28, and 52 accounted for 14, 11, and 11% of ΣPCB, respectively (we did not analyze for PCB-11). Twelve PCB congeners (PCB-31/28, 52, 49, 44, 95, 101, 110, 149, 118, 153, 138, and 180) were correlated with each other (r = 0.45−0.99, $p \leq 0.034$), with the exception of PCB-31/28 that was not correlated with PCB-180.

PCA was conducted with the 12 most abundant congeners representing the five homologue groups from tri- to hepta-PCB.[37] Congener profiles in outdoor air,[37] Aroclor PCB mixtures,[28] and exterior building sealants [29] were included for comparison. The results are presented as the PCA plots in Figure S4. The first two PCs account for 59% and 21% of the total variance. The Aroclor technical products separated into two groups with the 20 indoor locations and exterior building sealants spread in an arc between these two end-points (Figure S4). Aroclors 1254, 1260, and 1262, with their relatively high chlorine content scored low on PC1 and high on PC2 and visa versa for Aroclors 1232, 1242, and 1248. Offices and other locations grouped as Cluster I had a geometric mean concentration of 6.6 ng·m^{-3}. They share similar congener profiles with downtown Toronto outdoor air and one sealant profile. The remaining locations grouped as Cluster II included all the homes, which had lower chlorinated congeners and a lower geometric mean concentration of 2.0 ng·m^{-3}. This cluster also included one sealant profile and was similar to Aroclors 1248, 1232, and 1242. The similarity of indoor air to sealants is not surprising since sealants contribute significantly to the known stock of PCBs in Toronto.[41] As with PBDEs, it is puzzling that the locations (offices) with higher concentrations had congener profiles similar to outdoor air.

PBDE and PCB Distribution between Indoor Air and Dust. We evaluated the assumption of equilibrium partitioning between colocated measured PBDE and PCB concentrations in air and dust.[42] PBDE and PCB concentrations of individual congeners in the dust collected from the same 20 locations at the end of the air sampling period[5,43] were positively correlated with air concentrations (r = 0.55−0.86, $p \leq 0.016$) (Tables S6 and S7). Total PCB concentrations in air and dust were also correlated (r = 0.75, $p < 0.001$), but the same was not true for PBDEs (Figure S5). Thus, locations with elevated PCB concentrations in air tended to have higher concentrations in dust.

We next examined the relationship between partitioning of PBDEs and PCBs in air and dust to the octanol-air partitioning coefficient (K_{OA}) of the individual congeners. If the source of PBDEs and PCBs in dust were the result of partitioning between air and the organic phase of dust rather than abrasion of materials containing the chemicals,[44] then there should be a linear relationship between log (C_{air}/C_{dust}) and log K_{OA}.[45] This was the case for PCBs and PBDEs with less than 5 bromines but not for those with more than 5 bromines or log K_{OA} >11, for which there was no relationship (Figure 2). Three reasons could explain the results for PBDEs: (1) air and dust failed to reach equilibrium which was the conclusion reached by Weschler and Nazaroff

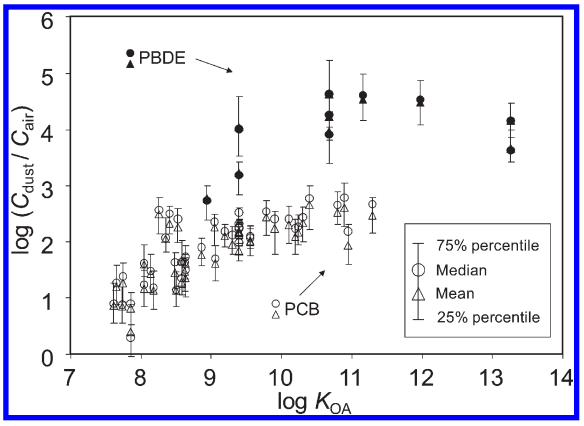


Figure 2. Dependence of dust/gas phase distributions of PBDEs and PCBs on their respective octanol/air partitioning coefficients (K_{OA}).

(2010) in their review of 66 SOCs; (2) measured gas-phase air concentration for congeners with high K_{OA} that were obtained using the PUF-disk passive sampler could have been overestimated due to the trapping of trace amounts of particle-phase PBDEs by the sampler;[46−49] (3) the source of higher molecular weight congeners to dust could have been physical abrasion of PBDE containing particles or fibers that would be relatively unavailable for gas-particle partitioning,[44] however then log (C_{dust}/ C_{air}) should exceed logK_{OA} rather than being less as is the case here.

Emissions and Fate of PBDEs and PCBs Indoors. Emissions of selected PBDEs and PCBs in the intensively studied office SSH were estimated using the Multimedia Indoor Model of Zhang et al. (2009) by solving for congener-specific emissions that must enter the room in order to achieve measured air concentrations. Measured PBDE and PCB concentrations in gas- and particle- phases of air, surface film on vertical glass windows and horizontal glass beads that were used to evaluate model assumptions and results are reported in Table S8 and Table S9. Congener profiles of PBDEs and PCBs in each phase are illustrated in Figure S6. Interpretation and discussion of media specific results are also included in SI.

When modeling PCBs, we assumed that steady-state conditions prevailed in the office, whereas for PBDEs we considered two scenarios − steady state and pseudo steady state. For the latter, we assigned upper and lower bound concentrations of PBDEs to the PUF in the office chairs based on concentrations reported in the literature, whereas no PBDE concentrations were assumed a priori for the former. We assumed particle deposition and resuspension rates reported by Bennett and Furtaw.[50] The air exchange rate was varied to obtain upper and lower bound estimates of emissions since Zhang et al. found that model-estimated emissions were highly sensitive to this variable. With these assumptions and emission rates calculated so that the modeled and measured air concentrations matched, the calculated PBDE and PCB concentrations in surface film of 74 and 180 ng·m^{-2}, respectively, were midway between measured film concentrations using window wipes and glass beads.

Model estimates of emissions of Σ_7BDE and Σ_8PCB in SSH were 87−550 ng·h^{-1} and 280−5870 ng·h^{-1}, respectively, which were 400−3000 fold and 100−200 fold higher than the contribution from outdoor air. Normalized to the area of the room, emissions of Σ_7BDE and Σ_8PCB were 6−40 and 20−430 ng·h^{-1}·m^{-2}, respectively. The range of Σ_7BDE emissions

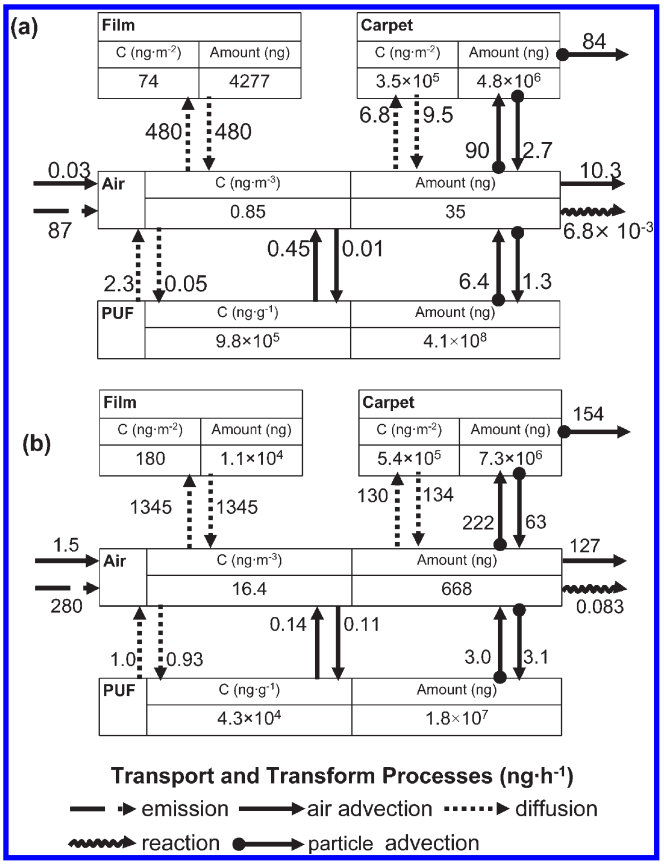


Figure 3. Results from the multimedia indoor model of Zhang et al. (2009) used to estimate emission rates and fate of (a) PBDEs and (b) PCBs in the SSH office. The emission rates were calculated to match modeled and measured air concentrations. Lower bound emission rates illustrated here were estimated assuming a lower bound air exchange rate of 0.19 h^{-1} and for PBDE, upper-bound concentrations in PUF of 10^6 ng·g^{-1}. Upper bound emission and fate are presented in Figure S7.

estimated herein encapsulated the value of 20 ng·h^{-1}·m^{-2} estimated for 12 US houses[38] and 22 ng·h^{-1}·m^{-2} estimated for a new office building by Batterman et al. (2010) for 21 congeners[51] and were considerably higher than ∼7 and 1 ng·h^{-1}·m^{-2} for a university office in Birmingham, UK with an older and new computer, respectively,[40] estimated by Zhang et al. who used the same model as used here.[15] The SSH office emissions were also comparable to the range of emission rates of 200−900 ng·h^{-1}·m^{-2} estimated for the City of Toronto as a whole using the Multimedia Urban Model.[19]

BDE-47 and -99 were the two dominant congeners, comprising ∼60% and ∼20% respectively of Σ_7BDE emissions. PCB emissions were dominated by PCB-138 and -28, which each contributing ∼25% of Σ_8PCB emissions.

Figure 3 illustrates lower bound emissions and the fate of PBDE and PCB indoors assuming a lower-bound air exchange rate of 0.19 h^{-1} and, for PBDE, upper-bound concentrations of 10^6 ng·g^{-3} in PUF. With this scenario, <10% of Σ_7BDE emission losses were via air advection to outdoors which is consistent with the choice of the lower-bound air exchange rate. However, this value changed to ∼85% of total losses to outdoors when using a higher bound air exchange rate of 8.69 h^{-1} (Figure S7). Assuming a high PBDE concentration in the PUF chairs, the PUF acted as a source of PBDE to the office, with a net flux of 7.8 ng·h^{-1}

from PUF-to-air. Carpet, due to its large surface area (SSH was fully carpeted) and dust deposition, acted as a sink for PBDEs depositing from air. The net flux from air-to-carpet was 84 $ng \cdot h^{-1}$ which equaled the chemical loss rate through dust removal (forced by the steady-state assumption for carpet). Dust removal contributed ~90 and 15% to PBDE loss from the indoor environment for low and high ventilation rates, respectively. For PCBs, losses via air advection and dust removal were about equal for the low ventilation scenario. This result is consistent with the higher vapor pressure and hence higher fraction of PCBs in the gas phase relative to PBDEs. However, ventilation losses increased to 97% of total losses assuming the high ventilation rate.

Although the room contained only 3 PUF chairs, the PUF was the greatest reservoir of PBDEs and PCBs of all compartments. The PUF acted as a sink for PBDEs and PCBs assuming high and low air exchange rates, except when upper bound PBDE concentrations in the PUF were assumed.

Considering these results, it is evident and logical that a room's contents and building materials are reflected in its air and dust concentrations and compound profiles. In general, offices have higher PBDE and PCB concentrations than homes. Even 27 years after construction, the SSH office had ~30 times higher PCB air concentration than outdoors. The PCBs were presumed to be incorporated in the building's construction materials. The PBDEs were presumed to be emitted from the electronic equipment first, followed by carpet and possibly PUF furniture that dated to just prior the 2004 restrictions on PBDE production. These results point to the indoor environment as a considerable reservoir for these now banned chemicals. This reservoir is slowly depleted by continual releases to the outdoor environment through building ventilation. The results suggest that personal exposure can be minimized by maximizing air ventilation rates, which may be contrary to efforts to minimize indoor energy losses designed to conserve energy.

■ ASSOCIATED CONTENT

Supporting Information. Detailed information on sampling locations, instrumental analysis, descriptive statistics of individual PBDE and PCB congener, QA/QC, further results of data interpretation and model application. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 416-978-1586. Fax: 416-946-5992. E-mail: miriam.diamond@utoronto.ca.

■ ACKNOWLEDGMENT

We are grateful to funding provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada and support to Zhang from Dept. of Geography, Univ. of Toronto and NSERC. We thank Prof. G. Arhonditsis of University of Toronto for advice on statistics. We also thank all those who volunteered to participate in the sampling campaign.

■ REFERENCES

(1) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* **2006**, *40*, 6247–6254.

(2) Stapleton, H. M.; Sjödin, A.; Jones, R. S.; Niehüser, S.; Zhang, Y.; Patterson, D. G.; Serum, J. Levels of Polybrominated Diphenyl Ethers (PBDEs) in Foam Recyclers and Carpet Installers Working in the United States. *Environ. Sci. Technol.* **2008**, *42*, 3453–3458.

(3) UNEP (2009) The Nine New POPs. An introduction to the nine chemicals added to the Stockholm Convention by the Conference of the Parties at its fourth meeting. Available online http://chm.pops.int/Programmes/NewPOPs/Publications/tabid/695/language/en-US/Default.aspx (accessed Nov 2010).

(4) Bromine Science Environmental Forum. Legislation - Regulatory Overview in the EU. Available online at http://www.bsef.com/regulation/eu_legislation/ (accessed May 2009).

(5) Harrad, S.; Ibarra, C.; Diamond, M.; Melymuk, L.; Robson, M.; Douwes, J.; Roosens, L.; Dirtu, A. C.; Covaci, A. Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States. *Environ. Int.* **2008**, *34*, 232–238.

(6) Harrad, S.; Diamond, M. New directions: Exposure to polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs): Current and future scenarios. *Atmos. Environ.* **2006**, *40*, 1187–1188.

(7) Erickson, M. D. *Analytical Chemistry of PCBs*, second *ed.;* Lewis Publishers: Boca Raton, FL, 1997.

(8) Herrick, R. F.; McClean, M. D.; Meeker, J. D.; Baxter, L. K.; Weymouth, G. A. An unrecognized source of PCB contamination in schools and other buildings. *Environ. Health Perspect.* **2004**, *112*, 1051–1053.

(9) Herrick, R. F.; McClean, M. D.; Meeker, J. D.; Baxter, L. K.; Weymouth, G. A. An unrecognized source of PCB contamination in schools and other buildings. *Environ. Health Perspect.* **2004**, *112*, 1051–3.

(10) Hu, D. F.; Martinez, A.; Hornbuckle, K. C. Discovery of Non-Aroclor PCB (3,3′-Dichlorobiphenyl) in Chicago Air. *Environ. Sci. Technol.* **2008**, *42*, 7873–7877.

(11) Rodenburg, L. A.; Guo, J.; Du, S. Y.; Cavallo, G. J. Evidence for Unique and Ubiquitous Environmental Sources of 3,3′-Dichlorobiphenyl (PCB 11). *Environ. Sci. Technol.* **2010**, *44*, 2816–2821.

(12) Wilford, B. H.; Harner, T.; Zhu, J. P.; Shoeib, M.; Jones, K. C. Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure. *Environ. Sci. Technol.* **2004**, *38*, 5312–5318.

(13) Menichini, E.; Lacovella, N.; Monfredini, F.; Turrio-Baldassarri, L. Relationships between indoor and outdoor air pollution by carcinogenic PAHs and PCBs. *Atmos. Environ.* **2007**, *41*, 9518–9529.

(14) Harrad, S.; Ibarra, C.; Robson, M.; Melymuk, L.; Zhang, X. M.; Diamond, M.; Douwes, J. Polychlorinated biphenyls in domestic dust from Canada, New Zealand, United Kingdom and United States: Implications for human exposure. *Chemosphere* **2009**, *76*, 232–238.

(15) Zhang, X. M.; Diamond, M. L.; Ibarra, C.; Harrad, S. Multimedia Modeling of Polybrominated Diphenyl Ether Emissions and Fate Indoors. *Environ. Sci. Technol.* **2009**, *43*, 2845–2850.

(16) Leech, J. A.; Nelson, W. C.; Burnett, R. T.; Aaron, S.; Raizenne, M. E. It's about time: A comparison of Canadian and American time-activity patterns. *J. Exposure Anal. Environ. Epidemiol.* **2002**, *12*, 427–432.

(17) Fraser, A. J.; Webster, T. F.; McClean, M. D. Diet Contributes Significantly to the Body Burden of PBDEs in the General US Population. *Environ. Health Perspect.* **2009**, *117*, 1520–1525.

(18) Roosens, L.; Abdallah, M. A. E.; Harrad, S.; Neels, H.; Covaci, A. Current Exposure to Persistent Polychlorinated Biphenyls (PCBs) and Dichlorodiphenyldichloroethylene (p,p′-DDE) of Belgian Students from Food and Dust. *Environ. Sci. Technol.* **2010**, *44*, 2870–2875.

(19) Jones-Otazo, H. A.; Clarke, J. P.; Diamond, M. L.; Archbold, J. A.; Ferguson, G.; Harner, T.; Richardson, G. M.; Ryan, J. J.; Wilford, B. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.* **2005**, *39*, 5121–5130.

(20) Diamond, M. L.; Melymuk, L.; Csiszar, S. A.; Robson, M. Estimation of PCB Stocks, Emissions, and Urban Fate: Will our Policies Reduce Concentrations and Exposure?. *Environ. Sci. Technol.* **2010**, *44*, 2777–2783.

(21) Harrad, S.; Hazrati, S.; Ibarra, C. Concentrations of polychlorinated biphenyls in indoor air and polybrominated diphenyl ethers in indoor air and dust in Birmingham, United Kingdom: Implications for human exposure. *Environ. Sci. Technol.* **2006**, *40*, 4633–4638.

(22) Hazrati, S.; Harrad, S. Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs): Factors influencing sampling rates. *Chemosphere* **2007**, *67*, 448–455.

(23) Diamond, M. L.; Gingrich, S. E.; Fertuck, K.; McCarry, B. E.; Stern, G. A.; Billeck, B.; Grift, B.; Brooker, D.; Yager, T. D. Evidence for organic film on an impervious urban surface: Characterization and potential teratogenic effects. *Environ. Sci. Technol.* **2000**, *34*, 2900–2908.

(24) Wu, R. W.; Harner, T.; Diamond, M. L. Evolution rates and PCB content of surface films that develop on impervious urban surfaces. *Atmos. Environ.* **2008**, *42*, 5696–5705.

(25) Melymuk, L. Are PCBs Really Legacy POPs? A Spatial Evaluation of PCBs in Toronto, Canada. University of Toronto, Toronto, 2007.

(26) Harner, T.; Shoeib, M.; Diamond, M.; Ikonomou, M.; Stern, G. Passive sampler derived air concentrations of PBDEs along an urban-rural transect: Spatial and temporal trends. *Chemosphere* **2006**, *64*, 262–267.

(27) Kemmlein, S.; Hahn, O.; Jann, O. Emissions of organophosphate and brominated flame retardants from selected consumer products and building materials. *Atmos. Environ.* **2003**, *37*, 5485–5493.

(28) Frame, G. M.; Cochran, J. W.; Bowadt, S. S. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. *J. High Resolut. Chromatogr.* **1996**, *19*, 657–668.

(29) Melymuk, L. *Personal communication*. 2008.

(30) Allen, J. G.; McClean, M. D.; Stapleton, H. M.; Webstert, T. F. Linking PBDEs in house dust to consumer products using X-ray fluorescence. *Environ. Sci. Technol.* **2008**, *42*, 4222–4228.

(31) Johnson, T.; Georgopoulous, P. *A Guide to Selected Algorithms, Distributions, and Databases Used in Exposure Models Developed by the Office of Air Quality Planning and Standards*. U.S. Environmental Protection Agency, Office of Research and Development: 2002.

(32) Wilford, B. H.; Harner, T.; Zhu, J.; Shoeib, M.; Jones, K. C. Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: implications for sources and exposure. *Environ. Sci. Technol.* **2004**, *38*, 5312–8.

(33) Gevao, B.; Al-Bahloul, M.; Al-Ghadban, A. N.; Ali, L.; Al-Omair, A.; Helaleh, M.; Al-Matrouk, K.; Zafar, J. Polybrominated diphenyl ethers in indoor air in Kuwait: Implications for human exposure. *Atmos. Environ.* **2006**, *40*, 1419–1426.

(34) Harrad, S.; Wijesekera, R.; Hunter, S.; Halliwell, C.; Baker, R. Preliminary assessment of UK human dietary and inhalation exposure to polybrominated diphenyl ethers. *Environ. Sci. Technol.* **2004**, *38*, 2345–2350.

(35) Wilford, B. H.; Shoeib, M.; Harner, T.; Zhu, J. P.; Jones, K. C. Polybrominated diphenyl ethers in indoor dust in Ottawa, Canada: Implications for sources and exposure. *Environ. Sci. Technol.* **2005**, *39*, 7027–7035.

(36) Balfanz, E.; Fuchs, J.; Kieper, H. Sampling and Analysis of Polychlorinated-Biphenyls (PCB) in Indoor Air Due to Permanently Elastic Sealants. *Chemosphere* **1993**, *26*, 871–880.

(37) Harner, T.; Shoeib, M.; Diamond, M.; Stern, G.; Rosenberg, B. Using passive air samplers to assess urban - Rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides. *Environ. Sci. Technol.* **2004**, *38*, 4474–4483.

(38) Batterman, S. A.; Chernyak, S.; Jia, C. R.; Godwin, C.; Charles, S. Concentrations and Emissions of Polybrominated Diphenyl Ethers from US Houses and Garages. *Environ. Sci. Technol.* **2009**, *43*, 2693–2700.

(39) Tittlemier, S. A.; Halldorson, T.; Stern, G. A.; Tomy, G. T. Vapor pressures, aqueous solubilities, and Henry's law constants of some brominated flame retardants. *Environ. Toxicol. Chem.* **2002**, *21*, 1804–1810.

(40) Hazrati, S.; Harrad, S. Causes of variability in concentrations of polychlorinated biphenyls and polybrominated diphenyl ethers in indoor air. *Environ. Sci. Technol.* **2006**, *40*, 7584–7589.

(41) Robson, M.; Melymuk, L.; Csiszar, S. A.; Giang, A.; Diamond, M. L.; Helm, P. A. Continuing sources of PCBs: the significance of building sealants. *Environ. Int.* **2010**, *36*, 506–13.

(42) Bergh, C.; Torgrip, R.; Emenius, G.; Östman, C. Organophosphate and phthalate esters in air and settled dust — a multi-location indoor study. *Indoor Air* **2011**, *21*, 67–76.

(43) Harrad, S. Unpublished data. Personal Communication with Dr. Harrad.

(44) Webster, T. F.; Harrad, S.; Millette, J. R.; Holbrook, R. D.; Davis, J. M.; Stapleton, H. M.; Allen, J. G.; Mcclean, M. D.; Ibarra, C.; Abdallah, M. A. E.; Covaci, A. Identifying Transfer Mechanisms and Sources of Decabromodiphenyl Ether (BDE 209) in Indoor Environments Using Environmental Forensic Microscopy. *Environ. Sci. Technol.* **2009**, *43*, 3067–3072.

(45) Weschler, C. J.; Nazaroffc, W. W. SVOC partitioning between the gas phase and settled dust indoors. *Atmos. Environ.* **2010**, *40*, 3609–3620.

(46) Abdallah, M. A. E.; Harrad, S. Modification and Calibration of a Passive Air Sampler for Monitoring Vapor and Particulate Phase Brominated Flame Retardants in Indoor Air: Application to Car Interiors. *Environ. Sci. Technol.* **2010**, *44*, 3059–3065.

(47) Tao, S.; Cao, J.; Wang, W.; Zhao, J.; Wang, Z.; Cao, H.; Xing, B. A passive sampler with improved performance for collecting gaseous and particulate phase polycyclic aromatic hydrocarbons in air. *Environ. Sci. Technol.* **2009**, *43*, 4124–9.

(48) Tao, S.; Liu, Y. N.; Xu, W.; Lang, C.; Liu, S. Z.; Dou, H.; Liu, W. X. Calibration of a passive sampler for both gaseous and particulate phase polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **2007**, *41*, 568–573.

(49) Chaemfa, C.; Wild, E.; Davison, B.; Barber, J. L.; Jones, K. C. A study of aerosol entrapment and the influence of wind speed, chamber design and foam density on polyurethane foam passive air samplers used for persistent organic pollutants. *J. Environ. Monit.* **2009**, *11*, 1135–1139.

(50) Bennett, D. H.; Furtaw, E. J. Fugacity-based indoor residential pesticide fate model. *Environ. Sci. Technol.* **2004**, *38*, 2142–2152.

(51) Batterman, S.; Godwin, C.; Chernyak, S.; Jia, C.; Charles, S. Brominated flame retardants in offices in Michigan, USA. *Environ. Int.* **2010**, *36*, 548–56.

Supporting Information

Sources, Emissions and Fate of Polybrominated Diphenyl Ethers (PBDEs) and Polychlorinated Biphenyls (PCBs) Indoors in Toronto, Canada

Xianming Zhang [1], Miriam Diamond [1], Matthew Robson [1], Stuart Harrad [2]*

[1] Department of Geography, University of Toronto, Toronto, Ontario, M5S 3G3, Canada

[2] Division of Environmental Health and Risk Management, Public Health Building, School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, United Kingdom

*Corresponding author phone: 416-978-1586; fax: 416-946-5992; e-mail: miriam.diamond@utoronto.ca.

TABLE S1. Usage of PBDE and PCB Technique Mixtures

	Product	Usage
PBDE [a]	Penta-BDE	polyurethane foam; carpet underlay; mattresses; vehicle interior; furniture; bedding
	Octa-BDE	thermal plastics; high-impact polystyrene; acrylonitrile-butadiene-styrene (ABS) polymer for equipment castings
	Deca-BDE	hard plastics for electric equipment component and castings; flame retardant rubbers; textile back coatings
PCB [b]	Aroclor 1016	production and sale was discontinued in late 1977; still present in capacitors now in use.
	Aroclor 1221	gas-transmission turbine hydraulics, rubber plasticizers, adhesives, and electrical capacitors before 1977; still present in many of the capacitors now in use.
	Aroclor 1242	heat transfer fluid, hydraulic fluids, rubber plasticizer, and in carbonless paper, adhesives and wax extenders before 1977; still present in transformers and capacitors now in use;
	Aroclor 1248	formerly used in hydraulic fluids, vacuum pumps, rubber plasticizers, synthetic resins, and adhesives.
	Aroclor 1254	hydraulic fluid, rubber plasticizers, synthetic resin plasticizers, adhesives, wax extenders, inks, cutting oils, pesticide extenders, sealants and caulking compounds before 1977; still present in transformers now in use.
	Aroclor 1260	electrical transformers, hydraulic fluids, plasticizer in synthetic resins before 1977; still present in many of the transformers and capacitors now in use.

[a] Reference (*1*)

[b] Reference (*2*)

TABLE S2. Detailed Information of the 20 Indoor Places in this Study

Sample I.D.	Type of environment	Room	Construction year of Building	Time since vacuumed	Room Ventilation	Number of foam chairs	Number of sofas	Number of beds	Other
CAN01	Home	Living room	1973/1974	2 weeks	Natural	6	2	0	0
CAN02	Home	Basement family room	mid 1970's	unknown	Mechanical	4	2	0	4 large foam toys and 9 large pillows
CAN03	Other	power plant Steam generator/ boiler room	1950's or 1960's	unknown	Mechanical	0	0	0	0
CAN04	Home	Living room/Dining room	1926	1 week	Natural	6	1	0	0
CAN05	Home	Bedroom(Student Residence)	2000	1 month	Natural	1	0	1	0
CAN06	Other	Infant Care Room	2003	2 days	Mechanical	0	0	0	3 foam-containing baby carriers
CAN07	Office	Office	1969	1 week	Mechanical	3	0	0	0
CAN08	Home	Living room/Dining room	early 1920's	1 week	Natural	1	1	0	0
CAN09	Home	Living room	1906	1 month	Natural	2	1	0	0
CAN10	Office	Hallway adjacent to offices	1920's	1 week	Natural	1	0	0	0
CAN11	Other	research Lab	1970's	1 day	Mechanical (& 8 fume hoods)	3	0	0	0
CAN12	Other	Gymnastics gym	unknown	1 day	Mechanical	0	0	0	1 foam pit, 1 foam floor, foam mats
CAN13	Home	Living room	1906	3 weeks	Natural	1	1	0	0
CAN14	Home	Living room	1948	1 week	Natural	4	1	0	0
CAN15	Home	Living room	1984	2 weeks	Mechanical	1	3	0	0
CAN16	Office	Office cubicle	1950	2 days	Mechanical	2	0	0	0
CAN17	Other	research lab	1926	5 months	Mechanical	0	0	0	0
CAN18	Office	Office	1961	unknown	Mechanical	7	0	0	0
CAN19	Office	Computer lab	1961	unknown	Mechanical	35	0	0	0
CAN20	Home	Living room/Dining room	1960's	2 weeks	Natural	4	1	0	0

TABLE S2. Detailed Information of the 20 Indoor Places in this Study (Continued)

Sample I.D.	Number of PCs/laptops	Number of fridges/freezers	Number of TVs	Other electrical equipment	Flooring type
CAN01	0	0	0	1 stereo	carpet (wall-to-wall)
CAN02	3	0	2	1 DVD, 1 Gameboy, 1 sewing machine	carpet (wall-to-wall)
CAN03	0	0	0	Gas-fired power generator	cement
CAN04	0	0	1	2 speakers, 1 DVD, 1 receiver, 1 VCR	carpet (wall-to-wall)
CAN05	0	0	0	0	carpet (wall-to-wall)
CAN06	0	0	0	1 stereo	linoleum
CAN07	0	0	0	1 printer, 1 fax machine	linoleum
CAN08	0	0	1	1 VCR, 2 speakers	carpet (area rug)
CAN09	0	0	0	0	carpet (area rug)
CAN10	0	0	0	1 printer	carpet (area rug)
CAN11	1	1	0	11 (various lab equipment)	linoleum
CAN12	0	0	0	1 stereo	carpet (wall-to-wall)
CAN13	0	0	1	1 VCR	carpet (area rug)
CAN14	0	0	0	0	carpet (wall-to-wall)
CAN15	0	0	1	3 speakers, 1 stereo	carpet (wall-to-wall)
CAN16	2	0	0	0	carpet (wall-to-wall)
CAN17	1	0	0	3 (various lab equipment)	linoleum
CAN18	2	0	0	1 printer, 1 fax machine	carpet (wall-to-wall)
CAN19	34	0	0	1 projector, 2 printers	linoleum
CAN20	3	1	1	1 printer, 1 DVD, 1 stereo, 1 microwave, 1 food processor	wood parquet

Multiple Indoor Phases Sampling

To estimate the emissions and fate of PBDEs and PCBs, PBDEs and PCBs in multiple phases of an office (SSH) were measured from August to October 2007. During the sampling period (56 days), a passive air sampler was deployed in the office as described in the main text. Active air sampling was also conducted for five three-day periods during the 56 days that the passive sampler was deployed. A low volume pump (Gast Manufacturing Inc.) was connected downstream of a sampling cartridge, housed with a glass fiber filter (GFF) (d=4.5cm, pore size=0.45□m) and two PUF plugs (d=4.5cm, l=4.0cm). GFF was used to collect particle-phase analytes and PUF plugs were used as sorbent of gas-phase analytes. Air flow rates were measured before and after each sampling period with a flowmeter (Sierra Instrument Inc.). To minimize the air sampled relative to the volume of the room, an air flow rate of 15 $L \cdot min^{-1}$ was used and in each period, the pump (controlled by a timer) was on for 12 h and off for 12 h alternatively for three times. A total of 540 L of air was sampled in each sampling period, yielding a total of 2.7 m^3 air sampled throughout the entire sampling campaign.

Surface films were collected by wiping the windows using pre-extracted Kimwipes and by using glass beads as a surrogate of an impervious surface. The former was based on the method used by Diamond et al. (*3*) Briefly, surface films were sampled by scrubbing the interior window surface with pre-cleaned Kimwipes, wetted with hexane (HPLC grade, Caledon Lab Ltd.). A 10 cm border around the window area was not scrubbed to avoid contamination of building materials. The actual area sampled was 127×163 cm. The window film was sampled at the beginning and in the end of the 56-day sampling period.

Glass beads have been used as a surrogate of impervious surface to maximize sampling surface area (*4*). During the 56-day sampling period, ~2.6×10^4 glass beads (d = 3 mm) arranged horizontally on 12 aluminum mesh trays allowed exposure from all directions. The surface area of the total glass beads was ~0.735 m^2. The top of the sampling trays was covered with pre-cleaned aluminum foil to avoid direct particle deposition on the beads. A schematic of the glass-bead sampling device is shown in Figure S1.

All glassware was rinsed three times with DCM before using. All the sampling media (PUF disks, glass beads, GFFs, PUF plugs, Kimwipes) were pre-cleaned by Soxhlet extraction with DCM at 60 °C for 16 h. These sampling media were dried under vacuum in a desiccator and then wrapped with pre-cleaned aluminum foil in sealed airtight bags before using. After sampling, the sampling media were wrapped with pre-cleaned aluminum foil and put into glass jars. The samples were stored at -18 °C before analysis.

Detail Information on Sample Extraction and Preparation

In the process of sample extraction, 150 mL pre-cleaned Soxhlet extractors were used for each PUF disk, each pair of PUF plugs, and the five GFFs. Two 250 mL pre-cleaned Soxhlet extractors were used for extracting the glass beads. Samples were treated with appropriate quantities (10 μL for each PUF disk and the five GFFs, 5 μL for each pair of PUF plugs and half of the glass beads) of PCB and PBDE internal standards (specifically PCB -34, -62, -119, -131 and -171, and ^{13}C PBDE -28, -47, -99, -153, -183 and -209) before extracting for 16 h at 60 °C using DCM.

Following extraction, crude extracts were solvent exchanged into hexane and adjusted to 4 mL. The extracts were separated into two fractions: 75% for PCB and PBDE analysis in this study and 25% for achieve and further study. The fractions for this study were treated with 2

mL concentrated sulfuric acid, were shaken for 30 s with Vortexer (IKA Work Inc.) and stored in the fridge for at least 6 h to allow the acid and organic layers to separate.

The samples were then fractioned on columns containing 2 g anhydrous sodium sulphate granular (VWR International) on top, followed by 8 g activated aluminum oxide (80-200 mesh, chromatographic grade, EMD Chemicals Inc.), which was activated at 200 °C for 12 h, 2g silver nitrate (Sigma-Aldrich Co.) impregnated aluminum oxide, and 2g anhydrous sodium sulphate. Prior to loading the samples, the columns were eluted with 25 mL hexane (Caledon Lab Ltd.). Then the organic layer of the samples was added to the columns and the acid layer in the sample vials was rinsed with hexane three times. The samples were eluted with 25 mL hexane followed by 65 mL 1:1 (v:v) DCM/hexane. The 65 mL elutes were collected in clean round bottom flasks, rotoevaporated to 1 mL, and then blown down under a steady stream of high purified (99.995%) nitrogen to incipient dryness and transferred to 300 µL inserts within 2 mL chromatography vials. 10 µL of 1.0 ng μL^{-1} PCB-29 and -129 were added as recovery standards. The samples were further reduced to 25 µL and then stored at -18 °C until further analysis.

Detailed Information on Instrumental Analysis of PCBs and PBDEs

For PCB analysis, separation was achieved using a 60 m DB-5 MS capillary column (0.25 mm i.d., 0.25 µm film thickness), with helium as carrier gas. 1 µL of the sample was injected in splitless mode. Both injector and interface temperatures were 280 °C and quadrupole temperature was 150 °C. The oven temperature program was: 140 °C for 2 min, 5 $°C \cdot min^{-1}$ to 215 °C and held for 5 min, then 2 $°C \cdot min^{-1}$ to 280 °C and held for 20 min.

PBDE separation was achieved using a 30 m DB-1 MS capillary column (0.25 mm i.d., 0.1 µm film thickness), with helium as carrier gas. 1 µL of the sample was injected in splitless

mode. Injector, interface and quadrupole temperatures were 250, 300 and 150 °C respectively. The oven temperature program was: 90 °C for 2 min, 10 °C·min^{-1} to 250 °C, then 0.8 °C·min^{-1} to 250 °C and held for 25 min, followed by 25 °C·min^{-1} to 325 °C and held for 15 min.

BDE-209 was analysed on a 15m DB-5MS capillary column (0.25 mm i.d., 0.25 μm film thickness), Injector, interface and quadrupole temperatures were 300, 320 and 150 °C respectively. The oven temperature program was: 100 °C for 1 min, 10 °C·min^{-1} to 300 °C, then 8 °C·min^{-1} to 320 °C and held for 10 min.

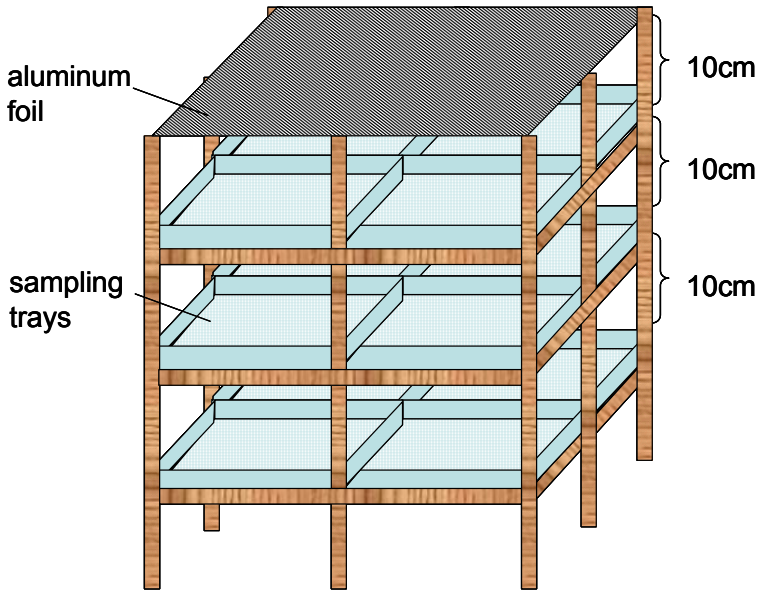


FIGURE S1. Schematic of the glass-bead sampling device.

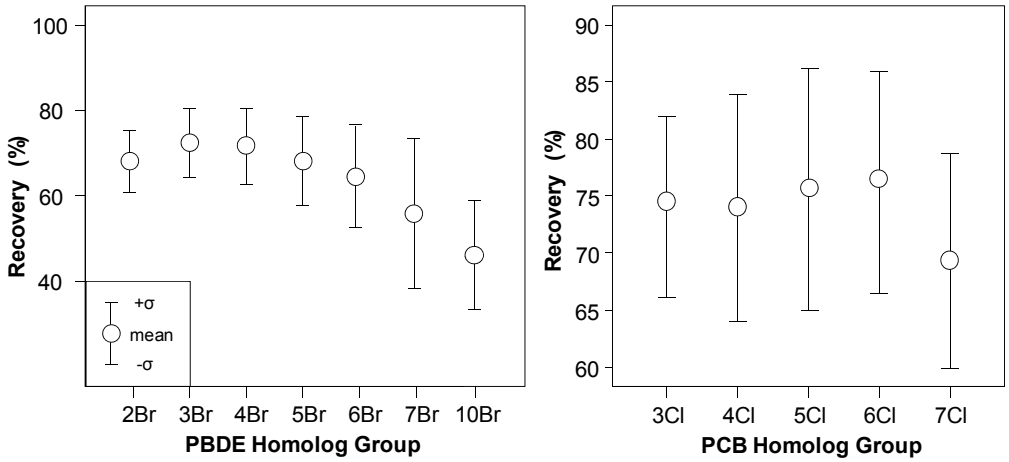


FIGURE S2. Recoveries of PBDEs and PCBs calculated from recovery standards in each homolog group

TABLE S3. Instrument Detection Limit (IDL) and Method Detection Limit (MDL) for PBDEs and PCBs

	PBDE			PCB				
	IDL	MDL		IDL	MDL		IDL	MDL
	pg	$ng \cdot m^{-3}$		pg	$ng \cdot m^{-3}$		pg	$ng \cdot m^{-3}$
17	0.18	0.0001	**19**	1.7	0.0009	**105**	3.4	0.002
28	0.84	0.0005	**18**	1.7	0.0009	**151**	3.5	0.002
49	0.34	0.0002	**17**	1.7	0.0009	**147**	3.6	0.002
71	0.24	0.0001	**34**	1.6	0.0009	**149**	3.6	0.002
47	0.16	0.0001	**29**	1.6	0.0008	**131**	4.6	0.003
66	0.27	0.0001	**31**	1.4	0.0007	**153**	1.7	0.001
77	1.6	0.0009	**28**	1.7	0.0009	**132**	2.3	0.001
100	0.40	0.0002	**33**	1.6	0.0009	**138**	1.8	0.001
119/120	0.63	0.0003	**52**	2.3	0.001	**158**	1.5	0.0008
99	0.66	0.0004	**49**	2.1	0.001	**129**	2.2	0.001
85	1.1	0.0006	**62**	1.7	0.0009	**128**	1.8	0.001
126	0.77	0.0004	**44**	2.3	0.001	**156**	1.8	0.001
154	1.07	0.0006	**74**	1.7	0.0009	**169**	1.9	0.001
153	2.3	0.001	**70**	7.2	0.004	**187**	3.8	0.002
138	3.1	0.002	**95**	2.1	0.001	**183**	3.5	0.002
156	6.6	0.004	**90/101**	2.1	0.001	**177**	2.1	0.001
184	4.9	0.003	**99/113**	2.1	0.001	**171**	1.8	0.001
183	3.1	0.002	**119**	1.8	0.001	**173**	2.4	0.001
191	4.0	0.002	**87**	2.4	0.001	**180**	2.1	0.001
196	16	0.009	**110**	1.8	0.001	**191**	1.7	0.0009
197	22	0.01	**118**	1.9	0.001	**170**	3.6	0.002
206	39	0.004						
207	30	0.003						
209	120	0.01						

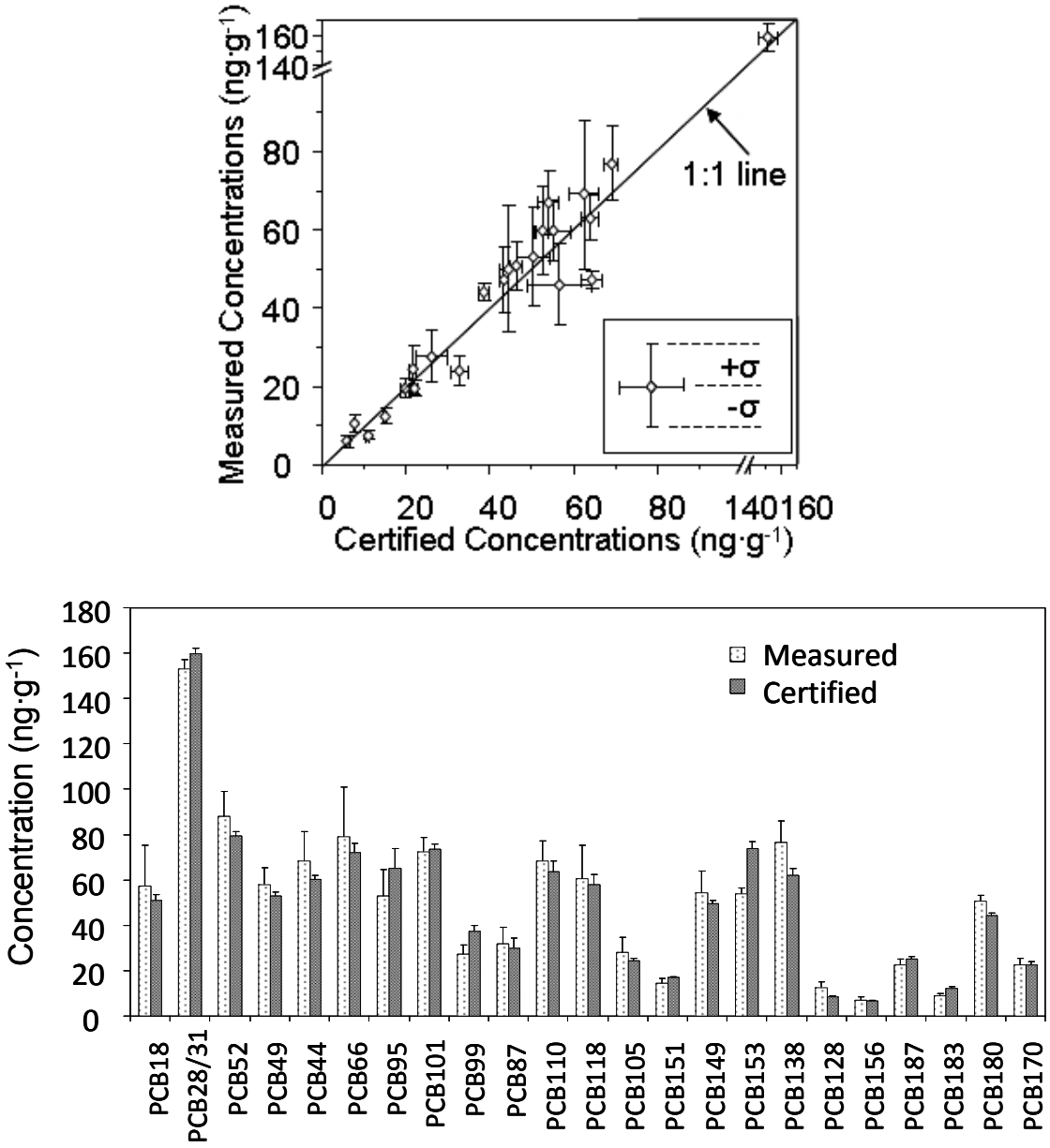


FIGURE S3. Measured and certified values of PCBs in SRM

TABLE S4. Descriptive Statistics for PBDE Air Concentrations (ng·m^{-3}) in the 20 Indoor Locations

Sample I.D.	PBDE Congeners										
	7	**15**	**17**	**28**	**47**	**49**	**66**	**77**	**85**	**99**	**100**
CAN01	<MDL	1.3E-03	2.2E-04	7.0E-04	1.5E-03	<MDL	<MDL	<MDL	<MDL	1.0E-03	<MDL
CAN02	5.8E-04	5.0E-03	3.7E-03	8.7E-03	4.2E-02	1.6E-03	4.4E-04	<MDL	<MDL	1.4E-02	3.8E-03
CAN03	1.9E-04	2.5E-04	2.7E-04	<MDL	4.5E-03	2.4E-04	1.4E-04	<MDL	<MDL	3.0E-03	7.1E-04
CAN04	<MDL	6.7E-03	2.4E-03	6.0E-03	5.7E-02	1.6E-03	5.6E-04	<MDL	<MDL	1.4E-02	4.3E-03
CAN05	7.7E-04	1.1E-03	2.3E-03	5.0E-03	2.5E-02	9.3E-04	3.2E-04	<MDL	<MDL	5.3E-03	1.0E-03
CAN06	1.7E-03	1.5E-02	1.5E-02	3.5E-02	2.8E-01	7.1E-03	3.0E-03	<MDL	1.8E-03	7.2E-02	2.0E-02
CAN07	<MDL	8.3E-04	1.3E-03	2.8E-03	1.3E-02	5.2E-04	1.6E-04	<MDL	<MDL	1.6E-03	<MDL
CAN08	6.5E-04	5.8E-03	1.2E-03	5.2E-03	1.9E-02	1.6E-03	8.8E-04	<MDL	<MDL	7.8E-03	1.2E-03
CAN09	<MDL	1.3E-03	2.0E-04	5.6E-04	1.8E-03	<MDL	<MDL	<MDL	<MDL	1.9E-03	<MDL
CAN10	2.2E-03	2.9E-03	3.3E-03	4.5E-03	1.3E-02	2.9E-03	2.7E-03	2.5E-03	3.6E-03	8.6E-03	5.1E-03
CAN11	<MDL	3.9E-04	8.2E-04	1.5E-03	6.7E-02	1.9E-03	6.5E-04	<MDL	<MDL	4.8E-02	1.8E-02
CAN12	1.6E-02	5.8E-02	1.2E-01	2.7E-01	5.1E+00	1.9E-01	4.0E-02	7.2E-02	2.8E-01	7.5E+00	1.5E+00
CAN13	<MDL	2.2E-03	1.4E-03	3.7E-03	1.8E-02	7.1E-04	1.5E-04	<MDL	1.2E-03	3.3E-03	9.5E-04
CAN14	<MDL	1.3E-03	2.6E-04	8.5E-04	3.0E-03	2.3E-04	1.4E-04	<MDL	<MDL	4.1E-03	5.4E-04
CAN15	2.6E-04	2.4E-03	5.8E-04	1.5E-03	4.8E-03	<MDL	<MDL	<MDL	<MDL	5.1E-03	1.1E-03
CAN16	4.3E-04	5.1E-03	1.0E-02	2.4E-02	1.4E-01	5.5E-03	2.0E-03	<MDL	2.0E-03	1.9E-02	8.0E-03
CAN17	<MDL	7.7E-04	9.3E-04	2.2E-03	1.4E-02	<MDL	<MDL	<MDL	<MDL	5.8E-03	<MDL
CAN18	4.1E-04	2.6E-03	4.7E-03	1.1E-02	8.2E-02	3.2E-03	1.4E-03	<MDL	1.2E-03	1.5E-02	5.2E-03
CAN19	<MDL	7.6E-03	1.2E-02	2.4E-02	2.4E-01	6.9E-03	3.0E-03	<MDL	1.0E-03	3.8E-02	1.4E-02
CAN20	<MDL	5.0E-03	4.9E-03	1.3E-02	8.3E-02	2.7E-03	9.4E-04	<MDL	<MDL	1.1E-02	4.0E-03
Mean	2.3E-03	6.3E-03	9.1E-03	2.2E-02	3.1E-01	1.4E-02	3.5E-03	3.7E-02	4.2E-02	3.9E-01	9.7E-02
Std. Deviation	4.8E-03	1.3E-02	2.6E-02	6.1E-02	1.1E+00	4.6E-02	9.7E-03	n.c.	1.1E-01	1.7E+00	3.7E-01
Geometric Mean	8.3E-04	2.6E-03	2.0E-03	5.4E-03	2.9E-02	2.1E-03	8.3E-04	1.3E-02	3.4E-03	1.1E-02	4.7E-03
Minimum	<MDL	2.5E-04	2.0E-04	<MDL	1.5E-03	<MDL	<MDL	<MDL	<MDL	1.0E-03	<MDL
25%ile	<MDL	1.2E-03	7.6E-04	1.9E-03	1.1E-02	8.7E-04	2.8E-04	<MDL	<MDL	3.9E-03	1.1E-03
Median	<MDL	2.5E-03	1.9E-03	5.0E-03	2.2E-02	1.8E-03	7.6E-04	<MDL	<MDL	8.2E-03	4.1E-03
75%ile	1.0E-03	5.0E-03	4.0E-03	9.9E-03	7.2E-02	3.1E-03	1.7E-03	<MDL	2.3E-03	1.4E-02	6.6E-03
Maximum	1.6E-02	5.8E-02	1.2E-01	2.7E-01	5.1E+00	1.9E-01	4.0E-02	7.2E-02	2.8E-01	7.5E+00	1.5E+00

<MDL: less than method detection limit; n.c.: standard deviation not calculated if <MDL for >15 of the 20 locations

TABLE S4. Descriptive Statistics for PBDE Air Concentrations (ng·m^{-3}) in the 20 Indoor Locations (Continued)

Sample I.D.	PBDE Congeners								
	119/120	126	138	153	154	183	184	191	ΣBDE
CAN01	<MDL	<MDL	<MDL	1.5E-03	5.8E-04	1.5E-03	<MDL	<MDL	8.3E-03
CAN02	<MDL	<MDL	<MDL	2.0E-03	8.2E-04	2.5E-03	<MDL	<MDL	8.5E-02
CAN03	<MDL	<MDL	<MDL	5.1E-03	1.5E-03	5.6E-03	<MDL	<MDL	2.2E-02
CAN04	1.0E-03	<MDL	<MDL	6.5E-03	2.3E-03	6.2E-03	<MDL	<MDL	1.1E-01
CAN05	<MDL	<MDL	<MDL	3.2E-03	1.0E-03	3.5E-03	<MDL	<MDL	5.0E-02
CAN06	<MDL	<MDL	<MDL	5.1E-03	3.5E-03	2.0E-03	<MDL	<MDL	4.6E-01
CAN07	<MDL	<MDL	<MDL	1.6E-03	4.5E-04	2.8E-03	<MDL	<MDL	2.5E-02
CAN08	3.8E-04	1.2E-02	<MDL	2.0E-03	6.0E-04	8.5E-04	<MDL	<MDL	5.8E-02
CAN09	<MDL	3.8E-03	<MDL	3.0E-03	9.9E-04	4.0E-03	<MDL	<MDL	1.8E-02
CAN10	<MDL	<MDL	6.6E-03	1.2E-02	8.6E-03	1.3E-02	6.7E-03	7.0E-03	1.0E-01
CAN11	7.8E-04	<MDL	<MDL	1.1E-02	3.5E-03	1.1E-02	<MDL	<MDL	1.6E-01
CAN12	1.3E-02	<MDL	5.6E-02	6.7E-01	6.2E-01	2.1E-02	4.2E-03	<MDL	1.6E+01
CAN13	<MDL	1.6E-02	<MDL	3.3E-03	1.0E-03	2.8E-03	<MDL	<MDL	5.6E-02
CAN14	<MDL	1.0E-02	<MDL	3.6E-03	1.2E-03	3.7E-03	<MDL	<MDL	2.9E-02
CAN15	<MDL	<MDL	<MDL	4.6E-03	1.4E-03	4.6E-03	<MDL	<MDL	2.6E-02
CAN16	<MDL	3.2E-02	<MDL	1.2E-03	7.3E-04	1.9E-03	<MDL	<MDL	2.5E-01
CAN17	<MDL	<MDL	<MDL	3.7E-03	1.3E-03	4.6E-03	<MDL	<MDL	3.3E-02
CAN18	<MDL	5.8E-04	<MDL	7.0E-03	2.5E-03	7.4E-03	<MDL	<MDL	1.4E-01
CAN19	<MDL	<MDL	<MDL	2.1E-03	1.2E-03	2.3E-03	<MDL	<MDL	3.5E-01
CAN20	<MDL	2.5E-02	<MDL	2.7E-03	9.9E-04	8.5E-04	<MDL	<MDL	1.5E-01
Mean	3.8E-03	1.4E-02	3.1E-02	3.8E-02	3.3E-02	5.1E-03	5.4E-03	7.0E-03	9.3E-01
Std. Deviation	n.c.	1.1E-02	n.c.	1.5E-01	1.4E-01	4.9E-03	n.c.	n.c.	3.7E+00
Geometric Mean	1.4E-03	8.6E-03	1.9E-02	4.5E-03	1.8E-03	3.6E-03	5.3E-03	7.0E-03	8.8E-02
Minimum	<MDL	<MDL	<MDL	1.2E-03	4.5E-04	8.5E-04	<MDL	<MDL	8.3E-03
25%ile	<MDL	<MDL	<MDL	2.1E-03	9.5E-04	2.2E-03	<MDL	<MDL	2.8E-02
Median	<MDL	<MDL	<MDL	3.4E-03	1.2E-03	3.6E-03	<MDL	<MDL	7.1E-02
75%ile	<MDL	1.8E-02	<MDL	5.1E-03	1.7E-03	4.9E-03	<MDL	<MDL	1.5E-01
Maximum	1.3E-02	3.2E-02	5.6E-02	6.7E-01	6.2E-01	2.1E-02	6.7E-03	7.0E-03	1.6E+01

TABLE S5. Descriptive Statistics for PCB Air Concentrations ($ng \cdot m^{-3}$) in the 20 Indoor Locations

Sample I.D.	PCB Congeners									
	18/17	**27**	**32/16**	**26/25**	**31/28**	**33**	**22**	**53**	**51**	**45**
CAN01	0.161	0.008	0.051	0.021	0.154	0.056	0.037	0.010	0.004	0.010
CAN02	3.522	0.283	1.407	0.526	2.509	0.961	0.605	0.160	0.058	0.194
CAN03	1.178	0.102	0.456	0.157	0.714	0.263	0.176	0.064	0.016	0.054
CAN04	0.256	0.156	0.098	0.035	0.236	0.094	0.079	0.018	0.012	0.021
CAN05	0.315	0.054	0.076	0.047	0.129	0.123	0.038	0.028	0.006	0.021
CAN06	0.154	0.016	0.048	0.033	0.108	0.065	0.021	0.009	0.004	0.032
CAN07	1.412	0.127	0.634	0.262	1.328	0.504	0.343	0.092	0.027	0.106
CAN08	0.726	0.245	0.270	0.140	0.637	0.384	0.218	0.049	0.017	0.081
CAN09	1.893	0.177	0.794	0.281	2.163	0.703	0.492	0.141	0.048	0.136
CAN10	0.589	0.135	0.268	0.085	0.357	0.311	0.144	0.038	0.007	0.039
CAN11	0.092	0.009	0.043	0.014	0.088	0.029	0.019	0.006	0.003	0.007
CAN12	5.099	0.407	2.378	1.074	5.018	1.927	1.293	0.634	0.126	0.400
CAN13	1.037	0.053	0.461	0.192	1.589	0.471	0.338	0.104	0.035	0.099
CAN14	2.007	0.188	0.842	0.330	2.294	0.745	0.522	0.150	0.051	0.145
CAN15	0.393	0.046	0.127	0.055	0.307	0.128	0.089	0.022	0.091	0.022
CAN16	1.329	0.053	0.335	0.106	0.567	0.241	0.164	0.054	0.021	0.077
CAN17	1.226	0.093	0.582	0.254	1.290	0.516	0.360	0.068	0.023	0.100
CAN18	4.863	0.345	2.098	0.765	3.937	1.462	1.006	0.250	0.079	0.249
CAN19	0.563	0.046	0.279	0.140	0.843	0.305	0.197	0.107	0.018	0.091
CAN20	0.563	0.161	0.208	0.102	0.520	0.168	0.144	0.043	0.015	0.069
Mean	1.369	0.135	0.573	0.231	1.239	0.473	0.314	0.102	0.033	0.098
Std.Dev.	1.483	0.113	0.665	0.272	1.352	0.494	0.337	0.140	0.033	0.095
Geomean	0.791	0.086	0.306	0.127	0.673	0.282	0.177	0.055	0.020	0.062
Minimum	0.092	0.008	0.043	0.014	0.088	0.029	0.019	0.006	0.003	0.007
25%ile	0.374	0.051	0.120	0.053	0.289	0.126	0.086	0.027	0.010	0.030
Median	0.881	0.115	0.307	0.140	0.676	0.308	0.187	0.059	0.019	0.079
75%ile	1.354	0.166	0.598	0.256	1.406	0.507	0.348	0.105	0.039	0.102
Maximum	5.099	0.407	2.378	1.074	5.018	1.927	1.293	0.634	0.126	0.400

TABLE S5. Descriptive Statistics for PCB Air Concentrations ($ng \cdot m^{-3}$) in the 20 Indoor Locations (continued)

Sample I.D.	PCB Congeners									
	52	**49**	**47**	**44**	**42**	**71/41/64**	**74**	**70/76**	**66**	**56/60**
CAN01	0.101	0.036	0.025	0.051	0.008	0.014	0.020	0.015	0.035	0.042
CAN02	0.887	0.430	0.305	0.528	0.116	0.165	0.226	0.136	0.327	0.285
CAN03	0.929	0.245	0.104	0.420	0.048	0.060	0.114	0.088	0.367	0.178
CAN04	0.142	0.045	0.050	0.063	0.011	0.060	0.049	0.018	0.108	0.047
CAN05	0.449	0.028	0.022	0.081	0.038	0.065	0.021	0.006	0.015	0.023
CAN06	0.100	0.024	0.015	0.038	0.006	0.010	0.026	0.008	0.043	0.036
CAN07	1.381	0.401	0.196	0.686	0.086	0.104	0.202	0.177	0.675	0.351
CAN08	0.769	0.146	0.086	0.256	0.068	0.142	0.095	0.074	0.200	0.166
CAN09	1.159	0.516	0.340	0.678	0.150	0.163	0.282	0.238	0.634	0.516
CAN10	0.694	0.059	0.039	0.165	0.051	0.061	0.161	0.021	0.041	0.066
CAN11	0.058	0.019	0.012	0.029	0.005	0.018	0.017	0.008	0.028	0.033
CAN12	21.260	4.447	1.171	8.580	0.625	0.766	2.144	2.082	10.270	3.649
CAN13	1.020	0.462	0.293	0.650	0.129	0.142	0.259	0.226	0.628	0.487
CAN14	1.229	0.548	0.360	0.719	0.159	0.173	0.299	0.252	0.672	0.547
CAN15	0.243	0.056	0.299	0.081	0.013	0.065	0.021	0.015	0.050	0.057
CAN16	1.073	0.251	0.093	0.386	0.033	0.065	0.104	0.077	0.321	0.139
CAN17	0.568	0.241	0.153	0.354	0.078	0.083	0.141	0.109	0.352	0.241
CAN18	1.861	0.768	0.470	1.081	0.223	0.248	0.424	0.317	0.982	0.699
CAN19	3.344	0.725	0.217	1.390	0.109	0.132	0.347	0.373	1.787	0.728
CAN20	0.336	0.131	0.099	0.171	0.031	0.116	0.102	0.051	0.135	0.122
Mean	1.880	0.479	0.218	0.820	0.099	0.133	0.253	0.215	0.884	0.421
Std.Dev.	4.625	0.964	0.263	1.864	0.138	0.161	0.461	0.454	2.251	0.794
Geomean	0.656	0.179	0.116	0.287	0.049	0.085	0.115	0.069	0.230	0.174
Minimum	0.058	0.019	0.012	0.029	0.005	0.010	0.017	0.006	0.015	0.023
25%ile	0.313	0.053	0.047	0.081	0.026	0.061	0.043	0.018	0.048	0.055
Median	0.828	0.243	0.129	0.370	0.059	0.094	0.128	0.083	0.324	0.172
75%ile	1.099	0.440	0.295	0.658	0.111	0.142	0.236	0.192	0.630	0.392
Maximum	21.260	4.447	1.171	8.580	0.625	0.766	2.144	2.082	10.270	3.649

TABLE S5. Descriptive Statistics for PCB Air Concentrations (ng·m^{-3}) in the 20 Indoor Locations (continued)

Sample I.D.	PCB Congeners									
	95	**91**	**84**	**90/101**	**99/113**	**83**	**97**	**87**	**111**	**110**
CAN01	0.030	0.005	0.004	0.026	0.011	0.004	0.010	0.003	0.024	0.020
CAN02	0.169	0.026	0.020	0.129	0.042	0.006	0.027	0.039	0.042	0.068
CAN03	0.814	0.064	0.081	0.642	0.125	0.014	0.095	0.181	0.045	0.340
CAN04	0.054	0.007	0.007	0.047	0.018	0.005	0.009	0.015	0.026	0.026
CAN05	0.027	0.003	0.004	0.019	0.009	0.004	0.005	0.005	0.009	0.014
CAN06	0.035	0.004	0.004	0.027	0.007	0.010	0.009	0.009	0.003	0.015
CAN07	0.957	0.099	0.125	0.874	0.221	0.023	0.147	0.269	0.063	0.459
CAN08	0.215	0.024	0.032	0.189	0.059	0.004	0.038	0.069	0.021	0.127
CAN09	0.312	0.043	0.045	0.312	0.100	0.009	0.068	0.108	0.038	0.188
CAN10	0.069	0.008	0.006	0.043	0.013	<MDL	0.017	0.018	0.009	0.036
CAN11	0.044	0.005	0.005	0.035	0.007	0.003	0.008	0.011	0.002	0.020
CAN12	12.645	1.326	1.658	10.839	2.850	0.377	1.983	3.658	0.877	6.210
CAN13	0.301	0.042	0.041	0.296	0.097	0.010	0.061	0.099	0.036	0.170
CAN14	0.331	0.045	0.047	0.331	0.106	0.010	0.073	0.115	0.041	0.199
CAN15	0.050	0.006	0.006	0.038	0.011	0.003	0.009	0.010	0.007	0.020
CAN16	0.387	0.041	0.043	0.296	0.080	0.015	0.050	0.082	0.025	0.126
CAN17	0.364	0.036	0.057	0.441	0.101	0.013	0.079	0.163	0.038	0.335
CAN18	1.192	0.080	0.123	1.077	0.176	0.020	0.129	0.249	0.061	0.479
CAN19	3.261	0.275	0.397	3.080	0.656	0.075	0.469	0.911	0.220	1.730
CAN20	0.112	0.012	0.013	0.096	0.025	0.009	0.019	0.030	0.008	0.052
Mean	1.068	0.107	0.136	0.942	0.236	0.032	0.165	0.302	0.080	0.532
Std.Dev.	2.823	0.293	0.369	2.430	0.632	0.085	0.440	0.815	0.193	1.390
Geomean	0.229	0.026	0.029	0.196	0.055	0.011	0.041	0.059	0.027	0.115
Minimum	0.027	0.003	0.004	0.019	0.007	<MDL	0.005	0.003	0.002	0.014
25%ile	0.053	0.007	0.006	0.042	0.012	0.005	0.010	0.014	0.009	0.024
Median	0.258	0.031	0.037	0.242	0.069	0.010	0.044	0.075	0.031	0.126
75%ile	0.371	0.044	0.050	0.364	0.102	0.013	0.075	0.129	0.041	0.240
Maximum	12.645	1.326	1.658	10.839	2.850	0.377	1.983	3.658	0.877	6.210

TABLE S5. Descriptive Statistics for PCB Air Concentrations ($ng \cdot m^{-3}$) in the 20 Indoor Locations (continued)

Sample I.D.	PCB Congeners									
	82	**118**	**105**	**136**	**151**	**135/148**	**149**	**134/143**	**146**	**153**
CAN01	<MDL	0.023	0.003	0.004	0.004	0.002	0.008	<MDL	0.002	0.005
CAN02	0.004	0.029	0.010	0.012	0.013	0.008	0.029	0.003	0.007	0.015
CAN03	0.018	0.168	0.046	0.158	0.189	0.086	0.396	0.017	0.029	0.172
CAN04	0.002	0.028	0.004	0.014	0.024	0.009	0.043	0.002	0.002	0.018
CAN05	0.007	0.039	0.004	0.003	0.003	0.002	0.008	<MDL	0.002	0.003
CAN06	0.003	0.010	0.002	0.006	0.005	0.002	0.011	0.002	0.003	0.004
CAN07	0.026	0.203	0.049	0.130	0.158	0.082	0.370	0.020	0.022	0.159
CAN08	0.007	0.073	0.021	0.022	0.026	0.017	0.069	0.005	0.010	0.037
CAN09	0.012	0.110	0.034	0.026	0.028	0.019	0.080	0.005	0.010	0.047
CAN10	0.009	0.017	0.010	0.007	0.008	0.002	0.015	0.002	<MDL	0.008
CAN11	0.002	0.013	0.003	0.008	0.008	0.005	0.019	0.003	0.003	0.008
CAN12	0.321	2.951	0.802	1.215	0.840	0.697	2.775	0.224	0.260	1.220
CAN13	0.013	0.095	0.030	0.024	0.026	0.015	0.068	0.004	0.007	0.039
CAN14	0.013	0.116	0.036	0.027	0.029	0.019	0.085	0.006	0.009	0.049
CAN15	0.003	0.010	0.003	0.006	0.005	0.005	0.012	<MDL	<MDL	0.006
CAN16	0.006	0.050	0.011	0.024	0.024	0.014	0.056	0.005	0.004	0.019
CAN17	0.018	0.248	0.073	0.075	0.101	0.060	0.281	0.016	0.022	0.154
CAN18	0.031	0.238	0.068	0.260	0.339	0.151	0.683	0.026	0.054	0.342
CAN19	0.097	0.875	0.263	0.561	0.684	0.350	1.618	0.075	0.151	0.921
CAN20	0.005	0.030	0.009	0.015	0.019	0.009	0.042	0.004	0.005	0.023
Mean	0.031	0.266	0.074	0.130	0.127	0.078	0.333	0.025	0.033	0.162
Std.Dev.	0.073	0.661	0.181	0.288	0.234	0.167	0.687	0.054	0.067	0.326
Geomean	0.010	0.071	0.018	0.029	0.032	0.017	0.075	0.008	0.010	0.036
Minimum	<MDL	0.010	0.002	0.003	0.003	0.002	0.008	<MDL	<MDL	0.003
25%ile	0.005	0.026	0.004	0.008	0.008	0.005	0.018	0.003	0.003	0.008
Median	0.009	0.062	0.016	0.023	0.025	0.014	0.062	0.005	0.008	0.030
75%ile	0.016	0.132	0.039	0.041	0.051	0.031	0.144	0.016	0.021	0.081
Maximum	0.321	2.951	0.802	1.215	0.840	0.697	2.775	0.224	0.260	1.220

TABLE S5. Descriptive Statistics for PCB Air Concentrations (ng·m^{-3}) in the 20 Indoor Locations (continued)

Sample I.D.	PCB Congeners									
	132	**141**	**138/164/163**	**128/162**	**179**	**176**	**178**	**187**	**183**	**185**
CAN01	0.002	0.003	0.004	<MDL	0.003	<MDL	<MDL	0.002	<MDL	<MDL
CAN02	0.009	0.007	0.011	<MDL	0.004	<MDL	<MDL	0.004	<MDL	<MDL
CAN03	0.098	0.058	0.140	0.016	0.058	0.014	0.007	0.056	0.015	0.006
CAN04	0.007	0.008	0.013	<MDL	0.016	0.003	0.001	0.012	0.002	0.002
CAN05	0.002	0.005	0.004	<MDL	0.003	<MDL	<MDL	0.001	<MDL	<MDL
CAN06	0.004	0.004	0.006	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
CAN07	0.105	0.063	0.162	0.016	0.054	0.015	0.007	0.067	0.020	0.008
CAN08	0.022	0.013	0.035	0.006	0.011	0.002	0.002	0.016	0.005	0.001
CAN09	0.027	0.015	0.042	0.008	0.010	0.002	<MDL	0.008	0.003	0.001
CAN10	0.008	0.007	0.009	<MDL	0.004	<MDL	<MDL	0.003	<MDL	<MDL
CAN11	0.005	0.007	0.010	<MDL	0.006	<MDL	<MDL	0.003	<MDL	<MDL
CAN12	1.088	0.338	1.305	0.210	0.109	0.035	0.015	0.104	0.042	0.008
CAN13	0.022	0.013	0.033	0.006	0.006	0.002	0.001	0.008	0.003	0.001
CAN14	0.028	0.015	0.046	0.007	0.011	0.002	0.002	0.009	0.004	0.001
CAN15	0.004	0.009	0.008	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
CAN16	0.020	0.010	0.024	<MDL	0.005	0.001	<MDL	0.005	0.001	<MDL
CAN17	0.109	0.055	0.210	0.037	0.034	0.009	0.004	0.046	0.012	0.004
CAN18	0.160	0.100	0.233	0.021	0.083	0.023	0.013	0.092	0.031	0.007
CAN19	0.479	0.264	0.748	0.089	0.176	0.052	0.034	0.258	0.092	0.022
CAN20	0.011	0.012	0.021	<MDL	0.005	<MDL	<MDL	0.008	0.003	<MDL
Mean	0.110	0.050	0.153	0.042	0.033	0.013	0.009	0.039	0.018	0.006
Std.Dev.	0.254	0.090	0.320	0.064	0.047	0.016	0.010	0.064	0.025	0.006
Geomean	0.023	0.018	0.036	0.019	0.014	0.006	0.005	0.013	0.008	0.003
Minimum	0.002	0.003	0.004	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25%ile	0.007	0.007	0.010	<MDL	0.005	<MDL	<MDL	0.004	<MDL	<MDL
Median	0.021	0.012	0.029	<MDL	0.011	0.006	<MDL	0.009	0.005	0.004
75%ile	0.049	0.027	0.074	0.026	0.032	0.014	0.009	0.043	0.017	0.007
Maximum	1.088	0.338	1.305	0.210	0.176	0.052	0.034	0.258	0.092	0.022

TABLE S5. Descriptive Statistics for PCB Air Concentrations ($ng \cdot m^{-3}$) in the 20 Indoor Locations (continued)

Sample I.D.	PCB Congeners						
	174	**177**	**171**	**172**	**180**	**170/190**	**∑PCB**
CAN01	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1.063
CAN02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	14.366
CAN03	0.033	0.018	0.008	0.003	0.029	0.010	9.984
CAN04	0.007	0.004	0.001	<MDL	0.007	<MDL	2.042
CAN05	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1.769
CAN06	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.979
CAN07	0.047	0.025	0.009	0.003	0.050	0.022	14.227
CAN08	0.007	0.003	<MDL	0.001	0.007	0.003	5.968
CAN09	0.005	0.002	0.001	0.001	0.004	0.002	13.229
CAN10	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	3.661
CAN11	0.002	<MDL	<MDL	<MDL	0.002	<MDL	0.786
CAN12	0.068	0.039	0.020	0.006	0.052	0.027	130.547
CAN13	0.004	0.002	<MDL	<MDL	0.004	0.001	10.256
CAN14	0.005	0.003	0.001	0.001	0.005	0.002	14.061
CAN15	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.411
CAN16	0.003	0.002	0.006	<MDL	0.003	0.002	6.929
CAN17	0.024	0.013	0.006	0.002	0.026	0.011	10.111
CAN18	0.044	0.024	0.009	0.003	0.032	0.011	28.790
CAN19	0.132	0.073	0.029	0.011	0.120	0.044	31.034
CAN20	0.004	0.002	<MDL	0.001	0.004	0.002	3.896
Mean	0.028	0.016	0.009	0.003	0.025	0.011	15.305
Std.Dev.	0.037	0.021	0.009	0.003	0.033	0.013	28.438
Geomean	0.012	0.007	0.006	0.003	0.011	0.006	6.520
Minimum	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.786
25%ile	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.319
Median	0.007	0.004	<MDL	<MDL	0.007	0.006	8.456
75%ile	0.034	0.020	0.009	0.003	0.029	0.011	14.103
Maximum	0.132	0.073	0.029	0.011	0.120	0.044	130.547

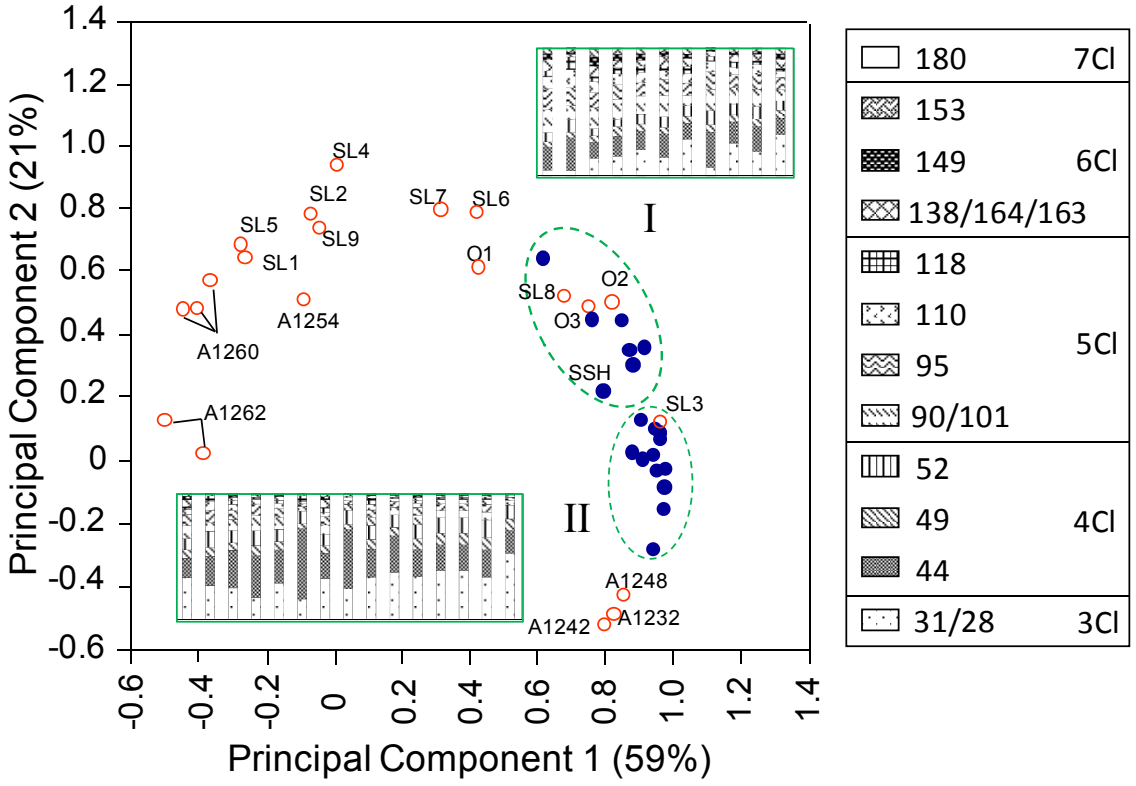


FIGURE S4. Plot of PCA scores of component 1 versus component 2 for PCBs of the indoor air samples analyzed in this study, outdoor air (O) (*5*), sealant (SL) (*6*) and Aroclor commercial PCB formulation (*7*). The PCB concentration profiles of the indoor air are separated into two clusters. Cluster I included CAN19, 03, 17, 12, 11, 07 and SSH. Cluster II included CAN18, 08, 16, 06, 05, 04, 10, 01, 15, 20, 09, 14, 13 and 02. The geomeans of the total 12 PCBs for Cluster I and II were 6.6 and 2.0 ng/m^3.

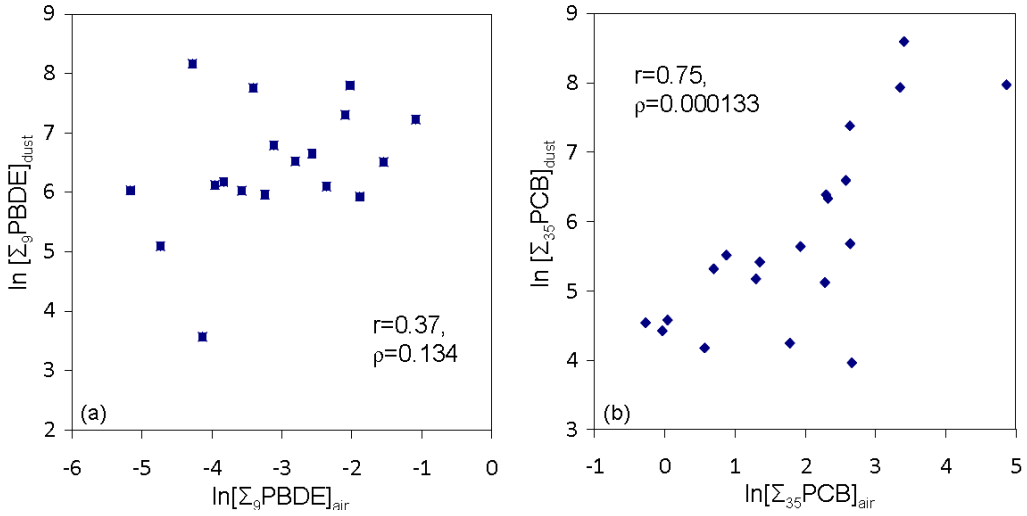


FIGURE S5. Correlations between log-transformed air concentrations (ng·m^{-3}) and dust concentrations (ng·g^{-1}) for ∑PBDEs (all congeners reported in this study except BDE-183, for which concentrations in dust were not available) and ∑PCBs.

TABLE S8. Correlations of ln [BDE]$_{air}$ and ln [BDE]$_{dust}$

PBDE Congeners	N	Pearson Correlation Coefficient	Sig. (2-tailed)
BDE-17	20	0.682 **	9.30×10^{-4}
BDE-28	20	0.797 **	2.60×10^{-5}
BDE-49	20	0.717 **	3.78×10^{-4}
BDE-47	20	0.708 **	4.79×10^{-4}
BDE-66	20	0.713 **	4.18×10^{-4}
BDE-100	20	0.648 **	2.00×10^{-3}
BDE-99	20	0.547 *	0.0126
BDE-154	20	0.668 **	1.29×10^{-3}
BDE-153	20	0.669 **	1.26×10^{-3}

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

TABLE S9. Correlations of ln $[PCB]_{air}$ and ln $[PCB]_{dust}$

PCB Congener	N	Pearson Correlation Coefficient	Sig. (2-tailed)
31/28	19	0.546 *	0.0157
44	20	0.733**	2.39×10^{-4}
49	19	0.738**	3.06×10^{-4}
52	20	0.741**	1.86×10^{-4}
90/101	20	0.853**	1.76×10^{-6}
95	20	0.857**	1.40×10^{-6}
110	20	0.851**	2.03×10^{-6}
118	20	0.794**	2.96×10^{-5}
138/164/163	20	0.823**	8.17×10^{-6}
149	20	0.797**	2.58×10^{-5}
153	20	0.828**	6.65×10^{-6}
180	14	0.651 *	0.0116

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

PBDEs and PCBs in Indoor Environmental Phases

PBDEs and PCBs concentrations in the bulk air (gas- and particle-phases), which were acquired through active sampling, were 0.95 and 7.84 $ng \cdot m^{-3}$. Gas-phase concentrations calculated from passive sampling data were ~3 times lower than from the active sampling which is likely due to uncertainty of passive sampling uptake rates used for calculation. The passive sampling rate can be greatly affected by the environmental characteristics of the indoor environment (*8*). The literature-reported uptake rates of similar types of passive samplers can vary by ~3 times (*9, 10*). Further discussion of the air concentrations refers to the data generated from active sampling.

Surface film sampled with glass beads had PBDE and PCB concentrations ~10 times higher than the window wipe samples. Reasons for this discrepancy are (a) greater particle deposition onto the horizontal glass bead trays versus the vertical windows, and

(b) lower sampling efficiency of wiping the window surface and Soxhlet extraction of the Kimwipes compared to Soxhlet extraction of glass beads. The PBDE concentrations (24.5 and 12.0 $ng \cdot m^{-2}$) in film measured with window wipes were comparable with the average value of 6.8 $ng \cdot m^{-2}$ reported by Butt et al. (2004) for interior urban films (*11*).

Comparing the chemical profiles of these indoor phases (Figure S6), two patterns were noted. Samples from PUF disks (passive sampling) and PUF plugs (gas phase from active sampling) displayed similar profiles, which were abundant in the lighter congeners. Consistent with the PUF passive samplers picking up some particle-phase chemicals, these samples had slightly greater portions of heavier congeners than in PUF plugs (*12, 13*). The congener profiles of particles and surface films had higher portions of heavy congeners than air which would be the case if the surface film consisted mainly of with air-borne particles (*3*).

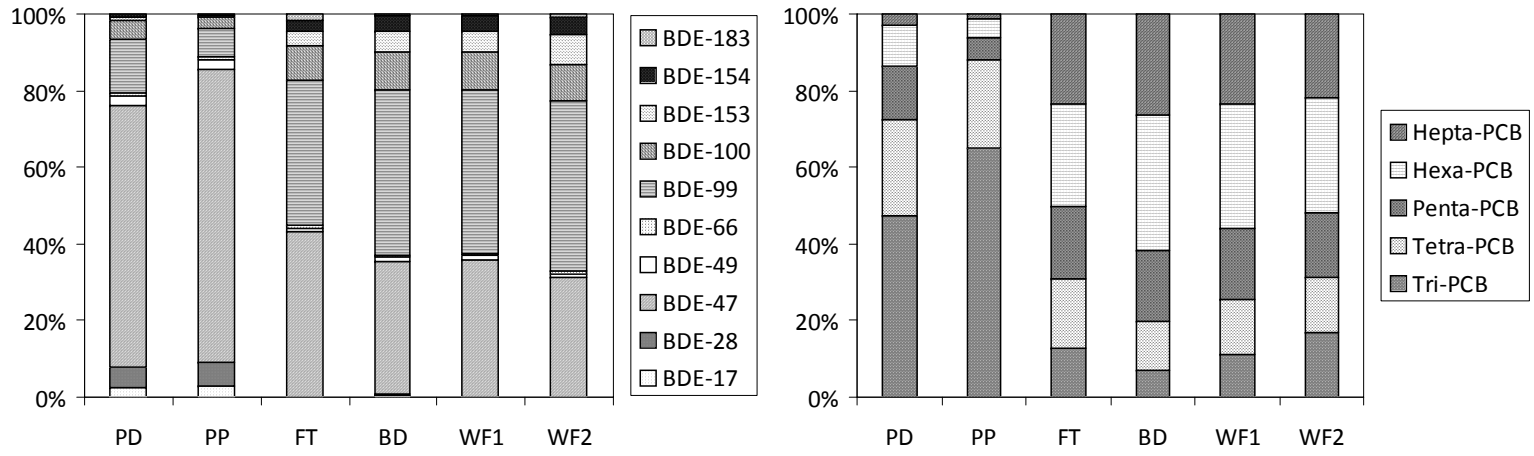


FIGURE S6. Congener profiles of BDE and homolog distributions of PCBs for multiple indoor environmental phases. PD: PUF disk; PP: PUF plug; FT: filter; BD: glass beads; WF1: window film sampled at the beginning of 1 month time period; WF2: window film sampled at the end.

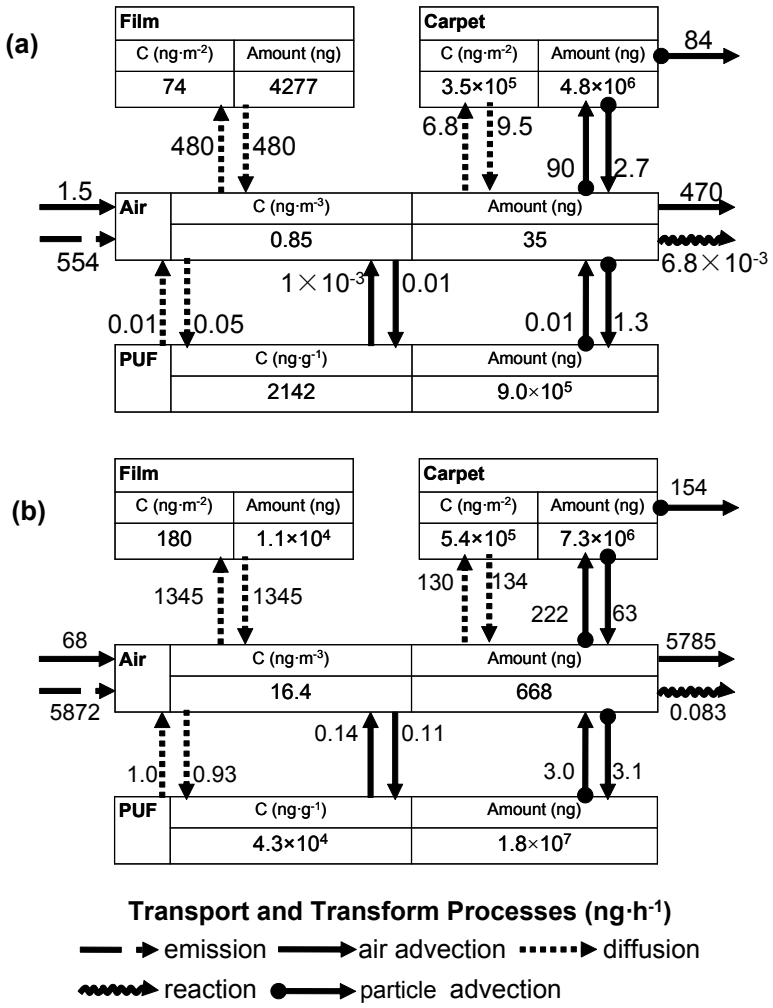


FIGURE S7. Modeling results of emission rates and fate of (a) PBDEs and (b) PCBs in the indoor environment. The emission rates were calculated using measured concentrations in air based on the mass balance of the air compartment. Higher bound emission rates illustrated here were estimated assuming a higher bound air exchange rate of 8.69 h^{-1} and for PBDE, lower-bound concentrations in PUF of 2×10^3 $ng\cdot g^{-1}$. Lower bound emission rates are presented in Figure 2.

TABLE S6. Concentrations of PBDEs in Multiple Indoor Phases

PBDE congener	PUF Disk (PD) $ng \cdot m^{-3}$	PUF Plugs (PP) $ng \cdot m^{-3}$	Filters (FT) $ng \cdot m^{-3}$	Beads (BD) $ng \cdot m^{-2}$	Window Film 1 (WF1) $ng \cdot m^{-2}$	Window Film 2 (WF2) $ng \cdot m^{-2}$
BDE-17	0.009	0.027	n.d.	0.98	n.d.	n.d.
BDE-28	0.018	0.055	n.d.	1.3	n.d.	n.d.
BDE-47	0.24	0.69	0.022	120.4	8.8	3.7
BDE-49	0.008	0.023	0.00062	3.5	0.27	0.11
BDE-66	0.003	0.009	0.00041	2.4	0.18	0.078
BDE-99	0.050	0.064	0.019	149.2	10.4	5.3
BDE-100	0.017	0.028	0.0046	33.7	2.4	1.2
BDE-153	0.003	0.004	0.0020	18.9	1.4	0.92
BDE-154	0.003	0.002	0.0014	14.2	0.99	0.58
BDE-183	n.d.	n.d.	0.00088	1.1	0.10	0.077
Σ_{10}BDE	**0.35**	**0.90**	**0.051**	**345.7**	**24.5**	**12.0**
BDE-206	n.d.	n.d.	n.d.	3.8	0.8	n.d.
BDE-207	n.d.	n.d.	n.d.	2.3	0.6	n.d.
BDE-209	n.d.	n.d.	n.d.	66.3	10.5	3.3

TABLE S7. Concentrations of PCBs in Multiple Indoor Phases

PCB homolog	PUF Disk (PD) $ng \cdot m^{-3}$	PUF Plugs (PP) $ng \cdot m^{-3}$	Filters (FT) $ng \cdot m^{-3}$	Beads (BD) $ng \cdot m^{-2}$	Window Film 1 (WF1) $ng \cdot m^{-2}$	Window Film 2 (WF2) $ng \cdot m^{-2}$
Tri-PCB	7.6	47	0.038	20	2.3	1.8
Tetra-PCB	4.0	17	0.053	34	3.0	1.6
Penta-PCB	2.3	4.2	0.056	50	3.8	1.8
Hexa-PCB	1.7	3.6	0.079	97	6.8	3.2
Hepta-PCB	0.48	0.79	0.070	71	4.9	2.4
ΣPCB	16	72	0.30	271	21	11

References

(1) World Health Organization., *Brominated Diphenyl Ethers*. International Program on Chemical Safety: WHO: Geneva, 1994.

(2) Spectrum Lab. Chemical Fact Sheet. *available online at http://www.speclab.com/compound/chemabc.htm (accessed May 2009)*.

(3) Diamond, M. L.; Gingrich, S. E.; Fertuck, K.; McCarry, B. E.; Stern, G. A.; Billeck, B.; Grift, B.; Brooker, D.; Yager, T. D. Evidence for organic film on an impervious urban surface: Characterization and potential teratogenic effects. *Environ. Sci. Technol.* **2000**, *34*, 2900-2908.

(4) Wu, R. W.; Harner, T.; Diamond, M. L. Evolution rates and PCB content of surface films that develop on impervious urban surfaces. *Atmos. Environ.* **2008**, *42*, 5696-5705.

(5) Harner, T.; Shoeib, M.; Diamond, M.; Stern, G.; Rosenberg, B. Using passive air samplers to assess urban - Rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides. *Environ. Sci. Technol.* **2004**, *38*, 4474-4483.

(6) Melymuk, L. Personal communication. **2008**.

(7) Frame, G. M.; Cochran, J. W.; Bowadt, S. S. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. *J. High Resolut. Chrom.* **1996**, *19*, 657-668.

(8) Tuduri, L.; Harner, T.; Hung, H. Polyurethane foam (PUF) disks passive air samplers: Wind effect on sampling rates. *Environ. Pollut.* **2006**, *144*, 377-383.

(9) Hazrati, S.; Harrad, S. Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs): Factors influencing sampling rates. *Chemosphere* **2007**, *67*, 448-455.

(10) Wilford, B. H.; Harner, T.; Zhu, J. P.; Shoeib, M.; Jones, K. C. Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure. *Environ. Sci. Technol.* **2004**, *38*, 5312-5318.

(11) Butt, C. M.; Diamond, M. L.; Truong, J.; Ikonomou, M. G.; Ter Schure, A. F. H. Spatial distribution of polybrominated diphenyl ethers in southern Ontario as measured in indoor and outdoor window organic films. *Environ. Sci. Technol.* **2004**, *38*, 724-731.

(12) Shoeib, M.; Harner, T. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36*, 4142-4151.

(13) Tao, S.; Liu, Y. N.; Xu, W.; Lang, C.; Liu, S. Z.; Dou, H.; Liu, W. X. Calibration of a passive sampler for both gaseous and particulate phase polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **2007**, *41*, 568-573.