

# Size-resolved particle measurements of polybrominated diphenyl ethers indoors: Implications for sources and human exposure

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## KEYWORDS

Polybrominated diphenyl ether (PBDE); flame retardant; air quality; size-resolved aerosol; particulate matter; inhalation exposure

## **ABSTRACT**

Polybrominated diphenyl ethers (PBDEs) are flame retardant polymer additives that are widely detected in outdoor and indoor environments. Release of PBDEs from consumer products leads to high concentrations indoors, but mechanisms of release are poorly understood. While ingestion of dust is a well-studied indoor PBDE exposure route, the importance of inhalation exposure is uncertain. To address these unknowns, dust was collected from household vacuum cleaners, and suspended particulate matter (PM) was collected from the same homes in St. John's, Canada using a cascade impactor. Size-fractionated PM samples (0.01-18  $\mu\text{m}$  diameter) were analysed for PBDEs. The sum of PBDEs in all PM ranged from  $8.7 \pm 0.5$  to  $15.7 \pm 0.5$   $\text{pg}/\text{m}^3$ , with >50% of PBDE mass in respirable PM (<1  $\mu\text{m}$ ). Mass loadings as a function of particle size suggested both abrasion and off-gassing led to the presence of PBDEs in PM. Variability in the PM mass loadings indicated emission mechanisms were both product- and location-dependent. Congener profiles in co-located vacuum dust and PM samples were different, indicating vacuum dust cannot accurately predict PBDE congeners in respirable PM. A calculated lower limit inhalation exposure to PBDEs (0.19  $\text{ng}/\text{day}$ ) is lower than exposure via diet or ingestion of dust, although the different biochemical pathways for inhalation compared to ingestion may have biological effects. This work highlights the importance of contaminant analysis in size-fractionated PM to assess human exposure via inhalation compared to traditional vacuum dust methods.

## **INTRODUCTION**

Polybrominated diphenyl ethers (PBDEs) are a class of halogenated organic flame retardants that slow flame propagation as bromine atoms sequester oxidizing agents following

molecular break-down at high temperatures [1]. Over the last three decades, three commercial mixtures have been used to treat household products: Penta-BDE, Octa-BDE, and Deca-BDE, named for the average degree of bromination of the diphenyl ether within the mixture [1]. Each mixture was used to treat specific kinds of products. Penta-BDE was added to polyurethane foam (e.g. couches, mattresses, carpet underlay, etc.) as well as textiles [1]. Octa-BDE was added to hard plastics and acrylonitrile-butadiene-styrene (ABS) resins primarily in circuit boards, and Deca-BDE was primarily used in hard plastic casing in electronics [2]. PBDEs and their metabolites are endocrine disruptors, binding to both receptors and enzymes in the human thyroid hormone pathway (e.g. [3]). PBDEs are possible carcinogens [4] and have been shown to negatively affect neurodevelopment in mammals, including humans [5].

Europe banned the use of Penta-BDE and Octa-BDE effective in 2004 [6], while manufacturing companies in the United States voluntarily ceased production of these mixtures around the same time [2]. All European and North American production of Deca-BDE ceased between 2008 and 2013 [2]. Despite this halt in production, PBDEs continue to be found ubiquitously in the environment (e.g. [7]), as well as human milk, adipose, and blood serum samples (e.g. [8]).

Human exposure to PBDEs has been demonstrated to occur through diet, ingestion of house dust, and human breast milk in infants [9–11]. Considering that North Americans spend ~90% of their time indoors [12], levels of PBDEs indoors are a concern. Concentrations of PBDEs are much higher indoors than outdoors, and ventilation of buildings is considered a major source of PBDEs to the environment [13]. Studies examining inhalation of gaseous and particulate PBDEs have found it to be a minor source of exposure compared to diet and ingestion of house dust [11,14–17]. Particles  $\leq 2.5 \mu\text{m}$  in diameter ( $\text{PM}_{2.5}$ ) are considered respirable,

because they reach the alveolar region of the lungs, with particles  $\leq 0.5 \mu\text{m}$  able to be taken up directly by the tissue. Previous inhalation studies have considered total PM, with the exception of a few recent studies examining  $\text{PM}_{2.5}$  that found PBDE enrichment in the inhalable size fraction [15–17].

The mechanism of PBDE release into indoor environments has not been fully established. The number of PBDE-containing commercial products in a given space is not reliably correlated with indoor concentrations of these compounds [18]. Probable mechanisms of release include volatilization of these semi-volatile compounds and mechanical abrasion of the products [18–20]. Determining the mass-distribution of PBDEs in size-fractionated suspended particulate matter (PM) can provide unique information regarding the mechanism of emission. Mechanical degradation or product off-gassing followed by condensation results in the presence of chemicals on different sizes of PM. Compounds found in PM because of direct emission resulting from mechanical abrasion would be expected in larger PM (i.e.  $> 1 \mu\text{m}$ ). In contrast, gas-particle partitioning following off-gassing would lead to enhancement in smaller PM (i.e.  $< 1 \mu\text{m}$ ) because of both the larger surface area and higher fraction of organic matter in small compared to large PM [21]. Measurements of size-resolved PBDE concentrations in PM can clearly distinguish between these two emission mechanisms, as well as aid in increasing the certainty of inhalation exposure risk.

To date, PBDEs in size-resolved PM have only been investigated outdoors. Samples collected using cascade impactors in Greece [22,23], China [24], and the Czech Republic [25] all measured enriched PBDEs in small particles. The present study used a cascade impactor to collect and fractionate suspended PM from the living areas of occupied homes in St. John's, Newfoundland and Labrador to investigate the size distribution of PBDEs in indoor air. To our

knowledge, this is the first study to examine PBDEs in size-resolved suspended PM indoors, and the first study to examine flame retardants in size-resolved suspended PM in occupied indoor environments. Using these unique measurements, we present: i) the distribution of PBDE congeners in the size-resolved particle samples and its association with indoor point-sources and emissions of PBDEs; ii) the relationship between PBDEs in household vacuum cleaner dust and particle-phase air samples collected from the same homes; and iii) health implications of PBDE exposure via inhalation. This study provides a proof-of-concept for the use of size-resolved PM measurements to determine indoor sources of PBDEs.

## **MATERIAL AND METHODS**

### *Chemicals*

All solvents used were OmniSolv® grade EMD millipore purchased through VWR (Oakville, ON). The calibration standard BDE-MXE was purchased from Wellington Laboratories (Guelph, ON), and the internal and injection standards FBDE-69, BDE-118, and BDE-208 from AccuStandard (New Haven, CT, USA). Silica gel was obtained from BDH Chemicals (Toronto, ON). The extraction method yields were determined by using the National Institute of Standards and Technology (NIST) standard reference material (SRM) for organic contaminants in house dust, SRM2585.

### *Air sampling*

Air samples were collected from the occupied living space of 3 homes in St. John's, NL between August 2014 and March 2015 while occupants used the space normally, with the exception that vacuuming and laundry were not undertaken during the study. One MOUDI collection from each home was undertaken during this timeframe. All three homes are heated with hot water radiators or baseboard radiative heaters and do not have air-exchange systems.

Windows were kept closed during sampling. Air exchange rates were not measured, but would likely be on the low end of measurements,  $>0.1 \text{ hr}^{-1}$  [26]. Temperatures during sampling were  $20 \pm 5 \text{ }^\circ\text{C}$ . Samples were collected by impaction using a Micro-Orifice Uniform-Deposit cascade Impactor, or MOUDI (MSP Corp. nano-MOUDI-II 122-R), coupled to a vacuum pump operating at a constant flow rate of 30 L/min (MSP Corp. MDI-122-0040) for a sampling period of 72 hours. In this instrument, sampled air moves around a series of 14 particle collection substrates, in contrast to typical filtration techniques where sampled air moves through the collected PM. As particles in the air sample approach an impaction stage, larger particles become impacted on the substrate due to their inertia, while smaller particles follow the flow of air to the next impaction stage. Particle size cut-off is sequentially reduced at each impaction stage within the sampler. Suspended PM was impacted on 14 separate glass fibre filters (GFFs), each collecting particles of a discrete size range (in  $\mu\text{m}$ ) as follows: 10-18, 5.6-10, 3.2-5.6, 1.8-3.2, 1.0-1.8, 0.56-1.0, 0.32-0.56, 0.18-0.32, 0.10-0.18, 0.056-0.10, 0.032-0.056, 0.018-0.032, 0.010-0.018, and  $<0.010$  in diameter. Before employing the GFFs as impaction substrates, the filters were baked at  $500 \text{ }^\circ\text{C}$  for 4 hours, immediately placed on impaction stages, enclosed in aluminum MOUDI sample holders, and kept in the refrigerator until transport to the site for assembly of the MOUDI sampler. Following the sampling event, impaction stages were transported back to the lab in the sample holders, where the GFFs were removed, transferred to sealed petri dishes, and stored at  $4 \text{ }^\circ\text{C}$  until extraction.

#### *Vacuum dust sampling*

Participants provided vacuum dust collected during normal cleaning of their homes prior to air sampling. Vacuuming was not undertaken during PM collection. The contents of vacuum cleaner bags were emptied by the participants and brought to the lab in clean low density

polyethylene (LDPE) plastic bags. A 1.5 mm<sup>2</sup> sieve was used to collect 0.1 g of the smallest fraction of dust. Three dust samples were collected from each LDPE bag, and placed in 15 mL polypropylene centrifuge tubes.

#### *Analytical procedure*

PBDEs were extracted from GFFs or vacuum dust by sonication for 15 min in 10 mL of an acetone/hexane/toluene solution at a ratio of 2:1:1. Samples were then centrifuged at 2400 rpm for 15 minutes and the supernatants collected. This process was repeated three times on each dust sample. The combined 30 mL of extract collected for each sample was reduced under N<sub>2</sub> gas to 2-3 mL. A preliminary range-finding study indicated that combination of the size fractions was necessary to detect concentrations above the limit of detection (LOD). The MOUDI extracts (n = 14/house) were combined into particle-size ranges (in μm) of: <0.01 - 0.1 (5 filters, ultrafine mode particles), 0.1 - 1.0 (4 filters, fine mode particles), 1 - 10 (4 filters, coarse mode particles), and 10 - 18 (1 filter, coarse mode particles), followed by N<sub>2</sub> evaporation, resulting in 4 samples of 2-3 mL. The samples were cleaned using heat-activated silica gel (60 - 120 mesh), baked at 500 °C for 4 h and kept above 110 °C until use. Samples were filtered through 6 mL SPE cartridges containing clean cotton and ~ 2 mL of silica gel pre-washed with 15 mL of hexane/toluene solvent (9:1), and eluted with 30 mL of the same solvent. The eluent was concentrated under N<sub>2</sub> gas to a final volume of ~225 μL.

Analysis of PBDEs was conducted with an Agilent 7890A gas chromatograph and 5976C mass spectrometer (GC/MS). Analytes were separated using a DB-5ht column (5% phenyl-methylpolysiloxane, 15 m, 0.25 mm i.d., 0.1 μm film thickness), with flow rate of 1 mL/min He after a 1 μL splitless injection at 320 °C. The oven program consisted of 100 °C for 5 minutes, followed by a temperature ramp of 25 °C/min to 250 °C, then 5 °C/min to 260 °C, and finally 25

°C/min to 325 °C with a 6.4 min hold, for a total run time of 22 min. The transfer line was maintained at 325 °C, with the source and quadrupole temperatures held constant at 150 °C. The MS was operated in electron capture negative ionization (ECNI) mode with methane as the ionization gas. Selected ion monitoring (SIM) mode identified ions with m/z of 79, 81, 160.8, 162.8, 403, 405, 406.5, 408.5, 483, 485, 562, 564. PBDEs were quantified with ion 79, while other ions were used for confirmation as described in Gómara *et al.* [27]. A total of 26 PBDE congeners were monitored using the method (BDEs -7, -15, -17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -156, -183, -184, -191, -196, -197, -206, -207, and -209, respectively). Instrumental detection limits (S/N = 3) ranged from injected masses of 0.009 – 0.5 ng for the observed congeners, where noise was defined as the standard deviation of the blank within the congener-specific retention windows (Table S1).

#### *Quality assurance*

In order to account for instrument variability, all quantification of PBDEs was done in relation to an internal standard F-BDE-69 (ISD), and injections were in triplicate. After the clean-up and blow-down, 5 µL of ISD at 200 ng/mL was added to each sample vial. Vacuum dust samples had enough total mass to allow 3 replicate extractions. Field blanks consisted of pre-baked GFFs transported to the sampling site and exposed to the ambient environment while the MOUDI sampling tower was being assembled. The accuracy of the method was determined using the NIST SRM for organic contaminants in house dust. The SRM includes certified PBDE concentration values for all congeners detected in this study, and was used to evaluate the efficiency of the extraction and clean-up method. Yields ranged from 93.1 - 108.2 % for congeners BDE-47, -99, -100, and -183, with BDE-209 recovered at 63.8% from three SRM extractions (Table S2). Yield values are statistically equivalent to the accepted values for BDE-



47, -99, -100, and -183 (t-test, 95% confidence). A matrix effect test was performed by adding 10 ng of BDE-118 and 20 ng of BDE-208 as injection standards to 200  $\mu$ L of Toluene or extracted house dust. Matrix suppression was quantified by comparing the signal-to-noise ratio of ions 79 and 486 for BDE-118 and BDE-208 respectively, between the solvent and complex-matrix samples (Table S3).

#### *Calculation of inhalation exposure*

Contaminant exposure by inhalation is calculated according to the formula

$$[(C_1F_1)+(C_2F_2)\dots+(C_nF_n)]R_R$$

where  $C_{1,2,n}$  is the concentration of the contaminant at a particular location, in this case a PBDE congener in the home,  $F_{1,2,n}$  is the fraction of the day spent at the same location, and  $R_R$  is respiration rate. Canadians spend approximately 90% of their time indoors [12], so a fraction of 0.9 is used in the following calculations. This assumes that the PBDE levels measured in the houses are representative of other indoor environments in which a person spends their time. An accepted approximation of the human adult respiration rate (age 21-60) is 15.9  $m^3/day$  [28].

The U.S. EPA calculates exposure by taking into account everything that breaches the body boundary rather than the absorbed fraction that makes it into the blood stream, as the latter is considered a matter that is addressed by pharmacokinetic dosage models [2]. As such, no absorption fraction is applied to the exposure calculation. The human absorption fractions of PBDE congeners through inhalation are unknown, but experimentally determined ingestion uptake rates in rats range from 0.78 - 0.94 for the five common Penta-BDE mixture congeners [29], and these rates are sometimes assumed for inhalation calculations in other studies [2].

## RESULTS AND DISCUSSION

### *PBDE congeners detected in MOUDI samples*

Human activities are known to affect suspended PM concentrations [30], so homes must be occupied and used normally during sampling to obtain a meaningful estimate of PBDE concentrations in PM. Because of the disruptive noise and size of the large vacuum pump required to operate the sampling equipment in the living area, this first survey had a small sample size. This is consistent with design for other studies using similar equipment to monitor indoor environments, which have been based on small sample sizes ( $\leq 10$ ) [31–33]. To minimize building-related differences between the homes, our three sampling sites were selected based on their heating and air-exchange methods. PBDEs were detected in the size-resolved suspended PM of all three houses.

Of the many PBDE congeners employed in the three commercial flame retardant mixtures, only 4 congeners were detected in PM samples collected by the MOUDI: BDEs 47, 99, 100, and 183. The presence of BDE-47, -99, and -100 is unsurprising given that they are often identified in dust and biological tissue, likely because they make up the largest percentages of the commercial Penta-BDE mix [10,34]. Similarly, the largest fraction of the Octa-BDE mix is comprised of BDE-183 [1]. The dominant congener in Deca-BDE, BDE-209, although present in vacuum dust, was not detected in any PM samples. The remaining discussion is focused on these five PBDE congeners.

Total measured PBDEs across all particle sizes ranged from  $8.7 \pm 0.5$  to  $15.7 \pm 0.5$   $\text{pg}/\text{m}^3$  (Figure 1). Measured mass loadings (i.e. mass per cubic meter of air sampled) from all blanks are reported in Table S4 and size-fractions of MOUDI samples at each sampling site in Figures S1-S3. Where at least two of the three replicate sample measurements fall either below the LOD or

the limit of quantitation (LOQ), mass loadings are reported as such. Where a single replicate measurement was below the LOD or LOQ, the average mass loading was determined using one-half LOD or one-half LOQ, respectively. The mass loadings are based on the total mass of PBDEs extracted from each aerosol size-fraction. There were no PBDE congeners present in the blanks above the LOD.

In general, measurements of semi-volatile species, such as PBDEs, in PM can be subject to blow-on (positive artifact) and blow-off (negative artifact) effects that could affect the accuracy of the results [35–37] (for more details, see Text S1). Measurements made using MOUDI samplers are only subject to blow-off effects, which could be caused by desorption of adsorbed molecules under the low pressures within the sampler. Blow-off effects have been shown to be negligible for compounds that partition almost entirely to PM [36], including BDE-183 and BDE-209 [38]. Blow-off studies have not been specifically undertaken with a MOUDI-II sampler, but results from one field inter-comparison showed no significant difference for the majority of semi-volatile compounds measured between a high-volume sampler and a MOUDI-II cascade impactor [39]. However, it remains possible that blow-off effects could affect the measurements reported here for the more volatile congeners (i.e. BDEs-47, -99, -100) for PM sizes collected at low pressures (i.e. fine and ultrafine PM). Error has been included to account for potential maximum blow-off based on theoretical predictions [37].

Due to the limited amount of mass collected in the PM samples, method detection limits could not be determined for each congener. Vacuum dust was used as a proxy to investigate matrix effects. Spiking vacuum dust with both penta-brominated BDE-118 and nona-brominated BDE-208 injection standards showed greater matrix suppression of the higher brominated congener (Table S3). Because the retention time and physical properties of BDE-208 and BDE-

209 are similar, it is likely that the signal for BDE-209 undergoes high levels of matrix suppression that are not accounted for by the internal standard, thereby reducing our sensitivity for BDE-209. Despite having made changes to the analytical method to optimize the detection of BDE-209 (e.g. high inlet temperature and long injection splitless time [40]), none was detected in any of the MOUDI PM samples.

Previous measurements of PBDEs in indoor air have looked at either primarily the gas phase, through passive sampling on polyurethane foam discs (e.g. [41,42]), or the sum of collected gas and PM phases (e.g. [43]). Thus, comparisons with previous studies are difficult. In general, concentrations observed in this study are much lower than indoor air concentrations reported in North America (e.g. [43]) and Asia (e.g. [15]). Concentrations are comparable to, though still smaller than, the sum of gas and PM levels reported in Europe (e.g. [13]). The PBDEs most commonly observed on indoor PM are BDE-47, -99, and -100, consistent with this work [15,43,44]. Studies of indoor PM in the Chinese cities, Guangzhou [15] and Shanghai [16,17], observed high PM loadings of BDE-209 (e.g. PM<sub>2.5</sub> concentrations from ~10 to >1000 pg/m<sup>3</sup>). In households in Hong Kong, China [15] and Michigan, USA [43], BDE-209 was not detected in any indoor PM samples. When indoor PM is sampled without sampling the gas phase, detection of BDE-209 is rare in North America, having been detected only in an indoor gymnastics facility [45]. The latter studies are consistent with the results of this work, where BDE-209 is not present in PM. However, as described above, matrix effects were higher for BDE-209, so it is possible that this congener is present, but obscured by matrix suppression when using GC-MS. BDE-183 has been occasionally detected in PM samples from North America and Asia [15,43] and was detected here in one of the three homes.

### *Comparison of congener profiles in PM and dust samples*

Concentrations measured in vacuum dust collected from these three houses were much lower than most previously reported values (e.g. [15]). Our observed concentrations are compared to results obtained by Dodson *et al.* [46] in their repeat sampling study in California, where vacuum dust was sampled from the same 16 houses, 5 years apart – before and after effects of the Penta-BDE phase-out had time to emerge (Table 1). PBDE concentrations in house dust dropped dramatically during that time, with Penta-BDE congeners falling by ~50%. Four years later it is unsurprising that the PBDE congeners measured in the current study are lower, in many cases, by an order of magnitude.

Since PBDE concentrations in vacuum dust are widely reported and used to calculate exposure via dust ingestion (e.g. [47]), it is important to determine whether concentrations of PBDE congeners in vacuum dust are representative of the congeners in suspended PM, and whether these reported values can be used to predict exposure via inhalation. Previous studies have shown inconsistent relationships between PBDE concentrations in dust and air (e.g. [15,17]). However, as described above, the definition and measurement of the term “air” varies between studies, which could contribute to the lack of consensus. Furthermore, given that sources vary between indoor locations, examination of paired dust and PM samples is likely to be most informative. PM in the 10-18  $\mu\text{m}$  size range is formed through mechanical abrasion, similar to formation processes for vacuum dust. Thus, this PM is the most likely to contain a similar congener profile as vacuum dust. Figure 2 shows the measured concentrations of BDE-47, -99, -100, -183, and -209, in triplicate samples collected from the household vacuum cleaners and the 10-18  $\mu\text{m}$  PM sample from each of the three houses (data in Table S7). Congener profiles for vacuum dust samples show no relationship with the paired PM samples. In general,

PM samples appear to be enriched in BDE-47 and lacking in BDEs-183 and -209 compared to the vacuum dust. Matrix effects could have reduced our ability to detect low levels of BDE-209 in PM, detection of this species in PM is unusual, even when concentrations are high in dust [43,44]. Congener profiles in vacuum dust also do not resemble those from any of the other PM size fractions. Notably, in House A, BDE-183 was detected in all PM below 10  $\mu\text{m}$ , but not the vacuum dust or the 10-18  $\mu\text{m}$  particles. In the other two houses, BDE-183 was not detected in any of the particles and was detected in the vacuum dust. These results suggest that formation mechanisms for PM and dust are inconsistent within homes. Thus, although data reporting PBDE concentrations in vacuum dust is widely available, congener profiles of PBDEs present in dust cannot be used to predict profiles of PBDEs present in PM, nor the respirable portion thereof.

#### *Mass loading of PBDEs in PM and mechanisms of emission*

Coarse and fine-mode particles have different mechanisms of formation, and different fates in the atmosphere [21,48]. Coarse mode particles ( $>1 \mu\text{m}$ ) are formed by mechanical processes, while smaller PM is formed by nucleation and condensation of precursor gases [21,48]. Release mechanisms for PBDEs from commercial products indoors are thought to be volatilization (e.g. [20]) and abrasion (e.g. [19]), leading to their presence in fine and coarse PM, respectively. Particles lost through air exchange and dry deposition are of similar importance in most indoor environments [49]. In indoor environments, dry deposition to rough household surfaces is fastest for coarse mode particles and fine mode particles with diameters less than 0.2  $\mu\text{m}$  [49]. Thus, fine mode particles between 0.2 and 1  $\mu\text{m}$  will have the longest lifetimes aloft. Particle number in atmospheric samples follows a log normal distribution. This underpins the bimodal size distribution of particle mass in the atmosphere [48] and the available particle surface area where PBDEs can sorb, both of which are inversely related to the size of the particle [21].

This makes strictly mass-based comparisons of PBDE concentrations of differently sized particles inappropriate. Instead, the mass loading distribution of particles calculated in the form of  $dM/d\log D_p$ , where  $m$  is the mass of analyte in the size range, and  $D_p$  is particle diameter [48], is representative for comparison purposes. The Penta-BDE congeners particle mass loading distributions from each sampling site are shown in this format in Figure 1. The PM mass loading size-distributions of PBDEs found in the Penta-BDE commercial mixture suggest that different products acting as indoor sources release PBDEs by different mechanisms. Coarse-mode PBDE-containing particles are likely formed by mechanical degradation of commercial products, such as small pieces of foam or plastic [19], while PBDEs associated with fine-mode particles are likely released by off-gassing followed by chemical partitioning or sorption. The size distributions observed in the three homes suggest that both mechanical degradation and off-gassing contribute to penta-BDEs in particles. House A has a high mass loading of the major components of the Penta-BDE mixture, BDEs-47, -99, and -100, in coarse particles compared to fine (0.1-1  $\mu\text{m}$ ) and ultrafine (0.01-0.1  $\mu\text{m}$ ) PM. To elucidate sources, coarse mode PM can be compared to ultrafine. There is possible overlap of coarse mode PM into the larger bins of the fine mode because of the size cut-off design of MOUDI sampling stages, reducing the utility of comparing coarse and fine PM as a few coarse particles contain significant relative mass. For all three congeners, mass loadings in coarse PM were higher than in ultrafine PM. However, mass loadings in the ultrafine and fine mode may be underestimated because of blow-off effects (see discussion above). Thus, statistical comparisons were undertaken for both the measured and upper-limit PBDE mass loadings. Loadings of BDEs-47 and -99 were statistically different under both conditions, within analytical error (Welch's t-test  $p < 0.01$ ). This suggests the dominant mechanism for release of Penta-BDE to indoor air in House A is mechanical abrasion. The

presence of all three BDEs in ultrafine and fine mode particles indicates that volatilization and subsequent partitioning or adsorption are also occurring. In contrast, House C has a higher loading of Penta-BDE congeners in small PM. All three Penta-BDE congeners qualitatively follow this trend, but only mass loadings of BDE-100 are statistically higher in ultrafine PM compared to coarse under both measured and upper-limit conditions (Welch's t-test  $p < 0.05$ ). Mass loadings in ultrafine and fine PM may be underestimated through sampling loss. This trend suggests that the major mechanism for release of these compounds to indoor air is through volatilization, with mechanical abrasion playing a lesser role. House B has inconsistent trends in the size distribution of PM for the two congeners that were measured in that location. BDE-47 was observed in higher amounts in coarse PM, while BDE-99 was enhanced in fine and ultrafine particles. Matrix effects in the sample collected from House B prevented quantitation of BDE-100. These trends suggest that sources to the air in House B have no dominant source, but similar contributions from both volatilization and mechanical abrasion.

Classes of PM with distinct formation mechanisms are expected for different houses, due to varying sources of Penta-BDE within the home. Household characteristics for those sampled here are outlined in Table 2. Possible sources of Penta-BDE commercial mixture in House A are carpet underlay, and polyurethane foam (PUF) used throughout the structure. House B has a couch and armchair set that are likely to contain Penta-BDE mixture, and the living area is carpeted. The age of the house and insulation is unknown. House C does not have any carpet or underlay, nor has the >100-year-old house undergone any recent renovations, however there are three couches in the living area of the home, including one second-hand couch that is of a vintage likely to contain Penta-BDE mixture.



Only House A contained PBDEs other than Penta-BDEs in the PM. In this home, BDE-183 was detected in ultrafine, fine, and coarse mode particles (Figure 3). The qualitative trend shows an enrichment in ultrafine PM, although it is not statistically higher. House A contains the largest number of plastic-containing electronics among the homes sampled. Elevated mass loadings in ultrafine PM is consistent with the known uses of BDE-183, primarily in circuit boards and hard plastics. Circuit board off-gassing, followed by condensation of BDE-183 onto pre-existing particles, would result in partitioning or adsorption to ultrafine PM.

It is clear from these results that neither of the proposed mechanisms for PBDE release into indoor air are consistently dominant. Rather, mechanisms likely depend on the types of commercial products present in the indoor environment and their frequency and duration of use. The results of this initial study demonstrate that this technique can be an effective tool to determine indoor sources and could be applied in larger-scale studies to fully explore the variability in indoor environments.

#### *Human exposure to PBDEs by inhalation of PM*

Just as particle sizes differ based on mechanisms of formation and deposition, likelihood of particles impacting the wall of the human respiratory tract is also affected by the size of a particle, with risk to human health generally increasing as particle size decreases. Implications of particle-mass distributions on inhalation exposure and human health impacts are therefore important to quantify.

The mean daily inhalation intake of PBDEs is 0.19 ng/day (Table S8), calculated based on mean concentrations of BDE-47, -99, -100, and -183 in the fraction of PM less than 10  $\mu\text{m}$  in diameter ( $\text{PM}_{10}$ ). The daily intake number presented here is lower than one other particle inhalation intake rate published in the literature, which calculates median inhalation exposures of

1.2 and 2.2 ng/day for a toddler and 25-year old male, respectively [15]. It should be noted that in the other published study, inhalation was dominated by BDE-209, which is not typically detected in PM (as described above). The PM exposures presented in this work are conservative estimates, as blow-off effects may cause an underestimate of measured PM concentrations, particularly in the ultrafine mode. In addition, personal exposure to PM has been shown to be much higher than measured indoor PM concentrations. Activities that re-suspend PM lead to a “personal cloud” effect causing higher PM concentrations directly surrounding people [50].

Figure 4 compares the calculated daily human exposure to PBDEs in PM (total, coarse-mode, and fine-mode) to published estimates for daily dietary and dust ingestion exposure. Exposure through inhalation of PM is about an order of magnitude lower than ingestion by dust and two orders of magnitude lower than ingestion. While the contribution to daily exposure of total suspended PM is minor when compared to other exposure sources, Mandalakis *et al.* [23] reiterate that it is the smallest particles that reach the deepest parts of the lungs, eliciting the greatest health effects. Because particles smaller than PM<sub>2.5</sub> are considered respirable, and particles <0.5 μm can penetrate the lining of the lung, fine and ultrafine PM is of greatest interest when considering the effects of human exposure. While exposure to PBDEs by inhalation is low, it is worth noting that >50 % of PBDE mass was observed in PM <1.0 μm. Coarse-mode PM include particles > 1 μm, and so contains some respirable particles (i.e. those between 1.0 and 2.5 μm). A lower limit of estimated inhalation exposure from respirable particles can be derived from mass loadings in the fine and ultrafine particles of 0.12 ng/day.

Exposure to PBDEs via inhalation is low in terms of ng/day when compared to other routes of exposure, as previously reported in PBDE exposure studies [11,14–17]. However, effects may also vary by mode of exposure due to human physiology. Contaminants that enter

the body through the lungs are pumped through the heart and directly to the rest of the body without passing through the liver, which is the case when contaminants are ingested. Given the endocrine and neurodevelopmental effects that exposure to PBDEs may cause, and the liver's role in detoxifying the body, direct delivery of inhaled PBDEs from the lungs to tissues via the bloodstream may incur different toxicological effects than ingestion, which could be important even at reduced PBDE concentrations.

## CONCLUSIONS

This study employed a novel sampling method, collecting size-fractionated PM from 3 households in St. John's, Canada, to assess the sources of PBDEs to indoor air and inhalation of PM as an exposure pathway for PBDEs. Four PBDE congeners (BDEs-47, -99, -100, and -183) were detected in particle samples. BDE-209 was not observed in any PM samples, consistent with previous studies. Penta-BDE congeners were found in all samples of PM, while BDE-183 was found in coarse, fine, and ultrafine PM from one home. The total concentrations of the four detected PBDE congeners across all particle sizes ranged from  $8.7 \pm 0.5$  -  $15.7 \pm 0.5$   $\text{pg/m}^3$ . Size distributions suggest that PBDEs are present in indoor air through a mixture of volatilization and mechanical abrasion mechanisms and that the prevalence varies between indoor environments. Further study is necessary to fully elucidate relationships between PBDE sources and PM size distribution. PBDEs are present in the respirable fraction of PM, and the toxicological effect of inhaled PBDEs remains unknown. An estimated lower limit of exposure to PBDEs through inhalation of  $\text{PM}_{10}$  is 0.19 ng/day. Over half of the mass was present in the fine and ultrafine mode particles, giving an exposure of 0.12 ng/day. The presence of different PBDE point sources within the home affect the particle mass distribution of PBDEs, which affects the implications of exposure. There was no relationship observed between congener profiles for vacuum dust and

PM from the same homes, indicating that vacuum dust has no predictive power for PM inhalation exposure.

## SUPPLEMENTAL DATA

Additional data and figures as outlined in the text.

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## TABLES

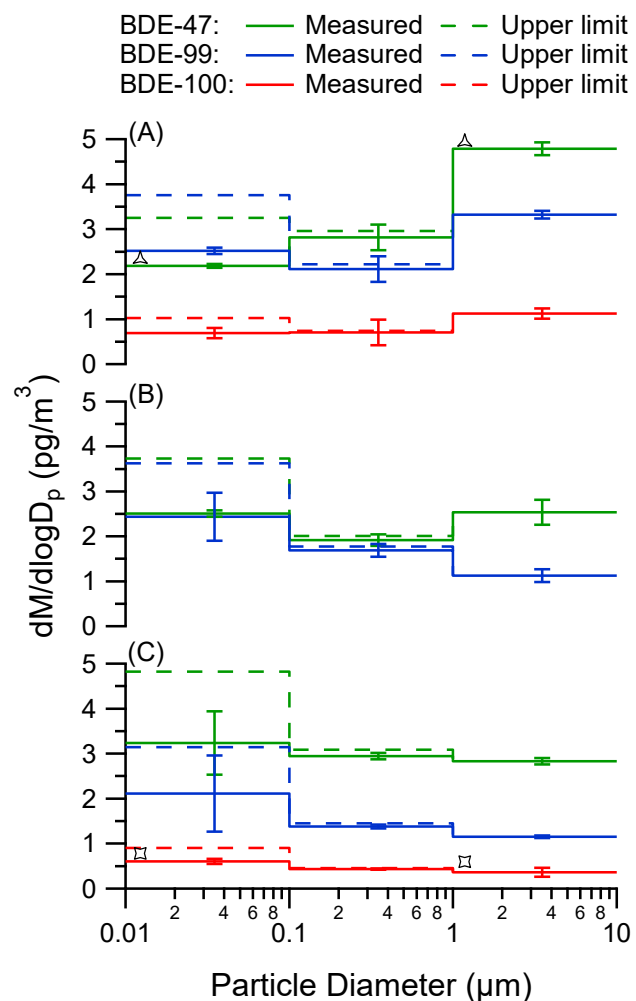
**Table 1.** Concentrations of PBDEs in vacuum-collected house dust (ng/g) in measurements from 16 Californian [46] and 3 St. John’s homes

PBDE Congener	2006		2011		This Study (2014-2015)	
	Range	Median	Range	Median	Range	Median
47	270-23 000	2 300	140-17 000	1 000	53-114	82
99	280-24 000	2 200	190-25 000	1 100	45-265	103
100	56-4 900	520	37-11 000	240	10-66	21
183	9-770	28	3-920	18	3-9	5
209	580-15 000	1 400	110-8 500	1 200	25-10 300	670

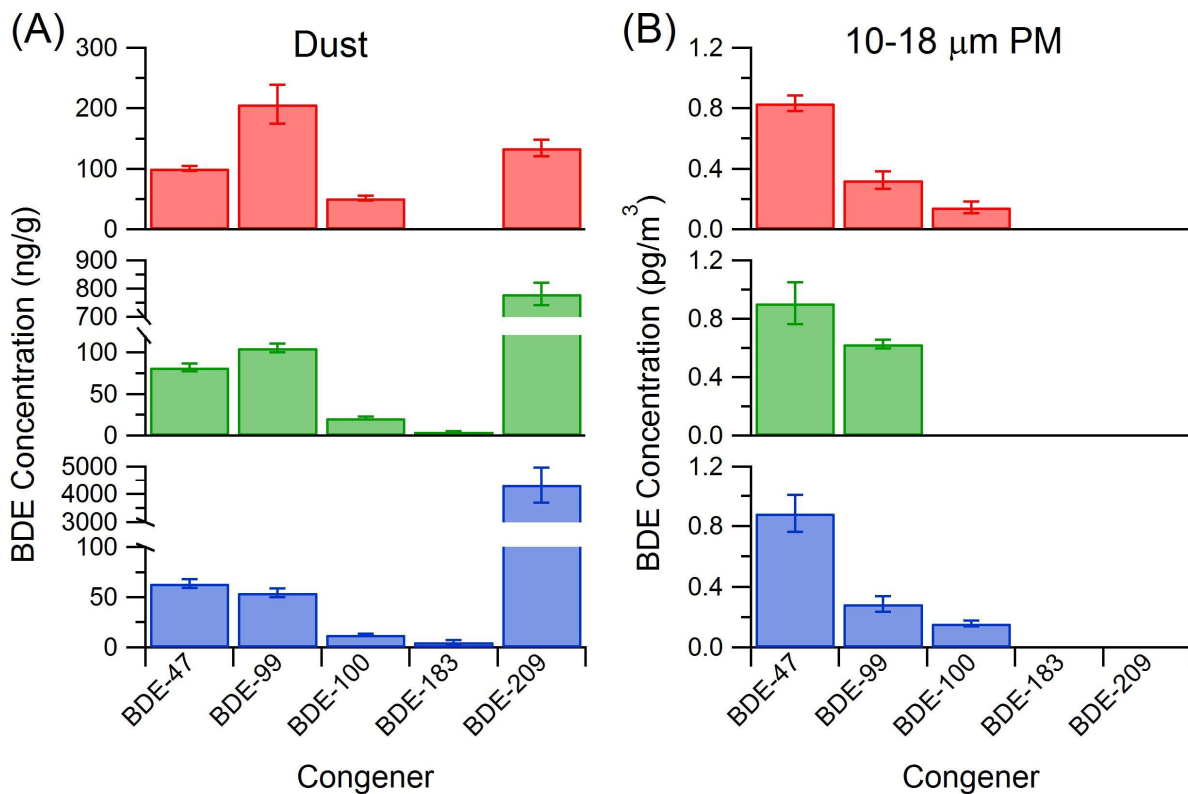
**Table 2.** Characteristics of sampling sites

Sampling Site	Possible sources of Penta-BDE mixture in the living area	Number of electronics likely to contain Octa- and/or Deca-BDE within the home
House A	carpet underlay, polyurethane foam	> 20
House B	carpet underlay, couch, armchair, desk chair	5
House C	couches (3), ottoman, desk chair	12

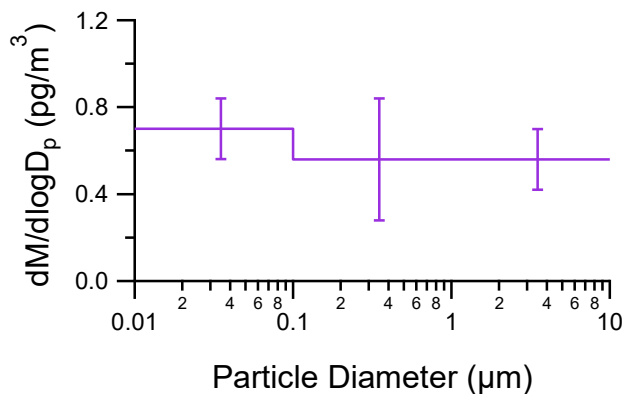
## FIGURES



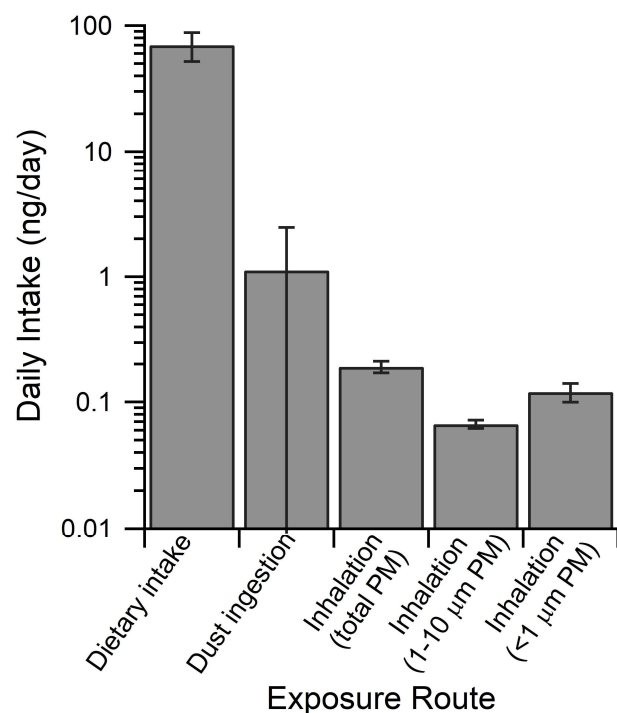
**Figure 1.** Particle-mass loading distributions of Penta-BDE congeners in MOUDI samples in: (A) House A; (B) House B; and (C) House C. Error bars represent the standard deviation of 3 replicate injections. Symbols indicate populations of ultrafine (0.01-0.1  $\mu\text{m}$ ) and coarse ( $>1 \mu\text{m}$ ) mode particles that are statistically different. Dashed lines represent the maximum underestimate of mass loadings due to sampling bias.



**Figure 2.** Congener levels for the five PBDE congeners detected in paired vacuum dust (A) and 10-18  $\mu\text{m}$  PM samples (B), for House A (red), House B (green), House C (blue). Error bars for dust and aerosol samples represent the standard deviation of 3 replicate extractions and 3 replicate injections, respectively.



**Figure 3.** Particle mass-loading distribution of BDE-183 in aerosol samples from House A. Error bars represent the standard deviation of 3 replicate injections.



**Figure 4.** Estimated daily intake of PBDEs from various sources. Mean dietary intake from [51] for United States adults aged 20 – 59, error bar represents standard deviation of age and sex; mean dust ingestion calculated using data from this study using the method of [10], error bar represents standard deviation between three homes; and mean inhalation of PM calculated as described in the text, error bars represent the standard deviation of three homes.

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