

## EVOLUTION OF FLAME RETARDANT CHEMICALS IN A NEWLY CONSTRUCTED BUILDING

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### Abstract

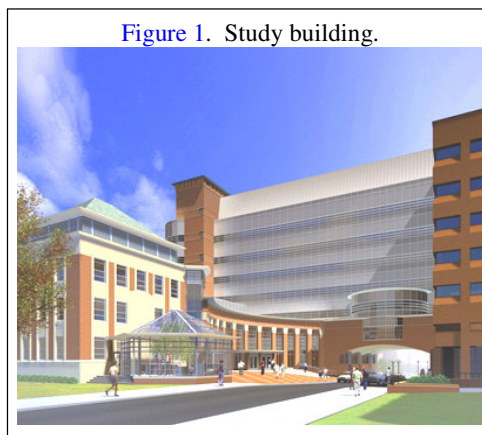
Brominated flame retardants (BFRs), including polybrominated diphenyl ethers (BDEs) and tetrabromobisphenol-a (TBBPa), are now widely distributed in the environment, including indoors. This study describes the evolution of BFRs in a newly constructed building. The building was monitored prior to occupancy, and then every 2-3 months, for multiple BDE congeners and TBBPa in dust, and airborne vapor and particles. A walkthrough inventory was conducted, and volatile organic compounds (VOCs) and air exchange rates based on perfluorocarbon tracers (PFTs) were measured. The most striking result is the rapid increase of BDE-209 in indoor dust, which rose exponentially from low levels just after building occupancy to ~10 µg/g after 9 months. For several BFRs (BDE-47, 99), airborne levels also increased, although changes and concentrations were less dramatic. Differences in trends among BFRs and VOCs suggest that equilibrium between BFR emissions and indoor concentrations (dust and air) has not yet been reached, and that multiple BFR sources are present. As seen in several studies, indoor BFR levels are high due to the presence of BDE-emitting materials and limited degradation and dispersal occurring indoors. This is the first study showing the rapid increase in indoor concentrations of BFRs after building construction and furnishing.

### Introduction

It is becoming recognized that brominated flame retardant (BFR) chemicals can be released from many sources, including building materials and furnishings, household/office products, chemical production, manufacturing (especially products that incorporate foams, plastics and textiles), and product disposal. Buildings contain a large reservoir of these persistent and bioaccumulative chemicals, and may represent an important environmental source of BFRs. Several studies have shown that levels of BFRs are highly elevated in buildings. *Objectives.* The objective of this study is to characterize indoor levels of BFRs in indoor dust, airborne particles, and the vapor phase in a newly constructed building with the specific aim of determining changes in concentrations and ultimately building emissions as the building is completed, furnished, and occupied.

### Materials and Methods

*Study design.* BFR concentrations in floor dust and air were tracked over a 7-month period in a newly-constructed mixed-use 7-floor building (Figure 1) that contains offices, classrooms, cafeterias, computer rooms, and laboratories. Monitoring was conducted just prior to occupancy in Aug. 2006, and then every 2 to 3 months until Feb. 2007. Sampling was conducted in an office suite on the 6<sup>th</sup> floor. Outdoor sampling was conducted simultaneously during most indoor sampling events. We also monitored volatile organic compounds (VOCs) and naphthalene in air in the same building at the same site, and collected floor dust and indoor samples in other buildings, which were analyzed for BFRs. Air exchange rates at the sampling site were determined for each sampling event. A walkthrough inventory/checklist was completed at each site and building.



*Sample collection.* Dust samples were collected by vacuuming a 1 m<sup>2</sup> area. Vapor and particulate samples were collected using a new medium-flow sampling system in which air first entered a PTFE cassette, which contained a 1 µm pore size PTFE filter to collect airborne particles, then a glass cartridge containing a pre-cleaned polyurethane foam (PUF) element, which collected vapor-phase BFRs. Air was sampled at a nominal flow rate

of 15 l/min over a one week period, giving a sample volume of  $\sim 150 \text{ m}^3$ . Sampling precision was determined using side-by-side tests. The possibility of breakthrough of vapor phase BFRs was evaluated using back-up adsorbents. Samples were returned to the laboratory in BFR-free containers and extracted within 24 hr for analysis (described below). Perfluorocarbon tracers (PFTs) used to measure air exchange rates (AERs) and VOCs were collected using passive thermally-desorbable Tenax-GR samples over the 1-week period, as described by Batterman et al.<sup>1</sup>

**Sample analysis.** Air and dust samples (PUF cartridge and filter separately) were Soxhlet-extracted for 24 hrs using hexane and dichloromethane, then cleaned and fractionated as described elsewhere.<sup>2,3</sup> Each sample was analyzed for 20 BDE congeners and tetrabromobisphenol-a using GC/MSD (Agilent 6890/5973, Palo Alto, CA) operating in negative chemical ionization mode. VOC and PFT samples were analyzed using another GC/MSD equipped with an automated short-path thermal desorption/cryofocusing system (Model 2000, Scientific Instrument Services, Ringoes NJ) operating in electronic impact mode for over 90 compounds following procedures detailed in Jia et al.<sup>4</sup>

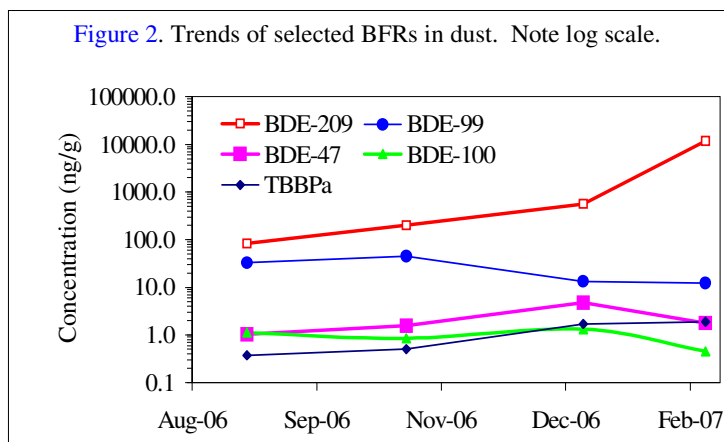
**Air exchange rates (AERs).** AERs were determined using PFTs, the constant injection rate method, adsorbent-based passive sampling of PFT concentrations and simple dilution models, as described elsewhere.<sup>5</sup> In brief, two hexafluorobenzene (HFB) and two octafluorotoluene (OFT) emitters were placed in the sampling area during the BFR measurement period. Total emission rates averaged 15.9 (range of 13.5–20.8) mg/hr for HFB and 10.5 (9.7–11.5) mg/hr for OFT. Airborne PFT concentrations were measured in replicate over the same period at two indoor locations, as described above. Building/room volume was measured directly. AERs were calculated using PFT emission rates and concentrations, and the room volume.

**Quality assurance.** In parallel with the analysis, the following quality control samples were processed: Blanks and standard reference dust were analyzed with each sample batch. Linearity, drift check, surrogate and spike recovery analyses were carried out. For the drift check, standards were run after every five samples and results were accepted only when standards varied by less than 10%. The estimated method detection limits (MDLs) for air samples (vapor and particles) are 0.01–0.02 ng/m<sup>3</sup> for tetra- and octa-BDEs, 0.2 ng/m<sup>3</sup> for nona-BDEs, 0.6 ng/m<sup>3</sup> for deca-BDE, and 0.1 ng/m<sup>3</sup> for TBBPa. For dust samples, the MDLs are 0.005–0.02 ng/g for tetra- and octa-BDEs, 0.4 ng/g for nona-BDE, 2.5 ng/g for deca-BDE, and 0.2 ng/g for TBBPa.

## Results and Discussion

Of the target BFRs, we detected BDEs-47, 99, 100, 209 and TBBP-A in most samples. Additionally, traces of BDEs-28, 49, 66, 85, 153, 154, 206, 207 and 208 were found in several samples.

**BFRs in dust.** In indoor dust, the predominant BFR was the deca-homologue, BDE-209. Its concentration increased more than exponentially over the study period (Figure 2), from  $\sim 100 \text{ ng/g}$  at the beginning of the study (Aug. 2005), to  $\sim 600 \text{ ng/g}$  at 6 months, and to over  $10,000 \text{ ng/g}$  in the latest measurements (Feb. 2007). BDE-209 composed  $\sim 50\%$  of the total PBDE in dust at the start of monitoring (August 2005) to  $94\%$  after 6 months. The other BDE congeners reflect the commercial penta-formula. For these BDEs, concentrations were modest ( $<45 \text{ ng/g}$ ), and concentration changes over the study period were small. TBBPa concentrations in dust increased over the study period (from  $0.4$  to  $2.0 \text{ ng/g}$ ; Figure 2), though the increase was much less dramatic than BDE-209. Generally, these data are comparable



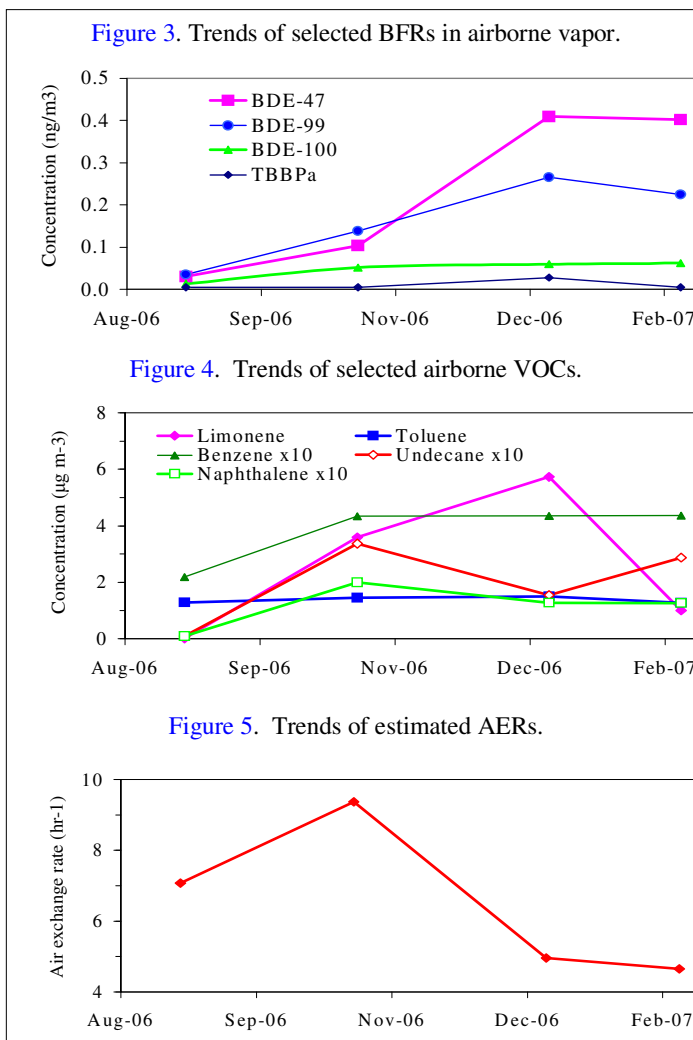
with the literature regarding PBDE levels in US houses, e.g., Stapleton et al.<sup>6</sup> reports that the total BDE concentrations averaged 4,600 ng/g (range from 160-8,000 ng/g), especially considering that our samples were taken from a newly constructed building. The continuing increase observed in the case study building suggests that the dust samples are not yet saturated with BFRs after nearly 1 year. Of course, dust sample measurements varied greatly, e.g., depending on the dust composition.

**BFRs in air.** Airborne vapor phase BFRs were dominated by BDEs-47 and 99, followed by BDE-100. Concentrations were near MDLs prior to occupancy, and tended to increase over the study period (Figure 3). The BDE composition and concentrations, which resemble those found in an office building described by Hazrati and Harrad,<sup>7</sup> can be explained by the application of BDEs in commercial foams, which can contain 5-30% of BDEs. The generally increasing airborne concentrations suggest that equilibrium has not been reached, but rather changes in emissions and air exchange must be considered.

The concentration of airborne particulate matter (PM) in the building was low, and the low sample mass collected (<2 mg) did not allow analysis of deca- and nona-BDEs. The BDEs detected (concentration range from <MDL to 70 pg/m<sup>3</sup>) varied significantly and reflected the technical penta-formula.

**VOCs in air.** Figure 4 shows the trend of selected VOCs in the case-study building. VOCs without a strong trend, e.g., benzene (and to an extent, toluene), largely reflect outdoor sources. Increasing levels of other VOCs, e.g., limonene and naphthalene, reflect emissions within the building. Other VOCs arise from both indoor and outdoor sources, e.g., toluene and undecane. Notably, trends of VOC concentrations differ significantly from those of the BFRs, and even those VOCs that increased significantly, e.g., limonene, appear to have reached a quasi-steady state or maximum soon after the building was occupied.

**AERs.** Figure 5 shows that AERs varied over a 2-fold range in the study office, from 4.6 to 9.4 hr<sup>-1</sup>. These rates represent air supplied to the office suite, which might come from other regions of the building and/or from outside air. AERs measured elsewhere in the building differed, and the lack of an inverse relationship between AER and indoor VOCs (e.g., limonene), suggest that the AER only partly reflects the supply of outside air.



*Summary.* BFRs, VOCs and PFTs in air showed different trends over the study period. The large increase of BDE-209 levels in indoor dust is remarkable. For the airborne contaminants, trends differed considerably. For VOCs, little partitioning between vapor and adsorbed phases was expected, and VOC concentrations will largely reflect a balance between emissions and AERs. We anticipate that indoor emissions of VOCs like limonene, associated with cleaning products in the building, are roughly constant over week-long monitoring periods used, and the rapid increase in VOC levels just after occupancy and then quasi-stabilization reflects the continuing use of such products. The strong negative correlation of VOC levels (associated with indoor sources) with AERs is anticipated. In contrast, BFRs are low volatility materials and extensive partitioning to surfaces (including dust) was expected. BFRs in building materials and contents (e.g., carpet, equipment, furniture, office supplies) may be emitted by volatilization (albeit at low rates) and by the generation of particles. Ultimately, these BFRs may absorb to or become incorporated into house dust. The differing trends seen for the various BDE congeners reflect different indoor sources and properties, specifically the penta-mix used in many flame-retarded soft furnishings, and deca-BDE used in hard plastics and textiles.<sup>8</sup> In the study building, several BDEs appear to be negatively correlated with AERs, specifically BDE-47 and 99, but BDE-100 levels continued to increase, suggesting that AER may have a smaller influence on other congeners and that additional time is needed for concentrations to equilibrate.

We recognize that trends evaluated at a single site in a single building are unlikely to be representative of all modern buildings, much less of other indoor spaces, and that additional monitoring is needed to evaluate the final levels of BFR attained in the case study building. Still, this study demonstrated the evolution of BFR levels in indoor air and dust, and the results are helpful in understanding the fate of and exposure to BFRs, and possibly the time needed to evaluate the effectiveness of mitigation efforts.

#### **Acknowledgements**

We acknowledge the support of our laboratory and field staff, including Alisson Stewart, Safia Ziani, Lindsey Lapointe, and Jo-Yu Chin. Melissa Hulting at the US EPA and Jon Dettling at the GLC provided helpful comments on methodology. We thank the US Environmental Protection Agency's Great Lakes National Program Office, and the Great Lakes Commission's Great Lakes Air Deposition Program for their financial support.

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