TRENDS AND MASS BALANCE OF FLAME RETARDANT CHEMICALS IN A NEW BUILDING

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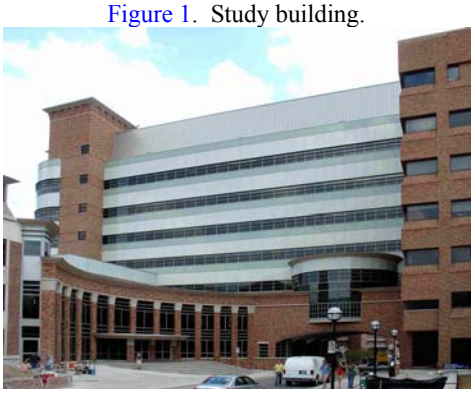
Abstract
Brominated flame retardants (BFRs), including polybrominated diphenyl ethers (BDEs) and tetrabromobisphenol-a (TBBPa), are known to be widely distributed in indoor environments although quantitative information regarding emission sources and exposure pathways remain elusive. This study describes the evolution and mass balance of BFRs in a newly constructed multiple-use building. The building was monitored prior to occupancy, and then every 2-3 months for over a year, for 21 BDE congeners and TBBPa in dust, air, and ventilation filters. We observed large increases of BFRs concentrations, with the most striking result being the rapid increase of BDE-209 in dust which rose exponentially from low levels and approached quasi-steady state levels after about eight months; airborne levels rose to steady levels after about five months. BDEs typical of the penta- and octa-formulations also rose dramatically, despite the voluntary ban on these products in North America. A mass balance among indoor and outdoor air, settled (floor) dust, and ventilation system filter dust quantifies transfers of BDEs from their primary sources to these compartments.

Introduction
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 numerous BFR-containing materials, and several studies have shown elevated levels of BFRs in buildings.[1] Buildings contain a large reservoir of these persistent and bioaccumulative chemicals, and collectively represent an important environmental source of BFRs.

This study has the following objectives: characterizing indoor levels of BFRs in a newly constructed commercial building; trending concentrations as the building is completed, furnished and occupied; and providing a mass balance among key indoor compartments. We construct time trends of BFRs by periodically collecting and analyzing dust, airborne particles and vapor-phase samples in the building. We also measure BFRs in ventilation filters and outside air. These data are used to show the evolution of BFR concentrations and a mass balance among the building compartments.

Materials and Methods
BFR concentrations in floor dust and air were tracked over a 15-month period in a newly-constructed mixed-use 7-floor building containing offices, classrooms, cafeterias, computer rooms, and laboratories (Figure 1). Monitoring started just prior to occupancy in Aug. 2006, and was repeated seven times subsequently until November 2007. Most samples were collected in an office suite on the 6th floor. We have previously described air and dust sampling in this building.[2] In brief, dust samples were collected by vacuuming a 1 m^2 area. Vapor and particulate samples were collected using a medium-flow sampling system over a 1 week period on filter and PUF adsorbent, with a typical sample volume of ~150 m^3. We also quantified sampling precision using side-by-side tests, and also evaluated the possibility of breakthrough of vapor phase BFRs using back-up adsorbents. Other

Figure 1. Study building.



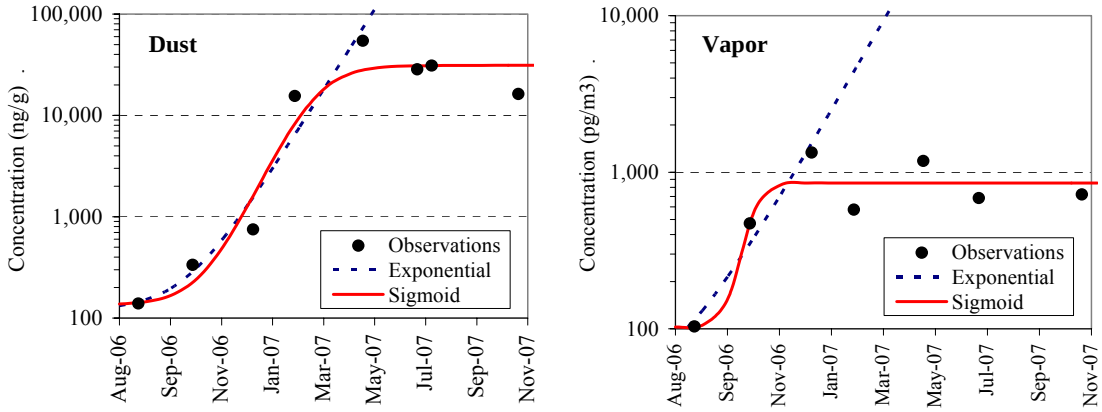
measurements included air exchange rates using perfluorocarbon tracers (PFTs), VOCs using passive thermally-desorbable Tenax-GR samples over the 1-week period analyzed by GC/MS,[3,4] and a detailed walkthrough survey. We collected both unused and used heating, ventilating and air conditioning (HVAC) filters for BFR analysis. The building's HVAC system utilized panel filters (5 cm deep pleated, 30% efficiency), followed by bag filters (53 cm deep, 65% efficiency). Each filter type was analyzed separately using composite samples (pieces of different sections of randomly selected filters). Pilot studies showed low extraction efficiencies for the bag filters, thus additional steps were taken, including separate extraction and analyses of the filter fabric and the backing layers. This yielded acceptable recoveries for all target congeners except BDE-49.

Twenty BDE congeners and tetrabromobisphenol-A BFRs were determined by Soxhlet extraction of samples using hexane and dichloromethane, cleaning and fractionating, and GC/MS analysis (Agilent 6890/5973, Palo Alto, CA) in negative chemical ionization mode. A separate run was made for BDE-209 using a faster temperature program that avoided decomposition of the congener. Calibration standards included TBBPa and BDEs 17, 28, 75, 49, 71, 47, 66, 100, 99, 85, 154, 153, 138, 166, 183, 190, 203, 208, 207, 206 and 209. For quality assurance purposes, each sample batch included blanks and checks using standard reference dust (NIST, Standard Reference Material 2585 "Organic Contaminants in House Dust"), as well as tests of linearity, drift, and spike recovery. These procedures are detailed elsewhere.[5,6] Replicate samples were averaged, and the sum of the 21 measured BDE congeners is reported as Σ_{21}BDE. BDEs concentrations in dust and vapor in the building were fit to trend models using exponential and logistic sigmoid forms. The Σ_{21}BDE mass balance used actual and a few estimated HVAC and building parameters.

Results and Discussion

Trends in settled dust. We detected BDEs-47, 99, 100, 209 and TBBP-A in most dust samples, and traces of BDEs-28, 49, 66, 85, 153, 154, 206, 207 and 208 in several samples. Figure 2 (left panel) shows trends of Σ_{21}BDE concentrations in dust and airborne vapor in the building. Prior to building opening (August 2006), BFRs in floor dust were at very low levels. For the next eight months, concentrations increased with a doubling time of 23 days (based on the exponential model fitting for Σ_{21}BDE). TBBPa also increased from trace levels at the study start (0.4 ±0.1 ng g^{-1}) to 270 ±250 ng g^{-1}. After May, 2007, concentrations in dust stabilized. This rapid increase and stabilization fits a logistic (sigmoid) model, and shows that nearly a year is required for dust samples to achieve a steady-state PBDE level. Each BDE congener and TBPPa showed comparable (100 to 1000-fold) increases over the study period. The compositions of BFRs in dust over the study period remained similar, primarily reflecting the commercial penta- and deca-formulations. BDE-209 was the predominant congener, increasing from 82 ng g^{-1} at the beginning of the study, to levels as high as 48,000 ng g^{-1} at mid-study, before an apparent stabilization at 6,900 to 9,300 ng g^{-1} at the end of the study. This result is significant in showing the evolution of BFR levels in a new building, and is one of the first results of its kind in the literature.

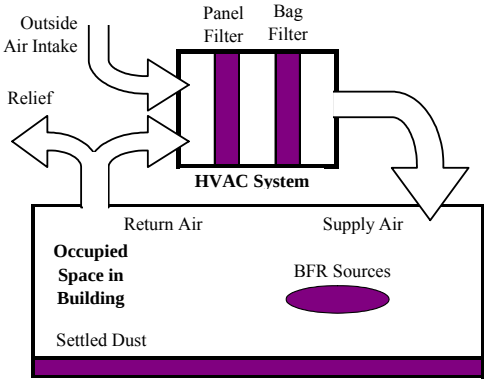
Figure 2. Σ_{21}BFR levels in dust and airborne vapor, and fits to exponential and sigmoid models..



Trends in indoor air. Indoor airborne concentrations of BFRs also fit a logistic trend (Figure 2, right panel), but more rapidly approached a steady level, reaching a steady-state level about five months after the building opened. The rate of increase was slightly slower (doubling time of 31 days). Indoor air was dominated by tetra- and penta-congeners, mostly BDEs-47, 99 and 71, though tri- through hexa-BDEs were detected in most samples. Vapor-phase Σ_{21}BDE concentrations increased from about 100 pg m^{-3} at the beginning of the study, a typical urban outdoor air concentration,[7] to about 930 pg m^{-3} at the end of the study. This trend, and the 10-fold increase in airborne BFR levels, are also striking.

HVAC filters. Traces of BFRs (Σ_{21}BDE concentration of 162 ng g^{-1}) were found in new HVAC panel filters, possible a result of storage or transit since these materials were not used in their manufacture. Filters used for three months, taken 1 year after the building opened, showed dramatic increases, e.g., the Σ_{21}BDE concentration was 10,600 ng g^{-1}, equivalent to a loading of 1.37 mg m^{-2} or a mass of 39 mg sequestered in the filter bank. Unused bag filters also showed traces of BFRs (Σ_{21}BDE concentration of 25 ng g^{-1}). After one year of use, concentrations increased to 6,600 ng g^{-1}, equivalent to 1.23 mg m^{-2} or 201 mg of BDEs in the filter bank, similar to the loadings on panel filters. The two filter types tended to collect different congeners, with the largest differences for BDE-99, which was preferentially collected on the panel filter, and BDE-209 and octa- and nona-congeners, which were preferentially collected on the bag filter.

Figure 3. Pathways and compartments considered in mass balance.



Mass balance. We calculated a BFR and PM mass balance among the compartments depicted in Figure 3 using the following assumptions: HVAC filters were exposed to an average PM_{10} level of 13 μg m^{-3}; 30% outside air was used (the remainder recirculated); panel and bag filter particle removal efficiencies were typical for the filters used (Fisk et al. 2002); the HVAC duty cycle was 70%; and the HVAC flow rate was 22 m^3 s^{-1}. Dust accumulations (loadings) were estimated as 600 g of PM_{10} in the panel filters over 3 months, and 4,460 g PM_{10} in the bag filters over 1 y. The 38 mg of Σ_{21}BDE determined for the panel filters (based on the measured area concentration multiplied by the filter area) divided by 600 g of PM gives a concentration in collected PM of 64 μg g^{-1}. For the bag filters (where 201 mg of Σ_{21}BDE was accumulated), the result is 45 μg g^{-1}. These values exceed floor dust measurements by a factor of 1.5-2, but they appear reasonable since HVAC filter dust excludes most sand, soil and other coarse, low sorption-capacity materials found in floor dusts. Assuming that BFR concentrations followed the trend in Figure 2, the HVAC filter combination would collect 420 mg y^{-1} of Σ_{21}BDE. To compare and confirm the BDE accumulations on HVAC filter dust, we calculated BDE fluxes through the filters using (independent) indoor and outdoor air measurements. With the measured indoor (930±290 pg m^{-3}) and outdoor (320±270 pg m^{-3}) concentrations, then air passing through the HVAC filters had a Σ_{21}BDE concentration of 750±220 pg m^{-3}. With complete capture of vapor and particulate phase BDEs on the HVAC filter dust, then 370 mg y^{-1} of Σ_{21}BDE would be collected by the HVAC filters, an estimate within 12% of that estimated using HVAC filter measurements. The agreement between airborne and HVAC filter measurements is remarkable. It implies that the HVAC filters capture essentially all of the airborne BDE passing through the filters, including vapor and particulate phases.

For floor dust, we applied the measured Σ_{21}BDE concentration of 33 μg g^{-1}, the measured dust loading of 1 g m^2, and assumed that the dust loading reflected 2 months of accumulation. For the office area of 3690 m^2, this represents a generation rate of 730 mg y^{-1}, not quite twice the airborne flux.

Synthesis. The literature contains little information regarding BDE levels in office environments, and BFR sources and fate are poorly understood. Our measurements of settled dust and indoor air in the case study

building (at the end of the study when levels stabilized) are in the upper range of levels previously reported, which is not too surprising given the density of electronic items, e.g., computers, in offices. On the other hand, high levels were not expected since this building was constructed and furnished after the voluntary ban in the USA of the penta- and octa-mixtures. The results suggest that workplace exposures (in offices) may be more important than previously recognized.

The mass balance indicates that HVAC filters, if suitably sampled, extracted, and analyzed, can be used to estimate airborne BDE levels. However, representative filter samples must be obtained (composite samples are recommended), filter efficiency must be high, corrections for background levels may be needed, and it may be difficult to extract and analyze BDEs from the filter matrix. Important transfers of BDEs from their primary sources occur via floor dust, air, and HVAC filters. Building filters and vacuum cleaner dust may need special handling to minimize exposures and environmental releases.

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