THE CONTRIBUTION OF VARIOUS INDOOR MICROENVIRONMENTS TO OUTDOOR CONTAMINATION OF PBDES AND OTHER HALOGENATED FLAME RETARDANTS IN STOCKHOLM, SWEDEN

Newton S*, Sellström U, de Wit CA

Department of Applied Environmental Sciences (ITM), Stockholm University, Sweden

Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardant (FR) chemicals that are used in a great number of products but also are found ubiquitously in the outdoor environment, including far from known sources[1]. PBDEs come in three commercial mixes known as Penta, Octa, and Deca. The Penta and Octa products have been banned globally under the Stockholm Convention and Deca has been banned for use in electronics in Europe[2]. However, the use of chemicals as FRs continues. PBDEs have been or are being replaced with new substances about which little is known or old substances that may have found new use[3]. Among the known PBDE replacements are 2-ethylhexyl 2,3,4,5-tetrabromobenozate (TBB) and di (2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH) which together replace the PentaBDE mixture and 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) which is replacing the Octa mixture. DecaBDE is being replaced by decabromodiphenyl ethane (DBDPE). Older FRs which are suspected to have recurring use include hexabromobenzene (HBB), pentabromotoluene (PBT), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH), and Dechlorane Plus. There are also a few FRs about which little has been reported including hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO) and octabromotrimethylphenylindane (OBIND).

The pathways by which FRs escape from the product and reach the outdoor environment has not been fully elucidated. Indoor air is known to contain higher levels of FRs than outdoor air due to the presence of flame retarded products but the percentage of the total outdoor inventory that comes from the indoor environment is not well understood. Björklund et al.[2] conducted a study in which outgoing air from ventilation systems was sampled and used together with published values of outdoor concentrations to estimate the contribution of the indoors to outdoor contamination of PBDEs. Their study estimated this contribution to be close to 90%. The current study seeks to expand on that study by sampling urban and rural outdoor air concurrently with indoor and outgoing air and separating gaseous phase compounds from those attached to particles. Also, soil and indoor dust from the air sampling sites were included and the number of analytes was expanded to include the FRs listed above.

Materials and Methods

Sampling

Dust, indoor air, and ventilation system air was sampled from four apartments, four furniture and electronic stores, two schools, four offices, and two laboratories during the winter and spring 2012 from various areas of Stockholm, Sweden. Outdoor air samples were taken at nine locations in total, creating two transects of the city: five in a north-south direction and five in an east-west direction with the center location in the city being the same for the two transects (Figure 1 below). Each transect goes from rural to urban to rural. Top soil samples were collected at each outdoor site as well.

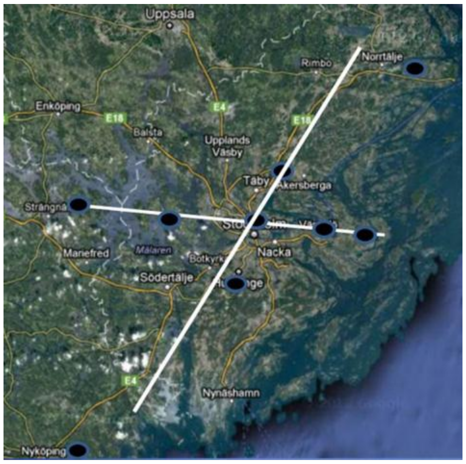

Figure 1 - Map of outdoor sampling sites

Further details about indoor air and dust sampling equipment and methodology as well as QA/QC can be found in Thuresson et al.[4] but are described here briefly. Indoor and ventilation system air samples were collected using a low volume active air pump (Leland Legacy, SKC Inc., Eight Four, PA, USA) branched to connect to four sampling trains. The pump was run at 12 L/minute (3 L/minute for each train) for 24 hours. The trains contained a glass fiber filter (GFF, 25mm diameter) followed by two polyurethane foam plugs (PUFs, 15mm diameter). Air from ventilation systems was sampled concurrently with indoor air at a point just before the air left the building. Dust was collected after air sampling was complete from the same area as the indoor air using pre-weighed cellulose filters in styrene-acrylonitrile holders that fit into a polypropylene nozzle connected to an industrial strength vacuum cleaner. From furniture and electronic stores, separate dust samples were collected directly from products and from settled dust around the products. Dust from apartments, offices, and schools was collected at least one meter above the ground and not directly from furniture or electronic products. Cars were sampled as well, however for dust only. Separate dust samples were taken from the upholstery and from the dash of the cars.

Outdoor air samples were collected using a high volume pump (~15-25 m^3/hour) with a GFF (25 cm diameter) and two PUFs. More details about sampling equipment and cleaning procedures can be found in Sellström et al.[5] Samples were taken for 48 hours (750 – 1200 m^3). Top soil (top 5 cm) was sampled from each location as well.

Extraction, Clean-up, and Instrumental Analysis

A previously developed method for fractionation and clean-up of PBDEs and novel FRs was adapted to include HBB, PBT, TBECH, Dechlorane Plus, HCDBCO, and OBIND by checking the elution of these compounds on the fractionation scheme[6]. The sampling method was then tested for all compounds by spiking the GFFs, running the sampler for 24 or 48 hours, and then analyzing the filter, front PUF, and back PUF separately.

The analytical method is given in detail in Sahlström et al.[6] but briefly described here. Dust, indoor air, and ventilation system samples were extracted using using 18 mL dichloromethane (DCM) in an ultrasonic bath for 30 minutes. The extraction was repeated and the extracts combined. Outdoor air and soil samples were extracted for 24 hours in Soxhlet extractors with 450 mL DCM. Filters and PUFs from air samples were analyzed separately. All extracts were solvent changed to *n*-hexane and reduced to 1 mL. The extracts were then fractionated into three fractions on an SPE column containing 2 g silica (deactivated with 2.5% H_2O) and 1 g Na_2SO_4. Fraction 1 was eluted with 30 mL *n*-hexane and contained PBDEs, DBDPE, TBECH, PBT, HBB, DP, HCDBCO, and OBIND. Fraction 2 was eluted with 10 mL 5% diethyl-ether (DEE) in *n*-hexane and contained TBB, TBPH, and BTBPE. Fraction 3 was eluted with 10 mL 50% DEE in *n*-hexane and contained the HBCDs. Fractions 1 and 3 were further cleaned using concentrated sulfuric acid while fraction 2 was eluted through a 0.5 g aminopropyl (NH_2) column with 12 mL *n*-hexane. Instrumental analysis was performed using a Trace GC Ultra coupled to a DSQ II MS (Thermo Scientific, Waltham, USA) operating in ECNI mode with ammonia as the moderating gas.

Results

Results from the filter spiking experiment show little to no breakthrough to the second PUF for most compounds (Figure 2 below). The only problematic compound was TBECH which had a total recovery of about 50% of which 7% was found on the second PUF indicating that some of this compound may be blowing through both PUFs. The least volatile compounds, i.e. BTBPE, OBIND, and BDE 209, stayed mostly on the filter. This indicates that blow-off of BDE-209 from particles to the PUF is unlikely.

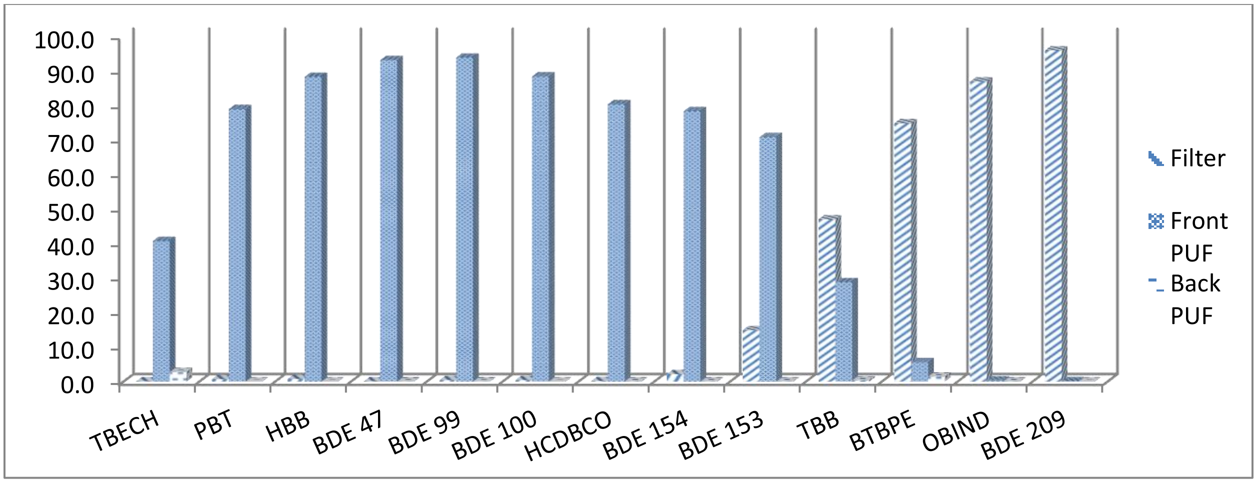

Figure 2 - Results from a filter spiking experiment to check sampling method.

First results from indoor air samples show detection of TBECH, HBB, PBT, Dechlorane Plus, TBB, and all PBDEs in offices and laboratories (Figure 3).

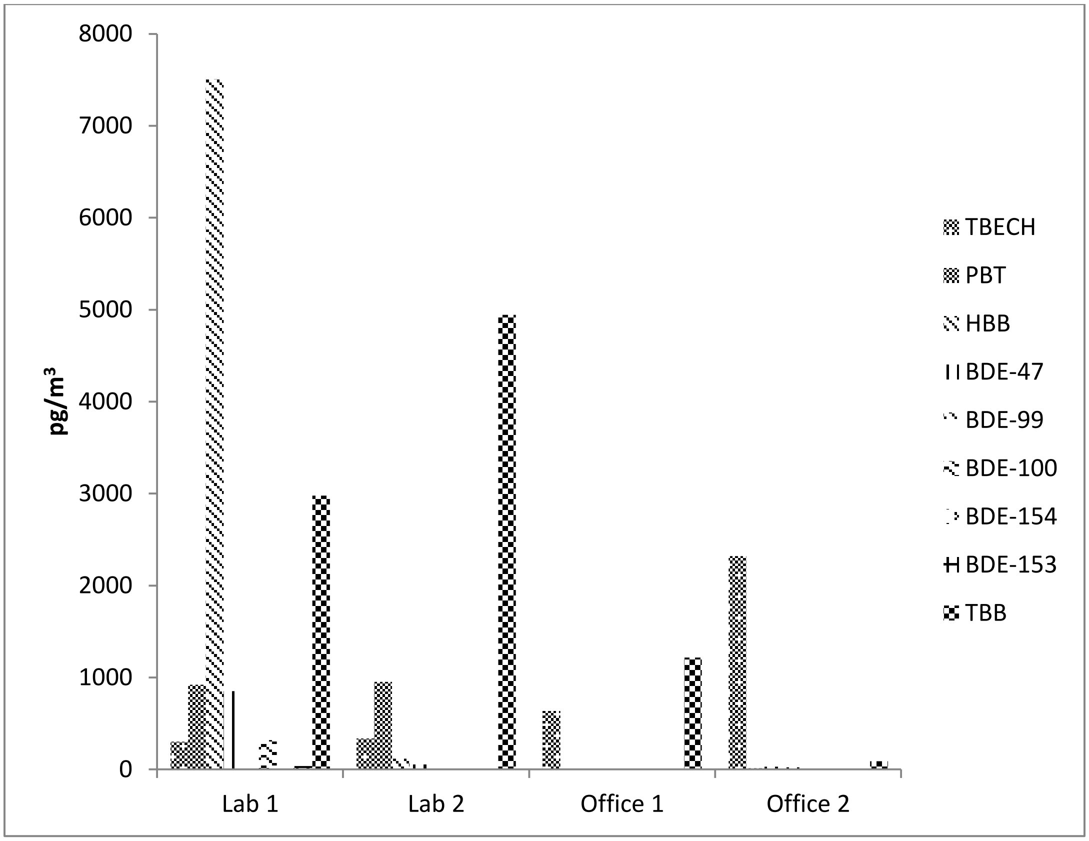

Figure 3 - Levels of BDEs and some other halogenated flame retardants in offices and laboratories from the same building.

TBB was a predominant pollutant in indoor air in this building with levels exceeding those of PBDEs. HBB, PBT, and TBECH were detected in all samples as well but at lower levels than TBB, except very high levels of HBB in lab 1. Dechlorane Plus was detected in the offices but not the labs. HCDBCO and OBIND were not detected in air but this was expected because of their low volatility.

These FRs are found in the outdoor environment[1, 7,.8] however it is not clear to what extent the indoor environment contributes to the contamination of the outdoor environment. Ventilation samples must be analyzed to compare indoor and outgoing concentrations and outdoor air samples must be analyzed to establish outdoor concentrations. Dust samples may reveal use of non-volatile flame retardants that were not detected in air samples. Analyzing these media together will draw a better picture of the path FRs take from product to environment, which is necessary in order to properly access human exposure to these substances.

References

1. de Wit, C. A.; Herzke, D.; Vorkamp, K., Brominated flame retardants in the Arctic environment -- trends and new candidates. Science of the Total Environment 2010, 408 (15), 2885-2918.
2. Björklund, J. A.; Thuresson, K.; Cousins, A. P.; Sellström, U.; Emenius, G.; de Wit, C. A., Indoor Air Is a Significant Source of Tri-decabrominated Diphenyl Ethers to Outdoor Air via Ventilation Systems. Environmental Science & Technology 2012.
3. Ma, Y.; Venier, M.; Hites, R. A., 2-Ethylhexyl Tetrabromobenzoate and Bis(2-ethylhexyl) Tetrabromophthalate Flame Retardants in the Great Lakes Atmosphere. Environmental Science & Technology 2011, 46 (1), 204-208.
4. Thuresson, K.; Bjorklund, J. A.; de Wit, C. A., Tri-decabrominated diphenyl ethers and hexabromocyclododecane in indoor air and dust from Stockholm microenvironments 1: Levels and profiles. Science of the Total Environment 2012, 414, 713-721.
5. Sellström, U.; Egebäck, A.-L.; McLachlan, M. S., Identifying source regions for the atmospheric input of PCDD/Fs to the Baltic Sea. Atmospheric Environment 2009, 43 (10), 1730-1736.
6. Sahlström, L.; Sellström, U.; De Wit, C. A. In Clean-Up Method for Determination of PBDEs, HBCDs and Emerging BFRs in Dust, Dioxin 2011, 2011.
7. Tomy, G. T.; Pleskach, K.; Arsenault, G.; Potter, D.; McCrindle, R.; Marvin, C. H.; Sverko, E.; Tittlemier, S., Identification of the Novel Cycloaliphatic Brominated Flame Retardant 1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane in Canadian Arctic Beluga (Delphinapterus leucas). Environmental Science & Technology 2007, 42 (2), 543-549.
8. Sagerup, K.; Herzke, D.; Harju, M.; Evenset, A.; Christensen, G. N.; Routti, H.; Fuglei, E.; Aars, J.; Strom, H.; Gabrielsen, G. W., New Brominate Flame Retardants in Arctic Biota. Norweigen Institute for Air Research (NILU): 2010.