

SOURCES AND MULTIMEDIA PARTITIONING OF BFRs INDOORS

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Introduction

Flammability standards ensure that, within North America and the U.K. (at least), foam furniture, electrical and electronic equipment and other products contain flame retardants (FRs). It's well known that semi-volatile (SVOCs) FRs, whether additive or reactive, migrate or abrade from the materials to which they were added. Allen et al. (2008) [1]; Harrad et al. (2006) [2]; de Wit et al. (2013) [3], have reported that sources of PBDEs and HBCDD to indoor air and/or dust include electric and electronic equipment, foam furniture and bedding. As expected, the dominant product source appears to depend on the room's furnishings (e.g., bedding in the bedroom or a TV and other electronic equipment in the living room), as well as dwelling characteristics such as air exchange rate. Data on product sources of "novel" brominated flame retardants (NBFRs) has not yet been reported.

Following emission from a product, SVOC FRs undergo multimedia partitioning within a dwelling, that influences their concentrations, fate and persistence. The fugacity paradigm predicts partitioning according to the organic carbon fraction and/or lipid content of each indoor compartment. Data support this prediction to varying extents (e.g., Weschler & Nazaroff (2010) [5], Zhang et al. (2006) [6]).

The goals of this research were to identify products that are dominant emission sources of PBDEs and NBFRs to indoor environments focusing on homes in Toronto, Canada, and secondly, to examine the multimedia behavior of these compounds indoors.

Materials and methods

To address the first goal, floor dust (2 m² floor area vacuumed, dust collected in nylon sock, sieved to <150 µm) from the most used room (usually TV room) and product surface wipes (medical wipes impregnated with isopropyl alcohol) were taken in 35 homes in Toronto during August 2012. The products wiped had Br levels > 0.1% as determined using XRF.

To address the second goal we conducted an intensive sampling campaign of 5 homes over 4 consecutive days in August 2010 and September 2011. Floor dust, window wipes and dermal wipes of the occupants were taken in 2 to 3 locations per home. In addition, measurements were made of air exchange rates, room volumes, room contents, etc. All samples were analyzed for the presence of 12 NBFRs and 12 PBDE congeners. Samples were extracted using pressurized solvent extractor, with cells packed with Sodium sulfate and florisil. Analysis was conducted on a GC-ECNI/MS, using a 15 m DB-5 column.

Results and discussion

XRF screening of >2000 products indicated the highest Br content of 4-13% in TV cases. Other items with elevated Br levels included a food dehydrator, heater, and multiplug and power surge bar. From the 35 home surface, we found that surface wipes of electronic products were dominated by BDE-209, 206 and 207 and numerous PBDE replacements, namely DBDPE, TDCPP, TBB, TBPH, HBB, PBEB, OBIND and syn-dechlorane plus. House dust was highest in BDE-99, 47, 209, TDCPP, TBB, TBPH, DBDPE and OBIND.

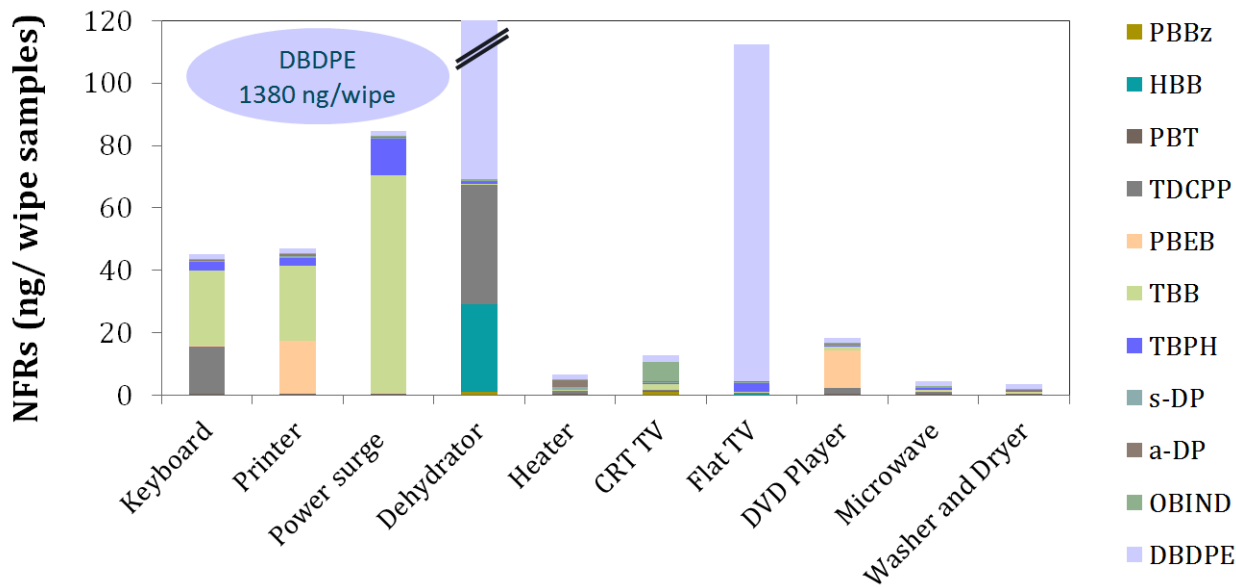


Figure 1 HFRs in product wipes

PBDE concentrations in dust were generally 10 times higher than NBFrs. Using Principle Components Analysis (PCA) (Figure 1), we found that the chemical profiles in dust most closely resembled that of products with lower molecular weight NBFrs, in particular TDCPP and TBB, which is indicative of flexible polyurethane foam found in foam furnishings rather than electronics. Chemical profiles of only two house dust samples were similar to NBFrs profiles of electronic products in those rooms. We conclude that HFRs in the most used room (generally the living room) of these 35 homes was not dominated by NBFrs in electrical equipment, but rather was consistent with NBFrs added to flexible polyurethane foam furniture.

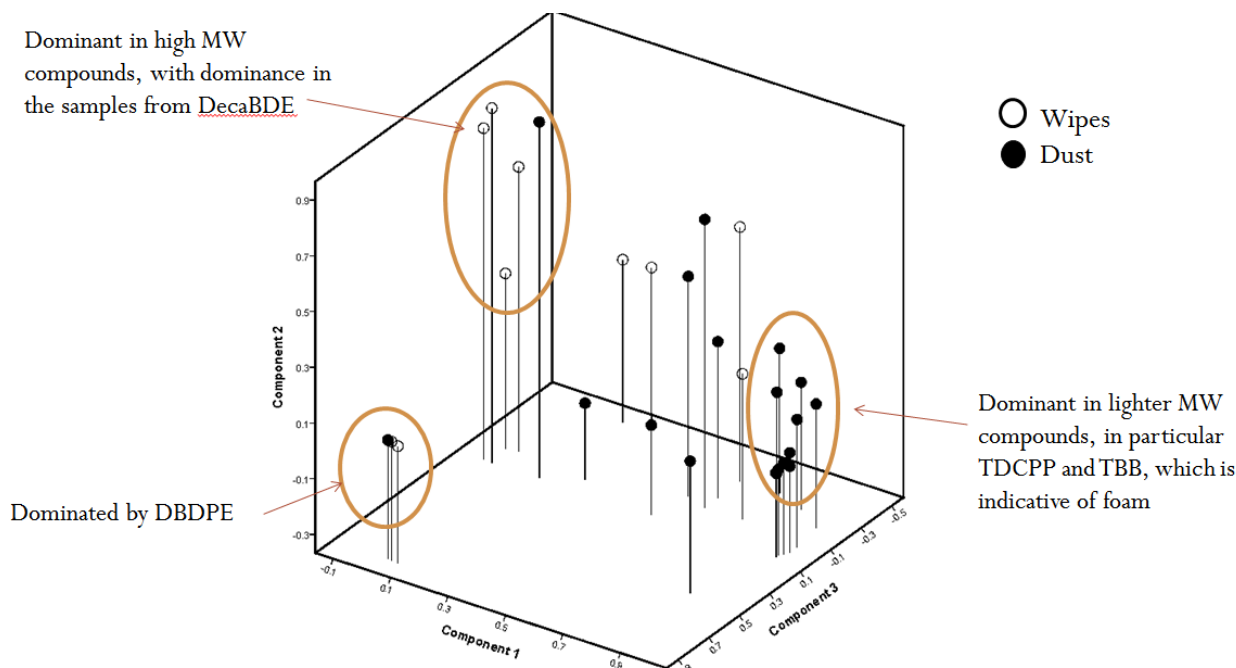


Figure 2 PCA for product wipes (white circles) and dust samples (black circles) collected from homes in Toronto

The intensive sampling campaign of 5 homes showed that concentrations of PBDEs and NBFrs varied as much between rooms as between homes. Concentrations were high in bedrooms and living rooms relative to kitchens. This observation is consistent with the number of potential sources in each of those rooms as well as the cleaning frequency. Concentrations in washrooms were lower than other rooms which is consistent with the lack of potential sources (e.g. few electronics and foam products in washrooms).

Many of the same NBFrs were present in both window film (Figure 2) and dust samples collected in the Toronto intensive study (TDCPP, PBEB, BDEs 47, 100, 99, 183, 209). Heavier PBDEs dominated in the window film profiles, with common congeners (hepta-, octa- and nonaBDEs) associated with photolytic debromination of decaBDE.

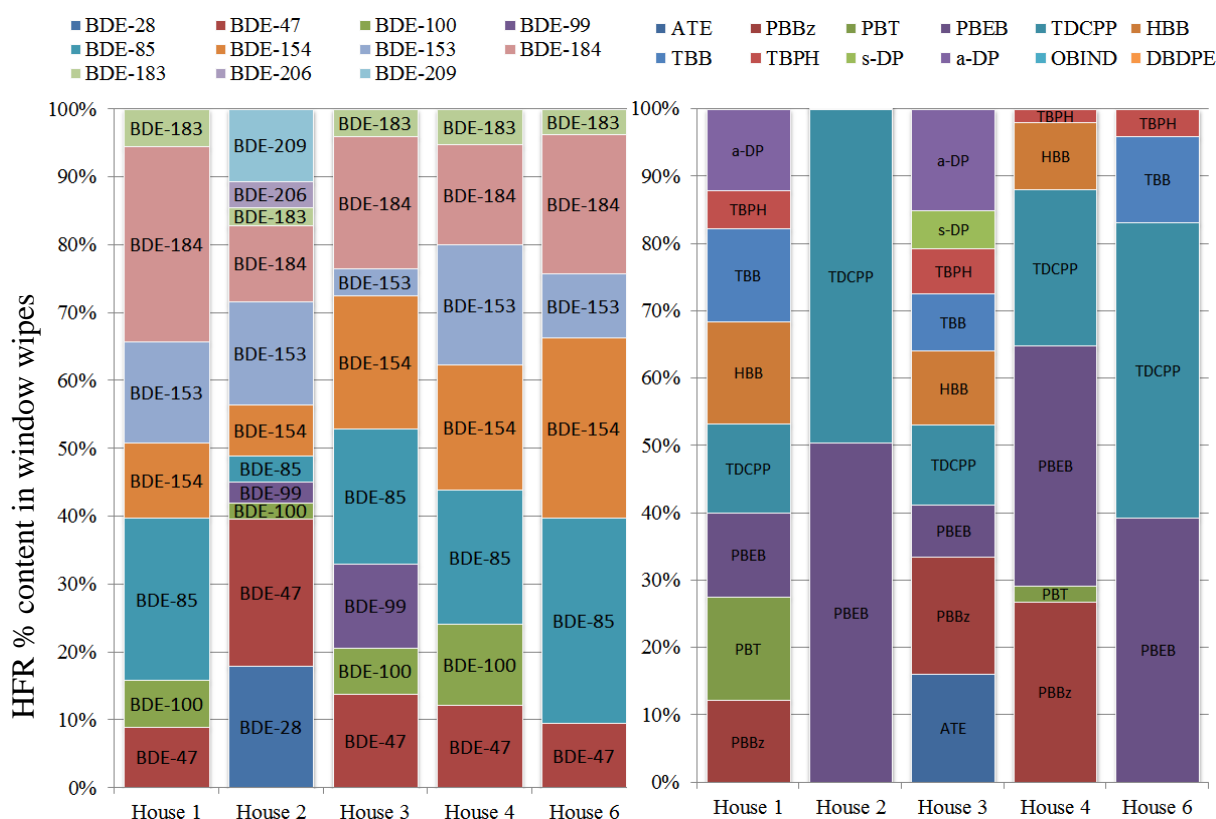


Figure 3 HFR contributions (%) in window films

PCA was also conducted for the intensive sampling campaign. The results showed that dust was dominated by lighter molecular weight NBFrs (e.g. TDCPP, TBB), which are consistent with emissions from foam applications. Window films were primarily driven by the presence of octaBDE and decaBDE congeners, as well as OBIND, DBDPE, and to some degree TDCPP and hence resembled both air and dust signatures, acting as an intermediate between the two. In comparison concentrations in dermal wipes were dominated by PBDE congeners 47, 99, and 100, producing a distinct signature from all other samples. The dermal signatures are more reflective of the dust samples, containing similar HFRs, which is expected because of hand contact with dusty surfaces. However the differences in dermal wipe profiles from dust could be an artifact of low NBFr detection frequencies compared to PBDE congeners. The predominance of these PBDE congeners in the dermal wipes is consistent with air, dust and serum measurements collected from a US cohort [7].

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