PBDES IN DUST: BETWEEN- AND WITHIN-HOME VARIATION LINKED TO XRF CHARACTERIZATION OF CONSUMER PRODUCTS

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Abstract

Efforts to associate PBDE levels in dust with the contents of homes have had limited success. One possible explanation is exposure misclassification due to large differences in PBDE concentrations between otherwise similar household products. As quantification of PBDEs in products is not feasible during home visits, we used a noninvasive surrogate, X-ray fluorescence (XRF), to quantify bromine concentrations. In a validation study, XRF-measured bromine in furniture foam was highly correlated with PBDEs measured by GC/MS ($r=0.96$, $p<0.001$). In a field study, we used XRF to measure the bromine content of household products in two rooms for each participant. We sampled dust from the same rooms and measured PBDE levels via GC/MS. XRF quantified bromine levels in furniture were correlated with pentaBDEs in dust in both bedrooms and living rooms ($r=0.65$, $p=0.002$; $r=0.49$, $p=0.03$). Bromine levels in bedroom electronics were highly correlated with decaBDEs in dust ($r=0.76$, $p<0.001$). Our study design allowed us to compare PBDE levels in dust between rooms and over two seasons. PBDE concentrations were correlated over the two seasons, with no statistically significant differences over time.

Introduction

Polybrominated diphenyl ethers (PBDEs) are commonly used as flame retardants in household consumer products such as electronics, certain fabrics, and furniture containing polyurethane foam (PUF). In principle, it should be possible to link PBDE concentrations in air and dust samples collected from indoor spaces to the consumer products in those spaces. However, previous attempts—relying primarily on counts of electronics and PUF-containing furniture—have had only modest success.[1-5] We hypothesized that this failure is due to wide variation in PBDE content between otherwise similar objects (e.g., chairs), leading to exposure misclassification and bias toward the null. We therefore employed a non-invasive, potential surrogate for PBDEs: the bromine content of objects measured using X-ray fluorescence (XRF). The study provided an opportunity to investigate three other important questions about household dust: the variation in PBDE dust concentrations within homes, the variation over time, and the dependence on method of collection.

Materials and Methods

We validated the XRF method using three samples of carpet padding and ten samples of foam collected from office chairs. A portable XRF analyzer (Innov-X Systems) was used to obtain ten-second bromine measurements of each sample (typically ten readings per sample). The samples were then analyzed for 36 PBDE congeners via gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC/MS).

The field investigation consisted of two visits to the same residences in the Greater Boston area (Massachusetts, USA), the first conducted from January to March 2006 (20 homes) and the follow-up conducted from October to November 2006 (19 homes). During both visits, we collected dust samples from measured areas of the main living area and bedroom using a Eureka Mighty-Mite canister vacuum cleaner and a crevice tool fitted with a cellulose extraction thimble.[5,6] We also collected dust from the participants' vacuum cleaner bag. The bedroom and main living area were selected as the two rooms that (a) would likely have the largest number of PBDE sources and (b) where participants would likely spend the majority of their time. A questionnaire was used to collect information about housing characteristics, household cleaning habits, and a detailed inventory of electronics and furniture in the bedroom and main living area. Dust samples were sieved (<500 µm) and analyzed via GC/MS.

During the second visit, the portable XRF was used to measure bromine in each consumer product in the bedroom and living room that could potentially act as a PBDE source to the indoor environment. Products were divided into sub-items to improve overall characterization. For instance, for a couch with multiple back and seat cushions, each cushion was analyzed separately as a sub-item. XRF measurements of electronics were obtained on the exterior plastic casings. We also measured the volume and surface area of items that were determined to have detectable levels of bromine. We constructed indices by multiplying bromine concentration by surface area, separating furniture and electronics.

Results and Discussion

In the validation phase, concentrations of PBDEs measured by GC/MS were strongly correlated with bromine concentrations measured via XRF: r=0.98 for the chair foam samples, r=0.97 for the carpet pad samples. These results are consistent with those of Li et al using KBr samples.[7] We are continuing the validation process with an assessment of hard plastics.

PBDE concentrations in dust separated into penta, octa and deca formulations as determined by factor analysis. On average, concentrations of pentaBDE and decaBDE were higher in the living room than the bedroom (Table 1). Results are also shown for bistribromophenoxyethane (BTBPE). By percent of total PBDEs, the dust samples were generally dominated by BDE 209, followed by BDEs 99, 100 and 47; however, the relative contributions of each congener vary substantially by sample. The highest recorded value of total PBDEs in household dust, 269,300 ng/g (mostly BDE 209), was found in one participant's vacuum bag. Concentrations were moderately correlated between rooms: r=0.45 (p=0.046) for penta BDE, r=0.48 (p=0.03) for octaBDE, r=0.56 (p=0.01) for decaBDE. These results suggest variation between rooms in the same home.

Investigator-collected dust samples were generally higher than concentrations in participants' vacuum cleaner bags. PBDE concentrations in vacuum cleaner bags were only moderately correlated with investigator-collected dust concentrations in rooms for pentaBDE and octaBDE (e.g., r=0.39, p=0.09, bedroom); results were stronger for decaBDE (r=0.77, p<0.001, bedroom). Vacuum cleaner bags may not be a suitable surrogate for researcher-collected dust; decaBDE may be an exception.

There was little difference in PBDE concentrations in dust between the two seasons. In bedrooms, pentaBDE was highly correlated between seasons (r=0.92, p<0.0001); the correlation coefficient for decaBDE was 0.57 (p=0.02). Correlations for living rooms was less strong: r=0.49 (p=0.05) for pentaBDE, r=0.59 (p=0.02) for decaBDE.

Area air samples were collected from the same rooms as the researcher-collected dust during the first (winter) sampling season.[1] For the bedroom, pentaBDE congeners were moderately correlated in air and dust (r=0.62, p=0.01), but not correlated for decaBDE (r=-0.27, p=0.25). There were no significant correlations between air and dust in the living rooms for either congener group.

XRF quantified bromine in furniture was a significant predictor of pentaBDEs in dust for both bedrooms and living rooms. Correlation coefficients between XRF measures (bromine concentrations*surface area) and dust concentrations were 0.62 (p=0.002) for the bedroom and 0.49 (p=0.02) for living rooms. For decaBDEs, we compared XRF measured bromine in electronics and decaBDE concentrations in dust. For bedrooms, we found a strong correlation (r=0.76, p=0.001). For living rooms, the correlation was not significant.

In all four scenarios, use of the XRF was an improvement over using counts of products. The correlations observed between XRF measurements and pentaBDEs indicate that the XRF is a useful tool for identifying sources of pentaBDEs in household furniture. For bedrooms, XRF measurements in electronics were a reliable predictor of decaBDEs in dust. For living rooms, use of XRF was an improvement over counts of electronics, but it was not statistically significant. This latter result may be partly due to further exposure misclassification: XRF does not distinguish between different brominated flame retardants. For example, tetrabromobisphenol-A (TBBPA) is used in ABS plastics in computers and other household electronics; the back casings of television sets primarily use decaBDE. The results in the bedroom, largely driven by bromine levels in television sets, were likely not affected by this misclassification. We are currently investigating the contribution of different electronic products to decaBDE levels in dust.

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Table 1. Summary statistics for PBDEs and BTBPE (ng/g) in Winter 2006 dust

	Living Room	***Bedroom***	***Vacuum Bag***
PBDE group	**GM (GSD)**	**GM (GSD)**	**GM (GSD)**
pentaBDE	5462 (2.9)	2613 (3.8)	1183 (3.5)
octaBDE	50 (3.5)	55 (5.8)	35 (3.4)
decaBDE	4702 (4.4)	1866 (5.6)	1939 (5.6)
BTBPE	16 (6.3)	8 (12.3)	11 (3.9)

GM=geometric mean; GSD=geometric standard deviation
pentaBDE=BDE 17,28/33,47,49,66,75,85/155,99,100,138,153,154;
octaBDE=BDE 183,196,197,203;
decaBDE=BDE 206,207,208,209

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