Linking PBDEs in House Dust to Consumer Products using X-ray Fluorescence

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Introduction. Polybrominated diphenyl ethers (PBDEs) are commonly used as flame retardants in household consumer products such as electronics, furniture containing polyurethane foam (PUF), certain fabrics, and a wide range of other products. 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, the attempts of several groups to do so—relying primarily on counts of electronics and PUF-containing furniture—have resulted in only modest success (Harrad et al., 2004; Stapleton et al., 2005; Wilford et al., 2005; Allen et al., 2006; Wu et al., 2006). Since product counts do not account for potentially large differences in PBDE content, a better method of characterizing PBDE sources is clearly needed.

We have therefore employed an innovative approach for obtaining a surrogate PBDE measure: testing for bromine using X-ray fluorescence (XRF). XRF technology, used for years to non-destructively test for the presence of lead in homes, illuminates a sample with high energy photons generated by a low-power x-ray source. Upon hitting an atom, photons dislodge electrons in inner orbitals. The vacancy is filled by outer orbital electrons which then release a fluorescent x-ray pattern which is unique by element. By measuring the scattered x-rays (both elastic and inelastic), the XRF can estimate density and calculate a concentration.

Accordingly, the primary objectives of our study were to determine whether bromine concentrations as determined using the XRF analyzer provide a valid method of estimating the PBDE content of consumer products, characterize the bromine content of different types of consumer products, and evaluate the relationship between the bromine content of consumer products and PBDEs in house dust.

Materials and Methods. The study was conducted in two phases: a lab-based validation of the XRF method and a field investigation of PBDEs using the XRF in residential settings. The validation phase included an assessment of 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 six 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 residences in the Greater Boston area (Massachusetts), the first conducted from January to March 2006 (20 homes) and the follow-up conducted from October to November 2006 (19 homes). During the first visit, we collected dust samples from the main living area and bedroom using a Eureka Mighty-Mite canister vacuum cleaner and a crevice tool fitted with a cellulose extraction thimble (Rudel et al., 2003). The main living area was defined as the room where participants spent the majority of their waking hours (not including the kitchen). 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 (<250 µm) and analyzed via GC/MS.

During the follow-up visit, the portable XRF was used to obtain up to three measurements of each consumer product in the bedroom and living room that could potentially act as a PBDE source to the indoor environment. Certain 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. Finally, we measured the volume and surface area of items that were determined to have detectable levels of bromine. A second round of dust samples were collected using the method described above (analysis pending).

Results and Discussion. In the validation phase, we found that XRF-measured bromine levels in chair foam samples ranged from 0.05 mg/g to 20.9 mg/g while GC/MS-measured PBDEs in the same samples ranged from 0.01 mg/g to 14.9 mg/g. Figure 1 presents the strong correlation between bromine and PBDEs in chair foam samples (r=0.98). Similarly, we found a strong correlation between XRF-measured bromine (0.03-1.8 mg/g) and GC/MS-measured PBDEs (0.3-3,889 µg/in^2) in carpet padding samples (r=0.97). These results suggest that XRF can reliably measure bromine as a surrogate for PBDEs in carpet padding and chair foam. Our results are consistent with those of Li et al (2006), who reported excellent agreement (r=0.99) between XRF-measured bromine and known quantities of potassium bromide (Li et al., 2006). We are continuing the validation process with an ongoing assessment of hard plastics.

Figure 1. Comparison of PBDEs via GC/MS and bromine via XRF in chair foam samples

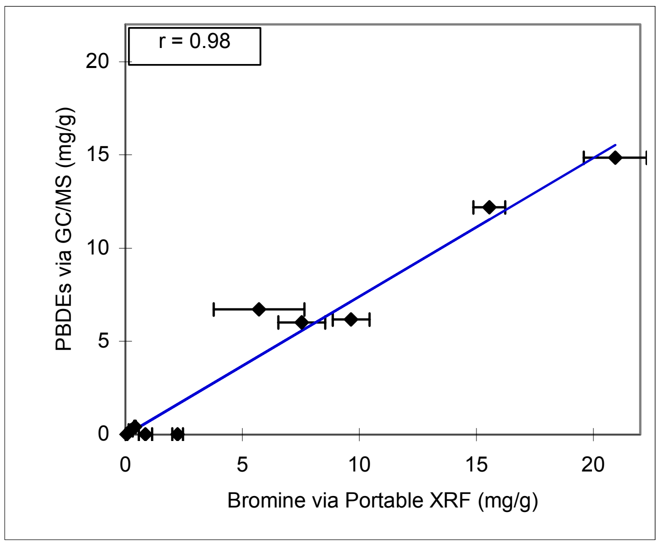


Table 1 presents a summary of the bromine content for electronics and furniture. The table shows the number of items measured, the percent of items in which bromine was detected above the limit of detection (LOD) of 10 ppm, and summary statistics. Bromine was detected in electronics more frequently and at higher concentrations than in furniture; in fact, the *minimum* detected bromine concentration in televisions was 12.6%. Of particular interest is the apparent high degree of variability in bromine content within product type. For instance, DVD players were found to contain bromine at levels ranging from 26 to 119,113 ppm. Accordingly, the limited ability of previous studies to link PBDEs in the indoor environment with product counts is likely explained by extensive measurement error.

The bromine measurements and product dimensions were used to calculate two indices of bromine loading for each room. One was calculated by multiplying the average bromine concentration of each product by its volume while the other was calculated similarly using product surface area instead of volume. The resulting values were summed separately for furniture and electronics for each room. The results presented here used bromine loadings weighted by product surface area; however, the evaluation of bromine loadings weighted by product volume were similar.

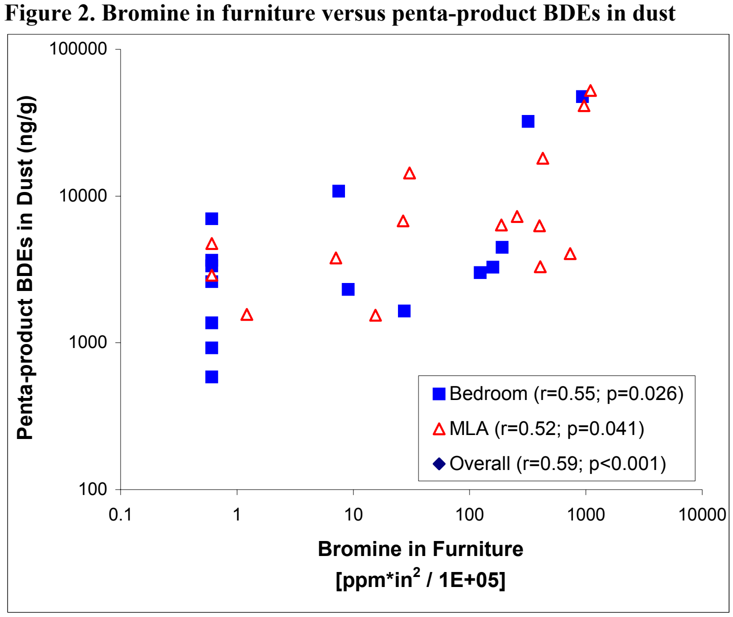
Figure 2 presents the comparison between penta-product BDEs in dust and the bromine content of furniture in the bedroom (r=0.55, p=0.03) and main living area (r=0.52, p=0.04). Overall, we found that XRF-measured bromine in furniture was significantly correlated with penta-product BDEs in dust (r=0.59, p<0.001). However, the correlations between XRF-measured bromine in electronics and deca-product BDEs in dust were not as strong in either the bedroom (r=0.40, p=0.1) or main living area (r=0.38, p=0.1).

The XRF method is easy, fast, and appears to be a promising surrogate measure for PBDE content, producing estimates of bromine source strength that can be linked to PBDEs in dust collected from the same rooms. When we analyzed the dust data using only questionnaire data, we found no associations between PBDEs and counts of furniture, electronics, or the presence of carpeting. But by returning to the same homes and using the XRF method, we reduced measurement error and found a clear association between consumer products and PBDEs in the indoor environment. While measuring bromine concentrations in plastics or foam does not identify the species of bromine-containing compound, even semi-quantitative estimates of PBDEs provide a

Table 1. Bromine concentrations in electronics and furniture

			Bromine (ppm)		
	n	%>LOD	Median	Min	Max
Electronics					
TVs	22	100	145,203	125,650	168,911
Powerstrips	27	96	96,084	<10	147,101
DVD Players	12	100	47,905	26.0	119,113
VCRs	6	100	46,428	26,213	120,670
Adapters	45	100	4,576	15.0	144,184
Cell Phones	5	80	4,530	<10	7,769
Receivers	6	67	2,291	<10	64,379
Laptops	6	100	498	17.5	964
CD Players	7	71	484	<10	144,007
Cable Boxes	8	88	193	<10	14,360
Remote controls	62	87	152	<10	14,827
Phones	16	81	147	<10	1,400
Alarm Clocks	16	88	104	<10	121,408
Speakers	29	28	5.0	<10	83,389
Furniture					
Futons	6	67	111	<10	3,220
Chairs	45	67	29.3	<10	20,820
Couches	16	81	28.5	<10	4,391
Carpet	6	67	23.5	<10	418
Mattresses	20	65	11.4	<10	1,210
Pillows	136	32	5.0	<10	3,512
Boxsprings	12	42	5.0	<10	147
Rugs	25	24	5.0	<10	116

Figure 2. Bromine in furniture versus penta-product BDEs in dust



preferable alternative to relying on product counts. Additionally, since the commercial deca-product (but not penta-product) is often used in conjunction with antimony trioxide in a 3:1 ratio (LCSP, 2005), it may be possible to use antimony (measured by XRF concurrently with bromine) as a marker for deca-BDE. Preliminary analyses indicate that bromine and antimony were detected in 100% of televisions, at a mean ratio of 3.6:1. Further investigation is necessary to evaluate the potential usefulness of antimony data for this purpose.

One potential limitation of the XRF is that the XRF only measures a short distance into materials and will not detect bromine-containing sources deep within a product, a potential source of measurement error if circuit boards contain PBDEs. Similarly, bromine-containing circuit boards located close to the surface (ie. remote controls) may also produce measurement error. On the other hand, we correlated bromine content against PBDEs in dust sampled six to nine months earlier. The extent to which PBDE levels in dust may change over time is unknown, but we expect to find a stronger correlation with PBDE levels in the second set of dust samples once results are available. In sum, we believe that XRF is a promising tool for characterizing the bromine content of products in homes that will inform our understanding of how PBDEs enter the indoor environment. The factors that determine whether PBDEs in consumer products will be released to the indoor environment require further exploration.

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References

Allen JG, McClean MD, Stapleton HM, Nelson JM, Sanchez G, Fraser AJ, and Webster TF. 2006. Presented at BFR 2006, Toronto, Ontario.

Harrad S, Wijesekera R, Hunter S, Halliwell C, and Baker R. 2004. Environmental Science & Technology 38(8): 2345-50.

Lowell Center for Sustainable Production. 2005. Report at: http://www.sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf

Li C, Romine H, and Petreas M. 2006. Presented at 232nd American Chemical Society National Meeting, San Francisco, CA.

Rudel RA, Camann DE, Spengler JD, Korn LR, and Brody JG. 2003. Environ Sci Technol 37(20): 4543-53.

Stapleton HM, Dodder NG, Offenberg JH, Schantz MM, and Wise SA. 2005. Environ Sci Technol 39(4): 925-31.

Wilford BH, Shoeib M, Harner T, Zhu J, and Jones KC. 2005. Environ Sci Technol 39(18): 7027-35.

Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, La Guardia M, McClean MD, and Webster TF. 2006. Environ Sci Technol In press.