Recent Studies on the Identification and Occurrence of PentaBDE Replacement Chemicals in Indoor and Outdoor Environments

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Introduction

Restrictions on the use of polybrominated diphenyl ethers (PBDEs) have resulted in an increased use of alternative flame retardant chemicals to comply with flammability standards. However, assessments to determine if these chemicals have the potential to impact human or environmental health have been hindered because the identity of the chemicals currently used and the types of products they are used in are not publicly available in most cases. Firemaster® 550 (FM550, a mixture containing 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), bis (2-ethylhexyl) 2,3,4,5- tetrabromophthalate (TBPH), and triphenyl phosphate (TPP)) and the chlorinated organophosphates (OPs) tris(1,3-dichloro-2-propyl)phosphate (TDCPP) and tris(1-chloro-2-propyl)phosphate (TCPP) have been identified as alternatives to PentaBDE for use in polyurethane foam and are currently used in the highest volumes to meet the California furniture flammability standard (Babich 2006; Stapleton et al. 2009). Despite their widespread use in indoor environments, relatively few environmental fate and toxicity data are available for TDCPP, TCPP, and TPP, and virtually no information is available for TBB and TBPH.

In this presentation we summarize the results of recent studies on the identification of PentaBDE replacement chemicals used in polyurethane foam and their occurrence in house dust, biosolids (i.e. sewage sludge), and aquatic environments. Included in these results is the identification of flame retardant chemicals in a polyurethane foam sample treated with Firemaster® 600 (FM600), a new PentaBDE replacement product distributed by Chemtura. Where possible, PentaBDE replacement chemical concentrations in these matrices are compared to those of PBDEs.

Materials and Methods

Chemical Identification

The FM550 technical mixture, obtained from Chemtura, was recently characterized (Stapleton et al. 2008; Klosterhaus et al. 2008; Klosterhaus et al. 2009). A sample of polyurethane foam treated with FM600 was obtained from a polyurethane foam manufacturer and analyzed using methods described by Stapleton et al 2009.

Indoor Environments: Consumer Product Foam and House Dust

Polyurethane foam (n=26) collected from furniture products, most of which were purchased in the U. S. after the 2004 phase-out of PentaBDE, were analyzed for brominated and chlorinated flame retardants (Stapleton et al. 2009). More recently, sampled foam from baby products (n=4), including a baby play mat, two portable crib mattress, and one head support from an infant stroller, were analyzed. PentaBDE replacements were also analyzed in house dust samples collected from homes in Boston in 2006 (Stapleton et al. 2008) and between 2002 and 2007 (Stapleton et al. 2009).

Biosolids (i.e. Sewage Sludge)
Biosolids collected in 2007-2008 from wastewater treatment plants (WWTPs) in the San Francisco Bay Area, CA, USA and Durham, NC, USA (two WWTPs in each location) were analyzed for TBB, TBPH, TDCPP, TCPP, and PBDEs using methods similar to those published previously by Stapleton et al. 2009. Biosolids collected in 2002, 2005, 2007, and 2008 from a WWTP in the mid-Atlantic region of the U.S. were analyzed for TBB, TBPH, and PBDEs using methods similar to those published by La Guardia et al. 2007.

Aquatic Environments: Sediments and Wildlife
Samples from San Francisco Bay were analyzed using previously published methods (Stapleton et al. 2008; Stapleton et al. 2009). Sediment (n=10), mussels (deployed *Mytilus californianus*; n=14), sport fish (white croaker and shiner surfperch; n=14), harbor seals (n=20 blubber samples), and bird eggs (double-crested cormorants; n=3) were analyzed for TBB and PBDEs. TBPH was only analyzed in sediments and bird eggs due to limited tissue sample mass. Cormorant eggs and sediments were screened for the presence of TDCPP, and TDCPP, TCPP, and TPP, respectively. In a separate study, La Guardia et al. collected sediments at a U.S. mid-Atlantic textile manufacturer's outfall and three sites downstream (up to 45 km away). These were also analyzed for TBB, TBPH and PBDEs (see La Guardia et al. 2007 for analytical method).

Results and Discussion

Chemical Identification
Chemicals in two PentaBDE replacement mixtures were characterized to facilitate studies of their occurrence, fate, and toxicity in the environment. Analysis of the FM550 technical mixture indicated it is primarily a mixture of mono-, di-, tri-, and tetra-isopropylphenyl phosphates (45%), TBB (30%), TPP (18%), and TBPH (9%), by weight. In the sample of polyurethane foam treated with FM600, concentrations of TBPH, TBB, and TPP were 1.48, 2.99, and 5.33 mg/g, respectively (isopropylphenyl phosphates were not quantified). The FM550 and FM600 technical mixtures appeared to be quite similar in composition; however, there were differences in the concentrations and composition of the isopropyl phenyl phosphates (IPPs). A comparison of a total ion chromatograph scan of an extract from the FM600 treated foam to that of the FM550 mixture clearly demonstrated a lack of several IPP isomers.

Foam in Furniture and Baby Products
Most of the furniture foam samples contained either TDCPP or TCPP at concentrations ranging from 1-5% or 0.5-2.2% by weight, respectively. PentaBDE and the brominated components of FM550 and FM600 (TBPH, TBB) were each detected in one foam sample. Of the two crib mattresses tested, one contained the FM550 and FM600 components (TBB, TBPH, TPP) and TDCPP, while the other contained only the FM550 and FM600 components. The play mat contained TDCPP. Based on these results, it appears that TDCPP, TCPP, and the chemicals in FM550 and FM600 (TBB, TBPH, and TPP)

are common replacements for PentaBDE in polyurethane foam.

House Dust

Detection frequencies of TBPH, TBB, TDCPP, TCPP, and TPP in Boston house dust samples ranged from 24 to 100%. Concentrations of TBPH and TBB ranged from 1.5 to 10,630 and <6 to 15,030 ng/g dry weight in the 2006 samples, and <300 to 47,110 and <450 to 75,000 ng/g dry weight in the 2002-2007 samples, respectively. Concentrations of TBPH and TBB were generally at least one order of magnitude lower than PBDE concentrations in these samples (Allen et al. 2007). In the samples collected between 2002 and 2007, concentrations of TDCPP, TCPP, and TPP ranged from <90 to 56,090, <140 to 5490, and <150 to 1,798,000 ng/g dry weight, respectively, and were in the same range as PBDEs.

Biosolids

PentaBDE replacement chemicals were detected in all biosolids samples analyzed. Mean concentrations (ng/g dry weight) of TBB and TBPH in the San Francisco Bay Area (SFBA) (2679 ± 5 and 502 ± 34 at WWTP #1; 354 and 92 at WWTP #2) were higher than those in Durham, NC (244 ± 156 and 29 ± 6 at WWTP #1; 102 ± 36 and 34 ± 5 at WWTP #2). Compared to PBDEs, TBB and TBPH concentrations were comparable or lower in the SFBA samples and lower in the Durham samples. TBB and TBPH (ng/g dry weight) were also detected in the mid-Atlantic U.S. biosolids and were highest in the 2002 sample (25,300 and 9,460, respectively). Their concentration decreased substantially over time to 410 and 40, respectively, in 2008. This decrease was likely the result of a local automotive interior parts manufacturer relocating out of the area in 2006.

Concentrations of TDCPP, TCPP, and TPP ranged from 700-105,000, 300-4,300, and 500-2,600 ng/g dry weight in SFBA biosolids, respectively, and were comparable to PBDE concentrations. In one biosolids sample from Durham, NC, concentrations of TDCPP and TCPP were 495 and 270 ng/g dry weight, respectively; these concentrations were lower than the PBDE levels detected. Detection of PentaBDE replacements in biosolids suggests these compounds are migrating from consumer products and likely entering aquatic environments via municipal wastewater effluent.

Aquatic Environments

TBB and TBPH were not detected in San Francisco Bay sediment (<0.03 ng/g dry weight) or wildlife (< 0.2-15 ng/g lipid). However, TBB and TBPH have been detected as high as 70 and 3860 ng/g lipid, respectively, in marine mammals from the Pearl River Delta (PRD), China (Lam et al., 2009). This may be related to higher chemical usage and disposal of these replacement products in the PRD. In river sediments collected downstream of a U.S. textile manufacturer outfall, concentrations of TBB and TBPH were 40 and 220 ng/g dry weight near the outfall and decreased to 0.3 and 8.1 ng/g, 45 km downstream. Concentrations of PentaBDE ranged from 130 ng/g dry weight at the outfall to 1.0 ng/g downstream.

Concentrations of TDCPP, TCPP, and TPP in San Francisco Bay sediments ranged from 1-19, <1-16 and <1-20 ng/g dry weight respectively. TDCPP was not observed in the cormorant eggs.

Conclusions

The lack of information on the chemical content of consumer products is a major impediment to evaluating the fate and potential impacts of chemicals in the environment. Chemical characterization of in-use products and technical mixtures highlights the extreme actions researchers must take in order to study the chemicals currently used in furniture, including baby products. The identification of TDCPP as a probable human carcinogen (Babich 2006, WHO 1998) and lack of fate and toxicity data for TBB and TBPH are a concern given the presence of these chemicals in house dust at ppm concentrations; human health risk assessments that consider dust as an exposure pathway are particularly warranted. The frequent detection of PentaBDE replacement chemicals in polyurethane foam, baby products, house dust, biosolids, and sediments indicates that further studies on the fate and potential toxicity of these chemicals are urgently needed.

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References

Allen, JG, McClean MD, Stapleton HM, Webster TF. 2008. Env Int 34:1085.

Babich, M. A. 2006. CPSC Staff Preliminary Risk Assessment of Flame Retardant (FR) Chemicals in Upholstered Furniture Foam, US CPSC, Bethesda, MD, USA

Davis EF, Stapleton HM. 2009. Environ Sci Technol 43:5739

Klosterhaus SL, Konstantinov A, Stapleton HM. 2008. BFR Workshop Abstract, Victoria, BC, Canada

Klosterhaus SL, Konstantinov A, Davis EF, Klein J, Stapleton HM. 2009. BFR Workshop Abstract, Ottawa, ON, Canada.

La Guardia MJ, Hale RC, Harvey E. 2007. Environ Sci Technol 41:6663

Lam JCW, Lau RKF, Murphy MB, Lam PKS. 2009. Environ Sci Technol 43:6944

Stapleton HM, Allen JG, Kelly SM, Konstantinov A, Klosterhaus S, Watkins D, McClean MD, Webster TF. 2008. Environ Sci Technol 42:6910

Stapleton HM, Klosterhaus S, Eagle S, Fuh J, Meeker JD, Blum A, Webster TF. 2009. Environ Sci Technol 43:7490

World Health Organization (WHO). 1998. Flame Retardants: Tris (chloropropyl) phosphate and tris (2-chloroethyl) phosphate. Environmental Health Criteria 209.