

Novel and High Volume Use Flame Retardants in US Couches Reflective of the 2005 PentaBDE Phase Out

Heather M. Stapleton,^{*,†} Smriti Sharma,[†] Gordon Getzinger,[†] P. Lee Ferguson,[†] Michelle Gabriel,[§] Thomas F. Webster,[‡] and Arlene Blum[§]

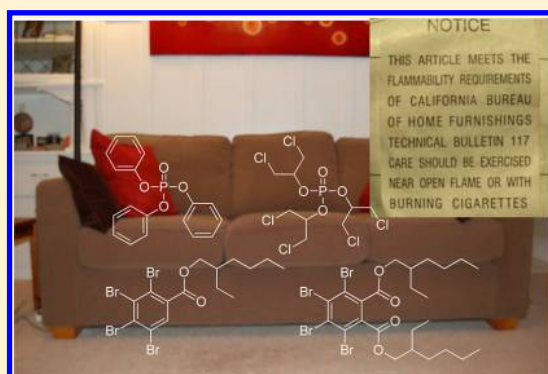
[†]Nicholas School of the Environment, Duke University, Durham, North Carolina, United States

[‡]Department of Environmental Health, Boston University School of Public Health, Boston, Massachusetts, United States

[§]Department of Chemistry, University of California, and Green Science Policy Institute, Berkeley, California, United States

S Supporting Information

ABSTRACT: California's furniture flammability standard Technical Bulletin 117 (TB 117) is believed to be a major driver of chemical flame retardant (FR) use in residential furniture in the United States. With the phase-out of the polybrominated diphenyl ether (PBDE) FR mixture PentaBDE in 2005, alternative FRs are increasingly being used to meet TB 117; however, it was unclear which chemicals were being used and how frequently. To address this data gap, we collected and analyzed 102 samples of polyurethane foam from residential couches purchased in the United States from 1985 to 2010. Overall, we detected chemical flame retardants in 85% of the couches. In samples purchased prior to 2005 ($n = 41$) PBDEs associated with the PentaBDE mixture including BDEs 47, 99, and 100 (PentaBDE) were the most common FR detected (39%), followed by tris(1,3-dichloroisopropyl) phosphate (TDCPP; 24%), which is a suspected human carcinogen. In samples purchased in 2005 or later ($n = 61$) the most common FRs detected were TDCPP (52%) and components associated with the Firemaster550 (FM 550) mixture (18%). Since the 2005 phase-out of PentaBDE, the use of TDCPP increased significantly. In addition, a mixture of nonhalogenated organophosphate FRs that included triphenyl phosphate (TPP), tris(4-butylphenyl) phosphate (TBPP), and a mix of butylphenyl phosphate isomers were observed in 13% of the couch samples purchased in 2005 or later. Overall the prevalence of flame retardants (and PentaBDE) was higher in couches bought in California compared to elsewhere, although the difference was not quite significant ($p = 0.054$ for PentaBDE). The difference was greater before 2005 than after, suggesting that TB 117 is becoming a de facto standard across the U.S. We determined that the presence of a TB 117 label did predict the presence of a FR; however, lack of a label did not predict the absence of a flame retardant. Following the PentaBDE phase out, we also found an increased number of flame retardants on the market. Given these results, and the potential for human exposure to FRs, health studies should be conducted on the types of FRs identified here.



INTRODUCTION

In the United States, a major driver of flame retardant (FR) use in residential furniture appears to be the California flammability standard, Technical Bulletin 117 (TB 117). This standard requires that polyurethane foam used in furniture withstand a 12 s open flame test with minimal loss of foam and no sustained ignition after the flame is removed. TB 117 was instituted in 1975 primarily to protect against home fires started by small open flames, such as candles, matches, and lighters.¹

To meet this standard, a variety of flame retardant chemicals have historically been used, but due to the proprietary nature of some FRs and the lack of a labeling requirement, it is very difficult to determine their presence or identity in products. It has been suggested that TB117 was primarily met by treating foam with PentaBDE prior to the 2005 phase-out, after which time TDCPP and FM 550 were primarily used. However, this is anecdotal, and no previous studies have investigated which FRs

were historically used in furniture, nor have they identified which FRs are now in common use.

Numerous studies dating back to the 1970s have raised concerns about the exposure and human health effects from both TDCPP and PentaBDE. TDCPP was found to be a mutagen more than three decades ago^{2,3} and was recently determined to be potentially neurotoxic.⁴ Based on its carcinogenicity, it was added to California's Proposition 65 List of Potential Carcinogens in 2011. In 2006, the Consumer Product Safety Commission conducted a risk assessment for several FRs used in upholstered furniture and specifically evaluated adult and children's exposure to TDCPP.⁵ While

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their report was limited to the use of modeled exposure data, their estimates suggested that both adults and children are receiving exposures that are 2 and 5 times higher, respectively, than the acceptable daily dose for noncancer end points. For cancer end points, they estimated that an adults lifetime individual cancer risk was 300 per million, based on a lifetime exposure to TDCPP treated furniture. Estimated cancer risk in children from two years of exposure to TDCPP treated furniture was 20 per million. The CPSC states that cancer risks greater than one in a million are considered relevant for regulatory consideration under the chronic hazard guidelines.

In the 1990s, several studies demonstrated that polybrominated diphenyl ethers (PBDEs) present in PentaBDE were biomagnifying in food webs and increasing in concentration in human tissues and the environment.^{6–8} Given the similarity in structure between PBDEs and thyroid hormones, a number of exposure studies with rodents, fish, and birds were conducted. Significant effects of PBDEs on thyroid hormone regulation and neurodevelopment were observed in these studies.^{9–12} By 2004 both the state of California and the European Union had banned the use of PentaBDE and another PBDE mixture, OctaBDE, from use in consumer products.¹³ These bans and similar ones in other states ultimately led to a voluntary agreement between the EPA and Chemtura, the sole chemical manufacturer in the US, to phase-out both PentaBDE and OctaBDE by January 1, 2005.¹⁴ The last and third PBDE mixture still in commercial use is DecaBDE is scheduled for phase-out in December of 2012 due to concerns about its neurotoxicity and potential to degrade into Penta- and OctaBDE components.¹⁵

The lack of labeling, and information on flame retardant use in consumer products, has hampered research investigating sources of human exposure to PBDEs and their replacements. Several US studies have found significant associations between PBDE body burdens, dietary sources,^{16,17} and house dust,^{18,19} suggesting both are significant sources of exposure. More recently, several of our authors demonstrated that PBDE residues on hands were strong predictors of serum PBDE levels in children²⁰ and in adults,²¹ suggesting hand to mouth contact is a significant source of exposure to these chemicals.

In 2011 we investigated the use of FR chemicals in foam from baby products such as nursing pillows, strollers, high chairs, and baby carriers.²² Such products are considered juvenile furniture and are required to meet the TB 117 standard. We found that 80% of the 101 products tested contained a FR, and all but one was halogenated.²² This was an important finding as there were no data available on the prevalence, identity, or levels of FRs in children's products containing foam. As a follow-up to that study, we are now investigating the use of FR in residential furniture purchased in the United States. One primary objective was to identify the types of FR chemicals commonly used in residential couches before and after the PentaBDE phase-out in 2005 as well as their concentrations in the foam. A second objective was to compare FR use in products sold within and outside of California (but all within the US). Studies have found higher levels of PBDEs in California house dust and residents, which may be due to TB 117.²³

MATERIALS AND METHODS

Materials. The internal standard used for PBDE, TBB, and TBPH analysis, 4-fluoro-2,3,4,6-tetrabromodiphenylether (FBDE 69), was purchased from Chiron (Trondheim,

Norway). Deuterated triphenyl phosphate (TPP) was purchased from Sigma Aldrich (St. Louis, MI), while deuterated tris(2-chloroethyl) phosphate (TCEP) and tris(1,3-dichloroisopropyl) phosphate (TDCPP) were synthesized by Dr. Vladimir Belov (Göttingen, Germany). PBDE calibration standards were purchased from AccuStandard (New Haven, CT), and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH) were purchased from Wellington Laboratories. TCEP and tris(4-butylphenyl) phosphate (TBPP) were purchased from Sigma-Aldrich (St. Louis, MI), while TDCPP and tris(2-methylphenyl) phosphate were purchased from ChemService (West Chester, PA). A commercial mixture of V6 was purchased from a flame retardant manufacturer in China (wishes to be anonymous) and purified to greater than 98%. All solvents used throughout this study were HPLC grade.

Foam Sample Collection. Polyurethane foam samples were solicited from volunteers during 2010–2011 using e-mail list-serves and requests at lectures and meetings that reached individuals from all over the US. To qualify for this study, the participant had to own a couch that met four criteria: 1.) The couch was purchased new by the owner and never reupholstered (No previously owned or used couches, sofa-beds, futons, or day beds were included in the study.); 2.) The owner knew the state and year of purchase of the couch; 3.) The couch was for home use, rather than for an office or public place; and 4.) The couch had a label that stated it contained polyurethane foam or the couch had no labels when purchased. The label could also state that the couch contained polyester fibers or other materials in addition to polyurethane foam.

The foam sample donor was instructed to cut or tear a 1/2 to 1 cubic inch foam sample from the couch, wrap the sample in aluminum foil, and seal it in an inner Ziploc bag which was placed into an outer Ziploc bag. The donor filled out a questionnaire including where and when the couch was purchased, the filling material as specified on the label, and whether a Technical Bulletin 117(TB117) or other flammability labels were found on the product. A product was considered to have a TB117 label if it contained the text: THIS ARTICLE MEETS THE FLAMMABILITY REQUIREMENTS OF CALIFORNIA BUREAU OF HOME FURNISHINGS TECHNICAL BULLETIN 117 (TB117). The questionnaire was placed in the outer Ziploc bag. The donor and sample information was logged into a database, unique ID numbers were given to each sample, and they were then shipped to Duke University for blind analysis of flame retardants.

Sample Analysis by Mass Spectrometry. All foam samples were first screened for flame retardant additives. Briefly, small pieces of foam (approximately 0.05 g) were sonicated with 1 mL of dichloromethane (DCM) in a test tube for 15 min. The DCM extract was syringe-filtered to remove particles and then transferred to an autosampler vial for analysis by GC/MS. All extracts were analyzed in full scan mode (collecting data on all mass spectra generated) using both electron ionization (GC/EI-MS) and electron capture negative chemical ionization (GC/ECNI-MS). Pressurized temperature vaporization injection was employed in the GC. GC/MS method details can be found in ref 24. Peaks observed in the total ion chromatograms were compared to a mass spectral database (NIST, 2005) and to authentic standards when available.

Table 1. Flame Retardant (FR) Measurements and Descriptive Statistics of Polyurethane Foam Samples ($n = 102$). (Values in parenthesis represent percentage of the total number of samples for that specific column)

flame retardant	number of detects	average FR level (mg/g)	purchased prior to 2005 ^a	purchased 2005 or later ^a	purchased in California ^b	purchased outside California ^b	yes TB 117 ^c	no TB 117 ^c
PentaBDE	17	20.23 ^d	16 (39%)	1 (2%) ^e	7 (29%)	9 (12%)	9 (14%)	8 (24%)
TDCPP	42	44.87	10 (24%)	32 (52%)	10 (42%)	30 (41%)	33 (50%)	9 (26%)
FM 550	13	19.76 ^f	2 (5%)	11 (18%)	3 (13%)	8 (11%)	12 (18%)	1 (3%)
V6/TCEP	1	41.77 ^g	0	1 (2%)	1 (4%)	0	1 (2%)	0
TBPP mix	8	7.90 ^h	0	8 (13%)	1 (4%)	7 (10%)	6 (9%)	1 (3%)
MPP mix	2	3.23 ⁱ	0	2 (3%)	0	2 (3%)	1 (2%)	1 (3%)
TDCPP and PentaBDE	2	22.64	2 (5%)	0	1 (4%)	1 (1%)	1 (2%)	1 (3%)
TDCPP and FM 550	2	19.06	0	2 (3%)	0	2 (3%)	2 (3%)	0
FR < 0.2 mg/g	3 ^j	0.11	1 (2%)	2 (3%)	0	3 (4%)	0	2 (6%)
none detected	12	-	10 (24%)	2 (3%)	1 (4%)	11 (15%)	1 (2%)	11 (32%)
totals	102		41	61	24	73	66	34

^aIndicates the number of samples collected from couches containing the FR and purchased during this time frame. ^bSome participants reported purchasing their couch online or through a catalog, and thus the state of purchase was not included in the sum ($n = 5$). ^cIndicates the number of samples that did or did not contain a TB 117 label on the product (no data available for 2 samples). ^dIncludes PBDE congeners plus TPP. ^eSample purchased in 2005. ^fMeasurement is the sum of TPP, TBB, and TBPH. ^gMeasurement is for V6 + TCEP. ^hMeasurement is the sum of TPP and tris(4-(tert-butyl)phenyl)phosphate (TBPP). ⁱIncludes measurement of TPP only. ^jTwo samples contained TDCPP; one sample contained BDE47 and BDE99.

If a potential flame retardant chemical was identified either by comparison to authentic standards or by a match to the NIST MS database (>90% match) during the initial screening, a second analysis of the foam sample, using a separate piece of the foam, was conducted for quantitation. To measure the FRs in foam, a piece of the foam was accurately weighed (approximately 100 mg) and then extracted using Accelerated Solvent Extraction (ASE 300 Dionex Corp., Sunnyvale, CA) with 100% dichloromethane (DCM). Extracts were reduced in volume to approximately 3 mL and transferred to a precleaned 4 mL amber vial. The mass of the extract was recorded, and then a 100 μ L aliquot was transferred to a 100 mL volumetric flask and diluted to 100 mL in DCM. One mL of the diluted extract was transferred to an autosampler vial, and the appropriate internal standards were added. A five point calibration curve was established for all analytes with concentrations ranging from 20 ng/mL to 2 μ g/mL. PBDEs were quantified by GC/ECNI-MS by monitoring bromide ions (m/z 79 and 81), and TBB and TBPH were monitored by molecular fragments m/z 357/471 and 463/515, respectively. TCEP and TDCPP were quantified by GC/EI-MS by monitoring m/z 249/251 and 381/383, respectively. TBPP was monitored in GC/EI-MS mode by monitoring m/z 479.5 and 480.5, respectively. V6 was detected and quantified using liquid chromatography–mass spectrometry. The HPLC (Agilent 1200; Agilent, Santa Clara, CA) separation was achieved with a Zorbax Eclipse XBD-C18 column (1.8 μ m, 4.6 \times 50 mm; Agilent). The mobile phase consisted initially of 60% methanol and 40% water at a flow rate of 0.4 mL min⁻¹ that was ramped to 100% methanol from 0 to 6 min and then maintained under isocratic conditions of 100% methanol to 12 min, after which the mobile phase returned to 60% methanol from 12 to 15 min. V6 was quantified by multiple reaction monitoring (MRM) using tandem mass spectrometry with positive atmospheric pressure chemical ionization (Agilent 6410B triple quadrupole spectrometer, Santa Clara, CA) by monitoring the transition from m/z 582.7 to 63.0 (quantifier), 582.7 to 360.8 (qualifier), and 582.7 to 234.8 (qualifier). The internal standard used was dTDCPP (108 ng). Fragmentor voltages were set at 160 V, and the collision energy was set at 55 V.

Ten foam extracts were also screened using HPLC-high resolution mass spectrometry (HPLC/HRMS) to provide more detail on potential structures of several unknown chemicals detected during the preliminary GC/MS screening. These analyses were conducted using a LTQ-Orbitrap Velos tandem mass spectrometer (ThermoFisher Scientific, Bremen, Germany) with a Thermo Fisher Scientific Accela series UPLC system. Sample extracts (25 μ L) were separated on a Hypersil Gold 100 \times 2.1-mm C₁₈ column with 1.9 μ m particles (ThermoFisher Scientific) using a flow rate of 0.4 mL/min and a linear gradient from 40 to 99% methanol/water in 15 min, followed by a 4-min hold at 99% methanol before returning to initial conditions for 3 min. Sample extracts were analyzed using positive polarity electrospray ionization (ESI) mode. Prior to analysis, mass calibration was performed daily by direct infusion of a calibration mixture prepared according to the instrument manufacturer's instructions. Mass spectral acquisition for initial sample screening was programmed into four scan events running concurrently throughout the chromatographic separation. The first scan event was programmed to acquire full-scan (50–2000 m/z), high-resolution ($R = 60,000$) Orbitrap MS data with external mass calibration (<2 ppm accuracy). The subsequent three scan events were low-resolution data-dependent MS/MS analyses in the LTQ ion trap analyzer, triggered by the three most intense ions selected from the previous high-resolution Orbitrap MS spectrum. After identifying chromatographic features of interest by unsupervised peak picking and molecular formula assignment (Exact-Finder 2.0, Thermo Scientific), subsequent targeted multistage HRMS experiments (HRMS² and HRMS³) were performed to acquire high-resolution accurate-mass fragmentation spectra for the structural elucidation of suspected contaminants. Conditions were similar to those reported in our previous paper.²²

As flame retardants are typically added to polyurethane foam at percent levels, we defined samples with detected concentrations (when authentic standards were available) less than 0.2 mg/g as having very small amounts. A majority of the samples contained FRs at levels >1.0 mg/g, while 3 samples contained detectable levels of FRs that ranged from 0.02 to 0.17 mg/g. Therefore, we set our threshold at 0.2 mg/g for “low detection”.

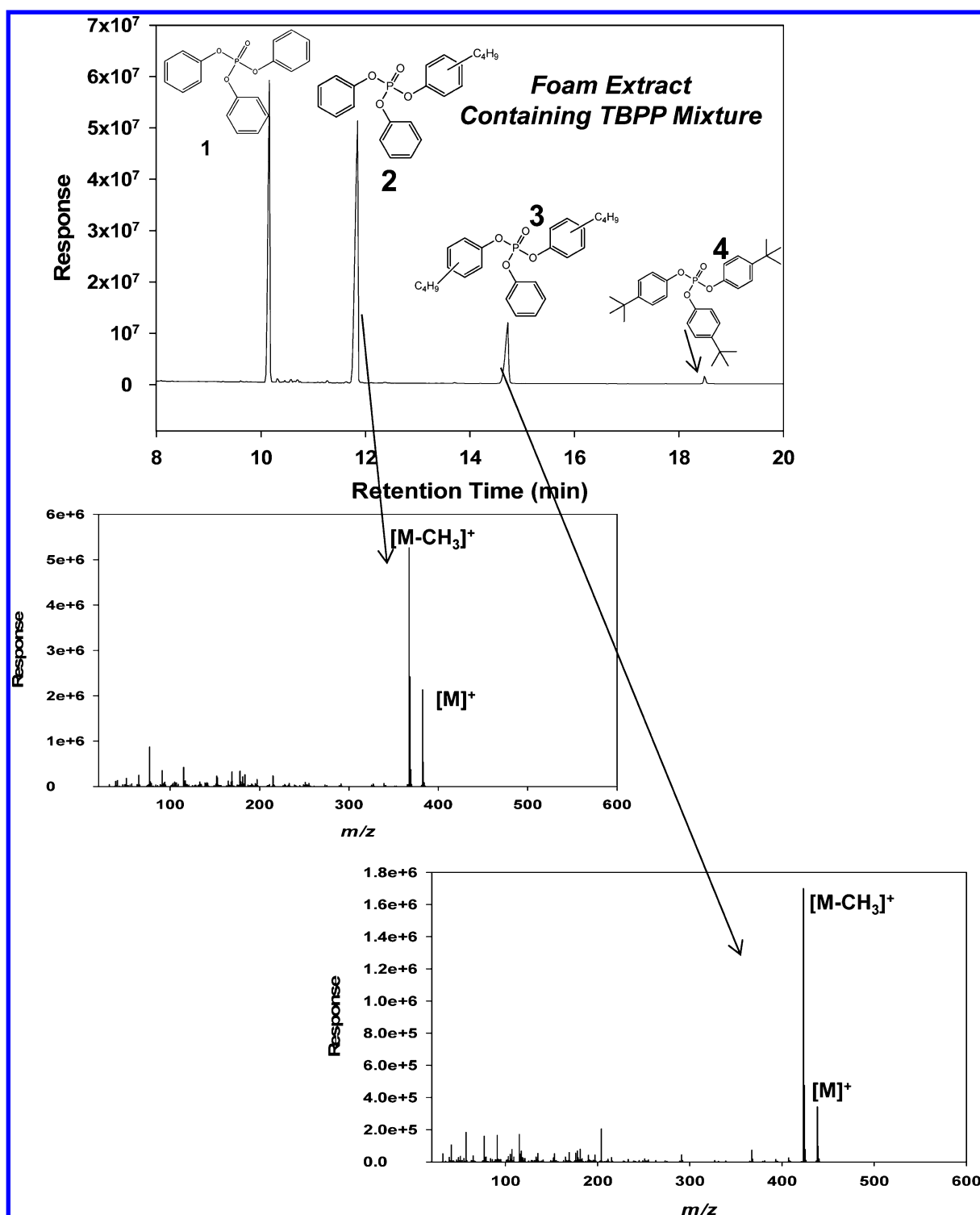


Figure 1. GC/MS total ion chromatogram from an extract of polyurethane foam treated with a mixture (TBPP mix) of aromatic phosphates including triphenyl phosphate (TPP) (1), 4-(*tert*-butyl)phenyl diphenyl phosphate (2), bis(4-(*tert*-butyl)phenyl) phenyl phosphate (3), and tris(4-(*tert*-butyl)phenyl) phosphate (TBPP) (4). Structures 2 and 3 are hypothesized based on high resolution mass spectrometry analysis and the confirmation of structure 4.

RESULTS AND DISCUSSION

A total of 102 polyurethane foam samples obtained from residential couches were collected for this study. When providing a sample, participants provided information on whether the couch contained a label indicating that it met the requirements of California's TB 117 flammability standard,

the US state where the couch was purchased, and the year of purchase. There were some cases in which the participant indicated that the couch was purchased online, thus information on the state of purchase was not included for 5 samples. Data were missing on TB 117 tags for two samples.

FR Screening. All foam sample extracts were first screened for potential flame retardant additives in both GC/EI-MS and

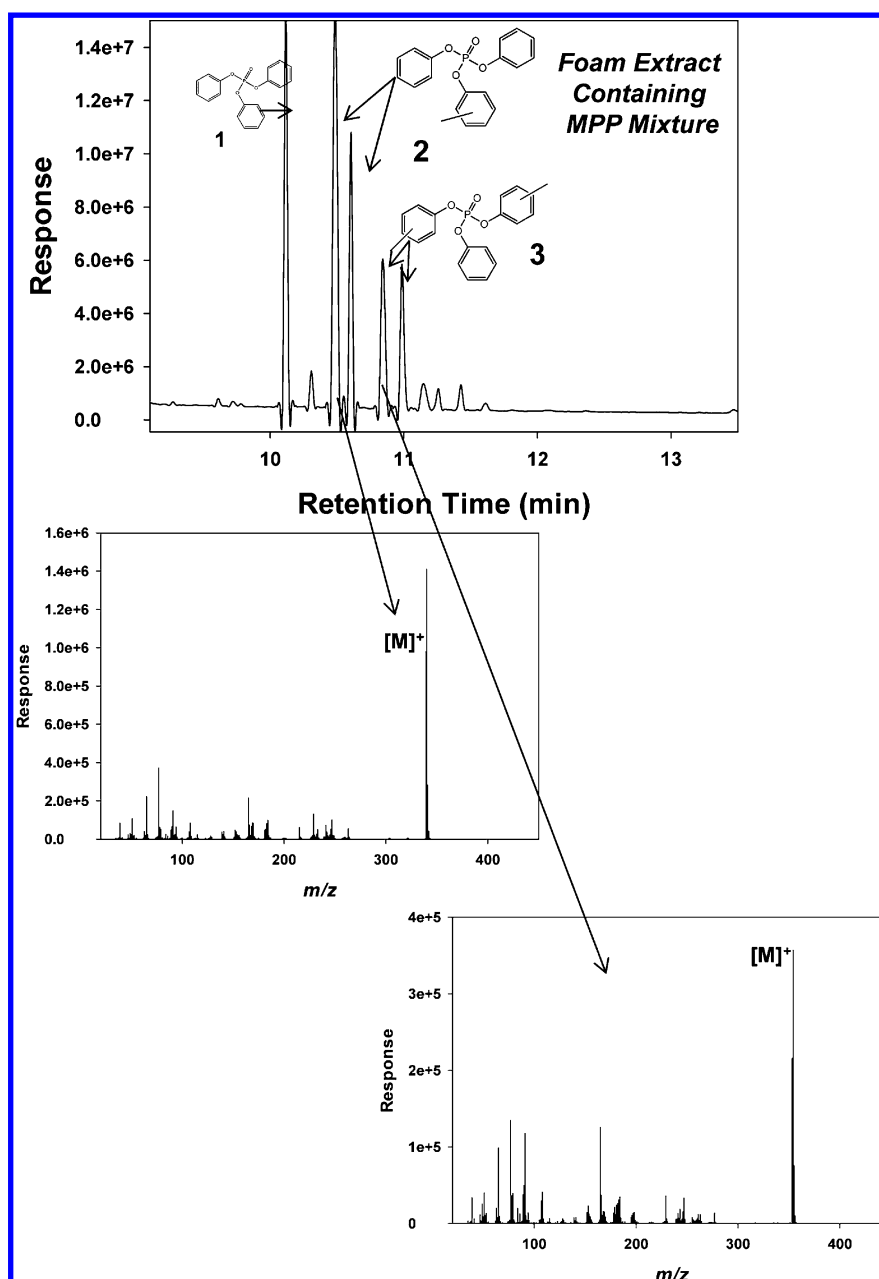


Figure 2. GC/MS total ion chromatogram from an extract of polyurethane foam treated with a mixture of aromatic phosphates including triphenyl phosphate (TPP) (1), two isomers of methylphenyl diphenyl phosphate (2), and two isomers of bis(methylphenyl) phenyl phosphate (3). Structures 2 and 3 are hypothesized based on comparison to NIST Mass Spectral Database (2005) and high resolution mass spectrometry analysis. The position of the methyl groups has not yet been determined.

GC/ECNI-MS modes. Preliminary screening indicated that 90 of the 102 samples (88%) contained a likely flame retardant chemical, either by comparison to authentic standards or by a significant (>90%) match to the NIST 2005 mass spectral database. The FRs detected and the sample information are presented in Table 1. No significant peaks were observed in the total ion chromatograms (TIC) for 12 of the sample extracts. Inspection of the TICs during the screening step revealed that 80 of the samples contained a flame retardant previously identified in our baby products study.²² These included FRs such as TDCPP, PBDE congeners commonly found in the PentaBDE commercial mixture, or chemicals found in the commercial mixture known as Firemaster 550 (FM 550). In our baby product study, we found that tris(2-chloroethyl)

phosphate (TCEP) was frequently associated with a new flame retardant mixture known as V6. Based on this, the detection of TCEP in one sample suggested the possible presence of V6. Therefore, this sample was further analyzed by LC/MSMS (V6 is not detectable by GC/MS), and the presence of V6 was confirmed during the LC/MSMS analysis by comparison with a purified commercial V6 mixture. The material safety data sheet for Albemarle's (Baton Rouge, LA) Antiblaze V6 reports the presence of TCEP as a 10% impurity, which is consistent with our findings. To our knowledge, V6 is manufactured both within and outside the USA.

Ten extracts contained significant responses in the TICs for several different types of triaryl phosphate compounds that are believed to be used as flame retardants. Eight of these extracts

were very similar in response and contained four significant peaks, as seen in Figure 1. The first and last eluting peaks were identified as triphenyl phosphate (TPP) and tris(4-(*tert*-butyl)phenyl)phenyl phosphate (TBPP) by comparison to authentic standards. TPP is a common organophosphate flame retardant that is used in a variety of halogenated and nonhalogenated flame retardant mixtures.²⁵ The second and third eluting peaks did not have authentic standards available, and thus Structures 2 and 3 in Figure 1 are hypothesized based on HPLC/HRMS analysis (see the Supporting Information). These four flame retardants together may be a mixture marketed by Supresta (Ardley, NY) known as AC073. Information in the EPA's 2005 report from the Furniture Flame Retardancy Partnership²⁵ states that AC073 contains TPP (38–48%) and three proprietary aryl phosphates in the approximate ratio of 40–46%, 12–18%, and 1–3%, which is very similar to the mass spectral signal responses observed in Figure 1.

The TICs of two foam extracts revealed the presence of TPP and at least 4 additional significant responses for structures containing organophosphate features (see Figure 2). Two of the significant responses were an 87 to 93% match to methylphenyl diphenyl phosphate (Structure 2 in Figure 2), while the other two responses were a 95–96% match to bis(4-methylphenyl) phenyl phosphate (Structure 3 in Figure 2), according to the NIST mass spectral database. The structures of the latter two compounds are hypothesized based on comparison to the NIST database and further analysis by HPLC/HRMS (see the Supporting Information). To the authors' knowledge, this mixture of flame retardants has not been reported in products or in the environment in the past.

FR Quantification. Following the screening analysis of the foam samples, quantitative measurements were then performed on all samples in which a FR was positively identified. Table 1 provides information on the average FR content measured in the foam samples. The most commonly detected flame retardant was tris(1,3-dichloroisopropyl)phosphate (TDCPP), in 42 of the 102 samples. The average concentration of TDCPP in the foam was 43.53 mg/g and ranged from 1.6 (couch purchased in 1999) to 110.2 (purchased in 2009) mg/g of foam.

PentaBDE was the second most frequently detected FR ($n = 17$) with an average concentration of 18.34 mg/g of foam and ranging from 6.54 to 43.17 mg/g of foam. All but one of these foam samples containing PentaBDE was purchased prior to 2005, the year of its phase-out in the U.S. The one remaining sample was purchased in 2005. These data suggest that since 2005, PentaBDE is no longer being used in new furniture. However, finding PentaBDE in 17% of the couches studied highlights the fact that, several years after the phase-out, the general population continues to be exposed to PentaBDE-containing products. Furthermore, because there is currently no strategy in place for the identification or safe disposal of FR containing furniture, this chemical will continue to be introduced into the outdoor environment via air, dust, and discarded furniture.

The third most common FR was a mixture of chemicals known to be associated with Chemtura's FM550 mixture. Thirteen samples contained TPP, a suite of isopropylated triarylphosphates, and two brominated compounds that are associated with FM 550, 2-ethylhexyl-tetrabromobenzoate (TBB), and bis(2-ethylhexyl) tetrabromophthalate (TBPH). No authentic standards were available for the isopropylated triaryl phosphates so they were not measured in this study. The

sum concentration of the remaining three compounds in the 13 samples averaged 19.76 mg/g of foam and ranged from 5.18 to 36.85 mg/g of foam. The values are similar to measurements made for these three chemicals in polyurethane foam collected from baby products.²² Since we were unable to measure the isopropylated triarylphosphates present in these samples, the total concentration of FRs actually applied to these samples is higher than reported here.

Quantification of TPP and TBPP was performed in the 10 samples found to contain mixtures of nonhalogenated organophosphate compounds (Figures 1 and 2). The 8 samples that contained both TPP and TBPP (Figure 1, listed as TBPP mix in Table 1) averaged a sum concentration of 7.53 mg/g of foam. It is likely that the two additional isomers (peaks 2 and 3 in Figure 1 for which no authentic standards were available) contribute a larger amount of the total flame retardant mass than TPP and TBPP. Only TPP was measured in the two samples containing a mixture of methylated phenyl phosphate (MPP) isomers (Figure 2, listed as MPP mix in Table 1) and averaged 3.23 mg/g. Again this value underestimates the true FR load in the foam since we could not measure the concentration of the remaining organophosphate FRs.

As mentioned already, one sample contained V6, a chlorinated organophosphate FR that contains two phosphate groups. Similar to what we found in our baby products study, both V6 and TCEP were detected together in one sample, measuring 36.30 and 5.47 mg/g of foam, respectively. Two samples purchased prior to 2005 contained TDCPP and PentaBDE, whereas two samples purchased in 2005 or after contained a mixture of TDCPP and FM 550. In our previous study on flame retardants in baby products, we also found some foam samples treated with more than one commercial mixture.²² Two possible explanations are as follows: (1) Manufacturers may be using a mixture containing multiple flame retardants or (2) Since the large mixing vats are not cleaned between batches of foam, flame retardants from one batch could be transferred into the next batch.

In summary, 85% of the samples contained FRs at greater than 0.2 mg/g, 3% contained small amounts (<0.2 mg/g), while 12% contained no detectable levels.

FR Trends Pre- and Post-2005. Since the phase-out of Penta- and OctaBDE commercial mixtures in the US starting in 2005, there have been no reports documenting the primary flame retardants currently used in residential furniture. In this study, we were able to evaluate trends in flame retardant use in furniture before and after the phase-out. Of the 102 samples analyzed, 41 samples were purchased between 1985 and 2004, 16 (39%) of which were found to contain PentaBDE along with TPP, which we found was associated with PentaBDE use in our previous analysis of baby products.²² The second most common flame retardant detected in samples purchased prior to 2005 was TDCPP, detected in 24% of samples as the sole FR and in 5% of samples in combination with PentaBDE. This observation suggests that TDCPP was being used as a FR at the same time as PentaBDE in residential furniture. This may explain why levels of TDCPP in indoor dust are just as high as PBDE levels.²⁴ Five percent of samples purchased prior to 2005 contained congeners associated with FM 550 (TBB, TBPH, TPP, and isopropylated TPP). These samples were purchased in 2002 and 2003, suggesting that use of FM 550 started at least three years prior to the phase-out of PentaBDE. Of the remaining samples purchased prior to 2005, 24% contained no trace of any flame retardant, and one sample contained very low

levels (<0.2 mg/g) of PentaBDE. This may indicate that prior to 2005, some manufacturers may not have been producing furniture to meet TB 117.

Samples purchased between 2005 and 2010 ($n = 61$) were found to contain a more varied group of FRs. A large majority of these samples (93%) contained high levels (>0.2 mg/g) of FRs, in contrast to couches purchased prior to 2005. This was a significant increase ($p < 0.01$) in FR use observed pre- and post-2005 using a Chi-Square test. The two most common FRs detected in the newer furniture were TDCPP and the FM 550 components (or a mixture of the two), in 74% of the samples purchased since 2005. While TDCPP was also detected in samples purchased before 2005, the increased detection of TDCPP in more recent furniture (52% compared to 24%) was statistically significant ($p < 0.01$). Sixteen percent of foam samples from couches purchased in 2005 or later were found to contain mixtures of nonhalogenated organophosphate based FRs, indicating that the use of nonhalogenated FRs is increasing. Of these samples, 13% contained TPP, TBPP, and several butylphenyl phosphate isomers (Figure 1), while 3% contained TPP and several methyl- or dimethyl- phenyl phosphate isomers (Figure 2). More research is needed to determine if these organophosphate FRs are detected in indoor air and dust.

FRs in Samples Purchased in and outside of California. Participants that donated foam samples from their couches were also asked whether or not their couch was purchased in California. Previous studies showing higher PBDE exposures in California residents^{23,26} suggest that more furniture may be treated with FRs in California compared to other states in the US. In our study, 24% of the samples were purchased within California, while 72% were purchased in other states (5 individuals reported buying their couches online). All but one of the samples purchased within California was treated with a flame retardant. The one sample from California that did not contain detectable levels of flame retardants was purchased in 1989. Of the 72 samples purchased outside California, 19% did not contain FRs over 0.2 mg/g. Overall, the prevalence of PentaBDE in California couches (29%) was about twice as high as those purchased elsewhere (12%), but the difference was not quite statistically significant ($p = 0.054$). Analysis of the data pre- and post-2005 suggests that furniture sold in California prior to 2005 was more likely to be treated with FR compared to furniture sold outside California ($p = 0.07$). FR applications increased overall in furniture post-2005 ($p < 0.01$), and there was no significant difference in FR use in furniture sold within or outside California after 2005. Thus, the higher prevalence of PentaBDE in California couches appears to be due to the higher prevalence of FR use prior to 2005 when PentaBDE was the dominant FR.

TB117 Labeling and the Use of FRs in Furniture. We also investigated whether the presence of a TB 117 label was associated with the use of FRs in a product. Of the samples analyzed, 64% contained a label indicating they met TB 117, and significant levels of FRs (>0.2 mg/g of foam) were detected in all but one of these samples (98%). Thirty-four % of samples did not have a TB117 label (no data were available for two), and in 40% of the cases, no identifiable FRs were observed, or levels were very low (<0.2 mg/g). Twenty-one samples (60%) that did not contain a TB 117 label did in fact have detectable levels of FRs present in the foam (>0.2 mg/g). These data suggest that the presence of a TB 117 label indicates that a FR is very likely present, but the absence of the label is

indeterminate, i.e., use of the label as a screen has good sensitivity but poor specificity.

In summary, our study has provided unique data on the types and amounts of flame retardants used in US residential furniture as well as examining time and geographic trends. We think it is unfortunate that such data are not publicly available to both environmental health scientists and consumers. Information on flame retardant applications in specific consumer products could help elucidate human exposure pathways and provide more insight into sources of flame retardants detected in the environment. One limitation of the current study is that we only examined residential couches. FR use in furniture designed for offices and other public places may differ as they are regulated separately in some locales. While we analyzed a relatively large number of samples (102), our sampling scheme was not random and therefore may not be easily generalizable to the US as a whole. For example, FR prevalence may be different in couches used by people not well represented in our sampling frame.

With the addition of TDCPP to California's Proposition 65 list in 2011, products containing this chemical are now required to have a label stating "This product contains a chemical known to the state of California to cause cancer". Our current study suggests that approximately 50% of the residential couches in use by average Americans are treated with TDCPP, indicating that a large percentage of the population may have increased cancer risks due to exposure to TDCPP treated furniture, according to the CPSC model.⁵ The addition of TDCPP to Proposition 65 may lead to decreased applications of TDCPP in furniture, but future studies are warranted to evaluate these trends.

Following the PentaBDE phase out we also found that a larger variety of FRs are now being used in residential furniture to meet TB 117, increasing the complexity of FR exposures. Given that these alternate FRs are additive, one might suspect that they will also migrate out of furniture over time, leading to exposure concerns in indoor environments, similar to PBDEs and TDCPP. Future studies evaluating human exposure, particularly children's exposure, to these mixtures of flame retardants in indoor environments are therefore also warranted.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional information supportive of our study identified above. Figures S1 through S3 display the mass spectrum of several organophosphate FRs previously unidentified. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: heather.stapleton@duke.edu.

Notes

The authors declare no competing financial interest.

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