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

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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 Firemaster®550 (FM 550) mixture (18%). Since the 2005 phase-out of PentaBDE, the use of TDCPP increased significantly. In addition, a mixture of non-halogenated 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. To the author's knowledge, this is the first report of TBPP and its isomers being used as a FR. 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 predicted the presence of FRs, both its absence was inconclusive: 98% of samples with a label and 57% of samples without a label contained flame retardant additives at levels > 0.2 mg/g foam. 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 second 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 TDCPP and FM 550 were primarily used. However, this is anecdotal and no previous studies have investigated which FRs were historically used, 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], and was recently determined to be potentially neurotoxic [3]. Based on its carcinogenicity, it was added to California's Proposition 65 List of Potential Carcinogens in 2011. 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 [4-6]. This led to animal studies where significant effects of PBDEs on thyroid hormone regulation and neurodevelopment, were observed [7-10]. 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 [11]. 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 [12]. The last and third PBDE mixture in commercial use, 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 [13].

The lack of labeling and information on use 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 [14, 15] and house dust [16, 17], 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 children [18] and in adults [19], 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. Such products are considered juvenile furniture and 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 [20]. This was an important finding as previous research had not evaluated 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. Studies have found higher levels of PBDEs in California house dust and residents, which may be due to TB 117 [21].

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), 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-methyl phenyl) phosphate was 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. 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 re-upholstered (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; 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, to 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 grams) were sonicated with 1 mL of dichloromethane (DCM) in a test tube for 15 minutes. 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 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 [22]. Peaks observed in the total ion chromatograms were compared to a mass spectral database (NIST, 2005) and to authentic standards when available.

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 pre-cleaned 4 mL amber vial. The mass of the extract was recorded and then a 100 microliter aliquot was transferred to a 100 mL volumetric flask and diluted to 100 mL in DCM. One mL of the diluted extracted 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 µg/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, 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 µm, 4.6 x 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 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) and 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 µL) were separated on a Hypersil Gold 100 x 2.1-mm C_{18} column with 1.9 µm particles (ThermoFisher Scientific) using a flow rate of 0.4 mL/min and a linear gradient from 40 to 99% methanol/water in 15 minutes, followed by a 4-min hold at 99% methanol before returning to initial conditions for 3-mins. 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 (ExactFinder 2.0, Thermo Scientific), subsequent targeted multistage HRMS experiments ($HRMS^2$ & $HRMS^3$) 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 [20].

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.

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 was 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 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 [20]. 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.

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 phosphate (TBPP) by comparison to authentic standard. TPP is a common organophosphate flame retardant that is used in a variety of halogenated and non-halogenated flame retardant mixtures [23]. 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 Supporting Info). These four flame retardants together may be a mixture marketed by Supresta (Ardlsey, NY) known as AC073. Information in the EPA's 2005 report from the Furniture Flame Retardancy Partnership [23] 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**. To the authors' knowledge, this mixture of flame retardants has not been reported in products or in the environment in the past.

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 Supplementary Info.) 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. Contrary to expectations that TDCPP would only be found in samples from 2005 or later, 10 of the samples purchased prior to 2005 contained TDCPP, beginning as early as 1988. Nevertheless, the fraction of samples containing TDCPP increased after 2004. 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 commonly FR was a mixture of chemicals known to be associated with Chemtura's FM550 mixture. Thirteen samples contained TPP and two brominated compounds that are associated with FM 550, 2-ethylhexyl-tetrabromobenzoate (TBB), and bis(2-ethylhexyl) tetrabromophthalate (TBPH). The sum concentration of these 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 [20]. FM 550 also contains a proprietary mixture of isopropylated triarylphosphates, for which we did not have a standard available, but which were visible in the TICs. Therefore, the total concentration of FRs in these samples is higher than reported here.

Quantification of TPP and TBPP was performed in the 10 samples found to contain mixtures of non-halogenated 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's 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. 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.

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 [20]. Two possible explanations are: (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 sum, 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, information has not been provided identifying the primary flame retardants currently used in commercial products. 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 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 [20]. The second most common flame retardant detected in samples purchased prior to 2005 was TDCPP, detected in 10 samples as the sole FR and in 2 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 be part of the reason that levels of TDCPP in indoor dust are just as high as PBDE levels [22]. Two samples purchased prior to 2005 contained congeners associated with FM 550 (TBB, TBPH, TPP and isopropylated TPP). These 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 11 samples purchased prior to 2005, 10 contained no trace of any flame retardant and one contained very low levels (<0.2 mg/g) of PentaBDE.

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 (> 1.0 mg/g) of FRs, in contrast to couches purchased prior to 2005, of which 25% were not found to be treated with a FR. This was a significant increase ($p<0.01$) in FR use 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 ($p<0.01$). Ten samples of foam from couches purchased in 2005 or later were found to contain mixtures of non-halogenated organophosphate based FRs, indicating that the use of non-halogenated FRs is increasing. Eight of these samples contained TPP, TBPP and several butylphenyl phosphate isomers (**Figure 1**), while two samples contained TPP and several methyl- or dimethyl-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 [21, 24] suggest that more furniture may be treated with FRs in California compared to other states in the US. In our study, 24 samples were purchased within California while 73 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 73 samples purchased outside California, 14 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 associated with the use FRs in a product. Of the samples analyzed, 65 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-five samples did not have a TB117 label (no data was available for two), and in 14 cases, no identifiable FRs were observed, or levels were very low (<1.0 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.

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. One limitation of the study is that we have 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.

Exposure and Health Concerns. Future studies should attempt to measure these halogenated and non-halogenated FRs in indoor environments as well as human tissues to determine the level of exposure the general public, and particularly children, are receiving in home environments. As mentioned previously, TDCPP is a suspected human carcinogen. 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 [25]. While their report was limited to 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 non-cancer endpoints. For cancer endpoints, 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. 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.

In summary, in our study of 102 couches, 85% contained FRs. We identified TBPP and its isomers as a novel FR and apparent PentaBDE replacement in furniture foam. FRs were found in all couches purchased since 2005 in California and 91% of couches purchased outside California. While PentaBDE was commonly found in furniture purchased prior to the 2005 phase-out, it was not the only FR used. In our study we found TDCPP in residential furniture purchased as early as 1988; however, its use increased significantly following the PentaBDE phase out.

With the addition of TDCPP to California's Proposition 65 list in 2011, beginning on October 28, 2012, products containing this chemical will be required to have a label stating "This product contains a chemical known to the state of California to cause cancer." This may lead to decreased use of TDCPP in residential furniture in the future. Following the PentaBDE phase out we 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 also additive, one might suspect that they will also migrate out of furniture over time, leading to exposure concerns in indoor environments, similar to PBDEs. Future studies evaluating human exposure, particularly children's exposure, to these mixtures of flame retardants in indoor environments are therefore warranted, particularly for TDCPP.

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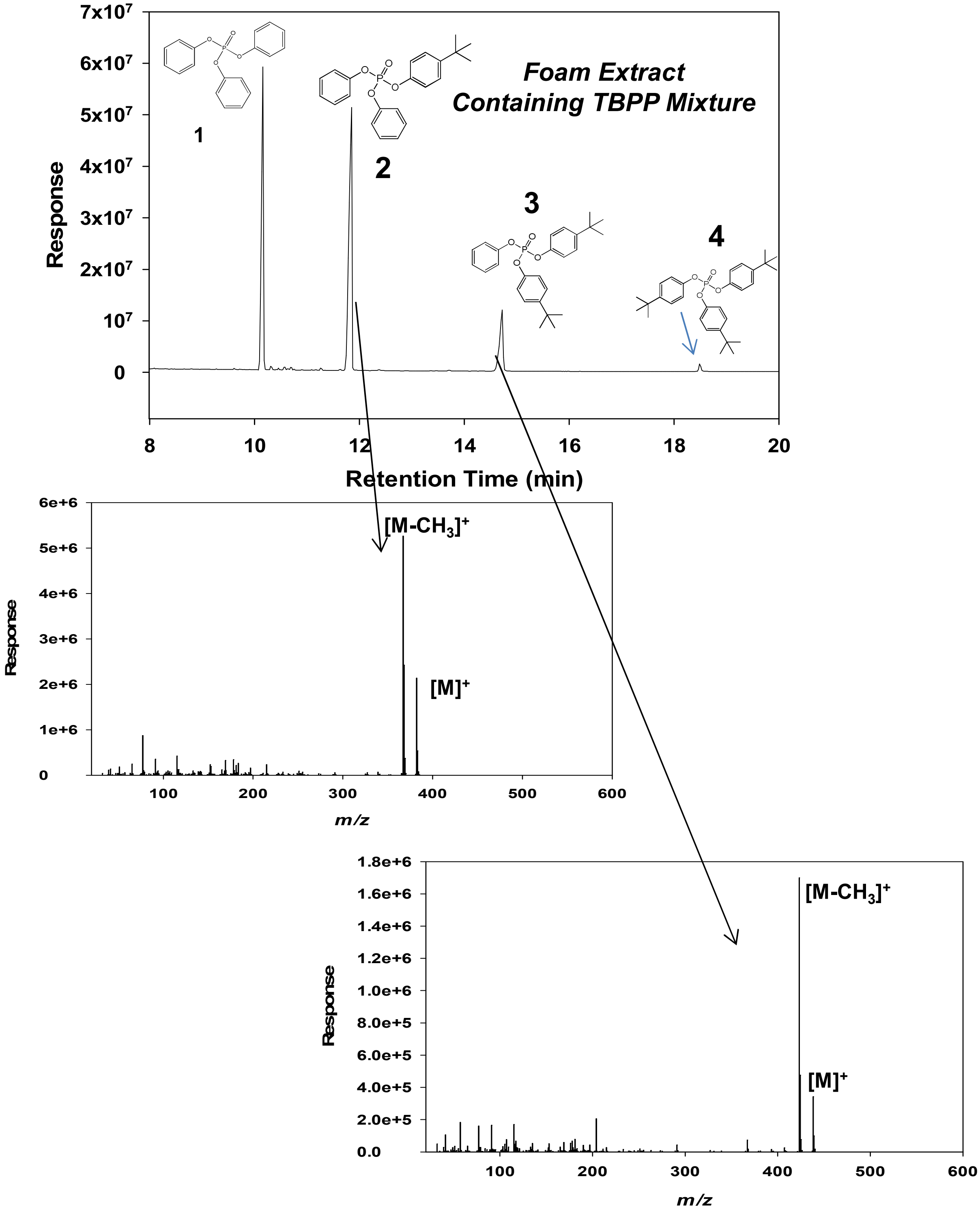

Figure 1. GC/MS total ion chromatogram from an extract of polyurethane foam treated with a mixture (TBPP Mix) of aromatic phosphates including triphenyl phosphate (TPP) (1), 4-(*tert*-butyl)phenyl diphenyl phosphate (2), bis(4-(*tert*-butyl)phenyl) phenyl phosphate (3) and tris(4-(*tert*-butyl)phenyl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

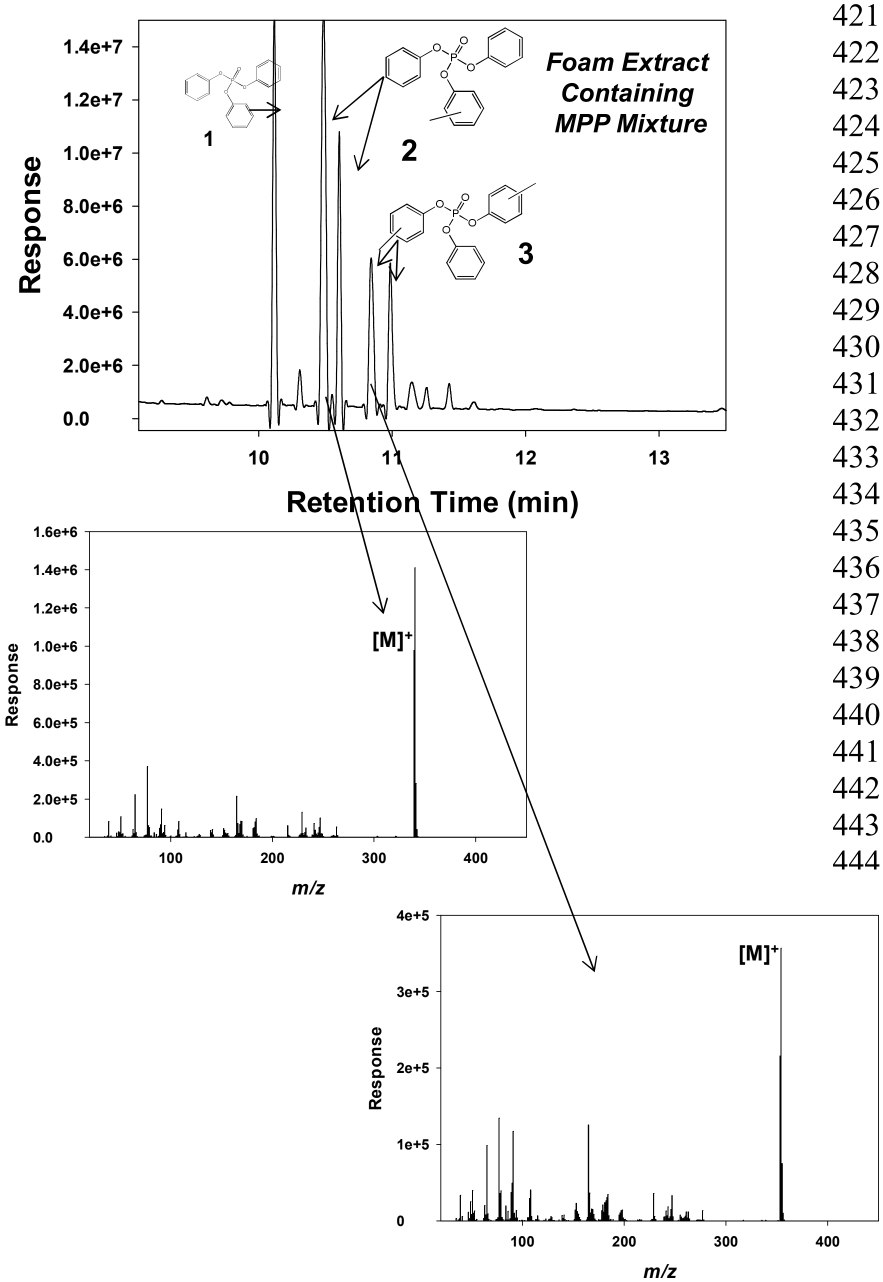

Figure 2. GC/MS total ion chromatogram from an extract of polyurethane foam treated with a mixture of aromatic phosphates including triphenyl phosphate (TPP) (1), two isomers of methylphenyl diphenyl phosphate (2), and two isomers of bis(methylphenyl) phenyl phosphate (3). Structures 2 and 3 are hypothesized 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

Table 1. Flame retardant (FR) measurements and descriptive statistics of polyurethane foam samples (n=102).

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**	**1[e]**	**7**	**9**	**9**	**8**
TDCPP	**42**	**44.87**	**10**	**32**	**10**	**30**	**33**	**8**
FM 550	**13**	**19.76[f]**	**2**	**11**	**3**	**8**	**12**	**1**
V6/TCEP	**1**	**41.77[g]**	**0**	**1**	**1**	**0**	**1**	**0**
TBPP Mix	**8**	**7.90[h]**	**0**	**8**	**1**	**7**	**6**	**1**
MPP Mix	**2**	**3.23[i]**	**0**	**2**	**0**	**2**	**1**	**1**
TDCPP and PentaBDE	**2**	**22.64**	**2**	**0**	**1**	**1**	**1**	**1**
TDCPP and FM 550	**2**	**19.06**	**0**	**2**	**0**	**2**	**2**	**0**
FR > 0.2 mg/g	**3[j]**	**0.11**	**1**	**2**	**0**	**3**	**0**	**3**
None Detected	**12**	**-**	**10**	**2**	**1**	**11**	**1**	**11**
Totals	**102**		**41**	**61**	**24**	**72**	**65**	**35**

a – Indicates the number of samples collected from couches containing the FR and purchased during this time frame. b – Some participants reported purchasing their couch online or through a catalog, and thus the state of purchase was not included in the sum (n=5). c -Indicates the number of samples that did or did not contain a TB 117 label on the product (no data for 2). d- Includes PBDE congeners plus TPP. e- Sample purchased in 2005. f- Measurement is the sum of TPP, TBB and TBPH. g- Measurement is for V6 + TCEP. h- Measurement is the sum of TPP and Tris(4-(tert-butyl)phenyl)phosphate (TBPP). i- Includes measurement of TPP only. j - Two samples contained TDCPP; one sample contained BDE47 and BDE99.

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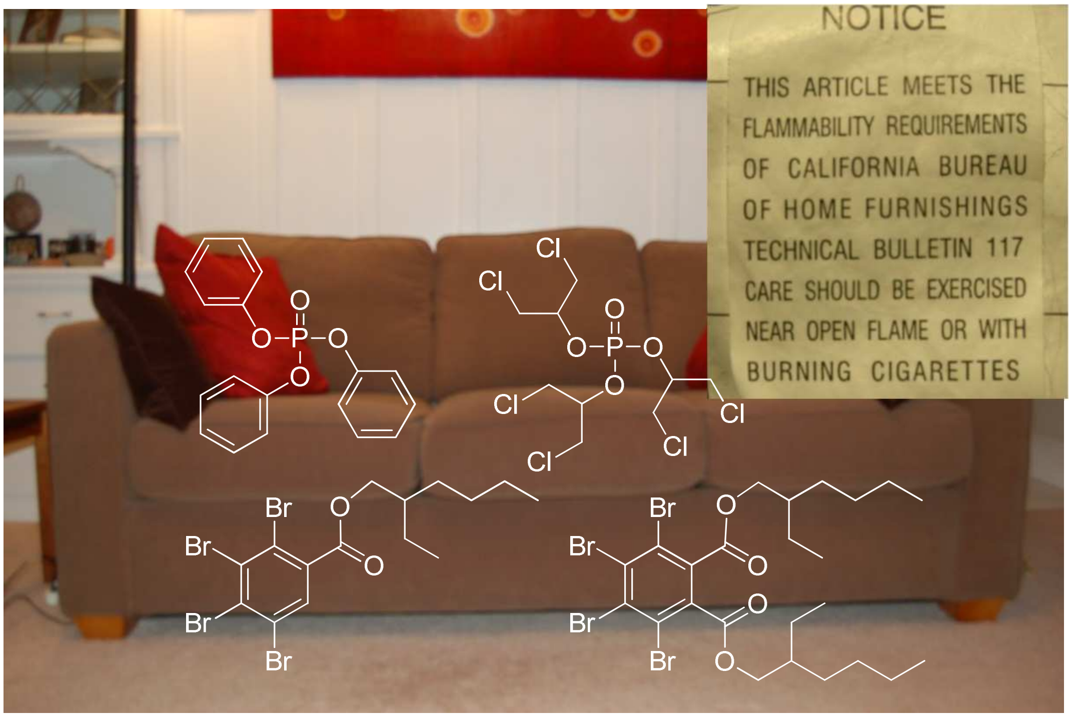
NOTICE
THIS ARTICLE MEETS THE
FLAMMABILITY REQUIREMENTS
OF CALIFORNIA BUREAU
OF HOME FURNISHINGS
TECHNICAL BULLETIN 117
CARE SHOULD BE EXERCISED
NEAR OPEN FLAME OR WITH
BURNING CIGARETTES

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