

IDENTIFICATION OF TRIS(1,3-DICHLORO-2-PROPYL) PHOSPHATE AND OTHER ORGANOPHOSPHATE FLAME RETARDANTS IN U.S. INDOOR ENVIRONMENTS

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Abstract

Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) and other organophosphate flame retardants (OPFRs) are being used as a replacement for PentaBDE in polyurethane foam. Samples of foam from furniture purchased in the USA was analyzed for BFRs and OPFRs, as was dust collected from Boston homes and air actively sampled from Boston offices. TDCPP and other OPFRs were found in a large fraction of the furniture. Concentrations of these compounds in dust and air were comparable to PBDEs. TDCPP is considered a probable human carcinogen. Increased attention is needed to alternatives to PBDEs and to their potential combined effects.

Introduction

Polybrominated diphenyl ethers (PBDEs) were manufactured as three commercial products: PentaBDE, OctaBDE and DecaBDE. PentaBDE was predominantly used in the USA until it was phased out in 2004. Its primary use was as a fire retardant in polyurethane foam for furniture. While large amounts of PentaBDE are still present in U.S. indoor environments, leading to ongoing exposure, other replacement fire retardants are taking its place. Study of these replacements is hindered by a lack of information regarding production volumes, uses, labeling, and, in some cases, identity of fire retardants. We previously reported on the presence in house dust of two components of one alternative, Firemaster 550: 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and bis (2-ethylhexyl) tetra-bromophthalate (TBPH).¹ We report here on the presence of another PentaBDE replacement, tris(1,3-dichloro-2-propyl) phosphate (TDCPP, CAS # 13674-87-8), in furniture, indoor air and house dust from the USA (See Figure 1). We also examined two other organophosphate flame retardants (OPFRs): tris (1-chloro-2-propyl) phosphate (TCPP, CAS 13674-84-5), and triphenyl phosphate (TPP, CAS 115-86-6).

Materials and Methods

Foam Sampling: Based on previous overviews of alternative fire retardants, particularly organophosphate compounds^{2,3}, we primarily targeted foam from furniture purchased from a large commercial retailer in the USA that reportedly no longer uses brominated flame retardants (BFRs). Foam samples were collected from several US cities. While all of the furniture was purchased in the USA, labels indicated that a number of items were manufactured in either Sweden or China. For exploratory purposes, foam was also sampled from a new baby stroller and the foam sound-proofing of a piece of laboratory equipment, a mechanical dust sieve. In each case, about 2-10 cm³ of foam were collected.

Air Sampling: Indoor air was collected from 31 offices during winter 2008/9 in the Boston, Massachusetts (USA) area using active sampling. We employed a glass-fiber filter (GFF) followed by a pre-cleaned polyurethane (PUF) plug; air was sampled for approximately 48 hours at 4 L/minute for a total volume of about 11 m³.⁴

Dust Sampling: Dust was collected from vacuum cleaner bags obtained from homes in Boston, Massachusetts area between 2002 and 2007. The samples were not collected from the same locations as the foam or air samples. Details on collection, treatment and storage of the dust samples are detailed elsewhere.⁵

Sample Extraction and Analysis. Samples were analyzed for the following organophosphate-based compounds: TDCPP, TCPP and TPP. We also measured several BFRs including PBDEs, TBB and TBPH. Our method for the analysis of the brominated

flame retardants measured in this study was reported previously.¹ The analysis of samples for the organophosphate compounds is briefly outlined here. Approximately 0.3 to 0.5 grams of sieved dust was accurately weighed, spiked with 50 to 100 ng of two quantification standards (4-fluoro-2,3,4,6-tetrabromodiphenyl ether (F-BDE 69) and ¹³C-labeled decabromodiphenyl ether (¹³C BDE 209), and extracted in stainless steel cells using pressurized fluid extraction (ASE 300, Dionex Inc.). Cells were extracted three times with 50:50 dichloromethane:hexane at a temperature of 100°C and at 1500 psi. Foam samples of approximately 0.2-0.3 grams in weight were also extracted using the same solvents on the ASE system but no internal standards were spiked into the ASE cell. Final extracts were reduced in volume to approximately 1.0 mL using an automated nitrogen evaporation system (Turbo Vap II, Zymark Inc.). Foam sample extracts of approximately 3.5 mL in volume were then accurately weighed in a 4 mL amber vial and a 50 µL aliquot was transferred to an autosampler vial, spiked with 100 ng of ¹³C CDE 141, and prepared for GC/MS analysis. Dust extracts were purified by elution through a glass column containing 4.0 g of 6% deactivated alumina. All analytes were eluted with 50 mL of a 50:50 mixture of dichloromethane:hexane. The final extract was then reduced in volume to 0.5 mL and 50 ng of the recovery standard, ¹³C CDE 141, was added prior to GC/MS analysis. Glass fiber filters and polyurethane foam plugs used to monitor air were extracted with petroleum ether in Soxhlets for 24 hours. Extracts collected from the Soxhlets were concentrated in volume to approximately 0.5 mL and spiked with the recovery standard (100 ng ¹³C CDE 141) and prepared for analysis by GC/MS.

Samples were analyzed using GC/MS operated in either electron impact mode (GC/EI-MS) for the detection of TCPP and TPP or electron capture negative ionization mode (GC/ECNI-MS) for TDCPP and the brominated flame retardants. The method for the analysis of BFRs measured in this study was reported previously.¹ A 0.25 mm (I.D.) x 15 m fused silica capillary column coated with 5% phenyl methylpolysiloxane (0.25 µm film thickness) was used for the separation of the analytes. Pressurized temperature vaporization (PTV) injection was employed in the GC. The inlet was set to a temperature of 80 °C for 0.3 minutes and then a 600 °C/min ramp to 275 °C was employed to efficiently transfer the samples to the head of the GC column. The oven temperature program was held at 40 °C for 1 min followed by a temperature ramp of 18 °C /min to 250 °C, followed by a temperature ramp of 1.5°C /min to a temperature of 260 °C, followed by a final temperature ramp of 25 °C/min to 300 °C which was held for an additional 20 min. The transfer line temperature was maintained at 300 °C and the ion source was held at 200°C. PBDEs were quantified by monitoring bromide ions (*m/z* 79 and 81). ¹³C BDE-209 was monitored by *m/z* 494.6 and 496.6; TDCPP was quantified by monitoring *m/z* 319 and 317 and TPP was quantified by monitoring *m/z* 326 and 325.

Results and Discussion

Foam: 26 foam samples from furniture—chairs, couches, futons, etc.—were collected and analyzed. All but one were purchased between 2004 and 2009. The one exception was an older futon purchased second-hand, probably manufactured before 2004. Of the 26 samples, 15 contained TDCPP, occurring at concentrations of 1-5% by weight. Four contained TCPP at concentrations of 0.5-2.2%. Two contained unidentified non-brominated compounds. Three contained no detectable amount of organophosphate or BFR. One contained TBB and TBPH (4.2%) and one contained PentaBDE (0.5%). The latter was the older futon discussed above. As our study was of limited scope and not designed as a random sample, it cannot be expected to reflect the prevalence of organophosphate flame retardants or BFRs in the foam furniture currently in use in the USA. Nevertheless, these results clearly indicate the presence of TDCPP and TCPP at percent levels in foam furniture in the US. Both the baby stroller and the foam sound-proofing contained TDCPP, the latter at 2.2%.

Indoor Air from Offices: TDCPP was detected in air from 87% of the 31 offices. Air concentrations were approximately log-normally distributed, ranging from <LOD to 4.4 ng/m³ with a geometric mean of 1.2 ng/m³. The latter is several times higher than the geometric mean indoor air concentrations we previously reported for PBDEs.⁴ Other compounds in the office air samples are still being analyzed.

Relatively few data exist on TDCPP concentrations in indoor air, with none reported for

North America. Marklund et al⁶ sampled air from 17 workplaces and homes (presumably in Sweden) using solid phase extraction columns. The concentrations of TDCPP ranged from <0.2 – 150 ng/m³ with a median of <5 ng/m³. Staaf et al⁷ sampled air from 29 indoor environments (presumably in Sweden). TDCPP concentrations ranged from <1 to 7 ng/m³ with a median of <1 ng/m³. Saito et al.⁸ recently reported finding TDCPP in air from 18 Japanese homes (median ND, range ND to 0.60 ng/m³) and 14 office buildings (median ND, range ND to 8.7 ng/m³). Reemstma et al⁹ recently reviewed these and other data but provided summary averages of only detected concentrations. Although comparisons are potentially complicated by differences in methods and sampled locations, our indoor air results appear comparable with previous results.

Residential dust: TDCPP and TPP were detected in over 96% of the dust samples. TCPP was detected in only 24%, but this low detection frequency may be due to a co-elution problem. TDCPP concentrations in dust ranged from <0.090 to 56 µg/g with a geometric mean of 1.9 µg/g. TPP concentrations ranged from <0.15 to 1800 µg/g with a geometric mean of 7.4 µg/g. TCPP concentrations ranged from <0.14 to 5.5 µg/g with a geometric mean of 0.57 µg/g. For comparison, the geometric mean concentrations of total PBDEs in these dust samples was 4.7 µg/g; geometric mean concentrations of TBPH and TBB were 0.65 and 0.84 µg/g, respectively. Concentrations of the organophosphate fire retardants were not significantly correlated with PBDEs. However, TPP was moderately correlated (Spearman=0.4) with TBPH and TBB. Note that TPP is one of the non-brominated components of Firemaster 550.¹ The relative proportions of different flame retardants varied between samples; in some samples the concentration of organophosphate compounds exceeded the BFRs.

Relatively few data exist for TDCPP in dust with none reported for North America. Marklund et al.¹⁰ collected dust from vacuum cleaner bags used from various kinds of indoor environments (presumably Swedish, n=15). TDCPP concentrations ranged from 0.2 to 67 µg/g with a median of 1.1 µg/g. Wensing¹¹ summarized two earlier German reports that found median concentrations of 1.2 and 1.7 µg/g in house dust. Takigami et al.¹² recently reported TDCPP concentrations in dust from a Japanese hotel (n=8), ranging from 0.07 to 18 µg/g with a median of 1.7 µg/g. Using microwave-assisted extraction, Garcia et al^{13,14} recently reported TDCPP in dust from indoor environments (presumably Spanish) including residences and cars, ranging from ND to 13 µg/g with a median of 0.3 µg/g. Although comparisons are potentially complicated by differences in methods and sampled locations, our indoor dust results appear comparable with previous results.

Exposure to TDCPP: TDCPP and a related compound, tris (2,3-dibromopropyl) phosphate (tris-BP), were removed from children's sleepwear in the US several decades ago.^{3,15} Unlike tris-BP, TDCPP found other uses, including as a fire retardant in polyurethane foam and other applications. Trade names include Fyrol FR2, Firemaster T33P, and Antiblaze 195. Studies report that TDCPP is mutagenic,¹⁵ carcinogenic in rats¹⁶ and dermally absorbed.¹⁷ The US Consumer Product Safety Commission considers TDCPP to be a probable human carcinogen,¹⁸ while the USEPA considers it to be moderate hazard for cancer, and a moderate hazard for reproductive and developmental effects.²

Relatively little is known about environmental concentrations or human exposure to TDCPP. TDCPP has been found in U.S. streams.¹⁹ It is unclear if exposure occurs via diet. The US Consumer Product Safety Commission¹⁸ recently estimated exposure to this compound using primarily modeled air concentrations, while ignoring inadvertent dust ingestion, thought to be a major route of exposure for PBDEs. Additional data regarding exposure to TDCPP are thus sorely needed. Based on geometric means of our data and nominal dust ingestion rates of 100 mg/d for young children and 20 mg/d for adults,²⁰ we estimate median exposure of TDCPP via inhalation to be about 20 ng/d, with dust ingestion on the order of 40 ng/d for adults and 200 ng/d for young children. These are very preliminary estimates for a number of reasons, including the uncertainty of dust ingestion exposure factors and the omission of dermal absorption. Another important issue is the combined exposure to the many flame retardants found in air and dust; such complex mixtures could potentially lead to additive, antagonistic or even synergistic effects. Use of a 95% upper bound on the concentration in dust of total flame retardants leads to an estimated exposure for children many orders of magnitude higher. Increased attention is needed to alternatives to PBDEs and to their potential combined effects.

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Figure 1. Structure of tris(1,3-dichloro-2-propyl) phosphate (TDCPP)

