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DOI:

[10.1016/j.emcon.2016.12.001](https://doi.org/10.1016/j.emcon.2016.12.001)

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Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Stubbings, WA, Drage, DS & Harrad, S 2016, 'Chlorinated organophosphate and “legacy” brominated flame retardants in UK waste soft furnishings: a preliminary study', *Emerging Contaminants*, vol. 2, no. 4, pp. 185-190. <https://doi.org/10.1016/j.emcon.2016.12.001>

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Chlorinated organophosphate and “legacy” brominated flame retardants in UK waste soft furnishings: A preliminary study



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ARTICLE INFO

Article history:

Received 13 January 2016

Received in revised form

28 November 2016

Accepted 1 December 2016

Available online 8 December 2016

Keywords:

Hexabromocyclododecane

Waste furniture

PBDEs

Tris(2-chloroisopropyl)phosphate

ABSTRACT

The Furniture and Furnishings (Fire Safety) Regulations 1988 is the major driver for the use of chemical flame retardants (FRs) in soft furnishings marketed in the UK. While these regulations specify the level of flame retardancy required, they do not specify how such levels should be achieved. Consequently, it remains unclear which FRs are present in UK soft furnishings. This is important not only to help assess what FRs we may be exposed to currently, but which FRs are currently entering the waste stream with concomitant potential for release into the environment. To address this data gap, concentrations of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and a range of chlorinated organophosphate flame retardants (OPFRs) were measured in samples of domestic and office waste soft furnishings products entering the UK waste stream in 2011 and 2012. This preliminary study measured the FR content of: carpets ($n = 4$), curtains ($n = 7$), mattress fabrics ($n = 2$), furniture foam ($n = 9$), and furniture upholstery textiles ($n = 10$). Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) were not found at significant concentrations (below detection limits in most samples) in any of the twenty two analysed products. In contrast, 7 of the 9 furniture foam samples were treated with tris(2-chloroisopropyl)phosphate (TCIPP) at a mean concentration of 1.9% w/w, with another single foam sample containing tris(1,3-dichloroisopropyl)phosphate (TDCIPP) and tris(2-chloroethyl)phosphate (TCEP) at 1.1 and 0.5% respectively. By comparison, PBDE concentrations are within the range reported previously for UK indoor dust [18], rather than the percent by weight levels required to impart flame retardancy.

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1. Introduction

In the UK, the use of flame retardants (FRs) in domestic and office furniture is driven by the Furniture and Furnishings (Fire Safety) Regulations 1988 (as amended in 1989, 1993 and 2010). To meet these regulations, a variety of FRs have been used. However, because the regulations do not stipulate the use of specific FRs, and it is not a labelling requirement to state which FR was used in a product, it is unclear which chemicals were applied, and at what concentration. These regulations do not apply to curtains and carpets, however, as these products are covered under UK General Product Safety Regulations 2005.

Historically, two main groups of FRs have been used to treat UK consumer products, brominated flame retardants (BFRs) and chlorinated organophosphate flame retardants (OPFRs), such as tris(2-chloroisopropyl)phosphate (TCIPP), tris(2-chloroethyl)phosphate (TCEP) and tris(1,3-dichloroisopropyl)phosphate (TDCIPP). Numerous studies have raised concern about the potential adverse environmental and human health effects associated with the use of these chemicals. Hexabromocyclododecane (HBCDD) has been identified as an endocrine disrupting chemical (EDC) that induces enzymes and alters thyroid homeostasis with potential to cause adverse effects in humans at relatively low exposure levels [9,10,29,30,34]. Several studies have indicated that polybrominated diphenyl ethers (PBDEs) can alter liver enzymes, disrupt thyroid homeostasis, and are associated with early onset of puberty, reduced fertility, and impaired neurological development [12,19,31].

TCIPP accumulates in the liver and kidneys [21], decreases cell number and alters neurodifferentiation [11], is irritating to skin and

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Peer review under responsibility of KeAi Communications Co., Ltd.

eyes of rats [21] and is considered potentially carcinogenic [22]. TCEP is toxic to aquatic organisms, causes reduced fertility and neurotoxic effects in rats and mice and is carcinogenic to animals [8,24,33]. Within the EU, TCEP is classified as a “potential human carcinogen” and has been listed as a “known carcinogen” by the Californian EPA since 1992 [7,23]. Another chlorinated OPFR, TDCIPP is also thought to be carcinogenic, with tumours observed in the liver, kidneys and testes of rats fed with TDCIPP for 2 years [4,5,33]. Within the EU, TDCIPP is classified as a level 2 carcinogen [16], with a recent study showing TDCIPP to display concentration-dependent neurotoxicity, inhibit DNA synthesis, and to decrease cell number and alter neurodifferentiation [11].

Anecdotal evidence exists that prior to the introduction of the 1988 UK fire safety regulations, UK soft furnishings were primarily treated with TCEP and TDCIPP and that after the introduction of these regulations, TCIPP was primarily used (pers. comm., Flexible Foam Research Ltd.). However, to our knowledge no previous studies have investigated which FRs were historically used in UK furniture, nor have they identified which FRs are now commonly used. Additionally, approximately 95% of Penta-BDE in Europe was used in flexible PUF widely used in domestic furniture [13].

Against this backdrop, this preliminary study measures concentrations of PBDEs, HBCDD and a range of chlorinated OPFRs, in 32 samples taken from 22 products (more than one material – e.g. foam filling and textile cover was taken from some products) of waste soft furnishings and furniture obtained from a variety of UK domestic and office locations to characterise the FRs present in this component of the UK waste stream. Materials studied are: carpets, curtains, mattress fabric, furniture PUF and furniture upholstery.

2. Sampling

Samples were obtained from a variety of domestic and office locations across the UK during 2011–2012. The following samples were taken: domestic sofa/chair (n = 5); domestic curtains (n = 4); domestic carpet (n = 4); domestic mattress (n = 1); office chair (n = 5); office carpet (n = 3). Table 1 shows the complete list of products surveyed, with information provided about the location from which the sample was taken, and where known, the country of manufacture.

Table 1
List of samples and materials analysed in the study.

Sample code	Furniture type	Materials sampled	Year of purchase	Year of manufacture	Additional information
Domestic 1	Dining chair	PUF	1995	u	Wembley
Domestic 2	Sofa	PUF & wool fabric	u	u	Harborne, Birmingham
Domestic 3	Sofa	PUF & cotton fabric	u	u	Ladywood furniture project
Domestic 4	Sofa	polyester fabric	2002	2001	Isleworth, Middx; made in Wales
Domestic 5	Armchair	PUF, cotton fabric & cotton batting	u	u	Harborne, Birmingham
Domestic 6	Curtain	cotton	u	u	Ladywood furniture project
Domestic 7	Curtain	cotton	u	1993	Ladywood furniture project
Domestic 8	Curtain	cotton	u	2001	Ladywood furniture project
Domestic 9	Curtain	cotton	u	2009	Haywards Heath, Sussex
Domestic 10	Carpet	blend ^a	2010	u	Wembley
Domestic 11	Carpet	blend ^a	1992	u	Wembley
Domestic 12	Carpet	polyester	1998	u	Wembley
Domestic 13	Carpet	wool	2002	u	Colchester, Essex
Domestic 14	Mattress	cotton or linen fabric & cotton and polyester batting	u	u	Harborne, Birmingham
Office 1	Desk chair	PUF & cotton fabric	u	u	University of Birmingham
Office 2	Desk chair	PUF & wool fabric	u	u	University of Birmingham
Office 3	Desk chair	PUF	1998	u	Wembley
Office 4	Sofa	PUF, fabric & polyester batting	u	u	University of Birmingham
Office 5	Stool	PUF & fabric	u	u	University of Birmingham
Office 6	Carpet	polyester	u	u	University of Birmingham, Room PH 210
Office 7	Carpet	polyester	u	u	University of Birmingham, Room PH 209
Office 8	Carpet	polyester	2008	u	Walton-on-Thames

^a Blend = 80/20 or 50/50 polypropylene wool; u = unknown.

As this study aimed to examine FR contamination of waste products, samples were required to meet two criteria: 1) the product must have been purchased within the UK, and 2) the product had to be ready for disposal and would otherwise enter the UK waste stream. Sample donors were asked to provide the year of purchase for donated items where known. Product manufacturer's labels were also collected where possible, in an attempt to further characterise items with respect to the year and place of manufacture. However, such labelling was not always available. Collected samples were wrapped in aluminium foil and sealed inside a plastic bag. When sampling from sofas and chairs, any accompanying textiles and composite layers were also taken along with the foam filling where possible.

3. Materials and methods

3.1. Sample preparation

Prior to analysis for FRs, carpet and curtain textile samples were cut into strips as small as possible (approx. 5 mm × 2 mm) and shaken thoroughly in a sealed plastic bag in an effort to ensure homogeneity. Approximately 1 g of each sample was then taken for analysis from this mixture. To determine initial concentrations of FRs in PUF samples, small pieces of foam (ca. 5 mm × 5 mm × 5 mm) were taken from random points from each sample totalling ca. 50 mg.

3.2. Extraction and clean up

In PUF, carpet, and curtain textile samples, PBDEs and HBCDDs were determined via a combined extraction and clean-up method based on that of Abdallah et al. [3]. Briefly, a 1 g aliquot of sample was added to a pre-packed accelerated solvent extractor (ASE) cell, containing florisil, hydromatrix and 44% acid-impregnated silica (Fig. 1). The cells were spiked with 100 ng of ¹³C₁₂-BDEs -47, -99, -153 and -209 and ¹³C₁₂-HBCDDs (α-, β- and γ-) and underwent pressured liquid extraction using an ASE 350 (Dionex). Target compounds were extracted using dichloromethane:n-hexane (3:2 v/v) at 90 °C, with three 5 min static cycles, with 2 min purge time. Extracts were concentrated to

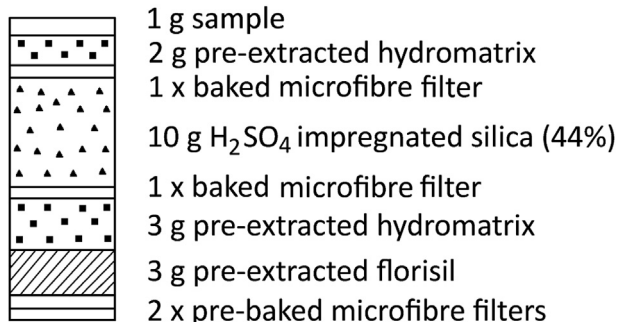


Fig. 1. Pre-packed ASE cell.

near-dryness using a Zymark Turbovap II (Hopkinton, MA, USA) sample evaporator and reconstituted in 200 µL of methanol containing 100 ng of ¹³C₁₂-BDE-100 and d₁₈-γ-HBCDD. As these analyses revealed no significant PBDE or HBCDD presence in the majority of furniture samples (Table 2), a similar procedure was followed to conduct initial semi-quantitative screening of samples for OPFR content. All initial screenings were one shot analyses with no replicates.

Following the detection of substantial amounts of chlorinated OPFRs in PUF samples, these samples were then subjected to fully quantitative analysis for these contaminants conducted in triplicate. To do so, 50 mg foam and 5 mL of ethyl acetate were added to a pre-washed test tube, vortexed for 1 min and sonicated for 5 min before being centrifuged for 2 min at 2000 rpm. The supernatant was transferred to a clean tube, the extraction was repeated and both supernatants were combined (10 mL total) and vortexed for 1 min 1 mL of sample was then transferred to a clean tube and diluted using 9 mL ethyl-acetate. Finally 10 µL of the first dilution was transferred to and diluted further using 90 µL methanol containing 90 ng d₁₅-labelled TPhP as internal standard (x 10,000 dilution in total).

3.3. Analysis

Target PBDEs (BDEs – 47, 85, 99, 100, 153, 154, 183, 209) and HBCDDs were measured on a LC-MS/MS system composed of a dual pump Shimadzu LC-20AB Prominence liquid chromatograph (Kyoto, Japan) equipped with a SIL-20A autosampler, a DGU-20A3 vacuum degasser coupled to a AB Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) operated in negative ion mode. For PBDEs the MS was operated in atmospheric photoionisation mode. Full details of PBDE analysis can be found elsewhere, [2]. For HBCDDs, the MS was operated in electrospray ionisation mode. Full parameters of HBCDD analysis can be found elsewhere [1].

Semi-quantitative screening of samples to check for the presence of OPFRs was conducted on an Agilent 6890 GC coupled to an Agilent 5973 MS on a 25 m × 0.22 mm × 0.25 mm HT-8 column operated in electron impact ionisation (EI) mode. Injection was performed in pulsed pressure 14.3 psi until 1.5 min and purge flow to split vent of 50 mL min⁻¹ after 1.25 min. The GC temperature program was 90 °C, hold 1.25 min, ramp 10 °C min⁻¹ to 240 °C, ramp 20 °C min⁻¹ to 310 °C, hold 16 min. Helium was used as a carrier gas with a flow rate of 1.0 mL min⁻¹. The mass spectrometer was run in selected ion monitoring (SIM) mode. Dwell times ranged between 20 and 30 ms. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively and the electron multiplier voltage was at 2200 V d₁₅-labelled tri-phenyl-phosphate (TPhP) was used as an internal standard to quantify

Table 2 Concentrations (mg kg⁻¹) of PBDEs, HBCDD and OPFRs in domestic soft furnishing samples.

Sample code	Material	Target analyte													
		BDE-47	BDE-85	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	α-HBCDD	β-HBCDD	γ-HBCDD	TCIPP	TCEP	TDClPP
Domestic 1	PUF	0.044	0.00056	0.0051	0.025	0.00080	0.0012	<LOD	3.4	0.068	0.062	0.16	8400	<0.00067	<0.0011
Domestic 2	PUF	3.8	<0.00024	<0.00011	<0.00014	<0.00017	0.00030	0.0076	25	0.74	0.81	0.35	17,000	<0.00067	<0.0011
Domestic 3	wool fabric	<0.0080	<0.00024	<0.00011	<0.00014	0.015	<0.00020	0.012	<0.00084	<0.0031	16	1.1	<0.00044	<0.00067	<0.0011
Domestic 3	PUF	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	0.083	0.083	0.069	0.073	0.71	<0.00044	<0.00067	<0.0011
Domestic 3	cotton fabric	<0.0080	<0.00024	<0.00011	<0.00014	0.020	<0.00020	0.016	0.18	15	20	<0.0039	<0.00044	<0.00067	<0.0011
Domestic 4	polyester	0.056	<0.00024	0.041	0.123	0.023	0.078	0.41	33	0.035	0.072	0.075	<0.00044	<0.00067	<0.0011
Domestic 5	PUF	0.075	0.0015	0.013	0.053	0.0036	0.0031	0.0015	1.6	0.11	0.040	0.14	8600	<0.00067	<0.0011
Domestic 5	cotton fabric	<0.0080	<0.00024	<0.00011	<0.00014	0.024	<0.00020	0.018	4.6	6100	1700	360	<0.00044	<0.00067	<0.0011
Domestic 5	cotton batting	<0.0080	<0.00024	<0.00011	<0.00014	0.011	<0.00020	0.0097	0.12	<0.0031	17	4.2	<0.00044	<0.00067	<0.0011
Domestic 6	cotton	0.27	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	3.1	0.015	0.093	0.18	<0.00044	<0.00067	<0.0011
Domestic 7	cotton	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	42	0.93	0.33	0.17	<0.00044	<0.00067	<0.0011
Domestic 8	cotton	<0.0080	<0.00024	<0.00011	0.049	<0.00017	<0.00020	<0.00015	0.026	0.20	0.10	0.72	<0.00044	<0.00067	<0.0011
Domestic 9	cotton	0.097	0.0036	0.0022	0.018	<0.00017	<0.00020	<0.00015	1.1	0.068	0.068	0.091	<0.00044	<0.00067	<0.0011
Domestic 10	blend ^a	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	0.097	<0.0031	<0.0034	<0.0039	<0.00044	<0.00067	<0.0011
Domestic 11	blend ^a	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	<0.00084	<0.0031	<0.0034	<0.0039	<0.00044	<0.00067	<0.0011
Domestic 12	polyester	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	<0.00084	0.050	<0.0034	0.040	<0.00044	<0.00067	<0.0011
Domestic 13	wool	0.0045	<0.00024	0.00072	0.0037	<0.00017	<0.00020	<0.00015	0.046	<0.0031	<0.0034	0.051	<0.00044	<0.00067	<0.0011
Domestic 14	cotton or linen fabric	<0.0080	<0.00024	<0.00011	<0.00014	0.021	<0.00020	0.017	<0.00084	16	8.2	11	<0.00044	<0.00067	<0.0011
Domestic 14	cotton & polyester batting	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	<0.00084	14	7.7	<0.0019	<0.00044	<0.00067	<0.0011

^a blend = 80/20 or 50/50 polypropylene wool.

triethyl phosphate (TEP), tri-n-propyl phosphate (TnPP), tri-iso-butyl phosphate (TiBP), Tri-n-butyl phosphate (TnBP), TCEP, TCIPP, tri (2-butoxyethyl) phosphate (TBOEP), TPhP, TDCIPP and tri-cresyl phosphate (TCP).

This initial screening was followed by a quantitative determination of OPFR concentrations in all samples in which the screening indicated them to be present. All OPFR concentrations were determined using a dual pump Shimadzu LC-20AB Prominence high pressure liquid chromatograph (Kyoto, Japan) equipped with a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA). The MS was operated in electrospray ionisation mode. A Varian Pursuit XRS3 C18 reversed phase analytical column (150 mm × 4.6 mm i.d., 3 μm particle size) was used for separation of target OPFRs (see [supplementary information for additional details](#)).

4. Results and discussion

Concentrations of PBDEs, HBCDD and OPFRs detected in domestic and office samples are presented in [Tables 2 and 3](#), respectively. In all but one sample (fabric from a domestic chair - discussed below), neither of the “legacy” BFR groups were found at concentrations required to impart flame retardancy.

The semi-quantitative screening analysis to check for the presence of ten OPFRs (TEP, TnPP, TiBP, TnBP, TCEP, TCIPP, TBOEP, TPhP, TDCIPP and TCP), revealed eight (all PUF) samples to contain at least one of these and subsequent quantitative analysis was conducted to determine concentrations of OPFRs.

In summary, TCIPP was found at percent levels in seven samples (domestic seat PUF (n = 3); office seat PUF (n = 4)) (0.84–3.8% by weight), with TDCIPP and TCEP detected at a similar elevated level in one sample (“office 3” chair PUF; 1.1% and 0.50% by weight respectively).

Our findings are largely consistent with reports that TCIPP was the preferred FR used in the production of UK PUF for domestic and office applications due to lower production costs than similar FRs such as TDCIPP [16]. However, this does not account for the observed presence of both TDCIPP and TCEP in significant concentrations in the “office 3” desk chair purchased in 1998, as TCEP has not been used in the production of UK PUF since the introduction of the 1988 flammability regulations (pers. comm., Flexible Foam Research Ltd.). A possible explanation is that the presence of TCEP in this one sample is due to its formation as reaction by-product formed in the manufacture of TDCIPP, which has been reported to lead to the presence of TCEP as an impurity in formulations containing TDCIPP [15]. TDCIPP is more commonly used as a flame retardant in US furniture where it was used as a drop-in replacement for Penta-BDE to meet the more stringent California Technical Bulletin of Home Furnishings 117 standard, exemplified by in the detection of TDCIPP in 50% of samples in a 2012 survey of US residential furniture PUF [25]. It is therefore possible that this item was manufactured outside of the UK (most likely the USA) and subsequently found its way into the UK market. Alternatively, we have reported previously that while TCIPP is the predominant OPFRs in dust from UK homes and offices, TDCIPP is present at broadly equivalent levels to TCIPP in dust from UK cars [6]. This was attributed to the fact that the more expensive TDCIPP rather than TCIPP is preferred in vehicle PUF owing to the latter’s inability to meet the more stringent flame retardancy requirements in vehicle PUF [16]. It is therefore also possible that the foam in this apparent “outlier” sample was originally intended for use in vehicles.

As noted earlier, elevated HBCDD concentrations (~8200 mg kg⁻¹ ΣHBCDD) were observed in the cotton upholstery fabric of the “domestic 5” armchair sample. However, the underlying PUF of

Table 3
Concentrations (mg kg⁻¹) of PBDEs, HBCDD and OPFRs in office soft furnishing samples.

Sample code	Material	Target analyte													
		BDE-47	BDE-85	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	α-HBCDD	β-HBCDD	γ-HBCDD	TCIPP	TCEP	TDCIPP
Office 1	PUF	0.094	0.0018	0.019	0.085	0.0034	0.0051	<0.00015	<0.00084	0.053	0.014	0.0085	17,000	<0.00067	<0.0011
Office 1	cotton fabric	<0.0080	<0.00024	<0.00011	<0.00014	0.023	<0.00020	0.019	<0.00084	<0.0031	7.7	<0.0039	<0.00039	<0.00067	<0.0011
Office 2	PUF	<0.0080	<0.00024	0.0023	0.0089	0.0016	0.0032	0.0030	0.14	0.010	0.0065	38,000	<0.00067	<0.0011	
Office 2	wool fabric	<0.0080	<0.0002	<0.00011	<0.00014	0.021	<0.00020	0.019	<0.00084	1.2	15	<0.0039	<0.00044	<0.00067	<0.0011
Office 3	PUF	0.073	0.031	0.02	0.096	0.0064	0.0087	0.0038	1.2	0.42	0.14	<0.00044	5000	11,000	
Office 4	PUF	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	0.015	<0.0031	<0.0034	16,000	<0.00067	<0.0011	
Office 4	synthetic fibre topped with PVC	<0.0080	<0.00024	<0.00011	<0.00014	0.031	0.030	0.020	<0.00084	26	4.3	<0.0039	<0.00067	<0.0011	
Office 4	polyester batting	<0.0080	<0.00024	<0.00011	<0.00014	0.0059	0.0020	0.0082	<0.00084	4.1	8.3	7.1	29,000	<0.00067	
Office 5	PUF	0.21	0.057	0.11	0.37	0.010	0.029	0.0093	0.69	0.18	0.11	0.20	<0.00067	<0.0011	
Office 5	wool fabric	<0.0080	<0.00024	<0.00011	<0.00014	0.029	<0.00020	0.022	<0.00084	19	3.8	<0.0039	<0.00067	<0.0011	
Office 6	polyester	0.055	0.034	0.022	0.11	0.026	0.078	0.011	0.22	0.46	0.24	<0.00044	<0.00067	<0.0011	
Office 7	polyester	<0.0080	<0.00024	0.0068	0.0088	<0.00017	<0.00020	<0.00015	0.041	0.40	0.18	<0.00044	<0.00067	<0.0011	
Office 8	polyester	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	0.0055	0.24	0.20	<0.00044	<0.00067	<0.0011	

the armchair was treated with TCIPP. HBCDD is reported to be used as a textile coating agent in polymer dispersions applied to cotton or cotton/synthetic blends for residential upholstery fabrics [32]. While the percentage of HBCDD present in the fabric (0.82% by weight) is relatively lower than reported previously for HBCDD-treated curtains used in Japanese domestic applications (~25,000 mg kg⁻¹; 2.5% by weight), there is a possibility that the fabric was treated with HBCDD and the concentration has dwindled during the armchair's lifecycle [26,28]. Often sofa and armchair upholstery can be removed for cleaning and this may result in the additive, unbound HBCDD being depleted. This level is lower than reported previously for HBCDD-treated curtains used in Japanese domestic applications, but likely still consistent with use for flame-retardancy purposes.

While some samples contained OPFRs or HBCDD, just over half of the samples analysed did not contain significant concentrations of our target FRs. With respect to the “domestic 3” sofa sample; this was obtained from a charity that redistributes used furniture at discounted rates to low-income households. Pertinently, the charity was unable to resell this sofa because it did not have the required fire safety labelling attached and therefore did not meet UK resale criteria. Therefore, it is a possibility that the sofa was manufactured prior to the 1988 fire safety regulations, which would explain why our target FRs were not detected. In the polyester fibre filling material from the “domestic 4” sample, the absence of detectable concentrations of our target FRs may be due to the inherently flame retardant nature of the fibres, which may mean that the addition of FRs was deemed unnecessary [17]. A similar explanation may account for the lack of target FRs found in our carpet samples. It is more common for the foam underlay of carpets to be treated with FRs. A further explanation for the absence of our target FRs from some samples could be that these samples were flame-retarded with a chemical not targeted in our study such as melamine or “novel” brominated flame retardants (NBFRs), which include: decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-DBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEH-TEBP) and hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO).

Despite approximately 95% of Penta-BDE sold in Europe being used in flexible PUF [13], our data do not indicate that any of the samples analysed had been treated with PBDEs. Indeed, concentrations are within the range reported previously for UK indoor dust [18], rather than the percent by weight levels required to impart flame retardancy. A caveat is that one cannot discount entirely the possibility that the tested items were flame-retarded at the point of manufacture, but that the PBDEs have migrated from the product over its lifecycle.

While the preliminary nature of this study precludes firm conclusions, it appears that concentrations of both PBDEs and HBCDD are highest in the samples of furniture foam as opposed to carpets and curtains. This may be due to the ability of foam to act as a passive sampler for airborne FRs present in the room from which the furniture originated.

While the information available on the year of manufacture of the studied items was incomplete, there does not appear to be any systematic relationship between the PBDE burden and the manufacture or purchase date. In this context, the presence of measurable levels of some congeners (PBDEs 47, 85, 99, 100, and 209) in the domestic curtain sample that was manufactured in 2009 (i.e. post-restrictions) is interesting. A possible explanation is that – in line with the previous paragraph – the curtain material has passively sorbed PBDEs from the indoor environment in which it was placed prior to sampling.

5. Conclusions

Overall, the concentrations detected in these samples indicate that 8 out of 10 surveyed furniture samples were treated with OPFRs – 7 contained TCIPP, with 1 containing TDCIPP and TCEP. Of these 10 items of furniture, 9 contained PUF and one polyester fibre filling material. Based on these limited data, 78% of sampled furniture PUF was treated with TCIPP with a mean concentration of 1.9% (by weight). While this percentage value should be not be taken as an exact indication of the prevalence of TCIPP in UK furniture PUF, it is broadly consistent with the fact that in 2000, 6800 tonnes (18%) of TCIPP within the EU was used in the production of flexible PUF [14]. This suggests that TCIPP has been the primary FR used in meeting UK flammability standards and regulations in furniture, and the results of this preliminary survey reflect this. The prevalence of TCIPP in waste furniture foam represents a potentially important route via which TCIPP may enter the waste stream, and is of substantial concern following disposal to landfill, given the potential for TCIPP leaching from PUF material [27].

Importantly in a legislative context, the PBDE and HBCDD concentrations detected in this study do not indicate any exceedances of the European Commission's proposed threshold for POPs free products of 1000 µg g⁻¹ (with the exception of the HBCDD concentration of the cotton upholstery fabric of the “domestic 5” armchair sample; 8200 µg g⁻¹).

Despite the fact that the fabric of one armchair (domestic 5) was possibly treated with HBCDD, the evidence of this preliminary study is that only a small proportion of soft furnishings and furniture waste now entering the UK waste stream were treated with PBDEs or HBCDD. This is in contrast to some other countries – e.g. Japan, where HBCDD is the most frequently used BFR for treatment of textiles, and concentrations of ~40,000 mg ΣHBCDD kg⁻¹ (~4%) have been reported in polyester textiles [20]. More significant vectors via which PBDEs and HBCDD may enter the UK waste stream is via their presence in expanded and extruded polystyrene foam building insulation, electronic waste (e-waste) and/or other soft furnishing categories not included in this preliminary study such as carpet underlay foams.

Acknowledgements

The authors acknowledge gratefully the provision of an Open Competition CASE studentship award to WAS by the UK Natural Environment Research Council (NERC ref. NE/I018352/1). Additional financial support to WAS from Ricardo-AEA is also acknowledged gratefully. The research leading to these results has received funding from DEFRA.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.emcon.2016.12.001>.

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