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Brandsma, S.H.

2014

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Brandsma, S. H. (2014). *Occurrence and Fate of Alternative Flame Retardants in the Environment*.

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4.1: Organophosphorus flame retardants (PFRs) and plasticizers in house and car dust and the influence of electronic equipment

Chemosphere (2014) In Press DOI: 10.1016/j.chemosphere.2014.02.036

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Abstract

All nine PFRs studied were detected in house and car dust from the Netherlands with the exception of tris(butyl) phosphate (TNBP) and tris(isobutyl) phosphate (TIBP) in car dust. Tris(2-butoxyethyl)phosphate (TBOEP, median $22 \mu\text{g g}^{-1}$) was dominant in house dust collected around and on electronics followed by tris(2-chloroisopropyl)phosphate (TCIPP, median $1.3 \mu\text{g g}^{-1}$), tris(2-chloroethyl)phosphate (TCEP, median $1.3 \mu\text{g g}^{-1}$) and tris(phenyl) phosphate (TPHP, median $0.8 \mu\text{g/g}$). Levels of TPHP and tris(methylphenyl) phosphate (TMPP, also known as TCP) in house dust on electronics were significantly higher than in house dust collected around electronics, suggesting that electronic equipment has limited contribution to the PFR levels in house dust, with the exception of TPHP and TMPP.

Car dust was dominated by tris(1,3-dichloroisopropyl) phosphate (TDCIPP) with the highest levels found in dust collected from the car seats ($1100 \mu\text{g g}^{-1}$). The mean TDCIPP and TCIPP levels observed in car dust were significantly higher than the levels observed in dust collected around electronics. Significantly higher mean TMPP levels in dust taken from car seats were found compared to dust collected around the equipment ($p < 0.05$). This is probably influenced by the use of TDCIPP, TCIPP in polyurethane foam (car seats) and the use of TMPP as plasticizer in car interiors.

Worldwide four PFR patterns were observed in house dust. The PFR pattern in the Netherlands of TDCIPP, TMPP, TCEP, TCIPP and TPHP in house dust is comparable to the pattern found in six other countries, which may point to identical sources of these PFRs in the indoor environment. However, the PFR levels between the countries and within countries showed high variation.

Abbreviations

PFRs, Organophosphorus flame retardants; TNBP, Tris(butyl) phosphate; TIBP, Tris(isobutyl) phosphate; TCEP, Tris(chloroethyl) phosphate; TCIPP, Tris(2-chloroisopropyl) phosphate; TDCIPP, Tris(1,3-dichloroisopropyl) phosphate; TBOEP, Tris(2-butoxyethyl) phosphate; TEHP, Tris(2-ethylhexyl) phosphate; TPHP, Tris(phenyl)phosphate; TMPP (or TCP), Tris(methylphenyl) phosphate; EHDPP, 2-Ethylhexyl diphenyl phosphate; PUF, polyurethane foam; BFRs, Brominated flame retardants; FR, Flame retardant; BDEs, Brominated diphenyl ethers; HBCD, Hexabromocyclododecane; BCMP-BCEP (or V6), 1,3 diyltetrakis(2-chloroethyl)bisphosphate; PBDPP, Resorcinol bis (diphenylphosphate); BPA-BDPP, Bis A bis (diphenylphosphate); PVC, Polyvinylchloride; PC, Polycarbonate; ABS, Acrylonitrile-butadiene-styrene; PPO, Polyphenylene oxide; HIPS, High impact polystyrene; Hexabromocyclododecane; TBBPA, Tetrabromobisphenol A; SRM, Standard reference material; ILS, Interlaboratory study; o, Ortho; m, Meta; p, Para; EH-TBB, 2-ethyl-2,3,4,5-tetrabromobenzoate; BEH-TEBP, bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate; PK, Pakistan; US, United states; SE, Sweden; BE, Belgium; DE, Germany; ES, Spain; RO, Romania; JP, Japan; NZ, New Zealand; KW, Kuwait; NL, the Netherlands.

Introduction

Organophosphorus flame retardants (PFRs) are produced in high volumes and used worldwide by manufacturers of electronic equipment, furniture, textile, and in the building industry in isolation material (Van der Veen and de Boer, 2012). Restriction over the years of some brominated flame retardant (BFRs) like Penta-bromodiphenylether (BDE), Octa-BDE and Deca-BDE technical mixtures has led to an increase in the use of PFRs. In 2006 the estimated total flame retardant (FR) consumption in Europe was 465,000 metric tonnes, with 20 % covered by PFRs, compared to 10 % for the BFRs (CEFIC, 2013). In addition to their use as FR, organophosphorus compounds are also used as plasticizers, stabilizers, lubricants in hydraulic fluids, antifoaming agents, and in floor polish, etc. (EFRA, 2013; Marklund et al., 2003; Van der Veen and De Boer, 2012).

The non-chlorinated organophosphorus compounds 2-ethylhexyl diphenyl phosphate, (EHDPP), tris(isobutyl) phosphate (TIBP), tris(2-ethylhexyl) phosphate (TEHP) tributyl phosphate (TNBP) and tris(2-butoxyethyl)phosphate (TBOEP) are primarily used as plasticizers. TNBP has been detected in wall and ceiling coverings and are used as additive in varnish, concrete, glue and airplane hydraulic fluids (Marklund et al., 2003; Saito et al., 2007). TBOEP is added to floor finish products (up to 0.5–8 % by weight) (Marklund et al., 2003; Kajiwara et al., 2011). TMPPP is further used as a plasticizer in PVC and as additive in hydraulic fluids (Van der Veen and De Boer, 2012). The chlorinated organophosphorus compound tris(2-chloroethyl)phosphate (TCEP), tris(2-chloroisopropyl)phosphate (TCIPP) and tris(1,3-dichloroisopropyl)phosphate (TDCIPP) are used as FR in polyurethane foam (PUF), textiles, plastics, wood preservation coating and unsaturated polyester resins (Ingerowski et al., 2001; WHO. 1998; Van der Veen and de Boer, 2012). TCEP is also found as impurity (4.5-7.5 %) in the technical mixture of 2,2-bis(chloromethyl)propane-1,3-diyltetrakis(2-chloroethyl)bisphosphate (BCMP-BCEP) (also known as V6) used in PUF in the automotive furniture. (EURAR, 2009, Fang et al., 2013). TCIPP and TDCIPP are used as substitutes for Penta-BDE in PUFs. They have been detected up to 5 % by weight in furniture foams (2004-2009) from the U.S. (Stapleton et al., 2009). Another non-halogenated organophosphorus compound, tris(phenyl) phosphate (TPHP), is also added to PUF in combination with other halogenated and non-halogenated mixtures like Penta-BDE (WHO. 1991; Stapleton et al., 2009). TPHP is also used as by-product in Firemaster 550 as alternative for Penta-BDE (Stapleton et al., 2009), and in the technical mixture of resorcinol bis (diphenylphosphate) (PBDPP) and bis phenol A bis (diphenylphosphate) (BPA-BDPP) (both alternatives for DecaBDE) (Waaaijers et al., 2013). PFRs are not covalently bound to the material but used as additives and therefore they can easily leach from products into the environment (Marklund et al., 2003)

PFR have been detected in house dust from different countries Sweden, Belgium, Spain, Germany, Romania, Japan, Philippines, New Zealand, Kuwait, Pakistan and the United States (US) (Marklund et al., 2003; Bergh et al., 2011; Van den Eede et al., 2011; García et al., 2007; Brommer et al., 2012; Ingerowski et al., 2001; Dirtu et al., 2012; Kanazawa et al., 2010; Kim et al., 2013; Ali et al., 2012, 2013; Dodson et al., 2012; Stapleton et al., 2009). The highest PFR levels were observed in house dust from Japan and the US. In general, TBOEP is one of the most abundant organophosphorus

compounds observed in house dust. The concentrations found in house dust often exceeded those of PBDEs, Hexabromocyclododecane (HBCD) and Tetrabromobisphenol A (TBBPA) in the same samples (Stapleton et al., 2009; van der Eede et al., 2011). In addition to house dust PFRs were also found in dust collected in hotels, day care centers, hospitals, shops, prisons, libraries, cinemas, aircrafts and public dance halls (Marklund et al., 2003; Takigami et al., 2009). Data on PFRs in dust collected from cars are limited. The limited data show that some PFRs in car dust from Germany, Pakistan, Kuwait and US were significantly higher than the levels observed in house dust from those countries (Brommer et al., 2012; Ali et al., 2013; and Carignan et al., 2013). The worldwide detection of PFRs in dust from various indoor environments indicates that humans can be exposed to PFRs by inhalation and ingestion of dust.

Limited toxicity data is available for PFRs, however, for some PFRs neurotoxicity and carcinogenicity are observed. The chlorinated PFRs TDCIPP and TCEP have been proven to be carcinogenic and TCIPP is a suspected carcinogen (WHO, 1998). Neurotoxic effects have also been observed for the non-chlorinated PFRs ortho-TMPP, TPHP and TNBP, while TBOEP is a suspected carcinogen (WHO, 1990, 1991, 2000). Dishaw et al. (2011) observed that TDCIPP, TCEP and TCIPP may affect neurodevelopment in PC12 cell studies. Meekers and Stapleton, (2010) concluded that TDCIPP and TPHP may be associated with decreased semen quality in men.

The aim of the current study was to investigate the indoor contamination of ten PFRs (Table 1) in the Netherlands as no data is available. Dust samples were collected in various houses and cars, and the influences of electronic equipment as source for PFRs in house dust was evaluated by taking dust samples on and around electronics. The PFR levels and patterns in house dust from the Netherlands was compared with those from other countries and a comparison was made between the PFR patterns and levels in house and car dust. This study also provides information on the comparison of two analytical methods (gas chromatography-mass spectrometry (GC-MS) versus liquid chromatography-mass spectrometry (LC-MS/MS) for the measurement of ten PFRs in dust.

Materials and Methods

Information about chemicals and suppliers is provided in the supplementary material of this manuscript. The abbreviations for the flame retardants and plasticizers in this manuscript are based on the abbreviation standards introduced by Bergman et al. (2012).

Sample collection

The dust samples used in this study are the same samples that have been collected in our previous study for the analysis of BPA-BDPP and PDBPP (Brandsma et al., 2013b). Detailed information on the dust sampling can be found there. Briefly, dust was collected using a DustreamTM dust collector (Indoor Biotechnologies Ltd, Wiltshire, United Kingdom) containing a disposable filter (mesh size 40

µm). For each sample a new filter was used. Eight houses from the Netherlands were sampled for dust in 2012. Two samples were collected in each house one directly on the electronics and one on the surface around the electronics (within one meter of the electronics). Floors were not included in the sampling. The electronics sampled were bought between 2006 and 2012, more information can be found in Table S4. In 2012 dust was also collected in eight cars from the Netherlands. Two samples were collected in each car, one from the seats and one from the dashboard. Two older cars (2003 and 2004) were included and the other six cars were manufactured between 2008 and 2012 (Table S5).

Sample extraction and cleanup

Detailed information on the sample extraction and cleanup is described in (Brandsma et al., 2013b). Briefly, 50 mg of dust was spiked with an internal standard solution containing TPHP-_{d15} and TNBP-_{d27} before it was extracted in two steps with acetone and toluene. Each extraction was performed by 1 min of Vortex mixing followed by 15 min of ultrasonication. The combined supernatant was filtered over dried sodium sulfate and evaporated under nitrogen to 1 mL of toluene. Finally, the extract was split into two; 0.5 mL was analyzed by GC-MS, the other 0.5 mL was redissolved in 1 mL methanol and analyzed with LC-MS/MS.

Table 1: Compound name, CAS-number, abbreviation and molar mass of the ten PFRs studied in this manuscript.

Compound	CAS no.	Abbreviation	Molar mass (g mol ⁻¹)
Tris(butyl) phosphate	126-73-8	TNBP	266.32
Tris(isobutyl) phosphate	126-71-6	TIBP	266.32
Tris(2-chloroethyl) phosphate	115-96-8	TCEP	285.49
Tris(2-chloroisopropyl) phosphate	13674-84-5	TCIPP	327.56
Tris(1,3-dichloroisopropyl) phosphate	13674-87-8	TDCIPP	430.9
Tris(2-butoxyethyl) phosphate	78-51-3	TBOEP	398.48
Tris(2-ethylhexyl) phosphate	78-42-2	TEHP	434,64
Tris(phenyl) phosphate	115-86-6	TPHP	326.29
Tris(methylphenyl) phosphate	1330-78-5	TMPP (TCP)	368.37
2-Ethylhexyl diphenyl phosphate	1241-94-7	EHDPP	362.4

Sample analysis

PFRs with GC-MS

Analysis of PFRs was performed on a HP6890 GC (Agilent Technologies, Amstelveen, The Netherlands) with a BPX5 capillary column (25 m x 0.22 mm ID, 0.25 μm film thickness, SGE Analytical Science, Rotterdam, the Netherlands). The injector temperature was 250 °C and the samples were injected in the pulsed splitless mode with a pulse pressure of 200 KPa for 1.5 min. Helium was used as a carrier gas with a flow of 1.3 mL min⁻¹. The oven temperature program was 110 °C held for 3 min, followed by an increase of 15 °C min⁻¹ to 190 °C. The temperature was then increased to 310 °C (10 °C min⁻¹) and held for 4 min. The MS was run in the electron impact ionization (EI) mode. The temperatures of the source and quadrupole were 230 and 150 °C, respectively. Selective ion monitoring (SIM) was performed, as given in Table S1.

PFRs with LC-MS/MS

The LC-MS/MS method used for the analyses of PFRs in dust was similar to the method used for the analyzed of BPA-BDPP and PBDPP in dust (Brandsma et al., 2013b). The MS was run in the MS-MS mode using multiple-reaction monitoring of the parent and daughter ions, as given in Table S2.

Quality control

Validation of the method

Validation of the dust sample treatment method was performed by a triplicate spike experiment of a dust certified reference material from NIST, coded SRM 2585, at two concentration levels. This SRM 2585 is not certified for the PFRs. However, it has recently been used in an interlaboratory study (ILS) for PFRs (Brandsma et al., 2013a) and also analyzed for PFRs by Van den Eede et al. (2011) and Bergh et al. (2012). Nine ~50 mg aliquots of SRM 2585 dust were weighed and three blanks were included. Three SRM 2585 samples were spiked at a high level (150 ng), three at a low level (50 ng) and three SRM 2585 samples were used unspiked. An exception was made for TBOEP, which was spiked ten times higher because the SRM 2585 contains a 10-fold higher TBOEP level compared to the other nine PFRs. Information about the blanks, detection limits and internal standards can be found in the supplementary material.

Results and discussion

Comparison GC-EI-MS versus LC-ESI-MS/MS

To compare the results of GC-EI-MS with LC-ESI-MS/MS, the spiked samples were analyzed with both techniques. Good recoveries (79-101 %) were observed for six of the ten PFRs with LC-ESI-MS/MS. However, for TDCIPP, TBOEP, EHDPP and TMPP ion suppression was observed for more than 50 % of the signal. Better results were observed with GC-EI-MS where seven PFRs showed good recoveries (82-112 %) for both the high and low level spike. Exceptions were TBOEP with some lower recovery (65 %) for the low spiked level and TEHP and total TMPP, which were somewhat high (140 % and 155 %, respectively). The results of the GC-EI-MS for all PFRs are listed in Table 2.

Table 2. Results of the triplicate spike experiment on SRM 2585 using GC-EI-MS and TPHP-d15 as internal standard. Indicated are the average recoveries, standard deviations (SD) and coefficients of variation (CV).

	Conc. Low spike ng	SD ng	CV (%)	Recovery	Conc. high spike ng	SD ng	CV (%)	Recovery	LOQ ng g ⁻¹
TIBP	53	0.8	2%	82%	178	3.5	2%	85%	50
TNBP	57	3.1	6%	87%	191	4.2	2%	89%	60
TCEP	61	3.4	7%	84%	205	9.1	4%	101%	70
TCIPP	52	2.6	6%	87%	174	5.6	3%	95%	60
TDCIPP	57	8.0	13%	107%	192	15	7%	112%	80
TBOEP	548	216	60%	65%	1840	244	18%	76%	120
TPHP	55	5.9	12%	86%	184	3.8	2%	89%	60
TMPP total	70	12	12%	150%	236	18	5%	155%	80
EHDPP	61	4.7	8%	95%	204	13	7%	98%	70
TEHP	64	6,5	7%	140%	214	21	8%	123%	80

Summarizing the result of the spiking experiment we concluded that GC-EI-MS is the preferred technique for analyzing PFRs. The dust samples from the Netherlands analyzed in this study were therefore further analyzed with only GC-EI-MS.

Validation

The results of the triplicate unspiked dust SRM2585 were compared with the literature data (see Table 3). The relative standard deviation of the triplicate analyses of PFRs in the dust SRM2585 ranged from 1 % to 10 %. Good agreement was observed for TNBP, TCEP, TCIPP, TBOEP, TPHP and EHDPP levels compared with the assigned values from the PFR ILS of Brandsma et al. (2013a). The TCEP, TCIPP total and TBOEP values compared well to the studies of Bergh et al. (2012) and Van den Eede et al. (2011). TDCIPP was 61 % higher than the assigned value of TDCIPP observed in the PFR ILS (Brandsma et al., 2013a). However, also in the studies of Bergh et al. (2012) and Van de Eede et al. (2011) higher TDCIPP levels were found (2300 and 2000 ng g⁻¹, respectively), which were more comparable to the TDCIPP level found in our study (2500 ng g⁻¹). The total TMPP level in this study was higher compared with the other three studies. It is rather difficult to quantify total TMPP, which

consists of ten different isomers. Total TMPP is reported in all studies as the sum of four isomers (*mmm*-TMPP, *mmp*-TMPP, *mpp*-TMPP and *ppp*-TMPP). The ILS showed a large variation for total TCP between the laboratories (coefficients of variation (CV) of 85 %), which is maybe due to the use of different technical mixtures for quantification. In the ILS no assigned value could be calculated and also Bergh et al. (2012) described a difference of -45 % compared to the study of Van den Eede et al. (2011). In the study of Bergh et al. (2012), the total TMPP level was close to the detection limit, which may have caused the higher uncertainty. The TEHP level in the present study was almost four times higher than the assigned value from the ILS of Brandsma et al. (2013a) and three times higher compared to that of the Bergh et al. (2012) study. Bergh et al. (2012) observed signal enhancement for TEHP related to the matrix. In our study less sample cleanup was performed compared to the studies of Bergh et al. (2012) and Van den Eede et al. (2011), which may cause signal enhancement and may explain the higher level observed in our study. This is consistent with the recovery data as we also found the recoveries of the spiked SRM exceeding 100 % (140 % for the low spike and 123 % for the high spike). Because of the high uncertainty for TEHP in this analysis, TEHP is not reported.

Table 3. PFR levels ($ng\ g^{-1}$) in dust SRM 2585 compared with literature data.

	ILS Brandsma et al. (2013a)			Bergh et al. (2012)			Van den Eede et al. (2011)			This study		
	Assigned value	Indicative value	CV (%)	Average (n=7)	STDE V	CV (%)	Average (n=5)	STDE V	CV (%)	Average (n=3)	STDE V	CV (%)
TIBP	-	17	93	<210			NA			<50		
TNBP	269	-	7	190	20	13	180	20	11	290	12	4%
TCEP	792	-	16	840	60	7	700	170	24	810	41	5%
TCIPP	944	-	28	880	140	16	820	100	12	750	28	4%
TDCIPP	1556	-	34	2300	280	12	2000	260	13	2500	12	1%
TBOEP	73464	-	44	82000	6500	8	49000	9600	20	81000	1850	2%
TPHP	1104	-	9	1100	100	9	990	70	7	890	49	5%
TMPP total	-	843	84	740	110	14	1070	110	10	1550	150	10%
EHDPP	963	-	21	1300	120	9	NA			1230	23	2%
TEHP	265	-	42	370	40	11	NA			1140	85	7%

NA =not analyzed.

House dust from the Netherlands

All nine PFRs studied were detected in dust from the Netherlands (Table 4). To our knowledge this is the first time these PFRs are detected in dust from the Netherlands. TBOEP dominates in dust samples taken around electronic equipment. The median TBOEP ($22\ \mu g\ g^{-1}$) level was ~20 times higher than the median levels of TCIPP ($1.3\ \mu g\ g^{-1}$), TCEP ($1.3\ \mu g\ g^{-1}$) and TPHP ($0.82\ \mu g\ g^{-1}$). TBOEP (median of $27\ \mu g\ g^{-1}$) was also predominant in house dust collected on the electronic equipment. TBOEP is mainly used as plasticizer in rubber and plastics and as polisher in floor finishing products (up to 0.5–8 % by weight) (Marklund et al., 2003; Kajiwara et al., 2011), which may explain the high levels observed in house dust. Dust collected on and around the electronic equipment show some similarity in PFR pattern (see Fig 2B) and concentrations (see Table 4). A Wilcoxon signed-rank test showed that only the mean levels of TPHP and TMPP are significantly different in the dust collected on and around the electronic equipment ($Z = -2.52$, $p = 0.012$; $Z = -2.52$, $p = 0.012$, respectively). TPHP was more abundant in dust collected on the electronic equipment than around the electronic equipment (8

times higher based on median concentration). The median TMPP was 3 times higher in dust collected on the electronic equipment. The finding of higher TPHP levels compared to TMPP is consistent with the results of Kajiwara et al. (2011) who observed that TPHP was the major PFR detected in electronic equipment (LCD televisions) from the Japanese market in 2008 followed by TMPP (some orders of magnitude lower), TDCIPP and TBOEP were only detected in some equipment at low concentration. This result may indicate that mainly TPHP and TMPP were emitted from the electronic equipment and that the other PFRs are not related to electronics but to other sources in the house (upholstery furniture, floor polish, carpet padding, wall covering, isolation materials, etc.). Because of the relatively small data set, more research is needed to confirm this finding. Recently, we found strong correlations between TPHP and both BPA-BDPP and PBDPP ($r=0.8-0.9$) in the same house dust collected on electronic equipment (Brandsma et al., 2013b). The technical BPA-BDPP and PBDPP mixtures used as alternative for DecaBDE in electronic equipment contain TPHP (up to 5 %) as by-product (Waaijers et al., 2013). This may explain the elevated TPHP levels in the dust taken from the electronic equipment compared to the TPHP levels in house dust taken around the electronic equipment.

Table 4. Median concentrations of PFRs in dust from houses and cars from the Netherlands ($ng\ g^{-1}$).

	Median n=8 around electronics	Range	Median n=8 on electronics	Range	Median n=8 Car dashboards	Range	Median n=8 Car seats	Range
TIBP	46	(30-180)	83	(LOQ-110)	<64	(<17-<270)	<13	(<9-<24)
TNBP	32	(10-200)	38	(LOQ-210)	<73	(<19-<310)	<14	(<10-<27)
TCEP	1300	(220-6900)	880	(520-2200)	2800	(1100-5700)	600	(240-5600)
TCIPP	1300	(480-3800)	1300	(580-4500)	5700	(1800-110000)	4300	(1400-110000)
TDCIPP	280	(70-3200)	680	(100-7400)	17000	(6000-150000)	110000	(3800-1100000)
TBOEP	22000	(4600-159000)	27000	(11000-52000)	11000	(<310-31000)	42000	(6300-230000)
TPHP	820	(680-11000)	6500	(1600-21000)	1700	(360-14000)	2400	(670-43000)
TMPP total	110	(<50-180)	330	(110-2300)	750	(<47-9500)	1400	(250-380000)
EHDPP	350	(300-2000)	680	(170-3700)	1500	(<42-3700)	750	(400-39000)
Σ PFRs	27000	(7400-167000)	42000	(28000-57000)	78000	(20000-133000)	200000	(74000-1700000)

Comparison of PFR patterns in eleven countries

In Figure 1 (A and B) the PFR pattern in house dust from the Netherlands (this study) is compared with those in other countries worldwide (Table S.3). TIBP and EHDPP, which were detected in house dust from the Netherlands, were excluded from Figure 1 (A and B) because it was infrequently detected or analyzed in the other studies. One exception was made in Figure 1 for the house dust samples from Spain because García et al. (2007) did not include TMPP.

Dirtu et al. (2012) compared dust levels from Romania with those from four other countries and concluded that the PFR pattern is heterogeneous among the countries. By comparing the PFR pattern

in house dust from eleven different countries we can confirm this in-homogeneity (Fig. 1A). If we restrict the pattern comparison to the compounds that are mainly used as FRs four main PFR pattern are observed (Fig. 1B). The pattern in dust from Spain, Romania, Belgium, Germany, Japan, Kuwait and the Netherlands is dominated by TCIPP. The second pattern is dominated by TCIPP, TDCIPP and TPHP and found in New Zealand and the US. The third and fourth pattern represents dust from Sweden and Pakistan, which is dominated by TDCIPP and TPHP respectively. Note, another study on PFRs in Swedish house dust by Marklund et al., (2003) showed a slightly different pattern compared to the study of Berg et al. (2011) (third pattern), less dominated by TDCIPP and more comparable to the second pattern. However, Marklund et al., (2003) only analyzed 2 house dust sample and, therefore, this study was not included in the country comparison shown in Fig. 1A and B.

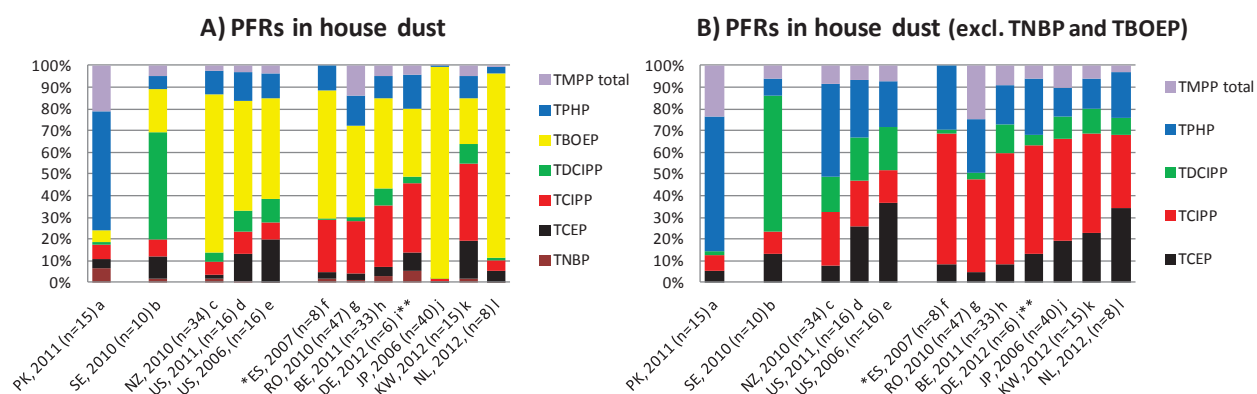


Figure 1 (A and B). Comparison of the PFR profile observed in Dutch house dust compared with PFR patterns observed in other countries. The differences between Fig. 1A and 1B is the exclusion of the plasticizers TNBP and TBOEP in Fig. 1B. * In the Spanish house dust studies TMPP was not analyzed ** Mean PFR levels were used instead of median for the German dust. a) Ali et al. (2013), b) Bergh et al., (2011), c) Ali et al., (2012), d) Dodson et al., (2012), e) Dodson et al., 2012, f) García et al., (2007), g) Dirtu et al., (2012) h) Van de Eede et al., (2011), i) Brommer et al., (2012), j) Kanazawa et al., (2010), k) Ali et al., (2013), l) this study. Studies not included in the country comparison are the one of Kim et al. (2013) who did not analyze TDCIPP, TCIPP and TBOEP, Ingerowski et al., (2001) who only analyzed TCIPP and TCEP, Stapleton et al., (2009) who only analyzed TDCIPP, TPHP and TCIPP and Marklund et al., (2003) who analyzed only two house dust samples.

Similarities in the PFR patterns may suggest similar sources in the indoor environment of the various countries. Chlorinated PFRs are used as additive FRs in PUF used in upholstery furniture, textiles, plastics, carpet padding, and isolation materials and can easily migrate from these products into the indoor environment (WHO, 1998; Stapleton et al., 2009; EFRA, 2013). In addition to the chlorinated PFRs TPHP was also dominating in most dust samples from the various countries (Figure 1B). The TPHP levels detected in house dust may be influenced by the use of Firemaster 550 (containing 18 % TPHP as by product). Stapleton et al. (2009) analyzed US dust samples for TBB and TBPH (the main compound observed in Firemaster 550) and found only a weak correlation ($r=0.4$) between TPHP, TBB

and TBPH. This finding was confirmed by Ali et al. (2012) and Dodson et al. (2012) who both found no strong correlation between TBB and TBPH with TPHP and concluded that the finding of TPHP in house dust could not only be related to Firemaster 550. TPHP is used as FR and plasticizer in various other products, which could also be one of the sources for TPHP observed in house dust. The use of BPA-BDPP and PBDPP technical mixtures containing the by-product TPHP as alternative for DecaBDE may contribute to the TPHP level, which was recently reported in house dust from the Netherlands (Brandsma et al., 2013b). In this study a strong correlation between TPHP and BPA-BDPP or PBDPP was found

We observed four major PFR patterns worldwide. However, the PFR levels vary considerably between the countries. For example in house dust, TBOEP varied from 1570000 ng g⁻¹ (median) in Japan to 17 ng g⁻¹ (median) in Kuwait, and TDCIPP varied from 10000 ng g⁻¹ (median) in Sweden to 60 ng g⁻¹ (median) in Romania (Kanazawa et al., 2010; Ali et al., 2013; Bergh et al., 20011; Dirtu et al., 2012, Table S3). Highest PFR levels were observed in house dust from Japan followed by dust from the US, which were both dominated by TBOEP (Kanazawa et al., 2010; Dodson et al., 2012). The median TPHP, TDCIPP, TCIPP, TCEP and TBOEP levels in house dust of Japan were 1-2 orders of magnitude higher than those from our study. The higher PFR levels observed in Japan may be related to the earlier phase out (voluntary) of the commercial PentaBDE mixture compared to the other countries (Dodson et al., 2012). Whereas the elevated PFR levels in the dust from US may be related to the stricter regulatory flammability standards compared to other countries.

In literature various reasons were given for the high variances observed between PFRs from the same location and between the different countries. For instance, Marklund et al. (2003) concluded that the distribution pattern of the PFRs was mainly influenced by building materials and consumer products (e.g. upholstery furniture, floor polish, carpet padding, wall covering, and isolation materials) used. Dirtu et al. (2012) suggested that the variances in the PFR pattern might be attributed to a multitude of factors since organophosphate compounds are not only used as FRs but also as plasticizers. Differences in regulation and restrictions between the countries also influence the use of PFRs (Dirtu et al., 2012). Different cleaning regimes per house may also influence the PFR levels (Brommer et al., 2012).

Car dust

The PFR levels observed in the car dust collected from dashboards and seats are listed in Table 3. All PFRs were detected in the car dust samples, with the exception of TIBP and TNBP. Significant differences in the dust collected from the dashboard and seats are found for the mean levels of TCEP, TDCIPP and TBOEP (Wilcoxon signed-rank test, $Z = -2.52$, $p = 0.01$; $Z = -2.20$, $p = 0.05$, $Z = -2.38$, $p = 0.02$, respectively). The mean TDCIPP and TBOEP levels in the dust collected from the seats are significantly higher than in the dust from the dashboards. In contrast, the mean TCEP level is significantly higher in the dust collected from the dashboard (Table 3). TDCIPP was predominant in all car dust samples with the exception of one sample from a dashboard in which TCIPP dominated (see

Figure 2A). The highest TDCIPP level ($1100 \mu\text{g g}^{-1}$) was found in dust from a car seat. TDCIPP is commonly used as FR in flexible and rigid PUF (Stapleton et al., 2009) and the high concentration found in seat dust indicate the emission from PUF. The presence of TDCIPP in dashboard dust indicates that it is spread throughout the car. One dust sample taken from a car seat (sample 4s Fig 2A and C) contained a very high TMPP concentration of $380 \mu\text{g g}^{-1}$ (Table 3). Brommer et al., (2012) detected up to $150 \mu\text{g g}^{-1}$ TMPP in two car dust samples from Germany. TMPP is used as a plasticizer for automobile car interior and in furniture upholstery (WHO, 1998, Brommer et al., 2012).

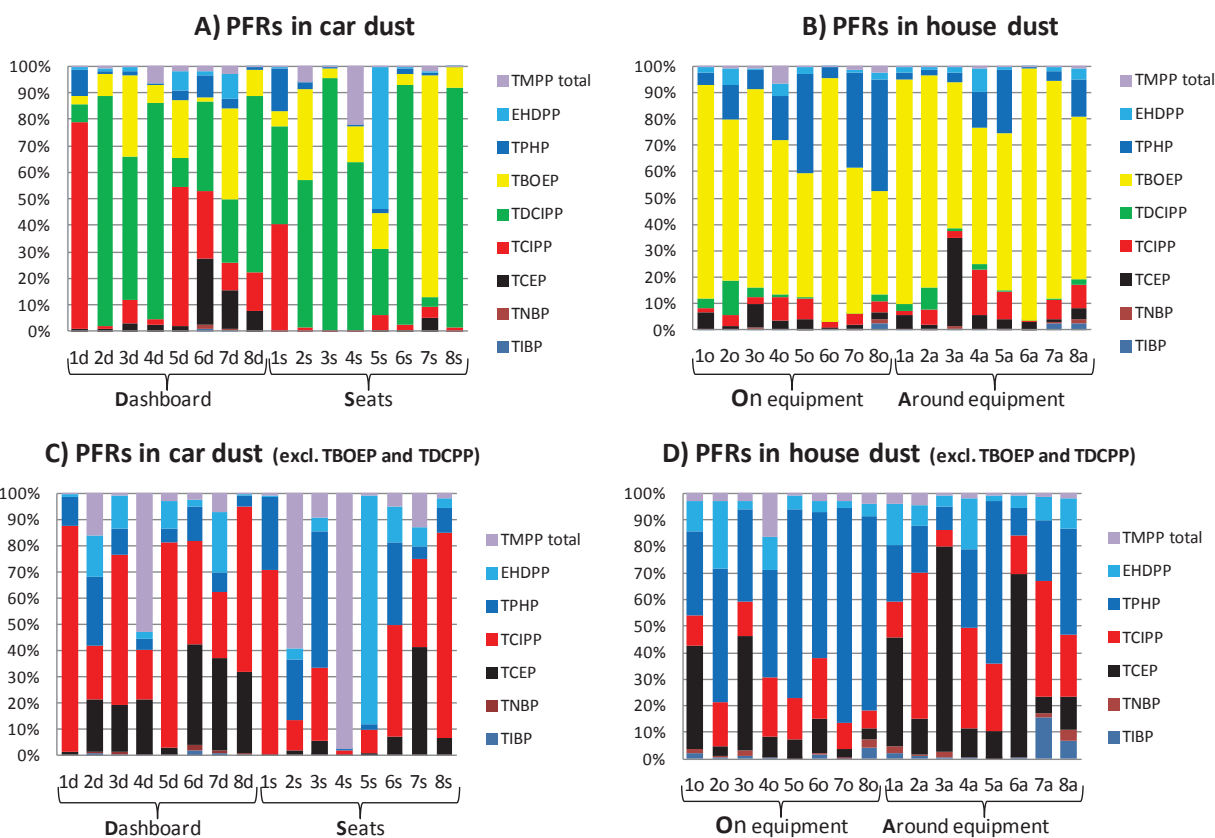


Figure 2A, B, C and D. The relative PFR concentrations in sixteen dust samples from eight different cars (A and C) and sixteen dust samples from eight different houses (B and D). In the car dust (figure 2A and 2C) the first eight samples (1d-8d) represent the dust taken from the dashboard and the numbers 1s-8s represent the dust samples taken from the seats. The samples 1d and 1s are from the same car, as are 2d en 2s, etc. In the house dust (figure 2B and 2D) the first eight samples (1o-8o) represent dust taken directly from the electronic equipment and the numbers 1a-8a represent dust collected around the equipment. The samples 1o and 1s are from the same house, as are 2o en 2s, etc. Figures 2C and 2D are similar than 2A and 2B with the exception of TBOEP and TDCIPP.

The PFR patterns and levels in the car dust from the Netherlands are comparable with the results of Brommer et al. (2012) in German car dust. Car dust from Kuwait and Pakistan showed different patterns, and was dominated by TCIPP and TPHP (Ali et al., 2013). Brommer et al. (2012) observed a negative correlation between the age of the car and the TDCIPP concentration suggesting that old

cars contain more TDCIPP. This could not be confirmed in our study because relatively new cars (2008-2011) also contained high levels of TDCIPP. The oldest car (2003) even had the lowest TDCIPP level and was dominated by TCIPP (sample number 1d and 1s in Figure 2A).

Car dust versus house dust

Significantly higher mean TDCIPP and TCIPP levels in car dust taken from the seats and dashboards than in dust collected around the electronic equipment and significantly higher mean TMPP levels in dust taken from car seats than in dust collected around equipment were found (ANOVA multiple comparison based on the log transformed PFR levels, $p < 0.05$). This is consistent with the results of Brommer et al. (2012) who observed significantly higher ($p < 0.05$) TDCIPP levels in cars than in office dust from Germany, and Ali et al. (2013) observed that the PFR levels were up to 20 times higher in car dust compared to house dust from Pakistan and Kuwait. Also in the US significantly higher mean TDCIPP levels were found in dust collected from vehicles and offices than in the dust collected in the main living areas and the bedrooms (Carignan et al., 2013).

We observed that the PFR patterns in car and house dust are also different. Figures 2A and B shows that TBOEP, mainly used as plasticizer and in floor polish, is predominant in house dust while TDCIPP, used in PUF, is predominant in car dust. On the other hand, if we exclude these dominating PFRs in house and car dust a more comparable PFR pattern is found (Fig. 2C and D). In addition, the median levels of these remaining compounds are low compared to those of TBOEP and TDCIPP. This may indicate that car dust can be a mixture of dust from cars and dust from other sources like houses and offices carried by the passengers into the cars. Therefore, low concentrations of PFRs in car dust are not necessarily related to the use of these PFRs in the car material. This hypothesis should be further verified.

Conclusions

Due to ion suppression of TDCIPP, TBOEP, EHDPP and TCP with LC-ESI-MSMS, GC-EI-MS is the preferred technique for analyzing PFRs in dust samples. To our knowledge this is the first data set on PFRs in house dust of the Netherlands. PFRs are detected in relatively high concentrations in house dust (up to $159 \mu\text{g g}^{-1}$ for TBOEP) and car dust (up to $1100 \mu\text{g g}^{-1}$ for TDCIPP). The sources for TBOEP and TDCIPP in house and car dust are probably the use of TBOEP in floor polish and the use of TDCIPP in PUF (car seats). Similarity in PFR patterns, based on TDCIPP, TMPP, TCEP, TCIPP and TPHP, was observed between house dust samples from the Netherlands, Belgium, Germany, Spain, Romania, Japan, New Zealand and Kuwait, which suggests similar sources of these PFRs in the indoor environment. However, the PFR levels between countries and within countries show a high variation. The results of this study suggest that electronic equipment has a limited contribution to the PFR levels in house dust, with the exception of TPHP and TMPP. The PFRs are probably more related to various other sources in the house like upholstery furniture, floor polish, carpet padding, wall covering,

isolation materials, etc. The lower PFR levels observed in car dust are probably not related to the use of these PFR in the cars but may come from house or office dust and carried into the car by the passengers.

Acknowledgements

The authors gratefully acknowledge the European Commission as the work was part of the FP7 ENFIRO project, (contract No. 226563). The authors are solely responsible for the contents of this paper, which does not necessarily represent the opinion of the European Community.

Appendix. Supplementary material

Materials

The solvents and chemicals used were all pro-analysis quality or HPLC grade, unless otherwise stated. *n*-Hexane, acetone, and methanol used for the extraction and cleanup were from Promochem, (Wesel, Germany) and toluene from Fisher Scientific (Loughborough, UK). tris(2-chloroethyl)phosphate (TCEP), tris(1,3-dichloroisopropyl)phosphate (TDCIPP), tris(phenyl) phosphate (TPHP), tris(methylphenyl) phosphate (TMPP or TCP), tris(butyl) phosphate (TNBP), 2-Ethylhexyl diphenyl phosphate (EHDPP), tris(2-ethylhexyl)phosphate (TEHP) and tris(2-butoxyethyl)phosphate (TBOEP) were supplied by Sigma-Aldrich Chemie B.V. (Zwijndrecht, the Netherlands). Tris(isobutyl) phosphate (TIBP) was supplied by Merck (Darmstadt, Germany) and tris(2-chloroisopropyl)phosphate (TCIPP) from Ehrenstorfer (Augsburg, Germany). The internal standards TPHP-_{d15} and TNBP-_{d27} were supplied by respectively, Sigma-Aldrich Chemie B.V. (Zwijndrecht, the Netherlands) and Cambridge Isotope Laboratories, Inc. (Andover, MA, USA).

Blank, detection limits and internal standards

The limit of quantification of the PFRs is listed in Table 1. Measurable blank levels were observed for tris(isobutyl) phosphate (TIBP), TCEP, TDCIPP and TPHP. The levels were low, TIBP was 3 times the LOQ, and the other three around 2 times the LOQ. The blank values were subtracted from the sample results.

Two internal standards (IS), TNBP-_{d27} and TPHP-_{d15}, were added to the dust samples. During the validation the PFR levels in the spiked dust samples were calculated with both IS. No statistical differences in PFR levels were found between the use of both internal standards (t-test, $p > 0.05$) using LC-ESI-MS/MS. For the calculation of the PFRs with GC-EI-MS TPHP-_{d15} was chosen instead of TNBP-_{d27}, because TPHP-_{d15} has a higher specific m/z than TNBP-_{d27} and it also elutes later in the chromatogram. Especially in the beginning of the chromatogram matrix may introduce noise in the low mass region, which may interfere with TNBP-_{d27} (Björklund et al., 2004, Quintana et al., 2007).

Table S1. GC-ESI-MS retention time and monitoring ions of the PFRs studied.

Compound	Acronym	qualifier	quantifier
Tris(butyl) phosphate d27 *	TNBP-d ₂₇	167	231, 99
Tris(butyl) phosphate	TNBP	155	211, 99
Tris(2-chloroethyl)phosphate	TCEP	249	251
Tris(isobutyl) phosphate	TIBP	155	211, 99
Tris(2-chloroisopropyl)phosphate	TCIPP	277	279, 201
Tris(1,3-dichloroisopropyl)phosphate	TDCIPP	381	379, 191
Tris(2-butoxyethyl)phosphate	TBOEP	299	199
Tris(2-ethylhexyl)phosphate	TEHP	99	211, 113
Tris(phenyl) phosphate d15 *	TPHP-d ₁₅	341	339, 239
Tris(phenyl) phosphate	TPHP	326	325, 215
Tris(methylphenyl) phosphate	TMPP (TCP)	368	277, 165
2-Ethylhexyl diphenyl phosphate	EHDPP	251	250, 362

* Internal standards

Table S2. LC-MS/MS retention times and ion transitions monitored for all PFRs studied.

Compound	Acronym	Retention time	Precursor Ion	Product Ion	Dwell	Fragmentor	Collision Energy
Tris(butyl) phosphate d27 *	TNBP-d ₂₇	15.6	294.4	166.1	20	100	15
			294.4	102.1	20	100	15
Tris(butyl) phosphate	TNBP	15.8	267.2	155.1	20	100	10
			267.2	99.1	20	100	10
Tris(2-chloroethyl)phosphate	TCEP	6.4	287	99.1	20	100	19
			285	63.1	20	110	18
Tris(isobutyl) phosphate	TIBP	15.8	267.2	155.1	20	75	8
			267.2	99.1	20	75	8
Tris(2-chloroisopropyl)phosphate	TCIPP	11.6	329	99	20	100	15
Tris(1,3-dichloroisopropyl)phosphate	TDCIPP	14.4	433	99.4	20	125	30
Tris(2-butoxyethyl)phosphate	TBOEP	16.4	399.4	299.2	20	125	15
			399.4	199.1	20	125	15
Tris(2-ethylhexyl)phosphate	TEHP	22.8	435.4	113.3	20	125	10
			435.4	99.1	20	125	10
Tris(phenyl) phosphate d15 *	TPHP-d ₁₅	16.4	342.2	160.2	20	175	40
			342.2	82.1	20	175	40
Tris(phenyl) phosphate	TPHP	16.5	327.2	152.1	20	175	35
			327.2	77.1	20	175	35
Tris(methylphenyl) phosphate	TMPP	17.1	369.2	165.2	20	175	35
			369.2	91.1	20	175	35
2-Ethylhexyl diphenyl phosphate	EHDPP	17.5	251.1	152.2	20	150	28
			251.1	77.2	20	150	28

* Internal standards

Table S3. Concentrations of PFRs (ng/g) in house dust of various countries.

authors	countries	sampling year	n	TMPP total (ng/g)	TPHP (ng/g)	TDCIPP (ng/g)	TCIPP (ng/g)	TCEP (ng/g)	TNBP (ng/g)	TBOEP (ng/g)
Ali et al., 2013	Pakistan	2011	15	67	175	<5	<20	15	<20	17
Berg et al., 2011a	Sweden	2010	10	1000	1200	10000	1600	2100	300	4000
Marklund et al., 2003*	Sweden	2003	2	NA	920	745	700	230	410	22000
Ali et al., 2012	New Zealand	2010	34	120	600	230	350	110	80	4020
Dodson et al., 2012	USA	2011	16	680	2800	2100	2200	2700	80	11000
Dodson et al., 2012	USA	2006	16	1000	3000	2800	2100	5100	32	12000
Garcia et al., 2007	Spain	2007	8	NA	1850	125	3800	510	230	9350
Dirtu et al., 2012	Romania	2010	47	500	500	60	860	100	45	1500
Van de Eede et al., 2011	Belgium	2011	33	240	500	360	1380	230	130	2030
Brommer et al., 2012*	Germany	2012	6	94	380	<80	740	200	130	730
Kanazawa et al., 2010	Japan	2006	40	<4000	5400	4000	18700	7500	1400	1570000
Ali et al., 2012	Kuwait	2012	15	190	430	360	1460	710	58	855
This study	Netherlands	2012	8	110	820	280	1300	1300	32	22000

* Mean PFR levels were used instead of median for the German dust and Swedish dust

Table S4 Houses from the Netherlands sampled for dust.

Sample code	Electronic sampled	Production year electronics	Sampled	Sampled
House 1	TV (flatscreen) and desktop computer	2007-2011	Directly on the electronics	Within 1 meter of the electronics
House 2	TV (flatscreen, desktop computer, receiver and game console	2007-2012	Directly on the electronics	Within 1 meter of the electronics
House 3	TV (flatscreen) and computer	2006-20010	Directly on the electronics	Within 1 meter of the electronics
House 4	TV (flatscreen), computer and game console	2008-2012	Directly on the electronics	Within 1 meter of the electronics
House 5	TV (flatscreen) and game console	2008-2010	Directly on the electronics	Within 1 meter of the electronics
House 6	TV (flatscreen), router, receiver and game console	2008-2010	Directly on the electronics	Within 1 meter of the electronics
House 7	TV (flatscreen) and game console.	2008-2012	Directly on the electronics	Within 1 meter of the electronics
House 8	TV (flatscreen)	2012	Directly on the electronics	Within 1 meter of the electronics

Table S4 Houses from the Netherlands sampled for dust.

Sample code	Manufactory year	Sampled	Sampled
Car 1	2003	Dashboard	Car seat
Car 2	2004	Dashboard	Car seat
Car 3	2008	Dashboard	Car seat
Car 4	2008	Dashboard	Car seat
Car 5	2010	Dashboard	Car seat
Car 6	2010	Dashboard	Car seat
Car 7	2011	Dashboard	Car seat
Car 8	2012	Dashboard	Car seat

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