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## Occurrence and Fate of Alternative Flame Retardants in the Environment

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## **4.2: Dust measurement of two organophosphorus flame-retardants, resorcinol bis (diphenylphosphate) (PBDPP) and bisphenol A bis (diphenylphosphate) (BPA-BDPP) used as alternatives for BDE209**

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## Abstract

Resorcinol bis (diphenylphosphate) (PBDPP) and bis phenol A bis (diphenylphosphate) (BPA-BDPP) are two halogen free organophosphorus flame retardant (PFRs) that are used as alternative for the decabromodiphenyl ether (Deca-BDE) technical mixture in TV/flatscreen housing and other electronic consumer products. In this study, dust samples were collected from various microenvironments in the Netherlands (houses, cars), Greece (houses) and Sweden (apartments, cars, furniture stores, electronics stores) and analyzed for PBDPP and BPA-BDPP. Additionally, the dust samples from the Netherlands were analyzed for decabromodiphenyl ether (BDE209) for comparison and for Tris(phenyl) phosphate (TPHP) which is a by-product in the PBDPP and BPA-BDPP technical product. BPA-BDPP was detected in almost all dust samples from the Netherlands, Greece and Sweden. Highest concentrations were found in dust samples collected on electronic equipment from all three countries with BPA-BDPP levels ranging from <math><0.1-1300\ \mu\text{g/g}</math> and PBDPP levels from <math><0.04-520\ \mu\text{g/g}</math>. PBDPP and BPA-BDPP levels in dust collected further away from the electronics (source) were usually lower. BDE209 levels in the Netherlands dust samples collected on and around the electronics were similar and much lower than the BPA-BDPP/PBDPP levels, indicating that the electronics were not the source of BDE209. Strong positive correlations were found between TPHP concentrations and those of PBDPP ( $r=0.805$ ) and BPA-BDPP ( $r=0.924$ ), probably due to TPHP being a by-product in commercial PBDPP and BPA-BDPP mixtures in electronics. To our knowledge this is the first time that PBDPP and BPA-BDPP were detected in dust samples from Europe.

## Introduction

Some brominated flame retardants (BFRs), such as the polybrominated diphenyl ethers (PBDEs) are persistent, bioaccumulative and show serious toxicological effects such as endocrine disruption (BSEF, 2010; Hites, 2004; Fångstrom et al., 2005; Schechter et al., 2005; She et al., 2007; Boon et al., 2002). Due to these negative effects, the three PBDE technical products, Penta-BDE (contains tri-hexa-BDEs), Octa-BDE (contains hexa-octa-BDEs) and Deca-BDE (contains primarily BDE209) were banned or phased-out in many countries, which led to an increase in production and use of alternative flame retardants (FRs), such as organophosphorus flame retardants (PFRs) (CEFIC, 2011). Several PFRs used as FRs in polyurethane foams are tris-(2-chloroisopropyl) phosphate (TCIPP), tris-(1,3-dichloroisopropyl) phosphate (TDCIPP) and tris-(2-chloroethyl) phosphate (TCEP), the latter being mainly used in polyester resins and PVC material (WHO, 1998; EFRA, 2013; Marklund et al., 2003). Relatively high PFRs levels ( $\mu\text{g/g}$  range) have been detected in house dust from different countries (EFRA, 2013; Van den Eede et al., 2011; Brommer et al., 2012; Ali et al., 2012). In general, PFR concentrations in house dust exceeded those of PBDEs, hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) in the same samples (Van den Eede et al., 2011; Brommer et al., 2012; Ali et al., 2012; Ali et al., 2013).

Two phosphorus-based FRs, PBDPP and BPA-BDPP (Figure 1) (also known by the abbreviations RDP and BDP) have been less studied. These two PFRs are used as an alternative for DecaBDE in TV/flat screen housings and other electronic consumer products but cannot be used in high impact polystyrene (HIPS) (LCSP, 2005).

Therefore, manufacturers have changed the polymer blends to polyphenylene oxide (PPO)/HIPS and polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS), to be able to use PBDPP and BPA-BDPP as alternatives for DecaBDE (LCSP, 2005; PBDE CAP, 2006). PBDPP and BPA-BDPP levels have only been reported in one dust sample in a study from Japan with a concentration of 1700 ng/g for PBDPP and 100 ng/g for BPA-BDPP (Matsukami et al., 2010). Little toxicity data for PBDPP and BPA-BDPP exist but they are of some concern as aquatic toxicity studies in the literature show varying results with moderate-low and high-low toxicity, respectively (Waijers et al., 2013). This variation may be due to the presence of tris(phenyl) phosphate (TPHP) as a by-product in the PBDPP and PBA-BDPP technical products (up to 5%); TPHP is known to be toxic for aquatic organisms ( $EC_{10} = 0.037$  mg/L for *Oncorhynchus mykiss*) (Waijers et al., 2013).

To assess indoor contamination from PBDPP and BPA-BDPP, assess possible sources and to estimate human exposure to these two FRs, dust sampling was performed in indoor microenvironments where products containing FRs are used. Sampling was carried out in the Netherlands (houses, cars), complemented by dust samples from similar microenvironments from Greece (houses) and Sweden (apartments, cars, furniture and electronics stores) to also determine how widespread these FRs are in other European countries. For dust samples from the Netherlands, analyses of BDE209 were included in order to study relationships with PBDPP and BPA-BDPP and test the hypothesis that these are being used as DecaBDE replacements. TPHP concentrations in the same dust samples were compared to PBDPP and BPA-BDPP concentrations to test the hypothesis that TPHP is present as a by-product.

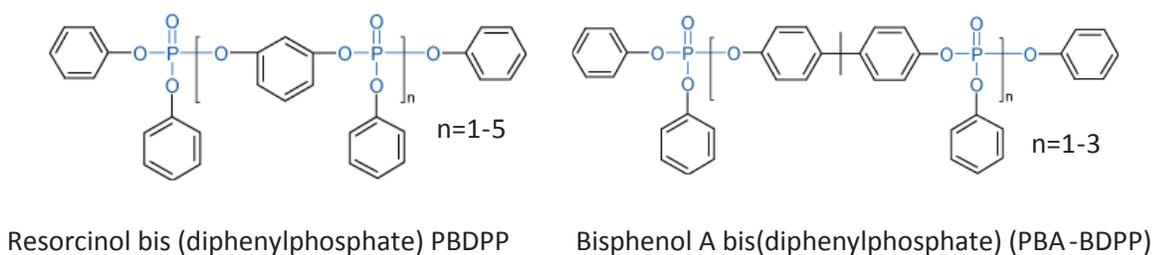


Figure 1. Structures of PBDPP and BPA-BDPP.

## 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). PBDPP (Fyrolflex RDP, technical grade, 95.5% purity) and BPA-BDPP (Fyrolflex BDP, technical grade, 96.5% purity) were obtained from ICL (Amsterdam, the Netherlands). TPHP were supplied by Sigma-Aldrich Chemie B.V. (Zwijndrecht, the Netherlands). The internal standards TPHP-<sub>d15</sub> and tris(butyl) phosphate (TNBP)-<sub>d27</sub> were supplied by respectively, Sigma-Aldrich Chemie B.V. (Zwijndrecht, the Netherlands) and Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Native and <sup>13</sup>C mass labeled BDE209 were from Wellington Laboratories (Guelph, Ontario, Canada). For the extraction/clean-up of the Swedish samples, methanol and dichloromethane (DCM, both LiChrosolv, Merck, Darmstadt, Germany) and diethyl ether (Stb BHT, HPLC, Labscan, Gliwice, Poland) were used. Isolute FL SPE columns (florisil, 200 mg / 3 mL) were from Biotage, Sweden. Sulfadimethoxine (SDIM, CAS: 122-11-2) from Sigma-Aldrich was used as volumetric standard. Formic acid (98-100%, reagent grade) was from Scharlau Chemie SA (Sentmenat, Spain) and water from a Milli-Q unit (Millipore AB, Solna, Sweden). Sulfadimethoxine (SDIM) (Sigma-Aldrich).

### Statistics

A Wilcoxon signed-rank test was performed to investigate possible significant differences for PBDPP, BPA-BDPP and BDE209 levels in dust collected on the electronics compared with those collected around the electronics. A Pearson correlation was performed to investigate the correlation between TPHP, PBDPP and BPA-BDPP in house dust from the Netherlands. ½ LOQ was used for the non-detects.

## **Sample collection**

### Netherlands and Greece

Dust was collected using a Dustream<sup>TM</sup> dust collector (Indoor Biotechnologies Ltd, Wiltshire, United Kingdom) attached to the end of the vacuum cleaner hose. The mesh side of the filter used inside the dust collector was 40 microns. House dust was collected in eight different houses in the Netherlands. At each location, two separate samples were collected, one sample directly from the electronic equipment (e.g. TVs, PCs, or game consoles) and the other one from the tables and sideboard around the equipment. The floor was not included in the sampling because this would introduce more matrices into the dust sample. To study spatial distribution from a possible source, in one of the eight houses, dust samples were collected on the TV, 0.1 m from the TV and 2-3 m from the TV. The samples were all taken 50 to 100 cm above the floor surface. Dust samples were also collected from eight different cars. In each car, two separate samples were collected, one from the dashboard and one from the seats (mainly the cushion of the seat).

The house dust collection in Greece was done with the same dust collector used for the sampling of the houses and cars in the Netherlands. House dust was collected in five different houses in Greece.

In three of the houses, two dust samples were collected: one directly from the electronic equipment and the other from the tables and sideboards around the equipment. In the other two houses the dust was only collected from the electronic equipment, and in one of these houses, two samples were taken, one from a PC and one from a TV. This resulted in six dust samples collected from electronic equipment and three samples from around electronic equipment.

After sampling the dust was removed from the filters. In most cases the total sample was taken into account. Hair and other larger particles were removed by hand from the dust.

### Sweden

Dust samples were collected from three apartments, four new cars, two electronics stores and two furniture stores using pre-weighed cellulose filters (7 cm diameter) in styrene-acrylonitrile holders inserted in a polypropylene nozzle (Krim. Teknisk Materiel AB, Bålsta, Sweden), attached to the intake nozzle of an industrial strength vacuum cleaner (Alto AERO 840) (Thuresson et al., 2012). In the apartments, samples were collected by vacuuming surfaces at least 1 m above the floor in the living room. No dust was sampled directly from electronic equipment. In the cars, separate dust samples were collected from the seats and the dashboards. In the electronics stores, separate samples were taken directly from the electronic devices (cables, TVs, PCs/laptops) and another sample from shelves or surfaces around the devices. In the furniture stores, separate samples were taken from the surfaces of several sofas (textile, leather) and from tables or surfaces near the sofas. After sampling hair and other larger particles were removed by hand before the filter were weighed again in order to obtain the actual dust weight.

### **Sample extraction and cleanup of the dust from the Netherlands and Greece**

#### PBDPP, BPA-BDPP, TPHP and BDE209

The dust samples mass was around 50 mg. Before extraction, the dust samples were spiked with a 50 µL of internal standard solution (TPHP-<sub>d15</sub> and TNBP-<sub>d27</sub> conc. 1600 ng/mL and <sup>13</sup>C<sub>12</sub>-BDE209 conc. 800 ng/mL). The extraction of the dust was performed in two steps. First, acetone was added to the dust sample and the mixture was vortexed for 1 min following by 15 min of ultrasonication. The supernatant was removed and transferred to a new tube. The extraction described above was repeated with toluene. The combined supernatant was evaporated to 1 mL of toluene and filtered over a 1 g dried sodium sulfate column through elution with 8 mL of acetone/ toluene mixture (1:1, v/v). This fraction was evaporated under nitrogen to a volume of 1 mL (toluene). The final extract was split into two; 0.5 mL of toluene was analyzed by GC-MS for BDE209, the other 0.5 mL was evaporated to almost dryness (ca. 10 µL) and re-dissolved in 1 mL methanol and analyzed with LC-MS/MS for the remaining PBDPP, BPA-BDPP and TPHP. If the vial contained particles, it was

centrifuged at 2000 rpm for 10 min. After centrifugation, 200  $\mu$ L of the top layer was transferred to a new vial (containing an insert).

#### Sample extraction and cleanup of the dust from Sweden

The method for the Swedish dust samples was originally developed and optimized to analyze 9,10-dihydro-9-oxa-10-phosphaphenanthrene (DOPO, not reported here). The method was adapted to also include PBDPP and BPA-BDPP and should be considered semi-quantitative for these two compounds because not a full validation was performed. The filters with the dust (0.3-325 mg) were transferred to glass test tubes with Teflon lined screw caps. The extraction was performed with methanol (3 x 10 mL) in an ultrasonic bath for 20 min. The test tube was centrifuged, the supernatant removed and combined and the sample volume reduced to 1 mL in a vacuum evaporator (Syncore<sup>®</sup> Line, Büchi, Flawil, Switzerland). The sample extract was then transferred to a new test tube and evaporated to almost dryness under gentle heating and a stream of nitrogen. The sample was re-dissolved in 0.4 mL DCM, ultrasonicated and fractionated on a Florisil column (prewashed with 15 mL DCM). Three fractions were collected: Fraction 1 (10 mL DCM) contained PBDPP and BPA-BDPP; Fraction 2 (5 mL DCM:diethyl ether 1:1), and Fraction 3 (12 mL MeOH) contained DOPO. The solvent was changed to methanol and a volumetric standard (SDIM) was added before the analysis. Although pre-studies had shown that PBDPP and BPA-BDPP eluted in Fraction 1, all fractions obtained were screened for the analytes. Some PBDPP and BPA-BDPP were detected in Fraction 2, so Fraction 1 and 2 were combined before the final analysis. Quantification was done by standard additions of the analytes at three different levels to aliquots of the sample.

### **Sample analysis**

#### PBDPP, BPA-BDPP and TPHP with LC-MS/MS (Netherlands, Greece)

Analysis of PBDPP, BPA-BDPP and TPHP in dust samples from the Netherlands and Greece was performed on a 1260 infinity high performance liquid chromatograph (HPLC) (Agilent Technologies, Amstelveen, the Netherlands) with a 150 x 3 mm Luna C18 (2) 3  $\mu$ m column (Phenomenex, Utrecht, the Netherlands). HPLC parameters were set according to Rodil et al. (2005). The HPLC was coupled to a 6410 triple quadrupole MS (Agilent Technologies, Amstelveen, the Netherlands) with an electrospray ionization (ESI) interface using the positive mode. Capillary voltage was set to 3500 volt with a source temperature of 350 °C, nebulizer gas of 45 psi with a flow of 8 L/min. The injection volume was 10  $\mu$ L. The MS was run in the MS-MS mode using multiple-reaction-monitoring of the parent and daughter ions, as given in Table S 1.

#### PBDPP and BPA-BDPP analysis with LC-MS/MS (Sweden)

PBDPP and BPA-BDPP in the Swedish dust samples were analyzed with an ultra-high performance liquid chromatograph (ACQUITY<sup>TM</sup> UPLC, Waters, Milford USA) coupled to a tandem-quadrupole mass

spectrometer (Xevo™ TQ-S). Nitrogen was used as desolvation and nebulizer gas, and argon as collision gas. The LC injection volume was 1 µL and the flow rate of the mobile phase was set at 0.4 mL/min. A C18 column (ACQUITY UPLC® HSS, 1.8 µm; 2.1x100 mm, Waters, Milford, USA) with a pre-column (ACQUITY UPLC™ HSS C18; 1.8 µm VanGuard™; 2.1 x 5mm) was used and kept at 65 °C. Methanol:H2O (20:80) was used as eluent A and 100% methanol as eluent B, both containing 0.2% formic acid. The following gradient was used: 0 min (0% B), 1 min (50% B), 3 min (95% B), 7 min (95% B) and 8.1 min (0% B). The tandem mass spectrometer was run in the ESI positive mode. Capillary voltage was set at 3000 V, source temperature 150 °C, cone voltage of 50, source offset of 30 V and desolvation temperature 350 °C. The desolvation gas flow was 650 L/h, cone gas flow 150 L/h, nebulizer gas flow of 7 bar and collision gas of 0.25 mL/min and the collision energy was set at 4 eV. For quantification two (precursor-product) transitions were measured with MRM: for BPA-BDPP (693-367) and (693-327) and for PBDPP (575-481) and (575-419).

### BDE209

Analysis of BDE209 was performed on a HP6890 GC (Agilent Technologies, Amstelveen, the Netherlands) with a DB-5 capillary column (15 m x 0.25 mm ID, 0.25 µm film thickness, J&W Scientific, Amstelveen, the Netherlands). The injector temperature was 275 °C and the samples were injected in the pulsed splitless mode with a pulse pressure of 277 KPa for 1.5 min. Helium was used as a carrier gas with a flow of 1.0 mL/min. The oven temperature program was 90°C held for 3 min, followed by an increase of 30 °C/min to 210 °C. The temperature was then increased to 315 °C (5 °C/min) and held for 10 min. The MS was run in the electron capture negative chemical ionization (ECNI) mode using methane as reagent gas. The temperatures of the source and quadrupole were 200 and 106 °C, respectively. Selected ion monitoring (SIM) was performed for  $m/z$  484 and 486 for BDE209 and 496 and 498 for the internal standard  $^{13}\text{C}_{12}$  BDE209.

## **Quality control**

### PBDPP, BPA-BDPP, TPHP and BDE209

For the validation of the analytical method a dust reference sample from NIST, coded SRM 2585, was used. This SRM is certified for BDE209 but not for TPHP, PBDPP and BPA-BDPP. Therefore, TPHP, PBDPP and BPA-BDPP were spiked (in triplicates) to aliquots (~50 mg) of SRM 2585 at high and low level (Table 2). Three un-spiked dust aliquots and three solvent blanks were also included. The recovery for TPHP- $d_{15}$  was 89% ± 19% (n=12). Acceptable recoveries (70-93%) have been observed for TPHP, PBDPP and BPA-BDPP for both the high and low level spike (Table 1). The TPHP, BPA-BDPP and PBDPP levels observed in the dust samples were not corrected for the recoveries. PBDPP and BPA-BDPP were not observed in the reference material SRM2585. However, SRM2585 does contain TPHP. The mean level observed in the un-spiked dust was 1110 ± 48 ng/g (n=3). This is comparable to the results observed in literature for TPHP in SRM2585; Van den Eede et al. (2011) found 990 ± 70 ng/g

(n=5) and Bergh et al. (2012) found  $1100 \pm 100$  ng/g (n=7). SRM 2585 was also used in an interlaboratory study for PFRs. The assigned value calculated for TPHP was  $1104 \pm 9$  ng/g (Brandsma et al., 2013).

SRM2585 dust was also analyzed for BDE209. The mean value (n=8) was  $2560 \pm 195$ ng/g, which is in good agreement with the certified value for BDE209 of  $2510 \pm 90$  ng/g.

Blank, detection limits and internal standards

The limit of quantification (LOQ) was calculated as 3 times the blank level. If no blank level was observed the LOQ was calculated by the signal-to-noise ratio (S/N=10).The LOQ values listed in Table 2 were calculated based on an maximum sample intake of 50 mg dust.

The LOQ for TPHP, PBDPP and BPA-BDPP is listed in Table 1. Measurable blank levels were only observed for TPHP with an average amount of 1 ng. The mean blank values were subtracted from the sample results.

Two internal standards (IS), TNBP-d<sub>27</sub> and TPHP-d<sub>15</sub>, were added to the dust samples. No statistical differences were observed between the PFR levels calculated for both internal standards (t-test, p > 0.05).

Table 1. Results of the triplicate spike experiment on SRM 2585.

	Amount Spiked ng	Average (n=3) ng	STDEV	Rel. STD (%)	Recovery	Amount spiked ng	Average (n=3) ng	STDEV	Rel. STD (%)	Recovery	LOQ ng/g
<b>TPHP</b>	55	62	6	9%	113%	184	231	13	6%	126%	60
<b>PBDPP</b>	147	136	11	8%	93%	493	441	25	6%	90%	30
<b>BPA-BDPP</b>	156	110	9	8%	70%	524	383	31	8%	73%	10

**Results and discussion**

PBDPP and BPA-BDPP in house dust samples from the Netherlands

PBDPP and BPA-BDPP were detected in high concentrations, up to  $\mu\text{g/g}$ , in house dust from the Netherlands (Table 2). BPA-BDPP was detected in all house dust samples and PBDPP in 63% of the dust samples. The highest concentrations were detected in the dust collected on the electronic equipment with BPA-BDPP levels up to  $1300 \mu\text{g/g}$ . In general, the BPA-BDPP concentrations are higher than those of PBDPP (10-200 times) with the exception of one dust sample collected around equipment in house 5 and in one dust sample from the equipment in house 3 (Fig. 2). The higher BPA-

BDPP concentrations may suggest a higher use of BPA-BDPP as flame retardant in TV/flat screen housings. Another possible reason for the higher BPA-BDPP concentrations observed could be the lower phosphorus content in BPA-BDPP as compared to PBDPP. This would make it less effective as flame retardant and more PBA-BDPP have to be added to the polymer in order to achieve the same fire safety rating (Levchik and Weil, 2006). Kemmlein et al. (2003) did emission studies in test chambers and observed a higher emission of BPA-BDPP (20 ng/m<sup>3</sup>) compared to PBDPP (13 ng/m<sup>3</sup>) from personal computers to the air. This indicates that BPA-BDPP leaches more readily from the polymer than PBDPP. A further explanation could be that PBDPP is less stable (thermally and hydrolytically). It was suggested by Levchik and Weil, (2003) that the use of PBDPP in polymers might deteriorate their long term aging performance, which could cause problems in recycling. This may be a reason for manufacturers to prefer BPA-BDPP instead of PBDPP in their product.

PBDPP and BPA-BDPP are used as alternatives for DecaBDE in TV/flat screen housings and other consumer products. Therefore, the dust samples from the Netherlands were also analyzed for BDE209 and compared to the PBDPP and BPA-BDPP levels observed in the same dust samples (Fig. 2). The BDE209 levels were 10-1000 times lower than the BPA-BDPP levels and in the same range as the PBDPP levels, with the exception of on dust sample with high PBDPP concentration collected on the electronic equipment of house 3. Both PBDPP and PBA-BDPP levels were higher in the dust sample collected on electronic equipment (Fig. 2a) than around the electronics (Fig 2b). This pattern was not observed for BDE209. A Wilcoxon signed-rank test showed that the levels of PBDPP and BPA-BDPP are significantly different on and around the electronic equipment ( $Z = -1.960$ ,  $p=0.050$ ;  $Z = -2.521$ ,  $p=0.012$ , respectively). The median PBDPP level around equipment were 38 ng/g and on equipment 2000 ng/g, and for BPA-BDPP 1300 ng/g around and 160000 ng/g on equipment. The BDE209 the levels are not significantly different on and around the equipment ( $Z = -1.120$ ,  $p=0.263$ ). This indicates that the electronic equipment was not a source of BDE209 and that PBDPP and BPA-BDPP are being used as alternative FRs for BDE209 in the electronics in most of the houses sampled.

Table 2. Median PBDPP and BPA-BDPP concentrations and ranges in ng/g in dust from the Netherlands, Greece and Sweden.

Sampling site	PBDPP		BPA-BDPP	
	Median	Range	Median	Range
<b>The Netherlands</b>				
On electronics (n=8)	2000	(<100-52000)	160000	(1100-1300000)
Around electronics (n=8)	38	(<30-2100)	1300	(190-100000)
Car seats (n=8)	7	(<2-9500)	13	(<2-170)
Car dashboards (n=8)	13	(<1.1-34000)	<5	(<2.9-<120)
<b>Greece</b>				
On electronics (n=6)	400	(<40-870)	240000	(<100-680000)
Around electronics (n=3)	1500	(<30-4400)	21000	(1500-50000)
<b>Sweden**</b>				
Apartments (n=3)	39	(25-97)	190	(170-230)
Car seats (n=4)	80	(10-120)	110	(16-330)
Car dashboards (n=4)	59	(8.1-220)	66	(21-110)
<i>Furniture stores</i>				
On textile sofas (n=2)	97	(57-140)	230	(130-330)
Around textile sofas (n=2)	170	(73-270)	470	(88-860)
On leather sofas (n=2)	380	(190-570)	190	(130-250)
Around leather sofas (n=2)	69	(45-94)	90	(60-120)
<i>Electronic stores</i>				
On cables (n=1)	280		1600	
Around cables (n=1)	77		260	
On flat screen TVs/PCs/laptops (n=4)	760	(80-1600)	160000	(8700-490000)
Around TVs/PCs/laptops (n=2)	370	(340-400)	11000	(440-21000)

\*\* The PBDPP and BPA-BDPP levels observed in the Swedish dust are semi-quantitative.

Results for some more commonly studied PFRs (tris 2-butoxyethyl phosphate (TBOEP), TCEP, TCIPP and TPHP) were also available for these same dust samples for comparison (Brandsma et al., 2014). Median BPA-BDPP concentration (1300 ng/g) in dust collected around the electronic equipment was lower than the median TBOEP concentration and comparable with the median TCEP, TCIPP and TPHP concentrations observed in the same samples. The median BPA-BDPP concentration was also comparable with the median TCEP, TCIPP and TPHP concentrations in house dust from Sweden, median TCIPP and TPHP concentrations in house dust from Belgium and Germany, and median TPHP concentrations in house dust from Spain (Van den Eede et al., 2011; Brommer et al., 2012; Ali et al., 2012; Bergh et al., 2010). The median PBDPP concentration (38 ng/g) observed in the dust collected around the electronic equipment in this study was much lower than the median BPA-BDPP concentration (1300 ng/g). In the dust samples collected on the electronic equipment PBA-BDPP was the predominant PFR (data for the other PFRs can be found in Brandsma et al. (2014)).

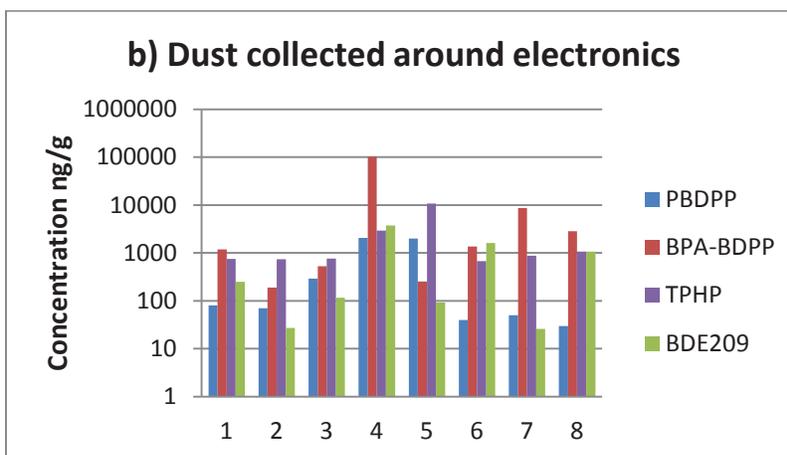
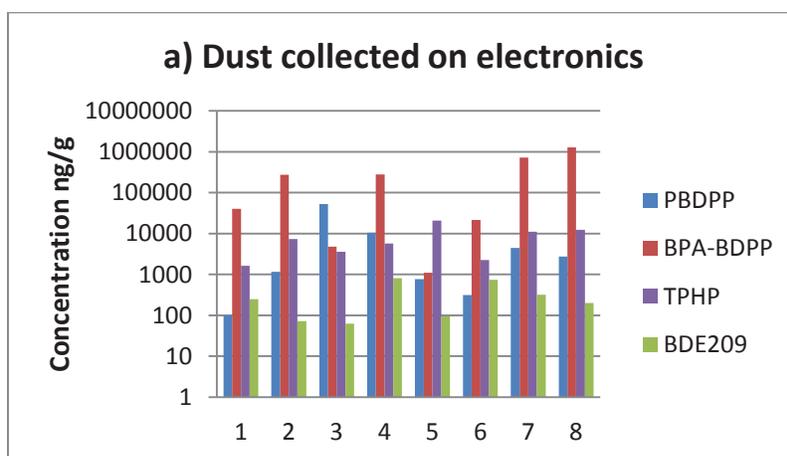


Figure 2. PBDPP, BPA-BDPP, TPHP and BDE209 concentrations (ng/g) in house dust samples collected a) on electronic equipment and b) around electronic equipment, from 8 houses in the Netherlands (logarithmic scale).

The median TPHP, PBDPP and BPA-BDPP concentrations were, respectively, 8, 50 and 120 times higher, respectively, in dust sampled from the electronic equipment than in dust samples around the electronics (Fig. 2), suggesting that PBDPP, BPA-BDPP and TPHP leach from the electronic equipments into the indoor environment. This is strengthened by the declining concentration gradient of TPHP, PBDPP and BPA-BDPP with increasing distance (for dust samples on top of, within 0.1 m and at 2-3 m) from a TV set, obtained from one house (Fig. 3).

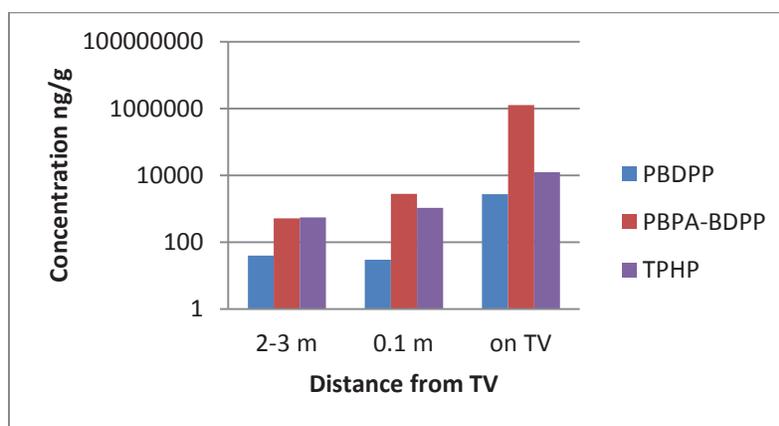


Figure 3. PBDPP, BPA-BDPP and TPHP concentrations (ng/g) in house dust samples from the Netherlands collected at different distances from a TV set (logarithmic scale).

### Correlations between PBDPP/BPA-BDPP and TPHP concentrations

TPHP is used as a plasticizer in polyester resins and PVC and as a flame retardant in different commercial flame retardant mixtures such as Firemaster 550 (up to 18% by weight) from Chemtura. Firemaster 550 also contains the brominated FRs 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEH-TEBP) (Stapleton et al., 2008). The commercial PBDPP and BPA-BDPP flame retardant mixtures also contain TPHP as a by-product, up to 5% (Waaaijers et al., 2013). Kajiwara et al. (2011) observed high TPHP levels in some consumer products from the Japanese market. Because it was unlikely that TPHP itself was used as a flame retardant in these products, Kajiwara et al. (2011) suggested that it was more likely that the TPHP observed in the consumer products was coming from the PBDPP and BPA-BDPP mixtures used in these products. The Firemaster 550 mixture was excluded as a source of the TPHP because the bromine content in the products was below the limit of detection. Ali et al. (2013) detected EH-TBB, BEH-TEBP and TPHP, the components in Firemaster 550, in house dust from Pakistani and Kuwaiti house dust. However, no statistically significant correlation was observed between EH-TBB and TPHP or BEH-TEBP and TPHP which may indicate that Firemaster 550 was not the only source of TPHP observed in those house dust samples.

To study if any relationships existed between the TPHP concentrations and those of PBDPP or BPA-BDPP, correlations were performed using the logarithms of TPHP concentrations plotted against those of PBDPP or BPA-BDPP for the seventeen house dust samples from the Netherlands (Fig. 4a and b). The results from house number 5 were not included in the calculation (represented by the red squares in Figure 4a and b) because this was the only house where the TPHP levels were higher than both the PBDPP and BPA-BDPP levels. The logarithmic transferred levels show a statistically significant positive correlation between TPHP with RDP or BDP (Pearson correlation,  $r=0.805$ ,  $p<0.05$  and  $r=0.924$ ,  $p<0.05$ , respectively). Also with the inclusion of house number 5 a significant correlation was

found (Pearson correlation,  $r=0.739$ ,  $p<0.05$  and  $r=0.512$ ,  $p<0.05$ , respectively). This strongly indicates that the finding of TPHP is related to the use of the commercial PBDPP and BPA-BDPP mixtures in electronic equipment. Another possible explanation may be that a mixture of PBDPP, BPA-BDPP and TPHP is used by the manufacturers because it is known that a combination of PBDPP with BPA-BDPP or/and TPHP is even more effective than using only one of these compounds and, therefore, more cost efficient (Levchik and Weil, 2006).

#### *PBDPP and BDP in car dust from the Netherlands*

PBDPP and BDP were also detected in some dust samples from cars of different makes from the Netherlands (Table 2). In most of the dust samples, PBDPP and BPA-BDPP concentrations were below the detection limits. PBDPP was in one dust sample taken directly from the dashboard of the car and in two dust samples from the car seats. The highest PBDPP concentration was found in the dust taken directly from the dashboard (34000 ng/g), which is comparable to the concentration found in dust collected from the electronic equipment in the houses sampled in the Netherlands (Table 2). PBDPP was also detected in the seat dust from the same car, although at 3.5 times lower concentration. This car was from 2010 and contained a navigation system that might be a possible source for PBDPP as it is known that PBDPP (and BPA-BDPP) are used in electronic equipment (LCSP, 2005). PBDPP is not detected in any other cars. BPA-BDPP was detected in three car dust samples collected from the seats. The BPA-BDPP concentrations were relatively low (48-148 ng/g), which may indicate that the foam or coating of the seats is not the source of BPA-BDPP or PBDPP. Car dust can be a mixture of dust from car and dust from sources like houses and offices carried by the passenger into the cars. Therefore, the detection of low concentrations of BPA-BDPP (and PBDPP) in car dust does not have to be related to the use of these PFRs in the car material.

#### *Distribution of PBDPP and BPA-BDPP in dust samples from other European countries*

To investigate how widespread PBDPP and BPA-BDPP are in other European countries dust was also collected in Greece and Sweden and the results are given in Table 2. In three of the Greek houses, PBDPP and BPA-BDPP were detected in the dust collected directly from electronic equipment, and were low or below detection limits for the other two. The highest PBDPP and BPA-BDPP concentrations were detected in dust collected from TVs. In all countries the BPA-BDPP concentrations, for most of the dust samples, were higher than those of PBDPP. The highest Swedish BPA-BDPP concentrations were detected in dust from electronic stores sampled from the surfaces of flat screen TVs, personal computers and laptops, similar to the results from both the Netherlands and Greece. Unlike the results from the Netherlands, PBDPP and BPA-BDPP were both detected in all car dust samples from Sweden, but at relatively low concentrations. Similar concentrations of PBDPP and

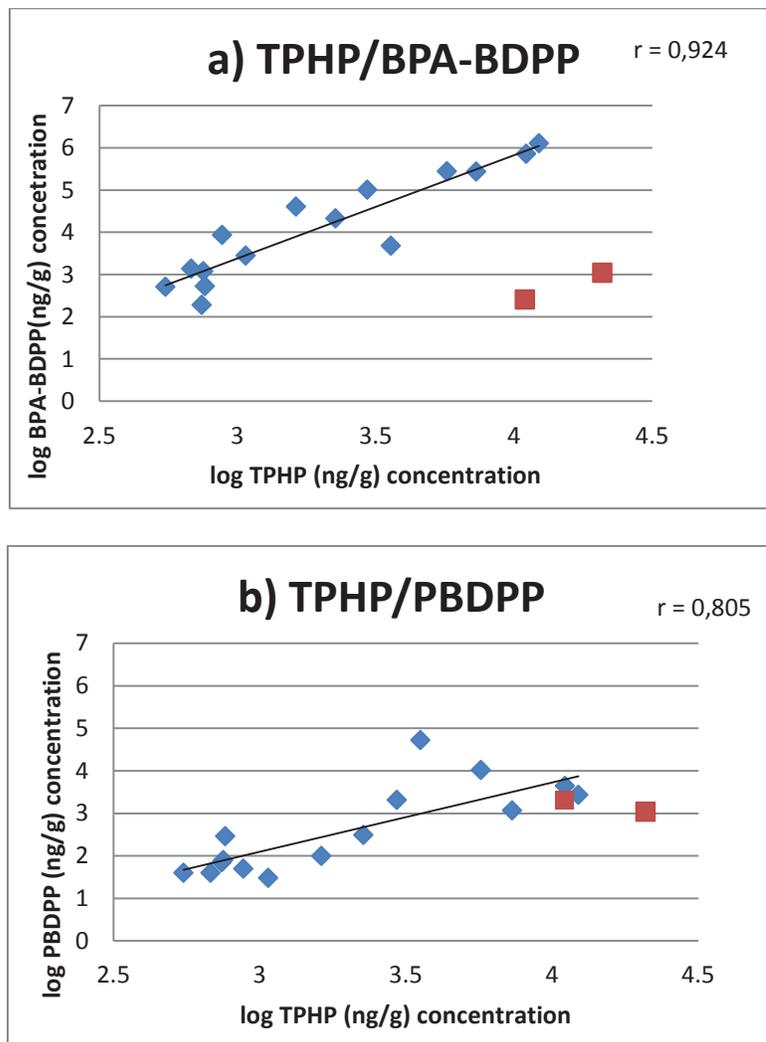


Figure 4. Relationship between the logarithmic concentrations of TPHP and a) log BPA-BDPP and b) log PBDPP concentrations in dust samples from the Netherlands. The red squares in both figures are concentrations from house 5 that were not included in the calculations. The black line is from linear regression.

BPA-BDPP were detected in both seat dust and dust from the dashboards. Lower PBDPP and BPA-BDPP concentrations were detected in dust from surfaces in the apartments, from the sofas and around the sofas in the furniture stores and on and around cables in one of the electronics stores. The PBDPP and BPA-BDPP concentrations in the dust samples from apartments in Sweden were in the same range as has been reported for BFRs such as PBDEs (including BDE209) in Swedish dust samples (medians of 320 ng/g in houses, 1100 ng/g in apartments) (Thuresson et al., 2012).

Generally, the BPA-BDPP concentrations in dust samples collected from electronic equipment in all three countries were high, with the highest concentrations found in one sample from the Netherlands (1300 µg/g) (Table 2). Therefore, electronic equipment is the most likely source of BPA-BDPP and possibly for PBDPP as well. The PBDPP and BPA-BDPP concentrations in dust samples on and around

electronic equipment were similar in all three countries which indicate that similar kinds of electronics are imported/used. In a study from Japan, the PBDPP concentration in one dust sample was 1700 ng/g, which is similar to the range found in dust collected around electronic equipment in our study, while the BPA-BDPP concentration (100 ng/g) were lower than in our study (Matsukami et al., 2010).

#### Human exposure to house dust

PBDPP and BPA-BDPP are relatively ubiquitous in dust samples from various indoor environments in the Netherlands, Greece and Sweden. This implies that Europeans are continuously exposed to these compounds via dust inhalation and ingestion. Estimations of the exposure to PBDPP, BPA-BDPP and TPHP through dust ingestion in ng/kg bw/d were calculated as described by Ali et al. (2012) and Brommer et al. (2012) for adults and (Table 3). The exposure estimates were based on a relatively small number of dust samples and are therefore only indicative. Only house dust samples from around the electronics (the Netherlands and Greece), and from Swedish apartments were used for the calculation of the exposure estimates because these were considered more representative of house dust than the dust samples taken on the electronics. The estimated exposure for house dust from the Netherlands may be overestimated because the calculation is based on dust collected around the electronics which may contain higher levels of BPA-BDPP and PBDPP than in “average” house dust. High, median and low estimated exposures to PBDPP, BPA-BDPP and TPHP were calculated for adults and toddlers assuming 100% absorption of PFRs from the ingested dust (Jones-Otazo et al., 2005). The estimated low exposure represents adults and toddlers that ingest 20 and 50 mg dust, respectively, daily at the 5<sup>th</sup> percentile dust concentration (Jones-Otazo et al., 2005). For the estimated median exposure for the adults and toddlers, the same daily dust ingestion of 20 and 50 mg, respectively, was used together with the median dust concentration. For the estimated high exposure for the adults and toddlers, a daily dust ingestion of 50 and 200 mg, respectively, was used together with the 95<sup>th</sup> percentile dust concentration (Jones-Otazo et al., 2005). Body weights of 70 kg for adults and 12.3 kg for toddlers were used. The highest exposure estimates for BPA-BDPP were 49 ng/kg bw/d for adults and 1125 ng/kg bw/d for toddlers, which are some orders of magnitude higher than the median BPA-BDPP estimated exposure levels for adults and toddlers of respectively, 0.4 and 5.2 ng/kg bw/d (Table 3). Brommer et al. (2012) recently reviewed the exposure estimated for PFRs via dust ingestion from Belgium, Germany and New Zealand. The median estimated exposure for BPA-BDPP in our study are comparably with the median exposure estimates of the predominant organophosphate compound, TBOEP from Belgium (0.7 ng/kg bw/d for adults and 8.2 ng/kg bw/d for toddlers) and New Zealand (0.9 ng/kg bw/d for adults and 13 ng/kg bw/d for toddlers) and some order of magnitudes higher than those of Germany (Brommer et al., 2012). The median estimated PBDPP exposure levels in adults and toddlers are lower than for BPA-BDPP, respectively 0.01 and 0.2 ng/kg bw/d.

The median BPA-BDPP estimated exposures for adults and toddlers are 8 times higher than the median BDE209 exposures via dust ingestion. Comparable results were found for PBDPP and BDE209. Because

toddlers ingest more dust from the floor than from any other high surfaces which was monitored in this study, the estimated exposure for the toddlers must be interpreted as a worst case scenario.

*Table 3. Estimated worst case exposure in ng/kg bw/d to PBDPP, BPA-BDPP, TPHP and BDE209 via dust ingestion.*

ng/kg bw/d	Country	PBDPP	BPA-BDPP	TPHP	BDE209
Adults (high)	Netherland	1.5	49	5.8	2.1
Adults (Median)	Netherland	0.01	0.4	0.2	0.05
Adults (low)	Netherland	0.005	0.06	0.2	0.008
Toddler (high)	Netherland	33	1125	132	49
Toddler (Median)	Netherland	0.2	5.2	3.3	0.7
Toddler (low)	Netherland	0.07	0.9	2.9	0.1
Adults (high)	Sweden	0.07	0.2		
Adults (Median)	Sweden	0.01	0.05		
Adults (low)	Sweden	0.008	0.05		
Toddler (high)	Sweden	1.5	3.7		
Toddler (Median)	Sweden	0.2	0.8		
Toddler (low)	Sweden	0.1	0.7		
Adults (high)	Greece	2.8	33		
Adults (Median)	Greece	0.01	3.4		
Adults (low)	Greece	0.005	0.7		
Toddler (high)	Greece	64	751		
Toddler (Median)	Greece	0.2	49		
Toddler (low)	Greece	0.08	10		

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## Appendix. Supplementary material

More information on the LC-MS/MS parameters used for the analysis of the dust samples from the Netherlands and Greece are given in Table S1. The individual BPA-BDPP and PBDPP observed in the dust samples from the Netherlands, Greece and Sweden are given in Table S2, S3 and S4.

Table S1. LC-MS/MS retention times and ion transitions monitored for all PFRs studied.

Compound	Acronym	Precursor Ion	Product Ion	Dwell	Fragmentor	Collision Energy
Tris(butyl) phosphate d27 *	TNBP-d27	294.4	166.1	20	100	15
		294.4	102.1	20	100	15
		435.4	99.1	20	125	10
Tris(phenyl) phosphate d15 *	TPHP-d15	342.2	160.2	20	175	40
		342.2	82.1	20	175	40
Tris(phenyl) phosphate	TPHP	327.2	152.1	20	175	35
		327.2	77.1	20	175	35
Bis-phenol A-bis (diphenyl phosphate)	BPA-BDPP	693.2	367.1	20	250	38
		693.2	327	20	250	38
Resorcinol bis (diphenyl phosphate)	PBDPP	575.1	481.1	20	225	45
		575.1	419	20	225	45

\* Internal standards

Table S2. PBDPP and BPA-BDPP concentrations in ng/g in dust from the Netherlands.

On electronics		Around electronics		Car dashboards		Car seats	
PBDPP	BPA-BDPP	PBDPP	BPA-BDPP	PBDPP	BPA-BDPP	PBDPP	BPA-BDPP
<100	40000	<80	1200	<80	<10	<11	<40
1200	270000	<70	190	<50	<120	<9	<9
52000	4800	290	530	<10	<8	<6	<6
11000	280000	2100	100000	<6	<3.6	<2	<10
770	1100	2000	260	34000	<20	9500	<3
310	22000	<40	1400	<30	<11	<17	150
4400	720000	<50	8700	<30	<20	50	170
2700	1300000	<30	2800	<1.1	<2.9	<37	50

Table S3. PBDPP and BPA-BDPP concentrations in ng/g in dust from Greece.

House no.	Items	PBDPP	BPA-BDPP
1	on electronics	870	7400
1	around electronics	4400	50000
2	on electronics	310	740000
2	around electronics	<30	12000
3	on electronics	490	680000
3	around electronics	<100	1500
4	on electronics	<40	<100
5	on electronics	<500	15300
5	on electronics	<100	710

Table S4. PBDPP and BPA-BDPP concentrations in ng/g in dust from Sweden.

	PDBPP	BPA-BDPP
Apartments	25	230
	39	190
	97	170
Car seats	120	329
	90	100
	70	127
	10	16
Car dashboards	60	50
	220	110
	62	80
	8.1	21
Furniture stores		
On textile sofas	140	330
	57	130
Around textile sofas	73	88
	270	860
On leather sofas	190	130
	570	250
Around leather sofas	94	120
	45	60
Electronic stores		
On cables	280	1600
Around cables	80	260
On flat screen etc.	590	490000
	80	8700
	940	290000
	1600	22000
Around TVs etc.	400	21000
	340	450

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