

## Impurities of resorcinol bis(diphenyl phosphate) in plastics and dust collected on electric/electronic material

Ana Ballesteros-Gómez, Alvaro Aragón, Nele Van den Eede, Jacob De Boer, and Adrian Covaci

*Environ. Sci. Technol.*, **Just Accepted Manuscript** • DOI: 10.1021/acs.est.5b05351 • Publication Date (Web): 21 Jan 2016

Downloaded from <http://pubs.acs.org> on January 21, 2016

### Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

1 **Impurities of resorcinol bis(diphenyl phosphate) in plastics and dust collected on**  
2 **electric/electronic material**

3

4 Ana Ballesteros-Gómez\*†, Álvaro Aragón †§, Nele Van den Eede‡, Jacob de Boert, Adrian Covaci‡

5

6 †VU University Amsterdam, Institute for Environmental Studies, De Boelelaan 1087, 1081 HV  
7 Amsterdam, the Netherlands

8 §Instituto Botánico, Universidad de Castilla-La Mancha, Campus Universitario s/n, 02071 Albacete, Spain

9 ‡Toxicological Center, University of Antwerp, Universiteitsplein 1, 2610 Antwerp, Wilrijk, Belgium

10

11 *\*Corresponding author*

12 E-mail: [a.m.ballesterosgomez@vu.nl](mailto:a.m.ballesterosgomez@vu.nl); [a.m.ballesterosgomez@gmail.com](mailto:a.m.ballesterosgomez@gmail.com)

13 Tel: + 31205983193

14 Fax +31205989553

15

16 **Abstract**

17 Resorcinol bis-(diphenylphosphate) (RDP) is an organophosphorus flame retardant widely used in  
18 electric and electronic equipment. It has been detected in house dust of several European countries  
19 according to recent literature. Similar to other flame retardants, RDP formulations and products treated  
20 with RDP, such as plastics, can contain RDP impurities, byproducts and breakdown products. In this  
21 study, we use screening methods based on wide scope solvent extraction and high resolution time-of-  
22 flight mass spectrometry for the identification of RDP related compounds in products and in dust. We  
23 analyzed both plastics from electrical/electronic equipment that contained RDP and indoor dust  
24 collected on and around surfaces of this equipment. A variety of compounds, namely TPHP,  
25 hydroxylated TPHP and RDP (*meta*-HO-TPHP and *meta*-HO-RDP), dihydroxylated TPHP, RDP with the loss  
26 of a phenyl group (RDP-[Phe]) and RDP oligomers were detected in plastics containing high levels of  
27 RDP. Regarding dust samples collected on electronics, TPHP *meta*-HO-TPHP, *meta*-HO-RDP, RDP-[Phe]  
28 and RDP oligomers were detected. High concentrations of *meta*-HO-TPHP (20-14,227 ng/g), TPHP (222-  
29 50,728 ng/g) and RDP (23-29,118 ng/g) were found in many of the dust samples, so that these  
30 compounds seem to easily migrate into the environment. These RDP impurities, byproducts and  
31 breakdown products are for the first time reported in indoor dust. *Meta*-HO-TPHP could be relevant for  
32 future biomonitoring studies concerning flame retardants.

33

34

35

36 **Keywords:** flame retardants; screening; RDP; triphenyl phosphate; dust; plastics; transformation  
37 products

## 38 Introduction

39 Flame retardants (FRs) have been added since the 1960s to a variety of materials (electronic equipment,  
40 textile, furniture, etc.) in order to prevent quick combustion and to delay the spread of fire.<sup>1</sup> After the  
41 phase-out of the toxic and persistent polybrominated diphenyl ethers (PBDEs), organophosphorus flame  
42 retardants (PFRs) have been increasingly used as suitable alternatives.<sup>2</sup> However, concern about their  
43 widespread presence and potential toxicity has also increased in the last years.<sup>3</sup> Resorcinol bis-(diphenyl  
44 phosphate) (RDP or PBDPP; CAS no. 125997-21-9) is a PFR used mainly in polymers of poly(p-phenylene)  
45 oxide (PPO)/ high impact polystyrene (HIPS) and of polycarbonate (PC)/ acrylonitrile butadiene styrene  
46 (ABS).<sup>4</sup> RDP is considered a suitable replacement for DecaBDE in electronic equipment.<sup>4,5</sup> The presence  
47 of RDP in environmental samples or in products has been scarcely reported,<sup>6-8</sup> although the first results  
48 indicate that RDP is widespread in indoor dust and that electric/electronic equipment, such as  
49 televisions, printers and power boards, is an important source in the indoor environment. High  
50 concentrations of RDP were found in dust collected on electronic equipment (<0.04-520 µg/g) from the  
51 Netherlands, Greece and Sweden.<sup>8</sup> The human toxicity of RDP is considered low to moderate according  
52 to a recent EPA report.<sup>4</sup> However, the aquatic toxicity of RDP is considered high (*Daphnia magna* 48-  
53 hour EC<sub>50</sub> = 0.7 mg/L) and the persistence and bioaccumulation potential are medium and high,  
54 respectively.<sup>4</sup> Lower persistence values (due to rapid primary biodegradation) have been also reported  
55 for RDP in a recent study.<sup>9</sup> Aquatic toxicity could partly be due to the presence of more polar impurities  
56 in RDP formulations (e.g. triphenyl phosphate, TPHP; typically 1-5 % w/w) and breakdown products  
57 (phenol, resorcinol).<sup>10</sup>

58 In the last years, new FRs have been identified for the first time in products and or in environmental  
59 samples, e.g. 2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl)bis(phosphate), known  
60 commercially as "V6",<sup>11,12</sup> or a triazine-based flame retardant [2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-  
61 triazine, TTBP-TAZ].<sup>13</sup> High resolution mass spectrometry plays an important role for the identification of

62 new contaminants (such as FRs) and their transformation products or impurities,. Not only FRs, but also  
63 new byproducts, impurities or degradation products have been very recently reported in environmental  
64 samples, such as those derived from tetrabromobisphenol A or tetrabromobisphenol S.<sup>14,15</sup> The  
65 persistency and toxicity of these impurities or related compounds, as well as their presence in the  
66 environment, is still largely unknown.

67 RDP impurities were recently identified in technical mixtures of RDP<sup>16-18</sup>, e.g. *meta*-hydroxy-triphenyl  
68 phosphate (*meta*-HO-TPHP) and hydroxyl-RDP. Together with TPHP, these impurities of RDP could also  
69 influence the total toxicity of RDP formulations. To the best of our knowledge, the presence of these  
70 impurities in environmental samples, such as indoor dust, has not yet been reported. In this study, we  
71 first investigate the presence of RDP impurities in plastics from electrical/electronic equipment in order  
72 to give a complete picture of RDP related compounds in the final processed product. The identified  
73 impurities were afterwards screened in indoor dust collected on electronics in order to study the  
74 possible migration of these compounds from the products into the environment. Suitable wide-  
75 screening methods based on solvent extraction and high-resolution time-of-flight-mass spectrometry  
76 (TOF-MS) were employed for both plastics and indoor dust.

77

## 78 **Experimental section**

### 79 ***Chemicals and reagents***

80 All solvents and reagents were of analytical grade and used as supplied. Acetone and methanol  
81 (MeOH) were from J.T. Baker® (Center Valley, USA). Tetrahydrofuran (THF) was acquired from Biosolve  
82 (Valkenswaard, The Netherlands). Dichloromethane (DCM, Picograde) and acetonitrile were obtained  
83 from Promochem® (Wesel, Germany) and toluene came from Fisher Scientific (Loughborough, UK). Milli-

84 Q water was obtained from ultrapure water purification Q-Pod system (Millipore, Bedford, USA). For  
85 sample treatment, micro-centrifuge filters (0.2  $\mu\text{m}$ , nylon) from Costar Spin-X obtained from Sigma-  
86 Aldrich were used for removing micro-particles from plastic sample extracts when necessary.  
87 Ammonium acetate was obtained from Sigma-Aldrich. TPHP and TPHP-d<sub>15</sub> were supplied by Sigma-  
88 Aldrich Chemie B.V. (Zwijndrecht, the Netherlands). Deuterated tri-*n*-butyl phosphate (TnBP-d<sub>27</sub>) was  
89 obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). RDP or PBDPP (Fyrolflex RDP,  
90 technical grade, 95.5% purity) was obtained from ICL (Amsterdam, the Netherlands). *Meta*-HO-TPHP  
91 was synthesized by the Organic Chemistry Synthesis Group from Duke University (NC, USA) and kindly  
92 donated by prof. Heather Stapleton (Duke University). The dust reference material SRM 2585 (organic  
93 contaminants in house dust) was obtained from the National Institute of Standards and Technology  
94 (NIST) and was employed for method validation. Information about this reference material can be found  
95 at NIST website ( <https://www-s.nist.gov/srmors/>, access December 2016)

#### 96 ***Apparatus and data processing***

97 A microTOF II with resolution >16,500 FWHM was used as detector and equipped with an LC-APCI II,  
98 direct probe-APCI or an LC-electrospray ionization (ESI)-ion booster source (Bruker Daltonics, Bremen,  
99 Germany). For LC, an InertSustain C18 (3  $\mu\text{m}$  particle size, 10 mm length) precolumn and an InertSustain  
100 C18 (3  $\mu\text{m}$  particle size, 2.1 mm i.d., 100 mm length) column were used as stationary phase (GL Sciences,  
101 Eindhoven, The Netherlands). For the mobile phase, Milli-Q water and MeOH were used in the following  
102 gradient: 50% MeOH (v/v) for 2 min, a linear gradient to 93% MeOH (v/v) in 25 min followed by 98%  
103 MeOH (v/v) for 10 min. The flow was 0.3 mL/min, the column temperature was set at 30 °C and the  
104 injection volume was 5  $\mu\text{L}$ . For internal calibration, an APCI-LC low concentration solution tuning mix  
105 from Agilent Technologies was used. The optimized TOF-MS parameters for the analysis of RDP and RDP

106 impurities by LC-(APCI)TOF-MS are given in Table S-1 of Supporting Information (SI). The instrumental  
107 detection limits were  $1 \text{ ng mL}^{-1}$  for *meta*-HO-TPHP and for TPHP and  $0.5 \text{ ng mL}^{-1}$  for RDP.

108 The software data analysis 4.0 and compass quant analysis from Bruker Daltonics were used for data  
109 processing (confirmation and quantification). MS internal calibration in each run was performed by  
110 infusing the calibration solution into the source within the first half a minute of the chromatogram by  
111 using a syringe pump (as designed by the supplier of the instrument). The internal calibration was  
112 performed by enhanced quadratic mode, with values  $<5 \text{ ppm}$  considered acceptable. Compounds were  
113 identified on the basis of mass accuracy and of mSigma values, that is the match factor between the  
114 measured isotopic pattern and the theoretical pattern for a given formula. Values below  $5 \text{ ppm}$  of mass  
115 error and below 100 of mSigma were considered acceptable for positive confirmation (mSigma  $<100$   
116 acceptable,  $<50$  good and  $<25$  excellent, as specified by the supplier of the Instrument and the software  
117 Bruker Daltonics).

### 118 ***Sample collection and preparation***

119 Electrical/electronic devices ( $n=25$ ) were analyzed, such as printers, routers, electrical adaptors, USB  
120 phone chargers, etc. They were bought in supermarkets in the Netherlands in 2015 ( $n=10$ ) or collected  
121 in Dutch houses and offices ( $n=15$ ). These samples were screened by a fast ambient mass spectrometry  
122 method<sup>19</sup> and ten samples containing RDP (five collected in houses and offices and other five bought in  
123 2015) were further investigated for this study. Aliquots of 25 mg were extracted with 5 or 50 mL of a  
124 mixture MeOH:THF (50:50, v/v) for screening and quantitation purposes, respectively. Samples were  
125 sonicated (60 min) and stirred (tube lateral shaker at  $200 \text{ Mot min}^{-1}$ ) for 24 h. Extracts were ultra-  
126 centrifuged (10,000 g, 5 min), then diluted 1:1, 1:10 or 1:100 with MeOH and ultra-centrifuged again  
127 (10,000 g, 5 min) to precipitate possible solids. The internal standard was added at the dilution step to a

128 final concentration after dilution of 250 ng mL<sup>-1</sup> of TPHP-d<sub>15</sub>. Aliquots of 5 µL were further analyzed by  
129 LC-(ESI/APCI)MS.

130 House dust samples ( $n=30$ ), were collected in different houses and offices in the Netherlands in 2015  
131 directly from the electronic equipment (e.g. televisions, computers, routers, printers or game consoles)  
132 that was present in each house/office and from the tables and sideboards around the equipment. Dust  
133 was collected using a Dustream<sup>TM</sup> dust collector (Indoor Biotechnologies Ltd., Wiltshire, United  
134 Kingdom) attached to the end of the vacuum cleaner hose. The mesh size of the filter used inside the  
135 dust collector was 40 µm and samples were not further sieved. Dust samples (~30 mg) were weighed in  
136 10 mL glass tubes and spiked with internal standards (TPHP-d<sub>15</sub> and TnBP-d<sub>27</sub>, 50 ng each). Then, 2 mL of  
137 2 M ammonium acetate and 2 mL of acetonitrile were added, vortex-mixed for 2 min and ultra-  
138 centrifuged (2000 g, 5 min). After the phase-separation by salting-out with ammonium acetate, the  
139 acetonitrile layer was separated and transferred into a glass tube. The liquid-liquid extraction was done  
140 3 times and all supernatants (~6 mL of acetonitrile) were combined and evaporated to near dryness (N<sub>2</sub>,  
141 40 °C). The extracts were reconstituted in 200 µL of methanol, vortexed for 30 s, ultracentrifuged 10,000  
142 g, 5 min) and transferred into a vial for analysis. Aliquots of 5 µL were further analyzed by LC-  
143 (ESI/APCI)MS.

144 The sample extracts were analyzed in both APCI and ESI (ion booster) and in positive and negative  
145 modes for screening purposes. The ESI (ion booster) source counts with an additional soft voltage and a  
146 vaporizer temperature for enhancing the ionization and for covering in this way a wider polarity range of  
147 compounds than a standard ESI source. For quantitation of TPHP, *meta*-HO-TPHP and RDP, samples  
148 were run in APCI(+) by monitoring [M+H]<sup>+</sup> as major ion. Calibration standards were prepared in  
149 methanol with concentrations in the range 1-5,000 ng/mL each containing 50 ng of the ISs (TPHP-d<sub>15</sub> and  
150 TnBP-d<sub>27</sub>). TPHP-d<sub>15</sub> was used as internal standard for the quantitation of *meta*-HO-TPHP, TPHP and RDP



151 in plastics. For the analysis of dust, TPHP-d<sub>15</sub> was used as IS of TPHP and TnBP-d<sub>27</sub> was used for *meta*-HO-  
152 TPHP and RDP in dust instead. The analytical figures of the quantitation method (*m/z* of the monitored  
153 ion, retention times and detection and quantitation limits) are given in Table S2. All the lab material was  
154 washed with methanol two times before use to prevent possible contamination. Procedural blanks (*n*=3)  
155 were run within each batch of samples and did not contain detectable levels of the target compounds  
156 (probably due to the relatively high instrumental LODs of the full scan MS detector and the simplicity of  
157 the method).

158

## 159 **Results and discussion**

### 160 **Extraction step for the screening/quantitation of RDP and RDP impurities**

161 Wide-scope extraction methods were investigated based on solvent extraction without further clean-up  
162 for preventing losses of compounds that could be of interest in the screening step. According to  
163 previous results,<sup>18</sup> mixtures of THF and MeOH are a suitable option for the extraction of a wide polarity  
164 range of plastic additives, including RDP and TPHP, and are compatible with the LC analysis. Plastic  
165 aliquots were extracted with 5 or 50 mL of THF:MeOH (50:50, v/v) for screening and quantitation  
166 purposes, respectively. The extraction method (with 50 mL THF:MeOH 50:50, v/v) was validated for the  
167 extraction of RDP, by analyzing a polymer material made of polycarbonate (PC)/acrylonitrile butadiene  
168 styrene (ABS) (70/30) that contained RDP at 20% (w/w). This material was prepared and validated for  
169 the European ENFIRO project. Recoveries were of 99±10% (*n*=3). Matrix effects in plastics extracts were  
170 acceptable in both ESI (recoveries of IS in the range 75-130%) and APCI (recoveries of IS in the range 85-  
171 120%) modes with relative standard deviations below 12%. Method detection limits for plastics were  
172 0.0005 w/w for *meta*-HO-TPHP and for TPHP and 0.00025 w/w for RDP. Method quantitation limits were  
173 0.001 w/w for *meta*-HO-TPHP and for TPHP and 0.0005 w/w for RDP.

174 The use of a salting-out extraction with acetonitrile for RDP and related compounds was previously  
175 investigated by our research group for the *in vitro* metabolism of RDP with microsomal preparations.<sup>16</sup>  
176 The method was successful for the extraction of a variety of RDP and RDP impurities and metabolites  
177 (yielding good apparent recoveries for all of them) and the simultaneous clean-up of the main matrix  
178 components (e.g. proteins and buffer) resulting in clear extracts.<sup>16</sup> We validated the same method for  
179 the analysis of the dust samples with LC-APCI(+)-TOF-MS analysis. The use of the mixture  
180 water:acetonitrile:ammonium acetate instead of only acetonitrile prevented the co-extraction of dust  
181 particles and of polar compounds that could interfere at the beginning of the LC chromatogram. The  
182 total recoveries of the target compounds (*meta*-HO-TPHP, TPHP and RDP) were assessed by spiking the  
183 dust certified reference material SRM 2585 (30 mg) at two concentration levels of 200 and 15,000 ng/g.  
184 Dust samples were spiked with 20-50  $\mu$ L of standards solutions and of internal standards in methanol  
185 and allowed to stand for around 6 h before extraction. In this way, the solvent was evaporated and we  
186 could mimic as much as possible the interaction of the compounds with the dust matrix. The true  
187 recoveries of the target compounds were estimated to be around 100% by assessing matrix effects in  
188 dust extracts that were spiked after extraction (with the target compounds and ISs at the same levels  
189 used for the calculation of the total method recoveries) and compared with equally spiked procedural  
190 blanks. Differently from the analysis of plastics, the use of APCI instead of ESI, drastically reduced matrix  
191 effects (recoveries without IS correction were below  $\sim$ 20% for ESI). Table 1 shows the validation results.  
192 TnBP-d<sub>27</sub> was a more suitable IS for *meta*-HO-TPHP and RDP, than TPHP-d<sub>15</sub> since the latter suffered  
193 from enhanced matrix effects (recoveries of 198 and 171%, respectively) due to a higher co-elution of  
194 matrix components in the elution window of TPHP. The same trend was observed in all dust samples  
195 (recoveries of TPHP-d<sub>15</sub> in the range 130-200%, average 165%) in contrast to the recoveries of TnBP-d<sub>27</sub>  
196 (range of 93-128%, average 109%). Method detection limits for dust were 10 ng g<sup>-1</sup> for *meta*-HO-TPHP

197 and for TPHP and 5 ng g<sup>-1</sup> for RDP. Method quantitation limits for dust were 20 ng g<sup>-1</sup> for *meta*-HO-TPHP  
 198 and for TPHP and 10 ng g<sup>-1</sup> for RDP.

199 The concentration of TPHP in the SRM 2585 was calculated as 1070±50 ng g<sup>-1</sup>. These values are in  
 200 accordance with the values of TPHP previously reported by other authors in this material (990±70 ng/g  
 201 <sup>20</sup>; 1,100±100 ng/g <sup>21</sup>).

202 **Table 1.** Total method recoveries of *meta*-HO-TPHP, TPHP and RDP

	<i>meta</i> -HO-TPHP	TPHP	RDP
TPHP-d <sub>15</sub>	<sup>a</sup> 67±1	<sup>a</sup> <b>102±5</b>	<sup>a</sup> 84±8
	<sup>b</sup> 67±2	<sup>b</sup> <b>103±2</b>	<sup>b</sup> 55±4
TnBP-d <sub>27</sub>	<sup>a</sup> <b>100±6</b>	-	<sup>a</sup> <b>103±1</b>
	<sup>b</sup> <b>104±2</b>		<sup>b</sup> <b>92±1</b>
Without IS	<sup>a</sup> 114±5	<sup>a</sup> 198±10	<sup>a</sup> 118±10
	<sup>b</sup> 103±1	<sup>b</sup> 171±1	<sup>b</sup> 92±1

<sup>a</sup>Spiked at 200 ng/g; <sup>b</sup>spiked at 15,000 ng/g; average±standard deviation (*n*=3) are shown; Optimal conditions used for quantitation of the samples are shown in bold

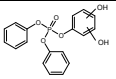
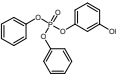
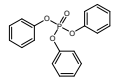
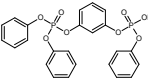
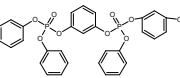
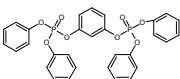
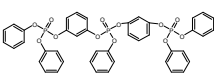
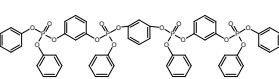
203

#### 204 Screening of RDP and RDP impurities in plastics and in indoor dust collected on electronics

205 Samples were run in ESI and APCI and in negative and positive modes for the screening of RDP-related  
 206 compounds. A detailed list of the compounds related to RDP and identified in plastics and in dust is  
 207 given in Table 2. A variety of RDP-related products, such as *meta*-HO-TPHP and RDP with the loss of a  
 208 phenyl ring (RDP-[Phe]) were observed in the samples. The impurity or related product of lowest relative  
 209 abundance, namely di-HO-TPHP, was only observed in plastics and not in dust. Regarding the RDP  
 210 oligomers, the dimer and the trimer were detected in the samples with high levels of RDP (above 0.03%  
 211 w/w in plastics and at levels of >3,000 ng/g in dust). For all hydroxylated compounds, only one isomer  
 212 was observed. For the monohydroxylated TPHP and RDP, *meta*- is the most probable position for the –  
 213 HO group in accordance with the RDP structure. This was confirmed for *meta*-HO-TPHP by matching the

214 retention time and spectra with those of the authentic standard. The only exception was HO-RDP in dust  
215 (not in plastics), that showed two isomers, one around 5-20 times more intense than the other. The  
216 most intense isomer in dust is most probably *meta*-HO-RDP taking into account that the retention time  
217 matched that of the HO-RDP isomer identified in plastics. This finding could suggest some biological or  
218 chemical degradation of RDP to other HO-isomer, such as *para*-HO-RDP. *Para*-HO-RDP was identified in  
219 our previous study as metabolite of RDP<sup>16</sup> and, as observed in the analysis of dust in this study, it eluted  
220 earlier than the *meta*-isomer in the LC chromatogram. Diphenyl phosphate (DPHP), was also observed in  
221 all the plastics that contained RDP, but it was not further investigated since it is not an specific  
222 compound deriving only from RDP, e.g. it could come also from a variety of arylphosphates, such as  
223 TPHP itself, 2-ethylhexyl diphenyl phosphate (EHDPHP) and bisphenol-A bis(diphenyl phosphate) (BDP).  
224

225 **Table 2.** RDP related products identified in plastics and in dust collected on and around electronics

Compound	Molecular Formula	Structure	Observed ions	Detection in plastic samples containing RDP <sup>a</sup> and in dust samples <sup>b</sup>
Dihydroxy-triphenyl phosphate (di-HO-TPHP) <sup>c</sup>	C18H15O6P		LC-ESI: [M-H] <sup>-</sup> LC-APCI: [M-H] <sup>-</sup>	3/10 <sup>a</sup> 0/30 <sup>b</sup>
Meta-hydroxy-triphenyl phosphate ( <i>meta</i> -HO-TPHP)	C18H15O5P		LC-ESI: [M-H] <sup>-</sup> , [M+Na] <sup>+</sup> , LC-APCI: [M-H] <sup>-</sup> , [M+H] <sup>+</sup> , [M+CH3OH+H] <sup>+</sup>	10/10 <sup>a</sup> 25/30 <sup>b</sup>
Triphenyl phosphate (TPHP)	C18H15O4P		LC-ESI: [M+H] <sup>+</sup> , [M+Na] <sup>+</sup> , LC-APCI: [M+H] <sup>+</sup> , [M+CH3OH+H] <sup>+</sup>	10/10 <sup>a</sup> 30/30 <sup>b</sup>
Resorcinol bis(diphenyl phosphate) with a loss of a phenyl group (RDP-[Phe])	C24H20O8P2		LC-ESI: [M-H] <sup>-</sup>	5/10 <sup>a</sup> 8/30 <sup>b</sup>
Hydroxy-Resorcinol bis(diphenyl phosphate) <sup>d</sup> (HO-RDP)	C30H24O9P2		LC-ESI: [M-H] <sup>-</sup> , [M+Na] <sup>+</sup> , LC-APCI: [M-H] <sup>-</sup> , [M+H] <sup>+</sup> , [M+CH3OH+H] <sup>+</sup>	6/10 <sup>a</sup> 5/30 <sup>b</sup>
Resorcinol bis(diphenyl phosphate) (RDP)	C30H24O8P2		LC-ESI: [M-H] <sup>-</sup> , [M+Na] <sup>+</sup> LC-APCI: [M+H] <sup>+</sup> , [M+CH3OH+H] <sup>+</sup>	10/10 25/30 <sup>b</sup>
RDP dimer [RDP(n2)]	C42H33O12P3		LC-ESI: [M+Na] <sup>+</sup> , [M+CH3CNNH3+H] <sup>+</sup> LC-APCI: [M+H] <sup>+</sup>	4/10 8/30 <sup>b</sup>
RDP trimer [RDP(n3)]	C54H42O16P4		LC-ESI: [M+Na] <sup>+</sup> , [M+CH3CNNH3+H] <sup>+</sup> LC-APCI: [M+H] <sup>+</sup>	2/10 3/30 <sup>b</sup>

226 <sup>a</sup>Plastics; <sup>b</sup>Dust; <sup>c</sup>The position of the –OH groups is unknown; <sup>d</sup>The most probable position is *meta*- as a breakdown  
227 product of RDP

## 228 Quantitation of RDP, TPHP and meta-HO-TPHP in plastics and indoor dust collected on electronics

229 Although samples were screened by LC with ESI(+/-) and APCI (+/-) sources as indicated in Table 2,  
230 APCI(+) was used for quantitation of TPHP, *meta*-HO-TPHP and RDP by monitoring [M+H]<sup>+</sup> as major ion  
231 with a *m/z* window of ±0.025 to achieve enough selectivity. APCI provided lower matrix effects and  
232 higher dynamic linear ranges in comparison with ESI. *Meta*-HO-TPHP could be also monitored by APCI(-)  
233 as [M-H]<sup>-</sup>, with the negative mode more selective in terms of matrix background noise. However, APCI(+)

234 was selected for quantitation of *meta*-HO-TPHP, since it provided around 5-fold better detection limits.  
235 *Meta*-HO-TPHP, TPHP and RDP were all present at quantifiable levels in the selected plastics that  
236 contained RDP (as shown in Table 3, Table S2 and Figure S2). However, only two samples contained high  
237 concentrations of RDP (11.6 and 12.8 %, w/w), while the other plastics contained RDP only at trace  
238 levels (0.001-0.08 %, w/w). The presence of different PFRs and FRs at low levels in the same product was  
239 reported before by our research group and could be due recycling or to cross-contamination during  
240 processing.<sup>7</sup>

241 The concentrations of TPHP and *meta*-HO-TPHP varied highly among different products (Table S3). The  
242 levels of these impurities were similar to those expected in RDP formulations in plastics containing the  
243 highest concentrations of RDP (e.g. TPHP was ~3.0 %, w/w and *meta*-HO-TPHP was 0.5%, w/w in the  
244 RDP formulation used in this study). Contrarily, they were very different in those containing trace levels  
245 of RDP. In these samples, TPHP was sometimes even at higher concentration levels than RDP itself. This  
246 could be due to cross-contamination (processing, recycling) from plastics that contained TPHP which  
247 was not related from RDP formulations. In any case, and despite the limited number of samples, the  
248 levels of *meta*-HO-TPHP and RDP and of TPHP and RDP in plastics containing RDP were highly correlated  
249 [Pearson correlation coefficient for *meta*-HO-TPHP and RDP (log data) 0.9577 with p-value 0.003 and  
250 Spearman correlation coefficient 0.9710 with p-value 0.001;  $n=6$ ; Pearson correlation coefficient for  
251 TPHP and RDP (log data) 0.9396 with p-value 0.0005 and Spearman correlation coefficient 0.9940 with  
252 p-value <0.0005;  $n=7$ ].

253

254

255

256

257 **Table 3.** Levels of *meta*-HO-TPHP, TPHP and RDP in plastics and in dust

Sampling site	<i>meta</i> -HO-TPHP	TPHP	RDP
In plastics containing RDP ( <i>n</i> =10), % w/w	0.01 <sup>a</sup> ; 0.003-0.4 <sup>b</sup> ; ( <i>n</i> =10) <sup>c</sup>	0.05 <sup>a</sup> ; 0.007-0.3 <sup>b</sup> ; ( <i>n</i> =10) <sup>c</sup>	0.03 <sup>a</sup> ; 0.001-12.8 <sup>b</sup> ; ( <i>n</i> =10) <sup>c</sup>
Dust, on and around electronics ( <i>n</i> =30), ng/g	86 <sup>a</sup> ; 20-14,227 <sup>b</sup> ; ( <i>n</i> =25) <sup>c</sup>	3,721 <sup>a</sup> ; 222-50,728 <sup>b</sup> ; ( <i>n</i> =30) <sup>c</sup>	431 <sup>a</sup> ; 23-29,118 <sup>b</sup> ; ( <i>n</i> =27) <sup>c</sup>

<sup>a</sup>Median, <sup>b</sup>range; <sup>c</sup>number of positive samples (above LOD). Detailed information of the levels found in plastics and in dust can be found in Tables S3 and S4 ; % w/w means percentage in weight

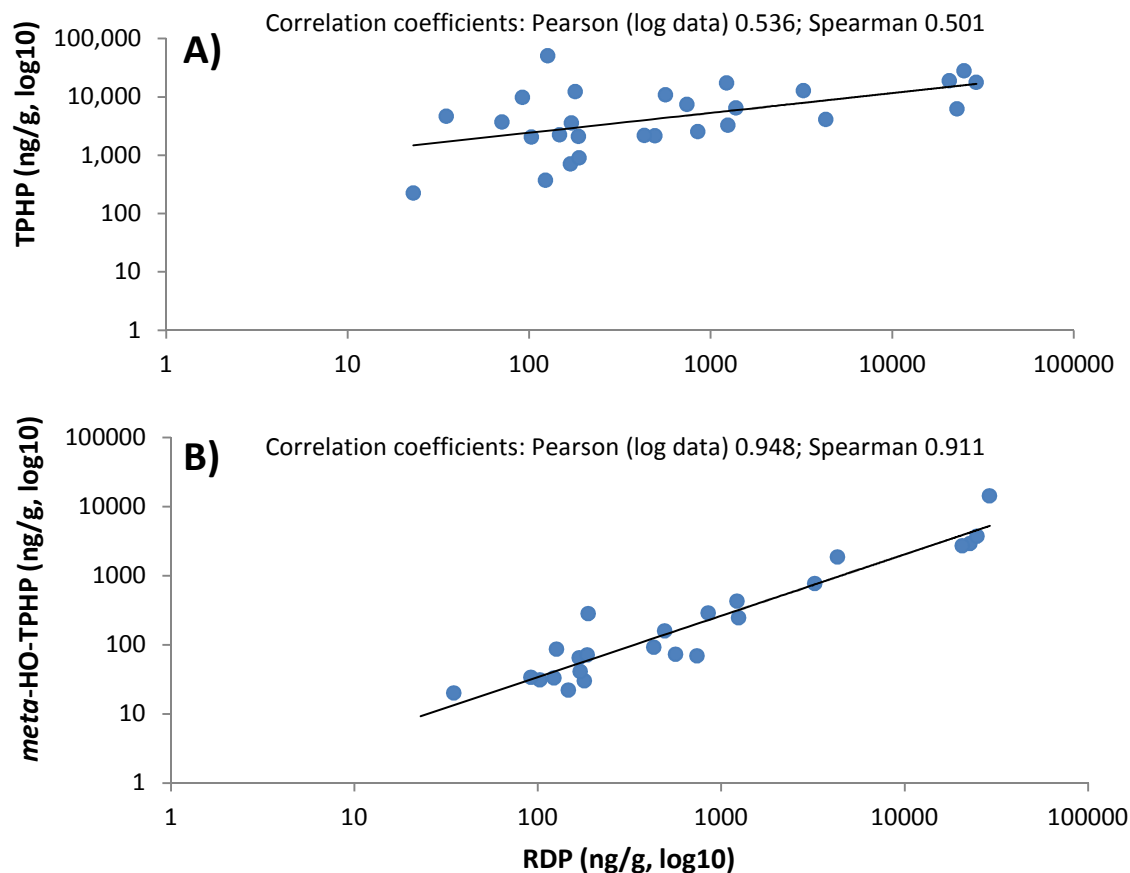
258

259 Regarding the analysis of 30 dust samples, the compounds TPHP (*n*=30), RDP (*n*=27), *meta*-HO-TPHP  
 260 (*n*=25), RDP-[Phe] (*n*=8) and *meta*-HO-RDP (*n*=5) (see Table 2). For *meta*-HO-TPHP, RDP and TPHP  
 261 concentrations are given in Tables 3 and S4. The median values were 86, 431 and 3,721 ng/g,  
 262 respectively. Despite the general lower levels of *meta*-HO-TPHP in dust in comparison with RDP and  
 263 TPHP, the maximum values also reached the µg/g range. The concentrations measured in dust for the  
 264 three compounds (222-50,728 ng/g for TPHP, 23-29,118 ng/g for RDP and 20-14,227 for *meta*-HO-TPHP)  
 265 are in agreement with those previously reported for RDP and TPHP and also for other FRs in samples  
 266 collected on/around electronics.<sup>8,12</sup>

267 The presence of TPHP in samples that did not contain RDP could be due to the use of TPHP in many  
 268 other FR and plasticizer formulations that do not contain RDP. In fact, only a moderate positive  
 269 correlation was found between the levels of TPHP and RDP in dust [Pearson correlation coefficient (log  
 270 data) 0.5356 with p-value 0.004; Spearman correlation coefficient 0.5012 with p-value 0.008; *n*=27, see  
 271 Figure 1)]. In contrast, *meta*-HO-TPHP was only present in those dust samples containing RDP, and the  
 272 concentrations of both compounds were very strongly correlated [Pearson correlation coefficient (log  
 273 data) 0.9479 with p-value <0.0001; Spearman correlation coefficient 0.9113 with p-value <0.0001;

14

274  $n=25$ , see Figure 1]. On the basis of these results, *meta*-HO-TPHP could be a suitable marker/tracer for  
275 the assessment of the exposure to RPD in future biomonitoring studies.



276 **Figure 1.** Correlation between the levels of TPHP and RDP ( $n=27$ ) and between *meta*-HO-TPHP and RDP  
277 ( $n=25$ ) in dust collected on/around electronics.

278 The concentrations of *meta*-HO-TPHP in dust were much higher than those that could be expected  
279 taking into account that it is only a minor impurity in RDP commercial formulations. So, the ratio of RDP  
280 (ng/g)/*meta*-HO-RDP (ng/g) in dust was in the range 0.7-11 (median= 4). In contrast, the ratio of RDP  
281 (w/w)/*meta*-HO-RDP (w/w) in the RDP formulation used in this study was much higher with a value of  
282  $\sim 196$  (corresponding to 0.5% w/w *meta*-HO-TPHP and 96% w/w RDP). The higher polarity and smaller  
283 molecular weight of *meta*-HO-TPHP could lead to an easier migration of this compound than RDP into  
284 the dust or possibly a chemical or biological hydrolysis of RDP could have taken place.



285 The levels of RDP-[Phe] and *meta*-HO-RDP in comparison with those of *meta*-HO-TPHP in the same dust  
286 samples (and under the same ionization mode) were similar and 10-100 smaller, respectively. Figure S1  
287 shows the extracted ion chromatograms of the target compounds in a dust sample extract. The lower  
288 detection frequency of RDP-[Phe] in dust could be due to higher detection limits for this compound in  
289 LC-ESI(-). The presence of matrix effects and higher background noise in ESI mode could have hampered  
290 the detection of RDP-[Phe] in dust at low levels. The future availability of true standards for RDP-[Phe]  
291 and *meta*-HO-RDP is highly desirable for a better assessment of the presence of these impurities.

292 Although we only investigated a limited number of samples, these results suggest that RDP and RDP  
293 impurities are commonly present in flame-retarded plastics from electric/electronic equipment  
294 (detected in 10 of 25 samples). Impurities seem to be present in plastics not only as a result of RDP used  
295 as main FR, but they are also present in plastics with trace levels of RDP, maybe due to cross-  
296 contamination during recycling or processing. Dust collected on electronics showed elevated  
297 concentrations (reaching the  $\mu\text{g/g}$  levels) of RDP, TPHP and *meta*-HO-RDP in most of the samples. These  
298 high spot levels on dust collected on electronics could be a significant route of human exposure via  
299 ingestion/dermal adsorption especially when touching these surfaces, e.g. by typing on a keyboard or  
300 switching on a TV. These results highlight the need to study not only the levels of the main FR, but also  
301 of their less-known impurities or degradation products, such as *meta*-HO-RDP derived from RDP. The  
302 analysis of other type of dust samples (not only collected on/around electronics) is highly desirable in  
303 future studies for a better assessment of the human exposure to these novel compounds. Typically,  
304 impurities of flame retardants share the same functional groups and basic structures with their parent  
305 compounds but are smaller and more polar. While impurities are usually be less persistent than the  
306 parent compound they can be also more toxic, as occurring for TPHP in comparison with RDP, for which  
307 some toxic properties have been reported (e.g. in chicken embryonic hepatocytes<sup>22</sup> and in developing  
308 zebrafish embryos.<sup>23,24</sup>). Giving these high spot levels, more data on the presence and potential toxicity

309 of *meta*-HO-TPHP is necessary in future monitoring studies to assess the human exposure and risks to  
310 this compound. Besides, due to its specificity and ubiquity as RDP impurity, *meta*-HO-TPHP could be a  
311 suitable marker/tracer of RDP. RDP-[Phe] and *meta*-HO-RDP could be also relevant for future studies.

312

### 313 **AUTHOR INFORMATION**

#### 314 ***Corresponding Author***

315 \*E-mail: a.m.ballesterogomez@vu.nl; [a.m.ballesterogomez@gmail.com](mailto:a.m.ballesterogomez@gmail.com); Tel: +31205983193; Fax  
316 +31205989553

#### 317 ***Notes***

318 The authors declare no competing financial interest.

### 319 **ACKNOWLEDGMENTS**

320 ABG acknowledges the funding by the Netherlands Organization for Scientific Research (NWO)  
321 (VENI2014-722.014.003). Dr. Pim Leonards and Dr. Sicco Brandsma are acknowledged for providing the  
322 plastic material containing RDP that was prepared under the FP7 ENFIRO project (contract No. 226563).  
323 Dr Álvaro Aragón thanks the Ministry of Education Culture and Sport of Junta de Comunidades de  
324 Castilla-La Mancha for his postdoctoral grant. Tim Jonkers is acknowledged for the collection of dust  
325 samples and plastics. Dr. David Gooden is gratefully acknowledged for synthesizing the meta-hydroxy-  
326 TPHP standard and Prof. Heather Stapleton for donating it.

### 327 **ASSOCIATED CONTENT**

#### 328 ***Supporting Information***

329 The Supporting Information provides detailed information about 1) the MS parameters used for the  
330 analysis, 2) analytical figures of the quantitation method (*m/z* of the monitored ion, retention times and  
331 detection and quantitation limits), 3) levels of RDP, TPHP and *meta*-HO-TPHP in individual plastic and

332 dust samples and 4) extracted ion chromatograms of the target compounds in a dust sample extract.

333 This information is available free of charge via the Internet at <http://pubs.acs.org/>.

### 334 **References**

- 335 1. Kemmlein, S.; Hahn, O.; Jann, O. Emissions of organophosphate and brominated flame  
336 retardants from selected consumer products and building materials. *Atmos. Environ.* **2003**, *37*,  
337 5485–5493.
- 338 2. Van der Veen, I.; de Boer, J. Phosphorus flame retardants: Properties, production,  
339 environmental occurrence, toxicity and analysis. *Chemosphere* **2012**, *88*, 1119–1153.
- 340 3. Wei, G.L.; Lia, D.Q.; Zhuo, M.N.; Liao, Y.S.; Xie, Z.Y.; Guo, T.L.; Li, J.J.; Zhang, S.Y.; Liang, Z.Q.  
341 Organophosphorus flame retardants and plasticizers: Sources, occurrence, toxicity and human  
342 exposure. *Environ. Pollut.* **2015**, *196*, 29–46.
- 343 4. U.S. Environmental Protection Agency (U.S. EPA). An Alternatives Assessment for the Flame  
344 Retardant Decabromodiphenyl Ether (DecaBDE)", 2014  
345 <http://www.epa.gov/dfe/pubs/projects/decaBDE/deca-report-complete.pdf>.
- 346 5. Lowell Center for Sustainable Production (LCSP). Decabromodiphenylether: An Investigation of  
347 Non-Halogen Substitutes in Electronic Enclosure and Textile Applications, 2005 [http://www.](http://www.sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf)  
348 [sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf](http://www.sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf).
- 349 6. Roth, T.; Urpi Bertran, R.; Pöhlein, M.; Wolf, M.; van Eldik, R. Gas chromatographic  
350 determination of phosphate-based flame retardants in styrene-based polymers from waste  
351 electrical and electronic equipment. *J. Chromatogr. A* **2012**, *1262*, 188–195.
- 352 7. Ballesteros-Gómez, A.; Brandsma S.H.; de Boer J.; Leonards P.E.G. Analysis of two alternative  
353 organophosphorus flame retardants in electronic and plastic consumer products: resorcinol bis-

- 354 (diphenylphosphate) (PBDPP) and bisphenol A bis (diphenylphosphate) (BPA-BDPP).  
355 *Chemosphere* **2014**, 116, 10-14.
- 356 8. Brandsma, S.H.; Sellström, U.; de Wit, C.A.; de Boer, J.; Leonards, P.E.G. Dust measurement of  
357 two organophosphorus flame-retardants, resorcinol bis (diphenylphosphate) (RBDPP) and  
358 bisphenol A bis (diphenylphosphate) (BPA-BDPP) used as alternatives for BDE209. *Environ Sci*  
359 *Technol.* **2013**, 47, 14434–14441.
- 360 9. Jurgens, S.S.; Helmus, R.; Waaijers, S.L.; Uittenbogaard, D.; Dunnebier, D.; Vleugel, M.; Kraak,  
361 M.H.S.; de Voogt, P.; Parsons, J.R. Mineralisation and primary biodegradation of aromatic  
362 organophosphorus flame retardants in activated sludge. *Chemosphere* **2014**, 111, 238–242.
- 363 10. LaFlamme, D.; Stone, A.; Kraege, C.; Department of Ecology Publication and Department of  
364 Health Publication of Washington. Alternatives to Deca-BDE in Televisions and Computers and  
365 Residential Upholstered Furniture. 2008  
366 <https://fortress.wa.gov/ecy/publications/summarypages/0907041.html>.
- 367 11. Stapleton, H.M.; Klosterhaus, S.; Keller, A.; Ferguson, P.L.; van Bergen, S.; Cooper, E.; Webster,  
368 T.F.; Blum, A. Identification of flame retardants in polyurethane foam collected from baby  
369 products. *Environ. Sci. Technol.* **2011**, 45, 5323–5331.
- 370 12. Fang, M.; Webster, T.F.; Gooden, D.; Cooper, E.M.; McClean, M.D.; Carignan, C.; Makey, C.;  
371 Stapleton, H.M. Investigating a novel flame retardant known as V6: measurements in baby  
372 products, house dust, and car dust. *Environ. Sci. Technol.* **2013**, 47, 4449-4454.
- 373 13. Ballesteros-Gómez, A; de Boer, J.; Leonards. P.E.G. A novel brominated triazine-based flame  
374 retardant (TTBP-TAZ) in plastic consumer products and indoor dust. *Environ. Sci. Technol.* **2014**,  
375 48, 4468–4474.
- 376 14. Qu, G.; Liu, A.; Wang, T.; Zhang, C.; Fu, J.; Yu, M.; Sun, J.; Zhu, N.; Li, Z.; Wei, G.; Du, Y.; Shi, J.; Liu,  
377 S.; Jiang, G. Identification of tetrabromobisphenol a allyl ether and tetrabromobisphenol a 2,3-

- 378 dibromopropyl ether in the ambient environment near a manufacturing site and in mollusks at a  
379 coastal region. *Environ. Sci. Technol.* **2013**, 47, 4760–4767.
- 380 15. Liu, A.; Tian, Y.; Yin, N.; Yu, M.; Qu, G.; Shi, J.; Du, Y.; Jiang, G. Characterization of three  
381 tetrabromobisphenol-S derivatives in mollusks from Chinese Bohai Sea: a strategy for novel  
382 brominated contaminants identification. *Sci. Rep.* **2015**, 11741 (5), 1-12
- 383 16. Ballesteros-Gómez, A.; Van den Eede, N.; Covaci, A. In vitro human metabolism of the flame  
384 retardant resorcinol bis(diphenylphosphate) (RDP). *Environ. Sci. Technol.* **2015**, 49, 3897-3904.
- 385 17. Matsukami, H.; Suzuki, G.; Takigami, H. Compositional analysis of commercial oligomeric  
386 organophosphorus flame retardants used as alternatives for PBDEs: Concentrations and  
387 potential environmental emissions of oligomers and impurities. *Environ. Sci. Technol.* **2015**, 49,  
388 12913–12921
- 389 18. Ballesteros-Gómez, A.; Jonkers, T.; Covaci, A.; de Boer, J. Screening of additives in plastics with  
390 high resolution time-of-flight mass spectrometry and different ionization sources: direct probe  
391 injection (DIP)-APCI, LC-APCI, and LC-ion booster ESI. *Anal. Bioanal. Chem.* DOI: 10.1007/s00216-  
392 015-9238-5
- 393 19. Ballesteros-Gómez, A.; Brandsma, S. H.; Leonards, P.E.G.; de Boer, J. Direct probe atmospheric  
394 pressure photoionization/atmospheric pressure chemical ionization high-resolution mass  
395 spectrometry for fast screening of flame retardants and plasticizers in products and waste. *Anal.*  
396 *Bioanal. Chem.* **2014**, 406, 2503-2512.
- 397 20. Van den Eede, N.; Dirtu, A.C.; Neels, H.; Covaci, A. Analytical developments and preliminary  
398 assessment of human exposure to organophosphate flame retardants from indoor dust. *Environ.*  
399 *Int.* **2011**, 37, 454–461.

- 400 21. Bergh, C.; Luongo, G.; Wise, S.; Östman, C. Organophosphate and phthalate esters in standard  
401 reference material 2585 organic contaminants in house dust. *Anal. Bioanal. Chem.* **2012**, 402, 51-  
402 59.
- 403 22. Su, G.; Crump, D.; Letcher, R.J.; Kennedy, S.W. Rapid in Vitro Metabolism of the Flame  
404 Retardant Triphenyl Phosphate and Effects on Cytotoxicity and mRNA Expression in Chicken  
405 Embryonic Hepatocytes. *Environ. Sci. Technol.*, **2014**, 48, 13511–13519.
- 406 23. McGee, S.P.; Konstantinov, A.; Stapleton, H.M.; Volz, D.C. Aryl phosphate esters within a major  
407 PentaBDE replacement product induce cardiotoxicity in developing zebrafish embryos: potential  
408 role of the aryl hydrocarbon receptor. *Toxicol. Sci.*, **2013**, 133, 144–156
- 409 24. Liu, C.; Wang, Q.; Liang, K.; Liu, J.; Zhou, B.; Zhang, X.; Liu, H.; Giesy, J.P.; Yu, H. Effects of tris(1,3-  
410 dichloro-2-propyl) phosphate and triphenyl phosphate on receptor-associated mRNA expression  
411 in zebrafish embryos/larvae. *Aquat Toxicol.* **2013**, 128-129,147-157.

412

413

414

415

416

417

418

419

420

421

422

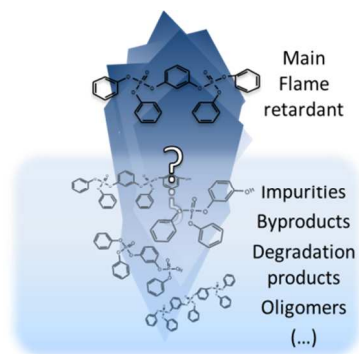
423

424

425

426 TOC

427



428