

1 **A Novel Brominated Triazine-based Flame Retardant (TTBP-TAZ) in Plastic Consumer Products**
2 **and Indoor Dust**

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21 **Abstract**

22 The presence of a novel brominated flame retardant named 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-
23 triazine (TTBP-TAZ) is reported for the first time in plastic parts of consumer products and indoor dust
24 samples. TTBP-TAZ was identified by untargeted screening and can be a replacement of the banned
25 polybrominated diphenyl ethers. Analysis techniques based on ambient mass spectrometry and on liquid
26 chromatography with atmospheric pressure chemical ionization combined with high resolution time-of-
27 flight mass spectrometry were developed for the screening, detection and quantification of this low
28 volatility and high molecular weight compound. TTBP-TAZ was present in 8 of 13 plastic parts of
29 consumer products (from mainly electric and electronic equipment acquired in 2012) at estimated
30 concentrations of 0.01-1.9 % by weight of the product (% w/w). It was not present in any of the older 13
31 plastic samples that were collected in a recycling park (manufacture date before 2006), this suggests a
32 recent use of TTBP-TAZ. It was also found in 9 of 17 house dust samples in the range of 160-22150 ng g⁻¹,
33 with the highest levels being found in samples collected on electronic and electrical equipment. These
34 preliminary results highlight the need for further research on TTBP-TAZ and the potential of using
35 alternative analysis methods for the identification of new flame retardants.

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38 **KEYWORDS:** Tris(2,4,6-tribromophenoxy)-1,3,5-triazine, TTBP-TAZ, FR-245, brominated flame
39 retardant

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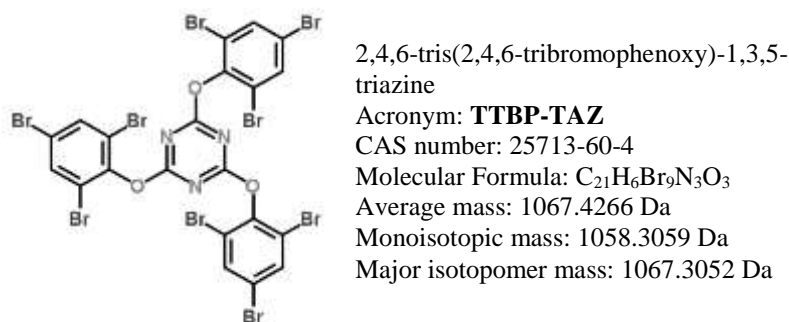
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43 **Introduction**

44 Brominated flame retardants (BFRs) are widely used in a variety of consumer goods (plastics, electric
45 and electronic equipment, textiles, furniture, building materials, etc.) to comply with flammability
46 standards. They are widely found in indoor and outdoor environments—e.g. dust, surface water, sediment
47 and human milk and blood (1-4). A number of adverse health effects have been reported for some BFRs,
48 including neurotoxicity, thyroid hormone effects and certain morphological effects (5), and lately even
49 estrogen/androgen hormone-related effects (6). On the basis of these toxic properties, the commercial
50 formulations of polybrominated diphenyl ethers (PBDEs), have been banned or phased out in the EU and
51 US. PentaBDE and OctaBDE were voluntarily phased out in the US after 2004 and banned by the EU
52 under the Directives 2003/11/EC and 2002/95/EC. In July 2008, a third PBDE mixture, DecaBDE, was
53 also banned by the European Court of Justice (Court Proceedings, 9.5.2008, C116/2-3) from use in
54 electrical and electronic equipment.

55 Restrictions on the use of PBDEs have resulted in an increased use of alternative flame retardants, such as
56 organophosphorous flame retardants (PFRs). In recent years, a number of new flame retardants have been
57 identified in products and environmental samples. The content of these compounds in daily products is
58 still largely unclear. Two chlorinated PFRs not previously recorded in the environment were recently
59 identified in polyurethane foam from baby care products (7), namely 2,2-bis(chloromethyl)propane-1,3-
60 diyl-tetrakis(2-chloroethyl)bis(phosphate), known commercially as “V6”, and the analogue 2,2-
61 bis(chloromethyl)propane-1,3-diyl tetrakis(1-chloropropan-2-yl) bis(phosphate), known as “U-
62 OPFR”. V6 was later reported in dust samples collected in houses and cars (8). Other two novel PFRs,
63 resorcinol bis(diphenylphosphate) (PBDPP) and bisphenol A bis(diphenylphosphate) (BPA-BDPP), have
64 recently been reported in house dust collected in Europe (9). To the best of our knowledge, new BFRs
65 have not been reported in indoor or outdoor environments since the detection of tetrabromobisphenol-A-
66 bis-(2, 3-dibromopropylether) (TBBPA-BDBPE) in dust in 2008 (10).

87 When looking for new compounds, in this case BFRs, alternative analysis techniques can be used for
88 screening and for providing information on the identity of the compound. Gas chromatography
89 (GC)/electron capture negative ionization quadrupole mass spectrometry (GC/ECNI qMS), GC/high
90 resolution MS (GC/HRMS) and GC ion trap MS (GC/ITMS) have been the most commonly used MS
91 techniques for the analysis of PBDEs (11). Liquid chromatography (LC) coupled to electrospray
92 ionization (ESI) with tandem triple quadrupole mass spectrometry has been used for the analysis of
93 hexabromocyclododecane (HBCDD), tetrabromobisphenol A (TBBPA), and PFRs (12,13). Recent
94 articles have shown the suitability of LC in combination with atmospheric pressure chemical ionization
95 (APCI) or with atmospheric pressure photoionization (APPI) for the analysis of BFRs that are not ionized
96 by ESI sources (14, 15). High resolution (HR) full-spectrum acquisition techniques, such as HR-time-of-
97 flight (TOF)-MS, have been increasingly used in the last decade for both targeted and untargeted analysis
98 (16) because it has a high sensitivity in full-scan acquisition mode and a strong elucidation capacity for
99 molecular structures. The combination of a soft ionization technique like APCI that generates mainly
100 molecular ions with HR-MS is especially suitable for compound identification.



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Figure 1. Structure of TTBP-TAZ

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84 In this study, we report for the first time the presence of 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine
85 or TTBP-TAZ, CAS number 25713-60-4 (Fig. 1), in plastics (plastic parts of electrical and electronic
86 equipment) and in indoor dust by using alternative analytical methods for BFRs analysis. TTBP-TAZ is a

87 novel brominated triazine-based BFR that is used in acrylonitrile butadiene styrene (ABS) and high
88 impact polystyrene (HIPS) (17) and could be used as replacement of the banned PBDEs in these
89 polymers. More detailed information about the commercial sources, viability of TTBP-TAZ as
90 replacement of BFRs and toxicity is given in Supporting information (SI). According to a recent study of
91 the European Food Safety Authority (EFSA), there are no analytical methods available for detecting
92 TTBP-TAZ (17). We identified this unknown brominated compound by untargeted screening in plastic
93 parts of consumer products and using a fast screening method, that is based on direct probe (DP) ambient
94 mass spectrometry coupled to APCI-HRTOF-MS. This method, recently developed by our research group
95 (18), does not require sample preparation or chromatographic separation that could hamper the detection
96 of potentially unknown compounds, since the solid sample is introduced directly into the MS source.
97 Secondly, we employed a solvent extraction method followed by LC-APCI-HR-TOF-MS analysis for the
98 confirmation of the screening results and for quantifying the levels of TTBP-TAZ in plastic and dust
99 samples.

100

101 **Experimental section**

102 *Materials and instrumental analysis*

103 All solvents and reagents were of analytical grade and used as supplied. Dichloromethane (DCM) and
104 methanol were obtained from Promochem (Wesel, Germany). Milli-Q water was obtained from the
105 ultrapure water purification Q-Pod system (Millipore, Bedford, USA). Tetrahydrofuran (THF) was
106 obtained from Sigma-Aldrich (Steinheim Germany). The target compound 2,4,6-tris(2,4,6-
107 tribromophenoxy)-1,3,5-triazine was obtained from Accustandard (New Haven, CT, USA) in ampoules of
108 $\sim 100 \mu\text{g mL}^{-1}$ in toluene (97% purity). Other TTBP-TAZ reagent, which was only tested for the presence
109 of impurities, was obtained from TCI Europe N.V. (Tokyo, Japan). 2,4,6-Tribromophenol (2,4,6-TBP)
110 was obtained from Sigma-Aldrich (Seelze, Germany) with 99.5% purity. For the calibration of the TOF-

111 MS we used an APCI tuning mix provided by Supelco (Bellefonte, PA, USA). For the validation of the
112 extraction methods we used the interlaboratory material IMEP-26 (19) and the dust certified reference
113 material from NIST, coded SRM 2585.

114 A microTOF II with resolution >16,500 FWHM was used as the detector and equipped with an LC-APCI
115 II source (Bruker Daltonics, Bremen, Germany). The source was also equipped with a direct probe
116 assembly which is mounted instead of the nebulizer sprayer on top of the vaporizer heater. An ESI source
117 was also tested for comparison. The LC system was an Agilent 1220 Infinity LC. A Kinetex core-shell
118 LC C18 column (2.1 mm x 100mm x 2.6 μ m), obtained from Phenomenex (Torrance, CA, USA) was
119 used as the stationary phase.

120 Besides TTBP-TAZ, other BFRs and PFRs were screened in the plastic samples purchased in 2012 by
121 LC-APCI(-) and LC-APCI(+), respectively (see Table S-1 of SI). The presence of other flame retardants
122 (namely BDE209, triphenyl phosphate or TPHP, PBDPP and BPA-BDPP) in most of the indoor dust
123 samples analyzed in this study have been recently reported by Brandsma et al. (9).

124 *Sample collection*

125 Twenty six consumer products that were mainly made of plastic and that were likely to contain flame
126 retardants (plastics that encased electric or electronic componentry) were collected for analysis. Older
127 plastic products ($n=13$) that were manufactured before 2006 were obtained from a recycling park in
128 Amsterdam (Netherlands) and included televisions ($n=6$), printers ($n=3$), a computer monitor and
129 scanners ($n=3$). The newer consumer products ($n=13$) were purchased from supermarkets in 2012 and
130 included electrical power boards ($n=2$), adaptors ($n=2$), televisions ($n=2$), toys ($n=4$) and other household
131 appliances (a heat sealer, a vacuum cleaner and an electrical plastic ornament).

132 House dust samples ($n=17$), were collected in nine different houses in the Netherlands directly from
133 electronic equipment (e.g. televisions, computers or game consoles) or from the tables and sideboards

134 around the equipment or from the floor in 2011. Dust was collected using a Dustream™ dust collector
135 (Indoor Biotechnologies Ltd., Wiltshire, United Kingdom) attached to the end of the vacuum cleaner
136 hose. The mesh size of the filter used inside the dust collector was 40 µm. The dust samples were not
137 further sieved.

138 More information about the plastic consumer products and the indoor dust samples analyzed in this study
139 can be found in the SI (Tables S-1 and S-2).

140 ***Rapid screening of TTBP-TAZ in plastic samples***

141 Plastic samples were first screened by direct probe-APCI(+)-HRTOF-MS on the basis of a novel
142 ambient MS technique recently reported by our research group (18). No sample treatment or
143 chromatographic separation was needed. A small amount of sample (few milligrams) was introduced
144 directly into the MS source through a capillary glass probe by a commercial direct probe assembly. The
145 glass probes were loaded with the sample by scratching the surface of the solid plastic products with the
146 probe to release small particles. Main particles outside the probe were removed with a lint-free cotton
147 cloth to prevent the contamination of the source. A drop of ~5 µL of calibration solution was added at the
148 outer surface of the probe before introducing it into the MS source for internal MS calibration.

149 The “smart formula” tool from Bruker data analysis software was used to identify the unknown
150 brominated peak corresponding to TTBP-TAZ in plastics. This tool generates possible molecular
151 formulae on the basis of mass accuracy and isotopic pattern. General parameters for formulae generation
152 were as follows: mass error tolerance was set at 5 ppm, H/C ratio from 0 to 3, number of rings and double
153 bonds were restricted to 0.5-40, electron configuration even. The option *automatically detect isotopic*
154 *mass* was activated and minor isotopomers in abundance (1-10% abundance) were selected for formulae
155 generation. This latter criterion facilitated the identification of the highly brominated compound. Values
156 of < 5 ppm of mass error and <100 of mSigma were considered acceptable for positive confirmation (as
157 specified by the supplier of the instrument and the software tools, Bruker Daltonics).

158 ***Confirmation and quantification method***

159 Small pieces of the plastic samples (~50 mg, obtained with a small cutter) were extracted with 20 mL
160 DCM by shaking for 24 h and sonication for 10 min. The extracts were diluted with methanol:THF 90:10
161 v/v for 10-100 times as required. The diluted extracts were ultra-centrifuged in Eppendorf microtubes
162 (10,000 rpm, 5 min) for precipitation of solids and aliquots of 2.5 µL were injected in the LC system.

163 The extraction of the dust (~ 50 mg) was performed in two solvent extraction steps, first with acetone
164 (10 mL) and then with toluene (10 mL). Each extraction step consisted of vortexing for 1 min and 15 min
165 of ultrasonication followed by centrifugation (3000 rpm, 5 min) to precipitate solids. The combination of
166 solvents was selected on the basis of our previous experience for obtaining good extraction efficiency for
167 PBDEs, new BFRs and PFRs (e.g. ref. 9). The combined clear supernatant was evaporated until almost
168 dry and reconstituted in 2 mL methanol:THF 90:10 v/v (vortexing 1 min). The final extracts were
169 ultracentrifuged (10,000 rpm, 5 min) in Eppendorf microtubes to precipitate remaining particles and
170 aliquots of 2.5 µL were injected in the LC system.

171 TTBP-TAZ was quantified both in plastic and in dust samples by external solvent-based calibration
172 (standards prepared in methanol:THF 90:10 v/v).

173 ***Sample analysis***

174 For the analysis of TTBP-TAZ by LC-APCI(+)-HRTOF-MS, the LC mobile phase consisted of water
175 (A):methanol (B), both containing 0.25% v/v formic acid at a flow rate of 0.3 mL min⁻¹. The gradient was
176 as follows: 60% B for 1.5 min and then to 100% B in 20 min, then 100% B for 10 min (for removal of
177 highly hydrophobic compounds) and finally re-conditioning for 8 min. The gradient was optimized for the
178 separation of the target compound from matrix components and from other flame retardants possibly
179 present in the sample. For the confirmation of the presence of TTBP-TAZ, the analysis was also made in
180 the negative APCI mode using a selective mass fragment instead of the parent ion (see Table 1). The LC
181 conditions for APCI(-) were the same as for APCI(+) but the mobile phase was methanol and water

182 without additives. Calibration standards were prepared in methanol:THF 90:10 v/v at concentrations
183 within the range of 5-1000 ng mL⁻¹. Procedural blanks (n=3) were run within each batch of samples and
184 did not contain quantifiable levels of TTBP-TAZ.

185 The optimized TOF-MS parameters for the analysis of TTBP-TAZ by LC-APCI and direct probe-APCI
186 are given in Table S-3 of SI.

187 The software data analysis 4.0 and compass quant analysis from Bruker Daltonics were used for data
188 processing (confirmation and quantification). MS internal calibration in each run was performed by
189 infusing the calibration solution into the source within the first minute of the chromatogram by using a
190 syringe pump (as designed by the supplier of the instrument). The internal calibration was performed by
191 enhanced quadratic mode, with values <5 ppm considered acceptable. The MS confirmation of the main
192 ions of TTBP-TAZ was based on mSigma values, that is the match factor between the measured isotopic
193 pattern and the theoretical pattern for a given formula (that is how similar the measured isotopic pattern of
194 TTBP-TAZ in samples was to the theoretical isotopic pattern of TTBP-TAZ) and on mass accuracy.
195 Values of less than 5 ppm of mass error and less than 100 of mSigma were considered acceptable for
196 positive confirmation (mSigma <100 acceptable, <50 good and <25 excellent, as specified by the supplier
197 of the instrument and the software Bruker Daltonics).

198

199 **Results and discussion**

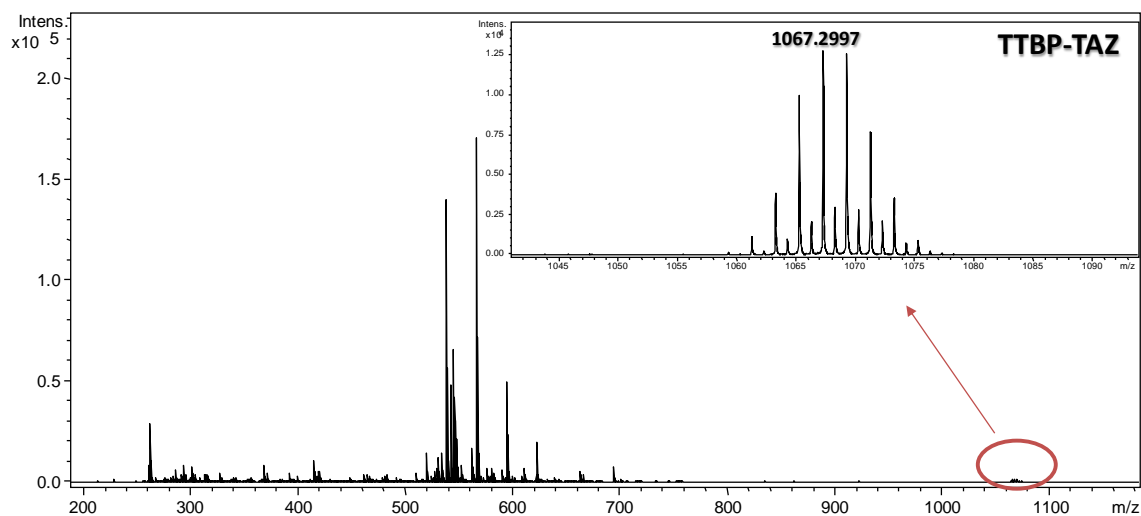
200 *Identification and analysis of TTBP-TAZ*

201 *Screening of TTBP-TAZ*

202 The identification of TTBP-TAZ was initially made by untargeted screening by direct probe APCI-
203 TOFMS analysis of the plastic samples in which the unknown brominated peak appeared in some of

204 them. This technique provides detection limits of about 0.1 % in weight of the product. On the basis of
205 the isotopic pattern observed for the unknown peak, a compound with nine bromine atoms was calculated
206 and the ion $[M+H]$ was expected as a major ion in positive mode on the basis of our previous experience
207 with the APCI source. Under these conditions two and four plausible formulae were generated for the
208 isotopomers with m/z 1063.2220 and with m/z 1065.3200, respectively. The mSigma value (based on the
209 isotopic pattern) was essential for the final identification and greatly limited the number of possible
210 formulae, e.g. 20 plausible molecular formulae instead of two were generated for the isotopomer with m/z
211 1063.2220 when the mSigma values were not taken into account. By connecting the generated formulae
212 with online libraries (e.g. Chemspider, Metlin) using the “compound crawler” tool of data analysis, the
213 only existing match was TTBP-TAZ.

214 The results of the screening were then confirmed by LC-APCI(+)-HRTOF as explained in the following
215 section. These results highlight how the direct probe analysis, which does not require sample preparation
216 or chromatography that could hamper the detection, is very suitable for the identification of unknown
217 flame retardants if they are at high enough concentration (around 0.1 % in weight). The direct probe-
218 APCI(+)-HRTOF-MS spectra of a power board sample containing TTBP-TAZ is shown in Fig. 2.



219
220 *Figure 2. DP-APCI(+)-HRTOF-MS spectra of the power board sample 1 containing TTBP-TAZ.*

221 ***LC-APCI-HRTOF method development***

222 TTBP-TAZ is a highly non-polar (Log Kow: 12.97), low volatility (vapor pressure, 2.02×10^{-25} Torr),
 223 heavy (average MW: 1067.43) compound (data from [17]). Because of these characteristics, the analysis
 224 by LC instead of by GC is highly desirable. Due to its high hydrophobicity, we also expected a better
 225 sensitivity by APCI ionization instead of the commonly used ESI. In fact, the sensitivity in the APCI
 226 positive mode was about 5-fold higher than in the ESI positive mode. The main ion observed in both
 227 APCI(+) and ESI(+) was $[M+H]^+$. In the APCI negative mode, a fragment corresponding to a loss of a
 228 tribromophenyl ring $[M-C_6H_2Br_3-H]^-$ was observed instead of the expected ion $[M-Br+O]^-$, that has been
 229 reported for other BFRs (14, 15). The $[M-Br+O]^-$ ion appeared only with a low signal (about 30 times
 230 less intense). As a consequence, APCI in the negative mode was 2-fold less sensitive than in the positive
 231 mode, but useful for confirmation. The main quantifier and qualifier ions are given in Table 1.

Table 1. Main ions of TTBP-TAZ in the APCI source

APCI mode	Ion	Ion molecular formula	^a Most intense isotopomer	^a Monoisotopic neutral mass
Positive	$[M+H]^+$ (quantifier)	C ₂₁ H ₇ Br ₉ N ₃ O ₃	1067.3052	1058.3059
Negative	$[M-C_6H_2Br_3-H]^-$ (qualifier)	C ₁₅ H ₄ Br ₆ N ₃ O ₃	753.5287	747.5352

^aValues calculated with Compass Isotope pattern tool of Data analysis software (Bruker Daltonics)

232
 233 MS-TOF parameters (mainly capillary exit and skimmer1, hexapole RF transfer time and pulse storage
 234 time) are dependent on the m/z value and influence the sensitivity. These parameters were optimized for
 235 the high m/z of interest in the positive mode (1067.3052) (see Table S-3 of SI). It is worth mentioning
 236 that tuning the TOF detector for the analysis of such a high molecular mass compound is important, as the
 237 values of some of the optimized MS-TOF parameters differ significantly from default values. This is
 238 essential for achieving maximum sensitivity (e.g. hexapole RF optimal value 752 V, default values 50-

239 100 V). These same values were also optimal for direct probe analysis being the vaporizer temperature set
240 at 300 °C to facilitate the desorption/ionization process directly from the solid.

241 The relatively long chromatographic separation time was used to separate TTBP-TAZ from other flame
242 retardants. It is worth mentioning that a significant improvement in peak shape was observed when using
243 the core-shell column employed in this article in comparison with an equivalent fully porous particles
244 C18 column.

245 *Brominated impurities*

246 A concentrated standard solution of TTBP-TAZ was investigated for the presence of other flame
247 retardants or structurally related impurities. 2,4,6-TBP, that is used in the synthesis of TTBP-TAZ and
248 that is a toxic compound (e.g. see the introduction of reference 21) was found in both the standard and the
249 plastic products purchased in 2012. The presence of 2,4,6-TBP was confirmed by mass accuracy, isotopic
250 patterns and retention time by the injection of a standard solution and the levels were estimated by
251 external calibration. The concentration of 2,4,6-TBP in the standard obtained from Accustandard was
252 about 0.09 % weight/weight (% w/w) and in the technical reagent supplied by TCI was about 0.02 %
253 w/w. 2,4,6-TBP was also detected in almost all the plastic samples that contained TTBP-TAZ. The
254 concentration values of 2,4,6-TBP are estimated or semi-quantitative since the method was not validated
255 for this compound.

256 *Analytical performance of the quantification method*

257 For the validation of the analysis of TTBP-TAZ in plastics and in dust and in order to assure an
258 accurate quantification without internal standard correction, we assessed the extraction efficiency and
259 possible matrix effects (ion enhancement or ion suppression) of the methods.

260 The extraction methods used for both plastic and dust samples were based on a solvent-extraction step
261 without further clean-up in order to minimize possible losses of the target compound. Due to the

262 unavailability of suitable reference materials for TTBP-TAZ, and to the difficulty of carrying out spiking
263 experiments at the high concentrations expected in the plastics, the extraction method for the analysis of
264 plastics was in-house validated for the analysis of PBDEs in the interlaboratory test material IMEP-26.
265 The selection of dichloromethane as the best extraction solvent for plastics is based on previous
266 investigations of our research group (that are out of the focus of this study). Kim et al. also reported DCM
267 as a good solvent for PBDEs in HIPS polymers (22).

268 IMEP-26 is made up of poly(ethylene terephthalate, PET) and contains high concentrations of some
269 PBDEs (~100-700 $\mu\text{g g}^{-1}$). The recoveries of PBDEs in the material IMEP-26 with the extraction method
270 used in this article (see *Confirmation and quantification method* section) were higher than 90%
271 (experiments made in triplicate). Since the molecular weight (average MW: 959.16) and polarity
272 (calculated log Kow 11.16; source: www.chemicalize.org) of decaBDE are close to those of TTBP-TAZ,
273 similar extraction efficiencies may be expected. However, the availability of a reference or an
274 interlaboratory material for TTBP-TAZ, is highly desirable for future studies for further validation of
275 recoveries.

276 The possible presence of matrix effects (ion suppression or enhancement), that could affect the
277 quantification, was assessed in the final extracts. Three types of plastic sample extracts that did not
278 contain TTBP-TAZ were spiked with concentrations of 0.05 and 0.2 $\mu\text{g mL}^{-1}$ of TTBP-TAZ. The
279 presence of ion suppression/enhancement was limited and the results were acceptable and in the ranges of
280 70-114% and 90-105%. These results are in accordance with the fact that APCI is known to be less
281 affected by matrix effects than for example ESI, due to a relatively stronger ionization process based on a
282 corona discharge.

283 Regarding the analysis of dust samples, the total recoveries were assessed by spiking the dust certified
284 reference material SRM 2585 from NIST at three concentration levels. Aliquots of ~50 mg were spiked at
285 150, 500 and 12000 ng g^{-1} and recoveries of 94 ± 11 , 112 ± 11 and $95\pm 7\%$ were found at these three levels.

286 Dust aliquots were spiked with 20-50 μL of TTBP-TAZ in DCM and allowed to stand for 12 h before
 287 extraction, so that all the solvent was evaporated and we could mimic as much as possible the interaction
 288 of TTBP-TAZ with the dust matrix. These acceptable recoveries show that TTBP-TAZ was also
 289 efficiently extracted from dust and that ion suppression or enhancement was scarce for the dust matrix.

290 The main analytical characteristics of the quantification method are given in Table 2. The instrumental
 291 detection (LODs) and quantification limit (LOQ) were calculated from blank samples determinations by
 292 using a signal-to-noise ratio of 3 and 10, respectively. The LOD and LOQ of the complete method were
 293 estimated from these values by considering a sample amount of 50 mg, 20 mL extraction solvent and a
 294 dilution factor of 1:10 (v/v) for plastic products, and an extraction volume of 2 mL for dust. In the case of
 295 plastics, the whole DCM extract could be evaporated and reconstituted in methanol:THF to improve
 296 detection limits if required. The instrumental LOQ of LC-APCI(+)-HR-TOFMS was low for plastic
 297 samples (0.0006 % in weight) and acceptable for the dust samples (60 ng g^{-1}).

Table 2. Analytical performance of the analysis of TTBP-TAZ with LC-APCI-TOF-MS

Retention time (min)	Instrument LOD (ng mL^{-1})	Calibration ^a Linear regression equation	R ²	^b Method LOD (% w/w)	^b Method LOQ (% w/w)	^c Method LOD (ng/g)	^c Method LOQ (ng/g)
18.9	0.5	$y = 417267x - 200$	0.9976	0.0002	0.0006	20	60

^a $n=7$, units $\mu\text{g mL}^{-1}$, ^bestimated on the basis of 50 mg sample, 20 mL dichloromethane extract and 1:10 dilution factor; ^cestimated on the basis of 50 mg sample and 2 mL methanol final extract.

298

299 *Analysis of TTBP-TAZ in plastics and dust*

300 The concentrations of TTBP-TAZ in the plastic products purchased in 2012 and in the dust are
 301 shown in Tables 3 and 4, respectively (more information can be found in tables S-1 and S-2 of SI). TTBP-
 302 TAZ was not found in the plastic products manufactured before 2006. This suggests that it has been used
 303 as a substitute of PBDEs after their phase-out (more information about the replacement of PBDEs is given

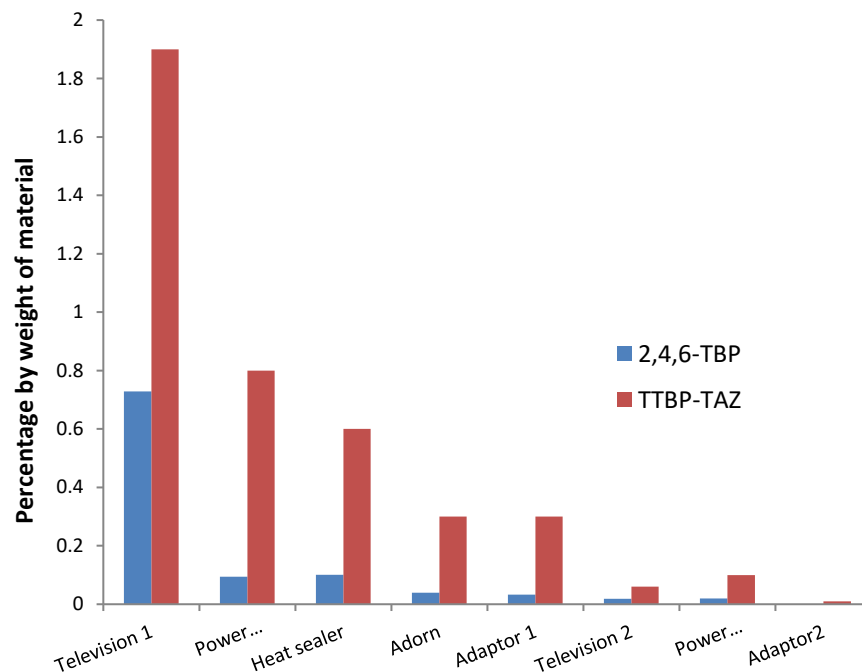
304 in SI). TTBP-TAZ was found in eight of the thirteen samples purchased in 2012 (all of them
 305 electric/electronic equipment). Concentrations ranged from 0.01-1.9 % weight/weight (w/w) and the
 306 highest level was found in a television. This value seems to be not high enough to comply with the
 307 flammability requirements. DecaBDE is for example added to HIPS at 10-15 percent by weight to meet
 308 fire safety standards (23). In fact, the main flame retardant in this sample was decabromodiphenylethane
 309 (DBDPE), whose concentration was estimated at a level of 16 % w/w. Both TTBP-TAZ and DBDPE are
 310 viable replacements of DecaBDE in HIPS (the most used polymer in televisions casings) (24), but we are
 311 not aware of the reasons for using a mixture of both compounds. The presence of other BFRs and PFRs in
 312 the plastic samples purchased in 2012 is given in Table S-1 of SI. The other most frequently detected
 313 BFRs in these samples were tetrabromobisphenol A (TBBPA) (detected in 11 samples), DBDPE
 314 (detected in 9 samples) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) (detected in 6 samples).
 315 Some PFRs were also detected but at low levels (estimated concentrations by external calibration below
 316 1% w/w). Although TTBP-TAZ was present in 8 of 13 plastic products purchased in 2012, it was not the
 317 major flame retardant in any of the samples analyzed. The presence of a variety of flame retardants,
 318 mainly at low levels below 1% w/w could be due to the presence of different polymers in the samples,
 319 cross-contamination in the factory or recycling.

320 *Table 3. TTBP-TAZ concentration ranges in weight percentage (% w/w) in plastic*
 321 *consumer products purchased in 2012*

Product	Number of samples containing TTBP-TAZ	Concentration range (% w/w)
Electrical power boards and adaptors (n=4)	4	(0.01-0.8)
Children toys (n=4)	0	-
Televisions (n=2)	2	(0.06, 1.9)
Other household appliances (n=3)	2	(0.3, 0.6)

326 2,4,6-TBP was also detected in all the plastic samples that contained TTBP-TAZ, except for the sample
327 with the lowest concentration of TTBP-TAZ (electrical adaptor 2, 0.01 % w/w of TTBP-TAZ). The
328 concentrations of 2,4,6-TBP in plastic samples were higher than those found in the standards of TTBP-
329 TAZ (0.02-0.09 % weight/weight, w/w) and ranged from 0.02 to 0.7 % w/w (see Figure 3). These higher
330 concentrations of 2,4,6-TBP in the plastic samples could be due to the lower purity of the TTBP-TAZ
331 formulations used in the preparation of the plastic polymers. Furthermore, 2,4,6-TBP can be used as a
332 flame retardant and as an additive/intermediate in formulations of other flame retardants or could even be
333 a degradation product (25,26). However, the fact that only the samples that contained TTBP-TAZ
334 contained also 2,4,6-TBP and that there was a strong direct correlation between the concentration of both
335 compounds (Pearson correlation, $r = 0.951$, $p < 0.001$, $n=8$; see Figure S-1 of SI) and not between TTBP-
336 TAZ and other major BFRs present in these samples (see Figure S-2 of SI), may indicate that the use of
337 TTBP-TAZ is a potential source of contamination of 2,4,6-TBP. Further investigation is needed to
338 determine if TTBP-TAZ is a relevant source of contamination of 2,4,6-TBP in the environment, due to
339 the limited number of samples of this preliminary study.

340



341

342 *Figure 3. Concentrations (percentage by weight of material) of 2,4,6-TBP in the plastic samples*
 343 *containing TTBP-TAZ. The concentration values of 2,4,6-TBP are estimated or semi-quantitative since*
 344 *the method was not validated for this compound*

345

346 Regarding the house dust samples, TTBP-TAZ was present in 9 of 17 samples, with the highest
 347 concentrations in the dust collected on electronic equipment (mainly computers and televisions).
 348 Concentrations were in the range of 1070-22150 ng-g⁻¹ on equipment and between 220 and 3950 ng-g⁻¹
 349 around equipment (see Table 4). Levels on equipment were about 5, 6 (n=2) and 30-fold higher than in
 350 the dust collected around the same equipment (see Table S-2 of SI). These findings suggest that the
 351 compound may be released from electronic equipment into the environment. TTBP-TAZ was also found
 352 in one of the floor dust samples at a concentration of 160 ng-g⁻¹.

353

354

Table 4. TTBP-TAZ average concentrations and ranges in ng g⁻¹ in dust

Sampling site	Number of samples containing TTBP-TAZ	Median	^a Range (ng g ⁻¹)
On electronics (n=8)	4	535	(1070-22150)
Around electronics (n=7)	4	220	(220-3950)
In floor dust (n=2)	1	-	(<20-160)

^aQuantitation limit 60 ng g⁻¹

355
356 The levels of TTBP-TAZ in house dust collected in 2011 (<20-3950 ng g⁻¹, samples collected on
357 electronics not included) were lower than those reported of TBBPA (535–9730 ng g⁻¹; ref. 27) or of TPHP
358 (<150-1798000 ng g⁻¹; ref. 28) but higher than those of DBDPE (<n.d.- 151 ng g⁻¹; ref. 29) and of BTBPE
359 (<2.5.- 8.1 ng g⁻¹; ref. 29), that were the other alternative BFRs more frequently detected in the products
360 purchased in 2012. The levels of TTBP-TAZ were also lower than those recorded in indoor dust of other
361 PFRs (e.g. 330-110000 ng g⁻¹ of TCEP; ref. 30) or of PBDEs (e.g. 230-3000 ng g⁻¹ of BDE 47; 70-3700 ng
362 g⁻¹ of BDE 99; 120-21000 ng g⁻¹ of BDE 209; ref. 31) and similar to the levels of V6 (<5-1117 ng g⁻¹; ref.
363 8).

364 These results show that TTBP-TAZ may be ubiquitous in dust from indoor environments in the
365 Netherlands and that people could be exposed to this compound via dust inhalation and ingestion. Plastic
366 products with electronic and/or electrical componentry, in which TTBP-TAZ was detected in 8 of the 13
367 of the samples purchased in supermarkets in 2012, could be a major source of emission to the
368 environment. Obviously, further research is needed to provide a more accurate estimation of the human
369 exposure to TTBP-TAZ through dust ingestion and source apportionment since we only report a limited
370 number of samples.

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376 **Supporting Information Available**

377 Detailed information about the commercial sources and uses of TTBP-TAZ, mass spectrometry detection
378 parameters and the plastic products and dust samples analyzed in this study can be found in the
379 Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org/>

380

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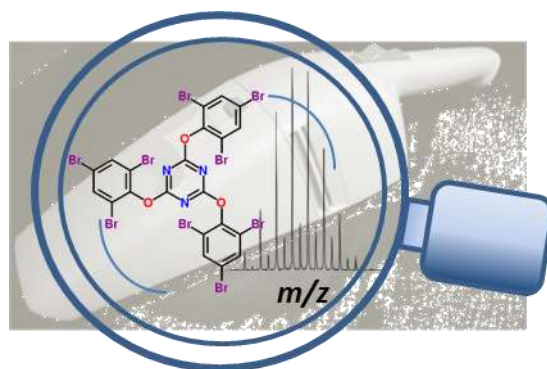
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469 **Table of Contents (TOC) and Abstract Art**

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