

# Assessment of brominated flame retardants in a small mixed waste electronic and electrical equipment (WEEE) plastic recycling stream in the UK

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24 flagged as having high Br concentrations (>2500 mg/kg) were subjected to further evaluation  
25 for BFR content *via* mass spectrometry analysis and the results compared with the XRF Br  
26 data. This revealed that in 22% of the 120 chips studied, XRF incorrectly identified the LPCL  
27 to be exceeded. Our data also identifies the presence of the novel BFRs decabromodiphenyl  
28 ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) in plastics derived from  
29 waste electronic and electrical equipment (WEEE). While the “light-MEP” samples contained  
30 POP-BFR concentrations below LPCLs, the “medium-MEP” and “heavy-MEP” fractions  
31 exceeded such limits. Management of the polymer chips by colour sorting resulted in  
32 significant reductions in concentrations of all BFRs in the clear polymers such that LPCL limits  
33 were not exceeded; however, concentration reductions in white polymers were insufficient to  
34 meet LPCLs.

35

## 36 **1. Introduction**

37 The move to a circular economy is vital for the development of industry and the protection of  
38 the environment (European Commission, 2018). Plastics are materials constantly in the  
39 spotlight and have received a substantial degree of public and political interest. Waste  
40 electronic and electrical equipment (WEEE) is one the fastest growing waste streams globally  
41 with an estimated 1.6 million tonnes generated in the UK, 12.3 million tonnes generated  
42 within the European Union (EU), and 44.7 million tonnes generated globally in 2016 (Baldé  
43 et al., 2017). Of this, the estimated proportion recycled in 2016 was 41.3% across the 28  
44 member states of the EU and 49.8% in the UK (Eurostat, 2020). It has been estimated that the  
45 average plastics content of WEEE is ~30% by weight (Schlummer et al., 2007).

46 A significant volume of WEEE plastic is collected but not currently recycled and is destined  
47 for disposal via incineration. This material is referred to as mixed engineering plastic (MEP),

48 which comprises a wide range of polymers that can contain hazardous legacy additives of  
49 potential concern when recycling the material (Drage et al., 2018). The current EU practice in  
50 material recycling of WEEE plastics separates only a fraction of light polyolefin blend  
51 polymers and all other MEP polymers are sent for disposal. However, at a small number of  
52 the largest facilities, a minor quantity of other polymers can also be separated for recycling  
53 using advanced techniques. In the UK, it is estimated that 134000 tonnes of “small mixed  
54 WEEE” (SMW) was collected from business and consumer waste in 2020, of which ~40000  
55 tonnes of SMW plastics are estimated to be collected (30% by weight), from which 27000  
56 tonnes of MEP are estimated to be generated (Comply Direct, 2020; pers. comm. Axion). In  
57 the EU, the SMW stream includes a broad range of WEEE items including: small household  
58 appliances, information technology and communications equipment, powered tools, toys and  
59 sports equipment, medical devices, control instruments, smoke detectors, and dispensers. It  
60 does not include other larger WEEE items such as: cathode ray tube and flat screen  
61 televisions and monitors, refrigeration equipment, large domestic appliances, and fluorescent  
62 lamps (Environment Agency, 2014). SMW accounted for 26-31% of total WEEE collected in  
63 the UK between 2015-2019 (Comply Direct, 2020).

64 A particular concern is that MEP contains brominated flame retardants (BFRs), of which  
65 polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are  
66 classed as persistent organic pollutants (POPs) under the United Nations Environment  
67 Programme (UNEP) Stockholm Convention. Typically, some polymers used in WEEE, most  
68 commonly acrylonitrile butadiene styrene (ABS), and high impact polystyrene (HIPS) are  
69 known to have been treated with BFRs at percent by weight levels in order to meet fire safety  
70 regulations (UNEP 2006; UNEP 2010). While the principal BFRs detected in EEE polymers  
71 are decabromodiphenyl ether (Deca-BDE), and tetrabromobisphenol-A (TBBP-A) (Drage et  
72 al, 2018), evidence exists of application of HBCDD in a limited proportion of EEE plastics

73 (Harrad et al, 2009; Drage et al, 2018). Uncontrolled recycling of POP-BFR (i.e. PBDE and  
74 HBCDD) contaminated WEEE polymers has led to the presence of these banned BFRs in  
75 recycled plastic products (e.g. children's toys and kitchen utensils) with consequent health  
76 and exposure implications (Guzzonato et al., 2017; Kuang et al., 2018; Fatunsin et al., 2020).  
77 As a result, the presence of these and other chemical contaminants in polymers has led to the  
78 classification of WEEE as hazardous waste. Moreover, EU Regulation 850/2004 *inter alia*  
79 specifies in Annex IV "low POP content limits" (LPCLs) that apply to PBDEs as a sum of all  
80 representative PBDE congeners; including Penta-, Octa-, and/or DecaBDE formulations, and  
81 also separately to HBCDD as a sum of all isomers (European Commission, 2004). Waste  
82 materials in which PBDE or HBCDD concentrations exceed the LPCL (1000 mg/kg; each)  
83 cannot be recycled or re-used and must be treated in such a way as to ensure the POP-BFR  
84 content is destroyed or irreversibly transformed - most likely in a high temperature  
85 incineration process, losing all value in the material and negatively impacting the  
86 environment. However, these LPCLs are currently under review with the aim of adopting a  
87 legislative limit value lowered to 500 mg/kg as quickly as possible and no later than 16<sup>th</sup> July  
88 2021 (European Commission, 2019). Furthermore, the EU has also introduced an  
89 unintentional trace contaminant (UTC) fixed threshold value for tetra-, penta-, hexa-, hepta-  
90 and decaBDE equal to or below 10 mg/kg for each homologue group (European Commission,  
91 2018), with UTC limits for HBCDD equal to or below 100 mg/kg, to be introduced no later  
92 than July 2021 (European Commission, 2019). These UTC limits are designed to prevent  
93 intentional and meaningful use of these chemicals in products while allowing recycling and  
94 enabling control and enforcement by being high enough to be detected by current detection  
95 methods.

96 In order to verify compliance with LPCLs and UTCs, concentrations of PBDEs and HBCDD  
97 must be determined in waste polymers. However, this currently requires the use of gas or

98 liquid chromatography coupled with mass spectrometry and is thus an expensive, time  
99 consuming, and destructive process. Recently, several studies have suggested the use of  
100 portable X-ray fluorescence (XRF) measurements of elemental Br as a surrogate measure of  
101 POP-BFR concentrations in EEE plastics (Gallen et al., 2014; Aldrian et al., 2015; Guzzonato  
102 et al., 2016; Sharkey et al., 2018). However, use of portable XRF spectrometry to identify  
103 items exceeding LPCL values has been shown in some instances (~6 % of 538 waste EEE,  
104 foam, and fabric samples tested in the Republic of Ireland; Harrad et al., 2019) to result in  
105 false exceedances (defined as situations where the concentration of bromine but not PBDEs  
106 or HBCDD exceeds the LPCL). This was attributed to the presence of other currently non-  
107 regulated Br-containing compounds used in EEE plastics such as TBBP-A and potentially  
108 decabromodiphenyl ethane (DBDPE) (Harrad et al., 2019). The “Sink/Float” method is the  
109 most commonly used method for separating BFR containing fractions and is simply based on  
110 the higher density of plastics containing BFRs (Sofies, 2020).

111 Identification of potentially recyclable waste polymers that comply with LPCL values is  
112 important as there is increasing global demand to meet sustainability targets and increase the  
113 proportion of waste plastics recycled for all key applications. The EU has set ambitious  
114 targets of recycling greater than 50% of all plastic waste generated in Europe by 2030  
115 (European Commission, 2018). Minimum recycling and reuse targets for different categories  
116 of WEEE are set out in Annex V to Directive 2012/19/EU on WEEE and range between 50%  
117 and 80% to be prepared for reuse and/or recycled, depending on the category (European  
118 Commission, 2012). Currently, large-scale, efficient separation of mixed plastics into  
119 individual polymers, or even specific grades so the materials can be reused and/or recycled, is  
120 at best a work in progress and at worst prohibitively expensive. For example, the use of near  
121 infra-red (NIR) technology widely used in plastic recycling facilities to sort polymers into  
122 different categories, is prevented by the presence of carbon black pigments and therefore

123 cannot be employed to sort MEP waste streams where a large proportion of polymers are  
124 black (WRAP, 2020). Current recovery activities at large scale WEEE recyclers in Europe  
125 only allow for separation of three of the >15 different polymer types (see Table S3; SI) with  
126 variable efficiencies. New polymer separation technologies such as Raman spectroscopy,  
127 mid-range infra-red spectroscopy (Mid-IR), and X-ray transmission (XRT) have high capital  
128 costs and are difficult to implement at larger scales. XRT for example may result in over  
129 sorting and larger volumes of plastic sent to incineration than if XRF were implemented.  
130 Moreover, the potential presence of PBDEs and HBCDD in WEEE creates a significant  
131 obstacle to achieving greater rates of recycling (European Commission, 2018). Due to the  
132 scale of the challenge, it is clear that innovative and creative solutions are required to  
133 transform the plastics industry into a full-circle recycling service. The manufacture of MEP  
134 material provides a potential route to utilise this otherwise unrecyclable mix of polymer  
135 material and recover some of its original value. Within a recycling context, MEP material is  
136 produced by sorting and combining heterogeneous mixtures of chipped or shredded polymers  
137 into predefined compositions to meet specific engineering characteristics. These are then  
138 passed through a melt extruder thus resulting in “homogenised” extruded pellets of MEP that  
139 can be utilised downstream to produce new recycled polymer products. Normally, a blend  
140 extrusion of different plastics would not be considered viable due to problems with  
141 engineering properties (such as incompatible melting or degradation points). However, due to  
142 high disposal costs via incineration, exploration of the possibility of creating a product that is  
143 composed of multiple polymer types, but with lowered engineering qualities (e.g. impact  
144 strength), has become a viable opportunity for specific product applications, providing they  
145 can also meet LPCLs and UTCs.

146 In order to effectively recycle this material, two developments are thus required: (1) a useable  
147 product from MEP that meets required engineering characteristics; and (2) enhanced

148 understanding of whether POP-BFRs are present and if so, which fractions of the overall  
149 MEP feedstock contain PBDEs and HBCDD at concentrations that do not exceed the LPCL.  
150 This knowledge can be used alongside an understanding of the engineering properties of such  
151 fractions to produce a final recycled product that is both useable in an engineering context  
152 while meeting the LPCLs.

153 Against this backdrop, this paper reports concentrations of both regulated and non-regulated  
154 BFRs within different fractions of a waste polymer stream consisting of SMW plastics.  
155 Additionally, we evaluate further the use of handheld XRF as a tool for screening for  
156 compliance with LPCL values. Identifying the presence of BFRs within individual polymer  
157 types prior to extrusion has given us a unique perspective on which polymers may be  
158 problematic in meeting LPCLs and the potential for MEP to be used as a viable product.

159

## 160 **2. Materials and methods**

### 161 **2.1 Chemicals**

162 All solvents used for extraction and both gas chromatography–mass spectrometry (GC-MS)  
163 and liquid chromatography–tandem mass spectrometry (LC–MS/MS) analyses were of HPLC  
164 grade (Fisher Scientific, Loughborough, UK). Concentrated sulfuric acid (99.7%) was  
165 purchased from Sigma–Aldrich (St. Louis, MA, USA).

166 Individual  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD standards,  $^{13}\text{C}_{12}$ - $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD,  $\text{d}_{18}$ - $\gamma$ -HBCDD, as  
167 well as individual standards of BDEs 28, 47, 77, 99, 100, 128, 153, 154, 183, 209,  $^{13}\text{C}_{12}$ -BDE  
168 209, and  $^{13}\text{C}_{12}$ -TBBP-A were purchased from Wellington Laboratories (Guelph, ON,  
169 Canada). A full list of all target analytes are presented in the Table S1 of the supporting  
170 information.



171 Certified reference materials (CRMs) for low density polyethylene (LDPE) (ERM-EC590)  
172 and polypropylene (PP) (ERM-EC591) were purchased from IRMM (Brussels, Belgium).

## 173 **2.2 Sampling**

174 Sample collection at the polymer recycling facility and extrusion of MEP pellets was  
175 conducted by Axion Recycling Ltd. All samples of polymeric material were provided by  
176 Axion Recycling Ltd. to the University of Birmingham. Axion Polymers are a major recycler  
177 of plastics derived from waste electronic and electrical equipment (WEEE). They operate one  
178 of the most advanced sorting and recycling facilities in Europe and already recycle over  
179 150,000 tonnes of shredder residue per annum.

180

## 181 **2.3 Sample treatment**

182 Batches of MEP chips were separated into three, roughly equal by mass, fractions using  
183 density separation: “Light-MEP”, “Medium-MEP”, and “Heavy-MEP”. The criteria for  
184 density separation are Axion's proprietary information and thus cannot be included here.  
185 Samples were generated from production by taking several grab samples of chipped (<15 mm  
186 diameter) MEP over time (typically 1 – 2 kg, up to 5 times per day) from each of these three  
187 fractions. Typically, the samples were then mixed well within their class before 2 kg of  
188 plastic chips were selected and extruded using a single screw lab scale extruder to form the  
189 “homogenised” MEP pellets, with subsamples (ca. 200 mg) of this extruded material taken  
190 for analysis. In all instances PVC chips were removed prior to extrusion. Batches of ~500 g  
191 of extruded pellets were prepared for each MEP fraction.

### 192 **2.3.1 FTIR analyses to characterise polymer type**

193 A representative random grab sample of the mixed polymer stream infeed was taken and the  
194 material dried. This was taken as part of a routine test conducted on a weekly basis to identify  
195 the constituent polymer of each chip. From this grab sample, 1 kg of chipped polymer (<15  
196 mm diameter) was selected with visible contaminants (e.g. metal, wires, printed circuit  
197 boards, wood, and rubber and other elastomers) removed. Polymer chips were selected and  
198 cleaned of any dirt or debris before the polymer type was determined using Fourier-transform  
199 infrared spectroscopy (FTIR) on site by Axion Recycling Ltd., Salford, UK. Using this  
200 process, 217 individual polymer chips were grouped by polymer type and sent to University  
201 of Birmingham for determination of concentrations of Br and BFRs (97 chips were analysed  
202 by MS for BFRs + 120 were screened by XRF (of which 27 were then analysed by MS for  
203 BFRs) = 217 total individual chips). The chips analysed in this study were obtained in  
204 September 2019.

205

### 206 **2.3.2 Determination of concentrations of Br**

207 Concentrations of Br in polymer chips were determined using a handheld XRF device (Niton  
208 XL3t 700 GOLDD+; Niton, UK). The sample to be analysed (minimum polymer sample  
209 thickness 2 mm) was mounted onto the sampling stand with a lead lined housing and the  
210 surface of the sample cleaned of any visible dust and dirt using a clean tissue. Measurement  
211 of Br was then carried out by irradiating for no fewer than 30 seconds using the large (X-ray)  
212 spot size, with the device locked into position and centred over the target area in the housing  
213 throughout the measurement period. Full methodology and QA/QC procedures have been  
214 reported previously (Sharkey et al., 2018). The limit of detection (LOD) of the Niton XRF  
215 Analyzer varies according to the element targeted, the matrix and the (X-ray) spot size used.

216 Overall, it ranges between 1-10 mg/kg. For Br in plastics using the large spot size, LOD = 3-  
217 8 mg/kg. Using the small spot size, LOD = 5-20 mg/kg with an average of ~10 mg/kg.

218

### 219 **2.3.3 Measurement of BFRs in MEP chips and extruded pellets**

#### 220 **2.3.3.1 Polymer extraction and extract purification**

221 The method used to extract BFRs from polymer samples and purify resultant extracts was  
222 adapted from a previously validated method (Abdallah et al., 2017), where dichloromethane  
223 (DCM) was used as extraction solvent and samples were not required to be pulverised prior  
224 to extraction. Extruded pellets were taken at random from a 500 g sample of MEP pellets, cut  
225 into small pieces ( $<2 \text{ mm}^2$ ) using metal shears, then mixed, and aliquots (ca. 200 mg)  
226 accurately weighed before being transferred into 15 mL glass centrifuge tubes. Each of the  
227 “white” and “clear” fraction extruded pellets were analysed in triplicate, whereby three (ca.  
228 200 mg) subsample aliquots were taken from the extruded pellets of each colour fraction.  
229 When analysing individual polymer chips pre-identified using FTIR, in almost all instances  
230 the whole chip was used and cut into smaller pieces ( $< 2 \text{ mm}^2$ ) to enhance extraction.

231 Samples were extracted by adding approximately 3 mL of DCM before vortexing for 2 min.  
232 followed by ultrasonication for 5 min to effect dissolution of the polymer. The resultant  
233 extract was collected in a separate centrifuge tube and the process repeated twice, collecting  
234 all DCM extracts in the same centrifuge tube. The combined extracts were then evaporated to  
235 approx. 2 mL at 40 °C under a gentle stream of nitrogen. Two mL of hexane were then added  
236 to the sample to precipitate dissolved polymer.

237 The sample was then evaporated to  $< 1 \text{ mL}$  and reconstituted in 2 mL in hexane (to ensure  
238 removal of DCM) and vortexed for 2 min. Approx. 2 mL of  $>98\%$  concentrated sulfuric acid  
239 was added to the sample and vortexed for 30 s. Samples were left for at least 1 h followed by

240 centrifugation at  $3000 \times g$  for 5 min to separate the aqueous and organic layers. 100  $\mu\text{L}$  of the  
241 clean supernatant hexane layer was collected in a glass tube and diluted to 10 mL in hexane.  
242 A further 100  $\mu\text{L}$  of the diluted sample was taken and spiked with 30 ng of all internal  
243 (surrogate) standards (IS) ( $^{13}\text{C}_{12}$   $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD, BDEs 77 and 128, and  $^{13}\text{C}_{12}$ -TBBP-  
244 A), except for  $^{13}\text{C}_{12}$ -BDE-209, of which 120 ng was added to the sample extract before  
245 reconstitution in 100  $\mu\text{L}$  toluene containing 0.2 ng/ $\mu\text{L}$   $^{13}\text{C}_{12}$ -BDE-100 and 0.2 ng/ $\mu\text{L}$   $\text{d}_{18}$ - $\gamma$ -  
246 HBCDD as recovery determination standard. BDEs 77 and 128 were used to quantify  
247 concentrations for BDEs 28, 47, 99, 100, 153, 154, and 184, and also NBRs: PBBz, HBBz,  
248 and BTBPE. While  $^{13}\text{C}_{12}$ -BDE-209 was used to quantify concentrations of BDE-209 and  
249 DBDPE,  $^{13}\text{C}_{12}$ -TBBP-A was used to quantify concentrations of TBBP-A. After  
250 reconstitution, the sample extract was transferred to a glass inserted auto-sampler vial for  
251 quantitative analysis of PBDEs, novel brominated flame retardants (NBFRs) and TBBP-A by  
252 GC-MS and HBCDD by LC-MS/MS.

253

#### 254 **2.3.3.2 GC-MS and LC-MS/MS methods**

255 Quantitative analysis of PBDEs, NBFRs, and TBBP-A was performed in a single injection on  
256 a ThermoFisher Trace 1310 gas chromatograph coupled to a ThermoFisher ISQ mass  
257 spectrometer. The mass spectrometer was operated in electron ionisation mode using  
258 selective ion monitoring (SIM). One  $\mu\text{L}$  of the purified extract was injected for analysis using  
259 a programmable temperature vaporiser (PTV) onto a Restek Rxi-5Sil MS column (15 m  $\times$   
260 0.25 mm  $\times$  0.25  $\mu\text{m}$  film thickness). Helium was used as the carrier gas at a flow rate of 1.5  
261 mL/min with methane as the reagent gas. More details on instrument conditions and ions  
262 monitored are provided in Abdallah et al. (2017).

263 HBCDDs were measured using a Shimadzu LC–20AB Prominence binary pump liquid  
264 chromatograph (Shimadzu, Kyoto, Japan), equipped with a SIL-20A auto-sampler, a DGU-  
265 20A3 vacuum degasser coupled to an AB Sciex API 2000 triple quadrupole mass  
266 spectrometer (Applied Biosystems, Foster City, CA, USA). Chromatographic separation was  
267 achieved using an Agilent Pursuit XRS3 C18 column (150 mm × 2 mm id, 3 µm particle size)  
268 and a mobile phase of (i) 1:1 methanol/water with 2 mM ammonium acetate and (ii)  
269 methanol at a flow rate of 180 µL/min. Molecular ionisation was achieved using an ESI  
270 source operated in negative ion mode. MS/MS detection operated in the multiple reaction  
271 monitoring mode was used for quantitative determination of HBCDD isomers based on m/z  
272 640.6→79, m/z 652.4→79 and m/z 657.7→79 for the native, <sup>13</sup>C<sub>12</sub>-labelled and d<sub>18</sub>-labelled  
273 diastereomers, respectively.

274

#### 275 **2.4 Quality assurance / quality control**

276 Two CRMs, low density polyethylene (LDPE - ERM-EC590), and polypropylene (PP -  
277 ERM-EC591), were used in determining method accuracy and precision in the analysis of  
278 PBDEs from plastic polymers. Five replicate (ca. 50 mg) analyses of each CRM were  
279 conducted using the extraction and clean-up method before commencement of analysis of  
280 polymer samples. The method precision and accuracy data obtained are considered  
281 satisfactory for these analyses (see Table S2; SI). Mean recoveries of PBDEs in the CRMs  
282 were generally very good (80-100% range) and are indicative that other BFRs (of similar  
283 physicochemical properties) would have similarly good recoveries.

284

#### 285 **2.5 Data analysis**

286 Basic and descriptive statistics were calculated using IBM SPSS Statistics 26, and Microsoft  
287 Excel 2016 software. Plots were generated using SigmaPlot 13 (Systat Software Inc.). The  
288 distribution of concentrations for each compound within the data set were evaluated for  
289 normality using Shapiro-Wilk test (due to the sample size being <50). The results, combined  
290 with visual inspection of frequency diagrams, revealed that both the  $\Sigma$ POP-BFR and  $\Sigma$ BFR  
291 concentration data were log-normally distributed. Hence, Pearson correlation coefficients  
292 were obtained for log-transformed data. Total Br concentrations from BFRs quantified *via*  
293 GC-MS analysis (MS-Br values) were calculated to facilitate comparison with the XRF  
294 measured total Br (XRF-Br) concentrations in these tests (see section S4, SI).

295

## 296 **2.6 Sample codes**

297 The naming convention used for samples is as follows: Density fraction-polymer type-sample  
298 ID number (e.g M-ABS-1 = Medium-MEP, ABS, sample ID 1.) Acronyms for all polymer  
299 types used in this paper can be found in Table S3 of the SI.

300

## 301 **3. Results and discussion**

### 302 **3.1 Characterisation of the MEP feed**

303 The SMW feed consists of a mixture of 15 predominant polymer types (Table S3).

### 304 **3.2 Characterisation of the extruded MEP**

305 Figure 1 provides a detailed overview of BFR concentrations within the three main extruded  
306 MEP fractions. A statistical summary of BFR concentrations for all extruded MEP fractions  
307 analysed is provided in Table S4, with concentrations of BFRs in four subgroupings within  
308 the “Medium-MEP” fraction shown in Figure 2. Unsurprisingly, given the relatively low

309 application of HBCDD in the polymers comprising MEP feedstock (Drage et al, 2018),  
310 concentrations of HBCDD were below LOQ in all samples analysed.

311 Within the “Light-MEP” fraction, BDE-209 dominates (arithmetic mean 410 mg/kg),  
312 followed by the Tri-Octa BDEs (arithmetic mean 67 mg/kg), DBDPE (arithmetic mean 35  
313 mg/kg), and TBBP-A (arithmetic mean 30 mg/kg). Notably, the arithmetic mean  $\Sigma$ PBDE and  
314 HBCDD concentrations within this fraction are low enough to comply with both current and  
315 prospective LPCLs (<1000 mg/kg and <500 mg/kg respectively). However, we do note that  
316 in one Light-MEP sample the BDE-209 concentration was 650 mg/kg and in another 500  
317 mg/kg. Additionally, we caveat that these results are based on only five replicate analyses and  
318 further testing is required to confirm that they consistently pass LPCLs before this fraction  
319 could be approved for recycling. We estimate that recycling of the “Light-MEP” fraction  
320 would result in an additional 9000 tonnes of SMW recycled per annum (see section S5; SI).

321 BFR concentrations are considerably higher in the “Medium-MEP” fraction when compared  
322 to the other MEP fractions examined. This is particularly true for the higher molecular weight  
323 BFRs, i.e. TBBP-A, BDE-209, and DBDPE. TBBP-A is the dominant BFR in this density  
324 range (arithmetic mean 15,000 mg/kg), followed by BDE-209 (arithmetic mean 6100 mg/kg),  
325 the Tri-Octa BDEs (arithmetic mean 2700 mg/kg), and DBDPE (arithmetic mean 660  
326 mg/kg).

327 Given these elevated concentrations in the overall “Medium-MEP” fraction, four additional  
328 sub-fractions of “Medium-MEP” were examined; referred to here as “Medium-MEP” a-d.  
329 These groupings were made to determine if proprietary refinements in the separation of the  
330 feed chips could yield lower BFR content in the extruded MEP pellets. The results of these  
331 analyses are given in Figure 2 and summarised in Table S4. One sample in the “Medium-  
332 MEP-c” group had a TBBP-A concentration of ~12% by weight. Moreover, all sub-fractions

333 contained PBDEs (principally BDE-209) at concentrations that exceed the EU's LPCL of  
334 1000 mg/kg.

335 The "Heavy-MEP" fraction contains considerably lower concentrations of BFRs than  
336 "Medium-MEP", but these still exceed those found in "Light-MEP" with consequent  
337 exceedances of the LPCL values. The greatest contributors to the BFR content of this fraction  
338 are BDE-209 (arithmetic mean 1000 mg/kg), DBDPE (arithmetic mean 800 mg/kg), TBBP-A  
339 (620 mg/kg), with a relatively low Tri-Octa-BDE contribution (arithmetic mean 99 mg/kg).

340 The variation in BFR concentrations observed within each density class is linked to the  
341 heterogeneity of the feed material. Within one pellet may be many different chips melted  
342 together and re-extruded. The exact blend is impossible to homogenise completely. SMW is a  
343 very diverse feed of different equipment, each piece of SMW equipment can be different  
344 depending on the manufacturer, country of origin, or year of production.

345

### 346 **3.3 Colour separated extruded MEP**

347 Within the "Medium-MEP" fraction, polymer feed chips were hand sorted into two further  
348 subdivisions based on colour before extrusion: white (opaque) chips and clear (transparent  
349 and translucent) coloured chips (see Fig. S3; SI). Polymer colour categories were measured  
350 large scale as part of a routine test conducted on a weekly basis on site by Axion Recycling to  
351 characterise the MEP polymer feed. Within the "Medium" fraction, "white" coloured  
352 polymers represented 18.8% of the MEP feed, "clear" coloured polymers represented 7.1%,  
353 while all other colours represented 74.1% (pers. comm. Axion Recycling Ltd., Salford, UK).

354 Table 1 provides an overview of the concentrations within the "white" and "clear" colour  
355 extruded MEP, with the unsorted "mixed colour" Medium-MEP also given as reference.

356 Sorting of the polymer chips by colour prior to extrusion results in a marked reduction of



357 Σtri-octa-BDEs in both the white (arithmetic mean: 51 mg/kg) and clear (arithmetic mean:  
358 1.5 mg/kg) MEP, when compared to the “mixed colour” (arithmetic mean: 890 mg/kg).  
359 However, sorting by colour makes little difference in reducing the concentration of BDE-209  
360 (arithmetic mean: 5000 mg/kg) and TBBP-A (arithmetic mean: 8300 mg/kg) in the “white”  
361 MEP. The reduction of POP-BFRs within the white sorted polymers is not sufficient to pass  
362 the EU LPCLs and therefore cannot be considered a viable means to do so. Conversely,  
363 significant reductions in BFR concentrations are observed for all target compounds in the  
364 “clear” sorted MEP resulting in the LPCLs being met. This is likely due to the composition of  
365 the polymers included, with an increase in the proportion of polymers containing no or low  
366 BFR concentrations (such as poly(methyl methacrylate); PMMA), resulting in a dilution of  
367 BFR concentrations. We estimate that recycling of the “clear” Medium-MEP fraction would  
368 result in an additional 639 tonnes of SMW recycled per annum.

369

### 370 **3.4 Concentrations of BFRs in individual chips of different polymer types**

371 Individual SMW polymer chips were separated, and their constituent polymer identified  
372 using FTIR prior to the extrusion process. The major polymer types for the “Medium-MEP”  
373 and “Heavy-MEP” fractions were identified in this fashion and five chips (ca. 200 mg each)  
374 per polymer type were analysed for their BFR content. The “Light-MEP” fraction was not  
375 examined here owing to the low concentrations of BFRs within this fraction resulting in  
376 compliance with the LPCL. In total, 97 individual chips comprising ten different polymer  
377 types were analysed for BFR content. Table 2 provides an overview of the concentrations of  
378 BFRs determined in each polymer type within each density fraction.

379 In the “Medium-MEP” fraction; individual chips identified *via* FTIR as: acrylonitrile  
380 butadiene styrene (ABS), polycarbonate-acrylonitrile butadiene styrene (PC-ABS),

381 polyamide (PA), polypropylene (PP), polystyrene-high impact polystyrene (PS-HIPS),  
382 PMMA, and polycarbonate (PC) were analysed for BFR content. As indicated by Table 2,  
383 PC-ABS and PA did not contain any of the targeted BFRs above detection limits. Moreover,  
384 consistent with its absence from extruded pellets, HBCDD was not detected in any individual  
385 polymer chips. Of the PC chips, while one sample contained 1100 mg/kg TBBP-A, no other  
386 BFRs were detected in the other PC chips. With respect to PP, one chip contained BDE-209  
387 and DBDPE at 200 mg/kg and 250 mg/kg, respectively. All ABS, PMMA, and PS-HIPS  
388 chips analysed contained TBBP-A in the range 190–28000 mg/kg, 24–55 mg/kg, and 5.1–  
389 47000 mg/kg, respectively. 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) was determined  
390 in 6 of 15 ABS chips mostly in the range of 0.90–40 mg/kg with one chip containing 27000  
391 mg/kg (2.7% wt.). Moreover, BDE-209 was detected in one PMMA sample at 96 mg/kg,  
392 while two PS-HIPS chips contained DBDPE at 140 and 330 mg/kg.

393 Notably, two additional non-regulated BFRs, pentabromobenzene (PBBz) and  
394 hexabromobenzene (HBBz), were also present in some PS-HIPS chips at 2.0-13 mg/kg and  
395 6.3-20 mg/kg, respectively. HBBz is a known FR additive used in polymers and EEE, and  
396 was detected in five chips, while PBBz was detected in four of the same five chips,  
397 suggesting a reductive debromination pathway of HBBz (Watanabe & Sakai, 2003). Tri-octa-  
398 BDE congeners were detected at relatively low levels in 9 of 15 “Medium-MEP” chips  
399 identified as ABS and in 6 of 13 chips identified as PS-HIPS.

400 One PS-HIPS chip was found to contain a mixture of PBBz (3.3 mg/kg), HBBz (16 mg/kg),  
401 BDE-153 (1.1 mg/kg), BDE183 (7.4 mg/kg), BDE-209 (25000 mg/kg), DBDPE (330 mg/kg),  
402 and BTBPE (51 mg/kg). While it is clear that the chip in question was predominantly treated  
403 with Deca-BDE, it is interesting that other FR compounds (e.g. HBBz, DBDPE, and BTBPE)  
404 are also present within the same chip albeit at much lower concentrations. Possible  
405 explanations include: that an unknown proprietary mixture was used to impart flame

406 retardancy, that there was some “carry over” of residues between batches during  
407 manufacturing, and/or in the case of PBBz and the lower brominated PBDEs, that some  
408 reductive debromination of compounds has taken place during the product lifecycle.  
409 However, the most likely explanation is that the chip contained some recycled material,  
410 supported by similar findings in a survey of Irish WEEE where quite a few items contained  
411 more than one BFR at appreciable concentrations (Drage et al., 2018; Sharkey et al. 2018).  
412 These data reveal that in general, ABS and PS-HIPS are the major contributors to the overall  
413 BFR concentrations in the “Medium-MEP” fraction. TBBP-A is known to be extensively  
414 used in as an additive in HIPS and ABS for EEE (Morf et al., 2003). This likely explains its  
415 ubiquity in these polymers in this study at substantial concentrations, often in the percent  
416 range and as high as 12% by weight.

417 In the “Heavy-MEP” fraction, individual chips of ABS, PC-ABS, PA, PP, polyvinyl chloride  
418 (PVC), POM, and polyethylene terephthalate (PET) were analysed for BFR content, with the  
419 results shown in Table 2.

420 PVC, PA, PP, POM did not contain any of the targeted BFRs above detection limits, with the  
421 only exception being one PP chip which contained 55 mg/kg TBBP-A. ABS, PC-ABS and  
422 PET were the only polymers containing BFRs in the “Heavy-MEP” fraction. Specifically, tri-  
423 octa BDE congeners were detected at relatively low levels in 2 of 9 “Heavy-MEP” ABS  
424 chips and BDE-209 in 3 of 9 samples. Meanwhile, seven ABS chips contained TBBP-A  
425 between 9.0–25,000 mg/kg, one PC-ABS chip contained DBDPE at 350 mg/kg, all ten PET  
426 chips contained TBBP-A in the range 13-1300 mg/kg, while one sample also contained  
427 DBDPE at 520 mg/kg and another, BTBPE at 52 mg/kg.

428 Overall, PBDEs were only detected in 21 out of the 97 chips analysed. This highlights the  
429 heterogeneity of BFR contamination of individual chips, because PBDEs and in particular

430 BDE-209 are ubiquitous within the extruded MEP mixtures. BFR analysis of a larger quantity  
431 of polymer identified individual chips is recommended for future research.

432

### 433 **3.5 Handheld XRF screening**

434 After the first round of analysis was completed (measuring BFR concentrations in individual  
435 polymers - detailed in the previous section) we then decided to screen the remaining 120  
436 FTIR-identified individual SMW polymer chips by handheld XRF to identify chips with Br  
437 concentrations consistent with the elevated presence of BFRs. Of the 120 individual chips  
438 tested by handheld XRF, this screening identified a total of 27 high Br concentrations (>2000  
439 mg/kg) within 14 of 20 ABS, 8 of 15 PS/HIPS, and 5 of 15 PET chips. The remaining 93  
440 chips tested (6 ABS, 10 PA, 22 PC-ABS, 10 PET, 10 PMMA, 8 POM, 10 PP, 7 PS/HIPS,  
441 and 10 PVC) were identified as having low Br concentrations (<2000 mg/kg, typically 0-250  
442 mg/kg) and were thus excluded from the next stage of analysis. The 27 high-Br content chips  
443 were then analysed for BFRs, with the paired Br and BFR concentrations for each of these  
444 chips given in Table 3.

445 The XRF Br overestimates both the BFR concentration and the POP-BFR concentration  
446 substantially in 26 of these 27 high BFR content samples with the exception of sample M-  
447 PS/HIPS-8. Whether the overestimation of BFR concentration is due to a systematic issue  
448 with XRF at these high concentrations (e.g. calibration of Br at higher concentrations) or the  
449 widespread presence of unknown BFRs is not possible to say. Pearson's correlation  
450 coefficient tests were performed, and a significant negative correlation was observed between  
451 the (log-transformed) XRF-Br and (log-transformed)  $\Sigma$ POP-BFR MS-analysis Br  
452 concentration data ( $r = -0.500$ ,  $p = 0.035$ ;  $n = 19$ , 8 chips contained no PBDEs or HBCDD so  
453 were excluded from the analysis). Despite this, no correlation was observed between the (log-

454 transformed) XRF-Br and (log-transformed)  $\Sigma$ BFR MS-analysis Br concentration data ( $r =$   
455  $0.052, p = 0.797; n = 27$ ). The correlation seen for  $\Sigma$ POP-BFR MS-analysis Br concentration  
456 data is owed to one sample (M-PS/HIPS-8 sample) skewing the trendline, with the correlation  
457 no longer significant when this sample is omitted from the analysis. For the Medium-MEP  
458 PS/HIPS-8 sample, XRF Br (10700 mg/kg) underestimates the POP-BFR concentration total  
459 MS-Br (20900 mg/kg), perhaps due to measurement inaccuracies of the portable XRF  
460 instrument and/or inhomogeneity of BFR distribution in the polymer chip sample analysed.  
461 For reference, Figure S1 (SI) provides the regression plot for the total Br concentrations  
462 derived from XRF-Br and MS-Br and Figure S2 the regression analysis between XRF-Br and  
463 MS-POP-BFR Br values. The inference of this overestimation of POP-BFR concentrations is  
464 that in 27 high Br samples tested, XRF incorrectly identified an individual chip as exceeding  
465 an LPCL of 1000 mg/kg. However, 93 “low-Br” (<2000 mg/kg) chips were not tested, of  
466 which 90 were shown to be <1000 mg/kg XRF-Br. For these 90 chips it is likely that MS-Br  
467 would also be <1000 mg/kg, thus the overall extent of false exceedances is expected to be  
468 much lower at 26 of 120 chips (~22%). This is still higher than previously reported in the  
469 Republic of Ireland where the rate of false exceedances for WEEE was ~11% (Harrad et al  
470 2019, WAFER project report). These observed inaccuracies could be due to the limited  
471 sample size.

472

### 473 **3.6 Exploration of the use of waste polymer management to reduce concentrations of** 474 **PBDEs and HBCDD in recycled polymer products.**

475 The findings of this study are consistent with the findings of the WAFER project which  
476 conducted a comprehensive survey of POP-BFRs within the Irish polymer waste stream  
477 (including WEEE plastics). In the WAFER project only 4.7% (n=2) of the 43 WEEE display

478 items examined contained PBDEs at concentrations >1000 mg/kg, yet the average  
479 concentration in such samples was 1900 mg/kg (Drage et al., 2018). Consistent with this, our  
480 data reveal that although PBDEs may only be present in a relatively small proportion of  
481 WEEE plastic chips in total, the relatively high PBDE concentrations (often in the percent  
482 range) of those few chips within the MEP feed mixture, results in PBDEs being present at  
483 concentrations approaching or exceeding the LPCL within homogenised extruded MEP  
484 pellets.

485 Our data reveals that while several polymer types (PA, PC, PC-ABS, PET, POM, and PVC)  
486 did not contain PBDEs, they were detected at substantial concentrations in ABS, PS-HIPS,  
487 and to a lesser extent PP and PMMA. This implies that effective sorting and separation of  
488 these polymer types from the SMW feed prior to extrusion could result in a recycled product  
489 that complies with LPCLs. Additionally, careful, effective management of the blend of  
490 polymer types within the feed chips prior to extrusion could allow extruded MEP pellets to  
491 meet current or proposed EU LPCLs, while also retaining desirable engineering properties  
492 (e.g. material strength and density) to deliver viable products. Furthermore, separations  
493 resulting in “Light-MEP” and colour separation (“clear” MEP) can also provide useful,  
494 simple, practical means of increasing the volume of WEEE plastic recycling.

495 The use of portable XRF analysis as a screening tool for determining compliance with POP-  
496 BFR LPCL values in the SMW polymer feed works to prevent POP-BFRs from entering the  
497 MEP recycling stream. However, our data indicates that its use as a screening tool for WEEE  
498 plastic results in a high proportion of false exceedances, where the measurement of XRF-Br  
499 overestimates exceedances of legislative limits on POP-BFR concentrations. This is mostly  
500 due to the high detection frequency of TBBP-A in these samples as well as other unidentified  
501 BFRs. Most of the Br content in the SMW polymer is attributed from the contribution of  
502 unknown brominated compounds not measured in this study. In turn, this can lead to an

503 overestimation of the volume of SMW polymer chips that are incorrectly identified as non-  
504 recyclable. However, TBBP-A is subject to the H14 criteria of hazardous waste for which  
505 waste can be classified as hazardous if TBBP-A is higher than 2500 ppm (Wagner and  
506 Schlummer 2020).

507 Furthermore, plastics recycling from WEEE treats ~ 1 tonne per hour. This volume cannot be  
508 pre-screened by handheld XRF. However, development of technologies such as XRT may  
509 provide future solutions.

510

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514

## 515 **References**

516 Abdallah, M.A-E.; Drage, D.S.; Sharkey, M.; Berresheim, H.; Harrad, S., 2017. A rapid  
517 method for the determination of brominated flame retardant concentrations in plastics and  
518 textiles entering the waste stream. *J. Sep. Sci.*. 40: 3873–3881.

519 <http://dx.doi.org/10.1002/jssc.201700497>

520

521 Aldrian, A., Ledersteger, A., Pomberger, R., 2015. Monitoring of WEEE plastics in regards  
522 to brominated flame retardants using handheld XRF. *Waste Manag.* 36, 297–304.

523 <http://dx.doi.org/10.1016/j.wasman.2014.10.025>

524

525 Baldé, C.P.; Forti, V.; Gray, V.; Kuehr, R.; Stegmann, P., 2017. The Global E-waste Monitor  
526 2017: Quantities, Flows, and Resources. United Nations University (UNU), International  
527 Telecommunication Union (ITU) & International Solid Waste Association (ISWA),  
528 Bonn/Geneva/Vienna. Available at: [https://collections.unu.edu/eserv/UNU:6341/Global-E-  
529 waste\\_Monitor\\_2017\\_electronic\\_single\\_pages\\_.pdf](https://collections.unu.edu/eserv/UNU:6341/Global-E-waste_Monitor_2017_electronic_single_pages_.pdf) [Accessed 2 May 2020].  
530  
531 Comply Direct, 2020. DEFRA confirm household WEEE collection targets for 2020.  
532 Available at: [https://www.complydirect.com/news/defra-confirm-household-weee-collection-  
533 targets-for-2020/](https://www.complydirect.com/news/defra-confirm-household-weee-collection-targets-for-2020/) [Accessed 20 October 2020].  
534  
535 Drage, D.S.; Sharkey, M.; Abdallah, M.A-E.; Berresheim, H.; Harrad, S., 2018. Brominated  
536 flame retardants in Irish waste polymers: Concentrations, legislative compliance, and  
537 treatment options, *Sci. Total Environ.*, 625, 1535–1543.  
538  
539 Environment Agency, 2014. Storage and Treatment of Small Mixed WEEE  
540 - Quick guide 413\_14.  
541  
542 European Commission, 2019. Regulation (EU) 2019/1021 of the European parliament and  
543 of the council of 20 June 2019 on persistent organic pollutants (recast). Available at:  
544 [https://eurlex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32019R1021&from=EN.  
545 \[Accessed 5 May 2020\].](https://eurlex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32019R1021&from=EN)  
546  
547 European Commission, 2018. European Strategy for Plastics in a Circular Economy.  
548 Available at: [https://ec.europa.eu/environment/circular-economy/pdf/plastics-strategy-  
549 brochure.pdf](https://ec.europa.eu/environment/circular-economy/pdf/plastics-strategy-brochure.pdf) [Accessed 1 May 2020].



550

551 European Commission, 2012. Directive (EU) 2012/19 of the European parliament and  
552 of the council of 4 July 2012 on waste electrical and electronic equipment (WEEE)  
553 (recast). Available at: [https://eur-lex.europa.eu/legal-](https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32019R1021&from=EN)  
554 [content/EN/TXT/PDF/?uri=CELEX:32019R1021&from=EN](https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32019R1021&from=EN) [Accessed 5 May 2020].

555

556 European Commission, 2004. Regulation (EC) No 850/2004 of the European Parliament and  
557 of the Council of 29 April 2004 on persistent organic pollutants and amending Directive  
558 79/117/EEC. Available at:

559 <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32004R0850> [Accessed 5  
560 May 2020].

561

562 Eurostat, 2020. Recycling rate of e-waste %. Available at:

563 [https://ec.europa.eu/eurostat/databrowser/view/t2020\\_rt130/default/table?lang=en](https://ec.europa.eu/eurostat/databrowser/view/t2020_rt130/default/table?lang=en) [Accessed  
564 5 May 2020].

565

566 Fatunsin, O.T.; Oluseyi, T.O.; Drage, D.S.; Abdallah, M.A-E.; Turner, A.; Harrad, S., 2020.

567 Children's exposure to hazardous brominated flame retardants in plastic toys. *Sci. Total*

568 *Environ.*, 720. <http://dx.doi.org/10.1016/j.scitotenv.2020.137623>

569

570 Gallen, C., Banks, A., Brandsma, S., Baduel, C., Thai, P., Eaglesham, G., Heffernan, A.,

571 Leonards, P., Bainton, P., Mueller, J.F., 2014. Towards development of a rapid and effective

572 non-destructive testing strategy to identify brominated flame retardants in the plastics of

573 consumer products. *Sci. Total Environ.* 491–492, 255–265.

574 <http://dx.doi.org/10.1016/j.scitotenv.2014.01.074>

575

576 Guzzonato, A.; Puype, F.; Harrad, S.J., 2017. Evidence of bad recycling practices: BFRs in  
577 children's toys and food-contact articles. *Environ. Sci.: Process. Impacts*, 19, 956–963.

578 <http://dx.doi.org/10.1039/c7em00160f>

579

580 Guzzonato, A.; Puype, F.; Harrad, S.J., 2016. Improving the accuracy of hand-held X-ray  
581 fluorescence spectrometers as a tool for monitoring brominated flame retardants in  
582 waste polymers. *Chemosphere* 159, 89–95.

583 <http://dx.doi.org/10.1016/j.chemosphere.2016.05.086>

584

585 Harrad, S.; Drage, D.S.; Abdallah, M.A-E.; Sharkey, M.; Berresheim, H., 2019. Evaluation of  
586 Hand-held XRF for Screening Waste Articles for Exceedances of Limit Values for  
587 Brominated Flame Retardants. (2014-RE-MS-2) Irish EPA Research Report 272 available at  
588 <http://www.epa.ie/pubs/reports/research/waste/research272.html> accessed 4<sup>th</sup> August 2020.

589

590 Harrad, S.; Abdallah, M.A-E.; Covaci A. 2009. Causes of variability in concentrations and  
591 diastereomer patterns of Hexabromocyclododecanes in indoor dust, *Env. Int.*, 35, 573–579.

592

593 Kuang, J.; Abdallah, M.A-E.; Harrad, S., 2018. Brominated flame retardants in black plastic  
594 kitchen utensils: Concentrations and human exposure implications. *Sci. Total Environ.*, 610:  
595 1138-1146. <http://dx.doi.org/10.1016/j.scitotenv.2017.08.173>

596

597 Morf, L., Taverna, R., Daxbeck, Z.H., Smutny, R., 2003. Selected polybrominated flame  
598 retardants PBDEs and TBBPA: substance flow analysis. Environmental Series No 338:  
599 Environmentally Hazardous Substances.

600

601 Schlummer, M.; Gruber, L.; Mäurer, A.; Wolz, G.; Eldik, R., 2007. Characterisation of  
602 polymer fractions from waste electrical and electronic equipment (WEEE) and implications  
603 for waste management. *Chemosphere* 67:1866-1876.

604

605 Sharkey, M.; Abdallah, M.A-E.; Drage, D.S.; Harrad, S.; Berresheim, H., 2018. Portable X-  
606 ray fluorescence for the detection of POP-BFRs in waste plastics. *Sci. Total Environ.*, 639:  
607 49–57. <http://dx.doi.org/10.1016/j.scitotenv.2018.05.132>

608

609 Sofies, 2020. Study on the Impacts of Brominated Flame Retardants on the Recycling of  
610 WEEE plastics in Europe. Available at: [https://www.bsef.com/wp-](https://www.bsef.com/wp-content/uploads/2020/11/Study-on-the-impact-of-Brominated-Flame-Retardants-BFRs-on-WEEE-plastics-recycling-by-Sofies-Nov-2020.pdf)  
611 [content/uploads/2020/11/Study-on-the-impact-of-Brominated-Flame-Retardants-BFRs-on-](https://www.bsef.com/wp-content/uploads/2020/11/Study-on-the-impact-of-Brominated-Flame-Retardants-BFRs-on-WEEE-plastics-recycling-by-Sofies-Nov-2020.pdf)  
612 [WEEE-plastics-recycling-by-Sofies-Nov-2020.pdf](https://www.bsef.com/wp-content/uploads/2020/11/Study-on-the-impact-of-Brominated-Flame-Retardants-BFRs-on-WEEE-plastics-recycling-by-Sofies-Nov-2020.pdf) [Accessed 24 January 2021].

613

614 United Nations Environment Programme (UNEP). 2006. Pentabromodiphenyl Ether, Risk  
615 Profile. Report of the Persistent Organic Pollutants Review Committee on the work of its  
616 second meeting, UNEP/POPS/POPRC.2/17/Add.1. Available at:  
617 [http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.2-17-](http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.2-17-Add.1.English.pdf)  
618 [Add.1.English.pdf](http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.2-17-Add.1.English.pdf) [Accessed 24 January 2020].

619

620 United Nations Environment Programme (UNEP), 2010. Technical review of the  
621 implications of recycling commercial Penta and Octabromodiphenyl ethers. Stockholm  
622 Convention document for 6th POP Reviewing Committee meeting  
623 (UNEP/POPS/POPRC.6/2). Available at:

624 <http://chm.pops.int/Portals/0/Repository/POPRC6/UNEP-POPS-POPRC.6-2.English.pdf>

625 [Accessed 24 January 2020].

626

627 Wagner, S.; Schlummer, M. 2020. Legacy additives in a circular economy of plastics:

628 Current dilemma, policy analysis, and emerging countermeasures. *Resour. Conserv. Recycl.*,

629 158: 104800. <http://dx.doi.org/10.1016/j.resconrec.2020.104800>

630 The Waste and Resources Action Programme (WRAP), 2020. Recyclability of black plastic

631 packaging Available at: <http://www.wrap.org.uk/content/recyclability-black-plastic->

632 [packaging-2](http://www.wrap.org.uk/content/recyclability-black-plastic-packaging-2) [Accessed 30 January 2020].

633

634 Watanabe, I.; Sakai, S., 2003. Environmental release and behavior of brominated flame

635 retardants. *Env. Int.*, 29: 665-682 [http://dx.doi.org/10.1016/S0160-4120\(03\)00123-5](http://dx.doi.org/10.1016/S0160-4120(03)00123-5)

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**Table 1: Statistical summary of concentrations (mg/kg) of BFRs in colour separated extruded MEP**

BFR		Colour sorted MEP		
		Mixed (n=20)	White (n=3)	Clear (n=3)
<b>Σtri-octa BDE<sup>1</sup></b>	<b>DF (%)</b>	100	100	100
	<b>Arithmetic mean</b>	890	51	1.5
	<b>Range</b>	150–5800	46–61	1.4–1.7
<b>BDE-209</b>	<b>DF (%)</b>	100	100	100
	<b>Arithmetic mean</b>	6100	5000	60
	<b>Range</b>	2100–9300	4100–6100	32–80
<b>DBDPE</b>	<b>DF (%)</b>	100	100	100
	<b>Arithmetic mean</b>	660	59	23
	<b>Range</b>	180–1700	40–90	22–26
<b>TBBP-A</b>	<b>DF (%)</b>	100	100	100
	<b>Arithmetic mean</b>	150,000	8300	140
	<b>Range</b>	7800–27000	7600–9100	110–190
<b>BTBPE</b>	<b>DF (%)</b>	0	100	0
	<b>Arithmetic mean</b>	<0.01	370	<0.01
	<b>Range</b>	<0.01	320–460	<0.01
<b>PBBz</b>	<b>DF (%)</b>	0	100	0
	<b>Arithmetic mean</b>	<0.01	0.69	<0.01
	<b>Range</b>	<0.01	0.45–0.97	<0.01
<b>HBBz</b>	<b>DF (%)</b>	0	67	0
	<b>Arithmetic mean</b>	<0.01	0.71	<0.01
	<b>Range</b>	<0.01	<0.01–1.1	<0.01

639 <sup>1</sup> Σtri-octa-BDE is defined here as the sum of six primary congeners: BDE-47, BDE-99, BDE-100, BDE-153,  
640 BDE-154, and BDE-183. DF = detection frequency; HBCDD was below limits of detection in all samples  
641 (<0.05 mg/kg). When calculating arithmetic means, samples beneath limits of detection were assumed to be  
642 equal to zero.

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**Table 2: Statistical summary of concentrations (mg/kg) of BFRs in 97 SMW individual polymer chips**

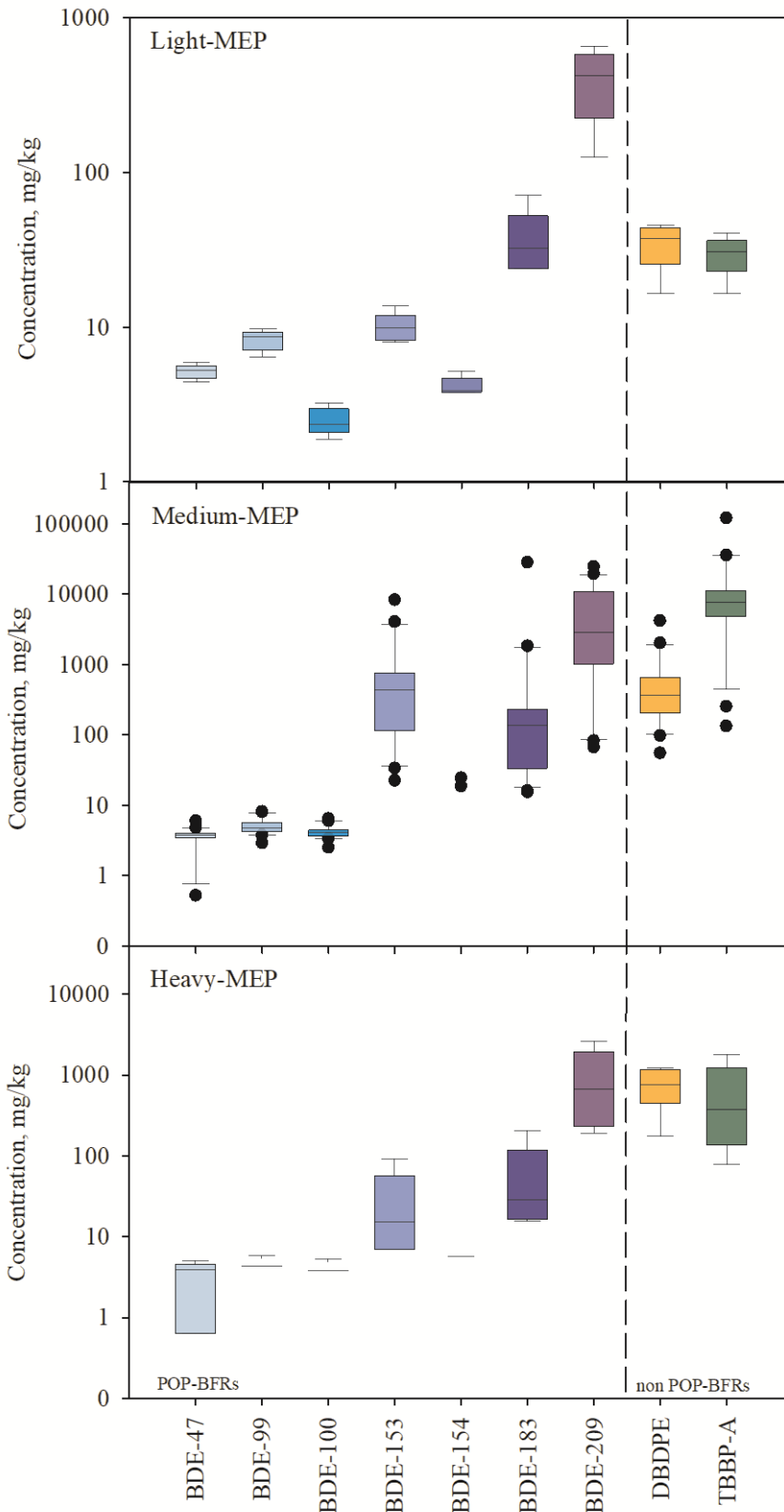
Polymer type	Σtri-octa BDE <sup>1</sup>			BDE-209			DBDPE			TBBP-A			BTBPE			PBBz			HBBz		
	DF (n)	Arith metic mean	Range	DF (n)	Arith metic mean	Range	DF (n)	Arith metic mean	Range	DF (n)	Arith metic mean	Range	DF (n)	Arith metic mean	Range	DF (n)	Arith metic mean	Range	DF (n)	Arith metic mean	Range
Medium-MEP ABS (n=15)	9	4.0	<0.01-18	1	43	<0.05-640	2	60	<0.2-480	15	13000	190-28000	6	1800	<0.01-27000	0	<0.01	<0.01	0	<0.01	<0.01
Medium-MEP PC-ABS (n=5)	0	<0.01	<0.01	0	<0.05	<0.05	0	<0.2	<0.2	0	<0.5	<0.5	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Medium-MEP PA (n=5)	0	<0.01	<0.01	0	<0.05	<0.05	0	<0.2	<0.2	0	<0.5	<0.5	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Medium-MEP PC (n=5)	0	<0.01	<0.01	0	<0.05	<0.05	0	<0.2	<0.2	1	210	<0.5-1100	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Medium-MEP PMMA (n=5)	0	<0.01	<0.01	1	19	<0.05-96	0	<0.2	<0.2	5	34	24-55	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Medium-MEP PP (n=5)	0	<0.01	<0.01	1	40	<0.05-200	1	49	<0.2-250	0	<0.5	<0.5	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Medium-MEP PS/HIPS (n=13)	6	1.1	<0.01-13	1	1900	<0.05-25000	2	25	<0.2-330	13	4600	5.1-47000	1	3.9	<0.01-51	4	1.6	<0.01-13	5	5.3	<0.01-20
Heavy-MEP ABS (n=9)	2	0.56	<0.01-2.5	3	87	<0.05-330	0	<0.2	<0.2	7	7600	<0.5-25000	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Heavy-MEP PC-ABS (n=5)	0	<0.01	<0.01	0	<0.05	<0.05	1	71	<0.2-350	0	<0.5	<0.5	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Heavy-MEP PA (n=5)	0	<0.01	<0.01	0	<0.05	<0.05	0	<0.2	<0.2	0	<0.5	<0.5	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Heavy-MEP PET (n=10)	0	<0.01	<0.01	0	<0.05	<0.05	1	52	<0.2-520	10	360	13-1300	1	5.2	<0.01-52	0	<0.01	<0.01	0	<0.01	<0.01
Heavy-MEP POM (n=5)	0	<0.01	<0.01	0	<0.05	<0.05	0	<0.2	<0.2	0	<0.5	<0.5	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Heavy-MEP PP (n=5)	0	<0.01	<0.01	0	<0.05	<0.05	0	<0.2	<0.2	1	11	<0.5-55	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01
Heavy-MEP PVC (n=5)	0	<0.01	<0.01	0	<0.05	<0.05	0	<0.2	<0.2	0	<0.5	<0.5	0	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01

<sup>1</sup> Σtri-octa-BDE is defined here as the sum of six congeners: BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183. DF = detection frequency; HBCDD was below limits of detection in all samples (<0.05 mg/kg). When calculating arithmetic means, samples beneath limits of detection were assumed to be equal to zero.

**Table 3: Paired analysis concentrations (mg/kg) of XRF-Br and MS-Br in 27 individual SMW polymer type chips**

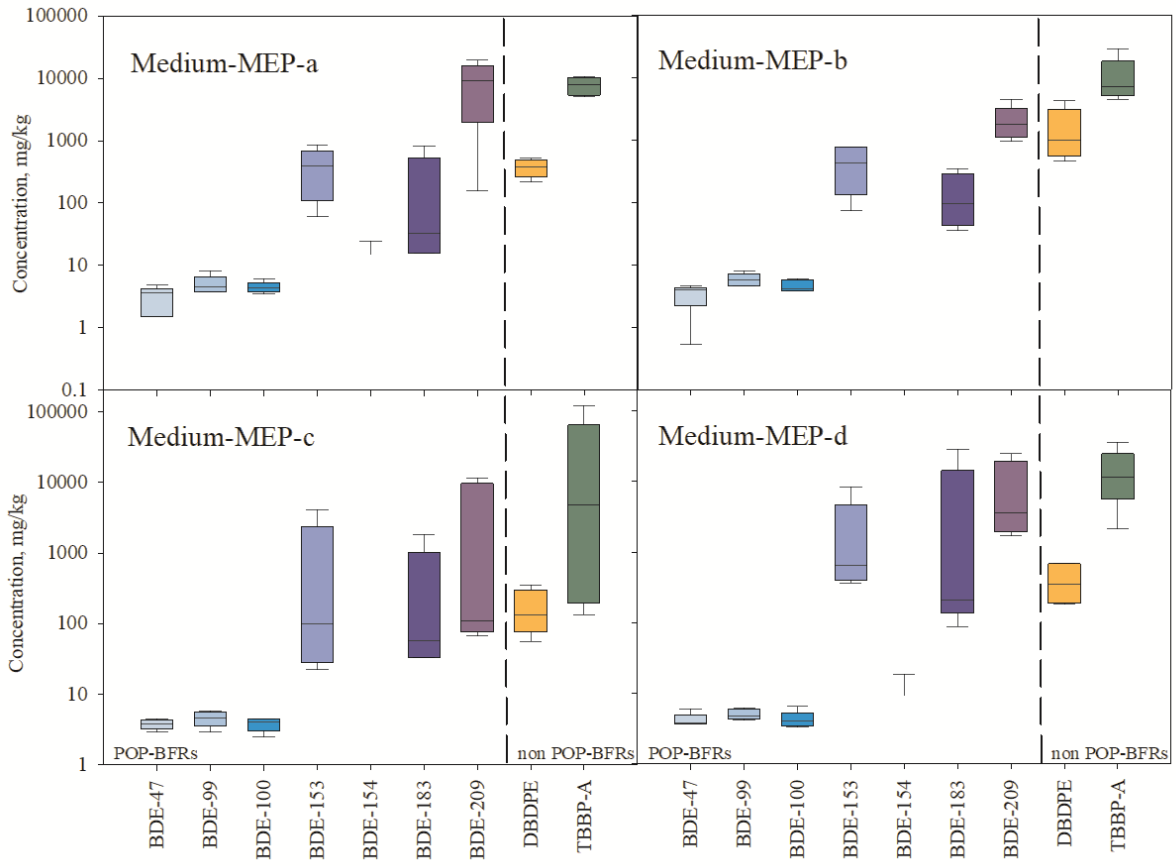
Polymer type / Sample ID	XRF-Br	MS-Br for individual BFR compounds									ΣPOP-BFRs <sup>1</sup> MS-Br	ΣBFRs MS-Br
		BDE-99	BDE-153	BDE-183	BDE-209	DBDPE	TBBP-A	BTBPE	PBBz	HBBz		
M-ABS-1	103000±2070	<0.00708	3.79	1.11	<0.0417	346	14,000	0.80	<0.00845	<0.00869	4.91	14400
M-ABS-2	107000±2590	<0.00708	<0.00745	3.10	<0.0417	<0.165	466	<0.0069	<0.00845	<0.00869	3.10	469
M-ABS-3	78800±1450	<0.00708	2.52	2.85	<0.0417	<0.165	13,600	3.9	<0.00845	<0.00869	5.37	13600
M-ABS-4	38100±487	<0.00708	0.069	2.97	<0.0417	<0.165	434	<0.0069	<0.00845	<0.00869	3.02	437
M-ABS-5	111000±2530	<0.00708	3.55	4.28	<0.0417	<0.165	16,200	0.63	<0.00845	<0.00869	7.83	16200
M-ABS-6	106000±2210	<0.00708	1.70	9.78	531	<0.165	1120	8.6	<0.00845	<0.00869	542	1670
M-ABS-7	104000±2130	<0.00708	2.84	<0.00774	<0.0417	397	14,100	28	<0.00845	<0.00869	2.84	14500
M-ABS-8	68800±1120	<0.00708	2.00	3.62	<0.0417	<0.165	11,400	<0.0069	<0.00845	<0.00869	5.62	11400
M-ABS-9	113000±2560	<0.00708	<0.00745	<0.00774	<0.0417	<0.165	365	18800	<0.00845	<0.00869	0.00	19200
M-ABS-10	94200±2130	<0.00708	1.06	<0.00774	<0.0417	<0.165	15,000	<0.0069	<0.00845	<0.00869	1.06	15000
M-PS/HIPS-1	129000±2870	2.81	<0.00745	<0.00774	<0.0417	<0.165	327	<0.0069	1.69	5.45	2.81	337
M-PS/HIPS-2	122000±2650	<0.00708	0.125	<0.00774	<0.0417	<0.165	197	<0.0069	<0.00845	<0.00869	0.125	197
M-PS/HIPS-3	106000±2120	<0.00708	<0.00745	<0.00774	160	<0.165	1020	<0.0069	2.70	14.4	160	1200
M-PS/HIPS-4	125,000±2880	<0.00708	1.18	<0.00774	<0.0417	<0.165	14,100	<0.0069	<0.00845	<0.00869	1.18	14100
M-PS/HIPS-5	88200±1700	<0.00708	<0.00745	<0.00774	<0.0417	<0.165	481	<0.0069	<0.00845	<0.00869	0.00	481
M-PS/HIPS-6	118000±2600	<0.00708	0.281	<0.00774	<0.0417	<0.165	7640	<0.0069	10.6	17.3	0.281	7670
M-PS/HIPS-7	88300±1710	<0.00708	<0.00745	<0.00774	<0.0417	<0.165	774	<0.0069	<0.00845	9.56	0.00	784
M-PS/HIPS-8	10700±130	<0.00708	0.827	5.75	20,900	272	712	36	2.78	13.6	20900	21900
H-ABS-1	79200±1490	<0.00708	<0.00745	<0.00774	176	<0.165	426	<0.0069	<0.00845	<0.00869	176	602
H-ABS-2	139000±3280	<0.00708	1.87	<0.00774	200	<0.165	14,600	<0.0069	<0.00845	<0.00869	202	14800
H-ABS-3	126000±2950	<0.00708	1.90	<0.00774	<0.0417	<0.165	14,900	<0.0069	<0.00845	<0.00869	1.90	14900
H-ABS-4	170000±4570	<0.00708	<0.00745	<0.00774	275	<0.165	534	<0.0069	<0.00845	<0.00869	275	809
H-PET-1	69900±1290	<0.00708	<0.00745	<0.00774	<0.0417	<0.165	304	<0.0069	<0.00845	<0.00869	0.00	304
H-PET-2	79900±1620	<0.00708	<0.00745	<0.00774	<0.0417	<0.165	778	<0.0069	<0.00845	<0.00869	0.00	777
H-PET-3	65000±1310	<0.00708	<0.00745	<0.00774	<0.0417	<0.165	316	<0.0069	<0.00845	<0.00869	0.00	316
H-PET-4	58000±1110	<0.00708	<0.00745	<0.00774	<0.0417	<0.165	163	<0.0069	<0.00845	<0.00869	0.00	163
H-PET-5	45700±780	<0.00708	<0.00745	<0.00774	<0.0417	<0.165	247	36	<0.00845	<0.00869	0.00	284

<sup>1</sup> ΣPOP BFRs is defined here as the sum of seven primary PBDE congeners (BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209) and HBCDD. BDE-47 and HBCDD were below limits of detection in all samples (<0.01 mg/kg and <0.05 mg/kg, respectively). M= Medium MEP; H=Heavy MEP



**Figure 1: BFR concentrations (mg/kg) for each MEP grade (“Light-MEP”,  $n=5$ ; “Medium-MEP”,  $n=20$ ; “Heavy-MEP”,  $n=5$ ). The boxes indicate the 25<sup>th</sup> to 75<sup>th</sup> percentiles, the whiskers indicate the 10<sup>th</sup> and 90<sup>th</sup> percentiles, the black line is the median, and the black dots represent outliers. The y-axis is plotted using log scale.**





**Figure 2: BFR concentrations (mg/kg) for each “Medium MEP” subgrouping a-d ( $n=5$  each). The boxes indicate the 25<sup>th</sup> to 75<sup>th</sup> percentiles, the whiskers indicate the 10<sup>th</sup> and 90<sup>th</sup> percentiles, the black line is the median, and the black dots represent outliers. The y-axis is plotted using log scale.**