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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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1	Assessment of brominated flame retardants in a small mixed waste electronic and
2	electrical equipment (WEEE) plastic recycling stream in the UK
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8	Keywords: BFRs; persistent organic pollutants; LPCL; polymers; e-waste; mixed
9	engineering plastics; XRF.
10	
11	Abstract
12	Identifying the presence of brominated flame retardants (BFRs) within individual polymer
13	types prior to extrusion has given us a unique perspective on which polymers may be
14	problematic in meeting European Union (EU) low persistent organic pollutant (POP) content
15	limits (LPCLs) and the potential for mixed engineering plastics (MEP) to be used as a viable
16	recycled product. Our findings suggest that careful management of the polymer types within
17	the feed chips prior to extrusion could deliver extruded polymer pellets that meet the EU LPCL
18	values for POP-BFRs (i.e. <1000 mg/kg). Within this study, three fractions of extruded
19	polymer pellets ("light", "medium", and "heavy" MEP) were created using density separation.
20	Each fraction was characterised for 28 legacy and novel BFRs with brominated diphenyl ether-
21	209 (BDE-209) (68-37,000 mg/kg) and tetrabromobisphenol-A (TBBP-A) (17-120,000
22	mg/kg) both predominant and ubiquitous. Portable X-ray fluorescence (XRF) was utilised to
23	measure Br in 120 individual MEP chips of various polymer types. Those chips that XRF

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

35

36 **1. Introduction**

The move to a circular economy is vital for the development of industry and the protection of 37 the environment (European Commission, 2018). Plastics are materials constantly in the 38 39 spotlight and have received a substantial degree of public and political interest. Waste electronic and electrical equipment (WEEE) is one the fastest growing waste streams globally 40 with an estimated 1.6 million tonnes generated in the UK, 12.3 million tonnes generated 41 42 within the European Union (EU), and 44.7 million tonnes generated globally in 2016 (Baldé et al., 2017). Of this, the estimated proportion recycled in 2016 was 41.3% across the 28 43 member states of the EU and 49.8% in the UK (Eurostat, 2020). It has been estimated that the 44 45 average plastics content of WEEE is ~30% by weight (Schlummer et al., 2007). A significant volume of WEEE plastic is collected but not currently recycled and is destined 46

47 for disposal via incineration. This material is referred to as mixed engineering plastic (MEP),

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

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

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

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

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liquid chromatography coupled with mass spectrometry and is thus an expensive, time 98 consuming, and destructive process. Recently, several studies have suggested the use of 99 100 portable X-ray fluorescence (XRF) measurements of elemental Br as a surrogate measure of POP-BFR concentrations in EEE plastics (Gallen et al., 2014; Aldrian et al., 2015; Guzzonato 101 et al., 2016; Sharkey et al., 2018). However, use of portable XRF spectrometry to identify 102 items exceeding LPCL values has been shown in some instances (~6 % of 538 waste EEE, 103 foam, and fabric samples tested in the Republic of Ireland; Harrad et al., 2019) to result in 104 false exceedances (defined as situations where the concentration of bromine but not PBDEs 105 106 or HBCDD exceeds the LPCL). This was attributed to the presence of other currently nonregulated Br-containing compounds used in EEE plastics such as TBBP-A and potentially 107 decabromodiphenyl ethane (DBDPE) (Harrad et al., 2019). The "Sink/Float" method is the 108 109 most commonly used method for separating BFR containing fractions and is simply based on the higher density of plastics containing BFRs (Sofies, 2020). 110 Identification of potentially recyclable waste polymers that comply with LPCL values is 111 important as there is increasing global demand to meet sustainability targets and increase the 112 proportion of waste plastics recycled for all key applications. The EU has set ambitious 113 targets of recycling greater than 50% of all plastic waste generated in Europe by 2030 114 (European Commission, 2018). Minimum recycling and reuse targets for different categories 115 of WEEE are set out in Annex V to Directive 2012/19/EU on WEEE and range between 50% 116 117 and 80% to be prepared for reuse and/or recycled, depending on the category (European Commission, 2012). Currently, large-scale, efficient separation of mixed plastics into 118 individual polymers, or even specific grades so the materials can be reused and/or recycled, is 119 120 at best a work in progress and at worst prohibitively expensive. For example, the use of near infra-red (NIR) technology widely used in plastic recycling facilities to sort polymers into 121 different categories, is prevented by the presence of carbon black pigments and therefore 122

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

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

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understanding of whether POP-BFRs are present and if so, which fractions of the overall 148 MEP feedstock contain PBDEs and HBCDD at concentrations that do not exceed the LPCL. 149 This knowledge can be used alongside an understanding of the engineering properties of such 150 fractions to produce a final recycled product that is both useable in an engineering context 151 while meeting the LPCLs. 152 153 Against this backdrop, this paper reports concentrations of both regulated and non-regulated BFRs within different fractions of a waste polymer stream consisting of SMW plastics. 154 Additionally, we evaluate further the use of handheld XRF as a tool for screening for 155 compliance with LPCL values. Identifying the presence of BFRs within individual polymer 156 types prior to extrusion has given us a unique perspective on which polymers may be 157 problematic in meeting LPCLs and the potential for MEP to be used as a viable product. 158

159

160 2. Materials and methods

161 **2.1** Chemicals

162 All solvents used for extraction and both gas chromatography–mass spectrometry (GC-MS)

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 α -, β - and γ -HBCDD standards, ¹³C₁₂- α -, β - and γ -HBCDD, d₁₈- γ -HBCDD, as

167 well as individual standards of BDEs 28, 47, 77, 99, 100, 128, 153, 154, 183, 209, ¹³C₁₂-BDE

168 209, and ${}^{13}C_{12}$ -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.

181 **2.3 Sample treatment**

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

2.3.1 FTIR analyses to characterise polymer type

A representative random grab sample of the mixed polymer stream infeed was taken and the 193 material dried. This was taken as part of a routine test conducted on a weekly basis to identify 194 the constituent polymer of each chip. From this grab sample, 1 kg of chipped polymer (<15 195 mm diameter) was selected with visible contaminants (e.g. metal, wires, printed circuit 196 boards, wood, and rubber and other elastomers) removed. Polymer chips were selected and 197 cleaned of any dirt or debris before the polymer type was determined using Fourier-transform 198 199 infrared spectroscopy (FTIR) on site by Axion Recycling Ltd., Salford, UK. Using this process, 217 individual polymer chips were grouped by polymer type and sent to University 200 201 of Birmingham for determination of concentrations of Br and BFRs (97 chips were analysed by MS for BFRs + 120 were screened by XRF (of which 27 were then analysed by MS for 202 BFRs) = 217 total individual chips). The chips analysed in this study were obtained in 203 204 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 surface of the sample cleaned of any visible dust and dirt using a clean tissue. Measurement 210 211 of Br was then carried out by irradiating for no fewer than 30 seconds using the large (X-ray) spot size, with the device locked into position and centred over the target area in the housing 212 throughout the measurement period. Full methodology and QA/QC procedures have been 213 214 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.

Overall, it ranges between 1-10 mg/kg. For Br in plastics using the large spot size, LOD = 3-8 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

The method used to extract BFRs from polymer samples and purify resultant extracts was 221 adapted from a previously validated method (Abdallah et al., 2017), where dichloromethane 222 (DCM) was used as extraction solvent and samples were not required to be pulverised prior 223 to extraction. Extruded pellets were taken at random from a 500 g sample of MEP pellets, cut 224 into small pieces ($<2 \text{ mm}^2$) using metal shears, then mixed, and aliquots (ca. 200 mg) 225 226 accurately weighed before being transferred into 15 mL glass centrifuge tubes. Each of the "white" and "clear" fraction extruded pellets were analysed in triplicate, whereby three (ca. 227 228 200 mg) subsample aliquots were taken from the extruded pellets of each colour fraction. When analysing individual polymer chips pre-identified using FTIR, in almost all instances 229 the whole chip was used and cut into smaller pieces ($< 2 \text{ mm}^2$) to enhance extraction. 230 Samples were extracted by adding approximately 3 mL of DCM before vortexing for 2 min. 231 followed by ultrasonication for 5 min to effect dissolution of the polymer. The resultant 232 extract was collected in a separate centrifuge tube and the process repeated twice, collecting 233 all DCM extracts in the same centrifuge tube. The combined extracts were then evaporated to 234 approx. 2 mL at 40 °C under a gentle stream of nitrogen. Two mL of hexane were then added 235 236 to the sample to precipitate dissolved polymer.

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

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240	centrifugation at 3000 × g for 5 min to separate the aqueous and organic layers. 100 μ 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 μ L of the diluted sample was taken and spiked with 30 ng of all internal
243	(surrogate) standards (IS) ($^{13}C_{12} \alpha$ -, β - and γ -HBCDD, BDEs 77 and 128, and $^{13}C_{12}$ -TBBP-
244	A), except for ${}^{13}C_{12}$ -BDE-209, of which 120 ng was added to the sample extract before
245	reconstitution in 100 μL toluene containing 0.2 ng/ μL $^{13}C_{12}\text{-}BDE\text{-}100$ and 0.2 ng/ μL $d_{18}\text{-}\gamma\text{-}$
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 C ₁₂ -BDE-209 was used to quantify concentrations of BDE-209 and
249	DBDPE, ¹³ 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.

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

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

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 \times 2 mm id, 3 μ m 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 μ L/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 \rightarrow 79, m/z 652.4 \rightarrow 79 and m/z 657.7 \rightarrow 79 for the native, ¹³ C ₁₂ -labelled and d ₁₈ -labelled
273	diastereomers, respectively.

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275 2.4 Quality assurance / quality control

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

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

Within the "Light-MEP" fraction, BDE-209 dominates (arithmetic mean 410 mg/kg), 311 followed by the Tri-Octa BDEs (arithmetic mean 67 mg/kg), DBDPE (arithmetic mean 35 312 mg/kg), and TBBP-A (arithmetic mean 30 mg/kg). Notably, the arithmetic mean Σ PBDE and 313 HBCDD concentrations within this fraction are low enough to comply with both current and 314 prospective LPCLs (<1000 mg/kg and <500 mg/kg respectively). However, we do note that 315 in one Light-MEP sample the BDE-209 concentration was 650 mg/kg and in another 500 316 mg/kg. Additionally, we caveat that these results are based on only five replicate analyses and 317 318 further testing is required to confirm that they consistently pass LPCLs before this fraction could be approved for recycling. We estimate that recycling of the "Light-MEP" fraction 319 would result in an additional 9000 tonnes of SMW recycled per annum (see section S5; SI). 320 BFR concentrations are considerably higher in the "Medium-MEP" fraction when compared 321 to the other MEP fractions examined. This is particularly true for the higher molecular weight 322 323 BFRs, i.e. TBBP-A, BDE-209, and DBDPE. TBBP-A is the dominant BFR in this density range (arithmetic mean 15,000 mg/kg), followed by BDE-209 (arithmetic mean 6100 mg/kg), 324 the Tri-Octa BDEs (arithmetic mean 2700 mg/kg), and DBDPE (arithmetic mean 660 325 mg/kg).

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

326

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



345

346 **3.3 Colour separated extruded MEP**

Within the "Medium-MEP" fraction, polymer feed chips were hand sorted into two further 347 subdivisions based on colour before extrusion: white (opaque) chips and clear (transparent 348 and translucent) coloured chips (see Fig. S3; SI). Polymer colour categories were measured 349 large scale as part of a routine test conducted on a weekly basis on site by Axion Recycling to 350 characterise the MEP polymer feed. Within the "Medium" fraction, "white" coloured 351 polymers represented 18.8% of the MEP feed, "clear" coloured polymers represented 7.1%, 352 353 while all other colours represented 74.1% (pers. comm. Axion Recycling Ltd., Salford, UK). Table 1 provides an overview of the concentrations within the "white" and "clear" colour 354 extruded MEP, with the unsorted "mixed colour" Medium-MEP also given as reference. 355 Sorting of the polymer chips by colour prior to extrusion results in a marked reduction of 356

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

369

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

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

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

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polyamide (PA), polypropylene (PP), polystyrene-high impact polystyrene (PS-HIPS), 381 PMMA, and polycarbonate (PC) were analysed for BFR content. As indicated by Table 2, 382 PC-ABS and PA did not contain any of the targeted BFRs above detection limits. Moreover, 383 consistent with its absence from extruded pellets, HBCDD was not detected in any individual 384 polymer chips. Of the PC chips, while one sample contained 1100 mg/kg TBBP-A, no other 385 BFRs were detected in the other PC chips. With respect to PP, one chip contained BDE-209 386 387 and DBDPE at 200 mg/kg and 250 mg/kg, respectively. All ABS, PMMA, and PS-HIPS chips analysed contained TBBP-A in the range 190-28000 mg/kg, 24-55 mg/kg, and 5.1-388 389 47000 mg/kg, respectively. 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) was determined in 6 of 15 ABS chips mostly in the range of 0.90–40 mg/kg with one chip containing 27000 390 mg/kg (2.7% wt.). Moreover, BDE-209 was detected in one PMMA sample at 96 mg/kg, 391 while two PS-HIPS chips contained DBDPE at 140 and 330 mg/kg. 392 393 Notably, two additional non-regulated BFRs, pentabromobenzene (PBBz) and hexabromobenzene (HBBz), were also present in some PS-HIPS chips at 2.0-13 mg/kg and 394 6.3-20 mg/kg, respectively. HBBz is a known FR additive used in polymers and EEE, and 395 was detected in five chips, while PBBz was detected in four of the same five chips, 396 suggesting a reductive debromination pathway of HBBz (Watanabe & Sakai, 2003). Tri-octa-397 BDE congeners were detected at relatively low levels in 9 of 15 "Medium-MEP" chips 398 399 identified as ABS and in 6 of 13 chips identified as PS-HIPS. One PS-HIPS chip was found to contain a mixture of PBBz (3.3 mg/kg), HBBz (16 mg/kg), 400 BDE-153 (1.1 mg/kg), BDE183 (7.4 mg/kg), BDE-209 (25000 mg/kg), DBDPE (330 mg/kg), 401 402 and BTBPE (51 mg/kg). While it is clear that the chip in question was predominantly treated with Deca-BDE, it is interesting that other FR compounds (e.g. HBBz, DBDPE, and BTBPE) 403 404 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

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

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

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

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

432

433 **3.5 Handheld XRF screening**

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

445 The XRF Br overestimates both the BFR concentration and the POP-BFR concentration

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) ΣPOP-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-

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

472

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

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

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

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

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

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

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

¹ Σtri-octa-BDE is defined here as the sum of six primary 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.

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644

Polymer type	Σtri-octa BDE ¹		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 (<i>n</i>)	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

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

 $^{1}\Sigma$ tri-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.

Polymer type /	XRF-Br			ΣPOP-BFRs¹	ΣBFRs							
Sample ID		BDE-99	BDE-153	BDE-183	BDE-209	DBDPE	TBBP-A	BTBPE	PBBz	HBBz	MS-Br	MS-Br
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

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

¹ΣPOP 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





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