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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Supporting Information

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S1 Target analytes

Table S1: List of chemical names, abbreviations, CAS numbers and monitored ions

Compound	Abbreviation	CAS #	Monitored ions
allyl 2,4,6-tribromophenyl ether	ATE	3278-89-5	370.3, 371.3
2-bromoallyl 2,4,6-tribromophenyl ether	BATE	99717-56-3	330.3, 448.2
2,4,4'-tribromodiphenyl ether	BDE-28	41318-75-6	405.3, 407.3
2,2',4,4'-tetrabromodiphenyl ether	BDE-47	5436-43-1	483.2, 485.2
2,2',4,4',5-pentabromodiphenyl ether	BDE-99	60348-60-9	403.3, 405.3
2,2',4,4',6-pentabromodiphenyl ether	BDE-100	189084-64-8	403.3, 405.3
2,2',4,4',5,5'-hexabromodiphenyl ether	BDE-153	68631-49-2	483.2, 485.2
2,2',4,4',5,6'-hexabromodiphenyl ether	BDE-154	207122-15-4	483.2, 485.2
2,2',3,4,4',5',6-heptabromodiphenyl ether	BDE-183	207122-16-5	560.9, 562.9
2,2',3,3',4,4',5,5',6,6'-decabromobiphenyl ether	BDE-209	1163-19-5	798.9, 800.9
di-(2-ethylhexyl) tetra-bromophthalate	BEHTBP	26040-51-7	464.2, 466.2
1,2-bis(2,4,6-tribromophenoxy) ethane	BTBPE	37853-59-1	356.3, 358.3
decabromodiphenylethane	DBDPE	84852-53-9	484.1, 486.1
syn-Dechlorane Plus®	*syn*-DP	135821-03-3	269.3, 270.3
anti-Dechlorane Plus®	*anti*-DP	135821-74-8	269.3, 270.3
2,3-dibromopropyl 2,4,6-tribromophenyl ether	DPTE	35109-60-5	329.3, 331.3
2-ethylhexyl 2,3,4,5-tetrabromobenzoate	EHTBB	183658-27-7	418.2, 420.2
1,2,3,4,5,6-hexabromobenzene	HBBz	87-82-1	547.2, 549.2
α-hexabromocyclododecane	α-HBCDD	134237-50-6	640.6 → 78.9
β-hexabromocyclododecane	β-HBCDD	134237-51-7	640.6 → 78.9
γ-hexabromocyclododecane	γ-HBCDD	134237-52-8	640.6 → 78.9
octabromotrimethylphenylindane	OBIND	155613-93-7	771, 773
1,2,3,4,5-pentabromobenzene	PBBz	608-90-2	469.1, 471.1
2,3,4,5,6-pentabromoethylbenzene	PBEB	85-22-3	499.2, 501.2
pentabromotoluene	PBT	87-83-2	485.2, 487.2
3,3',5,5'-tetrabrombisphenol-A	TBBP-A	79-94-7	526.2, 528.2
tetrabromo-*p*-xylene	pTBX	23488-38-2	419.2, 421.2
BDE-77 (internal/surrogate standard)	BDE-77	93703-48-1	483.2, 485.2
BDE-128 (internal/surrogate standard)	BDE-128	182677-28-7	483.2, 485.2
$^{13}C_{12}$-BDE-209 (internal/surrogate standard)		N/A	808.9, 810.9
$^{13}C_{12}$-BDE-100 (recovery determination standard)		N/A	415.3, 416.5
$^{13}C_{12}$-TBBP-A (internal/surrogate standard)		N/A	540.1
$^{13}C_{12}$-α-HBCDD (internal/surrogate standard)		N/A	652.4 → 79.0

$^{13}C_{12}$-β-HBCDD (internal/surrogate standard)		N/A	652.4 → 79.0
$^{13}C_{12}$-γ-HBCDD (internal/surrogate standard)		N/A	652.4 → 79.0
d_{18}-γ-HBCDD (recovery determination standard)		N/A	657.6 → 78.9

S2 QA/QC

Two certified reference materials (CRMs) were used in determining method accuracy in the analysis of PBDEs from plastics; ERM EC590-20G (Low density polyethylene; LDPE) and ERM EC591-20G (Polypropylene; PP). Five replicate analyses of each CRM were conducted before commencement of analysis of any plastic samples and satisfactory recovery data was obtained for these analyses. The certified PBDE values, measured arithmetic mean concentration ± standard deviation (SD), arithmetic mean recovery (%), and percent relative standard deviation (%RSD) are listed in Table S1. As the %RSDs are in all instances below 20%, the repeatability of the method is acceptable (EC Directive 2002/657/EC). The measured concentration values for ERM EC590-20G (within the limit of the standard deviation) fall within the range of 80-88% of the certified values for all target analytes. The difference in the arithmetic mean BDE-183 concentration range is within ± 10% of the limit of the certified value hence falls within suitable precision criteria and the measurements of the ERMEC590-20G CRM show the method has suitable trueness, precision, and accuracy i.e. is fit for purpose (EC Directive 2002/657/EC). The measured concentration values for ERMEC591-20G (within the limit of the standard deviation) fall within the range of 88-100% of the certified values for all target analytes. The difference in the arithmetic mean BDE-47, BDE-99, BDE-100, BDE-183 and BDE-209 concentration range are all within ± 10% of the limit of the certified value hence falls within suitable precision criteria and the measurements of the ERM EC591-20G CRM show the method has suitable trueness, precision, and accuracy i.e. is fit for purpose (EC Directive 2002/657/EC).

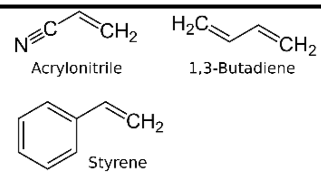
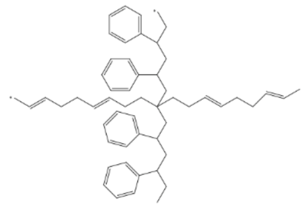
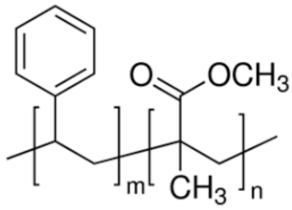
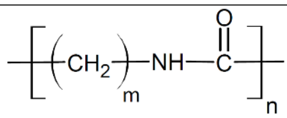
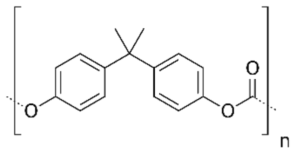
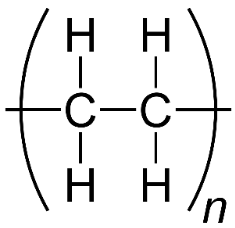
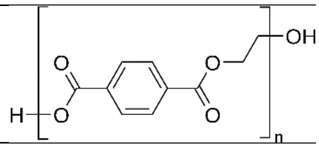
Table S2: Certified and measured concentrations of PBDEs in polymer CRMs

ERM EC590-20G – LDPE (*n*=5)				
Target analyte	Certified value (g kg^{-1})	Measured arithmetic mean (g kg^{-1}) ± standard deviation	Arithmetic mean recovery, %	%RSD
BDE-47	0.23 ± 0.04	0.226 ± 0.017	98	7.6
BDE-99	0.30 ± 0.030	0.301 ± 0.023	100	7.6
BDE-100	0.063 ± 0.005	0.061 ± 0.0062	97	10.1
BDE-153	0.047 ± 0.006	0.041 ± 0.0016	88	3.8
BDE-154	0.026 ± 0.0026	0.023 ± 0.0011	88	5.0
BDE-183	0.13 ± 0.012	0.117 ± 0.0068	89	5.8
BDE-209	0.65 ± 0.10	0.618 ± 0.021	95	3.4
ERM EC591-20G – PP (*n*=5)				
Target analyte	Certified value (g kg^{-1})	Measured arithmetic mean (g kg^{-1}) ± standard deviation	Arithmetic mean recovery, %	%RSD
BDE-47	0.25 ± 0.023	0.208 ± 0.0070	85	3.4
BDE-99	0.32 ± 0.04	0.274 ± 0.0098	86	3.6
BDE-100	0.066 ± 0.007	0.053 ± 0.0021	80	3.9
BDE-153	0.044 ± 0.006	0.039 ± 0.0019	88	5.0
BDE-154	0.026 ± 0.004	0.022 ± 0.0040	84	2.6
BDE-183	0.087 ± 0.008	0.074 ± 0.014	85	3.5
BDE-209	0.78 ± 0.09	0.636 ± 0.024	82	3.8

S3 Polymer types and MEP compositions

A key to the 15 most prevalent polymer types found in the SMW feed are presented in Table S3 along with their polymer chemical structures as reference.

Table S3: Polymer types present in MEP and their chemical structures

Polymer acronym	Full name	Chemical structure
ABS	Acrylonitrile butadiene styrene	
HIPS	High impact polystyrene	
MABS	Methyl methacrylate-acrylonitrile-butadiene-styrene	
PA	Polyamide	
PC	Polycarbonate	
PC-ABS	Polycarbonate-Acrylonitrile butadiene styrene	see PC and ABS
PE	Polyethylene	
PET	Polyethylene terephthalate	

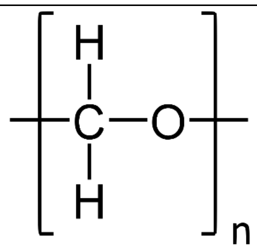
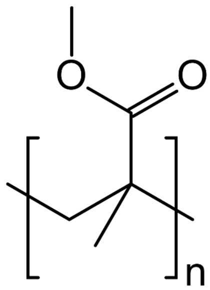
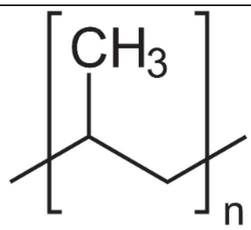
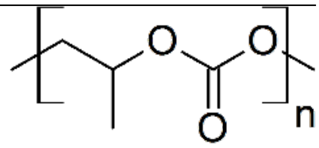
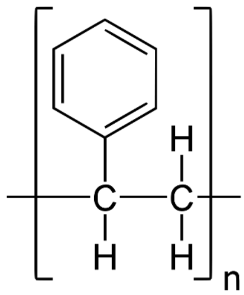
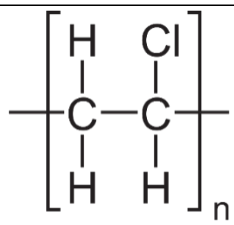
POM	Polyoxymethylene	
PMMA	Poly(methyl methacrylate)	
PP	Polypropylene	
PP-C	Polypropylene carbonate	
PP-Talc	Polypropylene-Talc filled	see PP
PS	Polystyrene	
PVC	Polyvinyl chloride	

Table S4: Statistical summary of concentrations (mg/kg) of BFRs in extruded MEP fractions (*n*=5 unless otherwise indicated)

MEP type	Σtri-octa-BDEs[1]			BDE-209			DBDPE			TBBP-A		
	Arithmetic mean	Median	Range	Arithmetic mean	Median	Range	Arithmetic mean	Median	Range	Arithmetic mean	Median	Range
Light-MEP	67	62	49–110	410	420	125–650	35	38	17–45	30	31	17-45
ΣMedium-MEP[2]	2700	570	68–37000	5900	2200	68–25000	680	350	56–4200	15000	7700	130–120000
Medium-MEP-a	640	204	<0.01–1700	9100	8300	160–20000	380	380	220–520	7800	7800	5100–11000
Medium-MEP-b	610	539	120–1100	2100	1800	960–4500	1700	990	460–4200	11000	7100	4500–29000
Medium-MEP-c	1400	150	68–6000	3900	110	68–12000	180	130	56–360	27000	4800	130–120000
Medium-MEP-d	8000	850	540–37000	9300	3600	1700–25000	420	350	180–690	14000	11000	2200–36000
Medium-MEP[3]	3.6	2.4	2.4–8.1	7900	5500	5200–16000	2000	1100	890–5100	2500	2100	1700–4000
Medium-MEP[4]	9.2	7.8	3.8–18	21000	20000	8700–37000	1900	2100	400–3400	14000	14000	7800–21000
Heavy-MEP	99	29	16–210	1000	670	190–2600	800	770	180–1200	620	370	79–1800

[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.
[2] n=20 (sum of all a-d fractions of Medium-MEP analysed)
[3] Medium-MEP "alt mix-1"
[4] Medium-MEP "alt mix-2"
HBCDD was below limits of detection in all samples (<0.05 mg/kg) and therefore was not included.
When calculating averages, samples beneath limits of detection were assumed to be equal to zero.

S4 Calculation of total Br concentrations from quantified BFRs (PBDEs, DBDPE, TBBP-A, BTBPE, PBBz, & HBBz) via MS-analysis to facilitate comparison between XRF and MS results.

Total Br concentration attributed to individual BDEs were calculated by determining the fractional quantity of bromine (*M[Br]* = 79.904 g mol^{-1} × *n* of Br) with respect to the relevant BDE congener ($M[BDE]_i$) (Royal Society of Chemistry) and adjusting the BFR concentration accordingly:

$$Br_i = \frac{M[Br]}{M[BDE]_i} \times [BDE]_i \qquad (1)$$

where Br_i is the concentration of bromine attributable to the specific PBDE congener ($[BDE]_i$) as determined by GC-MS. The total concentration of bromine from PBDEs in each sample, Br_{PBDE}, was then determined by summing the individual Br concentrations for each BDE congener (n = 7):

$$Br_{PBDE} = \sum_i^n Br_i \qquad (2)$$

Similar to PBDEs, DBDPE was quantified *([DBDPE]*) and converted to total bromine from using the molecular weight of DBDPE *(M[DBDPE])*, the atomic weight of 10 bromines and the concentration determined via GC-MS analogous to eq. 1 and 2. In the same fashion, bromine from TBBP-A ($Br_{TBBP\text{-}A}$), BTBPE (Br_{BTBPE}), PBBz (Br_{PBBz}), and HBBz (Br_{HBBz}) were directly quantified from GC-MS results, again using the molecular weights of Br (*M[Br]*) and TBBP-A, BTBPE, PBBz and HBBz (*M[TBBP-A]; M[PBBz]; M[HBBz]*) analogous to eq. 1 and 2. The total bromine concentration present in each sample resulting from these BFRs was then calculated in eq. 3 and is hereinafter considered to be the "true" concentration of bromine attributed to all quantified BFRs present:

$$Total\ Bromine = Br_{PBDE} + Br_{DBDPE} + Br_{TBBPA} + Br_{BTBPE} + Br_{PBBz} + Br_{HBBz} \qquad (3)$$

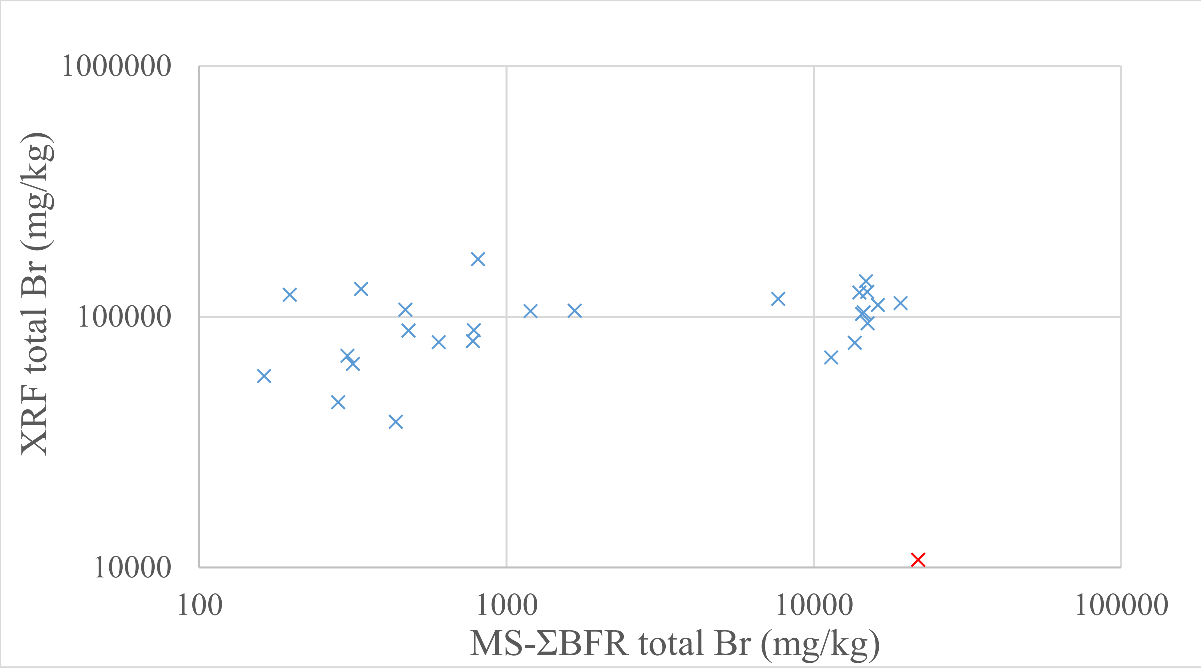


Figure S1: Regression analysis between total Br concentrations (mg/kg) measured by XRF and ΣBFR total Br concentrations (mg/kg) measured by GC-MS for polymer chip samples (n = 27). Blue crosses = XRF total Br overestimates; red cross = XRF total Br underestimates. The equation for the linear regression is: y = 0.0025x + 94115 (r^2 = 0.00000028, p =<0.0001).

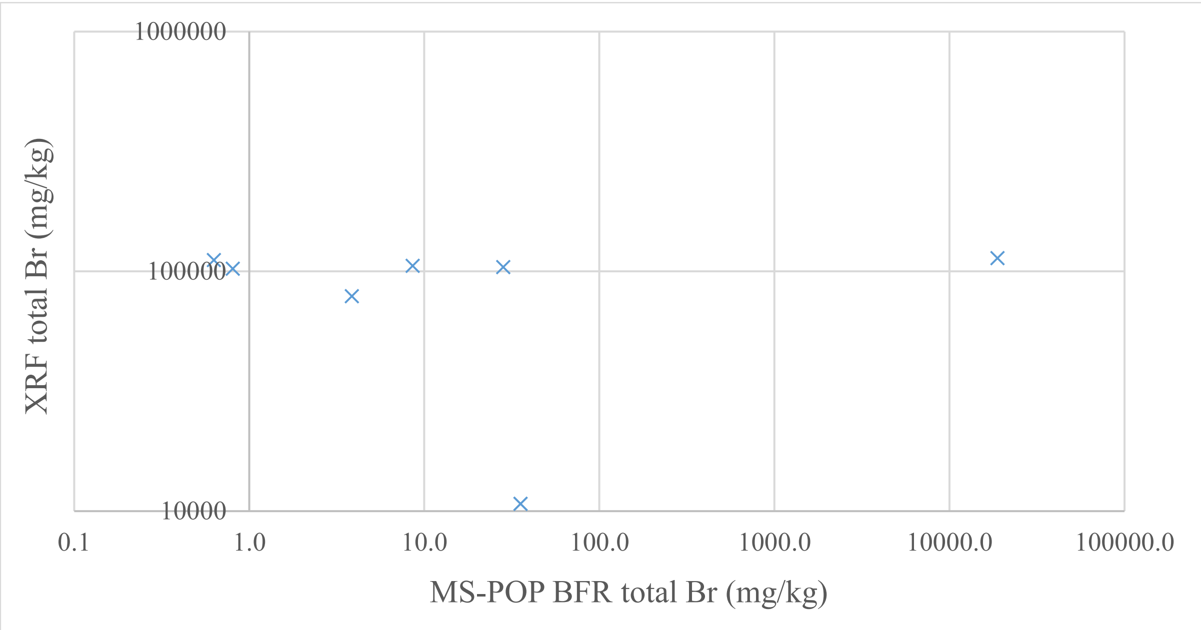


Figure S2: Regression between total Br concentrations (mg/kg) measured by XRF and total POP BFR Br concentrations (mg/kg) measured by GC-MS for polymer chip samples (n = 19). Blue crosses = XRF total Br overestimates. The equation for the linear regression is: y = 4.58x + 107121 (r^2 = 0.37, p =<0.0001).

S5 Calculation of additional recyclable MEP material due to sorting.

We estimate that recycling of the “Light-MEP” fraction would result in an additional 9000 tonnes of SMW recycled per annum.

The total volume of SWM polymers collected in the UK is 40,000 tonnes per annum for 2020 (Comply Direct, 2020). From this, 13000 tonnes are currently recycled as a PP fraction and are therefore not considered as MEP (pers. comm. Axion Recycling Ltd., Salford, UK).

The volume of SMW MEP generated is estimated as 27000 tonnes per annum.

The three MEP fractions (Light, Medium and Heavy) are roughly equal in mass (pers. comm. Axion Recycling Ltd., Salford, UK), therefore:

$$\frac{27000}{3} = 9000 \; tonnes \; per \; annum \quad (4)$$

Polymer colour categories were measured large scale as part of a routine test conducted on a weekly basis on site by Axion Recycling to characterise the polymer feed. “Clear” coloured polymers represented 7.1% of the Medium-MEP fraction (9000 tonnes) (pers. comm. Axion Recycling Ltd., Salford, UK)., therefore:

$$9000 \times 0.071 = 639 \; tonnes \; per \; annum \quad (5)$$

S6 Colour sorted MEP chips and extruded pellets.

Figure S3: Colour sorted MEP chips and pellets. Clockwise from the top left: “white” sorted MEP chips; extruded “white” MEP pellets; extruded “clear” MEP pellets; “clear” sorted MEP chips.