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WEEE PLASTIC SORTING FOR BROMINE CONTENT IS ESSENTIAL TO ENFORCE EU REGULATION

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SUMMARY: The plastics of waste of electric and electronic equipment (WEEE) are improved for fire safety by flame retardants, and particularly brominated flame retardants (BFR). As waste, the management of these plastic fractions must cope with the update of the regulation of waste hazard classification (2014), the publication of a technical standard on management of WEEE (2015), and a restriction of use for decabromodiphenylether in the product regulation (2017). Data of bromine and BFR concentrations in plastics from electric and electronic equipment (EEE) (n = 347 for Br analysis, n = 33 for BFR analysis, 2009 – 2013), and from WEEE processing facilities before and after sorting for bromine in four sites in France (n = 33 in 2014 and n = 32 in 2015) have been studied for chemical composition and for regulatory classification. After shredding, the lines sort for total bromine content (under or above 2000 mg/kg) in small household appliances (SHA), cathode ray tubes (CRT) and flat screens by X-ray fluorescence. In products, some items have no bromine (52/347 = 15%), while many items have at least one part with bromine (158/347 = 46%), and a large part of items have all parts brominated (137/347 = 39%). The most frequently brominated items are large household appliances, toys and tools (> 70% of brominated items). The bromine concentration of plastics is very heterogeneous (between items, and between parts of an item), and bromine is found where in unexpected categories, as observed by other authors in Italy, Australia, Austria, Czech Republic and UK. Obviously, a global unwanted loop of substances occurs via the international trade of plastic scrap. In waste, the most concentrated BFRs are decaBDE (3000 mg/kg) and tetrabromobisphenol A (8000 mg/kg). The bromine concentration of regulated brominated substances was identified in 2014 and 2015 to be up to 86% of total bromine in "old" waste (SHA, CRT), only 30% – 50% in "younger" waste (Flat screens), and a mean of only 8% in recent products (2009-2013). Regulated substances are a minority of all the brominated substances and the only practical way to sort is to measure on-line total bromine. Unsorted fractions of SHA, CRT and Flat screens have mean bromine concentration > 2000 mg/kg and CRT and Flat screens have decaBDE concentrations above the restriction of use concentration limit (for products) of 1000 mg/kg, and cannot be recycled as such. The sorting reduces the mean bromine concentration in the "Low Br" fraction in all sites, and reduces the decaBDE concentration below the restriction of use concentration limit. The "Low Br" fractions of SHA, CRT and Flat screens comply with all regulatory concentration limits and can be recycled. After sorting, the "High Br" fractions are all regulatory concern. In conclusion, sorting of small household appliances, cathode ray tubes and flat screen plastics is necessary to avoid

uncontrolled dispersion of regulated substances in recycled raw material. Other categories (large household appliances, electric and electronic tools, lighting equipment) should also be considered, since their total bromine content (unweighted mean concentration of parts) is high for some of these products.

1. INTRODUCTION

The mass flow of recycled plastics from WEEE separately sorted can be estimated in the EU to 0.7 Mt (= 3.5 Mt WEEE (Eurostat 2017)* 20.6% plastics in WEEE (Huisman et al. 2008)). The fraction that is recycled is not known by us but estimated by professionals to be greater than 50%. This 0.35 Mt could then represent > 5% of the 7.6 Mt of recycled plastics in EU (25.8 Mt collected * 29.7% recycled) (Plasticseurope 2017). This hypothesis is strengthened by the fact that flame retardants additives are now found in consumer products (see below) at concentrations consistent with a mixture rate > 5% (see below, this paper).

Recent developments in regulations and technical standards have changed the framework for the management of plastics from waste of electric and electronic equipment (WEEE). Detailed regulatory concentration limits are presented in this paper.

Numerous substances (75 according to Alaee et al. 2003) have been reported as potential brominated additives in plastics of EEE (alkanes, cycloalkanes, aromatics, alcohols, ethers, phthalates, epoxy resins, brominated polystyrene…). The c-octaBDE and c-decaBDE mixtures were typically incorporated into plastics at final weight loadings of 12% – 18% and 5 – 16%, respectively (Alaee et al., 2003; UNEP, 2007). Brominated flame retardants (BFRs) and antimony trioxide (a synergist of BFRs) are found in consumer plastics, WEEE or non-WEEE.

Turner and Filella (2017) investigated in the United Kingdom antimony, bromine and chlorine in plastic consumer products, with detailed results for antimony. The percentage of the 818 measured items (624 non-EEE) with antimony are (recalculated): Vehicle interiors 55%, Electronics 47%, Construction-plumbing 39%, Clothing-upholstery 36%, Leisure-sports 24%, Office-stationery 22%, Toys-hobbies 22%, Cleaning-storage 14%, Food-drinks 13%, Total 30%, Total non-EEE 28%. The percentage of items with brominated plastics are: Electronics 58%, Clothing-upholstery 39%, Vehicle interiors 34%, Construction-plumbing 30%, Leisure-sports 25%, Office-stationery 22%, Toys-hobbies 15%, Cleaning-storage 9%, Food-drinks 6%. Total 29%, Total non-EEE 21%. Bromine and/or antimony are found in all categories, including categories where no flame retardancy is expected. The authors conclude that many polymeric household items that have no reason to be fire-resistant are constructed, at least in part, from the recycled plastic components of end-of-life electronic products, and call for reconsideration of the means of disposal and recycling of Sb-rich electronic plastic waste. Obviously, a global unwanted loop of substances occurs via the international trade of plastic scrap, according to many professionals. The recyclers are aware of this question: “The Chinese government is determined to improve environmental conditions by imposing regulatory controls on the plastics recycling industry. … The ultimate objectives are to get rid of small recyclers who do not have proper recycling facilities; and to stop the importation and recycling of polluted scrap… The environmental authorities took to seizing factories, arresting owners, disconnecting utility supplies and destroying illegal workshops” (Patawari 2017).

In this study, data of bromine and BFRs in plastics from EEE, obtained from a service laboratory for commercial products quality control in 2009 to 2013, and from a WEEE processing facility before and after automated sorting for bromine in four sites of four companies in 2014 and in 2015 are presented and the following subjects discussed: distribution of the different BFRs, their concentrations and relation to total bromine content, the hazard and POP classification of these plastics, the consequences for management of these fractions, and the best way to enforce EU regulation and promote sustainable recycling of WEEE plastics.

2. MATERIALS AND METHODS

2.1 Campaign and samples

Data on bromine and BFRs in plastics from electric and electronic equipment (EEE) were obtained from a service laboratory for product quality control for compliance with the RoHS directive by the importers and resellers (SGS Multilab, Saint Etienne du Rouvray, France) from 2009 to 2013. Data on bromine and BFRs in plastics from WEEE processing facilities before and after sorting for bromine in four sites of four companies in 2014 and in 2015 in France (Table 1) were provided by OCAD3E (the French federation of producer responsibility organisation for WEEE), in collaboration with processing companies, the French Ministry for Ecology, and the National Institute for Industrial Safety and Environmental Protection (INERIS). The first set of data will be named EEE 2009-2013 and the second group WEEE 2014 and WEEE 2015 along the article.

In the 2009-2013 EEE campaigns, Br was determined in the visually different plastic parts (up to 76) of an item with a portable XRF (Niton) with a Br calibration, and with the in-borne instrument automatic correction for thickness. In a second step, laboratory analyses (total bromine, total antimony, polybromobiphenyls - PBB and polybromodiphenylethers - PBDE) were performed for some selected items (Table 1). The weight of each part is not known.

In the 2014 and 2015 WEEE campaigns, WEEE were sorted by categories in collection points, shredded and automatically sorted for total bromine content in two fractions: "Low Br (< 2000 mg/kg) and "High Br" (> 2000 mg/kg). In one site, this last fraction was further sorted with a floating bath in "high brominated low density" fraction and "high brominated high density" fraction.

Samples of the flow before and after the sorting for bromine were taken according to TS-50625-3-1:2015. During one day, ten samples were taken, mixed, quartered, divided in two and sent as laboratory samples for analysis. For a shredder delivering particles < 5 cm, 10 subsamples of 10 L were taken and reduced to a laboratory sample of 25 L, and for a shredder delivering 2 – 5 cm particles, 10 subsamples of 5 L were taken and reduced to 12 L. In 2014, sampling of flow with > 5 cm particles deviated from this procedure because a laboratory sample of 12 L was sent to the laboratory. This was corrected in 2015. For manual dismantling of cathode ray tubes (CRTs), pieces from 250 units were taken and sent to the laboratory.

The EEE and WEEE are classified in ten categories in the European WEEE Directive (EC 2012). For products, seven categories were analysed (Table 1). The WEEEs studied here were sorted in the collection points and at the processing facility in small household appliances (SHA), cathode ray tubes (CRT), and flat screens (Table 1). CRTs and flat screens can be assigned to Category 3 or 4.

Table 1: Campaigns, samples and analyses

Campaign	EEE 2009-2013			WEEE 2014	WEEE 2015
Equipment/Samples	Equipment-products for legal compliance	Parts of Equipment	Parts of Equipment	One day composite sample (shredder and sorter)	One day composite sample (shredder and sorter)
Parameters	Br (XRF)	Br (XRF)	Br (Laboratory), PBB, PBDE	Br (Laboratory), Sb, PBB, PBDE	Br (Laboratory), Sb, PBB, PBDE, HBCDD, TBBPA
EEE Categories (EC 2012) and short name in this paper					
1. Large household appliances (LHA)	26	1232	1		
2. Small household appliances (SHA)	14	310	2	4 inflow, 1 fines, 9 sorted	4 inflow, 9 sorted
3. Information and telecommunications equipment (IT)	173	1253	16	CRT: 4 inflow, 1 fines, 9 sorted; Flat screens: 2 inflow, 4 sorted	CRT: 4 inflow, 9 sorted; Flat screens: 2 inflow, 4 sorted
4. Consumer equipment and photovoltaic panels (Audio-Video)	48	219	3		
5. Lighting equipment (Lightings)	39	425	6		
6. Electrical and electronic tools (with the exception of large-scale stationary industrial tools) (Tools)	4	88	1		
7. Toys, leisure and sports equipment (Toys)	43	691	4		
Total laboratory samples	347	4218	33 parts of 22 items with brominated parts	33 (all in triplicates = 99)	32 (all 12 brominated in triplicates = 56)
Total Br analyses		4316 (4406 with triplicates)			
Total PBB PBDE analyses			98 (188 with triplicates)		
Total HBCDD TBBPA analyses					32 (56 with triplicates)

2.2 Analysis

The analyses were performed by the ISO 17025 service laboratory SGS Multilab (Saint-Etienne du Rouvray, France). A first sorting of the laboratory samples was carried out manually to eliminate the metallic parts. The sample was repeatedly shredded with a low-speed device (Blik model BB230) producing pieces less than 10 mm in size without heating. The sample was then cryo-grounded to 4 mm using a Retsch SM300 mill and quartered to 1 kg using a riffle divider. This sub-sample was cryo-grounded to 1 mm. For antimony, an aliquot sample was mineralised (ISO 13657, adapted) and analysed with ICP/OES (ISO 11885). For bromine, an aliquot was combusted in oxygen in a closed system (EN 14582) and assayed with ionic chromatography. Brominated flame retardants were determined per IEC 62321-6 with gas chromatography coupled with mass spectrometry (GC/MS). The expression of results in congeners and the limit of quantification are available on request.

For the WEEE 2014 campaign, the 33 laboratory samples were grounded and aliquots were analysed (extraction and analysis) in triplicates. The relative standard deviation (RSD) of the data higher than the limit of quantification (LOQ) are available on request**Errore. L'origine riferimento non è stata trovata.**. The mean RSD obtained of 13.5% has been judged satisfactory for these heterogeneous samples.

2.3 Classification for waste hazardousness, for POP regulation, for Br separation and for restriction of use of products

Products and waste must comply with their respective regulations. The hazard properties (HP) of waste in Europe are defined in the Commission Regulation 1357/2014 (EC 2014a) and the Decision 2014/955/UE (EC 2014b), except for the most frequent HP 14 ‘Ecotoxic’. For each hazard property, the (measured) concentrations or sum of concentrations of substances with hazard statement codes (from the “Regulation on classification, labelling and packaging of substances” (CLP 2008) tables and European Chemical Agency - ECHA site) are compared with waste-specific concentration limits (Table 2). The Decision 2014/955/UE includes persistent organic pollutants (POP) substances (use of POP concentration limit for classification of waste containing hexabromobiphenyls).

For HP 14 ‘Ecotoxic’, no method has yet been confirmed at the EU level. The EC proposes so-called “Method 1” (Table 2) without multiplying factors of the concentration (M-factors) for most ecotoxic substances. In this paper, the so-called “Method 2” with M-factors is also used. The M-factors of the substances with H400 and H410 hazard statement codes are all equal to 1 (according to ECHA site consulted Nov. 2016).

For bromine, a separation in fraction < or > 2000 mg/kg is recommended (CLC/TS 50625-3-1:2015). For decabromodiphenylether, a restriction of use in the EU REACh system applies since the first semester of 2017, with a concentration limit of 0.1% (1000 mg/kg).

Table 2: Classification of regulated substances: Hazard statement codes, hazard properties (HP) and POP classification, concentration limits (CL – mg/kg)

Substance	CAS	Hazard Statement Code	Hazard Property				POP		Separation	Restriction of use 2017
			HP	CL	Decision 2014/955/UE POP	CL	Rule	CL		
Br									2 000	
Sb_2O_3	1309-64-4	H351	HP 7	10 000 (Sb 8 400)						
HexaBB - PBB	36355-01-8	H350 1B	HP 7	1000	POP1	50	POP1	50		
TetraBDE	40088-47-9	H373	HP 5	100 000			POP2	∑ POP2 < 1 000		
TetraBDE	40088-47-9	H400 - H410	HP 14 Method 2***	∑ H410 < 25 000						
PentaBDE	32534-81-9	H373	HP 5	100 000			POP2	∑ POP2 < 1 000		
PentaBDE	32534-81-9	H400 - H410	HP 14 Method 2***	∑ H410 < 25 000						
HexaBDE	36483-60-0	H360 1B	HP 10	3000			POP2	∑ POP2 < 1 000		
HeptaBDE	68928-80-3	H360 1B	HP 10	3000			POP2	∑ POP2 < 1 000		

OctaBDE	117964-21-3	H360 1B	HP 10	3000						
NonaBDE	69278-62-2									
DecaBDE	1163-19-5	H319	HP 4	∑ H319, H315 < 200 000			**	**		1 000
HBCDD	3194-55-6	H319 - H335 - H315	HP 4	∑ H319, H315 < 200 000			POP3	1 000*		
HBCDD	3194-55-6	H361	HP 10	30 000						
HBCDD	3194-55-6	H400 - H410	HP 14 Method 2***	∑ H410 < 25 000						
TBBPA	79-94-7	H400 - H410	HP 14 Method 2***	∑ H410 < 25 000						
Variant HP 14 Method 1										
TetraBDE	40088-47-9	H400 - H410	HP 14 Method 1	∑ H410 < 2500						
PentaBDE	32534-81-9	H400 - H410	HP 14 Method 1	∑ H410 < 2500						
HBCDD	3194-55-6	H400 - H410	HP 14 Method 1	∑ H410 < 2500						
TBBPA	79-94-7	H400 - H410	HP 14 Method 1	∑ H410 < 2500						

HP 4 ‘Irritant’; HP 5 ‘Specific Target Organ Toxicity (STOT)/Aspiration’; HP 7: ‘Carcinogenic’; HP 10 ‘Toxic for reproduction’; HP 14 ‘Ecotoxic’.

* 1000 mg/kg subject to review by the European Commission by 20.4.2019

** Annex D fulfilled, annex E and F in technical committee (begin 2017).

*** M-factor of these substances = 1

3. RESULTS AND DISCUSSION

3.1 Bromine content

For EEE, some equipment have no bromine (< 100 mg/kg, 52/347 = 15%), while many others have at least one part with bromine (> 100 mg/kg, 158/347 = 46%), and a large part of equipment have all parts brominated (137/347 = 39%) (Table 4). A mean concentration of Br is calculated per category, assuming that all parts have the same weight, and that the concentrations below the limit of quantification (100 mg/kg) are equal to zero. According to professionals, at least in large household appliances, there are frequently only some small parts in contact with electric circuits and motors that are brominated, and the calculated mean could be overestimated. The most frequently brominated categories are LHA, Toys and Tools (> 70% of equipment), then SHA and Lightings (> 50% of equipment), and finally Audio-Video and IT (± 25% of equipment). A report commissioned by the WEEE Forum (European association speaking for thirty-one not-for-profit e-waste producer responsibility organisations) to contribute to a formulation of normative requirements with respect to depollution of WEEE, shows also that bromine concentrations > 2000 mg/kg are found in large household appliances (1 time/6 samples), small household appliances without screens (1/3), IT equipment without screens (3/3) and consumer equipment without screens (2/2) (Wäger et al. 2010). In mixed samples, bromine > 2000 mg/kg was found in mix of categories (2, 3, 4, 6, 7) (see Table 3 for categories number) 8 times/9 samples, in mix of categories (2, 6, 7) 2 times/4 samples and mix of categories (3, 4) 3 times/3 samples. Bromine concentrations are heterogeneous between parts of an equipment (i.e., large minimum - maximum differences) and between equipment of the same category, with the consequence that mean bromine concentrations can be very high. It seems unlikely that the separation of brominated plastics by using only EEE categories is possible. Moreover, the different parts of plastics of an equipment should be split. Other authors come to the same conclusion (Gallen et al. 2014 in Australia, Aldrian et al. 2015 in Austria, Puype et al. 2015 in Czech Republic, Cuzzonato et al. 2016 in Italy, Turner and Filella 2017 in UK).

All WEEE samples contain bromine (Tables 5 and 6). The mean concentration in the inflow fraction were 9343 mg/kg and 6597 mg/kg in 2014 and 2015, respectively, reduced to 2075 mg/kg and 2580 mg/kg for the "Low Br" fraction after sorting. Sorting is effective but needs to be improved to reach concentrations < 2000 mg/kg.

Table 3: Bromine content of EEE (sorted by decreasing bromine concentration for equipment with all parts brominated) (in blue, Br > 2000 mg/kg)

Equipment category	Equipment (number)	Parts (number)	Parts with Br > 100 mg/kg (number)	Br in all parts (mg/kg)	Br in parts with Br > 100 mg/kg (mg/kg)
6. Electrical and electronic tools (with the exception of large-scale stationary industrial tools)	4	88	10	5321	46829
5. Lighting equipment	39	425	44	3281	33125
1. Large household appliances	26	1232	89	3077	49348
2. Small household appliances	14	310	36	1755	20988
7. Toys, leisure and sports equipment	43	691	69	1238	12595
3. IT and telecommunications equipment	173	1253	91	992	17815
4. Consumer equipment and photovoltaic panels	48	219	24	895	8171
Total/Mean	347	4218	363	2013	26804

3.2 Distribution of BFR substances

In 2009-2013 EEE, the mean concentration of BFRs of 33 parts (1 LHA, 2 SHA, 16 IT, 3 Consumer, 6 Lights, 4 Toys) of 22 equipment (1 LHA, 1 SHA, 10 IT, 1 Audio-video, 4 Lights, 1 Tools, 4 Toys), mainly from 2013 are shown in Figure 1. These selected items come from a population of 4218 parts of 347 (Table 1). The regulated substances (underlined) account for only 18% of the identified substances (Figure 1). There are important differences between parts of an equipment. For example, the bromine concentration of parts of equipment with all parts brominated range from a minimum value of 100 – 1 600 mg/kg to a maximum value of 66 000 - 142 000 mg/kg for the seven EEE categories.

The mean concentrations of BFRs in WEEE of all samples are shown in Figures 2 and 3 for 2014 and 2015, respectively. DecaBDE has the highest mean BDE concentration. The sum of PBB and BDE is 473 mg/kg in EEE, and 2480 and 6270 mg/kg in WEEE in 2014 and 2015, respectively. When HBCDD and TBBPA are measured (WEEE 2015), TBBPA largely dominates (± 8000 mg/kg).

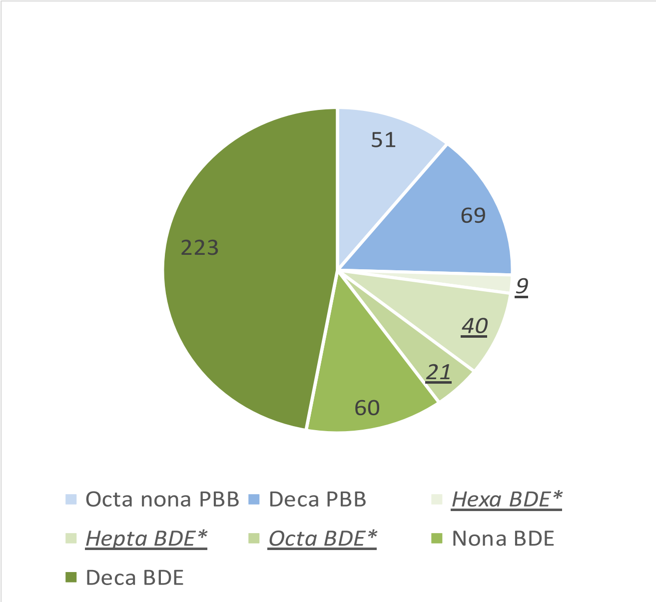

Figure 1: Concentration of brominated flame retardants in EEE 2009-2013 (mg/kg, 32 parts of 22 equipment, PBBs and PBDEs < LOQ not represented, HBCDD and TBBPA not measured; *classified substances are underlined)

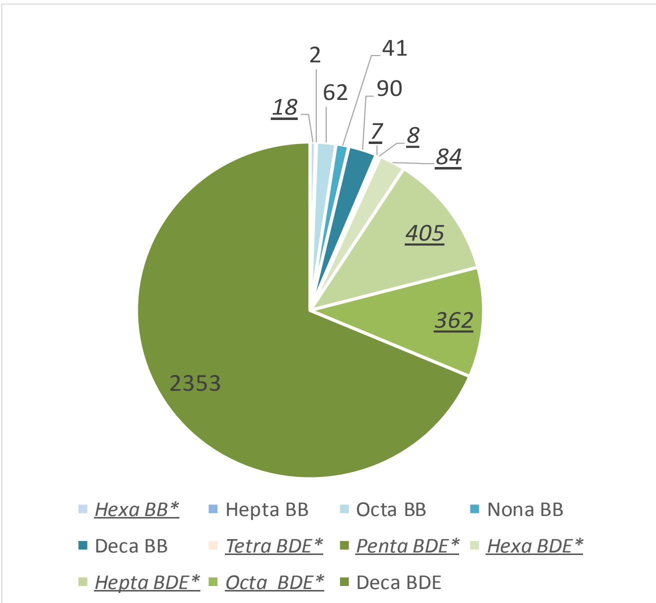

Figure 2: Concentration of brominated flame retardants in WEEE 2014 (mg/kg, n = 33, values > LOQ, PBBs and PBDEs < LOQ not represented, HBCDD and TBBPA not measured; * classified substances are underlined)

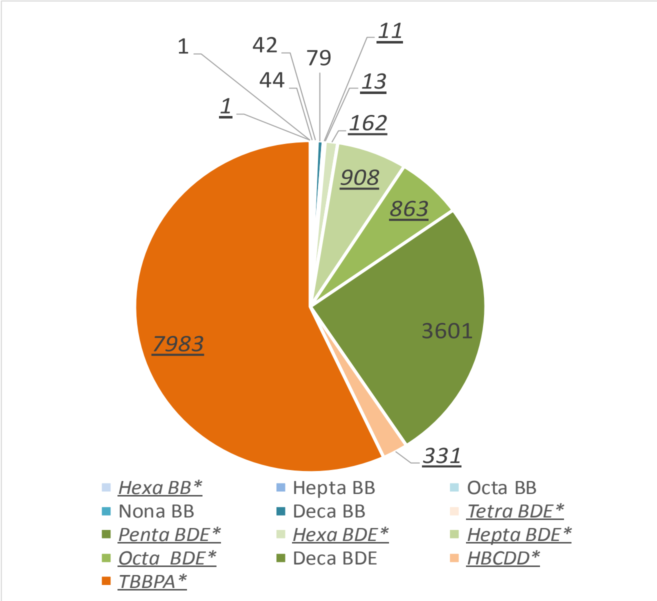

Figure 3: Concentration of brominated flame retardants in WEEE 2015 (mg/kg, n = 32, values > LOQ, PBBs and PBDEs < LOQ not represented; * classified substances are underlined)

3.3 Bromine balance

When the bromine in identified brominated compounds (calculated as the sum of the calculated bromine content in mono- to deca-BB (mass fraction of bromine 0.76 to 0.85), mono- to deca-BDE (0.66 to 0.83), HBCDD (0.75) and TBBPA (0.58)) is compared with the total bromine concentration, results are inconsistent for EEE (2009-2013 campaign) (Figure 4); the mean mass ratio being 0.08 with the highest one at only 0.33. Thus, most of the brominated compounds have remained unidentified. This might be explained by HBCDD and TBBPA not having been ~~not~~ measured. Two groups of samples are found in the 2014 WEEE campaign: a first group consistently showing a mass ratio of 0.42, with mainly SHAs and CRTs, and a second group characterised by a high bromine content but low identified bromine (Figure 5). This group is mainly formed of flat screens, probably less old than other waste. As mentioned above, HBCDD and TBBPA were neither measured in 2014 but they were measured in 2015. Samples in this latest campaign show similar behaviour as in 2014, with two distinct groups (Figure 6). When HBCDD and TBBPA are included in the calculation of the mass ratio (Figure 7), the first group mass ratio moves from 0.35 to 0.86. So, the bromine concentration of regulated brominated substances is identified up to 86% in 'older' waste (SHA, CRT) but only in the range 30-50% in 'younger' waste, and in mean only 8% in recent products (2009-2013).

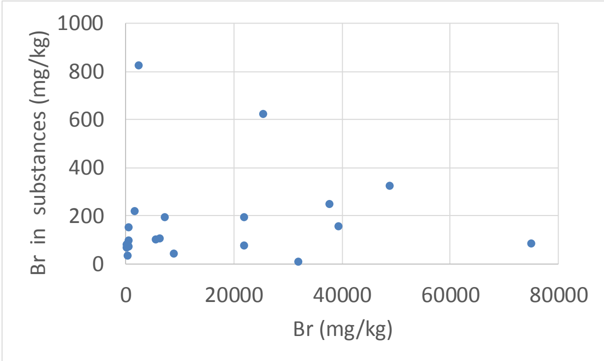

Figure 4: Bromine in measured substances as a function of total bromine in EEE (2009-2013) (n=22)

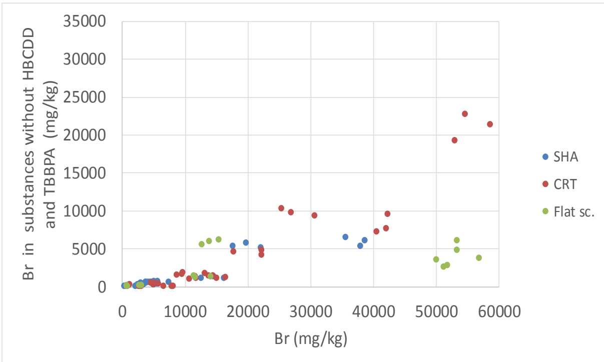

Figure 5: Bromine in measured substances as a function of total bromine in WEEE (2014) (n=99 with triplicates)

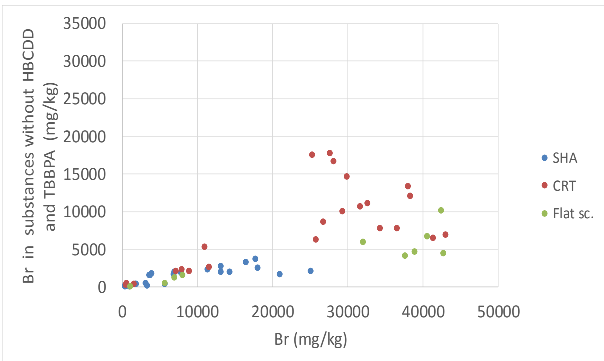

Figure 6: Bromine in measured substances (excepted HBCDD and TBBPA) as a function of total bromine in WEEE (2015) (n=56 with triplicates)

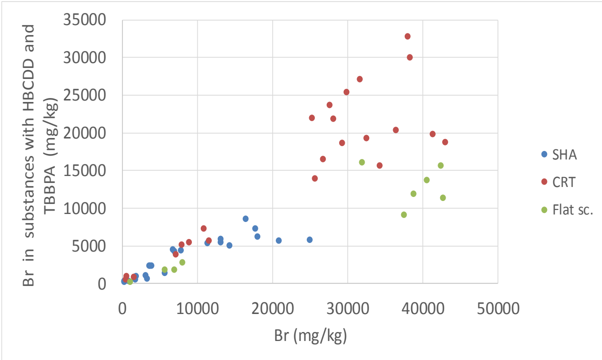

Figure 7: Bromine in measured substances (including HBCDD and TBBPA) as a function of total bromine in WEEE (2015) (n=56 with triplicates)

3.4 Classification for waste hazardousness, POP regulation, bromine separation and decaBDE resctriction of use for products

Detailed tables of concentrations and classification are presented in the next tables.

3.4.1 EEE

Mean concentrations of Br and substances in a selected set of brominated samples of 33 parts from 22 items are presented in Table 4 together with the corresponding classification results. The classification for HP 14 is not applicable due to the absence of measures for HBCDD and TBBPA. Few classifying substances are detected, and their concentrations are low. No EEE are classified as hazardous or POP with these analyses. In this selected set, mean bromine is > 2000 mg/kg in LHA, IT, Lights, Tools and Toys.

Table 4: Mean concentrations of Br, PBBs and PBDEs in EEE 2009-2013 and classification (data insufficient for HP 14)

EEE			LHA	SHA	IT	Audio-Video	Lights	Tools	Toys				
Concentration (mg/kg)	HP, POP	CL								n	Mean	Min	Max
Br		2000	32155		5624	1237	26463	75241	13006	22	15474	362	75241
Octa + Nona PBB					50		41		66	11	51	18	87
Deca PBB					51		45		211	8	69	15	211
Hexa BDE	HP 10	3000			9					2	9	5	13
Hepta BDE	HP 10	3000	10		91		23		36	4	40	10	91
Octa BDE	HP 10	3000					21			1	21	21	21
Nona BDE					39		82			6	60	24	112
Deca BDE		1000		133	192	398	218	100	267	22	223	54	991
Sum tetra-, penta-, hexa- and heptaBDE	POP	1000	10		100		23		36				
Sum tetra-, pentaBDE, TBBPA and HBCDD	HP 14	25000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.				
Classification HP, POP													
Management Br, Deca BDE (DB)			Br		Br		Br	Br	Br				

All other PBBs and PBDEs < LOQ. HBCDD and TBBPA not analysed (n.a.).

3.4.2 WEEE 2014

Mean concentrations of bromine and other substances are presented in Table 5, with the corresponding classification results. The classification for HP 14 is not applicable due to absence of measure of HBCDD and TBBPA. Sb is always lower than 8400 mg/kg in 2014 and 2015.

“High Br High density” CRTs and “High Br” CRTs exceed the concentration limits of POP regulation for the sum of tetra-, penta-, hexa- and heptaBDE (in red in the table). This is observed in the four processing sites (not shown).

“High Br” SHA is close to exceeding the concentration limits of POP regulation for the same sum (in orange in the table).

The inflow fractions have always a mean bromine concentration > 2000 mg/kg. The sorting for “Low Br” fraction of CRT should be improved.

DecaBDE has a mean concentration > 1000 mg/kg in the inflow fraction of CRT and Flat screens, and in the “High Br” fraction of CRT and SHA.

Table 5: Mean concentrations of Br, PBBs and PBDEs in WEEE 2014 from 4 sites and classification for waste hazardousness and for POP regulation (between brackets: concentration between 50% and 100% of the concentration limit)

WEEE 2014				Inflow			Fines		Low Br				High Br Low Density		High Br High Density		High Br		
Property/Category	HP, POP			SHA	CRT	Flat screens	SHA		SHA	CRT	Flat screens		SHA	CRT	SHA	CRT	SHA	CRT	Flat screens
Parameter (mg/kg)		CL																	
Br		2000		3495	11389	13143	4923		939	3458	1827		6110	27563	3837	20673	23854	36092	52720
HexaBB	POP	50															7		
HeptaBB																			
OctaBB														62					
NonaBB				2	4	2	2		2	3	2		2	158	2	2	2	3	2
DecaBB				10	29	10	10		10	10	10		11	328	10	10	12	18	10
Sum of PBBs				10	31	10	10		10	11	10		11	548	10	10	12	20	10
TetraBDE	HP 14			2			9								10			4	
PentaBDE	HP 14			3			12								15	4	2	10	
HexaBDE	HP 10	3000		4	18	2	12		2	3			5	14	22	465	127	294	5
HeptaBDE	HP 10	3000		20	121	8	49		5	11			25	99	201	2030	681	1702	28
OctaBDE	HP 10	3000		23	102	10	41		4	12			28	122	141	1913	682	1722	42
DecaBDE		1000		463	1098	4290	392		27	275	143		661	11000	352	1297	3620	8654	4625
Sum of PBDEs				540	1417	4585	546		37	312	149		755	11600	791	6223	5499	13441	5055
HBCDD	HP 14, POP	1000		n.a.	n.a.	n.a.	n.a.		n.a.	n.a.	n.a.		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
TBBPA	HP 14			n.a.	n.a.	n.a.	n.a.		n.a.	n.a.	n.a.		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Sum tetra-, penta-, hexa- and heptaBDE	POP	1000		28	139	12	82		9	14	4		30	114	248	2500	810	2009	33
Sum tetra-, pentaBDE, TBBPA and HBCDD	HP 14	25000		n.a.	n.a.	n.a.	n.a.		n.a.	n.a.	n.a.		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Classification HP, POP																POP	(POP)	POP	
Management Br, Deca BDE (DB)				Br	Br, DB	Br, DB	Br			Br			Br	Br, DB	Br	Br, DB	Br, DB	Br, DB	Br, DB

All other PBBs and PBDEs < LOQ. HBCDD and TBBPA not analysed (n.a.).

3.4.3 WEEE 2015

Mean concentrations of bromine and other substances is presented at Table 6 with the corresponding classification results.

In 2015 as in 2014, “High Br High density” CRTs and “High Br” CRTs exceed the concentration limits of POP regulation for the sum of tetra-, penta-, hexa- and heptaBDE (in red in the table) in the four processing sites (not shown). “High Br High density” CRTs are classified HP 10 ‘Toxic for reproduction’ due to hepta- and octaBDE concentrations. “Inflow” and “High Br Low density” CRTs approach the concentration limits of POP regulation for HBCDD and the sum of tetra-, penta-, hexa- and heptaBDE (in orange in the table). It is the same case for “High Br” SHA for the sum of tetra-, penta-, hexa- and heptaBDE. No waste are classified for HP 14 ‘Ecotoxic’, but “High Br” CRT fraction is close to the concentration limit. Classification for HP 14 is triggered by TBBPA.

The inflow fractions are consistently measuread with a mean bromine concentration > 2000 mg/kg. The sorting for “Low Br” fraction of CRT and Flat screens should be improved.

DecaBDE has a mean concentration > 1000 mg/kg in the inflow fraction of CRT and Flat screens, and in all the “High Br” fractions.

Table 6: Mean concentrations of Br, PBBs, PBDEs, HBCDD and TBBPA in WEEE 2015 from 4 sites and classification for waste hazardousness and for POP regulation (between brackets: concentration between 50% and 100% of the concentration limit)

WEEE 2015			Inflow			Low Br			High Br Low Density		High Br High Density		High Br		
Property/Category	HP, POP		SHA	CRT	Flat screens	SHA	CRT	Flat screens	SHA	CRT	SHA	CRT	SHA	CRT	Flat screens
Parameter (mg/kg)		CL													
Br		2000	3510	9398	6885	852	2884	4005	7200	30602	3753	27013	16685	35084	39020
HexaBB	POP	50													
HeptaBB															
OctaBB									2			48		33	
NonaBB			2	4	2	2	3	2	6	12	2	85	6	83	2
DecaBB			10	35	10	10	22	10	10	121	10	31	36	93	10
Sum of PBBs			10	37	10	10	24	10	7	134	7	164	39	208	10
TetraBDE	HP 14		7								15	3	4	6	
PentaBDE	HP 14		8								24	15	7	16	
HexaBDE	HP 10	3000	8	66	2	5	15		34	133	43	1353	103	266	11
HeptaBDE	HP 10	3000	35	388	6	19	96	3	201	561	168	8990	433	1540	46
OctaBDE	HP 10	3000	34	453	7	16	82	2	251	790	193	9177	332	1262	62
DecaBDE		1000	293	2768	1125	111	726	730	1707	12733	1487	2193	2046	7494	7020
Sum of PBDEs			420	4428	1219	162	1020	768	2297	14833	2017	23200	3309	12290	8035
HBCDD	HP 14, POP	1000	157	552	15	51	281	15	20	20	20	20	316	17	15
TBBPA	HP 14		843	3335	2100	180	1515	491	4223	15633	1118	8777	5868	21878	11877
Sum tetra-, penta-, hexa- and heptaBDE	POP	1000	58	456	10	25	113	6	237	696	250	10362	547	1829	59
Sum tetra-, pentaBDE, TBBPA and HBCDD	HP 14 Method 2	25000	1015	3889	2117	232	1798	508	4245	15656	1177	8815	6195	21917	11894
Classification HP, POP				(POP)						(POP)		HP 10, POP	(POP)	POP (HP 14)	
Management Br, Deca BDE (DB)			Br	Br, DB	Br, DB		Br	Br	Br, DB	Br, DB	Br, DB	Br, DB	Br, DB	Br, DB	Br, DB
Note : Sum HP 14	HP 14 Method 1	2500	1015	3889	2117	232	1798	508	4245	15656	1177	8815	6195	21917	11894

For EEE, the bromine concentration limit of 2000 mg/kg is exceeded for LHA, Tools, Lightings, IT and Toys (unweighted mean, potentially overestimated). Thus, a sorting of these categories for bromine should be recommended.

Classification of waste streams are very similar in 2014 and 2015. In both cases, sorting is necessary since inflow fractions of SHA, CRT and Flat screens have mean bromine concentrations > 2000 mg/kg and CRT and Flat screens have decaBDE concentrations above the restriction of use concentration limit of 1000 mg/kg for products. Unsorted fractions of these three categories cannot be recycled as such.

Sorting reduces the mean bromine concentration in the “Low Br” fraction in all sites, and the decaBDE concentration below the concentration limit of restriction of use. This implies that sorting for bromine of CRTs and Flat screens should be improved. The “Low Br” fractions of SHA, CRT and Flat screens comply with all regulatory concentration limits and can be recycled.

After sorting, the “High Br” fractions have the following regulatory concerns:

SHAs have a restriction of use for decaBDE in “High Br” fraction in 2014 but no restriction for “High Br Low Density” and “High Br High Density” in 2014, and have a restriction of use for decaBDE for all “High Br” fractions in 2015;

CRTs are POP for “High Br High Density” and “High Br” fractions, and hazardous HP 10 ‘Toxic for reproduction’ in the “High Br High Density” in 2015;

Flat screens have a restriction of use for decaBDE.

When the classification for HP 14 ‘Ecotoxic’ is done by Method 1 (proposed for classification at EU level) rather than by Method 2 with M-factors, CRT plastics are hazardous (Inflow CRT), and all the brominated fractions are hazardous excepted “High Br High Density” SHA. In total, seven fractions out of 13 are classified hazardous. Hazardous waste can be recycled, but must face user’s reluctance.

4. CONCLUSION

The EU Directive on WEEE management states that plastics containing BFRs should be sorted and managed separately from the non-brominated fraction. Existing literature and this study show that BFRs, and its practical surrogate parameter, total bromine, are found in WEEE and EEE plastics, but also in non-electric and electronic equipment plastics.

Classification of the fractions of WEEE before and after automated sorting is conclusive. The limit for sorting at 2000 mg/kg measured by XRF is validated, since all fractions below comply with regulation (excepted cathode ray tubes), and all fractions above this limit are of regulatory concern (bromine, decaBDE, hazard property, POP substances). This concentration limit can be used as a surrogate for full laboratory analysis and classification. Our results validate on-line sorting as done today in France.

Sorting should be extended to other categories than small household appliances and screens, because the BFRs used in plastic compounds change faster than regulations evolve (i.e., as shown in this study, 86% of identified bromine in “old waste” *versus* 30% to 8% in recent products), and other categories than the three considered here have bromine contents higher than 2000 mg/kg. Sorting is essential to avoid uncontrolled dispersion of regulated substances in recycled raw material.

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