



Full length article

Characterizing plastics from large household appliances: Brominated flame retardants, other additives and density profiles

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ABSTRACT

Large household appliances contain substantial amounts of plastics. At their end of life, these appliances are processed in waste electrical and electronic equipment (WEEE) treatment plants where a mixed plastic fraction is generally obtained after mechanical processing. This paper presents the results of a study conducted to investigate whether the practice of recycling these plastic streams without decontamination can be continued after the introduction of the 1000 mg/kg threshold value for the sum of polybrominated diphenyl ethers (PBDEs) in the 2019 recast of the European POP regulation. 25 samples of shredded mixed plastics from large household appliances were collected and analysed by two independent chemical laboratories with regard to various Brominated Flame Retardants (BFRs), heavy metals and tracers of common plastic additives. Results show that the currently applicable threshold values for recycling regarding heavy metals and BFRs are not exceeded in any of the analysed samples. However, relevant amounts of PBDEs (up to 791 mg/kg), tetrabromobisphenol-A (up to 1470 mg/kg) and antimony (up to 1200 mg/kg) were detected, all of which are currently under consideration for more stringent regulation in the EU. Results further show that due to limitations in analytical precision and representative sampling, the quantification of legacy substances in mixed WEEE plastic fractions is very challenging and the level of confidence with which decisions regarding legal compliance for recycling are taken is limited. It is strongly recommended that these challenges are taken into account when new threshold values are defined in order to enable a clean circular economy.

1. Introduction

Over half of all Waste Electrical and Electronic Equipment (WEEE) collected in Europe consists of large household appliances (Eurostat, 2017) which include cooling and freezing appliances (CFA) such as refrigerators, freezers and air conditioners, as well as non-cooling large household appliances (LHA) such as washing machines, dishwashers, tumble dryers and microwave ovens. These appliances contain a relevant share of plastics – roughly 15% in CFA (not including foams) and 10% in LHA (Eco-systèmes, personal communication, 2018) – which tends to increase over time due to the progressive substitution of metal by plastic parts. In the European commission's strategy on plastics (European Commission, 2018) which was adopted as part of the EU

Action plan for a circular economy (European Commission, 2015) electronics are therefore mentioned as "important applications for plastic use" and "a significant source of plastics waste that could be recycled". In addition, the recycling targets set in the European WEEE Directive (EU, 2012) are often impossible to achieve without a material recycling of the plastic fraction (Maris et al., 2015). This is due to the fact that these recycling targets are mass based and their achievability depends on the recovery rate of the materials most common in WEEE: ferrous metals, aluminium, copper and plastics. The metal content in large household appliances generally lies below the 80% recycling target set in the WEEE Directive and the target can thus not be reached by metal recycling alone (Swico/SENS/SLRS, 2021). However, Electrical and Electronic Equipment (EEE) usually remains in use for several years

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(around 10 years on average for large household appliances with considerably longer service life being possible) and WEEE plastics often contain hazardous substances, previously used as additives, which have since been restricted by regulations related to chemicals (e.g. REACH (EU, 2006), POP (EU, 2019)), products (e.g. RoHS (EU, 2011)) or wastes (e.g. WFD (EU, 2008), POP). These regulations impose restrictions on the treatment of wastes containing such legacy substances above defined threshold values, often prohibiting or severely limiting their recycling. This friction between increasing recycling targets and the desired elimination of hazardous additives reflects a larger conflict between two broad societal, and therefore political, demands; the push for a circular economy and the wish to render material cycles as toxic-free as possible. A delicate balance has to be found between maximising WEEE plastic recycling rates on the one hand, which may result in increasing dilution of toxics into secondary materials, and the complete elimination of toxics in both primary and secondary materials on the other hand, which may severely hinder or even halt WEEE plastic recycling.

The principal goal of our study was to provide comprehensive data on the characteristics of WEEE plastics from large household appliances and to assess the potential impacts of pending policy decisions in the field of WEEE plastic recycling regarding these material streams. The mass fractions of five heavy metals, seven Brominated Flame Retardants (BFRs) and various tracers of other common flame-retardants and fillers were analysed in a series of CFA and LHA shredded mixed plastic samples collected at different European WEEE treatment facilities. A special focus was set on BFRs, some of which (hexabromobiphenyl hexa-BB, polybrominated diphenyl ethers PBDEs, and hexa-bromocyclododecane HBCDD) are listed under the Stockholm convention and restricted under the POP regulation due to their persistence, bioaccumulation potential and toxicity (PBT). Previous studies have shown that, in comparison to other WEEE plastic streams, levels of restricted BFRs are relatively low in LHA- and very low in CFA plastics (Wäger et al., 2012). In the European WEEE treatment standards (EN 50625 series) plastics from large household appliances are

therefore considered free of the restricted BFRs (CENELEC, 2014) while for all other WEEE categories a threshold of 2000 mg/kg total Br is applied above which mixed plastic fractions need to undergo a BFR separation process in order to be recycled (CENELEC, 2015). In 2019 a stricter threshold value of 1000 mg/kg for the sum of PBDEs has been introduced with the recast of the POP regulation with the provision that the value be reviewed for a potential further reduction to 500 mg/kg. In the same year the Conference of the Parties to the Basel Convention adopted general technical guidelines with provisional low POPs limits for the sum of PBDEs of 1000 mg/kg, 500 mg/kg and 50 mg/kg (UNEP, 2019). Considering these developments towards a stricter regulation of PBDEs it is unclear whether the exemption of LHA and CFA plastics from BFR monitoring and separation as applied in the European WEEE treatment standards can still be justified. Some samples were analysed several times and by two independent laboratories regarding total Br and individual BFRs in order to gather more robust data and to assess potential uncertainties regarding the verification of the suggested new threshold values for PBDEs and restricted BFRs in general. In addition, density profiles of the collected samples were determined in order to investigate the effect of density-based BFR plastic sorting on potential recycling rates for LHA and CFA plastics.

2. Materials and methods

An overview of the methodological framework applied in our study is presented in Fig. 1.

2.1. Sampling

The sampling campaign took place at 19 WEEE treatment facilities located in 7 countries (France, Greece, Italy, the Netherlands, Portugal, Spain and Switzerland) between September and December 2017. Twenty-five composite plastic samples were collected during mechanical

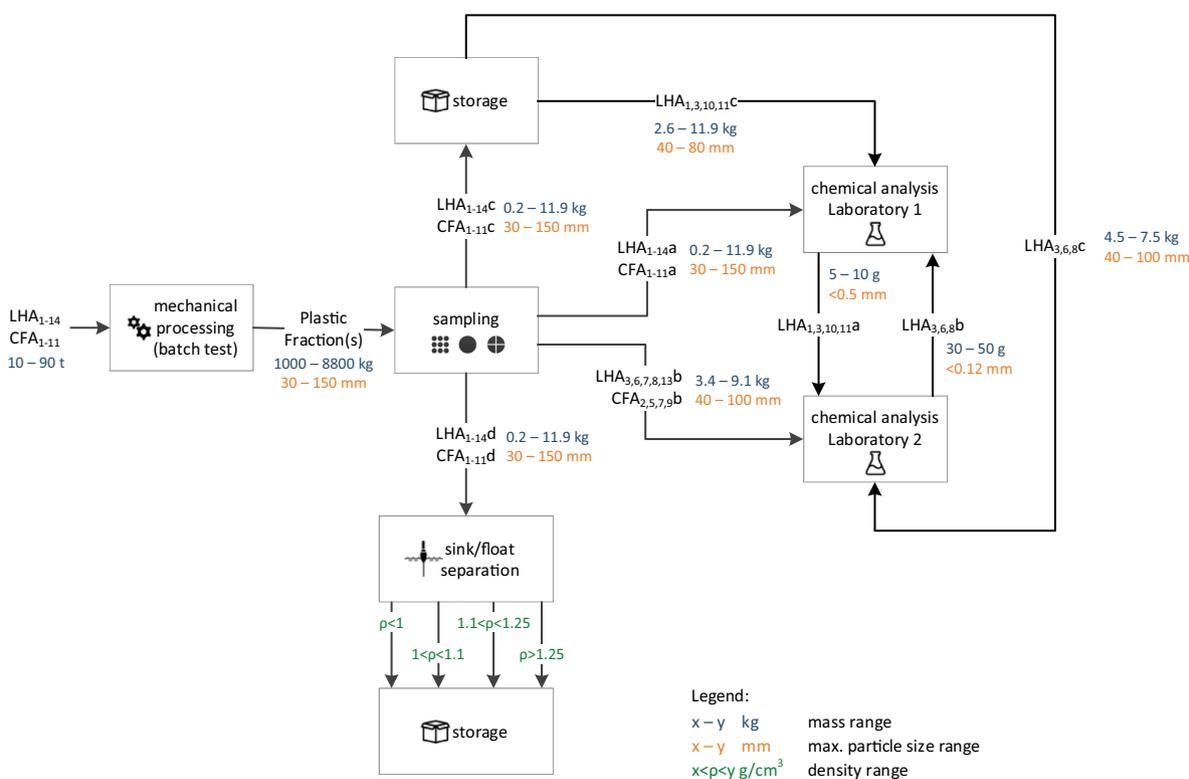


Fig. 1. Methodological framework for the assessment of additives (brominated flame retardants, heavy metals and tracers of common flame-retardants and fillers) in mixed plastic output fractions from mechanical batch processing of large household appliances (LHA) and cooling and freezing appliances (CFA) by chemical analysis and density characterization.

batch processing of CFA and LHA streams with batch inputs ranging between 10 and 90 tonnes. The sampling procedure, detailed in Section 1 of the Supporting Information, was developed following CLC/TS 50625-3-1:2015 (CENELEC, 2015) complemented by other relevant standards such as (LAGA PN 98, 2001) and (EN 14899:2005, 2005) and previous experiences (Haarman and Gasser, 2016; Wäger et al., 2012). Samples were taken from the mixed shredded plastic output fraction(s) produced during treatment operations before any BFR plastic separation processes. For each batch test composite samples were collected by taking 10 single grab samples of a prescribed minimum volume which were thoroughly mixed, piled up into a conical heap and the heap split into four equal parts. As a result four subsamples (field duplicates) were obtained per sampling batch, each having a similar weight and, presumably, a similar composition. The field duplicates were labelled (*a-d*) and used for the following purposes: *a*. Sample for chemical analysis in laboratory 1; *b*. Sample for chemical analysis in laboratory 2; *c*. Back-up sample for chemical analysis (either in laboratory 1 or laboratory 2); *d*. Sample for sink/float characterisation.

2.2. Chemical analysis

Analysed BFRs included compounds restricted by either POP or RoHS regulations – PBBs (Mono- to Deca-BB), PBDEs (Mono- to Deca-BDE) and HBCDD – as well as other BFRs shown in previous studies to be relatively abundant in WEEE plastics: tetrabromobisphenol-A (TBBPA), decabromodiphenyl ethane (DPDPE), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) and Hexabromobenzene (HBB) (BAFU, 2017a; Puype et al., 2015; Zennegg, 2011). Inorganic elements analysed included various heavy metals (Sb, Cd, Cr, Hg and Pb) as well as tracers of common flame-retardants and fillers (Br, Cl, P, Si, Mg, Ca, Al and Ti). In order to assess uncertainties resulting from eventual random or systematic variations introduced by analytical procedures samples were analysed in two different laboratories, both complying with (ISO/IEC 17025:2005, 2005) requirements. Initially, laboratory 1 analysed samples *a* from all batches and laboratory 2 analysed some randomly selected samples *b* while samples *c* were stored as back-up. Both laboratories used sample preparation methods based on (EN 15002:2015, 2015). Samples were first cleaned from non-polymeric materials (by either hand or magnet sorting) and the resulting fractions were weighted. Subsequently, grain size and volume of each sample were reduced in consecutive grinding, sieving and quartering steps resulting in grain sizes of 0.5 mm for laboratory 1 and 0.12 mm for laboratory 2. Both laboratories used methods based on the same standards for BFR characterisation (IEC 62321-6:2015, 2015), quantitative analysis of Al, Ca, Mg, P, Si, Sb, Cd, Pb and Ti (ISO 11885:2007, 2007) and determination of Br and Cl (EN 14582:2016, 2016) also described in (ASTM International D7359-08, 2008) and (IEC 62321-3-2:2013, 2013). For the determination of Hg laboratory 1 analysed test samples directly by cold vapour AAS based on (ISO 16772:2004, 2004) while laboratory 2 used a solid AAS analyser based on (ISO 11885:2007, 2007). Cr(VI) was analysed by laboratory 1 based on a method developed in-house. Test samples were suspended in ultrapure water at boiling temperature and under mechanical agitation for 10 min using a water volume to sample surface ratio of 50 mL – 50 cm². After filtration, phosphoric acid (H₃PO₄) and 1,5-Diphenylcarbazide (1,5-DPC) were added and the resulting coloration was measured by spectrometry at 540 nm. Laboratory 2 did not analyse Cr(VI). Further details regarding the applied methods and inter-laboratory variations in analytical procedures are given in Section 2 of the Supporting Information.

2.3. Density characterization

In addition to the chemical analyses a sink-float separation process was used to determine the density distribution of field duplicates *d* from all batches. Samples were successively immersed in baths of different densities: 1.00 g/cm³, 1.10 g/cm³ and 1.25 g/cm³. These density

thresholds were selected considering typical densities of BFR-rich and BFR-poor fractions and are also used in state-of-the-art WEEE plastic recycling facilities (Riise and Schwesig, 2016). After each bath floating and sinking fractions were separately collected and weighted. Solutions were prepared using demineralised water and magnesium sulphate (MgSO₄) and the density of each solution was continuously monitored using a hydrometer.

2.4. Data quality assessment

Several data quality indicators applying to both field and laboratory activities were selected to assess the reliability of results and identify potential sources of variability. The data quality assessment was focussed on the analyses of total Br and individual BFRs to support sound decision making in this area. Both laboratories (blindly) analysed three different certified reference materials (CRMs) to assess their analytical accuracy. These CRMs consist of granulates of low-density polyethylene (LDPE) and were produced under the responsibility of the Institute for Reference Materials and Measurements of the European Commission's Joint Research Centre. All three CRMs (ERM-EC590, ERM-EC680m and ERM-EC681m) have been certified for their content of total Br and, in the case of ERM-EC590, several BDE congeners as well as decabrominated biphenyl (BB-209). While the obtained benchmark results provide insights on the accuracy of the analytical methods applied, it has to be considered that, in contrast to CRMs, mixed WEEE plastics represent a heterogeneous matrix in which the elements to be analysed are non-homogeneously distributed and occur in low mass fractions which makes their analysis more challenging (Riber et al., 2007). The data quality assessment regarding analytical reproducibility therefore included the repetition of total Br analysis

- on prepared laboratory samples and under identical conditions (laboratory, analyst, method, equipment) with only the extraction and analysis step being repeated (*intra-laboratory repeatability*);
- using semi-quantitative X-ray fluorescence (XRF) analysis for a selection of samples where the initial analysis based on ion chromatography (IC) determined relatively high mass fractions of total Br (*inter-method reproducibility*); and the repetition of the analysis for total Br as well as individual BFRs
- by laboratory 1 for samples already prepared (and analysed) by laboratory 2 and vice-versa (*inter-laboratory reproducibility*);
- on field duplicates (subsamples *c*) for a selection of samples in which relatively high Br mass fractions were initially measured by either laboratory (*field reproducibility*).

2.5. Data handling

Laboratory 1 provided measurement results down to the limit of detection which was estimated individually for each measurement based on sample characteristics, sensitivity of the equipment at the moment of the analysis and eventual disturbances and dilutions. Laboratory 1 reported the measurement values indicating three significant figures. Laboratory 2 reported measurement results down to the limit of quantification calculated as 10 times the standard deviation resulting from a 7-fold determination of the blank value. Laboratory 2 reported the measurement values indicating two significant figures. For samples in which analytes could not be detected/quantified the reported detection or quantification limits were considered as the measured values, thus representing a worst-case scenario. Initial and supplementary analyses of Br and individual BFRs have provided multiple measurements for some lots. In such cases the average value of all results available for a specific lot was considered as this is the common practice when comparing mass fractions of specific substances in that lot with threshold values for these substances (BAFU, 2017b).

3. Results and discussion

3.1. Chemical and physical characterization

3.1.1. Brominated flame retardants

The average mass fractions of Br and individual BFRs measured by both laboratories in all samples from each lot (batch) are shown in Fig. 2. The standard deviation of Br measurements is displayed for lots with more than one available measurement value. The results of all chemical analyses can be found in tables S3 and S4 in Section 3 of the Supporting Information. A large share of the total Br measured in samples from several lots has an “unknown” origin i.e., its presence cannot be attributed to the individual BFR compounds measured. Such high shares (>60%) of unknown Br in WEEE plastic samples have been repeatedly observed in previous studies (Bantelmann, 2010; Morf et al., 2005; Schlummer et al., 2007; Straat and Nilsson, 2018; Wäger et al., 2012; Zennegg, 2011). Possible explanations include the presence of additive BFRs not analysed (more than 80 BFR compounds are commercially available, only seven were analysed in this study) and reactive BFRs i.e., covalently bound to the polymer matrix and therefore associated with low extraction rates during sample digestion. Total BFR loads in CFA plastic samples were measured below 500 mg/kg in all but one lot. This result aligns with the total Br measurements for CFA plastic samples, none of which exceeded 1000 mg/kg. For lot CFA11 a total BFR load of 1200 mg/kg was obtained. However, this result does not align with the total Br measurement (502 mg/kg) which indicates that the BFR content might have been overestimated in this lot. In LHA plastic samples higher total BFR loads were measured with several lots exceeding 1000 mg/kg. The maximum obtained measurements values for restricted BFRs in LHA plastic samples were <5 mg/kg (LOD) for hexa-BB, 791 mg/kg for Σ PBDEs and 115 mg/kg for HBCDD. The maximum obtained measurements values for restricted BFRs in CFA plastic samples were <5 mg/kg (LOD) for hexa-BB, 382 mg/kg for Σ PBDEs and <50 mg/kg (LOD) for HBCDD. The currently applicable legal threshold values (50 mg/kg for hexa-BB, 1000 mg/kg for Σ PBDEs and HBCDD) as specified in the European POP regulation were not exceeded in any of the samples. The 2000 mg/kg Br separation threshold above which plastics streams from other WEEE categories have to undergo a BFR separation process in order to be recycled was exceeded in 4 out of 14 LHA lots (max. measurement value: 5100 mg/kg) and none of the CFA lots (max. measurement value: 870 mg/kg). These results confirm the assumption that levels of restricted BFRs in mixed WEEE plastics from LHA and CFA are sufficiently low to guarantee legal compliance also regarding the lower threshold for PBDEs introduced in the 2019 recast of the POP regulation without the need to separate BFR-containing fractions, and that this assumption holds true even when the total Br content is above 2000 mg/kg.

However, the results also show that in case of a further reduction of the threshold value for Σ PBDEs to 500 mg/kg the assumption would lose its validity for LHA plastics as in various LHA samples values in close vicinity to 500 mg/kg Σ PBDE were obtained and in one sample this threshold was exceeded by over 50%.

3.1.2. Heavy metals

The currently applicable legal threshold values for heavy metals in homogeneous materials used in newly marketed EEE as defined in the RoHS Directive are 1000 mg/kg for lead, mercury and hexavalent chromium and 100 mg/kg for cadmium. The results of our study indicate that the mass fractions of Cd, Hg and Cr(VI) in WEEE plastics from CFA and LHA are well below the RoHS threshold values with measurements indicating mass fractions below 15 mg/kg in all but one sample for which laboratory 1 measured 43 mg/kg Hg. In the case of lead measurement ranges of 40 mg/kg – 960 mg/kg for CFA samples and 1 mg/kg (LOD) – 530 mg/kg for LHA samples were found. Possible sources of Pb in mixed WEEE plastics include lead-based polymer additives such as heat stabilisers in PVC or pigments as well as cross-contamination from other WEEE components during treatment (Wäger et al., 2012). Measurement values for antimony were found within the range of 20 mg/kg (LOD) – 1200 mg/kg for LHA and 20 mg/kg – 251 mg/kg for CFA samples. Both laboratories determined considerably higher median Sb mass fractions for LHA plastic samples. These results align with the previous observation that LHA plastics also contain higher amounts of BFRs, as in WEEE plastics Sb is almost exclusively found as antimony trioxide (Sb_2O_3) which is commonly used as a synergist with BFRs (Morf et al., 2007). Although its use is not restricted on a legal bases at present, antimony trioxide is listed under the CoRAP (community rolling action plan) list of substances (ECHA, 2019) which establishes the substances to be evaluated under REACH in the coming years. It is therefore possible that antimony trioxide will become a legacy substance in WEEE plastics in the future which might have potential implications for the recyclability of plastics from large household appliances considering the relatively high mass fractions of antimony found in some LHA plastic samples in our study.

3.1.3. Other additives

Besides BFRs and heavy metals, plastic samples were also analysed regarding their content of Ca, Si, Ti, Mg, Al, Cl and P which are major constituents of commonly used plastic additives. Ca in the form of calcium carbonate (CaCO_3) is the main filler found in polypropylene (PP) where it is used to reduce cost and increase stiffness (Rothon and Paynter, 2017). Si can be found in a wide range of fillers. Mainly in glass-fibre, which generally contains more than 50% SiO_2 but also other oxides such as Al_2O_3 , CaO and MgO (Chawla, 2016), magnesium silicate ($\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$, also known as talc, and aluminium silicate (Al_2SiO_5)

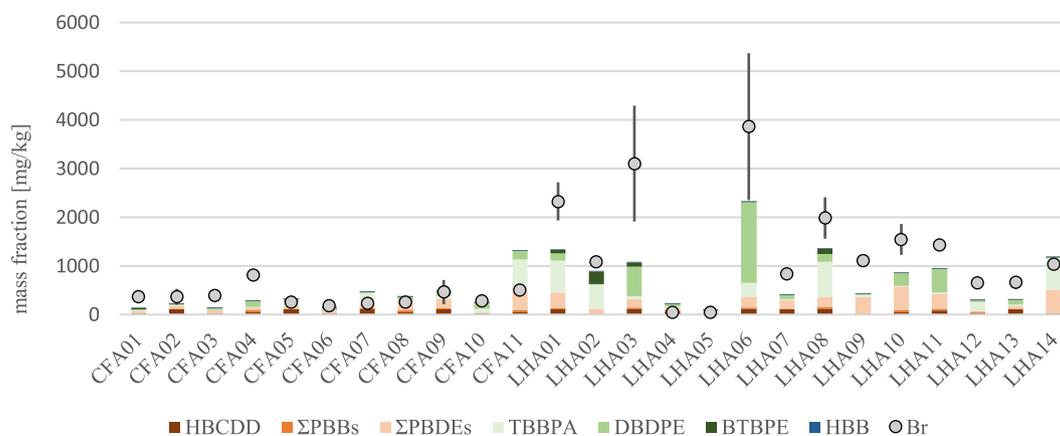


Fig. 2. Average of total Br and individual BFRs measured in samples from each lot. The standard deviation of total Br measurements is displayed for samples with more than one available measurement value.

(Maris et al., 2015). Glass-fibre is frequently added to PP and to a lesser degree to polystyrene (PS), polycarbonate (PC) and polycarbonate-acrylonitril butadiene styrol blend (PC-ABS). Ti can be found in WEEE plastics in the form of titanium dioxide (TiO_2) which is a low-cost and high-effective pigment used both as a white colourant and a filler (Datta et al., 2016). Mg and Al can both be found in flame retardants (e.g. as magnesium hydroxide $\text{Mg}(\text{OH})_2$ resp. aluminium trihydroxide $\text{Al}(\text{H}_2\text{O})_3$) and fillers (e.g. talc resp. aluminium silicate) (Maris et al., 2015). Cl is one of the main constituting elements of polyvinylchloride (PVC) and is used in flame retardant compounds (e.g. chlorinated organophosphates) while P indicates the use of phosphorus-based flame-retardants (e.g. aryl phosphate sometimes used in PC/ABS (Höroid, 2014)). Fig. 3 shows the measured mass fractions of these elements in LHA and CFA plastic samples. The sum of median mass fractions reaches 10.4% for LHA plastics and 3.9% for CFA plastics. Considering that these elements only represent a fraction of the molecules in which they are embedded and that other types of additives may be present but were not considered in our study, it can be assumed that the effective loads of additives in these plastic streams are considerably higher still. Main elements measured in LHA samples were Ca (5.5%), Si (2.5%), Mg (1.1%), Al (1.0%) and Cl (0.3%) by descending order of median mass fraction. The high abundance of Ca suggests widespread presence of PP filled with CaCO_3 in LHA plastic streams. Silica-based fillers further account for the relatively high levels of Si as well as the Mg and Al loads, part of which could potentially also be traced to Mg and Al based flame-retardants. Cl was only measured in low mass fractions which suggest that PVC and Cl based flame-retardants are rarely present in LHA plastics. Main elements measured in CFA samples were Cl (1.2%), Ca (1.2%), Al (0.6%), Si (0.5%) and Mg (0.2%) by descending order of median mass fraction. The higher levels of Cl measured in CFA plastic samples (1.2%) suggests more widespread use of PVC plastics and potentially Cl based flame-retardants in CFA. Moderate Ca levels indicate that CaCO_3 filled PP is also regularly used in CFA while the Si/Al/Mg ratio suggests the presence of some glass fibre and aluminium silicate fillers. P was measured in relatively low quantities in all samples from both LHA and CFA plastics (median = 0.02% and 0.04% respectively), which indicates that phosphorus-based flame-retardants are uncommon in these plastic streams. Ti measurements showed high discrepancies between the two laboratories with laboratory 1 obtaining Ti mass fractions between 2 mg/kg and 229 mg/kg and laboratory 2 between 4400 mg/kg and 10 000 mg/kg. According to laboratory 2, the chemical analysis of Ti is challenging and highly dependant on a full sample digestion. An over-estimation can result from a trivial mistake such as a cross contamination or a calibration mistake, however a systematic overestimation for all samples is unlikely as not all samples have been analysed at the same time and by the same analyst. A systematic underestimation on the other hand could be the result of insufficient sample digestion. The information received by laboratory 2 as well as the differences in sample preparation (laboratory 1 reduced grain size to 0.5 mm, laboratory 2 to

0.12 mm) suggest that laboratory 1 might have systematically underestimated Ti mass fractions due to insufficient sample digestion. However, a final conclusion regarding this issue cannot be made based on the available data. Despite these uncertainties the results suggest that titanium dioxide accounts for a minor share of the plastic additives identified in LHA and CFA plastics which are dominated by mineral fillers based on Ca, Si, Al and Mg.

3.1.4. Density profiles

Fig. 4 displays the results of the density analysis performed using density separation. The distribution (mass fraction) of samples amongst four different ranges of densities is indicated. Results show that LHA samples are relatively heavy. On average 70% of the total mass of the LHA plastics have a density above 1.10 g/cm^3 . CFA samples were found to be less dense with on average 80% of the total mass of CFA plastics having a density lower than 1.10 g/cm^3 . The obtained density distribution provides information on the polymer composition and additive content as plastic densities are dependant on these attributes. The highest density fraction ($>1.25 \text{ g/cm}^3$) likely contains a majority of PVC (soft and hard), rubber and highly filled PP and PC. This fraction also contains residual metallic particles that were not previously removed during sample preparation. Fractions with a density between 1.10 g/cm^3 and 1.25 g/cm^3 likely contain brominated plastics (mainly ABS and high-impact polystyrene HIPS), PC-ABS (with or without flame-retardants), medium-filled PP and soft PVC. Materials with a density in the $1.00\text{--}1.10 \text{ g/cm}^3$ range can be expected to consist of mainly ABS and HIPS (non-brominated), PS and medium filled PP. The lightest fraction (density $< 1.00 \text{ g/cm}^3$) contains a majority of unfilled PP and PE as well as residual wood and foam particles. These results align with the chemical analyses regarding non-brominated additives which showed that LHA and, to a lesser extent, CFA plastics contain significant loads of additives, particularly fillers such as calcium carbonate, glass-fibre, talc and aluminium silicate.

3.2. Data quality assessment

3.2.1. Analytical accuracy

The certified and measured mass fractions of BFRs (Deca-BB and PBDEs) and total Br for the analysed CRMs are shown in Fig. 5 (left and centre). Results suggest that both laboratories tend to overestimate BFR mass fractions, laboratory 1 obtaining a lower value only for Hepta-BDE, laboratory 2 for Hepta- and Octa-BDE. Laboratory 2 obtained measurement values within- or very close to the 95% confidence interval of the certified content for all compounds but Deca-BDE where the reported value lies 69% above the certified content. The results obtained by laboratory 1 are less accurate. The reported values lie 33% – 184% above the certified content for all compounds but Hepta-BDE for which the limit of quantification (5 mg/kg) was reported despite a certified content of 132 mg/kg. Results regarding total Br indicate that analysis by IC as

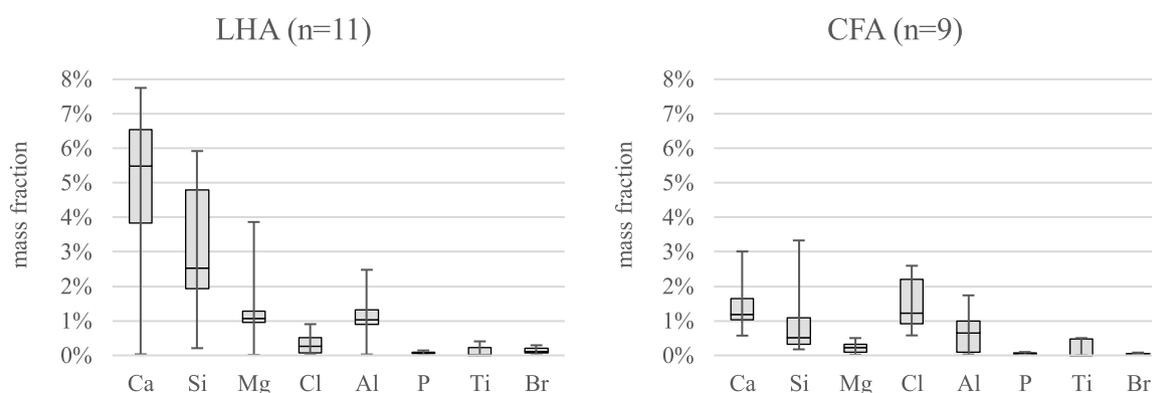


Fig. 3. Mass fractions for tracers of common additives in LHA and CFA plastic samples.

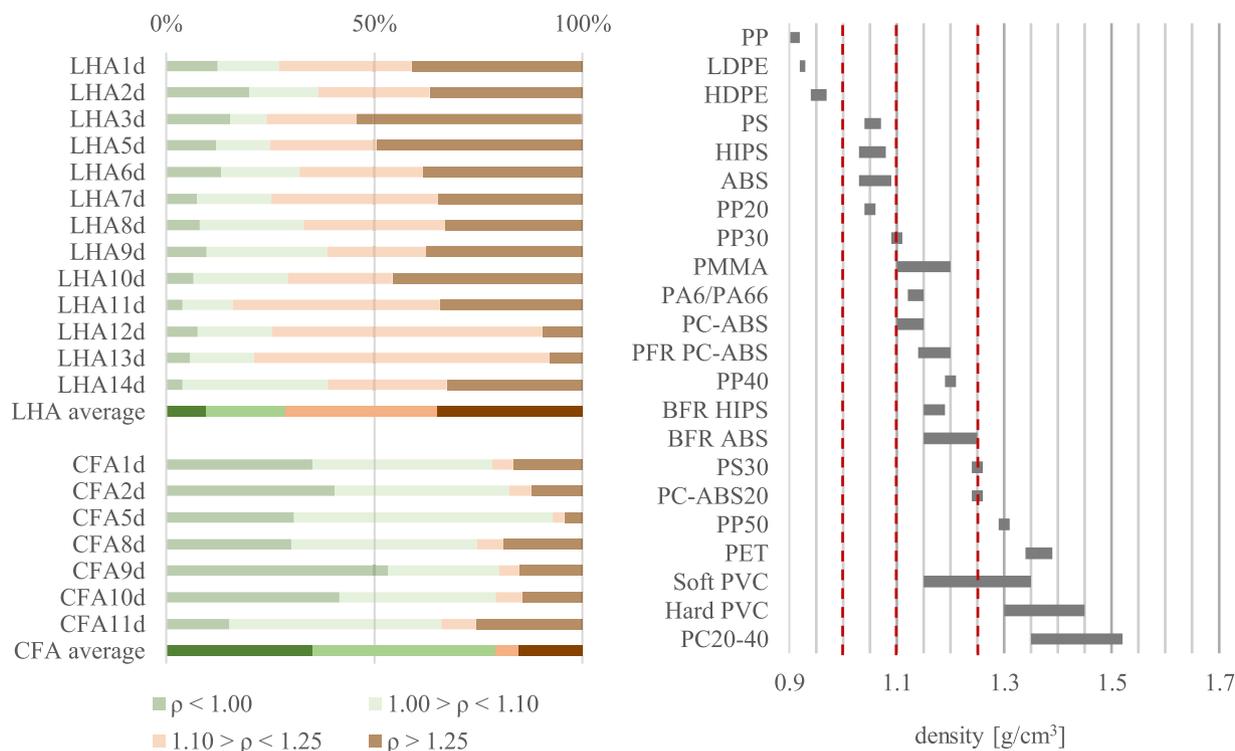


Fig. 4. Left: Density distribution of LHA and CFA plastic samples (density ρ in g/cm^3). Right: Density range of common WEEE plastics based on (Köhnlechner, 2014), (Omnexus - SpecialChem, 2019) and (Tange et al., 2012). Dashed vertical red lines represent density thresholds used for sink/float separation. PFR = Phosphorus Flame Retardants. BFR = Brominated Flame Retardants. PP20/30/40/50 = PP filled with 20/30/40/50% glass-fibre, talc or other mineral fillers. PS30 = PS filled with 30% glass-fibre. PC20–40 = PC with 20–40% glass-fibre. PC-ABS20 = PC-ABS filled with 20% glass-fibre.

performed by both laboratories provide relatively accurate measurements of Br mass fraction ranging from -14% to $+12\%$ compared to the certified content. Laboratory 1 tends to slightly underestimate Br content (-14% – -8%) while laboratory 2 obtained slightly higher values ($+3\%$ – $+12\%$). Furthermore, semi-quantitative analysis by XRF as performed by laboratory 1 seems to provide a relevant basis to crosscheck IC measurements with the obtained Br mass fractions being very close to the certified amounts for all reference materials. On the other hand, XRF analysis by laboratory 2 tends to underestimate the total Br content, the reported mass fractions ranging from -6% to -44% compared to the certified Br level.

3.2.2. Analytical reproducibility

Fig. 5 (right) shows the ranges of relative percent difference (RPD) values calculated for repeated measurements of total Br and BFRs.

$$RPD (\%) = \frac{|x_1 - x_2|}{\frac{x_1 + x_2}{2}} * 100 \quad (1)$$

Laboratory 2 performed total Br measurements for all samples in triplicate. RPD values regarding intra-laboratory repeatability of laboratory 2 were calculated using the minimum and maximum of the three obtained values. All other repeated analysis were done once for a selection of samples for which the initial measurement for total Br resulted in values above 1000 mg/kg . Measurement pairs from repeated analysis of total Br and individual BFRs were considered in the assessment of analytical reproducibility if deterministic values were reported for both the initial and repeated analysis, as well as when a deterministic value was reported only for one of the two measurements, in which case the reported detection or quantification limit was considered as the measured value for the non-deterministic result. In case both the initial and repeated measurement were reported to lie below the respective limits of detection or quantification the value pair was not considered in the assessment of analytical reproducibility. The median RPD value for

intra laboratory repeatability regarding total Br analysis by IC is 23% while the maximum observed RPD value is 87% . RPD values regarding inter-laboratory reproducibility (median = 18% , max = 84%) and inter-method reproducibility (median = 25% , max = 56%) were obtained in a similar range. The same applies for field reproducibility where, with the exception of one lot (LHA06, RPD = 119%), all RPD values were obtained below 50% . The observed RPD values between repeated measurements of BFRs were considerably higher with median values of 94% and 94% and maximum values of 139% and 191% , respectively, for inter-laboratory- and field reproducibility. The higher variability for inter laboratory reproducibility regarding individual BFR compounds compared to total Br aligns with the results regarding analytical accuracy which showed that both laboratories measure total Br levels more precisely than BFRs. The higher variability in field reproducibility can further be explained by the fact that the load of one specific BFR compound is less equally distributed amongst the plastic flakes of a sample than the load of total Br. When a sample is split into subsamples the distribution of individual BFRs amongst the obtained subsamples thus tends to be more variable than the distribution of total Br. The data quality assessment performed in our study shows that the quantification of contaminants in mixed WEEE plastics is subject to substantial uncertainties. RPD values for repeated measurements of total Br were generally obtained in the range of 10% – 50% which, according to laboratory 2, corresponds to the typical range for the combined expanded uncertainty regarding the determination of inorganic elements in solid waste samples. Inter-laboratory reproducibility and, with the exception of lot LHA06, field reproducibility analysis did not indicate the introduction of additional uncertainty which suggests that by adhering to the relevant standards along all sampling and analysis steps the uncertainty in total Br analysis for WEEE plastics can, in general, be minimized and is mostly driven by analytical uncertainty. In the case of BFRs laboratory 2 indicates the typical range for the combined expanded uncertainty regarding determination of BFR compounds in solid waste

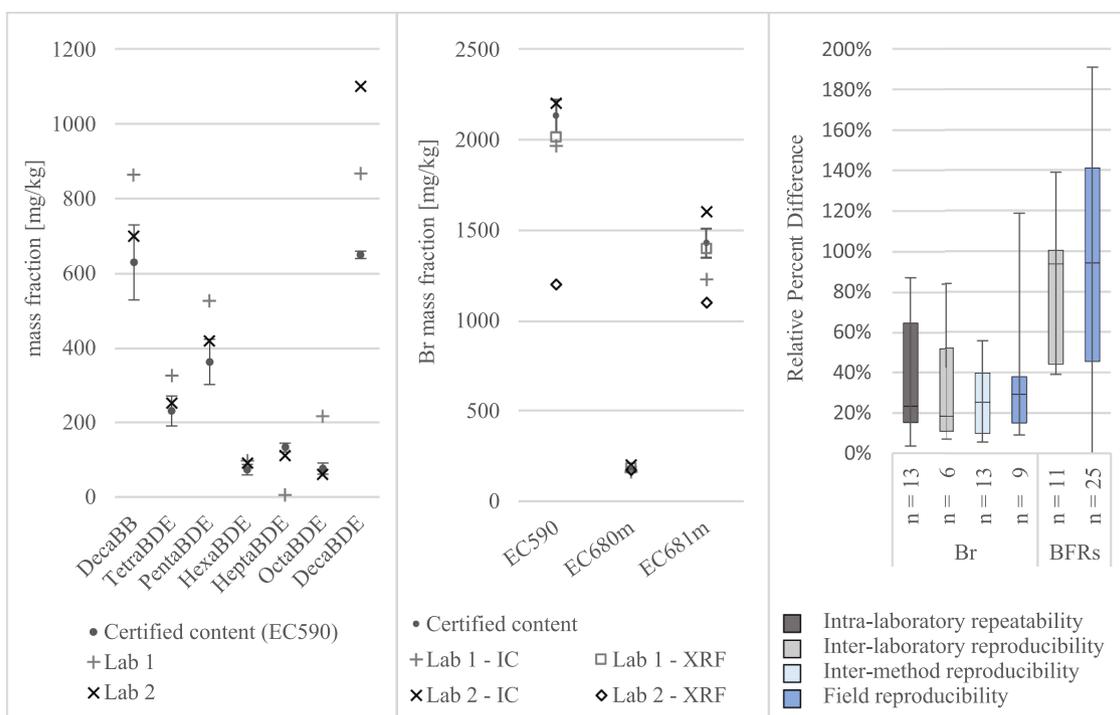


Fig. 5. *left:* Certified and measured mass fractions of brominated flame-retardants (PBDEs and decaBB). The error bars indicate the estimated expanded uncertainties of the certified value with a coverage factor $k = 2$ corresponding to a level of confidence of about 95%. *centre:* Certified and measured mass fractions of total Br. *right:* Range of relative percent difference (RPD) between repeated measurements of Br and individual BFRs. RPD values for inter laboratory reproducibility of BFR analysis are indicated based on repeated measurement of Σ PBDE and TBBPA. RPD values regarding field reproducibility of BFR analysis are indicated based on repeated measurements of Σ PBDE, TBBPA, DBDPE, BTBPE and HBCDD.

samples as 25% to 40%. Inter-laboratory reproducibility and field reproducibility analysis regarding individual BFRs resulted in significantly higher RPD values, thus indicating that in the case of BFR analysis relevant additional uncertainties were introduced during sampling and analysis steps.

3.2.3. Implications for the verification of threshold values

The data quality assessment performed in our study showed that despite the application of a detailed sampling plan based on relevant standards and previous experiences representative sampling regarding total Br could not be achieved for all lots and was even more challenging for individual BFR compounds. This could indicate that despite all efforts the homogenisation achieved during sampling was not sufficient. However, some authors also suggest that representative sampling regarding total Br in mixed WEEE plastic fractions is not actually possible using the sample sizes recommended by European WEEE treatment standards (7.5 – 25 liters recommended by the EN 50625 series) and that a minimum sample size of 60 – 250 litres would actually be required (Hennebert, 2019). While the representativeness of a sample could potentially be improved by increasing the sample size, this would also entail a high increase in cost and effort regarding sampling and sample preparation. In addition, we consider it unlikely that during day-to-day operations at WEEE treatment facilities the sampling procedures are carried out as carefully as during our study. It therefore has to be assumed that relevant uncertainties are introduced due to insufficient homogenisation when samples are taken under standard conditions and that a larger sample size might improve but cannot guarantee the representativeness of the obtained sample. Although the best currently available option, the verification of legal threshold values for restricted BFRs in mixed WEEE plastic fractions based on chemical analysis has its limits. The closer the mass fraction measured in the analysed sample is to the legal threshold value, the lower the level of confidence that the decision reached regarding legal compliance and the

need for BFR separation is valid for the sampled plastic fraction. This becomes more pronounced the closer the set threshold value gets to the limit of quantification and in the extreme case a threshold value below the limit of quantification is chosen. Such a situation would arise in case the 50 mg/kg provisional low POPs limit for Σ PBDEs suggested in the Basel Convention technical guidelines is introduced as a binding threshold value, since it is below the quantification limit for Σ PBDEs (100 mg/kg according to laboratory 2). In this scenario a conclusion regarding legal compliance could not be reached based on chemical analysis. Lacking alternative verification procedures such a situation would likely stop WEEE plastic recycling altogether.

3.3. Time trend of BFR and heavy metal mass fractions in LHA and CFA plastics

In order to investigate the time trend of BFR and heavy metal mass fractions in LHA and CFA plastics the results presented within this paper are plotted against the data published in (Wäger et al., 2012) in Fig. 6. This comparison is pertinent as similar sampling and analytical methods were applied in both studies. The comparison of median measurement values for LHA and CFA samples suggests that between 2009 and 2017 (years of the respective sampling campaigns for the two studies) total Br levels have increased in both LHA as well as CFA plastics. When comparing median BFR values it appears that PBDE levels have decreased in LHA plastics and remained low in CFA plastics, whereas TBBPA levels have increased in both waste streams. PBBs were, and are still, not found in measurable amounts in both LHA and CFA plastics. In the case of heavy metals levels of Cd and Hg remain very low, Pb mass fractions are decreasing in both LHA and CFA plastics and Cr(IV), previously found at substantial levels in both LHA and CFA plastic streams, was not detected in any of the samples analysed in our study. Mass fractions of Sb were found to be slightly higher in both LHA and CFA plastic streams compared to the values reported in 2012. These trends

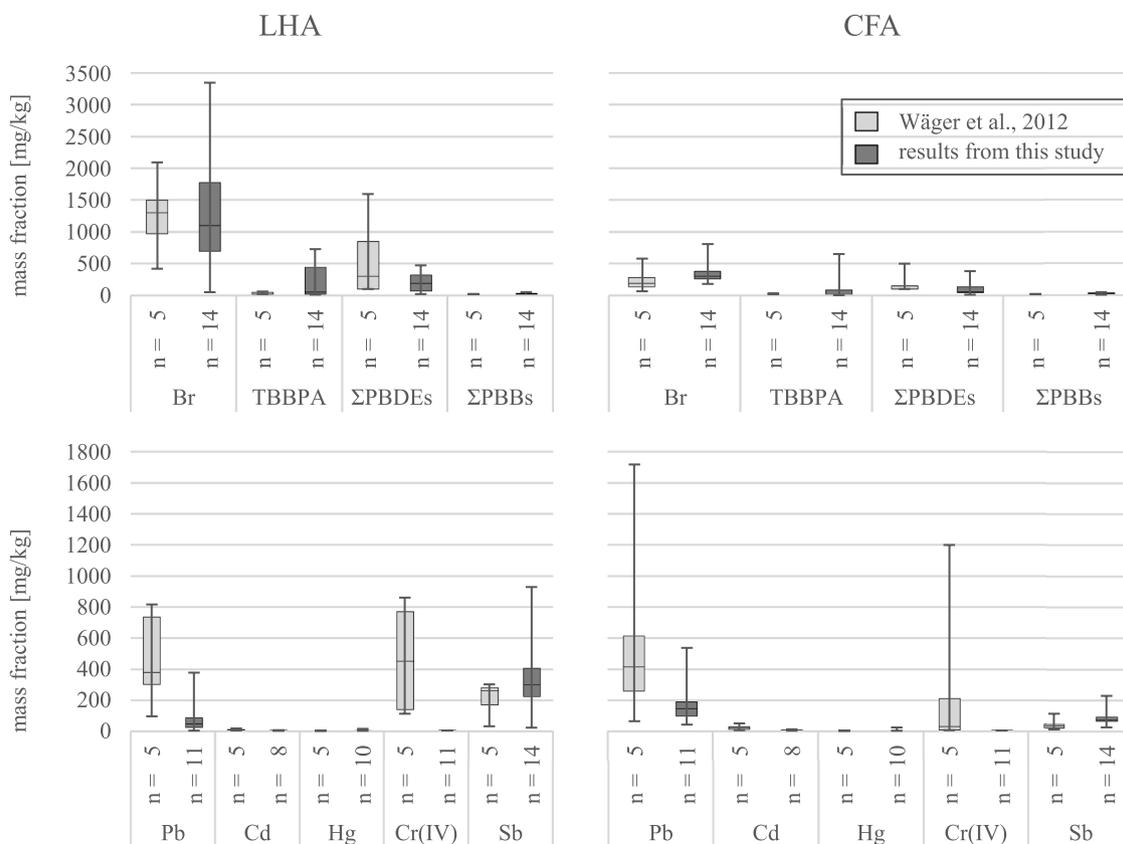


Fig. 6. Comparison of total Br, BFR and heavy metal analysis results with (Wäger et al., 2012).

indicate that restricted BFRs and heavy metals are progressively phased-out. At the same time an increase in total Br levels as well as TBBPA and antimony can be observed, indicating that this phase out is compensated by the use of non-restricted BFRs in synergy with antimony trioxide and that the overall BFR load is increasing. TBBPA and antimony trioxide are listed under the CoRAP list of substances to be evaluated under REACH (ECHA, 2019) and were also included in the latest review of substances to be regulated under the RoHS Directive where an inclusion has been suggested for TBBPA (European Commission, 2020). Considering these developments, TBBPA and antimony trioxide might soon become additional legacy substances in WEEE plastics, further inhibiting material recycling of these waste streams. This shows that the substitution of restricted additives by alternative chemicals does not solve the challenges in WEEE plastic recycling in the long run and that in order to increase the material recycling potential for WEEE plastics a general reduction in the use of flame retardants should be targeted instead. (Charbonnet et al., 2020) argues that the use of flame retardants is often driven by flammability standards which poorly represent real-world fire risks. The redesign of flammability standards based on more real-life fire scenarios could thus play a major role in decreasing flame retardant use and lead to improved framework conditions for a clean circular economy in the WEEE sector.

4. Conclusions

According to the results of our study mixed plastics from the processing of LHA and CFA waste streams do not contain hazardous substances above currently applied legal thresholds for recycling. The results are robust in the sense that samples were collected from a relatively large number of WEEE processing plants located in various European countries and according to a detailed sampling plan developed based on relevant standards and previous experiences. Despite repeated analyses by two independent laboratories the legal threshold values for

restricted BFRs and heavy metals were not exceeded in any sample even when considering maximum measurement values. The exemption from the 2000 mg/kg Br threshold value for mixed plastics from LHA and CFA, as currently applied in European WEEE treatment standards, therefore remains valid according to our study. However, in various LHA samples values in close vicinity to 500 mg/kg ΣPBDEs were obtained and in one sample this threshold was exceeded by over 50% while the levels of both TBBPA and antimony trioxide in LHA and CFA plastics have been increasing over the last years. Considering that PBDEs, TBBPA and antimony trioxide are under consideration for stricter regulation in the EU, it is likely that the exemption from BFR-separation for plastic streams from large household appliances will not remain valid in the future. Consequently, the BFR content in these plastic streams would have to be monitored in order to decide whether a BFR-separation process is required in the downstream treatment which, in the case of density separation, would lead to a material loss of 70% for LHA plastics and 20% for CFA plastics. The observed time trends regarding flame retardant use and regulation of chemicals thus show that the substitution of restricted chemicals with alternative additives does not improve material circularity in the long run, which would benefit much more from a general reduction regarding flame retardant use.

The results presented in this paper showcase that the transition to a clean circular economy is a balancing act in which policies need to be designed based on a holistic viewpoint. While updated flammability standards could lead to a general reduction of flame retardant use and thus increase the circularity of WEEE plastics in the future, legacy substances will remain a challenge in WEEE plastic recycling for many years to come. Although it is desirable to minimize the circulation of legacy substances during recycling processes as much as possible this comes at the cost of losing resources for the circular economy. The data quality assessment performed in our study shows that representative sampling of mixed WEEE plastics regarding Br and BFRs is very challenging and that the analytical precision for the determination of these substances is

limited. The level of confidence with which a decision is taken regarding the recyclability of WEEE plastics is therefore relatively low, especially when results are obtained in close vicinity of the threshold value. When specific tolerance levels for legacy substances in recyclates are set, the trade-offs between benefits and losses as well as whether or not the chosen tolerance level can be controlled and enforced with a satisfactory level of confidence should therefore be assessed carefully.

CRedit authorship contribution statement

Andreas Bill: Writing – original draft, Writing – review & editing, Visualization, Validation. **Arthur Haarman:** Funding acquisition, Conceptualization, Methodology, Investigation, Writing – original draft, Visualization, Validation, Project administration. **Michael Gasser:** Conceptualization, Methodology. **Heinz Böni:** Funding acquisition, Supervision. **Matthias Rösslein:** Methodology, Validation. **Patrick A. Wäger:** Funding acquisition, Supervision, Writing – review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.resconrec.2021.105956](https://doi.org/10.1016/j.resconrec.2021.105956).

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