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Bromine in plastic consumer products – evidence for the widespread recycling of electronic waste

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Abstract

A range of plastic consumer products and components thereof have been analysed by x-ray fluorescence (XRF) spectrometry in a low density mode for Br as a surrogate for brominated flame retardant (BFR) content. Bromine was detected in about 42% of 267 analyses performed on electronic (and electrical) samples and 18% of 789 analyses performed on non-electronic samples, with respective concentrations ranging from 1.8 to 171,000 μg g^{-1} and 2.6 to 28,500 μg g^{-1}. Amongst the electronic items, the highest concentrations of Br were encountered in relatively small appliances, many of which predated 2005 (e.g. a fan heater, boiler thermostat and smoke detector, and various rechargers, light bulb collars and printed circuit boards), and usually in association with Sb, a component of antimony oxide flame retardant synergists, and Pb, a heavy metal additive and contaminant. Amongst the non-electronic samples, Br concentrations were highest in items of jewelry, a coffee stirrer, a child's puzzle, a picture frame, and various clothes hangers, Christmas decorations and thermos cup lids, and were often associated with the presence of Sb and Pb. These observations, coupled with the presence of Br at concentrations below those required for flame-retardancy in a wider range of electronic and non-electronic items, are consistent with the widespread recycling of electronic plastic waste. That most Br-contaminated items were black suggests the current and recent demand for black plastics in particular is met, at least partially, through this route. Given many Br-contaminated items would

58 evade the attention of the end-user and recycler, their disposal by conventional
59 municipal means affords a course of BFR entry into the environment and, for food-
60 contact items, a means of exposure to humans.
61
62 **Keywords:** XRF; bromine; consumer products; electronic waste; recycling

1. Introduction

Plastic is the dominant component of waste electrical and electronic equipment (WEEE) and, having superior mechanical and thermal properties to plastics used in most other applications, is attractive for recycling. However, because a significant fraction of WEEE plastics contain brominated flame retardants (BFRs), there are constraints on how such materials are disposed of or reprocessed (Tange and Slijkhuis, 2009; Buekens and Yang, 2014). According to the 2001 Stockholm Convention and its various amendments, waste containing persistent organic pollutants (POPs) should be eliminated from the recycling stream and not intentionally diluted with compliant materials to prevent the reappearance of restricted chemicals in new products and minimise potential for release in to the environment (UNEP, 2011). BFRs classified accordingly include hexabromocyclododecane (HBCDD), hexabromobiphenyl, and the commercial polybrominated diphenyl ethers (PBDEs), penta-BDE and octa-BDE.

The discrimination between restricted and non-restricted BFRs in WEEE plastics by, for example, solvent extraction and gas chromatography, is timely and costly. Moreover, the number and variety of BFRs that have been employed in plastics means that many compounds may evade detection (Morf et al., 2005). The European Committee for Electrical Standardization (CENELEC) therefore stipulates that, in practice, waste containing (total) Br concentrations in excess of 2000 $\mu g\ g^{-1}$ by weight should be removed and destroyed or depolluted (Stenmarck et al., 2017). Dismantling and subsequent sorting by polymer type and Br content is, nevertheless, labour-intensive, and many countries, including the US and EU, have elected to bale WEEE

and ship it to China, India or Nigeria to be recycled or disposed of (Ni et al., 2013; Obaje, 2013; Haarman, 2016).

Despite attempts to 'close the loop' on harmful BFRs, they have recently been detected in a variety of consumer products that do not require flame retardancy or at concentrations insufficient to provide fire protection, including children's toys (Ionas et al., 2015), kitchen utensils (Samsonek and Puype, 2013), beaded garlands (Miller et al., 2016) and flooring products (Vojta et al., 2017). Thus, in many cases, recycled plastics from WEEE appear to have been used, in whole or in part, to manufacture contemporary electrical and non-electrical products that may not themselves be compliant.

In a recent article, we demonstrated the ubiquity of Sb amongst polymeric consumer products by means of a portable Niton x-ray fluorescence (XRF) spectrometer configured in a low density mode and with thickness correction (Turner and Filella, 2017). The metalloid was often encountered with similar or greater concentrations of Br in both electrical-electronic goods or components and non-electronic products, indicative of the presence of BFRs in association with oxides of Sb as flame retardant synergists. Here, we employ XRF spectrometry to determine total Br among a wider range of plastic consumer products as a proxy for evaluating the abundance and distribution of BFRs in the indoor setting. The approach has been validated by independent analytical methods and with customized, polymeric standards containing specific BFRs (Guzzonato et al., 2016), and is gaining increasing application in the WEEE recycling industry as a practical solution to accurately and rapidly monitor for

material compliance with limit concentrations (Löw, 2014; Gallen et al., 2014; Aldrian et al., 2015).

2. Materials and methods

2.1. Material access, collection and categorisation

A total of 1000 items and fixtures ('samples') of moulded hard and soft plastic construction (i.e. excluding foams, paints, rubbers, waxes and textiles) were accessed or sourced from domestic dwellings in Plymouth, offices and the nursery on the Plymouth University campus, a local primary school, a number of nationwide hardware stores and supermarkets, and a variety of local establishments serving fast and/or takeaway food and beverages.

Depending on their location and principal use, samples or distinct components thereof were categorised as electronic (encompassing both electronic and electrical items) and non-electronic. The former category embraces all items dependent on electric currents or electromagnetic fields in order to work, and includes small and large household appliances, IT equipment, lighting, toys and tools. The latter, broader category was further sub-categorised as food-hygiene (food packaging, drinks bottles, cutlery, flasks, lunch boxes, cosmetics, medicines), construction-storage (plumbing, worktops, fixtures, flooring, frames, cans, cases, hangers), tools-office (stationery, DIY, adhesive taping, book covers, noticeboards), leisure (toys, games, sports gear, hobbies, crafts, Christmas decorations, trophies) or clothing-accessories (raincoats, jewellery, straps, rucksacks, shoes, spectacles, hairbrushes, buttons). For each sample, and where evident, the place of manufacture and type of plastic were recorded, along with the colour of the area(s) to be measured (sometimes revealed below a layer of

paint); electronic products were also categorised as historic or non-historic according to the original WEEE Directive relating to collection, recycling and recovery targets for electrical goods (European Parliament and of the Council, 2003). While the surface or casing of most samples was investigated, some end-of-life electronic goods were dismantled and interior components analysed separately.

2.2. XRF analysis

Samples were analysed by energy-dispersive field-portable-XRF using a Niton XL3t 950 He GOLDD+ that was employed either in situ and handheld or in the laboratory and housed in a 4000 cm^3 Thermo Scientific accessory stand. The Niton XL3t employs a miniature x-ray tube that operates at up to 50 kV of high voltage and 200 μA of current as the source of sample excitation, and is fitted with a geometrically optimised large area silicon drift detector to detect characteristic x-rays from the sample. The instrument was operated in a 'plastics' mode through a standardless, fundamental parameters-based alpha coefficient correction model that is capable of simultaneously compensating for a wide variety of geometric and fluorescent effects. Because plastics are composed of light elements that are weak absorbers and relatively strong scatterers of x-rays, a thickness correction algorithm down to 50 μm that employs a compensation for mass absorption based on Compton scattering was also applied. Although a suite of elements may be determined in this mode, the present study focuses on Br as an indicator of BFR content, as well as Sb as a measure of the retardant synergistic content, Cl for the discrimination of PVC- and non-PVC-based materials, and Pb as a hazardous heavy metal that is often encountered as an additive or contaminant in WEEE and consumer plastics (Wäger et al., 2012).

In practice, sample thickness was determined through the flattest or smoothest (measurement) surface using 300 mm Allendale digital callipers, and to increase the effective depth and flatness of thin or hollow samples analysed in the accessory stand, items were cut (with scissors, pliers or a blade), folded or layered. The corrective algorithm was employed for all samples whose measured thickness was less than 20 mm, while an estimated value was applied to objects and components whose interiors were inaccessible or that were fixed to or components of walls, floors, windows, doors and appliances.

In the laboratory, samples were placed on the stainless steel base plate of the accessory stand with the measurement surface above the XRF detector window or, for samples smaller than the 10 mm window diameter, on to a SpectraCertified Mylar polyester 3.6 μm film that was carefully suspended above. On closing the stand shield, measurements with appropriate thickness correction and collimation (3 mm or 8 mm beam width) were activated through the laptop. Specifically, an initial, ~ 2-second matrix evaluation based on the measurement of characteristic chlorine peaks (and defining PVC as Cl > 15% by weight) was succeeded by counting periods equally distributed between a low energy range (20 kV and 100 μA) and main energy range (50 kV and 40 μA). A 45-second counting period was normally adopted, but periods of up to 200-seconds were employed for thinner, less attenuating materials. Spectra were quantified by fundamental parameter coefficients to yield elemental concentrations on a dry weight basis (in $\mu g\ g^{-1}$) and with a measurement counting error of 2σ (95% confidence) that were downloaded to the laptop via Niton data transfer (NDT) software. For quality control purposes, plastic reference discs supplied by the manufacturer and certified for $495 \pm 20\ \mu g\ g^{-1}$ Br and $1002 \pm 40\ \mu g\ g^{-1}$ Pb in

polyethylene (PN 180-554, batch SN PE-071-N), 96±10 μg g^{-1} Sb and 150±12 μg g^{-1} Pb in polyethylene (PN 180-619, LOT#T-81), and 996±50 μg g^{-1} Br and 1025±51 μg g^{-1} Sb in PVC (SN PVC-4C80, cal set #16) were analysed at the beginning and end of each 1-4 h sample measurement session.

For measurements of permanent fixtures or items too large to be contained within the accessory stand, the XRF was employed handheld using the trigger mechanism and touch-screen control panel. Here, the nose of the instrument was pressed firmly against the measurement surface, ensuring that the detector window was completely covered and that there was sufficient shielding and/or distance behind. Where feasible, and for extra protection to the operator from back-scattered radiation, a Thermo Scientific tungsten-PVC backscatter collar shield was clipped on to the nose. As above, reference discs were analysed at the beginning and end of each measurement session but while placed on a suitably solid and attenuating surface.

Precision and homogeneity were evaluated in the accessory stand by repeat measurements of selected samples positioned at the same location and at different locations above the detector window, while the effects of geometry were assessed by tilting regularly shaped samples at different angles (up to about 15^{o}) with respect to the plane of the steel base plate. The efficacy of the thickness correction algorithm was evaluated by analysing, with and without correction, sections cut from the flat, smooth surface of a plastic electrical casing that were incrementally stacked from about 1 to 10 mm.

2.3. FTIR analysis

For selected samples (n = 40), based on the XRF results and where plastic type was not indicated, component polymers were determined by Fourier transform infra-red (FTIR) spectroscopy using a Bruker ALPHA Platinum attenuated total reflection QuickSnap A220/D-01 spectrometer. Fragments were sliced from each sample using a stainless steel scalpel and clamped down on to the ATR diamond crystal before measurements, consisting of 16 scans in the range 4000 to 400 cm^{-1} and at a resolution of 4 cm^{-1}, were activated via Bruker OPUS spectroscopic software. Subsequent polymer identification involved a comparison of sample transmittance spectra with libraries of reference spectra.

3. Results

3.1. Sample categorisation and characteristics

The number and categorisation of the XRF measurements is shown in Table 1. Thus, a total of 1056 analyses were performed on 1000 different samples, with multiple measurements being performed on samples with distinctive components that could not be separated (e.g. laptop casing, screen frame and keyboard; thermos flask handle, rim and lid; the different coloured parts of various toys). In the electronic product category 267 analyses were performed, with the majority of samples or components (88%) being neutrally coloured (i.e. black, grey or white) and 16 being constructed of PVC. Samples that were labelled indicated a roughly equal split between pre- and post-WEEE Directive implementation (i.e. 2005) and a majority that was manufactured in east Asia (principally China, but also Taiwan and Thailand); some older items were marked as being “assembled” in Hong Kong or manufactured in the UK. Analyses of non-electronic items revealed a higher proportion of PVC-based materials in each sub-category with the exception of food-hygiene items, and a greater

236 percentage of non-neutral colours amongst the samples (and >50% in the food-
237 hygiene and leisure sub-categories); where indicated, most products were
238 manufactured in China, with a small proportion (< 10%) originating from the EU
239 (UK, Germany, Denmark and Austria).
240
241 *3.2. Elemental analyses*
242 Detection limits for Br (as 3σ) varied according to sample thickness and presence of
243 additional elements but within the operating conditions employed ranged from about 2
244 to 10 μg g^{-1}; detection limits for Sb and Pb ranged from about 60 to 120 μg g^{-1} and 5
245 to 10 μg g^{-1}, respectively. Regular analysis of the Niton reference discs revealed
246 elemental concentrations that were within 10% of certified values, while the precision
247 of measurements (of reference discs and a number of electronic and non-electronic
248 samples) was always better than 5%. Stacking offcuts of the same plastic casing to
249 between about 1 and 10 mm, or the thickness range encompassing more than 90% of
250 all samples, yielded results that were consistent when the thickness correction
251 algorithm was applied but that differed by around 15% (Br and Pb) or 30% (Sb) when
252 the algorithm was not factored in. Variations in sample geometry up to an angle of
253 about 15^{o} revealed no measurable impact on Br, Sb or Pb concentrations, and multiple
254 spatial measurements of various surfaces indicated an homogeneous dispersion of all
255 elements within the polymeric matrix.
256
257 Also shown in Table 1 are the categorisation and chemical characteristics of the
258 samples and components analysed. Thus, under the operating conditions described, Br
259 was detected in about 24% of all analyses performed, and among the categories,
260 detection ranged from about 12% for food-contact items to 42% for electronic

products. Within all categories, the number of Br-positive samples was greater in neutrally-coloured items; more specifically, on both a number and percentage basis, Br detection was greatest in black plastics. Overall, Sb was encountered in 185 analyses of which 106 were Br-positive and Pb was detected in 164 cases of which 88 were Br-positive, with the three elements co-existing in 46 cases. Antimony and Pb were most frequently detected in electronic samples and, while association of either or both elements with Br was most frequent amongst electronic items on a number basis, Pb was more frequently associated with the halogen on a percentage basis among the food-hygiene items. Co-associations of Br with Sb and/or Pb were most commonly encountered in electronic items that were neutrally coloured and in non-electronic samples that were black.

Table 1: Chemical characteristics, colour distribution and number of XRF analyses performed within each sample category. Shown in parentheses are the numbers of Br-positive results.

	electronic	food-hygiene	clothing-accessories	office-tools	storage-construction	leisure	total
no. analyses	267 (113)	172 (20)	78 (22)	118 (25)	130 (28)	291 (45)	1056 (253)
PVC	16 (3)	2 (0)	9 (0)	17 (3)	25 (6)	23 (0)	92 (12)
black	96 (54)	59 (13)	34 (17)	55 (18)	42 (19)	57 (28)	339 (149)
grey	65 (12)	1 (0)	9 (1)	7 (1)	17 (2)	12 (3)	111 (19)
white	73 (30)	15 (0)	4 (0)	9 (1)	30 (3)	15 (1)	146 (35)
other colours	33 (17)	97 (7)	31 (4)	47 (5)	41 (4)	207 (13)	460 (50)
Sb	76 (57)	19 (4)	14 (5)	17 (6)	24 (15)	35 (19)	185 (106)
Pb	59 (32)	11 (9)	14 (4)	24 (10)	24 (15)	32 (18)	164 (88)

A summary of the concentrations of Br amongst the different sample types is shown in Table 2. Concentrations spanned at least three orders of magnitude for each category and, overall, ranged from a few $\mu g\ g^{-1}$ to over 170,000 $\mu g\ g^{-1}$ (or 17% by weight). In the electronic category, concentrations exceeded 100,000 $\mu g\ g^{-1}$ in the

plastic casings of seven items (two plugs, two chargers, a fan heater, the DVD cover of a workstation hard drive and a DSL filter), only one of which was manufactured post-WEEE Directive. Concentrations between 10,000 μg g^{-1} and 100,000 μg g^{-1} were encountered in a higher proportion of small electrical items or components that had been manufactured post-WEEE Directive, including a number of printed circuit boards and remote controls, the collars of energy-saving lightbulbs, various components of several computer mouses and a smoke detector. Among the electronic goods, decreasing Br concentration was accompanied by a distinctive shift in the coloration of the plastic casing. Thus, of the 15 products ranked highest in terms of Br concentration, 10 were white and one was black, while of the 15 products ranked lowest, one was white and 10 were black.

Table 2: Distribution and summary statistics for Br concentrations (in μg g^{-1}) amongst the different sample categories.

	no. detected	10^0-10^1	10^1-10^2	10^2-10^3	10^3-10^4	10^4-10^5	>10^5	min.	max.	median
electronic	113	10	24	28	29	15	7	1.8	171,000	607
food-hygiene	20	6	8	5	1	0	0	2.6	3150	24
clothing-accessories	22	3	9	8	1	1	0	3.3	28,500	77
office-tools	25	6	14	3	2	0	0	4.1	1921	26
storage-construction	28	0	4	19	5	0	0	19	9410	244
leisure	45	7	18	10	8	3	0	3.5	14,500	75

Regarding non-electrical items, the highest concentrations (> 10,000 μg g^{-1}) were encountered in the stick-shaped beads of a necklace, the painted beads of two Christmas garlands and the main body of a child's puzzle from a Christmas cracker; concentrations above 1000 μg g^{-1} were found in a variety of samples from each sub-category that included a disposable coffee stirrer, the plastic decorations on a pair of earrings, various clothes hangers, a segment of sink piping, a picture frame and the

piping of a foot pump. Among the Br-positive non-electrical items (n = 140), 95 were black and only five were white, while FTIR analysis of a range of products revealed a variety of polymers, including Nylon, polyethylene and polypropylene, but a majority that was styrenic-based and consistent with the composition of most electronic goods analysed or indicated.

In Figure 1, the concentrations of Sb are plotted against the concentrations of Br, where both elements were detected, for electronic and non-electronic samples or components that are discriminated according to colour. Also shown is the line defining the optimum mass ratio of Sb to Br in commercial plastics amended with both BFRs and oxides of Sb as a synergist (Sb:Br = 0.61; Papazoglou, 2004). Regarding electronic items (Figure 1a), there was a significant (α = 0.05) correlation between the two elements overall with an association that was strongest amongst samples that were grey-coloured, while data that were close to the line of slope 0.61 were largely represented by small appliances or components that contained concentrations of Br above 50,000 μg g^{-1}. For the non-electronic items (Figure 1b), relationships between Sb and Br were neither significant overall nor on a colour basis, but there was a greater number and proportion of data across a broader concentration range that were close to the line of slope 0.61.

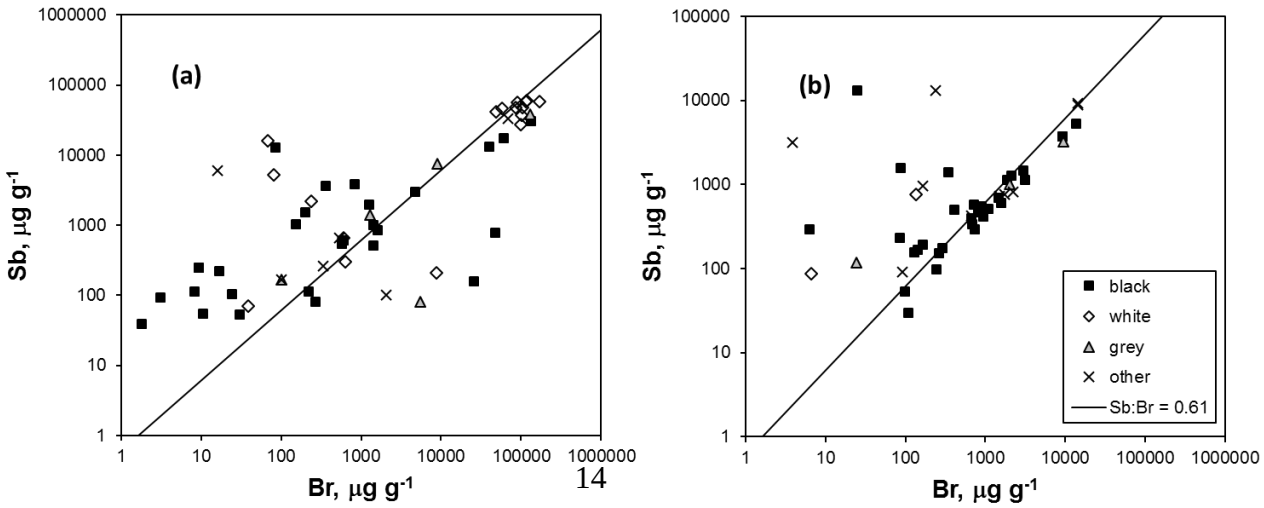

Figure 1: Concentrations of Sb versus concentrations of Br in (a) electronic and (b) non-electronic samples of different colour. The solid line represents the optimum mass ratio of Sb to Br in plastics amended with BFRs and synergistic Sb.

Figure 2 shows the concentrations of the heavy metal, Pb, versus the concentrations of Br in electronic and non-electronic samples. Although concentrations were not significantly correlated overall or on a colour basis for either sample type, the data serve as a useful illustration of the frequent occurrence of Pb in items of a variety of colour and application and of both PVC and non-PVC construction. Bromine-positive samples with the highest Pb concentrations (above several thousand μg g^{-1}) included USB and wire casings, various plumbing accessories, a luggage tag, the casing of a tape measure, two coat hangers, a clothes button and an office ring binder. Significantly, the heavy metal was detected in nearly one half of all Br-positive samples from the food-hygiene category, with the highest concentrations of about 100 μg g^{-1} returned for a coffee jug plunger and the lid of a thermos cup.

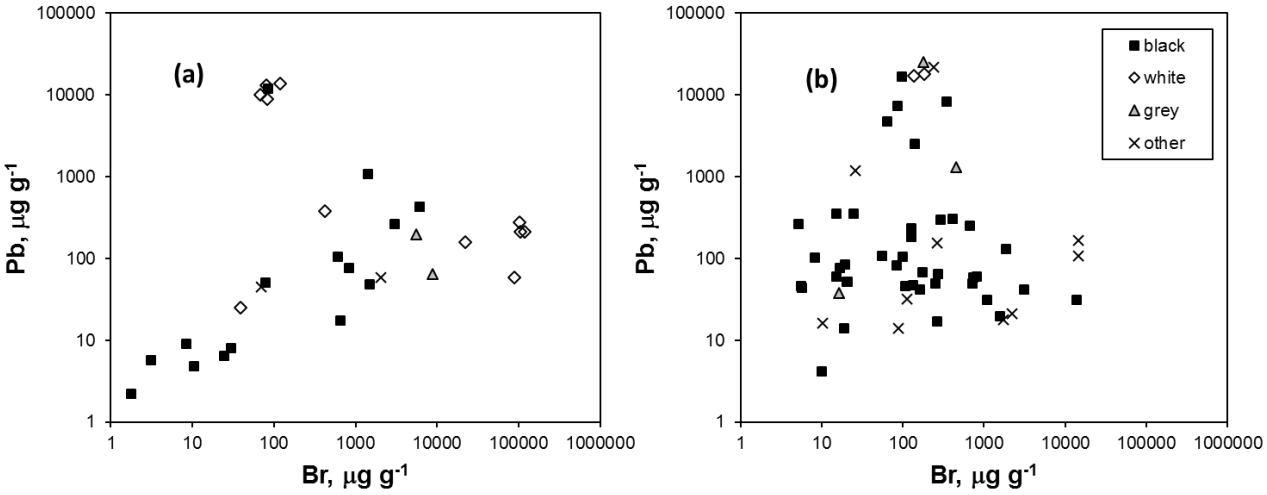

Figure 2: Concentrations of Pb versus concentrations of Br in (a) electronic and (b) non-electronic samples of different colour.

4. Discussion

This study has revealed the common occurrence of Br in plastic consumer products and appliances and components thereof. Although an implicit assumption thus far is that all Br-positive results returned by the XRF signify the presence of BFRs, it must be borne in mind that Br is also used in the green, halogenated copper phthalocyanine pigments, where typical Br concentrations in plastics are on the order of a few hundred $\mu g\ g^{-1}$ (Ranta-Korpi et al., 2014; Turner, 2017). On this basis, the limited number (n = 8) of green, non-electronic samples in the present study that contained relatively low quantities of both Br and Cu (including a raincoat, the lid of a confectionary tube, the handle of a sun lounger and a contemporary Lego block) can be discounted as BFR-positive. We infer, therefore, that of the 267 analyses of electronic samples and 789 analyses of non-electronic products, BFRs were detected in 113 and 132 cases, respectively.

Although it is difficult to assign a value for total Br concentration that provides adequate flame-retardancy to plastics because of the diversity of BFRs and types of polymer, Gallen et al. (2014) indicate a range of BFR content from about 5 to 10% by weight, which is equivalent to a range of Br concentration from about 3 to 8%. On this basis, retardancy from Br is most evident in historic (pre-WEEE Directive) and relatively small appliances that are often white, and absent in most newer, non-historic electronic products, regardless of their colour and size. This suggests that BFRs are being phased out by manufacturers of electronic goods and replaced with alternatives retardants based, for example, on phosphorus (Stapleton et al., 2009), or with materials that are inherently more fire-resistant (Laoutid et al., 2009). The occurrence of percentage concentrations of both Br and Sb in non-electronic products

that do not require flame-retardancy, however, like jewellery, Christmas decorations and toys, some of which had been purchased within the past twelve months, suggests that the plastic components of electronic products have been and/or are being used directly as recyclate. Moreover, the presence of Br and Sb across a wide range of electronic and non-electronic products at concentrations insufficient to provide flame-retardancy suggests that heterogeneous contamination of the recyclate stream by BFRs through the dilution of WEEE plastics is a widespread and pervasive issue cross the sector. This assertion is supported by recent studies reporting the total Br content in a range of consumer goods available in the US (Miller et al., 2016) and specific BFRs in a smaller number of consumer products purchased in the EU (Samsonek and Puype, 2013; Ionas et al., 2014; Leslie et al., 2016), Australia (Gallen et al., 2014) and Japan (Kajiwara et al., 2011).

The findings of many of the latter, independent studies are also consistent with our observations in that the majority of Br-contaminated consumer products are black in colour, despite BFRs being intentionally added to electronic goods of a range of (mainly neutral) colours. We surmise that this is related to the practical difficulties and costs associated with recycling (non-electronic) consumer plastics pigmented with carbon black. Specifically, while black materials account for 10-15% of all waste plastic, it cannot be sorted optically by polymer type because of the effective absorption of infra-red radiation by the pigment (Plastic Zero, 2014; Roh and Oh, 2016). With the consequent limited availability of recycled black plastic but a desire and demand for the production and use of black-coloured items, manufacturers may be deliberately or incidentally using black WEEE plastics, many of which contain

BFRs as well as Sb and Pb, as an alternative source of material for a range of consumer products.

The presence of BFRs in recycled products that evade the attention of the end-user of recycler, and in particular in food-contact items and small toys that are mouthable by young children, compromises consumer safety. Moreover, the subsequent disposal of contaminated (black) items via landfill or incineration affords a means of BFR (and Sb and Pb) release into the environment (Kajiwara et al., 2014). Once mobilised into air, water and soil, the persistence and lipophilicity of BFRs facilitates their subsequent long-range transport and accumulation by wildlife (Ackerman et al., 2008; Park et al., 2009). Furthermore, when thermally destroyed at temperatures typical of municipal incinerators, BFRs can also act as precursors in the formation of highly toxic polybrominated dibenzo-*p*-dioxins and dibenzofurans (Tang et al., 2014).

Ultimately, questions must be raised about the efficacy of both WEEE plastic processing in countries like China (Ni et al., 2013) and the CENELEC criterion for the destruction-depollution of waste based on exceedance of a Br concentration of 2000 $\mu g\ g^{-1}$ (Stenmarck et al., 2017). For example, is the screening and characterisation of materials sufficiently robust and are any regulations enforced, and is the CENELEC threshold itself conservative enough? In respect of the latter, we note that some nations are now proposing a stricter limit of 800 $\mu g\ g^{-1}$ total Br (Löw, 2014), corresponding to a worst-case scenario that all BFRs present are PBDEs and at a combined concentration of 1000 $\mu g\ g^{-1}$ (the Restriction of Hazardous Substances limit value for PBDEs in new and recyclable electronic equipment; RoHS, 2006). Until these issues are addressed, legacy BFRs, along with Sb and Pb, are predicted to

continue re-appearing in new consumer goods where they are neither intended nor expected.

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