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Black plastics: linear and circular economies, hazardous additives and marine pollution

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Abstract

Black products constitute about 15% of the domestic plastic waste stream, of which the majority is single-use packaging and trays for food. This material is not, however, readily recycled owing to the low sensitivity of black pigments to near infrared radiation used in conventional plastic sorting facilities. Accordingly, there is mounting evidence that the demand for black plastics in consumer products is partly met by sourcing material from the plastic housings of end-of-life waste electronic and electrical equipment (WEEE). Inefficiently sorted WEEE plastic has the potential to introduce restricted and hazardous substances into the recyclate, including brominated flame retardants (BFRs), Sb, a flame retardant synergist, and the heavy metals, Cd, Cr, Hg and Pb. The current paper examines the life cycles of single-use black food packaging and black plastic WEEE in the context of current international regulations and directives and best practices for sorting, disposal and recycling. The discussion is supported by published and unpublished measurements of restricted substances (including Br as a proxy for BFRs) in food packaging, EEE plastic goods and non-EEE plastic products. Specifically, measurements confirm the linear economy of plastic food packaging and demonstrate a

complex quasi-circular economy for WEEE plastic that results in significant and widespread contamination of black consumer goods ranging from thermos cups and cutlery to tool handles and grips, and from toys and games to spectacle frames and jewellery. The environmental impacts and human exposure routes arising from WEEE plastic recycling and contamination of consumer goods are described, including those associated with marine pollution. Regarding the latter, a compilation of elemental data on black plastic litter collected from beaches of southwest England reveals a similar chemical signature to that of contaminated consumer goods and blended plastic WEEE recyclate, exemplifying the pervasiveness of the problem.

Keywords

Black plastic; food packaging; waste electrical and electronic equipment; recycling; brominated flame retardants; heavy metals

1. Introduction

Because of their ease of manufacture, low cost, strength, versatility, inertness and insulating properties, plastics have become an invaluable commodity in a range of sectors, including packaging, construction, agriculture, healthcare, transport, clothing, communication and electronics (PlasticsEurope, 2016; Van Eygen et al., 2017). With such a diversity of applications, plastics may be tailored to precise needs through the addition of specific substances during manufacturing. Additives include materials and chemicals introduced intentionally for colour, heat stabilisation, plasticising, filling, impact modification, internal lubrication and flame retardancy, as well as catalytic residues arising from the polymerisation process itself (Hansen et al., 2013).

Both in spite of and because of their versatility and widespread use, plastics also pose a number of environmental threats. Thus, although most plastics are, in theory, recyclable, technological and economic constraints and the presence of additives that are harmful should they migrate from the polymeric matrix preclude the recycling of many products, at least into general consumer goods; as a consequence, a significant fraction of the plastic stream ends up in landfill or incinerated (Ignatyev et al., 2014). Moreover, through poor management and disposal practices from an individual level to an institutional basis, plastic littering has become a pervasive problem in the marine environment (Sheavly and Register, 2007). Here, not only do primary plastic objects and secondary plastic fragments have an aesthetic impact, they pose significant threats to wildlife (Li et al., 2016). Incidental or deliberate ingestion of plastic is a particular concern because it occurs across a wide

range of organisms and may result in blockage of or damage to the digestive tract (Santos et al., 2015; Jovanovic, 2017) as well as act as a vehicle for the bioaccumulation of chemical additives or pollutants adsorbed to the plastic surface (O'Connor et al., 2016; Massos and Turner, 2017).

Amongst these issues, black plastics pose a unique series of challenges and problems that have recently emerged. Thus, while there is a requirement for black products in various sectors, recycling of end-of-life black plastic is hampered by the availability of suitable technology to sort this material efficiently (Dvorak et al., 2011). As a consequence, the demand for black plastic appears to be met, in no insignificant part, by the recycling of plastic from waste electronic and electrical equipment (WEEE) (Chen et al., 2010; Haarman and Gasser, 2016). The presence of restricted chemical additives, residues or contaminants in WEEE plastic that cannot be identified or removed readily, however, has resulted in the appearance of potentially harmful chemicals in new black plastic consumer products intended for the preparation or storage of food or as toys for children (Chen et al., 2009; Kuang et al., 2018).

The present paper reviews the contemporary literature on the characteristics, life-cycles and environmental impacts of black plastics, and examines relevant regulations and conventions relating to the recycling and disposal of plastics that contain restricted chemical additives. The discussion is aided and directed by measurements of additives in black plastic electrical and non-electrical consumer products and in black plastic marine litter that have been garnered by the author's research group over the past few years or that have been undertaken for the specific purposes of the current review.

2. Nature and uses of black plastic

Most black plastics are coloured with carbon black, a group of industrial carbons created by the partial combustion of various hydrocarbons. Characterised by a small particle size and high oil absorption, carbon black is cheap to produce and has excellent colour strength, hiding power, solvent resistance and ultraviolet stability (Brewer, 2004). Addition of about 1% is usually sufficient as a colourant in unpigmented polymers but higher quantities (up to 40%) may be added to modify mechanical and electrical properties (Pfaff, 2017). The precise characteristics of plastic can be further refined by adjusting the size, morphology and dispersion of the particles within the polymeric matrix.

The properties of carbon black render it suitable for a wide range of plastics but it is particularly favourable for products used outdoors or where strength, conductivity or thermal stability is

91 required. Items employing carbon black therefore include automobile components, mouldings and
92 piping, ready meal trays, refuse bags, tarp and mesh, and housings and insulation for electrical and
93 electronic equipment (EEE). Carbon black is also used in products where colour is the principal
94 concern from an aesthetic perspective, like replica toys, jewelry and food packaging
95 (Plasticseurope.com, 2016).

96 In Table 1, a more specific list of consumer products that are wholly or partly constructed of black
97 plastic is given. Here, products are classified as follows: 'food-contact', where plastic is in direct or
98 indirect contact with food or beverages; 'storage and construction', with a range of applications in
99 the household but excluding storage of food; 'clothing and accessories', including articles that are in
100 direct contact with the skin or that are handled regularly; 'toys and hobbies', including objects
101 potentially mouthable by young children; 'office and garden' and other products used in the
102 workplace or outdoors; and 'EEE', or plastic casings of products that are battery- or mains-operated
103 and that have the propensity to generate heat (and including electrical varieties of products
104 categorised elsewhere such as toys, tools and sports equipment).

105

106 **3. Challenges for the recycling of black plastic**

107 *3.1. Non-EEE plastic*

108 Efficient recovery and recycling of non-EEE plastics relies on sorting into monopolymeric fractions
109 (and according to resin identification codes) that can be performed cheaply, reliably, safely and
110 automatically (Bezati et al., 2011). Currently available technology is based on spectral signatures
111 derived from near infra-red (NIR) reflectance spectroscopy (0.8 to 2.5 μm) where plastics are
112 identified according to stretching vibration modes of CH, CH_2 and CH_3 groups (Becker et al., 2017).
113 Plastics coloured with carbon black and other black pigments, however, exhibit very low reflectance
114 of light in the NIR spectral region and the signal-to-noise ratio of present sensors is insufficient to
115 allow classification according to polymer type (Rozenstein et al., 2017); identification may be
116 hampered further by the presence of additional additives and lacquer films (Becker et al., 2017).
117 Consequently, black plastics with no specific provision for recycling are typically confined to a linear
118 economy in which end-of-life material enters the unsorted residue of reprocessing facilities before
119 being sent for landfill or incineration and energy recovery rather than being reconstituted into
120 pellets for the production of new goods.

121 Alternative technologies to identify black plastics have recently been investigated that are based on
122 mid-wave infra-red spectroscopy (3 to 12 μm) but thus far these have not proved to be feasible on a

commercial scale (Becker et al., 2017; Rozenstein et al., 2017). A review into the problem by the UK government-funded recycling group, WRAP (Waste Resources Action Programme), concluded that, in combination with existing NIR technology, either alternative colourants or the addition of fluorescent markers would be the most suitable option to achieve a sufficient throughput of materials at a recovery or reprocessing facility (Dvorak et al., 2011). To this end, the PRISM project (Plastic Packaging Recycling using Intelligent Separation technologies for Materials) has recently secured funding to develop fluorescent materials from metal oxides for marking and coding plastics that are identified though an ultraviolet light source (Moore, 2016). In the meantime, WRAP has advised local UK authorities to check with their processor if black plastics are recycled and, if not, update their communications with householders stating clearly that black products are on the 'not recycled' list (letsrecycle.com 1).

3.2. EEE plastic

Although plastic used for housing or insulation of EEE may be a variety of (mainly neutral) colours, black is the dominant colour employed for appliances smaller than white goods such as fridges and washing machines (UNIDO, 2012). Unlike more general black household waste, the majority of which is food packaging, the disposal of end-of-life black plastic used in, for example, televisions, computers, phones, power tools, lighting equipment and electrical toys, is embraced by specific, existing legislation in the European Union that is outlined below. Typically, plastics used in such equipment, like high impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS) and polycarbonate (PC), have better mechanical and electrical properties than those used in most other consumer products (e.g. polyethylene terephthalate, PET, used in food packaging) but recycling is confounded by a number of additional challenges, including the potential environmental and health impacts associated with the presence of hazardous additives (Haarman et al., 2016).

4. Regulations relevant to EEE plastic

In order to better manage waste from EEE, contribute to a circular economy and enhance resource efficiency, the Directive on waste electrical and electronic equipment (WEEE) (Directive 2002/96/EC; European Parliament and Council, 2003a) and the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) (Directive 2002/95/EC; European Parliament and Council, 2003b) were introduced by the European Union and became effective from 2003 and 2005, respectively. The former directive focused on the creation of collection schemes for WEEE and was revised with effect from 2014 in order to tackle a rapidly

growing and diversifying waste stream (Directive 2012/19/EU; European Parliament and Council, 2012). The latter directive deals with the restriction and replacement of hazardous metals and specific brominated flame retardants (BFRs) in EEE and was recast with effect from 2013 (Directive 2011/65/EU; European Parliament and Council, 2011) and subsequently amended with effect from 2019 (Directive 2011/65/EU Annex II amendment; European Parliament and Council, 2015) in order to encompass a broader array of equipment and improve regulatory and legal clarity. Legislative or administrative procedures based on or similar to these directives have since been adopted in regions outside of the European Union, including India, China, Japan, Thailand, Latin America, Canada and various states in the US (Tanskanen and Butler, 2007; Bandyopadhyay, 2009; Terazono et al., 2015).

The production, use and processing of certain BFRs is also restricted according to additional and more general international agreements. The Stockholm Convention (Resource Futures International, 2001), which came into effect in 2004 and is currently ratified by 181 parties, requires developed nations to resource the elimination of the production and use of intentionally and unintentionally produced persistent organic pollutants (POPs) and manage and dispose of POPs by environmentally sound means. Although BFRs were not included in the list of chemicals in the original convention, several of those encompassed by the RoHS Directive were added in modifications that have since come into effect, albeit with exemptions relating to plastic recycling (UNIDO, 2017). The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal (UNEP, 2014) has been effective since 1992 and is currently ratified by 185 parties (but not the US). This convention was designed to reduce the movement of hazardous waste, particularly from developed to less developed nations, and includes the BFRs embraced by the Stockholm Convention. A critical and controversial loophole of the Basel Convention, however, is that exporters are able to designate WEEE as products that are “repairable” or to be “reused” rather than as hazardous waste, thereby potentially exempting non-functional electronic equipment from the obligations of the agreement (Perkins et al., 2014).

5. Hazardous additives in black plastics

Aside from pigments and dyes, additives are not necessarily specific to plastics of particular colours. However, the dominant use of black in food packaging and in EEE housings and insulation, coupled with the constraints on recyclability outlined above, mean that certain additives are likely to be more of an environmental and health concern when associated with black products. Potentially ‘hazardous’ substances in this context are the metalloid, antimony, and the four heavy metals and

two groups of BFR defined by the current RoHS Directive for WEEE materials (European Parliament and Council, 2011).

Antimony (Sb) is often homogeneously dispersed in PET, a plastic of high thermal stability and the most widely used for food packaging and cooking, as catalytic residue from the polycondensation of ethylene glycol and terephthalic acid. Its precise impacts on human health are still unclear but a toxicological similarity with arsenic ensures that it is gaining interest and remains a concern (Pierart et al., 2015). Because of toxicities that are better understood, cadmium (Cd), chromium (Cr) in its hexavalent form, mercury (Hg) and lead (Pb), and the polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants, are restricted by the RoHS Directive on homogeneous materials or components of EEE (including plastic housings and insulation) to concentrations of either 1000 ppm or 100 ppm (Cd only). Note that four phthalate plasticisers are also to be added to the restricted list for EEE products placed on the market from 2019, and that, despite compounds of Sb (and in particular, antimony trioxide, Sb_2O_3) commonly used as a halogenated flame retardant synergist (Felix et al., 2012), the metalloid itself has not been considered in the directive.

5.1. Measurement of hazardous additives in plastic

Determination of specific flame retardants and metals-metalloids in plastics may be accomplished by, for example, gas chromatography-mass spectrometry (GC-MS) and inductively coupled plasma mass spectrometry (ICP-MS), respectively, following decomposition of the matrix in a suitable solvent or mineral acid. Although these techniques are extremely sensitive, sample preparation can be both time- and resource-consuming and may generate significant quantities of hazardous waste (Chen et al., 2009; Mello et al., 2015). Accordingly, increasing use has been made of energy-dispersive x-ray fluorescence (XRF) spectrometry as a means of analysing plastics simultaneously for Br, as a proxy for BFRs, and Cd, Cr, Hg, Pb and Sb (Furl et al., 2012; Gallen et al., 2014; Aldrian et al., 2015; Massos and Turner, 2016). This approach relies on irradiating a sample with a high intensity, collimated x-ray beam (typically up to 50 kVp and 100 μA) and deconvoluting a spectrum of secondary x-rays generated by the material through a series of iterations. (Note that, unlike NIR, x-ray intensity is not affected by colour). XRF cannot discriminate different brominated compounds or oxidation states of Cr and detection limits on the order of tens of ppm mean that low levels of BFRs and metals may not be reported. However, the technique has the advantages of being rapid, non-destructive and, with handheld devices and suitable x-ray shielding, portable.

5.2. XRF-determination of black plastic additives for the present study

In the present study, concentrations of the elements listed above, plus Cl as a measure of chlorination and an indicator of polyvinyl chloride (PVC; operationally defined as [Cl] > 15% for the purposes of the XRF calibration), were determined in plastics using a Niton XL3t 950 GOLDD+ XRF according to protocols described in detail elsewhere (Turner and Solman, 2016) and as summarised below. Data for old and new black plastics, sourced from various households, offices, nurseries, schools, stores and fast-food establishments, have been compiled both from results of previous research into consumer plastics in general (Turner and Filella, 2017a; 2017b) and from new measurements where black products have been specifically targeted. Data for marine plastic litter that is coloured black have been distilled from published and unpublished results of several beach litter surveys undertaken around the English Channel and Atlantic coasts of south west England (Turner, 2016; Massos and Turner, 2017).

Thus, plastic products or specific components thereof ('samples'), and excluding rubbers, foams and textiles, were analysed by XRF in situ or in a laboratory test stand in a low density plastics mode with thickness correction and using an excitation beam width of 8 mm or 3 mm depending on sample size and accessibility. Counting was performed for periods of between 30 s and 200 s (depending on sample thickness, composition and analyte signal) that were equally distributed between a low energy range (20 kV and 100 μA) and main energy range (50 kV and 40 μA). X-ray spectra were quantified by fundamental parameter coefficients to yield concentrations on a dry weight basis (in ppm) and with a counting error of 2σ (95% confidence) that were downloaded to a laptop using Niton Data Transfer (NDT) software. For quality assurance purposes, reference discs supplied by the manufacturer and certified for concentrations of Cd, Cr, Hg, Pb and Sb in polyethylene (PN 180-619, LOT#T-18), Cd, Cr, Hg, Pb and Br in polyethylene (PN 180-554, batch SN PE-071-N) or Br and Sb in PVC (PVC-4C80) were analysed throughout each measurement session, while high quality virgin black pellets of various construction and with no added components (supplied by Algram Group Ltd, Plymouth) were used to check for false positives. Median detection limits under these operating conditions were < 10 ppm for Br, Cr and Pb, about 20 ppm for Hg and around 40 ppm for Cd and Sb, with precise values dependent on the nature of the sample but that were generally inversely related to material thickness.

6. Concentrations of hazardous additives in black consumer plastics

Results arising from the XRF-analyses of black plastic electrical and non-electrical consumer products are summarised in Table 2, where samples have been grouped according to the categorisation given in Table 1. Thus, in total, more than 600 samples were tested, with at least 70 considered in each

category and PVC encountered in 43 cases and across all categories. In Figure 1, examples of Br-positive samples among non-EEE products and Pb-positive samples among both EEE and non-EEE products are photographed to illustrate the range of items in which hazardous substances may be found.

Bromine was detected in almost one half of all black samples tested and in at least 20% of samples from each category, with concentrations overall ranging from 1.5 to 133,000 ppm and detection most frequent (on a percentage basis) in the EEE category. By comparison, analysis of samples coloured other than black and reported in Turner and Filella (2017b) revealed variable concentrations of Br in various older (pre-RoHS) white EEE and in only a limited number of non-EEE that were usually green and where the halogen is employed in phthalocyanine pigments (Ranta-Korpi et al., 2014).

Lead and Sb were detected in about one quarter of all black samples analysed and exhibited a more uniform distribution across the different categories than Br. Lead was most commonly detected in the clothing and accessories and toys and hobbies categories and least frequently in the food-contact category, and concentrations above 5000 ppm were always associated with PVC products. Antimony was most frequently detected in the EEE plastics, where concentrations spanned about three orders of magnitude, but was present across all other categories and with concentrations that were greatest either in the presence of high concentrations of Br or in PVC products. In the food-contact category, Sb was detected in 12 out of 14 PET trays tested (all of which were Br-negative) and at concentrations that were rather uniform (344 $\pm$ 89.0 ppm). However, the metalloid was never detected in other plastic products at similar concentrations and in the absence of Br, providing empirical evidence that black PET is not widely recycled into consumer goods.

Cadmium and Cr were detected in fewer black samples than the elements above but were present in items across all categories and, with the exception of Cd in a plastic brooch (35,000 ppm), concentrations spanned about two order of magnitude. On a percentage basis, Cd was most frequently encountered amongst office and garden equipment while Cr was most frequently detected in food contact items (including PET food trays). In contrast, Hg was detected in only eight samples across five categories and at concentrations that were always below 100 ppm.

Regarding black EEE plastics, 90 samples were identified from appropriate symbols and signage as post-RoHS Directive (or placed on the market since 2005) and 32 as pre-RoHS, with the remaining samples (unmarked components of absent larger items) unclear in this respect. A comparison of the descriptive statistics for Br, Cd, Cr, Pb and Sb in post- and pre-RoHS samples, shown in Table 3, indicates a similar percentage frequency of detection in both categories for all elements with the

285 exception of Pb, which was encountered in fewer cases post-RoHS. Moreover, a series of non-
286 parametric Mann-Whitney *U* tests, performed in Minitab 17, revealed that, among the elements,
287 only concentrations of Pb were statistically different ($\alpha < 0.05$) between the two categories (and
288 lower post-RoHS).

289

290 **7. Sources of hazardous additives in black plastics**

291 *7.1. Additives in EEE plastics*

292 Of the elements considered, Br was most commonly detected among the black plastic samples
293 analysed. Within the EEE category, its occurrence is attributed to the historical and contemporary
294 use of brominated flame retardants in thermosetting plastic housing and casings (Shaw et al., 2014).
295 Halogenated materials act as efficient and cost-effective flame retardants by interrupting the radical
296 chain reaction in the gas phase, and the variety of brominated compounds available allows specific
297 needs to be met in different plastics with a range of applications. Commercial mixtures of deca- and
298 octaBDE, trisbromophenol derivatives and brominated phosphates were commonly employed in
299 polymers for EEE before 2005 (UNEP, 2010), and usually in the presence of Sb_2O_3 as a synergist. The
300 Sb_2O_3 to BFR ratio was generally in the range of 0.2 to 0.5, or equivalent to a mass ratio of Sb to Br of
301 about 0.3 to 0.5, except where the metalloid caused molecular weight degradation of the matrix (a
302 particular problem in PC) (Papazoglou, 2004). Environmental concerns and implementation of the
303 RoHS Directive, however, resulted in the subsequent development of alternative brominated
304 compounds that are supposed to be safer and the wider use of halogen-free flame retardants like
305 hydrated minerals of aluminium and magnesium and phosphate esters (Liagkouridis et al., 2015).

306 The precise quantity of a compound or mixture required to achieve adequate flame retardancy
307 depends on the composition of the polymer, the application of the product, the type and nature of
308 retardant and its compatibility with the polymeric matrix, and the efficiency of any synergist.
309 Papazoglou (2004), however, suggest that a minimum of 3 to 5% by weight of a brominated
310 compound is required in most plastics, which is equivalent to a Br content of at least about 20,000
311 ppm. On this basis, only four out of 32 pre-RoHS black EEE products analysed as part of the present
312 study, and each containing Sb, are sufficiently flame retardant in terms of bromination, with a
313 further four samples of high Cl content likely to be retardant in terms of chlorination (Table 3).
314 Failure to detect Br in eleven pre-RoHS samples suggests that either non-halogenated flame
315 retardants were employed or the voltage of the product was sufficiently low to circumvent retardant
316 addition. In the remaining samples, the presence of Br over a wide range of concentrations (from

about 4 to 4000 ppm) that are too low to provide retardancy, coupled with a co-association with Sb, raises possibilities about material recycling.

A similar distribution of Br and Sb is evident in the post-RoHS samples (Table 3). Thus, here, only two samples contained sufficient Br (and Sb) to provide flame retardancy, presumably from unrestricted brominated compounds, with 31 products containing no measurable Br and probably attaining retardancy, where required, through non-brominated compounds. The remaining post-RoHS samples contained Br over a wide range of concentrations (from about 2 to 10,000 ppm) that are too low for retardancy but that were often co-associated with Sb, consistent with the material recycling assertion mentioned above.

Unlike Br and Sb, which have distinct functions in the manufacture and protection of EEE plastics, the sources of Cd, Cr and Pb in a variety of pre- and post-RoHS samples are less clear but likely to be more varied. Regarding plastics themselves, compounds of both Cd and Pb have been used as stabilisers in PVC (Titow, 2012) while Cr(VI) may be present in some polyethylene as residual chromium trioxide catalyst from the polymerisation process (Epacher et a., 2000). However, the presence of these metals in a wider array of (non-PVC) EEE plastics implies that many products may have been manufactured from a mixed recyclate. For example, Dimitrakakis et al. (2009) found that WEEE plastic may contain 15 or more different polymer types, with polymer identification not always possible (especially for black materials that evade NIR detection) and cross contamination during recycling inevitable. Regarding the present results, that Cd and Pb were always associated with Cl in the EEE samples tested suggests traces of PVC may have been recycled into new products. Alternatively (or additionally), since Cd, Cr(VI) and Pb have a wide variety of uses in non-plastic electronic equipment (as, for example, alloying elements, anticorrosion agents and activators, and in components of batteries, bonding agents, film pastes, solder, varnishes and ceramic capacitors), imperfect sorting of WEEE materials during dismantling may result in contamination of the plastic recyclate (Wäger et al., 2012). There also exists the possibility that the XRF results were skewed by secondary x-rays generated by metallic parts in the vicinity of the plastic being probed. However, where the co-existence of metallic and plastic components was evident or suspected, potential interferences were minimised by probing the edge of the sample using a 3-mm excitation beam width (Turner, 2018a); moreover, this effect would not explain the presence of Cd, Cr and Pb in plastic components with no metallic attachments, like battery compartment covers, support apparatus, protective caps, calculator cases and audio docking station adaptors, as well as their occurrence in the non-EEE samples reported in Table 2.

7.2. Additives in non-EEE plastics and evidence for the recycling of poorly-sorted WEEE

In non-EEE black plastic samples, relatively high concentrations of Cd and Pb may be attributed to the use of metal-based stabilisers in PVC products, while smaller quantities of Cr and Sb are likely the result of catalytic residues in polyethylene and PET, respectively. However, the widespread detection of these elements, and in particular Pb, across a broader range of materials, coupled with the extensive occurrence of Br among the samples tested that require no flame retardancy (and at concentrations insufficient to provide retardancy), calls for an alternative explanation.

Unlike other colours of plastic that can be readily identified by NIR spectrometry, there are technological and economic difficulties in the sorting and recycling of black plastics, as discussed earlier. With a high demand for black plastics in various sectors, it is suspected that polymers of this colour are often sourced for new consumer goods from end-of-life WEEE, and as implicated more specifically for both old and new EEE plastic above. New goods may be constructed entirely from black WEEE plastic, or may be blended with cleaner plastics (including those of other colours) and re-pigmented black.

In theory, and because industry-scale technology does not exist for removal of Br from plastic, sorting facilities should isolate plastics containing BFRs for disposal by appropriate means or for energy recovery in the metal or cement industries according to best available technologies (UNIDO, 2017). Although sorting may be accomplished by, for example, density separation in fluids or manual inspection according to age or ISO signage, with occasional spot checks using portable XRF for validation, poor, low-cost or inefficient practices allow materials impregnated with BFRs to re-enter the recyclate (Haarman and Gasser, 2016). This is a particular problem in (but vis not unique to) less developed nations, like India, Pakistan, Nigeria and China, which, despite the objectives of the Basel Convention, import significant quantities of WEEE from Europe, North America, Australia and Japan (Sepúlveda et al., 2010; Obaje, 2013), presumably as “used” or “repairable” goods. Here, large stockpiles that include older WEEE and restricted BFRs may be processed by inexperienced operatives without suitable screening technology at informal or unregulated facilities (UNIDO, 2017; Ni et al., 2013). (At the time of writing, China, the largest recipient of waste from overseas, has announced stringent restrictions on waste importation and introduced a licensing scheme that targets facilities with clean records and full regulation compliance, a system that will also allow the country to boost its own waste recycling rate; Letsrecycle.com 2.)

A consequence of this quasi-circular economy, coupled with imperfect international monitoring and regulatory loopholes, is that, unaware to the consumer and, in many cases, the manufacturer and retailer, BFRs and heavy metals like Pb end up in a heterogeneous assortment of items. These are exemplified in Figure 1 and include the ring of a baby's dummy, a disposable fork from a reputable supermarket, various kitchen utensils, the wheels of toy cars, games marbles and counters, necklace beads and pendants, clothes hangers, spectacle cases, plant pots, lawnmower blades, coffee plungers, thermos flasks and rawl plugs. Moreover, given the heterogonous mixture of EEE plastic types and vintages apparently recycled, coupled with potential blending with cleaner materials, concentrations of Br and Pb vary widely, with identical looking products from different suppliers sometimes containing relatively high concentrations of these elements and sometimes Br- and Pb-free. Significantly, consumer products analysed by XRF that returned concentrations of either element above 1000 ppm in the present study are RoHS non-compliant with respect to the heavy metal or potentially non-compliant with respect to BFRs. That is, limits designed for hazardous substances in WEEE are being breached for goods beyond the scope of the legislation, including products in regular contact with food, toys designed for young children, items of jewellery and a range of handles and grips.

Further, empirical evidence for the recycling of BFRs into non-EEE consumer goods is the co-existence and correlation of Sb with Br. Thus, in Figure 2, concentrations of the two elements are plotted against each other for both EEE plastics, with pre- and post-RoHS samples discriminated, and non-EEE products, where each sample category is discriminated. (Note that four highly chlorinated or PVC-based samples have been omitted where Sb was evidently used as a synergist for chlorine-based flame retardants.) Results of linear regression analysis of the data sets, shown in Table 4, reveal significant relationships in all cases, with slopes ranging from about 0.33 to 0.54 and that are consistent with the mass ratios of Sb-based synergists to BFRs in plastics defined above. Significantly, once 95% confidence intervals had been factored in, there was no statistical difference between the slope defining all non-EEE samples and that defining all EEE products.

A growing body of literature is reporting the occurrence of BFRs in a range of products where they are neither needed nor expected and present an unnecessary hazard to the consumer. For instance, Miller et al. (2016) used XRF to demonstrate the widespread occurrence of Br in plastic consumer goods that had been newly purchased on the US market, with mass spectrometry performed on black necklaces and garlands confirming the presence of several restricted BFRs. Samsonek and Puype (2013) and Kuang et al. (2018) detected various restricted BFRs in black thermos cups purchased in the EU and in black kitchen utensils purchased in the UK, respectively, while Chen et al. (2009) found several BFRs in toys bought on the Chinese market, including PBBs that had never been

produced in the country. Clearly, the reconstitution of WEEE into consumer products is a pervasive, global issue affecting plastics across a multitude of sectors and that is likely to have wide-ranging impacts on the environment and on human health.

8. Potential environmental and health impacts of hazardous additives in black plastics

The environmental impacts of plastics in general arise from the energy and resources involved in their production and transportation, the presence of broadly-used organic additives (e.g., phthalates), and the poor management of plastic waste and its disposal. With regard to black plastics, impacts are compounded and diversified because of inefficient and inadequate recycling and the presence of a range of harmful chemical additives.

8.1. PET packaging

Because of the potential toxicological profile of Sb (Gebel, 1997), its occurrence in black PET used in food packaging or cooking has been evaluated as a possible health hazard. Diffusible species of Sb are likely to be the monodentate glycolate (-Sb-OCH_2CH_2OH) and chelate ligand (-OCH_2CH_2O-) complexes, with inorganic Sb probably making a small contribution. Diffusion of Sb from the PET matrix depends on a number of factors, like degree of crystallinity of the polymer, the molecular weight distribution of the Sb-glycol complexes and the presence of additional additives that may act as sorbents for Sb (e.g. TiO_2 micro-particles), but is facilitated when the contents are heated, as in pre-packed ready meals (Haldimann et al., 2013). In some food trays exposed to high temperatures, migratable concentrations have been found to exceed the European Commission limit of 40 $\mu g\ kg^{-1}$ but not the WHO accepted tolerable daily intake of 6 $\mu g\ kg^{-1}$ body weight per day (Haldimann et al., 2007).

Black PET used for food packaging appears to be derived from virgin stock, with few uses of the polymer in EEE (Bhaskar et al., 2010) and no empirical evidence of recycling from this source (at least with respect to detectable Br or Pb). Moreover, it is a highly significant contributor to household plastic waste, with a recent study in Copenhagen finding that between 10 and 15% of rigid material (excluding WEEE) was black and largely derived from packaged food (Plastic Zero, 2014). In the UK alone, industry estimates that there are between about 30,000 and 60,000 tonnes per annum of rigid black plastic in the waste stream whose principal use was the packaging of food (Dvorak et al., 2011). Based on the mean concentration of Sb in PET trays (~ 350 ppm), it is estimated that up to 20 tonnes of the metalloid may also be disposed of annually via landfill and incineration. Regarding the latter route, Sb is a problematic element because of its propensity to leach from bottom ash at

concentrations that exceed limit values for use in secondary materials but through mechanisms that are currently unclear (Van Caneghem et al., 2016).

Disposal of Sb is also at odds with the EU's raw materials initiative. Thus, the metalloid is listed as one of the original fourteen critical raw materials which display a particularly high risk of supply shortage over the next decade and have a relatively high impact on the economy (European Commission, 2011). Specifically, Sb has an "import dependency" (mainly from China) of 100% and low "substitutability" and "recycling rate" scores. The recovery of Sb from various WEEE plastics by centrifugation of residues arising from polymer dissolution has been trialled in the laboratory but the upscaling necessary to attain a marketable secondary product is not currently feasible (Schlummer et al., 2016).

8.2. WEEE plastic and recycled WEEE plastic

WEEE plastic contains a wider array of hazardous chemical additives whose toxicities are relatively well-defined. Environmental impacts and human exposure arising from soil and water contamination and release of semi-volatile BFRs may, therefore, be significant at dismantling, recycling and moulding facilities, and especially at those that are unregulated or poorly managed (Zhang et al., 2012; Han et al., 2017). Local contamination may also occur through landfilling, with anaerobic conditions promoting the debromination of many highly brominated PBDEs into more toxic congeners (Tokarz et al., 2008). However, because black WEEE plastic appears to be ubiquitously recycled into components of toys, games and jewellery, products that are used to store, dispense, strain, stir or mouth food, and items for the storage and application of cosmetics, the wider population is exposed to these chemicals through a variety of pathways.

Unfortunately, very few studies have examined the migration or availability of additives from recycled WEEE plastic. Chen et al. (2009) estimated the exposure of PBDE flame retardants to young children from a number of hard plastic toys purchased in China (and using empirical measurements and data for EEE plastics) through inhalation, dermal contact and direct mouthing. Maximum total exposure was about 10 ng kg^{-1} body weight per day, with mouthing the greatest exposure contributor and comparable to that arising from human milk consumption for toddlers and higher than that resulting from fish consumption for infants. However, there was a significant degree of uncertainty in the calculations and it was predicted that exposure could be enhanced substantially for toys with higher BFR concentrations (the median value for PBDEs in the study was 53 ppm) and for longer mouthing periods or occasional swallowing of pieces that had been chewed off. More recently, Kuang et al. (2018) estimated the exposure of BFRs from black kitchen utensils purchased in the UK that had been in contact with food fried in oil at 160 ^{o}C. Daily exposures of up to 6 μg for

total BFRs and 4 μg for total PBDEs were reported, with the latter considerably exceeding corresponding UK exposure estimates determined independently for dust ingestion (up to 0.4 μg day^{-1}) and the diet (up to 0.075 μg day^{-1}) (Besis and Samara, 2012).

An additional problem associated with plastic products containing BFRs is the presence and formation of highly toxic polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs). These compounds may be present in technical mixtures of PBDEs as impurities but can be formed in significantly greater quantities during low temperature (< 500 ^{o}C) thermolysis (Wang et al., 2010). Here, many BFRs, including PBDEs and PBBs, act as precursors for the formation of PBDDs and, in particular, PCDFs, through debromination and hydrogenation reactions, with the yield increasing in the presence of Sb_2O_3 (Weber and Kuch, 2003). The mild thermal stress involved in the production, moulding or recycling of plastics may be sufficient to produce PBDD/Fs under many circumstances (Ebert and Bahadir, 2003), resulting in calls from some (now historical) sources for plastics containing PBDEs not to be recycled (Meyer et al., 1993). PBDD/Fs are also formed under conditions employed during the incineration of municipal waste. Here, generation is greatest in the economiser, where temperatures are reduced from those in the combustion chamber and superheater to values optimal for PBDD/F formation (250 to 450 ^{o}C) (Wang et al., 2010). The presence and formation of PBDD/Fs in plastic goods poses a risk of exposure to consumers while their generation during processing or combustion presents an occupational risk and has adverse impacts on local air quality. Significantly, UNEP (2010) assert that the formation of PBDD/Fs is the most important contributor to the total health impacts arising from the recycling of PBDEs.

9. Marine pollution

Where plastic waste has captured the attention of the public and scientific community to the greatest extent over the past few years is the marine environment. Here, plastic has impacts that are many and varied, ranging from aesthetics to the local economy, and from vessel damage to wildlife entanglement. Additives and contaminants in plastics beached around the coasts of southwest England have recently been investigated by XRF (Turner, 2016; Massos and Turner, 2017) allowing a direct a comparison to be made of black consumer goods in current or recent use with black plastic objects and fragments of less well-defined origin and age.

Published and unpublished data generated by our research group indicate that beached plastic that is black constitutes less than 5% of the total population sampled on a number basis, a value that is considerably lower than estimates of black plastic in domestic waste stream after exclusion of WEEE (up to about 15%; Plastic Zero, 2014). The discrepancy may be partly attributable to the difficulty in

513 detecting black objects against a dark background or where black stones or macroalgae are present.
514 However, in our experience there were no clear differences in the relative abundance of black
515 plastics retrieved from a variety of beaches, including those that were composed only of fine, pale
516 sand. It is more likely that a higher proportion of black plastic has a density greater than that of sea
517 water (1.03 g cm^{-3}) and a propensity to sink rather than be washed up in the coastal zone. For
518 example, the density of PET is about 1.4 g cm^{-3} while the densities of materials commonly employed
519 in EEE range from around 1.05 g cm^{-3} for ABS and HIPS to at least 1.3 g cm^{-3} for PVC; higher values
520 also arise in the presence of residues and functional additives.

521 The occurrence and concentrations of hazardous elements in beached black plastics from southwest
522 England are summarised in Table 5. Here, samples have been categorised as primary objects that
523 were recognisable (mainly bottle tops), secondary fragments that were not identifiable, and plastic
524 pellets that are used as feedstock by the plastic manufacturing industry or as biobeads in
525 wastewater treatment (Cornish Plastic Pollution Coalition, 2017). In total, 135 samples from over
526 2000 retrieved were black, with the relative abundance of this colour greatest among pellets. Only
527 one black sample was constructed of PVC, with all of those identified by Fourier Transform Infrared
528 spectrometry (n ~ 50) as polyethylene (PE) or polypropylene (PP) and whose densities (0.90 to 0.97 g
529 cm^{-3}, respectively) are consistent with the sorting of marine plastics on this basis as asserted above.

530 Among the elements analysed, Hg was never detected and Br, Cr and Pb were most frequently
531 encountered, with detection frequencies of the latter elements similar across each sample category
532 and comparable with corresponding frequencies for non-WEEE products shown in Table 2. Thus,
533 despite a narrower range of plastic types and potential alteration of the chemical makeup by aging
534 and weathering, the hazardous element signature of beached samples in terms of detection
535 frequency (and concentration range) is comparable to that of non-EEE consumer goods and blended
536 WEEE plastic. Significantly, the common occurrence of Br, Pb and Sb in black pellets (but not in
537 pellets of other colours), which are likely derived from a multitude of local, regional and distant
538 sources, confirms the pervasive, widespread use of recycled EEE by the global plastics industry.

539 The similarities of black plastic in marine waste and consumer goods are illustrated more specifically
540 in Figure 3 where the concentration of Sb is plotted against the concentration of Br for beached
541 samples (and with the exception of a single object of PVC where Sb was employed as a synergist in
542 the highly chlorinated matrix). Thus, a significant relationship is evident with a slope of about 0.6
543 and an intercept of around 70 ppm. Although the estimate of the gradient was associated with
544 relatively high degree of uncertainty, a value greater than estimates for the slopes defining the Sb-Br
545 relationships for all categories of non-EEE and EEE in Table 4 suggests that brominated compounds

546 may have a greater propensity for mobilisation into sea water from the aging matrix than
547 compounds of Sb (Turner, 2018b).

548 With a higher frequency of hazardous elements (and in particular Br, Pb and Sb) than other colours
549 of beached plastic litter, black items pose greater risks of chemical exposure to organisms that
550 inadvertently or incidentally ingest plastics (including invertebrates, fish, birds, crustaceans and
551 cetaceans; Law, 2017). Few investigations have been performed in respect of chemical additives (for
552 any colour of plastic), partly because the significance of restricted elements incorporated into the
553 matrix of plastic litter (rather than being adsorbed to its surface) has only recently been
554 demonstrated (Nakashima et al., 2012; Turner and Solman, 2016). Nevertheless, in a study of PBDEs
555 in the abdominal adipose of twelve Pacific short-tailed shearwaters, Tanaka et al. (2013) found
556 accumulation of both lower- and higher-brominated congeners. Accumulation of the former were
557 attributed to exposure through the diet since similar congeners were present in natural prey (pelagic
558 fish), while accumulation of the latter was attributed to exposure from ingested plastics since these
559 congeners were absent from its prey but more typical of flame-retarded plastics retrieved from its
560 digestive tract. Of significance in the context of the present discussion, photographs of the ingested
561 plastic captured by the authors reveal a relatively high proportion (and significantly greater than 5%)
562 of black fragments. Tanaka et al. (2015) provided further evidence for the accumulation of PBDEs by
563 procellariiform seabirds from ingested plastics by conducting leaching experiments on materials
564 compounded with deca-BDE. Thus, while small quantities of the BFR were mobilised by sea water
565 and acidified pepsin, up to 40% was released in a solution containing fish oil, a component of
566 stomach fluid while feeding.

567 More recently, a kinetic study of the mobilisation of hazardous elements from microplastics into a
568 digestive fluid that simulates the chemical conditions in the gizzard-proventriculus of the northern
569 fulmar has been undertaken (Turner, 2018b). Cadmium, Cr, Pb and Sb release could be modelled
570 using a pseudo-first-order diffusion equation with rate constants ranging from of 0.02 to 0.5 h^{-1},
571 while bioaccessibilities (as a percentage of total elemental content) ranged from < 1 for Cd in PE to >
572 20% for Pb in PVC. Nakashima et al. (2016) have also shown that up to about 0.1% of Pb in PVC can
573 leach into sea water, and that further leaching is possible should the surface become damaged by
574 abrasion such as might happen when beached. While not all plastics tested in these studies were
575 black, the more frequent occurrence of hazardous elements in black materials is of relevance in the
576 context of the current synopsis.

577

578 **9. Concluding remarks and recommendations**

While environmental and health impacts arise from the production and use of plastics in general, black plastics pose greater risks and hazards because of technical and economic constraints imposed on the efficient sorting and separation of black waste for recycling, coupled with the presence of harmful additives required for black plastic production or applications in the EEE and food-packaging sectors. By comparison, for example, while historical white EEE may contain restricted chemical additives, end-of-life white plastic in general is more readily sorted and, therefore, sourced more safely for recycling.

Black PET, the most common component of black plastic in household waste, is not generally recycled and therefore sits within a linear economy. Suggestions made to improve its recyclability include technologies that better label or identify black materials or the use of different black pigments (Dvorak et al., 2011; Plastic Zero, 2014) but a more sustainable option would be to use lighter coloured (and preferably clear) plastic to package food, and especially where thermal stress is not a constraining factor. This could be accomplished by making the public more aware of the problems associated with black plastic recycling and subsequently pressuring retailers and manufacturers for change. To this end, and at the time of writing, one of the largest supermarket chains in the UK has announced plans to phase out black plastic food packaging from their own products by the end of 2019 (Moore, 2018).

In contrast, black EEE plastic is contained within a complex, poorly quantified and largely undesirable and unregulated quasi-circular economy. The life cycle of this material is conceptualised in Figure 4, along with some of the key environmental impacts and exposure pathways associated with the disposal and recycling of restricted additives (of which brominated compounds, Pb and Sb are conceived as the most problematic). Thus, here, the demand for black plastic from the manufacturing industry is at least partly met from recycled WEEE plastic that should be free of restricted additives like BFRs and heavy metals. However, poor or inefficient isolation of compliant material has resulted in such a wide and uncontrolled dispersion of contaminants in black plastics that their eradication is now only possible through the manufacture of black goods from virgin materials. Realistically, the most acceptable immediate objective would be a reduction in the impacts of hazardous additives through the recycling of black plastic into goods where human exposure is minimal (e.g. pallets, lumber, communal refuse bins, guttering, road signs).

Given the nature and scale of these challenges and the long-term, widespread contamination of multi-use black plastics, it is recommended that future scientific research focus on the behaviour and migration of additives that have been recycled into sensitive consumer goods like food-contact items, drinks vessels and small toys. While a few publications have recently addressed restricted

612 BFRs in this respect, there is a complete lack of information on the migratability of heavy metals, and
613 in particular, Pb.

614

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621 **References**

622 Aldrian, A., Ledersteger, A., Pomberger, R., 2015. Monitoring of WEEE plastics in regards to
623 brominated flame retardants using handheld XRF. Waste Management 36, 297-304.

624 Bandyopadhyay, A., 2009. Development of Indian electronic waste management policy. Progress in
625 Environmental Science and Technology 2A/2B, 2151-2158.

626 Becker, W., Sachsenheimer, K., Klemenz, M., 2017. Detection of black plastics in the middle infrared
627 spectrum (MIR) using photon up-conversion technique for polymer recycling purposes. Polymers 9,
628 435, doi:10.3390/polym9090435

629 Besis, A., Samara, C., 2012. Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor
630 environments - a review on occurrence and human exposure. Environmental Pollution 169, 217–
631 229.

632 Bezati,F., Froelich, D., Massardier, V., Maris, E., 2011. Addition of X-ray fluorescent tracers into
633 polymers, new technology for automatic sorting of plastics: Proposal for selecting some relevant
634 tracers. Resources, Conservation and Recycling 55, 1214-1221.

635 Bhaskar, T., Mitan, N.M.M., Onwudili, J., Muto, A., Williams, P.T., Sakata, Y., 2010. Effect of
636 polyethylene terephthalate (PET) on the pyrolysis of brominated flame retardant-containing high
637 impact polystyrene (HIPS-Br). Journal of Material Cycles and Waste Management 12, 332-340.

638 Brewer, S.A., 2004. Carbon black pigments for plastics. In: Coloring of Plastics: Fundamentals, ed.
639 R.A. Charvat. John Wiley, Hoboken, NJ, pp. 159-174.

640 Chen, S.-J., Ma, Y.-J., Wang, J., Chen, D., Luo, X.-J., Mai, B.-X., 2009. Brominated flame retardants in
641 children's toys: Concentration, composition, and children's exposure and risk assessment.
642 Environmental Science and Technology 43, 4200-4206.

643 Chen, S.-J., Ma, Y.-J., Wang, J., Tian, M., Luo, X.-J., Chen, D., Mai, B.-X., 2010. Measurement and
644 human exposure assessment of brominated flame retardants in household products from South
645 China. Journal of Hazardous Materials 176, 979-984.

646 Cornish Plastic Pollution Consortium, 2017.
647 http://www.ramepbc.org/Biobead%20pollution%20on%20our%20beaches,%20CPPC,%20October%2
648 02017.pdf (accessed 4/18).

649 Dimitrakakis, E., Janz, A., Bilitewski, B., Gidarakos, E., 2009. Small WEEE: Determining recyclables and
650 hazardous substances in plastics. Journal of Hazardous Materials 161, 913-919.

651 Dvorak, R., Kosior, E., Noody, L., 2011. Development of NIR Detectable Black Plastic Packaging.
652 Waste Resources Action Programme, Banbury, UK, 64pp.
653 http://www.wrap.org.uk/sites/files/wrap/Recyclability%20of%20black%20plastic%20packaging.pdf
654 (accessed 2/18).

655

656 Ebert, J., Bahadir, M., 2003. Formation of PBDD/F from flame-retarded plastic materials under
657 thermal stress. Environment International 29, 711-716.

658 Epacher, E., Krohnke, C., Pukanszy, B., 2000. Effect of catalyst residues on the chain structure and
659 properties of a Phillips type polyethylene. Polymer Engineering and Science 40, 1458-1468.

660 European Commission, 2011. Communication from the Commission to the European Parliament, the
661 Council, the European Economic and Social Committee and the Committee of the Regions: Tackling
662 the challenges in commodity markets and on raw materials. EC, Brussels, 22pp.

663 European Parliament and Council, 2003a. Directive 2002/96/EC on waste electrical and electronic
664 equipment (WEEE). Official Journal of the European Union L37/24.

665 European Parliament and Council, 2003b. Directive 2002/95/EC on the restriction of the use of
666 certain hazardous substances in electrical and electronic equipment. Official Journal of the European
667 Union L37/19.

668 European Parliament and Council, 2011. Directive 2011/65/EU on the restriction of the use of certain
669 hazardous substances in electrical and electronic equipment (recast). Official Journal of the
670 European Union L174/88.

671 European Parliament and Council, 2012. Directive 2012/19/EU on waste electrical and electronic
672 equipment (WEEE) (recast). Official Journal of the European Union L197/38.

673 European Parliament and Council, 2015. Amendment to Annex II of Directive 2011/65/EU. Official
674 Journal of the European Union L137/10.

675 Felix, T., Pinto, O.P., Peres, A., Costa, J.M., Sayer, C., Morgan, A.B., Araujo, P.H.H., 2012. Comparison
676 of bismuth trioxide and antimony trioxide as synergists with decabromodiphenyl ether in flame
677 retardancy of high-impact polystyrene. Journal of Fire Sciences 30, 566-574.

678 Furl, C., Mathieu, C., Roberts, T., 2012. Evaluation of XRF as a screening tool for metals and PBDEs in
679 children's products and consumer goods. Environmental Assessment Program Report No. 12-03-009,
680 Washington State Department of Ecology, Olympia, WA, 69pp.

681 Gallen, C., Banks, A., Brandsma, S., Baduel, C., Thai, P., Eaglesham, G., Heffernan, A., Leonards, P.,
682 Bainton, P., Mueller, J.F., 2014. Towards development of a rapid and effective non-destructive
683 testing strategy to identify brominated flame retardants in the plastics of consumer products.
684 Science of the Total Environment 491-492, 255-265.

685 Gebel, T., 1997. Arsenic and antimony: comparative approach on mechanistic toxicology. Chemico-
686 Biological Interactions 107, 131-144.

687 Haarman, A., Gasser, M., 2016. Managing hazardous additives in WEEE plastic from the Indian
688 informal sector. A study on applicable identification & separation methods. Sustainable Recycling
689 Industries, St. Gallen, Switzerland, 66pp.

690 Haldimann, M., Blanc, A., Dudler, V., 2007. Exposure to antimony from polyethylene terephthalate
691 (PET) trays used in ready-to-eat meals. Food Additives and Contaminants 24, 860-868.

692 Haldimann, M., Alt, A., Blanc, A., Brunner, K., Sager, F., Dudler, V., 2013. Migration of antimony from
693 PET trays into food simulant and food: determination of Arrhenius parameters and comparison of
694 predicted and measured migration data. Food Additives and Contaminants A 30, 587-598.

695 Han, Z.X., Wang, N., Zhang, H.L., Zhao, Y.X., 2017. Bioaccumulation of PBDEs and PCBs in a small food
696 chain at electronic waste recycling sites. Environmental Forensics 18, 44-49.

697 Hansen, E., Nilsson, N.H., Lithner, D., Lassen, C., 2013. Hazardous Substances in Plastic Materials.
698 Oslo: COWI and the Danish Technological Institute on behalf of The Norwegian Climate and Pollution
699 Agency, 150 pp.

700 Ignatyev, I.A., Thielemans, W., Beke, R.V., 2014. Recycling of polymers: A review. Chemsuschem 7,
701 1579-1593.

702 Jovanovic, B., 2017. Ingestion of microplastics by fish and its potential consequences from a physical
703 perspective. Integrated Environmental Assessment and Management 13, 510-515.

704 Kuang, J., Abdallah, M.A.-E., Harrad, S., 2018. Brominated flame retardants in black plastic kitchen
705 utensils: Concentrations and human exposure implications. Science of the Total Environment 610-
706 611, 1138-1146.

707 Law, K.L., 2017. Plastics in the marine environment. Annual Review of in Marine Science 9, 205-229.

708 Letsrecycle.com 1. https://www.letsrecycle.com/news/latest-news/wrap-tells-councils-to-view-
709 black-trays-as-rubbish/ (accessed 12/17).

710 Letsrecycle.com 2. https://www.letsrecycle.com/news/latest-news/plastics-recyclers-dependent-
711 china/ (accessed 12/17)

712 Li, W.-C., Tse, H.-F., Fok, L., 2016. Plastic waste in the marine environment: A review of sources,
713 occurrence and effects. Science of the Total Environment 566, 333-349.

714 Liagkouridis, I., Cousins, A.P., Cousins, I.T., 2015. Physical–chemical properties and evaluative fate
715 modelling of 'emerging' and 'novel' brominated and organophosphorus flame retardants in the
716 indoor and outdoor environment. Science of the Total Environment 524-525, 416-426.

717 Massos, A., Turner, A., 2017. Cadmium, lead and bromine in beached microplastics. Environmental
718 Pollution 227, 139-145.

719 Mello, P.A., Diehl, L.O., Oliveira, J.S.S., Muller, E.I., Mesko, M.F., Flores, E.M.M., 2015. Plasma-based
720 determination of inorganic contaminants in waste of electric and electronic equipment after
721 microwave-induced combustion. Spectrochimica Acta Part B – Atomic Spectroscopy 105, 95-102.

722 Meyer, H., Neupert, M., Pump, W., 1993. Flammschutzmittel entscheiden über die
723 Wiederverwertbarkeit (Flame retardants are decisive for material recycling). Kunststoffe 83, 253–
724 257.

Miller, G.Z., Tighe, M.E., Peaslee, G.F., Peňa, K., Gearhart, J., 2016. Toys, décor, and more: evidence of hazardous electronic waste recycled into new consumer products. Journal of Environmental Protection 7, 341-350.

Moore, D., 2016. Funding for "Invisible Markers" to boost plastics recycling quality. CIWM Journal Online, 24/2/17 https://ciwm-journal.co.uk/funding-for-invisible-markers-to-boost-plastics-recycling-quality/ (accessed 12/17).

Moore, D., 2018. Waitrose To Reduce Black Plastic Trays Amid Plastics Review. CIWM Journal Online, 19/1/18 https://ciwm-journal.co.uk/waitrose-reduce-black-plastic-trays-amid-plastics-review/ (accessed 1/18).

Nakashima, E., Isobe, A., Kako, S., Itai, T., Takahashi, S., 2012. Quantification of toxic metals derived from macroplastic litter on Ookushi Beach, Japan. Environmental Science and Technology 46, 10099-10105.

Nakashima, E., Isobe, A., Kako, S., Itai, T., Takahashi, S., Guo, X.Y., 2016. The potential of oceanic transport and onshore leaching of additive-derived lead by marine macro-plastic debris. Marine Pollution Bulletin 107, 333-339.

Ni, K., Lu, Y., Wang, T., Shi, Y., Kannan, K., Xu, L., Li, Q., Liu, S., 2013. Polybrominated diphenyl ethers (PBDEs) in China: Policies and recommendations for sound management of plastics from electronic wastes. Journal of Environmental Management 115, 114-123.

Obaje, S.O. , 2013. Electronic waste scenario in Nigeria: Issues, problems and solutions. International Journal of Engineering Science Invention 2, 31-36.

O'Connor, I.A., Golsteijn, L., Hendriks, A.J., 2016. Review of the partitioning of chemicals into different plastics: Consequences for the risk assessment of marine plastic debris. Marine Pollution Bulletin 113, 17-24.

Papazoglou, E.S., 2004. Flame retardants for plastics. In: Handbook of Building Materials for Fire Protection, Harper, C.A., ed, McGraw-Hill, New York.

Perkins, D.N., Drisse, M.N.B., Nxele, T., Sly, P.D., 2014. E-waste: A global hazard. Annals of Global Health DOI: 10.1016/j.aogh.2014.10.001.

Pierart, A., Shahid, M., Sejalon-Delmas, N., Dumat, C., 2015. Antimony bioavailability: Knowledge and research perspectives for sustainable agricultures. Journal of Hazardous Materials 289, 219-234.

Pfaff, G., 2017. Inorganic Pigments. Walter de Gruyter GmbH, Berlin, 329 pp.

PlasticsEurope.com, 2016. Plastics – the facts 2016. An analysis of European plastics production, demand and waste data. www.plasticseurope.com (accessed 12/17).

Plastic Zero, 2014. Carbon Black Plastic - Challenges and ideas for environmentally friendly alternatives. Technical and Environmental Administration, Sustainability Unit, Copenhagen, 28 pp. http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=home.showFile&rep=file&fil=PLASTIC_ZERO_sort_plast_brochure_final_en.pdf (accessed 1/18).

Ranta-Korpi, M., Konttinen, J., Saarimaa, A., Rodriguez, M., 2014. Ash forming elements in plastics and rubbers. VTT Technical Research Centre of Finland, Espoo, Finland, 131pp.

763 Resource Futures International, 2001. Persistent Organic Pollutants and the Stockholm Convention:
764 A Resource Guide. A report prepared for the World Bank and CIDA, 22pp.

765 Rozenstein, O., Puckrin, E., Adamowski, J., 2017. Development of a new approach based on midwave
766 infrared spectroscopy for post-consumer black plastic waste sorting in the recycling industry. Waste
767 Management 68, 38-44.

768 Samsonek, J., Puype, F., 2013. Occurrence of brominated flame retardants in black thermo cups and
769 selected kitchen utensils purchased on the European market. Food Additives and Contaminants: Part
770 A, 30, 1976–1986.

771 Santos, R.G., Andrades, R., Boldrini, M.A., Martins, A.S., 2015. Debris ingestion by juvenile marine
772 turtles: An underestimated problem. Marine Pollution Bulletin 93, 37-43.

773 Schlummer, M., Popp, L., Trautmann, F., Zimmermann, D., Maurer, A., 2016. Recovery of bromine
774 and antimony from WEEE plastics. Electronics Goes Green 2016+, IEEE, Piscataway, NJ, DOI:
775 10.1109/EGG.2016.7829830

776 Sepúlveda, A., Schluep, M., Renauld, F.G., Streicher, M., Kuehr, R., Hagelüken, C., Gerecke, A.C.,
777 2010. A review of the environmental fate and effects of hazardous substances released from
778 electrical and electronic equipments during recycling: Examples from China and India. Environmental
779 Impact Assessment Review 30, 28-41.

780 Shaw, S.D.H., Jennifer, H., Berger, Michelle L., Subedi, B., Kannan, K., 2014. Brominated flame
781 retardants and their replacements in food packaging and house- hold products: uses, human
782 exposure, and health effects. In: Snedeker, S.M. (Ed.), Toxicants in Food Packaging and Household
783 Plastics, Molecular and Integrative Toxicology. Springer-Verlag, London. DOI: 10.1007/978-1-4471-
784 6500-2_3.

785 Sheavly, S.B., Register, K.M., 2007. Marine debris and plastics: Environmental concerns, sources,
786 impacts and solutions. Journal of Polymers and the Environment 15, 301-305.

787 Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M., Watanuki, Y., 2013.
788 Accumulation of plastic-derived chemicals in tissues of seabirds ingesting marine plastics. Marine
789 Pollution Bulletin 69, 219-222.

790 Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M.A., Watanuki, Y., 2015. Facilitated
791 leaching of additive-derived PBDEs from plastic by seabirds' stomach oil and accumulation in tissues.
792 Environmental Science and Technology 49, 11799-11807.

793 Tanskanen, P., Butler, E., 2007. Mobile phone take back – learning's from various initiatives.
794 Proceedings of the 2007 IEEE international symposium on electronics & the environment, 206-209.

795 Terazono, A., Oguchi, M., Iino, S., Mogi, S., 2015. Battery collection in municipal waste management
796 in Japan: Challenges for hazardous substance control and safety. Waste Management 39, 246-257.

797 Titow, W.V., 2012. Stabilisers: General aspects. In: PVC Technology, fourth edition, ed. W.V. Titow,
798 Elsevier, London, pp. 255-329.

799 Tokarz, J.A., Ahn, M-Y, Leng, J., Filley, T.R. and Nies, L., 2008. Reductive debromination of
800 polybrominated diphenyl ethers in anaerobic sediment and a biomimetic system. Environmental
801 Science and Technology 42, 1157-1164.

802 Turner, A., 2016. Hazardous metals, metalloids and other elements in marine litter. Marine Pollution
803 Bulletin 111, 136-142.

804 Turner, A., 2018a. In situ elemental characterisation of marine microplastics by portable XRF. Marine
805 Pollution Bulletin 124, 286-291.

806 Turner, A., 2018b. Mobilisation kinetics of hazardous elements in marine plastics subject to an avian
807 physiologically-based extraction test. Environmental Pollution 236, 1020-1026.

808 Turner, A., Filella, M., 2017a. Field-portable-XRF reveals the ubiquity of antimony in plastic consumer
809 products. Science of the Total Environment 584-585, 982-989.

810 Turner, A., Filella, M., 2017b. Bromine in plastic consumer products – Evidence for the widespread
811 recycling of electronic waste. Science of the Total Environment 601-602, 374-379.

812 Turner, A., Solman, K.R., 2016. Analysis of the elemental composition of marine litter by field-
813 portable-XRF. Talanta 159, 262-271.

814 UNEP, 2010. Technical review of the implications of recycling commercial pentabromodiphenyl ether
815 and commercial octabromodiphenyl ether. POPS/POPRC 6.2, United Nations Environment
816 Programme, Geneva, 41 pp.

817 UNEP, 2014. Basel Convention on the Control of Transboundary Movements of Hazardous Wastes
818 and Their Disposal. United Nations Environment Programme, Geneva, 119pp.

819 UNIDO, 2017. Guidance on best available techniques and best environmental practices for the
820 recycling and disposal of wastes containing polybrominated diphenyl ethers (PBDEs) listed under the
821 Stockholm Convention on Persistent Organic Pollutants. United Nations Industrial Development
822 Organization, Vienna, 111 pp.

823 Van Caneghem, J., Verbinnen, B., Cornelis, G., de Wijs, J., Mulder, R., Billen, P., Vandecasteele, C.,
824 2016. Immobilization of antimony in waste-to-energy bottom ash by addition of calcium and iron
825 containing additives. Waste Management 54, 162-168.

826 Van Eygen, E., Feketitsch, J., Laner, D., Rechberger, H., Fellner, J., 2017. Comprehensive analysis and
827 quantification of national plastic flows: The case of Austria. Resources, Conservation and Recycling
828 117, 183-194.

829 Wäger, P.A., Schluep, M., Müller, E., Gloor, R., 2012. RoHS regulated substances in mixed plastics
830 from waste electrical and electronic equipment. Environmental Science and Technology 46, 628-635.

831 Wang, L.-C., His, H.-C., Wang, Y.-F., Lin, S.-L., Chang-Chien, G.-P., 2010. Distribution of
832 polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans
833 (PBDD/Fs) in municipal solid waste incinerators. Environmental Pollution 158, 1595-1602.

834 Weber, R., Kuch, B., 2003. Relevance of BFRs and thermal conditions on the formation pathways of
835 brominated and brominated–chlorinated dibenzodioxins and dibenzofurans. Environment
836 International 29, 699-710.

837 Zhang, K., Schnoor, J.L., Zeng, E.Y., 2012. E-waste recycling: Where does it go from here?
838 Environmental Science and Technology 46, 10861-10867.

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Table 1: Categorisation and inventory of common consumer products that are constructed in part or in whole of black plastic.

Food-contact	Storage and construction	Clothing and accessories	Toys and hobbies	Office and garden	EEE
drinks stirrers	coat hangers and sizer labels	buttons and toggles	car chassis and wheels	stapler and scissor grips	televisions
coffee cup lids	bottles and lids	spectacle frames and sunglasses	caterpillar tracks	seating and handles	mobile phones
straws	tubes and caps	beads and necklaces	figures and animals	tarping and mesh	laptops and tablets
kitchen utensils	spectacle cases	bracelets and brooches	toy guns	lawnmower blades	cameras and lenses
thermos mugs and flasks	rucksacks	watch straps	trains and tracks	wire ties	games consols
food presentation trays	cases	masks	balls and marbles	bins and butts	media storage
ready meal trays	luggage tags	protective clothing and guards	games icons and figures	pens and lids	wire insulation
cutlery	carrier bags	shoes and boots	magnetic counters	taping	chargers, plugs and transformers
coffee plungers	folders	hair bands and clips	trophy bases	hosing	remote controls
bottles and bottle tops	refuse sacks	strapping and cord	tripods	furniture	electrical toys
coffee pods	boxes and crates	shoehorns	musical instruments	trolley wheels	radios
ice cream carton lids	CD and DVD cases	keyfobs	Xmas cracker toys	rivets	domestic appliances
draining boards	ink cartridges	umbrellas	Xmas decorations	foot pumps and adaptors	power tools
tupperware lids	suckers	hair brushes and combs	photo frames and book covers	plant pots	printers and copiers
lunch boxes	cable ties and strapping	belts	tweezers	garden tools	projectors
stoppers and caps	piping	wallets and purses	printing sets	signage	calculators
	caistors		building blocks	parcel packaging	lighting equipment
	tool grips		fidget spinners		DVD players

Table 2: Detection frequency and descriptive statistics for the elements determined by XRF in the different sample categories of black plastic. Concentrations are in ppm.

element	descriptor	Food-contact (*n* = 129; PVC = 1)	Storage and construction (*n* = 112; PVC = 11)	Clothing and accessories (*n* = 71; PVC = 2)	Toys and hobbies (*n* = 86; PVC = 4)	Office and garden (*n* = 97; PVC = 12)	EEE (*n* = 133; PVC = 11)
Br	*n*	29	57	38	49	32	88
	mean	594	2800	3850	1180	359	6280
	median	56.3	142	53.9	74.9	19.7	244
	min-max	2.6-6010	3.4-94,500	1.5-92,200	3.3-14,500	1.5-7000	1.8-133,000
Cd	*n*	8	7	6	4	10	8
	mean	79.0	77.5	6100	433	502	84.0
	median	67.5	56.3	146	317	246	52.9
	min-max	27.2-148	18.6-209	77.0-35,000	197-902	21.1-1590	18.8-287
Cr	*n*	35	15	15	11	12	20
	mean	58.6	41.3	283	80.6	119	108
	median	36.9	36.2	117	38.5	29.4	61.1
	min-max	19.4-278	18.3-99.4	19.1-1800	18.1-389	17.8-847	16.4-478
Hg	*n*	1	1	4	0	1	1
	mean	25.8	6.8	18.4		16	91.7
	median			12.8			
	min-max			4.8-43.4			
Pb	*n*	18	32	25	29	27	31
	mean	40.5	1170	473	629	2220	915
	median	44.5	48.5	50.6	76.3	103	76.1
	min-max	5.9-101	4.3-16,500	5.2-4670	5.6-9600	4.1-14,100	2.2-11,800
Sb	*n*	20	30	15	22	15	51
	mean	560	2780	4740	1490	2080	4760
	median	342	398	240	447	456	600
	min-max	137-3200	24.7-35,850	29.5-48,600	52.9-9190	99.5-17,700	38.8-56,900

Table 3: A comparison of detection frequency and descriptive statistics for the elements determined by XRF in pre- and post-RoHS EEE black plastics. Note that Hg was not detected in either category. Concentrations are in ppm.

element	descriptor	Pre-RoHS (*n* = 32; PVC = 4)	Post-RoHS (*n* = 90; PVC = 7)
Br	*n*	21	58
	mean	13,900	3930
	median	753	214
	min-max	3.7-101,000	1.8-133,000
Cd	*n*	3	4
	mean	58.9	52.1
	median	48.1	52.9
	min-max	29.2-99.7	18.8-83.9
Cr	*n*	4	15
	mean	127	106
	median	157	52.2
	min-max	20.5-172	16.4-478
Pb	*n*	12	18
	mean	1990	245
	median	101	28.9
	min-max	8.0-11,800	2.2-1650
Sb	*n*	15	32
	mean	9210	2920
	median	776	552
	min-max	53.4-56,900	38.8-30,100

Table 4: Results of regression analyses of Sb versus Br for the different black plastic sample categories.

category	*n*	slope	intercept, ppm	r^2	*p*
Food-contact	7	0.331	119	0.939	<0.001
Storage and construction	25	0.377	227	0.998	<0.001
Clothing and accessories	9	0.383	216	0.995	<0.001
Toys and hobbies	19	0.541	80.8	0.929	<0.001
Office and garden	6	0.480	167	0.919	0.003
All non-EEE	66	0.386	273	0.981	0.002
pre-RoHS EEE	12	0.464	-822	0.726	<0.001
post-RoHS EEE	24	0.229	695	0.966	<0.001
pre- and post-RoHS EEE	36	0.342	562	0.705	<0.001

Table 5: Detection frequency and descriptive statistics for the elements determined by XRF in beached black plastic litter. Note that Hg was not detected in any sample category. Concentrations are in ppm.

element	descriptor	Objects (n = 17; PVC = 1)	Fragments (n = 10; PVC = 0)	Pellets (n = 108; PVC = 0)	Total (n = 135; PVC = 1)
Br	*n*	9	4	46	59
	mean	26.2	245	298	253
	median	13.0	185	26.5	25.6
	min-max	9.2-94.7	16.9-591	4.5-4590	4.5-4590
Cd	*n*	1	1	8	10
	mean	123	79.8	85.6	88.8
	median			76.1	80.4
	min-max			63.1-139	63.1-139
Cr	*n*	5	7	56	68
	mean	47.3	40.9	53.9	52.1
	median	43.2	33.6	41.5	41.5
	min-max	24.1-70.1	24.3-81.7	21.5-538	21.5-538
Pb	*n*	7	5	34	46
	mean	47.1	71.2	77.8	72.4
	median	35.7	37.7	35.8	35.9
	min-max	8.5-109	11.0-149	11.2-941	8.5-941
Sb	*n*	1	2	10	13
	mean	6260	340	784	1140
	median		340	327	364
	min-max		150-531	74.0-2720	74.0-6260

888 Figure 1: Examples of EEE and non-EEE samples that were Pb-positive (a) and non-EEE samples that
889 were Br-positive (b).

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Figure 2: Concentrations of Sb versus concentrations of Br in non-EEE black plastic samples (a) and black plastic EEE casings (b).

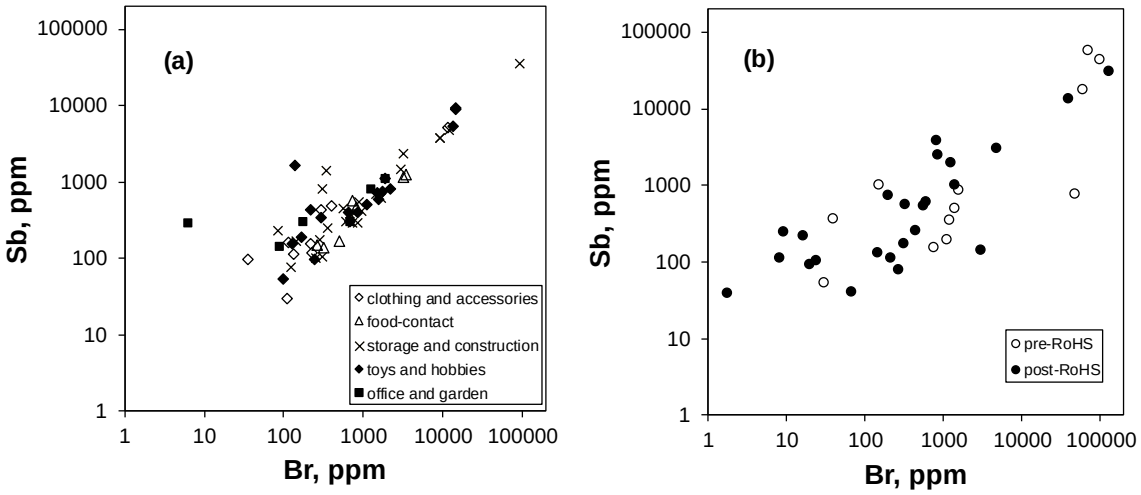

Figure 3: Concentrations of Sb versus concentrations of Br in beached black plastics. Note that Sb was not detected in distinct objects that were non-PVC-based.

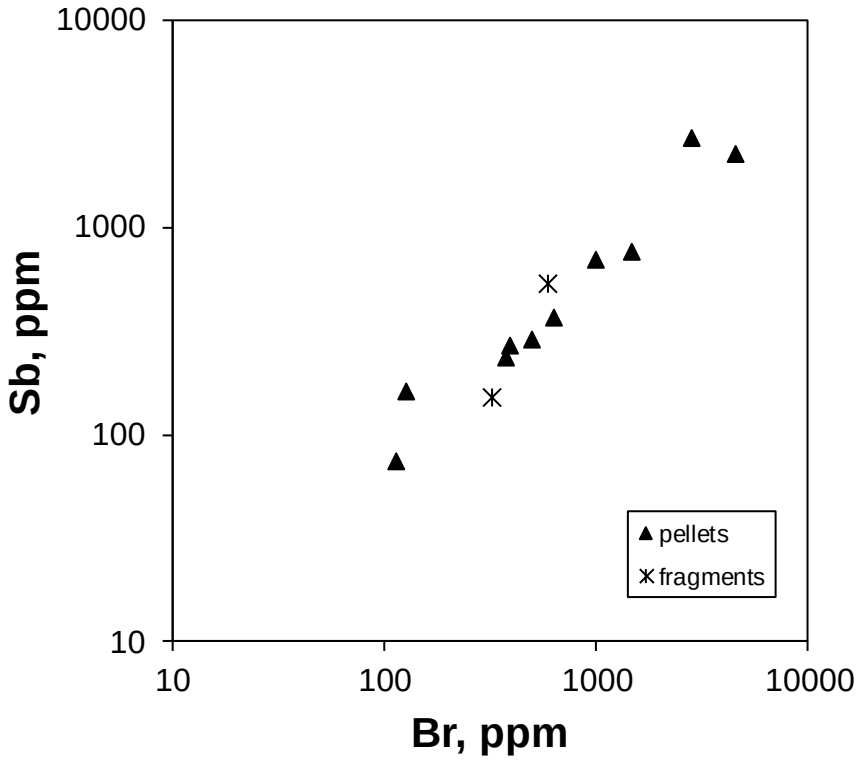

Figure 4: The life cycle of black plastic used in EEE. Solid lines represent the preferred pathways based on adequate testing for Br, while broken lines represent the non-preferred pathways along with exposure routes and environmental impacts of hazardous additives (brominated compounds, Pb and Sb).