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1 **Recycled electronic plastic and marine litter**

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12 **Abstract**

13 Black consumer plastics are often contaminated with hazardous chemicals because of technological
14 constraints on sorting dark plastic during recycling of municipal waste coupled with the convenience
15 of waste electrical and electronic equipment (WEEE) as a secondary source of black plastic. In this
16 study, samples of beached plastic litter ($n= 524$) from southwest England were categorised according
17 to origin, appearance and colour (black versus non-black) before being analysed by x-ray
18 fluorescence (XRF) spectrometry for elements that are characteristic of EEE. The small number of
19 items of WEEE retrieved ($n = 36$) were largely restricted to wiring insulation and constructed of lead-
20 stabilised polyvinyl chloride (PVC). Amongst the remaining samples, Br, Cd, Cr and Pb were
21 commonly detected in all categories of black plastics ($n= 264$) with maximum concentrations of
22 $43,400 \text{ mg kg}^{-1}$, 2080 mg kg^{-1} , 662 mg kg^{-1} and $23,800 \text{ mg kg}^{-1}$, respectively. Moreover,
23 concentrations of Br were significantly correlated with concentrations of the flame retardant
24 synergist, Sb ($n = 22$), and 35 samples were potentially non-compliant with regard to limits defined
25 by the Restriction of Hazardous Substances Directive. For plastics of other colours ($n =224$), Br and
26 Pb were detected in fewer samples and Br was co-associated with Sb in only two cases, with
27 occasional high concentrations Cd, Cr and Pb largely attributed to the historical use of cadmium
28 sulphide and lead chromate pigments. An avian physiologically-based extraction test applied to
29 selected samples cut to mm-dimensions revealed bioaccessibilities ranging from $< 0.1\%$ for Cr in a
30 green fragment to about 2.4% (or about 580 mg kg^{-1}) for Pb in black PVC. The recycling of WEEE into
31 consumer, industrial and marine (e.g. fishing) plastics that are mainly coloured black appears to be
32 an important vehicle for the introduction of hazardous chemicals into the environment and a source
33 of their exposure to wildlife.

34 **Keywords:** electrical and electronic; marine plastic; bromine; heavy metals; recycling; exposure

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37 **1. Introduction**

38 From both a human health and environmental perspective, one of the major concerns associated
39 with plastics, and in particular those available to the consumer, is the presence and potential
40 mobility of harmful chemicals (Lithner et al., 2011). Residues may remain in the polymeric matrix as
41 polymerisation catalysts, unreacted monomers or impurities, while other chemicals are added
42 intentionally to improve performance, functionality and ageing properties and include fillers,

43 plasticisers, pigments for colour, flame retardants, antistatic agents, lubricants, biocides and heat
44 and UV stabilisers (Gallo et al., 2018; Hahladakis et al., 2018).

45 Various international regulations have been introduced to restrict the amount or mobility of certain
46 hazardous chemicals in consumer plastics. For example, the European Packaging and Packaging
47 Waste Regulations stipulate that the aggregate concentrations of the heavy metals, Cd, Hg, Pb and
48 hexavalent Cr, should not exceed 100 mg kg⁻¹ in plastic packaging or packaging components except
49 for pallets and crates that are in a controlled distribution and reuse system (European Parliament
50 and Council of the EU, 1994; BIS, 2015). The same metals, plus certain brominated flame retardants
51 (polybrominated biphenyls, PBB, and polybrominated diphenyl ethers, PBDE) are encompassed by
52 the Restriction on Hazardous Substances (RoHS) Directive that deals with electrical and electronic
53 equipment (EEE), including EEE plastic (European Parliament and Council, 2003; BIS, 2011). Effective
54 since 2006, and forming the basis of similar regulations worldwide (Ilankoon et al., 2018), this
55 Directive stipulates that hazardous chemicals should be avoided and that concentrations are limited
56 in any homogeneous component of EEE to concentrations of 1000 mg kg⁻¹ or, for Cd, to 100 mg kg⁻¹.

57 While PBB and PBDE (as flame retardants) and compounds of Pb and Cd (as, for example, heat
58 stabilisers in PVC) have been used directly in historical EEE plastics, restricted chemicals used in
59 other (non-plastic) components of EEE, like soldered joints, corrosion protectors and switches, are
60 able to contaminate any plastic that is recovered (Wäger et al., 2012). Consequently, plastic recycled
61 from waste EEE (WEEE), unless properly screened and sorted, is a source of hazardous chemical
62 exposure in new goods, including consumer products (Turner and Filella, 2017; Cao et al., 2019). This
63 problem is particularly acute in black plastics because conventional and widely adopted near-
64 infrared sensors used to discriminate municipal waste plastic by resin code (polymer type) for
65 recycling are unable to detect a sufficient spectral signal from this colour (Rozenstein et al., 2017).
66 With black being a common and popular choice for EEE plastic housings, WEEE appears to be a
67 convenient source of plastic recyclate for new black goods (Turner, 2018a).

68 The marine environment is a significant recipient of vast quantities of contemporary and historical
69 plastic from a multitude of land-based and offshore sources. Much of this plastic is likely to have
70 been manufactured or recycled before regulations on hazardous chemicals were in place but
71 relatively little attention has been paid to additives and residues in marine waste and to whether
72 material is compliant or poses a threat to wildlife. A recent review by Hermabessiere et al. (2017)
73 highlighted the dearth of information in this respect but suggested that brominated flame
74 retardants, phthalate plasticisers, nonylphenols and bisphenol A are of greatest concern. However,
75 elemental measurements of marine plastic suggest that heavy metals are also a potential

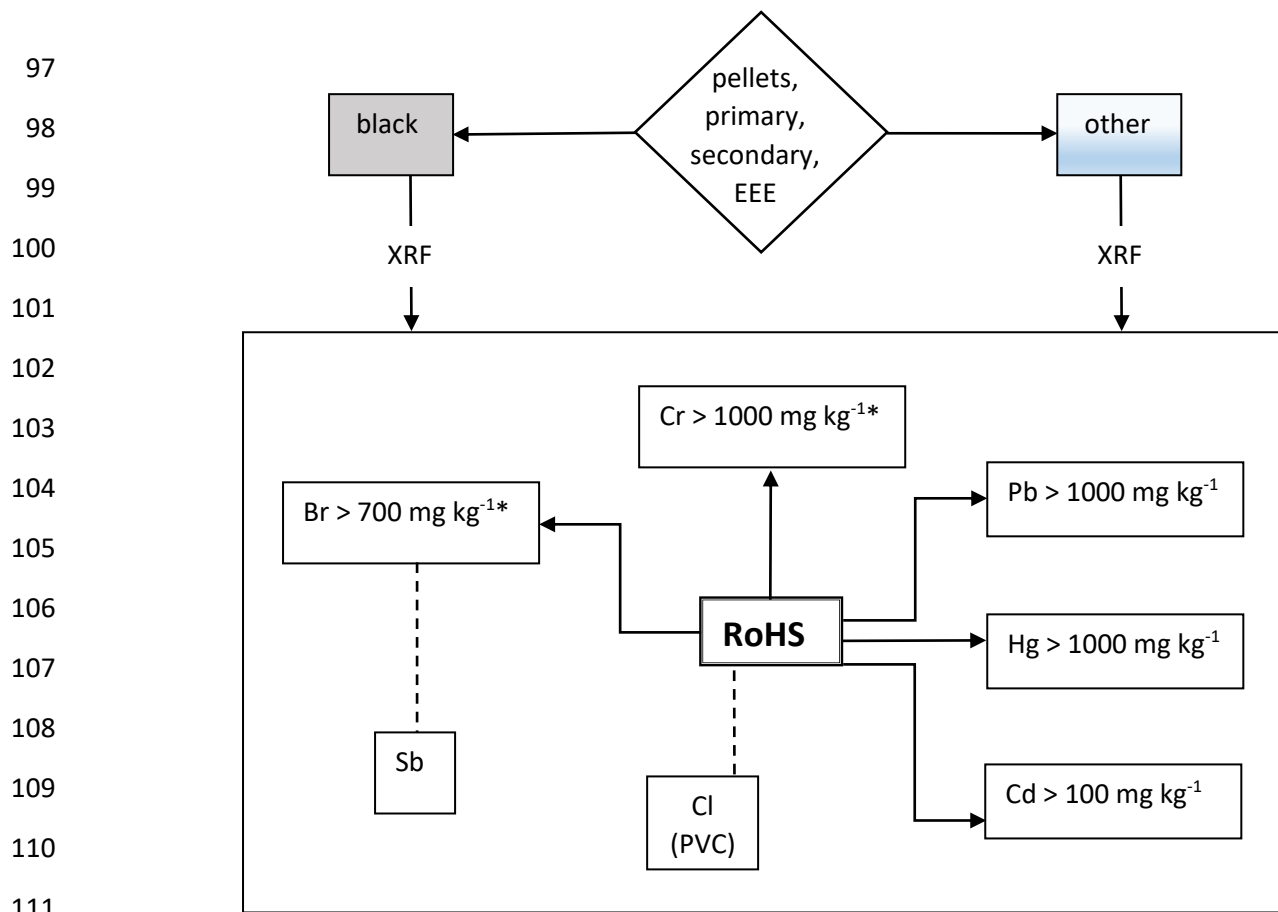
76 ecotoxicological risk (Turner, 2016; Massos and Turner, 2017), with chemical signatures bearing
77 similarities with WEEE plastic in many cases (Turner, 2018a).

78 In the present study, plastic samples, including WEEE material, are collected from beaches of south
79 west England and analysed in the context of the RoHS Directive in order to evaluate the presence
80 and origin of hazardous additives (and as conceptualised in Figure 1). Specifically, material is tested
81 by x-ray fluorescence (XRF) spectrometry for Cd, Pb, Hg, total Cr as a proxy for Cr(VI), and elemental
82 Br as a proxy for restricted brominated flame retardants, with compliance limits equal to those given
83 in the RoHS Directive and stated above with the exception of Br (set at 700 mg kg⁻¹, a representative
84 concentration of Br in 1000 mg kg⁻¹ of restricted brominated compounds). Antimony is also analysed
85 because of its co-association with many halogenated flame retardants as a flame quenching
86 synergist and Cl is analysed in order to discriminate polyvinyl chloride (PVC) from other types of
87 polymer. Samples are further categorised according to visual characteristics (e.g. primary versus
88 secondary plastics), and samples coloured black are compared with samples of other colours to test
89 the hypothesis that black plastics are more likely to be derived from recycled WEEE because of
90 difficulties in sorting and recycling this colour from the municipal waste stream. An avian
91 physiologically-based extraction test (PBET) is also applied to selected samples that had been grated
92 to mm-dimensions in order to evaluate elemental bioaccessibility to seabirds that incidentally or
93 deliberately ingest microplastics.

94

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96



112
113 **Figure 1:** Flowchart showing the categorisation of marine plastics and the elements analysed in the
114 present study, with RoHS-compliance limits indicated where applicable (asterisks denote potential
115 compliance limits).

116 **2. Methods**

117 *2.1. Sampling*

118 Samples of marine plastic (excluding rubbers) visible by eye were collected by hand during late 2018
119 and early 2019 from 50 m sections of the strandlines of five southwest- or northwest-facing sandy
120 beaches in south west England; namely, Thurlestone (50.26436, -3.86164), Sharrow (50.34753, -
121 4.25983), Tregonhawke (50.34043, -4.24220), Marazion (50.12380, -5.47642) and Crantock
122 (50.40799, -5.12553). In addition, plastic samples were retrieved from the south east-facing small
123 rocky-sandy cove of Picklecombe (50.34272, -4.17855) in Plymouth Sound, a more sheltered
124 embayment supporting a variety of industries and shipping activities.

125 In the laboratory, samples were rinsed under tap water to remove traces of surficial sea salts and
126 air-dried for 48 hours before being categorised as pellets (nurdles and water treatment bio-beads of

127 < 5 mm in diameter), primary plastics (distinct objects), secondary fragments whose origin could be
128 identified, secondary fragments of unknown origin, and objects and fragments of electrical and
129 electronic equipment. Within each category, samples were further divided by colour type into
130 plastics that were black (including charcoal and dark grey) and that were non-black.

131 2.2. XRF analysis

132 About 500 samples were characterised for a range of elements (but focussing on Cl, Br, Cd, Cr, Hg,
133 Pb, Sb) by field portable XRF spectrometry, with at least 30 selected from each category and colour
134 type where possible. Samples were placed in an accessory test stand with the flattest surface over
135 the detector window of a battery-powered Niton XL3t 950 He GOLDD+ XRF. Samples too big to fit in
136 the stand were cut to an appropriate size with scissors or a knife and any metal components
137 embedded in plastic (e.g. electrical wires) were removed with pliers. The XRF was operated remotely
138 in a plastics mode with thickness correction and after having measured sample thickness with digital
139 callipers, for successive counting periods of 25 s at 50 kV and 40 μ A and 15 s at 20 kV and 100 μ A.

140 For quality assurance purposes, two reference polyethylene discs were analysed after every 15
141 samples; specifically, disc PE-071-N (PN 180-554) contained Br, Cd, Cr, Hg and Pb at concentrations
142 similar to corresponding limits defined by the RoHS, and disc T-18 (PN 180-619) contained Cd, Cr, Hg,
143 Pb and Sb at concentrations < 200 mg kg⁻¹. Concentrations returned by the XRF were always within
144 10% of reference values with the exception of Sb (up to 16%) and, overall, replicate readings
145 revealed precisions of better than 90%. Median measurement detection limits, based on three
146 counting errors, were around 10 mg kg⁻¹ for Br, Cr, Hg and Pb, and about 25 mg kg⁻¹ and 40 mg kg⁻¹
147 for Cd and Sb, respectively.

148 2.3. Avian PBET

149 A physiologically-based extraction test (PBET) based on the digestive conditions encountered in the
150 gizzard-proventriculus of the northern fulmar (*Fulmarus glacialis*) was employed to evaluate the
151 bioaccessibility of hazardous elements in selected plastic samples (Turner, 2018b). Thus, eight
152 samples from different categories and of both colour type were cut to 1-2 mm pieces using a
153 stainless steel grater and 100 mg of each were weighed into individual, screw-capped polypropylene
154 centrifuge tubes. Digestive fluid was prepared in a 500 mL volumetric flask by dissolving 5 g of
155 pepsin (lyophilised powder from porcine gastric mucosa; Sigma-Aldrich) in a solution of 0.1 M NaCl
156 whose pH was adjusted to 2.5 by dropwise addition of 1 M HCl. Aliquots of 40 mL were added to
157 each centrifuge tube, plus a tube without solids as a control, and the contents incubated laterally in
158 a Fisher Scientific Isotemp SWB27 water bath set at 40°C and 100 rpm. After 120 h, 1 mL of fluid

159 from each reactor was pipetted into a new centrifuge tube and diluted to 5 mL with 2% HNO₃ and
160 stored under refrigeration awaiting analysis.

161 Extracts were analysed in triplicate for ⁸¹Br, ¹¹¹Cd, ⁵²Cr, ²⁰⁸Pb and ¹²¹Sb by collision cell-inductively
162 coupled plasma-mass spectrometry (ICP-MS) using a Thermo-Scientific iCAP RQ with a concentric
163 glass nebuliser and conical spray chamber. The instrument was calibrated externally using five mixed
164 standards (in the range 0 to 40 µg L⁻¹) of each element prepared in 2% HNO₃, and internal calibration
165 was achieved by the addition of 50 µg L⁻¹ of both ¹¹⁵In and ¹⁹³Ir to all standards and samples. Radio
166 frequency power was 1450 W and auxiliary, coolant, nebuliser and collision cell gas flows rates were
167 0.80 L Ar min⁻¹, 14 L Ar min⁻¹, 1.07 L Ar min⁻¹ and 4.288 mL 7 % H₂ in He min⁻¹, respectively; data were
168 acquired over a dwell period of 10 ms and with 50 sweeps per reading. Analytical precision between
169 replicates was generally better than 90% and limits of detection, based on three standard deviations
170 arising from blank measurements, ranged from about 0.01 µg L⁻¹ for Cd to 0.3 µg L⁻¹ for Br.

171

172 **3. Results**

173 *3.1. Visual and physical characteristics*

174 Table 1 shows the number of samples from each category that were analysed by XRF, along with the
175 number of samples that were constructed of PVC based on the intrinsic chlorine signal returned by
176 the instrument (> 150,000 mg kg⁻¹). Note that other polymers were not identified, largely because of
177 difficulties in obtaining infrared or Raman spectra for black plastics, but previous studies of beached
178 primary and secondary plastics (including pellets) of other colours from these environments indicate
179 a dominance of polyethylene and polypropylene (Massos and Turner, 2017). Note also that the
180 numbers in Table 1 do not reflect the relative abundance of each category or colour but were aimed
181 at providing a representative sample number of each type for comparative purposes. Significantly,
182 while the majority of bio-beads and electronic plastics were black, this colour comprised between
183 about 5% and 10% of other sample types on a number basis.

184 There was a limited number of electrical and electronic samples along the beach strandlines ($n =$
185 36), with the majority of such items retrieved from two locations and comprising offcuts of (mainly)
186 black, PVC-based wire and cable insulation whose electrical wires were still intact at the time of
187 sampling. Remaining samples from this category were non-PVC-based casings (or casing parts) from
188 small electronic communication equipment, including the front frames of a mobile phone and a
189 radio. None of the 137 pellet samples retrieved were constructed of PVC, and while bio-beads used

190 in water treatment were mainly black, pre-production pellets were a variety of colours but mainly
 191 white to off-white or translucent.

192 Black primary plastics ($n = 63$) included lids, combs, buttons, bottle tops, wire ties, toys and tubing
 193 but no items in this category were constructed of PVC; primary plastics of other colours ($n = 30$)
 194 included, additionally, lolly sticks, pens, cigarette lighters, bottle stoppers, golf tees and gun
 195 cartridges, with a single item (an orange bottle cap) constructed of PVC. Secondary plastics that
 196 were identifiable ($n = 109$) included fragments from cutlery, bottles, clothes hangers, handles,
 197 straps, fencing, fishing ropes and plant pots of different colours (including black) and four PVC-based
 198 items; secondary fragments of different colours that were not recognisable ($n = 149$) were generally
 199 smaller and more rounded and either flat or curved, and included a greater proportion of PVC-based
 200 items ($n = 8$).

201 **Table 1:** The number of beached plastic samples, by category and colour, analysed by XRF. Numbers
 202 in parentheses denote samples of PVC-construction.

	black	other colours	total
pellets	39	98	137
primary	63	30 (1)	93 (1)
secondary known	72 (3)	37 (1)	109 (4)
secondary unknown	90 (3)	59 (5)	149 (8)
EEE	26 (20)	10 (2)	36 (22)
total	290 (26)	234 (9)	524 (35)

204 *3.2. Chemical characteristics*

205 The number of cases in which Br, Cd, Cr, Hg, Pb and Sb were detected, along with summary statistics
 206 defining their concentrations, are shown for each plastic category and both colour type in Tables 2
 207 and 3. Bromine, Pb and Sb were detected more frequently, on a number and percentage (relative to
 208 total) basis, in black plastics than in other coloured plastic in each category. Overall, respective
 209 detection in black plastic and other plastic was about 40% and 16% for Br, 34% and 15% for Pb, and
 210 13% and 2% for Sb. Detection of Cd and Cr was more evenly distributed between categories and
 211 colour type, although the former was more abundant among secondary plastics, and Hg was only
 212 detected in one sample (a black radio cover).

213 Concentrations are highly variable and non-normally distributed within each category and for both
 214 colour types of plastic, and in particular among black plastics where concentrations of Pb span five
 215 orders of magnitude and concentrations of Br and Sb span three orders of magnitude. With respect
 216 to the RoHS limits shown in Figure 1, non-compliance (or potential non-compliance), also indicated

217 in Tables 2 and 3 and exemplified illustratively in Figure 2, occurs in 46 cases for black samples (and
218 mainly for Br, Cd and Pb) and in 26 cases for plastics of other colours (and largely for Cd and Pb),
219 with only one sample potentially non-compliant with respect to two elements (Cd and Cr in a green,
220 secondary unknown fragment).

221



222

223 **Figure 2:** Examples of beached plastics from south west England that were non-compliant or
224 potentially non-compliant with respect to RoHS regulations.

225

226 **Table 2:** Number of cases in which hazardous elements were detected and summary statistics for
227 their concentrations in the different categories of beached black plastics. Note that all

228 concentrations are in mg kg⁻¹ and that *n* > RoHS refers to the number of cases in which
 229 concentrations exceed corresponding RoHS limits.

		Br	Cd	Cr	Hg	Pb	Sb
pellets (<i>n</i> = 39)	<i>n</i>	24	5	19	0	16	6
	mean	272	105	73.8		69.2	606
	median	20.9	46.5	47.4		23.4	139
	min	4.4	35.1	17.4		7.9	74.0
	max	5020	321	249		494	2810
	<i>n</i> > RoHS	1	1	0	0	0	
primary (<i>n</i> = 63)	<i>n</i>	20	5	21	0	17	7
	mean	346	794	34.7		48.7	478
	median	31.5	461	29.0		33.0	359
	min	3.5	21.7	17.3		6.6	37.3
	max	1840	2080	64.6		159	884
	<i>n</i> > RoHS	4	5	0	0	0	
secondary known (<i>n</i> = 72)	<i>n</i>	20	5	23	0	22	10
	mean	377	598	38.8		863	540
	median	26.2	534	30.7		42.6	249
	min	3.8	24.9	19.3		4.3	210
	max	4100	1750	95.3		9490	2810
	<i>n</i> > RoHS	3	2	0	0	2	
secondary unknown (<i>n</i> = 90)	<i>n</i>	29	23	34	0	30	8
	mean	2190	261	66.8		943	2320
	median	28.7	212	34.4		79.0	74.9
	min	4.0	29.0	17.9		8.3	33.1
	max	43,400	1080	662		23,800	12,500
	<i>n</i> > RoHS	2	14	0	0	1	
EEE (<i>n</i> = 26)	<i>n</i>	13	0	1	1	14	6
	mean	217		22.0	8.6	35,600	20,400
	median	192				38,100	23,900
	min	29.9				58.7	189
	max	516				116,000	29,800
	<i>n</i> > RoHS	0	0	0	0	11	

230

231 **Table 3:** Number of cases in which hazardous elements were detected and summary statistics for
 232 their concentrations in the different categories of beached plastics of colours other than black. Note
 233 that all concentrations are in mg kg⁻¹ and that *n* > RoHS refers to the number of cases in which
 234 concentrations exceed corresponding RoHS limits.

		Br	Cd	Cr	Hg	Pb	Sb
pellets (<i>n</i> = 98)	<i>n</i>	8	5	55	0	9	1
	mean	6.3	74.1	30.3		29.7	46.4
	median	6.3	51.7	27.9		13.2	
	min	3.3	32.5	21.1		4.4	
	max	10.8	144	71.4		76.4	
	<i>n</i> > RoHS	0	2	0	0	0	
primary (<i>n</i> = 30)	<i>n</i>	4	3	10	0	3	1
	mean	61.5	1780	180		1430	1140
	median	29.3	587	28.7		634	
	min	9.5	55.8	19.2		28.7	
	max	178	4680	1270.0		3620	
	<i>n</i> > RoHS	0	2	1	0	1	
secondary known (<i>n</i> = 37)	<i>n</i>	14	3	11	0	9	3
	mean	109	379	158		461	498
	median	22.0	376	40.2		159	74
	min	4.7	29.6	20.5		5.8	67.0
	max	1070	731	598		1840	1350
	<i>n</i> > RoHS	1	3	0	0	3	
secondary unknown (<i>n</i> = 59)	<i>n</i>	11	9	15	0	10	0
	mean	45.9	905	363		1620	
	median	19.6	293	44.2		808	
	min	3.3	21.8	17.5		6.6	
	max	210	3130	2910		8950	
	<i>n</i> > RoHS	0	7	1	0	4	
EEE (<i>n</i> = 10)	<i>n</i>	1	0	3	0	3	0
	mean	309		185		7060	
	median			185		317	
	min			75.1		275	
	max			295		20,500	
	<i>n</i> > RoHS	0	0	0	0	1	

235

236 *3.3. Avian PBET results*

237 Concentrations of elements mobilised from eight plastic samples subject to the 120-h PBET are
238 shown in Table 4 along with total concentrations determined by XRF. Note that bioaccessibility (BA)
239 is operationally defined as the percentage of each element released by the PBET relative to the
240 corresponding total concentrations. Mobilised concentrations range from 1 mg kg⁻¹ to almost 600
241 mg kg⁻¹ (for Br and Pb in PVC, respectively), with values of BA ranging from about 0.1% for Cr in a
242 yellow plastic to over 2% for Pb in PVC.

243

244 **Table 4:** Concentrations of elements released from eight plastic samples after exposure to a 120-h avian PBET. Also shown are total concentrations in
 245 plastics determined by XRF, where detected, and measures of bioaccessibility (BA), defined as the percentage release relative to total concentration. In bold
 246 are RoHS exceedances or, denoted by an asterisk, potential exceedances.

sample	Br, mg kg ⁻¹	Br-XRF, mg kg ⁻¹	Br-BA, %	Cd, mg kg ⁻¹	Cd-XRF, mg kg ⁻¹	Cd-BA, %	Cr, mg kg ⁻¹	Cr-XRF, mg kg ⁻¹	Cr-BA, %	Pb, mg kg ⁻¹	Pb-XRF, mg kg ⁻¹	Pb-BA, %	Sb, mg kg ⁻¹	Sb-XRF, mg kg ⁻¹	Sb-BA, %	
primary, black				26.3	2080	1.27										
secondary unknown, black PVC	1.0	146	0.68							576	23,800	2.42				
secondary unknown, black	115	43,400*	0.26										270	12,500	2.16	
primary, black				21.4	1300	1.65										
secondary, black	52.4	4100*	1.28										57.4	1510	3.81	
secondary, green	16.0	1100*	1.45													
secondary unknown, green				2.4	104	2.26	2.7	2910*	0.09							
primary, yellow							16.3	1270*	1.28	41.9	3620	1.16				

247

248 **4. Discussion**

249 Although the results presented herein were derived from six beaches in one region of southwest
250 England, global commonalities in WEEE regulations, constraints on sorting black plastics and life
251 cycles of plastics (Turner, 2018a; Zheng et al., 2018) suggest that the findings are likely to be more
252 generally applicable to beached litter. Thus, it is evident that waste plastic which is clearly and
253 directly electronic or electrical in nature, either visibly or chemically, is not particularly abundant.
254 This may partly reflect the value of small electrical items compared with food packaging and other
255 waste that is discarded in situ and that there is less incentive to retrieve. WEEE as a composite of
256 plastic, glass and metal, for example, is also much denser than plastics comprised largely of
257 polyolefins that usually characterise beach litter (Massos and Turner, 2017; Karthik et al., 2018),
258 meaning that discarded WEEE, including any disposed of at sea, is unlikely to travel far from its point
259 of origin. In a recent paper, for example, Fortibuoni et al., 2019) observed large items of WEE from
260 scuba trawls in the coastal waters of the Adriatic Sea which were attributed to isolated instances of
261 in situ fly-tipping and illegal dumping. Accordingly, we may assume that WEEE retrieved from two
262 beaches in the present study that was composed of relatively dense PVC cable insulation and that
263 often encased conductive metal wire had been disposed of locally. An association of PVC insulation
264 with high concentrations of Pb in black cable insulation (but not in white) suggests that such material
265 may be relatively old as heavy metal-based stabilisers have been progressively phased out (VinylPlus,
266 2014). However, this characteristic alone does not allow discrimination between old material that
267 has been recently discarded and old material that has persisted in the environment.

268 Of greater significance, and in particular to lower density beached plastic that has the propensity for
269 longer-range transport, is material that has been recycled in whole or in part from WEEE. Given that,
270 apart from as brominated flame retardants, the only other known use of Br in plastic is a component
271 of the halogenated copper phthalocyanine pigments (Ranta-Korpi et al., 2014), the presence of the
272 element in plastic that is not coloured blue-green and that contains Cu is a useful proxy for
273 functional EEE or recycled WEEE. Accordingly, we may infer that of the 264 non-EEE black plastic
274 items of litter retrieved from the beach surveys, 93 (or 35%) have been derived through WEEE
275 recycling. (Note, however, that with detection of Br constrained to a few mg kg⁻¹, this figure may
276 represent an underestimate.) Regarding plastics of other colour type, only seven out of 224 items (or
277 3%) that are mainly white or grey, appear to contain residual WEEE plastic from recycling based on
278 the criteria above.

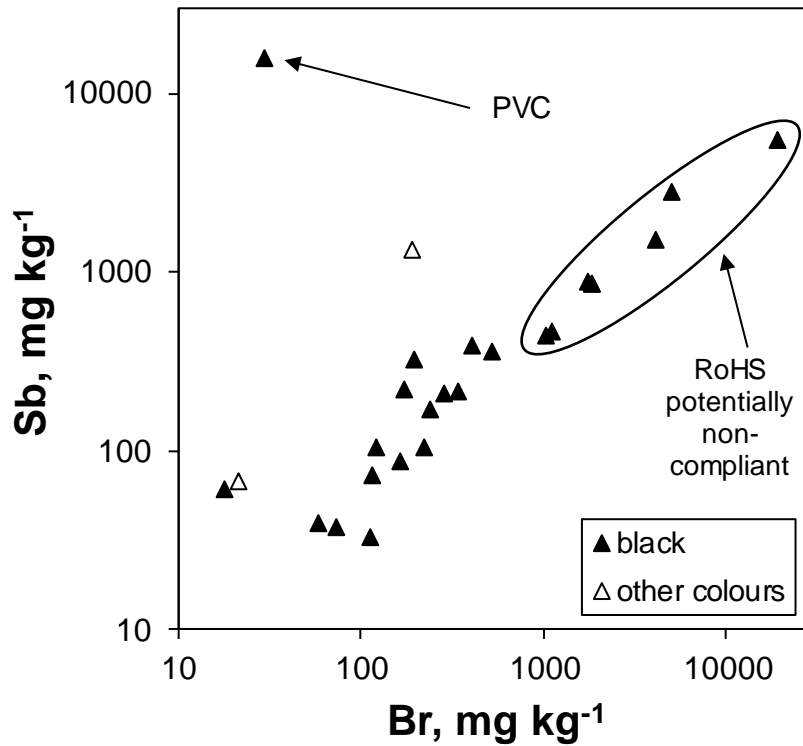
279 Further evidence for the presence of brominated flame retardants in beached plastic is the co-
280 association and correlation of Br with Sb. Thus, while Sb has a number sources and applications in

281 plastics, its dominant use is in the form of Sb_2O_3 as a flame quenching synergist for organohalide
282 compounds (Grause et al., 2011). In the present study, Br and Sb were detected together in 23
283 samples of black plastic across all categories and in two samples of plastic of other colour (note that
284 a relatively high detection limit of Sb is likely to have precluded identification of further
285 associations). The relationship between Sb and Br, illustrated in Figure 3, discriminates data
286 according to colour and whether the polymer is PVC-based. Thus, the principal outlier with a Sb
287 content of about $15,000 \text{ mg kg}^{-1}$ and a Br content of below 30 mg kg^{-1} is PVC cable insulation where,
288 presumably, Sb_2O_3 is used as a synergist for the chlorinated polymer itself, and the two non-black
289 samples are green fragments where both Br and Sb are likely to be present as components of
290 coloured pigments. Excluding these three data points ($n = 22$), statistical analyses reveal a Pearson's
291 moment correlation coefficient of 0.993 ($p < 0.001$) and a gradient and intercept of Sb-Br of $0.286 \pm$
292 0.013 ($p < 0.001$) and $203 \pm 127 \text{ mg kg}^{-1}$ ($p = 0.003$), respectively. The gradient of the relationship is
293 comparable to that defining both black plastic non-EEE consumer goods (0.386) and historical and
294 contemporary EEE items (0.342) (Turner, 2018a).

295 Given these quantitative similarities, and the fact that Br and Sb (and often in association with Cd
296 and/or Pb) was observed in samples of black plastic across all categories and of origins related to the
297 consumer (e.g. bottle lids, hair grips and a clothes hanger), marine applications (e.g. fragments of
298 rope, netting and traps) and industry (mainly bio-beads), suggests that the recycling of contaminated
299 WEEE plastic is a heterogeneous and pervasive issue that has been practised for some time. The
300 means by which hazardous chemicals and WEEE plastic are lost in nature and enter the marine
301 environment are illustrated within the more general life cycle of plastics in Figure 4. Thus, through
302 illegal or uncontrolled disposal, WEEE plastic enters the environment directly, while through
303 improper screening and sorting of WEEE according to RoHS criteria and the consequent and
304 incidental recycling of material into consumer goods and industrial and marine plastics, WEEE-
305 contaminated plastic enters the environment from a wide variety of land-based and marine waste
306 sources.

307 While, overall, the chemical signature of beached plastic is similar to that of contemporary consumer
308 goods (Turner, 2018a), there are some important differences between the two types of plastic. Thus,
309 firstly, beached plastic derived from consumer goods is likely to be older than goods in use and the
310 composition may reflect regulations (or lack of regulations) and practices that were in place
311 historically. Specifically, in the current context, WEEE-contaminated beached plastics are likely to be
312 older and contain a higher proportion of RoHS non-compliant additives or residues compared with
313 contemporary consumer goods where there has been a progressive dilution of older plastic with
314 newer materials through recycling. Secondly, beached plastics contain industrially-derived material

315 that is often derived from the direct recycling of WEEE and whose contribution to marine litter may
 316 be considerable in some locations (Turner et al., 2019). Thirdly, significant quantities of beached
 317 plastics are weathered and fragmented and are associated with a higher surface area and a greater
 318 propensity to leach additives than functional consumer goods.



319

320

321 **Figure 3:** Relationship between concentrations of Sb and Br in beached plastics of different colour
 322 type. Note the anomalous PVC-based sample of high Sb content and samples that are potentially
 323 non-compliant with respect to the RoHS.

324

Unlike consumer plastics, the presence or concentrations of hazardous chemicals in plastic litter in the marine environment is not regulated and has rarely been monitored. Significantly, the data shown in Tables 2 and 3 reveal that regulatory (RoHS) limits based on potential health and environmental risks arising from components of EEE, including EEE plastic, are breached or potentially breached in about 15% of black plastics collected in the study. By comparison, 10% of plastics of other colours exceed RoHS limits, and mainly for Cd, Cr and Pb in secondary fragments where lead chromates and cadmium sulphides were historically used as pigments for colour. Clearly, hazardous chemicals used in or derived from EEE are not expected in marine litter, and pose risks and exposure routes to receptors, including sediment, invertebrates, fish, birds and mammals, that

are not anticipated nor well-understood. The widespread occurrence of brominated flame retardants in black plastic is a particular concern in this respect because these compounds are synthetic and not contained in the normal diet. Moreover, there is evidence that a high proportion of dark microplastics (including those coloured black) is ingested by various seabirds (Ryan, 1987; Turner et al., 2019), although it is unclear whether such observations are related to plastic selectivity or availability.

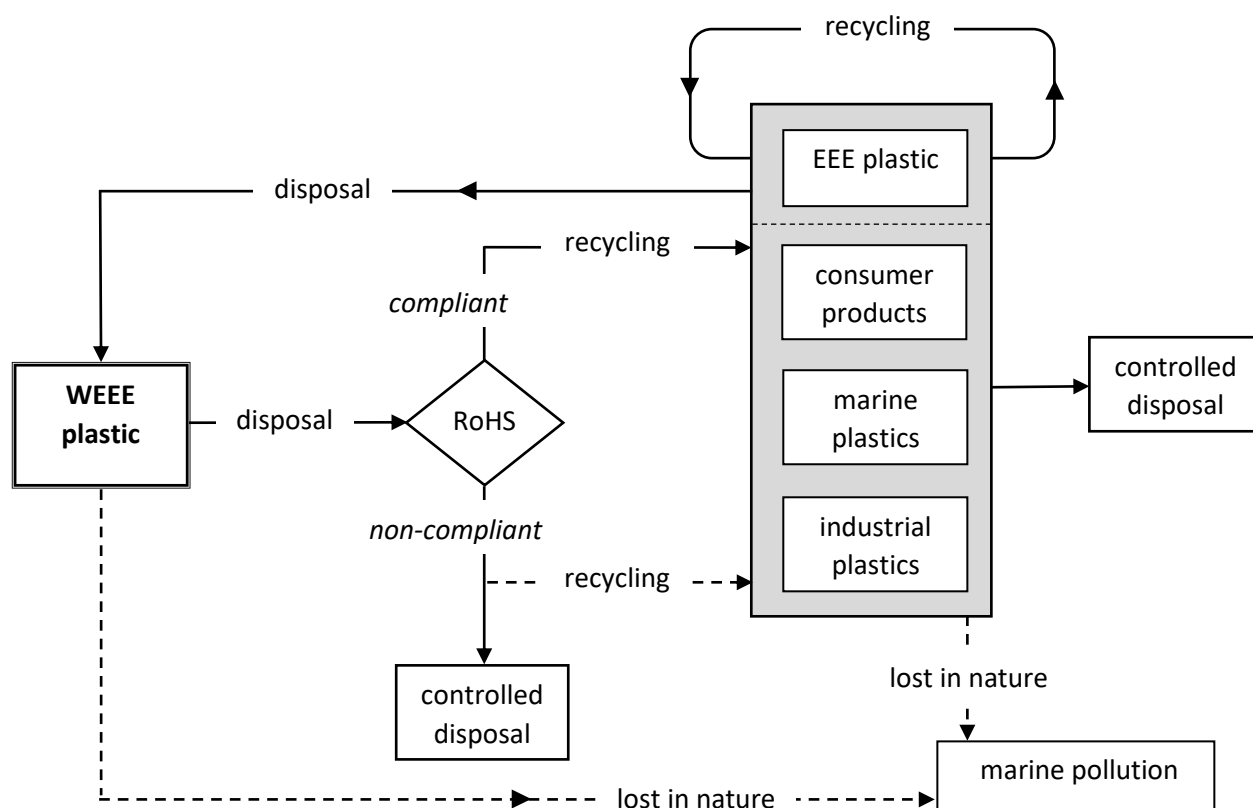


Figure 4: Flow chart showing the life cycle of WEEE plastic and routes of entry into the marine environment. Broken lines denote non-preferred or undesired pathways.

325 Regarding the five-day avian PBET results reported herein, bioaccessibility (but not necessarily
 326 bioavailability) of restricted elements (and including Sb) is variable but in the range of about 0.1% to
 327 2.4% and which can be greater than 100 mg kg⁻¹ in some cases. By comparison, an alternative avian
 328 PBET that includes lipophilic dietary components of Procellariiforms like fish oil has recently been
 329 tested on high density polyethylene compounded with decaBDE where it was shown that 40% of the
 330 brominated flame retardant could be mobilised (Tanaka et al., 2015), a mechanism that provided an
 331 explanation for the accumulation of specific PBDEs in the tissues of wild sea birds from the North
 332 Pacific Ocean.

333 Local contamination of the water column by brominated flame retardants and their subsequent
334 bioaccumulation may also result from the slow but continuous diffusive leaching from suspended or
335 deposited plastic debris (Rochman et al., 2014). This effect has been suggested as a means by which
336 certain brominated compounds are accumulated by juvenile yellowtail fish (*Seriola lalandi*) in the
337 North Pacific Central Gyre, a region remote from any land-based chemical emissions (Gassel et al.,
338 2013). For animals inhabiting or attached to larger pieces of plastic debris, both indirect (leaching)
339 and direct accumulation of hazardous chemicals from the substrate are possible. For example, Jang
340 et al. (2016) showed that mussels rafting on buoyant Styrofoam were able to accumulate
341 hexabromocyclododecane (flame retardant) additives from the underlying plastic, although the
342 precise mechanisms of uptake were not studied.

343 WEEE plastic is recognised as being potentially hazardous in terms of chemical additives and
344 regulations are in place to minimise their use in new EEE products. However, through improper
345 screening and sorting of WEEE, recycle derived from this stock, and in particular black plastic, is
346 readily contaminated. This introduces hazardous additives and residues into plastics more generally
347 and where they are not expected, affording a route of chemical exposure to humans and, through
348 pollution, marine wildlife. The impacts of chemicals in plastics that are introduced to the marine
349 environment are not fully understood but are gaining attention, with findings of the present study
350 also raising the case for classifying plastic litter by colour on the basis of origin and potential toxicity.

351

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356 **References**

357 BIS, 2011. RoHS Regulations: Government Guidance Notes. Department for Business, Innovation and
358 Skills URN 11/526, 38pp.

359 BIS, 2015. Packaging (Essential Requirements) Regulations: Government Guidance Notes.
360 Department for Business, Innovation and Skills
361 [https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/460891/BIS-15-460-packaging-essential-requirements-regulations-gov-guidance-notes.pdf)
362 [/460891/BIS-15-460-packaging-essential-requirements-regulations-gov-guidance-notes.pdf](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/460891/BIS-15-460-packaging-essential-requirements-regulations-gov-guidance-notes.pdf)
363 (accessed 5/19)

364 Cao, Z.G., Chen, Q.Y., Li, X.X., Zhang, Y.C., Ren, M.H., Sun, L.F., Wang, M.M., Liu, X.T., Yu, G., 2019.
365 The non-negligible environmental risk of recycling halogenated flame retardants associated with
366 plastic regeneration in China. *Science of the Total Environment* 646, 1090-1096.

367 European Parliament and Council of the EU, 1994. Directive 94/62/EC of 20 December 1994 on
368 packaging and packaging waste. Official Journal of the European Union L365.

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

372 Fortibuoni, T., Ronchi, F., Macic, V., Mandic, M., Mazziotti, C., Peterlin, M., Prevenios, M., Prvan, M.,
373 Somarakis, S., Tutman, P., Varezic, D.B., Virsek, M.K., Vlachogianni, T., Zeri, C., 2019. A harmonized
374 and coordinated assessment of the abundance and composition of seafloor litter in the Adriatic-
375 Ionian macroregion (Mediterranean Sea). *Marine Pollution Bulletin* 139, 412-426.

376 Gallo, F., Fossi, C., Weber, R., Santillo, D., Sousa, J., Ingram, I., Nadal, A., Romano, D., 2018. Marine
377 litter plastics and microplastics and their toxic chemicals components: the need for urgent
378 preventive measures. *Environmental Sciences Europe* 30, 13 [https://doi.org/10.1186/s12302-018-](https://doi.org/10.1186/s12302-018-0139-z)
379 [0139-z](https://doi.org/10.1186/s12302-018-0139-z)

380 Gassel, M., Harwani, S., Park, J.S., Jahn, A., 2013. Detection of nonylphenol and persistent organic
381 pollutants in fish from the North Pacific Central Gyre. *Marine Pollution Bulletin* 73, 231-242.

382 Grause, G., Karakita, D., Ishibashi, J., Kameda, T., Bhaskar, T., Yoshioka, Y., 2011. TG-MS investigation
383 of brominated products from the degradation of brominated flame retardants in high-impact
384 polystyrene. *Chemosphere* 85, 368-373.

385 Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P., 2018. An overview of chemical
386 additives present in plastics: Migration, release, fate and environmental impact during their use,
387 disposal and recycling. *Journal of Hazardous Materials* 344, 179-199.

388 Hermabessiere, L., Dehaut, A., Paul-Pont, I., Lacroix, C., Jezequel, R., Soudant, P., Duflos, G., 2017.
389 Occurrence and effects of plastic additives on marine environments and organisms: A review.
390 *Chemosphere* 182, 781-793.

391 Ilankoon, I.M.S.K., Ghorbani, Y., Chong, M.N., Herath, G., Moyo, T., Petersen, J., 2018. E-waste in the
392 international context – A review of trade flows, regulations, hazards, waste management strategies
393 and technologies for value recovery. *Waste Management* 82, 258-275.

394 Jang, M., Shim, W.J., Han, G.M., Rani, M., Song, Y.K., Hong, S.H., 2016. Styrofoam debris as a source
395 of hazardous additives for marine organisms. *Environmental Science and Technology* 50, 4951-4960.

396 Karthik, R., Roobin, R.S., Purvaja, R., Ganguly, D., Anandavelu, I., Raghuraman, m R., Hariharan, G.,
397 Ramakrishna, A., Ramesh, R., 2018. Microplastics long the beaches of southeast coast of India.
398 *Science of the Total Environment* 645, 1388-1399.

399 Lithner, D., Larsson, A., Dave, G., 2011. Environmental and health hazard ranking and assessment of
400 plastic polymers based on chemical composition. *Science of the Total Environment* 409, 3309-3324.

401 Massos, A., Turner, A., 2017. Cadmium, lead and bromine in beached microplastics. *Environmental*
402 *Pollution* 227, 139-145.

403

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

406 Rochman, C.M., Lewison, R.L., Eriksen, M., Allen, H., Cook, A.M., Teh, S.J., 2014. Polybrominated
407 diphenyl ethers (PBDEs) in fish tissue may be an indicator of plastic contamination in marine
408 habitats. *Science of the Total Environment* 476, 622-633.

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

412 Ryan, P. G., 1987. The incidence and characteristics of plastic particles ingested by seabirds. *Marine
413 Environmental Research* 23, 175-206.

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

417 Turner, A., 2018a. Black plastics: linear and circular economies, hazardous additives and marine
418 pollution. *Environment International* 117, 308-318.

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

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

423 Turner, A., Wallerstein, C, Arnold, R., 2019. Identification, origin and characteristics of bio-bead
424 microplastics from beaches in western Europe. *Science of the Total Environment* 664, 938-947.

425 VinylPlus, 2014. The European PVC industry's experience in replacing lead and cadmium-based
426 stabilisers [https://www.stabilisers.eu/wp-content/uploads/2015/11/VinylPlus_Contribution-
427 Cefic_Eu-Industry.pdf](https://www.stabilisers.eu/wp-content/uploads/2015/11/VinylPlus_Contribution-Cefic_Eu-Industry.pdf)

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

430 Zheng, Y., Bai, J., Xu, J., Li, X., Zhang, Y., 2018. A discrimination model in waste plastics sorting using
431 NIR hyperspectral imaging system. *Waste Management* 72, 87-98.