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Concentrations and migratabilities of hazardous elements in second-hand children’s plastic toys

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31 **Abstract**

32 About 200 second-hand plastic toys sourced in the UK have been analysed by x-ray
33 fluorescence spectrometry for hazardous elements (As, Ba, Cd, Cr, Hg, Pb, Sb, Se)
34 and Br as a proxy for brominated flame retardants. Each element was detected in > 20
35 toys or components thereof with the exception of As, Hg and Se, with the frequent
36 occurrence of Br, Cd and Pb and at maximum concentrations of about 16,000, 20,000
37 and 5000 $\mu\text{g g}^{-1}$, respectively, of greatest concern from a potential exposure
38 perspective. Migration was evaluated on components of 26 toys under simulated
39 stomach conditions (0.07 M HCl) with subsequent analysis by inductively coupled
40 plasma spectrometry. In eight cases, Cd or Pb exceeded their migration limits as
41 stipulated by the current EU Toy Safety Directive (17 and 23 $\mu\text{g g}^{-1}$, respectively),
42 with Cd released from yellow and red Lego bricks exceeding its limit by an order of
43 magnitude. Two further cases were potentially non-compliant based on migratable Cr,
44 with one item also containing > 250 $\mu\text{g g}^{-1}$ migratable Br. While there is no retroactive
45 regulation on second-hand toys, consumers should be aware that old, mouthable,
46 plastic items may present a source of hazardous element exposure to infants.

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51 **Introduction**

52 Mounting evidence for their acute and chronic toxicities at relatively low doses has
53 resulted in increasingly restricted use of many heavy metals and metalloids in
54 consumer products over the past few decades (1,2). Young children are particularly
55 susceptible to the health impacts of such elements because of their higher metabolic
56 rate, greater surface area to weight ratio, more rapid growth of organs and tissues, and
57 longer time period to develop diseases with latency periods compared with adults (3).
58 Infants are also potentially exposed to greater quantities of metals and metalloids in
59 consumer products through the mouthing of non-food objects as they seek oral
60 stimulation and explore taste, texture and shape. Consequently, products designed to
61 be used by (or in contact with) young children have received particularly stringent
62 regulatory attention in terms of both the concentrations and migratabilities of toxic
63 chemicals in accessible components.

64

65 The original European Council Directive 88/378/EEC on toy safety (4) stipulated
66 migratable limits for eight hazardous elements, listed in Table 1, that are based on the
67 ingestion of a small quantity of material and defined by two-hour extraction under
68 simulated gastric conditions (dilute HCl at 37 °C) according to the European standard,
69 EN 71-3 (5). An amended directive that applied to products placed on the market from
70 July 2013 provided revised limits on migration in dilute HCl that depended on the
71 matrix being tested (liquid or sticky; brittle, powder-like or pliable; material that can
72 be scraped off) (see Table 1), as well as limits for an additional number of elements
73 and different oxidation states of Cr (6). Precise concentration limits for some elements
74 have since been revised downwards in line with new scientific data, and there is
75 currently a proposal to substantially reduce the concentration limits of Pb because of a

76 growing body of scientific evidence that suggests there is no lower threshold of safety
 77 for its levels in blood (7).

78

79 *Table 1: Migratable limits (in $\mu\text{g g}^{-1}$) of eight hazardous elements in toys and as*
 80 *defined by the original and amended EC Toy Safety Directives. Note that different*
 81 *species of Cr are discriminated in the latter directive, and that limits for Ba, Cd and*
 82 *Pb have since undergone (or are currently being proposed for) further reduction, with*
 83 *revised values shown in parentheses.*

	88/378/EEC	2009/48/EC		
		brittle, powder, pliable	liquid, sticky	scraped-off
As	25	3.8	0.9	47
Ba	1000	4500 (1500)	1125 (375)	56000 (18,750)
Cd	50	1.9 (1.3)	0.5 (0.3)	23 (17)
Cr	60			
Cr (III)		37.5	9.4	460
Cr(VI)		0.02	0.005	0.2
Hg	60	7.5	1.9	94
Pb	90	13.5 (2.0)	3.4 (0.5)	160 (23)
Sb	60	45	11.3	560
84 Se	500	37.5	9.4	460

85

86 While the current Toy Safety Directive applies to new products, there is no retroactive
 87 regulation on the recycling or re-sale of older toys. Second-hand toys are an attractive
 88 option because they can be inherited directly from relatives and friends or obtained
 89 cheaply and readily from charity stores, flea markets and the internet (8). Moreover,
 90 in the UK the re-use of working, old and outgrown toys is actively encouraged
 91 through the Toy Recycling in Your Community ('Tric') scheme (9). Whereas liquid
 92 or sticky toys have a limited shelf-life and parents are likely to be wary of second-
 93 hand toys that are brittle or have visibly flaking paint, old plastic products often
 94 appear to be in good condition, presumably because of the durability of synthetic

95 polymers and the color-fastness of many pigments, and tend to be re-used more
96 extensively.

97

98 Despite the market for second-hand plastic toys and their abundance in homes,
99 waiting rooms, day-care centers and nurseries (8), there has been little scientific study
100 of the presence of hazardous elements in such items. Specifically, two studies
101 conducted in the US and employing a handheld x-ray fluorescence (XRF)
102 spectrometer report total concentrations of Pb in a variety of vintage plastic toys from
103 day centers and family homes that exceeded US limits of $100 \mu\text{g g}^{-1}$, but migration
104 from the matrix was not evaluated (8,10). Other metals and metalloids, including As,
105 Ba, Cd and Cr, are mentioned in the latter study, but none of these elements have US
106 mandatory limits in toys with the exception of Cd in jewelry.

107

108 The present study describes the first systematic investigation of the occurrence and
109 migratability of hazardous elements in second-hand plastic toys in the UK. Portable
110 XRF was used to determine the concentrations of the eight elements listed in the
111 original toy Safety Directive (and defined in Table 1) in addition to Br as a proxy for
112 brominated flame retardants (BFRs) and whose concentration is limited in electronic
113 plastic waste according to EU Directive 2002/95/EC (11). Based on the XRF results,
114 selected samples were subjected to extraction in dilute HCl in order to evaluate
115 element migratability and potential for exposure through ingestion.

116

117 **Experimental Section**

118 *Sample collection and categorization*

119 About 200 toys that were designed for young children, containing parts that were
120 small or accessible enough to be mouthed in part or in whole and that had been
121 acquired second-hand or second-generation, were sourced from two pre-school
122 nurseries, a primary school, various charity shops and five family homes within the
123 city of Plymouth, south west England. Toys were constructed entirely or largely of
124 synthetic, molded plastic (and not foam, rubber or textile) and excluded products that
125 housed electrical parts or that had been painted. Products and distinct components
126 thereof (e.g. different colored blocks, various body parts of figures, separate
127 constituents of games and puzzles) are listed in Table S1 of the Supporting
128 Information where they are categorized as follows: ‘activity’ (balls, marbles, yoyos,
129 tools, letters), ‘cars and trains’ (and other toys with wheels, plus accessories),
130 ‘construction’ (blocks and studded bricks), ‘food-related’ (bottle caps, cutlery,
131 crockery, model food), ‘figures’ (animals, dinosaurs, dolls, characters), ‘games and
132 puzzles’ (board games, shape sorters, numeracy toys), ‘jewelry’ (straps, beads, rings)
133 ‘sound-generating’ (rattles, whistles, bells, musical instruments) and ‘water’ (mainly
134 bath toys).

135

136 *XRF analysis*

137 Toys and components were analysed by energy-dispersive FP-XRF using a Niton
138 XL3t 950 He GOLDD+ that was configured nose-upwards in the laboratory and in a
139 4000 cm³ Thermo Scientific accessory stand. The instrument was operated in a low-
140 density, ‘plastics’ mode with thickness correction down to 50 µm. A suite of elements
141 may be determined in this mode but the present study focuses on the eight metals and
142 metalloids defined in the original Toy Safety Directive (listed in Table 1) and that are

143 generally regarded as most hazardous for children (12), as well as Cl and Br as
144 indicators of polyvinyl chloride (PVC) BFRs, respectively.

145

146 Where possible, sample thickness was determined through the measurement surface
147 using 300 mm Allendale digital calipers, while for hollow objects (mainly dolls, balls,
148 model food and sound-generating items) thickness was estimated from accessible
149 surfaces of objects of similar construction and rigidity. Samples were placed on the
150 stainless steel base plate of the accessory stand with the measurement surface above
151 the XRF detector window before analyses with appropriate thickness correction and
152 collimation (3 mm or 8 mm beam width depending on the accessibility and
153 homogeneity of the area to be probed) were activated remotely through a laptop for
154 counting periods of 40 s at 50 kV/40 μ A (main energy) and 20 s at 20 kV/100 μ A
155 (low energy). Spectra were quantified by fundamental parameters yielding elemental
156 concentrations in parts per million (μ g g⁻¹) and with a counting error of 2 σ that were
157 downloaded to the laptop via Niton data transfer (NDT) software.

158

159 Measurement detection limits (as 3 σ) varied depending on sample thickness and
160 composition, but median values based on counting errors arising from analyses that
161 failed to deliver a concentration ranged from < 10 μ g g⁻¹ for As, Br and Pb to about
162 300 μ g g⁻¹ for Ba. (A complete list of detection limits can be found in Table S1.)
163 Polyethylene and polyvinyl chloride (PVC) reference discs of 13-mm thickness and
164 that had been impregnated with As, Ba, Cd, Cr, Hg, Pb, Sb and Se (PN 180-619,
165 LOT#T-81), Cd, Cr, Br, Hg and Pb (PN 180-554, batch SN PE-071-N) or Br and Sb
166 (PVC-4C80) were analysed at regular intervals throughout each measurement session
167 and returned concentrations that were always within 10% of mean certified values. A

168 detailed comparison of metal concentrations in plastics derived by portable XRF and,
169 as an independent measure, by inductively coupled plasma (ICP) spectrometry
170 following digestion in H₂SO₄, is given elsewhere (13).

171

172 *Sample extraction*

173 Based on the results of XRF analysis, and subject to sufficient accessible material and
174 permission to sacrifice, 34 components of 26 plastic toys (and as described in Table
175 S1) were extracted in dilute HCl according to EN 71-3 for scraped off material (5).
176 Hard plastics were fractionated to < 2 mm through a stainless steel grater, with 100 to
177 300 mg of material collected on white A4 paper subsequently transferred to a series of
178 pre-weighed 50 ml polypropylene centrifuge tubes with the aid of a Nylon brush;
179 softer plastics (mainly PVC) or thin items were cut into small (< 5 mm) pieces using
180 stainless steel scissors or a scalpel before being transferred to centrifuge tubes
181 likewise. Ten ml of a solution of 0.07 M HCl, simulating the human gastric
182 environment and prepared by dilution of Fisher Scientific Trace Analysis grade acid
183 in Elga ultrapure water, was then pipetted into each tube and the screw-capped
184 contents inverted twice before being placed in a water bath at 37 °C for 2 h (1 h under
185 lateral agitation and 1 h without agitation). At the end of the incubations, 5 ml from
186 each tube were filtered through Whatman 0.45 µm PES syringe-cartridge filters into
187 10 ml polypropylene centrifuge tubes and diluted to 10 ml with 0.07 M HCl.

188

189 *Extract analysis*

190 Within 24 h of preparation, extracts were analysed for As, Ba, Br, Cd, Cr, Hg, Pb, Sb
191 and Se by ICP mass spectrometry using a Thermo X-series II (Thermo Elemental,
192 Winsford UK) with a concentric glass nebulizer and conical spray chamber. The

193 instrument was calibrated externally using five mixed standards prepared by serial
194 dilution of mixed standard solutions (LabKings, Hilversum, NL) in 0.07 M HCl, and
195 internally by the addition of 10 $\mu\text{g L}^{-1}$ of ^{115}In and ^{193}Ir to all samples, standards and
196 blanks. RF power was set at 1400 W and coolant, auxiliary, nebulizer and collision
197 cell gas flows rates were 13 L Ar min^{-1} , 0.70 L Ar min^{-1} , 0.75 L Ar min^{-1} and 3.5 mL
198 7% H_2 in He min^{-1} , respectively. Data were acquired over a dwell period of 10 ms,
199 with 50 sweeps per reading and three replicates. Limits of detection, based on three
200 standard deviations about multiple measurements of blanks ranged from 0.05 $\mu\text{g L}^{-1}$
201 for Cd and Pb to about 10 $\mu\text{g L}^{-1}$ for Br. Analyses of a reference drinking water (EP-
202 L-2; SPC Science, Quebec) after every ten samples revealed analyte concentrations
203 that were within 10% of certified values with the exception of Sb (within 15%).

204

205 **Results**

206 *Sample categorization and elemental concentrations*

207 The number and categorization of plastic toys and components considered in the
208 present study is summarized in Table 2. Thus, 285 XRF analyses were performed on
209 197 products, with multiple measurements undertaken on distinctly different
210 components of various toys like the wheels, base and body of a car, different colored
211 blocks in a set, and the constituent parts of a puzzle or game. Overall, 28 products
212 were constructed of PVC (defined by the XRF as having a Cl content greater than
213 15% by weight; 14), with the majority of this polymer encountered in the figures and
214 water categories. Also shown in Table 2 is the number of measurements in which each
215 hazardous element was detected by XRF. Thus, Hg was not detected in the products
216 analysed, and the sequence of decreasing number of cases detected among the
217 remaining elements was: Ba > Br/Cr > Sb > Cd/Pb > As > Se; with Ba and Br

218 encountered across all categories considered. Hazardous elements were most
219 frequently detected among plastic figures, construction toys, games and puzzles, and
220 jewelry, where, on average, more than one element was detected per measurement,
221 and detection was least frequent among activity products, cars and trains and toys
222 designed for use in water.

223

224 The total concentrations of each element, where detected by XRF, are illustrated in
225 Figure 1 in ascending order, with PVC- and non-PVC-based materials discriminated
226 and statistical summaries for each dataset annotated. Also shown is the number of
227 cases in which total concentrations exceed the respective migratable limits defined by
228 Directive 2009/48/EC and its subsequent amendments (see Table 1). (Note that the
229 higher migratable limit for Cr in its lower oxidation state is shown and, while Br is
230 not included in the Toy Safety Directive, the value presented is based on the
231 Restriction of Hazardous Substances concentration limit for certain brominated flame
232 retardants, but not total Br, in electronic plastics; 11.) While the two measures are not
233 directly comparable, total concentrations that exceed migratable limits should act as a
234 trigger for further investigation of a product. Thus, overall, there were 73 cases of
235 exceedance, encompassing 49 measurements and 31 products (of which seven were
236 PVC-based) from all categories with the exception of toys designed for water. Co-
237 associations of multiple elements exceeding their respective limit values were
238 encountered in two types of bead (Br-Cd-Pb-Sb), a number of Lego bricks (Cd-Se or
239 Cr-Sb), a small games mat (Ba-Pb), various games counters (Cd-Se) and figures (Cd-
240 Pb), and the plastic bowl of a bell (Cr-Sb).

241

242 *Table 2: Quantity and categorization of toy samples, along with the number of*
 243 *analyses performed and the number of cases in which each hazardous element was*
 244 *detected.*

	products (analyses)	PVC (analyses)	As	Ba	Br	Cd	Cr	Hg	Pb	Sb	Se
activity	38 (45)	4 (5)	1	12	7	0	2	0	2	0	0
cars and trains	25 (31)	1 (1)	1	7	3	1	1	0	2	2	0
construction	25 (46)	1 (1)	3	15	4	7	12	0	2	9	3
figures	39 (71)	11 (16)	5	24	18	10	13	0	15	10	1
food-related	21 (21)	2 (2)	0	5	3	0	7	0	0	0	0
games and puzzles	24 (41)	1 (1)	1	20	3	5	5	0	2	3	2
jewelry	8 (8)	0	1	5	4	2	3	0	4	3	0
sound-generating	7 (9)	0	0	2	3	0	1	0	0	1	0
water	10 (13)	8 (9)	0	3	3	0	0	0	0	0	0
245 total	197 (285)	28 (35)	12	93	48	25	44	0	27	28	6

246

247 *Hazardous element migratability*

248 Extraction tests were performed on 34 components of 26 toys that could be sacrificed
 249 and that were homogeneous, readily accessible and yielded sufficient quantities of
 250 plastic material on grating or slicing. These included many of the items where the
 251 XRF returned one or more hazardous element above its corresponding EU Directive
 252 migration limit (Table 1) in order to ascertain compliance/non-compliance, and
 253 samples of lower elemental concentrations but of a variety of color and type in order
 254 to explore possible controls on and variations in migratability. Significantly, and
 255 despite constraints on the amount of material required for extraction, a number of
 256 items tested (e.g. small blocks, counters and beads) were small enough to be ingested
 257 whole.

258

259 Table 3 presents results for all samples in which at least one element was detected in
 260 the extract by ICP ($n = 30$) in terms of both weight-normalized migratable
 261 concentration and percentage migration relative to total elemental content (i.e. a
 262 measure of bioaccessibility). Note that where the element was detected in the extract

263 but not by XRF, a lower limit of bioaccessibility is given that is based on the detection
264 limit returned by the Niton XL3t (and as shown in Table S1). Thus, while As and Se
265 were never detected in the extracts, Ba and Cd were encountered in 30 and 11 cases,
266 respectively, and in a variety of toys. Migratable concentrations ranged from $< 1 \mu\text{g g}^{-1}$
267 ¹ for Cd in two components to $> 100 \mu\text{g g}^{-1}$ for Ba, Br, Cd, Pb and Sb in at least one
268 case each, and bioaccessibility ranged from below 1% for Ba, Cd and Cr in a number
269 of products to over 10% for Cr in a molded food toy and Pb in a black bead. Among
270 the elements considered, and despite variations in percentage bioaccessibility,
271 statistically significant correlations between migratable concentrations and total
272 concentrations were exhibited by Cd ($n = 11, r = 0.825, p = 0.002$) and Pb ($n = 7, r =$
273 $0.972, p < 0.001$).

274

275 With respect to the current EU Directive, non-compliance occurred for Cd in four
276 yellow or red building bricks from two Lego sets, and for Pb in two body parts of a
277 PVC-based model dinosaur and on both surfaces of a child's PVC tape measure.

278 Although concentrations of extractable Cr were compliant in respect of total
279 migration, it is suspected that a number of brightly colored items or parts (a building
280 block, model dinosaur and tape measure) and a black bead were non-compliant in
281 respect of Cr(VI) since the co-association of Cr and Pb suggests the presence of the
282 pigment, lead chromate. Overall, therefore, various components from four toys were
283 non-compliant, with a further two products potentially non-compliant.

284

285 *Table 3: Migratable concentrations (in $\mu\text{g g}^{-1}$) and percentage bioaccessibilities (in*
286 *parentheses and relative to total concentrations) of hazardous elements detected in*
287 *the extracts of different toys or components thereof that are numbered and lettered*

288 according to the identification given in Table S1 and that are classified as PVC- or
 289 non-PVC-based. Note that figures in bold denote non-compliance or potential non-
 290 compliance according to the current EU Toy Safety Directive and the proposed,
 291 revised limit for Pb.

sample/component, colour	category	Ba	Br	Cd	Cr	Pb	Sb
1a. tape measure, red	activity (PVC)	13.2 (0.28)			0.34 (>0.50)	137 (3.4)	
1b. tape measure, white	activity (PVC)	7.8 (>0.1)				163 (3.6)	
2. building brick, pink	construction (PVC)	6.9 (0.74)		0.18 (0.18)			
3. building brick, purple	construction	3.8 (>1.6)					
4. Sticklebrick, green	construction	6.6 (>4.7)					
5. megablock, yellow	construction	24.1 (5.1)			3.2 (0.77)	16.0 (1.2)	
6a. Lego brick, yellow	construction	62.5 (7.1)		217 (3.1)			
6b. Lego brick, grey	construction	10.1 (>2.3)		11.3 (0.87)			
6d. Lego brick, red	construction	394 (3.8)		274 (1.4)			
6e. Lego brick, red	construction	79.8 (3.5)		18.0 (0.19)			1.1 (>0.93)
7. building block, red	construction	58.2 (2.6)		7.9 (0.30)			
8. Lego brick, yellow	construction	10.2 (2.6)		105 (1.6)			
10a. dinosaur model, red	figure (PVC)	68.7 (8.1)		8.6 (8.9)	4.4 (3.5)	41.1 (4.0)	6.3 (1.5)
10b. dinosaur model, grey	figure (PVC)	71.3 (4.9)		8.8 (7.3)	4.5 (2.8)	43.7 (3.9)	
11. farm animal, white	figure (PVC)	3.4 (>1.4)					
12. dinosaur model, brown	figure (PVC)	3.6 (1.0)			0.59 (>2.8)		
13. helmet, grey	figure	2.5 (>2.4)					
14. molded food, brown-red	food-related (PVC)	3.1 (1.0)			18.6 (1.8)		
15. molded food, yellow	food-related (PVC)	6.4 (3.8)					
16. molded food, red	food-related	2.6 (>1.9)			0.76 (0.26)		
17. plate, yellow	food-related	4.3 (>2.0)			1.8 (2.6)		
18. bowl, yellow	food-related	3.3 (>1.7)			1.6 (5.6)		
19. spoon, green	food-related	6.6 (3.9)					
20. molded food, brown	food-related	2.1 (1.4)					
22a. cup, orange	games and puzzles	1.2 (0.11)		0.83 (0.03)			
22b. mat, brown	games and puzzles	23.9 (0.02)				6.6 (1.1)	
23. counter, red	games and puzzles	14.3 (0.19)		6.6 (0.27)			
24. cylinder, blue	games and puzzles	2.1 (>1.9)					
25. bead, black	jewellery	50.5 (4.1)	257 (1.8)		4.5 (20.4)	18.2 (10.8)	104 (1.2)
26. bell, orange	sound-generating	7.9 (>8.5)			3.65 (0.32)		

292

294 Discussion

295 The results of the present study reveal high concentrations of many elements listed by
 296 the original EU 88/3781/EEC Toy Safety Directive (4) in products that remain in
 297 circulation, being handed-down by parents, recycled via charity shops, and donated to
 298 or purchased (historically) by nurseries, hospitals and schools. Both the frequencies of
 299 detection and median elemental concentrations are greater than corresponding values
 300 for new plastic toys sourced from major retailers (15,16) but are more in line with

301 measurements reported for new, low cost items purchased from bargain stores and
302 road-side vendors (16,17,18). Regarding older plastic toys, similar conclusions to the
303 present study have been reached for Pb in toys in day care centers in Nevada (10) and
304 for several hazardous metals in products purchased in the 1970s and 1980s in the
305 USA but whose precise source was not specified (8). The latter studies, however,
306 implicitly relate exposure and health hazard to total elemental concentrations in
307 plastic, in line with current US restrictions, rather than migratable levels. The results
308 shown in Table 3 clearly indicate a wide variation in bioaccessibility on a percentage
309 basis for any given element, with correlations between total and migratable
310 concentrations significant only for Cd and Pb. Presumably, this reflects variations in
311 product composition, age and usage, but suggests that total concentration is not,
312 necessarily, a good proxy for exposure through ingestion.

313

314 Elemental concentrations extracted by dilute HCl in this study that exceed current or
315 proposed EU migratable limits include Cd and Pb (and potentially Cr) in various
316 building blocks and bricks, and in PVC figures. In these products, Pb appears to have
317 been employed in compounds used as stabilizers in PVC or, in association with
318 Cr(VI), as the brightly colored yellow pigment, $PbCrO_4$, whose precise hue may be
319 varied through to red by addition of $PbMoO_4$ or $PbSO_4$ (19). Cadmium was evident as
320 a stabilizer in one PVC-based component (the black caterpillar track from an
321 excavating vehicle) but was more generally encountered in a variety of brightly-
322 colored toys. Here, the compound CdS, or a mixture of CdS and ZnS, is likely to have
323 been employed as a yellow pigment, with successively darker hues of orange and red
324 effected by the progressive replacement of S by Se (19). Consistent with this
325 assertion, Se was absent from all yellow toys that were Cd-positive, while the mass

326 ratio of Cd:Se increased from about 4 in an orange games cup to about 7.3 in a dark
327 red counter.
328
329 Cadmium and Pb-based pigments found widespread use in plastics because of their
330 pure, brilliant shades, opacity, light-fastness and weather-resistance, and, at least
331 when new, high chemical resistance and little tendency to migrate (20). Accordingly,
332 such pigments had a key role in manufacture of colorful toys before health and
333 environmental concerns resulted in their restriction and replacement by safer organic
334 and inorganic alternatives. Of the toys analysed in the present study, the highest levels
335 of total and migratable Cd were encountered in some, but not all, red and yellow
336 studded Lego bricks. Specifically, those in sets that appear to have been purchased in
337 the 1970s yielded migratable Cd concentrations that sometimes exceeded the EU
338 migration limit by an order of magnitude, while those purchased in the 1990s, and that
339 were visually indistinguishable from the older bricks, contained no detectable Cd. The
340 introduction of high quantities of Cd in Lego bricks is likely to have coincided with
341 the introduction of acrylonitrile butadiene styrene (ABS) as a replacement for
342 cellulose acetate as the material of construction in the 1960s (21) since Cd
343 sulphoselenides were favorable colorants for styrenic-based polymers at the time (22);
344 when, precisely, Cd-based chemicals in Lego were subsequently replaced by safer
345 pigments, however, is unclear. Given their popularity, durability, collectability and
346 compatibility with newer products, older, ABS-based Lego sets, and in particular
347 those containing brightly-colored pieces, should be treated with caution.
348
349 One element not embraced by the original or amended Toy Safety Directive but of
350 concern from a health perspective is Br. Although the halogen is found in the organic

351 pigment, copper phthalocyanine green 36, that has limited use in plastics (23), its
352 most important application in synthetic polymers is as a constituent of free radical-
353 scavenging BFRs. These chemicals represent a wide variety of organic compounds
354 designed to increase resistance to ignition and slow down developing fires in heat-
355 generating materials like electronic casings and construction materials. Because many
356 commonly-employed BFRs are persistent, bioaccumulative and toxic, their use in new
357 and recycled electrical products is restricted according to EU Directive 2002/95/EC
358 (11). Accordingly, and given the practical and analytical difficulties in discriminating
359 BFRs (including those that are unregulated; 24), Br should be absent from non-
360 electrical plastics that are not pigmented with copper phthalocyanine (14). That nearly
361 40 non-green (and mainly neutrally-colored) products or components thereof were Br-
362 positive in the present study, and usually at levels well below those required for flame
363 retardancy (between about 3 and 8% by weight; 24), suggests many children's toys
364 have been manufactured, directly or indirectly, from recycled waste electrical casings.
365 This issue has been highlighted more generally in new consumer products, including
366 toys (25,26,27), but the presence of Br in older toys raises the possibility that residues
367 of the more hazardous BFRs that were banned 15 years ago and are subject to more
368 stringent regulation, like polybrominated diphenyl ethers and polybrominated
369 biphenyls, remain in plastics that are available to young children. Because of the
370 relatively small molecular weight of most BFRs, they also have a greater propensity
371 to migrate compared with many other organic additives (28). This is evident from the
372 extraction of considerable quantities of Br from an item of jewelry presented in Table
373 3.
374

375 With the introduction and refinement of the Toy Safety Directive, the design and
376 development of safer and more sustainable products, and the publicity generated by
377 new goods violating chemical standards, there is clearly good reason for the plastic
378 manufacturing industry to eliminate hazardous elements from new toys. The latest
379 statistics provided by the US Consumer Product Safety Commission (29) confirm a
380 steady decline in the number of recalls based on the presence of hazardous substances,
381 and in particular Pb. However, the attraction of second-hand products to consumers in
382 terms of cost, convenience and recyclability is acting as a conduit for exposing
383 ‘legacy’ chemicals to the current generation of young children. For consumer
384 products more generally, some authorities have advocated a ‘right to know’ policy,
385 whereby goods are labelled should they contain any toxic constituents (3, 30).
386 Because of the plethora and variety of old toys on sale or passed down whose precise
387 ages and origins are unknown, this approach would be difficult to implement in the
388 current context. However, a specific recommendation of this investigation is that
389 consumers should be aware of the potential risks associated with small, mouthable,
390 and brightly colored (and in particular red and yellow) old plastic toys or components.
391 The present study has also provided evidence for the occurrence of historical BFRs in
392 some second-hand toys that are neutrally colored; this finding is part of a broader and
393 more complex issue concerning the recycling of electronic plastic waste and one that
394 warrants further study (14,31).

395

396 **Declaration**

397 The author declares no competing financial interests.

398

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403

404 **Associated content**

405 **Supporting information available**

406 A brief description of each toy and component, XRF results with counting errors, and
407 cases of potential non-compliance are provided in Table S1.

408

409

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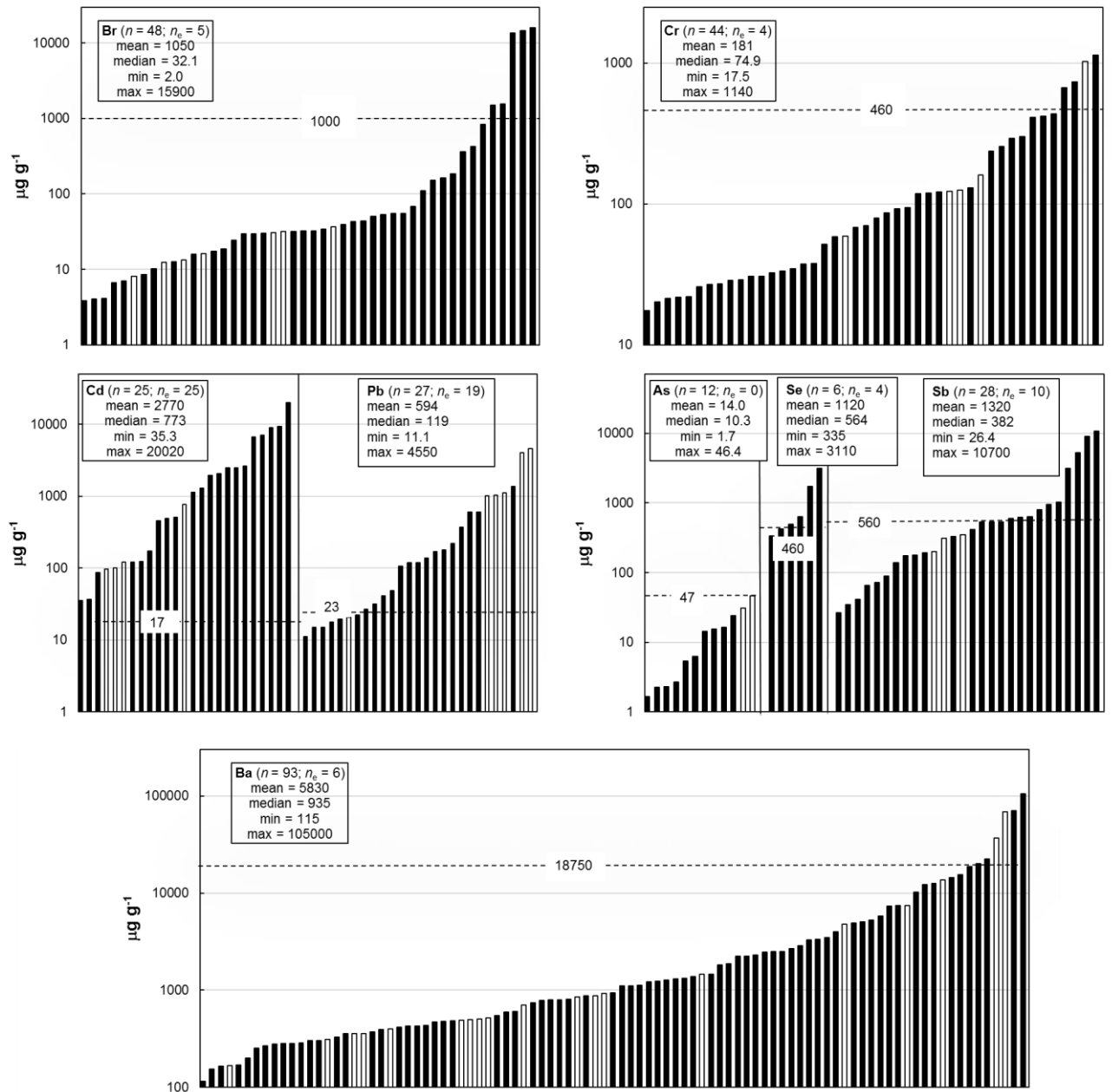
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525 Figure 1: Total concentrations of the hazardous elements detected in the toys and
 526 components thereof by XRF. Concentrations are shown in ascending order and open
 527 bars denote samples composed of PVC. Dashed lines represent the current or
 528 proposed (Pb) EC Toy Safety Directive migration limits, and shown inset are
 529 summary statistics for each element (n_e = number of samples exceeding the
 530 corresponding migration limit).



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