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# Mobilisation kinetics of hazardous elements in marine plastics subject to an avian physiologically-based extraction test.

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3 **Mobilisation kinetics of hazardous elements in marine**  
4 **plastics subject to an avian physiologically-based**  
5 **extraction test**

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27 **Abstract**

28 Samples of plastic collected from two beaches in southwest England ( $n = 185$ ) have  
29 been analysed by XRF spectrometry for elements that are hazardous or restricted in  
30 synthetic polymers (namely, As, Ba, Br, Cd, Cr, Hg, Pb, Sb and Se). Overall, one or  
31 more restricted element was detected in 151 samples, with 15 cases exhibiting non-  
32 compliance with respect to the Restriction of Hazardous Substances (RoHS)  
33 Directive. Twelve plastics that were RoHS-non-compliant were subsequently  
34 processed into microplastic-sized fragments and subjected to an avian  
35 physiologically-based extraction test (PBET) that simulates the chemical conditions in  
36 the gizzard-proventriculus of the northern fulmar. Kinetic profiles of metal and  
37 metalloid mobilization in the PBET were fitted using a pseudo-first-order diffusion  
38 model with rate constants ranging from  $\sim 0.02$  to  $0.5 \text{ h}^{-1}$ , while profiles for Br were  
39 better fitted with a parabolic diffusion model and rate constants of  $7.4$  to  $9.5 (\mu\text{g L}^{-1})^{-1}$   
40  $\text{h}^{-1}$ . Bioaccessibilities, based on maximum or equilibrium concentrations mobilized  
41 relative to total (XRF) concentrations, ranged from  $< 1 \%$  for Cd and Se in  
42 polyethylene and polypropylene to over  $10\%$  for Br in a sample of expanded  
43 polystyrene and Pb in a sample of PVC. Calculations suggest that ingested plastic  
44 could contribute about  $6\%$  and  $30\%$  of a seabird's exposure to and accumulation of Pb  
45 and brominated compounds, respectively.

46

47 **Capsule:** The kinetics of mobilisation and measures of bioaccessibility have been  
48 determined for hazardous elements in marine plastics using an avian digestive extract  
49

50 **Keywords:** microplastics; heavy metals; brominated flame retardants; avian  
51 bioaccessibility; mobilization kinetics

52 **1. Introduction**

53 Because of their relatively low manufacturing costs, versatility, imperviousness to  
54 water and low density, plastics have a wide variety of applications in the packaging,  
55 storage, plumbing, construction, medical, furniture, electronic, agriculture,  
56 transportation and maritime sectors. Although many thermoplastics can be readily  
57 recycled, there are environmental issues associated with plastic use and consumption  
58 that have been well-publicised over the past few decades, including energy  
59 requirements for their production from crude oil, emissions associated with disposal  
60 by landfill or incineration, littering and marine pollution. Regarding the latter,  
61 floating, deposited and beached plastics pose risks to marine wildlife, and in particular  
62 to procellariiform seabirds through entanglement and ingestion (Phillips et al., 2010;  
63 Wilcox et al., 2015). The inadvertent or incidental consumption of indigestible  
64 plastics by birds feeding or foraging may result in starvation, damage to the digestive  
65 tract and reduced growth. Moreover, if plastics are associated with toxic chemicals,  
66 these have the potential to undergo mobilisation under the acidic conditions of the  
67 gizzard and subsequent absorption in the higher pH environment of the small  
68 intestine.

69

70 With respect to hydrophobic organic pollutants that have adsorbed to the surface of  
71 plastics from sea water, it is unclear whether ingestion provides a significant vector  
72 for their bioaccumulation since model calculations suggest an overwhelming  
73 contribution to body burden from the diet (Herkze et al., 2016). However, empirical  
74 studies have revealed that organic chemicals present in plastics as functional additives  
75 and occurring at concentrations many orders of magnitude higher than adsorbed  
76 pollutants are often readily mobilised in the simulated digestive juices of

77 procellariiforms (Tanaka et al., 2015). Regarding inorganic chemicals, compounds of  
78 hazardous metals and metalloids were often added to historical plastics at percentage  
79 concentrations as fillers, pigments, stabilisers and flame retardants (Hansen et al.,  
80 2013), while substantial quantities of residual catalysts and intermediates may also be  
81 present if such materials had been expanded or extruded (Turner and Lau, 2016).  
82 Accordingly, older marine plastics are often characterised by the presence of  
83 chemicals like lead chromate, cadmium sulphoselenide and antimony-based  
84 synergists, many of which have since been restricted or phased out (Turner, 2016).  
85  
86 In a recent article, a limited number of individual, beached microplastics (< 5 mm)  
87 containing one or more hazardous elements were subjected to an avian  
88 physiologically-based extraction test (PBET) (Massos and Turner, 2017). Although  
89 mobilisation of small but significant quantities of Cd and Pb was evident, an  
90 evaluation of the mechanisms and kinetics of dissolution was thwarted by  
91 concentrations that were close to control levels or instrumental detection limits. In the  
92 present study, such constraints are circumvented by undertaking PBETs on larger and  
93 controlled quantities of microplastics that have been prepared from primary and  
94 secondary macroplastics in order to assess the potential for hazardous element  
95 exposure to sea birds. The samples for study were retrieved from local beaches and  
96 selected on the basis of non-compliance according to the Restriction of Hazardous  
97 Substances Directive on electronic plastics (RoHS, 2006); that is, in a homogeneous  
98 material of any new or recycled product, concentration limits are 100  $\mu\text{g g}^{-1}$  for Cd,  
99 1000  $\mu\text{g g}^{-1}$  for Cr(VI), Hg and Pb, and 1000  $\mu\text{g g}^{-1}$  for specific brominated flame  
100 retardants and where total Br is a commonly employed proxy (Guzzonato et al.,  
101 2016). Additional, potentially hazardous elements were also considered that are

102 commonly co-associated with RoHS-elements and that have restrictions on migration  
103 from plastics according to the original European toy safety standard, EN 71-3:1994  
104 (Cordeiro et al., 2012); namely: As, Ba, Se and Sb.

105

## 106 **2. Materials and methods**

### 107 *2.1. Sampling and sample processing*

108 Samples of plastic were collected from two sand-gravel beaches in Plymouth Sound,  
109 south west England (Firestone Bay: 50.36054, -4.16252; and Mount Batten:  
110 50.35771, -4.12755). Distinctive objects and fragments of plastic and pieces of  
111 expanded or extruded polymer of between about 5 and 250 mm in length, but  
112 excluding food packaging that had been discarded in situ, were retrieved after high  
113 water from the most recent strandline using plastic tweezers and transferred to a  
114 polyethylene storage box. In the laboratory, samples were rinsed in Millipore Milli-Q  
115 water through a 2-mm sieve and with the aid of a Nylon brush in order to remove  
116 debris and silt before being dried at 40°C for 24 hours.

117

### 118 *2.2. XRF analysis*

119 Samples were analysed by energy-dispersive field-portable-XRF for a suite of  
120 elements, of which those that are restricted in plastics according to the RoHS  
121 Directive or EN71 Standard are the focus of the present study (i.e. As, Ba, Br, Cd, Cr,  
122 Hg, Pb, Sb, Se). Thus, in the laboratory, a battery-powered Niton XRF analyser  
123 (model XL3t 950 He GOLDD+) was fixed, nose-upwards, into a Thermo Fisher  
124 Scientific accessory test stand (PN 420-017) and connected to a laptop computer via  
125 USB and operated under conditions detailed elsewhere (Turner and Solman, 2016).  
126 Samples were measured for thickness through the flattest (measurement) surface

127 using digital callipers before being placed on a 20 cm<sup>2</sup>, 3.6 µm thick polyester film  
128 that was suspended above the detector window. With the shield of the stand closed,  
129 measurements in a low density ‘plastics’ mode and with appropriate thickness  
130 correction were activated through the laptop for 60 seconds, comprising an initial scan  
131 for Cl to discriminate polyvinyl chloride- (PVC-) and non-PVC-based plastics, and  
132 subsequent periods of counting of 40 seconds at 50 kV and 40 µA and 20 seconds at  
133 20 kV and 100 µA. Spectra were quantified by fundamental parameters to yield  
134 elemental concentrations on a dry weight basis (in µg g<sup>-1</sup>) and a counting error of 2σ  
135 (95% confidence) that were downloaded to the laptop using Niton data transfer (NDT)  
136 PC software. False positives for As in the presence of Pb (resulting from spectral  
137 overlap of As-Kα = 10.54 keV and Pb-Lα = 10.55 keV) were eliminated on  
138 examination of individual spectra displayed by the NDT software.

139

140 For quality assurance purposes, two Niton polyethylene discs that had been  
141 impregnated with various elements were analysed at regular intervals throughout each  
142 measurement session. Specifically, disc 1 (PN 180-554, batch SN PE-071-N) contains  
143 Br, Cd, Cr, Hg and Pb at or close to their respective RoHS limits, while disc 2 (PN  
144 180-619, LOT#T-18) contains all elements listed in the original toy safety standard at  
145 concentrations ranging from about 50 µg g<sup>-1</sup> (As) to 700 µg g<sup>-1</sup> (Ba). Measured versus  
146 certified concentrations resulting from all analyses of both discs and shown in Figure  
147 1 reveal agreement within 10% in all cases with the exception of Br in disc 1 and Hg  
148 in disc 2 (agreement within 12%). Also shown in Figure 1 are indicative measurement  
149 limits of detection for each element, based on mean counting errors derived from all  
150 disc analyses multiplied by 1.5 (i.e. 3σ).

151

152 2.3. *FTIR analysis*

153 The composition of samples for the extraction tests, selected on the basis of RoHS-  
154 non-compliance and as described below, were determined by Fourier transform infra-  
155 red (FTIR) spectroscopy using a Bruker ALPHA Platinum attenuated total reflection  
156 QuickSnap A220/D-01 spectrometer. Sample offcuts of about 20 mg were clamped  
157 down on to the ATR diamond crystal before measurements, consisting of 16 scans in  
158 the range 4000 to 400  $\text{cm}^{-1}$  and at a resolution of 4  $\text{cm}^{-1}$ , were activated via Bruker  
159 OPUS spectroscopic software. Identification involved a comparison of sample  
160 transmittance spectra with libraries of reference spectra.

161

162 2.4. *PBET*

163 The avian extraction test was modelled on the digestive characteristics of the  
164 proventriculus-gizzard of the northern fulmar, *Fulmarus glacialis*, a procellariform  
165 known to ingest substantial quantities of microplastics and an OSPAR indicator  
166 species of plastic pollution (OSPAR, 2008; Avery-Gomm et al., 2012). Samples were  
167 first manually processed to a size of < 3 mm using a stainless steel grater or scalpel  
168 before ~100 mg portions were accurately weighed into individual 60 ml screw-capped  
169 polypropylene centrifuge tubes. Forty ml of a digestive fluid, comprising 1% pepsin  
170 (lyophilised powder from porcine gastric mucosa; Sigma-Aldrich) in 0.1 M NaCl  
171 solution whose pH had been adjusted to 2.5 by addition of 1 M HCl, was then added  
172 to each tube, including three without solids and which served as controls. Tubes were  
173 subsequently capped and the contents incubated in a shaking water bath set at 100  
174 rpm and 40 °C. After time intervals of about 1, 2, 5, 15, 25 and 160 h, and taking care  
175 not to abstract plastic fragments, 1-ml aliquots of extract from each tube were pipetted



176 into individual Sterilin tubes where they were diluted to 5 ml with 2% HNO<sub>3</sub> and  
177 stored at 4 °C and in the dark pending analysis.

178

### 179 *2.5. Extract analysis*

180 PBET extracts were analysed in triplicate for the restricted elements considered by  
181 collision cell-ICP-MS using a Thermo X-series II (Thermo Elemental, Winsford UK)  
182 with a concentric glass nebuliser and conical spray chamber. The ICP was calibrated  
183 externally using five mixed standards and five blanks prepared in 2% HNO<sub>3</sub> and  
184 operated under conditions described elsewhere (Turner and Holmes, 2015). Limits of  
185 detection, based on three standard deviations arising from blank measurements,  
186 ranged from about 0.5 µg L<sup>-1</sup> for Cd, Pb and Se to about 10 µg L<sup>-1</sup> for Br.

187

## 188 **3. Results and Discussion**

### 189 *3.1. Sample characteristics*

190 A total of 185 samples of primary and secondary plastics were analysed by XRF, and  
191 a summary of the concentrations of hazardous and restricted elements is given in  
192 Table 1. Detection frequency ranged from about 2% for Se to over 40% for Ba and  
193 Cr, and overall, one or more element was detected in 151 cases. Non-detection was  
194 usually associated with distinct objects (e.g. bottle lids, toys, straws) while the highest  
195 concentrations of one or more restricted elements were generally encountered in both  
196 primary and secondary plastics that were either brightly coloured and/or of PVC-  
197 construction, and in neutrally- or brightly-coloured pieces of expanded plastic. Non-  
198 compliance according to RoHS criteria (RoHS, 2006) was observed in 12 samples  
199 based on Cd or Pb concentrations, with potential non-compliance occurring in three  
200 additional samples based on total Br concentrations in excess of 1000 µg g<sup>-1</sup> and in

201 two cases and in association with non-compliance of Pb where total Cr exceeded 1000  
202  $\mu\text{g g}^{-1}$ . Regarding the latter, the mass ratio of Cr:Pb of about 1:4 suggests that Cr in  
203 these samples exists as Cr(VI) in the form of the pigment,  $\text{PbCrO}_4$  (Turner and  
204 Solman, 2016), implying non-compliance in respect of both metals. Based on these  
205 observations, 12 out of 15 non-compliant (or potentially non-compliant) samples were  
206 selected for extraction tests, with three not considered where Cd concentrations were  
207 marginally above its RoHS threshold. These samples are illustrated in Figure 2 and  
208 characterised according to results from both FTIR and XRF analyses in Table 2.

209

### 210 *3.2. PBET results and kinetic modelling*

211 The concentrations of elements extracted from ~100 mg of plastics in 40 ml of avian-  
212 PBET fluid and corrected for concentrations in the corresponding controls are shown  
213 as a function of time in Figure 3. In most cases, elemental concentrations increase in a  
214 biphasic fashion with relatively rapid initial mobilisation followed by a slower and  
215 more protracted period in which equilibrium appears to be approached or attained  
216 within the timeframe of the experiment. In the case of Br, initial mobilisation is  
217 evidently extremely rapid with equilibrium conditions not met by the end of the  
218 incubation, and with respect to Cr and, in three cases, Pb, there appears to be a period  
219 of relaxation (e.g. adsorption or precipitation) following initial mobilisation.

220

221 The timed PBET data were fitted using one of two kinetic models based on the  
222 diffusion-controlled and surface reaction-controlled dissolution of solids as outlined  
223 by Ruby et al. (1992) and Turner and Price (2008). Thus, a pseudo-first-order  
224 diffusion model, derived from a modified form of the Noyes-Whitney equation,

225 predicts that the rate of mobilisation is proportional to the magnitude of the  
226 concentration gradient around the particles, and whose solution is:

227

$$228 \quad \ln(C_e - C) = \ln C_e - k_1 S t \quad (1a)$$

229

230 Here,  $C$  and  $C_e$  represent the observed (time-dependent) and equilibrium aqueous  
231 elemental concentrations, respectively,  $S$  is the surface area of undissolved solid, and  
232  $k_1$  is a combined (forward and reverse) pseudo-first-order rate constant. In the case  
233 where the initial mobilisation is too rapid to be modelled, a constant,  $a$ , may be  
234 introduced that defines an effective starting concentration:

235

$$236 \quad \ln(C_e - C) = \ln C_e - k_1 S t + \ln a \quad (1b)$$

237

238 An alternative, diffusion-controlled and parabolic model derived from Fick's second  
239 law for the dissolution of a semi-infinite slab is:

240

$$241 \quad C = 2(C_e - C)(\sqrt{D/\pi})t^{1/2} = k_2 t_{1/2} \quad (2a)$$

242

243 where  $D$  is the diffusion coefficient of the aqueous element. Likewise, accounting for  
244 extremely rapid initial mobilisation, a constant,  $b$ , defining an effective starting  
245 concentration can be introduced:

246

$$247 \quad C = 2(C_e - C)(\sqrt{D/\pi})t^{1/2} + b = k_2 t_{1/2} + b \quad (2b)$$

248

249 Models 1 and 2 were applied to the data in Figure 3 to determine which mechanism(s)  
250 and kinetics best describe metal mobilisation in the simulated avian proventriculus-  
251 gizzard. For model 1a, concentrations at equilibrium were defined as those measured  
252 at the end of the incubations and, for simplicity,  $S$  was assumed to be constant and  
253 was not factored into the calculations. The rate constant was derived from linear  
254 regression analysis of  $\ln(C_e - C) - \ln C_e$  versus  $t$ , forced through the origin, with the  
255 number of data points ( $n$ ) constrained to those whose concentrations were less than  
256  $C_e$ . Model 1b was employed where regression analysis of  $\ln(C_e - C) - \ln C_e$  versus  $t$   
257 and without forcing returned a significant y-intercept. For model 2, and given that  $D$  is  
258 a constant, both  $k_2$  and  $b$  were derived from the slope and intercept arising from linear  
259 regression analysis of  $C$  versus  $t_{1/2}$ .

260

261 The results, as rate constants, regression coefficients defining the linearised data and,  
262 for model 1,  $C_e$ , are shown in Table 3, while model fits using these values are  
263 annotated on Figure 3. Thus, for all elements with the exception of Br, model 1  
264 provided the better fits, with only two cases (Ba in expanded polystyrene and Cd in a  
265 fragment of polyethylene) requiring an intercept to account for initial, rapid  
266 mobilisation. Model 2 successfully fitted Br data for two samples (expanded  
267 polyurethane and expanded polystyrene), requiring intercepts of more than 70% of the  
268 corresponding values of  $C_e$  in both cases. Also shown in Table 3 are maximum and  
269 equilibrium elemental bioaccessibilities ( $BA_{\max}$  and  $BA_e$ , respectively) for each time-  
270 course modelled. Bioaccessibilities, on a percentage basis, were calculated by  
271 converting the highest or final aqueous concentrations to a weight basis and  
272 normalising to the corresponding total (XRF) elemental concentrations.

273

274 *3.3. Implications for exposure to seabirds*

275 Regarding the two beaches sampled in the present study, the amount of RoHS non-  
276 compliant material retrieved on a number basis was about 8%. With the restrictions or  
277 phasing out of harmful additives in plastics, this percentage reflects the relative  
278 abundance of historical material washed up on the strandline and is, likely,  
279 representative of the more general plastic population suspended at sea where  
280 procellariiforms and other seabirds feed. Despite PVC being denser than sea water, its  
281 presence on the strandline suggests that small fragments may evade deposition while  
282 carried in the water column or be transported locally as bed-load. The fact that  
283 fragments of PVC have been observed in the digestive tracts of seabirds, including  
284 procellariiforms (Furtado et al., 2016), is consistent with the former assertion and may  
285 reflect the propensity of small particles to be suspended at the sea surface microlayer  
286 (Song et al., 2015) or the tendency of many pursuit plunging birds to feed well below  
287 the surface (Tavares et al., 2017).

288

289 The avian PBET results of this study predict various degrees of mobilisation of  
290 hazardous elements once non-compliant plastics have been ingested, with Br and Pb  
291 exhibiting the greatest concentrations in the simulated digestive fluid and yielding the  
292 highest bioaccessibilities on a percentage basis (and in excess of 10% and 20%,  
293 respectively, in one case each). Pseudo-first-order fits to most metal-metalloid data  
294 with rate constants on the order of  $0.05 \text{ h}^{-1}$  suggest that mobilisation may be  
295 constrained by the penetrability of the digestive fluid into the hydrophobic, non-  
296 porous plastics (Nakashima et al., 2016); as such, equilibrium is attained within the  
297 timeframe in which non-food material is trapped in the proventriculus-gizzard (weeks  
298 to months; Avery-Gomm et al., 2012). In some cases, where competing or transient

299 reactions are evident (e.g. Cr and Pb), mobilisation in the digestive tract may exceed  
300 equilibrium values within the first few days of ingestion, suggesting that accessibility  
301 would be greater should material be regurgitated and expelled during this period. In  
302 contrast, mobilisation of Br from the more porous expanded plastics appears to  
303 proceed continuously after an initial, extremely rapid period of mobilisation. Here, it  
304 is suspected that the substrate is modified or partially consumed at the onset of  
305 digestion with subsequent mobilisation of Br not constrained by fluid penetration.  
306 These observations suggest that significant release of brominated compounds is likely  
307 immediately after ingestion and that further release is dependent on the precise time of  
308 entrapment in the digestive tract rather than the hydrophobicity of the polymeric  
309 surface.

310

311 The significance of microplastics as a source of exposure to hazardous elements  
312 compared to exposure arising from the diet was evaluated using the results from the  
313 present study, an estimate for the fraction of plastic in ingested fulmar food of  $4.75 \times$   
314  $10^{-5}$  (Herkze et al., 2017) and dry weight concentrations of elements reported for  
315 muscle tissue of Atlantic fish typical of the fulmar diet. With measurements for the  
316 latter restricted to Cd and Pb, and with respective median concentrations of about 0.01  
317 and  $0.03 \mu\text{g g}^{-1}$  (Julshamn et al., 2013; Karl et al., 2016), fractional exposure arising  
318 from ingested plastics is predicted to be about 0.95 and 0.98, respectively, based on  
319 the highest elemental concentrations in beached materials reported in Table 2 (that is,  
320  $4310 \mu\text{g g}^{-1}$  for Cd and  $38,200 \mu\text{g g}^{-1}$  for Pb). Using the maximum bioaccessible  
321 concentrations of Cd and Pb in plastics on a dry weight basis derived from the data in  
322 Table 3 ( $36.3 \mu\text{g g}^{-1}$  for Cd and  $928 \mu\text{g g}^{-1}$  for Pb), respective fractional exposures are  
323 reduced to around 0.15 and 0.6. Clearly, these figures are overestimates that require

324 selective ingestion of the most contaminated materials, and more realistic measures  
325 must account for the relative abundance of Cd- and Pb-positive items within the  
326 available plastic population. Thus, based on weighted average concentrations and a  
327 frequency of RoHS-non-compliance among the samples tested by XRF of about 4%,  
328 fractional exposures to the fulmar arising from plastic become about 0.007 and 0.06  
329 for Cd and Pb, respectively.

330

331 Regarding Br, if it is assumed that the total concentration in plastic is equivalent to the  
332 combined concentrations of brominated flame retardants (BFRs) (Massos and Turner,  
333 2017), calculations may be performed using available data on BFRs in Atlantic prey.  
334 Jenssen et al. (2007) report maximum, summed concentrations of various BFRs in cod  
335 lipid that are equivalent to whole body concentrations on a dry weight basis of about 1  
336 ng g<sup>-1</sup>. Undertaking calculations as above yield a maximum fractional exposure to  
337 BFRs due to ingested plastic of 0.99, which is reduced to 0.90 when bioaccessibility  
338 is factored in and about 0.3 once the abundance of Br-positive plastics have been  
339 taken into account.

340

341 Assuming that hazardous chemicals in ingested prey are entirely accessible and that  
342 absorption across the intestinal epithelium is independent of the source or speciation  
343 once mobilised, ingested plastics are, on average, predicted to contribute about 0.7%,  
344 6% and 30% to the respective net accumulations of Cd, Pb and Br (as BFRs) in the  
345 fulmar. The high contribution for the latter is qualitatively consistent with the  
346 relatively small size of BFR molecules and their greater propensity to migrate from  
347 the polymeric matrix than particulate, metallic additives (Hansen et al., 2013; Jang et  
348 al., 2016), and the accumulation of specific BFRs by procellariiforms that are present

349 in plastic but absent in prey (Tanaka et al., 2013). Thus, although ingested plastics  
350 appear to represent a negligible source of relatively high molecular weight  
351 hydrophobic organic pollutants to pelagic seabirds (Herkze et al., 2017), they may act  
352 as a significant vehicle for the accumulation of lower molecular weight BFRs and for  
353 metallic additives.

354

355

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360

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461 seabirds is global, pervasive, and increasing. *Proceedings of the National Academy of*  
462 *Sciences of the United States of America* 112, 11899-11904.

463 Table 1: Summary statistics for the elemental concentrations in 185 beached plastic samples along with the number of cases of RoHS non-compliance (or, for Br and Cr,  
 464 potential non-compliance).

|                              | <b>As</b> | <b>Ba</b> | <b>Br</b> | <b>Cd</b> | <b>Cr</b> | <b>Hg</b> | <b>Pb</b> | <b>Sb</b> | <b>Se</b> |
|------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| <i>n</i>                     | 14        | 80        | 49        | 9         | 86        | 8         | 28        | 14        | 4         |
| mean, $\mu\text{g g}^{-1}$   | 97.7      | 744       | 202       | 1270      | 201       | 35.3      | 2130      | 1270      | 568       |
| median, $\mu\text{g g}^{-1}$ | 31.4      | 494       | 34.3      | 845       | 69.9      | 23.4      | 75.4      | 244       | 547       |
| min, $\mu\text{g g}^{-1}$    | 7.3       | 118       | 6.0       | 57.0      | 18.3      | 8.3       | 2.6       | 37.4      | 319       |
| max, $\mu\text{g g}^{-1}$    | 368       | 8680      | 2370      | 4310      | 1330      | 90.0      | 38200     | 15000     | 858       |
| RoHS-non-compliance          |           |           | 3         | 7         | 2         | 0         | 5         |           |           |

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475 Table 2: Characteristics and elemental concentrations (in  $\mu\text{g g}^{-1}$ ) of the samples used in the extraction tests and as photographed in Figure 2. Note that As and Hg were not  
 476 detectable. (PE = polyethylene; PP = polypropylene; PVC = polyvinyl chloride; E-PS = expanded polystyrene; E-PU = expanded polyurethane.)

| sample | thickness, mm | type | Ba  | Br   | Cd   | Cr   | Pb    | Sb  | Se  |
|--------|---------------|------|-----|------|------|------|-------|-----|-----|
| 1      | 2.6           | PP   | 246 | 3.2  | 1380 |      |       |     | 319 |
| 2      | 10.4          | E-PU | 188 | 2370 |      | 486  |       |     |     |
| 3      | 2.1           | PP   | 479 |      |      | 1090 | 4260  | 242 |     |
| 4      | 2.9           | PE   | 325 |      | 2060 | 18.4 |       |     | 469 |
| 5      | 1.6           | PE   | 704 |      | 4310 |      |       |     | 858 |
| 6      | 1.7           | PE   |     |      | 57.0 | 716  | 3680  |     |     |
| 7      | 15.0          | E-PS |     | 1070 |      | 191  |       |     |     |
| 8      | 21.7          | E-PS | 253 | 1750 |      | 199  |       |     |     |
| 9      | 3.8           | PP   | 737 |      |      | 1330 | 6130  | 247 |     |
| 10     | 2.8           | PVC  |     | 15.4 |      |      | 4090  |     |     |
| 11     | 3.2           | PP   | 515 |      | 2340 |      |       |     | 625 |
| 12     | 7.0           | PVC  | 360 | 305  |      |      | 38200 | 108 |     |

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478 Table 3: Results of fitting models 1 or 2 to the data in Figure 3, along with  
 479 equilibrium and maximum aqueous concentrations and bioaccessibilities (ns = results  
 480 of regression analysis non-significant).

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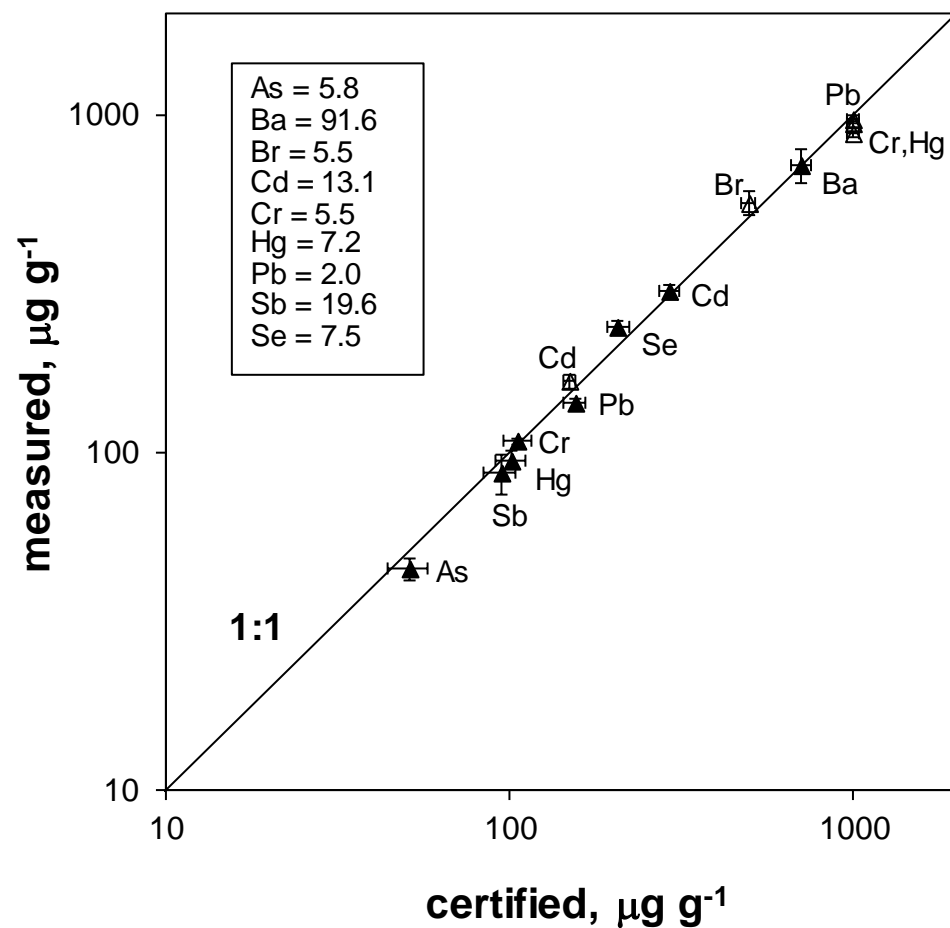
|                     |                                   | 1             | 2         | 3         | 4         | 5         | 6         | 8         | 9         | 10     | 11        | 12        |
|---------------------|-----------------------------------|---------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|--------|-----------|-----------|
| Ba                  | $k_1, h^{-1}$                     | 0.0426        |           |           |           |           |           | 0.0288    | 0.0562    |        |           |           |
|                     | $r^2 (n)$                         | 0.996 (6)     |           |           |           |           |           | 0.916 (5) | 0.982 (6) |        |           |           |
|                     | $C_e, \mu g L^{-1}$               | 31.4          |           |           |           |           |           | 11.6      | 104       |        |           |           |
|                     | $a, \mu g L^{-1}$                 |               |           |           |           |           |           | 5.0       |           |        |           |           |
|                     | $BA_e, \%$                        | 5.11          |           |           |           |           |           | 1.83      | 5.64      |        |           |           |
| Br                  | $k_2, (\mu g L^{-1})^{-1} h^{-1}$ |               | 9.47      |           |           |           |           | 7.4       |           |        |           |           |
|                     | $r^2 (n)$                         |               | 0.928 (7) |           |           |           |           | 0.966 (7) |           |        |           |           |
|                     | $C_e, \mu g L^{-1}$               |               | 412       |           |           |           |           | 471       |           |        |           |           |
|                     | $b, \mu g L^{-1}$                 |               | 291       |           |           |           |           | 373       |           |        |           |           |
|                     | $BA_e, \%$                        |               | 6.95      |           |           |           |           | 10.8      |           |        |           |           |
| Cd                  | $k_1, h^{-1}$                     | 0.0614        |           |           | 0.0339    | 0.0326    | 0.0749    |           |           |        | 0.0444    |           |
|                     | $r^2 (n)$                         | 0.956 (6)     |           |           | 0.907 (6) | 0.954 (6) | 0.880 (6) |           |           |        | 0.993 (6) |           |
|                     | $C_e, \mu g L^{-1}$               | 90.7          |           |           | 14.9      | 23.8      | 1.43      |           |           |        | 38.0      |           |
|                     | $a, \mu g L^{-1}$                 |               |           |           | 6.0       |           |           |           |           |        |           |           |
|                     | $BA_e, \%$                        | 2.63          |           |           | 0.29      | 0.22      | 1.00      |           |           |        | 0.65      |           |
| Cr                  | $k_1, h^{-1}$                     |               |           |           |           |           |           |           | 0.558     |        |           |           |
|                     | $r^2 (n)$                         |               |           |           |           |           |           |           | 0.899 (3) |        |           |           |
|                     | $C_e, \mu g L^{-1}$               |               |           |           |           |           |           |           | 77.0      |        |           |           |
|                     | $C_{max}, \mu g L^{-1}$           |               |           |           |           |           |           |           | 81.9      |        |           |           |
|                     | $BA_{max}, \%$                    |               |           |           |           |           |           |           | 2.32      |        |           |           |
| Pb                  | $k_1, h^{-1}$                     |               |           | 0.297     |           |           | 0.282     |           | 0.0595    | 0.179  |           | 0.0387    |
|                     | $r^2 (n)$                         |               |           | 0.336 (3) |           |           | ns (3)    |           | 0.969 (6) | ns (3) |           | 0.809 (6) |
|                     | $C_e, \mu g L^{-1}$               |               |           | 83.7      |           |           | 49.7      |           | 832       | 1640   |           | 3070      |
|                     | $C_{max}, \mu g L^{-1}$           |               |           | 128       |           |           | 70.0      |           |           | 2320   |           |           |
|                     | $BA_e, \%$                        |               |           | 0.79      |           |           | 0.54      |           | 5.43      | 16.04  |           | 3.21      |
| Sb                  | $k_1, h^{-1}$                     |               |           | 0.0538    |           |           |           |           | 0.0419    |        |           |           |
|                     | $r^2 (n)$                         |               |           | 0.982 (6) |           |           |           |           | 0.995 (6) |        |           |           |
|                     | $C_e, \mu g L^{-1}$               |               |           | 27.6      |           |           |           |           | 27.9      |        |           |           |
|                     | $BA_e, \%$                        |               |           | 4.56      |           |           |           |           | 4.52      |        |           |           |
|                     | Se                                | $k_1, h^{-1}$ | 0.0358    |           |           | 0.0243    | 0.0217    |           |           |        |           | 0.0631    |
| $r^2 (n)$           |                                   | 0.818 (6)     |           |           | 0.935 (6) | 0.737 (6) |           |           |           |        | 0.719 (6) |           |
| $C_e, \mu g L^{-1}$ |                                   | 18.2          |           |           | 7.42      | 9.89      |           |           |           |        | 23.3      |           |
| $BA_e, \%$          |                                   | 2.28          |           |           | 0.63      | 0.46      |           |           |           |        | 1.49      |           |

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483 Figure 1: Measured versus certified concentrations of elements in Niton polyethylene reference discs 1 ( $\Delta$ ) and 2 ( $\blacktriangle$ ). Errors represent two  
484 standard deviations about the mean of 12 analyses (measured) and the 95% confidence interval for an unspecified number of measurements  
485 (certified). Shown inset are indicative measurement limits of detection.

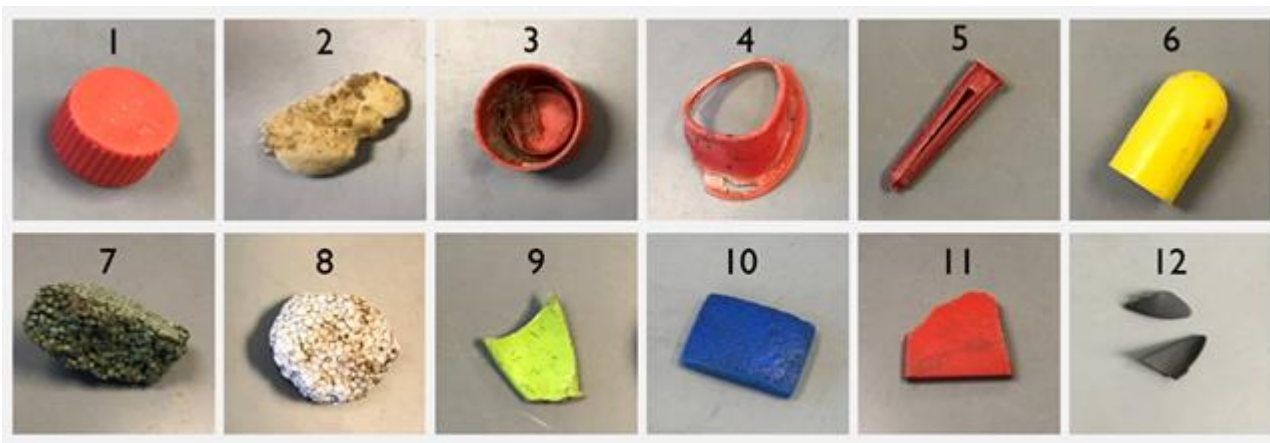
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488 Figure 2: The primary and secondary plastics characterised in Table 2 and used to prepare the microplastics for the extraction tests.



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498 Figure 3: Elemental concentrations extracted from ~100 mg of sample, and as coded in the Cr panel, by 40 ml of avian-PBET fluid. (Note that  
499 all elements evaded detection in sample 7.) Errors denote the standard deviation about the mean of three analyses and lines represent model fits  
500 according to equation 1 or equation 2 (Br only) using the coefficients given in Table 2.

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