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Turner, Andrew

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Andrew Turner[*]

School of Geography, Earth and Environmental Sciences

Plymouth University

Drake Circus

Plymouth PL4 8AA

UK

[*]Corresponding author. Tel: +44 1752 584570; Fax: +44 1752 584710; e-mail: aturner@plymouth.ac.uk

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Abstract

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

2

1. Introduction

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

procellariiforms (Tanaka et al., 2015). Regarding inorganic chemicals, compounds of

hazardous metals and metalloids were often added to historical plastics at percentage

concentrations as fillers, pigments, stabilisers and flame retardants (Hansen et al.,

2013), while substantial quantities of residual catalysts and intermediates may also be

present if such materials had been expanded or extruded (Turner and Lau, 2016).

Accordingly, older marine plastics are often characterised by the presence of

chemicals like lead chromate, cadmium sulphoselenide and antimony-based

synergists, many of which have since been restricted or phased out (Turner, 2016).

In a recent article, a limited number of individual, beached microplastics (< 5 mm)

containing one or more hazardous elements were subjected to an avian

physiologically-based extraction test (PBET) (Massos and Turner, 2017). Although

mobilisation of small but significant quantities of Cd and Pb was evident, an

evaluation of the mechanisms and kinetics of dissolution was thwarted by

concentrations that were close to control levels or instrumental detection limits. In the

present study, such constraints are circumvented by undertaking PBETs on larger and

controlled quantities of microplastics that have been prepared from primary and

secondary macroplastics in order to assess the potential for hazardous element

exposure to sea birds. The samples for study were retrieved from local beaches and

selected on the basis of non-compliance according to the Restriction of Hazardous

Substances Directive on electronic plastics (RoHS, 2006); that is, in an homogeneous

material of any new or recycled product, concentration limits are 100 μg g^{-1} for Cd,

1000 μg g^{-1} for Cr(VI), Hg and Pb, and 1000 μg g^{-1} for specific brominated flame

retardants and where total Br is a commonly employed proxy (Guzzonato et al.,

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^2, 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^{-1}) 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^{-1} (As) to 700 μg g^{-1} (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 cm^{-1} and at a resolution of 4 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_3 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_3 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 $\mu g\ L^{-1}$ for Cd, Pb and Se to about 10 $\mu g\ L^{-1}$ 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 $\mu g\ g^{-1}$ and in

201 two cases and in association with non-compliance of Pb where total Cr exceeded 1000

202 μg 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, 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 $$\ln(C_e - C) = \ln C_e - k_1 St \qquad (1a)$$

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 $$\ln(C_e - C) = \ln C_e - k_1 St + \ln a \qquad (1b)$$

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

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

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

3.3. Implications for exposure to seabirds

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

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

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 $\mu g\ g^{-1}$ (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 $\mu g\ g^{-1}$ for Cd and 38,200 $\mu g\ g^{-1}$ 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 $\mu g\ g^{-1}$ for Cd and 928 $\mu g\ g^{-1}$ 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^{-1}. 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.

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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).

|	As	Ba	Br	Cd	Cr	Hg	Pb	Sb	Se
n	14	80	49	9	86	8	28	14	4
mean, $\mu g\ g^{-1}$	97.7	744	202	1270	201	35.3	2130	1270	568
median, $\mu g\ g^{-1}$	31.4	494	34.3	845	69.9	23.4	75.4	244	547
min, $\mu g\ g^{-1}$	7.3	118	6.0	57.0	18.3	8.3	2.6	37.4	319
max, $\mu g\ g^{-1}$	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 µg 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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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, µg L⁻¹	31.4						11.6	104			
	a, µg L⁻¹							5.0				
	BA_e, %	5.11						1.83	5.64			
Br	k_2, (µg L⁻¹)⁻¹h⁻¹		9.47					7.4				
	r^2 (n)		0.928 (7)					0.966 (7)				
	C_e, µg L⁻¹		412					471				
	b, µg 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, µg L⁻¹	90.7			14.9	23.8	1.43				38.0	
	a, µg 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, µg L⁻¹								77.0			
	C_{max}, µg L⁻¹								81.9			
	BA_e, %								2.32			
	BA_{max}, %								2.46			
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, µg L⁻¹		83.7				49.7		832	1640		3070
	C_{max}, µg L⁻¹		128				70.0			2320		
	BA_e, %		0.79				0.54		5.43	16.04		3.21
	BA_{max}, %		1.20				0.66			22.7		
Sb	k_1, h⁻¹		0.0538						0.0419			
	r^2 (n)		0.982 (6)						0.995 (6)			
	C_e, µg 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, µg 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 (Δ) and 2 (▲). 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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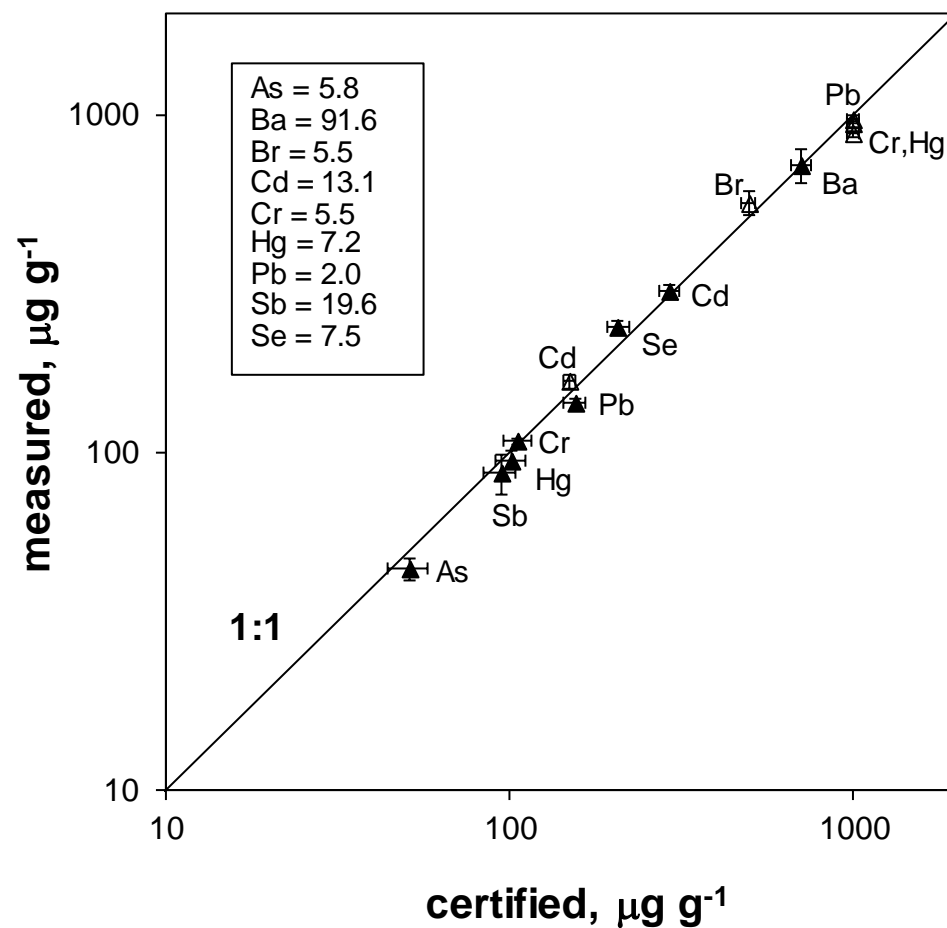
488   Figure 2: The primary and secondary plastics characterised in Table 2 and used to prepare the microplastics for the extraction tests.

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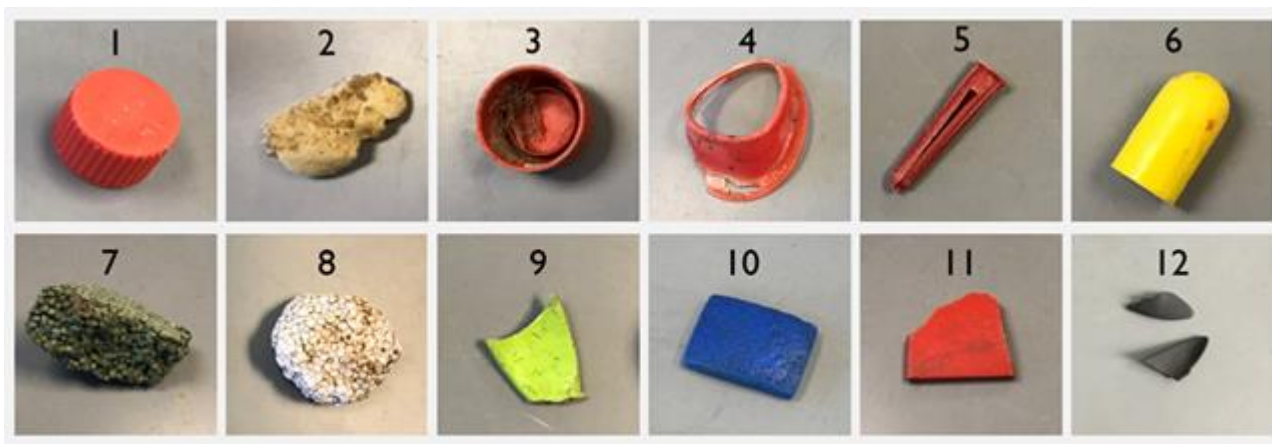
498   Figure 3: Elemental concentrations extracted from ~100 mg of sample, and as coded in the Cr panel, by 40 ml of avian-PBET fluid. (Note that

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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