

2020-09-01

# Mobilisation kinetics of Br, Cd, Cr, Hg, Pb and Sb in microplastics exposed to simulated, dietary-adapted digestive conditions of seabirds

Smith, EC

<http://hdl.handle.net/10026.1/15745>

---

10.1016/j.scitotenv.2020.138802

Science of The Total Environment

Elsevier BV

---

*All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.*

1  
2  
3 **Mobilisation kinetics of Br, Cd, Cr, Hg, Pb and Sb in**  
4 **microplastics exposed to simulated, dietary-adapted**  
5 **digestive conditions of seabirds**

6  
7  
8 **Elliot C. Smith, Andrew Turner\***

9  
10 *School of Geography, Earth and Environmental Sciences*

11 *Plymouth University*

12 *Drake Circus*

13 *Plymouth PL4 8AA*

14 *UK*

15  
16  
17  
18 \*Corresponding author. Tel: +44 1752 584570; Fax: +44 1752 584710; e-mail:  
19 [aturner@plymouth.ac.uk](mailto:aturner@plymouth.ac.uk)

20  
21 Accepted 17 April 2020

22 <https://doi.org/10.1016/j.scitotenv.2020.138802>

39 **Abstract**

40 Samples of beached plastics and historical and contemporary consumer plastics  
41 containing hazardous elements derived from reaction residues or functional additives  
42 have been micronised and subject to extraction conditions representative of the  
43 digestive environment of seabirds. Mobilisation of Br, Cd, Cr, Hg, Pb and Sb into  
44 NaCl solution, an avian physiologically-based extraction test (PBET) and a dietary-  
45 adapted PBET (DA-PBET) incorporating fish oil as part of the avian diet was  
46 monitored by ICP-MS over a 168-h period. Kinetic data were subsequently fitted  
47 using pseudo-first-order and parabolic diffusion models in order to derive rate  
48 constants for the release of hazardous elements during avian digestion of  
49 microplastics. Rate constants were variable and dependent on the nature and origin of  
50 plastic, type of residue or additive, extractant solution employed and model applied.  
51 Resulting estimates of bioaccessibility, defined as the equilibrium or maximum  
52 concentration of an element mobilised over the time course relative to its total  
53 concentration, were variable but considerable in many cases. Specifically, maximum  
54 values of about 65% of Cd and 100% of Pb were observed in consumer  
55 polycarbonate-acrylonitrile butadiene styrene exposed to the avian PBET and beached  
56 polyurethane exposed to the DA-PBET, respectively. The potential health risks of  
57 hazardous elements in microplastics are addressed and criteria for classification based  
58 on the European Toy Safety Directive migration (mobilisation) limits are proposed.

59

60

61 **Keywords:** microplastics; additives; metals; mobilisation kinetics; avian PBET;  
62 bioaccessibility

63

## 64 **1. Introduction**

65 Although the sources, distribution and physical impacts of microplastic litter have  
66 received considerable attention over the past few decades (Ng et al., 2006; Hall et al.,  
67 2015; Lin et al., 2016), less well studied are the nature, occurrence, mobility and fate  
68 of chemical residues and additives (Kwon et al., 2017; Luo et al., 2019). Residues  
69 may remain as reactants or catalysts from the manufacturing process of certain  
70 plastics or may be more widely distributed amongst plastics through the recycling and  
71 blending of end-of-use materials (Turner, 2018a). Additives are deliberately  
72 formulated into plastics, either physically or chemically, for specific functions that  
73 include flame retardancy, colour, fastness, opacity, lubrication, strength, heat  
74 resistance and stabilisation (Pritchard, 1997). While most contemporary additives are  
75 regarded as safe, many historical additives are now restricted or inhibited on health  
76 and environmental grounds. For example, the Restriction of Hazardous Substances  
77 (RoHS) Directive provides limit values of Cd, Cr(VI), Hg, Pb and certain brominated  
78 flame retardants in new or recycled electrical and electronic plastics (European  
79 Parliament and Council, 2003; 2011), while the Toy Safety Directive specifies  
80 migration limits for various metals and metalloids, including Cd, Cr(VI), Hg, Pb and  
81 Sb, from plastic toys into a fluid mimicking a child's stomach (European Parliament  
82 and Council of the EU, 2009). Despite these restrictions, however, potentially harmful  
83 residues and additives remain in products in circulation and are particularly common  
84 in marine litter where a heterogeneous assortment of plastics of variable sources and  
85 ages are encountered (Massos and Turner, 2017; Shaw and Turner, 2019).

86

87 While most residues and additives are either designed, or at least considered, to  
88 remain in the polymeric matrix, aging and weathering in the environment facilitates

89 their gradual mobilisation (Hansen et al., 2013; Nakashimi et al., 2016). Significant in  
90 this respect is the propensity of hazardous additives, such as those listed in the RoHS,  
91 to be released into the digestive tract of animals that inadvertently or incidentally  
92 ingest plastics because mobilisation may result in their entry into the systemic  
93 circulation and subsequent accumulation. The release of small but significant  
94 quantities of Cd and Sb (typically < 1% of corresponding total values) from various  
95 micronised plastics into near-neutral surfactant- and protein-rich fluids simulating the  
96 digestive conditions of deposit-feeding invertebrates over a six-hour time period has  
97 recently been demonstrated by Martin and Turner (2019) and James and Turner  
98 (2020). In an earlier study, Turner (2018b) showed greater release (ranging from <  
99 1% to > 20%) of various hazardous elements from polyolefins, polyvinyl chloride and  
100 expanded plastics over a more extended timeframe into an acidic solution that mimics  
101 the digestive chemistry of a seabird. Using a similar approach Tanaka et al. (2015)  
102 demonstrated mobilisation of trace quantities of the polybrominated diphenyl ether  
103 flame retardant, deca-BDE, impregnated in polyethylene. However, mobilisation was  
104 increased 50-fold when oils that simulate the presence of food were added to the  
105 acidified extractant.

106

107 In the present study, we hypothesize that the mobilisation of a variety of hazardous  
108 elements present in a wider variety of weathered and unweathered plastics are  
109 impacted by the presence of relatively hydrophobic dietary components in the avian  
110 digestive environment. Accordingly, we compare the kinetics of element mobilisation  
111 from micronised plastics (microplastics) in a standard physiologically-based  
112 extraction test (PBET) with those in a dietary-adapted-PBET (DA-PBET) in which  
113 fish oil is added. In the absence of any guidelines or limit values for environmental

114 plastics, measures of bioaccessibility arising from the experiments are related to  
115 available migration limits as defined by the Toy Safety Directive in order to evaluate  
116 the potential health implications of the different samples.

117

## 118 **2. Materials and methods**

### 119 *2.1. Microplastic sample characteristics and preparation*

120 Nine samples of plastic that had been archived from previous studies (e.g. Turner,  
121 2018c; Turner and Solman, 2016) were selected for the present experiments. The  
122 origin and characteristics of the samples, shown in Table 1, indicate five different  
123 types of polymer, and five primary or secondary beached plastics that have been  
124 exposed to the environment and four historical or contemporary consumer plastics  
125 that have not undergone such exposure. Also shown in Table 1 are the concentrations  
126 of elements that are hazardous according to the RoHS Directive and determined by X-  
127 ray fluorescence spectrometry; namely, Br (a proxy for brominated flame retardants),  
128 Cr (as an upper bound indicator of Cr(VI)), Cd, Hg, and Pb. Although Sb is not in the  
129 current iteration of the RoHS, it is also included because it is used as a flame retardant  
130 synergist with brominated compounds (note its association with Br) and is regulated  
131 by the Toy Safety Directive. Significantly, all samples are non-compliant or  
132 potentially non-compliant (depending on the form of Br and speciation of Cr) with  
133 respect to the 1000  $\mu\text{g kg}^{-1}$  or 100  $\mu\text{g kg}^{-1}$  (Cd only) limit values specified by the  
134 RoHS Directive (European Parliament and Council, 2011).

135

136 About 1 g of each plastic sample was formulated to “microplastic” of less than 1 mm  
137 in at least two dimensions using a stainless steel grater. Microplastics were stored in

138 individual polyethylene specimen bags and in the dark pending use in the  
139 experiments.

140

141 **Table 1:** Characteristics of the microplastics used in the study. Polymer types were  
142 identified by Fourier-Transform infrared spectrometry and elemental concentrations  
143 (in  $\mu\text{g g}^{-1}$  and where nd = not detected) were determined by X-ray fluorescence  
144 spectrometry according to methods outlined elsewhere (Massos and Turner, 2017).

sample	type	description	Br	Cd	Cr	Hg	Pb	Sb
1	polypropylene	boot stud remover - black	nd	766	1180	nd	9160	109
2	polyethylene	child's shape sorter toy - yellow	nd	6880	26.0	nd	nd	nd
3	polyvinyl chloride	washing machine drainage hose - grey	73.7	nd	nd	nd	22,900	nd
4	polycarbonate + acrylonitrile butadiene styrene	jewellery beads - black, painted red	15,100	34.3	nd	nd	123	8960
5	polyethylene	water treatment medium (beached) - black	3320	nd	nd	nd	22.4	1970
6	glass-reinforced polyurethane	foam fragment (beached) - brown	50.2	nd	116	nd	4860	nd
7	polyethylene	unidentified fragment (beached) - green	1260	35.9	4970	nd	121	674
8	polyethylene	shot gun cartridge (beached) - red	6.3	1780	nd	nd	nd	nd
9	polyethylene	unidentified fragment (beached) - red	nd	969	85.5	480	21.9	nd

145

## 146 2.2 Extraction reagents

147 Extractions consisted of a 0.1 M solution of NaCl, a simulated avian physiologically-  
148 based extraction test (PBET) and a dietary adapted PBET (DA-PBET). Sodium  
149 chloride solution, simulating the pre-digestive conditions in the oesophagus and crop  
150 of seabirds, was prepared by dissolving 5.844 g of Aristar NaCl (VWR Chemicals  
151 BDH) in 1 L of high purity Elga LabWater (18.2 M $\Omega$ .cm resistivity). The standard  
152 avian PBET was based on methods outlined elsewhere (Turner, 2018b) and modelled  
153 on the chemistry of the proventriculus-gizzard of the northern fulmar, *Fulmarus*  
154 *glacialis*, a procelliform known to ingest substantial quantities of microplastics  
155 (Avery-Gomm et al., 2012) and an indicator species of plastic pollution according to  
156 the Oslo and Paris Convention for the Protection of the Marine Environment of the  
157 North-East Atlantic (OSPAR, 2008). Here, 10 g of pepsin (lyophilised powder from  
158 porcine gastric mucosa; Sigma-Aldrich) were dissolved in 1 L of 0.1 M NaCl solution  
159 whose pH was adjusted to 2.5 by the dropwise addition of 1 M HCl (prepared from  
160

161 Fisher Scientific TraceMetal grade concentrated HCl). The DA-PBET was designed  
162 to simulate digestive conditions that, additionally, include oils arising from the diet.  
163 We used oil from menhaden, fish of the genera *Brevoortia* and *Ethmidium* that are  
164 consumed by a diverse range of predators and that represent an important food source  
165 for many marine birds (Buchheister et al., 2017). Standard refined menhaden oil,  
166 comprising ~ 20-35 % omega-3 fatty acids as triglycerides and of density 0.93 g ml<sup>-1</sup>,  
167 was purchased from Sigma-Aldrich.

168

### 169 2.3. Extraction procedure

170 Extractions were performed on 100 mg of each micronised sample in a series of  
171 screw-capped polypropylene centrifuge tubes using 50 ml NaCl solution, 50 ml PBET  
172 solution, and 40 ml PBET solution plus 10 ml menhaden oil (DA-PBET). The  
173 contents of the tubes were incubated under continuous lateral agitation in a water bath  
174 (Clifton, Nickel Electro Ltd, Weston-super-Mare, UK) set at 100 rpm and 40 °C. At  
175 time intervals of approximately 0.5, 1, 3, 6, 24, 48, 96 and 168 h, 4 ml aliquots of  
176 NaCl or PBET solution were pipetted from each tube, taking care not to abstract any  
177 oil from the DAPBET, and filtered through 0.45 µm Whatman membrane filters  
178 (Sigma-Aldrich) with the aid of a Terumo syringe. Filtrates were transferred to  
179 individual Sterilin tubes to which 80 µl aliquots of 2% HNO<sub>3</sub> (prepared from Fisher  
180 Scientific TraceMetal grade concentrated HNO<sub>3</sub>) were added before the contents were  
181 stored at room temperature and in the dark. Controls were performed likewise for  
182 each extractant but in the absence of micronised microplastics.

183

184 In some acidified extracts from the PBET and DA-PBET a precipitate was observed  
185 to form on storage. Here, extracts were centrifuged at 3000 rpm for 10 min using an



186 MSE Super Minor centrifuge (Heathfield, UK), with 1 ml aliquots of supernatant  
187 subsequently diluted to 4 ml 2% HNO<sub>3</sub> in new Sterilin tubes.

188

#### 189 *2.4. Extract analysis*

190 Sample extracts were analysed in triplicate for Br, Cd, Cr, Hg, Pb and Sb by collision-  
191 cell inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo  
192 Scientific iCAP RQ ICP-MS (Thermo Elemental, Winsford, UK) with a concentric  
193 glass nebuliser and conical spray chamber. Radio frequency power was 1550 W and  
194 coolant, auxiliary, nebuliser and collision cell gas flow rates were set at 14 L Ar min<sup>-1</sup>,  
195 0.8 L Ar min<sup>-1</sup>, 1.05 L Ar min<sup>-1</sup> and 5 ml He min<sup>-1</sup>, respectively. Extracts were  
196 analysed in triplicate, and data were obtained over a dwell time of 10 ms with 50  
197 sweeps per reading. The instrument was calibrated using four mixed standards (in the  
198 range 2 to 20 µg L<sup>-1</sup>) and one blank prepared from LabKings and SCP Science  
199 standard solutions in 0.1 M NaCl. For quality assurance purposes, a certified reference  
200 drinking water (EP-L, SCP Science) was analysed in triplicate during each session  
201 and a standard was analysed after every ten samples as a check for instrumental drift.  
202 Limits of detection after normalisation to dry mass of microplastic ranged from about  
203 0.003 µg g<sup>-1</sup> for Cd, Cr and Pb in the DA-PBET to 0.44 µg g<sup>-1</sup> for Br in NaCl solution  
204 and precision (as relative standard deviation) among replicate analyses was usually  
205 between 3 and 10%.

206

#### 207 *2.5. Timed data fitting*

208 Data arising from the timed experiments were fitted with two diffusion models that  
209 are based on those outlined by Ruby et al. (1992). The linearised solution to the first  
210 model is as follows:

211

$$\ln(C_e - C) = \ln C_e - k_1 t + \ln C_0 \quad (1a)$$

213

214 where  $C$  and  $C_e$  represent the elemental concentrations mobilised from the  
215 microplastic on a weight basis at time  $t$  and at equilibrium, respectively,  $k_1$  is a  
216 combined, forward and reverse pseudo-first-order rate constant of units  $\text{h}^{-1}$ , and  $C_0$  is  
217 the weight-normalised concentration mobilised at  $t = 0$ . The latter is effectively a  
218 constant that accounts for the very rapid, initial mobilisation that is often observed to  
219 occur in such experiments but that cannot otherwise be modelled by a standard  
220 diffusion-controlled reaction (Turner, 2018b). The value of  $k_1$  was obtained from the  
221 gradient arising from linear regression analysis of  $\ln(C_e - C) - \ln C_e$  versus  $t$ , using  
222 Microsoft Excel Office 365, with the value of  $C_0$  derived from the intercept of the  
223 linear regression,  $a$ , as follows:

224

$$C_0 = C_e(1 - e^a) \quad (1b)$$

226

227 The linearised solution to the second, parabolic model of mobilisation is as follows:

228

$$C = k_2 t^{1/2} + C_0 \quad (2)$$

230

231 where  $k_2$  is a parabolic diffusion rate constant of units  $\mu\text{g} [\text{g}(\text{h})^{1/2}]^{-1}$  and, as above,  $C_0$   
232 is the weight-normalised concentration mobilised at  $t = 0$ . Values of  $k_2$  and  $C_0$  were  
233 obtained directly from the gradient and intercept, respectively, arising from linear  
234 regression analysis of  $C$  versus  $t^{1/2}$  using Microsoft Excel.

235

236

### 237 **3. Results and Discussion**

#### 238 *3.1. Elemental mobilisation among the different microplastics and extractants*

239 The concentrations of potentially hazardous elements detected in the microplastic  
240 extracts on a mass basis and corrected for corresponding control concentrations,  $C$  (in  
241  $\mu\text{g g}^{-1}$ ), are shown as a function of time in Figures 1 to 6. Note that analytical error  
242 bars were often smaller than the symbol size and are not shown for clarity. There is a  
243 net increase in concentration for all elements (where detected) and all extractants over  
244 the time course, and in most cases concentrations either increase continuously over  
245 time or exhibit an initial, rapid increase followed by an approach to apparent  
246 equilibrium. For a given element, however, differences in the precise timed profiles  
247 are evident among the different samples and between the different extractant  
248 solutions.

249

250 Mobilisation of Br (Figure 1) was detected in the three microplastics where the  
251 element appeared to have been added (or recycled) as a constituent of a brominated  
252 flame retardant. Amongst the extractants, mobilisation was greatest in the DA-PBET  
253 for polyethylene (samples 5 and 7) but greatest in NaCl solution (i.e. without  
254 acidification or digestive additives) for the mixed polycarbonate-acrylonitrile  
255 butadiene styrene (sample 4). Cadmium mobilisation (Figure 2) was detected in two  
256 microplastics (samples 2 and 8) where the metal had been added as the pigment  
257 cadmium sulphide yellow, CdS, or cadmium sulphoselenide red, Cd<sub>2</sub>SeS (confirmed  
258 from the sample X-ray fluorescence spectra), and in two microplastics (samples 1 and  
259 4) where it was present as a contaminant (likely through recycling); significantly, Cd  
260 release was not detected in polyethylene (sample 9) where the metal had been added

261 with Hg (presumably as the pigment cadmium mercury red,  $\text{CdHgS}_2$ ), although  
262 measurable mobilisation of Hg itself by the DA-PBET was evident (Figure 4).  
263 Cadmium mobilisation was always greater in the PBET and DA-PBET than in NaCl  
264 solution, with maximum release effected by the PBET and the DA-PBET in two cases  
265 each. Chromium mobilisation (Figure 3) was detected from polypropylene (sample 1)  
266 and polyurethane (sample 6) where the metal was likely present as a contaminant or  
267 residual catalyst but not in polyethylene (sample 7) where it was present at the highest  
268 total concentration as a pigment (and most likely chromium oxide green;  $\text{Cr}_2\text{O}_3$ ). In  
269 both cases of detectable Cr mobilisation, the DA-PBET released considerably greater  
270 quantities of the metal than the PBET and NaCl solution.

271

272 Lead mobilisation was detected in four cases (Figure 5); in polypropylene (sample 1)  
273 and polycarbonate-acrylonitrile butadiene styrene (sample 4), where the metal was  
274 likely present as a contaminant, release was greatest by the PBET, while for polyvinyl  
275 chloride (sample 3) and polyurethane (sample 6), where the metal was likely present  
276 as part of a stabilising compound or catalytic residue, respectively, release was  
277 greatest for the DA-PBET. Mobilisation of Sb (Figure 6) was detected in the  
278 microplastics where it was co-associated with Br (samples 4, 5 and 7) and in the  
279 microplastic where it was likely present as a contaminant through recycling (sample  
280 1). Mobilisation was greatest for the DA-PBET in all cases with the exception of  
281 sample 4; here, the PBET mobilised the greatest quantity of the metalloid and the DA-  
282 PBET mobilised the lowest concentration.

283

284 *3.2. Kinetic modelling of timed data*

285 Rate constants and values of  $C_0$  derived from the timed mobilisation data shown in  
286 Figures 1-6 are given in Table 2. The criterion for assigning a value of either  $k_1$  or  $k_2$   
287 was based on the shape of the timed profile (approach to equilibrium or a more  
288 continuous increase in concentration with time, respectively) and the model regression  
289 fit that yielded the greater significance. Where  $k_1$  was assigned, the value of  $C_e$ ,  
290 defined as the concentration measured at the termination of the experiment, is also  
291 shown. Note that any concentrations exceeding this value through the time course  
292 were neglected in the derivation of the rate constant (i.e.  $n < 7$  in the regression).  
293 Where  $k_2$  was assigned (and denoted with an asterisk in Table 2), the final  
294 concentration measured in the time course is given but here is defined as the  
295 maximum concentration,  $C_{\max}$  (and  $n = 8$  in the regression). Where neither model  
296 returned a significant fit but mobilisation was detected,  $C_{\max}$  is shown.

297

298 **Table 2:** Constants defining the timed data show in Figures 1 to 6 for elemental  
299 mobilisation from 9 samples of microplastics in NaCl solution, the PBET and the DA-  
300 PBET. Note that ns = not significant, and values highlighted in yellow or orange  
301 denote, respectively, non-compliance or potential non-compliance with respect to the  
302 European Toy Safety Directive (European Parliament and Council of the EU, 2009).

303

304

305

306



328  
329  
330  
331  
332  
333  
334  
335  
336  
337  
338  
339  
340  
341

342 Rate constants arising from model 1 range from  $0.0094 \text{ h}^{-1}$  for Cr in sample 1 exposed  
343 to the PBET to  $0.472 \text{ h}^{-1}$  for Cr in sample 6 exposed to the DA-PBET. Values of  $C_0$   
344 were usually positive and in many cases exceeded 50% of  $C_e$  (e.g. Pb in sample 6),  
345 suggesting significant instantaneous mobilisation into the extractants. Rate constants  
346 arising from model 2 range from  $0.119 \mu\text{g} [\text{g}(\text{h})^{1/2}]^{-1}$  for Cd in sample 1 exposed to  
347 NaCl solution to  $34.1 \mu\text{g} [\text{g}(\text{h})^{1/2}]^{-1}$  for Sb in sample 4 exposed to the PBET, and here  
348 values of  $C_0$  were always relatively close to the origin.

349

### 350 *3.3. Elemental bioaccessibilities*

351 Table 3 provides operational measures of elemental avian bioaccessibility, BA (%), or  
352 the percentage of total element that is available in the pre-digestive environment of

353 the oesophagus and crop (NaCl), the digestive environment of the proventriculus and  
 354 gizzard in the absence of food (PBET) and the digestive environment in the presence  
 355 of food (DA-PBET) over a timeframe of 168 h. (Note that non-food material may be  
 356 trapped in the proventriculus-gizzard of many seabirds for weeks to months; Avery-  
 357 Gomm et al., 2012.) Values of BA are calculated from the equilibrium or maximum  
 358 (i.e., final) concentrations of elements mobilised over the time courses and reported in  
 359 Table 2 relative to corresponding total elemental concentrations determined by X-ray  
 360 fluorescence spectrometry and given in Table 1. Where an element was detected by  
 361 X-ray fluorescence but not detected by an extractant an upper limit is given based on  
 362 the ICP-MS detection limit in the relevant medium.

363

364 **Table 3:** Percentage bioaccessibilities of hazardous elements in the different  
 365 extractants tested and calculated from  $C_e$  or  $C_{max}$  relative to total concentration.

366

sample	Br			Cd			Cr			Hg	Pb			Sb		
	NaCl	PBET	DA-PBET	NaCl	PBET	DA-PBET	NaCl	PBET	DA-PBET	DA-PBET	NaCl	PBET	DA-PBET	NaCl	PBET	DA-PBET
1				0.226	0.687	1.41	0.473	1.18	2.19		2.51	4.86	3.22	1.56	3.76	9.08
2				0.346	0.683	0.953										
3	<0.600	<0.039	<0.004								0.430	5.25	8.67			
4	4.90	0.038	0.094	16.9	64.7	53.6					0.488	26.4	14.6	2.49	4.91	1.25
5	0.274	1.33	1.61											0.660	0.746	1.8
6	<0.880	<0.058	<0.006				0.431	0.980	5.34		41	56	106			
7	0.095	0.349	2.14	<0.096	<0.014	<0.009	<0.001	<0.001	<0.001		<0.004	<0.010	<0.002	0.964	1.07	2.26
8				0.183	0.680	0.300										
9				<0.001	<0.001	<0.001	<0.004	<0.004	<0.004	0.048						

367

368 For a given element, values of BA vary considerably amongst the microplastics and  
 369 extractants. For Br, BA ranges from < 1% for samples 3 and 6 in all extractants to  
 370 about 5% for sample 4 exposed to NaCl. For Cd, BA is < 1 % in most cases with the  
 371 exception of sample 4 where values exceed 50% in the PBET and DA-PBET; in all  
 372 samples where the metal was detected in the extractants, BA was greater in the PBET



373 or DA-PBET than in the near-neutral NaCl solution. For Cr, BA ranges from <  
374 0.005% in samples 7 and 9 to > 2% for samples 1 and 6 exposed to the DA-PBET.  
375 Values of BA for Pb range from < 0.01% in sample 7 to about 100% in sample 6  
376 exposed to the DA-PBET, and in all cases BA was greater in the PBET or DA-PBET  
377 than in NaCl solution. Regarding Sb, BA ranges from 0.66% in sample 5 exposed to  
378 NaCl to over 9% for sample 1 exposed to the DA-PBET, and in all microplastics the  
379 maximum value of BA results from exposure to the PBET or DA-PBET.

380

#### 381 *3.4. Mechanisms of element mobilisation*

382 Hazardous elements may be incorporated into the plastic as ions, complexes or  
383 compounds, or bound irreversibly to the polymeric backbone (Town et al., 2018). In  
384 addition, at least for the beached plastics, there may be a small amount of element  
385 adsorbed to the surface from the marine environment (Holmes et al., 2012).  
386 Neglecting desorption of environmentally acquired elements, the fundamental  
387 mechanism of element mobilisation from the microplastics in the present study is  
388 diffusion from the plastic matrix into a saline (NaCl) aqueous medium. Free ions and  
389 small complexes may diffuse through the particle matrix whereas larger complexes or  
390 those bound irreversibly are immobile, with the permeability (or crystallinity) of the  
391 polymer determining the size limit of diffusible complexes. Presumably, therefore, the  
392 rapid, instantaneous mobilisation that we observe arises from the release of elements  
393 that are located at (but incorporated into) the particle surface and not required to  
394 diffuse through the plastic matrix.

395

396 The rate of mobilisation of elements from the microplastics may be facilitated by  
397 altering the composition of the aqueous medium, or, more specifically, making

398 conditions more favourable for the formation of free ions or small complexes and  
399 molecules. To this end, the use of an acidic digestive medium is predicted to increase  
400 the concentration of metal ions relative to a near-neutral solution. Mobilisation may  
401 also be facilitated if a medium is introduced that interacts with the plastic matrix by,  
402 for example, exposing a greater surface area to the aqueous phase through polymer  
403 chain loosening (Sun et al., 2019). Accordingly, it is possible that the hydrophobic  
404 fish oil is able to partially modify the integrity of plastic structure or even act as a  
405 solvent for the extraction of relatively hydrophobic organic compounds of bromine  
406 (Tanaka et al., 2015).

407

408 The observations in the present study are partly consistent with the assertions above in  
409 that mobilisation and bioaccessibility of the metals (Cd, Cr and Pb) are enhanced  
410 under the acidic conditions of the PBET and DA-PBET relative to unacidified NaCl  
411 solution, with the presence of fish oil usually enhancing but sometimes inhibiting  
412 metal release. Acidified conditions also promote the mobilisation of Br and Sb in  
413 most cases, but NaCl releases greater quantities of both elements than the PBET  
414 and/or the DA-PBET from sample 4. The polymeric composition of this sample  
415 (acrylonitrile butadiene styrene-polycarbonate) suggests a rather amorphous structure  
416 of relatively low permeability and high thermal stability, at least compared with  
417 expanded polyurethane, polyvinyl chloride and the polyolefins (Keller, 2017).

418 Anomalous mobilisation results for sample 4 in the presence of fish oil (for Br and Sb  
419 as well as Cd and Pb) may, therefore, reflect the poor penetrability of the relatively  
420 large triglyceride molecules into the plastic and, possibly, a propensity to block the  
421 migration of other solutes into and out of the matrix.

422

423 *3.5. Implications for exposure to seabirds and setting safety guidelines*

424 Despite kinetic modelling of the mobilisation of potentially hazardous elements from  
425 microplastics under simulated digestive conditions being relatively straightforward,  
426 the extent of mobilisation exhibits a complex dependence on the type of plastic, the  
427 nature of the additive or reaction residues and the composition of the extractant  
428 solution. Mobilisation is, however, considerable in many cases, with a reduction in pH  
429 facilitating elemental release for metals and the presence of food oil having a more  
430 variable but usually positive effect on the dissolution of both inorganic and  
431 brominated compounds. For more meaningful upper estimates of chemical  
432 bioaccessibility in microplastics and their risks to fish-consuming seabirds, it is  
433 recommended that both a standard avian PBET and a DA-PBET be employed and that  
434 the higher result be adopted.

435

436 Currently, there exist no chemical standards for waste environmental plastics that are  
437 based on health grounds. The RoHS Directive limits have recently been employed as  
438 a screening criterion for compliance of primary and secondary beached plastics (Shaw  
439 and Turner, 2019) but the total content of a potentially hazardous chemical does not  
440 address its potential for migration or its bioaccessibility to an animal. Accordingly, we  
441 propose that the Toy Safety Directive limits on the migration of metals and metalloids  
442 (but not brominated compounds) are of most relevance when evaluating the potential  
443 health impacts of marine plastic ingestion to mammals. Here, limit values are based  
444 on the potential impacts arising from the ingestion of 8 mg of material per day and  
445 migration into 0.07 M HCl for 2 h at 37°C (BSI, 1994; European Commission, 2016).  
446 Current or proposed migration limits for material that can be “scraped off” toys,  
447 including plastics, by biting and sucking are 17  $\mu\text{g g}^{-1}$  for Cd, 0.2  $\mu\text{g g}^{-1}$  for Cr(VI),

448 94  $\mu\text{g g}^{-1}$  for Hg, 23  $\mu\text{g g}^{-1}$  for Pb and 560  $\mu\text{g g}^{-1}$  for Sb (European Parliament and  
449 Council of the EU, 2009). Based on these limits, and for an equivalent weekly (168 h)  
450 intake of 56 mg of microplastic by a seabird, five of the current samples that include  
451 beached plastics and both historical and contemporary consumer products would be  
452 non-compliant with respect to at least one element and at least one extractant; non-  
453 compliance occurs for Pb in four cases, Cd in two cases, and Cr in one case (sample  
454 1) if it is assumed that a Pb-Cr association is indicative of lead chromate and the  
455 higher oxidation state of the metal.

456

457 Clearly, the overall risk to a seabird is more complex as plastic ingestion varies  
458 greatly between and among species (Lavers and Bond, 2016; Roman et al., 2019) and  
459 the quantities of plastic ingested that contain hazardous elements will depend on  
460 availability in the water column, foraging ecology, and any selectivity based on, for  
461 example, colour (Kain et al., 2016; Tavares et al., 2017). Nevertheless, microplastics  
462 should not be overlooked as a source of harmful additives and residues to animals that  
463 digest material for extended periods of time under acidic and oily conditions.

464

#### 465 **4. Conclusions**

466 Significant quantities of hazardous elements (Br, Cd, Cr, Hg, Pb, Sb) associated with  
467 residues and historical additives in plastics can be mobilised under simulated gastric  
468 conditions representative of seabirds, and in particular where the diet is considered as  
469 part of the digestive chemistry. Although the kinetics of mobilisation can be modelled  
470 by simple diffusion equations, the magnitude of the constants associated with these  
471 models appear to exhibit a complex dependence on the nature of the additive and the  
472 type and condition of the plastic. It is suggested that limits of chemical migration (or

473 mobilisation) stipulated by the European Toy Safety Directive afford a means of  
474 evaluating the potential risks of microplastics to mammals in the marine environment.  
475 On this basis, five out of nine plastics tested in the present study returned non-  
476 compliant concentrations for at least one element and one digestive fluid simulant.

477

#### 478 **Acknowledgements**

479 Dr Robert Clough, Dr Andrew Fisher and Mr Andy Arnold (UoP) are thanked for  
480 technical assistance and advice throughout the study. This work was supported in part  
481 by a Higher Education Innovation Fund grant.

482

#### 483 **References**

484 Avery-Gomm, S., O'Hara, P.D., Kleine, L., Bowes, V., Wilson, L.K., Barry, K.L.,  
485 2012. Northern fulmars as biological monitors of trends of plastic pollution in the  
486 eastern North Pacific. *Marine Pollution Bulletin* 64, 1776-1781.

487

488 BSI, 1994. *Safety of Toys – part 3: Migration of Certain Elements*. British  
489 Standard BS EN 71-3, London.

490

491 Buchheister, A., Miller, T.J., and Houde, E. 2017. Evaluating Ecosystem-based  
492 reference points for Atlantic menhaden. *Marine and Coastal Fisheries Dynamics  
493 Management and Ecosystem Science* 9, 457-478.

494

495 Claessens, M., De Meester, S., Van Landuyt, L., De Clerk, K., Janssen, C.R., 2011.  
496 Occurrence and distribution of microplastics in marine sediments along the Belgian  
497 coast. *Marine Pollution Bulletin* 62, 2199-2204.

498

499 European Commission, 2016. Toy Safety Directive 2009/48/EC. An explanatory  
500 guidance document (Revision 1.9 CORR). Europese Commissie, Brussel.

501

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

505

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

509

510 European Parliament and Council of the EU, 2009. Directive 2009/48/EC of the  
511 European Parliament and of the Council of 18 June 2009 on the safety of toys.  
512 Official Journal of the European Union L170/1.

513

514 European Parliament and the Council of the European Union, 2009. Directive  
515 2009/48/EC on the safety of toys. Official Journal of the European Union L170, 1.

516

517 Hall, N.M., Berry, K.L.E., Rintoul, L., Hoogenboom, M.O., 2015. Microplastic  
518 ingestion by scleractinian corals. *Marine Biology* 162, 725-732.

519

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

523

524 Holmes, L., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic  
525 resin pellets in the marine environment. *Environmental Pollution* 160, 42-48.

526

527 James, E., Turner, A., 2020. Mobilisation of antimony from microplastics added to  
528 coastal sediment. *Chemosphere* (submitted).

529

530 Kain, E.C., Lavers, J.L., Berg, C.J., Raine, A.F., Bond, A.L., 2016. Plastic ingestion  
531 by Newell's (*Puffinus newelli*) and wedge-tailed shearwaters (*Ardenna pacifica*) in  
532 Hawaii. *Environmental Science and Pollution Research* 23, 23951-23958.

533

534 Kwon, J.H., Chang, S., Hong, S.H., Shim, W.J., 2017. Microplastics as a vector of  
535 hydrophobic contaminants: Importance of hydrophobic additives. *Integrated*  
536 *Environmental Assessment and Management* 13, 494-499.

537

538 Lavers, J.L., Bond, A.L., 2016. Ingested plastic as a route for trace metals in Laysan  
539 Albatross (*Phoebastria immutabilis*) and Bonin Petrel (*Pterodroma hypoleuca*) from  
540 Midway Atoll. *Marine Pollution Bulletin* 110, 493-500.

541

542 Lin, V.S., 2016. Research highlights: impacts of microplastics on plankton.  
543 *Environmental Science – Processes and Impacts* 18, 160-163.

544

545 Luo, H.W., Xiang, Y.H., He, D.Q., Li, Y., Zhao, Y.Y., Wang, S., Pan, X.L., 2019.  
546 Leaching behavior of fluorescent additives from microplastics and the toxicity of  
547 leachate to *Chlorella vulgaris*. *Science of the Total Environment* 678, 1-9.

548

549 Martin, K., Turner, A., 2019. Mobilization and bioaccessibility of cadmium in coastal  
550 sediment contaminated by microplastics. *Marine Pollution Bulletin* 146, 940-944.

551

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

554

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

558

559 Ng, K.L., Obbard, J.P., 2006. Prevalence of microplastics in Singapore's coastal  
560 marine environment. *Marine Pollution Bulletin* 52, 761-767.

561

562 OSPAR, 2008. Background document for the EcoQO on plastic particles in stomachs  
563 of seabirds. London, 355/2007.

564

565 Pritchard, G., 1997. *Plastic Additives: An A-Z Reference*. Chapman and Hall,  
566 London, 633pp.

567

568 Roman, L., Bell, E., Wilcox, C., Hardesty, B.D., Hindell, M., 2019. Ecological drivers  
569 of marine debris ingestion in procellariiform seabirds. *Scientific Reports* 9, article no.  
570 916. DOI: 10.1038/s41598-018-37324-w

571



572 Ruby, M.V., Davis, A., Kempton, J.H., Drexler, J.W., Bergstrom, P.D., 1992. Lead  
573 bioavailability: dissolution kinetics under simulated gastric conditions. *Environmental*  
574 *Science and Technology* 26, 1242-1248.  
575

576 Shaw, E.J., Turner, A., 2019. Recycled electronic plastic and marine litter. *Science of*  
577 *the Total Environment* 694, 133644.  
578

579 Sun, B., Hu, Y., Cheng, H., Tao, S., 2019. Releases of brominated flame retardants  
580 (BFRs) from microplastics in aqueous medium: Kinetics and molecular-size  
581 dependence of diffusion. *Water Research* 151, 215-225.  
582

583 Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M.A., Watanuki,  
584 Y., 2015. Facilitated leaching of additive-derived PBDEs from plastic by  
585 seabirds' stomach oil and accumulation in tissues. *Environmental Science and*  
586 *Technology* 49, 11799-11807.  
587

588 Tavares, D.C., de Moura, J.F., Merico, A., Siciliano, S., 2017. Incidence of marine  
589 debris in seabirds feeding at different water depths. *Marine Pollution Bulletin* 119, 68-  
590 73.  
591

592 Town, R.M., van Leeuwen, H.P., Blust, R., 2018. Biochemodynamic features of metal  
593 ions bound by micro- and nano-plastics in aquatic media. *Frontiers in Chemistry*  
594 <https://doi.org/10.3389/fchem.2018.00627>  
595

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

598

599 Turner, A., 2018b. Mobilisation kinetics of hazardous elements in marine plastics  
600 subject to an avian physiologically-based extraction test. *Environmental Pollution*  
601 236, 1020-1026.

602

603 Turner, 2018c. Concentrations and migratabilities of hazardous elements in second-  
604 hand children's plastic toys. *Environmental Science and Technology* 52, 3110-3116.

605

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

608

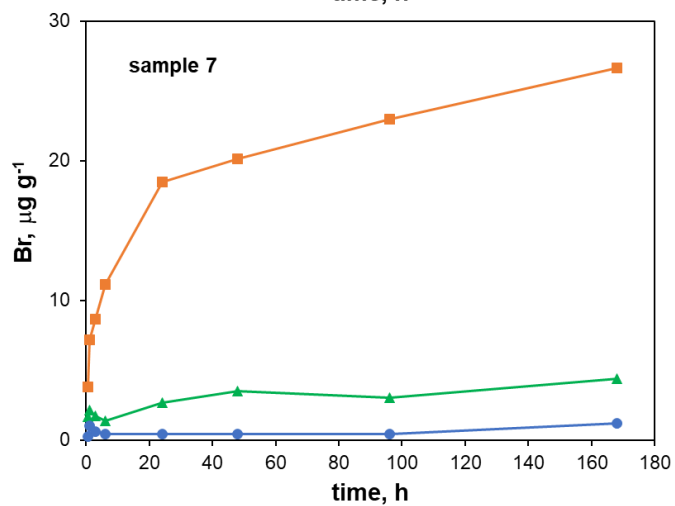
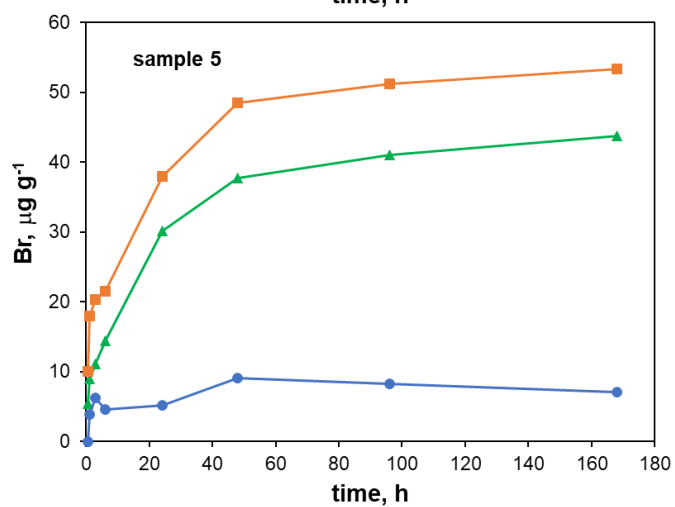
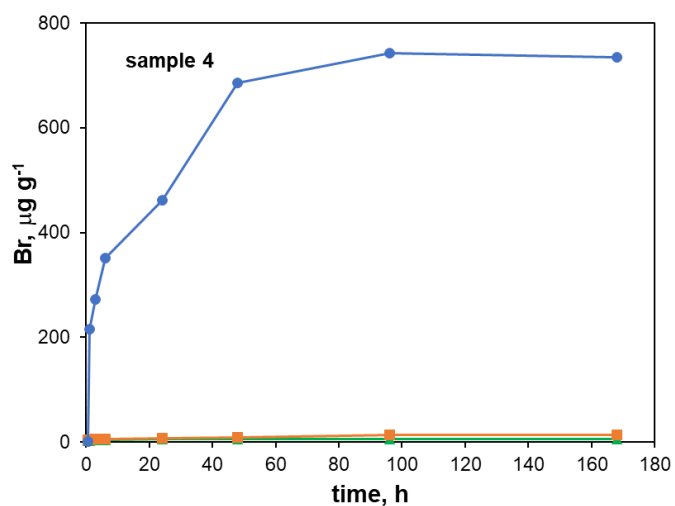
609

610 Figure 1: Mobilisation of Br from micronised plastic samples as a function of time in

611 NaCl solution (blue circles), the PBET (green triangles) and DA-PBET (orange

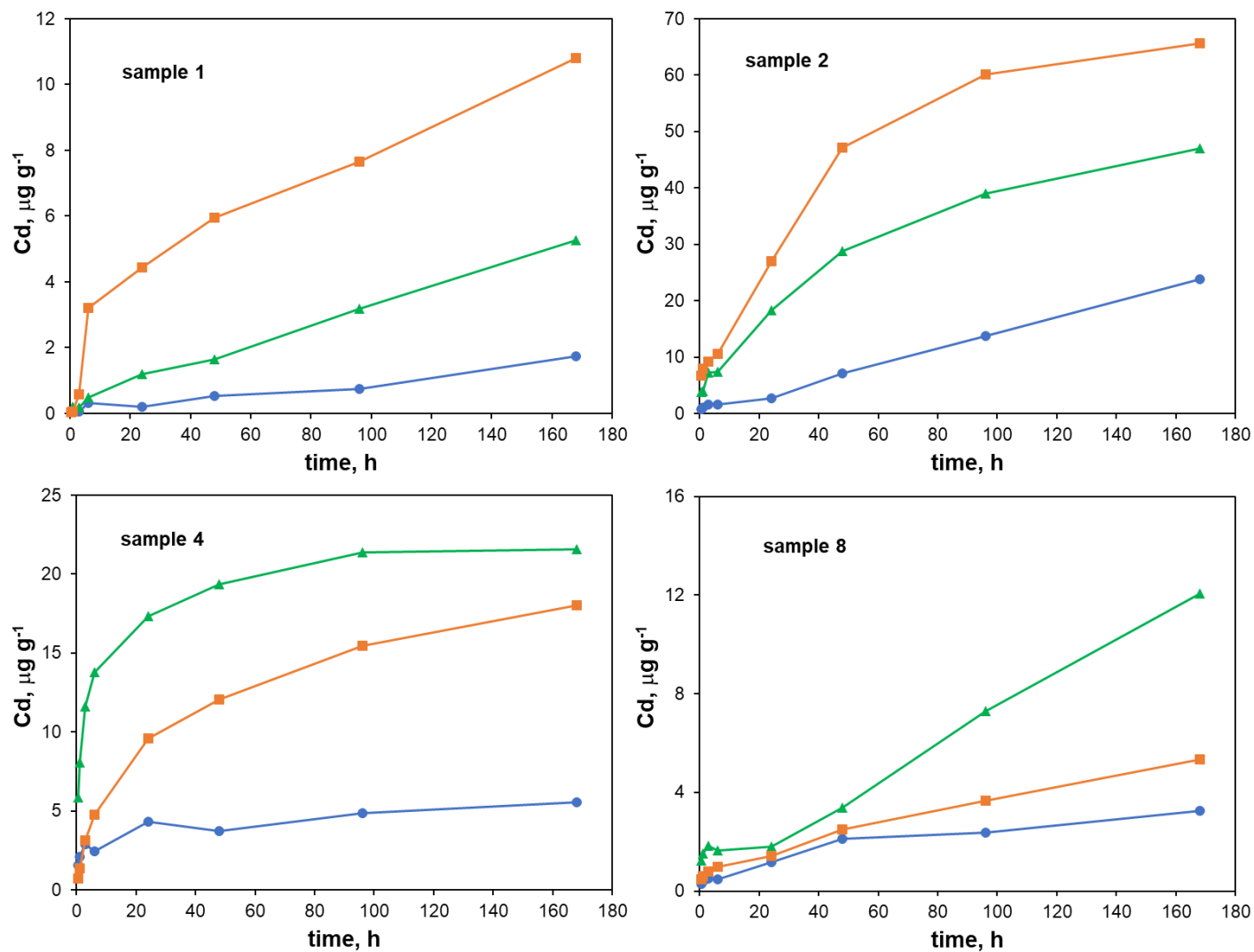
612 squares).

613



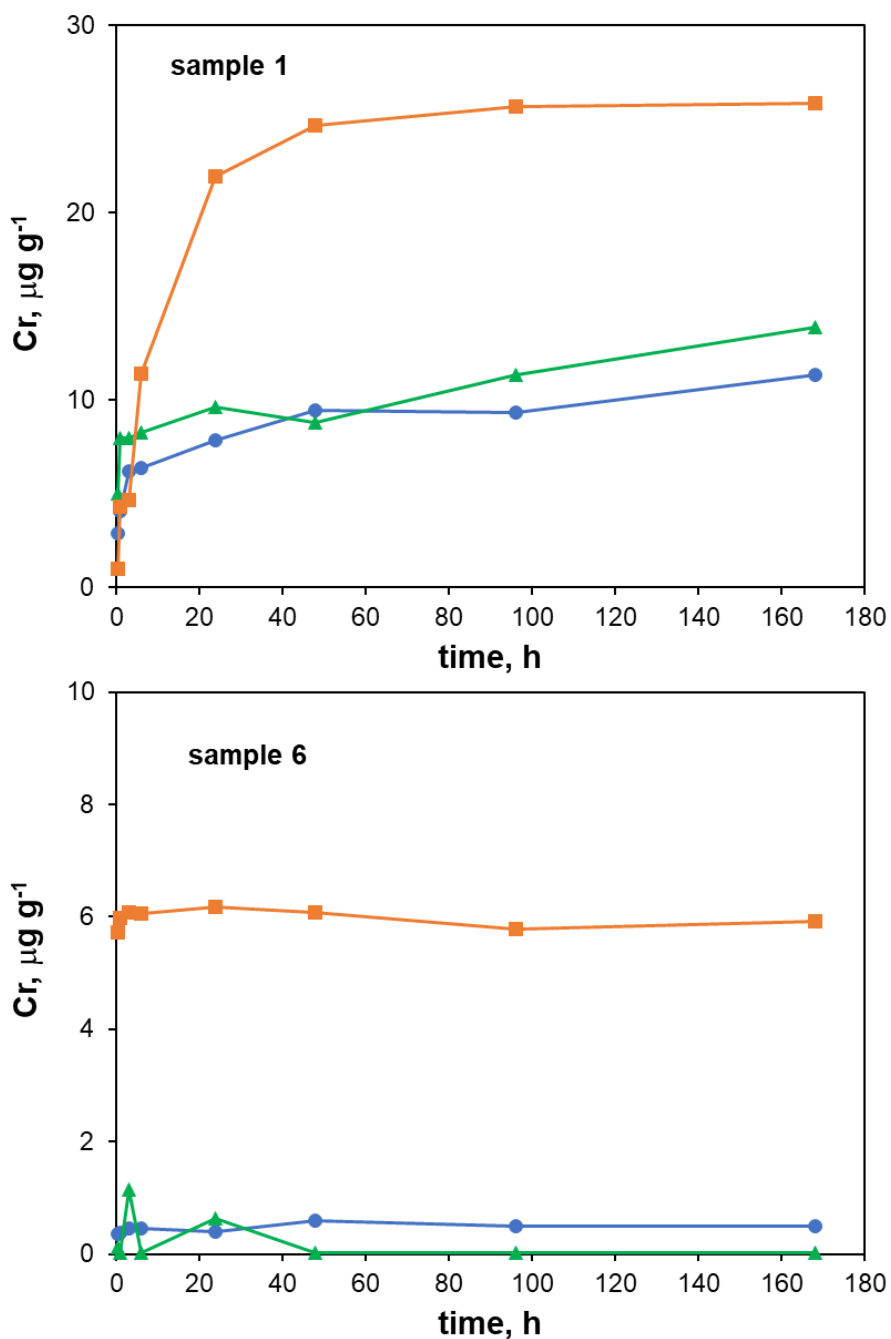
614

615 Figure 2: Mobilisation of Cd from micronised plastic samples as a function of time in NaCl solution (blue circles), the PBET (green triangles)  
616 and DA-PBET (orange squares).  
617

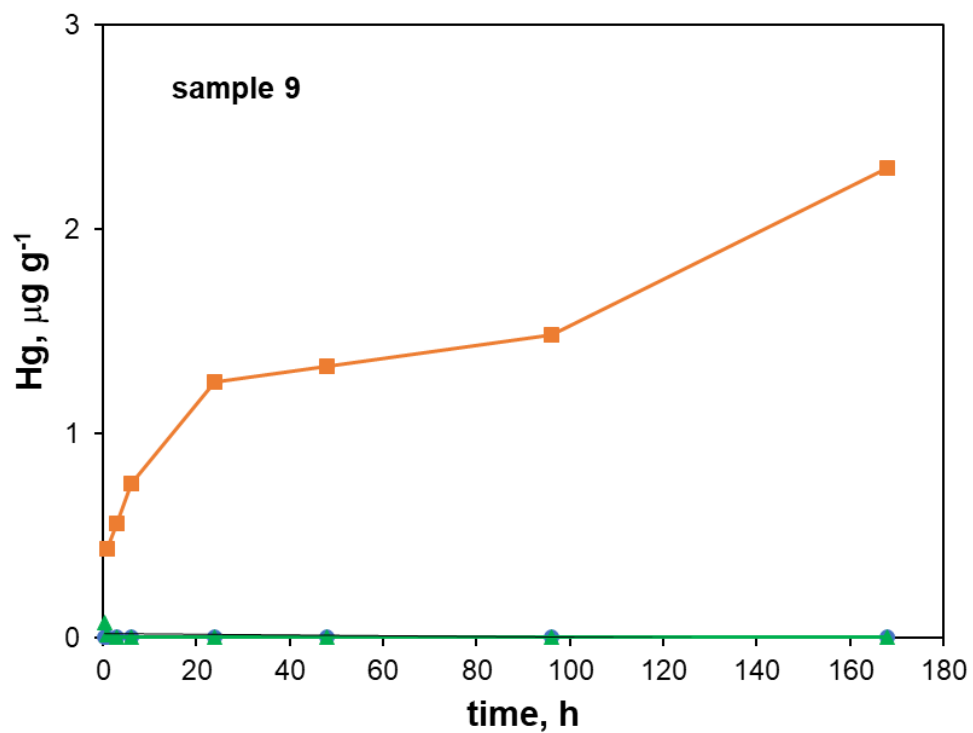


618 Figure 3: Mobilisation of Cr from micronised plastic samples as a function of time in  
619 NaCl solution (blue circles), the PBET (green triangles) and DA-PBET (orange  
620 squares).

621  
622

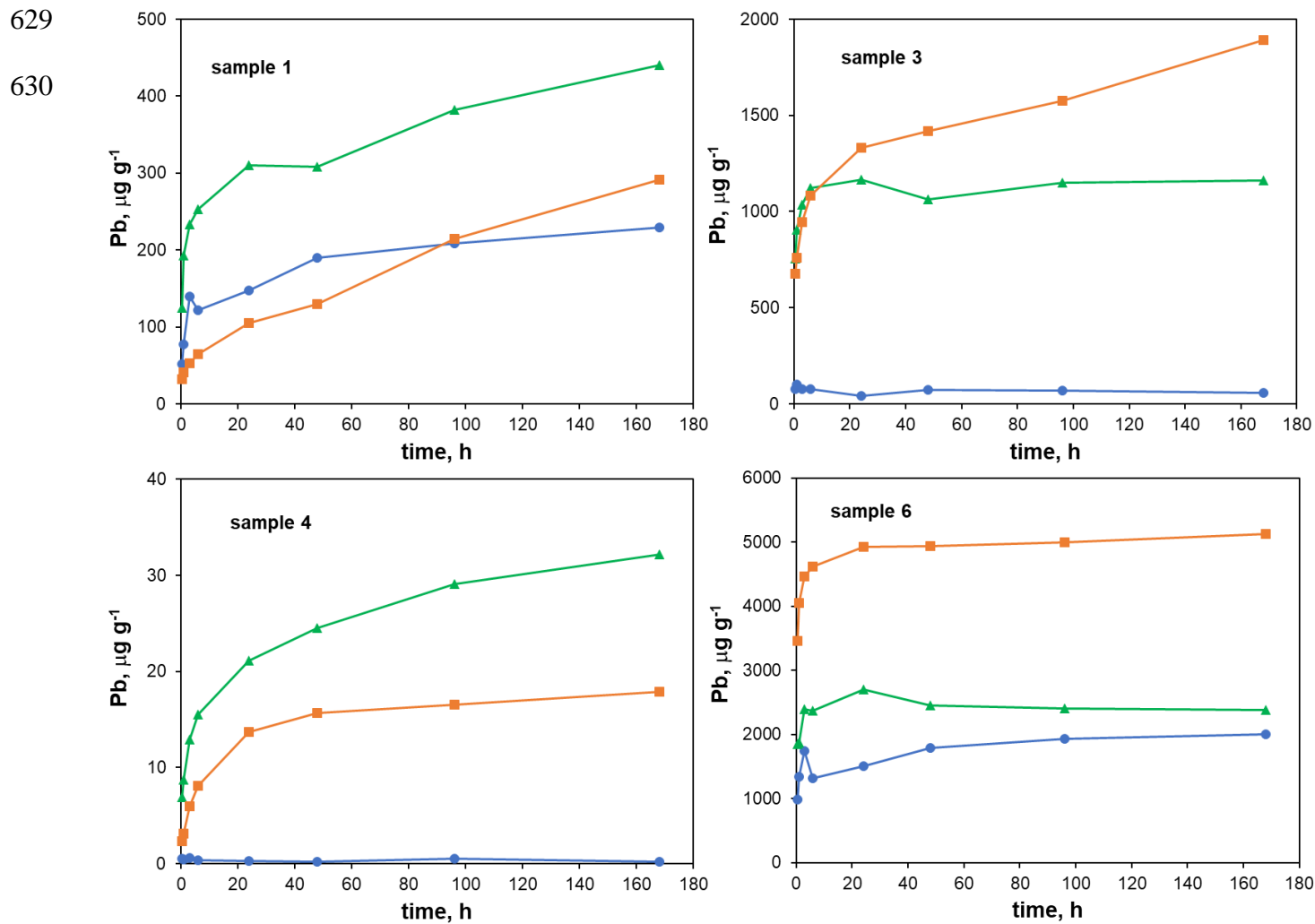


623 Figure 4: Mobilisation of Hg from a micronised plastic sample as a function of time in  
624 NaCl solution (blue circles), the PBET (green triangles) and DA-PBET (orange  
625 squares).



626

627 Figure 5: Mobilisation of Pb from micronised plastic samples as a function of time in NaCl solution (blue circles), the PBET (green triangles)  
628 and DA-PBET (orange squares).



631 Figure 6: Mobilisation of Sb from micronised plastic samples as a function of time in NaCl solution (blue circles), the PBET (green triangles)  
632 and DA-PBET (orange squares).

