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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
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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

147 2.2 Extraction reagents

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

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⁻¹,
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% HNO₃ (prepared from Fisher
180 Scientific TraceMetal grade concentrated HNO₃) 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% HNO₃ 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⁻¹,
195 0.8 L Ar min⁻¹, 1.05 L Ar min⁻¹ and 5 ml He min⁻¹, 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⁻¹) 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⁻¹ for Cd, Cr and Pb in the DA-PBET to 0.44 µg g⁻¹ 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

$$212 \quad \ln(C_e - C) = \ln C_e - k_1 t + \ln C_0 \quad (1a)$$

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 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

$$225 \quad C_0 = C_e (1 - e^a) \quad (1b)$$

226

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

228

$$229 \quad C = k_2 t^{1/2} + C_0 \quad (2)$$

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, Cd₂SeS (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, 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; Cr_2O_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).

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342 Rate constants arising from model 1 range from 0.0094 h^{-1} for Cr in sample 1 exposed
343 to the PBET to 0.472 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 | | 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

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482

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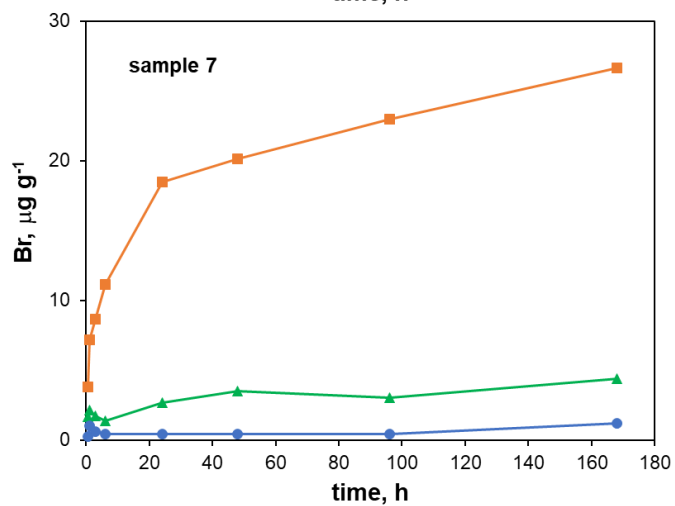
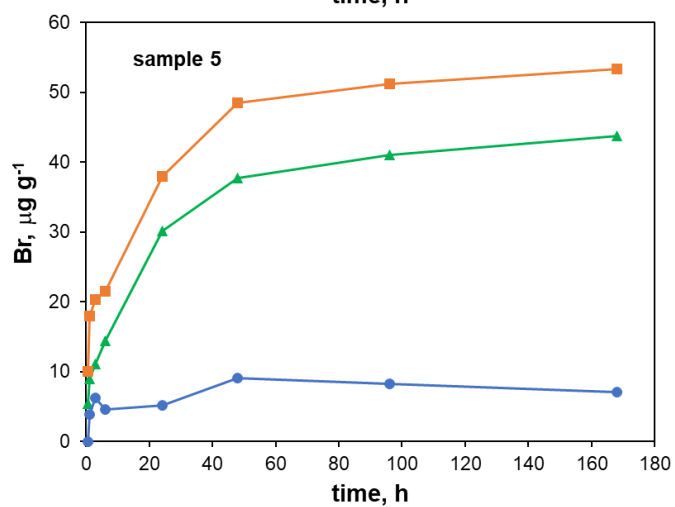
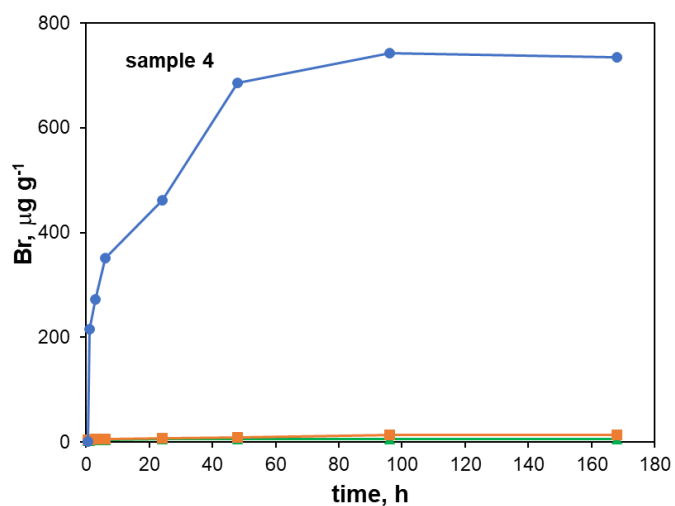
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610 Figure 1: Mobilisation of Br from micronised plastic samples as a function of time in

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

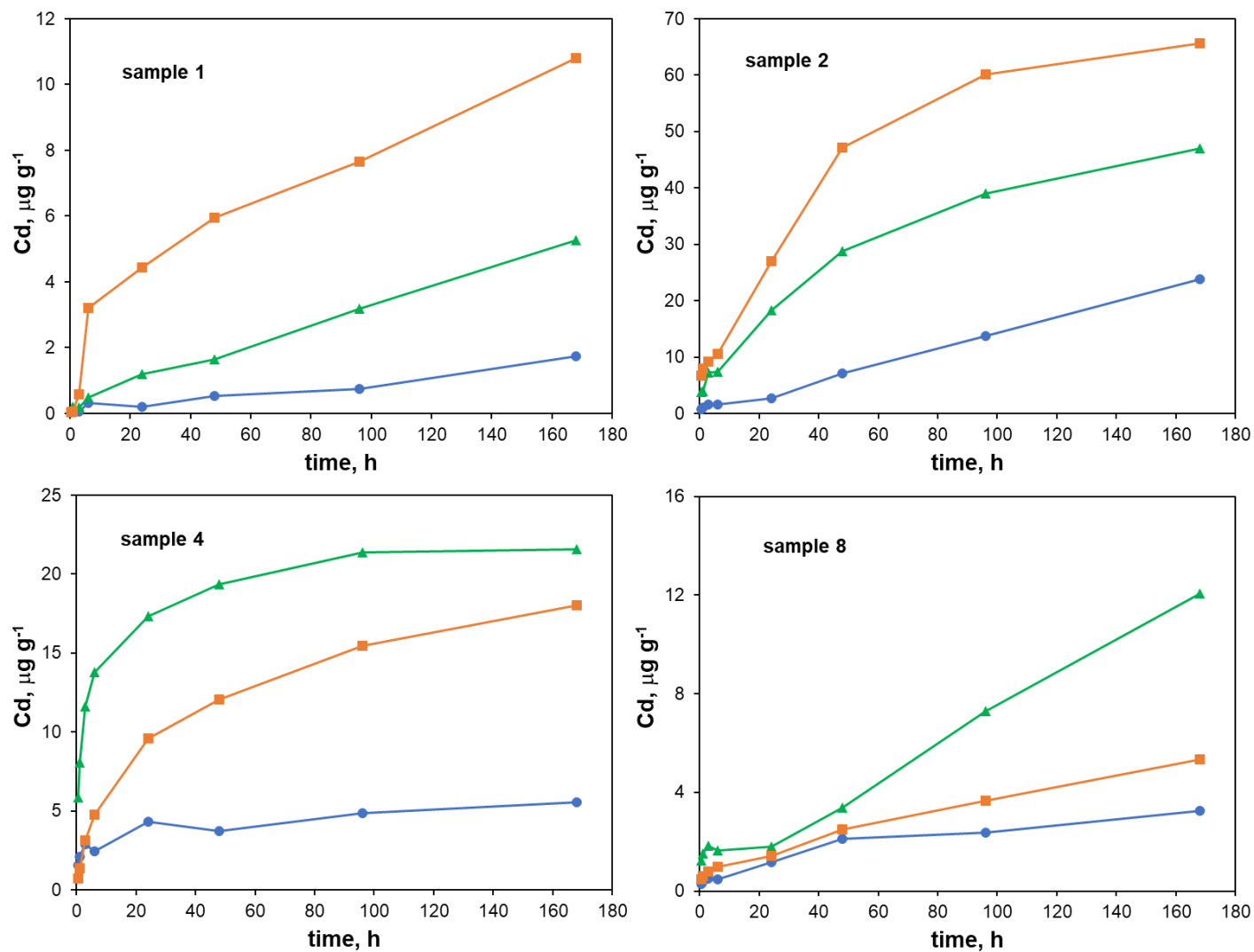
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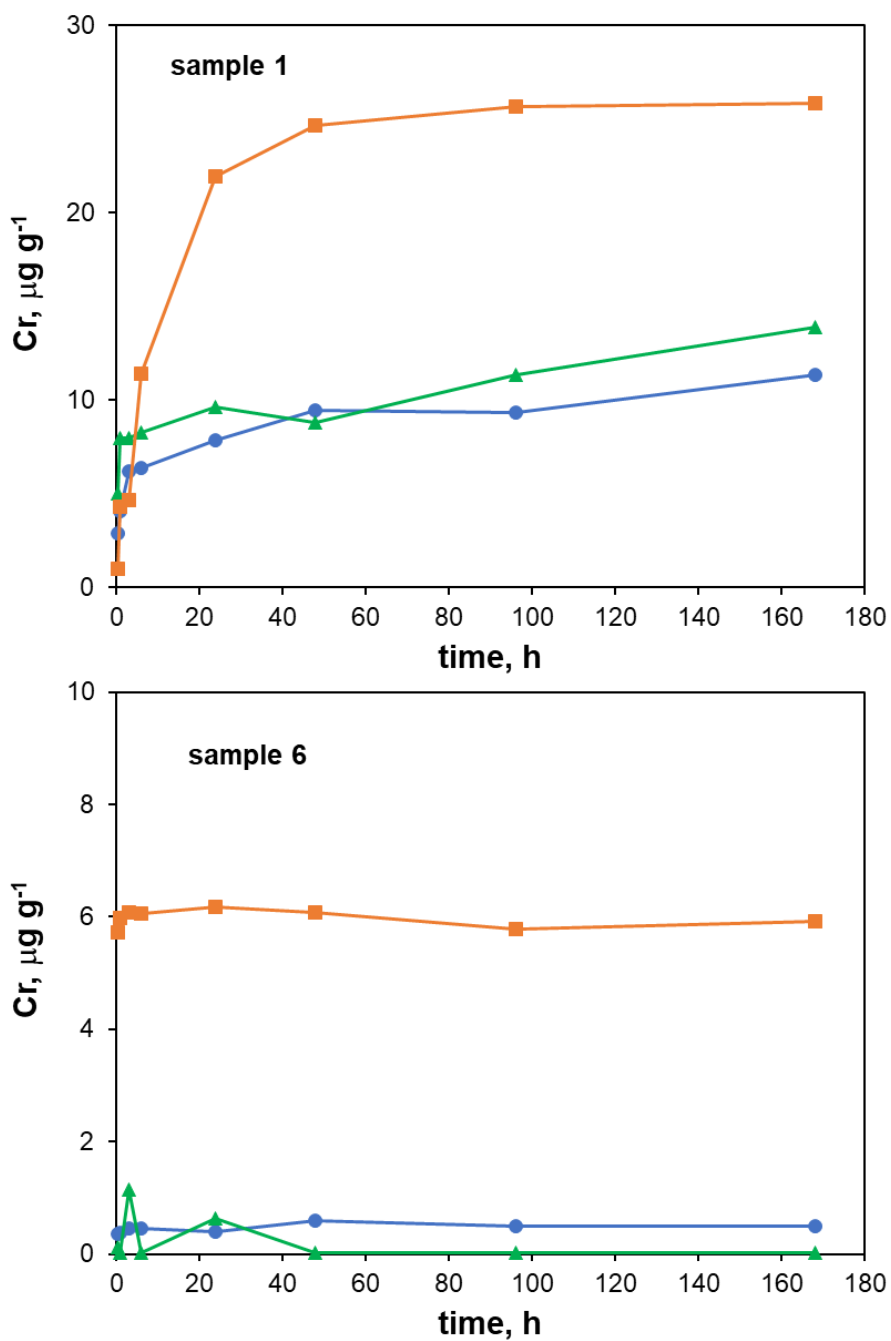
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615 Figure 2: Mobilisation of Cd from micronised plastic samples as a function of time in NaCl solution (blue circles), the PBET (green triangles)
616 and DA-PBET (orange squares).
617

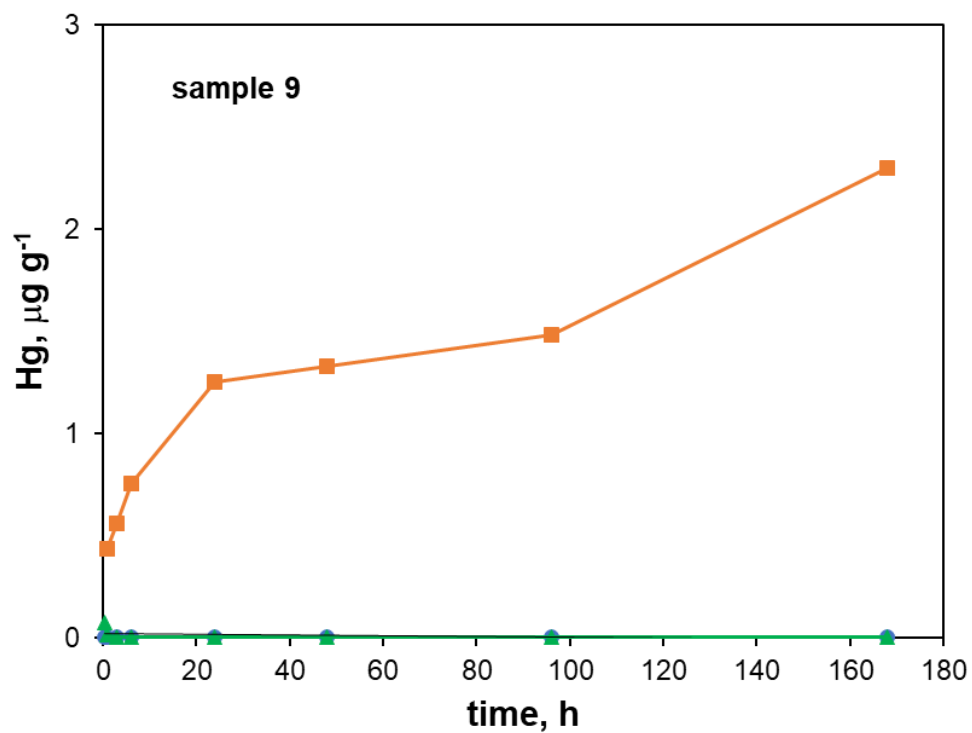


618 Figure 3: Mobilisation of Cr from micronised plastic samples as a function of time in
619 NaCl solution (blue circles), the PBET (green triangles) and DA-PBET (orange
620 squares).

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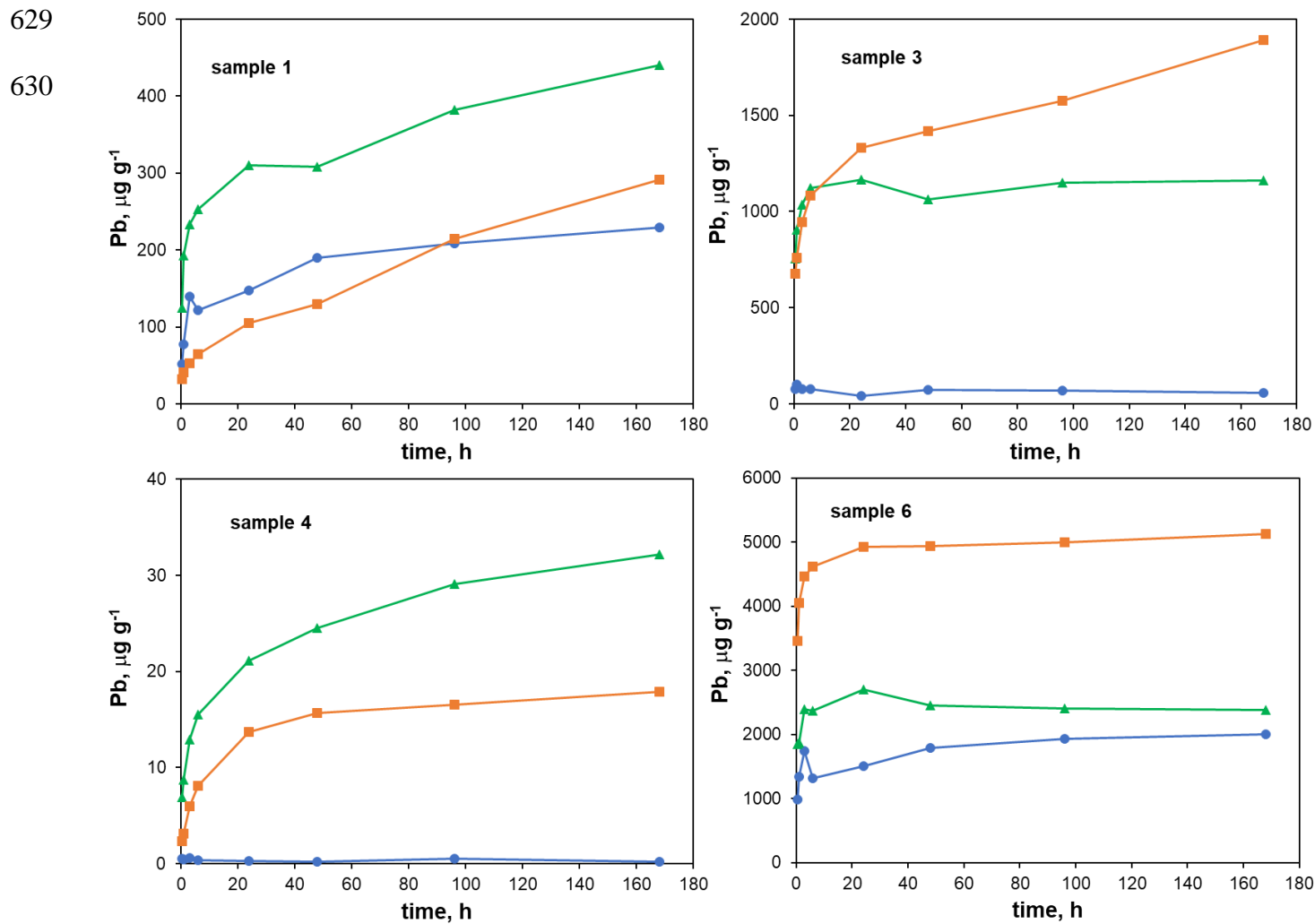


623 Figure 4: Mobilisation of Hg from a micronised plastic sample as a function of time in
624 NaCl solution (blue circles), the PBET (green triangles) and DA-PBET (orange
625 squares).



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).

