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**Elemental concentrations and bioaccessibilities in
beached plastic foam litter, with particular reference
to lead in polyurethane**

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24 **Abstract**

25 Seventy samples of foamed plastic collected from a high-energy, sandy beach in SW
26 England have been characterised by FTIR and XRF. Most samples were polyurethane
27 (PU; $n = 39$) or polystyrene (PS; $n = 27$) that were associated with variable
28 concentrations of Br-Cl, Fe and Zn, indicative of the presence of halogenated flame
29 retardants, iron oxides and Zn-based additives, respectively. Many samples of rigid
30 PU contained Pb, historically used as a catalyst, at concentrations of up to 16,000 μg
31 g^{-1} . A physiological extraction test that simulates the conditions in the gizzard of
32 plastic-ingesting seabirds was applied to selected samples and results revealed that
33 while Br and Zn were not measurably bioaccessible, Pb mobilisation progressed
34 logarithmically over a period of time with maximum accessibilities after 220 h of ~
35 10% of total metal. Foamed PU is a source of bioaccessible Pb in the marine
36 environment that has not previously been documented.

37

38 **Keywords:** plastics; polyurethane; foams; seabirds; lead; flame retardants

39 **1. Introduction**

40 Because of their wide usage in society, coupled with a high durability, poor
41 degradation and low density, plastics are widely distributed throughout the global
42 ocean and littoral zone (Li et al., 2016). The impacts of plastic waste in the marine
43 environment are many and varied and include a reduction in aesthetic and amenity
44 value, damage to vessels and fishing gear, a threat to public safety and adverse effects
45 on wildlife (Gregory, 2009). Regarding the latter, plastics can cause alterations to
46 benthic community structure, entanglement, strangulation and suffocation, and
47 starvation and choking via ingestion when material is mistaken for food (Baulch and
48 Perry, 2014; Sigler, 2014; Wilcox et al., 2016). Through the association of chemicals
49 with the polymeric matrix or the adsorption of aqueous species to the polymer
50 surface, ingestion can also act as a vehicle for the transfer of contaminants into the
51 foodchain (Ashton et al., 2010; Rochman et al., 2013; Tanaka et al., 2013).

52

53 Beached plastic items categorised by OSPAR include multi-pack yokes, bags, bottles,
54 engine oil containers, injection gun containers, cigarette lighters, toys, crates, food
55 packaging, lobster pots, rope, cord, netting and foams (OSPAR Commission, 2010).

56 With respect to foams, different size categories of expanded or extruded polystyrene
57 (PS) pieces are specified but polyurethane (PU) is not mentioned. This is perhaps
58 surprising because beach surveys that we have recently conducted have revealed an
59 abundance of foamed PU that, in some cases, represents the dominant form of plastic
60 litter on a number basis (Turner, 2016; Turner and Solman, 2016). The widespread
61 occurrence of PU waste may be attributed to its extensive application in the domestic,
62 industrial, transportation and maritime settings, with an annual demand among
63 synthetic polymers that is exceeded only by polyethylene, polypropylene and

64 polyvinyl chloride (Plastics Europe, 2015). PU foam may be classified as flexible or
65 rigid, with the former being open-cell, porous and having a density typically between
66 10 and 80 kg m⁻³, and the latter being closed-cell, semi-porous to non-porous and
67 having a density ranging from 30 to 400 kg m⁻³. Flexible PU foam is used for
68 packaging and as cushioning in furniture and bedding, under carpets and in
69 automobile and aircraft seating, while rigid PU foam is used principally as an
70 insulator in buildings, refrigerators, pipelines, vehicles and storage facilities.
71 Additional, maritime applications of rigid foam involve flotation, buoyancy, support
72 and void filling in boats, pontoons, docks, baffles and barrels (Szycher, 1999).
73
74 PU is formed by reacting a diisocyanate or polyisocyanate with an oligomeric polyol
75 (polyester or polyether) to produce a urethane linkage, with the precise properties of
76 the product dependent on the nature (e.g. molecular weight) of the reactants and the
77 preparation process. For the formation of PU foam, a blowing reaction is also required
78 in which a gas is either added or created. Additives used in the production of PU
79 include tertiary amine or metal salt catalysts for the polymerisation and blowing
80 reactions, fillers, pigments for colour, halogenated flame retardants, smoke
81 suppressants and plasticisers. Based on these characteristics and the carcinogenic and
82 mutagenic properties of its component monomers, Lithner et al. (2011) ranked
83 polyurethanes among the most hazardous polymers in current production.
84 Accordingly, PU waste is a potential source of a variety of highly toxic contaminants
85 to the environment whose concentrations, mobilities and fates are largely unknown.
86
87 In the present study, foamed plastic waste has been collected from a section of a high-
88 energy, macrotidal sandy beach in south west England and classified by polymer type

89 using Fourier transform infra-red (FTIR) spectrometry. The elemental composition of
90 the foams is ascertained by field portable-x-ray fluorescence (FP-XRF) spectrometry
91 configured in a 'plastics' mode for the analysis of low density samples, and the
92 bioaccessibilities of the predominant elements in selected foams (and mainly PU) is
93 determined by means of a physiological solution that simulates the digestive fluids
94 encountered in the gizzard of a plastic-ingesting marine bird.

95

96 **2. Materials and methods**

97 *2.1. Sampling and sample location*

98 Whitsand Bay is a protected coastal region a few km to the west of Plymouth Sound
99 that is characterised by an expansive, sandy beach. The beach faces south west and
100 directly towards the western English Channel and is backed by high cliffs that, at high
101 tide, fragment the region into a series of rocky coves. During October 2015, pieces of
102 foamed plastic that were visible to the naked eye were collected by hand from a ~30
103 m-wide transect of the beach at Tregantle (50.3525, -4.2719) between the high water
104 line and the backshore. Samples were stored in a series of clear polyethylene bags and
105 transported to the laboratory where individual items were cleared of sand and other
106 debris under running tap water and with the aid of a Nylon brush before being dried
107 under vacuum desiccation at room temperature for 48 to 96 h. Samples were then
108 weighed on a five-figure balance and measured for thickness through the flattest
109 surface using 300 mm Allendale digital callipers before being stored individually in
110 labelled polyethylene specimen bags and in the dark pending analysis.

111

112 *2.2. FTIR analysis*

113 In order to identify the polymeric composition of the foams, samples were analysed
114 by FTIR spectroscopy. Initially, samples were analysed by attenuated total reflection-
115 (ATR-) FTIR using a Bruker ALPHA Platinum ATR QuickSnap A220/D-01
116 spectrometer. Samples were cut to a suitable size using a stainless steel scalpel before
117 being firmly clamped down on to the ATR diamond crystal in order to ensure good
118 contact and sufficient penetration of the evanescent wave. Measurements, consisting
119 of 16 scans in the range 4000 to 400 cm^{-1} and at a resolution of 4 cm^{-1} , were activated
120 via Bruker OPUS spectroscopic software, and polymer identification involved a
121 comparison of sample transmittance spectra with libraries of reference spectra. Where
122 identification was not definitive, sample offcuts were re-analysed by photoacoustic
123 FTIR using a Bruker Vertex 70 spectrometer coupled with an MTEC 300
124 photoacoustic cell that was purged with He. Measurements were recorded as an
125 average of 32 scans in the range 4000 to 400 cm^{-1} and at a resolution of 8 cm^{-1} with
126 activation and identification undertaken as above.

127

128 *2.3. XRF analysis*

129 Sample surfaces were analysed for a suite of elements, of which Br, Cl, Fe, Pb and Zn
130 are the focus of the present study, by energy dispersive field portable-XRF using a
131 battery-powered Niton XRF analyser (model XL3t 950 He GOLDD+). The
132 instrument was operated in a plastics mode that employs a compensation for mass
133 absorption coefficient based on Compton scatter and corrects for sample thickness
134 down to 0.05 mm. The XRF was used in the laboratory in a bench-top accessory stand
135 and was connected to a laptop computer via USB and a remote trigger. Samples were
136 placed on 3.6 μm polyester film and positioned centrally and with the measurement
137 surface face downwards over the XRF detector window. On closing the steel shield of

138 the stand, measurements, with appropriate thickness correction, were activated
139 through the laptop for a total period of 120 seconds (60 seconds each at 50 kV/40 μ A
140 and 20 kV/100 μ A). Spectra were quantified by fundamental parameters to yield
141 elemental concentrations on a dry weight basis (in μ g g^{-1}) with a counting error of 2σ
142 (95% confidence). At the end of each measurement session data were downloaded to
143 the laptop using Niton data transfer (NDT) PC software.

144

145 Limits of detection, as $1.5 \times 2\sigma$, varied according to the precise density, shape and
146 thickness of sample, but mean values were about 20 μ g g^{-1} for Br and Pb, 40 μ g g^{-1}
147 for Zn and 300 μ g g^{-1} for Cl and Fe. Multiple analyses ($n = 5$) of two Niton reference
148 plastics (PN 180-554, batch SN PE-071-N, and PN 180-619, LOT#T-18) that had
149 been impregnated with Br and Pb revealed measured concentrations that were within
150 10% of reference concentrations.

151

152 2.4. PBET

153 In order to evaluate the bioaccessibility of Pb and other elements (with the exception
154 of Cl), selected foams ($n = 8$) of varying appearance and polymeric and elemental
155 composition (based on XRF and FTIR analyses) were subjected to an avian
156 physiologically-based extraction test (PBET). The extraction was modelled on the
157 digestive characteristics of the northern fulmar, *Fulmarus glacialis*, a procellariiform
158 seabird known to ingest substantial quantities of plastic debris. Because dissected
159 specimens have revealed ingested plastic within the proventriculus-gizzard but not
160 within the duodenum (Furness, 1985; Robards et al., 1995), the PBET described
161 below replicates conditions encountered in the former components of the digestive
162 tract.

163

164 Briefly, the extraction fluid was prepared by dissolving 10 g of pepsin (lyophilised
165 powder from porcine gastric mucosa; Sigma-Aldrich) in one litre of 0.1 M NaCl
166 solution and adjusting the pH by dropwise addition of 1 M HCl to 2.5. Shavings of
167 about 0.1 g of each foam sample were weighed into individual 60 ml screw-capped
168 polypropylene centrifuge tubes before 40 ml of extraction fluid was added. All tubes,
169 including a control containing no solid, were then capped and incubated in a shaking
170 water bath set at 100 rpm and at 40 °C, or the average body temperature of marine
171 birds (Warham, 1996), for a period of about 220 h. Although this is longer than
172 typical proventriculus-gizzard retention times for food in piscivorous birds, ingested
173 plastic may remain trapped in this part of the digestive tract for periods of weeks or
174 months (Avery-Gomm et al., 2012). At pre-determined time-intervals, 1 ml aliquots of
175 extract, including triplicate aliquots at selected intervals, were pipetted in to individual
176 Sterilin tubes where they were diluted to 5 ml with 2% HNO₃ and stored at 4 °C and
177 in the dark pending analysis.

178

179 *2.5. Analysis of extracts*

180 Extracts were analysed for ⁷⁹Br, ⁵⁶Fe, ²⁰⁸Pb and ⁶⁶Zn by collision cell-inductively
181 coupled plasma-mass spectrometry (ICP-MS) using a Thermo X-series II
182 (ThermoElemental, Winsford UK) with a concentric glass nebuliser and conical spray
183 chamber. The instrument was calibrated externally using five mixed standards and
184 five blanks prepared in 2% HNO₃ and operated under conditions described elsewhere
185 (Turner and Holmes, 2015). Limits of detection, based on three standard deviations
186 arising from blank measurements, ranged from about 0.03 µg L⁻¹ for Pb to about 10
187 µg L⁻¹ for Br and Fe.

188

189 **3. Results**

190 *3.1. Sample characteristics*

191 Overall, 70 samples were retrieved from Whitsand Bay, with a selection illustrated in
192 Figure 1. Sample mass ranged from a few mg to > 10 g and thickness through the
193 flattest (measurement) surface ranged from about 2 to 40 mm. FTIR spectra revealed
194 that the majority of samples were polystyrene (PS; $n = 27$) or polyurethane (PU; $n =$
195 39), with the presence of ester-based plasticisers and inorganic fillers evident in many
196 of the latter type that were rigid.

197

198 Samples of expanded PS were always white and were usually smooth and well-
199 rounded through erosion and weathering, with brown, oxidic deposits visible on the
200 surface in many cases. The fewer number of extruded PS samples appeared to be
201 more fragmented and exhibited a broader colour range of browns, yellows and blues.
202 Most PU samples were rigid (or semi-rigid), brittle and well-rounded, displaying a
203 variety of shades of brown and yellow but with discolourations on the surface of
204 deeper shades of brown or black often evident. Although dissection of these samples
205 usually revealed a paler interior, no significant change in IR spectra were observed
206 across individual sections. Five PU samples were flexible, with a squarer and less
207 smooth or torn appearance and colours that were yellow, brown, blue or green.
208 Remaining, non-PS and non-PU samples ($n = 4$) were elasticated rubber or acrylic- or
209 PVC-based expanded polymers that were black, pink or yellow and that appeared to
210 be derived from neoprene products, beach footwear and rubber toys.

211

212 *3.2. Elemental concentrations*

213 XRF analysis of sample surfaces revealed the occurrence of different combinations of
214 As, Ba, Bi, Cr, Cu, Sb, Sn, Ti and V among the foams, with median concentrations of
215 a few hundred $\mu\text{g g}^{-1}$ or less for each element. Bromine, Cl, Fe, Pb and Zn were,
216 however, more commonly encountered and at variable concentrations that are
217 summarised in Table 1. Concentrations of Br, Cl and Fe in samples of PS spanned
218 two to three orders of magnitude in each case, with maximum concentrations of about
219 12,000, 70,000 and 30,000 $\mu\text{g g}^{-1}$, respectively. Lead always occurred at
220 concentrations less than 70 $\mu\text{g g}^{-1}$, while Zn was detected in 21 samples with a median
221 concentration on the order of 100 $\mu\text{g g}^{-1}$. No statistically significant correlations were
222 observed between any pair of elements, but the highest concentrations of Br were
223 generally associated with the lowest concentrations of Pb.

224

225 Concentrations of Br, Cl, Fe, Pb and Zn in the PU samples spanned two or three
226 orders of magnitude and mean and median concentrations of Cl, Pb and Zn were
227 considerably higher than respective concentrations in samples of PS. Although no
228 statistically significant correlations among the elements were observed, the highest
229 concentrations of Br were often accompanied by relatively low concentrations of Pb
230 and vice versa. PU samples of a flexible nature contained variable concentrations of
231 Br, Cl and Fe and relatively low concentrations of Zn ($\sim 100 \mu\text{g g}^{-1}$) but Pb was never
232 detected. Among the remaining ('other') expanded polymers, concentrations of
233 detectable Br were about 10 $\mu\text{g g}^{-1}$, concentrations of Cl, Fe and Zn were on the order
234 of a few thousand $\mu\text{g g}^{-1}$, and Pb was not detected.

235

236 Spatial analysis of the surfaces of selected PS and rigid PU samples revealed a degree
237 of heterogeneity whose relative standard deviation ($\sigma_{n-1}/\bar{x} \times 100\%$; $n = 5 - 10$) was

238 generally less than 30% for Br, Cl, Fe, Pb and Zn. Analysis of sample sections
239 revealed no statistically significant differences between surficial and internal
240 concentrations with the exception of Fe. Here, concentrations within samples of both
241 PU and discoloured, expanded PS were often an order of magnitude lower than
242 corresponding concentrations measured on the surface.

243

244 3.3. *PBET results*

245 Of the elements analysed in the PBETs, Br and Zn were never detected at
246 concentrations above those in the respective controls, while Fe and Pb were detected
247 throughout the time-courses in two and four cases, respectively. Specifically, Fe was
248 detected in extracts of one sample of rigid PU and a sample of expanded PS that was
249 partially covered in brown, oxidic deposits, while Pb was detected in extracts of four
250 samples of rigid PU.

251

252 The time-courses of the PBETs in which Pb was detected are shown in Figure 2.
253 Extracted concentrations exhibit a biphasic distribution with rapid release within the
254 first day followed by a slower, more protracted period of mobilisation. Because
255 equilibrium does not appear to be approached, a pseudo-first-order diffusion model
256 only partially fitted the data; specifically, and employing a “quasi-equilibrium”
257 concentration as the last measured point in the time series, such a model
258 overestimated concentrations within the first few days and underestimated
259 concentrations thereafter. Better fits in each case were obtained using a modified
260 version of a diffusion-controlled and parabolic model based on Fick’s second law
261 (Ruby et al., 1992):

262

263 $[Pb(t)] = kt^{1/b}$ (1)

264

265 Here, $[Pb(t)]$ is the time-dependent concentration in $\mu\text{g L}^{-1}$, k is a rate constant in μg
266 $\text{L}^{-1} \text{h}^{-1/b}$, and b is a coefficient whose theoretical value is 2 but in this case is
267 empirically adjusted. Best fits to the data are annotated on Figure 2 while the fitted
268 constants are shown in Table 2. Also shown in Table 2 are total Pb concentrations,
269 $[Pb_T]$ ($\mu\text{g g}^{-1}$), and as determined by surficial XRF measurements, alongside the
270 maximum concentrations of Pb extracted, $[Pb_{\text{max}}]$ ($\mu\text{g g}^{-1}$), at the end-point of each
271 time-course. The latter are on the order of $1000 \mu\text{g g}^{-1}$, with the percentage of total Pb
272 released at the end-point (or bioaccessibility) ranging from about 4 to 10. By
273 comparison, the maximum percentage bioaccessibilities of Fe in PU and PS were
274 about 4 and 12, respectively, with values of k and b of $22.9 \mu\text{g L}^{-1} \text{h}^{-1/b}$ and 2.25, and
275 $118 \mu\text{g L}^{-1} \text{h}^{-1/b}$ and 3.72, respectively.

276

277 **4. Discussion**

278 Although plastic foams have been mentioned or categorised in several publications
279 dealing with marine litter in general (Moore et al., 2001; Topcu et al., 2013; Nuelle et
280 al., 2014; Ryan, 2015), the present study appears to be the first to specifically focus on
281 expanded and extruded materials as waste and address their composition and potential
282 hazards. Because of the diversity of applications in the industrial, domestic,
283 transportation and maritime settings, foams have a wide variety of sources to the
284 marine environment. While some sources to the beached litter pool may be local (e.g.
285 toys, footwear and flotation devices), the low density, well-roundedness and/or
286 discolouration of many of the samples of PS and PU observed here suggest that most

287 fragments are likely to have travelled considerable distances and undergone
288 significant ageing since their original site of disposal.
289

290 Of the foams identified and characterised, the rigid (and semi-rigid) PU types are of
291 greatest concern from an environmental perspective because of their relative
292 abundance and the concentrations of hazardous elements or elements that are
293 indicative of hazardous chemicals in the polymeric matrix. For instance, high
294 concentrations of Br and/or Cl in many rigid PU (and PS) foams likely reflect the
295 addition of various halogenated flame retardants to the polymer, especially when the
296 materials had been used for insulation. Bromine in the foam products analysed herein
297 was not, however, measurably accessible to the avian PBET using ICP-MS. This
298 suggests that in aged, expanded polymers, at least, residual brominated flame
299 retardants are largely bound in the polymeric matrix through various functional (e.g.
300 hydroxyl) groups rather than being mechanically mixed into the formulation (Szycher,
301 1999).

302

303 The presence of Fe and Zn in many of the foams, and in particular in PU, may be
304 attributed to the use of additional additives in foam manufacture. For instance,
305 synthetic iron oxides are used as high opacity pigments for colour (yellows, browns
306 and black) (Szycher, 1999) while various zinc compounds have been used as
307 pigments, catalysts, flame retardants (through char production) and smoke suppressors
308 (Forrest, 2001). It is also likely that the Fe content of foamed plastics is augmented by
309 the precipitation of natural iron oxides on to the polymer surface while suspended in
310 sea water. This effect was apparent from the visible discoloration of many of the aged

311 PS samples and is consistent with higher concentrations of Fe on the surfaces of many
312 samples of PS and PU than in their respective interiors.

313

314 The only reference to Pb in PU foams is as various organic lead salts (lead benzoate,
315 lead oleate, lead 2-ethylhexoate) and organolead compounds (e.g. tetramethyl lead)
316 that were historically used as chain extension and gelation catalysts (Huber, 1987;
317 Carraher, 2005). Up to 0.05% of the lead salt catalysts were typically added during the
318 reaction (Doyle, 1971), although it is conceivable that significantly greater quantities
319 may have been employed where rapid foam formation was sought (Overmars, 1970).

320

321 Because Fe and Zn are not particularly toxic and exhibit relatively low (and frequently
322 undetectable) accessibilities in the PU matrix, they are not likely to be of great
323 concern in the marine environment or to wildlife that inadvertently consume plastics.
324 In contrast, however, elevated concentrations of the highly toxic, priority pollutant,
325 Pb, are accompanied by maximum bioaccessibilities up to about ten per cent that,
326 presumably, reflect the solubilities of organic lead salts (rather than organolead
327 compounds) in the PU matrix under the low pH conditions of the simulated avian
328 gizzard. Clearly, therefore, certain types of (older) PU have the potential of acting as a
329 significant source of local Pb contamination that may be readily transferred into the
330 foodchain. For example, since beach sediment around the southern coast of south west
331 England typically contains total Pb at concentrations of about $10 \mu\text{g g}^{-1}$ (Schuwerack
332 et al., 2007), the intertidal zone need only be contaminated by the addition a few parts
333 per thousand of abraded PU particulates to result in an order of magnitude increase in
334 the local Pb content.

335

336 We are unaware of studies that report the precise mass of foamed plastics in the
337 dissected digestive environments of seabirds but assume that they are encountered on
338 a regular basis since this category (and, specifically, PU) is mentioned as part of the
339 OSPAR Ecological Quality Objective for marine litter in fulmars (Franeker et al.,
340 2011). Based on the observations in the present research, the mobilisation of Pb from
341 ingested foams will be dependent on retention time in the gizzard, the absolute
342 concentration of Pb and the constants defining its rate of release. As a specific
343 example, ingestion and regurgitation of just 10 mg of PU foam (or a small fraction of
344 the total mass of plastic encountered in fulmars from remote locations; Trevail et al.,
345 2015) containing $15,000 \mu\text{g g}^{-1}$ of total Pb could result in the mobilisation of about 15
346 μg of the metal into the avian digestive environment after a period of ten days. While
347 this figure may be regarded as an upper-bound estimate for the conditions considered
348 because Pb is likely to undergo partial precipitation or readsorption in the higher pH
349 environment of the duodenum (Turner and Hambling, 2012), bioaccessibility in the
350 gizzard (or stomach) is often regarded as a good proxy for overall Pb bioavailability
351 (Furman et al., 2006).

352

353 Exposure of Pb to birds is known to cause both lethal and sublethal effects. The latter
354 may be observed at concentrations as low as about $5 \mu\text{g g}^{-1}$ in the liver and feathers,
355 and include loss of appetite, drooped wings, lethargy, tremors, and impaired
356 locomotion and balance (Burger and Gochfeld, 2001). Although Pb exposure from
357 leaded paints and lead-based gunshot pellets are well documented in respect of both
358 seabirds and waterfowl (Finkelstein et al., 2003; Bingham et al., 2015; Kim and Oh,
359 2015), the present study has highlighted a widespread, historical source of relatively
360 bioaccessible Pb in the marine environment that has thus far not been recognised.

361 Greater systematic reporting of the occurrence of foamed litter on beaches, in the
362 oceans and ingested by organisms is called for, while further studies are required to
363 evaluate the wider impacts of Pb in PU foam in the marine environment and on
364 wildlife that are exposed to or consume plastics.

365

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370

371 **References**

372 Ashton, K., Holmes, L., Turner, A., 2010. Association of metals with plastic
373 production pellets in the marine environment. *Marine Pollution Bulletin* 60, 2050-
374 2055.

375

376 Avery-Gomm, S, O'Hara, P.D., Kleine, L., Bowes, V., Wilson, L.K., Barry, K.L.,
377 2012. Northern fulmars as biological monitors of trends of plastic pollution in the
378 eastern North Pacific. *Marine Pollution Bulletin* 64, 1776-1781.

379

380 Baulch, S., Perry, C. Evaluating the impacts of marine debris on cetaceans. *Marine*
381 *Pollution Bulletin* 80, 210-221.

382

383 Bingham, R.J., Larsen, R.T., Bissonette, J.A., Hall, J.O., 2015. Widespread ingestion
384 of lead pellets by wild chukars in northwestern Utah. *Wildlife Society Bulletin* 39, 94-
385 102.

386

387 Burger, J., Gochfeld, M. 2001. Effects of chemicals and pollution on seabirds. In:
388 Biology of Marine Birds, ed. E.A. Schreiber and J. Burger. CRC, Boca Raton, pp.485-
389 526.

390

391 Carraher, C.E. Jr., 2005. Organolead-containing polymers. In: Macromolecules
392 Containing Metal and Metal-like Elements, Volume 4. Abd-El-Aziz, A.S., Carraher,
393 C.E., Pittman, C.U., Zeldin, M. (eds), Wiley & Sons, Hoboken, NJ, p311-328.

394

395 Doyle, E.N., 1971. Development and Use of Polyurethane Products. McGraw-Hill,
396 New York, 352pp.

397

398 Finkelstein, M.E., Gwiazda, R.H., Smith, D.R., 2003. Lead poisoning of seabirds:
399 Environmental risks from leaded paint at a decommissioned military base.
400 Environmental Science and Technology 37, 3256-3260.

401

402 Forrest, M.J. 2001. The Chemical Characterization of Polyurethanes. RAPRA Review
403 Reports, Shrewsbury, UK.

404

405 Franeker, J.A., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., Hansen,
406 P.L., Heubeck, M., Jensen, J.K., Le Guillou, G., Olsen, B., Olsen, K.-A., Pedersen, J.,
407 Stienen, E.W.M., Turner, D.M., 2011. Monitoring plastic ingestion by the northern
408 fulmar *Fulmarus glacialis* in the North Sea. Environmental Pollution 159, 2609-2615.

409

410 Furman, O., Strawn, D.G., Heinz, G.H., Williams, B., 2006. Risk assessment test for
411 lead bioaccessibility to waterfowl in mine-impacted soils. *Journal of Environmental*
412 *Quality* 35, 450-458.

413

414 Furness, R.W., 1985. Plastic particle pollution - accumulation by procellariiform
415 seabirds at Scottish colonies. *Marine Pollution Bulletin* 16, 103-106.

416

417 Gregory, M.R., 2009. Environmental implications of plastic debris in marine settings -
418 entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions.
419 *Philosophical Transactions of the Royal Society of London B* 364, 2013-2025.

420

421 Huber, F., 1987. *Pb Organolead Compounds: Part 1: Tetramethyllead*. Springer,
422 Berlin, 194 pp.

423

424 Kim, J., Oh, J.-M., 2015. Trace element contamination in nestling black-tailed gulls
425 (*Larus crassirostris*) in Korea. *Ecotoxicology* 24, 770-778.

426

427 Li, W.C., Tse, H.F., Fok, L., 2016. Plastic waste in the marine environment: A review
428 of sources, occurrence and effects. *Science of the Total Environment* 566-567, 333-
429 349.

430

431 Lithner, D., Larsson, A., Dave, G., 2011. Environmental and health hazard ranking
432 and assessment of plastic polymers based on chemical composition. *Science of the*
433 *Total Environment* 409, 3309-3324.

434

435 Moore, S.L., Gregorio, D., Carreon, M., Weisberg, S.B., Leecaster, M.K., 2001.
436 Composition and distribution of beach debris in Orange County, California. *Marine*
437 *Pollution Bulletin* 42, 241-245.
438
439 Nuelle, M.T., Dekiff, J.H., Remy, D., Fries, E., 2014. A new analytical approach for
440 monitoring microplastics in marine sediments. *Environmental Pollution* 184, 161-169.
441
442 OSPAR Commission, 2010. Guideline for monitoring marine litter on the beaches in
443 the OSPAR maritime area. OSPAR Commission, London, 84pp.
444
445 Overmars, H.G.J., 1970. Organolead compounds and polyurethane foam produced by
446 the use thereof as catalysts. US patent 3547841A.
447
448 Plastics Europe, 2015. *Plastics – The Facts 2014/2015*. An analysis of European
449 plastics production, demand and waste data. Association of Plastics Manufacturers,
450 Brussels, 34pp.
451
452 Robards, M.D., Piatt, J.F., Wohl, K.D., 1995. Increasing frequency of plastic particles
453 ingested by seabirds in the sub-arctic north Pacific. *Marine Pollution Bulletin* 30, 151-
454 157.
455
456 Rochman, C.M., Hoh, E., Korobe, T., Teh, S.J., 2013. Ingested plastic transfers
457 hazardous chemicals to fish and induces hepatic stress. *Scientific Reports* 3, 3263
458 DOI: 10.1038/srep03263.
459

460 Ruby, M.V., Davis, A., Kempton, J.H., Drexler, J.W., Bergstrom, P.D., 1992. Lead
461 bioavailability: dissolution kinetics under simulated gastric conditions. *Environmental*
462 *Science and Technology* 26, 1242-1248.
463
464 Ryan, P.G., 2015. Does size and buoyancy affect the long-distance transport of
465 floating debris? *Environmental Research Letters* 10, article 084019, DOI:
466 10.1088/1748-9326/10/8/084019.
467
468 Schuwerack, P.-M.M., Neal, M., Neal, C., 2007. The Dart estuary, Devon, UK: a case
469 study of chemical dynamics and pollutant mobility. *Hydrology and Earth System*
470 *Sciences* 11, 382-398.
471
472 Sigler, M., 2014. The effects of plastic pollution on aquatic wildlife: current situations
473 and future solutions. *Water, Air and Soil Pollution* 225, article 2184, DOI:
474 10.1007/s11270-014-2184-6.
475
476 Szycher, M., 2013. *Szycher's Handbook of Polyurethanes*, second edition. CRC
477 Press, Boca Raton, London, 1126pp.
478
479 Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M., Watanuki, Y.,
480 2013. Accumulation of plastic-derived chemicals in tissues of seabirds ingesting
481 marine plastics. *Marine Pollution Bulletin* 69, 219-222.
482

483 Topcu, E.N., Tonay, A.M., Dede, A., Ozturk, A.A., Ozturk, B., 2013. Origin and
484 abundance of marine litter along sandy beaches of the Turkish Western Black Sea
485 coast. *Marine Environmental Research* 85, 21-28.
486

487 Trevail, A.M., Gabrielsen, G.W., Kuhn, S., van Frankener, J.A., 2015. Elevated levels
488 of ingested plastic in a high Arctic seabird, the northern fulmar (*Fulmarus glacialis*).
489 *Polar Biology* 38, 975-981.
490

491 Turner, A., 2016. Heavy metals, metalloids and other hazardous elements in marine
492 plastic litter. *Marine Pollution Bulletin* (in press).
493

494 Turner, A., Hambling, J., 2012. Bioaccessibility of trace metals in sediment,
495 macroalga and antifouling paint to the wild mute swan, *Cygnus olor*. *Water, Air and*
496 *Soil Pollution* 223, 2503-2509.
497

498 Turner, A., Holmes, L., 2015. Adsorption of trace metals by microplastic pellets in
499 fresh water. *Environmental Chemistry* 12, 600-610.
500

501 Turner, A., Solman, K.R., 2016. Analysis of the elemental composition of marine
502 litter by field-portable-XRF. *Talanta* 159, 262-271.
503

504 Warham, J., 1996. *The Behaviour, Population Biology and Physiology of the Petrels*.
505 Academic, London, 616pp.
506

507 Wilcox, C., Mallos, N.J., Leonard, G.H., Rodriguez, A., Hardesty, B.D., 2016. Using
508 expert elicitation to estimate the impacts of plastic pollution on wildlife. *Marine*
509 *Policy* 65, 107-114.
510

Table 1: Distributions and summary statistics for the concentrations of Br, Cl, Fe, Pb and Zn ($\mu\text{g g}^{-1}$) in samples of beached foams from Whitsand Bay.

	no. detected	10^1 - 10^2	10^2 - 10^3	10^3 - 10^4	10^4 - 10^5	$>10^5$	min.	max.	mean	median
<i>Polystyrene (n = 27)</i>										
Br	23	12	7	3	1		12	11,500	1,190	97
Cl	27		1	13	14		554	69,000	14,900	11,300
Fe	27		1	14	12		477	27,600	9,560	9,030
Pb	11	11					11	61	23	19
Zn	21	9	12				42	245	118	123
<i>Polyurethane (n = 39)</i>										
Br	34	23	9	2			21	5,820	440	68
Cl	38			4	7	27	1,160	518,000	214,000	226,000
Fe	39		1	18	20		799	26,900	11,300	10,100
Pb	19	6		5	8		11	15,700	7,030	4,240
Zn	17	9	6	1	1		47	23600	1630	76
<i>Other (n = 4)</i>										
Br	2	2					10	12	11	11
Cl	4			3	1		2,100	17,700	6,130	5,440
Fe	4		2	2			391	4,030	1,180	749
Pb	0									
Zn	4			4			2630	3230	2810	4190

Table 2: Constants and concentrations defining the mobilisation of Pb from the four samples of rigid PU whose kinetic profiles are illustrated in Figure 2. (Note that terms are defined in the text and lettered samples do not correspond to those illustrated in Figure 1.)

sample	$[\text{Pb}_T], \mu\text{g g}^{-1}$	$[\text{Pb}_{\text{max}}], \mu\text{g g}^{-1}$	$[\text{Pb}_{\text{max}}]/[\text{Pb}_T], \%$	$k, \mu\text{g L}^{-1} \text{h}^{-1/b}$	b	r^2
a	13,800	516	3.7	522	6.84	0.897
b	14,500	1380	9.5	903	4.26	0.986
c	15,700	977	6.2	363	2.97	0.993
d	15,300	846	5.5	477	3.73	0.989

Figure 1: A selection of foams (between 4 and 8 cm in length) collected from Whitsand Bay: (a) light brown flexible polyurethane; (b) well-rounded and discoloured polystyrene; (c) elasticated pink rubber; (d) well-rounded and dark brown rigid polyurethane; (e) yellow-brown rigid polyurethane; (f) partly discoloured yellow-brown rigid polyurethane.

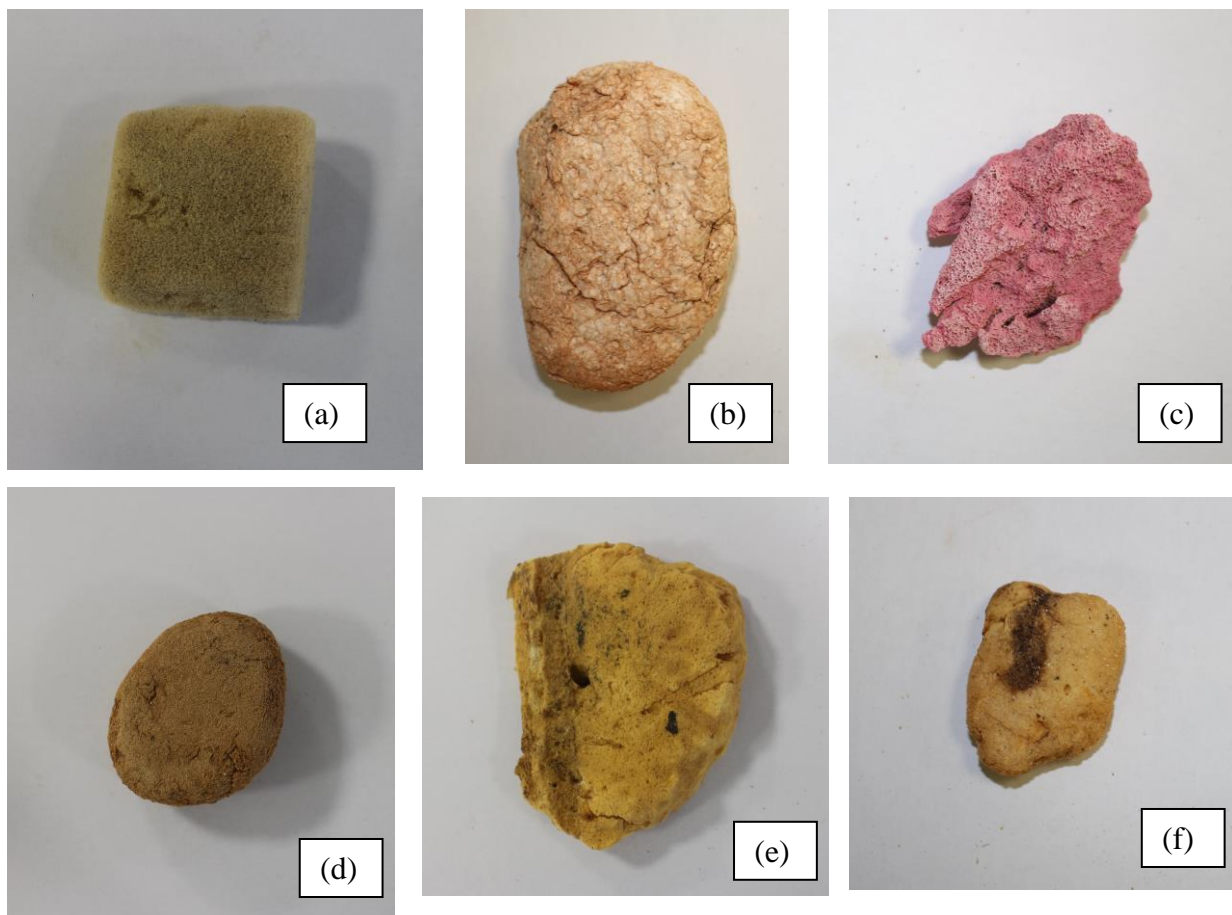


Figure 2: Kinetic profiles for the mobilisation of Pb from four samples of rigid polyurethane by the avian PBET. Annotated are best-fits to the data according to equation 1 and errors represent one standard deviation about the mean of three independent measurements. Concentrations of Pb (in $\mu\text{g g}^{-1}$) and rate constants defining the profiles are given in Table 2. (Note that lettered samples do not correspond to those illustrated in Figure 1.)

