2019-05-10

Identification, origin and characteristics of bio-bead microplastics from beaches in western Europe.

Turner, Andrew

http://hdl.handle.net/10026.1/13399

Identification, origin and characteristics of bio-bead microplastics from beaches in western Europe

Andrew Turner*, Claire Wallerstein[a] & Rob Arnold[a]

*School of Geography, Earth and Environmental Sciences,

Plymouth University

Drake Circus

Plymouth PL4 8AA, UK

aturner@plymouth.ac.uk

[a]Rame Peninsula Beach Care

56 Fore Street

Kingsand

Torpoint PL10 1NA, UK

23 **Abstract**

24 Primary microplastics have been collected from 17 beaches along the Atlantic, English Channel and

25 southern North Sea coasts of western Europe. Based on visual characteristics, these plastics were

26 differentiated as either relatively smooth, lentil- or disc-shaped pre-production pellets (or nurdles),

27 which were usually a few mm in diameter and were mainly white to off-white, or rougher and more

28 irregular pellets that were slightly larger and usually black. The latter appeared to be bio-beads, or

29 plastics that are specifically manufactured for use as biomedia in certain sewage water treatment

30 (SWT) plants, and possibly in other industrial wastewater treatment applications. Identification of

31 bio-beads was confirmed following the acquisition of identical samples from a SWT plant in

32 southwest England and a French supplier of bio-beads. Infrared and x-ray fluorescence analysis

33 revealed that bio-beads have, at least historically, been constructed of plasticised polyethylene and,

34 unlike pre-production pellets, contained variable quantities of potentially toxic elements: Br, Cd, Cr,

35 Hg, Pb and Sb; with a distinctive Br to Sb ratio indicative of brominated flame retardants and

36 antimony-based retardant synergists. It is asserted that bio-beads have been manufactured from a

37 heterogeneous mix of recycled polyethylene and end-of-life electrical and electronic plastic, with

38 concentrations of Br, Cd, Cr or Pb in about 50 bio-beads (out of 500 analysed) non-compliant or

39 potentially non-compliant with respect to current regulations on hazardous plastic waste.

40 Concentrations of Br, Cd, Cr, Pb and Sb extracted from individual bio-beads by a simulated avian

41 digestive fluid were variable, with maximum values of about 14, 0.8, 1.3, 20 and 1.4 $\mu g\ g^{-1}$,

42 respectively. The presence and, in many cases, dominance of bio-beads among beached primary

43 microplastics is discussed with regard to the classification of microplastics and potential impacts on

44 wildlife.

45

46 **1. Introduction**

47 Plastic pre-production pellets, or nurdles, are the industrial raw material used by the thermoplastics

48 industry for melting and injection moulding-extrusion (Redford et al., 1997). Typically, pre-

49 production pellets are a few mm in diameter and several tens of mg in weight and are manufactured

50 in a range of colours. The volume of plastic shipped globally, coupled with spillages and losses during

51 transportation, handling and processing, has ensured that these pellets are one of the most

52 abundant and pervasive forms of primary marine microplastic in aquatic systems, and in particular in

53 environments favourable for the deposition of low density material (Takada, 2006; Moreira et al.,

54 2016). On some coastal beaches, for example, the number of pre-production pellets can exceed

55 several thousand per m^3 and may be encountered at depths of up to 2 m (Kusui and Noda, 2003;

56 Turra et al., 2014), while on lake beaches, pellets may comprise more than 90% of plastic debris on a

57 number basis (Zbyszewski and Corcoran, 2011).

58 Because of their buoyancy, colour and size, pre-production pellets are often consumed by birds and

59 fish that mistake them for food or prey, resulting in potential obstruction of the gastrointestinal

60 tract, suffocation, starvation and internal injuries (Pierce et al., 2004; Colabuono et al., 2009).

61 Ingestion may also enable chemicals and contaminants that are associated with the plastic, either as

62 additives or that have adsorbed to the surface during suspension, to bioaccumulate (Endo et al.,

63 2005; Turner, 2018a).

64 Recently, the Cornish Plastic Pollution Coalition, a grouping of over 30 voluntary organisations based

65 in south-west England, suggested that many of the primary microplastics retrieved from local

66 beaches, and in some cases the majority of such plastics, are not in fact conventional pre-production

67 pellets (CPPC, 2018). Thus, although many microplastics are of similar dimensions to these pellets,

68 they are not smooth or regular in form but are amorphous, wrinkled and/or ridged. The intricacy of

69 some of these designs suggests that they have been deliberately engineered for a specific purpose

70 rather than being manufactured by simple extrusion for pre-production use. Thus, the authors

71 asserted that these microplastics were bio-beads, used in a number of local sewage water treatment

72 (SWT) plants as part of the filtration process. Specifically, biological aerated flooded filter (BAFF)

73 plants employ pellets as a buoyant, high surface area substrate for the attachment of a biofilm of

74 bacteria used to digest compounds such as ammonia (Gray, 2004). Wastewater is passed in a

75 flooded condition, a process that requires a smaller area of land than an equivalent activated sludge

76 process and that is able to treat high salinity sewage.

77 A visit by the Cornish Plastic Pollution Coalition to a SWT works in Plympton (Plymouth) serving

78 85,000 people revealed that approximately 43 billion bio-beads were in operation in a series of

79 reactors. An abundance of bio-beads in storage and on the ground was noted that were consistent in

80 form and colour distribution to those collected on beaches from the region. It was also established

81 how readily spillages and losses could occur during reactor top-ups, leaks and accidents. Nationally,

82 at least 55 plants serving 2 million people appear to employ this technology, with available

83 information suggesting that bio-beads have been purchased from FLI Water (Kempston, Bedford)

84 who source them from a French company (Plasti-Negoce, Lormaison, Picardie). The majority of bio-

85 beads used are black which, presumably, is one of the cheaper colours to source. Thus, although

86 SWT plants are designed to remove suspended solids and deliver clean effluent water (Murphy et al.,

87 2016), some facilities appear to act as a direct source of microplastic pollution to the environment.

88   In the present study, primary microplastics collected from beaches of south-west England and

89   throughout the English Channel and parts of the southern North Sea are examined in order to

90   explore the wider distribution and occurrence of bio-beads. Both bio-beads and pre-production

91   pellets are analysed non-destructively by Fourier transform infrared (FTIR) spectroscopy and x-ray

92   fluorescence (XRF) spectrometry in order to attempt to chemically discriminate the two types of

93   microplastic and ascertain the nature and sources of plastics employed. The wider implications of

94   bio-beads for plastic identification and classification and for impacts on wildlife are also addressed.

95   **2. Methods**

96   *2.1. Sampling campaigns*

97   Several thousand microplastics were collected by hand, either by the authors or by colleagues,

98   through inspections of visible accumulations of litter along the sand or silt strandlines of beaches,

99   harbours and estuaries at locations shown in Figure 1 that are encompassed by OSPAR regions II

100   (Greater North Sea, including the English Channel) and III (Celtic Seas, extending into the Atlantic

101   Ocean) and where plastic pollution is of greatest concern (QSR, 2010). In most cases (Cornwall, Scilly

102   Islands, Jersey, southern England, Wales) unsorted beached microplastics were retrieved during

103   2017 or early 2018; in other cases, however, French and Dutch colleagues supplied suspected bio-

104   beads isolated from archived plastics that dated back to 2011 and that had been stored dry in

105   darkened air-tight containers. Samples were foil-wrapped and returned or posted to the laboratory

106   at Plymouth University where, as necessary, they were visually sorted by colour and type (pre-

107   production pellets, bio-beads and any secondary fragments that were generally angular, film-like or

108   fibrous). In addition, bio-beads were collected by hand from spillages around the reactors at

109   Plympton SWT works, Plymouth, in January 2017, and new bio-beads were sourced directly from the

110   manufacturer, Plasti-Negoce, in March 2018 (Figure 1). A selection of individual primary

111   microplastics of each type (pre-production pellets and bio-beads) and from each location or source

112   was weighed on a five-figure balance (Sartorius Genius) and measured for diameter through the

113   widest axis and for height through the thickest part using digital callipers.

114   *2.2. XRF analysis*

115   All or a selection of at least 20 primary microplastics from each location or source, as indicated in

116   Figure 1 and totalling 616 (537 bio-beads and 79 pre-production pellets), were analysed for twelve

117   elements that are proxies for important additives in plastics and/or are potentially toxic

118   contaminants (Ba, Br, Cd, Cl, Cr, Cu, Fe, Hg, Pb, Sb, Ti, Zn) using an energy-dispersive Niton XL3t He

119   GOLDD+ portable XRF. The instrument was configured nose upwards in a shielded laboratory test-

120   stand and activated remotely by a laptop via USB connection. Samples were measured for thickness

121   through the measurement surface (usually the smoothest or flattest face) using digital callipers

122   before being suspended above the detector window on 3.6 μm Mylar film with the aid of a pair of

123   tweezers and real-time video footage projected on the laptop through a CCD camera located next to

124   the x-ray source. Samples were counted in a standardless plastics mode with thickness correction for

125   20 seconds at 40 μA and 50 kVp and 10 seconds at 100 μA and 20 kVp. Spectra arising from sample

126   counting were quantified by fundamental parameter coefficients to yield elemental concentrations

127   in $\mu g\ g^{-1}$ and a measurement error of 2σ (95% confidence) that were downloaded to the laptop via

128   Niton data transfer software.

129   For quality assurance and instrument performance purposes, two 13 mm-thick Niton reference

130   plastics that had been impregnated with various elements (PN 180-554 batch SN PE-071-N and PN

131   180-619 LOT#T-18) were analysed at regular intervals throughout each measurement session. To

132   evaluate measurement precision and the importance of the thickness correction algorithm, selected

133   samples were analysed in quintuplicate after varying thickness correction had been applied between

134   1 and 6 mm (approximating the range of sample thicknesses determined using the callipers). Median

135   precisions were found to range from < 5% for Br, Cr and Ti to about 15% for Cd and Cl, and errors in

136   thickness estimation of at least 50% were required to produce significant errors in reported

137   concentration (relative to the concentration returned for true thickness and according to a series of

138   paired t-tests; $\alpha = 0.05$) for elements whose fluorescent energies are less than 10 keV (Cl, Cr, Cu, Fe,

139   Ti, Zn).

140   Limits of detection under the operating conditions of the XRF are dependent on sample thickness,

141   density and chemical composition. Median values, based on the analysis of 50 pellets and 50 bio-

142   beads from various locations and derived from counting errors multiplied by 1.5 (i.e. 3σ), were

143   similar for the two types of microplastic for a given element and ranged from < 10 $\mu g\ g^{-1}$ for Br and

144   Pb to several hundred $\mu g\ g^{-1}$ for Ba and Cl.

145   ***2.3. FTIR analysis***

146   A selection of primary microplastics of varying size, form, colour and, according to XRF analysis,

147   composition, and sampled from different environments, including those supplied by the

148   manufacturer and totalling 30, was analysed by attenuated total reflectance FTIR (ATR-FTIR)

149   spectrometry using a Bruker Vertex 70. The ATR diamond crystal was cleaned with isopropanol

150   before whole samples or offcuts thereof were clamped against the crystal and spectra recorded with

151   16 scans in the region 4000 to 600 cm^{-1} and at a resolution of 4 cm^{-1}. After being smoothed,

152   baseline-corrected and normalised via Bruker OPUS 7 software, spectra were compared with

153 libraries of reference spectra for the identification of component polymers and were visually

154 inspected for signs of polymer modification.

2.4. Extraction tests and analysis

156 In order to evaluate the mobility of potentially toxic contaminants from bio-beads, 11 samples from

157 various locations (and including the STW plant) were extracted under conditions approximating

158 those encountered in the digestive tract of a seabird (Turner, 2018a). Thus, whole bio-beads were

159 weighed into individual 10-ml polypropylene centrifuge tubes before the addition of 5-ml aliquots of

160 0.07 M HCl (Fisher Scientific Trace Analysis Grade in Elga ultrapure water). The contents were then

161 placed in a Fisher Scientific Isotemp SW27 water bath for 24 h at 40 $^\circ$C and under lateral shaking at

162 100 rpm before extracts were pipetted into clean centrifuge tubes and stored for up to two weeks

163 under refrigeration pending analysis.

164 Concentrations of Br, Cd, Cr, Cu, Fe, Hg, Pb, Sb and Zn in the HCl-extracts were determined by

165 inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo Scientific iCAP RQ analyser

166 with a Glass Expansion micromist nebuliser and cyclonic spray chamber. The instrument was

167 calibrated with a blank and three mixed and matrix-matched standards in the range 10 to 100 μg L^{-1},

168 and RF power was set at 1.5 KW with coolant, nebuliser and auxiliary flows of 1.4, 1.07 and 0.8 L Ar

169 min^{-1} and a replicate (n = 3) read time of 10 ms.

170

3. Results

3.1. Appearance and physical characteristics of new and SWT bio-beads

173 A total of 25 bio-beads were returned from Plympton SWT works, where BAFF media have been

174 employed for over 20 years. Here, 16 bio-beads were black (including charcoal or dark grey), while

175 the remainder were white to off-white or blue-green (Figure 2). The majority of these used bio-

176 beads had a distorted and irregular cylindrical form and were amorphous-looking, with poorly-

177 defined faces which, in some cases, appeared to be pitted, bumpy or concertinaed. Occasional bio-

178 beads, however, were more defined in shape with at least one distinctive face that was usually

179 circular.

180 The physical characteristics of a selection of SWT bio-beads are summarised in Table 1. Briefly, bio-

181 bead mass ranges from around 28 to 53 mg and averages about 38 mg, while the diameter

182 measured across the widest axis of the bio-bead, d_1, ranges from about 3.2 to 4.5 mm, and height

183   measured through the thickest part, d_2, ranges from about 3.1 to 5.7 mm. The aspect ratio of the

184   bio-beads (d_1:d_2) ranges from around 0.6 to 1.3, with an average that is close to unit value.

185   All new bio-beads supplied by Plasti-Negoce (n = 15) were black, irregular cylinders with a rough

186   texture throughout and no smooth faces evident (Figure 2). These were less variable in size and

187   aspect than the bio-beads retrieved from the SWT plant, with an average mass of about 41 mg, an

188   average diameter and height of about 3.6 and 4.8 mm, respectively, and an average aspect ratio of

189   0.76.

190   Microscopic images, exemplified in Figure 3, revealed that new bio-bead surfaces were uneven

191   throughout and edges were jagged. Used bio-beads, however, were generally smoother and more

192   eroded on surfaces and edges where concertinaing was absent, and were characterised by deposits

193   of brown, white or black particulates on their surfaces.

194   ***3.2. Appearance and physical characteristics of beached primary microplastics***

195   Nearly all of the primary microplastics collected from various estuarine and coastal beaches

196   throughout the region under study could be categorised either as bio-beads, based on the

197   description above, or pre-production pellets (nurdles); occasional, distinctive components of fishing

198   equipment or children's toys-jewellery were the only other type of primary microplastic evident.

199   Pre-production pellets were generally smooth and disc- or lentil-shaped with a distinctive depression

200   often visible on one side (Figure 2), although some were well-defined cylinders that reflect simple

201   extrusion of the polymer, and the majority were white to off-white or translucent, with the latter

202   often accompanied by yellowing resulting from photo-oxidative weathering. Based on

203   measurements of 40 random samples from various beaches, and as summarised in Table 1, pre-

204   production pellet mass averaged 23 mg and ranged from about 15 to 38 mg. Average dimensions

205   were 4.1 mm and 2.2 mm for d_1 and d_2, respectively, with a mean aspect ratio of around 2. In

206   contrast, beached bio-beads were mainly black and less frequently grey, green-blue, or white to off-

207   white. Measurements of 67 random samples from different beaches, and summarised in Table 1,

208   revealed that bio-beads were more variable in mass and size than pre-production pellets but were,

209   overall, larger. Thus, bio-bead mass averaged over 40 mg and ranged from about 13 to 74 mg, and

210   both d_1 and d_2 average about 4 mm, but with a relatively large range of values that resulted in a

211   mean aspect ratio close to unit value.

212   The microscopic images shown in Figure 3 highlight the differences between beached bio-beads and

213   pre-production pellets. Specifically, the latter generally have a better-defined, regular shape and

214   exhibit a relatively smooth surface while the former are mostly irregular with a rougher surface that

215 allows extraneous material to be more readily accumulated during suspension or beaching.

216 Accumulation appears to be particularly favourable where the surface is concertinaed, an effect

217 most evident on blue-green bio-beads, or where there were cracks and bumps. Note also that some

218 bio-beads that were usually black, grey or dark green were distinctly smoother and more regular

219 than most of the other bio-beads. Although it was originally suspected that these samples may have

220 been pre-production pellets, similar characteristics to some of the smoother used bio-beads from

221 the SWT plant and a form that precludes ready extrusion for pre-production pelletisation, including

222 distortion and doming, suggested otherwise.

223 *3.3. Polymeric composition of bio-beads and pre-production pellets*

224 Results of FTIR analysis, exemplified in Figure S1, revealed that all bio-beads tested (*n* = 22),

225 including those supplied by Plasti-Negoce, were constructed of polyethylene and, based on a

226 carbonyl peak of varying intensity at around 1730 cm^{-1}, contained variable quantities of ester-based

227 plasticiser. For the SWT and beached bio-bead spectra, a broad peak between 3700 and 3000 cm^{-1}

228 that was considerably reduced when the internal structure of the plastic was exposed after

229 dissection suggests the presence of absorbed water and/or hydrolysis of the surface. Although

230 methyl bending deformation evident in many black samples at 1377 cm^{-1} was initially attributed to

231 chain length reduction through weathering and aging, the presence of this absorption peak in new

232 bio-beads suggests that low density polyethylene may also be an inherent component of the plastic

233 matrix (Jung et al., 2018).

234 FTIR spectra for the pre-production pellets analysed (*n* = 8) revealed plastics composed of either

235 polyethylene or polypropylene with variable quantities of plasticiser. There was less evidence of

236 water absorption and/or hydrolysis at the surface and absorption peaks were less evident at 1377

237 cm^{-1}.

238 *3.4. Elemental composition of bio-beads and pre-production pellets*

239 Table 2 reports summary statistics for the concentrations of the twelve elements analysed by

240 portable XRF in the different primary microplastics. All new bio-beads sourced from the

241 manufacturer contained measurable quantities of Fe, Ti and Zn, while some bio-beads contained

242 detectable Ba, Cu and Cl. Likewise, all bio-beads that had been employed in SWT reactors contained

243 measurable Fe, Ti and Zn and some bio-beads contained detectable Ba, Cu and Cl. However,

244 concentrations of a given element were more variable than in the new bio-beads, with standard

245 deviations close to the mean and a concentration range that spanned more than an order of

246 magnitude in some cases. In addition, many used bio-beads contained measurable quantities of the

8

247 more toxic elements: Br, Cr, Pb and Sb; concentrations of which spanned up to two orders of

248 magnitude.

249 For the bio-beads collected from various beaches, the frequency of detection of each element

250 overall was similar to that of the used bio-beads but with Cd and Hg present in a number of cases.

251 Concentrations of each element were highly variable, with a range spanning two or more orders of

252 magnitude for Br, Fe and Ti. The correlation matrix shown in Figure 4 reveals associations with a

253 Pearson's moment correlation coefficient (r) above 0.75 occur in eight cases that are limited to

254 combinations between six elements (Br, Cd, Cu, Hg, Pb, Sb) and a coefficient above 0.9 for Br-Sb and

255 Cd-Hg; in contrast, no associations with a coefficient above 0.5 are evident among the elements Cl,

256 Fe and Ti.

257 Regarding the beached pre-production pellets, Cd, Cu and Sb were never detected and

258 concentrations of Br, Hg and Pb were only returned in one case each. Overall, detection frequency

259 (as a percentage of samples analysed) in pre-production pellets was lower than in new bio-beads for

260 Ba, Cl, Fe, Ti and Zn and lower than or equal to used bio-beads for all elements with the exception of

261 Cr. Compared with beached bio-beads, detection frequency, mean concentration and median

262 concentration were lower for all elements considered with the exception of Cl (a higher mean) and

263 Cr (a higher detection frequency and median). The results of correlation analysis shown in Figure 4

264 reveal only one association (Ba-Cr) with a coefficient exceeding 0.5.

265 The heterogeneity in bio-bead composition overall was also reflected by high elemental variability at

266 each location where bio-beads were reported and provided, with evidence of geographical patterns

267 limited to differences in detection frequencies between regions. Specifically, Ba appeared to be

268 more commonly detected towards the east-southeast (for example, 65% in Texel compared with <

269 40% at Perranporth and Freshwater West) while Cl appeared to be more commonly detected

270 towards the west (less than a third in the Netherlands and northern France compared with up to

271 80% in Jersey and Cornwall).

272 *3.5. Elemental extraction from bio-beads*

273 Table 3 presents a summary of the concentrations of various elements extracted from 11 bio-beads

274 by the simulated avian digestive solution. Iron and Zn were detected in all extracts and at the highest

275 concentrations, with respective maximum values of 1120 and 161 $\mu g\ g^{-1}$ encountered in a bio-bead

276 from the SWT. Relative to the total concentrations returned by the XRF, percentage extraction for

277 both metals ranged from about 10 to over 100. Mercury was never detected in the extracts and

278 remaining elements were detected in between 1 (Cr) and 11 (Br, Pb) cases with average

279   concentrations always below 10 µg g^{-1} and, with the exception of Cu, percentage extractions less

280   than 1%.

281   **4. Discussion**

282   ***4.1. Sources and distributions of bio-beads***

283   Bio-beads are primary microplastics that are used as filtering media in many biological aerated

284   flooded filter SWT works. The results of the present study indicate that bio-beads are polyethylene-

285   based, irregularly-shaped and usually black, and are, on average, larger and heavier than plastic

286   production pellets (nurdles). Bio-beads are distributed throughout a wide region of western Europe

287   with a range of about 900 km from the Scilly Islands in the west to Texel in the east evident in the

288   present study. Because of the nature of the sampling, including subsampling from archived and

289   previously manipulated stocks, it was not possible to precisely quantify the relative abundance of

290   beached bio-beads and other visible primary microplastics. Nevertheless, observations indicated

291   that the occurrence of bio-beads varied considerably throughout the region, being relatively

292   uncommon in the Scilly Islands, for example, but the dominant form of primary microplastic at

293   Camber Sands. A previous, more quantitative distributional approach undertaken by the Cornish

294   Plastic Pollution Coalition (CPPC, 2018) also indicated a widely varying abundance of bio-beads

295   relative to other primary microplastics but one that had no clear geographical patterns, with relative

296   abundances of about 20% reported on one beach on the Atlantic coast of Cornwall to 90% on an

297   English Channel beach near to the border of France and Belgium.

298   The incidence of bio-beads beyond the region under study is not clear because a variety of different

299   types and sizes of plastic biomedia are used in SWT globally (Bailly et al., 2018). However, we note

300   that they have recently been reported along the Atlantic coast of south west France and the western

301   coast of Denmark (CPPC, 2018), while XRF analysis of archived black microplastics collected from the

302   Mediterranean island of Malta (Turner and Holmes, 2011) and performed as part of the present

303   study revealed similar chemical characteristics to those of bio-beads reported herein. An

304   examination of internet images of beached microplastics also suggests that the presence of bio-

305   beads may extend beyond Europe.

306   Bio-beads may enter the environment during handling at SWT plants and during their processing and

307   transportation by the manufacturers or suppliers. However, the principal environmental source

308   appears to be related to loss from SWT reactors, an assertion confirmed by the presence of

309   polycyclic aromatic hydrocarbons, characteristic of urban runoff, adsorbed to the surfaces of bio-

310   beads but not to other primary microplastics (i.e. pre-production pellets) collected from Cornish

311 beaches (Hideshige Takada, pers. comm). Large-scale loss of bio-beads to the environment may

312 occur when the retaining mesh of the reactors fails. As an example, the utility company, South West

313 Water, was alerted to a spillage of over 5 billion bio-beads into the Truro River, south west England,

314 in 2010, when the 3-mm steel mesh of a reactor split (CPPC, 2018). Although the company

315 subsequently attempted to clear bio-beads from the environment, this incident exemplifies the lack

316 of any fail-safe containment mechanism to trap lost bio-beads to any meaningful degree.

317 The requirement to occasionally top-up reactors with bio-beads suggests that spillages may also take

318 place during maintenance, or that continuous loss occurs through partial damage to the mesh or

319 through encapsulation by sludge. Abrasion of bio-beads with the interior reactor walls may also

320 facilitate escapement should the primary or secondary diameter be denuded to a value that is less

321 than the 3-mm pore size of the steel mesh. Table 1 shows that the minimum values of both d_1 and d_2

322 for the new and used bio-beads exceeds this value but that d_2 for beached bio-beads may be less

323 than 2 mm.

324 Within the UK, the Cornish Plastic Pollution Coalition report that eight out of the twelve national

325 water companies use bio-beads at more than 55 SWT plants that serve about two million people,

326 and that a further two companies use, or have used, a type of plastic bead medium but could not

327 provide specific details (CPPC, 2018). However, given the rather vague, ambivalent and contradictory

328 responses to requests for information from some companies we contend that this figure may

329 represent a significant underestimate. Available information suggests, but cannot confirm, that bio-

330 beads are not used for treating sewage in neighbouring countries, despite their abundance on sandy

331 beaches outside the UK and the parent company of FLI Water being based in Ireland. Their exclusive

332 use by British utility companies would require bio-beads to be readily transported throughout the

333 region, and to both the west and east, by ocean currents, or that additional industries employ bio-

334 beads for water treatment.

335 *4.2. Chemical characteristics and signature of bio-beads*

336 Bio-beads are chemically complex and many are associated with relatively high concentrations of

337 potentially toxic elements (and in particular, Cd, Pb and Sb) and/or brominated compounds. This

338 observation, coupled with the use of combinations of brominated compounds, Cd, Pb and Sb in

339 electronic plastic as contaminants or in order to engender flame retardancy to heat-generating

340 articles (Turner and Filella, 2018), suggests that many bio-beads are, or have been, manufactured,

341 directly or indirectly, from end-of-life waste electrical and electronic equipment (WEEE). Potentially

342 harmful chemicals are supposed to be removed from the WEEE stream but poor or inefficient

343 practices have resulted in contamination of recycled consumer goods (Turner, 2018b). This is a

particular problem for black products because domestic waste plastic coloured in this way is difficult to identify and recycle at municipal sorting facilities (Rozenstein et al., 2017) and, being inherently black, most electrical equipment casings afford a convenient and cheap alternative recyclate. Consistent with this problem, Br, Cd, Pb and Sb were most frequently encountered in bio-beads that were black or that appeared to have been blended from black plastic (e.g. dark green).

In addition to the widespread, heterogeneous contamination of bio-beads from (likely) WEEE plastic, many samples contain one or more toxic or potentially toxic chemical additives that exceed the respective limits defined by the Restriction of the use of certain Hazardous Substances in electrical and electronic equipment (RoHS) Directive (European Parliament and Council, 2003) (Table 4). Strictly, therefore, these bio-beads should be classified as 'hazardous' themselves. Specifically, and with respect to electrical goods placed on the market in Europe after 2006, the metals Cd, Cr (as Cr VI) and Pb are restricted to concentrations of 100 $\mu g\ g^{-1}$, 1000 $\mu g\ g^{-1}$ and 1000 $\mu g\ g^{-1}$, respectively, in homogenous materials or components of EEE, while concentrations of the polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants are restricted to concentrations of 1000 $\mu g\ g^{-1}$. (Note that, despite compounds of Sb commonly used as halogenated flame retardant synergists (Papazoglou, 2004), the potentially toxic metalloid itself has not been considered in the directive.) Accordingly, 20 samples from a variety of locations but with a relatively high proportion on the East Looe river estuary are RoHS-non-compliant (or derived from non-compliant products) with respect to Cd and four samples are non-compliant with respect to Pb. One sample from the Scilly Islands is potentially non-compliant with respect to Cr (XRF cannot discriminate Cr III and Cr VI) and 26 samples from throughout the region are potentially non-compliant with respect to Br in that concentrations exceed 700 $\mu g\ g^{-1}$ Br (the approximate concentration of Br in 1000 $\mu g\ g^{-1}$ of penta-PBDE, one of the more commonly used lower brominated congeners). Potential Br non-compliance occurs in a sample from Plympton STW and in a relatively high proportion of samples collected from Texel and Marazion but was not observed in the Scillies or at East Looe, where Pb and either Cd or Cr non-compliance (or potential non-compliance) was observed. Overall, there were 51 cases of potential RoHS-exceedance among 49 samples that were all black and that had been retrieved from all locations studied with the exception of Cayeux-sur-mer, Freshwater West Bay and Kimmeridge Bay.

The heterogeneous distribution of restricted chemicals among the bio-beads, both within and between locations and at concentrations both above and below their respective RoHS limits, suggests that the bio-beads have been derived from a variety of multiple sources or a single (or limited number of) source(s) whose supply is either chemically heterogeneous or is variable in make-up over time. The lack of restricted chemicals detected in the new bio-beads obtained from Plasti-

378   Negoce, the only apparent supplier of bio-beads within the UK, is consistent with the latter

379   explanation and sourcing raw material that is linked with the availability, historical processing and

380   degree of contamination of black plastic. Thus, it is possible that better practices in sorting non-

381   compliant materials from the WEEE stream or the phasing out of restricted chemicals has resulted in

382   a reduction in contamination of the raw material. On this basis, we may assert that bio-beads from

383   Texel, for example, where restricted chemicals are abundant and, in the case of Br, frequently

384   exceed RoHS limits, are older than ones from the Scillies or the northern coast of France. That said,

385   however, recent studies into contemporary consumer goods suggests that contamination of black

386   plastic is a long-term but highly variable problem and that once contaminants are introduced and

387   blended into the recyclate are difficult to eliminate (Turner, 2018b).

388   Further evidence for the use of recycled WEEE to manufacture bio-beads is the correlations between

389   the concentrations of restricted elements (Figure 4), and in particular that between Br, indicative of

390   the quantity of brominated flame retardants, and Sb, representative of the amount of antimony-

391   based compounds (and mainly Sb_2O_3) used as flame retardant synergists. The association of Br and

392   Sb for bio-beads where both elements were detected is illustrated in Figure 5. Here, data are

393   discriminated by location but most data-points, including those from the SWT plant, lie within 20%

394   of the best-fit regression line forced through the origin. Significantly, the gradient of the best-fit line

395   (Br-Sb = 1.45) is lower than that defining pre- and post-RoHS EEE plastics (Br-Sb = 2.92) and as

396   determined by portable XRF and reported by Turner (2018b). Given that different types of polymer

397   may require different kinds and quantities of halogenated flame retardant and synergist for

398   protection (Papazoglou, 2004), the discrepancy in gradients may be partly attributed to the apparent

399   use of recycled polyethylene in bio-beads compared with the use of a multitude of polymers in EEE

400   (including polystyrene, polypropylene and acrylonitrile butadiene styrene). However, it is also

401   possible that differential release of flame retardants and synergist occurs while bio-beads are

402   suspended in sewage water or seawater; specifically, a greater gradient defining EEE than bio-beads

403   requires a higher propensity for the mobilisation of brominated compounds from the polymeric

404   matrix than compounds of Sb. The mobilisation of either or both Br and Sb also has implications for

405   the chemical quality of effluent water discharged from SWT plants that employ plastic biomedia.

4.3. Elemental mobility from bio-beads

407   Results of the extraction tests reveal relatively high but variable mobilities of Fe and Zn from the bio-

408   beads, consistent with the adherence, entrapment, adsorption or (co-)precipitation of material at

409   the polymer surface. That extractable concentrations were greatest in a bio-bead from the SWT

410   plant suggests phases derived from sewage water are more labile than those derived from the

coastal environment or that the phases derived from sewage water plants desorb readily when beads are released to the environment. The restricted elements, Br, Cd, Cr, Pb and Sb, are less available to extraction, both in terms of absolute concentration and percentage relative to total concentration, presumably because high proportions are associated with the plastic matrix rather than material physically or chemically attached to the polymer surface. This assumption was subsequently confirmed by analysis of the interiors of a selection of bio-beads (after slicing with pliers) returning concentrations that were almost identical to those derived from whole bio-bead analyses performed through the plastic surface. Nevertheless, given the potential or known toxicities of these elements to marine wildlife, including potential impacts on physiology, reproduction, survival, growth, neurobehaviour and endocrine systems (Burger and Gochfeld, 2000; De Andres et al., 2016; Sebastiano et al., 2016), their mobilities are of concern for organisms that inadvertently ingest bio-beads into an acidic digestive system. The ingestion of bio-beads by the herring gull, *Larus argentatus*, has recently been reported to the authors by a fisherman working on the Truro River, downstream of a major spill at a sewage water treatment plant in early 2010. The regurgitated contents from one individual are illustrated in Figure 6, with plastic contributing more than 40% to the total matter on a dry mass basis (about 3.2 g) and bio-beads dominating the microplastic pool.

4.4. Concluding remarks

Bio-beads are small, irregularly shaped plastics derived from waste water treatment processes that constitute a significant fraction of microplastic pollution on beaches of western Europe. Bio-beads are often black and associated with Br, Cd, Pb and Sb in quantities that are characteristic of plastic recycled from WEEE. Their distinctive physical and chemical characteristics warrant classification that is both separate from pre-production pellets (nurdles) and is based on colour for monitoring, scientific and risk assessment purposes. With respect to BAFF treatment plants that employ bio-beads, it is recommended that more stringent prevention and remediation plans are adopted in order to minimise the occurrence and potential impacts of spillages and leakages in the environment.

References

Bailly, C., Barreau, C., Bencivengo, P., Verdet, F., Maison, P., Bost, G., Wallerstein, C., 2018. Sewage filter media and pollution of the aquatic environment. Surfrider Foundation Europe, Biarritz, 154pp.

Burger, J., Gochfeld, M., 2000. Metals in albatross feathers from Midway Atoll: Influence of species, age, and nest location. Environmental Research 82A, 207-221.

Colabuono, F.I., Barquete, V., Domingues, B.S., Montone, R.C., 2009. Plastic ingestion by procellariiformes in Southern Brazil. Marine Pollution Bulletin 58, 93–96.

CPPC, 2018. Bio-bead pollution on our beaches. A Cornish Plastic Pollution Coalition report, second edition. http://www.ramepbc.org/CPPC_Bio-bead_Pollution_on_our_Beaches_2nd_Edition_July_2018.pdf (accessed 9/18).

De Andres, E., Gomara, B., Gonzalez-Paredes, D., Ruiz-Martin, J., Marco, A., 2016. Persistent organic pollutant levels in eggs of leatherback turtles (*Dermochelys coriacea*) point to a decrease in hatching success. Chemosphere 146, 354-361.

Endo, S., Takizawa, R., Okuda, K., Takada, H., Chiba, K., Kanehiro, H., Ogi, H., Yamashita, R., 2005. Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: Variability among individual particles and regional differences. Marine Pollution Bulletin 50, 1103-1114.

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

Gray, N., 2004. Biology of Wastewater Treatment (2nd edition). Series on Environmental Science and Management. Imperial College Press, London, 1421pp.

Jung, M.R., Horgen, F.D., Orski, S.V., Rodriguez, V., Beers, K.L., Balazs, T., Jones, T., Work, T.M., Brignac, K.C., Royer, S.-J., Hyrenbach, K.D., Jensen, B.A., Lynch, J.M., 2018. Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms. Marine Pollution Bulletin 127, 704-716.

Kusui, T. Noda, M., 2003. International survey on the distribution of stranded and buried litter on beaches along the Sea of Japan. Marine Pollution Bulletin 47, 175–179.

Moreira, F.T., Balthazar-Silva, D., Barbosa, L., Turra, A., 2016. Revealing accumulation zones of plastic pellets in sandy beaches. Environmental Pollution 218, 313-321.

Murphy, F., Ewins, C., Carbonnier, F., Quinn, B., 2016. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. Environmental Science and Technology 50, 5800-5808.

OSPAR, 2010. Guideline for monitoring marine litter on the beaches in the OSPAR maritime area. OSPAR Commission, London, 84pp.

481 Papazoglou, E.S., 2004. Flame retardants for plastics. In: Handbook of Building Materials for Fire
482 Protection, Harper, C.A., ed, McGraw-Hill, New York.

483 Pierce, K.E., Harris, R.J., Larned, L.S., Pokras, M.A., 2004. Obstruction and starvation associated with
484 plastic ingestion in a Northern gannet *Morus bassanus* and a Greater shearwater *Puffinus gravis*.
485 Marine Ornithology 32, 187–189.

486 QSR, 2010. Quality status report 2010. OSPAR Commission, London
487 http://qsr2010.ospar.org/en/index.html (accessed 9/18).

488 Redford, D.P., Trulli, H.K., Trulli, W.R., 1997. Sources of plastic pellets in the aquatic environment. In
489 Coe, J.M. and Rogers, D.B. (Eds.) Marine Debris: Sources, Impacts, and Solutions. Springer-Verlag,
490 New York, 335-343.

491 Rozenstein, O., Puckrin, E., Adamowski, J., 2017. Development of a new approach based on midwave
492 infrared spectroscopy for post-consumer black plastic waste sorting in the recycling industry. Waste
493 Management 68, 38-44.

494 Sebastiano, M., Bustamante, P., Costantini, D., Eulaers, I., Malarvannan, G., Mendez-Fernandez, P.,
495 Churland, C., Blevin, P., Hasuselmann, A., Dell'Omo, G., Covaci, A., Eens, M., Chastel, O., 2016. High
496 levels of mercury and low levels of persistent organic pollutants in a tropical seabird in French
497 Guiana, the Magnificent frigatebird, *Fregata magnificens*. Environmental Pollution 214, 384-393.

498 Takada, H., 2006. Call for pellets! International Pellet Watch Global Monitoring of POPs using
499 beached plastic resin pellets. Marine Pollution Bulletin, 52 1547-1548.

500 Turner, A., 2018a. Mobilisation kinetics of hazardous elements in marine plastics subject to an avian
501 physiologically-based extraction test. Environmental Pollution 236, 1020-1026.

502 Turner, A., 2018b. Black plastics: linear and circular economies, hazardous additives and marine
503 pollution. Environment International 117, 308-318.

504 Turner, A., Holmes, L., 2011. Occurrence, distribution and characteristics of beached plastic
505 production pellets on the island of Malta (central Mediterranean). Marine Pollution Bulletin 62, 377-
506 381.

507 Turner, A., Filella, M., 2017. Bromine in plastic consumer products – Evidence for the widespread
508 recycling of electronic waste. Science of the Total Environment 601-602, 374-379.

509 Turra, A, Manzano, A.B., Dias, R.J.S., Mahiques, M.M., Barbosa, L., Balthazar-Silva, L., Moreira, F.T.,
510 2014. Three-dimensional distribution of plastic pellets in sandy beaches: shifting paradigms.
511 Scientific Reports 4, Article number: 4435.

512 Zbyszewski, M., Corcoran, P.L., 2011. Distribution and Degradation of Fresh Water Plastic Particles
513 Along the Beaches of Lake Huron, Canada. Water Air and Soil Pollution 220,365–372.

514

515

516

517 Table 1: Summary statistics for the mass and dimensions (d_1 = diameter, d_2 = height) of a selection of
518 new bio-beads sourced from Plasti-Negoce, used beads collected from Plympton SWT plant,
519 beached bio-beads and beached pre-production pellets.

		new bio-beads	SWT bio-beads	beached bio-beads	beached pre-production pellets
mass, mg	n	10	16	67	40
	mean±sd	41.14±7.00	37.66±7.01	42.25±13.11	23.06±4.95
	min	23.98	27.90	12.9	14.98
	max	49.59	53.45	73.94	37.62
d_1, mm	n	10	16	67	40
	mean±sd	3.58±0.30	3.88±0.37	3.96±0.57	4.08±0.36
	min	3.08	3.17	2.87	2.83
	max	4.09	4.47	5.67	4.58
d_2, mm	n	10	16	67	40
	mean±sd	4.79±0.73	4.03±0.70	3.90±0.84	2.20+0.41
	min	3.52	3.10	1.87	1.59
	max	6.09	5.66	7.14	3.10
d_1:d_2	n	10	16	67	40
	mean±sd	0.76±0.10	1.00±0.21	1.06±0.27	1.92±0.44
	min	0.59	0.61	0.58	1.06
	max	0.88	1.27	1.74	2.52

520

521

522

523

524

525

526

527

528

529

530

531

532

533

534

Table 2: Summary statistics for the elemental composition of new, used (SWT) and beached bio-beads and beached pre-production production pellets. All concentrations are in µg g^{-1}.

		Ba	Br	Cd	Cl	Cr	Cu	Fe	Hg	Pb	Sb	Ti	Zn
new bio-beads (n = 15)	no. detected (%)	10 (66.7)	0	0	5 (33.3)	0	2 (13.3)	15 (100)	0	0	0	15 (100)	15 (100)
	mean±sd	409±89.7			1130±677		21.2	160±22.9				9830±1560	495±46.8
	median	386			855		21.2	160				10,200	496
	min	300			786		20.2	122				6850	420
	max	606			2340		22.2	201				12,276	588
SWT bio-beads (n = 25)	no. detected (%)	17 (68.0)	17 (68.0)	0	16 (64.0)	7 (28.0)	7 (28.0)	25 (100)	0	11 (44.0)	11 (44.0)	25 (100)	25 (100)
	mean±sd	1410±1840	204±235		659±360	42.0±14.4	34.1±23.6	1130±1020		38.6±18.8	192±135	2970±1550	320±244
	median	548	85.3		685	37.3	31.1	768		38.9	131	3270	262
	min	318	7.8		215	24.9	14.3	116		9.4	58.9	809	58.6
	max	5500	739		1210	62.4	83.5	3670		69.9	420	5240	854
beached bio-beads (n = 497)	no. detected (%)	280 (56.5)	247 (49.7)	73 (14.7)	269 (54.2)	169 (34.0)	145 (29.2)	490 (98.5)	14 (2.8)	231 (46.4)	71 (14.3)	487 (97.9)	428 (86.1)
	mean±sd	869±604	283±892	93.9±60.8	1250±1200	77.2±137	56.7±53.6	509±670	19.5±4.3	105±379	621±1010	5200±4310	236±223
	median	768	35.5	73.9	827	37.0	41.8	323	19.4	38.6	307	4460	222
	min	342	5.40	35.1	180	17.4	13.5	50.4	12.0	8.1	77.8	59.0	16.3
	max	8020	6730	312	8140	1400	363	10,900	26.1	5380	4730	35,100	1590
beached pre-production pellets (n = 79)	no. detected (%)	9 (11.4)	1 (1.3)	0	25 (31.6)	35 (44.3)	0	72 (91.1)	1 (1.3)	1 (1.3)	0	21 (26.6)	4 (5.1)
	mean±sd	610±115	12.0		1380±1330	40.9±9.7		197±271	20.4	22.2		4600±5900	83.9±41.6
	median	635	12.0		940	41.9		101	20.4	22.2		87.1	89.7
	min	417	12.0		212	18.5		35.9	20.4	22.2		14.7	30.2
	max	781	12.0		6280	62.7		1700	20.4	22.2		13,900	126

543   Table 3: Summary statistics for the concentrations of elements (in $\mu g\ g^{-1}$) extracted from bio-beads under simulated avian digestive conditions.

	Br	Cd	Cr	Cu	Fe	Hg	Pb	Sb	Zn
no. detected	11	8	1	10	11	0	11	2	11
mean±sd	7.6±2.6	0.34±0.24	1.3	3.0±1.9	366±421		6.0±6.2	1.3	53.2±53.0
median	7.2	0.28		2.2	111		3.3	1.3	44.6
min	3.1	0.08		1.0	34.1		0.6	1.1	8.8
max	13.5	0.77		5.6	1120		20.0	1.4	161

544

545

546

547

548

549

550

551

552

553

554

555

556

557

558

559   Table 4: Number of cases in which bio-beads were non-compliant (Cd, Pb) or potentially non-compliant (Br, Cr) with respect to corresponding RoHS limits
560   (and as indicated).

561

Location	Br > 700 μg g^{-1}	Cd > 100 μg g^{-1}	Cr > 1000 μg g^{-1}	Pb > 1000 μg g^{-1}
Plasti-Negoce				
Plympton STW	1			
Freshwater West				
Burnham on Sea	2			
Perranporth	1	1		
St Mary's			1	1
Marazion	4			
Truro-Tresillian	1			
East Looe		11		2
Tregantle	2	2		1
Kimmeridge Bay				
Camber Sands	2			
Texel	8	1		
Wimereux	2	2		
Cayeux-sur-mer				
Le Havre		1		
Bel Royal	1	2		
Greve d'Azette	2			
total	26	20	1	4

562

20

563

564 Figure 1: Location of the sampling sites in the present study, including the French manufacturer of
565 bio-beads. Numbers in parentheses denote the number of bio-beads analysed by XRF from each site.

566
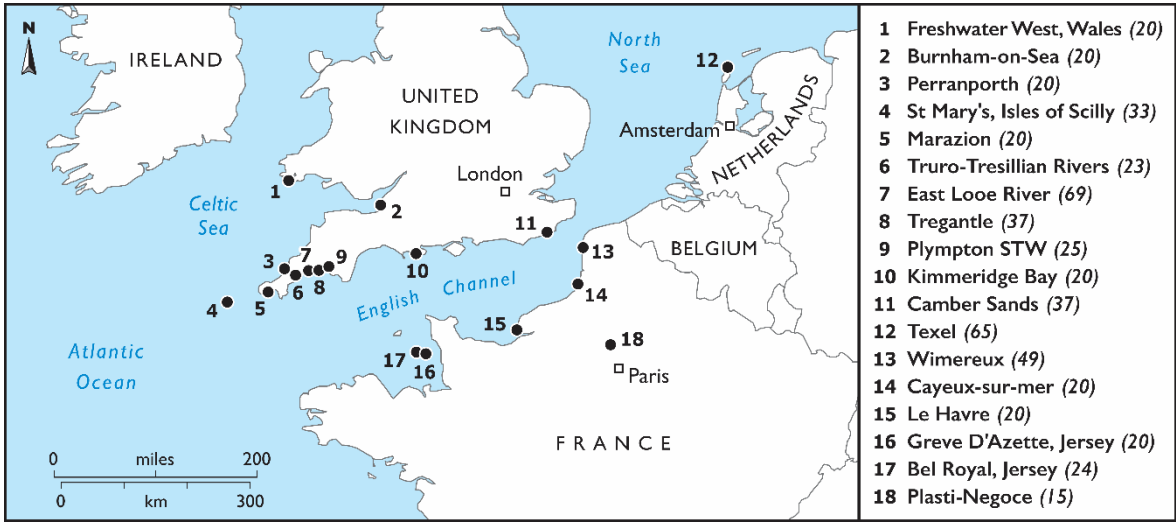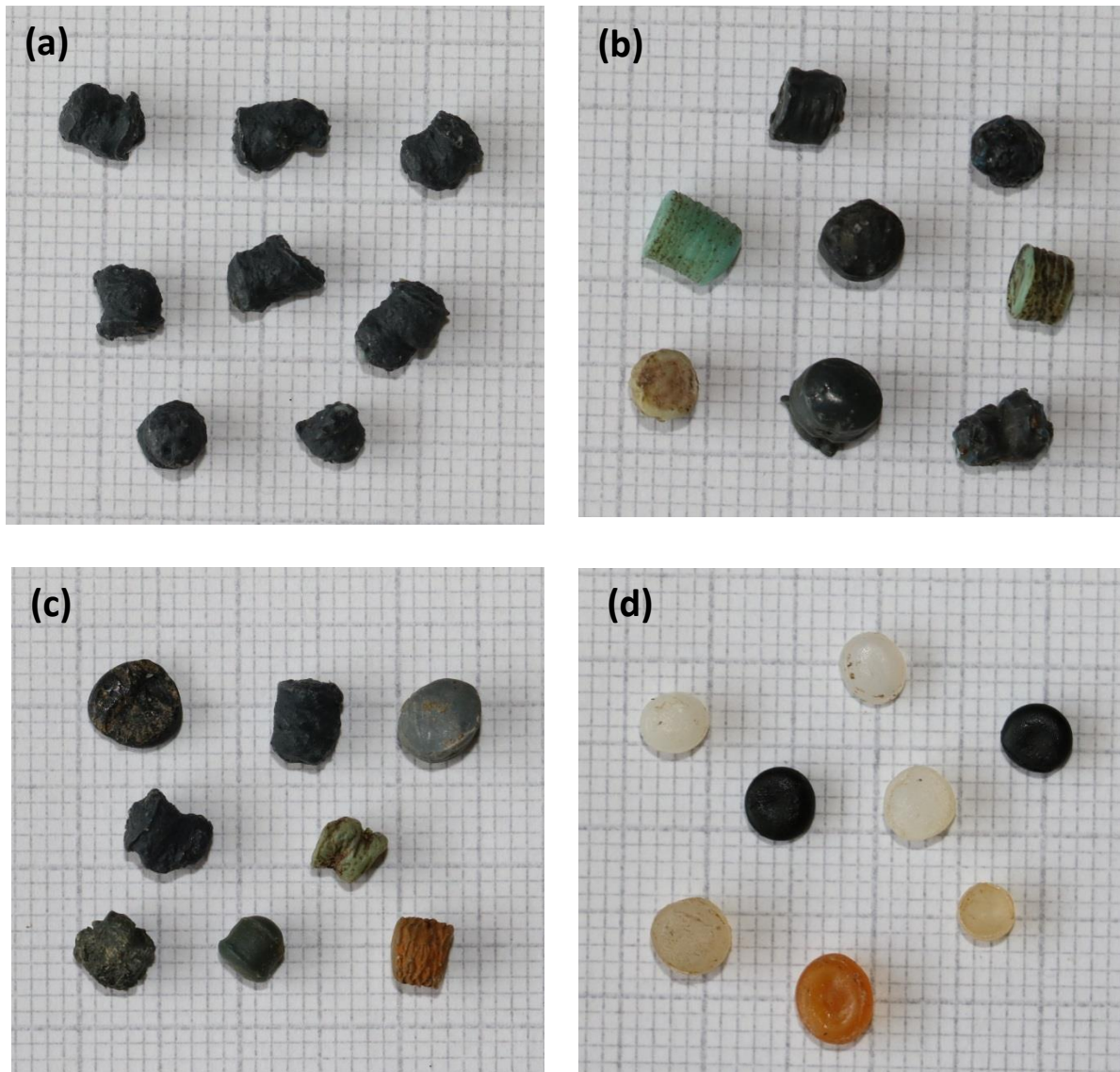
567

568

569

570

571

572

573

574

Figure 2: Photographs of a selected of samples on cm-scaled graph paper. (a) Bio-beads supplied by Plasti-Negoce, (b) bio-beads retrieved from Plympton SWT works, (c) bio-beads collected from Camber Sands and East Looe, and (d) pre-production pellets collected from Tregantle, Perranporth and Camber Sands.

Figure 3. Microscopic images of selected bio-beads and pre-production pellets. (a) A bio-bead supplied by Plasti-Negoce, exhibiting a rough surface and jagged edges; (b) an irregular black bead from Plympton SWT works showing evidence of erosion and material accumulation; (c) a smoother, more cylindrical black bead from the STW; (d) a blue-green bead from the STW revealing material accumulation along the concertinaed edges; (e) an irregular black bio-bead from Cayeux-sur-Mer with visible accumulation of brown and white material; (f) an irregular black bead from Camber Sands with evidence of yellow-brown material accumulation; (g) a smoother and more regular black bead from the Scilly Islands; (h) a translucent pre-production pellet from East Looe that had undergone yellowing; (i) a black pre-production pellet from the Scilly Islands.
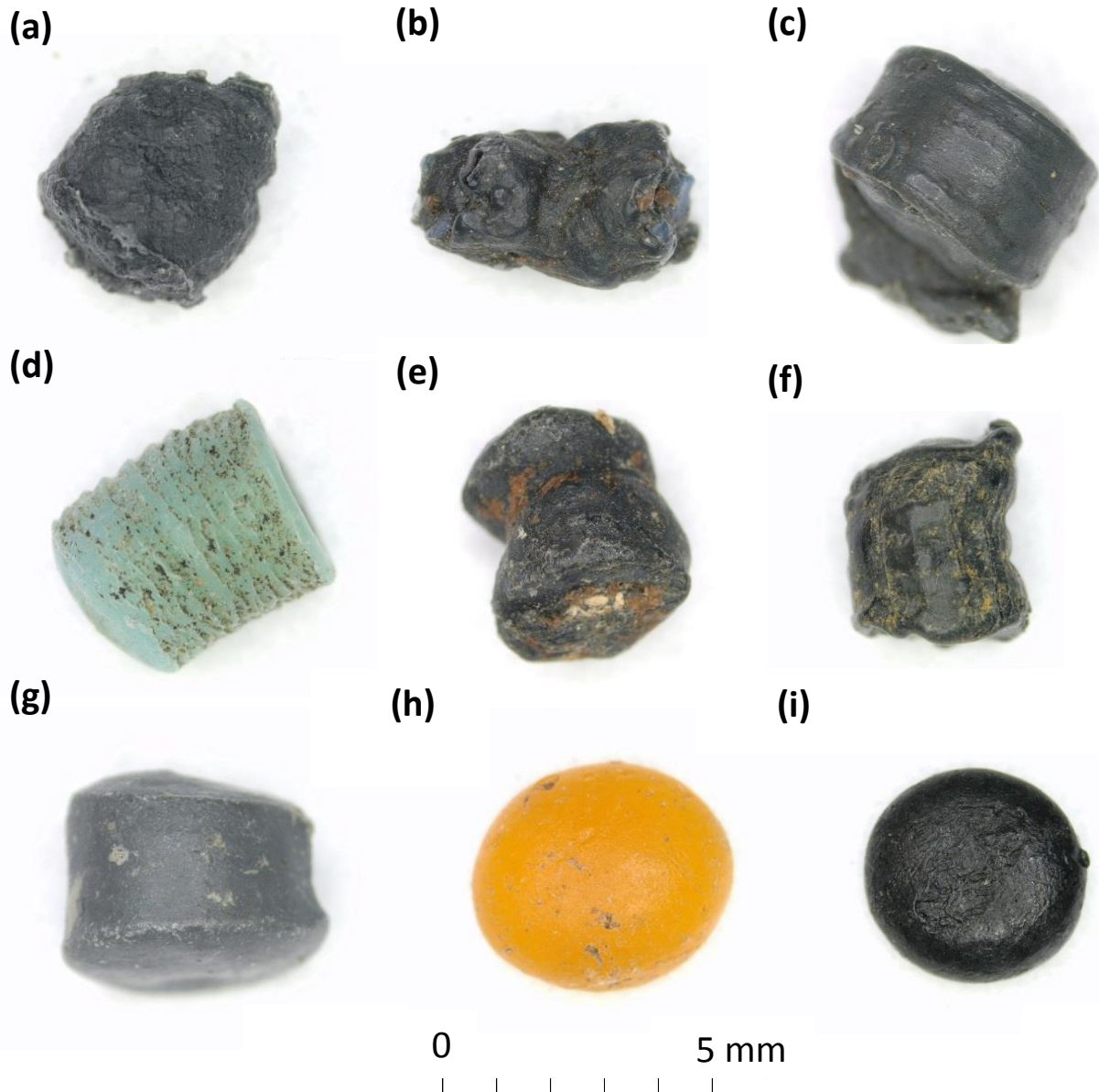
Figure 4: Correlation matrix showing associations between different elements for the beached bio-beads (▲, *r* > 0.5; ▲▲, *r* > 0.75; ▲▲▲, *r* > 0.9) and pre-production pellets (◊, *r* > 0.5).

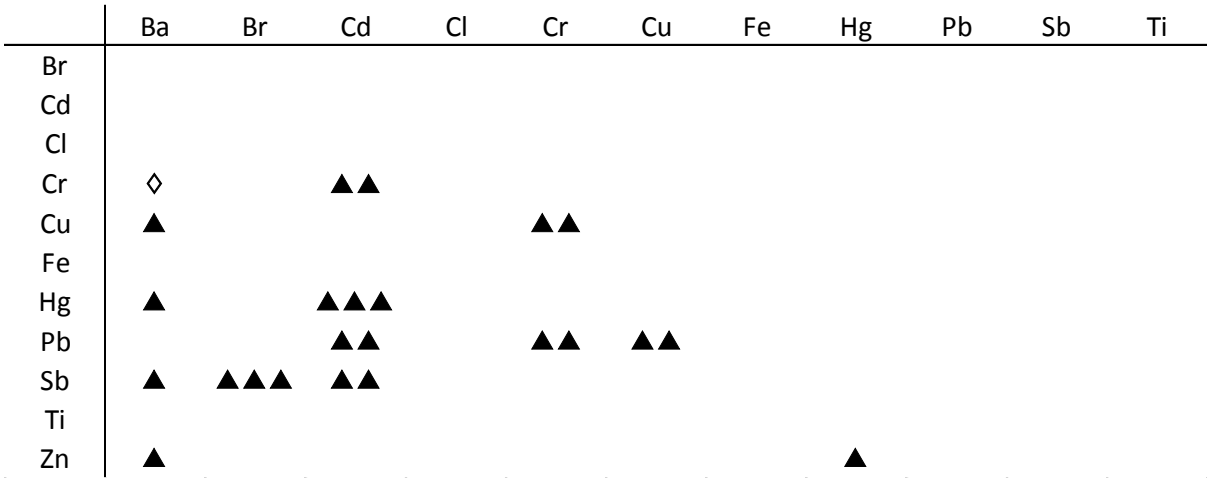|	Ba	Br	Cd	Cl	Cr	Cu	Fe	Hg	Pb	Sb	Ti
Br											
Cd											
Cl											
Cr	◊		▲▲								
Cu	▲				▲▲						
Fe											
Hg	▲		▲▲▲								
Pb			▲▲		▲▲	▲▲					
Sb	▲	▲▲▲	▲▲								
Ti											
Zn	▲							▲			

Figure 5: Relationship between Br and Sb in SWT bio-beads and beached bio-beads (*n* = 89, *r* = 0.983, *m* = 1.45, *p* < 0.01). Note that Sb was not detected in samples form Freshwater West.
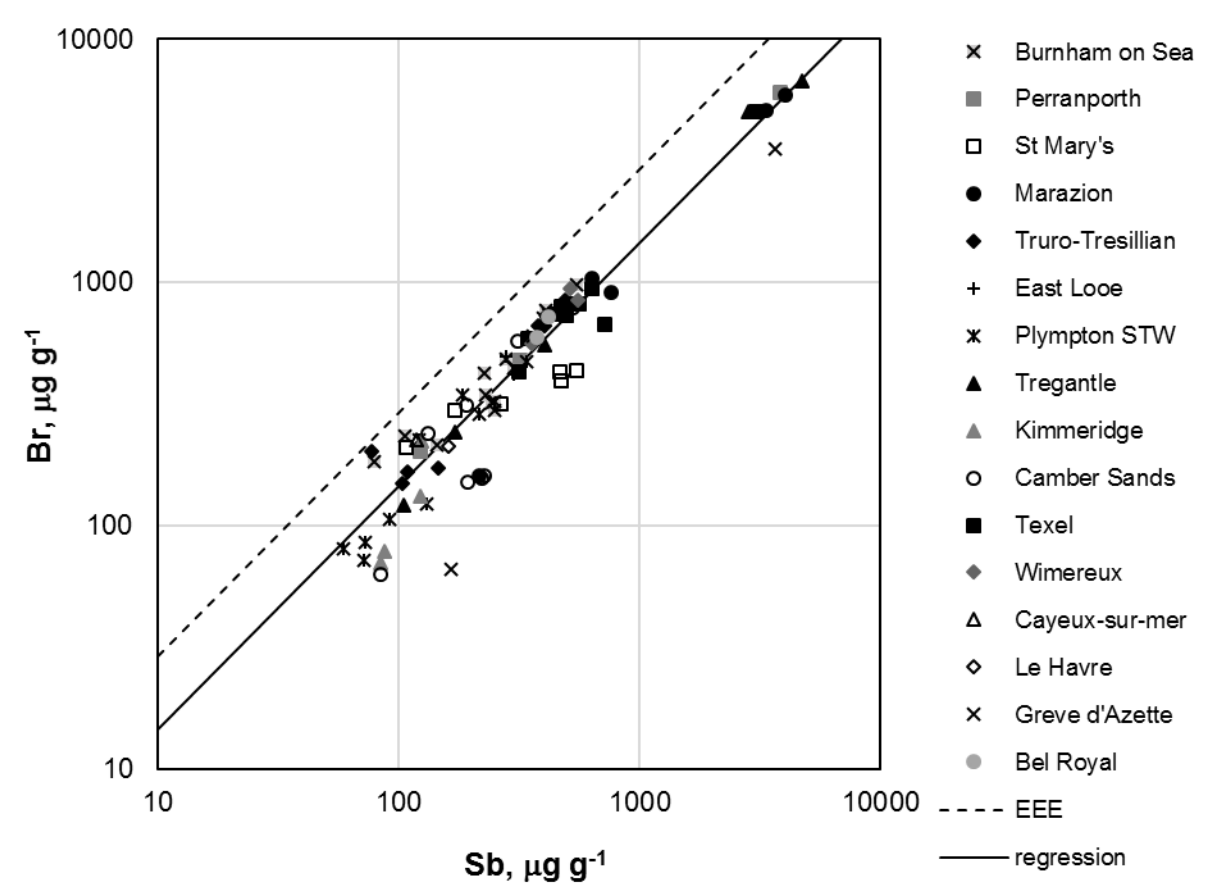
589 Figure 6: Material regurgitated by *L. argentatus* illustrating the presence of pre-production pellets,
590 bio-beads and various secondary microplastics amongst food and other material (seaweed,
591 crabshell, barnacle fragments).

592

593

594

595

596

597

598

599

600

601

602

603

604