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Cadmium, lead and bromine in beached microplastics

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26 **Abstract**

27 Samples of microplastic ($n = 924$) from two beaches in south west England have been
28 analysed by field-portable-x-ray fluorescence (FP-XRF) spectrometry, configured in a
29 low-density mode and with a small-spot facility, for the heavy metals, Cd and Pb, and
30 the halogen, Br. Primary plastics in the form of pre-production pellets were the
31 principal type of microplastic ($> 70\%$) on both beaches, with secondary, irregularly-
32 shaped fragments representing the remainder of samples. Cadmium and Pb were
33 detected in 6.9% and 7.5% of all microplastics, respectively, with concentrations of
34 either metal that exceeded $10^3 \mu\text{g g}^{-1}$ usually encountered in red and yellow pellets or
35 fragments. Respective correlations of Cd and Pb with Se and Cr were attributed to the
36 presence of the coloured, inorganic pigments, cadmium sulphoselenide and lead
37 chromate. Bromine, detected in 10.4% of microplastics and up to concentrations of
38 about $13,000 \mu\text{g g}^{-1}$, was mainly encountered in neutrally-coloured pellets. Its strong
39 correlation with Sb, whose oxides are effective fire suppressant synergists, suggests
40 the presence of a variety of brominated flame retardants arising from the recycling of
41 plastics originally used in casings for heat-generating electrical equipment. The
42 maximum bioaccessible concentrations of Cd and Pb, evaluated using a physiological
43 extraction based on the chemical characteristics of the proventriculus-gizzard of the
44 northern fulmar, were about $50 \mu\text{g g}^{-1}$ and $8 \mu\text{g g}^{-1}$, respectively. These concentrations
45 exceed those estimated for the diet of local seabirds by factors of about 50 and 4,
46 respectively.

47

48 **Keywords:** cadmium; lead; bromine; microplastics; pellets; flame retardants

49 **Capsule:** XRF analysis of beached microplastics reveals the common occurrence of
50 the hazardous elements, Cd, Pb and Br

51 **1. Introduction**

52 Plastic litter is a global problem that has a variety of environmental, social, aesthetic
53 and economic impacts. In the marine environment, floating, deposited and beached
54 plastics pose risks to marine wildlife, principally through entanglement and ingestion.
55 Regarding the latter, the extent of the impacts bears some inverse relationship to
56 particle size in that the smaller the plastic, the greater its potential to affect a wider
57 range of organisms through, for example, blockages and internal abrasions (Wesch et
58 al., 2016). Ingestion of microplastics, or plastics of diameter < 5 mm (Arthur et al.,
59 2009), may occur intentionally (e.g. when particles are mistaken for food),
60 incidentally (e.g. during filter feeding), via consumption of contaminated prey, or,
61 regarding cetaceans, through inhalation (Lusher, 2015).

62
63 Microplastics in the marine environment can be classified as primary or secondary
64 according to their origin (Hidalgo-Ruz et al., 2012). Thus, primary microplastics are
65 those that have been manufactured for a specific purpose and usually enter the
66 environment from spillages or via wastewater. Primary microplastics are frequently
67 identifiable and include pre-production pellets used for the moulding of finished
68 articles and microbeads employed as ex-foliating agents in cosmetic and personal care
69 products. Secondary microplastics are those derived from the gradual breakdown and
70 fragmentation of larger objects or fragments (macroplastics) that have entered the
71 environment from a variety of additional sources such as shipping, fishing activities
72 and coastal littering.

73
74 Another concern regarding ingested microplastics is their propensity to release
75 additives from the polymeric matrix while transiting or trapped in the gastro-intestinal

76 tract. In this respect, most focus has been on organic compounds added to plastics to
77 enhance their performance, durability and safety, like plasticisers, antioxidants and
78 flame retardants (Tanaka et al., 2013; Jang et al., 2016; Narvaez Valderrama et al.,
79 2016). However, recent research using field-portable-x-ray fluorescence (FP-XRF)
80 spectrometry configured in a low density, ‘plastics’ mode has reported high
81 concentrations of many hazardous elements in beached marine litter, and in particular
82 the toxic heavy metals, cadmium and lead (Turner and Solman, 2016; Turner, 2016).
83 Inorganic compounds of these metals were used as heat and UV stabilisers in
84 polyvinyl chloride (PVC) and as coloured pigments in other plastics before being
85 restricted or phased out (Hansen et al., 2010).

86

87 Based on these observations, it would be reasonable to hypothesise that hazardous
88 elements are present in primary and secondary microplastics, and that particle
89 ingestion affords a potential route of their exposure to a range of marine organisms.
90 To this end, therefore, we examine the elemental concentrations and distributions in
91 primary and secondary microplastics retrieved from two beaches in south west
92 England using FP-XRF. Coupled with a ‘small-spot’ facility that collimates the x-ray
93 beam to a width of 3 mm, this technique is able to provide rapid, quantitative
94 information on the elemental content of plastics down to about 1 mm in diameter and
95 0.1 mm in thickness. The focus of the study is on elements that are both hazardous
96 and restricted in plastics (RoHS, 2006; Hansen et al., 2010; European Chemicals
97 Agency, 2016); namely, the halogen, Br, as an indicator of brominated compounds
98 that are used as flame retardants, and the heavy metals, Cd and Pb. In order to
99 evaluate the avian bioaccessibility of these elements, selected samples are digested in

100 a physiological fluid that mimics the chemistry of a seabird proventriculus-gizzard
101 and the digests analysed by inductively coupled plasma-mass spectrometry (ICP-MS).

102

103 **2. Materials and methods**

104 *2.1. Sampling and sample processing*

105 Samples were collected from two high-energy, macrotidal, sandy beaches in south
106 west England that are popular with tourists, surfers and other recreational users
107 (Figure 1). Whitsand Bay, on the south (English Channel) coast of Cornwall
108 comprises an expansive, 8-km, south west-facing beach that is backed by steep cliffs.
109 Woolacombe, on the north (Atlantic Ocean) coast of Devon is a 3-km, west-facing
110 beach that is flanked by shallow, grassy sand dunes.

111

112 Selective sampling was undertaken on single occasions and about an hour after high
113 water during December 2015 (Woolacombe) and January 2016 (Whitsand). Samples
114 of non-porous, moulded plastics that were visible to the naked eye were retrieved
115 from a 10 m transect of the strandline using plastic tweezers and stored in a clear,
116 polyethylene box. (Note that small items of foamed plastic were not considered
117 because of their friability and difficulties in identification, while small pieces of
118 filamentous waste were not sampled because strands were generally too thin to
119 perform XRF analysis.) Sample size was screened in situ with a clear plastic ruler and
120 measured more accurately with callipers in the laboratory (see below). Our working
121 definition of microplastics was < 5 mm in at least two dimensions and no more than
122 10 mm in any one dimension, with visibility and analytical constraints resulting in a
123 minimum primary particle diameter of about 1 mm. This size range is consistent with

124 the diameters of plastics typically recovered from the digestive environments of
125 different seabirds (Hidalgo-Ruz et al., 2012).

126

127 In the laboratory, samples from each beach were rinsed in Millipore Milli-Q water
128 through a sieve and with the aid of a Nylon brush in order to remove debris and
129 epiphytes before being dried at 40°C for 24 hours. After recording the total dry
130 weights using a two figure balance, samples were divided according to appearance as
131 primary plastics (identifiable objects) or secondary plastics (unidentifiable fragments
132 derived from the breakdown of primary products) and coded according to colour.

133

134 *2.2. FTIR analysis*

135 The component polymers of selected samples ($n = 30$) were determined by Fourier
136 transform infra-red (FTIR) spectroscopy using a Bruker ALPHA Platinum attenuated
137 total reflection QuickSnap A220/D-01 spectrometer. Samples were clamped down on
138 to the ATR diamond crystal before measurements, consisting of 16 scans in the range
139 4000 to 400 cm^{-1} and at a resolution of 4 cm^{-1} , were activated via Bruker OPUS
140 spectroscopic software. Identification involved a comparison of sample transmittance
141 spectra with libraries of reference spectra.

142

143 *2.3. XRF analysis*

144 Samples were analysed for a suite of elements, of which Cd, Pb and Br are the focus
145 of the present study, by energy dispersive FP-XRF using a battery-powered Niton
146 XRF analyser (model XL3t 950 He GOLDD+) configured in a 'plastics' mode.

147 Although the general approach has been described and independently validated

148 elsewhere (Turner and Solman, 2016), the current study makes use of the instrument's

149 'small-spot' facility for probing samples smaller than the 10-mm diameter of the
150 detector window. Here, 3-mm collimation is applied to the beam by means of a
151 tapered, tungsten alloy tube of appropriate distal exit aperture diameter that is aligned
152 over the x-ray source via a geared shutter mechanism.

153

154 In the laboratory, the instrument was fixed, nose-upwards, into a Thermo Fisher
155 Scientific accessory test stand (PN 420-017) and connected to a laptop computer via
156 USB. Each sample was measured for thickness through the flattest (measurement)
157 surface using digital callipers before being placed on a 20 cm², 3.6 µm thick polyester
158 film that was suspended above the detector window. The sample was positioned
159 centrally over the window using plastic tweezers, a process aided by referring to real-
160 time video footage projected on the laptop through a CCD camera located next to the
161 x-ray source. On closing the shield of the stand, measurements, with appropriate
162 thickness correction, were activated through the laptop for 60 seconds, comprising
163 periods of counting of 40 seconds at 50 kV and 40 µA and 20 seconds at 20 kV and
164 100 µA. Spectra were quantified by fundamental parameters to yield elemental
165 concentrations on a dry weight basis (in µg g⁻¹) and a counting error of 2σ (95%
166 confidence) that were downloaded to the laptop using Niton data transfer (NDT) PC
167 software.

168

169 Limits of detection, defined as 3σ and calculated by fundamental parameters, varied
170 according to the precise density, shape, thickness and composition of sample, and
171 ranged from about 30 to 50 µg g⁻¹ for Cd, 5 to 20 µg g⁻¹ for Pb and 4 to 10 µg g⁻¹ for
172 Br. Multiple analyses ($n = 20$) of two Niton reference plastics that had been
173 impregnated with Cd, Pb and Br (PN 180-554, batch SN PE-071-N) and Cd and Pb

174 (PN 180-619, LOT#T-18) revealed measured concentrations that were within 5% of
175 certified values.

176

177 2.4. PBET

178 In order to evaluate element bioaccessibility in the microplastics, ten samples of
179 varying colour, appearance and elemental composition (based on XRF analysis) were
180 subjected to a marine avian physiologically-based extraction test (PBET) (Turner and
181 Lau, 2016). The extraction was modelled on the digestive characteristics of the
182 proventriculus-gizzard of the northern fulmar, *Fulmarus glacialis*, a procellariform
183 known to ingest substantial quantities of microplastics. Briefly, digestive fluid was
184 prepared by dissolving 10 g of pepsin (lyophilised powder from porcine gastric
185 mucosa; Sigma-Aldrich) into one litre of 0.1 M NaCl solution and adjusting the pH by
186 addition of 1 M HCl to 2.5. Selected samples were weighed into individual 60 ml
187 screw-capped polypropylene centrifuge tubes to which 40 ml of extraction fluid was
188 added. All tubes, including a control containing no solid material, were then capped
189 and incubated in a shaking water bath set at 100 rpm and at 40 °C. After a period of
190 about seven days (168 h), 1 ml aliquots of extract from each tube were pipetted into
191 individual Sterilin tubes where they were diluted to 5 ml with 2% HNO₃ and stored at
192 4 °C and in the dark pending analysis.

193

194 2.5. Analysis of extracts

195 Cadmium, Pb and Br were determined in the PBET extracts by collision cell-ICP-MS
196 using a Thermo X-series II (Thermo Elemental, Winsford UK) with a concentric glass
197 nebuliser and conical spray chamber. The ICP was calibrated externally using five
198 mixed standards and five blanks prepared in 2% HNO₃ and operated under conditions

199 described elsewhere (Turner and Holmes, 2015). Limits of detection, based on three
200 standard deviations arising from blank measurements, were about $0.5 \mu\text{g L}^{-1}$ for Cd
201 and Pb and about $10 \mu\text{g L}^{-1}$ for Br, or, on a dry weight basis and for a representative
202 mass of microplastic of 35 mg, about $0.6 \mu\text{g g}^{-1}$ and $11 \mu\text{g g}^{-1}$, respectively.

203

204 **3. Results and Discussion**

205 *3.1. Sample characteristics*

206 In total, 924 samples of microplastic that satisfied the size criteria outlined above
207 were analysed by FP-XRF, with a summary of their categorisation and colour coding
208 given in Table 1. The total mass of material retrieved from Whitsand ($n = 436$) was
209 16.35 g, with an average individual mass of microplastic of 37.2 mg, while from
210 Woolacombe ($n = 488$), the total mass was 16.50 g with an average individual mass of
211 33.8 mg. On both beaches, the only identifiable pieces of primary plastic were
212 cylindrical and disk-shaped pre-production pellets, and these comprised about 90%
213 and 75% of all samples from Whitsand and Woolacombe, respectively. Colour coding
214 revealed that the majority of primary, pelletised plastics from both beaches were
215 white-clear (including translucent and off-white), with the next most abundant colours
216 being black and orange-brown; the latter category included a large number of aged,
217 translucent pellets whose distinctive amber colouration is likely to have been caused
218 by the photo-oxidative formation of by-products having quinonoidal structures (Endo
219 et al., 2005). The most common colours encountered in secondary, fragmented and
220 irregularly-shaped microplastics were white and red, while colour differences between
221 the two beaches included a relatively high number of purple pellets from Whitsand,
222 and the absence of red and grey primary plastics from Woolacombe.

223

224 FTIR analysis revealed that most samples considered were polyethylene or
225 polypropylene, with the remainder being of polystyrene construction. Out of all
226 samples analysed by XRF, and based on chlorine content measured at 2.62 and 2.82
227 keV, only three (white fragments from Woolacombe) were classified as polyvinyl
228 chloride (PVC). Significantly, therefore, it would appear that nearly all samples have
229 a density less than that of sea water across its normal temperature range.

230

231 *3.2. Occurrence and concentrations of Cd, Pb and Br*

232 Also shown in Table 1 are the numbers of microplastics in which Cd, Pb and Br were
233 detected by XRF. Overall, Cd was detected in about 7% of all samples, and was more
234 abundant on a number basis in pellets and on a percentage basis in fragments.

235 Although the number of cases in which Cd was detected was greatest among white
236 microplastics, the highest percentages of detectable Cd were encountered in purple
237 and red samples. Within the purple category, Cd was detected exclusively in
238 production pellets, while in red samples the metal was detected in both pellets and
239 fragments.

240

241 Lead was detected in 7.5% of all samples analysed and, like Cd, was more abundant
242 on a number basis in plastic pellets and on a percentage basis in plastic fragments.

243 Regarding colour categories, the number of cases in which Pb was detected was
244 greatest among black samples, while the highest percentages of detectable Pb were
245 encountered in grey, purple and black plastics; Pb occurred least frequently in white-
246 clear microplastics, with only one out of nearly 500 pellets of this colour containing
247 measurable quantities of the metal.

248

249 Bromine was detected in more than 10% of all samples analysed, and in a greater
250 number of pellets than fragments but in similar percentages of the two types of
251 microplastic. Overall, and on both a number basis and percentage basis, Br was most
252 frequently detected amongst samples that were neutrally-coloured (black, grey and
253 white-clear).

254

255 Table 2 summarises the occurrences and co-associations (but not correlations) of the
256 three elements on both beaches and among the two types of microplastic. Thus, in
257 total, one or more of the elements was encountered in 182 samples, or about 20% of
258 all microplastics analysed. Cadmium and Pb were detectable in the same sample in
259 eight cases, Cd and Br in three cases and Pb and Br in 20 cases, while all three
260 elements co-existed in five, additional cases. Co-associations were more common at
261 Whitsand ($n = 28$) than at Woolacombe ($n = 8$) and, overall, were most frequent
262 among black pellets ($n = 16$).

263

264 The distribution of Cd, Pb and Br concentrations for both beaches and among the two
265 types of microplastic is shown in Table 3. For Cd, concentrations spanned two orders
266 of magnitude and from about 40 to 3400 $\mu\text{g g}^{-1}$, with mean and median concentrations
267 higher in plastic fragments than in production pellets. Although the highest Cd
268 concentration was recorded in a grey pellet, most samples containing concentrations
269 above 1000 $\mu\text{g g}^{-1}$ were red in colour, with concentrations exceeding 100 $\mu\text{g g}^{-1}$, or
270 the RoHS (2006) maximum level for the metal, also encountered in green, black and
271 orange microplastics.

272

273 Regarding Pb, concentrations spanned more than three orders of magnitude and from
274 about 3 to over 5000 $\mu\text{g g}^{-1}$. Mean and median concentrations were higher in
275 fragments than in primary microplastics, with concentrations in excess of the RoHS
276 (2006) maximum Pb level of 1000 $\mu\text{g g}^{-1}$ encountered in a number of red, yellow and
277 green fragments and in a single, yellow pellet.

278

279 Concentrations of Br spanned more than three orders of magnitude and from about 4
280 to over 13,000 $\mu\text{g g}^{-1}$. Median concentrations were similar among both fragments and
281 pellets from the two beaches, with an elevated mean concentration in Whitsand
282 fragments attributed to an exceptionally high concentration in a grey pellet.

283 Concentrations exceeded the RoHS (2006) limit values for various brominated
284 compounds (but not Br itself) of 1000 $\mu\text{g g}^{-1}$ in six cases, and samples containing the
285 halogen at concentrations above 100 $\mu\text{g g}^{-1}$ were restricted to samples of neutral
286 colour.

287

288 *3.3. Relationships with other elements and composition of additives*

289 Despite lack of inter-element correlations among Cd, Pb and Br, correlations were
290 observed with additional elements analysed by XRF. Thus, concentrations of Pb in
291 pellets and fragments from both beaches were highly correlated with concentrations of
292 Cr, where detected, and with a slope derived from linear regression of about 2 (Figure
293 2). The majority of samples conforming to this relationship were red fragments and
294 yellow fragments and pellets, qualitatively consistent with the presence of the
295 pigments, lead chromate molybdate sulphate red ($\text{Pb}(\text{Cr,S,Mo})\text{O}_4$) and lead chromate,
296 (PbCrO_4), respectively. In addition to Pb, these pigments contain Cr in its hexavalent
297 form (although XRF is not able to verify elemental speciation) which, because of its

298 carcinogenicity and toxicity to reproduction, is also both hazardous and restricted in
299 plastics (Hansen et al., 2010; European Chemicals Agency, 2016), with an RoHS
300 (2006) limit value of 1000 $\mu\text{g g}^{-1}$.

301

302 Concentrations of Cd in the microplastics were correlated with concentrations of Se,
303 where detected, and with a slope of about 5 (Figure 3). Here, samples were restricted
304 to both pellets and fragments that were red or orange in colour, consistent with the use
305 of the pigment, cadmium sulphoselenide, a solid solution of CdS and CdSe whose
306 colour can be bright orange or bright red depending on the ratio of Se to S. Although
307 no hazards have been classified for the pigment itself by the European Chemicals
308 Agency (2016), compounds of both Cd and Se are known to be highly toxic (Ayres
309 and Hellier, 1998).

310

311 Bromine concentrations were highly correlated with concentrations of Sb, where
312 detected, and with a slope of about 2 derived from linear regression analysis of the
313 data (Figure 4); moreover, microplastics exhibiting this relationship were restricted to
314 pellets that were neutrally-coloured, and mainly black. These observations are
315 consistent with microplastics impregnated with both a variety of brominated
316 compounds as halogenated flame retardants and oxides of antimony as fire
317 suppressant synergists (Dupont et al., 2016). However, although the mass ratio of Br
318 to Sb is similar to that employed in the plastic casings of heat-generating electronic
319 and electrical goods (Papazoglou, 2004), the concentrations of Br measured herein are
320 too low to provide adequate flame retardancy. This suggests that pellets are not the
321 feedstock for the electronics industry itself but have been derived from diluted,

322 recycled electrical waste and are destined for the more general manufacturing market
323 (Leslie et al., 2016).

324

325 *3.4. Implications for plastic-consuming seabirds*

326 Previous research has shown that trace metals are able to interact with microplastics
327 suspended in sea water through adsorption onto the aged and coated surface, with
328 resulting concentrations from this process that are typically below $1 \mu\text{g g}^{-1}$ (Rochman
329 et al., 2014; Turner and Holmes, 2015; Brennecke et al., 2016). More recently,
330 however, XRF analysis of marine litter has revealed considerably higher
331 concentrations of metals and other hazardous elements in many plastics that are an
332 inherent part of the polymeric matrix (Turner, 2016). The present study has confirmed
333 that this inherent load is also encountered in beached microplastics of both primary
334 and secondary origin. Since the densities of the majority of samples analysed herein
335 are less than the density of sea water they are positively buoyant and amenable to
336 seabirds and other organisms that mistake them for food while filtering, skimming,
337 hydroplaning or diving (Acampora et al., 2014).

338

339 The total quantity of Cd, Pb and Br per g of microplastic was estimated for Whitsand
340 and Woolacombe from the overall mean elemental concentration (for pellets and
341 fragments combined) multiplied by the fraction of total samples in which the
342 corresponding element was detected. For Cd and Pb, estimates of $30 \mu\text{g}$ were obtained
343 for both beaches, while for Br, estimates of $59 \mu\text{g}$ and $37 \mu\text{g}$ were obtained for
344 Whitsand and Woolacombe, respectively. The quantities of plastic-bound Cd and Pb
345 exceed the respective mean quantities in local beach sand ($< 1 \mu\text{g}$ and about $10 \mu\text{g}$)
346 and in local crab tissue (1 and $2 \mu\text{g}$) (Schuwerack et al., 2007), the latter representing

347 an important dietary component of many seabirds (Schwemmer and Garthe, 2005).
348 Comparisons for Br are not as straightforward since its occurrence in microplastics is
349 attributed to the presence of a complex mixture of halogenated flame retardants.
350 However, that the concentration of Br as brominated flame retardants in marine
351 sediment and shellfish is generally a few tens of ng g^{-1} or lower (Munschy et al.,
352 2015; Suhring et al., 2015) suggests a quantity of equivalent Br in microplastic that is
353 orders of magnitude greater.

354

355 Critical to the uptake of Cd, Pb and Br from ingested microplastics is the accessibility
356 or mobility of the elements from the polymeric matrix. Results of the avian PBETs
357 were rather limited in that concentrations of the three elements in the digestive fluid
358 after a 168-h period of incubation were close to the corresponding detection limits of
359 the ICP-MS. Nevertheless, Pb was detected in the digests of two yellow fragments
360 (one polyethylene and one polypropylene) containing measurable Cr, with
361 concentrations of about 4 and 8 $\mu\text{g g}^{-1}$ or bioaccessibilities (relative to the respective
362 total Pb concentrations returned by the XRF) of about 0.1% and 0.2%. Cadmium was
363 detected in the digest of one red polyethylene fragment containing measurable Se, and
364 at a concentration of 52 $\mu\text{g g}^{-1}$ and with a bioaccessibility of about 2%. Thus,
365 accessible concentrations of Pb in the microplastics tested are greater than but a
366 similar order of magnitude to concentrations of dietary Pb (based on its presence in
367 local crab meat) while accessible concentrations of Cd are about fifty times greater
368 than dietary concentrations. These comparisons suggest that a seabird having 1 g of
369 coloured microplastics containing lead chromate or cadmium sulphoselenide trapped
370 in its gizzard-proventriculus for a period of seven days would be exposed to the same
371 quantity of Pb or Cd from the ingestion of about 4 g or 50 g of food.

372

373 **4. Conclusions**

374 This study has shown that the abundance and type of non-porous, moulded
375 microplastics from two sandy beaches of different aspect on the south west peninsula
376 of England are broadly similar. Specifically, the stock is composed of primary plastics
377 in the form of production pellets and smaller quantities of secondary, unidentifiable
378 fragments. Cadmium and Pb were detected in about 7% of over 900 samples analysed
379 by XRF, with the highest concentrations usually encountered in red and yellow pellets
380 or fragments and in association with Se and Cr, respectively (or as the coloured
381 pigments, cadmium sulphoselenide and lead chromate, respectively). Bromine was
382 detected in over 10% of samples analysed but was mainly encountered in neutrally-
383 coloured pellets; a co-association with Sb is consistent with the occurrence of a
384 variety of halogenated flame retardants in primary plastics that had been recycled
385 from the casings of heat-generating electronic equipment. Although the avian
386 bioaccessibilities of Cd, Pb and Br in microplastics are low, accessible concentrations
387 of Cd and Pb in brightly coloured fragments may exceed corresponding
388 concentrations in the seabird diet by factors of 50 and 4, respectively.

389

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393

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494 Table 1: The number of primary pellets and secondary fragments retrieved from 10 m sections of each
 495 beach, along with their colour distributions and the occurrence of Cd, Pb and Br.

	black	blue	green	grey	orange-brown	red	purple	white-clear	yellow	total
Whitsand pellets	55	16	15	13	34	4	15	213	22	387
Whitsand fragments	1	9	4	4	5	13	0	11	2	49
Woolacombe pellets	36	10	6	9	30	0	1	266	7	365
Woolacombe fragments	1	15	13	0	6	18	1	63	6	123
total	93	50	38	26	75	35	17	553	37	924
%	10.1	5.4	4.1	2.8	8.1	3.8	1.8	59.8	4.0	100
cadmium										
Whitsand pellets	5	2	1	1	1	4	12	6	0	32
Whitsand fragments	0	0	1	1	2	2	0	0	0	6
Woolacombe pellets	3	0	0	1	1	0	0	10	0	15
Woolacombe fragments	1	1	0	0	1	3	0	5	0	11
total	9	3	2	3	5	9	12	21	0	64
%	9.7	6.0	5.3	11.5	6.7	25.7	70.6	3.8	0.0	6.9
lead										
Whitsand pellets	14	2	0	5	1	0	5	0	1	28
Whitsand fragments	1	4	1	1	0	2	0	1	2	12
Woolacombe pellets	10	3	2	2	0	0	0	0	0	17
Woolacombe fragments	1	2	1	0	1	3	0	2	2	12
total	26	11	4	8	2	5	5	3	5	69
%	28.0	22.0	10.5	30.8	2.7	14.3	29.4	0.5	13.5	7.5
bromine										
Whitsand pellets	22	2	2	9	5	0	0	10	0	50
Whitsand fragments	1	3	0	1	1	1	0	2	0	9
Woolacombe pellets	13	0	1	3	1	0	0	10	0	28
Woolacombe fragments	1	1	4	0	1	0	0	2	0	9
total	37	6	7	13	8	1	0	24	0	96
%	39.8	12.0	18.4	50.0	10.7	2.9	0.0	4.3	0.0	10.4

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497 Table 2: Number of cases in which Cd, Pb and Br co-existed, along with the total
 498 number of samples in which one or more of the elements was detected.

	Cd-Pb	Cd-Br	Pb-Br	Cd-Pb-Br	Cd, Pb, Br
Whitsand pellets	9	3	13	3	85
Whitsand fragments	2	1	3	0	18
Woolacombe pellets	1	3	5	1	49
Woolacombe fragments	1	1	1	1	30
total	13	8	22	5	182

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505 Table 3: The distribution of Cd, Pb and Br concentrations among the samples (in $\mu\text{g g}^{-1}$)
 506 ¹⁾ and the colour category in which the maximum elemental concentration was
 507 recorded.

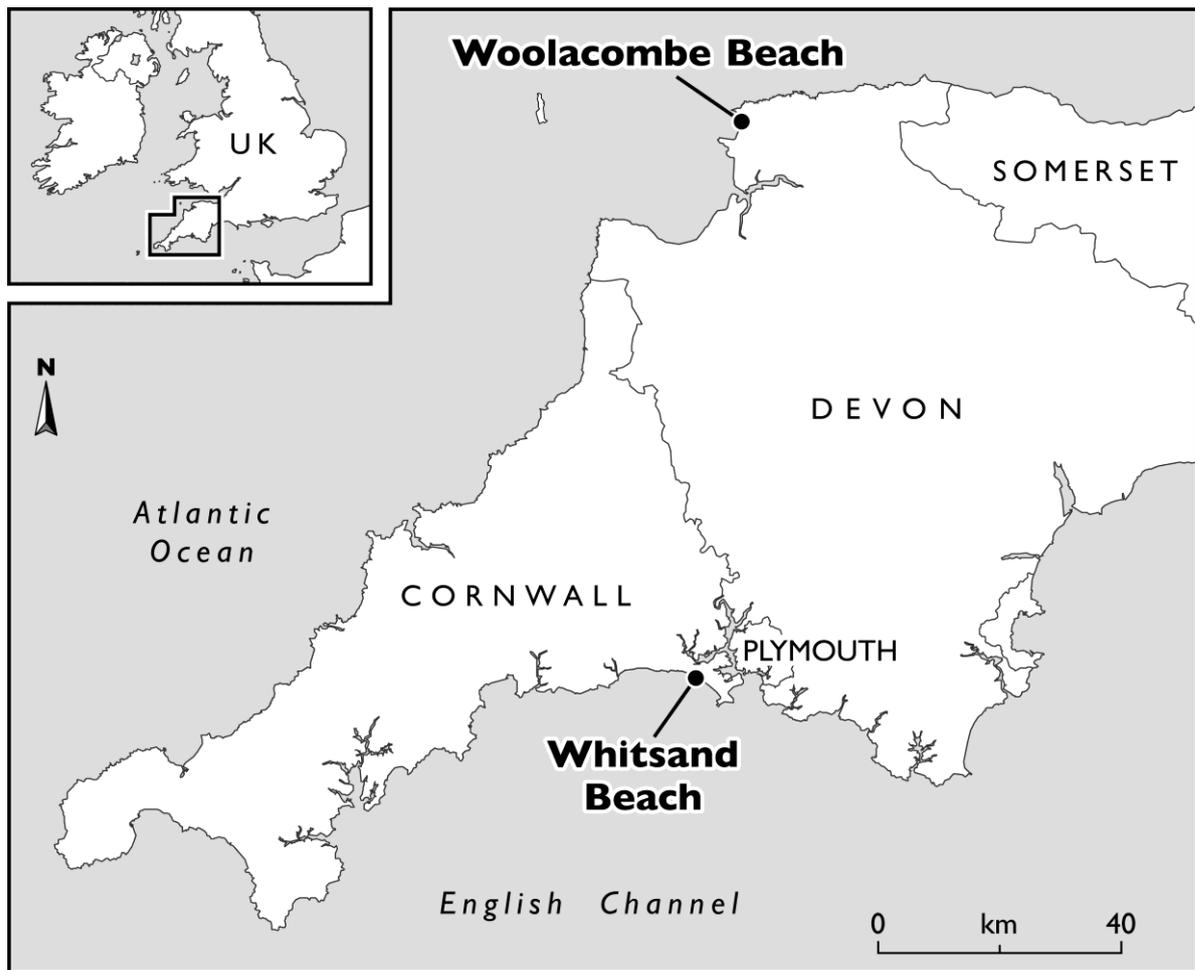
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	< 10	10-10 ²	10 ² -10 ³	10 ³ -10 ⁴	> 10 ⁴	mean	median	min	max	max colour
cadmium										
Whitsand pellets	0	23	6	3	0	232	64	38	1980	red
Whitsand fragments	0	1	2	3	0	895	974	66	1610	red
Woolacombe pellets	0	13	1	1	0	334	64	39	3390	grey
Woolacombe fragments	0	3	3	5	0	968	509	45	2622	red
lead										
Whitsand pellets	1	22	4	1	0	241	36	3.4	5330	yellow
Whitsand fragments	0	4	5	3	0	554	241	17	1660	red
Woolacombe pellets	0	14	3	0	0	108	36	12	941	black
Woolacombe fragments	0	4	4	4	0	1210	605	32	4820	yellow
bromine										
Whitsand pellets	18	21	8	3	0	241	18	4.0	4590	black
Whitsand fragments	0	8	0	0	1	1490	18	10	13,300	grey
Woolacombe pellets	5	17	5	1	0	283	25	6.6	4980	white
Woolacombe fragments	3	5	0	1	0	247	18	7.9	2050	white

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511 Figure 1: Locations in south west England for the sampling of microplastics.



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514 Figure 2: Concentration of Pb versus concentration of Cr in pellets (●) and fragments
515 (▲) from Whitsand and in pellets (○) and fragments (Δ) from Woolacombe.

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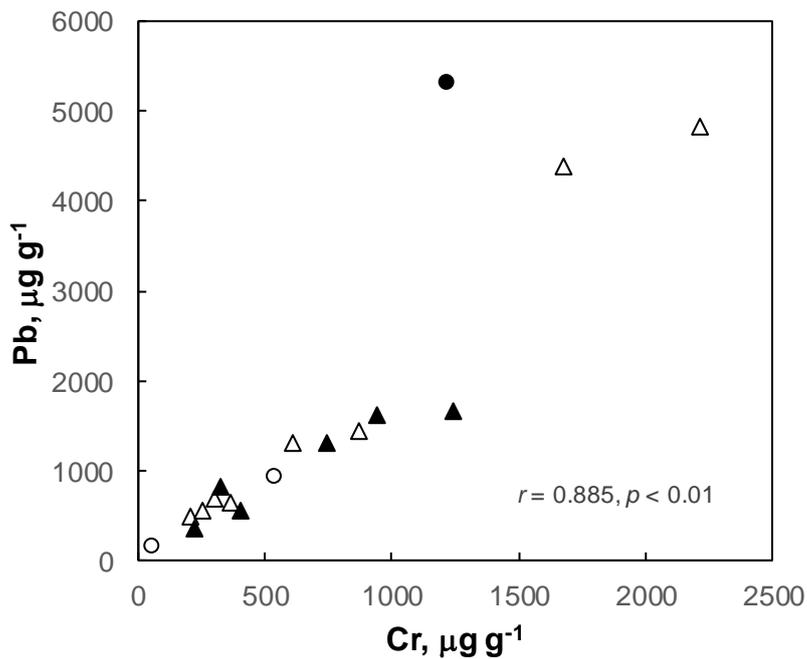
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526 Figure 3: Concentration of Cd versus concentration of Se in pellets (●) and fragments
527 (▲) from Whitsand and in pellets (○) and fragments (Δ) from Woolacombe.

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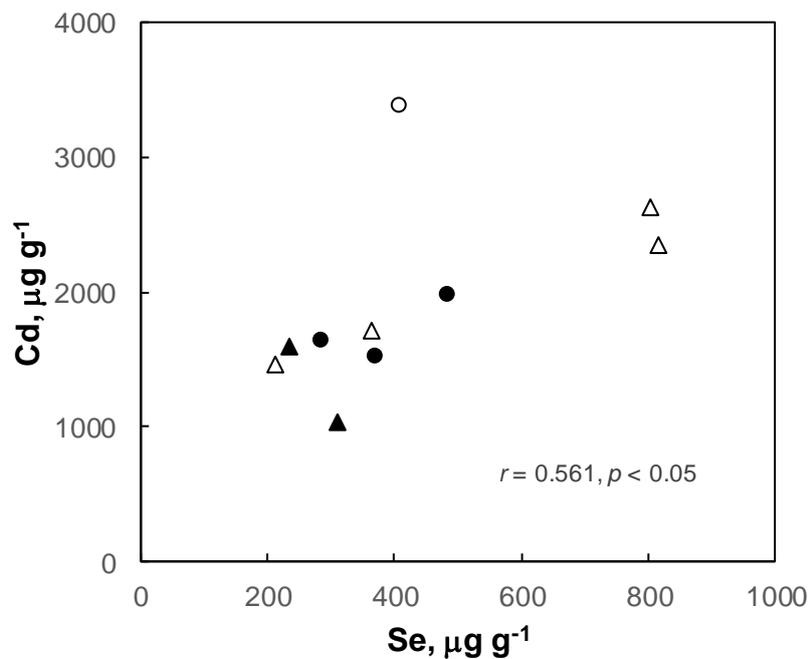
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539 Figure 4: Concentration of Br versus concentration of Sb in pellets from Whitsand (●)
540 and Woolacombe (○).

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