

1 **Marine pollution from pyroplastics**

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21 **Abstract**

22 Items of marine plastic litter are conventionally classified as primary or secondary, depending on
23 whether they are distinct objects or angular fragments, respectively. “Pyroplastic” is an additional
24 type of plastic litter that is described here, based on observations made on beached samples from
25 south west England. Pyroplastics are derived from the informal or more organised burning of
26 manufactured plastics and may be angular “plastiglomerates”, comprising pieces of plastic debris
27 within a matrix, or rounded plastic “pebbles”, where agglomerated material has been weathered
28 and smoothed into more brittle and neutrally-coloured geogenic-looking clasts. Beached
29 pyroplastics are usually positively buoyant because of a polyethylene or polypropylene matrix, and
30 exhibit a bimodal mass distribution attributed to the breakage of larger clasts (> 20 mm) into smaller
31 fragments (<5 mm). XRF analysis reveals variable quantities of Pb in the matrix (up to 7500 $\mu\text{g g}^{-1}$),
32 often in the presence of Cr, implying that material in many samples pre-dates restrictions on the use
33 of lead chromate. Low concentrations of Br and Sb relative to pieces of manufactured plastics in the
34 marine environment suggest that pyroplastics are not directly or indirectly derived from electronic
35 plastic. Calcareous worm tubes on the surfaces of pyroplastics dense enough to be temporarily
36 submerged in the circalittoral zone are enriched in Pb, suggesting that constituents within the matrix
37 are partly bioavailable. Evading ready detection due to their striking visual similarity to geogenic
38 material, pyroplastics may contribute to an underestimation of the stock of beached plastics in many
39 cases.

40 **Keywords:** pyroplastic; plastiglomerates; marine litter; weathering; XRF; lead

41

42 **1. Introduction**

43 Marine pollution from plastics is a growing global problem that results from a complex interplay
44 between demand, consumption, disposal and recycling of the material. Because of their persistence,
45 hydrophobicity and low density, plastics in the marine environment have a variety of well-
46 established economic, visual and ecological impacts (Wilcox et al., 2016; Krelling et al., 2017) in
47 addition to emerging potential consequences on health and food security (Santillo et al., 2017;
48 Barboza et al., 2018).

49 While suspended, deposited or beached, plastics undergo gradual and progressive mechanical,
50 chemical and photo-oxidative breakdown (Song et al., 2017; Cai et al., 2018). Consequently, plastics
51 may be classified as primary, bearing the recognisable integrity of the original plastic structure, or
52 secondary, where objects have been broken down into smaller fragments or pieces whose primary

53 source is often difficult to establish. Examples of primary plastics include shot-gun cartridges, bottles
54 and bottle tops, straws, cutlery, pellets, pens, cigarette lighters, cotton buds, food packages, toys,
55 strapping and rope.

56 Recently, an additional type of non-manufactured marine plastic was described by Corcoran et al.
57 (2014). “Plastiglomerates” are indurated, multi-composite materials made hard by the agglutination
58 of rock and other materials with molten plastic, the source of the latter being attributed to the
59 informal, open (e.g. campfire) burning of plastic waste. Plastiglomerates may be classified as in situ,
60 where the material is adhered to a rocky substrate, or clastic, where conglomerates are discrete
61 entities. This type of marine plastic is, therefore, composed of a melted polymeric matrix of
62 unknown origin(s) that encapsulates sand, rock, shell fragments, wood and various pieces of
63 anthropogenic debris, with a resultant bulk density of about 2 to 3 g cm⁻³.

64 Over the past two years, the Cornwall Plastic Pollution Coalition, a group of voluntary organisations,
65 has reported the occurrence of plastics on beaches throughout the county of Cornwall, south west
66 England, that have undergone burning in situ or ex situ. Their appearance is similar to the
67 plastiglomerates described by Corcoran et al. (2014) but encapsulated material is usually plastic
68 (rather than rock or sand) and many samples do not appear to have agglomerated any significant
69 quantities of extraneous material. Consequently, these samples have a relatively low bulk density
70 and most will float in sea water. “Pyroplastics”, as they are hereafter referred to, may be encrusted
71 on rocky outcrops towards the back beach and cliffs, or encountered along the strandline as distinct
72 clasts, with crusts eventually breaking off and becoming a series of clasts.

73 In the present paper, a variety of pyroplastics collected from various beaches are described and
74 defined, with particular emphasis on material retrieved from Whitsand Bay, a large, protected,
75 sandy and southwest-facing embayment to the west of Plymouth (Uncles et al., 2015; Figure 1). A
76 selection of samples is subject to analysis by Fourier Transform Infrared (FTIR) spectrometry in order
77 to define their polymeric makeup and by x-ray fluorescence (XRF) spectrometry in order to identify
78 inorganic additives and co-contaminants. Attempts are made to determine the origin and age of
79 pyroplastics and to evaluate their potential environmental impacts and chemical hazards.

80

81 **2. Methods**

82 Through calls and descriptions on social media from mid-2018 to early 2019, pyroplastics were
83 reported on and retrieved from sandy beaches throughout the county of Cornwall, including
84 Whitsand Bay (Figure 1), and then from places farther afield, both in the UK and overseas. As part of

85 organised beach cleans or from informal beach-combing about 400 samples out of several thousand
86 collected from the strandline, foreshore and rocky outcrops were forwarded to the University of
87 Plymouth. Recording the abundance of pyroplastics was not an objective of the present study and
88 was confounded by the difficulty in identifying material (especially where they assumed a geological
89 appearance), but during a systematic clean of a beach on Whitsand Bay it was noted that several
90 samples were often retrieved per metre of strandline.

91 In the laboratory, a subset of 165 samples from the beaches of Whitsand Bay and 30 samples
92 collected from elsewhere were classified by density according to whether or not they floated in tap
93 water at room temperature contained in a 30 cm diameter glass dish or a half-filled 30-L laboratory
94 sink. Cleaned and dried samples were then photographed, weighed on a five-figure Sartorius Genius
95 balance and measured for primary diameter (longest axis; d_1) and secondary diameter (shortest axis
96 but through the thickest part; d_2) using digital callipers. Samples were coded for colour (or colours)
97 and the abundance and nature of encapsulated materials.

98 Samples were subsequently analysed for various elements that are indicative of additives,
99 contaminants and extraneous material (Br, Cd, Cl, Cr, Cu, Fe, Pb, Sb, Zn) using a battery-operated
100 Niton XL3t He GOLDD+ XRF spectrometer described in detail elsewhere (Turner and Solman, 2016).
101 The instrument was configured nose upwards in a laboratory test-stand and activated remotely by a
102 laptop. The region of the sample to be probed (usually the central part with the flattest and
103 smoothest face) was placed above the detector window and counted in a standardless plastics mode
104 with thickness correction (where sample thickness was less than 10 mm) for 20 seconds at 40 μ A
105 and 50 kVp and 10 seconds at 100 μ A and 20 kVp. Spectra arising from sample counting were
106 quantified by fundamental parameter coefficients to yield elemental concentrations in $\mu\text{g g}^{-1}$ and a
107 measurement error of 2σ (95% confidence). For samples too large to fit in the test stand (> 20 cm in
108 length) measurements were made likewise but the instrument was operated hand-held using the
109 trigger mechanism with samples cradled in a folded radiation apron placed on a stainless steel
110 bench. Elements were also determined in the calcareous worm tubes attached to two pyroplastics
111 and, as a non-plastic control of similar density, a tarball. Here, the crushed contents of five \sim 100 mg
112 deposits scraped from each sample were analysed by XRF in a higher density soils mode for counting
113 periods of 45 seconds at 40 μ A and 50 kVp and 15 seconds at 100 μ A and 20 kVp.

114 For quality assurance and instrument performance purposes, two 13 mm-thick Niton reference
115 plastics that had been impregnated with various elements (PN 180-554 batch SN PE-071-N and PN
116 180-619 LOT#T-18) were analysed at regular intervals throughout each measurement session;
117 concentrations returned by the XRF were always within 15% (and usually within 10%) of certified

118 values. Precision, evaluated by quintuplicate measurements of the same area of six samples of
119 varying size, colour and appearance, ranged from < 5% for Cl, Fe and Pb to about 15% for Cd and Sb.

120 Thirty of the Whitsand pyroplastics and five samples collected elsewhere that had been
121 characterised above were analysed by attenuated total reflectance FTIR (ATR-FTIR) spectrometry
122 using a Bruker Vertex 70. A stainless steel scalpel was employed to scrape a piece of a few mg from
123 different regions of the surface and, in some cases, the subsurface (below 1 mm). Samples were
124 clamped against the diamond crystal before spectra were acquired with 16 scans in the region 4000
125 to 600 cm^{-1} and at a resolution of 4 cm^{-1} . After being smoothed, baseline-corrected and normalised
126 via Bruker OPUS 7 software, spectra were compared with libraries of reference spectra for the
127 identification of component polymers and were visually inspected for signs of polymer modification.

128

129 **3. Results**

130 *3.1. Visual and physical characteristics*

131 Pyroplastics were supplied from beaches in Cornwall and from the Orkneys (Scotland), County Kerry
132 (Ireland) and north west Spain, and were reported on the coast of Vancouver (Canada). Samples
133 were broadly similar in appearance, colour, size range and chemical makeup, but for the purposes of
134 further classification and quantification, pyroplastics are restricted to those from the beaches of
135 Whitsand Bay where a greater number had been collected in a more systematic manner.

136 Figure 2 and Figure S1 illustrate pyroplastics collected from Whitsand Bay from which a subset was
137 forwarded to the University, while Figure 3 shows six larger clasts, graded according to degree of
138 agglomeration and angularity, that had been sampled from this subset. Pyroplastics are distinctly
139 different from manufactured plastics, having a geological or industrial appearance, often being
140 agglomerated and heterogeneous, and generally being considerably thicker and less angular than
141 secondary fragments. Pyroplastics are defined by an amorphous matrix formed by the burning or
142 melting of plastic that is usually characterised by a single, neutral colour (black-charcoal-grey, off-
143 white or brown), with occasional hues of green, blue, pink or yellow, and is accompanied by cracks
144 and fractures, pits and cavities. Breaking the brittle matrix usually revealed a brighter and shinier
145 internal structure (for example, a charcoal exterior would be accompanied by an anthracite-looking
146 interior).

147 Samples (a) through to (f) in Figure 3 are of similar dimensions but exhibit decreasing roundness and
148 increasing angulation and roughness and an accompanying increase in apparent degree of
149 association of the melted matrix with extraneous material. The more rounded pyroplastics of any

150 sphericity (but usually high) that appear to contain relatively little agglomerated extraneous material
 151 (similar to samples (a) to (c)) could be considered as singular entities or “plastic pebbles”, while
 152 more angular pyroplastics of generally low sphericity (similar to samples (d) to (f)) could be
 153 described better as “plastiglomerates”. Agglomerated extraneous material is mainly plastic, and
 154 includes pellets, remains of straws, food packaging, bottle tops and rope, and fragments of unknown
 155 origin. Extraneous plastics of varied colours and shapes may be bonded (or fused) to the surface of
 156 the matrix or partially encapsulated, and may be intact or partly melted themselves.

157 Despite this classification, there is clearly a continuum of pyroplastics that makes distinction
 158 imprecise; moreover, occasional samples have additional characteristic features. For example, a few
 159 pebble-like pyroplastics had long filamentous plastic fragments fused at one end to the matrix
 160 (Figure S2), while some large plastiglomerates were extremely flat and rough and appeared to be
 161 composed of multiple matrices of different (but mainly neutral) colours or textures.

162 **Table 1:** Summary statistics defining the mass and dimensions of the pyroplastic samples from
 163 Whitsand Bay ($n = 165$).

	mass, g	d_1 , mm	d_2 , mm	d_1/d_2
median	0.358	12.9	6.58	2.04
minimum	0.097	5.64	3.72	0.422
maximum	274	240	40	7.50
kurtosis	69.9	31.6	6.18	11.3
skewness	7.61	4.88	2.39	2.82

164

165
 166 Table 1 shows summary statistics defining the mass and dimensions of the subset of 165 pyroplastics
 167 supplied from the beaches of Whitsand Bay. Distributions of all measures were skewed to the right
 168 with heavy tails or outliers. Mass ranged from less than 100 mg to about 270 g, with a median value
 169 that was about 350 mg and a distribution that was bimodal (with relatively few clasts between 5 and
 170 10 g). Primary diameter (d_1) ranged from about 6 to 240 mm (median = 12.9 mm) and secondary
 171 diameter (d_2) ranged from about 4 to 40 mm (median = 6.6 mm), with the two measures combined
 172 to give aspect ratios (d_1/d_2) ranging from 0.42 to 7.5 (median = 2.0). In general, higher aspect ratios
 173 were accompanied by more angular plastiglomerates that appeared to contain relatively high
 174 quantities of visible extraneous agglomerated plastics while lower aspect ratios were associated with
 175 rounded pebbles containing relatively few (or no) visible extraneous plastics.

176 All pyroplastics were less dense than water at room temperature with the exception of five relatively
 177 large clasts. Three of the latter samples were plastiglomerates that had extensive and curved

178 accumulations of calcareous deposits from the tube-building worm, *Spirobranchus triqueter*, on at
 179 least one face, with matted patches of what appeared to be the bryozoan, *Electra pilosa*, attached to
 180 one sample. The remaining two denser clasts were smooth and pebble-like with no visible
 181 extraneous material on their surfaces.

182 *3.2. Chemical characteristics*

183 Spectra arising from ATR-FTIR analysis of different regions of selected pyroplastics, and as
 184 exemplified in Figure 4, revealed that the polymeric matrix consisted of either (or both) polyethylene
 185 or polypropylene, even in samples that were denser than tap water. FTIR results also suggested the
 186 presence of non-aromatic plasticisers and terminal methyl groups (indicative of chain breakage) in
 187 many cases, but no clear spectral differences were evident between the surface and interior of any
 188 sample tested.

189 XRF analysis of the entire subset of samples from Whitsand Bay indicated that no pyroplastics were
 190 constructed in whole of polyvinyl chloride (PVC), but that one distinctive object encapsulated by a
 191 large plastiglomerate was PVC-based. XRF also revealed a variety of elements indicative of polymeric
 192 additives and residues and small quantities of inorganic extraneous matter (e.g. sand) in some cases.
 193 Concentrations of elements in the central surface region of the melted matrix (or in highly
 194 agglomerated samples, the most abundant matrix material) are shown in Table 2. Here, the number
 195 of cases in which each element was detected is shown along with an indicative range of detection
 196 limits (which vary for a given element dependent on sample thickness and composition), while
 197 statistical parameters are the same as those reported in Table 1.

198 **Table 2:** Detection frequency, indicative limit of detection (LOD) and concentration summary
 199 statistics for the elements in the pyroplastic samples from Whitsand Bay ($n = 165$). Also shown are
 200 the number of cases in which elemental concentrations exceed or potentially exceed their
 201 corresponding Restriction of Hazardous Substances (RoHS) limits (Br as certain brominated
 202 compounds $\sim 700 \mu\text{g g}^{-1}$; Cd = $100 \mu\text{g g}^{-1}$, Cr and Pb = $1000 \mu\text{g g}^{-1}$).

	Br	Cd	Cr	Cu	Fe	Pb	Sb	Zn
no. detected	120	46	72	93	165	128	12	137
LOD, $\mu\text{g g}^{-1}$	5-10	10-30	10-15	15-30	30-60	10-30	20-40	10-30
median, $\mu\text{g g}^{-1}$	7.8	62.4	53.5	31.4	773	76.0	54.8	62.3
minimum, $\mu\text{g g}^{-1}$	2.9	14.9	17.4	11.8	34.2	5.1	27.0	11.0
maximum, $\mu\text{g g}^{-1}$	346	1100	1430	581	45600	7510	196	2720
kurtosis	37.0	17.8	15.4	39.9	56.5	46.2	-0.83	24.5
skewness	5.71	3.89	3.52	5.59	7.05	5.98	0.95	4.84
no. exceeding RoHS	0	18	1			13		

203

204 Percentage detection ranged from about 7 for Sb to 100 for Fe, and median concentrations are
205 greatest for Fe, lowest for Sb and similar among the remaining elements. Concentrations of each
206 element are highly variable and span up to three orders of magnitude, and with the exception of Sb,
207 distributions exhibit considerable skewness to the right and have heavy tails or outliers. Pearson's
208 moment correlation analysis revealed that statistically significant relationships ($p < 0.05$) were
209 restricted to the following elemental pairs: Cd-Sb, Cr-Pb and Cd-Fe; with the greatest number of co-
210 associations and the strongest correlation between Cr and Pb and as illustrated by the linear
211 regression results in Figure 6.

212 XRF analysis of different areas of the same sample also resulted in variable results, and in particular
213 where the matrix consisted of distinctly different components or colours or contained agglomerated
214 material. Such heterogeneity is exemplified by the distributions of Pb and Cr concentrations in a
215 large, multi-coloured plastiglomerate in Figure 6. However, when elemental concentrations were
216 normalised with respect to concentrations of an element exhibiting some general co-association or
217 correlation (such as Pb and Cr; see above), ratios were rather consistent, as exemplified by the
218 relationship inset in Figure 5.

219 Lead was also detected in the calcareous tubes of *S. triqueter* attached to the plastiglomerate
220 illustrated in Figure 6 with a mean concentration of $12.2 \mu\text{g g}^{-1}$. By comparison, the mean Pb
221 concentration in the worm tubes scraped from a pyroplastic whose Pb content was $< 50 \mu\text{g g}^{-1}$ was
222 $8.5 \mu\text{g g}^{-1}$ (but with no statistical difference noted between the mean tube concentrations according
223 to a two-sample *t*-test; $p = 0.078$) and Pb in the tubes on a beached tarball was always below the
224 detection limit of about $6 \mu\text{g g}^{-1}$.

225

226 **4. Discussion**

227 Pyroplastics are evidently formed from melting or burning of plastic and are distinctly different from
228 manufactured (primary and secondary) marine plastics in terms of origin, appearance and thickness.
229 Since pyroplastics have been retrieved by colleagues from Atlantic beaches in Spain and Pacific
230 beaches of Vancouver, they are not a regional phenomenon, and it is suspected that their
231 distribution may be widespread but that documentation is lacking because of a distinctly geogenic
232 appearance. It is likely that the samples described here are related to the plastiglomerates reported
233 on Hawaiian beaches by Corcoran et al. (2014), but a key difference is bulk density, with those
234 retrieved from Hawaii agglomerating rocks and stones rather than other plastics. We did not observe
235 significant agglomeration of dense material but it is possible that such clasts are more abundant on

236 the seafloor offshore. Several of the densest pyroplastics reported here returned relatively high
237 concentrations of Fe, suggesting agglomeration of sand, and were partially covered in calcareous
238 tubes of *S. triqueter*. The latter observation, coupled with the absence of more delicate fouling
239 species, is consistent with a period submerged in the circalittoral zone that is subject to movement
240 and disturbance through tidal and wave action.

241 The sources of pyroplastics are unclear but there are a number of possibilities. Corcoran et al. (2014)
242 attribute plastiglomerate formation to the in situ burning of plastic and other waste in bonfires on
243 beaches or rocky outcrops, with smaller clasts then formed by mechanical disintegration. There is
244 clear evidence of bonfires on the beaches of Whitsand Bay, with encrustations of burned plastic on
245 rocks towards the cliffs. It is suspected that fires are used as campfires or barbeques, or are
246 employed to deliberately but informally burn beach waste or spent fishing equipment. This source is
247 consistent with the occurrence of identifiable remnants of plastics typical of the marine
248 environment, like nurdles and netting, agglomerated into pyroplastics, and could also introduce
249 extraneous matter like sand and wood into the matrix.

250 More organised burning of waste, including plastics, appears to take place on many small islands
251 where limited or primitive facilities for waste disposal exist. For example, inhabitants of some
252 Caribbean islands are known to burn waste that results in partially melted plastics entering the sea
253 (Witherington and Witherington, 2011). Although the fetch of Whitsand Bay to the south west
254 extends across the North Atlantic, closer to Cornwall it has been reported that domestic waste burnt
255 in open fires on the Channel Island of Sark (170 km south east of Whitsand Bay) has been dumped at
256 sea from the harbour wall (Delaney, 2018). In such cases, pyroplastics would be expected to contain
257 a more diverse array of plastics from the domestic waste stream, with possible agglomeration of
258 buoyant marine plastics if material had not fully cooled on disposal.

259 In England there are about 20,000 landfills that had been constructed before the Control of Pollution
260 Act in 1974, with many located on low value coastal land (O'Shea et al., 2016). Being poorly
261 engineered, leakage of chemicals and materials has frequently been reported through both erosion
262 and collapse (Pope et al., 2011; Njue et al., 2012). It is possible, therefore, that partially burned
263 plastic dumped in historical coastal landfills or resulting from the more general burning of bulk waste
264 and organic matter before disposal is able to escape into the littoral zone. Here, pyroplastics would
265 be expected to be composed of an assortment of older domestic plastics but contain no marine
266 litter.

267 The disposal of plastic garbage from ships, including incineration ashes generated onboard, has been
268 prohibited since the implementation of the MARPOL 73/78-Agreement/Annex V (Regulation for the

269 Prevention of Pollution by Ship Waste) of 1989, although only ships of 400 gross tonnage and above
270 are required to carry out a garbage management plan (Chen and Liu, 2013). Current protocols
271 typically involve reducing the volume of shipborne plastic waste, often by shredding and partial
272 melting, and disposal of residual material in port. However, the rationale for the MARPOL agreement
273 suggests that previous practice may have involved the direct disposal of large quantities of melted
274 plastic into the marine environment, with the composition of resulting pyroplastics largely reflecting
275 the contents of ship waste.

276 Regardless of the sources of pyroplastics and whether they are generated in situ, at sea or on land,
277 many of those of positive buoyancy will end up in the turbulent swash zone where they are shaped
278 by mechanical abrasion into more rounded and geogenic-looking pebbles. Evading ready recognition
279 on the strandline, they are not classified under any category of marine litter according to OSPAR
280 (2010) guidelines and potentially result in underestimates of the plastic inventory on beaches.
281 Moreover, their brittleness means that they are a ready source of secondary microplastics and
282 nanoplastics through impactation and shattering (Efimova et al., 2018), a characteristic that may well
283 explain the bimodal size distribution we have observed.

284 Presumably, the age of deposition of pyroplastics is related to the degree of erosion and roundness
285 and apparent agglomeration, although there is no clear means of quantifying this effect. With
286 respect to age of manufacture of the plastic itself, a qualitative assessment may be gained from the
287 distribution of certain additives within the matrix. Specifically, there is both a high occurrence and
288 concentration of cadmium and lead among the samples, and in particular in the well-rounded clasts.
289 These heavy metals are either no longer used or are highly regulated in consumer, electrical and
290 packaging plastics, although small quantities appear in various goods through the recycling of
291 improperly sorted historic waste (Turner, 2018). Significantly, limits for Cd and Pb in electrical
292 plastics, defined by the Restriction of Hazardous Substances (RoHS) Directive (European Parliament
293 and Council, 2003) as $100 \mu\text{g g}^{-1}$ and $1000 \mu\text{g g}^{-1}$, respectively, are exceeded in the pyroplastics
294 analysed herein in 18 and 13 cases, respectively (Table 2).

295 Until a few decades ago, both Cd and Pb were used as heat and UV stabilisers in PVC and as
296 pigments to colour most types of plastic. Given that PVC was absent among the pyroplastics and that
297 there was no clear relationship between Cd or Pb and chloride (indicative of residual PVC), we
298 surmise that the metals are present in the samples as pigments. The principal pigment of Pb used in
299 plastics was lead chromate (PbCrO_4), effecting a range of reds, yellows and greens with high tinting
300 strength and opacity by either itself or on mixing with other compounds. Among the pyroplastics
301 there was a strong correlation between Pb and Cr concentrations determined by XRF (Figure 5), with

302 a gradient defining the linear regression of Pb versus Cr similar to the mass ratio of the metals in
303 pure PbCrO_4 (~ 4); moreover, within the same sample, Pb and Cr exhibited a similar relationship that
304 is exemplified for the pyroplastic shown in Figure 6. Despite the presence of brightly-coloured
305 leaded (and likely, cadmium-based) pigments, the matrix of pyroplastics assumes a neutral
306 appearance (and most commonly grey or charcoal) through the mixing of multiple colours and hues
307 A simple laboratory test involving melting brightly coloured polyethylene fragments in a steel
308 canister under a series of Bunsen burners and rapidly cooling the contents under tap water resulted
309 in a dark grey plastic matrix encapsulating various coloured streaks, as illustrated in Figure S3.

310 Compared with contemporary consumer goods (Turner and Filella, 2017) and other beached plastics
311 collected from the region that have undergone similar degrees of environmental exposure (Massos
312 and Turner, 2017; Wallerstein et al., 2019) there is a distinct lack of bromine and antimony in the
313 pyroplastics. Specifically, the median concentration of Br is $7.8 \mu\text{g g}^{-1}$, Sb was only detected in twelve
314 pyroplastics, and Br and Sb co-existed in just seven samples. Given the principal use of bromine in
315 plastics is as brominated flame retardants (BFRs) in electrical and electronic housings and insulation,
316 and that BFRs are usually associated with antimony as a retardant synergist, there is little evidence
317 of electrical and electronic waste among the pyroplastic samples, either directly or through the
318 presence of recycled material. This may reflect the fact that many pyroplastics pre-date the
319 introduction of brominated flame retardants (the 1960s; Janssen, 2005) or the general recycling of
320 electronic plastic into consumer goods, a practice that is currently not legal but that is facilitated
321 through a series of loopholes (Turner, 2018). Alternatively, it is possible that, because the presence
322 of BFRs and Sb render plastic more difficult to burn, such materials are deliberately avoided in the
323 first place or remain as more discrete (i.e. non-agglomerated) residues after burning. (Aside from its
324 high density, this would also explain the absence of PVC in the beached pyroplastics, a material
325 whose halogen content ensures an inherent flame retardancy.)

326 In addition to underestimating the stock of beached plastic and their propensity to readily form
327 microplastics and nanoplastics, a concern of pyroplastics is the potential for heavy metals to be
328 mobilised or enter the foodchain. The mobility of Pb was evaluated by determining its concentration
329 in calcareous worm tubes on a lead-rich pyroplastic (illustrated in Figure 6), a lead-poor pyroplastic
330 and a beached tarball containing no detectable lead. That mean Pb concentrations in the tubes were
331 greatest on the lead-rich pyroplastic and not detected on the tarball suggests that there is potential
332 for transfer of additives or residues in plastic to organisms that use the material as a substrate. A
333 similar conclusion was reached by Jang et al. (2016) for marine mussels inhabiting styrofoam that
334 accumulated the flame retardant, hexabromocyclodecane, from the matrix but further studies in this

335 area are required in order to evaluate the significance of contaminant transfer from plastics more
336 generally.

337 In summary, pyroplastics are a non-manufactured type of marine plastic litter that appear to be
338 derived from the informal or more organised burning of waste that may take place in situ or ex situ.
339 They typically consist of a neutrally-coloured matrix agglomerating more distinct pieces of plastic
340 and other debris, but weathering in the circalittoral zone shapes material into geogenic-looking
341 pebbles that readily evade detection during beach-cleaning. Pyroplastics require their own
342 classification within the umbrella of marine litter, and are a source of finer plastic particulates
343 through mechanical breakdown and a potential source of contaminants for organisms that inhabit or
344 ingest them.

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350

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410 **Figure 1:** Locations in Cornwall, south west England, where pyroplastics have been collected (filled
411 circles) in relation to major embayments and centres of population.

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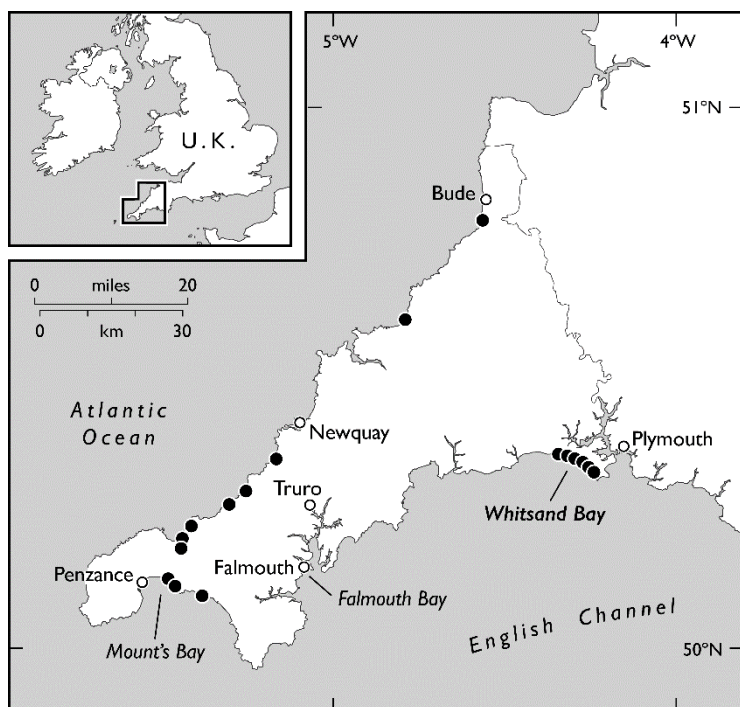


Figure 2: Pyroplastics retrieved from the strandline at Whitsand Bay.

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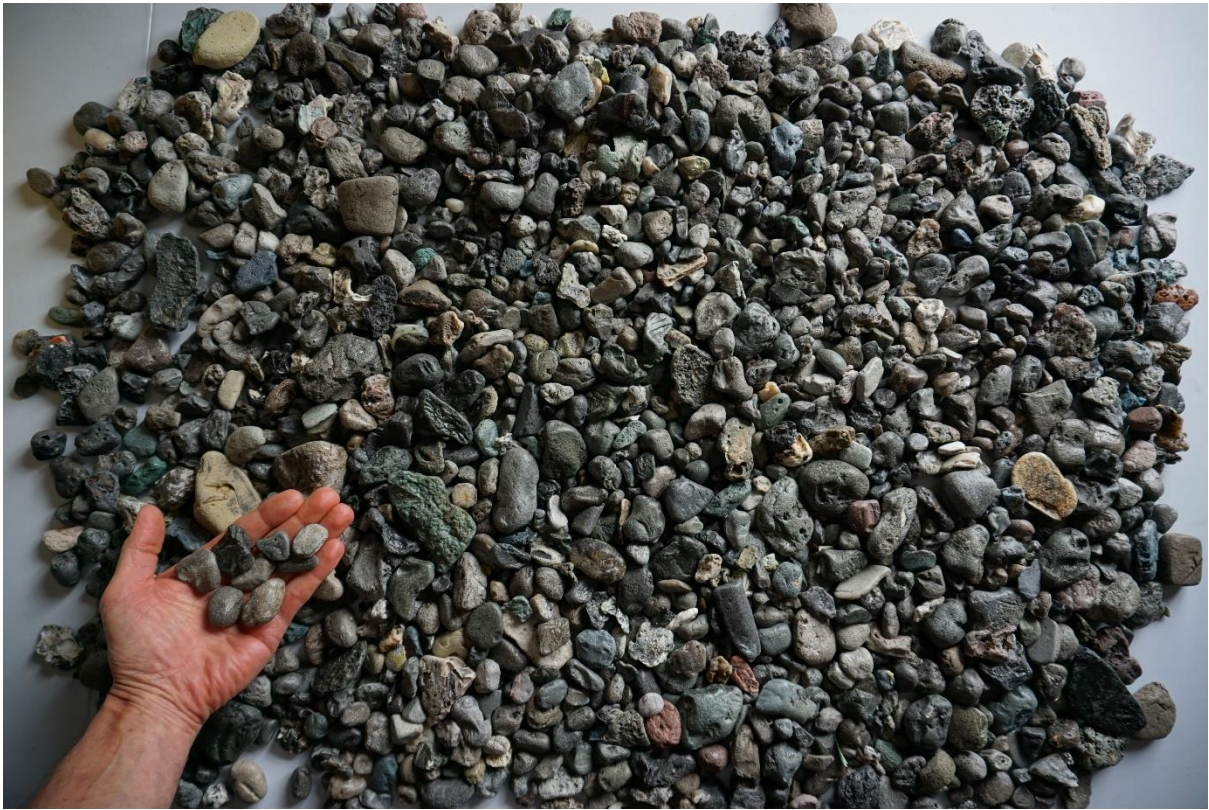
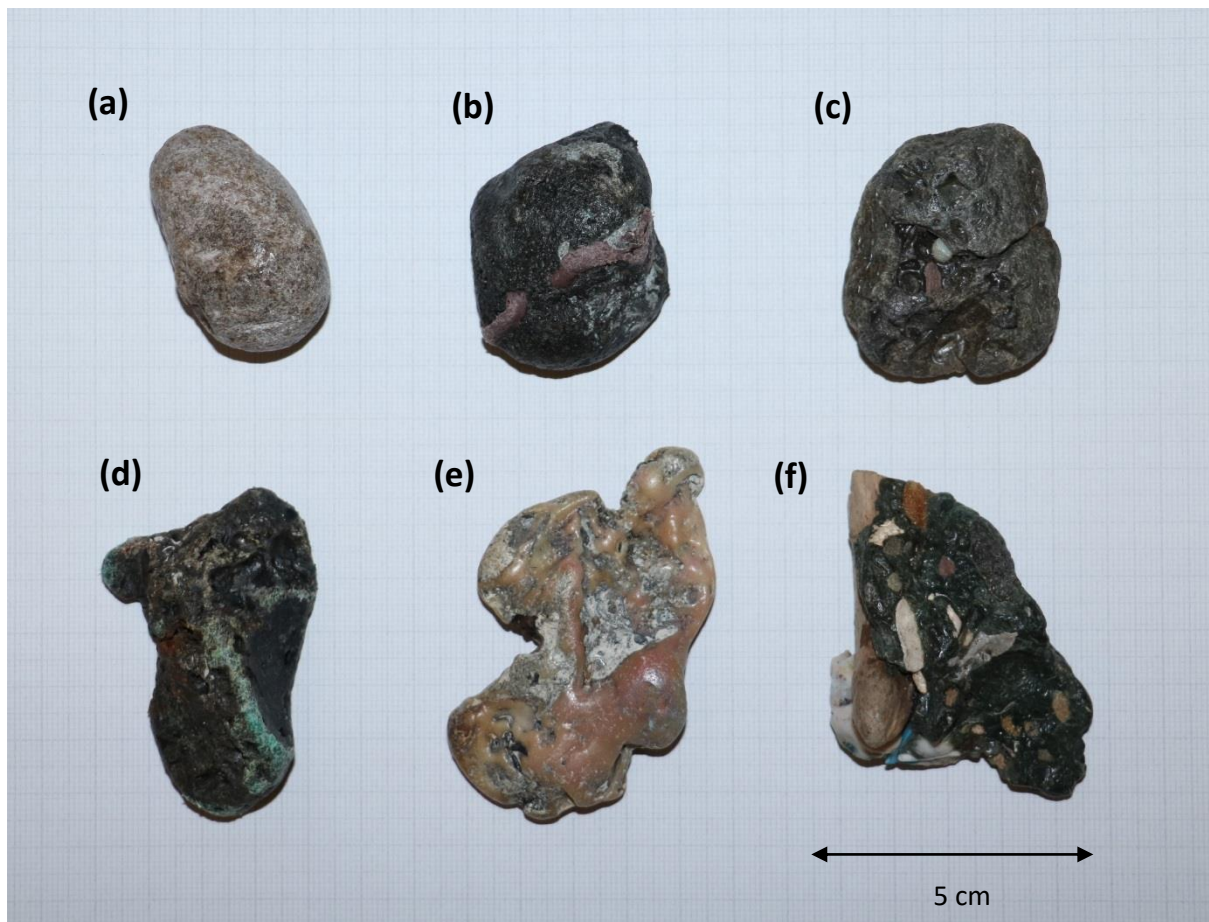


Figure 3: A selection of samples collected from Whitsand Bay exhibiting increasing agglomeration and angulation from (a) through to (f).



414 **Figure 4:** FTIR spectra for the surface and subsurface (> 1 mm) of a charcoal-coloured pyroplastic
415 from Whitsand Bay, which were library-matched from characteristic absorption bands at 2914, 2847,
416 1470 and 718 cm^{-1} to high density polyethylene.

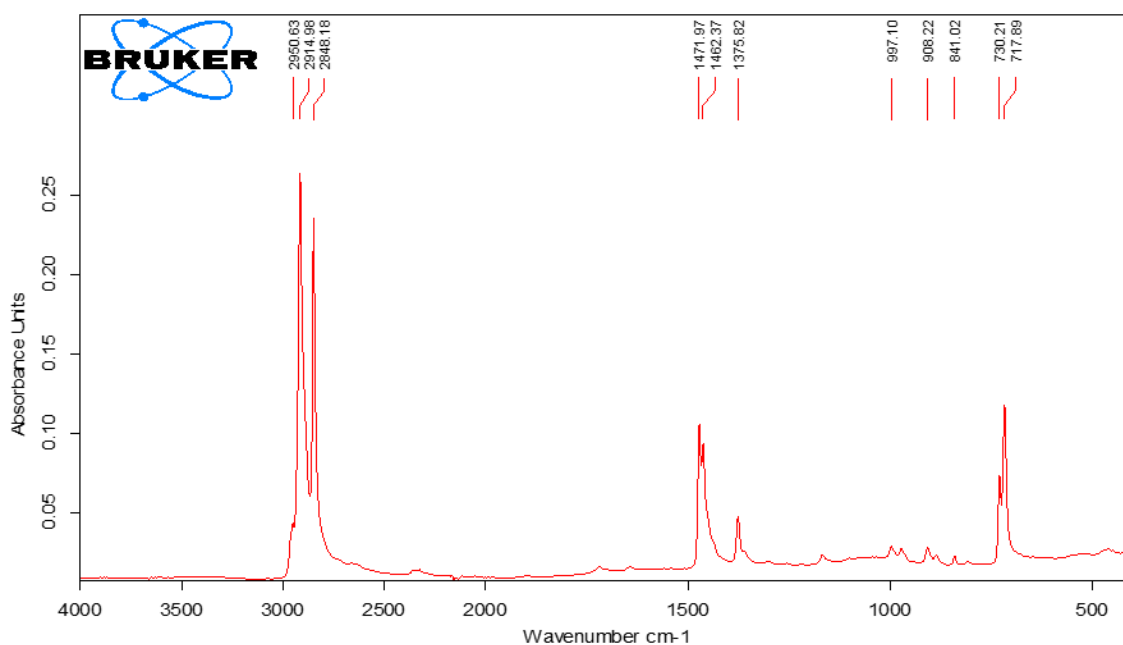
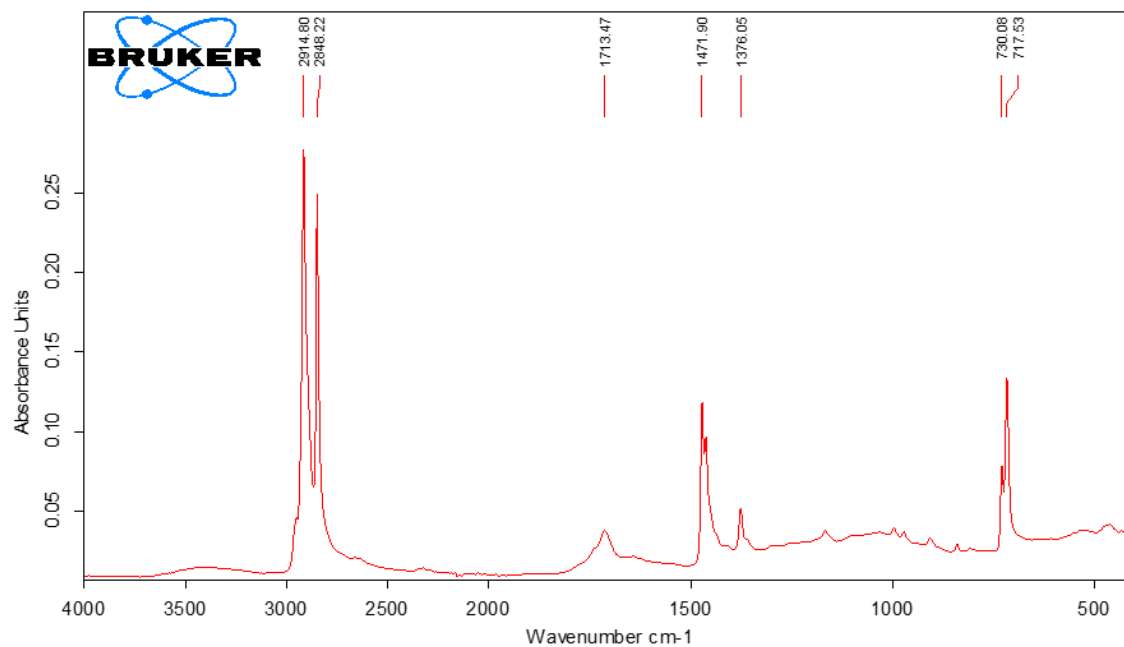
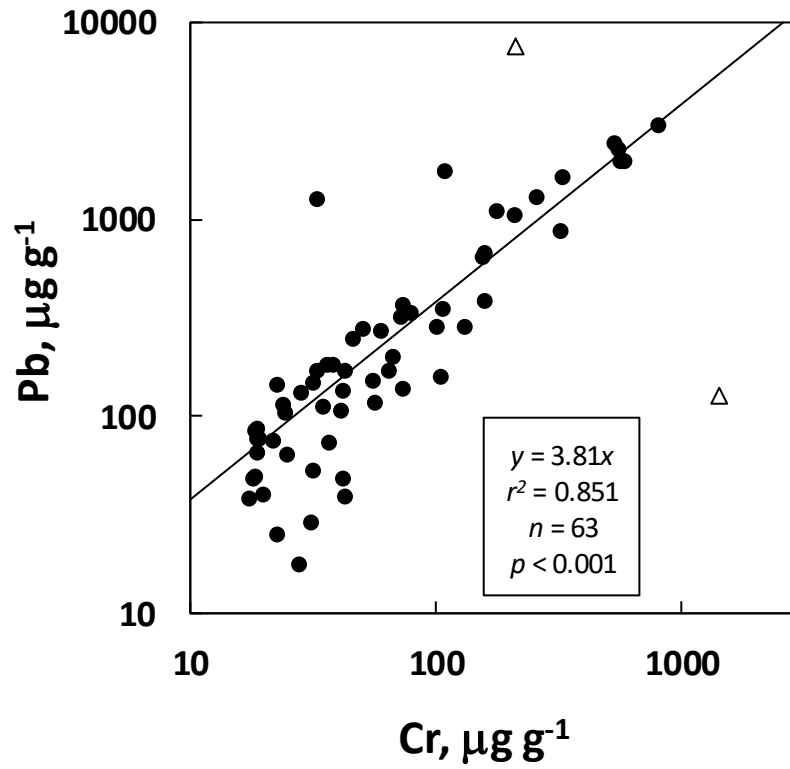


Figure 5: Relationship between Pb and Cr in the pyroplastics from Whitsand Bay. The statistical summary defines the linear regression of the data excluding data points with the highest Pb content and the highest Cr content (shown as open triangles).



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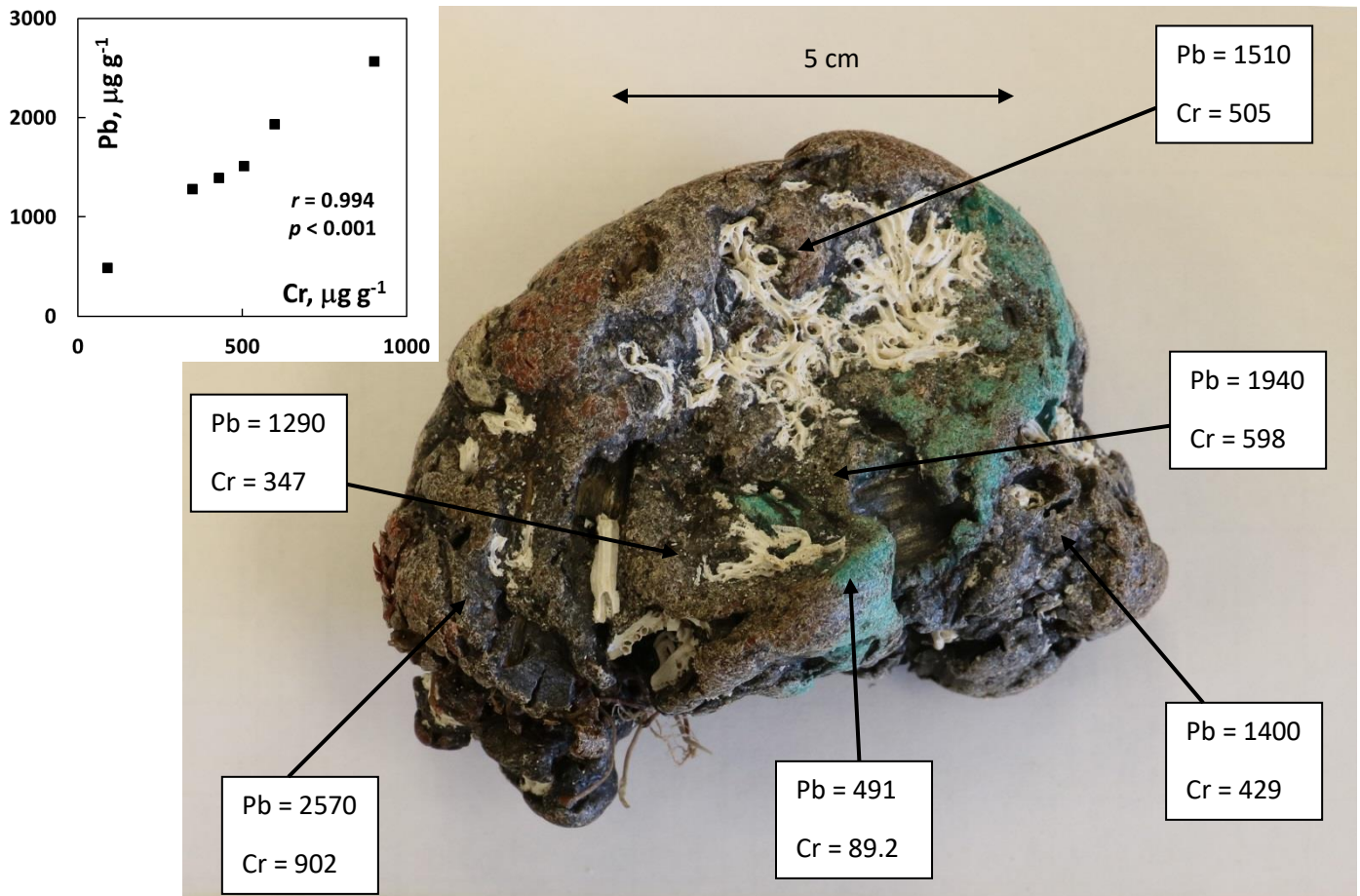
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Figure 6: Concentrations of Pb and Cr (in $\mu\text{g g}^{-1}$) across different regions of a pyroplastic hosting calcareous deposits of the tube-building worm, *S. triqueter*. Inset is the relationship between Pb and Cr concentrations in the sample.



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