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Heavy metals, metalloids and other hazardous elements in marine plastic litter

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22 **Abstract**

23 Plastics, foams and ropes collected from beaches in SW England have been analysed
24 for As, Ba, Br, Cd, Cl, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn and Zn by field-portable-x-ray
25 fluorescence spectrometry. High concentrations of Cl in foams that were not PVC-
26 based were attributed to the presence of chlorinated flame retardants. Likewise, high
27 concentrations of Br among both foams and plastics were attributed to the presence of
28 brominated flame retardants. Regarding heavy metals and metalloids, Cd and Pb were
29 of greatest concern from an environmental perspective. Lead was encountered in
30 plastics, foams and ropes and up to concentrations of 17,500 $\mu\text{g g}^{-1}$ due to its
31 historical use in stabilisers, colourants and catalysts in the plastics industry.
32 Detectable Cd was restricted to plastics, where its concentration often exceeded 1000
33 $\mu\text{g g}^{-1}$; its occurrence is attributed to the use of both Cd-based stabilisers and
34 colourants in a variety of products.

35

36 **Keywords:** marine plastic; FP-XRF; ropes; foams; heavy metals; flame retardants

37 **1. Introduction**

38 Marine litter is a global problem, with sources of waste related to a variety of human
39 activities that are both marine-based and land-based. Accumulation of litter is found at
40 the sea surface, on the seabed and washed up on beaches and, because of the
41 persistence and buoyancy of many processed materials, often represents a
42 transboundary issue and one that affects regions remote from urbanisation or
43 shipping. Marine plastics in particular have received a great deal of attention over the
44 past two decades because of their scale of production, poor rates of recycling and
45 durability (Browne et al., 2010).

46

47 Aside from the aesthetic and economic impacts, plastic waste also poses a hazard to
48 navigation and a threat to the health and safety of humans and wildlife. Regarding the
49 latter, the potential of plastic products and fragments for entanglement, strangulation
50 and ingestion are well-documented for fish, birds and mammals (Carson, 2013; Yorio
51 et al., 2014; McIntosh et al., 2015). Less understood, however, is the role of plastics in
52 providing a vector for exposure to and accumulation of chemicals that are adsorbed to
53 or incorporated within the polymeric matrix. Moreover, the majority of studies in this
54 respect have targeted persistent organic micropollutants, like polychlorinated
55 biphenyls and polycyclic aromatic hydrocarbons (Frias et al., 2010; Rochman et al.,
56 2013; Gauquie et al., 2015).

57

58 Given the widespread contemporary and historical use of metals and metalloids by the
59 plastics industry, it is perhaps surprising that very little attention has been paid to the
60 occurrence and impacts of these elements in marine litter (Ashton et al., 2010;
61 Nakashima et al., 2012). Compounds of many metals and metalloids are currently

62 used as catalysts, biocides, pigments for colour and UV and heat stabilisers and, while
63 many of the more hazardous compounds, including those of Cd, Cr, Hg and Pb, have
64 been phased out or banned, they are still likely to be encountered at elevated
65 concentrations in litter derived from or containing older plastic products. According to
66 a recent report prepared on behalf of the Norwegian Environmental Protection
67 Agency (Hansen et al., 2013), for instance, certain historical materials or products are
68 expected to contain concentrations of Hg up to 3000 $\mu\text{g g}^{-1}$ and concentrations of Cd,
69 Cr and Pb up to 50,000 $\mu\text{g g}^{-1}$. Such concentrations are orders of magnitude greater
70 than corresponding values one would expect to find in even the most contaminated
71 marine sediments.

72

73 In the present paper, a variety of heavy metals and metalloids (As, Ba, Br, Cd, Cl, Cr,
74 Cu, Hg, Ni, Pb, Se, Sb, Sn and Zn) and other elements that are potentially indicative
75 of hazardous chemicals (Br, Cl) are analysed in samples of marine plastic litter
76 collected from five beaches across south west England. Specifically, the focus is on
77 objects and/or fragments of plastic, foam and rope, and analysis is performed by a
78 field-portable-x-ray fluorescence spectrometer in a mode that is configured for the
79 analysis of low density materials according to protocols described in detail elsewhere
80 (Turner and Solman, 2016).

81

82 **2. Materials and methods**

83 *2.1. Sampling and sample locations*

84 Five beaches of contrasting aspect, profile, size, sediment characteristics, fetch, wave
85 climate and usage, and that were not subjected to routine litter collection and were
86 free of buildings, were visited just after high water on single occasions between late

87 August and late September 2015 (Figure 1). Chapel Porth (CP) and Constantine Bay
88 (CB) are west- (Atlantic-) facing sandy beaches that are popular destinations for both
89 tourists and surfers. While the sweeping arc of Constantine Bay is backed by a
90 network of sand dunes, Chapel Porth is set in a sheltered cove that is bound by high,
91 steep cliffs. Porth Kidney (PK) is an expansive, north-facing and dune-backed beach
92 in St Ives Bay that lies at the mouth of a small, protected estuary (Hayle), while
93 Saltram (SA) is a small, silty-sandy intertidal region on the east bank of a shallow,
94 urbanised estuary (Plym) that is close to a recently capped landfill site. Mount Batten
95 (MB) is a south-facing pebble-sand beach in Plymouth Sound, a bay that receives
96 freshwater inputs from the Plym and Tamar estuaries and, being protected to the south
97 by a 1.6 km breakwater, is a natural harbour for naval and commercial ships and a
98 popular location for yachting.

99

100 On each beach, pieces of plastic litter that were visible to the naked eye were
101 collected by hand from a transect of the high (or highest) water line. This line was
102 readily apparent from the accumulation of debris and macroalgae and was either
103 located on the beach itself (SA, PK), along the seaward edge of the dune system (CB),
104 or on boulders and rocks at the landward limit of the backshore (MB, CP). Depending
105 on the abundance of material, the lengths of the transects varied between about 10 m
106 and 200 m, ensuring that at least 50 samples were collected in each case.

107

108 For the purposes of the present study, plastic litter is defined as relatively mobile, low
109 density, poorly-degradable, manufactured or processed material. Items falling within
110 this description were categorised on collection as ‘plastics’ (non-porous, moulded
111 objects or fragments, and including rubber), ‘foams’ (pieces of open- or closed-cell

112 expanded and extruded polymer) or ‘ropes’ (fragments of rigging, cord, netting and
113 fishing line). While, strictly, all samples are plastic-based, this categorisation is
114 consistent with distinct groupings within the OSPAR classification of plastic litter
115 based on visual appearance (OSPAR Commission, 2010). From a practical
116 perspective, this classification also reflects the requirement for different approaches to
117 sample preparation and differences in absorption of x-rays that relate to density and
118 the presence of air within the matrix (Turner and Solman, 2016). While components
119 of these categories made up the majority of the litter pool (> 90% on a number basis),
120 items neglected included pieces of masonry, objects and fragments that were
121 composed principally or wholly of metal, pieces of glass or ceramic, paper and
122 cardboard waste, and machined wood. Also neglected were foils or films of food
123 packaging that had evidently been recently discarded as earlier, independent analyses
124 of a variety of contemporary packaging failed to detect any of the elements under
125 study.

126

127 Categorised litter collected from each beach was stored in a series of clear
128 polyethylene bags and transported to the laboratory. Here, individual items were
129 cleared of sand and other debris under running tap water and with the aid of a Nylon
130 brush before being dried at 40 °C in an oven for 12 h or, for foams, under desiccation
131 at room temperature for 48 h. Samples were then weighed on a three- or five-figure
132 balance, depending on their size, and stored individually in labelled polyethylene
133 specimen bags at room temperature and in the dark until required for XRF analysis.

134

135 *2.2. XRF analysis*

136 All samples were analysed by energy dispersive FP-XRF using a battery-powered
137 Niton XRF analyser (model XL3t 950 He GOLDD+) for elements of a hazardous
138 nature (or elements indicative of hazardous compounds) and/or regarded as important
139 marine contaminants (that is, As, Ba, Br, Cd, Cl, Cr, Cu, Hg, Ni, Pb, Se, Sb, Sn and
140 Zn). The instrument was operated in a plastics mode that is capable of quantifying the
141 concentrations of up to 18 elements, whose fluorescent peaks range from 2.62 keV
142 (Cl- K_{α}) to 32 keV (Ba- K_{α}), in complex, low density materials through a fundamental
143 parameters-based alpha coefficient correction model. Fundamental parameters
144 eliminates the requirement for sample-specific standards, has a wide dynamic range
145 and is independent of the size and shape of the surface (Bosco, 2013).

146

147 For the analysis of samples in the plastics mode, the instrument has a thickness
148 correction algorithm down to 0.05 mm that employs a compensation for mass
149 absorption coefficient based on Compton scatter so that variations in material density
150 are factored in. Thickness correction was applied to all plastics whose depth was less
151 than 10 mm and to all foams and ropes regardless of sample depth. Sample thickness
152 was measured through the flattest ('measurement') surface using 300 mm Allendale
153 digital callipers, and to increase the effective depth and flatness of the thinnest
154 samples of plastic or rope, items were often cut (with scissors, pliers or a blade),
155 folded or layered and, where necessary, held in place using crocodile clips.

156

157 The XRF was used in the laboratory in a bench-top accessory stand and was
158 connected to a laptop computer via USB and a remote trigger. Samples were placed
159 on 3.6 μm polyester film and positioned centrally and with the measurement surface
160 face downwards over the XRF measurement window. On closing the steel shield of

161 the stand, measurements with appropriate thickness correction were activated through
162 the laptop for a total period of 120 seconds (60 seconds each at 50 kV/40 μ A and 20
163 kV/100 μ A). Spectra were quantified by fundamental parameter coefficients to yield
164 elemental concentrations on a dry weight basis (in μ g g^{-1}) and with a counting error of
165 2σ (95% confidence). At the end of each 2-6 h session, spectra and elemental
166 concentrations were downloaded to the laptop using Niton data transfer (NDT) PC
167 software.

168

169 Element-specific limits of detection of the Niton XL3t are dependent on a number of
170 factors, including mode of instrument application, counting time, and sample density,
171 composition and thickness. In the plastics mode and for a counting time of 120
172 seconds, detection limits are generally lowest and below 40 μ g g^{-1} for each sample
173 category (plastics, foams and ropes) for As, Br, Cr and Pb and highest and above 70
174 μ g g^{-1} for each category for Ba, Sb and Sn (Turner and Solman, 2016). Note that in
175 the case of As, overlap of its K_{α} fluorescence peak with the L_{α} peak of Pb coupled
176 with the relatively low intensity of the As- K_{β} line means that concentrations cannot be
177 effectively calculated for samples with Pb:As ratios in excess of about 10
178 (Environmental Protection Agency, 2007). Arsenic concentrations reported herein are,
179 therefore, restricted to those returned by the XRF where Pb was not detectable.

180

181 Table 1 shows the results of multiple analyses ($n = 5$) of two Niton reference plastics
182 (PN 180-554, batch SN PE-071-N, and PN 180-619, LOT#T-18); these are
183 polyethylene discs of thickness 13 mm and diameter 31 mm that have been
184 impregnated with various elements. Where certified concentrations are reported,

185 measured concentrations are within 10% of reference concentrations in most cases
186 and within 15% in all cases.

187

188 *2.3. FTIR analysis*

189 In order to identify the component polymers in the plastics, foams and ropes, a range
190 of samples from each beach ($n = 100$ in total) were analysed by attenuated total
191 reflection-Fourier transform infra-red spectroscopy (ATR-FTIR) using a Bruker
192 ALPHA Platinum ATR QuickSnap A220/D-01 spectrometer. Samples were cut to a
193 suitable size, where necessary, using a stainless steel scalpel, before being firmly
194 clamped down on to the ATR diamond crystal. Measurements, consisting of 16 scans
195 in the range 4000 to 400 cm^{-1} and at a resolution of 4 cm^{-1} , were activated via Bruker
196 OPUS spectroscopic software, with subsequent identification involving comparisons
197 of transmittance spectra with libraries of reference spectra.

198

199 **3. Results**

200 *3.1. Sample characteristics*

201 Table 2 presents a summary of the different categories of samples collected, in terms
202 of both number and mass. The total number of samples retrieved was 573, with at
203 least 70 samples being collected from each beach. Plastics comprised about a half of
204 the number of samples in total, and on individual beaches percentage contributions of
205 plastics to the total sample number ranged from about 4% (MB) to 78% (SA). Foams
206 comprised about a third of all samples on this basis, with the percentage contribution
207 ranging from 18 (SA) to 57 (MB), while values for ropes were 16% overall and
208 relative contributions ranged from about 4% (SA) to 36% (CB).

209

210 The total mass of material retrieved was about 1 kg, and the mass of individual items
211 ranged from about 2 mg to 50 g. Overall, and on three individual beaches, plastics
212 were the dominant material on a mass basis. The mass contribution of foams to the
213 total loading was about a half of that of plastics, but on two beaches (MB and PK)
214 foams represented the dominant material category. Overall, the mass contribution of
215 ropes was the lowest of the three categories considered but on a location basis relative
216 contributions were highly variable and ranged from about 1% to 36% of total mass
217 (SA and CP, respectively). Sample thickness ranged from about 0.3 mm for a number
218 of plastic films to more than 40 mm for several foams, and primary diameter or length
219 ranged from about 3 mm for various plastic fragments and pellets to more than 10 cm
220 for a number of plastic objects and pieces of foam and rope.

221

222 More than half of the samples in the plastics category were unidentifiable fragments
223 of varying size. Many samples that were recognisable as either fragments or whole
224 objects could be classified according to the OSPAR marine litter monitoring
225 guidelines (OSPAR Commission, 2010), and in descending order of abundance, as
226 bottle caps and lids, production pellets, injection gun caps, lolly sticks, cutlery and
227 straws, toys, shotgun cartridges, cigarette lighters, pens and strapping bands. Other
228 recognisable fragments not categorised by OSPAR appeared to be derived from
229 garden furniture and fencing, adhesive taping, piping, plant pots, vials and a traffic
230 safety barrier. Likewise, and regarding foams, most items were unidentifiable
231 fragments of varying size, but fast food containers, polystyrene cups, foam sponge
232 and miscellaneous polystyrene pieces were consistent with OSPAR classifications;
233 note that polyurethane and expanded rubber, which were abundant on some beaches,
234 do not appear to have equivalent or distinct classifications. According to OSPAR,

235 rope samples could be classified, in decreasing order of abundance, as rope *per se*
236 (and by definition of diameter > 1 cm), netting, tangled nets-cord-rope, string and
237 cord (diameter < 1 cm), fishing line and ‘other’ textiles.

238

239 3.2. Elemental content of litter

240 Tables 3 to 5 show the concentrations of the different elements in the three categories
241 of litter. Here, data are pooled for the five locations in order to evaluate elemental
242 differences among the different types of material, and elements are shown in order of
243 descending number of cases detected and in terms of both concentration distributions
244 and summary statistics. Regarding plastics (Table 3), Cl was the most abundant
245 element, being detected in 225 out of 279 samples and at concentrations up to about
246 50% by weight. Zinc was the most abundant heavy metal detected and at
247 concentrations up to about 25,000 $\mu\text{g g}^{-1}$. Among the remaining elements that were
248 detected in more than ten cases, maximum concentrations were at least 1000 $\mu\text{g g}^{-1}$
249 with the exception of Cu. Median detectable concentrations were greatest and above
250 500 $\mu\text{g g}^{-1}$ for Cd, Cl and Ba and lowest and below 50 for Cr, Br, As and Ni. With
251 respect to the foams (Table 4), and as above, the most abundant element was Cl, being
252 detected in 195 out of 203 cases and up to concentrations of 63% by weight;
253 compared with plastics, however, the median concentration was two orders of
254 magnitude higher. The second most abundant element in the foams was Br, with
255 maximum and median concentrations of about 18,000 $\mu\text{g g}^{-1}$ and 250 $\mu\text{g g}^{-1}$,
256 respectively. Chromium, Cu, Pb, Sn and Zn were all detected in more than 10% of
257 samples analysed with median concentrations above 100 $\mu\text{g g}^{-1}$ and maxima ranging
258 from about 1000 $\mu\text{g g}^{-1}$ (Cr) to more than 25,000 $\mu\text{g g}^{-1}$ (Zn). Likewise, in the ropes
259 category (Table 5) Cl was the most abundant element, being detected in 85 out of 91

260 samples, but median and maximum concentrations (about 1500 $\mu\text{g g}^{-1}$ and 50,000, μg
261 g^{-1} , respectively) were lower than in both plastics and foams. Bromine, Cr, Cu, Pb and
262 Zn were detected in more than 40% of rope samples, with median concentrations
263 ranging from 26 $\mu\text{g g}^{-1}$ for Br to 139 $\mu\text{g g}^{-1}$ for Pb and maxima that were about an
264 order of magnitude higher than corresponding medians.

265

266 Overall, and across all litter categories, Cl was detected in the most cases (505 out of
267 573), with Br, Pb, Zn, Cu and Cr detected in more than 100 samples each, and Hg and
268 Se were detected in the fewest cases (3 and 5 samples, respectively); overall median
269 concentrations were greater than 1000 $\mu\text{g g}^{-1}$ for Ba, Cd and Cl and less than 50 $\mu\text{g g}^{-1}$
270 for As.

271

272 **4. Discussion**

273 Only a limited number of previous studies have addressed associations of heavy
274 metals and other hazardous elements with marine litter. Specifically, Ashton et al.
275 (2010) determined the concentrations of metals that could be extracted by acid from
276 beached plastic production pellets in south west England and found aluminium-
277 normalised enrichment factors, relative to extraneous material (e.g. silt), that exceeded
278 unit value in a few cases. Holmes et al. (2012) studied the kinetics of uptake of heavy
279 metals from sea water by production pellets and found that aged pellets were more
280 effective accumulators than virgin pellets, while Rochman et al. (2014) conducted a
281 12-month study in San Diego Bay and demonstrated that many metals could be
282 accumulated by different types of plastic in the long-term.

283

284 Although plastics clearly have the ability to accumulate or adsorb heavy metals,
285 resultant, absolute concentrations are typically on the order of a few ng g^{-1} to a few μg
286 g^{-1} (Ashton et al., 2010). In the plastic matrix itself, however, the results of the present
287 study and the limited data reported by Nakashima et al. (2012) for metals (and mainly
288 Pb) in a variety of plastics retrieved from a number of Japanese beaches reveal
289 elemental concentrations that are highly variable but that may exceed a few percent by
290 weight in many cases. The present study also reveals that metals and other elements
291 are not just restricted to moulded plastic products and fragments, but are also
292 encountered in foams and ropes.

293

294 Plastics with high concentrations of Cl (typically above 20%) were classified as
295 polyvinyl chloride (PVC) by the XRF, an identification that was used to correct for
296 mass absorption and density in the fundamental parameters calculations and that was
297 subsequently confirmed by selected FTIR analyses. Many foams, with the exception
298 of those that appeared to have been used for used for food packaging, were also
299 classified as PVC by the XRF, and while FTIR confirmed that some of these samples
300 were PVC-based, the majority analysed by this technique were identified as
301 elasticated rubbers or expanded-extruded polystyrene and polyurethane. Elasticated
302 rubber likely includes neoprene, or polychloroprene, a polymer resistant to burning
303 which is used for cushioning, padding and thermal insulation (e.g. wet suits and
304 waders). Regarding polystyrene and polyurethane foams, while Cl is not an inherent
305 component of the respective polymers, it is a constituent of various flame retardants,
306 such as Dechlorane Plus and chlorinated organophosphates, that have been added to
307 products used for insulation or in soft furnishings (Katz and Milewski, 1987; King et
308 al., 2009).

309

310 Bromine is also a component of many flame retardants, including those added to
311 expanded-extruded polymers employed for thermal insulation and furnishings in both
312 buildings and in transportation, and in plastics used for construction and electronic
313 equipment. Hexabromocyclododecane (HBCD) was the principal flame retardant
314 added to both expanded and extruded polystyrenes used for building insulation but
315 was recently banned in the European Union under the EU Reach programme (Koch-
316 Jugl et al., 2015) and in the US safer alternatives are currently being sought (US EPA,
317 2014). Depending on their use, flexible and rigid polyurethanes are often impregnated
318 with a variety of brominated flame retardants. Polybrominated diphenyl ethers
319 (PBDEs) were the main type used in flexible furnishings until health concerns at the
320 beginning of the century led to the phase-out of certain congeners (Keimowitz et al.,
321 2015), while bromine-containing polyols have been commonly added to rigid
322 polyurethanes used for construction and insulation within the EU (Weil and Levchik,
323 2004).

324

325 Figure 2 shows a scatter plot of the concentration of Br versus the concentration of Cl,
326 where both elements were detected, for the plastics, foams and ropes categories of
327 marine litter. While there was no significant correlation in the data, either overall or
328 within a specific sample category, the distribution clearly shows a greater degree of
329 both chlorination and bromination among the foams compared with the plastics and
330 ropes. The latter two categories exhibit similar distributions because the dominant
331 component materials, as identified by FTIR, were the same (polyethylene and
332 polypropylene), while greater concentrations of Cl and Br associated with the
333 expanded-extruded samples is due to the incorporation of flame retardants in the

334 matrix. Presumably, therefore, the relative abundance of Cl and Br in polymeric
335 foams reflects the type of flame retardant in the material, while low concentrations of
336 both elements (including no detection) indicate the absence of such additives. Lack of
337 flame retardants suggests use of the foams other than in construction, insulation or
338 furnishing, or application in certain (marine) settings where fire would not be a
339 concern (e.g. pontoons, buoys, boat hulls, life jackets).

340

341 Compounds of heavy metals and metalloids are added to plastics as fillers, heat and
342 UV stabilisers, pigments for colour, release agents, activators, biostabilisers,
343 antimicrobial agents, catalysts and intermediates. In expanded and extruded materials,
344 and in particular in rigid polyurethane, some compounds of Sb and Zn also serve as
345 flame retardants and/or smoke suppressants (Zatorski et al., 2008) (note that Zn was
346 frequently measured at concentrations exceeding $1000 \mu\text{g g}^{-1}$ in the polyurethane
347 foams in the present study; Table 4). Antifouling agents containing Cu(I), Zn, Sn, Pb
348 or Hg are (or have been) added to marine paints to prevent biofouling, and such
349 formulations may have also been applied to netting and ropes if used for aquaculture
350 (Guardiola et al., 2012).

351

352 Among the heavy metals studied, Cd and Pb are of greatest concern because of their
353 risks to health and the environment and their widespread occurrence and elevated
354 concentrations in a variety of litter samples. Cadmium was detected at concentrations
355 above $100 \mu\text{g g}^{-1}$ in 11 samples of beached plastic, of which only one was clearly
356 classifiable (a shot gun cartridge). Although Cd has been used as a heat and UV
357 stabiliser in some PVC products at concentrations up to about $30,000 \mu\text{g g}^{-1}$ by weight
358 (Tamaddon and Hogland, 1993), it has been more widely employed in a variety of

359 plastics for colour and at concentrations up to about 10,000 $\mu\text{g g}^{-1}$ (Hansen et al.,
360 2013). Cadmium sulphide and Cd sulphoselenide pigments provide a range of colours
361 that can be adjusted by partial replacement of Cd^{2+} by Zn^{2+} (yellow to green) or
362 replacement of sulphur by selenium (forming oranges and reds) (Pritchard, 1998). In
363 the samples of plastic where Cd was detected, Se was reported in 5 cases, with the
364 mass ratio of Cd to Se ranging from about 3 to 8 and colours that were mainly orange
365 or green. Although Cd in plastic has been restricted or banned under various
366 Directives, it is likely to be encountered in certain products still in use in the domestic
367 and urban settings (Hansen et al., 2013), thereby explaining its widespread occurrence
368 in beached marine litter.

369

370 Lead was detected in a range of plastics, ropes and foams in the present study. Among
371 the plastics, the highest concentrations were encountered in various fragments that
372 were mainly red or yellow but occasionally green, white or grey. Ropes and netting
373 that contained Pb in excess of a few hundred $\mu\text{g g}^{-1}$ were always orange, while foams
374 containing Pb in excess of 1000 $\mu\text{g g}^{-1}$ were usually rigid polyurethane. Lead was
375 commonly employed as a heat and UV stabiliser in PVC, and in a number of pigments
376 (but largely lead chromates) provided a wide range of colours in a variety of plastics.
377 Concentrations of Pb added to plastics were variable but generally less than 50,000 μg
378 g^{-1} by weight (Hansen et al., 2013) until various Directives resulted in the
379 discontinuation or phase-out of lead compounds by the plastics industry.

380

381 Among the 43 plastic samples in which Pb was detected, only three were PVC
382 (according to the XRF classification based on Cl content); however, where both Pb
383 and Cr were both measurable ($n = 22$) there was a significant relationship between the

384 two metals with a slope that was close to the mass ratio of Pb to Cr in lead chromate
385 (about 4; Figure 3a). No rope samples containing Pb were classified as PVC by the
386 XRF but, as above, a significant relationship between Pb and Cr ($n = 24$) with a slope
387 close to the Pb to Cr mass ratio in lead chromate was observed among the nine
388 samples in which both metals were detected (Figure 3b). Regarding the foams, there
389 was no significant relationship between Pb and Cr where both metals were present (n
390 $= 26$) and the concentration of Cr exceeded that of Pb in most cases (Figure 3c).
391 Overall, however, the highest concentrations of Pb among the foams were
392 encountered where Cr was not detected.

393

394 The observations above suggest that lead chromates are the most abundant form of Pb
395 among the plastics and ropes but that expanded-extruded polymers, and in particular
396 rigid polyurethanes, contain Pb derived from a different source. Although it is unclear
397 why Pb is so abundant among the polyurethane samples, Szycher (2013) makes
398 reference to a few heavy metals, including Pb, as possible leachable toxins in such
399 polymers, while Carraher (2005) notes the catalytic properties of monomeric,
400 organolead compounds in the formation of some foams produced in the 1960s.

401

402 The presence of plastic litter containing hazardous elements represents a potential
403 source of localised contamination in the marine environment. For example, the
404 highest concentrations of Cd and Pb in the plastics category are three to four orders of
405 magnitude higher than the respective median concentrations in sandy sediment from
406 the south west coast of the UK (0.5 and $12.6 \mu\text{g g}^{-1}$; Schuwerack et al., 2007);
407 consequently, the presence of just 0.1% of plastic fragments among the sediment may
408 result in an order of magnitude elevation in the net content of Cd and Pb. Clearly, the

409 risks and impacts associated with these elements will depend on their mobilities and
410 bioaccessibilities in the polymeric matrix. Most metallic compounds are added to
411 plastics as finely-divided solids that are incorporated into the polymer while in a
412 liquid phase, meaning that dispersed particles are retained physically within the
413 matrix and have little tendency to migrate, at least from new or undamaged products
414 (Pritchard, 1998). With wear and tear, abrasion and degradation, however, or the very
415 effects that plastics are subjected to while suspended or beached in the marine
416 environment, particles may be released (Hansen et al., 2013). Of particular concern in
417 this respect are PVC-based materials, where the release of Cl appears to facilitate the
418 migration of other components (Piorek 2004). The nature and kinetics of hazardous
419 element mobilisation from a variety of plastics, foams and ropes are currently under
420 investigation.

421

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425

426 **References**

427 Ashton, K., Holmes, L., Turner, A., 2010. Association of metals with plastic
428 production pellets in the marine environment. *Marine Pollution Bulletin* 60, 2050-
429 2055.

430

431 Bosco, G.L. 2013. Development and application of portable, hand-held x-ray
432 fluorescence spectrometers. *Trends in Analytical Chemistry* 45, 121-134.

433

434 Browne, M.A., Galloway, T.S., Thompson, R.C., 2010. Spatial patterns of plastic
435 debris along estuarine shorelines. *Environmental Science and Technology* 44, 3403-
436 3409.

437

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

441

442 Carson, H.S., 2013. The incidence of plastic ingestion by fishes: From the prey's
443 perspective. *Marine Pollution Bulletin* 74, 170-174.

444

445 Environmental Protection Agency, 2007. Method 6200 - Field portable x-ray
446 fluorescence spectrometry for the determination of elemental concentrations in soil
447 and sediment.

448 <http://www3.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/6200.pdf>
449 Accessed 12/15.

450

451 Frias, J.P.G.L., Sobral, P., Ferreira, A.M., 2010. Organic pollutants in microplastics
452 from two beaches of the Portuguese coast. *Marine Pollution Bulletin* 60, 1988-1992.

453

454 Gauquie, J., Devrese, L., Robbens, J., De Witte, B., 2015. A qualitative screening and
455 quantitative measurement of organic contaminants on different types of marine plastic
456 debris. *Chemosphere* 138, 348-356.

457

458 Guardiola, F.A., Cuesta, A., Meseguer, J., Esteban, M.A., 2012. Risks of using
459 antifouling biocides in aquaculture. *International Journal of Molecular Sciences* 13,
460 1541-1560.
461

462 Hansen, E., Nilsson, N.H., Lithner, D., Lassen, C., 2013. Hazardous substances in
463 plastic materials. COWI and the Danish Technological Institute on behalf of The
464 Norwegian Climate and Pollution Agency, Oslo. 150 pp.
465

466 Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals by
467 plastic resin pellets in the marine environment. *Environmental Pollution* 160, 42-48.
468

469 Katz, H.S., Milewski, J.V., 1987. *Handbook of Fillers for Plastics*. Van Nostrand
470 Reinhold, New York.
471

472 Keimowitz, A.R., Strunsky, N., Wovkulich, K., 2016. Organophosphate flame
473 retardants in household dust before and after introduction of new furniture.
474 *Chemosphere* 148, 467-472.
475

476 King, D.A., Walker, J., Harman, D.J., 2009. Ten-year storage studies on flame
477 retarded polyurethane foam. *Cellular Polymers* 28, 325-343.
478

479 Koch-Jugl, J, Beer, I, Bolland, T., Dettling, F., Stolzenberg, H.C., Tietjen, L., Wurbs,
480 J., Debiak, M., 2015. Hexabromocyclododecane (HBCD): Answers to frequently
481 asked questions. Federal Environment Agency (UBA), Dessau-Roßlau, Germany.
482

483 McIntosh, R.R., Kirkwood, R., Sutherland, D.R., Dann, P., 2015. Drivers and annual
484 estimates of marine wildlife entanglement rates: a long-term case study of Australian
485 fur seals. *Marine Pollution Bulletin* 101, 716-725.

486

487 Nakashima, E., Isobe, A., Kako, S., Itai, T., Takahashi, S., 2012. Quantification of
488 toxic metals derived from macroplastic litter on Ookushi beach, Japan. *Environmental*
489 *Science & Technology* 46, 10099-10105.

490

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

493

494 Piorek, S., 2004. Feasibility of analysis and screening of plastics for heavy metals
495 with portable x-ray fluorescence analyser with miniature x-ray tube. GPEC 2004
496 Paper abstract #14.

497

498 Pritchard, G., (ed.) 1998. *Plastic additives: An A-Z reference*. Springer, Dordrecht,
499 632pp.

500

501 Rochman, C.M., Hoh, E., Korobe, T., Teh, S.J., 2013. Ingested plastic transfers
502 hazardous chemicals to fish and induces hepatic stress. *Scientific Reports* 3, 3263
503 DOI: 10.1038/srep03263.

504

505 Rochman, C.M., Hentschel, B.T., Teh, S.J., 2014. Long-term sorption of metals is
506 similar among plastic types: implications for plastic debris in aquatic environments.
507 *PLOS ONE* 2014, 9, article number e85433.

508

509 Schuwerack, P.-M.M., Neal, M., Neal, C., 2007. The Dart estuary, Devon, UK: a case
510 study of chemical dynamics and pollutant mobility. *Hydrology and Earth System*
511 *Sciences* 11, 382-398.

512

513 Szycher, M., 2013. *Szycher's Handbook of Polyurethanes*, second edition. CRC
514 Press, Boca Raton, London, 1126pp.

515

516 Tamaddon, F., Hogland, W., 1993. Review of cadmium in plastic waste in Sweden.
517 *Waste Management and Research* 11, 287-295.

518

519 Turner, A., Solman, K.R., 2016. Analysis of the elemental composition of marine
520 litter by field portable x-ray fluorescence spectrometry. *Talanta* 159, 262-271.

521

522 US EPA, 2014. Flame retardant alternatives for hexabromocyclododecane (HBCD).
523 EPA publication 740R14001, 230 pp.

524 https://www.epa.gov/sites/production/files/2014-06/documents/hbcd_report.pdf

525 accessed 3/16.

526

527 Weil, E.D., Levchik, S.V., 2004. Commercial flame retardancy of polyurethanes.
528 *Journal of Fire Sciences* 22, 183-210.

529

530 Yorio, P., Marinao, C., Suarez, N., 2014. Kelp Gulls (*Larus dominicanus*) killed and
531 injured by discarded monofilament lines at a marine recreational fishery in northern
532 Patagonia. *Marine Pollution Bulletin* 85, 186-189.

Table 1: A comparison of measured and reference concentrations (in $\mu\text{g g}^{-1}$) in two impregnated Niton polyethylene disks. Errors denote either the 95% confidence level (reference) or one standard deviation (measured).

material	As	Ba	Br	Cd	Cr	Hg	Pb	Sb	Se
PN 180-554									
reference			495 \pm 20	150 \pm 6	995 \pm 40	1000 \pm 40	1002 \pm 40		
measured ($n=5$)			497 \pm 3	135 \pm 5	1063 \pm 7	912 \pm 5	964 \pm 21		
PN 180-619									
reference	51 \pm 7	704 \pm 45		292 \pm 20	106 \pm 10	101 \pm 10	155 \pm 12	94 \pm 10	207 \pm 15
measured ($n=5$)	46 \pm 2	761 \pm 25		295 \pm 5	116 \pm 8	93 \pm 3	136 \pm 2	98 \pm 3	228 \pm 4

Table 2: The numbers and masses of the items in different categories of marine litter retrieved from each beach.

beach	plastics			foams			ropes			total	
	n	total, g	median (min-max), g	n	total, g	median (min-max), g	n	total, g	median (min-max), g	n	combined mass, g
Chapel Porth	50	173.09	2.32 (0.17-27.92)	38	43.18	0.34 (0.01-15.02)	13	119.64	1.55 (0.20-40.10)	101	335.91
Constantine Bay	61	76.24	0.45 (0.02-13.49)	34	22.79	0.36 (0.01-5.43)	54	47.61	0.50 (0.13-6.81)	149	146.64
Mount Batten	41	98.30	0.95 (0.03-17.40)	70	100.90	0.23 (0.002-22.15)	11	7.95	0.69 (0.11-2.28)	122	207.15
Porth Kidney	67	38.61	0.19 (0.01-11.8)	47	42.43	0.07 (0.004-11.48)	10	3.22	0.26 (0.02-1.09)	124	84.26
Saltram	60	129.75	0.55 (0.009-20.19)	14	63.24	0.61 (0.09-49.80)	3	2.22	0.53 (0.13-1.56)	77	195.21
total	279	515.99	0.54 (0.009-27.92)	203	272.54	0.26 (0.002-49.80)	91	180.64	0.56 (0.02-40.10)	573	969.17

Table 3: Distributions and summary statistics for the elemental concentrations in beached plastics ($n = 279$). All concentrations are in $\mu\text{g g}^{-1}$ and elements are ordered according to descending number detected.

	no. detected	10^0 - 10^1	10^1 - 10^2	10^2 - 10^3	10^3 - 10^4	10^4 - 10^5	$>10^5$	min.	max.	median
Cl	225		23	117	68	4	13	22	532,000	672
Zn	139	1	83	43	8	4		5.1	26,700	58
Cr	127		113	13	1			21	1240	37
Cu	71	1	49	21				9.9	718	52
Br	53	16	29	6	1	1		4.7	17,900	20
Pb	43	8	15	7	10	3		6.3	17,500	87
Ba	39			11	24	3	1	236	143,000	1691
Sb	18			15	2	1		154	12,600	262
Sn	16		3	9	4			34	2090	211
Cd	11			5	6			117	4640	1270
As	8	6	2					4	21	8
Ni	7		6	1				17	555	29
Se	5			5				214	563	334
Hg	3		1	2				54	273	156

Table 4: Distributions and summary statistics for the elemental concentrations in beached foams ($n = 203$). All concentrations are in $\mu\text{g g}^{-1}$ and elements are ordered according to descending number detected.

	no. detected	10^0 - 10^1	10^1 - 10^2	10^2 - 10^3	10^3 - 10^4	10^4 - 10^5	$>10^5$	min.	max.	median
Cl	195			3	20	96	76	743	633,000	65,700
Br	155		38	86	28	3		12	17,600	244
Cr	148		23	125				23	940	252
Zn	120		19	68	31	2		26	25,300	248
Cu	39		4	32	3			71	1910	219
Pb	34	1	15	11	6	1		6.7	17,000	111
Sn	26		3	20	3			53	2280	209
As	12		9	3				25	210	62
Ba	12			6	6			298	4622	1000
Sb	4		1	2	1			67	5820	259
Ni	2			2				224	410	317
Cd	0									
Hg	0									
Se	0									

Table 5: Distributions and summary statistics for the elemental concentrations in beached ropes ($n = 91$). All concentrations are in $\mu\text{g g}^{-1}$ and elements are ordered according to descending number detected.

	no. detected	10^0 - 10^1	10^1 - 10^2	10^2 - 10^3	10^3 - 10^4	10^4 - 10^5	$>10^5$	min.	max.	median
Cl	85			35	30	20		189	49,900	1510
Cu	63		42	20	1			26	1225	76
Br	51	3	46	2				6.3	247	26
Zn	40	1	32	7				9.1	535	35
Cr	39		27	12				25	908	72
Pb	36	1	14	18	3			9.5	3770	139
Sn	8		4	4				49	467	121
As	3	1	2					6.6	17	15
Ba	2			2				196	356	278
Ni	2		1	1				37	735	386
Sb	1			1				122	122	122
Cd	0									
Hg	0									
Se	0									

Figure 1: Locations of the five beaches in SW England sampled in the present study.

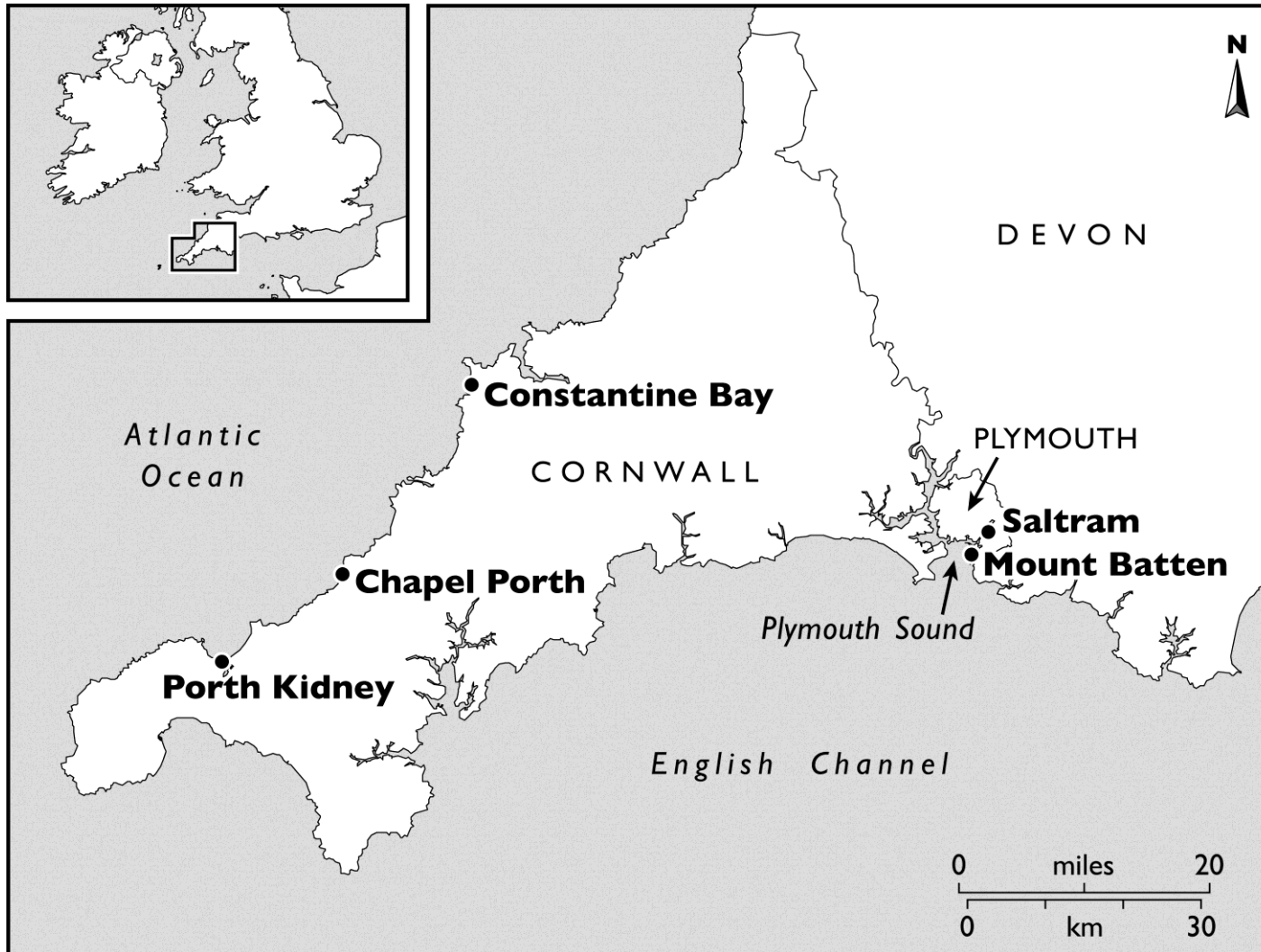


Figure 2: Concentration of Br versus concentration of Cl in the beached plastics (\blacktriangle), foams (\triangle) and ropes (\times).

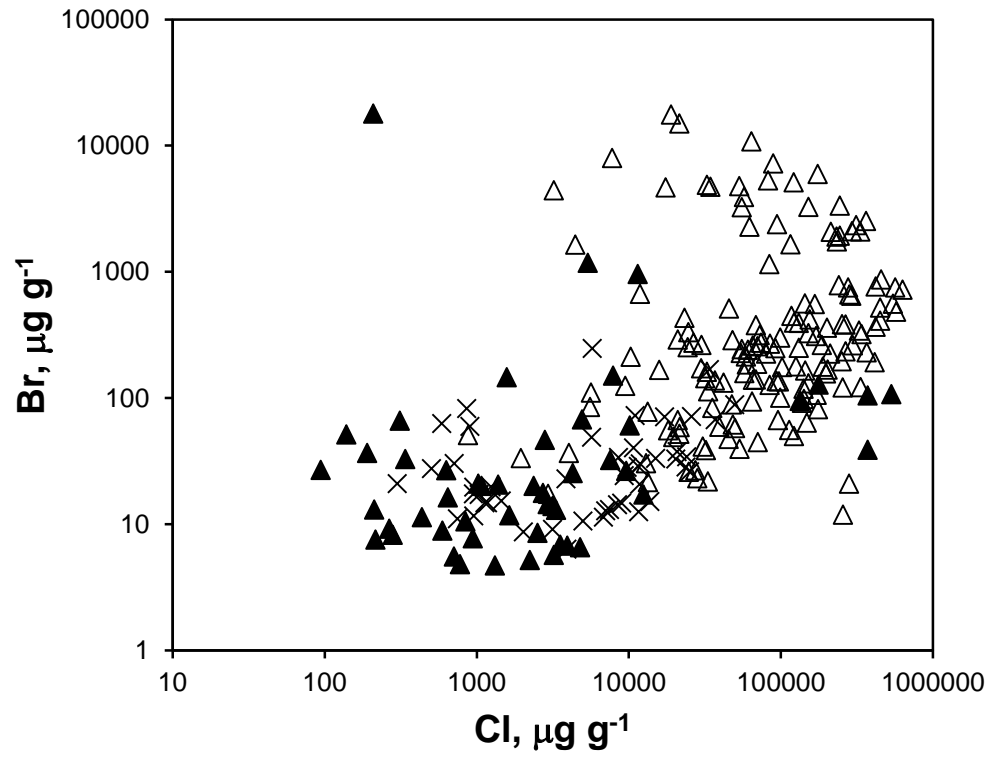


Figure 3: Concentration of Pb versus concentration of Cr in beached litter: (a) plastics; (b) ropes; (c) foams. Also shown are the lines defining the mass ratio of Pb to Cr in lead chromate (4:1) and, for plastics and ropes, best fit regression lines.

