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**Analysis of the elemental composition of marine litter
by field-portable-XRF**

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22 **Abstract**

23 Marine litter represents a pervasive environmental problem that poses direct threats to
24 wildlife and habitats. Indirectly, litter can also act as a vehicle for the exposure and
25 bioaccumulation of chemicals that are associated with manufactured or processed
26 solids. In this study, we describe the use of a Niton field-portable-x-ray fluorescence
27 (FP-XRF) spectrometer to determine the content of 17 elements in beached plastics,
28 foams, ropes and painted items. The instrument was used in a 'plastics' mode
29 configured for complex, low density materials, and employed a thickness correction
30 algorithm to account for varying sample depth. Accuracy was evaluated by analysing
31 two reference polyethylene discs and was better than 15% for all elements that had
32 been artificially impregnated into the polymer. Regarding the litter samples, limits of
33 detection for a 120 second counting time varied between the different material
34 categories and among the elements but were generally lowest for plastics and painted
35 items with median concentrations of less than $10 \mu\text{g g}^{-1}$ for As, Bi, Br, Cr, Hg, Ni, Pb,
36 Se and Zn. Concentrations returned by the XRF were highly sensitive to the thickness
37 correction applied for certain elements (Ba, Cl, Cr, Cu, Fe, Sb, Ti, Zn) in all matrices
38 tested, indicating that accurate measurement and application of the correct thickness is
39 critical for acquiring reliable results. An independent measure of the elemental
40 content of selected samples by ICP spectrometry following acid digestion returned
41 concentrations that were significantly correlated with those returned by the XRF, and
42 with an overall slope of $[\text{XRF}]/[\text{ICP}] = 0.85$. Within the FP-XRF operating
43 conditions, Cl, Cr, Fe, Ti and Zn were detected in more than 50% and Hg and Se in
44 less than 1% of the 367 litter samples analysed. Significant from an environmental
45 perspective were concentrations of the hazardous elements, Cd, Br and Pb, that
46 exceeded several thousand $\mu\text{g g}^{-1}$ in many cases.

47

48 **Keywords:** marine litter; XRF; plastics; ropes; foams; metals

49 **1. Introduction**

50 The accumulation of marine litter in the open ocean and on beaches is a significant
51 and pervasive global problem. Discarded solid waste has a multitude of both land-
52 based and marine-based sources and arises through a lack of awareness and poor or
53 ineffective waste management practices. As well as representing an aesthetic problem
54 on the foreshore and a nuisance to boaters, manufactured or processed items of waste
55 that are composed of persistent, durable and low-density materials, like plastics,
56 rubbers and ropes, pose serious threats to wildlife through ingestion, suffocation and
57 entanglement [1]. Ingestion of small fragments of litter also affords a route of
58 exposure to and accumulation of chemicals that are associated with these materials
59 [2]. Such chemicals are either an inherent component or degradation product of the
60 solid itself, or may have accumulated from sea water during suspension and
61 transportation of the litter [3].

62
63 Although hydrophobic organic pollutants, including polychlorinated biphenyls and
64 polycyclic aromatic hydrocarbons, have been well-studied in this respect [4-6], recent
65 attention has also focussed on the association of various trace metals, like Cd, Cu, Cr,
66 Ni, Pb and Zn, with plastic litter. Thus, controlled laboratory experiments have shown
67 that small quantities of metal can rapidly adsorb onto the plastic surface from sea
68 water [7] while mild acid digestion of beached plastics has revealed that greater
69 quantities of metals can gradually accumulate in natural films coating the polymer [8].
70 More important from a bulk concentration perspective, however, is the association of
71 certain metals with plastics and other synthetic solids arising from the manufacturing
72 process itself [9]. For example, many metals and metalloids and their compounds are
73 used, or have been used before restrictions came into place, as colourants, fillers,

74 stabilisers, catalysts, biocides and flame retardants and at concentrations of up to
75 several per cent on a dry weight basis [10]. While most additives are designed to be
76 non-migratable from the virgin matrix, leaching may be facilitated by ageing and
77 abrasion of the solid [9], or the very conditions that marine litter are subjected to
78 during transport in sea water and subsequent beaching.

79

80 The analysis of metals in manufactured and processed solids by wet chemical means,
81 involving the complete digestion of the material in concentrated acid and subsequent
82 analysis by, for example, inductively coupled plasma (ICP), spectrometry is rather
83 time-consuming and labour-intensive. More appropriate for the analysis of beach
84 litter, therefore, is a non-destructive technique that allows the rapid throughout of
85 samples of diverse composition and that can be used to explore the spatial distribution
86 of metals within a single- or multiple-component sample. With the miniaturisation of
87 x-ray sources, reduction in battery power requirements, and improvements in detector
88 resolution, detection limits, precision and standardless calibrations, field-portable-x-
89 ray fluorescence (FP-XRF) spectrometry meets these needs [11].

90

91 Nakashima et al. [9] recently employed energy dispersive FP-XRF spectrometry
92 (alpha-6500, Innov-X) to determine the concentrations of five metals-metalloids (As,
93 Cr, Pb, Sb, Sn) in a number of plastic items retrieved from a beach in south west
94 Japan. Measurements were corrected using element-specific and material-specific
95 regression equations that related XRF measurements to those returned by ICP after
96 HNO₃-H₂SO₄ digestion. Unfortunately, however, data reported in the article were
97 limited to mean concentrations of Pb in polyethylene, polypropylene and polyvinyl
98 chloride (PVC) and a mean concentration of Sn in PVC. Moreover, little information

99 was provided on the XRF methodology itself, including counting time, fluorescent x-
100 ray energy ranges, potential interferences, thickness considerations, and the mode and
101 internal calibration of the instrument.

102

103 In the present paper, we describe the use of a Niton FP-XRF spectrometer to
104 determine the concentration of a larger suite of elements ($n = 17$) in a wide variety of
105 samples of marine litter (including plastics, rubbers, expanded-extruded materials,
106 processed corks, ropes, netting and painted surfaces) retrieved from four different
107 beaches. We use the instrument in a ‘plastics’ mode that is specifically configured for
108 the analysis of complex, low density materials, and evaluate the effects of sample
109 thickness, density and heterogeneity and various aspects of quality control, including
110 a comparison with independent ICP measurements based on analysis of acid digests.
111 The advantages and limitations of the XRF technique used both in situ and ex situ are
112 also discussed.

113

114 **2. Materials and methods**

115 *2.1. Sampling and sample locations*

116 Four beaches in south west England were visited just after high water on single
117 occasions between late August and late September, 2015. Saltram beach is a small,
118 sandy, intertidal region on the east bank of a shallow, urbanised estuary (Plym) that is
119 close to a recently capped landfill site. Mount Batten is a south-facing pebble-sand
120 beach in Plymouth Sound, a bay that receives freshwater inputs from the Plym and
121 Tamar estuaries and, being protected to the south by a 1.6 km breakwater, is a natural
122 harbour for naval and commercial ships and a popular location for yachting.

123 Constantine Bay and Porth Kidney are sandy beaches on the north (Atlantic) coast of
124 Cornwall and are popular destinations for both tourists and surfers.

125

126 On each beach, visible pieces of litter were collected by hand from a transect of the
127 high (or highest) water line. The length of each transect varied between about 10 m
128 and 200 m depending on the abundance of material (and ensuring that at least 50
129 samples were collected in each case). Litter retrieved included whole objects and
130 fragments of plastic and rubber, pieces of low density expanded-extruded plastic and
131 rubber and fragments of processed cork (the latter being visually very similar to many
132 expanded polymers), offcuts of rope, fabric and netting, and painted wood, fibreglass
133 and synthetic resin; hereafter, these components are classified as plastics, foams,
134 ropes and painted surfaces, respectively. Note that litter not considered in the present
135 study included metal objects, pieces of glass, paper items, unpainted wood and films
136 of food packaging that appeared to have been recently discarded in situ.

137

138 Litter from each beach was stored in a series of clear polyethylene bags and
139 transported to the laboratory where individual items were cleared of sand and other
140 debris under running tap water and with the aid of a Nylon brush before being dried at
141 40 °C in an oven for 12 h or, for foams, under desiccation at room temperature for up
142 to 96 h. Samples were then weighed on a five-figure balance and stored individually
143 in labelled polyethylene specimen bags and in the dark pending analysis.

144

145 2.2. XRF analysis

146 Samples of litter were analysed by energy dispersive FP-XRF using a battery-
147 powered, field portable (1.3 kg) Niton XRF analyser (model XL3t 950 He GOLDD+).

148 The instrument employs a miniature, low power x-ray tube with an Ag transmission
149 anode operating at up to 50 kV of high voltage and 200 μ A of current as the source of
150 sample excitation, and is fitted with a geometrically optimised large area silicon drift
151 detector to detect and register characteristic x-rays from the sample. The
152 concentrations of As, Ba, Bi, Br, Cd, Cl, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, Sn, Ti and
153 Zn, whose fluorescent peaks range from 2.62 keV (Cl- K_{α}) to 32 keV (Ba- K_{α}), were
154 determined in a plastics mode through a fundamental parameters-based alpha
155 coefficient correction model. This iterative approach accounts for background matrix
156 effects by describing measured fluorescent x-ray intensities using mathematical
157 equations that tie together the physics of the interaction of x-rays with sample
158 components [12]. Fundamental parameters eliminates the requirement for sample-
159 specific standards, has a wide dynamic range and is independent of the size and shape
160 of the surface [11].

161

162 Because polymers are composed of light elements, and primarily carbon and
163 hydrogen, they are weak absorbers of x-rays, and below a critical, saturation
164 thickness, d_{sat} , the measured intensity of x-rays will be dependent on both the analyte
165 concentration and the thickness of the sample, d . For polyethylene, d_{sat} , is about 9
166 mm, while for polyvinyl chloride (PVC) the abundance of chloride results in a d_{sat} of
167 about 5 mm. For polymers containing heavier elements as, for example, contaminants
168 and additives, d_{sat} is reduced compared with that of the pure material, while in
169 expanded-extruded synthetic polymers, ropes and corks, the presence of air results in
170 densities that are reduced compared with those of the corresponding unexpanded or
171 air-free equivalents and d_{sat} is increased. For the analysis of polymeric materials in the
172 plastics mode, the Niton XL3t 950 GOLDD+ has a thickness correction algorithm

173 down to 0.05 mm that employs a compensation for mass absorption coefficient based
174 on Compton scatter so that variations in density are factored in. In practice, the
175 thickness of each sample needs to be measured (in mm) before being analysed and if
176 it falls below d_{sat} , the corrective algorithm should be applied with the appropriate
177 (measured) thickness.

178

179 In the present study, thickness correction was employed for all plastic samples of $d <$
180 10 mm, including those identified by the XRF as PVC (based on Cl content), and to
181 expanded-extruded polymers, ropes and corks of $d < 100$ mm (effectively all samples
182 in these categories). Thickness itself was determined through the flattest
183 ('measurement') surface using 300 mm Allendale digital callipers, and to increase the
184 effective depth and flatness of thin or hollow samples, items were often cut (with
185 scissors, pliers or a blade), folded or layered and, where necessary, held in place using
186 crocodile clips. Regarding the painted surfaces, a thickness correction of 0.05 mm was
187 applied in order to ensure that measurements were made of the surface film while
188 minimising interferences from the underlying wooden or polymeric substrates.

189

190 The XRF was used in the laboratory in a bench top accessory stand (with the nose
191 upwards) and was connected to a laptop computer via USB and a remote trigger.

192 Samples were placed on to a SpectraCertified Mylar polyester 3.6 μm film with the
193 measurement surface facing downwards. The slide was then positioned such that the
194 sample lay directly and centrally over a 3 mm small-spot collimator above the 8 mm
195 XRF measurement window, a process aided by referring to real-time video footage
196 generated by an integrated CCD camera adjacent to the detector. On closing the steel
197 shield of the stand, measurements with appropriate thickness correction were

198 activated through the laptop for a total period of 120 seconds; specifically, counting
199 was performed for 60 seconds each in a low energy range (20 kV and 100 μ A: Cl, Cr
200 and Ti) and main energy range (50 kV and 40 μ A: all remaining elements). Spectra
201 were quantified by fundamental parameter coefficients to yield elemental
202 concentrations on a dry weight basis (in μ g g^{-1}) and with a counting error of 2σ (95%
203 confidence). At the end of each 2-6 h sample measurement session, spectra and
204 elemental concentrations were downloaded to the laptop using Niton data transfer
205 (NDT) PC software.

206

207 *2.3. Sample digestion and analysis by ICP*

208 As an independent and more sensitive measure of the elemental content of marine
209 litter, a variety of samples ($n = 18$), encompassing all material categories with the
210 exception of painted surfaces and that had already been tested by XRF, were digested
211 in Fisher Scientific TraceMetal grade acids (and ammonia) and analysed by
212 inductively coupled plasma-optical emission spectroscopy (ICP-OES). Thus, offcuts
213 or slices of plastic, foam (including cork) and rope of between about 50 mg and 200
214 mg were prepared with a stainless steel blade before being accurately weighed into
215 individual 100 ml borosilicate Tecator tubes. Three ml of concentrated sulphuric acid
216 was added to each tube and the contents heated to 300°C for about 2 h in an
217 aluminium digestion block. To the resulting digests, concentrated HNO₃ was carefully
218 added dropwise until the solutions changed from black to pale yellow or colourless.
219 After the covered contents had been allowed to cool overnight, digests were
220 transferred to 50 ml glass volumetric flasks and diluted to mark with 2% HNO₃. To
221 any digests containing a visible precipitate (presumably PbSO₄ and/or BaSO₄),

222 concentrated ammonia solution was added dropwise until the solids cleared.
223 Procedural controls were undertaken likewise but in the absence of litter samples.
224
225 Digests were analysed for all elements detected by XRF and that were measurable by
226 ICP-OES (thereby excluding Cl and Br) using a ThermoScientific iCAP 7400. The
227 instrument was calibrated using four mixed standards and a blank prepared by serial
228 dilution of CPI International standards in 2% HNO₃, and settings in both UV and
229 visible light were as follows: exposure time = 2 s; RF power = 1150 W; nebuliser,
230 coolant and auxiliary gas flows = 0.50, 12 and 0.5 L min⁻¹, respectively; viewing
231 height = 12 mm; uptake time = 50 s; wash time = 15 s.

232

233 *2.4. FTIR analysis*

234 In order to identify the component polymers in the plastics, foams and ropes, selected
235 samples ($n = 50$) were analysed by attenuated total reflection-Fourier transform infra-
236 red spectroscopy (ATR-FTIR) using a Bruker ALPHA Platinum ATR QuickSnap
237 A220/D-01 spectrometer. Samples were cut to a suitable size, where necessary, using
238 a stainless steel scalpel, and then firmly clamped down on to the ATR diamond crystal
239 in order to ensure good contact and sufficient penetration of the evanescent wave.
240 Measurements, consisting of 16 scans in the range 4000 to 400 cm⁻¹ and at a
241 resolution of 4 cm⁻¹, were activated via Bruker OPUS spectroscopic software, with
242 subsequent identification involving comparisons of transmittance spectra with
243 libraries of reference spectra.

244

245 **3. Results and Discussion**

246 *3.1. Sample characteristics*

247 A total of 376 litter samples retrieved from four beaches of south west England were
248 analysed in the present study, of which 149 were categorised as plastics, 149 as foams
249 (including processed corks), 68 as ropes and 10 as painted surfaces. The mass of
250 individual items of plastic ranged from less than 10 mg for various unidentifiable
251 fragments to over 10 g for relatively large fragments and specific objects (e.g. toys, a
252 bodyboard clip and a cigarette lighter); thickness through the flattest surface, d ,
253 ranged from about 0.3 mm for several flexible films after folding or stacking to more
254 than 10 mm for many of the largest fragments and objects. The mass of the foams
255 ranged from less than 3 mg to 50 g and d ranged from about 0.5 to 40 mm, with most
256 items being fragments of various size, shape and colour (but mainly off-white or
257 yellow-brown). The mass of ropes ranged from about 20 mg for a small fragment of
258 fabric to over 40 g for a multi-coloured offcut of rigging, with d , after any deliberate
259 intertwining of fishing line or frayed netting, ranging from about 2 to 12 mm. The
260 mass of painted surfaces ranged from about 1.7 to 150 g, with the bulk of the material
261 representing the underlying substrate, and in all cases d (of the surface) was assumed
262 to be 0.05 mm (see above).

263

264 FTIR analysis of selected samples revealed that plastic items and fragments were
265 mainly polyethylene or polypropylene but a few were polyvinyl chloride (PVC), and
266 that offcuts of rope and netting were generally polyethylene or polypropylene but
267 fishing lines were Nylon. Many pieces of expanded-extruded polymer could not be
268 identified definitively but those yielding clear spectra were predominantly polystyrene
269 or polyurethane with some fragments composed of elasticated rubber, PVC, rayon or
270 acrylic. Because information on cork was not contained in the reference libraries, such

271 samples were verified by comparisons of spectra with those derived from direct
272 measurements of a series of cork stoppers.

273

274 *3.2. Detection limits*

275 FP-XRF is able to detect elements that elicit a sufficiently strong fluorescence signal
276 relative to background intensity that is free from interferences arising from the matrix
277 and from the interactions of other elements (peak overlaps and absorption and
278 enhancement effects). The limit of detection (LOD) is, therefore, dependent on the
279 element (or its x-ray activity and the energies of its fluorescence peaks), detector
280 resolution, mode of application of the instrument, counting time, sample thickness,
281 physical and chemical composition of the material, and statistical criteria used for
282 defining detection. The Niton XLT3t series of analysers define LODs that are specific
283 to the characteristics of the sample and the counting time as three standard deviations
284 ($1.5 \times 2\sigma$, or 99.7% confidence interval), and measurements are reported in the NDT
285 output only where concentrations exceed this threshold with calculated detection
286 limits provided otherwise. The lower LODs specified by the manufacturer for
287 elements in 'clean' polymers of unspecified thickness that are relatively free of inter-
288 element spectral interferences and for a 30-second total counting time in plastics
289 mode range from less than $10 \mu\text{g g}^{-1}$ (As, Bi, Br, Hg, Pb and Se) to $100 \mu\text{g g}^{-1}$ (Ba) in
290 polyethylene and from less than $20 \mu\text{g g}^{-1}$ (As, Br, Cd and Pb) to more than $100 \mu\text{g g}^{-1}$
291 (Fe) in PVC.

292

293 LODs based on the analysis of the more varied and complex litter samples are shown
294 in Table 1. Here, the median, minimum and maximum calculated limits for each
295 element and for each category of sample are provided for a total counting time of 120

296 seconds and with appropriate thickness correction where applicable (see below), along
297 with the numbers and percentages of samples that were not detected in each case.
298 Within a specific material category, LODs vary widely for a given element, reflecting
299 the sensitivity of detection to sample composition and thickness and the presence of
300 and interferences arising from other elements in the matrix. For most elements, and
301 within a given category, LODs span one or two orders of magnitude among the
302 samples. With respect to the different material categories, and based on median
303 values, LODs are higher in foams than in plastics and ropes, presumably because of
304 the greater contribution of air in the former (air promotes multilateral reflections and
305 inhibits fluorescent x-rays from reaching the detector [13]). Painted surfaces exhibit
306 the lowest LODs, likely because samples in this category contained fewer elements
307 and lower concentrations of Cl as potential interferents (attenuating or enhancing
308 secondary x-rays). Among the elements, LODs were generally lowest, and below 40
309 $\mu\text{g g}^{-1}$ for each category of material, for As, Br, Cr and Pb, and highest, and above 70
310 $\mu\text{g g}^{-1}$ for each category, for Ba and Cl.

311

312 *3.3. Thickness correction and reference materials*

313 Table 2 shows the results of multiple analyses ($n = 5$) of two reference materials
314 manufactured by Niton (PN 180-554, batch SN PE-071-N, and PN 180-619, LOT#T-
315 18); these are polyethylene discs of 31 mm in diameter impregnated with various
316 elements and whose thicknesses ($d \sim 13$ mm) are above the saturation level for the
317 material. Thus, without thickness correction, the FP-XRF delivers concentrations that
318 are usually within 10% of the respective reference values; for comparison, an
319 ‘acceptable’ difference from certified values of $\pm 20\%$ for each analyte is stipulated
320 by the US Environmental Protection Agency (EPA) [14]. Also shown in Table 2 are

321 results of analyses of a 3.4 mm section of PN 180-619 with appropriate thickness
322 correction applied. Measured concentrations are within 12% of corresponding
323 concentrations returned by analysis of the whole disc without thickness correction
324 with the exception of Ba, whose measured concentration in the section was 40%
325 greater than that in the whole disc.

326

327 Figure 1 illustrates the effect of varying the thickness correction on the concentrations
328 returned, and after normalisation to the measured concentrations without thickness
329 correction (and as annotated), for reference material PN 180-554; these results
330 illustrate how different elements respond to the corrective algorithm in polyethylene.
331 Thus, for Cr and to a lesser extent Hg, adjusting thickness correction towards its lower
332 limit of 0.05 mm results in progressively lower normalised concentrations, while for
333 Cd the same adjustments result in a progressively higher concentrations; normalised
334 concentrations of Br and Pb, on the other hand, exhibit relatively little dependence on
335 the magnitude of the thickness correction applied. Despite different concentrations of
336 several elements being returned that were dependent on the thickness correction
337 applied, relative error did not display any clear dependence on this variable.

338

339 *3.4. Thickness correction and plastic litter*

340 Figure 2 exemplifies the effects of applying different thickness corrections to four
341 plastic (polyethylene and polypropylene) samples of varying size, colour, condition-
342 age and elemental composition and where $d < d_{\text{sat}}$. Here, a wider range of elements
343 detected are normalised to the corresponding concentrations measured after applying
344 correction for the measured thickness, and whose values are annotated on each panel.
345 For a given element, the precise effects and trends are different, both among the

346 samples and from the reference material (Figure 1), presumably because of the
347 interactive effects that the presence of additional elements have on each other in more
348 complex materials and the consequent corrections applied by fundamental parameters.
349 In general, however, and with adjustments in thickness correction towards the lower
350 limit, Ba and Sb are subject to a significant increase in normalised concentration
351 while Cl, Cu, Fe, Ti and Zn exhibit a decrease in normalised concentration. Chlorine
352 exhibited the greatest dependency on thickness correction in respect of the latter, and
353 among the samples Cu, Fe and Zn exhibited a dependency whose significance
354 appeared to exhibit an inverse dependency on the measured concentration with
355 appropriate correction applied. Bromine, Cd, Pb and Se exhibited a dependency on
356 thickness correction that was relatively small, with concentration differences across
357 the range of corrections that varied by no more than 20%. As with the reference
358 materials, relative errors did not display any clear dependence on thickness correction,
359 but were inversely related to the absolute concentration of the element in the sample.

360

361 *3.5. Thickness correction and foam and rope litter*

362 Figure 3 shows the effects of applying different thickness corrections to six different
363 samples containing air within their structures; namely, an expanded polystyrene, two
364 expanded, rigid polyurethanes, a Nylon fishing line that had been intertwined and
365 secured between two crocodile clips, a fragment of cork and an offcut of multi-
366 coloured rope. Because d_{sat} is unknown and, likely, highly variable among such
367 samples, sub-saturation was assumed in all cases. Thus, as above, the concentrations
368 of different elements detected are normalised to the corresponding concentrations
369 measured after applying correction for the measured thickness, and whose values are
370 annotated on each panel. The findings are broadly consistent with those ascertained

371 from analyses of the plastics (Figure 2) in that adjustments in thickness correction
372 towards the lower limit of 0.05 mm are accompanied by an increase in normalised
373 concentration of Ba (note that Sb was not detected in these samples) and a reduction
374 in normalised concentration for all other elements detected. The latter effect was most
375 significant for Cl, Fe and Zn and least evident for Br and Pb, and, for the cork and two
376 of the expanded polymers, was always most pronounced at thickness corrections
377 below 2-6 mm such that trends were approximately asymptotic to unit value.

378

379 *3.6. Measurement precision and sample heterogeneity*

380 Regular assessment of precision is recommended by the US EPA [14] when using FP-
381 XRF as an important component of quality control considerations. The precision of
382 concentrations delivered by the Niton XL3t 950 He GOLDD+ on beached marine
383 litter was ascertained on a wide range of samples, in terms of material category, size,
384 thickness, colour, condition and elemental content, that were fixed in position relative
385 to the detector and measured repeatedly ($n = 4$ to 6) with appropriate thickness
386 correction. Precision was defined as the relative standard deviation (as a percentage)
387 arising from the repeat measurements of each sample, and results are shown in Table
388 3. Precision was highly variable, both among the different elements and between the
389 different material categories, but in all cases was better than 30% and in most cases
390 better than 20%, a recognised ‘acceptable’ objective for FP-XRF measurements [15].
391 Precision displayed a dependency on absolute concentrations (i.e. measurements of
392 higher elemental concentrations were more precise) and was also dependent on the
393 characteristics of the sample; specifically, measurements were most precise for
394 relatively thick, dense and homogeneous materials and least precise for thin,
395 expanded-extruded and more heterogeneous items.

396

397 When the same sample of plastic was located in different positions or with different
398 orientations above the detector, repeat measurements became more variable, reflecting
399 the different response of the detector to variations in geometry and thickness and to
400 inherent variability in the composition and surface conditions of the polymer. Samples
401 composed of regions of visibly different colour or texture or with areas of obvious
402 discolouration, and in particular those in the foams and painted surfaces categories,
403 often exhibited considerable variations in elemental concentrations that reflected
404 significant compositional changes and/or heterogeneous contamination. Figure 4
405 exemplifies the spatial, surface variability of various elements on a piece of painted
406 fibreglass backed with resin that appeared to have been derived from a boat, while
407 Figure 5 illustrates both the surface and depth distribution of different elements in a
408 fragment of cork that had evidently been treated or contaminated. Note an order of
409 magnitude difference in concentrations of Bi, Cl and Pb among the different colours
410 of paint and two orders of magnitude differences in Fe and Zn concentrations in the
411 different regions of cork.

412

413 *3.7. Summary of elemental concentrations in marine litter*

414 Table 4 summarises the concentrations of the elements that were detected in each
415 material category of beached marine litter, with appropriate thickness correction
416 applied. Note that the lowest concentrations reported here for some elements are
417 lower than minimum LODs given in Table 1 because detection is dependent on the
418 precise composition and thickness of the sample and the presence of interfering
419 elements; thus, for example, what may not be detected in one sample may be detected
420 at a lower concentration in another sample which is thicker, denser and ‘cleaner’.

421 Note also that, in the case of As, overlap of its K_{α} fluorescence peak with the L_{α} peak
422 of Pb and the relatively low intensity of the As- K_{β} line means that As concentrations
423 cannot be effectively calculated for samples with Pb:As ratios in excess of about 10
424 [14]. Because false positives may often be returned for the metalloid by FP-XRF in
425 the presence of Pb [16], As concentrations given in Table 4 are restricted to those
426 returned where Pb was not detectable.

427

428 In the plastics category, all elements were detected, albeit in less than ten cases for
429 As, Bi, Cd, Hg, Sb, Se, Sn and Ni. Among the remaining elements, concentrations
430 spanned at least an order of magnitude, and in the case of Cl, Fe, Pb, Ti and Zn, at
431 least three orders of magnitude. Regarding Cl, two samples whose concentrations
432 exceeded $350,000 \mu\text{g g}^{-1}$ (or 35% by weight) were returned as PVC by the XRF, an
433 identification that was confirmed by subsequent FTIR analysis. Bismuth, Cd, Hg and
434 Se were never detected in the foams but many of the remaining elements returned a
435 higher number (and proportion) of detectable cases in this category compared with the
436 plastics. For example, Br, Pb and Sn were detectable in about 15, 13 and 2% of plastic
437 samples compared with respective percentages of 75, 20 and 14%, of foam samples.
438 Median concentrations were about an order of magnitude greater in foams than in
439 plastics for Br, Cr, Fe and Zn; for Cl, the difference was more than two orders of
440 magnitude and 35 samples were returned with concentrations in excess of $150,000 \mu\text{g}$
441 g^{-1} (or 15% by weight) and identified as PVC by the XRF. Clearly, many of these
442 samples were not PVC-based (most of those analysed by FTIR were identified as
443 expanded-extruded polystyrene or polyurethane) but such a classification based on a
444 high chlorine content is a practical requirement for the appropriate fundamental
445 parameter coefficients to be applied.

446

447 In the ropes category, Ba, Bi, Cd, Hg, Sb and Se were never detected and median
448 concentrations of Ni and Pb were higher and Br and Zn lower than the respective
449 median concentrations in both plastics and foams; however, compared with the latter
450 categories, concentrations of most detectable elements in ropes encompassed
451 considerably lower ranges in concentrations. Analysis of the painted surfaces returned
452 no detectable Cd, Cr, Ni, Sb, Se, Sn and As and median concentrations of Ba and Ti
453 that were higher and Cl, Cu and Fe lower than respective median concentrations in the
454 plastics, foams and ropes categories. With the exception of Pb and Zn, the range of
455 elemental concentrations in the painted surfaces was lower than in any of the
456 remaining categories. Overall, and for all categories, Cl, Fe and Ti were detected in
457 the most (> 300) and Hg and Se in the least (≤ 3) number of cases; maximum
458 concentrations exceeded $10,000 \mu\text{g g}^{-1}$ (or 1% by weight) for Ba, Br, Cl, Fe, Pb, Ti
459 and Zn but were never greater than $500 \mu\text{g g}^{-1}$ for Bi and Hg.

460

461 *3.8. Independent analysis of marine litter by ICP following acid digestion*

462 As an independent measure of the elemental content of beached litter, selected
463 samples were analysed for all elements except Br and Cl by ICP-OES following
464 $\text{H}_2\text{SO}_4\text{-HNO}_3$ digestion. Samples encompassed a variety of plastic fragments,
465 expanded polymers (including polyurethane and polystyrene), ropes and a piece of
466 cork but excluded painted surfaces. (Note that while paints could not be completely
467 isolated from their substrates, a comparison of discrete paint fragment analysis by FP-
468 XRF and ICP given elsewhere reveals good agreement between the two approaches
469 [16].) The results of the present study revealed no false negatives among the samples
470 and for all elements considered; that is, lack of detection by the XRF was not

471 accompanied by a measurement by ICP that exceeded the corresponding LOD of the
472 XRF. Excluding the impacts of Pb on the detection of As by XRF (see above), false
473 positives were returned in three cases for Cr (two plastic fragments and a piece of
474 polystyrene foam); thus, here, the XRF reported concentrations of Cr (albeit less than
475 $100 \mu\text{g g}^{-1}$) in samples that failed to return a measurement by the more sensitive ICP-
476 OES.

477

478 Concentrations of various elements detected by both approaches are compared in
479 Figure 6 and statistical summaries for the data and for individual elements are shown
480 in Table 5. Correlation analysis revealed significant relationships between [XRF] and
481 [ICP] for all elements with the exception of Ba, and slopes, when forced through the
482 origin, of less than 1.4 with the exception of Cu (about 8), Sn (4) and Zn (2.5)
483 (exclusion of two expanded samples resulted in a reduction of the Cu and Zn slopes to
484 2.5 and 1.8, respectively). Despite most slopes being greater than 1, however, or the
485 XRF on average returning concentrations greater than those delivered by the ICP, the
486 relationship defining the data overall and forced through the origin ($y = 0.850x$; $r =$
487 0.775 ; $p < 0.01$; $n = 89$) indicates a slope below unit value. This discrepancy may be
488 attributed to the weighting placed on the two data points defining the highest
489 concentrations of Fe; thus, neglecting these points results in a slope of 1.24 ($r = 0.858$;
490 $p < 0.01$; $n = 91$).

491

492 Given that FP-XRF provides a measurement of the elemental content at a particular
493 location on the sample whereas ICP involves complete destruction of a sample (that
494 likely displays some degree of heterogeneity), coupled with possible incomplete
495 digestion of some samples on acid treatment and the presence of precipitate in other

496 cases, the two approaches could be considered as providing more than acceptable
497 agreement overall according to EPA criteria [14]. Based on the results for individual
498 elements, the quantitative performance of the XRF appears to be considerably better
499 for elements like Cd, Pb, Sb and Se than for Cu, Sn and Zn, and in particular in
500 expanded-extruded materials where accurate thickness correction is critical.

501

502 *3.8. Advantages and limitations of FP-XRF for the analysis of marine litter*

503 FP-XRF affords a cost-effective, non-destructive means of measuring elements in a
504 variety of materials sampled from the pool of litter washed up on beaches, including
505 plastics and rubbers, synthetic foams, corks, painted surfaces, ropes, fabrics and
506 netting. With respect to the Niton XL3t 950 He GOLDD+, because it does not employ
507 a radioactive source for the excitation of samples, training, usage and transport are not
508 constrained by additional safety considerations and licensing and its excitation source
509 is not subject to regular replacement. In the plastics mode, the instrument is able to
510 analyse samples with very little preparation down to a few mg in weight and less than
511 3 mm in diameter, including plastic production pellets, individual spheres of expanded
512 polystyrene, and small fragments of (micro)plastic, foam and rope, with a minimum
513 LOD of less than $10 \mu\text{g g}^{-1}$ and a precision of better than 10% in many cases. The
514 instrument is particularly useful for measuring the spatial and depth distributions of
515 elements in larger items and on heterogeneous surfaces which exhibit variable degrees
516 of contamination.

517

518 Although samples whose thickness is greater than saturation are preferable in that the
519 analysis is more sensitive and returns relatively low counting errors, an algorithm in
520 the plastics mode is able to correct for measurements made on thinner samples in

521 most cases. While sample thickness has a relatively small impact on concentrations
522 returned for some elements, like Br, Pb and Se, it has a significant impact on
523 measurements of others, including Ba, Cl, Cr, Cu, Ti and Zn, and particularly in
524 materials containing air, like expanded-extruded polymers and ropes, and whose
525 thickness is below a few mm. It is critical, therefore, to apply the corrective algorithm
526 if the latter elements are considered in samples comprised of low density materials
527 and where $d \ll d_{\text{sat}}$.

528

529 An additional advantage of FP-XRF, and which has been reported in practice in the
530 literature, is the ability to test beach litter samples in situ [9]. Pilot studies undertaken
531 with the Niton XL3t 950 He GOLDD+ on one beach involved activating the
532 instrument through the touch screen display in order to measure samples in contact
533 with or in close proximity to the detector window and that had been temporarily fixed
534 to a white plastic tray using adhesive putty. While this approach proved useful for the
535 relatively rapid screening of some elements and the approximate abundance of others,
536 detection limits and counting errors were relatively high and precision relatively low.
537 This is because of the shorter counting time employed in our pilot study (20 seconds
538 each in the main and low energy ranges), hand-held vibrations of the XRF nose and
539 inconsistent positioning of samples in front of the detector window.

540

541 In situ application of the FP-XRF was also subject to practical difficulties associated
542 with accurately measuring sample thickness, cleaning, drying and cutting-folding
543 samples, orientating the flattest surface towards the detector, and measuring samples
544 smaller than the diameter of the measurement window (i.e. < 8 mm); for a single
545 operator of the instrument, these difficulties had a significant impact on the

546 throughput of samples. Safety was an additional concern since the analysis of
547 irregular surfaces or shapes of low density tends to create excess secondary (back
548 scattered and fluorescent) radiation. Given these constraints and considerations, and
549 our requirements for weighing, archiving and additional testing, a laboratory approach
550 involving a customised stand is recommended for the more accurate and systematic
551 characterisation of beached marine litter.

552

553 From an environmental perspective, the most important finding of the present study
554 was the occurrence and elevated concentrations of hazardous elements in many
555 samples and from all material categories considered. Most significant in this respect
556 are the heavy metals, Cd and Pb, at concentrations in excess of 1000 $\mu\text{g g}^{-1}$ in various
557 plastics objects and fragments, Pb and Br (the latter a component of brominated flame
558 retardants) up to concentrations of 2% in expanded-extruded polymers, and Pb at
559 concentrations of several thousand $\mu\text{g g}^{-1}$ in fragments of rope, netting and processed
560 cork and in paint used on wood and fibreglass. The mobilities and bioaccessibilities of
561 these elements are important considerations for risk assessment and management
562 purposes and are the subject of ongoing research.

563

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568

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Table 1: Median, minimum and maximum limit of detection (LOD, $\mu\text{g g}^{-1}$) for each element and in the four categories of litter for a total counting time of 120 seconds and with appropriate thickness correction applied. Also shown are the numbers and percentages of cases where elements were not detected in each category and which were used to quantify the LODs. *Original res version in Excel file.*

	plastics (n=149)					foams (n = 149)					ropes (n = 68)					painted surfaces (n = 10)				
	n < LOD	% < LOD	median	min	max	n < LOD	% < LOD	median	min	max	n < LOD	% < LOD	median	min	max	n < LOD	% < LOD	median	min	max
As	143	96.0	3.4	1.8	231	138	92.6	23	2.9	420	59	86.8	5.6	2.3	47	6	60	1.5	1.5	1.9
Ba	132	88.6	492	217	2011	140	94.0	498	185	1734	68	100	468	281	912	8	80	384	342	454
Bi	145	97.3	12	5.5	66	149	100	49	7.1	361	68	100	17	8.4	79	9	90	5.3	3.9	72
Br	126	84.6	6.7	2.9	30	37	24.8	36	9.9	75	36	52.9	7.7	4.6	21	3	30	14	1.8	14
Cd	144	96.6	52	25	147	149	100	57	22	197	68	100	53	33	104	10	100	28	24	38
Cl	22	14.8	100	19	260	6	4.0	1233	468	1788	5	7.4	341	81	459	0	0			
Cr	72	48.3	14	2.7	46	41	27.5	35	8.7	305	36	52.9	14	4.9	31	10	100	1.5	1.5	1.7
Cu	114	76.5	24	7.9	123	120	80.5	145	17	562	21	30.9	34	21	100	8	80	6.0	3.8	16
Fe	28	18.8	25	15	56	1	0.7	625	625	625	1	1.5	56	56	56	0	0			
Hg	148	99.3	13	6.0	109	149	100	68	8.7	287	68	100	15	9.2	48	8	80	3.8	2.8	12
Ni	146	97.9	20	8.4	173	147	98.7	142	21	544	66	97.1	31	20	102	10	100	6.0	4.9	10
Pb	130	87.2	7.3	3.4	47	120	80.5	30	12.0	98	40	58.8	9.1	5.4	25	4	40	2.8	2.5	3.8
Sb	144	96.6	85	31	243	145	97.3	85	34	326	68	100	82	51	160	10	100	57	47	77
Se	147	98.7	11	4.8	126	149	100	45	6.0	215	68	100	11	7.0	34	10	100	3.5	2.6	14
Sn	146	98.0	72	34	221	127	85.2	76	26	275	67	98.5	73	44	133	10	100	37	24	38
Ti	13	8.7	8.9	2.5	28	6	4.0	314	95	1768	1	1.5	16	16	16	0	0			
Zn	76	51.0	12	6.4	36	60	40.3	91	17	238	40	58.8	15	10	34	3	30	6.1	5.1	6.4

Table 2: A comparison of reference and measured concentrations ($\mu\text{g g}^{-1}$) in two polyethylene discs supplied by Niton and that had been impregnated with various elements. Note that reference concentrations are given with estimates of errors at the 95% confidence level arising from an unspecified number of analyses while measured concentrations are shown as the mean with one standard deviation ($n = 5$). *Original version in Excel file.*

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 with no thickness correction			497 \pm 3	135 \pm 5	1060 \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 with no thickness correction	46 \pm 2	761 \pm 25		295 \pm 5	116 \pm 8	93 \pm 3	136 \pm 2	98 \pm 3	228 \pm 4
PN 180-619: 3.4 mm section									
measured with thickness correction	44 \pm 4	1060 \pm 130		319 \pm 12	124 \pm 2	82 \pm 5	138 \pm 7	109 \pm 19	209 \pm 5

Table 3: Number of cases detected and median, minimum and maximum precisions (as % relative standard deviation) for each element and in the four categories of litter for a total counting time of 120 seconds and with appropriate thickness correction applied. *Original res version in Excel file.*

	plastics (n=6)				foams (n = 5)				ropes (n = 3)				painted surfaces (n = 6)			
	n > LOD	median	min	max	n > LOD	median	min	max	n > LOD	median	min	max	n > LOD	median	min	max
As	4	14.2	6.0	24.6	2	12.0	10.5	13.5	3	13.0	10.6	21.1	4	5.2	0.6	19.9
Ba	2	10.4	3.1	17.7	0				0				2	4.8	1.3	8.3
Bi	0				0				0				1	24.6	24.6	24.6
Br	0				5	4.5	1.5	12.0	1	1.3	1.3	1.3	3	4.8	1.1	10.6
Cd	3	1.6	0.6	7.9	0				0				0			
Cl	5	5.9	3.1	11.5	5	1.6	0.6	4.3	3	6.4	2.9	7.5	6	2.7	0.1	17.0
Cr	6	3.9	1.1	13.8	4	4.7	4.0	7.9	3	2.3	1.5	2.5	0			
Cu	1	16.5	16.5	16.5	4	13.8	9	21.8	1	7.5	7.5	7.5	0			
Fe	5	3.1	1.2	8.8	5	3.6	0.8	11.1	3	4.0	0.8	18.2	6	3.7	0.1	4.7
Hg	0				0				0				0			
Ni	2	17.6	15.9	19.4	0				0				0			
Pb	4	1.7	0.9	4.3	2	4.0	3.1	4.8	3	2.6	1.3	3.6	5	2.0	0.4	16.5
Sb	3	9.8	2.3	18.4	0				2	21.7	17.8	25.5	0			
Se	1	2.9	2.9	2.9	0				0				0			
Sn	0				2	12.6	8.7	16.5	0				0			
Ti	6	2.6	0.6	10.8	5	8.7	1.5	21.2	2	2.5	2.5	2.5	6	0.9	0.5	6.4
Zn	6	4.7	2.0	14.2	4	7.7	5.6	10.0	1	15.7	15.7	15.7	6	3.1	1.1	7.7

Table 4: Number of cases detected and median, minimum and maximum concentrations ($\mu\text{g g}^{-1}$) for each element and in the four categories of litter for a total counting time of 120 seconds and with appropriate thickness correction applied. *Original res version in Excel file.*

	plastics (n=149)				foams (n = 149)				ropes (n = 68)				painted surfaces (n = 10)			
	n > LOD	median	min	max	n > LOD	median	min	max	n > LOD	median	min	max	n > LOD	median	min	max
As	1	6.2	6.2	6.2	9	56	25	210	2	27	17	36	0			
Ba	17	1710	329	10,700	9	1090	298	20,400	0				2	4070	4030	4100
Bi	4	88	20	198	0				0				1	79	79	79
Br	23	32	4.8	1180	112	218	12	17,600	32	20	6.6	91	7	37	5.6	61
Cd	5	1940	117	4640	0				0				0			
Cl	127	594	4.3	408,000	143	60,700	744	572,000	63	958	189	20,400	10	39	9.6	614
Cr	77	34	21	717	108	210	23	940	32	63	25	909	0			
Cu	35	60	22	718	29	203	71	1910	47	76	27	808	2	14.0	10	18
Fe	121	136	20	28,700	148	7570	279	120,000	67	1160	88	29,200	10	90	11	400
Hg	1	272	272	272	0				0				2	7.3	4.0	11
Ni	3	29	19	74	2	220	220	220	2	386	37	735	0			
Pb	19	58	6.3	13,200	29	119	6.7	17,000	28	199	13	3770	6	175	3.6	10,700
Sb	5	228	154	6260	4	259	67	5819	0				0			
Se	2	457	351	563	0				0				0			
Sn	3	486	35	2090	22	209	53	2280	1	83	83	83	0			
Ti	136	387	5.6	63,900	143	867	18	30,400	67	386	16.8	3140	10	2920	3.5	454
Zn	73	39	13	26,700	89	229	25	25,300	28	30	15	535	7	92	6.0	1570

Table 5: Parameters defining the relationships between FP-XRF and ICP-OES measurements of various marine litter samples. The slope, m , correlation coefficient (significant at $p < 0.01$), r , and number of data points, n , are shown for each element and, for Cu and Zn (and in parentheses), after exclusion of two foam samples. *Original res version in Excel file.*

element	m	r	n
Ba	1.48*	ns	4
Cd	1.05	0.969	4
Cr	1.33	0.550	12
Cu	8.02 (1.72)	0.849 (0.871)	7 (5)
Fe	0.75	0.948	15
Pb	1.39	0.795	11
Sb	1.34	0.999	3
Se	1.18	0.999	2
Sn	4.03	0.997	3
Ti	1.17	0.984	18
Zn	2.54 (1.59)	0.641 (0.999)	12 (10)

*Since the relationship for Ba was not significant, the slope is represented as the average ratio defining the concentrations derived from the two approaches.

Figure 1: Elemental concentrations in the reference polyethylene disc, PN-180-554, as a function of thickness correction applied and for a total counting time of 120 seconds. Note that concentrations are normalised to values shown in the legend (in $\mu\text{g g}^{-1}$ and derived without thickness correction). *High res version in Excel file.*

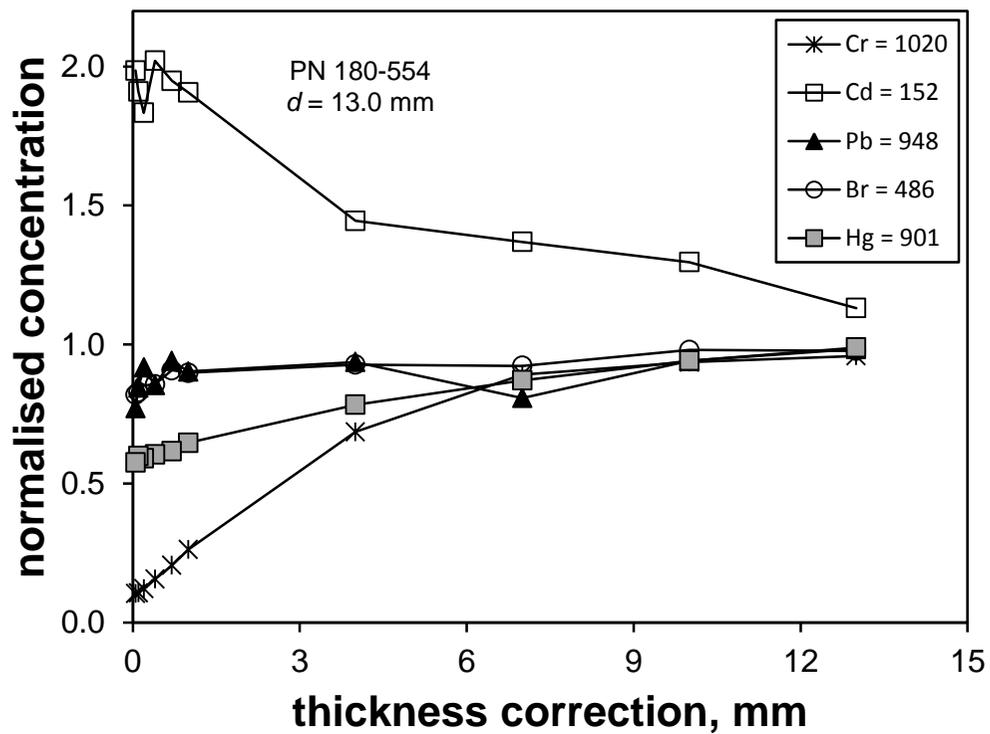


Figure 2: Elemental concentrations in various plastic (polyethylene and polypropylene) litter samples as a function of thickness correction applied and for a total counting time of 120 seconds. Note that concentrations are normalised to values shown in the legend (in $\mu\text{g g}^{-1}$ and derived with appropriate thickness correction). *High res version in Excel file.*

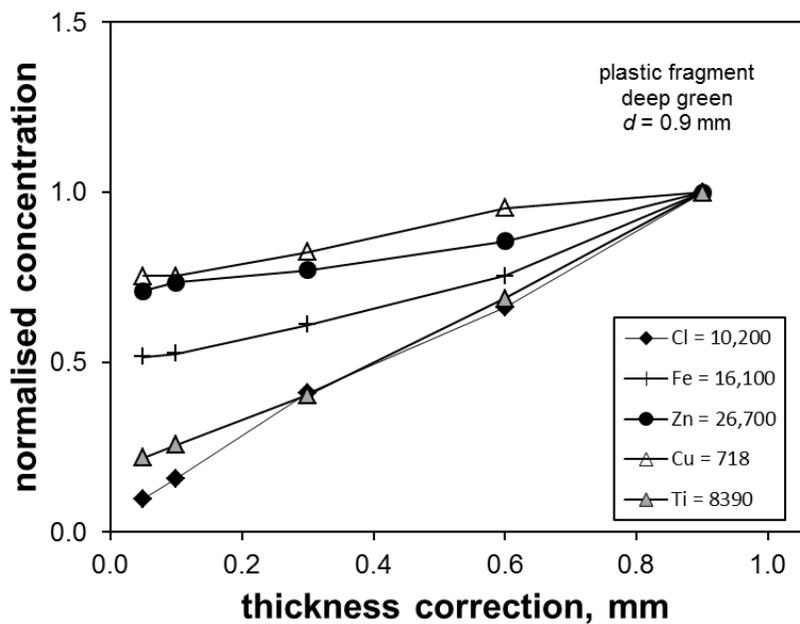
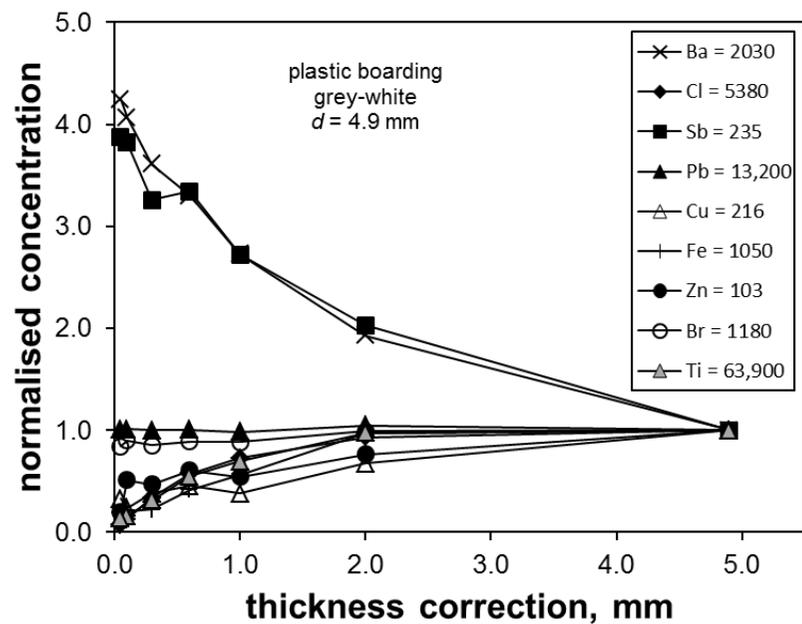
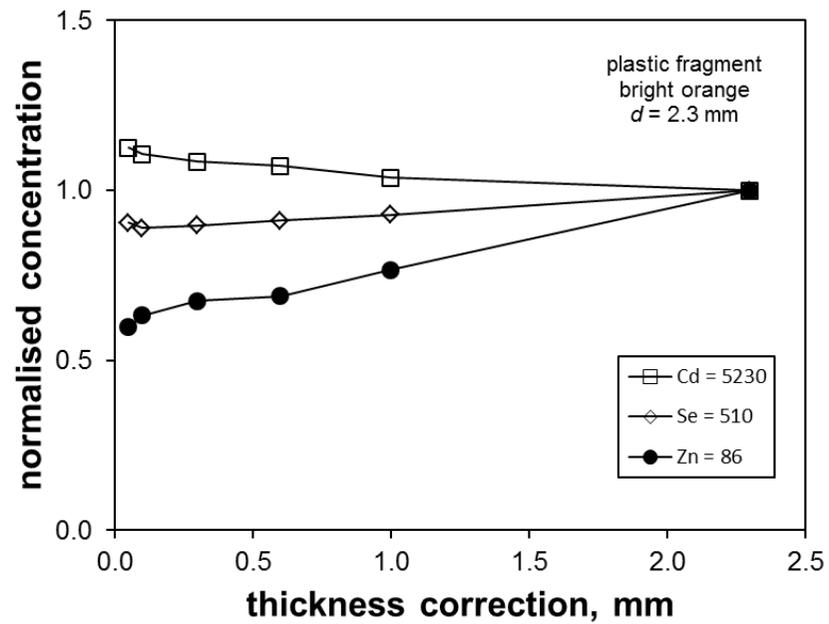
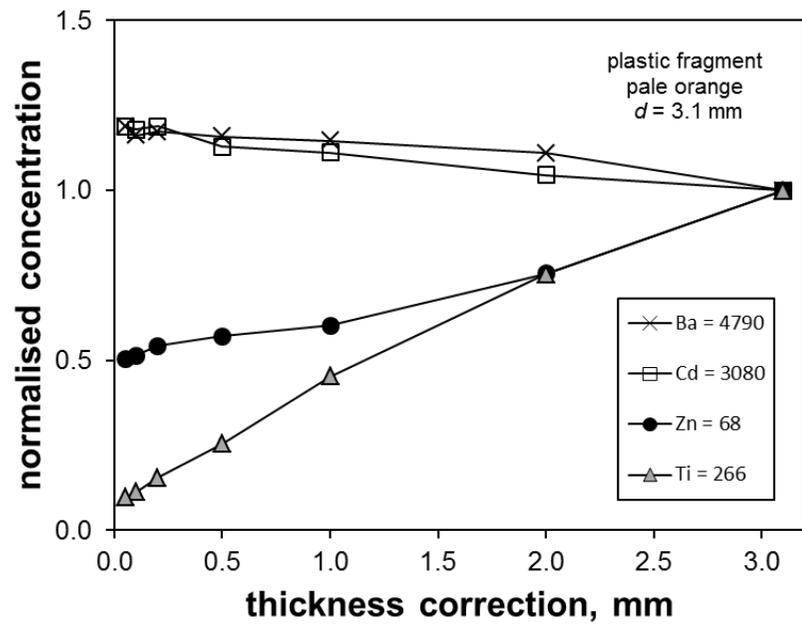


Figure 3: Elemental concentrations in various foams (including a fragment of cork) and ropes as a function of thickness correction applied and for a total counting time of 120 seconds. Note that concentrations are normalised to values shown in the legend (in $\mu\text{g g}^{-1}$ and derived with appropriate thickness correction). EPS = expanded polystyrene; EPU = expanded polyurethane. *High res version in Excel file.*

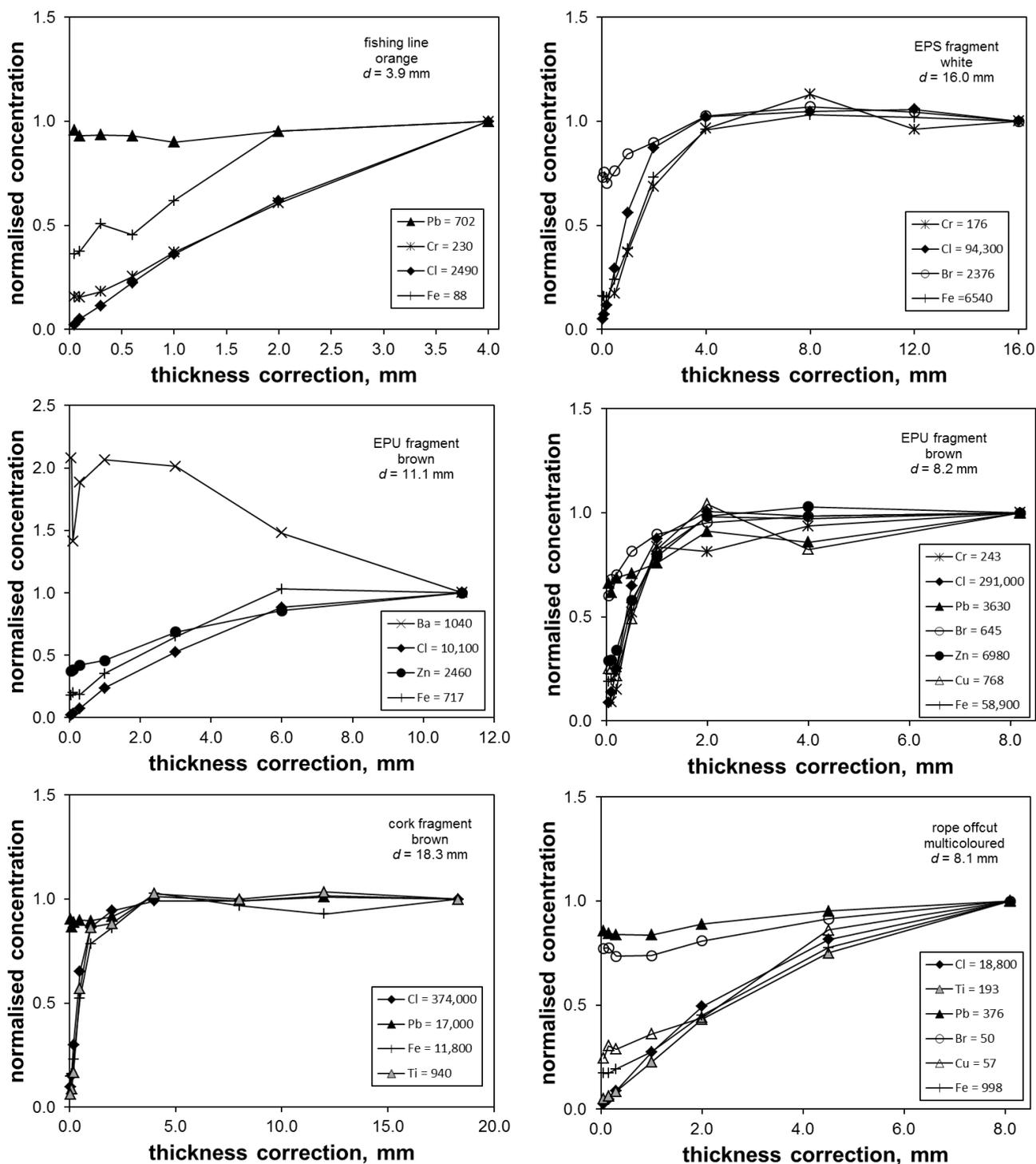


Figure 4: Spatial distribution of various elements (in $\mu\text{g g}^{-1}$) measured at the surface of a fragment of painted acrylic-fibreglass with resinous backing. (for colour reproduction on the web)

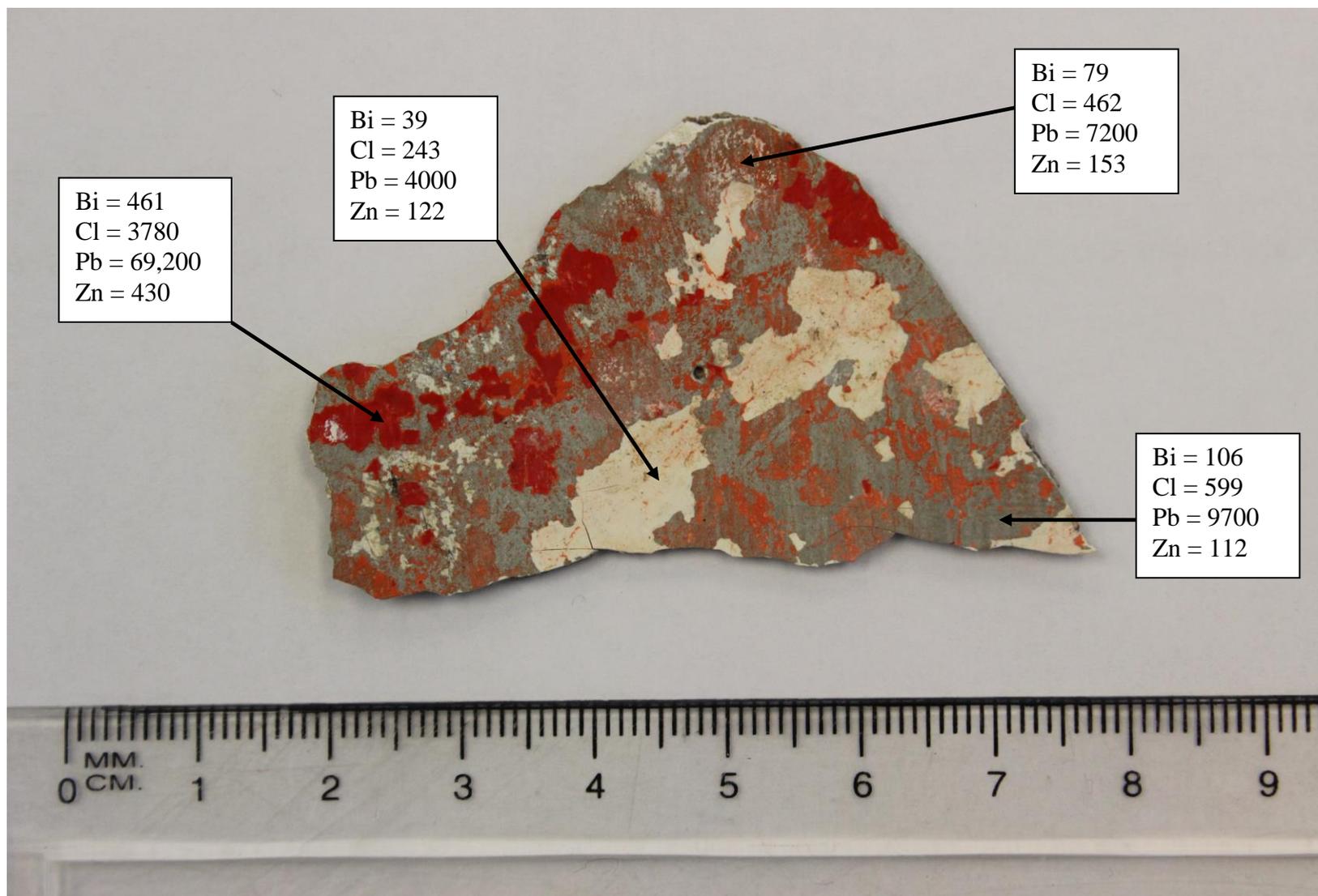


Figure 5: Spatial and depth distribution of various elements (in $\mu\text{g g}^{-1}$) in a fragment of cork that had been sliced with a stainless steel scalpel. (for colour reproduction on the web)

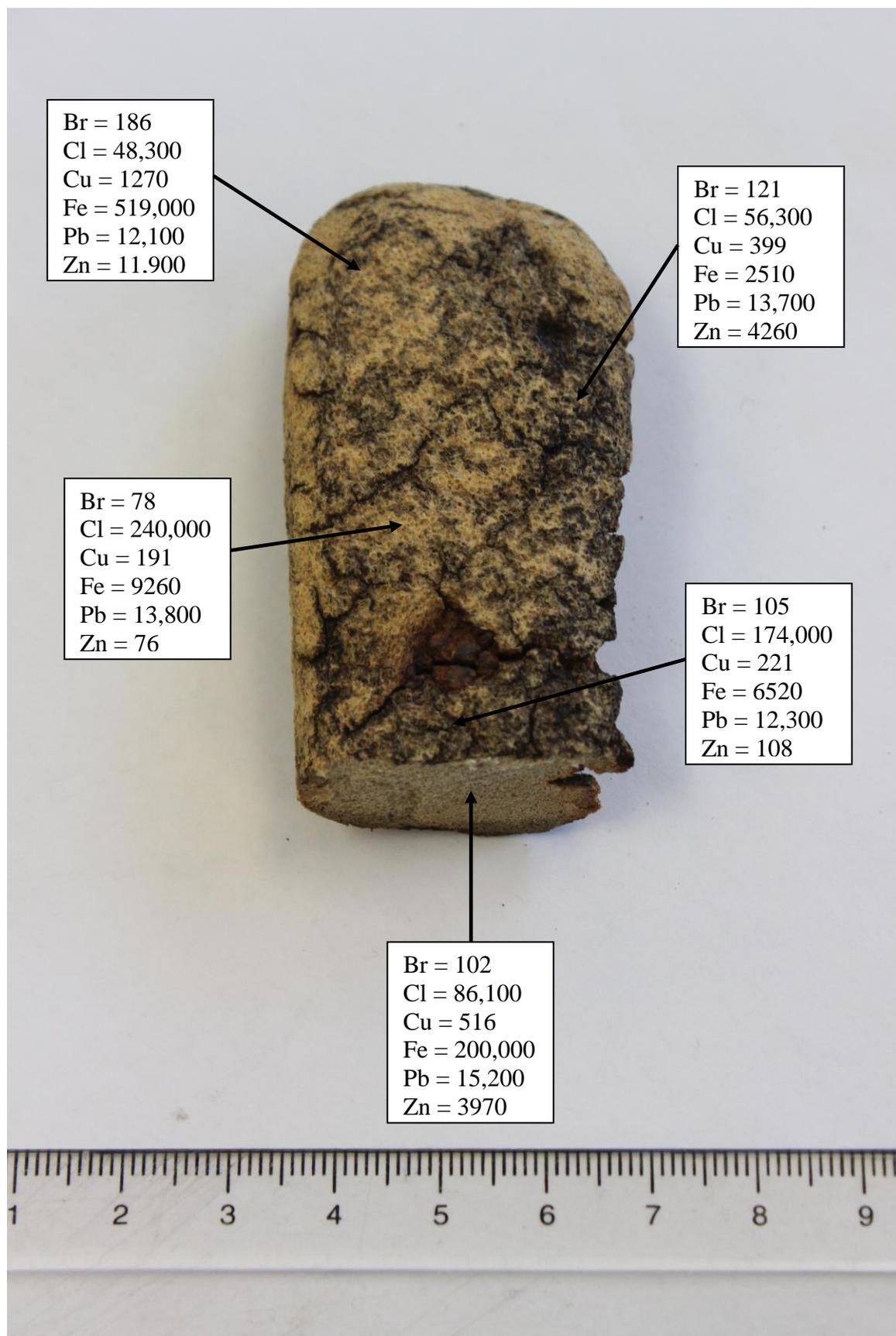


Figure 6: A comparison of the concentrations of elements in various samples of marine litter returned by the FP-XRF and by ICP-OES following acid digestion. Annotated are lines defining unit slope and ratios of [XRF] to [ICP] of 10:1 and 1:10. *High res version in Excel file.*

