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# **Lead pollution of coastal sediments by ceramic waste**

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20 **Abstract**

21 Ceramic fragments and fractionated (< 2 mm) sediment have been sampled from two  
22 beaches in southwest England, along with sediment from a control beach where ceramic  
23 waste was lacking. Analysis of the glazed ceramic surfaces by X-ray fluorescence (XRF)  
24 spectrometry returned concentrations of Pb up to 729,000 mg kg<sup>-1</sup>, while XRF analysis of  
25 sediment samples revealed high but heterogeneous concentrations of Pb at the two sites  
26 impacted by ceramic waste (median = 292 and 737 mg kg<sup>-1</sup>) compared with the control  
27 beach (median ~ 20 mg kg<sup>-1</sup>). These observations are attributed to the disposal of  
28 contemporary and historical ceramic products, and the subsequent attrition of material and  
29 contamination of local sediment. Extraction of a milled ceramic composite (Pb = 2780 mg  
30 kg<sup>-1</sup>) by 1M HCl, revealed a high (34%) environmental mobility and availability of Pb;  
31 extraction in a solution of protein, however, suggested a low (0.1%) bioaccessibility to  
32 sediment-ingesting invertebrates.

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34 **Keywords:**

35 Ceramic fragments; glaze; lead; sediments; contamination

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46 **1. Introduction**

47 Heavy metals enter rivers, estuaries and coastal waters through natural erosion in the  
48 catchment and from a variety of anthropogenic sources, including municipal and industrial  
49 waste, stormwater, metal mining and processing, boating and shipping activities and  
50 agriculture (Cave et al., 2005; Pan and Wang, 2012). Sediment is the principal receptacle of  
51 metals in these environments, mainly because its high surface area and chemical reactivity  
52 allow charged species to readily undergo exchange reactions, adsorption and co-precipitation  
53 at the particle surface (Turner and Millward, 2002). Metals may also be present in sediment  
54 when associated with discrete, contaminated particulates, like fly ash, paint fragments, tyre-  
55 wear particles and microplastics (Pratt and Lottermoser, 2007; Massos and Turner, 2017)  
56 which, in some instances, make a significant contribution to overall metal loading. For  
57 example, tyre wear particles enriched in Zn, which serves as an activator or accelerator for  
58 the rubber vulcanization process, may contribute up to 10% of the sedimentary reservoir in  
59 the vicinity of major highways (Voparil et al., 2004), while antifouling paint fragments  
60 containing high levels of Cu as a biocide make considerable contributions to the sediment  
61 loading in the vicinity of boat repair facilities (Singh and Turner, 2009).

62

63 While measuring heavy metals in intertidal sediments from the Tamar estuary, southwest  
64 England, using a portable X-ray fluorescence (XRF) spectrometer (Turner and Taylor,  
65 2018), we noted elevated concentrations of Pb at various locations towards the estuary  
66 mouth. At one site, concentrations of Pb, but not other metals, were an order of magnitude  
67 higher than concentrations in the upper catchment that is impacted heavily by historic  
68 mining activities. Sediments at this site were coarse (sand-gravel-pebble) compared with the  
69 fine silts of the upper catchment but were characterised by an abundance of visible fragments  
70 of ceramic debris that were usually off-white or brown but occasionally brightly-coloured.  
71 Subsequent inspection of other beaches in the region revealed that ceramic debris was

72 commonly present where sediment was relatively coarse, especially towards the high water  
73 line. Since lead oxide was (and, in some cases, still is) employed as a flux in the glazing of  
74 ceramics (Beldi et al., 2016), it is hypothesized that the presence and attrition of such  
75 material may act as a significant source of local Pb contamination.

76

77 In this study, sediments and glazed ceramics have been collected from two beaches in the  
78 Plymouth Sound region of southwest England and analysed directly and non-destructively  
79 for Pb using XRF; an additional beach with little ceramic waste evident was sampled for  
80 sediment as a control. In order to evaluate the mobility and environmental significance of Pb  
81 from this source, a composite of glazed ceramics was prepared by milling and subjected to  
82 XRF analysis and to different chemical treatments, with extracts analysed by conventional  
83 inductively coupled plasma techniques.

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85

## 86 **2. Materials and methods**

### 87 *2.1. Study sites*

88 Plymouth Sound, south west England is an open, macrotidal bay facing the English Channel  
89 whose inner waters are up to 40 m deep and are sheltered by a 1600 m breakwater. The  
90 coastline is steeply sloping and rocky, with numerous small coves and beaches. The Tamar  
91 and Plym estuaries enter the Sound from the north west and north east, respectively, and  
92 supply the majority of freshwater to the system. The inner Sound and lower estuaries are  
93 urbanised and support a number of maritime, shipping, naval and fishing industries as well  
94 as various water sports.

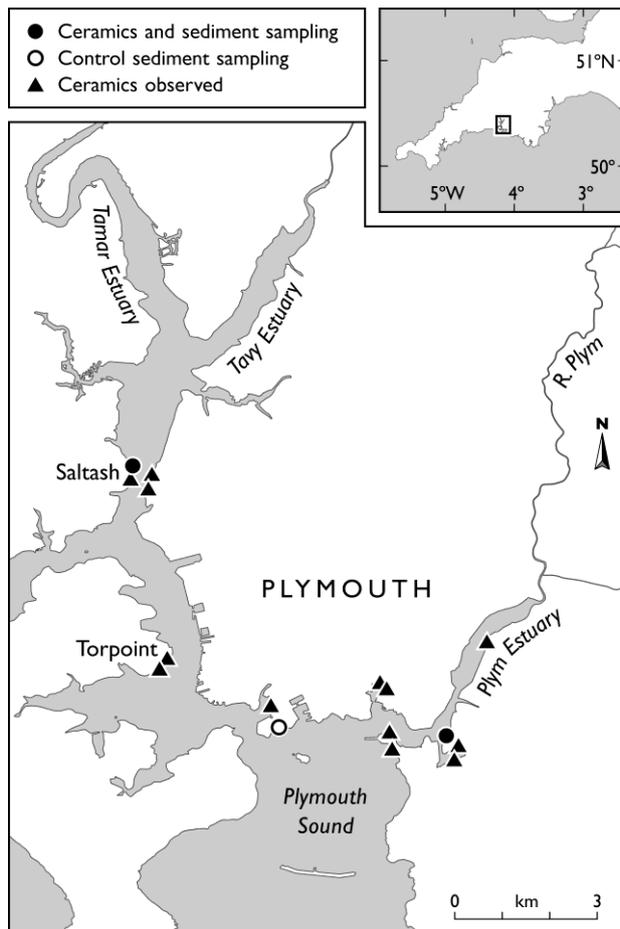
95

### 96 *2.2. Sampling*

97 Samples were collected during March and September of 2017 from three sand-gravel-pebble  
98 beaches around the coastal zone of Plymouth and at the locations shown in Figure 1;  
99 specifically, at Oreston on the lower Plym estuary, Saltash on the lower Tamar estuary, and  
100 Firestone Bay in Plymouth Sound. Previous visits to a number of sites and counting with 0.5  
101 m<sup>2</sup> quadrats had revealed that ceramic fragments were most abundant at the former two  
102 locations, especially in the upper reaches of the intertidal zone, while the latter location was  
103 relatively free of such material.

104

105 Three surficial (< 1 cm) intertidal sediment samples of about 200 g were collected using a  
106 plastic spatula at three sites from each location that were approximately 20 m apart. Samples  
107 were returned to the laboratory in resealable polyethylene bags where they were oven-dried  
108 in open crucibles at 40 °C overnight. Dried samples were then sieved through a 2 mm nylon  
109 mesh and the fine fraction transferred to new polyethylene bags. Fragments of ceramics that  
110 were clearly visible to the naked eye were collected manually from a 1 m<sup>2</sup> quadrat centred on  
111 the sediment sample sites and counted into a series of polyethylene bags. In the laboratory,  
112 ceramics were cleaned with a nylon brush under running water and dried as above before  
113 being stored in air-tight polyethylene boxes.



114

115 **Figure 1: Locations for sampling and where ceramic waste was observed in the**  
 116 **Plymouth Sound region of southwest England.**

117

118 *2.3. Sediment analysis*

119 Sediments were analysed directly in their bags and at six different positions through the face

120 of each polyethylene sample bag using a Niton XL3t 950 He GOLDD+ portable XRF

121 housed in a 4000 cm<sup>3</sup> laboratory accessory stand. Measurements for Pb and a suite of other

122 metals whose fluorescent energies were not significantly attenuated by polyethylene (Bi, Cu,

123 Rb, Sb, Sn, Zn) were conducted in a ‘mining’ mode and with a beam width of 8 mm

124 (equivalent to a measurement area of 50 mm<sup>2</sup>) for a total time of 60 s, comprising successive

125 counting periods of 30 s at 50 kV/40 μA (main filter), 15 s at 20 kV/100 μA (low filter) and

126 15 s at 50 kV/40 μA (high filter). Spectra arising from sample counting were quantified by

127 fundamental parameter coefficients to yield metal concentrations in  $\text{mg kg}^{-1}$  and with a  
128 measurement counting error of  $2\sigma$  (95% confidence).

129

130 The detection limit for Pb in sediment, based on errors arising from samples returning the  
131 lowest concentrations, was around  $9 \text{ mg kg}^{-1}$ . Multiple analyses of a reference sediment  
132 (GBW07318) that had been packed into a polyethylene XRF sample cup (Chemplex series  
133 1400, 21-mm internal diameter) and collar-sealed with  $3.6 \mu\text{m}$  SpectraCertified Mylar  
134 polyester film returned concentrations of Pb, Cu and Zn that were within 15 % of certified  
135 values ( $66\pm 6$ ,  $66\pm 7$  and  $165\pm 15 \text{ mg kg}^{-1}$ , respectively).

136

#### 137 *2.4. Ceramic analysis*

138 Selected ceramic samples were analysed by XRF in a 'plastics' mode and a 'lead paint'  
139 mode. In the plastics mode, a thickness correction of 0.05 mm was applied that accounted for  
140 the film-like characteristics of the glaze. The central area of the glazed surface was measured  
141 (and on both internal and external surfaces where possible) for Pb with a beam width of 8  
142 mm and for a total time of 60 s, comprising successive counting periods of 40 s with the  
143 main filter and 20 s with the low filter. Concentrations were returned by fundamental  
144 parameters in  $\text{mg kg}^{-1}$  with a detection limit, as defined above, of about  $6 \text{ mg kg}^{-1}$ . Where the  
145 surface was patterned or multi-coloured, different areas were probed by moving the sample  
146 with respect to the detector window, a process aided by live imagery generated by the CCD  
147 camera adjacent to the x-ray source. Samples of different colour, condition and Pb  
148 concentration were also analysed by XRF in a lead paint mode. Here, the instrument was  
149 operated at 8 mm and for a counting period of 30 s at 50 kV and  $40 \mu\text{A}$ , and returned  
150 concentrations of Pb through fundamental parameters in  $\text{mg cm}^{-2}$ . Concentrations of Pb  
151 determined in six standard reference paint films (SRM 2570 to 2575; National Institute of  
152 Standards & Technology) were within 15% of corresponding certified values.

153

154 *2.5. Ceramic composite*

155 A fine, working composite sample of ceramics, representing aged (eroded and abraded)  
156 material, was prepared from various fragments of different visual and chemical  
157 characteristics. Thus, six fragments from Oreston and six from Saltash were crushed into a  
158 powder in a tungsten bowl at 700 rpm for 30 s and 1400 rpm for 20 s using a Retsch RS100  
159 puck mill. The powder was transferred into two separate resealable polyethylene bags under  
160 a dust extractor, with one bag analysed directly by XRF in its mining mode as above and  
161 material in the second bag used in the extraction tests described below.

162

163 *2.6. Extraction tests*

164 The powdered composite was subject to extraction in cold 1 M HCl (Fisher Scientific Trace  
165 analysis grade) and 5 g L<sup>-1</sup> bovine serum albumin (BSA; >96% fraction V, Sigma Aldrich)  
166 The former extract is designed as a simple means of evaluating the general mobility or  
167 bioavailability of heavy metals and is often used in the first tier of sediment quality  
168 assessment (McCready et al., 2003), while the latter extract provides a more specific  
169 estimation of metal bioaccessibility to deposit-feeding invertebrates (Kalman and Turner,  
170 2007). Thus, three 1 g portions of the composite were weighed into individual 100 ml acid-  
171 cleaned Pyrex beakers and 50 ml of 1 M HCl added. The contents, plus three beakers  
172 containing acid and no solids, were left at room temperature with occasional agitation for a  
173 period of 6 h before being filtered through Whatman 0.45 µm filters into individual 60 ml  
174 polypropylene centrifuge tubes. This process, including corresponding controls, was  
175 repeated using BSA solution in place of HCl.

176

177 *2.7. Extract analyses*

178 Concentrations of Pb in the HCl-extracts of the milled composite were determined by  
179 inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Thermo  
180 Scientific iCAP 7400 analyser with a MiraMist PEEK nebuliser and cyclonic spray chamber.  
181 The instrument was calibrated using four matrix-matched standards in the range 0.2 to 20 mg  
182 L<sup>-1</sup> and a matrix-matched blank. Instrument RF power was set at 1.2 KW, coolant, auxiliary  
183 and nebuliser flows were 12, 0.5 and 0.5 L Ar min<sup>-1</sup>, respectively, and replicate ( $n = 3$ ) read  
184 time was 2 s. Lead concentrations in the BSA-extracts were determined by inductively  
185 coupled plasma-mass spectrometry (ICP-MS) using a Thermo Scientific iCAP RQ analyser  
186 with a Glass Expansion micromist nebuliser and cyclonic spray chamber. The instrument  
187 was calibrated with a blank and three matrix-matched standards in the range 10 to 100 µg L<sup>-1</sup>  
188 <sup>1</sup>, and RF power was set at 1.5 KW with coolant, nebuliser and auxiliary flows of 1.4, 1.07  
189 and 0.8 L Ar min<sup>-1</sup> and a replicate ( $n = 3$ ) read time of 10 ms.

190

### 191 **3. Results**

#### 192 *3.1. Characteristics of the ceramic samples*

193 Ceramic fragments were abundant amongst the sand-gravel-pebbles of the upper intertidal  
194 zones of Oreston and Saltash, with up to several hundred pieces per m<sup>2</sup> visible at the surface  
195 where counting had been performed. Fragments were evident at many other locations in the  
196 region (Figure 1), with abundance greater in more sheltered embayments than on beaches  
197 facing directly on to Plymouth Sound. In total, 48 ceramic samples were analysed from  
198 Oreston and 24 fragments were analysed from Saltash, with a selection of samples illustrated  
199 in Figure 2. Samples were an heterogeneous assortment of rounded or angular fragments of  
200 earthenware, stoneware and porcelain of different sizes, colours and degrees of aging.



201

202 **Figure 2:** A selection of ceramic fragments retrieved from Oreston and Saltash and  
203 presented on cm-scaled paper.

204

205 The primary length of most fragments ranged from about 2 to 5 cm, with thicknesses usually  
206 around 3-6 mm but that exceeded 1 cm in isolated cases and masses that varied between  
207 about 2 and 20 g. Most samples exhibited an inherent curvature and glazing on both  
208 surfaces, with many fragments having a distinctive lip or base area and a few fragments  
209 characterised by a ribbed or ridged surface; other samples, however, were flat and often  
210 unglazed on one side. The décor below glazed surfaces was most commonly white to off-  
211 white or brown-beige, with blue-green and yellow fragments also present, while the paste of  
212 most samples was off-white or brown. A few samples were decorated in different colours  
213 and lipped areas were occasionally coloured differently to the main, curved surfaces. The  
214 glazing of some ceramics appeared to be in relatively good condition but the majority of

215 samples exhibited various degrees of crazing. Other evidence of aging and erosion was the  
216 presence of cracks and pits on the surface, areas where the glazing and décor had been  
217 completely dislodged from the underlying ceramic body, and regions of inorganic fouling  
218 and algal growth.

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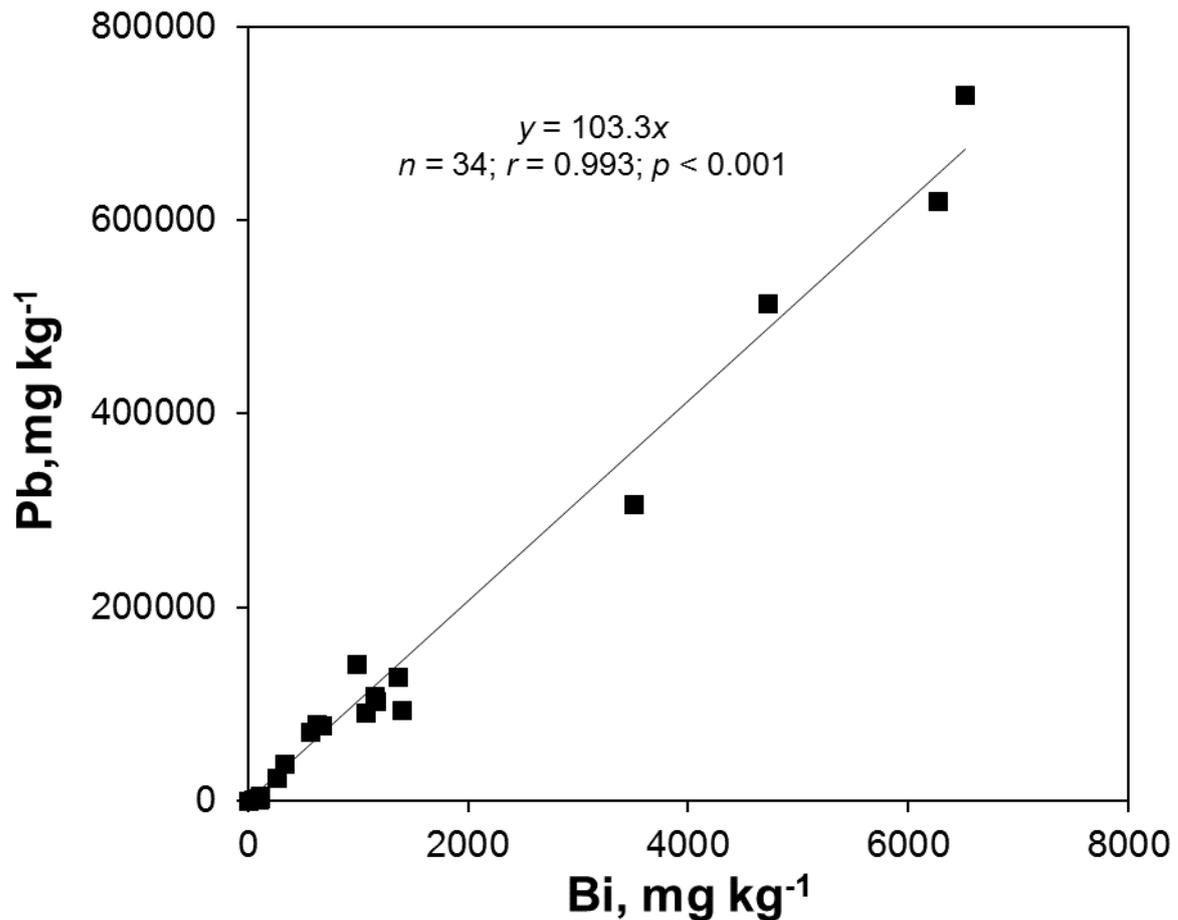
### 220 *3.2. Lead concentrations in the ceramic samples*

221 Concentrations of Pb in the glazed surfaces of the ceramic samples from Oreston and Saltash  
222 that had been analysed by XRF are summarised in Table 1. Here, concentrations are based  
223 on single measurements performed in the centre of the outer surface. Note that multiple  
224 measurements over a reasonably uniform surface returned concentrations with a relative  
225 standard deviation of < 20% and that measurements of inner surfaces were often constrained  
226 by accessibility or distance to the XRF detector window. Lead was detected in all 24 samples  
227 analysed from Saltash and in 45 out of 48 samples analysed from Oreston, with  
228 concentrations that were highly variable and that, overall, ranged from < 10 mg kg<sup>-1</sup> to about  
229 70% by weight. There was no clear relationship between Pb concentration and sample  
230 thickness, curvature or décor colour but concentrations below 100 mg kg<sup>-1</sup> were usually  
231 encountered in samples that appeared to be relatively clean, angular and new.

232

233 Other heavy metals (and metalloids) that were detected by the XRF in many (but not all)  
234 ceramic samples analysed included Bi, Cu, Sb, Sn and Zn and with median concentrations of  
235 451, 62, 563, 1160 and 296 mg kg<sup>-1</sup>, respectively. While the concentrations of the latter  
236 elements exhibited no clear co-association with concentrations of Pb, concentrations of Bi  
237 (where detected) and Pb exhibited a striking and highly significant linear relationship that is  
238 shown in Figure 3.

239



240

241 Figure 3: Concentrations of Pb versus concentrations of Bi in the ceramic fragments.

242

243 Lead was also measured in selected samples ( $n = 15$ ) on an areal basis using a lead paint  
 244 mode and with units of  $\text{mg cm}^{-2}$  that are consistent with many Pb-based paint assessments  
 245 and regulations (Clark et al., 2006). The concentrations arising from this approach ranged  
 246 from 0.03 to 23.1  $\text{mg cm}^{-2}$  and were highly correlated with concentrations determined in  
 247 plastics mode and in  $\text{mg kg}^{-1}$  ( $r = 0.989$ ;  $p < 0.001$ ), with a best-fit linear regression line  
 248 defining the data of  $y = 29,900x$ , or a conversion factor between the two measures of 29.9  
 249  $\text{cm}^2 \text{g}^{-1}$ . The lead paint mode also returns a depth index that provides a semi-quantitative  
 250 evaluation of the depth of the layer of Pb. An average value of 1.5 and no values above 2 for  
 251 the samples tested confirms that the metal is located at or near the surface of the ceramics.

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**Table 1:** Frequency distribution and summary statistics for Pb concentrations (in mg kg<sup>-1</sup>) in the glazed surfaces of ceramic samples from Oreston and Saltash.

	< 10 <sup>2</sup>	10 <sup>2</sup> -10 <sup>3</sup>	10 <sup>3</sup> -10 <sup>4</sup>	10 <sup>4</sup> -10 <sup>5</sup>	>10 <sup>5</sup>	mean	median	min	max
Oreston (n = 48)	6	10	5	22	5	45,000	29,300	79.0	402,000
Saltash (n = 24)	4	4	3	6	7	121,000	29,900	9.3	729,000

*3.3. Lead concentrations in the ceramic composite and release by HCl and BSA*

The concentration of Pb in the ceramic composite prepared by milling 12 individual fragments and determined by XRF in mining mode was 2780 ± 286 mg kg<sup>-1</sup> (n = 6). Other heavy metals were detected but at significantly lower concentrations; specifically, concentrations of Bi, Sn and Zn were 36.7 ± 6.2, 46.5 ± 11.7 and 477 ± 62 mg kg<sup>-1</sup>, respectively, and Cu was undetected. Lead mobilised by 1M HCl and determined by ICP was 953 ± 91.6 mg kg<sup>-1</sup>, or 34% of total Pb determined by XRF, while the corresponding values mobilised by 5 g BSA L<sup>-1</sup> were 2.5 ± 0.86 mg kg<sup>-1</sup> and 0.1%.

*3.3. Lead concentrations in the sediment samples*

Concentrations of Pb in the three fractionated (< 2 mm) sediments taken from each location and measured at six different positions through the face of the polyethylene bag are summarised in Table 2. At the control location (Firestone Bay), mean concentrations are similar among the three samples and, overall, concentrations range from about 11 to 30 mg kg<sup>-1</sup>. At the locations impacted by ceramic waste, both mean and individual concentrations of Pb are more variable, with concentrations ranging from about 80 to 1400 mg kg<sup>-1</sup> at Oreston and 310 to 1000 mg kg<sup>-1</sup> at Saltash. On average, Pb concentrations at these locations are greater than the control location by factors of 20 or more.

276 In order to account for granular and mineralogical variations among the sediment samples,  
277 Pb data were normalised with respect to a geochemical proxy. While Al or Fe are  
278 conventionally employed as proxies (Schiff and Weisberg, 1999; Ho et al., 2012), the  
279 fluorescent energies of the former are too low to be analysed by portable XRF in air and the  
280 region is impacted by high and variable concentrations of the latter through acid mine  
281 drainage in the upper Tamar catchment (Mighanetara et al., 2009). Accordingly, Rb was  
282 selected as a normaliser because of its propensity to substitute for K in fine-grained clays  
283 and its ready determination by XRF (Rae, 1995; Lewis and Turner, 2018). Concentrations of  
284 Rb, shown in Table 2, reveal relatively invariant concentrations within the same sample and  
285 between samples taken from the same site, suggesting that local variations in Pb  
286 concentration are not the result of variations in sediment granulometry but are the result of  
287 heterogeneous contamination. Variations in Rb concentration between locations, however,  
288 suggest that grain size varies across the region; specifically, higher concentrations at Oreston  
289 and Saltash than Firestone suggest a finer distribution of material at the former locations.

290

291 Rubidium-normalised Pb concentrations were used to compute mean enrichment factors, EF,  
292 for sediments at Oreston and Saltash as follows:

293

$$294 \quad EF = ([Pb]/[Rb])/([Pb]_b/[Rb]_b)^{-1}$$

295

296 where the denominator represents baseline Rb-normalised Pb concentrations that are derived  
297 from mean concentrations of the metals at Firestone Bay. Values of EF exceeding unity,  
298 shown in Table 2, confirm that the locations impacted by ceramic waste are contaminated by  
299 Pb, with the extent of Pb contamination ranging from about 5.4 for one sediment at Oreston  
300 to over 13 for a sample from Saltash.

301

302 **Table 2:** Summary statistics for Pb concentrations and mean concentrations of Rb in the  
 303 three < 2 mm sediment samples from each location that were analysed at six different  
 304 positions through the face of the polyethylene bag. EF denotes mean enrichment factors for  
 305 Pb based on normalisation with respect to Rb.

				Pb		Rb	EF
		mean+1 sd	median	min	max	mean+1 sd	
Firestone Bay	(i)	19.5 <sub>+8.3</sub>	15.1	11.4	30.1	50.3 <sub>+9.2</sub>	
	(ii)	21.0 <sub>+5.2</sub>	22.3	14.5	28.3	47.5 <sub>+3.3</sub>	
	(iii)	20.9 <sub>+6.3</sub>	22.0	11.4	28.3	48.6 <sub>+6.7</sub>	
Oreston	(i)	414 <sub>+488</sub>	292	81.3	1390	180 <sub>+27.7</sub>	5.35
	(ii)	564 <sub>+256</sub>	485	304	987	165 <sub>+23.8</sub>	7.95
	(iii)	501 <sub>+190</sub>	425	307	804	168 <sub>+11.4</sub>	6.93
Saltash	(i)	518 <sub>+181</sub>	461	370	872	146 <sub>+8.1</sub>	8.25
	(ii)	481 <sub>+119</sub>	467	307	660	144 <sub>+22.8</sub>	7.77
	(iii)	751 <sub>+172</sub>	737	570	1010	133 <sub>+18.7</sub>	13.13

306

#### 308 4. Discussion

309 While OSPAR (2010) includes ceramics in their categorisation of marine litter, only a  
 310 handful of studies appear to have referred to this type of waste while classifying beached  
 311 materials (Ioakeimidis et al., 2014; Buhl-Mortensen and Buhl-Mortensen, 2016). The results  
 312 of this study are, therefore, significant in revealing the extent of heterogeneous  
 313 contamination by ceramic debris that is possible in the intertidal zone. Although quantitative  
 314 analysis was restricted to two beaches around Plymouth Sound, inspections of other local  
 315 beaches revealed varying degrees of contamination in many other cases (Figure 1), with  
 316 accumulations most often observed among gravel-pebble deposits of the upper intertidal  
 317 zone but also apparent on fine, intertidal mudflats. Clearly, it is likely that other  
 318 environments of similar (historic) usage and setting are subject to comparable contamination  
 319 by ceramic debris.

320

321 Potential sources of ceramics to the region under study include historic landfill sites and  
322 various construction projects and manufacturing industries. However, fragments typical of  
323 those sampled would be too large and dense to be transported and redistributed across  
324 Plymouth Sound, suggesting that sources are more localised. That ceramic debris was more  
325 abundant in the vicinity of informal boating activities (repair, maintenance and renovation)  
326 implies material may be partly derived from the disposal and fragmentation of shipboard  
327 sanitary equipment and tiles. This practice may also attract the tipping of additional  
328 municipal wastes, including crockery and garden ceramics, in the immediate vicinity (Turner  
329 and Rees, 2016), with lighter material like plastics, ropes and foams more readily swept  
330 away or recognised and collected as litter. More generally, however, it is suspected that  
331 material has accumulated in the intertidal zone over extended periods of time (centuries)  
332 through the historic use of utilitarian and, later, decorated products for the storage,  
333 transportation and trading of a wide range of goods, including food, wine, chemicals and  
334 molasses. Because of their natural colours, these fragments blend into the sand-gravel-pebble  
335 substrate and have, therefore, evaded collection and disposal as waste.

336

337 The majority of the ceramic fragments retrieved in the present study were glazed, with  
338 surfaces that were usually characterised by high concentrations of Pb. This observation is  
339 consistent with the pervasive use of lead oxide (PbO) as a flux of low melting point, wide  
340 firing range and high refractive index. Other oxides that were evident in some of the samples  
341 and that co-existed with high concentrations of Pb included those of Sn and Zn. However,  
342 the striking correlation of Bi with Pb suggests that bismuth trioxide ( $\text{Bi}_2\text{O}_3$ ) has been used  
343 extensively as a component of ceramic fluxes in tandem with PbO (and at a mass ratio of  
344 Pb:Bi of about 100).

345

346 High concentrations of Pb in the glaze affords the potential for heterogeneous contamination  
347 of local sediment as the ceramics break down through weathering and abrasion; this is  
348 reflected by high (but variable) EF values at Oreston and Saltash for sediments fractionated  
349 to < 2 mm. It is unclear how thick the glazed layer of the ceramics is but the Pb  
350 concentration of the milled composite of 2800 mg kg<sup>-1</sup> is assumed to be a representative  
351 value for the bulk material (that includes the paste) as a contaminant. Thus, assuming a  
352 background sediment concentration of Pb for the region of 20 mg kg<sup>-1</sup> based on results for  
353 the control location and a sediment concentration of 400 mg kg<sup>-1</sup> representative of sites  
354 contaminated by ceramic debris, mass balance requires that, on average, ceramic-derived  
355 material contributes about 14% to the total mass of (< 2 mm) sediment in contaminated  
356 settings.

357

358 The mobility or general availability of Pb in the milled composite of ceramics was evaluated  
359 using cold 1M HCl. With respect to estuarine and coastal sediments, this fraction is often  
360 assumed to represent metal bound in non-residual fractions and where the majority of  
361 anthropogenic metals reside, as well as providing a general proxy for monitoring the  
362 bioavailability and biological effects of heavy metals (Riddle et al., 2003; Bettioli et al.,  
363 2008). While the percentage of total Pb mobilised from the ceramic composite (around 34%)  
364 is lower than that typically mobilised from contaminated sediments (in excess of 80% has  
365 been reported; McCready et al., 2003), it is nevertheless significant and indicates that the  
366 weathered and eroded glaze of ceramics may be an important source of mobile Pb in coastal  
367 sediments impacted by visible debris. In contrast, however, the availability of Pb in the  
368 composite to the protein, BSA, is only about 0.1% of its total content and is considerably  
369 lower than the percentage mobilised in contaminated sediment (around 10%; Kalman and  
370 Turner, 2007). Thus, despite its high mobility under acidic conditions, Pb in ceramic debris

371 is not predicted to be particularly accessible in non-acidic digestive conditions typical of  
372 sediment-feeding invertebrates or under near-neutral aqueous conditions more generally.

373

## 374 **5. Conclusions**

375 This study has highlighted the potential significance of glazed surfaces as a source of Pb to  
376 estuarine and coastal sediments that are visibly impacted by ceramic wastes. At the sites  
377 under investigation, the presence of glazed ceramics that have been eroded to sizes < 2 mm  
378 result in increases in Pb concentrations relative to a regional baseline of about an order of  
379 magnitude and enrichment factors normalised to Rb of between 5 and 13. Lead arising from  
380 glazed ceramic surfaces has a mobility of more than 30% as evaluated by extraction in cold  
381 HCl, but is unlikely to be assimilated by deposit-feeding invertebrates because of its poor  
382 solubility in a surrogate digestive protein. While the specific findings of the study are  
383 localised, it would be reasonable to assume that the broad impacts documented are more  
384 generally applicable where ceramic waste is observed.

385

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390

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