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# Observational Study Unveils the Extensive Presence of Hazardous Elements in Beached Plastics from Lake Geneva

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1 **Observational study unveils the extensive presence of hazardous**  
2 **elements in beached plastics from Lake Geneva**

3

4 Montserrat Filella<sup>1,\*</sup>, Andrew Turner<sup>2</sup>

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6 <sup>1</sup>Institute F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva,  
7 Switzerland

8 <sup>2</sup>School of Geography, Earth and Environmental Sciences, Plymouth University, Drake  
9 Circus, Plymouth PL4 8AA, UK

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14 **Abstract**

15

16 Over 3000 samples of plastic litter have been retrieved from twelve pebble beaches around the  
17 shores of Lake Geneva. The plastic stock consisted of identifiable objects of various size and  
18 colour, including bottles, bottle tops, cotton buds, pens, toys and straws, an heterogeneous  
19 assortment of fragments whose origin was either discernible or unknown, and pieces or blocks  
20 of expanded polymer (polystyrene or polyurethane foam). Analysis of 670 samples by portable  
21 x-ray fluorescence (XRF) spectrometry revealed high concentrations of hazardous elements or  
22 compounds among many plastics. These included Cd, Hg and Pb (with maximum  
23 concentrations of 6760, 810 and 23,500 ppm, respectively) as stabilisers in PVC-based  
24 materials and/or brightly-coloured sulphide or chromate pigments in primary and secondary  
25 plastics, and Br (with a maximum concentration of 27,400 ppm) as a proxy for brominated  
26 flame retardants in both plastics and foams. The abundance of hazardous elements in beached  
27 plastics that have been restricted or banned reflect the age and residence time of the plastic  
28 stock in the lake, coupled with a relatively high length of shoreline to surface area of the system.  
29 The migratability of hazardous elements from the polymeric matrix is likely to determine their  
30 environmental impacts and is recommended as a future area of research.

31

32

33 **Keywords:** Lake Geneva; beaches; plastics; portable-XRF; hazardous elements; Hg; Pb, Cd

## 34 1. Introduction

35

36 The accumulation and impacts of anthropogenic litter in marine environments has been well-  
37 documented and publicised over the past few decades. In contrast, and despite often easier and  
38 more ready access, littering in the freshwater environment has received far less attention, with  
39 systematic investigations of rivers and lakes appearing in the literature only recently (Eriksen  
40 et al., 2013; Imhof et al., 2013; Hoellein et al., 2014; Klein et al., 2015; Turner and Holmes,  
41 2015; Zhang et al., 2015; 2016; Cable et al., 2017). Although they share many similarities with  
42 the oceans in terms of usage and anthropogenic pressures, lakes have a smaller fetch, greater  
43 enclosure, higher ratio of shoreline to open water, smaller (if any) tidal or haline influence on  
44 circulation and transport, and greater sensitivity of water characteristics to local weather  
45 conditions. Anthropogenic inputs in lakes are, therefore, likely to be more localised and  
46 characterised by a greater land-based and direct human signatures, with a higher proportion of  
47 buoyant litter, and in particular low density plastics, ending up beached at the land-water  
48 interface (Hoffman and Hittinger, 2017).

49

50 Regardless of their precise source, plastics deposited on the shores and beds of lakes and  
51 suspended in the lentic water column are likely to pose the same problems to wildlife as marine  
52 plastics. In this respect, entanglement and ingestion are of greatest concern, with the former  
53 having the propensity to suffocate, impair mobility, disrupt feeding and maim, and the latter  
54 posing a significant risk of obstruction or damage to the linings of digestive tracts and, through  
55 reduced feeding drive, starvation (Gregory, 2009). Ingestion also has the potential to transfer  
56 toxins associated with polymers to organisms that consume plastics either directly or through  
57 contaminated prey. The majority of studies in this area have targeted persistent organic  
58 micropollutants, like polychlorinated biphenyls and polycyclic aromatic hydrocarbons, that are  
59 sorbed to the plastic surface (Frias et al., 2010; Rochman et al., 2013; Gauquie et al., 2015;  
60 Ziccardi et al., 2016; Hong et al., 2017). However, attention has recently been paid to the  
61 occurrence and impacts of chemical elements in litter, like metals, metalloids and halogens, that  
62 are either adsorbed to the plastic or incorporated into the polymer itself (Nakashima et al., 2016;  
63 Boucher et al., 2016; Turner, 2016; Turner and Solman, 2016; Brennecke et al., 2016). While  
64 recent empirical evidence and models suggest that the exposure and accumulation of adsorbed  
65 compounds or elements may have been overstated in the literature (Herzke et al., 2016),  
66 inorganic additives of the plastic matrix, including flame retardants, catalysts and heavy metal-  
67 based pigments, appear to represent a more significant source of contaminants to the foodchain  
68 (Rani et al., 2015; Massos and Turner, 2017).

69

70 In order to improve our understanding about potentially toxic elements present in plastics in the  
71 lentic environment, the present study determines their concentrations in plastic litter collected  
72 from twelve beaches around Lake Geneva (or Lac Lemman), one of western Europe's largest  
73 bodies of freshwater. Selected samples are analysed by portable x-ray fluorescence (XRF)  
74 spectrometry using established and validated protocols (Turner and Solman, 2016) for the  
75 discrimination of PVC- and non-PVC-based materials and the presence and concentration of  
76 elements that are restricted in plastics according to EU Directive 2002/95/EC on the Restriction  
77 of Hazardous Substances (RoHS, 2006) and are potentially hazardous to wildlife; namely, the  
78 heavy metals, Cd, Hg and Pb, and the halogen, Br, as a proxy for brominated flame retardants.  
79 Other, ancillary metals and metalloids (As, Sb, Se and total Cr) are also considered because of  
80 their restriction according to other European Directives (e.g. 2009/48/EC on toy safety;  
81 European Parliament and the Council of the European Union, 2009) or whose co-association  
82 with the principal elements provides evidence for the types of pigments or retardants present.

83

84 **2. Materials and methods**

85

86 **2.1 Study area and plastic sampling**

87

88 Lake Geneva is an elongated, mesotrophic, perialpine lake at an altitude of 372 m above mean  
89 sea level whose catchment area of 8000 km<sup>2</sup> (including the lake itself) houses a resident  
90 population of about 1.1 M according to 2011 data (CIPEL, 2017). With a surface area of 580  
91 km<sup>2</sup>, a maximum length and width of 72.3 km and 14 km, respectively, and a maximum depth  
92 of 310 m, it has a water volume of 89 km<sup>3</sup>, making it one of the largest lakes and largest  
93 freshwater reservoirs in western Europe. The main tributaries to the lake are the Rhône and  
94 Dranse rivers, and the theoretical residence time, based on volume and freshwater input is about  
95 11 years.

96

97 Twelve pebble beaches along the Swiss and French shores of Lake Geneva (Figure 1 and Table  
98 1) were sampled for the present study. Since the lake is heavily used for recreational purposes  
99 and most of the beaches are routinely cleaned, particularly in summer, sampling took place on  
100 three consecutive days in mid-March (and before the Easter holiday break) in 2016. Despite  
101 targeting a period outside of the main holiday season, however, organised litter cleaning was  
102 witnessed on some of the Swiss beaches, resulting in a lower amount of material retrieved at  
103 these locations. Although litter tended to accumulate with wood and other natural debris along  
104 strand lines, all material across the entire beach that was visible at the surface to the naked eye  
105 and that was wholly or largely constructed of plastic was retrieved by hand. Samples from each  
106 beach were returned to the laboratory in a series of clear, polyethylene zip-lock bags where they  
107 were cleared of any visible extraneous material, grouped according to sample site, counted,  
108 photographed and weighed.

109

110

111 **2.2 XRF analysis**

112

113 Selected samples of various size, colour and texture from each location were analysed by  
114 energy-dispersive XRF using a battery-powered Niton analyser (model XL3t 950 He  
115 GOLDD+) for a suite of elements, of which As, Br, Cd, Cl, Cr, Hg, Pb, Sb and Se are the focus  
116 of the present study, under operating conditions described and validated elsewhere (Turner and  
117 Solman, 2016). Briefly, the instrument was configured in a plastics mode that is capable of  
118 quantifying elemental concentrations in complex, low density materials through a fundamental  
119 parameters-based alpha coefficient correction model and a thickness correction algorithm down  
120 to 0.05 mm. The XRF was employed in the laboratory in a bench-top accessory stand and was  
121 operated remotely by a laptop via USB. The surface of the sample to be probed (usually the  
122 thickest and flattest part) was positioned centrally over the detector window on 3.6 µm polyester  
123 film before measurements, with 8-mm collimation and appropriate thickness correction, were  
124 activated through the laptop for a total period of 120 s (60 s each at 50 kV/40 µA and 20 kV/100  
125 µA). Spectra were quantified by fundamental parameters to yield elemental concentrations on  
126 a dry weight basis (in µg g<sup>-1</sup>) and with a counting error of 2σ (95% confidence).

127

128 For quality assurance purposes, two Niton reference plastics (PN 180-619, LOT#T-18 and PN  
129 180-554, batch SN PE-071-N) were analysed likewise and at regular intervals during each  
130 measurement session. A comparison of mean measured concentrations and certified values,  
131 shown in Table 2, reveals agreement to within 10% in all cases with the exception of Sb in the  
132 former disc; here, the mean measured concentration was 15% lower than the average certified  
133 value.

134

135 Measurement limits of detection of the Niton XL3t are dependent on a number of factors,  
136 including analyte fluorescence intensity, mode of instrument application, counting time, and  
137 sample density, composition and thickness. For the samples considered here and under the  
138 operating conditions described above, detection limits were generally lowest and below  $10 \mu\text{g g}^{-1}$   
139  $\text{g}^{-1}$  for As, Br, Cr and Pb and highest and above  $70 \mu\text{g g}^{-1}$  for Ba, Sb and Sn. Note that in the  
140 case of As, overlap of its  $K\alpha$  fluorescence peak with the  $L\alpha$  peak of Pb coupled with the  
141 relatively low intensity of the As- $K\beta$  line means that concentrations cannot be effectively  
142 calculated for samples with Pb:As ratios in excess of about 10 (Environmental Protection  
143 Agency, 2007). Arsenic concentrations reported herein are, therefore, restricted to those  
144 returned by the XRF where Pb was not detected.

145

### 146 **2.3. FTIR analysis**

147

148 Fourier transform infra-red (FTIR) spectroscopy was employed to obtain a high resolution  
149 infrared spectrum of absorbance by the samples that identifies the type of polymer/s present.  
150 Thus, based on the XRF results, selected samples ( $n = 40$ ) were determined by FTIR using a  
151 Bruker ALPHA Platinum attenuated total reflection QuickSnap A220/D-01 spectrometer.  
152 Sample offcuts of up to about 20 mg were clamped down on to the ATR diamond crystal before  
153 measurements, consisting of 16 scans in the range  $4000$  to  $400 \text{ cm}^{-1}$  and at a resolution of  $4 \text{ cm}^{-1}$ ,  
154 were activated via Bruker OPUS spectroscopic software. Identification involved a  
155 comparison of sample transmittance spectra with libraries of reference spectra.

156

### 157 **2.4. Data treatment and analysis**

158

159 Data from the XRF were converted to Excel files using Niton Data Transfer (NDT) software.  
160 Regressions and correlations were performed in Excel 2010 using the data analysis ToolPak  
161 add-in, with an alpha level of 0.05 adopted as a measure of defining statistical significance.

162

## 163 **3. Results and discussion**

164

### 165 **3.1. Number and type of plastic samples**

166

167 The majority of anthropogenic material observed on each beach was plastic, with manufactured  
168 wooden and metallic debris present in lesser quantities and glass entirely absent. The plastic  
169 items retrieved from the 12 locations are illustrated in Figure S1 and quantified in Table 1 in  
170 terms of total number, number analysed by XRF and average weight. Overall, 3349 samples  
171 were collected, with a total mass of about 4 kg. Items could be classified as primary plastic  
172 objects that were usually identifiable (e.g. bottle tops and stoppers, straws, cotton buds,  
173 cartridges, clothes pegs, toys, pens, cigarette lighters, cable ties), secondary plastic fragments  
174 that were identifiable (e.g., irregular pieces or remains of wire insulation, piping, taping, plant  
175 pots, sheeting-wrapping, food wrappers, cups and bottles), secondary plastic fragments that  
176 were unidentifiable, or fragments of expanded plastic (hereafter referred to as foam) that were  
177 unidentifiable. XRF analysis was restricted to 670 items because of time and resource  
178 constraints, with measurements prioritised on the basis of sample variety and reduced by  
179 avoiding items that were visually similar in construction, texture and colour, both within and  
180 between different sites.

181

182 The number of items retrieved and the distribution of items in terms of classification and size  
183 varied considerably among the beaches and with no clear geographical pattern. For instance,  
184 the plastic stock at Petite Rive was dominated by primary plastics but at Rupalet comprised a  
185 high proportion of secondary fragments, and while foams were absent from Crans-près-Céligny

186 and comprised a low proportion of the plastic pool at La pêcheirie they were abundant on the  
187 beaches at Rupalet and Les marines; plastics at La pêcheirie were also dominated by a high  
188 number of small items whereas those at Rupalet comprised far fewer items that, on average,  
189 were considerably larger. Variations in the amount and type of plastic accumulated among the  
190 beaches may be attributable to many factors, including proximity to inhabited areas and  
191 tributaries, recent history of beach cleaning, circulation and currents in the lake and beach  
192 aspect and slope, but a detailed analysis and source apportionment was not the objective of the  
193 present study.

194

### 195 **3.2. Occurrence and concentrations of hazardous elements**

196

197 Table 3 shows the frequency of detection and summary statistics for the hazardous elements  
198 and ancillary elements in all beached lake plastics analysed by XRF, while Figure 2 illustrates,  
199 in ascending order, all concentrations returned for Br, Cd, Hg and Pb, along with photographs  
200 of samples with the highest concentrations and/or that exceed respective RoHS limits.

201

202 Bromine was detected in over 20% of the samples analysed, with concentrations ranging from  
203 about 3 to 27,000 ppm. Concentrations of total Br exceeding 1000 ppm were encountered in 21  
204 items that are photographed in Figure 2a and that were either fragments of foam or neutrally-  
205 coloured or green primary and secondary plastics. Based on Cl content returned by the XRF,  
206 none of these samples was of PVC-construction, with FTIR analysis revealing that foams were  
207 polyurethane- or polystyrene-based and that remaining samples were composed of  
208 polyethylene, polypropylene or acrylonitrile butadiene styrene. Bromine is used in some  
209 plastics in the pigment copper phthalocyanine (Lewis, 2004), explaining its occurrence in the  
210 two green items illustrated in Figure 2, but its use in brominated flame retardants (BFRs), often  
211 in association with Sb-based flame retardant synergists, accounts for its presence in the  
212 remaining samples. Here, BFRs may have been added deliberately to items requiring flame  
213 retardancy, like soft furnishings, electronic casings and insulating materials, or incorporated  
214 inadvertently into items not requiring flame retardancy, like flotation aids and food packaging,  
215 via contamination of the recyclate stream (Turner and Filella, 2017). Where Sb was detected  
216 among these samples ( $n = 7$ ), the two elements exhibited a significant relationship (Figure 3a),  
217 with a gradient of about 3.5 that is similar to the mass ratio of Br:Sb in plastics impregnated  
218 with many historical and contemporary BFRs (Papazoglou, 2004; Turner and Filella, 2017).  
219 Assuming that Br occurs in the form of one or more restricted brominated compound in samples  
220 that are not green, at least 19 items retrieved from the lake are potentially non-compliant with  
221 respect to the RoHS limit for BFRs of 1000 ppm.

222

223 Cadmium was detected in about 16% of lake samples analysed by XRF, with concentrations  
224 ranging from about 20 to 7000 ppm, and exceedance of the RoHS limit for Cd in plastics of  
225 100 ppm occurred in 57 samples which are photographed in Figure 2b. The heavy metal was  
226 never detected in foams and was most frequently encountered in brightly coloured (and green,  
227 yellow, orange and red) plastic objects and fragments that FTIR indicated were generally  
228 polyethylene-based; Cd also occurred in a limited number neutrally-coloured fragments that  
229 were usually of PVC construction. The presence of Cd in PVC may be attributed to its use as a  
230 stabiliser in the form of a stearate or laurate (Titow, 1986), while its widespread occurrence  
231 among coloured plastics is a consequence of the brilliance and light-fastness of the pigments,  
232 cadmium yellow (CdS) and cadmium red (CdSe). Thus, the former was employed in plastics to  
233 provide a bright yellow colour, with progressive replacement of S by Se resulting in  
234 successively darker hues of red and combination with viridian ( $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) providing a range  
235 of light greens (Rangos, 2004). Accordingly, and amongst the Cd-positive lake samples, Se was  
236 only detected where red or orange was the principal colour while Cr was detected across a

237 variety of green items. Quantitatively, the relationships between Cd and Se concentrations,  
238 shown in Figure 3b, could be defined by a slope that was greater for red samples (Cd:Se =  
239 0.224) than for orange samples (Cd:Se = 0.139), while concentrations of Cd and Cr were  
240 statistically unrelated.

241  
242 The present study appears to be the first to provide systematic data on Hg in plastic litter in the  
243 aquatic environment. Thus, while traces of the metal were detected in various samples,  
244 concentrations above 100 ppm, and as photographed in Figure 2c, were restricted to plastic  
245 objects and fragments that were always red or reddish-brown and, where analysed by FTIR, of  
246 polyethylene construction. Mercury has been used as a catalyst in some polyurethanes,  
247 accounting for residues in a number of foams sampled herein, but it does not appear to have  
248 had widespread use as a pigment in plastics (Hansen et al., 2013). As part of a literature review  
249 into solid products in municipal waste that contain Hg, the US EPA (1992) found no published  
250 data on the use of Hg-based pigments but suggested that most of those manufactured were likely  
251 used by the plastics industry. A subsequent synopsis of colour pigments in plastics by Rangos  
252 (2004) mentions Hg-Cd pigments that were developed in the 1950s as a more cost-effective and  
253 brighter alternative to cadmium sulphoselenides, with Hg replacing part of the Cd and  
254 eliminating the requirement for Se in providing a colour range from deep orange to maroon.  
255 However, being inferior to sulphoselenides in terms of light-fastness and heat stability, Hg-  
256 based pigments never gained popularity. Regarding the lake samples measured here, Cd was  
257 present in ten red plastics where Hg was detected, and in all items where the concentration of  
258 Hg exceeded 100 ppm, with Se present in just one case. Overall, concentrations of the two  
259 heavy metals were significantly related (Figure 3c), with a slope of 0.167 that affords an insight  
260 into the chemical makeup and stoichiometry of the pigment encountered herein

261  
262 Lead was detected in almost one quarter of all samples analysed, encompassing a wide variety  
263 of primary and secondary plastics in terms of size, colour and polymer, and in fragments of  
264 polyurethane foam. Concentrations ranged from about 5 to 24,000 ppm, with exceedance of the  
265 RoHS for the metal of 1000 ppm occurring in 65 cases and as illustrated in Figure 2d; samples  
266 above 5000 ppm were dominated by PVC-based materials and those below, where measured  
267 by FTIR, constructed largely of polyethylene. The presence of Pb in PVC reflects its use as a  
268 stabiliser in compounds like lead sulphates and lead stearates (Titow, 1986), while its  
269 occurrence in polyolefins may be attributed to the use of various leaded pigments that include  
270 cremnitz white ((PbCO<sub>3</sub>)<sub>2</sub>·Pb(OH)<sub>2</sub>), red lead (Pb<sub>3</sub>O<sub>4</sub>) and chrome yellow (PbCrO<sub>4</sub>), with  
271 orange and red variants of the latter being effected by the addition of PbSO<sub>4</sub> or PbMoO<sub>4</sub>  
272 (Hummel, 2002; Rangos, 2004). There was a striking, significant relationship between Pb and  
273 Cr in samples that were non-PVC-based and not green (where Cr in its lower oxidation state is  
274 often used as a pigment) with a slope of 5.01 that is marginally greater than the mass ratio of  
275 Pb:Cr in pure lead chromate (about 4) (Figure 3d). This suggests that lead chromate and its  
276 variants have commonly been employed, in whole or in part (e.g. with Cd-based pigments), to  
277 colour plastics retrieved from the lake that are yellow, brown, red or orange.

### 278 279 **3.3. Comparison with beached marine plastics**

280  
281 The present study is one of only a limited number that have published information on plastics  
282 in western Europe's largest lake (Faure et al., 2012; Faure et al., 2015) or addressed the  
283 occurrence of hazardous elements associated with different polymeric matrices in freshwater  
284 (Imhof et al., 2016). Several of the findings of our investigation are similar to those arising from  
285 studies of beaches in Atlantic Europe; specifically, there is a heterogeneous assortment of  
286 primary and secondary plastics and foams, coupled with a plastic pool that is dominated by  
287 polyolefins and with a relatively low abundance of higher density materials like PVC which,

288 presumably, has a propensity for sedimentation (Turner, 2016; Fok et al., 2017; Massos and  
289 Turner, 2017). Unlike marine plastic surveys, however, there was an absence of primary  
290 production pellets and very little filamentous commercial fishing waste, like rope, netting and  
291 cord, retrieved from the shores of the lake. Production pellets are often the dominant form of  
292 plastic waste on oceanic beaches on a number basis and, with respect to microplastics (< 5 mm  
293 in diameter), on a mass basis (Massos and Turner, 2017), with the principal sources related to  
294 spillages during transportation (including shipment at sea) and improper handling at processing  
295 facilities (Duis and Coors, 2016). Lack of commercial plastic transportation on the lake coupled  
296 with efficient waste water treatment in the catchment may account for a limited supply of pellets  
297 to the system (Driedger et al., 2015), with a coarse-grained substrate acting to sieve out any  
298 residual pellets and other microplastics from the beach surface. Regarding filamentous debris,  
299 and compared with the marine environment, smaller-scale commercial fishing operations and  
300 more quiescent conditions ensure that there is less scope for losing gear and a better chance of  
301 its recovery, while a limited number of registered users means that there is a greater  
302 responsibility and incentive to retrieve fishing waste.

303

304 Compared with equivalent studies conducted on marine beaches (Turner, 2016), hazardous  
305 elements appear to occur in higher abundance in plastics retrieved from Lake Geneva. Since  
306 many of these compounds have been restricted or phased out over the past few decades (Hansen  
307 et al., 2013), we may infer that a significant proportion of the plastic stock in Lake Geneva is  
308 historical; specifically, the presence of Hg-based pigments suggests that some materials are at  
309 least sixty years old. While this does not necessarily imply that such plastics have been in the  
310 lake for this length of time, significant rounding and discolouration of most expanded foam  
311 samples from the lake is consistent with the protracted periods of weathering and erosion.  
312 Moreover, modelling studies in other lakes suggest that buoyant plastics may reside in enclosed  
313 water bodies for timescales considerably longer than hydraulic flushing times (Cable et al.,  
314 2017), meaning that the entrapment of low density plastics for decadal periods is entirely  
315 feasible in Lake Geneva.

316

### 317 **3.4. Potential impacts of hazardous elements on wildlife**

318

319 The impacts of hazardous elements and compounds in plastics are largely related to their  
320 propensity to migrate from the polymeric matrix and accumulate in biota and there are three  
321 potential means by which this may take place. Thus, firstly, a chemical may slowly leach into  
322 the surrounding aqueous medium while plastic is suspended in the water column, providing a  
323 general increase in its concentration and availability. Since additives, including pigments, are  
324 not designed to leach from plastics, this process is predicted to be slow and of limited  
325 importance in circulating water, even after the surface has become weathered and abraded  
326 (Nakashima et al., 2016). Secondly, and more significantly, small suspended plastics may be  
327 ingested by organisms mistaking items for food, with chemical accumulation occurring via  
328 partial but accelerated dissolution under the acidic or enzyme-rich conditions of the gastro-  
329 intestinal tract (Massos and Turner, 2017). Although the beached plastics retrieved from Lake  
330 Geneva were relatively large because of the sieving effect mentioned above, smaller, (non fiber-  
331 type) microplastics that are significant in the water column (Faure et al., 2015) are likely derived  
332 from and have a chemical signature similar to the material characterised herein. Thirdly, it is  
333 possible that invertebrates may accumulate hazardous chemicals by inhabiting static (e.g.  
334 trapped) or moored plastics or by grazing on associated biofilms. For instance, Jang et al. (2016)  
335 recently showed that marine mussels inhabiting styrofoam buoys were able to accumulate the  
336 BFR, hexabromocyclododecane, that had been impregnated in the polymer during its  
337 manufacture.

338

339 **4. Conclusions**

340

341 The present study is among the first to describe both the type and characteristics of beached  
342 plastics in Lake Geneva and the occurrence of hazardous elements in fresh water plastic litter.  
343 The results reveal the ubiquity of restricted hazardous elements and compounds, including  
344 brominated flame retardants, often in association with antimony-based synergists, and  
345 cadmium-, mercury- and lead-based stabilisers and/or pigments, among primary and secondary  
346 plastics and fragments of foam. The abundance of hazardous elements in beached lake plastics  
347 may be attributed to the decadal residence times of low density material in the lake, the age of  
348 the plastic stock in the system and the relatively high length of shoreline to surface area of the  
349 enclosed water body. The impacts of plastic-bound toxic elements on lake wildlife are unknown  
350 but should form the basis of future empirical investigations.

351

352 **Supporting information**

353

354 Figure S1 is a photographic catalogue of the beaches and samples retrieved from Lake Geneva.

355

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357

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361 **References**

- 362
- 363 Boucher C., Morin M., Bendell L.I. (2016). The influence of cosmetic microbeads on the  
364 sorptive behavior of cadmium and lead within intertidal sediments: A laboratory study.  
365 *Regional Studies in Marine Science* 3, 1-7.
- 366 Cable, R.N., Beletsky, D., Beletsky, R., Wigginton, K., Locke, B.W., Duhaime, M.B. (2017).  
367 Distribution and modeled transport of plastic pollution in the Great Lakes, the World's  
368 largest freshwater resource. *Front. Environ. Sci.* 5:45. doi.org/10.3389/fenvs.2017.00045
- 369 CIPEL (2017). Programme Quinquennal 2011-2015. Campagne 2016. Rapports sur les Etudes  
370 et Recherches Entreprises dans le Bassin Lémanique. Nyon: CIPEL.
- 371 Driedger, A.G.J., Dürr, H.H.; Mitchell, K.; Van Cappellen, P. (2015). Plastic debris in the  
372 Laurentian Great Lakes: A review. *J. Great Lakes Res.* 41, 9-19.
- 373 Duis, K. and Coors, A. (2016). Microplastics in the aquatic and terrestrial environment:  
374 sources (with a specific focus on personal care products), fate and effects. *Environ. Sci.*  
375 *Europe* 28:2. doi: 10.1186/s12302-015-0069-y.
- 376 Environmental Protection Agency (2007). Method 6200 - Field Portable X-ray Fluorescence  
377 Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.  
378 <https://www.epa.gov/sites/production/files/2015-12/documents/6200.pdf> (accessed 9/17).
- 379 Eriksen, M., Mason, S., Wilson, S., Box, C., Zellers, A., Edwards, W., Farley, H., Amato, S.  
380 (2013). Microplastic pollution in the surface waters of the Laurentian Great Lakes. *Mar.*  
381 *Pollut. Bull.* 77, 177-182.
- 382 European Parliament and the Council of the European Union (2009). Directive 2009/48/EC of  
383 the European Parliament and of the Council of 18 June 2009 on the Safety of Toys.  
384 Official Journal of the European Union L170/1. [http://eur-lex.europa.eu/legal-](http://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX%3A32009L0048)  
385 [content/en/TXT/?uri=CELEX%3A32009L0048](http://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX%3A32009L0048)
- 386 Faure, F., Corbaz, M., Baecher, H., De Alencastro, L.F. (2012). Pollution due to plastics and  
387 microplastics in Lake Geneva and in the Mediterranean Sea. *Archives des Sciences* 65,  
388 157-164.
- 389 Faure, F., Demars, C., Wieser, O., Kunz, M., De Alencastro, L.F. (2015). Plastic pollution in  
390 Swiss surface waters: nature and concentrations, interaction with pollutants. *Environ.*  
391 *Chem.* 12, 582–591.
- 392 Fok, L., Cheung, P.K., Tang, G.D., Li, W.C. (2017). Size distribution of stranded small plastic  
393 debris on the coast of Guangdong, South China. *Environ. Poll.* 220, 407-412.
- 394 Gregory, M. (2009). Environmental implications of plastic debris in marine settings—  
395 entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions.  
396 *Philos. Trans. R. Soc. Lond. B Biol. Sci.* 364, 2013-2025.
- 397 Hansen, E., Nilsson, N.H., Lithner, D., Lassen, C. (2013). Hazardous Substances in Plastic  
398 Materials. Oslo: COWI and the Danish Technological Institute on behalf of The  
399 Norwegian Climate and Pollution Agency, 150 pp.
- 400 Herzke, D., Anker-Nilssen, T., Nost, T.H., Gotsch, A., Christensen-Dalsgaard, S., Langset, M.,  
401 Fangel, K., Koelmanns, A.A. (2016). Negligible impact of ingested microplastics on  
402 tissue concentrations of persistent organic pollutants in northern fulmars off coastal  
403 Norway. *Environ. Sci. Technol.* 50, 1924-1933.
- 404 Hoellein, T., Rojas, M., Pink, A., Gasior, J., Kelly, J. (2014). Anthropogenic litter in urban  
405 freshwater ecosystems: distribution and microbial interactions. *PLoS One* 9(6), e98485.
- 406 Hoffman, M.J., Hittinger, E. (2017). Inventory and transport of plastic debris in the  
407 Laurentian Great Lakes. *Mar. Poll. Bull.* 115, 273-281.
- 408 Hong S.H., Shim W.J., Hong L. (2017). Methods of analysing chemicals associated with  
409 microplastics: a review. *Anal. Methods* 9, 1361-1368.

410 Hummel, D. (2002). *Atlas of Plastic Additives: Analysis by Spectrometric Methods*. Berlin:  
411 Springer, 541 pp.

412 Imhof, H.K., Ivleva, N.P., Schmid, J., Niessner, R., Laforsch, C. (2013). Contamination of  
413 beach sediments of a subalpine lake with microplastic particles. *Curr. Biol.* 23, R867-  
414 R868.

415 Imhof, H.K., Laforsch, C., Wiesheu, A.C., Schmid, J., Anger, P.M., Niessner, R., Ivleva, N.P.  
416 (2016). Pigments and plastic in limnetic ecosystems: A qualitative and quantitative study  
417 on microparticles of different size classes. *Water Res.* 98, 64-74.

418 Jang, M., Shim, W.J., Han, G.M., Rani, M., Song, Y.K., Hong, S.H. (2016). Styrofoam debris  
419 as a source of hazardous additives for marine organisms. *Environ. Sci. Technol.* 50, 4951-  
420 4960.

421 Klein, S., Worch, E., Knepper, T.P. (2015). Occurrence and spatial distribution of  
422 microplastics in sediment of the Rhine-Main Area in Germany. *Environ. Sci. Technol.* 49,  
423 6070-6076.

424 Lewis, P.A. (2004). "Organic colorants," in: *Coloring of Plastics: Fundamentals, 2nd Edition*,  
425 ed. R.A. Charvat (Hoboken, NJ: John Wiley), 100-126.

426 Massos, A. and Turner, A. (2017). Cadmium, lead and bromine in beached microplastics.  
427 *Environ. Poll.* 227, 139-145.

428 Nakashima, E., Isobe, A., Kako, S., Itai, T., Takahashi, S., Gou, X. (2016). The potential of  
429 oceanic transport and onshore leaching of additive-derived lead by marine macro-plastic  
430 debris. *Mar. Poll. Bull.* 107, 333-339.

431 Papazoglou, E.S. (2004). "Flame retardants for plastics," in *Handbook of Building Materials*  
432 *for Fire Protection*, ed. C. A. Harper (New York: McGraw-Hill).

433 Rangos, G. (2004). "Inorganic colored pigments," in *Coloring of Plastics: Fundamentals, 2<sup>nd</sup>*  
434 *Edition*, ed. R. A. Charvat (Hoboken, NJ: John Wiley), 127-145.

435 Rani M., Shim W.J., Han G.M., Jang M., Al-Odaini N.A., Song Y.K., Hong S.H. (2015).  
436 Qualitative analysis of additives in plastic marine debris and its new products. *Arch*  
437 *Environ. Contam. Toxicol.* 69, 352-366.

438 Rochman C.M., Hoh E., Korobe T., Teh S.J. (2013). Ingested plastic transfers hazardous  
439 chemicals to fish and induces hepatic stress. *Sci. Reports* 3, 3263.  
440 DOI:10.1038/srep03263.

441 RoHS (2006). Restriction of Hazardous Substances, EU Directive 2002/95/EC  
442 <http://www.rohsguide.com/rohs-substances.htm> (accessed September 2017).

443 Titow, W.V. (1986). "Stabilisers: General Aspects," in *PVC Technology, 4<sup>th</sup> Edition* (London:  
444 Elsevier), 255-334.

445 Turner, A. (2016). Hazardous metals, metalloids and other elements in marine litter. *Mar. Poll.*  
446 *Bull.* 111, 136-142.

447 Turner, A. and Filella, M. (2017). Bromine in plastic consumer products – Evidence for the  
448 widespread recycling of electronic waste. *Sci. Total Environ.* 601-602, 374-379.

449 Turner, A. and Holmes, L. (2015). Adsorption of trace metals by microplastic pellets in fresh  
450 water. *Environ. Chem.* 12, 600-610.

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

453 U.S. EPA (1992). Characterization of Products Containing Mercury in Municipal Solid Waste  
454 in the United States, 1970 to 2000, report EPA530-S-92-013. U.S. Environmental  
455 Protection Agency, 22 pp.

456 Verlis, K.M., Campbell, M.L., Wilson, S.P. (2013). Ingestion of marine debris plastic by the  
457 wedge-tailed shearwater *Ardenna pacifica* in the Great Barrier Reef, Australia. *Mar. Poll.*  
458 *Bull.* 72, 244-249.

459 Zhang K, Gong W, Lv J, Xiong X, Wu C. (2015). Accumulation of floating microplastics  
460 behind the Three Gorges Dam. *Environ. Pollut.* 204, 117-123.

461 Zhang K, Su J, Xiong X, Wu X, Wu C, Liu J. (2016). Microplastic pollution of lakeshore  
462 sediments from remote lakes in Tibet plateau, China. *Environ Pollut.* 219, 450-455.  
463

464 Table 1: Name and location of each beach and information about the number (and average  
 465 weight) of samples retrieved and the number of XRF analyses performed.

Beach	Location	Date	Number of samples	Number of analyses	Mean weight per object / g
Jardin Botanique, Geneva, CH	46°13N, 6°08'E	17 March 2016	168	24	1.4
Crans-près-Céligny, CH	46°36N, 6°22'E	15 March 2016	18	4	1.2
Gland, CH	46°25'N, 6°17'E	15 March 2016	170	48	1.2
Rupalet, CH	46°27'N, 6°21'E	15 March 2016	34	13	3.0
Pêcherie, CH	46°27'N, 6°22'E	15 March 2016	804	109	0.76
Budaz, CH	46°29'N, 6°44'E	15 March 2016	71	14	2.8
Maladaire, CH	46°26'N, 6°52'E	15 March 2016	544	88	0.90
Les marines, Villeneuve, CH	46°24'N, 6°55'E	15 March 2016	152	41	1.2
Bret-Locum, F	46°24'N, 6°45'E	16 March 2016	262	55	1.6
Chauffours, F	46°24'N, 6°41'E	16 March 2016	630	149	1.4
Petite Rive, F	46°24'N, 6°37'E	16 March 2016	320	79	1.1
St-Disdille, Thonon-les-Bains, F	46°24'N, 6°30'E	16 March 2016	166	46	2.1

466

467

468 Table 2: A comparison of measured and certified concentrations of elements in two Niton reference plastic discs, with errors representing two standard deviations  
 469 about the mean in all cases.

CRM		As	Cd	Br	Cr	Hg	Pb	Sb	Se
PN 180-619, LOT#T-18	measured ( n = 12)	48 ± 8	264 ± 22		114 ± 12	97 ± 12	143 ± 8	80 ± 13	238 ± 16
	certified	51 ± 7	292 ± 20		106 ± 10	101 ± 10	155 ± 12	94 ± 10	207 ± 15
PN 180-554, PE 071-N	measured ( n = 8)		154 ± 36	524 ± 78	974 ± 89	908 ± 34	949 ± 81		
	certified		150 ± 6	495 ± 20	995 ± 40	1000 ± 40	1002 ± 40		

470  
 471

472 Table 3: Frequency of detection and summary statistics for the hazardous elements in beached Lake Geneva plastics.

473

Element	Number (%) of positives	Median, ppm	Minimum, ppm	Maximum, ppm	1Q, ppm	3Q, ppm
Antimony	73 (10.9)	183	33.1	27100	87.2	655
Arsenic <sup>a</sup>	63 (9.4)	6.3	1.7	26.4	3.9	11.2
Bromine	146 (21.8)	64.6	2.9	27400	18.2	314
Cadmium	107 (15.9)	1120	23	6760	224	2320
Chromium	326 (48.6)	48.8	17.0	77100	27.7	183
Lead	153 (22.8)	585	5.9	23500	48.6	2390
Mercury	17 (2.5)	68.6	3.3	810	17.1	510
Selenium	34 (5.1)	394	156	1670	244	808

474 <sup>a</sup>Excludes results arising from the spectral interference by lead.

475

## Figure legends

Figure 1. Location of the 12 beaches sampled in Lake Geneva.

Figure 2a. Distribution of measured bromine concentrations. The picture shows all objects with concentrations higher than 1000 ppm and in descending order from left to right and from top to bottom.

Figure 2b. Distribution of measured cadmium concentrations. The picture shows all objects with concentrations higher than 1000 ppm and in descending order from left to right and from top to bottom.

Figure 2c. Distribution of measured mercury concentrations. The picture shows all objects with concentrations higher than 100 ppm and in descending order from left to right and from top to bottom.

Figure 2d. Distribution of measured lead concentrations. The picture shows all objects with concentrations higher than 1000 ppm and in descending order from left to right and from top to bottom.

Figure 3. (a) Br versus Sb **concentrations** in samples where  $\text{Br} > 1000$  ppm; (b) Se versus Cd **concentrations** in red (●) and orange (○) plastics; (c) Hg versus Cd **concentrations** in Hg-positive samples; (d) Pb versus Cr **concentrations** in non-PVC-based samples that were not coloured green; **the line corresponds to the mass ratio of Pb to Cr in pure lead chromate.**

**Values in figures correspond to best fit regression lines.**

Figure 1

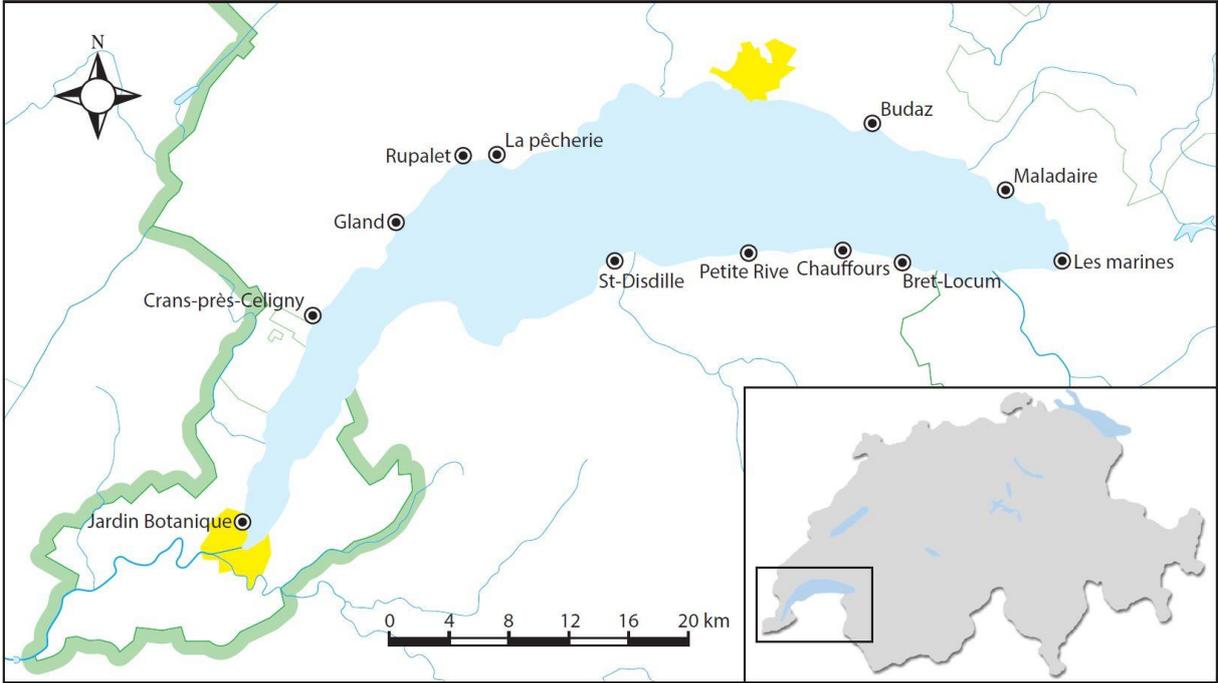


Figure 2 a

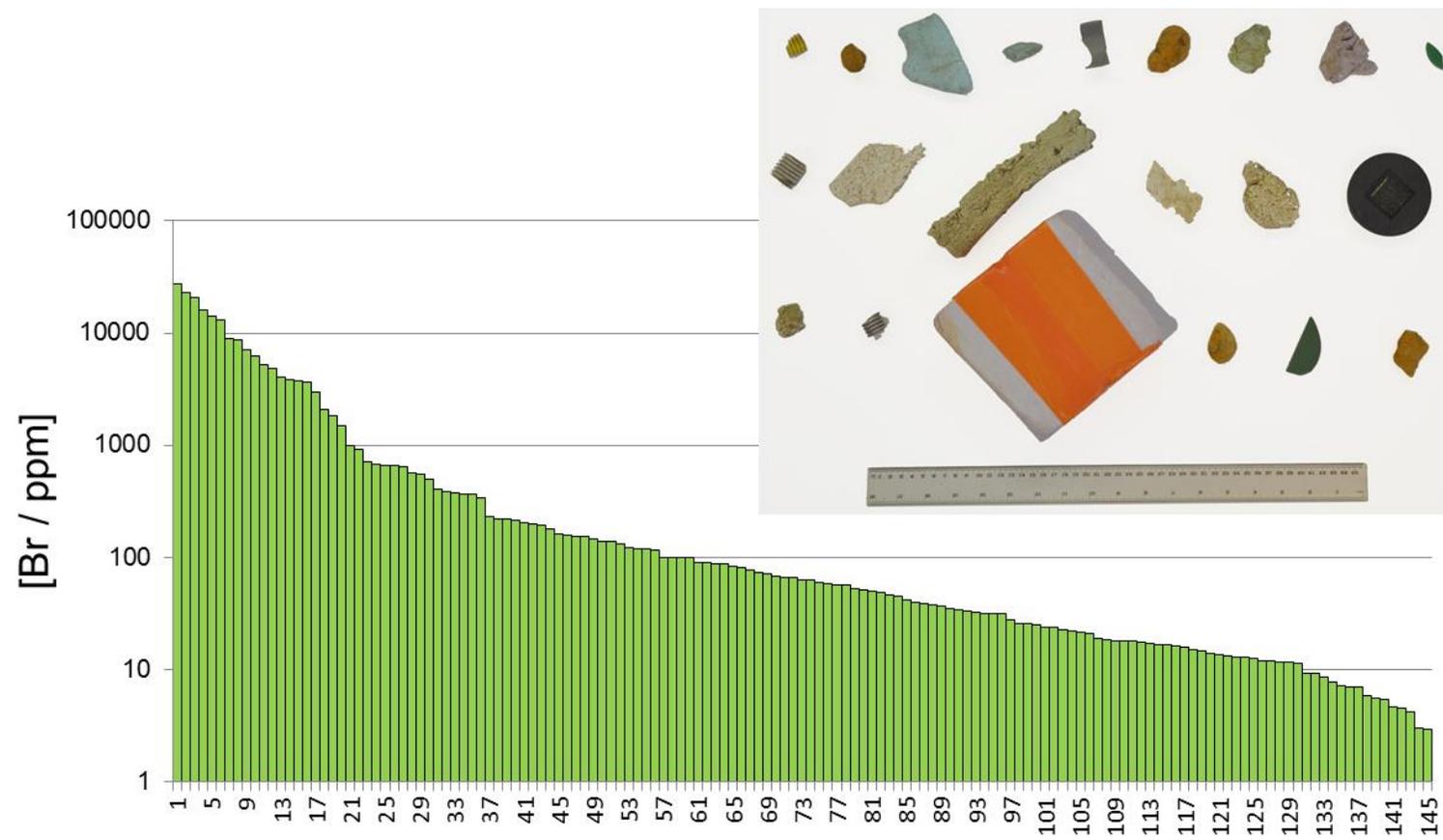


Figure 2 b

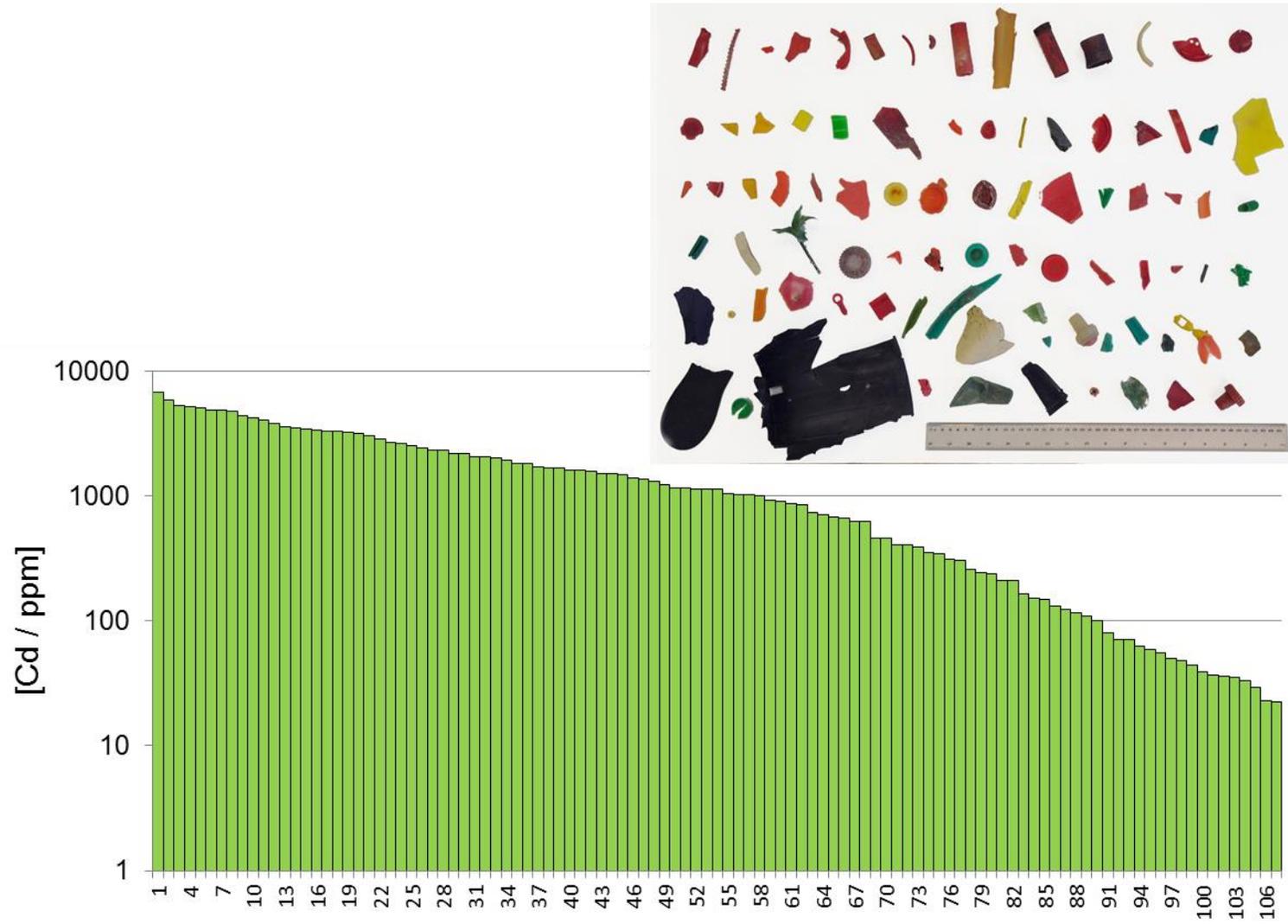


Figure 2c

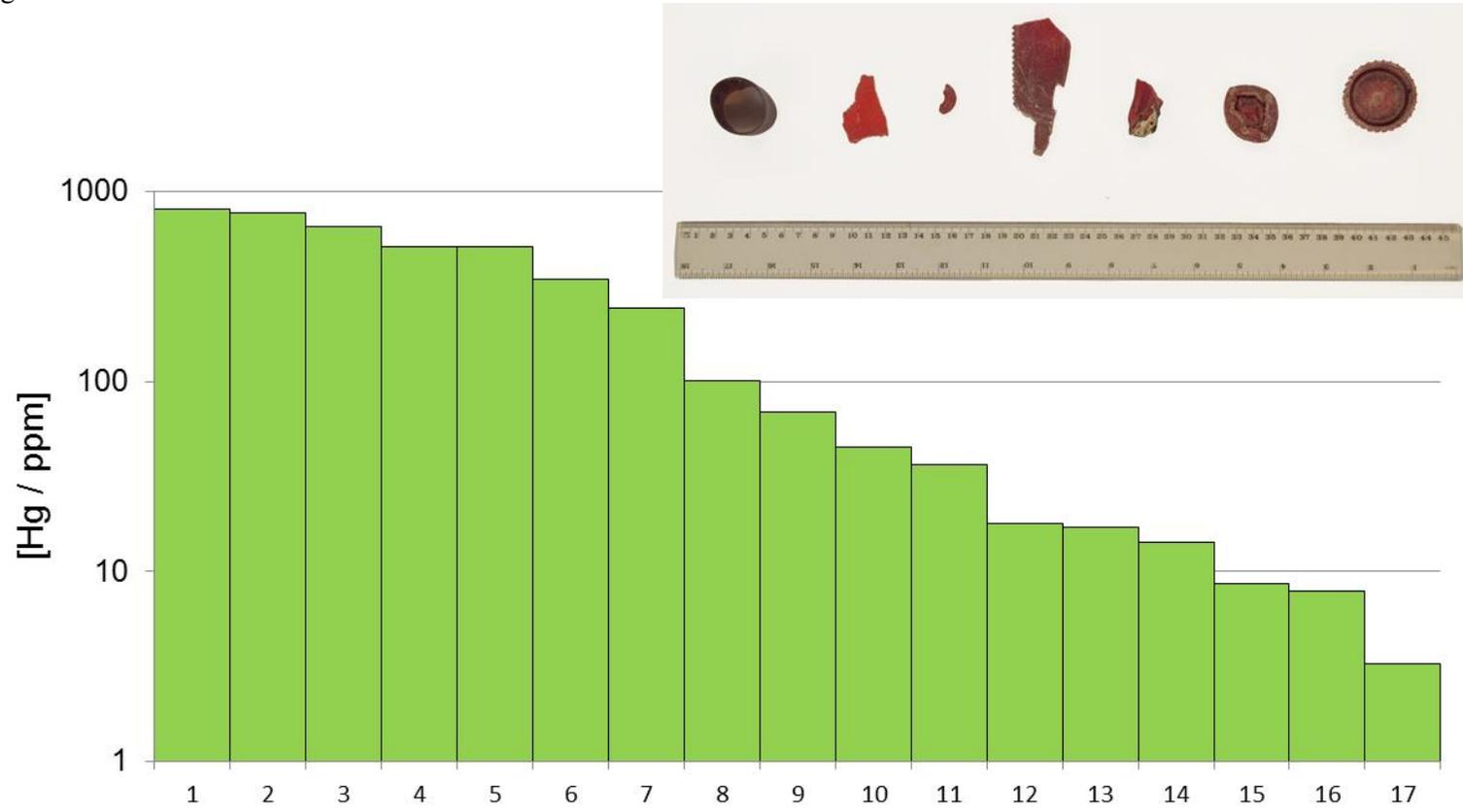


Figure 2d

