

2021-07-30

Polyvinyl chloride in consumer and environmental plastics, with a particular focus on metal-based additives

Turner, Andrew

<http://hdl.handle.net/10026.1/18133>

10.1039/d1em00213a

Environmental Science: Processes & Impacts

Royal Society of Chemistry (RSC)

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

1 **Polyvinyl chloride in consumer and environmental plastics, with a**
2 **particular focus on metal-based additives**

3

4 Andrew Turner

5 School of Geography, Earth and Environmental Sciences, University of Plymouth, Drake
6 Circus, Plymouth PL4 8AA, UK

7 aturner@plymouth.ac.uk

8 ORCID: 0000-0003-0505-4561

9

10 Montserrat Filella*

11 Department F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva,
12 Switzerland

13 montserrat.filella@unige.ch

14 ORCID: 0000-0002-5943-1273

15

16

17 *Author for correspondence

18

19 Accepted 29th July 2021

20 **DOI**

<https://doi.org/10.1039/D1EM00213A>

22

23 **Abstract**

24 Polyvinyl chloride (PVC) is one of the most widely used thermoplastics but is also a material
25 of concern because of the generation and release of harmful chemicals during its life cycle.

26 Amongst the chemicals added to PVC are metal-based stabilisers **and Sb-based halogenated**
27 **flame retardant synergists**. However, very little quantitative information exists on these
28 additives, and in particular in PVC lost to the environment. In this study, the distribution of
29 PVC amongst consumer plastics in societal circulation and plastics retrieved **from marine and**
30 **lacustrine beaches** and agricultural soils are compared, along with the presence and
31 concentrations of Ba, Cd, Pb, Sb, Sn and Zn **as proxies for common metal-based additives**
32 **and determined by X-ray fluorescence spectrometry**. About 10% of consumer plastics and
33 2% of environmental plastics were **constructed of PVC**, with the discrepancy attributed to the
34 long service lives and managed disposal of PVC used in the construction sector and the
35 propensity of the plastic to sink in aquatic systems and evade detection. Metal-based
36 additives, defined as having a metal concentration $> 1000 \text{ mg kg}^{-1}$, were present in about 75%
37 of consumer and environmental PVC, with Ba and Pb most abundant and Cd and Zn least
38 abundant in both types of sample, **and median** concentrations statistically different only for
39 Ba. Metals also appeared to be present as contaminants (defined as concentrations $< 1000 \text{ mg}$
40 kg^{-1}) arising from manufacturing or recycling. Metals in PVC are believed to pose little risk
41 when the material is in use, but experimental **evidence in the literature suggests** that
42 significant mobilisation and exposure may occur from PVC microplastics when ingested by
43 wildlife.

44

45 Keywords: polyvinyl chloride; PVC; stabilisers; metals; XRF; environment; microplastics

46

47

48 Introduction

49 Polyvinyl chloride (PVC) is a vinyl polymer with the chemical formula $(C_2H_3Cl)_n$ whose key
50 properties are given in Table 1. First patented in 1913 and commercially produced in 1933,
51 this thermoplastic has had widespread uses in various sectors because of its durability,
52 inherent flame retardancy, excellent chemical and mechanical properties and ability to
53 accommodate a wide range of additives through its high polarity. PVC resins may be either
54 rigid (unplasticised), and produced mainly by extrusion or moulding, or flexible (plasticised),
55 where plasticisers are added in high proportions (up to 50%) to engender softness and
56 elasticity. Recent estimates indicate that PVC accounts for 12-25% of all plastic
57 manufactured globally and is exceeded only by polypropylene and/or polyethylene.²⁻⁴
58 Unplasticised PVC is used in plumbing, construction, cladding, fencing, seating, drainage
59 systems and in hard, interior and exterior automotive parts, while applications of plasticised
60 PVC include hosing, electrical cable insulation, flooring, medical devices, elastic automotive
61 parts, waterproof clothing and inflatable toys.

62 Despite its extensive production and wide applications, PVC has been referred to as a
63 “contested” versatile material because of concerns about risks to human health from its life
64 cycle that have been raised by scientific research and regulatory bodies.⁵ These concerns
65 mainly **result from** the generation and release of harmful chemicals during production, usage
66 and disposal of the material. Thus, although PVC is considered relatively inert, the generation
67 of chlorine itself is associated with hazardous **by-products**, while the long-term physical and
68 chemical breakdown of the plastic and its disposal via combustion are responsible for
69 environmental emissions of various toxic organochlorine substances and additives.⁶
70 Regarding the latter, of greatest concern has been the use of phthalic acid esters as
71 plasticisers, and cadmium- and lead-based primary thermal stabilisers to prevent
72 dehydrohalogenation and to neutralise **hydrochloric acid (HCl)**.⁷⁻⁸ Use of the most harmful

73 phthalates is subject to various recent or pending restrictions. For instance, in Europe, one of
74 the phthalates most widely used in PVC (di(2-ethylhexyl) phthalate) was registered under the
75 European Union's REACH legislation in 2010, with use after 2015 requiring authorisation.⁹
76 **Regarding cadmium (Cd) and lead (Pb) compounds**, European producers and stakeholders
77 voluntarily phased out their intentional introduction into PVC in 2007 and 2015,
78 respectively.¹⁰ Preferred alternative, phthalate-free plasticisers that have been used or are
79 being developed include citrates, benzoates, aliphatic esters and bio-based compounds,¹¹ and,
80 while safer metal-based stabilisers are still in use (**such as salts of barium, Ba, and zinc, Zn,**
81 **and organotin compounds**), there have been efforts to replace all metal compounds with
82 organophosphites.¹²

83 Despite its widespread use and the presence of harmful additives, there is relatively little
84 documentation of the occurrence, distribution and characterisation of PVC in the environment
85 compared with other plastics,^{13,14} with many reviews failing to discuss or even mention the
86 **polymer**^{15,16}. Moreover, where the toxicity of the plastic is studied empirically, there is often
87 a distinct lack of material characterisation and identification or quantification of the additives
88 present.¹⁷⁻²¹ To this end, we present a compilation of data derived in our laboratory from X-
89 ray fluorescence analyses on the relative abundance of PVC in both consumer plastics and
90 plastics lost to the environment (environmental plastics). Specifically, we report and compare
91 the degree of chlorination and concentrations of metals (including the **metalloid antimony,**
92 **Sb**) used **in stabilising additives** and **halogenated** flame retardant synergists in consumer and
93 environmental samples of PVC. **We use this information and the more general properties of**
94 **the plastic** to gain insights into its environmental behaviour, fate and impacts.

95 **Materials and methods**

96 **Samples**

97 Moulded hard and soft plastics, excluding foams, paints, rubbers, waxes and textiles, were
98 considered in the present study. Consumer plastics ($n = 1056$) were accessed or sourced from
99 households, university offices, schools, shops and restaurants in Plymouth (SW England) and
100 as described in Turner and Filella ²². Items or distinct components thereof were grouped as
101 electronic (mainly housings and wire insulation of small and large domestic appliances),
102 food-hygiene (food-contact and packaging for food, cosmetics and medicines), construction-
103 storage (plumbing, fixtures, flooring, frames, cans, cases, hangers), tools-office (stationery,
104 DIY, adhesive taping, book covers), leisure (toys, games, sports gear, hobbies, crafts) or
105 clothing-accessories (raincoats, jewellery, straps, rucksacks, shoes, buttons).

106 Environmental plastics ($n = 1980$) were collected and analysed as part of previous
107 studies²³⁻²⁵ or for the purposes of the present research. Plastics were grouped as: beached
108 plastic litter (mainly articles and fragments > 5 mm in size), beached fishing equipment
109 (mainly netting and rope fragments) and beached “small” plastics (visible, primary and
110 secondary particles < 5 mm in length or diameter) retrieved from the coastal strandlines of
111 southwest England; beached litter obtained from the shores of Lake Geneva (mainly articles
112 and fragments > 5 mm; note that fishing gear and small plastics were largely absent here);
113 and agricultural plastic waste (> 5 mm) sampled from fields of Luxembourg and central
114 Spain. Environmental samples were cleaned under tap water and dried before being analysed.

115 **XRF analysis**

116 Samples were analysed by standardless energy-dispersive field-portable-XRF using a Niton
117 XL3t 950 He GOLDD+ that was operated in a low-density “plastics” mode and employed a
118 thickness correction algorithm down to 50 µm. Most samples were analysed in the laboratory

119 within an accessory stand and via a laptop after thickness of the measurement surface had
120 been measured with digital callipers or estimated from the known thickness of similar
121 products. An initial, ~ 2 s analysis of characteristic chlorine peaks determined whether the
122 sample was constructed of PVC or an alternative (and usually lighter) plastic, with PVC
123 **operationally** defined as having a chlorine content > 15% by weight. This was succeeded by
124 counting periods up to 200 seconds (depending on sample size and thickness) distributed
125 equally or in a 2:1 ratio between a “main” energy range (50 kV and 40 µA) and a “low”
126 energy range (20 kV and 100 µA). Spectra were quantified by fundamental parameter
127 coefficients to yield elemental concentrations on a dry weight basis (in mg kg⁻¹) and with a
128 measurement counting error of **2σ (95% confidence)** that were downloaded to the laptop via
129 Niton data transfer software. In addition to Cl, elements of interest were those used in metal-
130 based stabilisers in PVC (Ba, Cd, Pb, Sn, Zn) and the halogenated flame retardant synergist,
131 Sb.

132 **For performance checks**, Niton (UK) and Modern Analytical Techniques (New Jersey)
133 polyethylene and PVC reference discs certified for different combinations and concentrations
134 of Ba, Cd, Pb and Sb (PN 180-554, batch SN PE-071-N; PN 180-619, LOT#T-81; SN PVC-
135 4C80, cal set #16) were analysed during each sample measurement session. Concentrations
136 returned were always within 15% and usually within 10% of certified values.

137 For permanent fixtures or items too large to be contained within the accessory stand, the
138 XRF was employed handheld under the operating conditions described above. The detector
139 window was placed firmly over the measurement surface and the instrument was operated
140 using the trigger mechanism and touch-screen control panel. Reference discs placed on a
141 solid, attenuating surface were analysed at regular intervals, with concentrations returned that
142 were always within 20% and usually within 15% of certified values.

143 XRF detection limits for a given element, and based on three counting errors, vary
144 according to the composition, thickness and density of material and the mode of operation of
145 the instrument. However, detection limits for the plastic samples in the present study usually
146 ranged from about 5 to 15 mg kg⁻¹ for Pb, 20 to 50 mg kg⁻¹ or Cd, Sb, Sn and Zn, and 50 to
147 300 mg kg⁻¹ for Ba and Cl.

148 FTIR analysis

149 As a check on the ability of the XRF to discriminate PVC from other plastics, selected
150 samples returning a range of Cl concentrations ($n = 41$) were analysed by Fourier transform
151 infra-red (FTIR) spectroscopy using a Bruker ALPHA Platinum attenuated total reflection
152 QuickSnap A220/D-01 spectrometer. Flakes of ~ 1 mg were sliced from each sample in the
153 region analysed by XRF using a stainless steel scalpel before being clamped down on to the
154 ATR diamond crystal. Measurements, consisting of 16 scans in the range 4000 to 400 cm⁻¹
155 and at a resolution of 4 cm⁻¹, were activated via Bruker OPUS spectroscopic software.
156 Polymer identification involved a comparison of sample transmittance spectra with libraries
157 of reference spectra and a hit quality of > 70%.

158 Results and discussion

159 Identification of PVC

160 Figure 1 shows the results of FTIR analysis of selected consumer and environmental samples
161 along with the corresponding Cl concentrations determined by XRF. In red (and hatched) and
162 blue are samples defined as PVC and non-PVC, respectively, according to XRF criteria. In
163 the majority of cases, there is a clear distinction in Cl content between PVC and other plastics
164 and XRF correctly identifies PVC. The one false negative involved a complex, multi-
165 component fragment of beach litter in which the different resolutions of each technique may

166 have contributed to the discrepancy (FTIR requires a surface flake of ~ 1 mm while XRF
167 collimation is either 3 mm or 8 mm in diameter). In support of XRF as a rapid and non-
168 destructive means of identifying PVC, a recent study found that an Oxford Instruments
169 portable device operated in a “soils” mode and tested on various consumer and environmental
170 samples was 100% accurate for this plastic.²⁶

171 **PVC amongst consumer and environmental samples**

172 Within the constraints above, Table 2 presents a summary of the PVC samples encountered in
173 each group of the consumer and environmental plastics considered in the present study. Note
174 that XRF is unable to directly discriminate plasticised and unplasticised forms of the
175 polymer, but samples were **readily defined** as “flexible” or “rigid” based on their appearance
176 and elasticity. Amongst the plastics in circulation with consumers ($n > 1000$), the storage-
177 construction group exhibited the greatest percentage contribution of PVC to total plastic
178 samples (~ 20), with PVC articles including hosing and piping, frames for windows and
179 doors, vinyl flooring and storage wallets, while the food-hygiene group displayed the lowest
180 percentage contribution (~ 1), with PVC items limited to two tablet blister packs. Overall,
181 about 9% of plastics on a number basis were constructed of PVC. However, given that many
182 of these samples were relatively large construction items, the percentage of the polymer in
183 consumer circulation on a mass or volume basis is likely to be closer to the production figure
184 of 20% reported by the British Plastics Federation.⁴ Regarding plastics lost to the
185 environment ($n \sim 2000$), about 2% overall, and mainly comprised of relatively small (< 10
186 cm) objects and fragments, were constructed of PVC, with percentage contributions in the
187 different groups ranging from less than one for beached marine fishing gear (rope) and small
188 plastics to about five for beached lake samples.

189 **Chlorine content and metal-based functional additive concentrations in consumer and**
190 **environmental PVC**

191 Also shown in Table 2 is a summary of the number of samples in each category and group
192 containing functional and deliberately added stabilisers based on the five metals: Ba, Cd, Pb,
193 Sn, Zn. Here, the presence of a functional stabiliser was assumed when the concentration of
194 an individual metal exceeded 1000 mg kg⁻¹; this is equivalent to a minimum metal-based
195 stabilising compound content in PVC of about 2000 mg kg⁻¹ reported by Baitz et al.²⁷ Note
196 that the presence of each metal in this form is not mutually exclusive and that “absent” means
197 that there was no evidence of any functional metal-based stabiliser. Specifically, Ba and Pb
198 exhibited the greatest number of co-associations as additives while Sn exhibited the fewest
199 number of associations with any other metal. Note also that metal concentrations lower than
200 1000 mg kg⁻¹ were assumed to be present as contaminants of PVC manufacture or recycling
201 or through acquisition from the environment. The number of PVC samples containing Sb as a
202 halogenated flame retardant synergist (principally in wire insulation²⁸), and likewise defined
203 by its presence above 1000 mg kg⁻¹, is also given in Table 2. A quantitative summary of the
204 concentrations of the different elements present as functional additives in the consumer and
205 environmental PVC samples (and where, by operational definition, [Cl] > 150,000 mg kg⁻¹
206 and other elements > 1000 mg kg⁻¹) is provided in Table 3. Also shown are results of a series
207 of Mann-Whitney tests performed in Minitab v19 that compare median concentrations of
208 each element in consumer and environmental samples.

209 Regarding Cl, concentrations ranged from about 150,000 mg kg⁻¹ in both consumer and
210 environmental PVC samples that were flexible to over 600,000 mg kg⁻¹ in two rigid
211 consumer plastics. Assuming that there are no significant contributions from other, chlorine-
212 bearing additives in the samples, the measured Cl content can be used to estimate the PVC
213 content (= [Cl]*100/56.7, and ranging from 27 to 112%), with the remaining mass

214 contribution providing an estimate of the total additive content of the sample. Thus, lower Cl
215 concentrations are predicted to be associated with a relatively high proportion of plasticisers,
216 stabilisers, fillers, rubbers and pigments (up to 74% by weight), while concentrations
217 approaching the theoretical Cl content of PVC (567,000 mg kg⁻¹) are predicted to contain a
218 relatively small proportion of additives. These estimates are consistent with information
219 provided by Baitz et al.²⁷ that suggests the PVC content of consumer and industrial articles
220 ranges from about 25% for vinyl flooring to 92% for hard food and mechanical packaging
221 and piping (or an additive content ranging from about 75% to 8%, respectively). The makeup
222 of samples whose measured Cl content exceeds the theoretical maximum for PVC cannot,
223 however, be explained on this basis. Here, we suspect that the component polymer is
224 chlorinated PVC, a direct derivative of PVC (containing about 670,000 mg kg⁻¹ of Cl) that
225 offers a higher temperature service range and greater corrosion and chemical resistance.²⁹

226 Overall, the median Cl concentration in the environmental samples was significantly
227 greater than the median value in the consumer plastics ($p = 0.040$). Based on the
228 dehydrochlorination of PVC that occurs during photodegradation,³⁰ one might expect
229 environmental plastics to have a lower Cl content than unweathered consumer samples.
230 However, according to Table 2, there was a higher proportion of rigid samples among
231 environmental plastics (about 61%) than consumer plastics (about 42%), suggesting an
232 inherently lower plasticiser content (or higher Cl content) of samples lost to the environment.

233 Based on the measured concentration of Ba, Cd, Pb, Sn and Zn, functional metal-based
234 stabilisers were evident in about 75% of all consumer samples constructed of PVC ($n = 92$).
235 Barium-based compounds appeared to be the most commonly employed stabiliser (although
236 other uses of Ba compounds, such as an inert filler, cannot be excluded) and the metal was
237 encountered in all groups with the exception of food-hygiene and up to concentrations of
238 about 75,000 mg kg⁻¹. In flexible and semi-rigid PVC, mixed salts of Ba and Cd were used

239 until safer alternatives based on Ba and Zn salts of fatty acids or phenolates were introduced.⁸
240 By contrast, Cd-based stabilising compounds were only present in two samples (and in
241 association with Ba) within the storage-construction group and at concentrations of about
242 1500 mg kg⁻¹, and Zn-based compounds were present in eight samples (and usually in the
243 presence of Ba) across a range of groups at concentrations ranging from about 1000 to 4000
244 mg kg⁻¹. Organotin stabilisers, such as dibutyltin maleate or di-n-alkyltin mercaptides, are
245 usually employed in rigid PVC⁸ but were encountered in 18 hard and flexible consumer
246 samples at concentrations up to about 5000 mg Sn kg⁻¹ and were the only stabilisers detected
247 in the food-hygiene group. Lead-based compounds were found in 23 consumer samples over
248 a wide concentration range (about 1600 to 25,000 mg Pb kg⁻¹), reflecting the broad array of
249 lead soaps and salts used as stabilisers in PVC, including stearates, phthalates, sulphates,
250 carbonates and phosphites,³¹ and the durability and long service life of PVC products
251 containing leaded compounds.²⁷ Significantly, and unlike the case for other plastics,
252 including polyethylene, polypropylene and polystyrene,^{23,32} Pb was never detected in the
253 presence of Cr, suggesting that lead chromate is not commonly employed as a colour pigment
254 in PVC.

255 A similar percentage of environmental PVC samples (*n* = 46) contained functional
256 metal-based stabilisers. Distributions and concentration ranges of the different metals were
257 comparable with those of consumer samples, with Ba and Pb most abundant and Cd and Zn
258 least abundant, and a significant difference in median concentrations of environmental and
259 consumer samples was only evident for Ba (*p* = 0.035). Antimony, as a synergist, exhibited
260 similar distributions between consumer and environmental samples of PVC, with no
261 statistically significant difference in median concentrations. In summary, therefore, it would
262 appear that the stocks of PVC in societal circulation and lost to the environment through
263 littering, loss and poor waste management have broadly common chemical signatures.

264 **Residual metal concentrations**

265 Table 4 shows summary statistics for metals and Sb detected in consumer and environmental
266 PVC samples at concentrations below 1000 mg kg⁻¹. Here, it is assumed that concentrations
267 are too low to function as additives and are therefore present as residues from the
268 manufacturing or recycling of PVC. Note that while acquisition of metals from the
269 environment is possible (through adsorption, for example), concentrations arising from this
270 route are much lower than the detection limit of the XRF.³³⁻³⁵ When PVC is mechanically
271 recycled, functional additives are retained, an approach that is favoured during the controlled
272 reconstitution of the same type of product. However, less controlled and more open
273 mechanical recycling may result in additives being introduced into different types of product
274 (such as Sb in non-electrical goods) or being dispersed at lower concentrations into more
275 general, blended recyclates which are often mixed with virgin PVC.³⁶

276 The data suggest that residual contamination is common and heterogeneous in both
277 consumer and environmental samples of PVC, with a range in elemental concentrations, a
278 variety of co-occurrences amongst the elements, and their presence with stabilisers (above
279 1000 mg kg⁻¹) in both rigid and flexible forms of the plastic. In total, 47 consumer samples
280 and 27 environmental samples (or about 50% and 60% of total PVC samples, respectively)
281 contained detectable residuals, and median concentrations of Sb and Sn were significantly
282 lower in environmental samples than in consumer samples, possibly because of their greater
283 mobilization under environmental conditions. We note a low incidence of residual Pb
284 amongst the samples compared with its occurrence as a functional additive which,
285 presumably, reflects efforts to eliminate or recover the metal chemically or to recycle it in a
286 more controlled manner.³⁶ Overall, seven consumer samples and two environmental samples
287 were “clean” and free of detectable metals and Sb.

288 **Differences in PVC abundance between consumer and environmental samples**

289 Despite similarities in the abundance and concentration range of the elemental constituents of
290 PVC in consumer goods and environmental samples, the polymer itself is considerably less
291 abundant amongst the plastic groups in the latter category. Moreover, the polymer was
292 entirely absent from the several hundred pre-production pellets retrieved amongst the small
293 beached plastics in southwest England, despite the plastic being processed by injection
294 moulding.³⁷ The low quantities of PVC samples retrieved from the environment compared
295 with its occurrence in consumer plastics and its global production may be attributed to a
296 number of factors.

297 First, a significant fraction of plastic litter in the environment is derived from food
298 packaging^{38,39} and the data in Table 2 appear to suggest that the contemporary and recent use
299 of PVC in this sector is limited. More specifically, in the marine environment, large
300 quantities of plastic waste are derived from fishing activities, and in particular fragments and
301 offcuts of cord, netting and rope, where PVC has few uses.⁴⁰ Secondly, many of the
302 applications of PVC are large, “long-life”, construction articles whose disposal is more
303 carefully managed and regulated than other, smaller or single-use consumer plastics.⁴¹
304 Specifically, Baitz et al.²⁷ report that the lifespans of construction PVC articles may be up to
305 30 years, and that about 70% of PVC produced has a service life of at least a decade. Thirdly,
306 the higher density of PVC (the polymer density is about 1.4 g cm⁻³ according to Table 1 but
307 this may be increased by the presence of metal-based additives) compared with other
308 consumer plastics means that a greater proportion of this material that is discharged into
309 surface waters, lost at sea or entering water treatment facilities is likely to sink. In theory,
310 therefore, PVC has a greater propensity to evade both long-range transport in surface waters
311 and beaching along strandlines where plastics are often sampled and studied. Rather, it is

312 predicted to settle relatively rapidly and accumulate in benthic environments that are more
313 inaccessible and less well researched.^{42,43}

314 **PVC microplastics and metal mobilisation and toxicity**

315 Environmental microplastics of smaller (sub-mm) dimensions than the small plastics referred
316 to above have been subject to extensive scientific scrutiny over the past few years and,
317 despite PVC receiving less attention than other plastics, like polyethylene, polypropylene and
318 polystyrene, the **recent literature** mentioning PVC suggests that it is ubiquitous.⁴⁴⁻⁴⁹ The
319 nature and concentration of additives in microplastics of sub-mm dimensions is difficult to
320 determine readily or accurately. However, it would be reasonable to assume that the chlorine
321 content and signatures of metal- and Sb-based additives and residuals reported above apply to
322 microscopic particles.

323 Metal-based additives and synergists in PVC products in-life are assumed to be inert and
324 pose no significant health or environmental risks until disposal or unless exposed to fire.²⁷
325 However, release is more likely from environmental PVC that has weathered and become
326 micronised and that is exposed to physico-chemical conditions favouring the dissolution of
327 inorganic compounds.^{28,50,51} The inadvertent ingestion and digestion of microplastics by
328 aquatic organisms and birds provides a means by which these conditions are met, and
329 examinations of the gastro-intestinal tracts of bivalves^{42,52-56} have confirmed that PVC
330 particles are often present. As part of previous research, selected consumer and
331 environmental samples reported in the current paper were micronised (mm-sized) to study the
332 release of metals from PVC (and other plastics) in simulated digestive fluids.^{57,58}

333 Mobilisation followed diffusion kinetics **and mobilities (relative to total contents)** ranged
334 **from ~0.01% for Sb from** a micronised beached fragment of PVC in a protein-rich
335 invertebrate digestive solution after six hours' incubation to about 10% for Pb from a
336 micronised PVC pipe bend in an acidic avian extraction test after a period of seven days.

337 Metal mobilisation is not necessarily equivalent to metal accumulation, nor should it
338 imply toxicity. However, two studies have reported a direct link between acute toxicity and
339 the mobilisation of a metal-based additive from PVC particles into the aqueous phase. Thus,
340 first, Lithner et al.⁵⁹ attributed most of the observed immobility of *Daphnia magna* to the
341 mobilisation of Zn ions from plasticised PVC (with leachate prepared from 250 g of rubber
342 glove cuttings per L of deionised water). Secondly, Boyle et al.¹⁹ showed that zebrafish
343 larvae exposed to 150 µm PVC particles (of unspecified origin and presumably rigid) at up to
344 500 mg L⁻¹ for 24 h increased expression of metallothionein 2, a metal-binding protein, but
345 not biomarkers of estrogenic or organic contaminants, with subsequent analysis of PVC
346 leachates revealing that the release of Pb was responsible. Although performed under
347 environmentally unrealistic conditions (excessive particle concentrations), these studies
348 suggest the potential for both restricted and unrestricted metal-based additives, and in both
349 plasticised and unplasticised PVC, to exert toxic responses in aquatic organisms. Clearly, a
350 greater understanding of the presence and mobilities of metal additives is required for PVC
351 that is lost to the environment.

352 Conclusions

353 The data presented here suggests that, at least on a number basis, PVC is more abundant
354 amongst consumer articles than plastics lost to the environment. This may be attributed to the
355 relatively low contribution of PVC to common litter and fishing gear, the use of PVC in
356 larger, long-lasting products whose disposal is more carefully managed, and the propensity of
357 PVC to sink and evade ready detection in many aquatic systems. Environmental PVC has a
358 greater chlorine content than consumer PVC, **possibly because** of a greater abundance of rigid
359 (unplasticised) plastics in the environment. However, the concentrations and distributions of
360 metal-based additives and Sb-based flame retardant synergist is similar between the two

361 categories of PVC, despite differences in the relative abundance of the material and
362 regulations that have been introduced to reduce Cd and Pb. These additives are believed to
363 pose little risk when PVC is in use, but experimental evidence indicates that significant
364 mobilisation and exposure may occur from PVC microplastics that are ingested by wildlife.

365

366 **References**

- 367 1 A. L. Andrade, Poly(vinyl chloride), in *Polymer Data Handbook*, ed. M. E. James, Oxford
368 University Press, 1999, pp.928–934.
- 369 2 R. Geyer, J. R. Jambeck and K. L. Law, Production, use, and fate of all plastics ever made,
370 *Science Advances* 2017, **3**, e1700782.
- 371 3 L. Ye, C. Qi, J. Hong and X. Ma, Life cycle assessment of polyvinyl chloride production and its
372 recyclability in China, *Journal of Cleaner Production* 2017, **142**, 2965–2972.
- 373 4 British Plastics Federation, Polyvinyl chloride PVC, 2021.
374 <https://www.bpf.co.uk/plastipedia/polymers/pvc.aspx#:~:text=PVC%20is%20a%20versatile%20material,coverings%2C%20fashion%20and%20footwear%2C%20packaging>, (accessed April
375 2021).
- 377 5 G. Akovali, Plastic materials: Polyvinyl chloride (PVC), in *Toxicity of Building Materials*, ed.
378 F. Pacheco-Torgal, S. Jalali and A. Fucic, Woodhead Publishing Series in Civil and Structural
379 Engineering, 2012, pp. 23–53.
- 380 6 J. Leadbitter, PVC and sustainability, *Progress in Polymer Science*, 2002, **27**, 2197–2226.
- 381 7 A. O. Earls, I. P. Axford and J. H. Braybrook, Gas chromatography–mass spectrometry
382 determination of the migration of phthalate plasticisers from polyvinyl chloride toys and
383 childcare articles, *Journal of Chromatography A*, 2003, **983**, 237–246.
- 384 8 J. E. McGrath, M. A. Hickner and R. Höfer, *Polymers for a Sustainable Environment and
385 Green Energy*, Elsevier, Amsterdam, 2012.
- 386 9 European Council for Plasticisers and Intermediates, European Parliament targets DEHP
387 plasticizer in recycled PVC, *Additives for Polymers*, 2016, **2**, 11.
- 388 10 VinylPlus, The European PVC industry's experience in replacing lead and cadmium-based
389 stabilisers, 2014. https://www.stabilisers.eu/wp-content/uploads/2015/11/VinylPlus_Contribution-Cefic_Eu-Industry.pdf, (accessed April
390 2021).

- 392 11 T. T. Bui, G., Giovanoulis, A. P. Cousins, J. Magner, I. T. Cousins and C. A. de Wit, Human
393 exposure, hazard and risk of alternative plasticizers to phthalate esters, *Science of the Total*
394 *Environment*, 2016, **541**, 451–467.
- 395 12 V. Ambrogi, C. Carfagna, P. Cerruti and V. Marturano, Additives in polymers, in *Modification*
396 *of Polymer Properties*, ed. C. F. Jasso-Gastinel and J. M. Kenny, William Andrew Publishing,
397 2017, pp. 87–108.
- 398 13 H. A. Nel, G. H. S. Smith, R. Harmer, R. Sykes, U. Schneidewind, I. Lynch and S. Krause,
399 Sources, transport, and accumulation of different types of plastic litter in Sediment,
400 *Environmental Pollution*, 2020, **264**, 114696.
- 401 14 C. Bertoldi, L. Z. Lara, F. A. D. Mizushima, F. C. G. Martins, M. A. Battisti, R. Hinrichs and
402 A. N. Fernandes, First evidence of microplastic contamination in the freshwater of Lake
403 Guaiba, Porto Alegre, Brazil, *Science of the Total Environment*, 2021, **759**, 143503.
- 404 15 G. Erni-Cassola, V. Zadjelovic, M. I. Gibson and J. A. Christie-Oleza, Distribution of plastic
405 polymer types in the marine environment; A meta-analysis, *Journal of Hazardous Materials*,
406 2019, **369**, 691–698.
- 407 16 M. Padervand, E. Lichtfouse, D. Robert and C. Wang, Removal of microplastics from the
408 environment: A review, *Environmental Chemistry Letters*, 2020, **18**, 807–828.
- 409 17 M. Oliveiro, T. Tato, S. Schiavo, V. Fernandez, S. Manzo and R. Beiras, Leachates of
410 micronized plastic toys provoke embryotoxic effects upon sea urchin *Paracentrotus lividus*,
411 *Environmental Pollution*, 2019, **247**, 706–715.
- 412 18 Y. M. Wu, P. Y. Guo, X. Y. Zhang, Y. X. Zhang, S. T. Xie and J. Den, Effect of microplastics
413 exposure on the photosynthesis system of freshwater algae, *Journal of Hazardous Materials*,
414 2019, **375**, 219–227.
- 415 19 D. Boyle, A. I. Catarino, N. J. Clark and T. B. Henry, Polyvinyl chloride (PVC) plastic
416 fragments release Pb additives that are bioavailable in zebrafish, *Environmental Pollution*,
417 2020, **263**, 114422.
- 418 20 S. Pignattelli, A. Broccoli and M. Renzi, Physiological responses of garden cress (*L. sativum*)
419 to different types of microplastics, *Science of the Total Environment*, 2020, **727**, 138609.

- 420 21 L. Zimmermann, S. Göttlich, J. Oehlmann, M. Wagner and C. Volker, What are the drivers for
421 plastic toxicity? Comparing the toxicity of plastic chemicals and particles to *Daphnia magna*,
422 *Environmental Pollution*, 2020, **267**, 115392.
- 423 22 A. Turner and M. Filella, Bromine in plastic consumer products – Evidence for the widespread
424 recycling of electronic waste, *Science of the Total Environment*, 2017, **601-602**, 374–379.
- 425 23 A. Turner and K. R. Solman, Analysis of the elemental composition of marine litter by field-
426 portable-XRF, *Talanta*, 2016, **159**, 262–271.
- 427 24 A. Massos, A. Turner, Cadmium, lead and bromine in beached microplastics, *Environmental
428 Pollution*, 2017, **227**, 139–145.
- 429 25 M. Filella and A. Turner, Observational study unveils the extensive presence of hazardous
430 elements in beached plastics from Lake Geneva, *Frontiers in Environmental Science*, 2018, **6**, 1
431 doi:10.3389/fenvs.2018.00001.
- 432 26 A. P. M. Michel, A. E. Morrison, V. L. Preston, C.T . Marx, B. C. Colson and H. K. White,
433 Rapid identification of marine plastic debris via spectroscopic techniques and machine learning
434 classifiers, *Environmental Science and Technology*, 2020, **54**, 10630–10637.
- 435 27 M. Baitz, J. Kreissig, E. Byrne, C. Makishi, T. Kupfer, N. Frees, N. Bey, M.S. Hansen, A.
436 Hansen, T. Bösch, V. Borghi, J. Watson and M. Mirnada, Life Cycle Assessment of PVC and
437 of principal competing materials. Final Report for the European Commission, Brussels. 2004.
438 https://pure.au.dk/portal/files/13386408/pvc-final_report_lca.pdf, (accessed May 2021).
- 439 28 P. V. Mercea, C. Losher, M. Petrasch and V. Tosa, Migration of stabilizers and plasticizer from
440 recycled polyvinylchloride, *Journal of Vinyl and Additive Technology*, 2018, **24**, E112–E124.
- 441 29 T. Walsh, The plastic piping industry in North America, in *Applied Plastics Engineering
442 Handbook*, ed. M. Kutz, William Andrew Publishing, 2011, pp. 625–644.
- 443 30 C. A. D'Aquino, W. Balmant, R .L. L. Ribeiro, M. Munaro, J. V. C. Vargas and S. C. Amico, A
444 simplified mathematical model to predict PVC photodegradation in photobioreactors, *Polymer
445 Testing*, 2012, **31**, 638–644.
- 446 31 Y. B. Liu, W. Q. Liu and M. H. Hou, Metal dicarboxylates as thermal stabilizers for PVC,
447 *Polymer Degradation and Stability*, 2007, **92**, 1565-1571.

- 448 32 C. Maier and T. Calafut, *Polypropylene: The Definitive User's Guide and Databook*, William
449 Andrew, Norwich NY, 1998, 431 pp.
- 450 33 K. Ashton, L. Holmes and A. Turner, Association of metals with plastic production pellets in
451 the marine environment, *Marine Pollution Bulletin*, 2010, **60**, 2050–2055.
- 452 34 M. Carbery, G. R. MacFarlane, W. O'Connor, S. Afrose, H. Tayloer and T. Palanisami,
453 Baseline analysis of metal(loid)s on microplastics collected from the Australian shoreline using
454 citizen science, *Marine Pollution Bulletin*, 2020, **152**, 110914.
- 455 35 I. Martins, Y. Rodriguez and C. K. Pham, Trace elements in microplastics stranded on beaches
456 of remote islands in the NE Atlantic, *Marine Pollution Bulletin*, 2020, **156**, 111270.
- 457 36 J. Ooms and J. G. Cuperus, Impact of Lead Restrictions on the Recycling of PVC, Tauw BV,
458 Deventer, NL, 2013. [https://vinylplus.eu/uploads/Modules/Documents/2013_07_13-
459 impact_lead-restrictions_pvc_recycling-tauw.pdf](https://vinylplus.eu/uploads/Modules/Documents/2013_07_13-impact_lead-restrictions_pvc_recycling-tauw.pdf), (accessed May 2021).
- 460 37 T. Garbacz, Structure and properties of cellular injection molded products, *Polimery*, 2013, **58**,
461 295–303. In Polish.
- 462 38 C. Y. Barlow and D. C. Morgan, Polymer film packaging for food: An environmental
463 assessment, *Resources Conservation and Recycling*, 2013, **78**, 74–80.
- 464 39 T. Kiessling, K. Knickmeier, K. Kruse, D. Brennecke, A. Nauendorf and M. Thiel, Plastic
465 Pirates sample litter at rivers in Germany - Riverside litter and litter sources estimated by
466 schoolchildren, *Environmental Pollution*, 2019, **245**, 545–557.
- 467 40 N. A. Welden and P. Cowie, Degradation of common polymer ropes in a sublittoral marine
468 environment, *Marine Pollution Bulletin*, 2017, **118**, 248–253.
- 469 41 A. E. Schwarz, T. Lighart, E. Boukris and T. van Harmelen, Sources, transport, and
470 accumulation of different types of plastic litter in aquatic environments: A review study,
471 *Marine Pollution Bulletin*, 2019, **143**, 92–100.
- 472 42 C. A. Peters, E. Hendrickson, E. C. Minor, K. Schreiner, J. Halbur and S. P. Bratton, Pyr-
473 GC/MS analysis of microplastics extracted from the stomach content of benthivore fish from
474 the Texas Gulf Coast, *Marine Pollution Bulletin*, 2018, **137**, 91–95.

- 475 43 P. Xu, G. Peng, L. Su, Y. Gao, L. Gao and D. Li, Microplastic risk assessment in surface
476 waters: A case study in the Changjiang Estuary, China, *Marine Pollution Bulletin*, 2018, **133**,
477 647–654.
- 478 44 Q. Zhou, C. Tian and Y. Luo, Various forms and deposition fluxes of microplastics identified in
479 the coastal urban atmosphere, *Kexue Tongbao*, 2017, **62**, 3902–3910. In Chinese.
- 480 45 C. C. Cheang, Y. Ma and L. Fok, Occurrence and composition of microplastics in the seabed
481 sediments of the coral communities in proximity of a metropolitan area, *International Journal*
482 *of Environmental Research and Public Health*, 2018, **15**, 2270.
- 483 46 C. Du, H. D. Liang, Z. P. Li and J. Gong, Pollution characteristics of microplastics in soils in
484 southeastern suburbs of Baoding City, China, *International Journal of Environmental Research*
485 *and Public Health*, 2020, **17**, 845.
- 486 47 A. A. Franco, J. M. Arellano, G. Albendin, R. Rodriguez-Barroso, S. Zahedi, M. Quiroga and
487 M. D. Coello, Mapping microplastics in Cadiz (Spain): Occurrence of microplastics in
488 municipal and industrial wastewaters, *Journal of Water Processing Engineering*, 2020, **38**,
489 101596.
- 490 48 D. Kankanige and S. Babel, Identification of micro-plastics (MPs) in conventional tap water
491 sourced from Thailand, *Journal of Engineering and Technological Sciences*, 2020, **52**, 95–107.
- 492 49 M. Ghayebzadeh, H. Taghipour and H. Aslani, Abundance and distribution of microplastics in
493 the sediments of the estuary of seventeen rivers: Caspian southern coasts, *Marine Pollution*
494 *Bulletin*, 2021, **164**, 112044.
- 495 50 R. M. Town, H. P. van Leeuwen and R. Blust, Biochemodynamic features of metal ions bound
496 by micro- and nano-plastics in aquatic media, *Frontiers in Chemistry*, 2018, **6**, 627.
497 doi:10.3389/fchem.2018.00627
- 498 51 J. Meng, B. Xu, F. Liu, W. Li, N. Sy, X. Zhou and B. Yan, Effects of chemical and natural
499 ageing on the release of potentially toxic metal additives in commercial PVC microplastics,
500 *Chemosphere*, 2021, **283**, 131274.
- 501 52 C. Fang, R. H. Zheng, H. Z. Chen, F. K. Hong, L. S. Lin, H. Lin, H. G. Guo, C. Bailey, H.
502 Segner, J. L. Mu and J. Bo, Comparison of microplastic contamination in fish and bivalves

- 503 from two major cities in Fujian province, China and the implications for human health,
504 *Aquaculture*, 2019, **512**, 734322.
- 505 53 A. Gomiero, P. Strafella, K. B. Oysaed and G. Fabi, First occurrence and composition
506 assessment of microplastics in native mussels collected from coastal and offshore areas of the
507 northern and central Adriatic Sea, *Environmental Science and Pollution Research*, 2019, **26**,
508 24407–24416.
- 509 54 G. Pellini, A. Gomiero, T. Fortibuoni, C. Ferrà, F. Grati, A.N. Tassetti, P. Polidori, G. Fabi and
510 G. Scarcella, Characterization of microplastic litter in the gastrointestinal tract of *Solea solea*
511 from the Adriatic Sea, *Environmental Pollution*, 2018, **234**, 943–952.
- 512 55 S. Avery-Gomm, M. Valliant, C. R. Schacter, K. F. Robbins, M. Liboiron, P. Y. Daoust, L. M.
513 Rios and I. L. Jones, A study of wrecked Dovekies (*Alle alle*) in the western North Atlantic
514 highlights the importance of using standardized methods to quantify plastic ingestion, *Marine
515 Pollution Bulletin*, 2016, **113**, 75–80.
- 516 56 R. Furtado, D. Menezes, C. J. Santos and P. Catry, White-faced storm-petrels *Pelagodroma
517 marina* predated by gulls as biological monitors of plastic pollution in the pelagic subtropical
518 Northeast Atlantic, *Marine Pollution Bulletin*, 2016, **112**, 117–122.
- 519 57 E. James and A. Turner, Mobilisation of antimony from microplastics added to coastal aquatic
520 environments: A review study, *Marine Pollution Bulletin*, 2020, **161**, 111776.
- 521 58 E. C. Smith and A. Turner, Mobilisation kinetics of Br, Cd, Cr, Hg, Pb and Sb in microplastics
522 exposed to simulated, dietary-adapted digestive conditions of seabirds, *Science of the Total
523 Environment*, 2020, **733**, 138802.
- 524 59 D. Lithner, I. Nordensvan and G. Dave, Comparative acute toxicity of leachates from plastic
525 products made of polypropylene, polyethylene, PVC, acrylonitrile–butadiene–styrene, and
526 epoxy to *Daphnia magna*, *Environmental Science and Pollution Research*, 2012, **19**, 1763–
527 1772.
- 528

529 Table 1: Key properties and characteristics of unplasticised PVC.¹

CAS number	9002-86-2
molecular weight of repeat unit	62.5 g mol ⁻¹
mass percentage of Cl	56.7
glass transition temperature	344-380 K
tensile strength	56.6 Mpa
530 density @ 20 °C	1.391-1.431 g cm ⁻³

531

532 Table 2: Total number of consumer and environmental plastics (by group) analysed by XRF
 533 and the corresponding number of samples defined as PVC and as rigid PVC. Also shown are
 534 the numbers of PVC samples containing functional metal-based stabilisers, no metal-based
 535 stabilisers (“absent”) and Sb as a flame retardant synergist.

	samples	PVC	rigid	PVC with metal-based stabiliser						Sb
				Ba	Cd	Pb	Sn	Zn	absent	
<u>Consumer</u>										
Electronic	267	16	3	10	0	11	2	2	1	6
Food-hygiene	172	2	2	0	0	0	2	0	0	0
Clothing-accessories	78	9	2	4	0	0	2	1	2	0
Office-tools	118	17	9	8	0	3	3	2	4	3
Storage-construction	130	25	13	11	2	8	4	2	5	2
Leisure	291	23	10	12	0	1	5	1	9	0
<i>Total</i>	<i>1056</i>	<i>92</i>	<i>39</i>	<i>45</i>	<i>2</i>	<i>23</i>	<i>18</i>	<i>8</i>	<i>21</i>	<i>11</i>
<u>Environmental</u>										
Beached (marine)	306	10	4	3	0	2	2	3	2	2
Beached (marine, fishing)	91	0	0	0	0	0	0	0	0	0
Beached (marine-micro-)	923	3	3	0	0	0	0	0	1	0
Beached (lacustrine)	603	31	20	9	2	13	3	1	7	3
Agricultural soils	57	2	1	0	0	0	1	0	1	0
<i>Total</i>	<i>1980</i>	<i>46</i>	<i>28</i>	<i>12</i>	<i>2</i>	<i>15</i>	<i>6</i>	<i>4</i>	<i>11</i>	<i>5</i>

536

537

538 Table 3: Summary statistics for the concentrations of the different elements as functional
 539 stabilisers in consumer and environmental samples of PVC (defined as $> 150,000 \text{ mg kg}^{-1}$ for
 540 Cl and $> 1000 \text{ mg kg}^{-1}$ for metals and Sb) and results of median value comparisons using a
 541 series of Mann-Whitney tests.

		Cl	Ba	Cd	Pb	Sn	Zn	Sb	
consumer	<i>n</i>	92	45	2	23	18	8	11	
	mean, mg kg^{-1}	304000	16800	1630	11800	2700	2120	7530	
	median, mg kg^{-1}	286000	9210	1630	12100	2500	1580	6730	
	min, mg kg^{-1}	151000	1100	1580	1610	1020	1100	1390	
	max, mg kg^{-1}	635000	75500	1680	25100	5100	4350	17700	
environmental	<i>n</i>	46	12	2	15	6	4	5	
	mean, mg kg^{-1}	342000	43900	3440	10100	2290	5000	9140	
	median, mg kg^{-1}	360000	3370	3440	9200	2020	3750	6510	
	min, mg kg^{-1}	151000	1130	2640	1140	1020	1260	1460	
	max, mg kg^{-1}	532000	319000	4240	19000	4550	11200	23000	
542	<u>difference in medians</u>	<u>p-value</u>	0.040	0.035	0.245	0.634	0.484	0.203	0.981

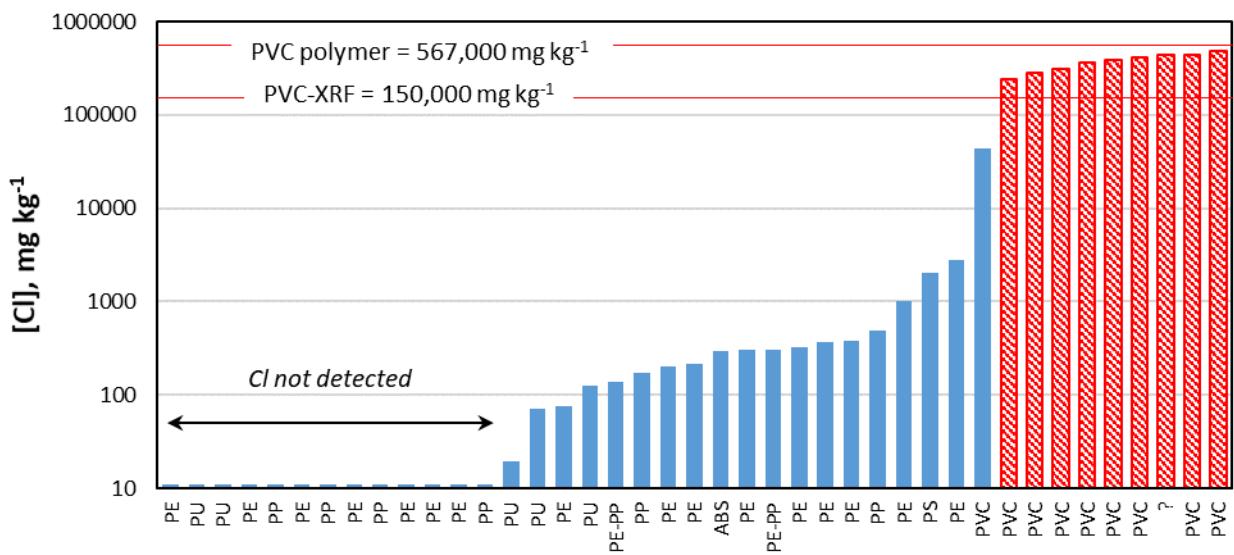
543

544 **Table 4: Summary statistics for the concentrations of the different metals and Sb as residues**
 545 **in consumer and environmental samples of PVC (defined as < 1000 mg kg⁻¹) and results of**
 546 **median value comparisons using a series of Mann-Whitney tests.**

		Ba	Cd	Pb	Sn	Zn	Sb	
consumer	<i>n</i>	4	10	5	20	23	5	
	mean, mg kg ⁻¹	628	257	393	300	306	279	
	median, mg kg ⁻¹	643	226	546	226	254	279	
	min, mg kg ⁻¹	373	120	86	39	34	135	
	max, mg kg ⁻¹	852	476	621	913	866	470	
environmental	<i>n</i>	15	5	1	4	18	5	
	mean, mg kg ⁻¹	396	300	37	51	330	96	
	median, mg kg ⁻¹	388	250	37	57	274	77	
	min, mg kg ⁻¹	180	36	37	34	36	55	
	max, mg kg ⁻¹	735	857	37	103	805	226	
547	difference in medians	<i>p</i> -value	0.147	0.668	nd	0.011	0.646	0.037

548

549 Figure 1: A selection of plastics analysed by XRF and shown in ascending order of Cl content
550 along with the polymer identified by FTIR (ABS = acrylonitrile butadiene styrene; PE =
551 polyethylene; PP = polypropylene; PS = polystyrene; PU = polyurethane; ? = uncertain and
552 hit quality < 70%). **Data shown in red and hatched** are samples defined as PVC by XRF ([Cl]
553 > 150,000 mg kg⁻¹). Also annotated is the theoretical Cl content of pure PVC.



554