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1 **Letter: Metals in microplastics: determining which**  
2 **are additive, adsorbed, and bioavailable**

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13 **Abstract:** Microplastics from the North Atlantic Gyre deposited on Guadeloupe beaches  
14 were sampled and characterized. A new method was developed to identify which elements  
15 were present as additives in these microplastics. The method used both acidic leaching and  
16 acidic digestion. Using this original method, several elements (Al, Zn, Ba, Cu, Pb, Cd, Mn,  
17 Cr) were identified as pigments. Furthermore, some elements used as additives to plastics  
18 (especially the non-essential elements) seem to contribute to most of the acidic leaching,  
19 suggesting that these additives can leach and readsorb onto the surface of microplastics,  
20 becoming bioavailable. Based on the element content in the acidic leaching, only Cd should  
21 represent a danger for fish when ingested. However, further studies are needed to determine  
22 the potential synergetic effect on health caused by the ingestion of several elements and  
23 microplastics.

24

25 **Keywords:** microplastics, metals, metalloids, bioavailability, additive, adsorption, leaching

26

## 27 **Introduction**

28 Thousands of metric tons of plastics debris<sup>1</sup> have been released into the environment since  
29 the 1950s, and the public is becoming ever-more aware of the negative impacts of plastic  
30 debris on living organisms. These impacts can occur directly through the presence or  
31 accumulation of plastics, or indirectly via their associated pollutants (organic and inorganic),  
32 also known as the Trojan horse effect<sup>2</sup>. From the various chemicals possibly carried by  
33 plastics debris, metal and metalloid elements are most used, by relative mass, in plastics<sup>3</sup>.  
34 Metals and metalloids are added as plasticizers, flame retardants, antioxidants, pigments,  
35 and more.<sup>4</sup> (Throughout this paper, when the word “elements” is used, it is to mean metal  
36 and metalloid elements.) As other carbon-based particles are released in the environment,  
37 aging plastics debris can act as a support for biofilms or, in response to (photo)chemical  
38 oxidation of their surface functional groups, both biofilms and surface groups can adsorb  
39 metalloids<sup>5,6</sup>.

40 Metals and metalloids can be highly toxic when inadvertently consumed in aging plastic  
41 debris, as these elements are released from the sorbent under acidic digestive conditions  
42 (i.e., they become bioavailable through biological digestion processes). There is now clear  
43 evidence that chemicals associated with nanoplastics impact aquatic organisms’ metabolism  
44 much more than the same pristine polymer without metal additives<sup>7</sup>. Measuring metals’  
45 relative bioavailability remains challenging, given their surface and/or core distribution in the  
46 plastics. From the surface to the core, element exchangeability and bioavailability decrease.  
47 However, after a long residence time in the environment, plastics can undergo highly  
48 oxidative conditions, which partly alter the surface of plastics and can induce the release of  
49 additives (i.e. elements). To evaluate the potential health risks induced by the ingestion of  
50 plastics by the biota, it is thus crucial to determine the total concentrations of each element  
51 and to discriminate between which elements are labile, and which are incorporated into

52 plastic structures. However, the most important point is to determine which additives can be  
53 leached over time and become bioavailable for the biota.

54 The additive elements can be identified by measuring the depth distribution of element  
55 concentrations in the plastic by laser ablation (LA) inductively coupled plasma mass  
56 spectrometry (ICP-MS)<sup>9</sup>. However, only a few elements can be measured in plastic reference  
57 materials this way, and it is a time-consuming method. Another possibility is to perform a  
58 double extraction of elements: (i) from an acidic leaching to determine which elements are  
59 labile and (ii) from an acidic digestion to determine total element concentrations. Numerous  
60 studies have determined total metals concentrations in plastics by X-ray fluorescence  
61 spectrometry (XRF)<sup>9-28</sup>, but this will be the first time for this joint approach consisting of  
62 coupling acidic leaching and digestion to ICP-MS or ICP-AES (atomic emission  
63 spectrometry) measurements. Our innovative approach aims to determine which elements  
64 are additive or adsorbed to the plastics, and their bioavailability to the biota.

## 65 **Material & Methods**

### 66 **Geographic area and collection**

67 Fragments and pellets of plastic were collected in November 2018 on the beaches of Sainte  
68 Marie Bay in Guadeloupe (16°23'43.6"N 61°24'21.9"W). This bay is exposed to the North  
69 Atlantic Gyre, which is known to be an area of plastic accumulation. The top 3 cm of sand  
70 composed of sargassum, sand, and plastics were manually collected. Size separation was  
71 performed using 2 sieves, with 1 cm and 2 mm grids. Microplastics and pellets from 2 mm to  
72 1 cm were separated by visual morphologic aspects. Only microplastics were used in the  
73 present study. The collected microplastics were subdivided in 7 colours: Blue, Green,  
74 Orange, Red, Yellow, Black, Grey, and White.

## 75 **Acidic leaching and acidic digestion**

76 Microplastics were first washed with deionized (DI) water under agitation to desorb (detach)  
77 any biofilms and natural organic matter residues that often occur with microplastics in the  
78 environment<sup>25</sup>. Then 1 g of each coloured microplastic was mixed with 0.1 M HNO<sub>3</sub> (ultrapure  
79 grade) for 48 h. Microplastics were then removed from the solution by filtration through a 0.2  
80 µm filter. The solution (<0.2 µm) was further analysed by ICP-MS. Finally, microplastic  
81 pieces were acid-digested using a multistep procedure with a microwave oven (UltraWAVE  
82 system from Milestone; 110°C for 10 min, then 180°C for 10 min, 230°C for 20 min and  
83 230°C for 5 min). Prior to elemental analyses, samples were evaporated, dried, and then  
84 resolubilized with HNO<sub>3</sub> at 0.37 M.

## 85 **Metal concentrations analysis**

86 Metal concentrations were measured by Inductively Coupled Plasma-Mass Spectrometry  
87 (ICP-MS) from Agilent Technologies (7700x Model, Agilent). The ICP-MS analyses  
88 introduced He gas into a collision cell to suppress any interference from Ar. All limits of  
89 quantification are presented in Table S1. The digestion process was validated using  
90 reference materials (ERM-EC 680 and ERM-EC 681) from the Joint Research Centre of the  
91 European Commission (JRC, Ispra, Italy) (see SI Section S1 for further information).

## 92 **Results and discussion**

93 In the present work, only microplastics from 2 mm to 1 cm, a size that can be easily ingested  
94 by the marine and terrestrial biota, were studied<sup>31,32</sup>. Figure 1 presents the workflow and the  
95 hypotheses for the bioavailability of microplastic-associated elements. The percentage of  
96 elements released by the washing step was less than 0.1% of the total element  
97 concentrations (see Figure 1). This fraction of water-leached elements can be considered to  
98 be the most easily exchangeable fraction, and is thus negligible. The acidic leaching releases  
99 elements that can be desorbed from the microplastic surface. The pH conditions are aligned

100 to those encountered in the stomach digestion of animals (i.e. bioavailable fraction by  
101 ingestion route). The surface layer of environmentally-aged microplastics can be altered by  
102 wear and tear in the environment. For those altered microplastics, the acidic leached fraction  
103 represents both (i) the adsorbed environmental elements and (ii) the elements released from  
104 the microplastic alteration that were subsequently bound in the altered layer, namely a part of  
105 the additive metals. The acidic digestion is a total mineralization of the microplastic debris  
106 under extreme conditions (i.e., microwave process using concentrated acid and high  
107 temperatures). Such conditions are not environmentally relevant, but they facilitate the  
108 determination of less bioavailable metals. Microplastic debris is therefore providing a metal  
109 source rather than transfer vector. Based on this metal screening, acid digestion increases  
110 the bioavailable metals by four orders of magnitude (Figure 1), illustrating the importance of  
111 additives in the metal distribution in microplastics.

112

### 113 **Identification of the elements nature in the different coloured microplastics**

114 All elements can potentially be adsorbed on the microplastic surface through specific sites  
115 (i.e., carboxylic). Comparing the concentrations of elements determined after acidic leaching  
116 and total digestion can provide information on the additive or adsorbed origin of metals.

117 In Figure S2, the concentrations of (a) Cu (b) Cd (c) Zn (d) Pb (e) Ni (f) Ba (g) Cr (h) V and (i)  
118 As were compared for the acidic leaching and digestion, by subtracting the acid-leached  
119 concentrations from the total digestion concentrations ( $S = [\text{Digestion}] - [\text{Leaching}]$ ) for each  
120 colour (Figure 2 and S1-2 for Al). High S values of this microplastics suggested that S could  
121 be used to distinguish between additive or adsorbed elements.

122 Due to their close behaviour, a linear relationship between Fe and Mn concentrations can be  
123 established. Only one sample is far from the linear relationship, so the relationship is good  
124 enough to determine the additive origin of some samples for Fe, Mn and Al (SI Section S2 for

125 further information). Thus, using Figure 2 and elements identified in the literature as additives  
126 (Table S2 and S3), the additives elements can be identified as follows:

127 • **Blue:** Both Cu and Ba present large S values (814 and 2360 nmol g<sup>-1</sup>, respectively) in  
128 blue plastics compared to other colours of microplastics. This might be explained by the  
129 use of the inorganic blue pigments BaCuSi<sub>2</sub>O<sub>6</sub> and 2CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>.

130 • **Red:** Ba and V have high S values (189 and 8 nmol g<sup>-1</sup>, respectively) in red plastics  
131 compared to other colours of microplastics. However, to our knowledge those elements  
132 are not used as red pigments, but Ba is a well-known filler in plastics. Unfortunately, very  
133 little information is available on V as an additive. However, trace elements were found in  
134 fly ash used for building materials, concrete modification, composite and polyester  
135 mortar, which might explain its presence as additive<sup>3</sup>.

136 • **Green:** Five elements present large S values in the green microplastics: Pb (615.90  
137 nmol g<sup>-1</sup>), Cr (485.68 nmol g<sup>-1</sup>), Cu (344.21 nmol g<sup>-1</sup>), Ba (141.40 nmol g<sup>-1</sup>) and Cd (60.50  
138 nmol g<sup>-1</sup>). The presence of Cd, Cr and Cu should be explained by the use of green  
139 pigments, such as phthalocyanine green (Cu organic complex), Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O,  
140 CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O, and/or a mix of CdS and Cr<sub>2</sub>O<sub>3</sub>.

141 Pb and Ba are not used as green pigments, but they are used as yellow pigments as  
142 Pb<sub>3</sub>(SbO<sub>4</sub>)<sub>2</sub>, PbCrO<sub>4</sub> or Pb<sub>2</sub>SnO<sub>4</sub> and BaCrO<sub>4</sub>, which likely explains their presence. Since  
143 Sb and Sn were not analysed in our study, it is impossible to know if Pb<sub>3</sub>(SbO<sub>4</sub>)<sub>2</sub> and  
144 Pb<sub>2</sub>SnO<sub>4</sub> were used in this sample. The presence of Cr as an additive might confirm the  
145 use of PbCrO<sub>4</sub> and BaCrO<sub>4</sub>.

146 The use of Pb and Ba for other properties can not also be excluded. Pb and Ba are also  
147 largely used in plastic formulations as heat stabilisers, antioxidants, UV stabilisers (Pb),  
148 and fillers (Ba). The presence of Cd and Pb as additives in green microplastics from this  
149 sampling site was confirmed by El Hadri et al.<sup>8</sup> using LC-ICP-MS (Table S4).



- 150 • **Orange:** Five elements have large S values in orange plastics: Al ( $122.82 \mu\text{mol g}^{-1}$ ), Zn  
151 ( $8820.68 \text{ nmol g}^{-1}$ ), Cd ( $426.48 \text{ nmol g}^{-1}$ ), Ba ( $68.32 \text{ nmol g}^{-1}$ ), and V ( $53.20 \text{ nmol g}^{-1}$ ).  
152 The presence of Cd might be explained by the use of the orange pigment CdS. The  
153 presence of Zn, Ba and V might be explained either by their use as yellow pigments or  
154 for other properties. Other yellow pigments include  $\text{BiVO}_4$ ,  $\text{K}_2\text{O}_4\text{ZnCrO}_4(\text{H}_2\text{O})_3$ ,  $\text{BaCrO}_4$ .  
155 However, Ba and Zn are also well-known fillers and Zn is also a flame retardant. To our  
156 knowledge, no common orange, red or yellow pigments contain Al. Thus, Al's presence  
157 in this sample as an additive is likely due to its use as flame retardant. Note that El Hadri  
158 et al.<sup>8</sup> showed that Cd was present as an additive in orange microplastics by LC-ICP-MS  
159 analysis (Table S4).
- 160 • **Grey and Black:** Five elements have large S values in grey and black plastics: Cu  
161 ( $402.12 \text{ nmol g}^{-1}$ ), Pb ( $180.13 \text{ nmol g}^{-1}$ ), Cr ( $174.77 \text{ nmol g}^{-1}$ ), Mn ( $75.72 \text{ nmol g}^{-1}$ ) and  
162 Cd ( $49.77 \text{ nmol g}^{-1}$ ). Large Mn and Cd concentrations could be explained by the use of  
163 Cd-Mn pigments. The presence of Cu, Pb and Cr as additives are either explained by  
164 their use as a mix of different pigments to obtain the black colour, or their use for  
165 properties other than pigments in this sample. Note that the presence of Pb as an  
166 additive was also highlighted by El Hadri et al.<sup>8</sup> in grey microplastics from the same field  
167 site analysed by LC-ICP-MS (Table S4).
- 168 • **Yellow and White:** No element has a large S in yellow or white microplastics. Therefore,  
169 no additive elements are highlighted in these microplastics.

## 170 **Release of additives**

171 The S calculation helped to identify which elements are additives in the microplastics we  
172 collected from the Guadeloupe beaches. However, this method does not give any  
173 information about the source of the acid-leached elements: are they coming from the  
174 environment or are they coming from the alteration of microplastics? Looking at the  
175  $[\text{metal}]/[\text{metal}]_{\text{acidic leaching}}$  and  $[\text{metal}]/[\text{metal}]_{\text{acidic digestion}}$  ratio for metals identified as additives in

176 the orange and grey and black samples (see Section 3.1), two different behaviours are  
177 exhibited (Figure 3). Cu, Pb, Cr and Cd exhibit similar  $[\text{metal}]/[\text{metal}]_{\text{acidic leaching}}$  and  
178  $[\text{metal}]/[\text{metal}]_{\text{acidic digestion}}$  values. In these microplastics, the acidic leached concentrations,  
179 namely adsorbed Cu, Pb, Cr and Cd, may therefore originate from the alteration of plastics  
180 and the subsequent adsorption of released additives.

181 In contrast, Mn, Al and Zn present larger  $[\text{metal}]/[\text{metal}]_{\text{acidic digestion}}$  values than  
182  $[\text{metal}]/[\text{metal}]_{\text{acidic leaching}}$  values. These additives are therefore either not leached in significant  
183 amounts, or they are progressively released from the plastic surface to the external  
184 environment. All these elements are known as oligo-elements. Manganese is usually used as  
185 Mn(IV) oxide for grey pigment in plastic formulations. Microorganisms are able to reduce  
186 Mn(IV) to Mn(II), releasing the Mn from the plastic to the solution. Aluminium and Zn as  
187 additives are also solubilized and potentially consumed by the biota as oligo-elements,  
188 disappearing from the system as a consequence. By contrast Pb, Cr and Cd are non-  
189 essential elements for living organisms and should therefore not be preferentially consumed.

### 190 **Bioavailability of adsorbed and additive elements**

191 Numerous studies have shown that plastics are ingested accidentally by animals. Plastics  
192 can injure animals through both the plastic itself, and through pollutants adsorbed on the  
193 plastic surface that can be released by digestion processes (conditions similar to acidic  
194 leaching). If the largest concentrations measured in the plastics correspond to additive  
195 elements, additive elements are less (or not) released by acid than adsorbed elements.  
196 Ecotoxic parameters only discuss acidic leached concentrations of elements that may be  
197 dangerous to animals due to their release in acidic stomach conditions.

198 The ECOTOX (<https://cfpub.epa.gov/ecotox/search.cfm>) database contains the Lowest  
199 Observed Effect Concentrations (LOEC [ $\text{mg} (\text{kg}\text{-food})^{-1}$ ]) that have been determined for Fe,  
200 Cu, Zn, As, Cd and Pb for several fish (Table S5). Note that LOEC were determined for

201 acute tests by ingesting one dose of each element. Concentrations measured after acidic  
202 leaching for Fe, Cu, Zn, As and Pb are lower than the LOEC (minimal and maximal values)  
203 for all microplastics samples (Table S5). Cadmium concentrations in the blue and grey and  
204 black microplastics were below the LOEC minimal value but higher for the green, orange,  
205 red, yellow and white microplastics. However, fish do not only eat plastics (100% food ≠  
206 100% plastic); they tend to ingest the plastic along with real food. From Cd concentrations  
207 measured in the acidic leaching and for an LOEC of  $0.07 \text{ mg (kg food)}^{-1}$ , it is possible to  
208 calculate the maximal percentage of plastic in food for which the LOEC is attained. The  
209 percentage of microplastic in the fish's food has be higher than 72% (Green), 71% (White),  
210 24% (Yellow), 21% (Orange) and 16% (Red) to observe effects due to Cd from plastics.  
211 These percentages show that it is highly improbable that fish will eat sufficient plastics by  
212 accident to present a danger for them.

213 Our results suggest that our microplastic samples are not very dangerous for fish, when  
214 ingested in one dose. However, here, we only studied the possible danger posed by (i) the  
215 ingestion of a single dose of metal adsorbed by plastics, whereas chronic ingestion could  
216 also be a potential danger for biota. We did not consider the potential synergetic health  
217 effects of the elements being in mixtures in plastics. As well, plastics themselves can hurt  
218 ecosystems. It would thus be interesting to study the effects of chronic ingestion of metals  
219 adsorbed onto plastics and verify their toxicity or lack of it.

## 220 **Conclusion**

221 It is crucial to determine the origin of elements contained in plastic debris, since the response  
222 of additives and sorbed metalloids to physico-chemical conditions can vary. In our study, we  
223 provided a new and simple method to determine the additive *versus* sorbed elements in  
224 microplastics. This method consists of measuring and comparing the concentrations of  
225 elements released from two processes: acidic leaching and total digestion. Using this

226 method, a large number of element concentrations can be determined simultaneously. Our  
227 method also determines the bioavailable elements for living organisms.

228 The colour of the microplastic debris of the North Atlantic Gyre that is deposited on  
229 Guadeloupe beaches depends on the heterogeneous elements it contains. Several elements  
230 were probably used as pigments (Cd, Cu, Cr, and possibly Pb, Ba, and V). When plastics are  
231 altered by the addition of these elements, the additives seem to be mobile. Only Cd seems to  
232 be a danger when ingested by fish. Considering the percentage of plastic potentially ingested  
233 by fish, Cd levels do not seem to reach the LOEC. However, further research is needed to  
234 determine if microplastics and associated elements affect the health of the biota, and what  
235 effects the chronic consumption of plastics with additive elements might have.

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## Supporting information:

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### **Metals in microplastics: determining which are**

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### **additive, adsorbed, and bioavailable**

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## Section S1: Materials and methods

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317 Quantitative analyses were performed using a conventional external calibration procedure (7  
 318 external standard multi-element solutions were purchased from Inorganic Venture, USA). A  
 319 300 ppb mixed solution of rhodium and rhenium was injected with the sample in-line in the  
 320 nebulizer. This solution was used as an internal standard for all measured samples, to  
 321 correct any instrumental drift and matrix effects. Calibration curves were calculated based on  
 322 the intensity ratios between the internal standard and the analysed elements. An SLRS-6  
 323 water standard was used to check the accuracy of the measurement procedure.

324 The matrix of reference materials (ERM-EC 680 and ERM-EC 681) is composed of  
 325 polyethylene supplemented with various concentrations of inorganic additives including As,  
 326 Cd, Cr, Pb and Zn. Concentrations were validated for As (-0.56 and 9.26% of error), Cd (-  
 327 1.04 and 0.82%), Cr (-0.8 and 3.16% of error), Pb (10.19 and 3.54% of error) and Zn (-0.68  
 328 and -7.75% of error).

329 *Table 1: Quantification limit of the ICP-MS.*

Element	Isotope	Mode	<1000	< 100 ppb	< 10 ppb	<1 ppb	<0,5ppb	< 0,1 ppb
			ppb	ppb	ppb	ppb	ppb	ppb
Al	27	No Gas	3%	5%	5%	5%	5%	10%
V	51	He	3%	5%	5%	5%	5%	10%
Cr	52	He	3%	5%	5%	5%	5%	10%
Cr	53	He	3%	5%	5%	5%	5%	10%
Mn	55	He		3%	3%	5%	5%	10%
Fe	56	He	3%	5%	5%	10%		
Fe	57	He	3%	5%	5%	10%		
Co	59	He		3%	3%	5%	5%	10%
Ni	60	He		3%	3%	5%	5%	10%
Ni	62	He		3%	3%	5%	5%	10%
Cu	65	He	3%	3%	3%	5%	5%	10%

Zn	66	No Gas		3%	3%	5%	5%	10%
Zn	66	He	3%	3%	3%	5%	5%	10%
As	75	He		3%	3%	5%	5%	10%
Cd	111	No Gas		3%	3%	5%	5%	10%
Ba	138	No Gas	3%	3%	3%	3%	5%	10%
Pb	208	No Gas			3%	3%	5%	10%

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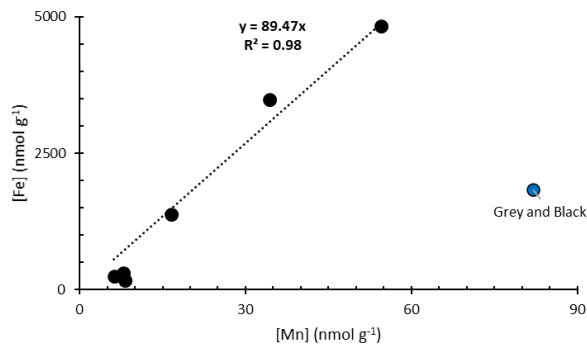


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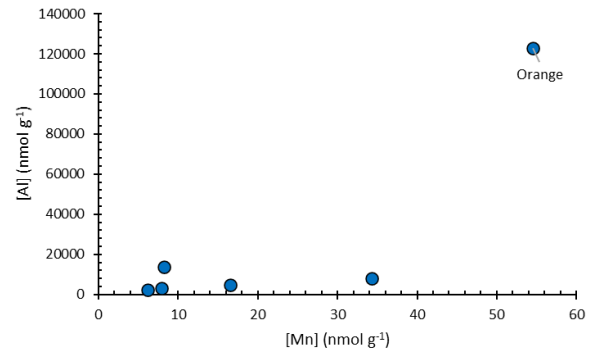
## **Section S2: Identification of the elements nature**

332 Due to their similar chemical behaviour, Fe and Mn concentrations in water are usually  
333 related by a linear relationship. Interestingly, Fe and Mn also show this linear relationship in  
334 all the coloured microplastics, except for the grey and black microplastics (Figure S1a).  
335 There are three factors that lead us to state that Fe and Mn are present as sorbent elements  
336 in all samples, except for the grey and black sample: (i) to our knowledge, Fe is used as an  
337 additive only as an inorganic pigment (Table S1 and 2), (ii) Mn is used only as an inorganic  
338 pigment for the grey colour (Table S1 and 2), and (iii) Fe and Mn concentrations are linearly  
339 linked. Similarly, a linear relationship is highlighted between Al and Mn concentrations,  
340 except for the orange microplastics (Figure S1b and c). Both microplastics samples (grey  
341 and black for Mn and orange for Al) could, therefore, be additives. Comparing the S values of  
342 Al, Mn and Fe (Figure 2a)), those two samples (grey and black for Mn and orange for Al)  
343 present high S values. We can thus identify elements as additives based on their S values.

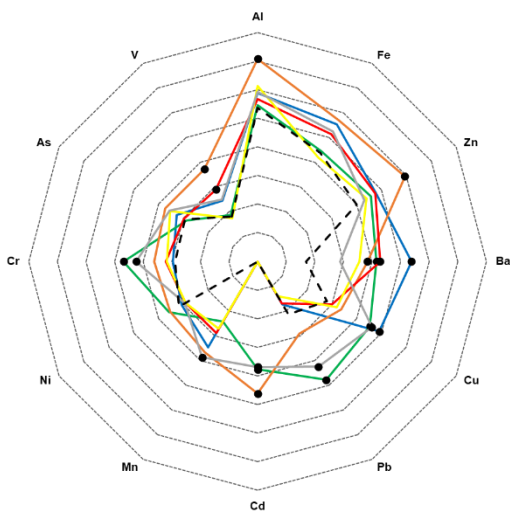
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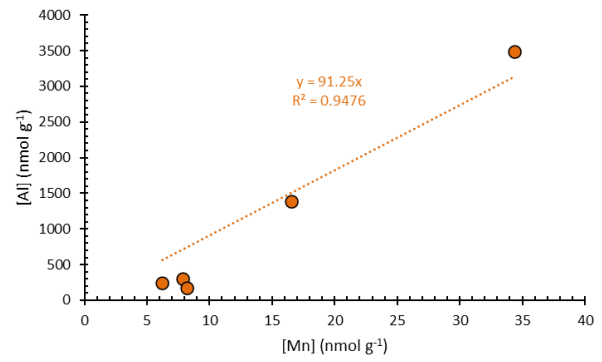
a)



b)

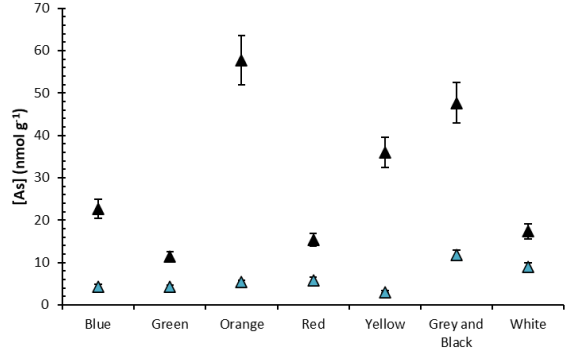
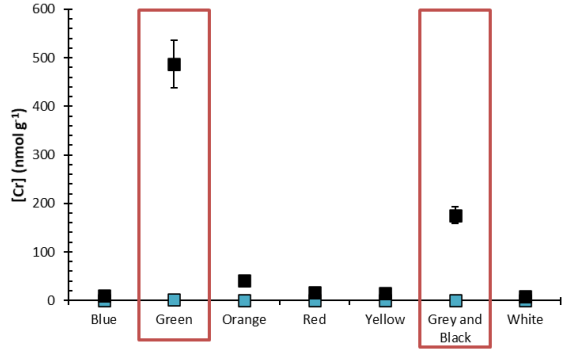
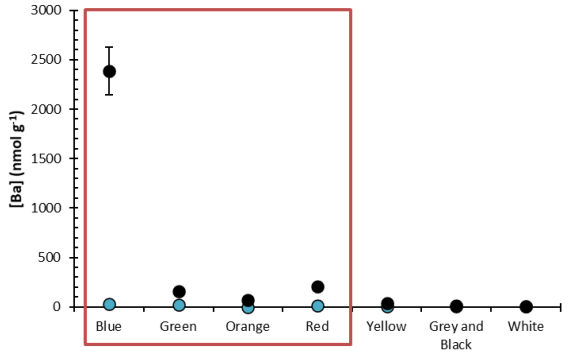
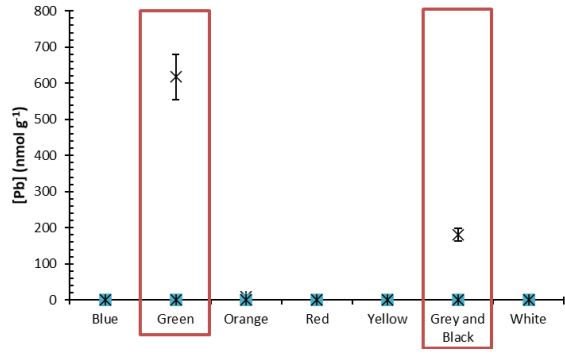
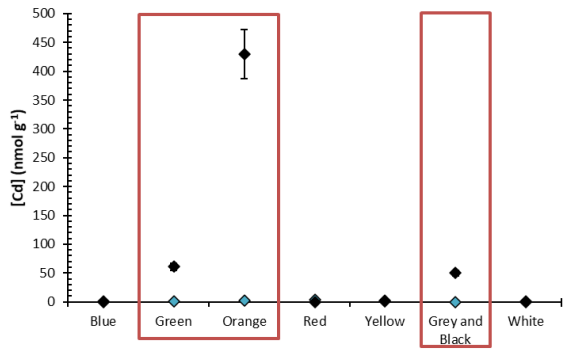
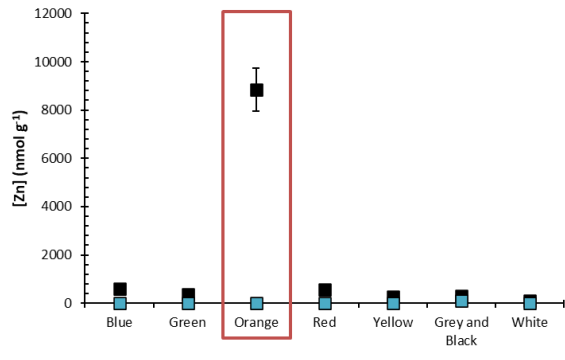
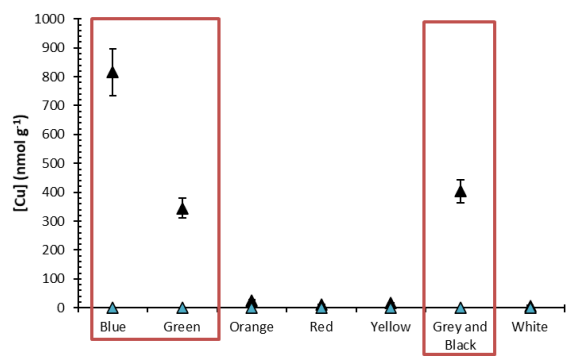
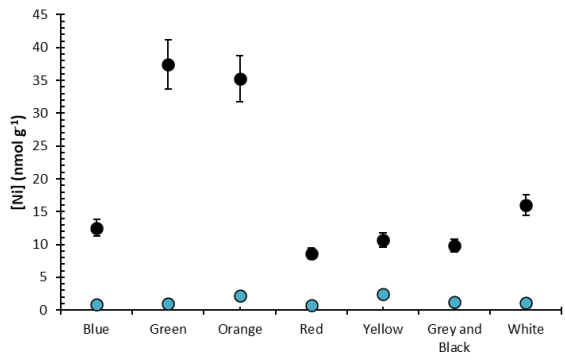


c)



d)

346 Figure 1: Linear relationship between (a) Fe and Mn and (b) Al and Mn concentrations with the orange  
 347 microplastics and (c) without the orange microplastics. d) S values obtained from acidic leaching and digestion for  
 348 Al, Fe, Zn, Ba, Cu, Pb, Cd, Mn, Ni, Cr, As and V elements; high S values indicate these are additives in  
 349 microplastics.





350 *Figure 2: Element concentrations measured in the acidic leachate after total acidic digestion. Red rectangles*

351 *highlight the high differences in extraction concentrations.*

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## Section S3: Tables

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354 *Table 2: Summary of elements that are used as pigments. Most of the data comes from the Internet site*355 *<https://colourlex.com/pigments/pigments-colour/>.*

Colour	Name of the pigment	Composition
Blue	Han Blue	$\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$
	Egyptian blue	$\text{BaCuSi}_2\text{O}_6$
	Blue Verditer	$\text{CaCuSi}_4\text{O}_{10}$
	Manganese Blue	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Vivianite	$\text{BaMnO}_4 \cdot \text{BaSO}_4$
	Cerulean Blue	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
	Prussian Blue	$\text{CoSnO}_3$
	Smalt	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$
	Azurite	contain Co
	Cobalt Blue	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Ultramarine	$\text{CoAl}_2\text{O}_4$
Red	Pompeiiian Red	$\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$
	Chrome Red	Iron oxide + clay and quartz
	Cadmium Red	$\text{PbO PbCrO}_4$
	Red Lead	$\text{Cd}(\text{S,Se})$
	Red Ochre	$\text{Pb}_3\text{O}_4$
	Vermilion	Hematite (Iron oxide)
	Realgar	$\text{HgS}$
Yellow	Raw Sienna	$\text{As}_4\text{S}_4$
	Bismuth Vanadate	Iron oxide + small amounts of Mn oxides
	Yellow	$\text{BiVO}_4$
	Zinc Yellow	$\text{K}_2\text{O } 4\text{ZnCrO}_4(\text{H}_2\text{O})_3$
	Lemon Yellow	$\text{BaCrO}_4$
	Cobalt Yellow	$\text{K}_3[\text{Co}(\text{NO}_2)_6]$
	Naples Yellow	$\text{Pb}_3(\text{SbO}_4)_2$
	Cadmium Yellow	$\text{CdS}$
	Yellow Ochre	Iron oxides
	Orpiment	$\text{As}_2\text{S}_3$
Chrome Yellow	$\text{PbCrO}_4$	

	Lead-Tin Yellow	$Pb_2SnO_4$
Green	Phthalocyanine Green	Cu organic complex
	Cobalt Titanate Green	$Co_2TiO_4$
	Verdigris	$Cu(CH_3COO)_2 \cdot H_2O$
	Green Earth	$K[(Al, Fe^{III}), (Fe^{II}, Mg)(AlSi_3, Si_4)O_{10}(OH)_2]$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
	Viridian	$Cr_2O_3 \cdot 2 H_2O$
	Emerald Green	$3 Cu(AsO_2)_2 \cdot Cu(CH_3COO)_2$
	Cadmium Green	mix of CdS and $Cr_2O_3$
Orange	Antimony Orange	$2 Sb_2S_3 \cdot Sb_2O_3$
	Cadmium Orange	CdS
	Chrome Orange	$PbO \cdot PbCrO_4$
	Orange Ochre	Iron oxides
	Realgar	AsS, $As_2S_2$ or $As_4S_4$
Grey and Black	Spinel black	$MnFe_2O_4$
	Manganese Black	Manganese and Iron oxides
White	Titanium Dioxide White	$TiO_2$
	Calcite	$CaCO_3$
	Zinc White	ZnO
	Lead White	$2 PbCO_3 \cdot Pb(OH)_2$

356 Table 3 : Additive information from Hahladakis et al., 2018.

Element	Use
Al	- Special effects (such as fluorescence). - Flame retardant
Zn	- Inorganic pigments - Fillers - Flame retardant as zinc borate
As	- Biocides
Fe	- Inorganic pigments
Mn	- Inorganic pigments (cadmium-manganese based possible)
Cu	- Special effect (such as fluorescence)
Cr	- Inorganic pigments
Ba	- Fillers
Pb	- Stabilisers, Antioxidants and UV stabilisers - Heat stabilisers - Inorganic pigments - Special effect (such as fluorescence)
Cd	- Stabilisers, Antioxidants and UV stabilisers - Heat stabilisers

	- Inorganic pigments
<b>Ca</b>	- Fillers

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359 *Table 4: Summary of the results obtained by El Hadri (2020) from microplastics collected at the same sampling*

360 *site measured by LC-ICP-MS. Two behaviours were identified in the samples: additive (Add) and sorbed (Sor)*

<b>Colour</b>	<b>Orange</b>	<b>White</b>	<b>Yellow</b>	<b>Blue</b>	<b>Beige</b>	<b>Green</b>	<b>Grey</b>
<b>Cd</b>	Add	Add/Sor	Add/Sor	Sor	Add	Add	Sor
<b>As</b>	Sor	Sor	Sor	Sor	Sor	Sor	Sor
<b>Zn</b>	Sor	Sor	Add	Add	Add	Add	Sor
<b>Pb</b>	S	Sor	S	Sor	Sor	Add	Add

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363 Table 5: Element concentrations measured after acid leaching and the lowest observed effect concentration  
 364 (LOEC) determined for each element in this study. LOEC data is from the Internet database:  
 365 <https://cfpub.epa.gov/ecotox/>

		Fe	Cu	Zn	As	Cd	Pb
Blue	[mg (kg pl.) <sup>-1</sup> ]	0.87	0.09	0.51	0.25	0.05	0.18
Green	[mg (kg pl.) <sup>-1</sup> ]	1.02	0.06	0.56	0.24	<b>0.10</b>	0.27
Orange	[mg (kg pl.) <sup>-1</sup> ]	1.94	0.06	0.57	0.24	<b>0.33</b>	0.04
Red	[mg (kg pl.) <sup>-1</sup> ]	0.22	0.04	0.32	0.37	<b>0.42</b>	0.00
Yellow	[mg (kg pl.) <sup>-1</sup> ]	0.52	0.04	0.38	0.12	<b>0.29</b>	0.04
Grey and Black	[mg (kg pl.) <sup>-1</sup> ]	3.29	0.08	7.41	0.68	0.03	0.15
White	[mg (kg pl.) <sup>-1</sup> ]	0.38	0.07	0.43	0.57	<b>0.10</b>	0.00
LOEC min	[mg (kg food) <sup>-1</sup> ]	560	0.28	100	28	0.07	7.20
LOEC max	[mg (kg food) <sup>-1</sup> ]	560	1780	5926	732	615	802.92

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## Figures:

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### **Metals in microplastics: determining which are**

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### **additive, adsorbed, and bioavailable**

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383

384 Charlotte Catrouillet<sup>a\*</sup>, Mélanie Davranche<sup>a</sup> Imane Khatib<sup>a</sup>, Corentin Fauny<sup>a</sup>, Aurélie Wahl<sup>a</sup>,

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Julien Gigault<sup>a,b\*</sup>.

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387 <sup>a</sup>*Univ. Rennes, CNRS, Géosciences Rennes - UMR 6118, F-35000 Rennes, France*

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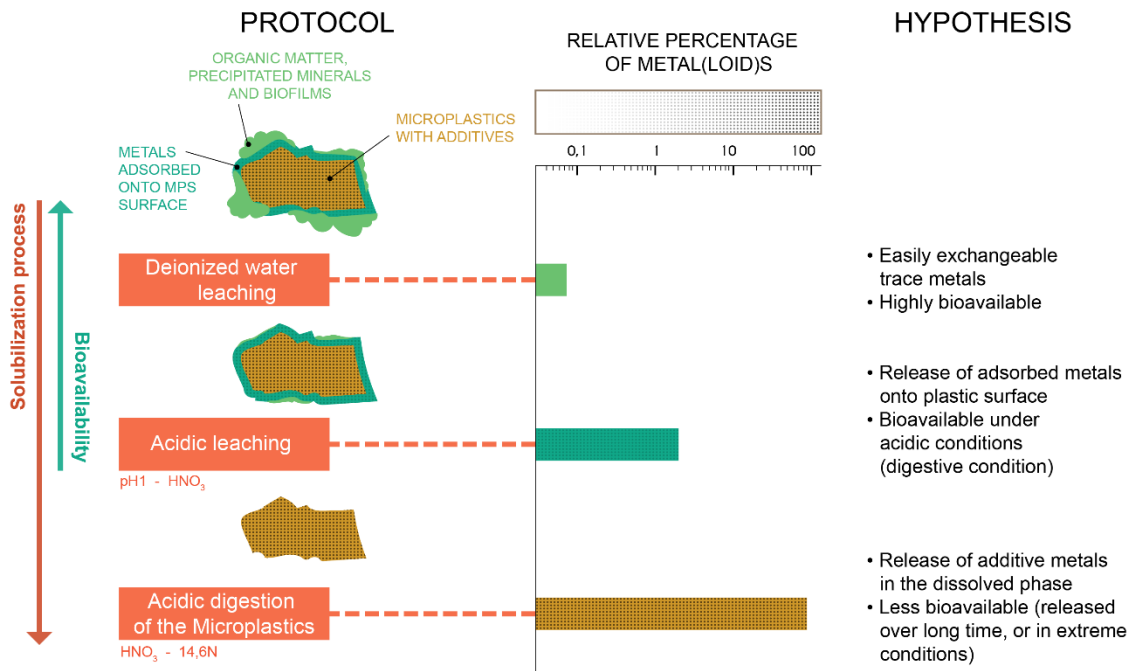
<sup>b</sup>*TAKUVIK CNRS/ULaval, UMI3376, Université Laval, Quebec City, QC, Canada*

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390 \*Corresponding authors: [julien.gigault@takuvik.ulaval.ca](mailto:julien.gigault@takuvik.ulaval.ca) and [391](mailto:charlotte.catrouillet@univ-</a></p></div><div data-bbox=)

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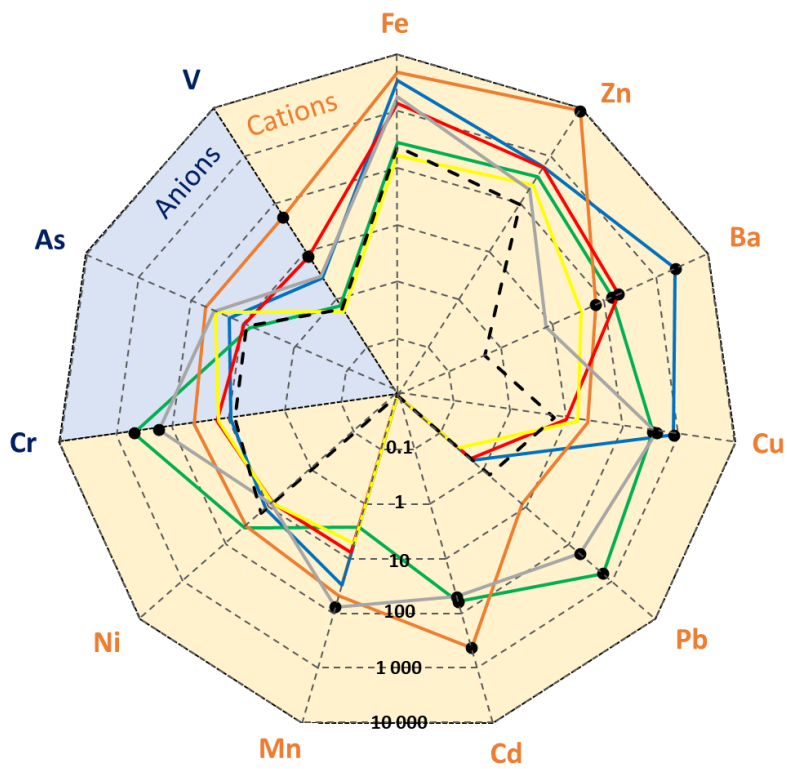
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394 *Figure 3: Protocol developed in our study and linked hypothesis*

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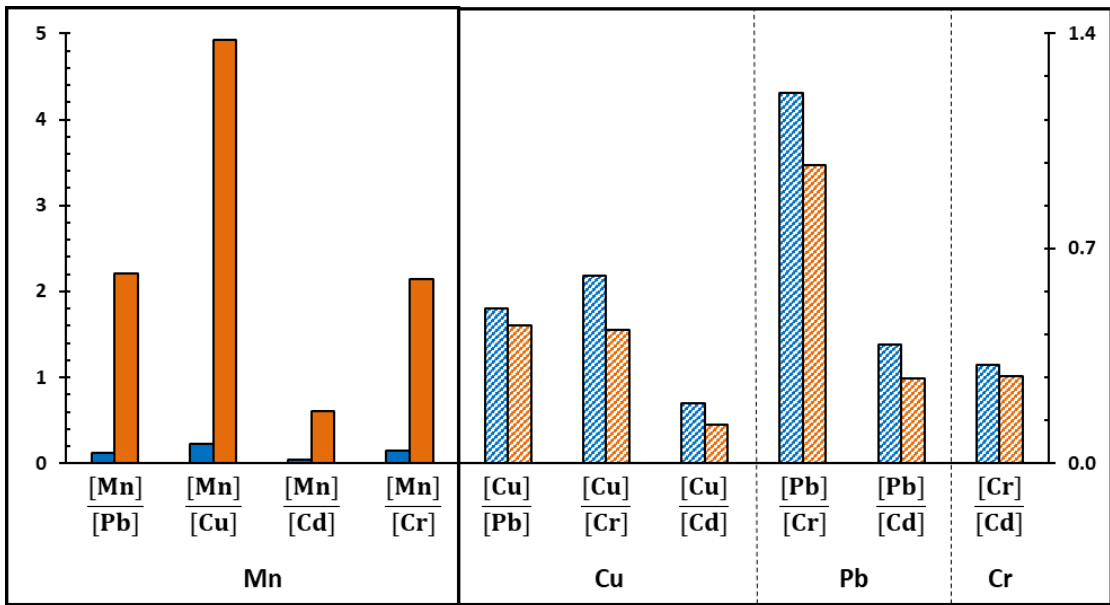
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399 *Figure 4: S values obtained from acidic leaching and digestion for Fe, Zn, Ba, Cu, Pb, Cd, Mn, Ni, Cr, As and V.*

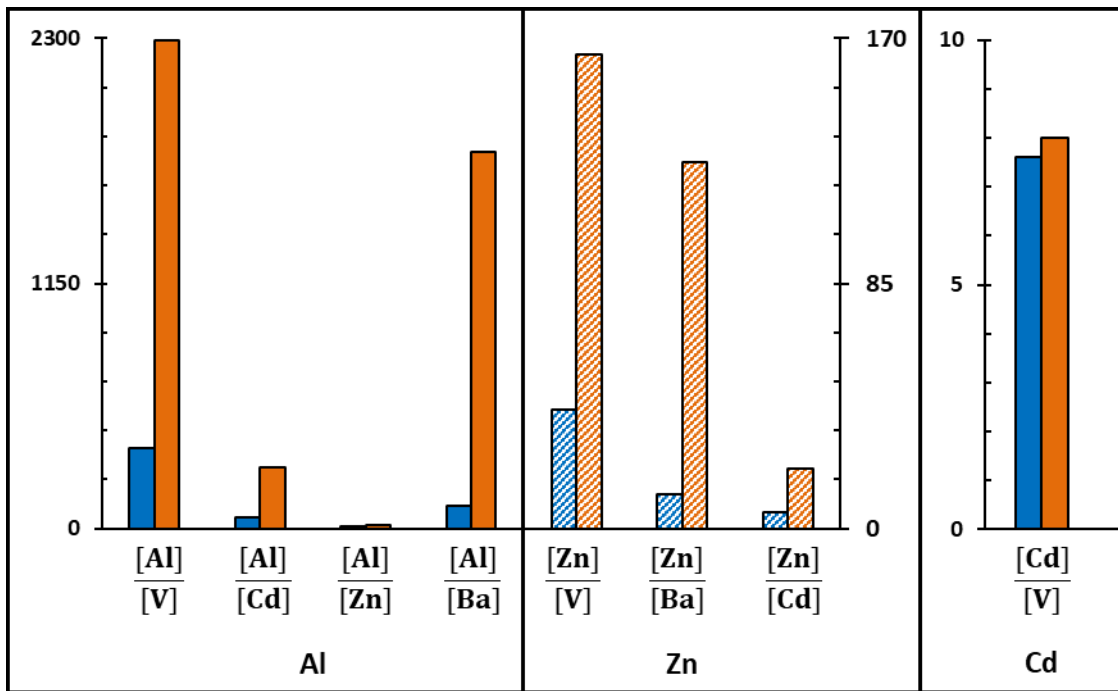
400 *For Al, see FIGURE 1 in SI. Metal(loid)s, with low S values (close to the centre) are mainly sorbed onto*

401 *microplastics. Metal(loid)s, with high S values are additives in the microplastics.*

402



a)



b)

■ Acidic leaching ■ Acidic digestion

403 *Figure 5: Metal/Metal ratio of concentration in the acidic leaching and acidic digestion in the a) grey and black*  
404 *sample and b) orange sample. Cu, Pb, Cr and Cd have similar concentration ratios. Cu, Pb, Cr and Cd adsorption*  
405 *may originate from the alteration of plastics. Note that if one metal is present at higher concentrations in the acidic*  
406 *digestion than in the acidic leaching, this metal imposes a different metal/metal ratio. Thus, Cu/Mn, Pb/Mn, Pb/Cu,*  
407 *Cr/Mn, Cr/Cu and Cr/PB ratios were not represented for part a). Similarly, Zn/Al, Cd/Al and Cd/Zn were not*  
408 *represented for part b).*

409