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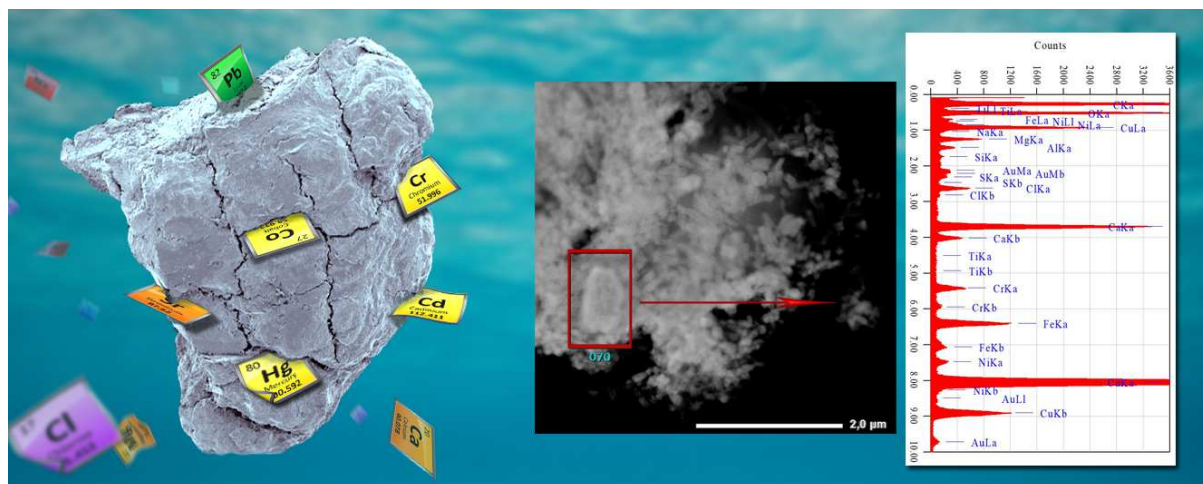
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Trace metals in polyethylene debris from the North Atlantic subtropical gyre

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KEYWORDS: Microplastic; plastic debris; metals' accumulation; polyethylene; polymer

ABSTRACT

Plastic pollution in the marine environment poses threats to wildlife and habitats through varied mechanisms, among which are the transport and transfer to the food web of hazardous substances. Still, very little is known about the metal content of plastic debris and about sorption/desorption processes, especially with respect to weathering. In this study, plastic debris collected from the North Atlantic subtropical gyre was analyzed for trace metals; as a comparison, new packaging materials were also analyzed. Both the new

23 items and plastic debris showed very scattered concentrations. The new items contained
24 significant amounts of trace metals introduced as additives, but globally, metal
25 concentrations were higher in the plastic debris. The results provide evidence that
26 enhanced metal concentrations increase with the plastic state of oxidation for some
27 elements, such as As, Ti, Ni, and Cd. Transmission electron microscopy showed the
28 presence of mineral particles on the surface of the plastic debris. This work demonstrates
29 that marine plastic debris carries complex mixtures of heavy metals. Such materials not
30 only behave as a source of metals resulting from intrinsic plastic additives but also are able
31 to concentrate metals from ocean water as mineral nanoparticles or adsorbed species.

32 CAPSULE

33 Plastic debris collected from the North Atlantic subtropical gyre was analyzed for trace metals.

34 Marine plastic debris carry complex mixtures of heavy metals but it is evidence that plastic oxidation
35 favors their adsorption.

36

37 **Introduction**

38 Reports of plastic debris found in marine and terrestrial habitats have led to a growing
39 awareness of the hazards from plastic pollution¹. Subtropical gyre accumulations are
40 emblematic², but plastic pollution is found throughout the oceans, as well as in bays³,
41 estuaries⁴ and terrestrial environments such as rivers⁵ and lakes⁶. However, the research
42 remains young, and we need to better understand the effect of plastic pollution on
43 ecosystems. The direct impacts of plastic on wildlife are entanglement and ingestion⁷.
44 Instances of ingestion that result in ulceration or starvation are increasing and are found
45 throughout the ecosystem⁸. As an indirect impact, plastic debris is transported by ocean

46 currents over very large distances and serves as a novel habitat for various organisms,
47 leading to the spreading of biological species across oceans⁹⁻¹¹. Another concern is the
48 chemical pollution associated with plastic debris¹². Various classes of chemicals are carried
49 by plastics; some are listed as priority pollutants, and others are even classified as toxic
50 substances^{1, 13, 14}. However, identifying all the substances that could be transported by
51 plastics is far from easy, and the transfer of these substances to the marine environment
52 and biota has only been approached to a limited extent¹⁵⁻¹⁷.

53 To better understand the interaction of plastic debris with chemicals and toxic elements, it
54 is important to first differentiate plastics from polymers. The term polymer refers to the
55 macromolecule, whereas the term plastic describes a manufactured product. A plastic is a
56 material made of a polymer (or sometimes a mixture of several polymers) to which
57 additives have been added to produce the required properties for a given application¹⁸. The
58 chemicals transported by plastics can be categorized according to their origin: 1) molecules
59 from the polymerization process, 2) compounds introduced during the formulation step,
60 namely, the additives, and 3) molecules or elements sorbed onto plastic during the use of
61 the item or during its stay in the environment. All these chemicals are not covalently bound
62 to the polymer, and sorption and desorption processes are involved; these processes are
63 complex mechanisms influenced by external conditions such as pH, the salinity of the
64 surrounding media^{19, 20}, UV light and shear stress, but the two latter factors are seldom
65 considered.

66 Regarding the metal content in plastic debris, the most attention has been paid to beached
67 preproduction pellets^{13, 21-25}. Preproduction pellets (from 1 mm to 5 mm) are generally
68 made of raw resin and used in the manufacturing of plastics, where they are melted into
69 objects. Although pure polymers are generally acknowledged to be rather inert toward
70 ions, the sorption of trace metals by new and beached preproduction PE pellets has been

71 proved^{21, 23, 24}. It has been demonstrated that metal sorption is enhanced with pellet
72 weathering^{13, 24}; the increases in polarity, surface area and porosity promote trace-metal
73 binding²⁴. The accumulation of metals may also be mediated by biofilm development¹³.
74 Imhof *et al.* recently reported the presence of paint particles in freshwaters²⁶. They
75 demonstrated that the proportion of paint among microplastics in Lake Granada (Italy) was
76 increased in smaller plastic debris (in the range 50 – 500 μm) and that the debris contained
77 a high variety of metals such as Cd, Pb and Cu. Most of field data regarding metal sorption
78 onto plastic concerns beached pellets, but Turner *et al.* developed a field survey using
79 portable XRF and analyzed beached plastic debris²⁷⁻²⁹. In comparison, the concentrations
80 of several metals were two to three orders of magnitude higher in plastic debris than in
81 pellets (e.g., Cd concentrations were between 1.09 and 76.7 ng/g in beached pellets^{23, 24},
82 while values ranged from 25 to 147 $\mu\text{g/g}$ in beached debris²⁷; all samples were from
83 England).

84 Regarding the transfer of metals to the trophic chain, it has been suggested that metals are
85 mostly sorbed onto the pellet surface and are therefore likely bioavailable by ingestion²⁴.
86 High levels of ingested plastic in sea birds have been recently correlated with increasing
87 concentrations of Cl, Fe, Pb, Mn and Rb in feathers³⁰. These preliminary studies suggest
88 that the transfer and accumulation of trace metals by plastic debris must be further
89 investigated.

90 In the present study, we analyzed the trace metal content in plastic debris collected from
91 the North Atlantic subtropical gyre. This is the first report of trace metal content in plastic
92 debris from the open ocean. A large variety of plastics are present in the environment³¹, but
93 the most abundant in the open ocean is polyethylene (PE)^{32, 33}; the discussion is thus
94 focused on PE. For comparison, we also analyzed preproduction pellets and new
95 packaging materials to understand whether the metals found in debris result from

96 manufacturing, formulation or sorption that occurs after release to the environment. Trace
97 metal contents are discussed in terms of the oxidation state, size and color of the debris.
98 The concentrations measured here are compared to published data for beached debris and
99 for debris from coastal areas^{13, 21, 23-25, 27} and rivers³⁴.

100 **EXPERIMENTAL SECTION**

101 **Sample origin**

102 Mesoplastics (0.5 - 20 cm) were collected from a boat in the North Atlantic subtropical
103 gyre in May 2014 and June 2015 during the French 7th Continent Expedition. The
104 mesoplastics were visible from the sailing vessel *Guyavoile* and floated at the sea surface.
105 Thirteen PE mesoplastics were selected for trace metal analysis, as they covered a large
106 range of sizes, colors and types of items; a complete description is given in Table SI1. The
107 mesoplastics were cut into small pieces with a ceramic knife for purpose analysis, stored in
108 sealed plastic bags and frozen at -5°C until analysis. Microplastics (0.1 - 0.5 cm) were
109 collected in a manta net equipped with a mesh size of 300 µm. On the boat, 5 mixtures of
110 microplastics were prepared; for each mixture, a total of 15 microplastics were collected
111 with a plastic tweezer and placed in a plastic bag that was sealed and stored at -5°C. The
112 GPS locations of the four net tows are given in Table SI2. Each mixture of microplastics
113 was chosen to be representative of the mixture usually collected in the survey area in terms
114 of size and color. The average length and weight of the microplastics collected in this area
115 were 1.5 mm (±0.3 mm) and 2 mg (±0.2 mg), respectively. The samples were mostly white
116 (80%). Several fibers were also present in the samples; the fibers were approximately one
117 millimeter in diameter and were attributed to fishing lines because clothing fibers are
118 typically thinner³³. For Polyethylene virgin pellets, six samples of PE (CAS 9002-88-4)
119 (also referred to as prefabrication pellets) were obtained as reference materials. Three PE

120 pellets were purchased from Sigma Aldrich (Saint Louis, MO, USA), and three were
121 purchased from Goodfellow (Huntingdon, UK). A full physicochemical characterization of
122 these pellets is given elsewhere³⁵. Twenty-two new PE packaging materials (high density
123 and low density) were randomly selected from supermarkets; items such as milk bottles,
124 white and colored plastic containers, tubes and caps were analyzed for their trace metal
125 contents. These items are described in the Supporting Information (Table SI3). A full
126 physicochemical characterization of these pellets is given in ter Halle *et al.*³⁵.

127 **Fourier transform infrared (FTIR) spectroscopy**

128 Infrared spectra were recorded using a Thermo Nicolet Nexus spectrometer equipped with
129 a diamond crystal ATR accessory and a deuterated triglycine sulfate (DTGS) detector. A
130 full description of the procedure is given elsewhere, together with the method used to
131 calculate the carbonyl index (I_{CO})³⁵.

132 **Trace metal analysis**

133 Each plastic sample (between 35 and 130 mg) was solubilized (in duplicate for several
134 samples) by acid digestion with bi-distilled HNO_3 using a multistep procedure with a
135 microwave oven (MARS 5 system CEM; 110°C - 3 min, then 160°C - 3 min and 200°C -
136 15 min). Trace element concentrations were obtained by measurement on a quadrupole
137 ICP-MS (inductively coupled plasma mass spectrometer, Agilent 7500, ®Perkin Elmer) at
138 the GET laboratory (Toulouse, France). The international geostandard ERM-EC680K PE
139 (low level) was used to check the validity and reproducibility of both the acid digestion
140 and ICP-MS analyses. Indium and rhenium were used as internal standards for the ICP-MS
141 measurements. Blank tests indicated that the level of contamination induced by the acid
142 digestion procedure was negligible. The total Hg concentration (Hg_T) was measured in
143 duplicate or triplicate by atomic absorption spectrometry (Advanced Mercury Analyzer,

144 AMA254, ®LECO) after combustion and gold-trapping directly on the dried plastic debris.
145 The recoveries of Zn, Cd, Sb, Pb and Hg from the ERM-EC680K standard were close to
146 100%, whereas those of Cr, As and Sn were 55%, 63%, and 53%, respectively, suggesting
147 that the measured Cr, Sn and As concentrations may be slightly underestimated in the
148 microplastic debris. Limits of detection were respectively 91 and 11 ng.g⁻¹ for Ca and K,
149 0.85 ng.g⁻¹ for Al and Zn, 0.64 ng.g⁻¹ for Fe, respectively 0.27 and 0.12 ng.g⁻¹ for Cr and
150 Sn, between 0.01 to 0.08 ng.g⁻¹ for Cd, Co, Ti, As, Sr, Ba, Sb, Mn, V, Ni, Cu and Pb, and
151 lower than 0.01 ng.g⁻¹ for Mo, Th and U.

152 **Transmission electron microscopy**

153 Transmission electron microscopy (TEM) and scanning transmission electron microscopy
154 (STEM) studies were performed using a JEOL cold-FEG JEM-ARM200F operated at 200
155 kV and equipped with a probe Cs corrector reaching a spatial resolution of 0.078 nm.
156 Energy-dispersive X-ray (EDX) spectra were recorded on a JEOL CENTURIO
157 SDD detector. To visualize the presence of metals on the MD0518-4 sample, the surface of
158 the debris was gently scrubbed. The extracted particles were analyzed by TEM/EDX. More
159 than 150 observations were collected.

160 **Soda washing of the mesoplastic**

161 In a Teflon beaker at room temperature, 100 mg of the mesoplastic 14MD0518-4 was
162 mixed with 5 mL of a NaOH solution (1 mol L⁻¹) for 48 hours. A blank control was
163 subjected to the same experiment without mesoplastic. The sample mass balance after
164 washing exhibited a loss of 5.14 mg. The treated mesoplastic was analyzed for trace metal
165 content according to the same protocol. The mesoplastics and NaOH solution were
166 evaporated at 70°C, and the residues were collected in a HNO₃ solution (10 M) for ICP-
167 MS analysis.

168 **Statistical analyses**

169 Multivariate statistical analysis (MSA), including principal component analysis (PCA),
170 hierarchical cluster analysis (HCA) Pearson or Spearman's correlation analysis, is largely
171 used in environmental studies to explore the origins of major or trace elements by reducing
172 the dataset to the main influencing factors (called "principal components"), based on the
173 similarities and differences among samples and relationships among variables in order to
174 highlight the natural and/or anthropogenic origins of elements in different reservoirs (river
175 waters, soils, rocks, mineral water bottles, etc.). Principal component analysis uses an
176 orthogonal transformation to convert possibly correlated variables into a set of independent
177 variables called "principal components" (PCs), allowing the accurate description of
178 complex systems. The rows of the starting data matrix for PCA analysis represent the
179 samples (i.e., 42 observations, including 10 mesoplastics, 22 packaging materials, 6 pellets
180 and 4 microplastics), and the columns represent the variables, representing the elemental
181 concentrations (15 elements, including Al, Ti, Cr, Mn, Ba, Fe, Co, Ni, Cu, Zn, As, Cd, Pb,
182 and Mo) and their carbonyl index. PCA analyses were performed with R software (version
183 3.4.3).

184 **RESULTS AND DISCUSSION**

185 **Metal concentrations in PE virgin pellets**

186 The trace metal concentrations in PE virgin pellets were almost all below the $\mu\text{g.g}^{-1}$ level
187 or the ICP-MS detection limit, except for Ti, Cr and Mo (Table SI4). Titanium
188 concentrations reached $5 \mu\text{g.g}^{-1}$ in HDPE-3 mm but were an order of magnitude lower in
189 the other samples. The chromium concentration reached $10 \mu\text{g.g}^{-1}$ in LDPE-1 mm pellets;
190 this sample also presented $23 \mu\text{g.g}^{-1}$ of Mo. This value is approximately 10 times greater
191 than those observed for the other samples.

192 Considering the molecules originating from the polymerization processes, in addition to
193 free radical initiation, polyethylene (PE) is polymerized using transition-metal catalysts.
194 Catalytic polymerization accounted for approximately 73% of the global PE production in
195 2008³⁶. Transition-metal catalysts used for PE production include i) Ziegler-Natta, ii)
196 supported Cr and iii) single-site catalysts. Ziegler-Natta catalysts are derived from
197 inorganic Ti compounds (activated with organo-Al compounds). The most common
198 supported Cr catalysts are the so-called “Phillips catalysts”, which are supported on
199 refractory oxides, most often silica, and contain small amounts of Mo³⁶. Most commercial
200 single-site catalysts include Zr, Hf or Ti; the use of transition metals such as Pd, Fe or Ni
201 emerged in the mid-1990s.

202 These noticeable amounts of Cr and Mo indicate that the sample LDPE-1 mm was
203 probably synthesized using a Cr-supported catalyst. For the other samples, we could not
204 clearly determine which catalyst had been used, as no trace metals appeared at a high
205 concentration.

206 **Metal concentrations in new packaging materials**

207 In total, 23 packaging materials (for cosmetics, food, beverages, etc.) randomly selected
208 from everyday life were analyzed; these items were made of high- or low-density PE.
209 These PE packaging materials showed very scattered metal concentrations (Table SI5). On
210 average, there were no significant differences between HDPE and LDPE packaging. All
211 metal concentrations were higher in the packaging materials than in the virgin pellets.
212 There is one exception, a LDPE-1 mm pellet that presented high Cr and Mo contents.

213 Antioxidants and UV stabilizers are often based on Ti (usually added at values between 0.5
214 and 5% w/w³⁷). Other metals, such as Cd, Zn, Ba and Pb, are used as stabilizers in PE
215 packaging in typical amounts between 0.05 and 3% w/w³⁸. Pigments are usually

216 incorporated in plastics in proportions between 0.01 and 10% w/w; mixed metal oxides
217 based on Ti, Cr, Ni, Sb, Mn, Co, Al, Zn, Fe or Cu are often used as pigments³⁶. For
218 example, Cu is used in the form of copper oxides, St is used in the nitrate or chlorate form
219 as a red colorant³⁹, and chromates and cadmium sulfoselenide are used as orange
220 colorants⁴⁰. Fillers are typically made of calcium carbonate or zinc oxide and can be
221 incorporated at up to 50% w/w⁴¹. For example, Ba sulfate is a white pigment that promotes
222 brightness. However, this additive is also an inert white filler that promotes resistance to
223 acid and alkalis and provides very good weathering resistance³⁶. Zinc distearate is used as
224 a stabilizer in the polymer industry and as a lubricant in the manufacturing of plastic
225 moldings in industrial processes. Some metal-based compounds are used as antimicrobial
226 agents; Cu, Mn, Co, Ni, Zn, Ag and Cd are used in sulfonamides, and organotin
227 compounds are used as biocides in plastic⁴². In Europe, Pb has been phased out as a plastic
228 additive³⁶, and Cd use is still under discussion; according to the Restriction of Hazardous
229 Substances (RoHS) Directive for any new or recycled product, the concentration limits for
230 Cd are set at 100 $\mu\text{g}\cdot\text{g}^{-1}$ ⁴³. Additionally, potentially hazardous elements are restricted (As,
231 Ba, Se and Sn) because of their properties of migration from plastics³⁷. A Norwegian
232 report has mapped the prioritized hazardous substances used in plastic materials⁴⁴: arsenic
233 (antimicrobial and plasticizer), Br (brominated flame retardant), Cd (pigment; heat- and
234 UV-stabilized only in PVC), Cr (catalyst and pigment) Co (light-blue pigment in PET), B
235 (buffering agent), Pb (pigment; heat- and UV-stabilized in PVC), Hg (catalyst for
236 polyurethane), organic tin compounds (biocides), etc. These inorganic additives confer a
237 wide range of interesting properties to plastic for various applications. It seems challenging
238 to replace metal-based pigments with organic ones, especially from an economic point of
239 view; furthermore, organic pigments do not present the same stability as inorganic ones³⁶.
240 In the literature and in legislative documents, it is stated that the migration rate of

241 inorganic metal salts is very limited compared to those of other substances (like
242 monomers, residual solvents or other even larger organic molecules)^{36, 38}. However,
243 migration evaluation tests are performed on new plastics; there are no data under advanced
244 weathering conditions such as those encountered by marine plastic debris.

245 Titanium concentrations in the packaging materials ranged between 0.4 and 849.5 $\mu\text{g}\cdot\text{g}^{-1}$,
246 with a median value of 140.9 $\mu\text{g}\cdot\text{g}^{-1}$. This corresponds to typical loads of Ti in PE
247 plastics³⁶. Copper contents were significantly higher in the colored (150 $\mu\text{g}\cdot\text{g}^{-1}$ on average)
248 than in the white packaging materials (0.44 $\mu\text{g}\cdot\text{g}^{-1}$ on average) or the pellets (0.09 $\mu\text{g}\cdot\text{g}^{-1}$).
249 The average Ba concentration was particularly high in the colored packaging materials
250 (225 $\mu\text{g}\cdot\text{g}^{-1}$), while the Ba values were below 1 $\mu\text{g}\cdot\text{g}^{-1}$ in the white items and in the virgin
251 pellets. The highest Ba concentrations were obtained for 5 packaging materials, which
252 corresponded to rigid lids or caps with dark colors (red, purple, brown). Lead
253 concentrations in the packaging materials were above 1 $\mu\text{g}\cdot\text{g}^{-1}$ (2.25 and 1.6 $\mu\text{g}\cdot\text{g}^{-1}$) for
254 only 2 items, and Cd concentrations were below 0.83 $\mu\text{g}\cdot\text{g}^{-1}$. Zinc concentrations ranged
255 from 0.06 to 0.25 $\mu\text{g}\cdot\text{g}^{-1}$ in the PE virgin pellets but reached up to 331 $\mu\text{g}\cdot\text{g}^{-1}$ in a brown
256 LDPE lid and averaged 25.9 $\mu\text{g}\cdot\text{g}^{-1}$ in the packaging materials. Strontium concentrations in
257 the packaging materials ranged from LD (0.05 $\mu\text{g}\cdot\text{g}^{-1}$) to 56 $\mu\text{g}\cdot\text{g}^{-1}$ in a red LDPE soda
258 sample, while Sr values for the prefabrication pellets were below the detection limit.

259 **Metal concentrations in plastic debris from the North Atlantic subtropical gyre**

260 Plastic debris were characterized by FTIR spectroscopy and were mostly made of
261 polyethylene (90%) and in the present study the discussion is focused on polyethylene. The
262 total metal concentrations varied strongly from one debris material to another (Table SI6 and
263 SI7). The complexity of the metal mixtures found on plastic debris has already been addressed
264 by Rochman et al.¹³. Globally, the metal concentrations were higher in the plastic debris

265 (mesoplastics and microplastics) than in the new packaging materials, except for Ba, Co, Cu,
266 and Sn.

267 The average Ti concentration in the plastic debris ($1404 \mu\text{g}\cdot\text{g}^{-1}$) was significantly higher than
268 that in the packaging materials ($222.5 \mu\text{g}\cdot\text{g}^{-1}$, Figure 1). Several hypotheses could explain
269 these results: 1) the plastic debris derived from old manufactured objects, and their dated
270 formulation used higher amounts of Ti; 2) titanium is a UV stabilizer, and the debris materials
271 that persist the most might be those containing the highest amount of Ti; and 3) the Ti present
272 in the debris resulted from sorption.

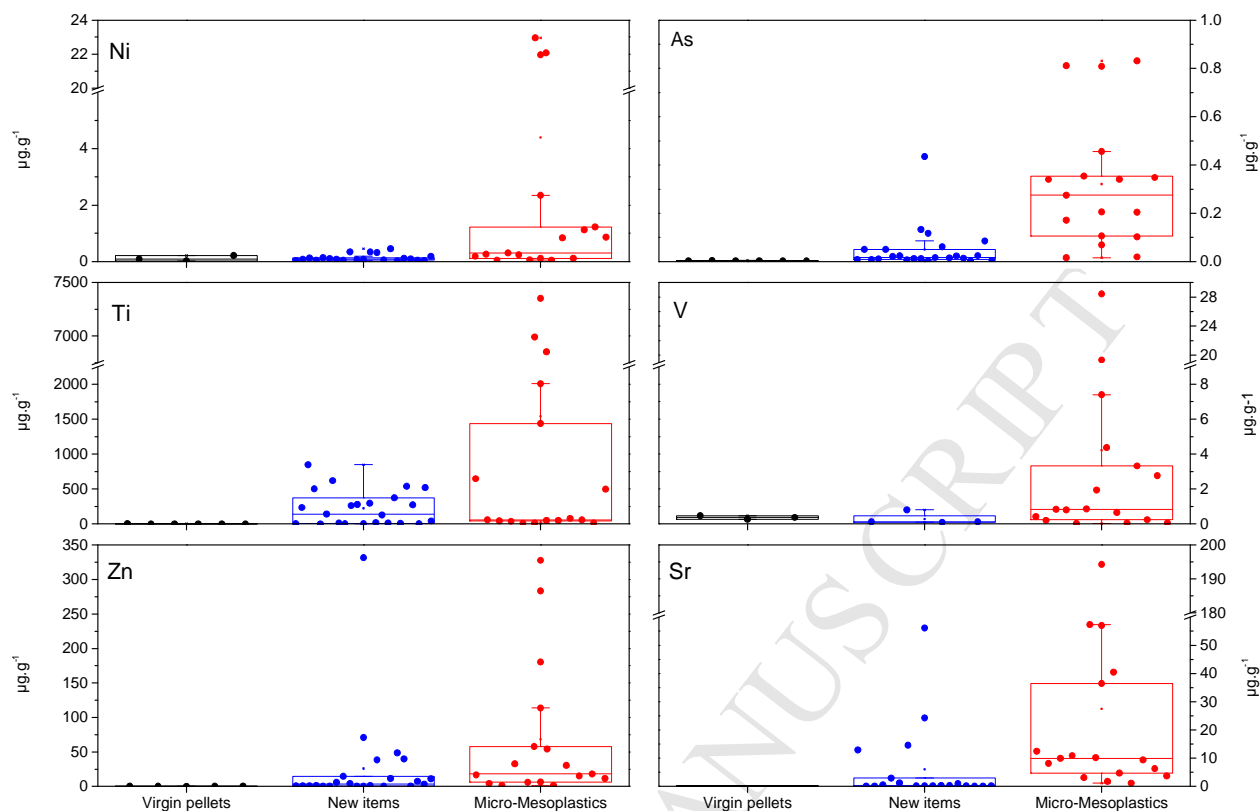
273 Vanadium, Ni and Sr concentrations in the plastic debris were significantly higher than in the
274 new packaging materials. As these trace metals have not been identified as plastic additives,
275 their presence might therefore result from sorption processes.

276 Arsenic contents were significantly higher in the plastic debris (from 0.1 to $0.8 \mu\text{g}\cdot\text{g}^{-1}$) than in
277 the new packaging materials ($0.05 \mu\text{g}\cdot\text{g}^{-1}$). Arsenic was once commonly used in formulations,
278 but its use is now restricted⁴⁴. High concentrations of As in the plastic debris might thus result
279 from the age of the manufactured objects from which the mesoplastics were derived or from a
280 sorption process.

281 Zinc contents were higher in the plastic debris (average $54 \mu\text{g}\cdot\text{g}^{-1}$) than in the new packaging
282 materials ($26 \mu\text{g}\cdot\text{g}^{-1}$). The presence of zinc might be attributed to additives (pigments, fillers,
283 etc.) and/or sorption processes. The molybdenum concentration was 10 times higher in plastic
284 debris than in new packaging materials. Molybdenum is largely used in catalyst formulations;
285 however, this increase suggests sorption processes. The cadmium concentration was the
286 highest in the mesoplastic 14MD0518-4, reaching $4284 \mu\text{g}\cdot\text{g}^{-1}$ in this material and an average
287 of $278 \mu\text{g}\cdot\text{g}^{-1}$ in the plastic debris, but less than $0.012 \mu\text{g}\cdot\text{g}^{-1}$ in the packaging materials. The
288 cadmium content in the plastic debris thus seems to be accounted for by sorption. Regarding

289 the exception of 14MD0518-4, this object might have been a container for a product enriched
290 in Cd, such as a phytopharmaceutical product^{45, 46}. The average Ba concentration in the plastic
291 debris was 70.9 $\mu\text{g}\cdot\text{g}^{-1}$. In the packaging materials, the Ba concentration was very high in two
292 samples: the purple P30 (1538 $\mu\text{g}\cdot\text{g}^{-1}$) and brown P7 (871 $\mu\text{g}\cdot\text{g}^{-1}$) samples; indeed, Ba is often
293 used in red and brown pigments. Excluding those two extreme values, the concentration of Ba
294 was 5 times higher in the mesoplastics than in the packaging materials. The same observation
295 can be made for Sn, with a high value in the green P24 packaging material that distorted the
296 calculation of the average concentration. Without those extreme samples, the Sn concentration
297 was 2 times higher in the plastic debris than in the packaging materials. Both elements
298 highlight not only the heterogeneity of the samples but also the complexity of the mechanisms
299 involved in the trace metal presence in plastic debris. Titanium, V, Ni, Zn, As, Sr, Mo, Cd and
300 Ba concentrations were higher in the plastic debris than in the packaging materials; the ratio
301 of average concentrations ranged between 2 (for Sn) and 190 000 (for Cd, see Figure SI1).

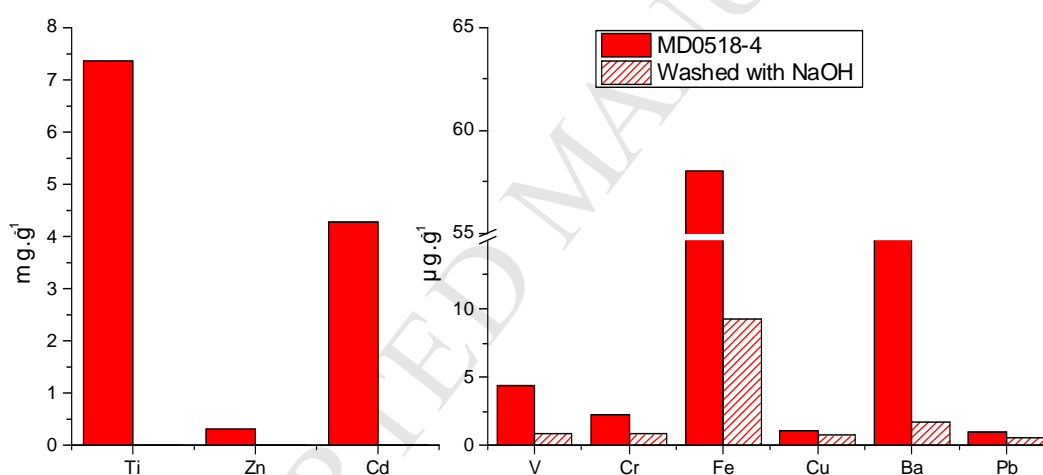
302 The present data were compared to the literature data for coastal areas (Table SI8). Generally,
303 the mesoplastics collected in coastal areas^{27, 47} and here in the open ocean presented higher
304 trace metal contents (specifically Cd and Cr) than did beached pellets^{23, 24}. For example, the
305 Zn content in plastic debris was more than 36-fold higher than in beached pellets. These
306 differences can be explained by the higher initial metal amount in plastics than in raw pellets
307 but also by the higher sorption capacity of plastics, due to their higher polarity conferred by
308 additives, than that of prefabrication pellets. The general tendency is that the mesoplastics
309 from English coastal areas^{27, 47} or Chinese littoral areas³⁴ and the ones from the open ocean
310 here present the same order of magnitude of contamination. This result is remarkable and
311 different compared with data for organic pollutants, whose concentration is lower in plastic
312 debris from the open ocean than in that from coastal areas⁴⁸.



313
 314 Figure 1: Trace metal element concentrations in virgin pellets (n=6), new packaging materials
 315 (n=23) and mesoplastics collected in the North Atlantic subtropical gyre (n=13) during the sea
 316 campaign 7th Continent Expedition 2015. Whiskers correspond to 1.5 times the interquartile
 317 range. All values are reported and represented by crosses (unless they are below the
 318 quantification limit), minimum and maximum values are represented by squares, and mean
 319 values are represented by a point.

320 To determine where the metallic elements may be located on the mesoplastic, the
 321 mesoplastic 14MD0518-4 was washed with NaOH (1 M) for 48 hours at ambient
 322 temperature. The slightly brown-colored biofilm was mostly removed from the mesoplastic
 323 after treatment (as confirmed by scanning electron microscopy, data not shown). The
 324 resulting mesoplastic surface was crumbly, suggesting that this washing step might have
 325 also removed a part of this crumbly layer. Control virgin pellets treated under the same
 326 conditions showed no weight loss and no physical alteration (verified by SEM, data not

327 shown). Most metal concentrations significantly decreased after washing (Figure 2 and
 328 Table SI9). All Ti and Cd were removed (99 to 100%), and almost all Zn (97%) and 80%
 329 of V were leached (V concentrations dropped from $4.4 \mu\text{g.g}^{-1}$ to $0.89 \mu\text{g.g}^{-1}$). The
 330 chromium concentration decreased from 2.2 to $0.85 \mu\text{g.g}^{-1}$ (61%), and Ni decreased from
 331 22 to $2.6 \mu\text{g.g}^{-1}$ (88%). Most of the metals were therefore removed from the plastic debris,
 332 except Co, Cu, As and Sr. The drastic decrease in concentrations indicates that the metals
 333 were probably located on the sample surface: either 1) in the biofilm, 2) deposited as small
 334 mineral particles, or 3) sorbed to the plastic surface layers or onto precipitated mineral
 335 particles. Accumulation patterns needs to be better understood²².

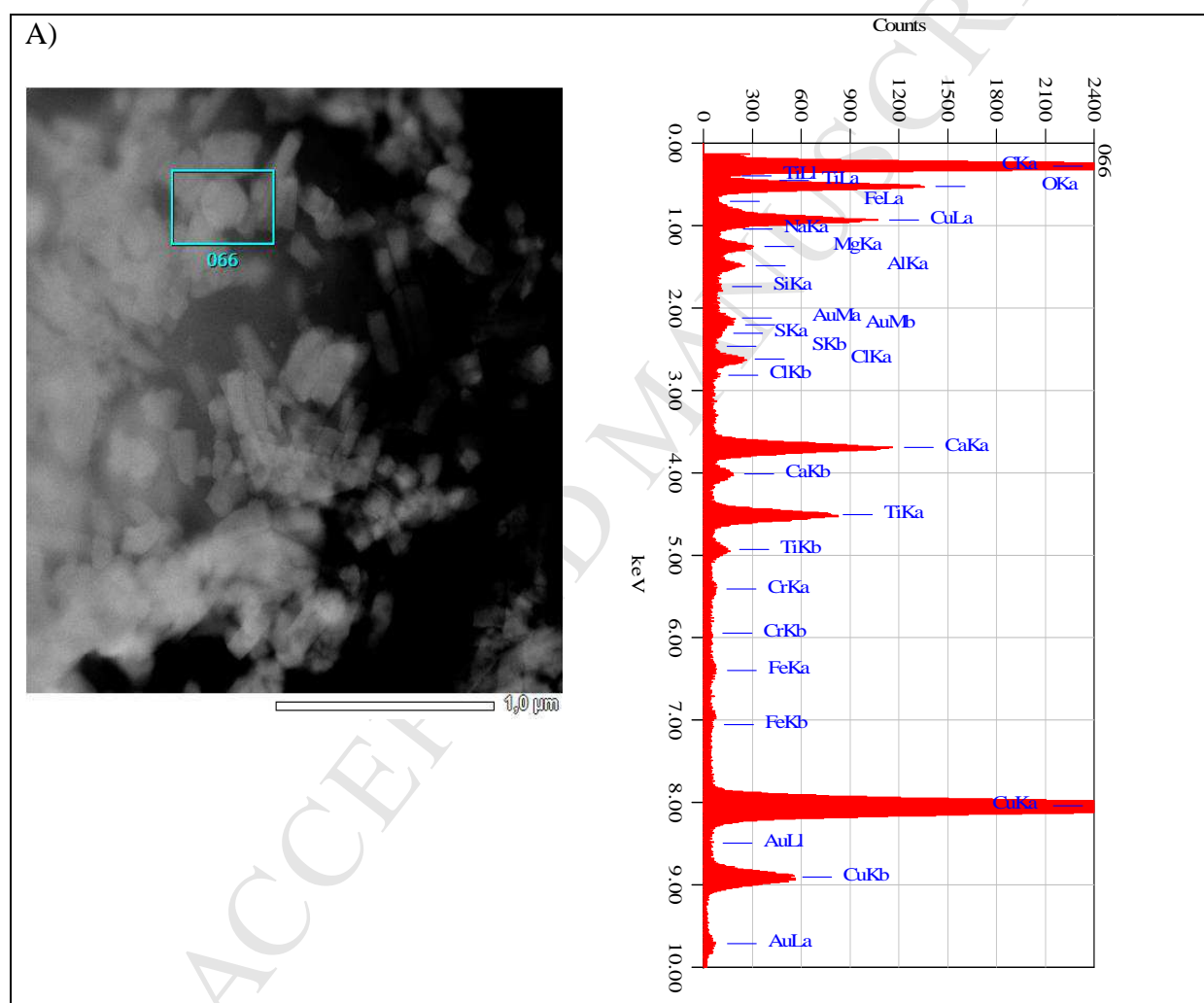


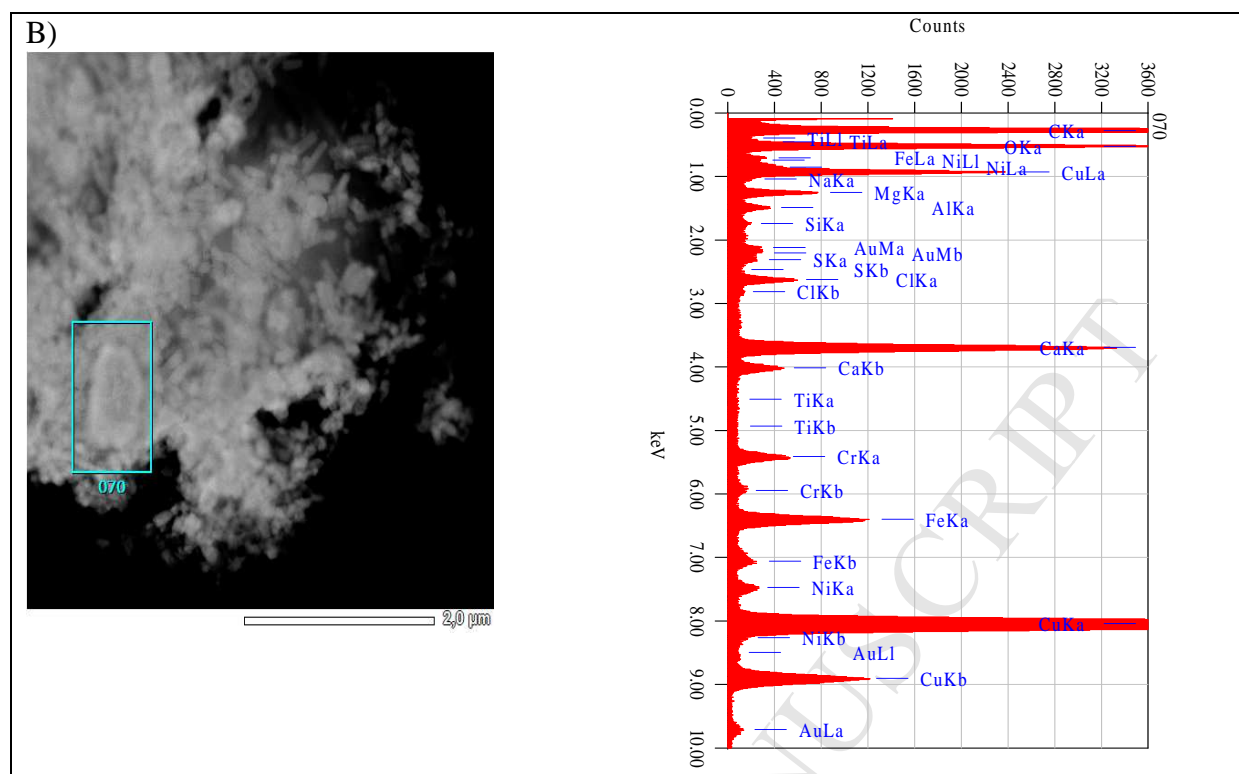
336
 337 Figure 2: Metal concentrations in mg.g^{-1} (left) and in $\mu\text{g.g}^{-1}$ (right) for the PE mesoplastic
 338 MD0518-4 sample before (plain bars) and after washing with NaOH (diagonal stripes).

339 The EDX analysis of the particles collected by gently scrubbing the surface of the
 340 mesoplastic 14MD0518-4 showed the systematic presence of the following elements in the
 341 background: C, O, Na, Cl, K, and Ca (Figure SI3). However, we also observed the
 342 presence of particles with very heterogeneous compositions. There were relatively large
 343 particles that contained Ti, for example (Figure 3A). Nanometric particles containing Fe

344 were also observed (approximately 10 nm, Figure SI4). Barium was also detected in some
345 areas; the particles were a few 10s of nm in size (Figure SI5). Chromium and Au were
346 detected as 10-nm particles (Figure SI6 and SI7). Some mineral particles of Cr, Fe, Ni, and
347 Au were observed (Figure 3B). The TEM/EDX images highlighted that metals were
348 located at the debris surface and sometimes as nanoparticles.

349





350 Figure 3: Observation by TEM (on the left) of particles extracted from the surface of the
 351 mesoplastic MD0518-4. On the right is given the elemental composition corresponding to the
 352 rectangular delimited area. A) The area shown in the rectangular frame is a few hundred
 353 nanometers in size, and the presence of Ti is clear. B) In the area shown by the rectangular
 354 frame (a few hundred nanometers in size), the particles contain significant amounts of various
 355 trace metals: Cr, Fe, Ni, and Au.

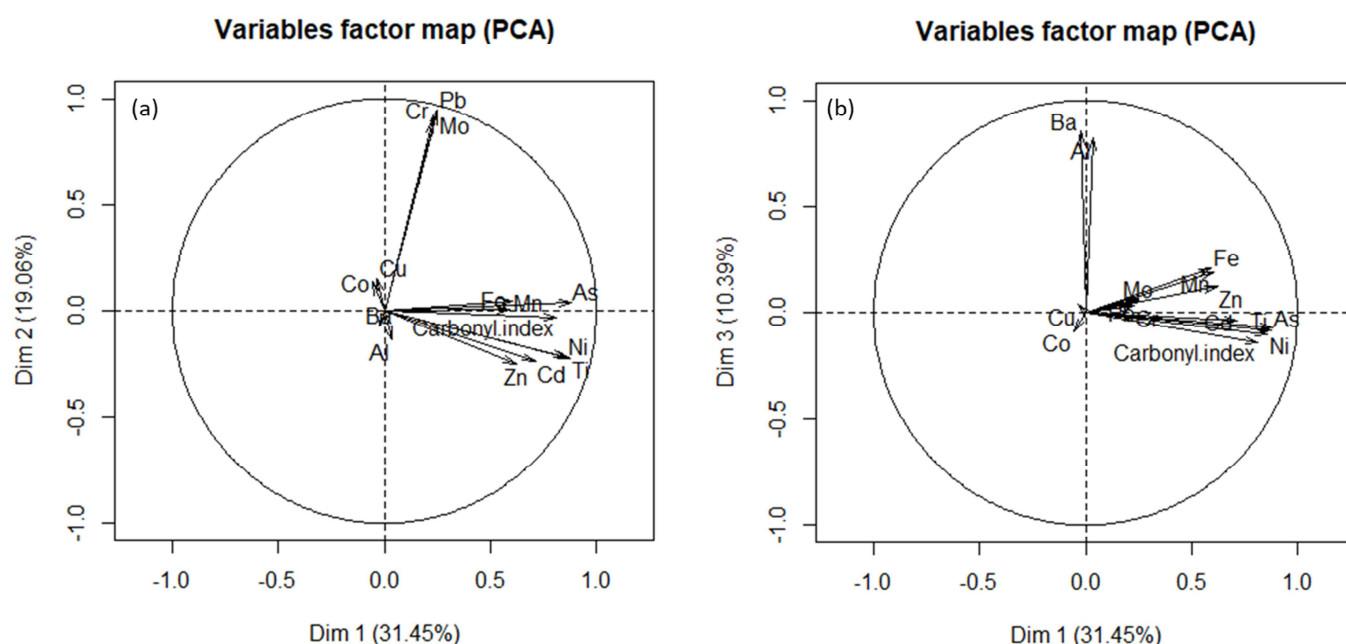
356 **Relation between elements and samples: statistical overview**

357 PCA was conducted in order to explore the origins of trace elements in plastics. Figure 4
 358 presents the biplots of the variable correlations with respect to the first two principal
 359 components. Five independent factors with eigenvalues exceeding 1 were extracted,
 360 accounting for 75% of the total variance. Three of the factors, explaining 61% of the variance,
 361 were examined in this paper: the first PC accounts for 31.5% of the variance, the second for
 362 19.0%, and the third for 10.4%. This value is the result of the high variability of the data
 363 owing to the heterogeneity of the samples and to the heterogeneity of the observations for

364 each type of samples (namely, pellets, packaging materials, and meso- and microplastics).
 365 Hierarchical clustering (Figure SI8) shows that the first sampling campaign strongly differed
 366 from the second and that the pellet and packaging samples differed. Examination of the
 367 dataset provides evidence that the elemental content of Ti was notably higher in the first
 368 campaign.

369 Considering the high elemental concentrations in mesoplastics, PC 1 was mainly
 370 attributed to the Ti, Ni, As and carbonyl indices. Cd and Zn showed loadings between 0.619
 371 and 0.880. PC2 was related to Pb, Mo and Cr, with loadings ranging from 0.898 to 0.948. PC
 372 3 was attributed to Ba and Al, with loadings of 0.852 and 0.822, respectively. The discussion
 373 of PCA focuses on the results for PC1, PC2 and PC3. The loadings for PC4 and PC5 were
 374 less than 0.630, and these PCs are not discussed.

375



376
 377 Figure 4: Principal component analysis results. (a) Biplot represents variable correlations with
 378 respect to the first two principal components (PC1 (31.45%) and PC2 (19.06%), total variance
 379 explained: 48%), and (b) Biplot represents variable correlations with respect to PC1 and PC3
 380 (10.39%) for the whole dataset (pellets, packaging, and meso- and microplastics for all the
 381 sampling campaigns).

382
383 Minor metals, such as Fe and Mn, were correlated either with As (for Fe) or with Mo, Ti and
384 Zn (for Mn). In all samples, Mn concentrations remained relatively low ($<2 \mu\text{g}\cdot\text{g}^{-1}$), while Fe
385 concentrations reached their maximum in micro- and mesoplastics, averaging $25 \mu\text{g}\cdot\text{g}^{-1}$
386 (average concentration among the data used for the PCA), which was higher than the values
387 found in pellets and packaging materials. TEM/EDX observations revealed Fe nanoparticles
388 on the weathered layers of the plastic debris; Fe was therefore mainly present here as
389 precipitated minerals. Several studies have demonstrated that polymers and plastics can trap
390 Fe particles⁴⁹⁻⁵¹. SEM/EDS only provided evidence of nano sized minerals, some of them
391 were identified as Fe oxides which are known to be strong adsorbent of As. Moreover, no As
392 was detected by EDS, indicating that As concentration are too low to allow the precipitation
393 of As as mineral. The correlation with As is explained by the high affinity of As for Fe-
394 oxides. If any other metals are correlated with Fe and Mn, they cannot act significantly as a
395 sorbent for other chemical elements. As a consequence, the results obtained here show that
396 there is no significant trace metal sorption process on the Fe and Mn oxides present on the
397 weathered layers of plastic debris. This was also observed with the second PCA, which was
398 performed without the samples from the first campaign. The carbonyl index, which
399 fingerprints the plastic degradation progress, was correlated with some chemical elements,
400 such as As, Cd, Ni, Fe and Ti (the Spearman coefficients for the carbonyl index with As, Cd,
401 Ni, Fe and Ti were 0.64, 0.51, 0.51, 0.58 and 0.50, respectively). These correlations provide
402 evidence that degradation drives the increase in some chemical element concentrations on
403 plastic debris. In contrast, a significant positive correlation also existed among Pb, Cr and Mo,
404 which explains PC2. These 3 elements are commonly used together in formulations. Their
405 presence in plastics can therefore be explained as residues of the plastic fabrication process.

406 PC3 displayed a positive correlation between Al and Ba (Spearman coefficient =
407 0.41): Ba is used in plastics as a stabilizer or pigment, and Al is used as a pigment. Several

408 samples, notably yellow or purple plastic debris materials, presented high amounts of both Al
409 and Ba, suggesting that these elements may be used together in the formulation of plastics.
410 However, we cannot exclude that Ba and Al precipitated on the weathered surface layer of the
411 altered plastics debris, since both Ba and Al minerals were detected by TEM/EDX,
412 PCA statistical analysis shows that the amounts of chemical elements are mainly a
413 consequence of their use as additives in PE formulation. Their increase in meso- and
414 microplastics compared with their values in packaging may be, for several of the elements,
415 correlated to the carbonyl index (Figure 4); we can thus conclude that plastic degradation
416 might be a significant factor in the increase in quantities of chemical elements.

417 In summary the analysis of plastic debris collected in the North Atlantic subtropical gyre
418 revealed wide-ranging concentrations of metals. The metal concentrations followed the order
419 of plastic debris > new packaging materials > preproduction pellets. The results demonstrated
420 that there are two main source of metals on plastic debris are i) the additives initially
421 incorporated in the plastic and ii) the metals resulting from adsorption and precipitation on
422 plastics.

423 **Conclusion**

424 Plastic debris represents a potential source of toxic metals that can be released in the ocean
425 through weathering but also represents a sink as a support for nanoparticles or trace elements.
426 However, further studies are needed to identify the exact mechanisms that account for the
427 increase in metal concentrations on plastics debris (formation of new binding sites, use of
428 weathering layers as a precipitation nucleus, etc.). This study demonstrates that the
429 ingredients introduced in plastics, however, could present environmental and health concerns
430 even if they are designed not to leach from the product during its use. Plastic debris can be a

431 potential source of metals for aquatic organisms as well as sea birds, and the associated risk
432 should be further assessed.

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564

565

Plastic debris collected from the North Atlantic subtropical gyre was analyzed for trace metals

It is evidence that plastic oxidation favors the adsorption of some such as As, Ti, Ni, Cd

The presence of mineral particles on the surface of the plastic debris was evidenced by microscopy

Plastics initially contain important amounts of metals resulting from intrinsic plastic additives

Marine plastic debris carry complex mixtures of heavy metals