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Trace metals in polyethylene debris from the North Atlantic subtropical gyre

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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

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

CAPSULE

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

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

Introduction

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

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

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

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

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

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

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

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

EXPERIMENTAL SECTION

Sample origin

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

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

Fourier transform infrared (FTIR) spectroscopy

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

Trace metal analysis

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

AMA254, ®LECO) after combustion and gold-trapping directly on the dried plastic debris. The recoveries of Zn, Cd, Sb, Pb and Hg from the ERM-EC680K standard were close to 100%, whereas those of Cr, As and Sn were 55%, 63%, and 53%, respectively, suggesting that the measured Cr, Sn and As concentrations may be slightly underestimated in the microplastic debris. Limits of detection were respectively 91 and 11 ng.g⁻¹ for Ca and K, 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 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 lower than 0.01 ng.g⁻¹ for Mo, Th and U.

Transmission electron microscopy

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

Soda washing of the mesoplastic

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

Statistical analyses

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

RESULTS AND DISCUSSION

Metal concentrations in PE virgin pellets

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

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

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

Metal concentrations in new packaging materials

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

Antioxidants and UV stabilizers are often based on Ti (usually added at values between 0.5 and 5% w/w³⁷). Other metals, such as Cd, Zn, Ba and Pb, are used as stabilizers in PE 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 $\mu\text{g.g}^{-1}$ 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

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

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

Metal concentrations in plastic debris from the North Atlantic subtropical gyre

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Relation between elements and samples: statistical overview

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

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

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

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

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

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

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

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

Conclusion

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

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

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References

1. Rochman, C. M.; Browne, M. A.; Halpern, B. S.; Hentschel, B. T.; Hoh, E.; Karapanagioti, H. K.; Rios-Mendoza, L. M.; Takada, H.; Teh, S.; Thompson, R. C., 2013. Classify plastic waste as hazardous. *Nature* 494, 169-171.
2. Law, K. L.; Moret-Ferguson, S. E.; Goodwin, D. S.; Zettler, E. R.; De Force, E.; Kukulka, T.; Proskurowski, G., 2014. Distribution of Surface Plastic Debris in the Eastern Pacific Ocean from an 11-Year Data Set. *Environ. Sci. Technol.* 48, 4732-4738.
3. Schlining, K.; von Thun, S.; Kuhn, L.; Schlining, B.; Lundsten, L.; Stout, N. J.; Chaney, L.; Connor, J., 2013. Debris in the deep: Using a 22-year video annotation database to survey marine litter in Monterey Canyon, central California, USA. *Deep Sea Res. Part 1 Oceanogr. Res. Pap.* 79, 96-105.
4. Bakir, A.; Rowland, S. J.; Thompson, R. C., 2014. Transport of persistent organic pollutants by microplastics in estuarine conditions. *Estuar. Coast. Shelf. S.* 140, 14-21.
5. Eerkes-Medrano, D.; Thompson, R. C.; Aldridge, D. C., 2015. Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Res* 75, 63-82.
6. Eriksen, M.; Mason, S.; Wilson, S.; Box, C.; Zellers, A.; Edwards, W.; Farley, H.; Amato, S., 2013. Microplastic pollution in the surface waters of the Laurentian Great Lakes. *Mar. Pollut. Bull.* 77, 177-182.
7. Wright, S. L.; Thompson, R. C.; Galloway, T. S., 2013. The physical impacts of microplastics on marine organisms: A review. *Environ. Pollut.* 178, 483-492.
8. Gall, S. C.; Thompson, R. C., 2015. The impact of debris on marine life. *Mar. Pollut. Bull.* 92, 170-179.
9. Goldstein, M. C.; Carson, H. S.; Eriksen, M., 2014. Relationship of diversity and habitat area in North Pacific plastic-associated rafting communities. *Mar. Biol.* 161, 1441-1453.
10. Zettler, E. R.; Mincer, T. J.; Amaral-Zettler, L. A., 2013. Life in the "Plastisphere": Microbial Communities on Plastic Marine Debris. *Environ. Sci. Technol.* 47, 7137-7146.
11. Carlton, J. T.; Chapman, J. W.; Geller, J. B.; Miller, J. A.; Carlton, D. A.; McCuller, M. I.; Treneman, N. C.; Steves, B. P.; Ruiz, G. M., 2017. Tsunami-driven rafting: Transoceanic species dispersal and implications for marine biogeography. *Science* 357, 1402-1405.

12. Engler, R. E., 2012. The Complex Interaction between Marine Debris and Toxic Chemicals in the Ocean. *Environ. Sci. Technol.* **46**, 12302-12315.
13. Rochman, C. M.; Hoh, E.; Hentschel, B. T.; Kaye, S., 2013. Long-Term Field Measurement of Sorption of Organic Contaminants to Five Types of Plastic Pellets: Implications for Plastic Marine Debris. *Environ. Sci. Technol.* **47**, 1646-1654.
14. Lithner, D.; Larsson, A.; Dave, G., 2011. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. *Sci Total Environ* **409**, 3309-3324.
15. Rochman, C. M.; Kurobe, T.; Flores, I.; Teh, S. J., 2014. Early warning signs of endocrine disruption in adult fish from the ingestion of polyethylene with and without sorbed chemical pollutants from the marine environment. *Sci Total Environ* **493**, 656-661.
16. Tanaka, K.; Takada, H.; Yamashita, R.; Mizukawa, K.; Fukuwaka, M.; Watanuki, Y., 2013. Accumulation of plastic-derived chemicals in tissues of seabirds ingesting marine plastics. *Mar. Pollut. Bull.* **69**, 219-222.
17. Wardrop, P.; Shimeta, J.; Nuggeoda, D.; Morrison, P. D.; Miranda, A.; Tang, M.; Clarke, B. O., 2016. Chemical Pollutants Sorbed to Ingested Microbeads from Personal Care Products Accumulate in Fish. *Environ. Sci. Technol.* **50**, 4037-4044.
18. *Emission scenario document on plastic additives. OECD Environmental Health and Safety Publications*; Paris, 2004.
19. Turner, A., 2018. Concentrations and Migratabilities of Hazardous Elements in Second-Hand Children's Plastic toys. *Environ. Sci. Technol.* **52**, 3110-3116.
20. Turner, A., 2018. Mobilisation kinetics of hazardous elements in marine plastics subject to an avian physiologically-based extraction test. *Environ. Pollut.* **236**, 1020-1026.
21. Holmes, L. A.; Turner, A.; Thompson, R. C., 2014. Interactions between trace metals and plastic production pellets under estuarine conditions. *Mar Chem* **167**, 25-32.
22. Rochman, C. M.; Hentschel, B. T.; Teh, S. J., 2014. Long-Term Sorption of Metals Is Similar among Plastic Types: Implications for Plastic Debris in Aquatic Environments. *PLoS ONE* **9**.
23. Holmes, L. A.; Turner, A.; Thompson, R. C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. *Environ. Pollut.* **160**, 42-48.
24. Ashton, K.; Holmes, L.; Turner, A., 2010. Association of metals with plastic production pellets in the marine environment. *Mar. Pollut. Bull.* **60**, 2050-2055.
25. Brennecke, D.; Duarte, B.; Paiva, F.; Cacador, I.; Canning-Clode, J., 2016. Microplastics as vector for heavy metal contamination from the marine environment. *Estuar. Coast. Shelf. S.* **178**, 189-195.
26. Imhof, H. K.; Laforsch, C.; Wiesheu, A. C.; Schmid, J.; Anger, P. M.; Niessner, R.; Ivleva, N. P., 2016. Pigments and plastic in limnetic ecosystems: A qualitative and quantitative study on microparticles of different size classes. *Water Res* **98**, 64-74.
27. Turner, A.; Solman, K. R., 2016. Analysis of the elemental composition of marine litter by field-portable-XRF. *Talanta* **159**, 262-271.
28. Turner, A., 2017. Trace elements in fragments of fishing net and other filamentous plastic litter from two beaches in SW England. *Environ. Pollut.* **224**, 722-728.
29. Turner, A., 2016. Heavy metals, metalloids and other hazardous elements in marine plastic litter. *Mar. Pollut. Bull.* **111**, 136-142.
30. Lavers, J. L.; Bond, A. L., 2016. Ingested plastic as a route for trace metals in Laysan Albatross (*Phoebastria immutabilis*) and Bonin Petrel (*Pterodroma hypoleuca*) from Midway Atoll. *Mar. Pollut. Bull.* **110**, 493-500.
31. Anderson, A.; Andrady, A.; Hidalgo-Ruz, V.; Kershaw, P. J. *Sources, fate and effects of microplastics in the marine environment: a global assessment*; GESAMP Joint group of experts on the scientific aspects of marine environmental protection: 2015.
32. Moret-Ferguson, S.; Law, K. L.; Proskurowski, G.; Murphy, E. K.; Peacock, E. E.; Reddy, C. M., 2010. The size, mass, and composition of plastic debris in the western North Atlantic Ocean. *Mar. Pollut. Bull.* **60**, 1873-1878.

33. ter Halle, A.; Ladirat, L.; Gendre, X.; Goudouneche, D.; Pusineri, C.; Routaboul, C.; Tenailleau, C.; Duployer, B.; Perez, E., 2016. Understanding the Fragmentation Pattern of Marine Plastic Debris. *Environ. Sci. Technol.* **50**, 5668-5675.
34. Wang, J. D.; Peng, J. P.; Tan, Z.; Gao, Y. F.; Zhan, Z. W.; Chen, Q. Q.; Cai, L. Q., 2017. Microplastics in the surface sediments from the Beijiang River littoral zone: Composition, abundance, surface textures and interaction with heavy metals. *Chemosphere* **171**, 248-258.
35. Ter Halle, A.; Ladirat, L.; Martignac, M.; Mingotaud, A. F.; Boyron, O.; Perez, E., 2017. To what extent are microplastics from the open ocean weathered? *Environ. Pollut.* **227**, 167-174.
36. Murphy, J., *Additives for plastic handbook*. Elsevier Advanced Technology: Oxford, UK, 2003.
37. Cordeiro, F.; Baer, I.; Robouch, P.; Emteborg, H.; J., C.-G.; Korsten, B.; B., d. I. C., IMEP-34: Heavy metals in toys according to EN 71-3:1994. JCR. In Luxembourg, 2012; p 58pp.
38. *Hazardous substances in plastic materials*, COWI Danish Technological Institute; 2013.
39. Bylan, C., *Developments in colorants for plastics*. 2003; Vol. 14, p 85.
40. Marier, C.; Calafut, C., *Polypropylene: the Definitive User's Guide and Databook*. Norwich NY, 1998.
41. Lazzeria, A.; Zebarjadb, S. M.; Parcellac, M.; Cavalierd, K.; Rosam, R., 2005. Filler toughening of plastics. Part 1-The effect of surface interactions on physico-mechanical properties and rheological behaviour of ultrafine CaCO₃/HDPE nanocomposites. *Polymer* **46**, 827-844.
42. Rizzotto, M., Chapter 5 Metal complexes as antimicrobial agents In *A search for antibacterial agents*, Bobbarala, V., Ed. 2012; p 73.
43. RoHS. Restriction of hazardous Substances, Eu Directive 2002/95/EC, <http://www.rohsguide.com/rohs-substances.htm>. In 2006 (accessed May 2017).
44. Hansen, E.; Nilsson, N. H.; Lithner, D.; Lassen, C., Hazardous substances in plastic materials, COWI and the Danish technological institute on behalf of thr Norwegian Climate and Pollution Agency. In Oslo, 2010; p 150 pp.
45. Nziguheba, G.; Smolders, E., 2008. Inputs of trace elements in agricultural soils via phosphate fertilizers in European countries. *Sci Total Environ* **390**, 53-57.
46. Jiao, W. T.; Chen, W. P.; Chang, A. C.; Page, A. L., 2012. Environmental risks of trace elements associated with long-term phosphate fertilizers applications: A review. *Environ. Pollut.* **168**, 44-53.
47. Massos, A.; Turner, A., 2017. Cadmium, lead and bromine in beached microplastics. *Environ. Pollut.* **227**, 139-145.
48. Hirai, H.; Takada, H.; Ogata, Y.; Yamashita, R.; Mizukawa, K.; Saha, M.; Kwan, C.; Moore, C.; Gray, H.; Laursen, D.; Zettler, E. R.; Farrington, J. W.; Reddy, C. M.; Peacock, E. E.; Ward, M. W., 2011. Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. *Mar. Pollut. Bull.* **62**, 1683-1692.
49. Belzile, N.; Devitre, R. R.; Tessier, A., 1989. Insitu Collection of Diagenetic Iron and Manganese Oxyhydroxides from Natural Sediments. *Nature* **340**, 376-377.
50. Fakih, M.; Davranche, M.; Dia, A.; Nowack, B.; Petitjean, P.; Chatellier, X.; Gruau, G., 2008. A new tool for in situ monitoring of Fe-mobilization in soils. *Appl Geochem* **23**, 3372-3383.
51. Al-Sid-Cheikh, M.; Pedrot, M.; Dia, A.; Guenet, H.; Vantelon, D.; Davranche, M.; Gruau, G.; Delhay, T., 2015. Interactions between natural organic matter, sulfur, arsenic and iron oxides in re-oxidation compounds within riparian wetlands: NanoSIMS and X-ray adsorption spectroscopy evidences. *Sci Total Environ* **515**, 118-128.

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