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

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

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

Introduction

Thousands of metric tons of plastics debris¹ have been released into the environment since the 1950s, and the public is becoming ever-more aware of the negative impacts of plastic debris on living organisms. These impacts can occur directly through the presence or accumulation of plastics, or indirectly via their associated pollutants (organic and inorganic), also known as the Trojan horse effect². From the various chemicals possibly carried by plastics debris, metal and metalloid elements are most used, by relative mass, in plastics³. Metals and metalloids are added as plasticizers, flame retardants, antioxidants, pigments, and more.⁴ (Throughout this paper, when the word “elements” is used, it is to mean metal and metalloid elements.) As other carbon-based particles are released in the environment, aging plastics debris can act as a support for biofilms or, in response to (photo)chemical oxidation of their surface functional groups, both biofilms and surface groups can adsorb metalloids^{5,6}.

Metals and metalloids can be highly toxic when inadvertently consumed in aging plastic debris, as these elements are released from the sorbent under acidic digestive conditions (i.e., they become bioavailable through biological digestion processes). There is now clear evidence that chemicals associated with nanoplastics impact aquatic organisms’ metabolism much more than the same pristine polymer without metal additives⁷. Measuring metals’ relative bioavailability remains challenging, given their surface and/or core distribution in the plastics. From the surface to the core, element exchangeability and bioavailability decrease. However, after a long residence time in the environment, plastics can undergo highly oxidative conditions, which partly alter the surface of plastics and can induce the release of additives (i.e. elements). To evaluate the potential health risks induced by the ingestion of plastics by the biota, it is thus crucial to determine the total concentrations of each element and to discriminate between which elements are labile, and which are incorporated into

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

The additive elements can be identified by measuring the depth distribution of element concentrations in the plastic by laser ablation (LA) inductively coupled plasma mass spectrometry (ICP-MS)⁸. However, only a few elements can be measured in plastic reference materials this way, and it is a time-consuming method. Another possibility is to perform a double extraction of elements: (i) from an acidic leaching to determine which elements are labile and (ii) from an acidic digestion to determine total element concentrations. Numerous studies have determined total metals concentrations in plastics by X-ray fluorescence spectrometry (XRF)^{9–28}, but this will be the first time for this joint approach consisting of coupling acidic leaching and digestion to ICP-MS or ICP-AES (atomic emission spectrometry) measurements. Our innovative approach aims to determine which elements are additive or adsorbed to the plastics, and their bioavailability to the biota.

Material & Methods

Geographic area and collection

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

Acidic leaching and acidic digestion

Microplastics were first washed with deionized (DI) water under agitation to desorb (detach) any biofilms and natural organic matter residues that often occur with microplastics in the environment²⁵. Then 1 g of each coloured microplastic was mixed with 0.1 M HNO₃ (ultrapure grade) for 48 h. Microplastics were then removed from the solution by filtration through a 0.2 µm filter. The solution (<0.2 µm) was further analysed by ICP-MS. Finally, microplastic pieces were acid-digested using a multistep procedure with a microwave oven (UltraWAVE system from Milestone; 110°C for 10 min, then 180°C for 10 min, 230°C for 20 min and 230°C for 5 min). Prior to elemental analyses, samples were evaporated, dried, and then resolubilized with HNO₃ at 0.37 M.

Metal concentrations analysis

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

Results and discussion

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

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

Identification of the elements nature in the different coloured microplastics

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

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

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

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

- **Blue:** Both Cu and Ba present large S values (814 and 2360 nmol g⁻¹, respectively) in blue plastics compared to other colours of microplastics. This might be explained by the use of the inorganic blue pigments BaCuSi₂O₆ and 2CuCO₃·Cu(OH)₂.
- **Red:** Ba and V have high S values (189 and 8 nmol g⁻¹, respectively) in red plastics compared to other colours of microplastics. However, to our knowledge those elements are not used as red pigments, but Ba is a well-known filler in plastics. Unfortunately, very little information is available on V as an additive. However, trace elements were found in fly ash used for building materials, concrete modification, composite and polyester mortar, which might explain its presence as additive³.
- **Green:** Five elements present large S values in the green microplastics: Pb (615.90 nmol g⁻¹), Cr (485.68 nmol g⁻¹), Cu (344.21 nmol g⁻¹), Ba (141.40 nmol g⁻¹) and Cd (60.50 nmol g⁻¹). The presence of Cd, Cr and Cu should be explained by the use of green pigments, such as phthalocyanine green (Cu organic complex), Cu(CH₃COO)₂·H₂O, CuCO₃·Cu(OH)₂, Cr₂O₃·2H₂O, and/or a mix of CdS and Cr₂O₃.
Pb and Ba are not used as green pigments, but they are used as yellow pigments as Pb₃(SbO₄)₂, PbCrO₄ or Pb₂SnO₄ and BaCrO₄, which likely explains their presence. Since Sb and Sn were not analysed in our study, it is impossible to know if Pb₃(SbO₄)₂ and Pb₂SnO₄ were used in this sample. The presence of Cr as an additive might confirm the use of PbCrO₄ and BaCrO₄.
The use of Pb and Ba for other properties can not also be excluded. Pb and Ba are also largely used in plastic formulations as heat stabilisers, antioxidants, UV stabilisers (Pb), and fillers (Ba). The presence of Cd and Pb as additives in green microplastics from this sampling site was confirmed by El Hadri et al.⁸ using LC-ICP-MS (Table S4).

- Orange:** Five elements have large S values in orange plastics: Al ($122.82 \mu\text{mol g}^{-1}$), Zn ($8820.68 \text{ nmol g}^{-1}$), Cd ($426.48 \text{ nmol g}^{-1}$), Ba ($68.32 \text{ nmol g}^{-1}$), and V ($53.20 \text{ nmol g}^{-1}$). The presence of Cd might be explained by the use of the orange pigment CdS. The presence of Zn, Ba and V might be explained either by their use as yellow pigments or for other properties. Other yellow pigments include BiVO_4 , $\text{K}_2\text{O}_4\text{ZnCrO}_4(\text{H}_2\text{O})_3$, BaCrO_4 . However, Ba and Zn are also well-known fillers and Zn is also a flame retardant. To our knowledge, no common orange, red or yellow pigments contain Al. Thus, Al's presence in this sample as an additive is likely due to its use as flame retardant. Note that El Hadri et al.⁸ showed that Cd was present as an additive in orange microplastics by LC-ICP-MS analysis (Table S4).
- Grey and Black:** Five elements have large S values in grey and black plastics: Cu ($402.12 \text{ nmol g}^{-1}$), Pb ($180.13 \text{ nmol g}^{-1}$), Cr ($174.77 \text{ nmol g}^{-1}$), Mn ($75.72 \text{ nmol g}^{-1}$) and Cd ($49.77 \text{ nmol g}^{-1}$). Large Mn and Cd concentrations could be explained by the use of Cd-Mn pigments. The presence of Cu, Pb and Cr as additives are either explained by their use as a mix of different pigments to obtain the black colour, or their use for properties other than pigments in this sample. Note that the presence of Pb as an additive was also highlighted by El Hadri et al.⁸ in grey microplastics from the same field site analysed by LC-ICP-MS (Table S4).
- Yellow and White:** No element has a large S in yellow or white microplastics. Therefore, no additive elements are highlighted in these microplastics.

Release of additives

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

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

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

Bioavailability of adsorbed and additive elements

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

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

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

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

Conclusion

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

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

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

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Supporting information:

**Metals in microplastics: determining which are
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Section S1: Materials and methods

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

The matrix of reference materials (ERM-EC 680 and ERM-EC 681) is composed of polyethylene supplemented with various concentrations of inorganic additives including As, Cd, Cr, Pb and Zn. Concentrations were validated for As (-0.56 and 9.26% of error), Cd (-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 and -7.75% of error).

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%

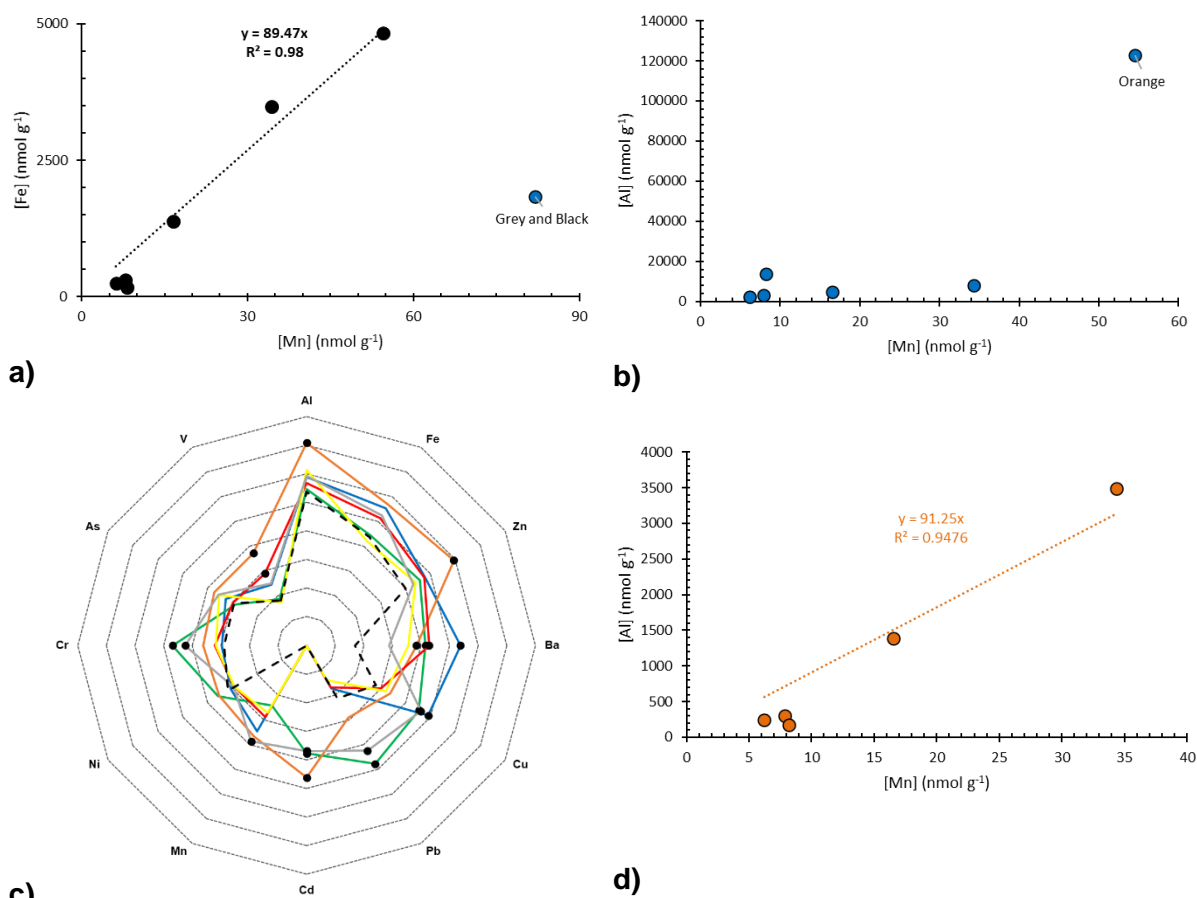
Zn	66	No Gas		3%	3%	5%	5%	10%
Zn	66	He	3%	3%	3%	5%	5%	10%
As	75	He		3%	3%	5%	5%	10%
Cd	111	No Gas		3%	3%	5%	5%	10%
Ba	138	No Gas	3%	3%	3%	3%	5%	10%
Pb	208	No Gas			3%	3%	5%	10%

330

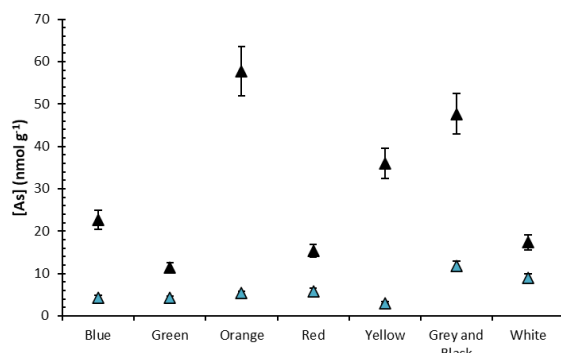
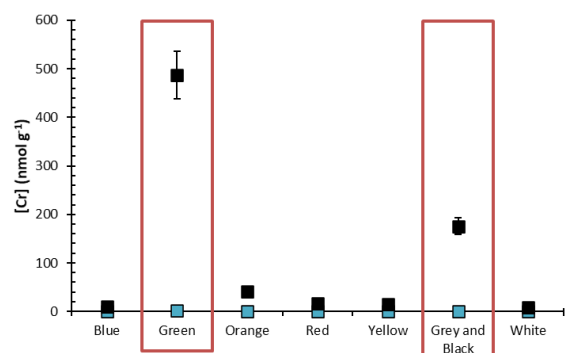
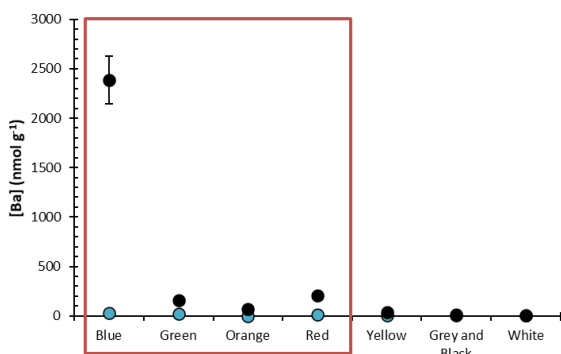
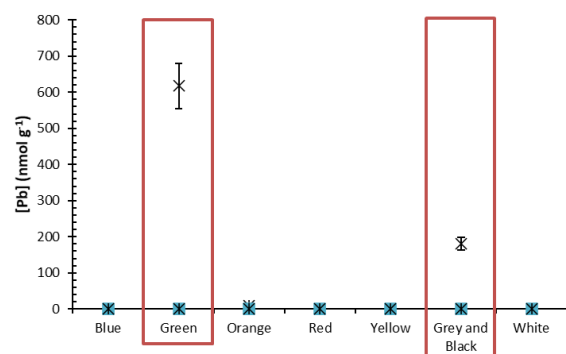
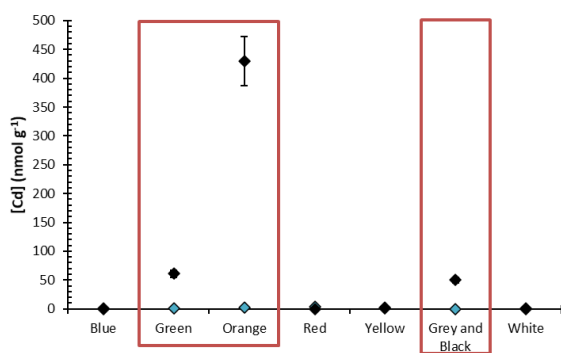
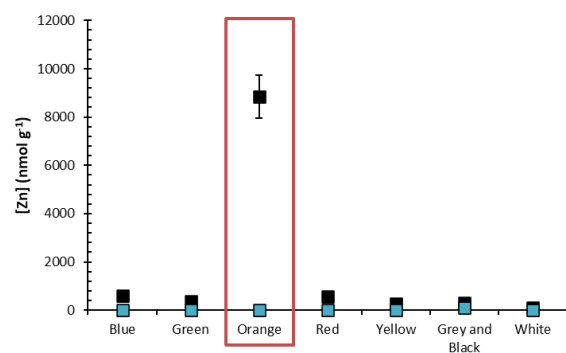
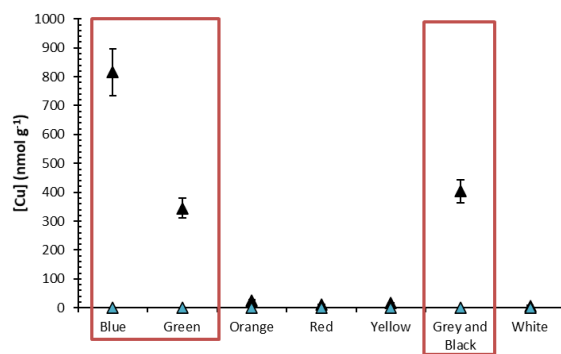
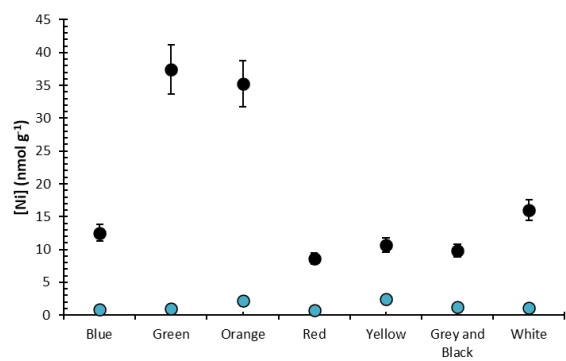
Section S2: Identification of the elements nature

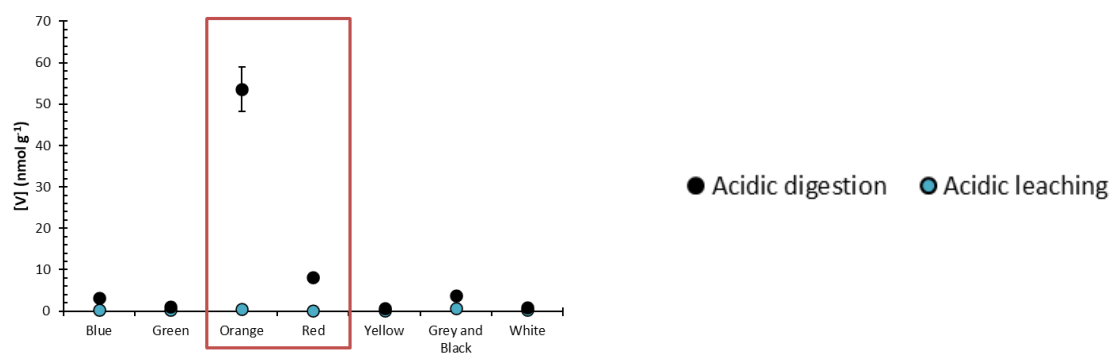
Due to their similar chemical behaviour, Fe and Mn concentrations in water are usually related by a linear relationship. Interestingly, Fe and Mn also show this linear relationship in all the coloured microplastics, except for the grey and black microplastics (Figure S1a). There are three factors that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

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c) Figure 1 : Linear relationship between (a) Fe and Mn and (b) Al and Mn concentrations with the orange microplastics and (c) without the orange microplastics. d) S values obtained from acidic leaching and digestion for Al, Fe, Zn, Ba, Cu, Pb, Cd, Mn, Ni, Cr, As and V elements; high S values indicate these are additives in 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	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	CoAl_2O_4
		$\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$
Red	Pompeiiian Red	Iron oxide + clay and quartz
	Chrome Red	PbO PbCrO_4
	Cadmium Red	$\text{Cd}(\text{S}, \text{Se})$
	Red Lead	Pb_3O_4
	Red Ochre	Hematite (Iron oxide)
	Vermilion	HgS
	Realgar	As_4S_4
Yellow	Raw Sienna	Iron oxide + small amounts of Mn oxides
	Bismuth Vanadate	BiVO_4
	Yellow	$\text{K}_2\text{O } 4\text{ZnCrO}_4(\text{H}_2\text{O})_3$
	Zinc Yellow	BaCrO_4
	Lemon Yellow	$\text{K}_3[\text{Co}(\text{NO}_2)_6]$
	Cobalt Yellow	$\text{Pb}_3(\text{SbO}_4)_2$
	Naples Yellow	CdS
	Cadmium Yellow	Iron oxides
	Yellow Ochre	As_2S_3
	Orpiment	PbCrO_4
	Chrome Yellow	

	Lead-Tin Yellow	Pb_2SnO_4
Green	Phthalocyanine Green Cobalt Titanate Green Verdigris Green Earth Malachite Viridian Emerald Green Cadmium Green	Cu organic complex Co_2TiO_4 $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ $\text{K}[(\text{Al}, \text{Fe}^{\text{III}}), (\text{Fe}^{\text{II}}, \text{Mg})(\text{AlSi}_3, \text{Si}_4)\text{O}_{10}(\text{OH})_2]$ $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ $\text{Cr}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$ $3 \text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{CH}_3\text{COO})_2$ mix of CdS and Cr_2O_3
Orange	Antimony Orange Cadmium Orange Chrome Orange Orange Ochre Realgar	$2 \text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$ CdS $\text{PbO} \cdot \text{PbCrO}_4$ Iron oxides AsS, As_2S_2 or As_4S_4
Grey and Black	Spinel black Manganese Black	MnFe_2O_4 Manganese and Iron oxides
White	Titanium Dioxide White Calcite Zinc White Lead White	TiO_2 CaCO_3 ZnO $2 \text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$

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
Ca	- 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)*

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

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

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

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Figures:

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Metals in microplastics: determining which are additive, adsorbed, and bioavailable

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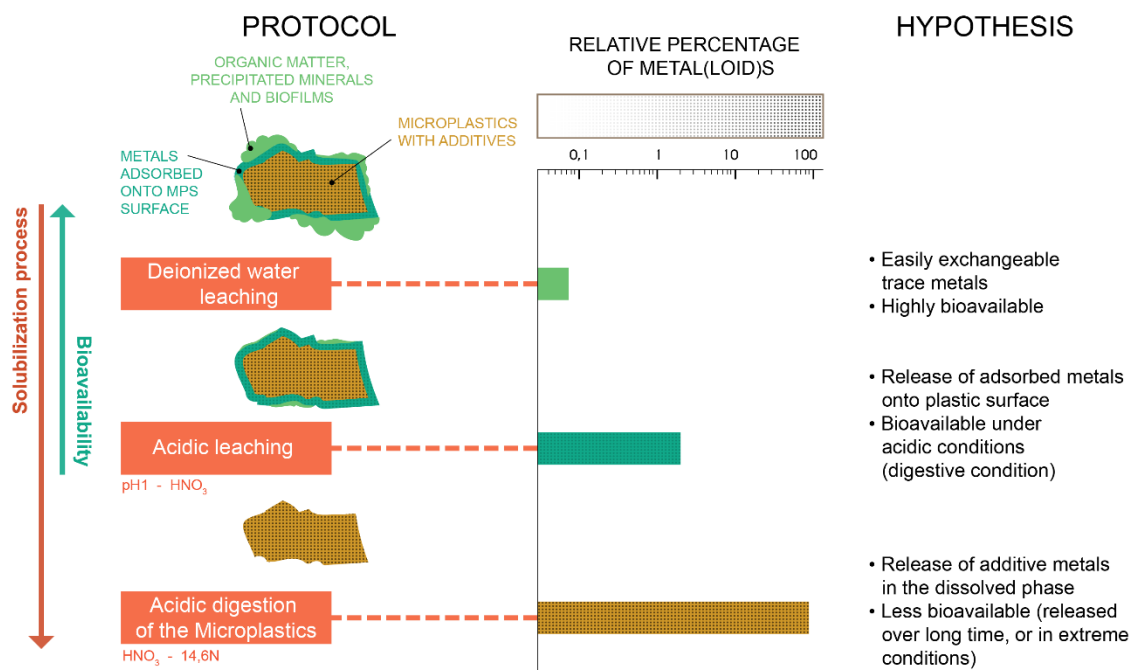


Figure 3: Protocol developed in our study and linked hypothesis

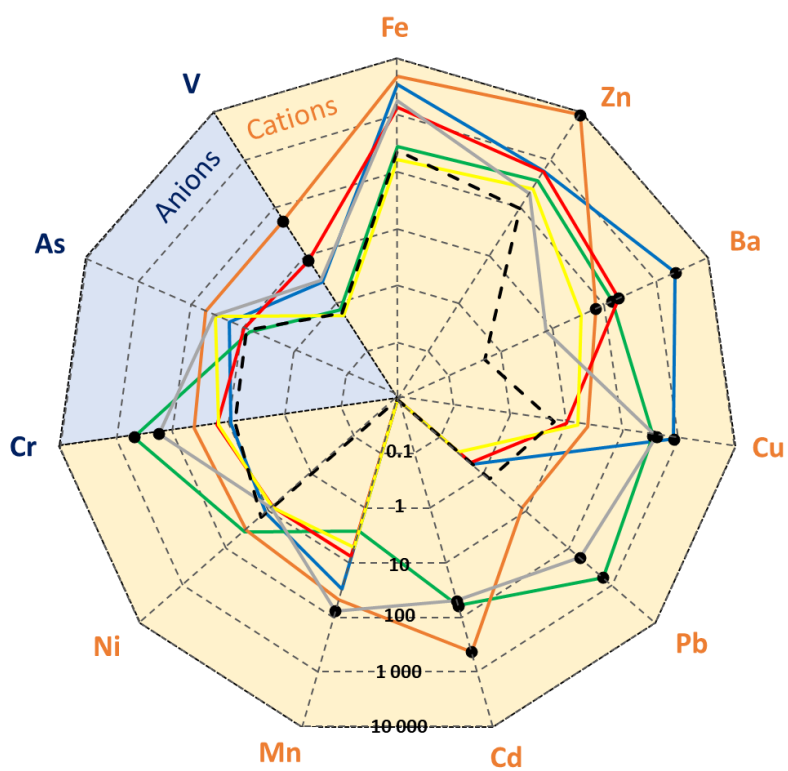
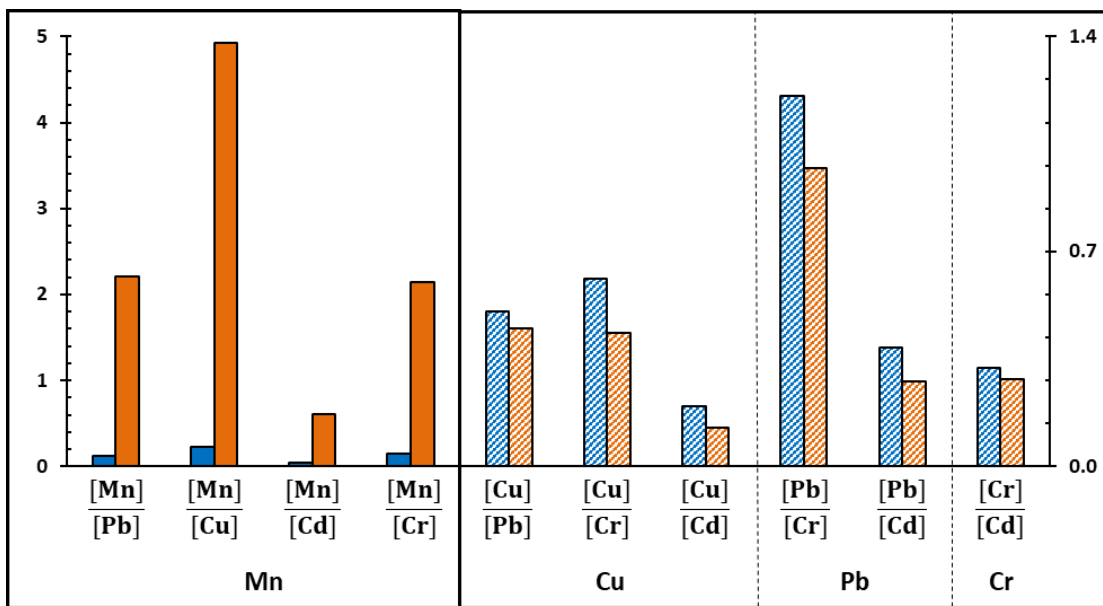
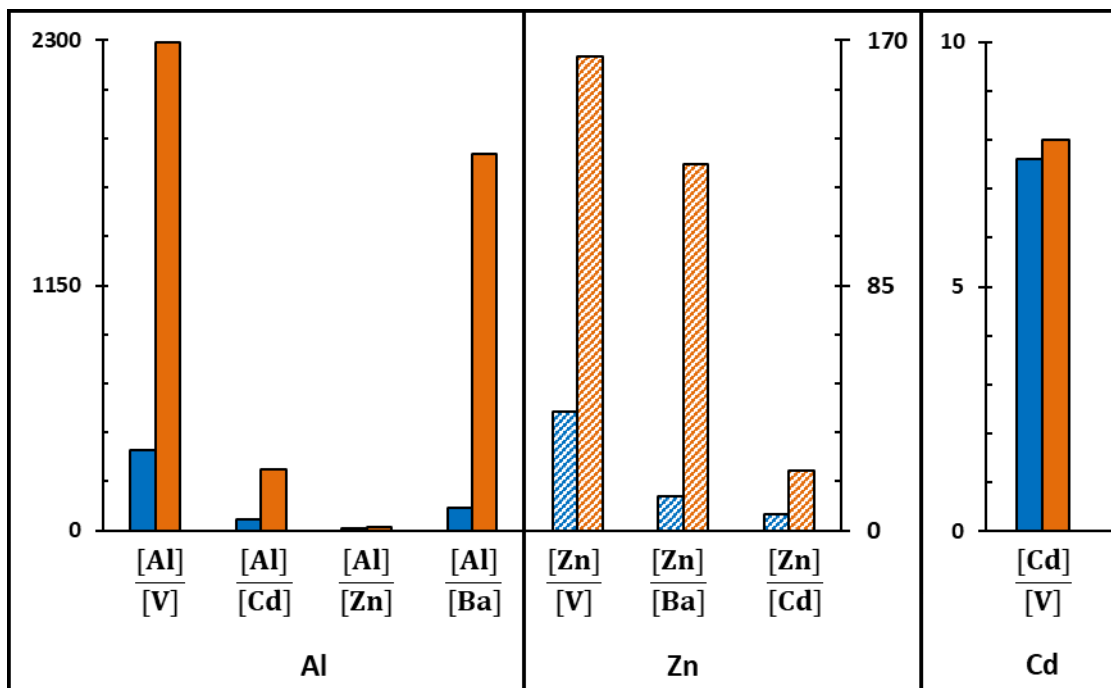


Figure 4: S values obtained from acidic leaching and digestion for Fe, Zn, Ba, Cu, Pb, Cd, Mn, Ni, Cr, As and V. For Al, see FIGURE 1 in SI. Metal(loid)s, with low S values (close to the centre) are mainly sorbed onto microplastics. Metal(loid)s, with high S values are additives in the microplastics.



a)



b)

■ Acidic leaching ■ Acidic digestion

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