Supporting information:

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

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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 S1: Quantification limit of the ICP-MS.

Element	*Isotope*	Mode	<1000 ppb	< 100 ppb	< 10 ppb	<1 ppb	<0,5ppb	< 0,1 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%

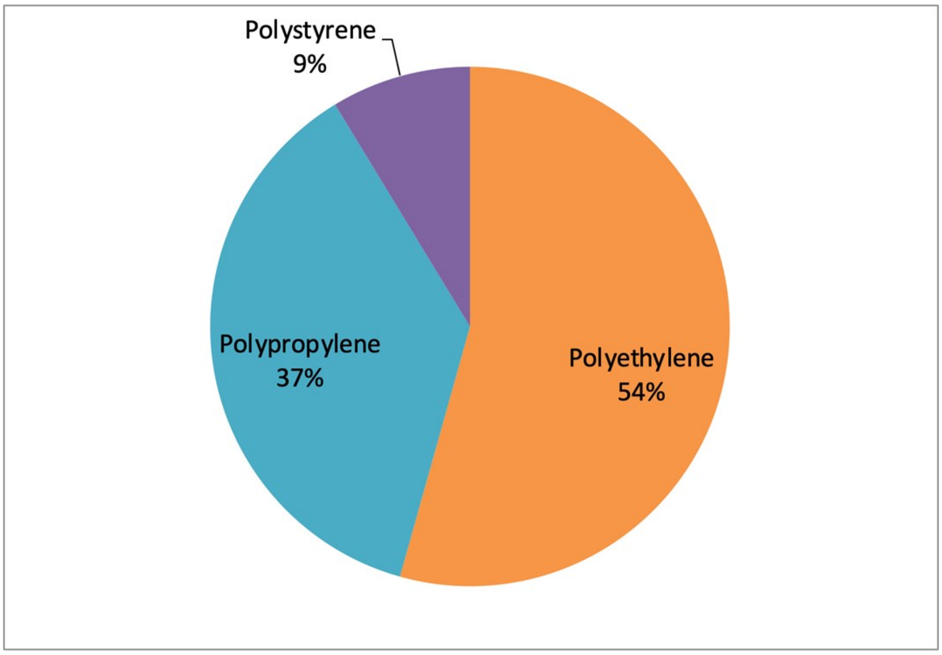

Figure S1: Distribution of the microplastics' composition analyzed by FTIR.

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 S2a)), those two samples present high S values. We can thus identify elements as additives based on their S values.

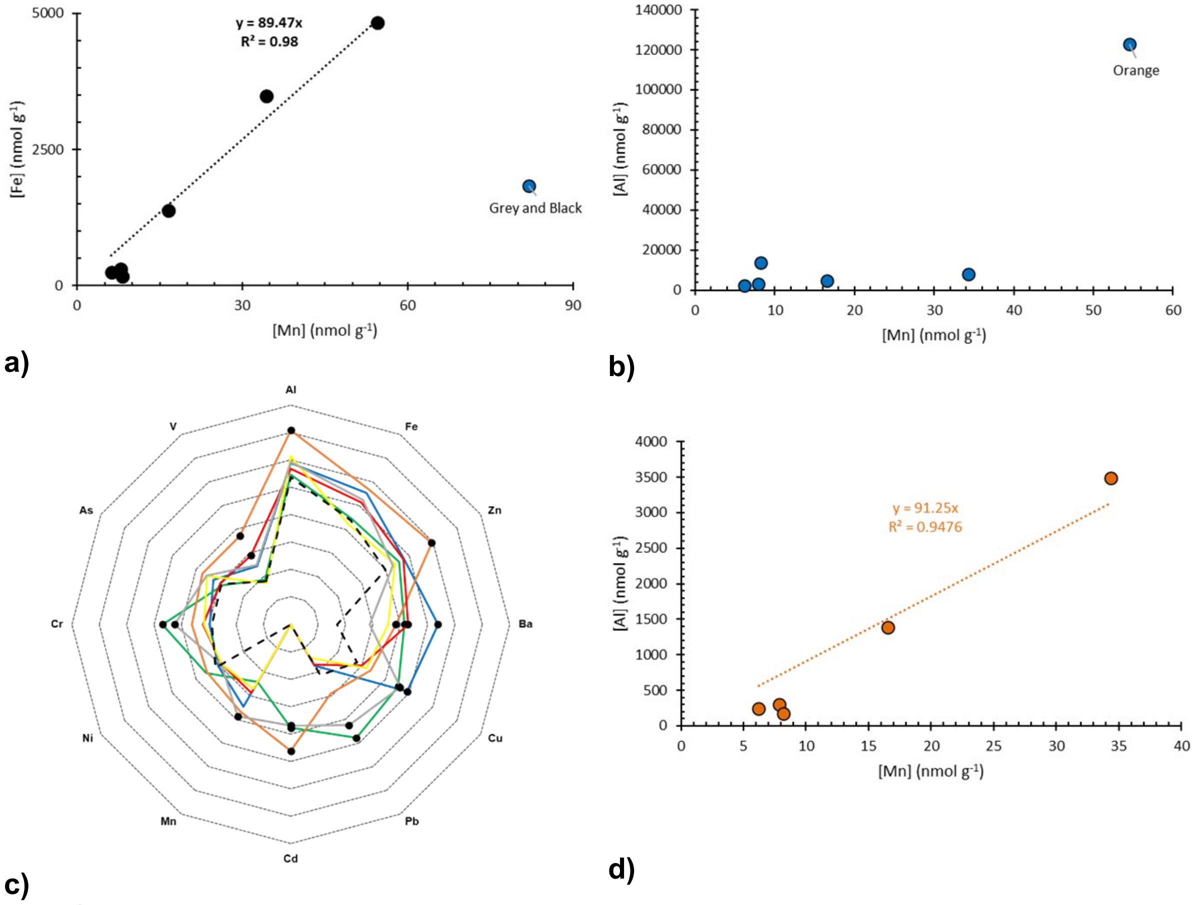

Figure S2 : Linear relationship between (a) Fe and Mn and (b) Al and Mn concentrations with the orange microplastics and (c) without the orange microplastics. d) S values obtained from acidic leaching and digestion for Al, Fe, Zn, Ba, Cu, Pb, Cd, Mn, Ni, Cr, As and V elements; high S values indicate these are additives in microplastics.

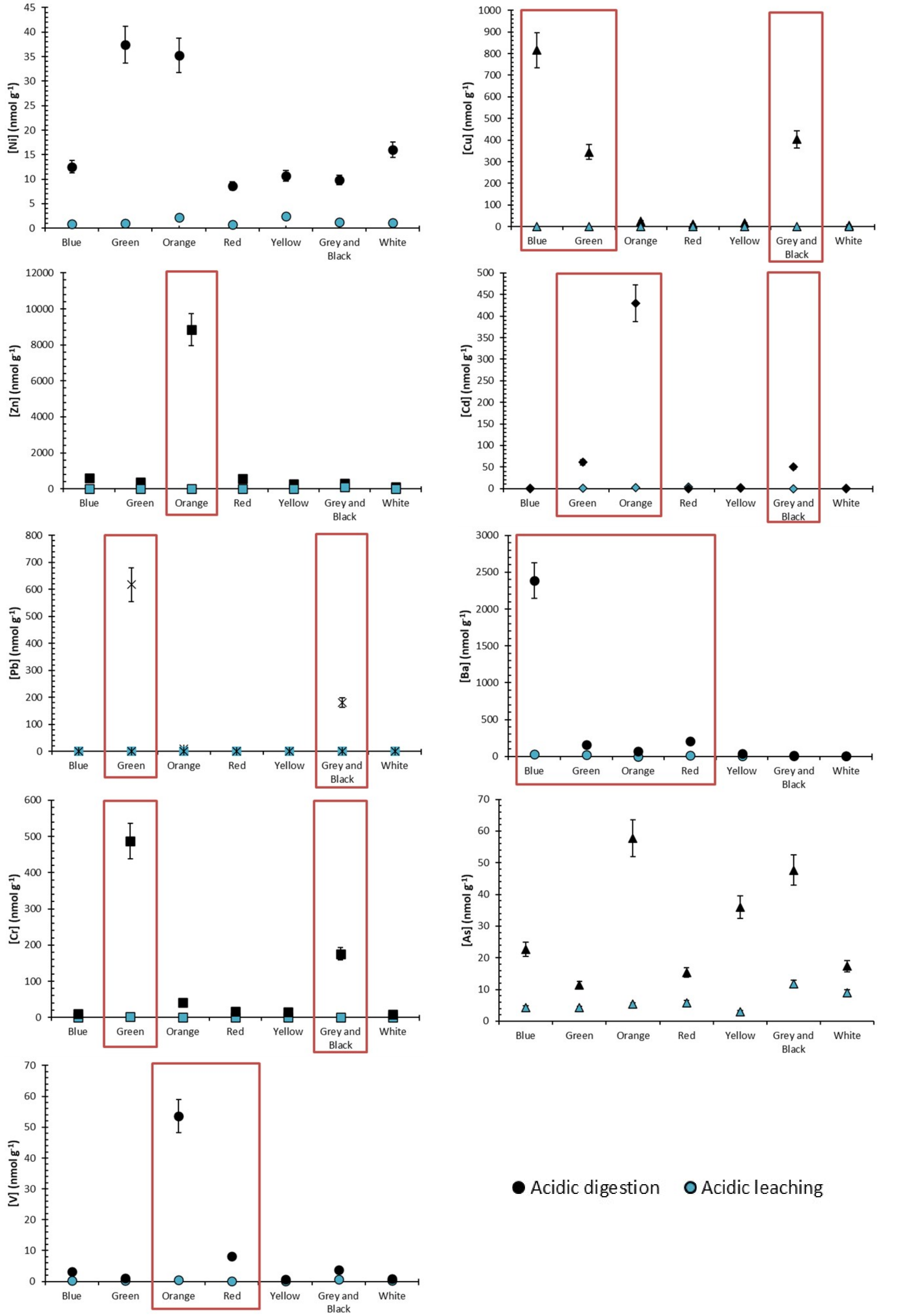

Figure S3: Element concentrations measured in the acidic leachate after total acidic digestion. Red rectangles highlight the high differences in extraction concentrations.

Section S3: Tables

Table S2: Summary of elements that are used as pigments. Most of the data comes from the Internet site https://colourlex.com/pigments/pigments-colour/.

Colour	Name of the pigment	Composition
Blue		$YIn_{1-x}Mn_xO_3$
	Han Blue	$BaCuSi_2O_6$
	Egyptian blue	$CaCuSi_4O_{10}$
	Blue Verditer	$2CuCO_3 \cdot Cu(OH)_2$
	Manganese Blue	$BaMnO_4 \cdot BaSO_4$
	Vivianite	$Fe_3(PO_4)_2 \cdot 8H_2O$
	Cerulean Blue	$CoSnO_3$
	Prussian Blue	$Fe_4[Fe(CN)_6]_3 \cdot xH_2O$
	Smalt	contain Co
	Azurite	$2CuCO_3 \cdot Cu(OH)_2$
	Cobalt Blue	$CoAl_2O_4$
	Ultramarine	$Na_7Al_6Si_6O_{24}S_3$
Red	Pompeiian Red	Iron oxide + clay and quartz
	Chrome Red	$PbO\ PbCrO_4$
	Cadmium Red	Cd(S,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 Yellow	$BiVO_4$
	Zinc Yellow	$K_2O\ 4ZnCrO_4(H_2O)_3$
	Lemon Yellow	$BaCrO_4$
	Cobalt Yellow	$K_3[Co(NO_2)_6]$
	Naples Yellow	$Pb_3(SbO_4)_2$
	Cadmium Yellow	CdS
	Yellow Ochre	Iron oxides
	Orpiment	As_2S_3
	Chrome Yellow	$PbCrO_4$
	Lead-Tin Yellow	Pb_2SnO_4
Green	Phthalocyanine Green	Cu organic complex
	Cobalt Titanate Green	Co_2TiO_4
	Verdigris	$Cu(CH_3COO)_2 \cdot H_2O$
	Green Earth	$K[(Al,Fe^{III}),(Fe^{II},Mg](AlSi_3,Si_4)O_{10}(OH)_2$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
	Viridian	$Cr_2O_3 . 2\ H_2O$
	Emerald Green	$3\ Cu(AsO_2)_2 \cdot Cu(CH_3COO)_2$
	Cadmium Green	mix of CdS and Cr_2O_3
Orange	Antimony Orange	$2\ Sb_2S_3 \bullet Sb_2O_3$
	Cadmium Orange	CdS
	Chrome Orange	$PbO \bullet PbCrO_4$
	Orange Ochre	Iron oxides
	Realgar	AsS, As_2S_2 or As_4S_4
Grey and Black	Spinel black	$MnFe_2O_4$
	Manganese Black	Manganese and Iron oxides
White	Titanium Dioxide White	TiO_2
	Calcite	$CaCO_3$
	Zinc White	ZnO
	Lead White	$2\ PbCO_3 \cdot Pb(OH)_2$

Table S3 : 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

Table S4: Summary of the results obtained by El Hadri (2020) from microplastics collected at the same sampling 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

Table S5: 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