

**Assessing sources and fractions of metals associated with beached plastic litter: a case study in Lake Como (Italy)**

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**Electronic supporting information: Tables S1-S5 and Figs. S1-S5**

**Table S1** Acid digestion data for all the samples analysed. Average values and relative standard deviations (RSD) of three replicates analyses per sample are reported.

<b>Sample</b>		<b>Al</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>
<b>PEvir1</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	245.884	12.043	0.039	0.511	0.256	10.712	0.040	0.369	13.846
	RSD [%]	10.8	11.3	20.9	39.8	7.4	12.1	123.7	5.2	33.7
<b>PEenv2</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	250.320	7.652	0.063	0.690	1.699	128.900	0.083	0.762	30.418
	RSD [%]	0.1	19.5	39.6	28.0	27.8	1.6	102.1	40.2	14.0
<b>PEenv3</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	145.738	27.004	0.100	1.620	9.488	79.255	0.095	1.424	0.783
	RSD [%]	4.0	11.4	0.9	35.9	2.6	0.8	0.7	4.2	68.0
<b>PPvir1</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	68.720	1.167	0.004	0.247	0.120	4.915	0.004	0.132	0.076
	RSD [%]	5.7	8.8	18.8	37.1	21.8	15.9	67.9	39.6	-
<b>PPenv2</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	91.399	6.313	0.175	0.934	4.431	195.178	0.104	0.561	0.930
	RSD [%]	41.2	77.0	84.9	23.9	24.5	94.1	34.3	16.7	32.6
<b>PPenv3</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	74.417	1.015	0.006	0.272	0.596	49.605	0.006	0.207	0.446
	RSD [%]	0.3	17.1	14.2	68.4	4.2	2.3	34.6	37.0	13.8
<b>PETvir1</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	0.446	2.560	0.004	0.109	0.454	71.708	0.683	0.309	0.262
	RSD [%]	0.0	48.4	0.0	0.0	30.7	35.4	9.2	0.0	33.4
<b>PETenv2</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	4.524	1.074	0.013	0.479	0.485	62.419	0.227	0.308	0.281
	RSD [%]	137.2	127.7	0.0	0.0	34.7	17.7	12.3	0.0	79.9
<b>PETenv3</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	20.645	1.570	0.038	1.311	0.998	74.752	0.095	1.004	0.400
	RSD [%]	10.4	106.5	7.3	3.2	3.4	4.9	0.9	7.7	25.7

<b>Sample</b>		<b>Zn</b>	<b>As</b>	<b>Sr</b>	<b>Ag</b>	<b>Cd</b>	<b>Sn</b>	<b>Ba</b>	<b>Pb</b>	<b>U</b>
<b>PEvir1</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	49.478	<LOD	0.472	0.048	0.002	13.033	0.500	0.086	0.005
	RSD [%]	138.1	-	1.7	0.4	71.0	4.5	38.8	12.0	19.9
<b>PEenv2</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	95.497	0.018	0.942	0.125	0.072	27.097	1.331	0.193	0.008
	RSD [%]	124.0	53.6	24.2	104.7	10.5	8.7	2.5	15.0	5.8
<b>PEenv3</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	27.252	0.093	0.618	0.233	0.041	77.946	1.178	0.834	0.006
	RSD [%]	14.4	18.1	2.9	128.2	4.1	44.0	2.4	11.5	2.2
<b>PPvir1</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	4.660	<LOD	0.049	0.203	0.000	7.595	0.838	0.048	0.000
	RSD [%]	113.7	-	73.3	-	67.6	0.8	127.9	30.7	103.8
<b>PPenv2</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	609.941	0.208	19.861	1.145	0.010	33.900	1151.877	0.607	0.011
	RSD [%]	34.5	94.0	88.8	140.8	97.8	40.1	87.0	33.2	75.7
<b>PPenv3</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	2.289	<LOD	0.061	0.188	0.023	14.606	0.561	0.125	0.001
	RSD [%]	40.3	-	0.3	-	2.0	5.5	116.3	93.7	-
<b>PETvir1</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	2.237	0.020	0.048	0.098	0.042	33.897	<LOD	0.093	<LOD
	RSD [%]	57.0	0.0	65.3	17.8	38.4	6.0	-	13.2	-
<b>PETenv2</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	2.566	0.000	0.104	3.426	0.003	47.588	0.244	0.160	0.009
	RSD [%]	30.8	0.0	7.8	135.6	30.7	10.2	0.0	1.0	3.8
<b>PETenv3</b>	Average [ $\mu\text{g}/\text{cm}^3$ ]	4.197	0.052	0.169	0.289	0.117	59.263	<LOD	0.302	0.004
	RSD [%]	9.5	99.2	16.3	39.4	72.6	4.7	-	45.1	0.8

**Table S2** Sequential extractions data and 2% HNO<sub>3</sub> direct extraction data for all the samples analysed (expressed as µg/cm<sup>3</sup>). Average values of three replicates per sample are reported.

Sample	Extraction	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
		[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]
<b>PEvir1</b>	HNO <sub>3</sub> 2%	0.383	0.008	0.001	<LOD	0.081	4.192	0.001	0.194	<LOD
	Ammonium nitrate 1M	0.504	<LOD	<LOD	0.007	0.085	0.146	<LOD	0.407	2.069
	Acid acetic 0.1M	2.400	0.003	<LOD	<LOD	0.021	0.467	<LOD	0.199	0.929
	Hydrogen peroxide 30% v/v	<LOD	0.002	<LOD	<LOD	<LOD	<LOD	<LOD	0.008	0.058
<b>PEenv2</b>	HNO <sub>3</sub> 2%	2.543	0.042	0.007	<LOD	1.632	4.893	0.008	0.456	0.405
	Ammonium nitrate 1M	0.460	<LOD	0.003	0.120	1.490	1.441	0.004	0.376	0.174
	Acid acetic 0.1M	1.405	0.007	0.002	0.003	0.223	1.706	0.001	0.038	0.123
	Hydrogen peroxide 30% v/v	0.249	0.050	0.002	<LOD	0.059	0.328	0.002	0.022	0.136
<b>PEenv3</b>	HNO <sub>3</sub> 2%	3.428	0.114	0.012	<LOD	5.708	10.013	0.033	0.173	0.250
	Ammonium nitrate 1M	0.087	<LOD	0.002	0.020	4.323	0.803	0.016	0.166	0.180
	Acid acetic 0.1M	1.596	0.025	0.004	<LOD	1.309	3.909	0.010	<LOD	<LOD
	Hydrogen peroxide 30% v/v	1.553	0.268	0.004	<LOD	0.239	0.929	0.003	0.010	0.031
<b>PPvir1</b>	HNO <sub>3</sub> 2%	<LOD	<LOD	<LOD	<LOD	0.042	0.322	<LOD	0.105	<LOD
	Ammonium nitrate 1M	0.061	<LOD	<LOD	0.046	0.096	0.200	<LOD	<LOD	0.345
	Acid acetic 0.1M	0.238	0.001	<LOD	<LOD	0.015	0.795	<LOD	0.140	0.271
	Hydrogen peroxide 30% v/v	<LOD	0.002	<LOD	<LOD	0.009	<LOD	<LOD	0.001	<LOD
<b>PPenv2</b>	HNO <sub>3</sub> 2%	3.126	0.106	0.009	0.011	1.791	8.072	0.009	0.130	0.528
	Ammonium nitrate 1M	0.382	0.024	0.004	<LOD	2.466	0.636	0.009	0.045	<LOD
	Acid acetic 0.1M	1.507	0.019	0.003	<LOD	0.332	3.457	0.002	<LOD	<LOD
	Hydrogen peroxide 30% v/v	2.849	0.856	0.006	<LOD	0.101	2.313	0.002	0.030	0.073
<b>PPenv3</b>	HNO <sub>3</sub> 2%	0.038	0.029	0.002	<LOD	0.262	1.784	0.001	0.124	<LOD
	Ammonium nitrate 1M	0.318	0.001	<LOD	<LOD	0.065	0.096	<LOD	0.106	<LOD
	Acid acetic 0.1M	0.495	0.006	<LOD	<LOD	0.042	1.290	<LOD	0.021	0.053
	Hydrogen peroxide 30% v/v	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.003	0.005
<b>PETvir1</b>	HNO <sub>3</sub> 2%	<LOD	0.001	<LOD	<LOD	0.037	1.109	0.002	0.164	<LOD
	Ammonium nitrate 1M	0.251	0.002	<LOD	<LOD	0.034	0.107	0.002	0.135	1.688
	Acid acetic 0.1M	0.552	0.003	<LOD	0.009	0.021	0.798	<LOD	0.308	0.237
	Hydrogen peroxide 30% v/v	0.154	0.088	0.001	<LOD	0.008	<LOD	<LOD	0.021	0.034
<b>PETenv2</b>	HNO <sub>3</sub> 2%	2.386	0.070	0.002	<LOD	0.347	5.484	0.005	0.206	0.023
	Ammonium nitrate 1M	0.139	<LOD	<LOD	<LOD	0.192	0.918	0.002	0.141	0.161
	Acid acetic 0.1M	1.419	<LOD	<LOD	<LOD	0.033	2.016	<LOD	0.115	0.166
	Hydrogen peroxide 30% v/v	<LOD	0.039	<LOD	<LOD	0.008	<LOD	<LOD	0.034	<LOD
<b>PETenv3</b>	HNO <sub>3</sub> 2%	2.649	0.121	0.007	0.070	0.172	15.157	0.006	0.110	0.075
	Ammonium nitrate 1M	0.107	<LOD	<LOD	<LOD	0.108	0.275	0.002	<LOD	0.534
	Acid acetic 0.1M	1.234	0.010	<LOD	<LOD	0.007	2.706	<LOD	0.241	0.217
	Hydrogen peroxide 30% v/v	0.198	0.010	0.002	<LOD	0.021	0.245	<LOD	0.027	<LOD

Table S2 Continues

Sample	Extraction	Zn	As	Sr	Ag	Cd	Sn	Ba	Pb	U
		[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]	[µg/cm <sup>3</sup> ]
PEvir1	HNO <sub>3</sub> 2%	<LOD	0.001	0.017	<LOD	0.001	4.115	0.368	<LOD	<LOD
	Ammonium nitrate 1M	1.010	0.001	0.012	<LOD	<LOD	0.156	0.014	0.083	<LOD
	Acid acetic 0.1M	1.467	0.001	0.005	<LOD	<LOD	0.458	0.023	0.021	<LOD
	Hydrogen peroxide 30% v/v	<LOD	<LOD	<LOD	0.001	<LOD	0.012	<LOD	<LOD	<LOD
PEenv2	HNO <sub>3</sub> 2%	<LOD	0.028	0.218	<LOD	0.001	45.586	0.894	0.109	0.001
	Ammonium nitrate 1M	0.363	0.012	0.151	<LOD	<LOD	1.154	0.743	0.020	<LOD
	Acid acetic 0.1M	<LOD	0.009	0.017	<LOD	<LOD	0.498	0.337	0.054	<LOD
	Hydrogen peroxide 30% v/v	0.040	0.004	0.004	0.004	<LOD	0.610	0.045	0.003	<LOD
PEenv3	HNO <sub>3</sub> 2%	1.609	0.068	0.236	0.025	0.003	53.772	0.256	0.304	0.002
	Ammonium nitrate 1M	0.774	0.030	0.139	<LOD	0.001	0.676	0.245	0.016	<LOD
	Acid acetic 0.1M	<LOD	0.023	0.014	<LOD	<LOD	1.345	0.118	0.103	0.001
	Hydrogen peroxide 30% v/v	<LOD	0.011	0.004	<LOD	<LOD	1.011	0.057	0.002	<LOD
PPvir1	HNO <sub>3</sub> 2%	<LOD	<LOD	0.001	0.010	<LOD	2.515	0.016	<LOD	<LOD
	Ammonium nitrate 1M	0.292	0.001	0.012	<LOD	<LOD	0.057	0.256	0.099	<LOD
	Acid acetic 0.1M	<LOD	0.002	0.004	0.001	<LOD	0.430	0.228	0.027	<LOD
	Hydrogen peroxide 30% v/v	<LOD	<LOD	0.001	<LOD	<LOD	0.028	0.039	<LOD	<LOD
PPenv2	HNO <sub>3</sub> 2%	0.723	0.053	0.371	0.000	0.001	20.599	10.559	0.236	0.002
	Ammonium nitrate 1M	0.925	0.027	0.541	0.000	0.001	0.242	17.362	0.038	<LOD
	Acid acetic 0.1M	0.190	0.019	0.206	<LOD	<LOD	0.954	11.527	0.092	0.001
	Hydrogen peroxide 30% v/v	0.112	0.011	0.079	0.010	<LOD	1.673	4.537	0.010	<LOD
PPenv3	HNO <sub>3</sub> 2%	0.305	0.007	0.032	0.020	0.003	17.409	0.059	0.019	0.003
	Ammonium nitrate 1M	<LOD	<LOD	0.010	0.002	0.006	0.035	<LOD	<LOD	<LOD
	Acid acetic 0.1M	0.851	<LOD	0.003	<LOD	<LOD	0.238	0.007	0.013	<LOD
	Hydrogen peroxide 30% v/v	<LOD	<LOD	<LOD	<LOD	<LOD	0.025	<LOD	<LOD	0.001
PETvir1	HNO <sub>3</sub> 2%	<LOD	<LOD	<LOD	<LOD	0.006	2.231	0.028	<LOD	<LOD
	Ammonium nitrate 1M	0.884	<LOD	0.002	0.001	0.005	0.051	<LOD	0.046	<LOD
	Acid acetic 0.1M	1.244	0.008	0.014	<LOD	<LOD	0.610	0.427	0.070	<LOD
	Hydrogen peroxide 30% v/v	0.586	<LOD	0.005	<LOD	<LOD	0.079	0.092	<LOD	<LOD
PETenv2	HNO <sub>3</sub> 2%	<LOD	0.023	0.058	0.004	0.021	73.860	0.333	0.063	0.002
	Ammonium nitrate 1M	0.002	<LOD	0.046	<LOD	0.017	0.074	0.208	<LOD	<LOD
	Acid acetic 0.1M	1.405	<LOD	0.003	0.002	0.002	0.867	<LOD	0.110	0.001
	Hydrogen peroxide 30% v/v	<LOD	<LOD	<LOD	<LOD	<LOD	0.058	<LOD	<LOD	<LOD
PETenv3	HNO <sub>3</sub> 2%	<LOD	0.010	0.034	0.022	0.001	22.987	0.263	0.181	0.004
	Ammonium nitrate 1M	0.842	<LOD	0.016	<LOD	<LOD	0.448	<LOD	0.028	<LOD
	Acid acetic 0.1M	1.116	<LOD	<LOD	<LOD	<LOD	1.085	<LOD	0.085	0.003
	Hydrogen peroxide 30% v/v	3.022	<LOD	0.026	0.005	0.002	0.095	<LOD	0.025	<LOD

**Table S3** Characteristic peaks and corresponding wavelengths used for polymer type identification with attenuated total reflectance FTIR spectroscopy.

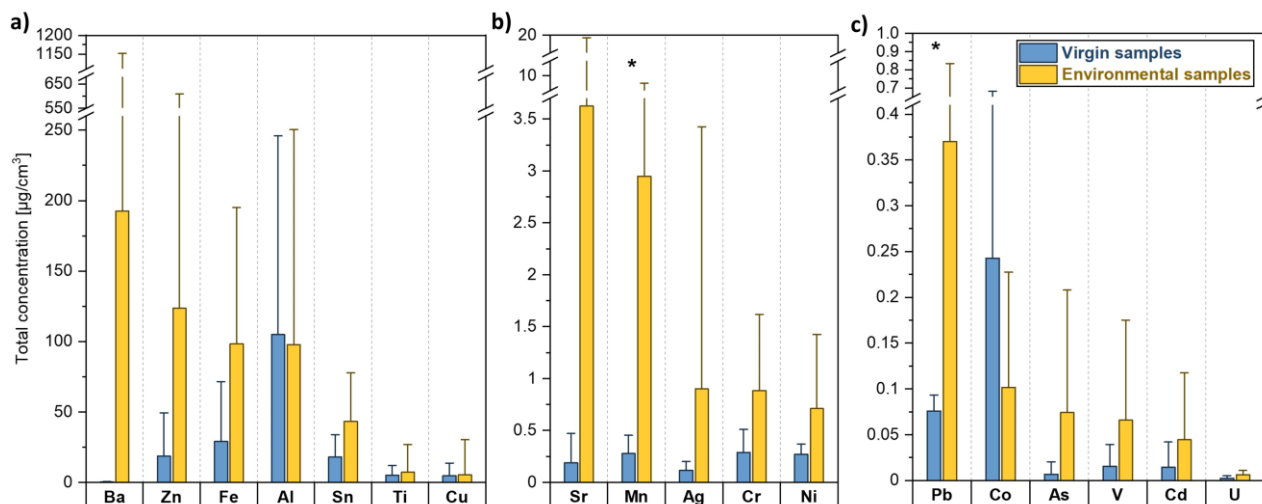
Polymer type	Characteristic peaks used for recognition
PE	C-H bonds (stretching at 2919 cm <sup>-1</sup> and 2851 cm <sup>-1</sup> ) and CH <sub>2</sub> (bending at 1473 cm <sup>-1</sup> and 1462 cm <sup>-1</sup> , rocking at 730 cm <sup>-1</sup> and 717 cm <sup>-1</sup> ).
PP	C-H stretching (2950 cm <sup>-1</sup> , 2915 cm <sup>-1</sup> , 2838 cm <sup>-1</sup> ), CH <sub>2</sub> bending (1455 cm <sup>-1</sup> ), CH <sub>3</sub> bending (1377 cm <sup>-1</sup> ), CH bending, CH <sub>3</sub> rocking and C-C stretching (1166 cm <sup>-1</sup> ), CH <sub>3</sub> rocking, CH <sub>3</sub> bending and CH bending (972 cm <sup>-1</sup> ), CH <sub>2</sub> rocking and C-CH <sub>3</sub> stretching (840 cm <sup>-1</sup> ).
PET	C=O stretching (1715 cm <sup>-1</sup> ), C-O stretching of aromatic esters (1245 cm <sup>-1</sup> ), C-O stretching of aliphatic esters (1100 cm <sup>-1</sup> ) and C-H bending (720 cm <sup>-1</sup> ).

**Table S4** Trace metals in Lake Como water sample determined through ICP-MS analysis. Average values after three replicates are reported.

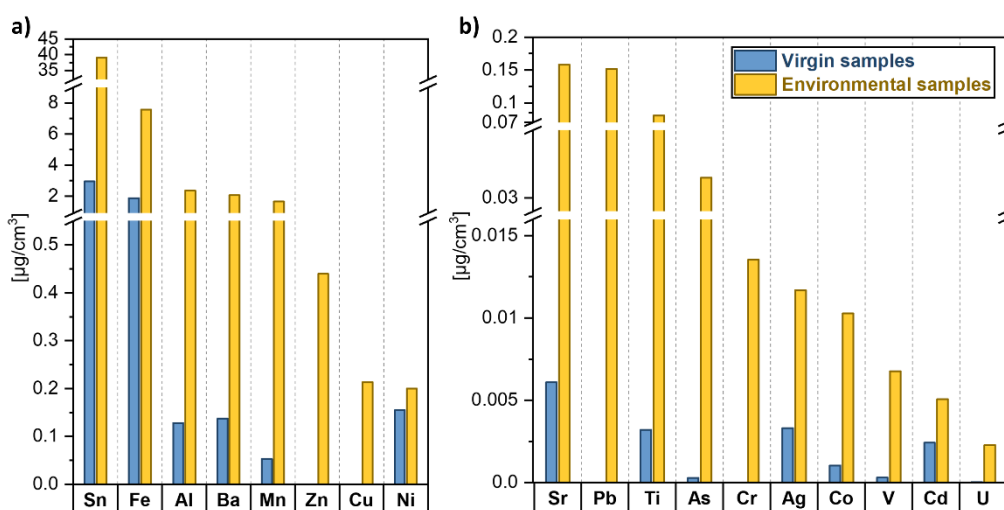
Metal	Sr	Zn	Al	Ba	As	Fe	Ni	Cu	U
[µg/l]	146.388	20.895	15.811	9.630	3.248	3.135	0.938	0.822	0.669
Metal	Cr	V	Mn	Ag	Sn	Pb	Co	Cd	Ti
[µg/l]	0.517	0.291	0.151	0.081	0.072	0.063	0.055	0.030	0.014

**Table S5** Major ions in Lake Como water sample determined through IC analysis. Average values after three replicate analyses are reported.

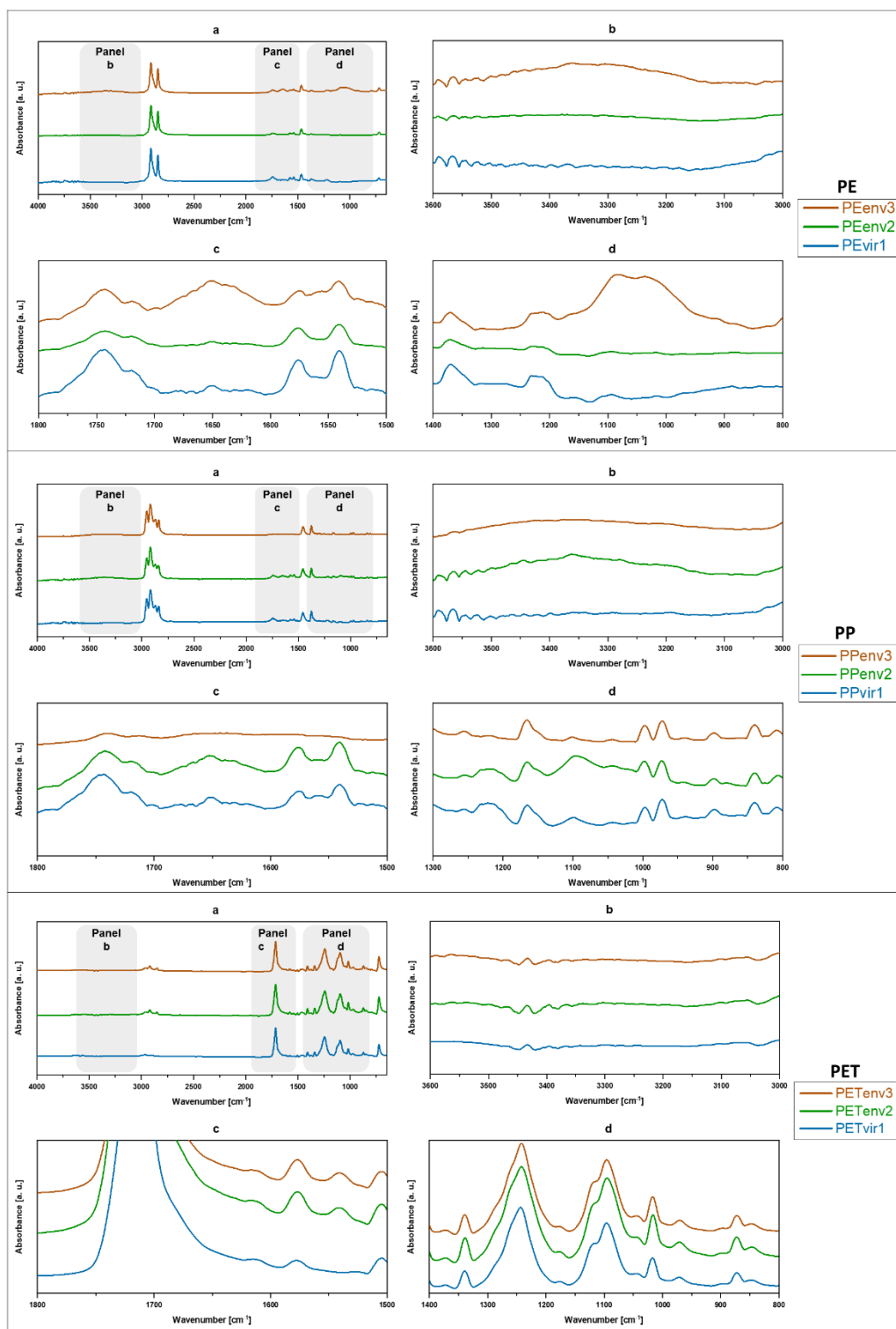
Anions	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>
[mg/l]	0.07	13.72	<LOD	1.73	<LOD	21.58
Cations	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	
[mg/l]	<LOD	3.66	1.57	4.14	15.74	



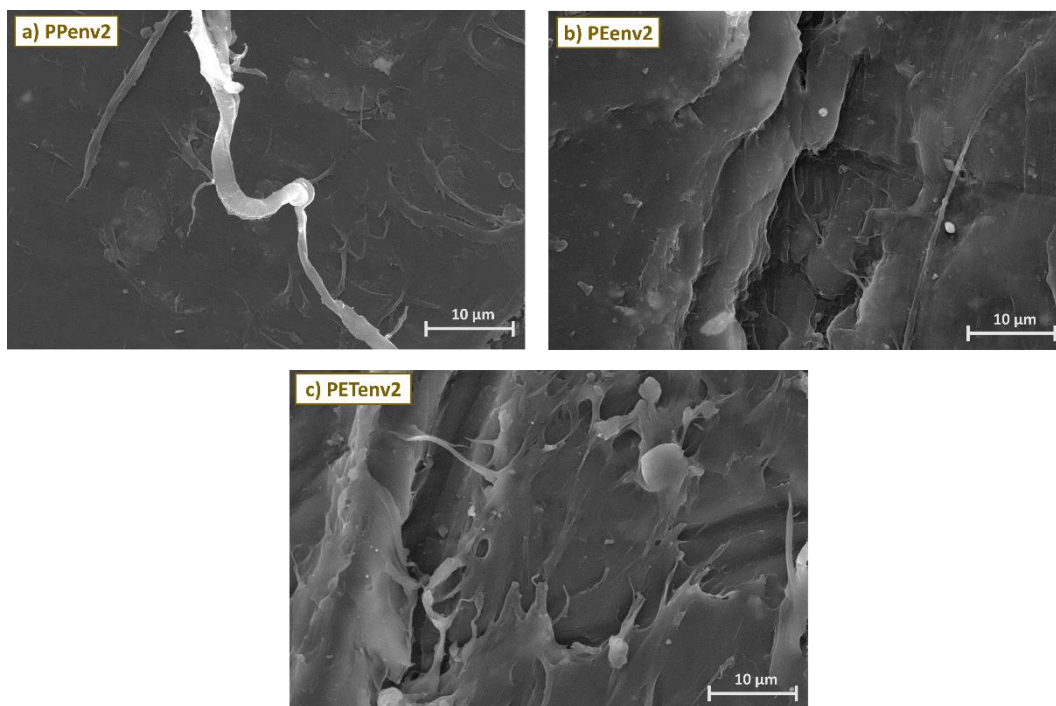
**Fig. S1** Total metal loads determined with acid digestion in virgin and environmental samples. Mean values derived from all the samples analyzed are displayed, with the maximum values detected indicated by the whisker. Metal concentrations are ordered and separated in three graphs (a, b and c) for graphical reasons only. Significantly different data ( $p < 0.05$ ) after Mann-Whitney test are indicated by asterisk. Raw data are reported in **Table S1**.



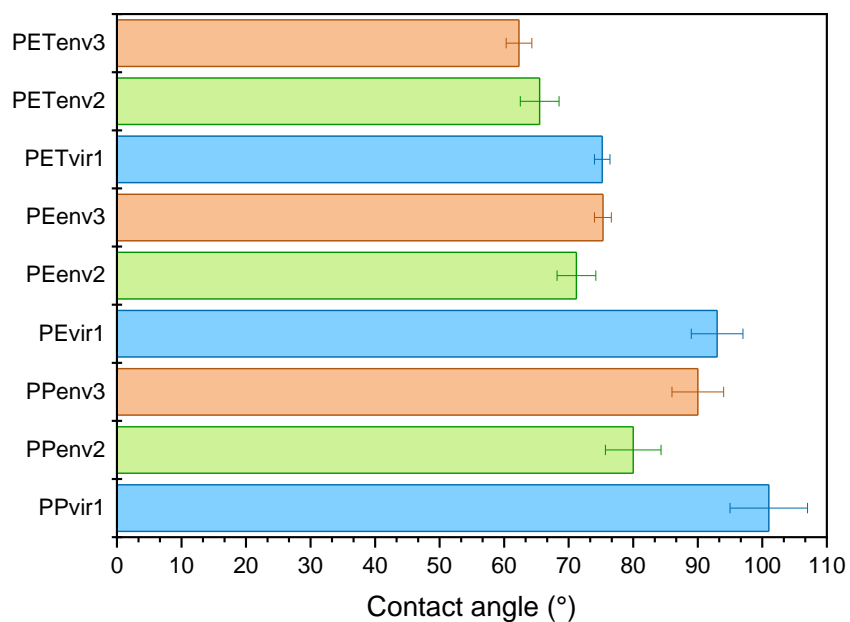
**Fig. S2** Labile metals in plastic samples, determined via 2%  $\text{HNO}_3$  extraction. Mean values distinguished for virgin and environmental samples are displayed. Metals are displayed in two different graphs (a and b) on the basis of their concentrations solely for graphical reasons. Raw data are listed in **Table S2**.



**Fig. S3** FTIR Spectra of the different polymer types: PE; PP; PET. Environmental samples (env) and virgin samples (vir) are shown. For every polymer, the whole spectral window is displayed in figure (a), whereas the other three panels indicate the specific spectral windows analysed at 3600-3000 cm<sup>-1</sup> (b), 1800-1500 cm<sup>-1</sup> (c) and 1400-800 cm<sup>-1</sup> (d).



**Fig. S4** Supplementary SEM micrograph of environmental samples. The rugged and wrinkled texture is evident, and some filamentous morphologies are observable.



**Fig. S5** Contact angle values of all virgin (in blue) and environmental samples (in green and red). The whiskers show the standard deviation after 3 replicates.