Net4mPlastic project

Activity 4.2

D 4.2.2. - Collection of plastic and microplastic items and identification of the plastic and origin

October, 2021

Project Acronym	NET4mPLASTIC
Project ID Number	10046722
Project Title	New Technologies for macro and Microplastic Detection and Analysis in the Adriatic Basin
Priority Axis	3
Specific objective	3.3
Work Package Number	4
Work Package Title	Demonstration activities: testing and improvement of developed methodologies
Activity Number	4.2
Activity Title	Lab's analysis on plastic and microplastic wastes on coastal and marine environments
Partner in Charge	TIPH
Partners involved	University of Trieste
Status	Final
Distribution	Public

Version control

Data	Vers	Prep	Resp	Appr	Rev	Comment
06.10.2021	1.0	UniTS			Final	

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1 Introduction

This document reports on the analysis carried out on plastic debris samples collected by the University of Ferrara and sent to the University of Trieste for analysis on June 28, 2021. Collection sites were: Po Delta, Pescara and Teramo. Plastic debris were sorted and indentified by means of Image analysis and Fourier-Transform Infrared Spectroscopy

2 Materials and methods

2.1 Samples identification and classification

Samples in the form of debris of different composition, size and shape were received inside 61 packages (paper envelopes). Each package was identified by a number written on the outside of the envelope (from P1000-100 to P1000-160). Envelopes from P1000-100 to P1000-114 and P1000-130 to P1000-160 were collected in Po Delta site; P1000-121 to P1000-128 in Pescara; P1000-115 to P1000-120 in Teramo. Envelopes were opened; digital picture (with an appropriate scale) of their content was taken, then samples were counted and classified according to their color and shape. A unique id number was assigned to every object inside the package (for instance: P100-100-a, b, c etc.). The type of samples was defined as “pellet” (PL), “fragment” (FR) or “filament” (FL). Objects labeled as “pellets” are spherical or cylindrical in shape, and typically are small granules used as raw material in plastic production. Objects labeled as “filaments” are thin and have a high aspect ratio (ratio between longer and shorter dimensions). Irregular objects were categorized as “fragments”. The color was attributed according to the best match to the following: black (BLK), blue (BLU), brown (BRW), green (GNR), grey (GRY), orange (ORA), pink (PNK), red (RED), sky blue (SKY), transparent (TRS), white (WHT), yellow (YEL).

2.2 Sample size

Samples sizes (dimensions and area) were measured directly on the pictures with the help of an image-editing software (GIMP); aspect ratio was defined as the ratio between the longer and the shorter measured dimension.

2.3 Sample composition

Sample composition was assessed by means of Fourier-Transform Infrared Spectroscopy (FT-IR). FT-IR spectra were acquired via a Thermo-Nicolet Nexus 470 spectrometer, equipped with an Attenuated

Total Reflectance (ATR) accessory, in the 4000-500 cm^{-1} spectral range. Different plastic materials were identified by comparison with known reference spectra of the most common polymers; the most important vibrational bands were used as fingerprints as suggested by Jung et al (2018). These bands are shown in Table 1Table 3. Other compounds (such as sand, calcium carbonate or cellulose) were identified by their characteristic vibrational bands reported in Table 2. Strong peaks in the 1400-1440 cm^{-1} region ($CaCO_3$ vibrational mode 2) or in the 1100 cm^{-1} region (SiO_2), when superimposed to the polymer spectra, were related to the presence of sand (carbonate or siliceous origin) in the plastic debris. The ratio between the peak intensity and the main peak of the polymer spectrum was also calculated. Spectra with only a broad, not well-defined vibrational band in the 1000-1050 cm^{-1} region (compatible with C-O-C stretch in polysaccharides) were assigned (also after visual examination of the sample) to fragments of algae or paper (cellulose). Samples with only $CaCO_3$ vibrational bands (aragonite?) were identified as fragments of shells or exoskeleton (biological origin).

Table 1: vibrational bands used to identify the most common polymers. Most intense peak for each polymer is labeled with (#)

polymer	**Vibrational bands (cm^{-1})**	**assignment**
Low-density polyethylene (LDPE); High-density polyethylene (HDPE)	2915 / 2845	CH_2 stretch (#)
	1472 / 1462	CH_2 bend (NB: single peak in HDPE; multi peak in LDPE)
	730 / 717	CH_2 rock
	2915 / 2845	CH_2 stretch
	1472 / 1462	CH_2 bend
	1377	CH_3 bend
	730 / 717	CH_2 rock
Polypropylene (PP)	2950 / 2915 / 2838	CH & CH_2 stretch (#)
	1455	CH_2 bend
	1377	CH_3 bend
	1166	CH bend; CH_3 rock; C-C stretch
	997	CH_3 rock; CH_3 bend; CH bend
	972	CH_3 rock; C-C stretch
	840	CH_2 rock; C-CH_3 stretch
Polystyrene (PS)	3024	arom. CH stretch
	2847	CH_2 stretch
	1601	arom. ring stretch
	1492	arom. ring stretch
	1451	CH_2 bend

	1027	arom. CH bend
	694	arom. ring out of plane bend (#)
Acrylonitrile butadiene styrene (ABS)	2922	CH & CH_2 stretch
	1602	arom. ring stretch
	1494	arom. ring stretch
	1452	CH_2 bend
	966	=C-H bend
	759	arom. ring out of plane bend (#)
Ethylene Vinyl acetate (EVA)	2917 / 2848	CH & CH_2 stretch (#)
	1740	C=O stretch
	1469	CH_2 & CH_3 bend
	1241	C-O bend
	1020	CH_2 rock
	720	CH_2 rock
Polyurethane (PU)	2865	CH & CH_2 stretch
	1731	C=O stretch (#)
	1531	C-N stretch
	1451	CH_2 bend
	1223	C(=O)O stretch
Polyamide (PA)	3298	NH stretch
	2932 / 2858	CH & CH_2 stretch
	1634	C=O stretch (Amide-I) (#)
	1538	NH bend, C-N stretch (Amide-II)
	1464	CH_2 bend
	1372	CH_2 bend
	1274	NH bend, C-N stretch
	1199	CH_2 bend
	687	NH bend, CO bend

Table 2: vibrational bands used to identify other compounds

	Vibrational bands (cm^{-1})	**assignment**
$CaCO_3$	1400 - 1450	$CaCO_3$ v3 mode
	855 - 875	$CaCO_3$ v2 mode
SiO_2	1100	Si-O-Si stretch (asymm)
	801	Si-O-Si stretch (symm)
	471	Si-O bend
algae, cellulose	1000 - 1030	C-O-C (polysaccharides?)

3 Results

Sample classification, size and composition is reported in Table 3. A total number of 317 debris were categorized (240 from Po Delta, 67 from Pescara, 10 from Teramo). Type, shape and color codes are those reported in para. 2.1 and 2.2. Site code: “D” for Po Delta; “P” for Pescara; “T” for Teramo. The composition was assessed as reported in para 2.3. Envelopes labeled as “P1000-104”; “P1000-107”; “P1000-130” and “P1000-158” were empty (no samples were found inside); Envelopes “P1000-129”, “P1000-135” and “P1000-138” were missing (no envelope with that successive number was delivered: discontinuity in the numbering). When measurable, the ratio between the SiO_2 or $CaCO_3$ peak intensity and the main peak of the polymer spectrum is also reported.

Pictures of all samples are shown in Figure 1. Some representative spectra are shown in Figure 2, Figure 3 and Figure 4. Representative shapes and colors are shown in Figure 9 and Figure 10.

Table 3: sample ID, classification and size

Envelope ID		Sample ID	Site	Type	color	Area (mm^2)	Dim L1 (mm)	Aspect ratio	Composition	SiO_2	$CaCO_3$
P1000	100	1	D	PL	WHT	18.55	4.86	1.0	PS	0.26	
P1000	101	1	D	FR	WHT	4.71	3.99	1.7	alga		
P1000	102	1	D	PL	BLK	31.57	6.34	1.0	LDPE	0.28	0.2
P1000	103	a	D	FL	GRN	15.20	16.89	18.8	LDPE	1.29	0.29
P1000	103	b	D	FR	BRW	3.14	2.06	1.4	alga		
P1000	103	c	D	FR	WHT	1.12	1.14	1.2	$CaCO_3$		1
P1000	104	EMPTY	D	-	-	-	-	-	-	-	-
P1000	105	1	D	FR	WHT	2.40	1.60	1.1	HDPE		
P1000	106	1	D	FR	WHT	5.66	3.84	1.3	HDPE	0.18	
P1000	107	EMPTY	D	-	-	-	-	-	-	-	-
P1000	108	1	D	FR	YEL	62.72	11.10	2.0	LDPE	0.40	0.27
P1000	109	a	D	FR	SKY	1.86	3.10	5.2	PP	0.75	
P1000	109	b	D	FR	SKY	1.25	2.50	5.0	PP		
P1000	110	a	D	FL	GRN	20.15	23.67	27.8	LDPE	0.62	
P1000	110	b	D	FL	GRN	14.90	17.50	20.6	LDPE	0.51	
P1000	110	c	D	FL	GRN	35.00	41.12	48.3	LDPE	0.34	
P1000	110	d	D	FL	WHT	10.23	12.82	16.1	PP	1.23	
P1000	110	e	D	FL	WHT	11.76	14.74	18.5	PP	0.44	

P1000	110	f	D	FR	SKY	4.60	3.09	2.1	LDPE	0.47	0.15
P1000	110	g	D	FR	BLU	4.04	2.23	1.2	HDPE	0.28	0.12
P1000	110	h	D	FR	YEL	8.96	3.83	1.6	$CaCO_3$		1
P1000	110	i	D	FR	BLK	5.90	2.77	1.3	HDPE	0.46	0.15
P1000	110	j	D	FR	BRW	11.58	3.51	1.1	LDPE	2.94	0.5
P1000	111	1	D	PL	TRS	4.15	2.30	1.0	HDPE		
P1000	112	a	D	FR	WHT	39.42	14.60	5.4	LDPE	0.63	
P1000	112	b	D	FR	WHT	24.84	9.20	3.4	LDPE	0.42	
P1000	113	a	D	FR	RED	4.69	2.33	1.2	PP	0.77	
P1000	113	b	D	FR	WHT	6.43	2.82	1.2	PS	0.37	0.32
P1000	113	c	D	FR	GRN	7.25	3.26	1.5	LDPE	0.69	0.35
P1000	113	d	D	FR	YEL	5.06	2.39	1.1	alga		
P1000	114	1	D	FR	WHT	47.16	7.20	1.1	LDPE	0.57	
P1000	115	1	T	FR	GRN	3.52	2.20	1.4	HDPE	0.21	0.22
P1000	116	1	T	PL	BLK	2.59	1.82	1.0	alga		
P1000	117	a	T	PL	GRY	11.72	3.86	1.0	LDPE	0.42	0.44
P1000	117	b	T	PL	BLK	10.06	3.58	1.0	LDPE	0.34	0.35
P1000	117	c	T	PL	BLK	15.42	4.43	1.0	LDPE	0.48	0.7
P1000	117	d	T	FR	WHT	5.65	3.98	1.4	LDPE	1.38	0.59
P1000	117	e	T	FR	YEL	20.77	12.61	7.7	LDPE	0.59	0.23
P1000	118	1	T	FR	BLK	5.34	4.09	1.6	PP	0.45	0.63
P1000	119	1	T	FR	BRW	6.78	4.77	1.7	PU		
P1000	120	1	T	FR	WHT	24.21	7.61	2.4	LDPE	0.44	0.24
P1000	121	a	P	PL	WHT	15.59	4.46	1.0	PP	0.63	0.80
P1000	121	b	P	FL	GRN	24.89	31.43	39.7	LDPE	0.49	0.69
P1000	121	c	P	FR	GRN	22.79	6.48	1.8	LDPE	0.68	0.70
P1000	122	a	P	PL	WHT	8.13	3.22	1.0	LDPE	0.27	0.22
P1000	122	b	P	FR	WHT	28.91	5.84	1.2	$CaCO_3$		1
P1000	122	c	P	FR	WHT	14.94	4.50	1.4	$CaCO_3$		1
P1000	123	a	P	FR	GRN	5.95	2.67	1.2	LDPE	0.37	0.53
P1000	123	b	P	FR	WHT	6.70	3.81	1.1	LDPE	0.73	1.23
P1000	123	c	P	FR	WHT	5.53	3.02	1.6	LDPE	0.49	0.75
P1000	123	d	P	FR	WHT	5.08	2.77	1.5	PS	0.54	0.51
P1000	123	e	P	FR	WHT	5.29	5.94	6.7	LDPE	0.67	2.67
P1000	124	a	P	PL	WHT	11.84	3.88	1.0	LDPE	0.48	0.68
P1000	124	b	P	PL	BLK	11.84	3.88	1.0	ABS	1.44	2.56
P1000	124	c	P	PL	BLK	12.44	3.98	1.0	LDPE	0.68	0.85
P1000	124	d	P	PL	BLU	12.14	3.93	1.0	LDPE	0.43	0.63
P1000	124	e	P	PL	YEL	11.55	3.83	1.0	PP	0.64	0.89

P1000	124	f	P	FR	WHT	6.08	2.91	1.4	LDPE	0.60	1.09
P1000	124	g	P	FR	GRN	7.88	3.69	1.7	LDPE	0.62	0.96
P1000	124	h	P	FR	GRN	4.50	2.38	1.3	PP	0.73	1.27
P1000	125	1	P	PL	WHT	6.29	2.83	1.0	LDPE	1.63	2.63
P1000	125	2	P	PL	WHT	2.96	1.94	1.0	PS	0.44	0.52
P1000	125	3	P	PL	WHT	13.97	4.22	1.0	LDPE	1.48	0.85
P1000	125	4	P	PL	YEL	19.60	5.00	1.0	LDPE	1.38	2.96
P1000	125	5	P	PL	TRS	55.89	8.44	1.0	PP	0.75	2.50
P1000	125	6	P	FR	WHT	5.76	4.72	3.9	PP	0.94	2.00
P1000	125	7	P	FR	WHT	36.87	7.38	1.5	LDPE	0.14	0.31
P1000	125	8	P	FR	YEL	22.12	6.99	2.2	LDPE	0.81	1.38
P1000	125	9	P	FR	GRY	15.55	5.72	2.1	PP	1.38	3.23
P1000	125	10	P	FR	WHT	38.54	7.55	1.5	LDPE	1.76	2.12
P1000	125	11	P	FR	WHT	13.04	5.11	2.0	PS	0.40	0.43
P1000	125	12	P	FR	BLK	23.97	13.93	4.0	HDPE	0.30	0.35
P1000	125	13	P	FR	GRY	32.53	8.88	2.4	LDPE	1.52	2.70
P1000	125	14	P	FR	GRY	6.29	2.83	1.0	PP	1.17	2.42
P1000	125	15	P	FR	PNK	8.41	5.05	3.0	PP	1.17	1.57
P1000	125	16	P	FR	YEL	3.54	2.55	1.8	LDPE	0.28	0.26
P1000	125	17	P	FR	BRW	1.39	1.33	1.0	$CaCO_3$		1
P1000	125	18	P	FL	GRY	5.66	8.49	12.8	$CaCO_3$		1
P1000	126	a	P	PL	WHT	17.04	4.66	1.0	LDPE	0.31	0.31
P1000	126	b	P	FL	TRS	19.45	34.01	59.5	LDPE	0.27	0.27
P1000	127	1	P	PL	TRS	14.25	4.26	1.0	LDPE	0.26	0.25
P1000	127	2	P	PL	WHT	13.04	4.07	1.0	LDPE	0.63	1.28
P1000	127	3	P	PL	WHT	15.95	4.51	1.0	LDPE	0.22	0.51
P1000	127	4	P	PL	WHT	19.64	5.00	1.0	LDPE	0.19	0.43
P1000	127	5	P	PL	WHT	19.64	5.00	1.0	LDPE	0.41	0.84
P1000	127	6	P	PL	YEL	15.95	4.51	1.0	LDPE	2.44	3.38
P1000	127	7	P	PL	BLK	14.66	4.32	1.0	LDPE	0.22	0.33
P1000	127	8	P	FR	WHT	19.50	7.35	1.4	LDPE	0.39	0.22
P1000	127	9	P	FR	WHT	21.50	6.11	1.7	PP	1.21	1.37
P1000	127	10	P	FR	WHT	11.42	6.85	2.1	PP	0.52	1.38
P1000	127	11	P	FR	GRY	4.63	5.56	3.3	LDPE	1.03	0.97
P1000	127	12	P	FR	GRY	9.09	3.27	1.2	LDPE	0.22	0.28
P1000	127	13	P	FR	GRY	6.55	2.65	1.1	LDPE	0.22	0.36
P1000	127	14	P	FR	GRY	1.92	2.22	1.3	$CaCO_3$		1
P1000	127	15	P	FR	YEL	14.09	5.31	2.0	PP	1.05	1.50
P1000	127	16	P	FR	RED	8.87	5.99	2.0	LDPE	0.38	0.69

P1000	127	17	P	FR	WHT	17.49	5.25	1.6	PS	0.46	0.50
P1000	127	18	P	FR	SKY	2.63	1.85	1.3	PP	0.24	0.43
P1000	127	19	P	FR	BLU	2.02	1.42	1.0	PP	0.56	0.88
P1000	127	20	P	FR	GRN	13.43	8.70	5.6	LDPE	0.84	1.63
P1000	127	21	P	FR	GRY	9.95	5.37	2.9	LDPE	0.34	0.88
P1000	127	22	P	FR	GRN	10.08	3.89	1.5	LDPE	1.86	2.86
P1000	128	1	P	PL	GRN	13.14	4.09	1.0	HDPE	1.11	2.93
P1000	128	2	P	PL	YEL	8.23	3.24	1.0	LDPE	1.94	3.75
P1000	128	3	P	FR	BLK	13.65	5.34	2.1	LDPE	0.71	1.29
P1000	128	4	P	FR	BRW	10.31	5.34	1.4	$CaCO_3$		1
P1000	128	5	P	FR	BLU	2.25	1.65	1.2	HDPE	0.25	0.47
P1000	128	6	P	FR	RED	0.58	1.08	1.0	PP	1.03	1.80
P1000	129	missing		-	-	-	-	-	-	-	-
P1000	130	EMPTY	D	-	-	-	-	-	-	-	-
P1000	131	1	D	FR	BLU	3.06	2.16	1.5	LDPE	0.93	0.56
P1000	132	1	D	FR	WHT	15.33	4.12	1.1	HDPE	0.90	0.97
P1000	133	1	D	FL	YEL	9.26	9.95	10.7	PP	0.29	
P1000	134	1	D	FR	WHT	9.78	3.53	1.0	PS	0.39	
P1000	135	missing	D	-	-	-	-	-	-	-	-
P1000	136	1	D	PL	GRY	16.31	4.56	1.0	LDPE	0.79	
P1000	137	1	D	FR	WHT	5.24	2.74	1.4	PP		
P1000	138	missing	D	-	-	-	-	-	-	-	-
P1000	139	1	D	FR	WHT	23.23	5.44	1.0	PS	0.96	0.31
P1000	140	a	D	PL	WHT	10.81	3.71	1.0	LDPE	0.15	
P1000	140	b	D	FR	WHT	5.25	2.59	1.0	PS	0.58	
P1000	140	c	D	FR	WHT	5.48	2.64	1.0	PS	0.44	
P1000	140	d	D	FR	WHT	3.66	3.43	3.2	PS	0.81	
P1000	140	e	D	FR	WHT	3.64	2.70	2.0	PS	0.83	
P1000	140	f	D	FR	TRS	2.37	4.22	7.5	LDPE	0.23	
P1000	140	g	D	FR	YEL	7.96	10.12	12.9	HDPE	0.11	
P1000	140	h	D	FR	RED	10.86	10.73	5.3	LDPE	0.08	
P1000	141	a	D	PL	WHT	8.63	3.32	1.0	PP	2.20	
P1000	141	b	D	FR	BLU	12.21	4.00	1.3	PP	0.73	
P1000	142	a	D	PL	WHT	11.91	3.89	1.0	PP	2.70	0.62
P1000	142	b	D	FR	WHT	3.31	2.05	1.0	PS	0.55	2.04
P1000	142	c	D	FR	WHT	2.23	1.68	1.0	PS	0.67	2.78
P1000	142	d	D	FR	WHT	1.83	1.53	1.0	PS	0.41	2.56
P1000	142	e	D	FR	WHT	4.02	2.26	1.0	PS	1.04	4.35
P1000	142	f	D	FR	WHT	2.98	1.95	1.0	PS	0.53	1.72

P1000	142	g	D	FR	WHT	5.94	2.89	1.4	PS	1.45	4.55
P1000	142	h	D	FR	TRS	6.12	4.84	1.9	PP	0.63	
P1000	143	a	D	PL	BLK	14.27	4.26	1.0	LDPE		
P1000	143	b	D	FR	BRW	1.36	1.32	1.0	alga		
P1000	143	c	D	FR	BRW	1.70	1.89	2.1	alga		
P1000	144	1	D	PL	WHT	13.04	4.07	1.0	LDPE	0.13	
P1000	144	2	D	PL	WHT	8.41	3.27	1.0	PP	0.08	0.10
P1000	144	3	D	FR	BRW	13.84	4.20	1.0	PS	1.09	0.38
P1000	144	4	D	FR	BRW	21.79	7.59	1.3	LDPE	0.36	
P1000	144	5	D	FR	WHT	24.82	7.96	1.3	PP	0.50	
P1000	144	6	D	FR	WHT	24.10	7.65	2.4	PP	0.73	
P1000	144	7	D	FR	WHT	9.33	4.44	2.1	HDPE	0.34	
P1000	144	8	D	FR	WHT	15.68	5.19	1.7	LDPE	0.98	0.51
P1000	144	9	D	FR	TRS	9.15	6.05	2.0	PP	0.24	
P1000	144	10	D	FR	GRY	7.80	7.90	8.0	LDPE	0.19	
P1000	144	11	D	FR	BRW	6.33	2.84	1.0	PS	0.75	0.21
P1000	144	12	D	FR	BRW	2.52	1.79	1.0	PS	0.53	
P1000	144	13	D	FR	WHT	6.61	2.90	1.0	PP	0.50	
P1000	144	14	D	FR	BRW	2.69	1.85	1.0	PS	1.03	
P1000	144	15	D	FR	WHT	6.84	4.81	3.4	PS	0.56	
P1000	144	16	D	FR	WHT	6.22	2.96	1.4	PS	0.70	0.23
P1000	144	17	D	FR	BLK	1.49	1.85	1.2	cellulosa		
P1000	144	18	D	FR	WHT	2.72	2.59	2.5	PS	0.43	
P1000	144	19	D	FR	WHT	2.77	1.73	1.1	PS	0.73	
P1000	144	20	D	FR	WHT	2.32	1.98	1.7	PS	0.80	
P1000	145	1	D	PL	WHT	19.05	4.92	1.0	LDPE	0.22	
P1000	145	2	D	FR	WHT	15.69	4.47	1.0	PS	0.87	0.33
P1000	145	3	D	FR	WHT	17.03	5.23	1.6	LDPE	0.31	
P1000	145	4	D	FR	WHT	30.53	7.20	1.7	LDPE	0.24	
P1000	145	5	D	FR	WHT	16.58	5.76	1.0	LDPE	4.50	0.58
P1000	145	6	D	FR	WHT	6.63	4.17	1.3	LDPE	0.30	
P1000	145	7	D	FR	WHT	11.47	4.09	1.5	LDPE	0.19	
P1000	145	8	D	FR	WHT	18.64	4.39	1.0	LDPE	0.20	
P1000	145	9	D	FR	WHT	6.23	2.65	1.1	LDPE	0.32	
P1000	145	10	D	FR	WHT	5.25	4.62	2.0	HDPE	0.21	
P1000	145	11	D	FR	BRW	19.28	5.30	1.5	?? EVA		
P1000	145	12	D	FR	BRW	24.28	6.82	1.9	LDPE	0.20	
P1000	145	13	D	FR	WHT	21.12	6.06	1.7	LDPE	0.44	
P1000	145	14	D	FR	WHT	31.10	6.52	1.4	PS	0.96	0.30

P1000	145	15	D	FR	WHT	10.39	5.83	1.6	LDPE	0.23	0.92
P1000	145	16	D	FR	WHT	10.39	3.64	1.0	PS	0.86	
P1000	145	17	D	FR	BRW	7.95	3.18	1.0	PS	0.84	
P1000	145	18	D	FR	WHT	6.72	3.41	1.7	PP	1.33	
P1000	145	19	D	FR	WHT	10.12	3.26	1.0	LDPE	0.68	0.30
P1000	145	20	D	FR	WHT	4.78	3.71	1.4	LDPE	0.50	
P1000	145	21	D	FR	YEL	4.48	2.95	2.0	PE/PP	0.62	0.34
P1000	145	22	D	FR	BLK	4.14	2.88	2.0	LDPE	0.23	
P1000	145	23	D	FR	BLU	2.84	2.50	2.2	PP	0.30	
P1000	145	24	D	FR	GRY	7.90	6.14	4.8	LDPE	0.17	
P1000	145	25	D	FR	GRY	19.53	4.77	1.2	LDPE		
P1000	145	26	D	FR	BRW	14.77	5.00	1.7	PE/PP		
P1000	145	27	D	PL	BLK	14.35	4.28	1.0	PP	0.17	
P1000	145	28	D	PL	BLK	12.47	3.99	1.0	PP	0.09	
P1000	145	29	D	PL	BLK	9.50	3.48	1.0	PP	1.26	
P1000	145	30	D	PL	BLK	5.65	2.68	1.0	PP	1.58	
P1000	145	31	D	FR	WHT	11.19	3.77	1.3	PP	0.63	
P1000	145	32	D	FL	WHT	7.74	9.71	12.2	PP	0.57	
P1000	145	33	D	FL	WHT	6.72	11.59	20.0	PP		
P1000	145	34	D	FR	SKY	24.26	5.58	1.3	LDPE	0.40	
P1000	145	35	D	FR	GRN	2.28	2.10	1.9	LDPE	0.18	
P1000	145	36	D	FR	GRN	1.96	1.59	1.3	PE/PP	0.31	
P1000	145	37	D	FR	SKY	4.68	2.39	1.2	LDPE		
P1000	145	38	D	FR	GRN	6.12	3.84	2.4	LDPE	0.37	
P1000	145	39	D	FR	GRN	2.49	1.81	1.3	PP	0.16	
P1000	145	40	D	FR	GRN	7.94	3.04	1.2	LDPE	0.43	0.33
P1000	145	41	D	FR	GRN	2.09	1.52	1.1	LDPE	0.13	
P1000	145	42	D	FR	YEL	5.25	3.62	2.5	LDPE	0.19	
P1000	145	43	D	FR	ORA	8.38	3.04	1.1	PA	0.54	
P1000	145	44	D	FR	RED	1.54	1.52	1.5	LDPE	0.06	
P1000	145	45	D	FR	TRS	4.64	2.46	1.3	LDPE	0.10	
P1000	145	46	D	FR	TRS	6.93	3.99	2.3	LDPE	0.27	
P1000	145	47	D	FR	WHT	3.97	2.61	1.7	PP	0.44	
P1000	145	48	D	FR	YEL	6.83	3.77	2.1	LDPE	0.24	
P1000	145	49	D	FR	BRW	10.00	4.93	2.4	LDPE	0.48	
P1000	145	50	D	FR	WHT	5.46	3.77	2.6	PP	0.08	
P1000	145	51	D	FR	WHT	4.11	3.33	2.7	PP	0.13	
P1000	145	52	D	FR	GRY	5.88	2.90	1.4	PE/PP	0.13	
P1000	145	53	D	FR	WHT	4.96	3.26	2.1	?? EVA		

P1000	145	54	D	FR	WHT	4.25	3.91	3.6	LDPE	0.73	0.27
P1000	145	55	D	FR	WHT	2.39	2.54	1.3	PP		
P1000	145	56	D	FR	WHT	5.11	4.28	1.8	LDPE	0.25	
P1000	146	1	D	PL	WHT	14.53	4.30	1.0	PP	0.80	
P1000	147	1	D	PL	WHT	4.42	2.37	1.0	PE/PA	0.07	
P1000	147	2	D	PL	WHT	7.95	3.18	1.0	LDPE	0.21	
P1000	147	3	D	PL	WHT	5.63	2.68	1.0	LDPE	0.24	
P1000	147	4	D	PL	BLK	5.21	2.58	1.0	LDPE	1.14	
P1000	147	5	D	PL	BLK	7.21	3.03	1.0	PP	1.50	
P1000	147	6	D	FR	WHT	12.19	3.94	1.0	PS	0.24	
P1000	147	7	D	FR	WHT	14.74	4.29	1.3	LDPE	0.12	
P1000	147	8	D	FR	WHT	10.87	4.14	1.6	LDPE	0.31	0.55
P1000	147	9	D	FR	YEL	16.83	5.05	1.5	LDPE	0.78	
P1000	147	10	D	FR	WHT	16.05	6.11	2.3	LDPE	0.37	
P1000	147	11	D	FR	WHT	5.84	2.73	1.0	PS	0.82	0.18
P1000	147	12	D	FR	WHT	2.37	1.62	1.1	PP		
P1000	147	13	D	FR	YEL	3.00	2.83	1.3	PP	0.24	
P1000	147	14	D	FR	WHT	5.22	3.33	2.1	LDPE	0.30	
P1000	147	15	D	FR	WHT	5.47	2.93	1.6	LDPE	0.93	
P1000	147	16	D	FR	YEL	2.85	2.63	1.2	LDPE		
P1000	147	17	D	FR	BLU	25.42	7.76	1.2	LDPE	0.24	
P1000	147	18	D	FR	GRN	8.43	4.66	1.3	LDPE	0.81	0.33
P1000	147	19	D	FR	GRN	6.10	4.08	1.4	PP	0.13	
P1000	147	20	D	FR	GRN	11.00	6.84	2.1	LDPE	0.19	
P1000	147	21	D	FR	GRN	5.04	4.08	1.7	HDPE	0.22	
P1000	147	22	D	FR	GRN	1.33	1.78	1.2	HDPE		
P1000	147	23	D	FR	GRN	5.12	2.87	1.6	LDPE		
P1000	147	24	D	FR	GRN	10.30	7.47	5.4	LDPE	0.70	
P1000	147	25	D	FR	WHT	7.63	4.43	2.6	LDPE	0.23	0.17
P1000	147	26	D	FR	YEL	7.13	2.76	1.1	HDPE	0.07	
P1000	147	27	D	FR	GRN	4.14	2.18	1.2	PP	0.26	
P1000	147	28	D	FR	GRN	3.07	3.56	4.1	LDPE	0.09	
P1000	147	29	D	FR	GRY	2.88	3.85	5.2	LDPE	0.83	0.12
P1000	147	30	D	FR	RED	2.96	1.84	1.1	PP	0.16	
P1000	147	31	D	FR	WHT	2.48	1.72	1.2	PP	0.17	
P1000	147	32	D	FR	WHT	1.06	1.61	1.2	PP	0.15	
P1000	147	33	D	FR	WHT	2.15	1.49	1.0	PP	0.17	
P1000	147	34	D	FR	GRY	2.56	2.47	2.4	PP	0.26	
P1000	147	35	D	FR	ORA	1.18	1.78	1.3	PP	0.35	

P1000	147	36	D	FR	WHT	2.13	1.61	1.2	PP	0.14	
P1000	147	37	D	FR	BLK	4.12	2.76	1.8	LDPE	0.21	
P1000	147	38	D	FR	TRS	2.40	1.61	1.1	PP	0.38	
P1000	147	39	D	FR	BLU	2.03	2.53	3.1	PP	0.32	
P1000	147	40	D	FR	BLU	0.95	1.03	1.1	PP	0.56	
P1000	147	41	D	FR	WHT	4.80	2.47	1.0	PS	0.45	
P1000	147	42	D	FR	PNK	4.02	3.33	1.4	LDPE	0.17	
P1000	148	1	D	PL	TRS	15.13	4.39	1.0	PP	0.90	
P1000	148	2	D	PL	WHT	11.21	3.78	1.0	LDPE	3.07	
P1000	148	3	D	PL	WHT	9.93	3.56	1.0	LDPE	0.20	
P1000	148	4	D	PL	GRY	11.88	3.89	1.0	PP	1.13	
P1000	148	5	D	PL	BLK	11.21	3.78	1.0	PP	0.66	
P1000	148	6	D	PL	BLU	27.76	5.94	1.0	LDPE	0.20	
P1000	148	7	D	FR	RED	10.00	3.33	1.1	LDPE	0.11	
P1000	148	8	D	FR	GRN	9.76	3.44	1.2	LDPE	0.24	
P1000	148	9	D	FR	YEL	21.70	10.56	5.1	HDPE	0.38	
P1000	148	10	D	FR	BLU	11.51	6.28	1.7	LDPE	0.14	
P1000	148	11	D	FR	BRW	10.40	5.94	1.7	LDPE	0.66	
P1000	148	12	D	FR	BRW	20.34	6.78	2.3	LDPE		
P1000	148	13	D	FR	WHT	12.57	4.00	1.0	PS	0.90	
P1000	148	14	D	FR	WHT	9.93	3.56	1.0	PS	0.90	
P1000	148	15	D	FR	WHT	13.20	5.06	1.9	LDPE	0.16	
P1000	148	16	D	FL	WHT	17.83	21.39	25.7	PP	0.19	
P1000	148	17	D	FR	WHT	26.15	6.11	1.4	LDPE	0.16	
P1000	148	18	D	FR	WHT	12.92	4.06	1.0	LDPE		
P1000	148	19	D	FR	WHT	15.06	8.27	2.3	PP		
P1000	148	20	D	FR	WHT	29.34	6.79	1.6	HDPE	0.27	0.25
P1000	148	21	D	FR	WHT	10.45	5.74	1.6	LDPE	0.19	
P1000	148	22	D	FR	TRS	16.27	4.32	1.1	HDPE	0.05	
P1000	148	23	D	FR	TRS	5.85	5.93	6.0	PP	0.15	
P1000	148	24	D	FR	WHT	3.60	2.16	1.3	PP	0.51	
P1000	148	25	D	FR	WHT	8.14	3.77	1.7	LDPE	0.20	
P1000	148	26	D	FR	WHT	10.30	3.27	1.0	LDPE	0.24	
P1000	148	27	D	FR	BRW	12.97	5.68	2.5	LDPE		
P1000	148	28	D	FR	BRW	12.57	4.63	1.7	PS	0.66	
P1000	148	29	D	FR	BRW	6.61	2.90	1.0	PS	0.49	
P1000	148	30	D	FR	BRW	2.18	1.67	1.0	HDPE	0.51	
P1000	148	31	D	FR	RED	6.08	5.19	2.2	PP	0.38	
P1000	148	32	D	FR	RED	7.10	3.02	1.3	PP	0.39	

P1000	148	33	D	FR	WHT	5.37	2.90	1.6	LDPE	0.29	
P1000	148	34	D	FR	BRW	3.19	2.35	1.7	PS	0.46	0.54
P1000	148	35	D	PL	WHT	0.67	0.93	1.0	PS	0.14	
P1000	148	36	D	FR	BRW	3.06	1.98	1.0	LDPE	0.31	0.24
P1000	148	37	D	FR	BLK	6.37	2.72	1.2	LDPE	0.39	0.20
P1000	148	38	D	FR	GRN	1.07	2.04	1.9	LDPE	0.20	0.13
P1000	148	39	D	FR	BLU	1.52	2.47	4.0	LDPE	0.14	
P1000	148	40	D	FR	PNK	1.92	1.73	1.6	PP	1.91	
P1000	148	41	D	FR	PNK	2.28	1.60	1.1	PP		
P1000	148	42	D	FR	GRN	3.65	4.07	2.3	PP	0.33	
P1000	148	43	D	FR	YEL	3.93	2.96	1.1	LDPE		
P1000	148	44	D	FR	WHT	2.51	2.90	1.7	PS	0.28	
P1000	148	45	D	FR	WHT	5.03	2.72	1.5	PP	0.23	
P1000	148	46	D	FR	WHT	9.91	3.21	1.0	PS	0.77	
P1000	148	47	D	FR	BRW	1.68	2.10	1.3	LDPE		
P1000	148	48	D	FR	BLK	1.26	1.85	2.7	PP	0.63	
P1000	148	49	D	FR	GRN	0.88	1.42	2.3	HDPE	0.12	
P1000	148	50	D	FR	BRW	0.88	1.30	1.9	PP		
P1000	148	51	D	FR	ORA	1.22	1.79	2.6	PP		
P1000	148	52	D	FR	BLU	1.72	1.48	1.0	PP	0.73	
P1000	149	1	D	FL	WHT	10.94	29.08	77.3	PP	0.43	
P1000	150	1	D	FR	WHT	10.84	4.03	1.5	PP	0.80	
P1000	151	a	D	FR	WHT	14.57	3.87	1.0	cellulosa		
P1000	151	b	D	FR	TRS	12.00	6.29	1.6	LDPE	0.22	0.16
P1000	152	1	D	FR	YEL	16.09	6.24	2.4	LDPE	0.25	0.16
P1000	153	1	D	FR	GRN	1.59	1.56	1.5	ABS		
P1000	154	1	D	FR	WHT	1.69	2.10	1.3	CaCO3		
P1000	155	1	D	FR	WHT	3.42	4.25	5.3	CaCO3		
P1000	156	1	D	FR	BRW	3.40	2.63	2.0	alga		
P1000	157	1	D	FR	WHT	6.62	2.90	1.0	PS	0.26	0.20
P1000	158	EMPTY	D	-	-	-	-	-	-	-	-
P1000	159	1	D	FR	BLU	1.21	2.04	1.7	PP	0.54	
P1000	160	1	D	FR	BLK	1.91	1.56	1.0	LDPE		


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123 a b c d e
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19 20 21 22 23 24
25 26

Figure 1 –pictures and ID number of the analyzed samples

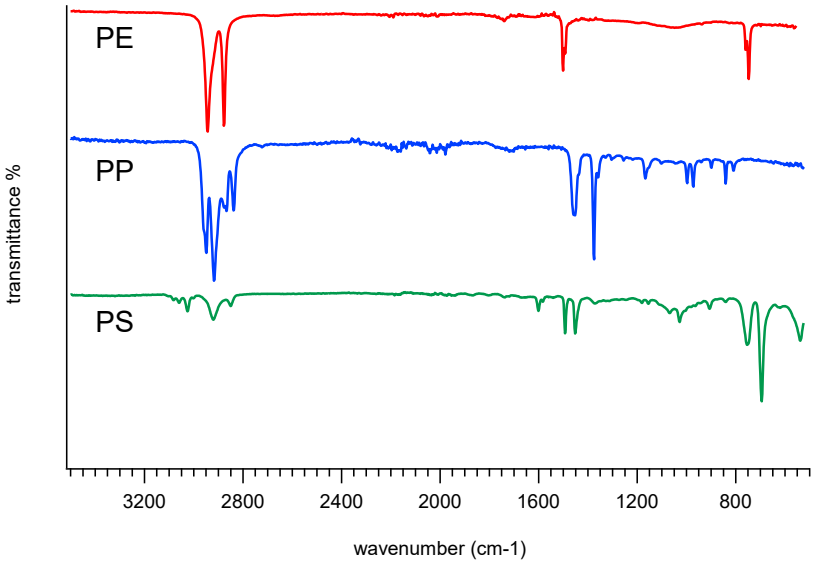

Figure 2 – representative FTIR spectra of most common polymers identified among the analyzed plastic debris: PE (red curve), PP (blue curve) and PS (green curve).

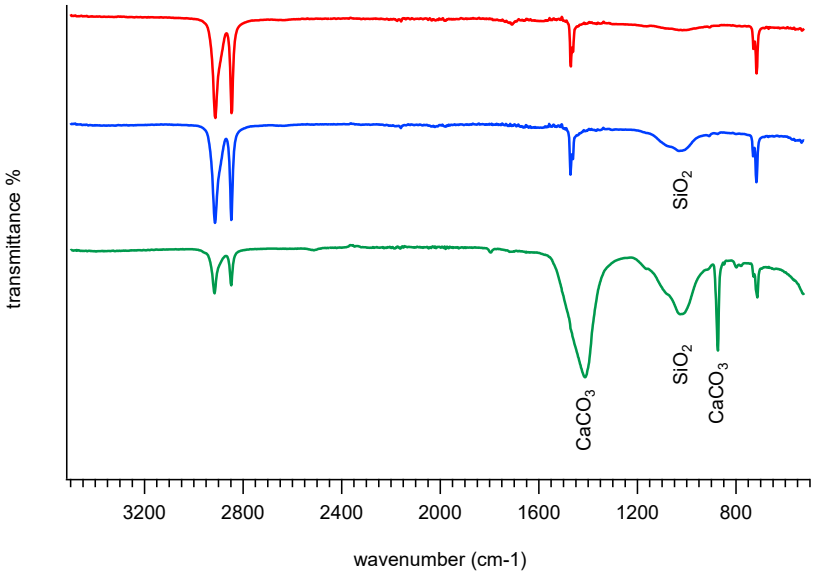

Figure 3 – representative FTIR spectra of PE samples without contaminants (red curve), with SiO_2 (blue curve) and with SiO_2 and $CaCO_3$ (green curve).

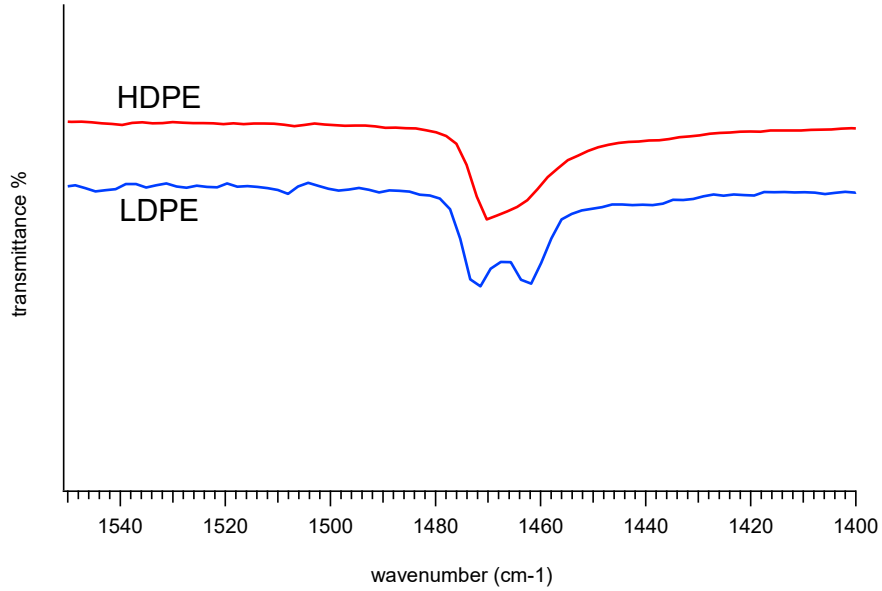

Figure 4 – representative FTIR spectra of HDPE (red) and LDPE (blue) samples: details of the spectral region centered on CH_2-bend vibration: a band splitting can be noticed in LDPE.

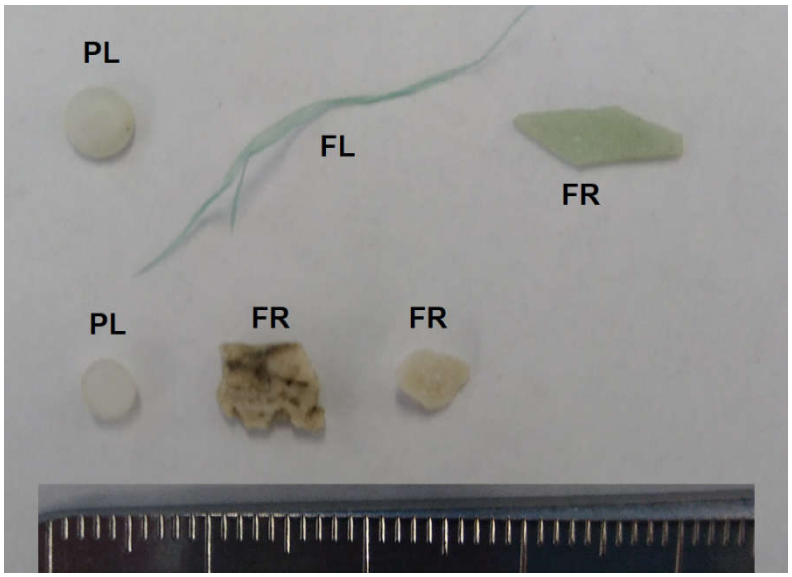

Figure 5 – representative debris shape: pellet (PL), filament (FL) and fragment (FR)

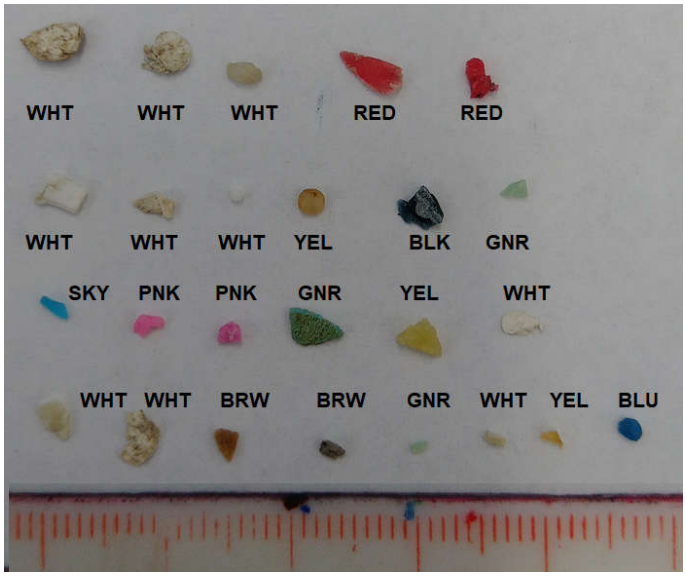

Figure 6 – representative debris color (for color codes refer to para. 2.1)

4 Discussion

Among the different polymers produced worldwide, the most common plastics found in marine waste include polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), polyurethane (PUR), polyethylene terephthalate (PET) and nylon (polyamide – PA) (Thushari 2020, Solomon 2016, Andrandy 2014). Table 4 shows the common applications of these plastics and their specific gravity.

Table 4: common plastics found in marine waste, their common application and specific gravity

Plastic type		**Common application**	**Specific gravity**
Low density polyethylene	LDPE	Plastic bags, film, packaging	0.91 – 0.93
High density polyethylene	HDPE	Bottle caps, storage containers	0.92 – 0.95
Polypropylene (PP)	PP	Ropes, storage containers, bottle caps	0.90 – 0.92
Polystyrene - expanded	EPS	Boxes, packaging	0.01 – 1.00
Polystyrene	PS	Utensils, cups	1.05 – 1.10
Polyvinyl chloride	PVC	Pipes, containers, insulators, films	1.20 – 1.30
Polyamide (Nylon)	PA	Ropes, fishing nets	1.15 – 1.20
Polyethylene terephthalate	PET	Bottles	1.35 – 1.40
Polyurethane	PU	Adhesives, foams	variable

A total number of 317 fragments have been categorized by means of visual analysis and then identified by FTIR. Of these, 78.5% were labeled as “fragments” (irregular shape), 17% as “pellets” (cylindrical or spherical) and 4.4% as “filaments” (very elongated, thin sheets). Fragments and filaments are most likely secondary microplastics (originated from the breakdown of large plastic items), while pellets (which represents almost the 20% of the total) can be categorized as primary microplastics (originally and intentionally manufactured in that size). These pellets are pre-production plastic pellets, made of raw resin, which are usually melted and used in the manufacturing of everyday plastic items. They somehow entered the environment before plastic objects production stage (most likely lost during transportation) and were subsequently found in areas of marine waste concentration. A summary of debris categories, sizes and aspect ratio is reported in Figure 7 and Figure 8. It is possible to notice that the majority of

debris are between 1 and 2 mm (considering their greater measured size), and about ¾ have an aspect ratio below 2. About 5% of the collected object are clearly elongated (aspect ratio > 10).

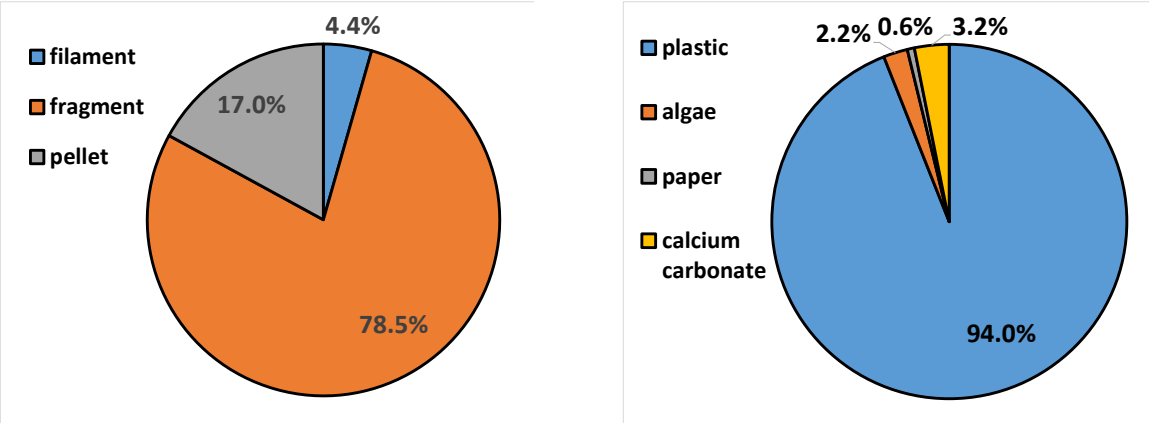

Figure 7 – debris classification, according to shape (left) and composition (right)

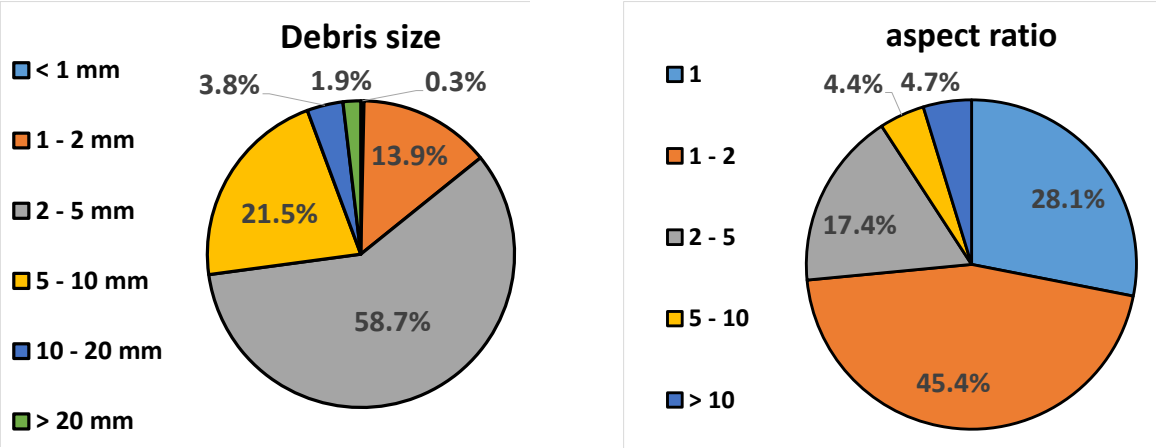

Figure 8 – debris size and aspect ratio

About 94% of the collected objects were plastic debris, while 6% were non-plastic (calcium carbonate 3.2%, algae 2.2%; paper 0.6%). Chart showing composition and color of analyzed fragments are shown in Figure 9 and Figure 10.

In the 85.2% of these plastic debris it was possible to identify a clear signal related to the presence of SiO_2; in the 42.2% of these latter, also $CaCO_3$ signal was noticeable. Given their sampling location (most likely Adriatic beaches – there was no information about the sampling location on the envelopes) it is possible to speculate a contamination of the samples with sand and/or shells.

All the identified plastics have a density lower than that of the water, therefore they are most likely are floating objects. No PET debris were found, even if this plastic is usually extensively found in marine waste. It is worth remembering that PET density is greater than water density, therefore PET objects do not float.

PE alone (HDPE + LDPE) represents more than half (54.7%) of the total collected plastic fragments. PP has the second share (27.2%). Polyolefin fraction (LDPE + HDPE + PP) is more than 80% of the collected plastics. About 15% of the collected objects were made of PS; given their softness, shape (round or roundish) and density (<1) most of these PS debris were recognized as expanded polystyrene (EPS). Of the "other plastics" fraction (3.7% of the total plastic objects), most of them (63.6%) were, again, polyolefin-based blends or copolymers (PE/PP, PE/PA and elastomers). The other fractions are represented by acrylonitrile butadiene styrene (ABS – 18.2%), polyurethane (PU – 9.1%) and polyamide (PA – 9.1%).

Figure 11 shows the data organized according to the different sampling site (240 objects from Po Delta site, 67 object from Pescara site and only 10 object from Teramo site were analyzed: the statistical significance should be taken into account). Again, it is possible to clearly notice a preponderance of polyolefin plastics (PE and PP). LDPE fraction seems to be higher in Pescara (58%) and Teramo (60%) than in Po Delta (40%). On the other hand, PP and PS fractions are higher (28% and 16%, respectively) in Po Delta than in Pescara (20% and 6%) and Teramo (10% and 0%). No PS debris were collected in Teramo (again, it is worth remembering that only 10 objects from Teramo were analyzed). The "other plastic" fraction (3.8% in Po Delta, 1.5% in Pescara and 10% in Teramo) is composed by 78% other polyolefin blends, 11% PA and 11% ABS in Po Delta. In Pescara the only "other" object is ABS, in Teramo the only "other" object is PU.

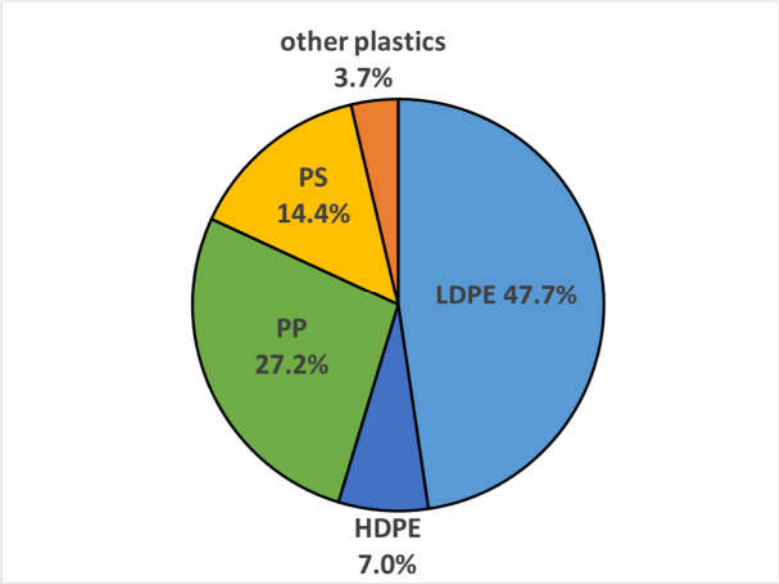

Figure 9 – relative abundance of polymers among the analyzed plastic objects

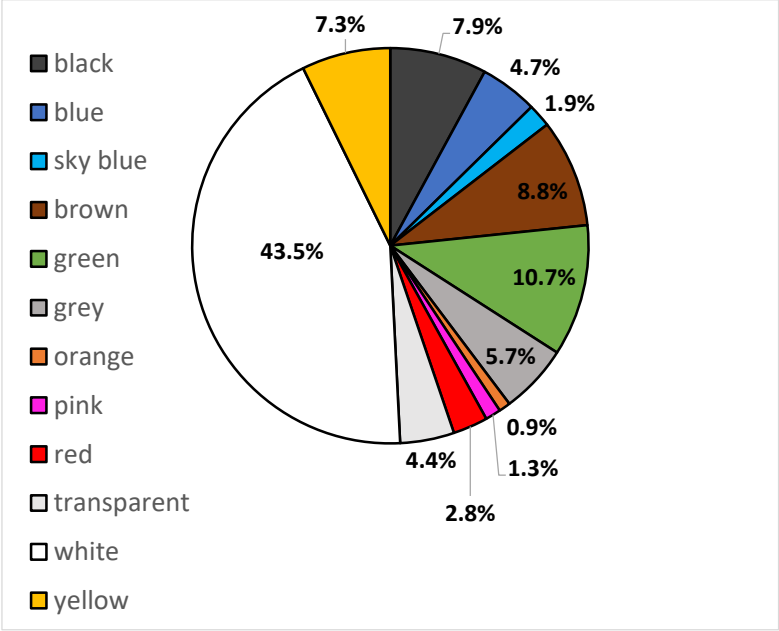

Figure 10 –colors of the analyzed plastic objects

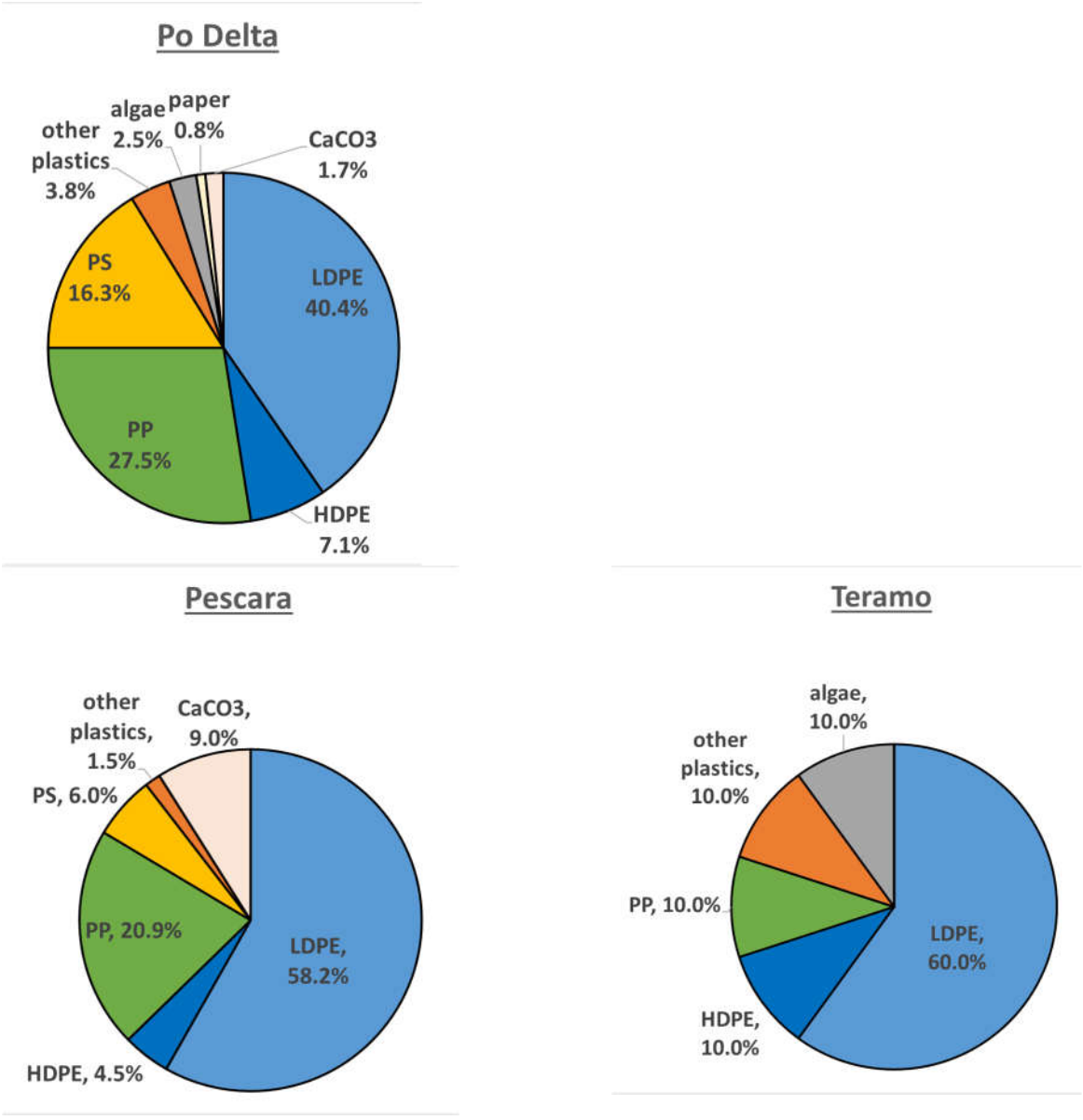

Figure 11 – relative abundance according to the different sampling sites. (Nr. of analyzed objects - Po delta: 240; Pescara: 67; Teramo: 10).

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