NET4mPLASTIC PROJECT

Activity 4.2

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Identification and classification of plastic debris via Image analysis, Fourier-Transform Infrared Spectroscopy and Raman Spectroscopy

November 2019

CONTRIBUTING PARTNERS	UNITS

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1 Introduction

This document reports on the analysis carried out on samples collected by the University of Ferrara and sent to the University of Trieste for analysis on November 2019.

2 Materials and methods

2.1 Received samples

Samples were received in two different sets:

- SET-A - 10 envelopes (labelled “Garibaldi P1-P3-P4”, “Estensi P1-P3-P5” and “Logonovo P2”), with relatively large plastic fragments
- SET-B - 2 sets of 5 glass microfiber filters (labelled “Pelosa2” and “Pelosa4”) + 2 clean filters

2.2 Samples identification

Large plastic samples of SET-A were labelled according to the envelope (for instance, “Garibaldi P3 LMP fragments” and a successive number: 1,2 and 3).

Small object analysed on filters of SET-B were identified according to the filter label (P2 or P4), a successive number identifying the filter (1,2,3,4 or 5) and a letter (for instance: P2-1-a)

2.3 Sample size

Samples sizes 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.

2.4 Sample analysis

Samples from SET-A were analysed 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.

Samples from SET-B were analysed means of optical microscopy (Nikon Eclipse 50i) and micro-focused Raman Spectroscopy (B&W Tech i-Raman Plus portable spectrometer).

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 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. Samples with only $CaCO_3$ vibrational bands were identified as fragments of shells or exoskeleton (biological origin). Samples with only SiO_2 bands were identified as sand grains or glass fragments.

Table 1: vibrational bands used to identify the most common polymers.

polymer	Vibrational bands (cm^{-1})	assignment
Polyethylene	2915 / 2845	CH_2 stretch
	1472 / 1462	CH_2 bend
	730 / 717	CH_2 rock
Polypropylene (PP)	2950 / 2915 / 2838	CH & CH_2 stretch
	1455	CH_2 bend
	1377	CH_3 bend
	972	CH_3 rock; C-C stretch
	840	CH_2 rock; C-CH_3 stretch
Polystyrene (PS)	1601	arom. ring stretch
	1492	arom. ring stretch
	1451	CH_2 bend
	1027	arom. CH bend
	694	arom. ring out of plane bend
Polyethylene terephthalate (PET)	1713	C=O stretch
	1241	C-O stretch
	1094	C-O stretch
	720	arom. CH out of plane 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

3 Results

3.1 SET-A (macroplastic fragments)

Sample classification, size and composition is reported in Table 3. A total number of 18 pieces were categorized. Type, shape and color codes are those reported in para. 2.2 and 2.3. The composition was assessed as reported in para 2.4. When measurable, the presence of SiO_2 or $CaCO_3$ signal is reported as "x" in the last columns. Samples pictures are shown in Figure 1. Some representative spectra are shown in Figure 2, Figure 3 and Figure 4.

Table 3: sample ID, classification and size

Sample ID		type	color	Dim L1 (mm)	Aspect ratio	Composition	SiO_2	$CaCO_3$
Garibaldi P1 LMP	1	FL	RED	19.8	10.3	PS		x
Garibaldi P3 LMP	1	FR	GRN	6.1	1.5	PP	x	x
Garibaldi P3 LMP	2	FR	GRN	3.6	1.2	PE	x	x
Garibaldi P3 LMP	3	FR	GRN	2.9	1.1	PE	x	x
Garibaldi P3 LMP	4	FR	GRN	3.0	1.4	PE	x	x
Garibaldi P3 LMP	5	FR	YEL	3.9	1.5	PE		
Garibaldi P3 LMP	6	PL	WHT	6.2	1.0	PE	x	x
Garibaldi P3 LMP	7	PL	BLK	5.2	1.0	PE	x	x
Garibaldi P4 LMP	1	FR	BLU	4.7	1.5	PE	x	x
Garibaldi P4 LMP	2	FR	YEL	5.3	1.9	PE	x	x
Garibaldi P4 LMP	3	PL	WHT	5.2	1.0	PE	x	x
Estensi P1 LMP	1	FR	GRY	4.1	1.9	PET	x	
Estensi P1 LMP	2	PL	WHT	5.1	1.0	PE	x	x
Estensi P3 LMP	1	PL	WHT	6.0	1.0	PE	x	x
Estensi P5 LMP	1	FR	RED	3.6	2.1	PE		
Estensi P5 LMP	2	FR	RED	3.8	1.6	PE		
Estensi P5 LMP	3	FR	RED	4.3	1.4	PE		
Logonovo P2	1	FR	BLU	11.3	3.1	PE	x	

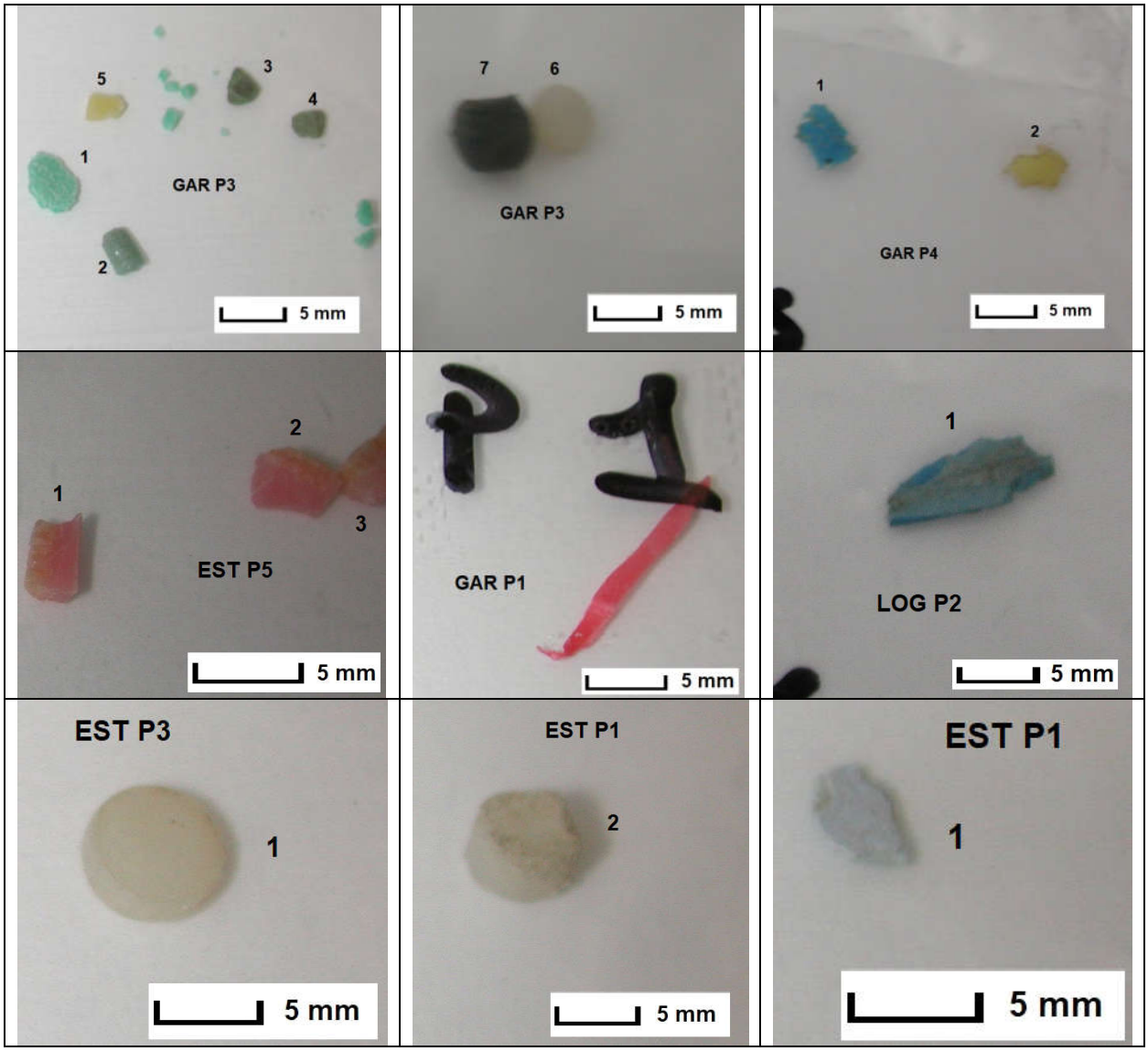

Figure 1 – sample pictures

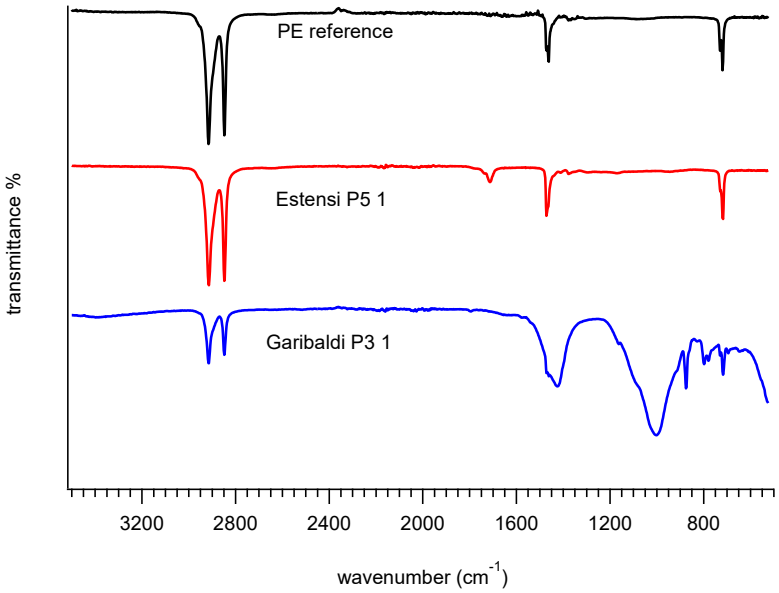

Figure 2 –FTIR spectra for PE reference, Esternsi P5-1 sample (PE fragment, with degradation-related C=O peak at 1700 cm^{-1}) and Garibaldi P3-1 (PE pellet with SiO_2 and $CaCO_3$ contamination)

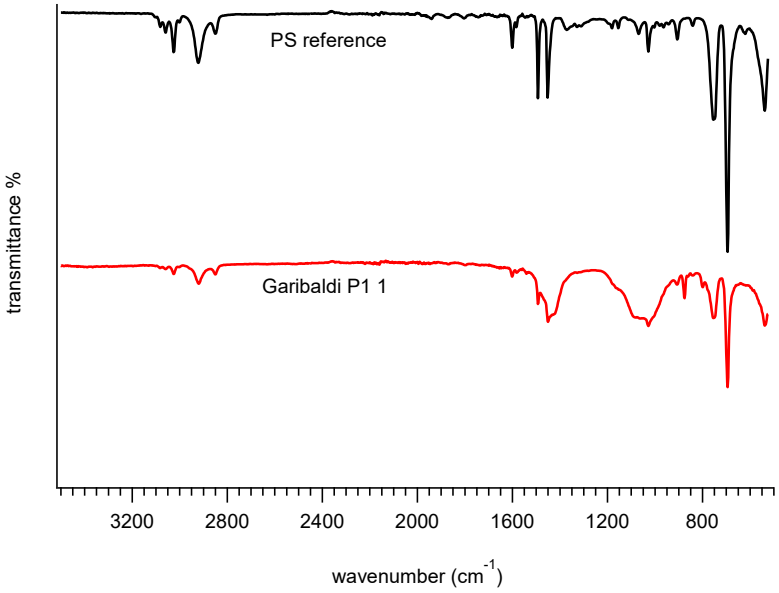

Figure 3 – FTIR spectra for PS reference and Garibaldi P1-1 (PS filament with SiO_2 and $CaCO_3$ contamination)

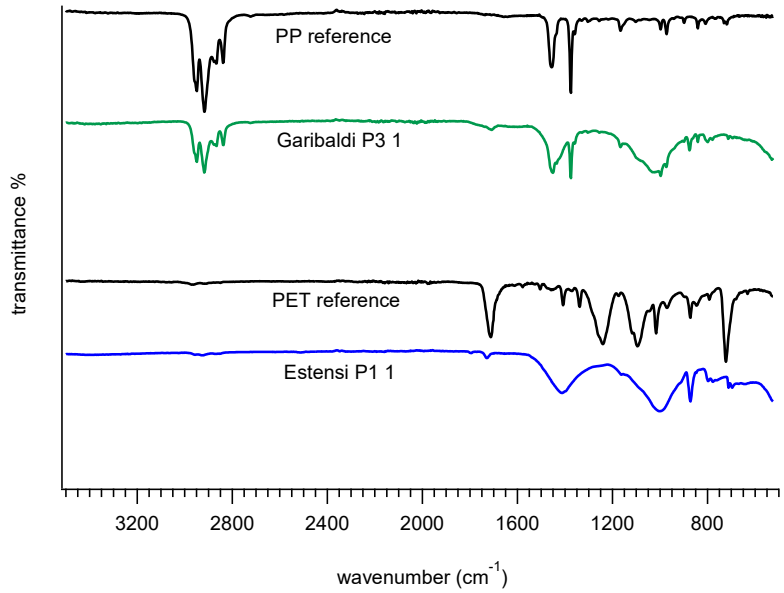

Figure 4 – FTIR spectra of PP and PET reference compared with Garibaldi P3-1 (PP fragment with SiO_2 and $CaCO_3$ contamination) and Estensi P1-1 (PET fragment with SiO_2 and $CaCO_3$ contamination)

3.1 SET-B (microfiber filters)

Figure 5 shows a representative picture of one filter and details of its surface; Figure 6 shows micrographs of some objects found on the filter surface. Several grain-like, glassy objects are noticeble. It was not possible to acquire Raman spectra directly on the glass filters due to the strong background noise of the substrate. The objects were therefore transferred on fluorite substrate for Raman measurements. A total of 121 spectra were collected by micro-focused Raman; nevertheless, only a 2 of these (<2%) were related to objects identified as "plastic". Most of the analysed objects were identified as SiO_2 or $CaCO_3$. Cross-checking the spectroscopy data with the micrographs, it is clear that these objects were simply grain of sand, glass fragments or shells. The only two microplastic found among analysed debris were identified as PET. Representative Raman spectra are shown in Figure 7.

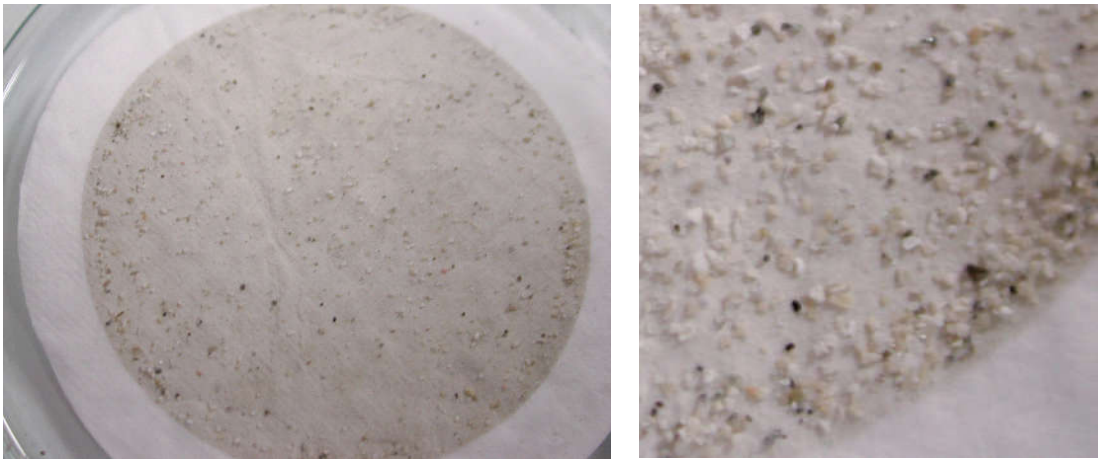

Figure 5 – sample picture of a filter and details of filter surface: several "grains" are noticeable

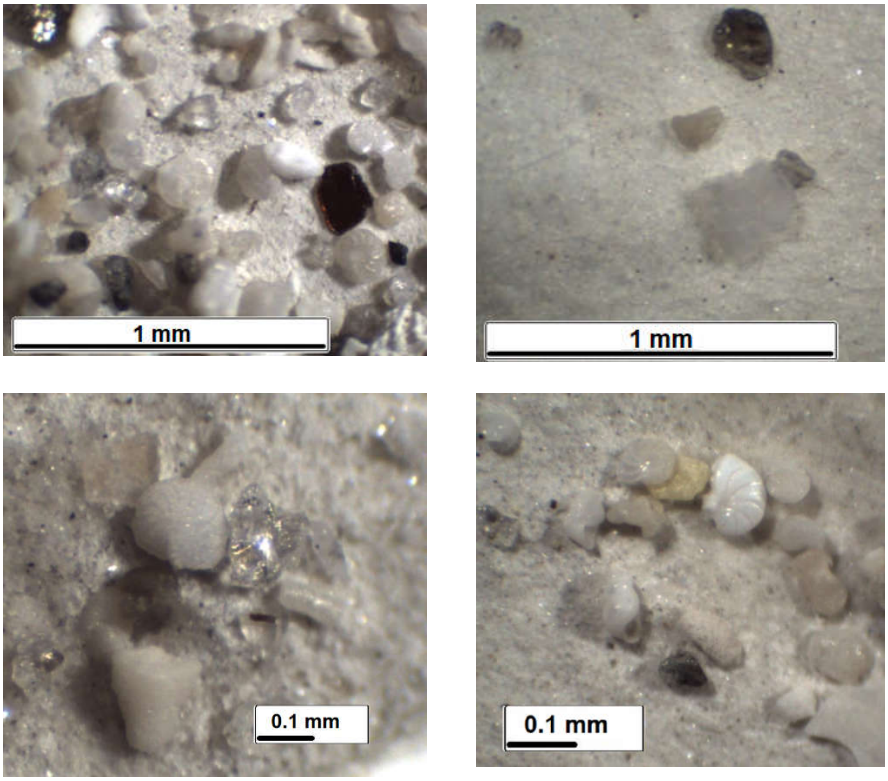

Figure 6 – representative micrographs (details) of typical objects found on filters

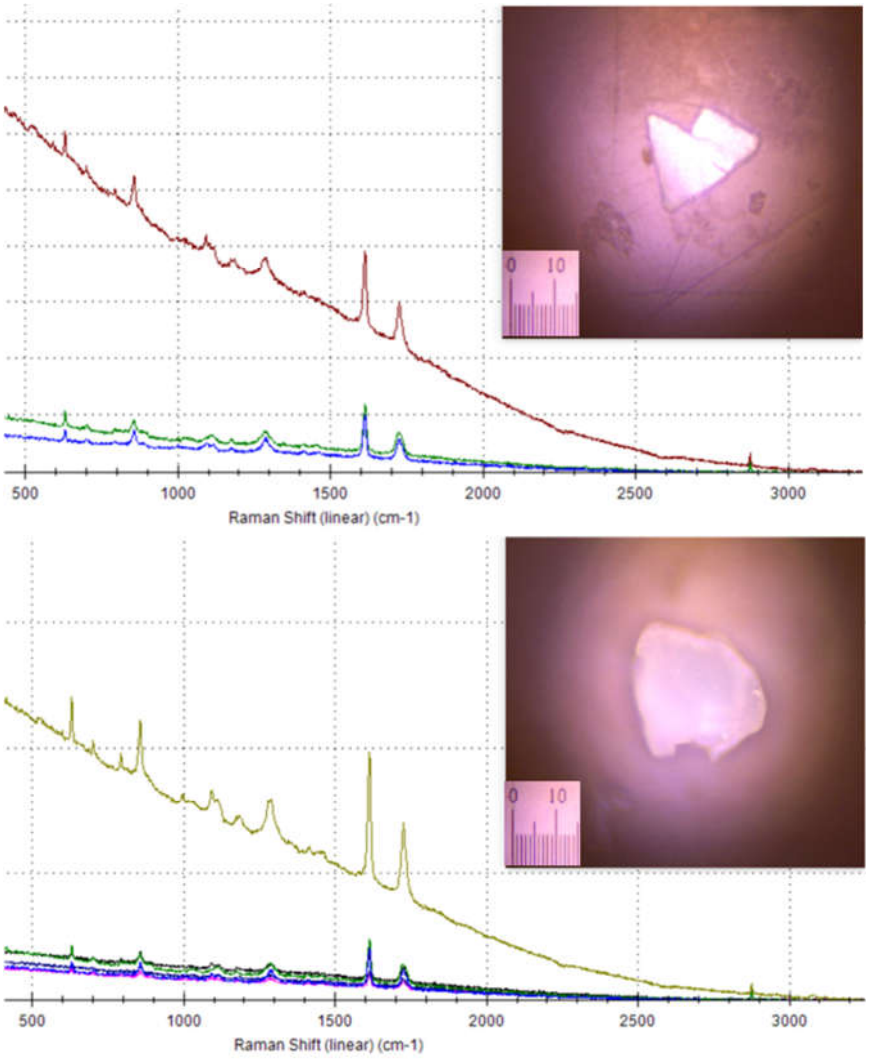

Figure 7 – Micrographs and Raman spectra of the only two microplastics found on the filters, identified as PET

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) (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	PUR	Adhesives, foams	variable

About a hundred of microscopic objects were analysed on filters of SET-B; only a few (<2%) were identified as plastic; the remaining objects (>98%) were minerals (sand, glass or shells). It is possible to conclude that SET-B method was not particularly suited for microplastic collection and analysis.

A total number of 18 macro-fragments of SET-A have been categorized by means of visual analysis and then identified by FTIR. The number of received objects is low to be statistically significant. Nevertheless, of the plastic macro-fragments (dimensions: min: 2.9 mm; max: 19.8 mm, average: 5.8 ±3.9 mm), 67% were categorized as “fragments” (irregular shape), 6% as “filaments” (very elongated, thin sheets) and 28% as “pellets” (cylindrical or spherical). Fragments and filaments are most likely secondary microplastics (originated from the breakdown of large plastic items), while pellets (which represents almost the 28% of the total) are pre-production

plastic pellets, made of raw resin, which are usually melted and used in the manufacturing of everyday plastic items. Hence these are primary microplastics (originally and intentionally manufactured in that size). 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.

In the 78% of these plastic debris it was possible to identify a clear signal related to the presence of SiO_2 and or $CaCO_3$. Given their sampling location (North Adriatic) it is possible to speculate a contamination of the samples with siliceous or carbonate sand and/or shells.

All the identified plastics (except one) have a density lower than that of the water, therefore they are most likely are floating objects. Only one PET debris was 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 sink. PE alone represents more than 80% of the total collected plastic fragments. A summary of debris categories, color and composition is reported in Figure 8.

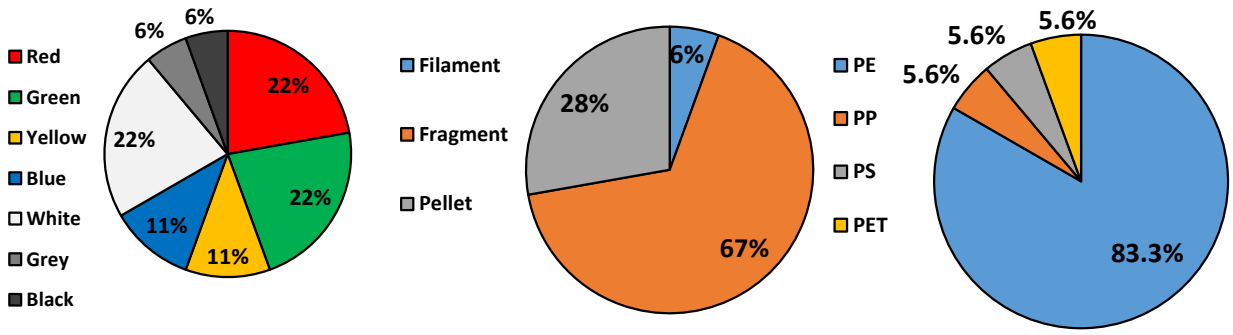

Figure 8 – debris classification, according to color, shape and composition

References

Jung et al., Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms, Marine Pollution Bulletin 127: 704-716 (2018)

Solomon and Palanisami, Microplastics in the Marine Environment: Status, Assessment Methodologies, Impacts and Solutions, Journal of Pollution Effects & Control 4: 1000161 (2016), doi.org/ 10.4172/2375-4397.1000161

Andrandy, Microplastics in the marine environment, Marine Pollution Bulletin 62: 1596-1605 (2011), doi.org/10.1016/j.marpolbul.2011.05.030