HyperSpectral Imaging based approach for monitoring of micro-plastics from marine environment

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Abstract The possibility to develop a sensor based procedure in order to monitor plastic presence in the marine environment was explored in this work. More in detail, this study was addressed to detect and to recognize different types of microplastics coming from sampling in different sea areas adopting a new approach, based on HyperSpectral Imaging (HSI) sensors. Moreover, a morphological and morphometrical particle characterization was carried by digital image processing. Morphological and morphometrical parameters, combined with hyperspectral imaging information, give a full characterization of each investigated particle, concurring to explain all the transportation, alteration and degradation phenomena suffered by each different polymer particle. Obtained results can represent an important starting point to develop, implement and set up monitor strategies to characterize marine microplastics. Moreover, the procedure developed in this work is fast, not expensive and reliable, making its utilization very profitable.

1 Introduction

Plastic debris in the marine environment are considered as a global problem: the increasing plastic production and its improper disposal when plastics become wastes heighten the build-up of these materials in the

environment, contaminating especially oceans [1]. Recent studies have shown as five large-scale accumulation regions of floating plastic debris exist in the oceans [2]. Once in the sea water, plastics undergo degradation processes (i.e. UV radiation, atmosphere oxidative properties and seawater hydrolytic properties) that induce their fragmentation, leading to an increasing amount of small plastic particles, called microplastics. Microplastics are defined as "plastic particles smaller than 5 m" according to the International Research Workshop on the Occurrence, Effects and Fate of Microplastic Marine Debris in September 2008 [3]. Due to their small size, microplastics can easily enter in the marine food chain, being ingested by marine biota [4]. The persistence of microplastics in the sea fauna (i.e. mussels) has implications for predators, including birds, crabs, starfish, predatory whelks [5] and humans. Microplastics can absorb persistent bio-accumulative and toxic compounds from seawater before being transferred to the marine organisms as food [6] causing health problems in each step of the food chain. In particular, toxic chemicals as persistent organic pollutants (POPs) are endocrine disruptors that produce dangerous effects. Moreover, some researches highlighted as the microplastics presence in the circulatory system can impede blood flow, damaging cardiac activity and tissues vascularization but also the ingested plastic can abrade the gut cavity [7]. Several studies indicate microplastic toxicological risks but concentrations in nature are not well known [8]. In order to obtain a better knowledge of the impacts due to the microplastics presence in the marine environment, most studies have focused on quantifying their abundance. A detailed monitoring of microplastics from the sea water is thus needed, in order to assess a reliable evaluation of the marine situation in terms of plastic presence [4]. Indeed, quantitative measurements are important in order to assess the risk and to realize monitoring purposes, but also to allow temporal and spatial comparison of pollutants [9]. In this work, the classical digital imaging and the innovative hyperspectral imaging approaches were combined in order to obtain a full classification of marine microplastic samples. A morphological and morphometrical analysis by digital images was coupled with the investigation of hyperspectral images that allows to identify, to recognize and to classify different types of polymers starting from known reference plastics. The fulfillment of a fast and non-destructive monitoring system, able to characterize and recognize different types of marine microplastics, can make the successive

operations, aiming to prevent and combat their production and spread, much more effective and targeted.

2 Materials and methods

2.1 Samples

The investigated marine microplastic samples were collected from the Mediterranean Sea along the northern coast of the Adriatic Sea and off the coast of Forlì-Cesena and Ferrara areas, during two measurement campaigns carried out by ISPRA (Italian National Institute for Environmental Protection and Research) and ARPAE (Regional Agency for Prevention, Environment and Energy of Emilia-Romagna, Italy), in October 2014 in the framework of the international project called Derelict Gear Management System in the Adriatic Region – DeFishGear, funded with the financial assistance of the IPA Adriatic Cross-Border Cooperation Programme [10]. The investigated area was divided in two transects, Cesenatico and Porto Garibaldi, and a station called Lido di Volano: the sampling was carried out in the first few meters of water column where the particles tend to float on the surface. For each transect, samples were collected at 500 m, 3 km, 10 km and 20 km off shore, while for the sampling at Lido di Volano station microplastics were taken at 10 km off shore. The collected number of microplastic samples was 643: 469 in the Cesenatico transect, 153 in the Porto Garibaldi transect and 21 in the Lido di Volano station. According to the particle shape, samples were classified as filaments, films, foam, fragments, granules, other, pellets and uncategorized. For the analyses shown in this work, fragment class was selected and 293 samples were thus analyzed (Table 1.1).

Table 1.1: Total and percentage number of microplastic samples belonging to the fragment class in each transect/station

	Cesenatico Transect	**Porto Garibaldi Transect**	**Lido di Volano Station**
N°fragments	186	97	10
% fragments	64	33	3

The 293 microplastic samples were grouped in about 10-12 particles and they were acquired by digital camera and hyperspectral imaging

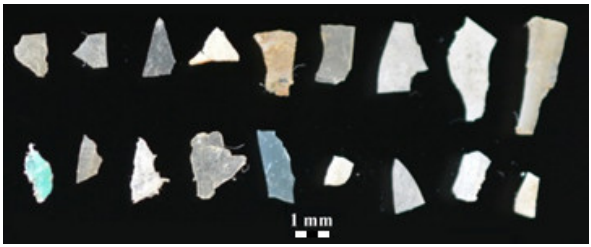


Figure 1.1: Marine microplastics from the Cesenatico Transect sample

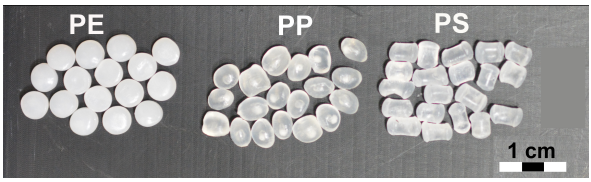


Figure 1.2: Virgin PP, PE and PS samples used as references for the identification of microplastics

working in the short wave infrared range (1000-2500 nm) (Figure 1.1). In total 25 digital images for morphological and morphometrical analysis and the corresponding 25 hyperspectral images were thus obtained.

In order to recognize the polymer type of each microplastic fragment, the SWIR spectra of virgin polypropylene (PP), virgin polyethylene (PE) and virgin polystyrene (PS) samples coming from an industrial production plant were used as references. Comparing the particle spectra with those of known reference polymers, the identification of polymer constituting the analyzed microplastic samples was performed. A classification model was also built and validated applying it on hyperspectral images rapresenting marine microplastics (Figure 1.2).

2.2 Image acquisition systems

Both classical and hyperspectral imaging acquisitions were carried out at "RawMaLab" (Raw Materials Laboratory) of the Department of Chemical Engineering, Materials & Environment (Sapienza - University of Rome, Italy). In order to acquire digital images of microplastic samples

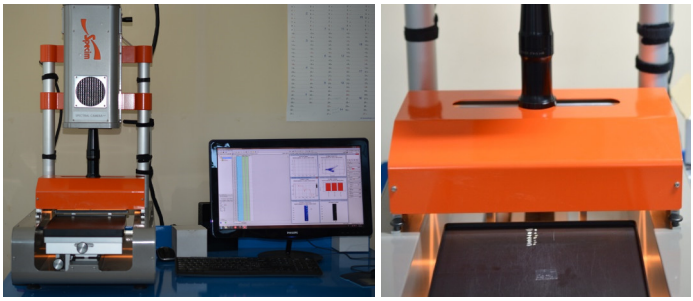
for morphological and morphometrical analyses, a Nikon D5200 camera was adopted. The 25 digital images thus obtained were processed adopting the Image-Pro Plus software by Media Cybernetics. More in detail, the following parameters were measured for each fragment particle:

- Area (mm^2);
- Axis major (mm);
- Axis minor (mm);
- Diameter max (mm);
- Diameter min (mm);
- Diameter mean (mm);
- Perimeter (mm);
- Roundness as the ratio between the perimeter^2 and the $4\pi \cdot area$;
- Fractal dimension.

The 25 hyperspectral images were acquired using the SISUChema XL^{TM} Chemical Imaging Workstation (Specim, Finland) (Figure 1.3), equipped with an ImSpector^{TM} N25E imaging spectrograph (Specim, Finland) working in the short wave infrared range (SWIR: 1000-2500 nm). The analytical station is controlled by a PC unit equipped with specialized acquisition/pre-processing software (Chemadaq^{TM}), to handle the different units and the sensing device constituting the platform and to perform the acquisition and the collection of spectra. Images were acquired scanning line by line the samples, with a width of 320 pixels and a number of frames variables according to the desired length. Calibration for black and white references was automatically performed.

The analyzed images were acquired with a macro lens and a field of view of 10 mm. 256 wavelengths were collected. Spectral data analyses were performed using PLS-Toolbox^{TM} under Matlab® environment.

The procedure for the analysis of the hyperspectral data was developed in different steps. First of all, Regions Of Interest (ROIs) were selected on each acquired particle in the hyperspectral images in order to obtain SWIR spectra to compare with plastic reference spectra for



a b

Figure 1.3: An overview of the SISUChema XL^{TM} chemical imaging workstation (Specim, Finldand) (a) and a detail of the macro lens acquiring microplastics (b)

a preliminary sample identification. Starting from reference plastics of known type, Principal Component Analysis (PCA) was applied in order to perform an exploratory analysis, useful to set the classes for the further classification purpose. In order to build a classification model, Partial Least-Squares Discriminant Analysis (PLS-DA) was adopted and it was validated applying the model to the hyperspectral images.

3 Results

3.1 Morphological and morphometrical analysis

Morphological and morphometrical results obtained for the investigated microplasic particles are reported in Table 1.2, in terms of mean, standard deviation, max and min values. Area ranges between 0.26 and 37.07 mm^2, Axis Major between 0.15 and 8.74 mm, Axis Minor varies between 0.30 and 6.57 mm, Diameter max ranges between 0.68 and 9.74 mm, Diameter min between 0.11 and 5.29 mm while Diameter mean is between 0.56 and 6.76 mm, Perimeter ranges between 1.92 and 27.77 mm. The mean value for the Roundness is around 1.6: only a very elongated particle was found in the Cesenatico transect with 39.21 as Roundness value. The Fractal Dimension of the analyzed microplastics ranges between 1.01 and 1.41 with a mean value of 1.06.

Table 1.2: Total and percentage number of microplastic samples belonging to the fragment class in each transect/station

	Cesenatico				Porto Garibaldi				Lido di Volano			
	Mean	**St.Dev**	**Max**	**Min**	**Mean**	**St.Dev**	**Max**	**Min**	**Mean**	**St.Dev**	**Max**	**Min**
Area (mm^2)	3.68	4.28	24.65	0.27	3.01	4.52	37.07	0.26	5.04	7.83	26.11	0.47
Axis Max (mm)	2.75	1.51	8.74	0.82	2.24	1.29	7.54	0.15	2.75	1.97	7.3	0.84
Axis Min (mm)	1.51	0.81	4.99	0.31	1.38	0.92	6.57	0.3	1.74	1.28	4.73	0.74
Diameter Max (mm)	2.83	1.59	9.74	0.83	2.29	1.31	8.19	0.68	2.58	1.88	6.96	0.98
Diameter Min (mm)	1.35	0.72	4.42	0.11	1.23	0.8	5.29	0.22	1.5	1.15	3.99	0.56
Diameter Mean (mm)	1.87	0.95	5.49	0.56	1.63	0.98	6.76	0.56	2.02	1.47	5.61	0.77
Perimeter (mm)	7.79	4.2	22.89	2.13	6.4	3.91	27.77	1.92	8.12	5.69	21.18	2.75
Roundness	1.78	2.8	39.21	0.36	1.45	0.35	3.22	1.08	1.59	0.82	3.91	1.17
Fractal Dimension	1.06	0.02	1.13	1.01	1.07	0.04	1.41	1.02	1.06	0.02	1.1	1.02

Starting from the mean diameter of each analyzed particle, according to the ranges set by literature for microplastics [11] [12] [13] as small (0.35-1.00 mm), medium (1.00-4.75 mm) and large (4.75-5.00 mm), samples were grouped and counted (Figure 1.4). Medium particles are the most abundant in each transect/station, followed by the small ones. Large microplastics, with mean diameter ranging between 4.75-5.00 mm and more than 5.00 mm, are very few and they are concentrated into the Cesenatico transect mainly. The low presence of large particles is probably due to all the degradation processes occurred in the sea water (i.e. UV radiation and seawater wavy motion) inducing their fragmentation.

3.2 Hyperspectral imaging

In order to collect microplastic particle spectra, some ROIs (Regions of Interest) were selected in each of the 25 HSI acquisitions (Figure 1.5).

The analyzed microplastics were classified as PE, PP and PS: 245 are PE particles, 32 are made of PP and 1 particle is constituted by PS (Table 1.3). 14 particles are not identified because of their black color that makes difficult the spectrum recognition. In Cesenatico transect, samples are more affected by the presence of unidentified particles. After the preliminary analysis that allowed to identify the most abundant polymers in the microplastic samples, a procedure for automatic recognition of plastic types was carried out.

The acquired raw and preprocessed spectra of PP, PE and PS references plastics are reported in Figure 1.6. After pre-processing stage,

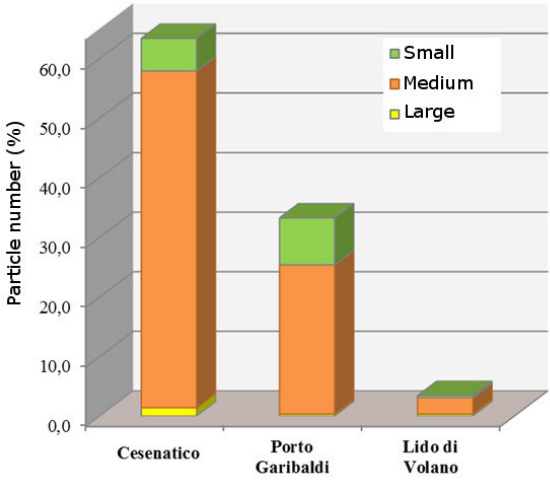


Figure 1.4: Microplastic particle number (%) grouped in small, medium and large per each transect/station according to [11] [12] [13]

Table 1.3: Number of particles and percentage values constituted by PE, PP, PS and unidentified (NI) for each transect/station

	Cesenatico		**Porto Garibaldi**		**Lido di Volano**	
	n°particles	%	n°particles	%	n°particles	%
PE	160	86	75	77	10	100
PP	12	6	20	21	0	0
PS	0	0	1	1	0	0
NI	14	8	1	1	0	0

PCA was applied as exploratory data analysis. The analysis of the score plot allows to identify three different groups according their spectral signature.

In Figure 1.7 score plot PC1-PC2 obtained after removal of some border pixels is shown. All the pixels represented in Figure 1.7 were selected as training dataset for PLS-DA model.

The obtained values of Sensitivity and Specificity are shown in Table 1.4.

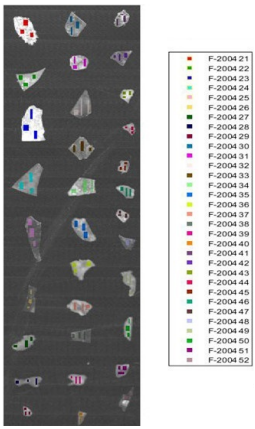


Figure 1.5: An example of the ROI selection on a SWIR-HSI image

Table 1.4: Sensitivity and Specificity for the PLS-DA model built for the recognition of microplastic types: PP, PE and PS

	Sensitivity		**Specificity**	
	Calibration	*Cross validation*	*Calibration*	*Cross validation*
PE	1.000	1.000	0.999	0.999
PP	1.000	1.000	1.000	1.000
PS	1.000	1.000	1.000	1.000

The results in terms of "class most probable" predictions are shown in Figure 1.8 : the class with the highest probability is assigned to each pixel in the image. Obtained results are very good, allowing to distinguish 3 PP particles, 9 PE particles and 1 PS particle clearly.

4 Conclusions

The study was carried out to obtain a full characterization of marine microplastics in order to monitor their presence in the marine environment. A morphological and morphometrical analysis was combined with SWIR-HSI analysis in order to evaluate particle sizes, shapes and polymer types. Moreover, a SWIR-HSI based procedure was developed in

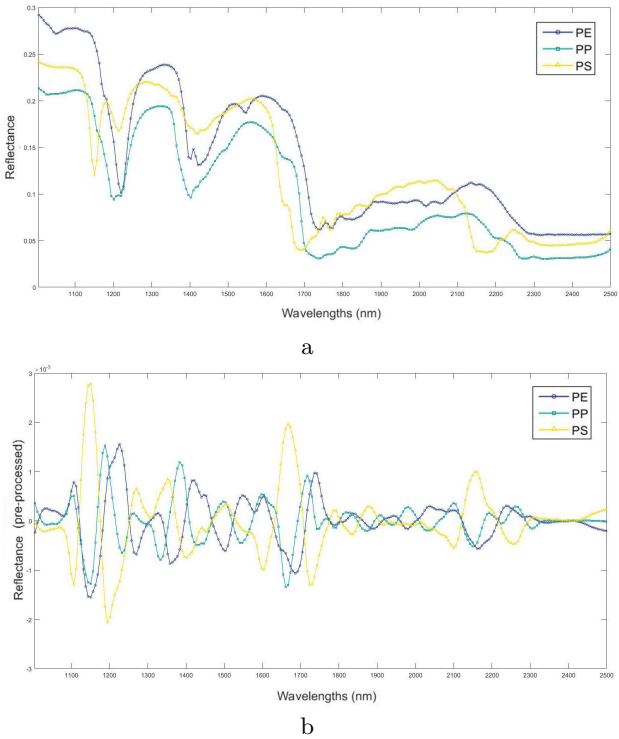


Figure 1.6: Raw spectra (a) and preprocessed spectra (b) after the application of 2nd Derivative e Mean Center algorithms of PE, PP and PS reference samples

order to implement an automatic recognition of PP, PE and PS in a hyperspectral image representing microplastic particles coming from sea water. More in detail, Partial Least-Squares Discriminant Analysis, after application of Principal Component Analysis, was used to build a model able to recognize/classify PP, PE and PS particles. The proposed HSI-based approach presents a lot of advantages: it is reliable, fast and non-destructive, allowing low-cost analysis. As confirmed by the results, the HSI can be profitably utilized to clearly discriminate PP, PE and PS

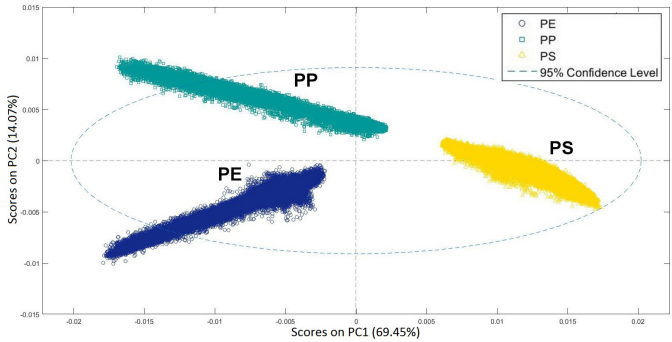


Figure 1.7: PC1-PC2 score plot as resulting after pixels removal from the training dataset in the SWIR wavelength field (1000-2500 nm)

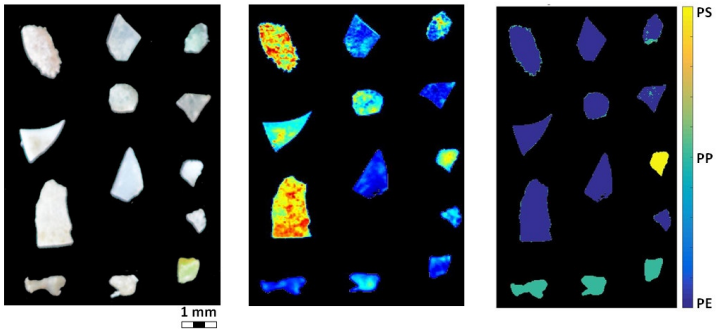


Figure 1.8: Digital image (a), hyperspectral image (b) and prediction map (c) obtained as result of the PLS-DA classification model

in the analyzed samples. Obtained results can be considered as an important starting point to develop monitor strategies for marine microplastic characterization. Further studies will be devoted to correlation between morphological and morphometrical parameters and the different degradation processes of marine microplastics related to the polymer types.

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