MARINE PLASTICS CHARACTERIZATION PROTOCOL

WP4 – Activity 4.2–Fishing for litter catches: composition and quantities definition

DELIVERABLE 4.2.5

Partner in Charge: LP

Partners involved: LP, PP1, PP2, PP4

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Summary

Introduction

This document aims to develop a short procedures collection to perform a qualitative and quantitative assessments about composition and status of plastic fraction present in the Marine Litter (ML) recovered during Fishing for Litter (FfL) activities in Italian and Croatian coastal areas. The proposed composition analysis points out how:

- to examine items constituting plastic litter in the FfL waste,

- to characterize materials to identify thermoplastic polymer (1) together with the contemporary description of macroscopic parameter (2) such as color, typology of assembly (single, poly or multilayered materials),

- to classify waste items by assignment to a previously stated category.

This latter activity can be carried out using definitions proposed in the "Guidance on Monitoring of Marine Litter in European Seas" [Hanke, 2013] in order to allow the comparison with existing data and the tracking of the potential source of the waste.

The marine litter recovered from the FfL activity during normal commercial fishing operations is disposed of at a specific collection site granted for this purpose by the municipal or port authorities concerned. In this step, all materials constituting the recovered marine litter are mixed and without a perspective of further treatments other than landfill disposal; actually, the recovery of waste from the sea is only a first step in solving the issue of Marine Litter present on sea floor. A further effort in the field of the waste management of FfL materials is necessary and should be applied to a sustainable solution regarding its disposal. All solutions should agree with the provisions of the Communitarian Directive 2008/98/EC, where a well-defined hierarchy is envisaged by the integrated management of waste, with a decreasing level of preference to be applied, from the prevention / reduction of waste production, reuse, recycling (recovery of materials) and energy recovery until, finally, to landfill disposal. While the prevention / reduction could be faced by a political and cultural approach such as the increase of the awareness of the population towards the problem of ML or the reduction of the use of disposable plastics, the following steps in the hierarchical management of ML require sound technological and scientific efforts for the classification and estimation of plastic waste, such as waste category and chemical composition. Therefore, these practices need to be leaded forward a more sustainable and less environmentally impacting recovery of plastic marine waste, avoiding finalizing the actions toward an exclusive landfill disposal.

Quantifications of the total amount and macroscopic composition of FfL waste collected at disposal in selected fishing ports within the project were routinely carried out for the main material groups (plastic, wood, metal, fishing gear etc.) and results are reported in the deliverables D4.2.1 and D4.2.3. In the context of this activity, specific sampling campaigns were implemented with the aim to perform a detailed investigation related to the ML plastic fraction, supporting a selected number of aforementioned monitoring. The obtained results are reported in deliverable D4.2.4.

The investigation approach was developed following key points below listed:

- **Individuation of sampling periods in relationship with other data (seasonality, change of oceanographic conditions, different bathymetric zones, etc.);**
- **Adoption of a suitable methodology of waste sample collection and sample preparation to be combined with the contemporary quantification of the ML collected during FfL activities;**
- **Choice of criteria for macroscopic description and classification of collected items;**
- **Selection and implementation of analytical techniques for the individuation of plastic ML polymeric composition;**
- **Search and formulation of a degradation status indicator.**

1. **Sampling and sample preparation for analysis**

   1.1. Sampling site selection and planning of monitoring campaigns

The selection of sampling stations could be determined by the presence of waste disposal sites authorized by pertinent authorities. Moreover, these sites are generally present in port areas, so it is necessary to check in advance the need to request access permission and check available access options to areas where the storage containers for ML are present. If disposal sites are available, the choice can be steered by:

- **logistical accessibility to the sites;**
- **type of fishing carried out in the area;**
- **amount of waste delivered;**
- **number of fishing boat involved in FfL activities;**

- **fishing area.**

The first point has a strong practical relevance due to the performance conditions for sampling activity, while other aspects represent indications that can be influenced by the purpose of each specific study or monitoring.

The same constraints expressed in the last two points can also determine the development of a planning of the monitoring activity, especially if they can change during the assessment time. Moreover, meteorological and oceanographic change, or sedimentological and geomorphological feature modifications during the monitoring, can affect the fate of plastic litter discharged in the marine environment. The choose of period for a sampling campaign must consider also potential causes triggering processes of dispersion and accumulation of ML on the sea floor in relationship with the aims of the projects. Therefore, it is important to record all available information in order to support the results obtained. For example, presence of rivers or streams and their hydrological behavior or marine currents should be taken into account in relationship to the fishing area involved.

1.2. Sampling methodology

Based on preliminary and previous activities on marine waste monitoring, for each sampling campaign and selected area, about 100 items of plastic waste were collected. This number was indicated because it represents an adequate compromise between performing representative analyses of marine waste in relation to time and the logistic constraints generally found during common monitoring practices.

It is advisable to sample items for the analysis at the same time as other marine litter quantification activities. That permits to better define the sampling strategy and to retrieve significant information in order to track source and consistency of the disposed Marine Litter. Therefore, the materials, to be collected into special bags used to dispose of the waste recovered during Fishing for Litter activities, is first subjected to a visual inspection during the contemporary evaluation of quantity and typology of Marine Litter. In this step, it is important to individuate and select five (or more) FfL bags, choosing those with most heterogeneous and abundant content in terms of plastic items. An important practical aspect of this step is represented by the fact that a first separation is carried out between waste materials. During the project ML-REPAIR the weight estimation of different categories of litter is performed following the procedure here described.

In the first step **A) Fishing Related Items (FRI)** are separated from **B) Other Items (OI)**; in the second step these two macro categories are further subdivided, obtaining different groups based on typology of fishing gear: for **FRI (a1_Mussel Nets**, **a2_Gill Nets**, **a3_Other Nets**, **a4_Pots & Traps**, **a5_Ropes**, **a6_Cables**, **a7_Foderone [Bottom Panels]** and **a8_Other**), while for **B) OI** recovered waste is separated according to a compositional approach: **b1_Plastic**, **b2_Metal**, **b3_Rubber**, **b4_Glass**, **b5_Paper**, **b6_Textile**, **b7_Wood** and **b8_Mixed**.

These materials are physically separated and spread on the working ground, allowing the selection of items to pick up for the characterizations in field and laboratory. Plastic litter is recovered principally from **b1**, **b3** (for scientific purposes synthetic rubber and other elastomers can be considered as part of the plastic polymer category) and from the plastic fraction in **A)** (which often represents the largest fraction of this macro category).

The overall **Plastic Marine Litter Sample (PMLS)** is, therefore, assembled collecting approximately **100 plastic items** by means of the following procedure:

- **estimate** the **plastic fraction weight** or **plastic items number** collected in each FfL bag up to a total of 5 bags;

- **assign** an **identification code** to each FfL bag involved in the sampling (the ID used in the "FFL samples – data collection form" for the ML-REPAIR project)**;**

- **select 100 items** in **proportion** to their **bag weight** with respect to the total weight of all 5 FfL bags or in **proportion** to the **number of items** per bag with respect to the total number obtained from all FfL bags. The latter selection is preferable because less affected by the presence of big items in the bag and is simpler to be performed. If the total number of collected plastic items is <100, additional samples should be selected from further bags (annotating the ID of supplementary bags selected) until that value is reached;

- **select sections** of approximately **5/6 cm in size** from the chosen items (for the **bottles** take the **upper section,** including the **cap**, the **seal ring** and **expiration date,** if present**)** by **cutting** them with **scissors** or **nippers.** If the partial item does not allow to individuate its category of items for further classification, mark the piece and annotate the referring mark;

- for **each FfL bag separate fragments** according to **RFI** and **OI** categories and collected **subsamples** in separate containers. Simple plastic bags (such as freezer bags) can be used

as samples containers. If possible, rinse the fragments roughly with tap water before putting them in the bag. **Merge** the two subsample containers in a single container related to the FfL bag. Label the container with the following data:

- **Location** (State international code and sampling site location, preferably with geographic coordinates)
- **Date** of sampling campaign
- **FfL bag ID** ("FFL samples – data collection form" for ML-REPAIR project)
- **Macro category acronym** (for subsample container)

1.3. Safety regulations and personal protection devices

Disposal containers for FfL bags are generally available in port areas, which are assimilable to industrial area. From an administrative point of view, it could be necessary to request accession permission to related authorities. Another important issue in such activities in port areas is relative to safety rules and practice to be strictly followed. Such rules can be specific for each site; therefore, it is very important to ask for specific instructions to managing authorities before accessing the site.

Moreover, it is anyway imperative to adopt good safety practices:

-pay attention and avoid hindering the movement of vehicles and personnel in operation.

When operating near disposal site containers, it is important to control presence of cutting or abrading objects, as well as pest or other animals (rats, gulls, etc.) that may constitute a health risk for the operators. Personal protective equipment is highly recommended if not even mandatory when operating in such areas; the equipment to be adopted may be the following:

- **work gloves cutting and abrasion resistant**
- **puncture resistant gloves**
- **safety shatterproof glasses**
- **Dust masks (if necessary)**
- **Safety work trousers with tear-resistant fabric**
- **Disposable non-woven suit (e.g. Tyvek)**

- **Safety shoes with toe cap and reinforced sole**

All the actions carried out in the field or in the laboratory must be in accordance with the national laws and regulations regarding safety in the workplace, based on **Council Directive 89/391/EEC — Measures to improve the safety and health of workers at work**. For Italian operators the referring text is the **D. Lgs. n. 81/2008 "Testo unico in materia di salute e sicurezza nei luoghi di lavoro"**. For Croatian operators the referring text is Act of June 5, 2014 on Occupational Safety (Text No. 1334), **NN 71/2014 "Zakon o zaštiti na radu".**

1.4. Sample preparation for analysis

Treatment and preparation of PMLS can be performed in the field or in the laboratory in relationship to availability of facilities in proximity of disposal site. It is required to clean the surface of analyzed PMLS fragments. In order to correctly characterize their polymer composition through spectroscopic analytical techniques (Raman, Fourier Transform InfraRed-FTIR, Near Infrared Spectroscopy-NIR). In order to facilitate the application of the proposed protocol to routinely monitoring activities, an effort was done to test and select cleaning procedures and related agents, which are implementable by using chemicals cheap and easy to find on the market, and with minimum hazard for the operator.

Plastic items recovered on the seafloor are subjected to various physical, chemical and, particularly, biological processes. Items can be buried by sediment, damaged by currents (abrasion, dent and breakage), covered by algal or bacterial biofilm and encrusted by colonial benthic organisms, bivalve molluscans or worms.

A cleaning step must be performed **at sampling site** by **rinsing roughly** each item and fragment with **tap water** in order to massively remove the sediment deposits. In some cases, such incrustations can be removed also by drying samples and shaking them.

A second washing step to be performed **in the laboratory or facility site** using **brushes** allows to remove residual silt and clay. If possible, such step should include also the elimination of dent or other crushing, which do not permit to effectively clean the collected ML fragments.

In the following cleaning steps other incrustations must be removed, such as biofilm and bioorganic deposits, through a mild oxidative reaction, and biogenic carbonates by means of acid dissolution.

1.4.1. Removal of biofilm and bioorganic deposits

In the third cleaning step, a mild oxidation was selected as best procedure in order to eliminate the biological fouling that generally covers the surface of ML plastic fragments. In order to avoid the use of reagents in liquid form, such as H_2O_2 (Hydrogen Peroxide) solutions, which exhibits issues for storage and handling, the choice was directed towards a solid salt commonly used as a bleaching substance in commercial detergents, **Sodium Percarbonate**. This is preferable to Sodium Perborate, which is recently suspected of posing some environmental concern. It is possible to find it commercially in formulations without additives. The **Sodium Percarbonate** is a solid adduct of sodium carbonate and hydrogen peroxide, whose formula is **2 Na_2CO_3 3 H_2O_2** (CAS Number 15630-89-4). The solubility in water is approx. 150 g/L and the molar mass is 156.98 g/mol. A **80-100 g/L water solution of sodium percarbonate has been demonstrated to be a good oxidizing agent** for cleaning ML plastic items, but the concentration can be increased, based on the organic load, toward its limit of solubility. Plastic fragments can be **left to soak for one or two days in the solution at room temperature**. Then they should be rinsed thoroughly with tap water (or demineralized water, if possible).
During such operations, it is important to wear protective glasses and protective gloves since Sodium Percarbonate is an irritant and oxidizing agent, as clearly declared on the packaging.

1.4.2. Biogenic carbonate encrustation dissolution

In the fourth step, the carbonate fouling can be removed by acid dissolution, by applying a water solution of a weak organic acid. **Citric acid** has been adopted in order to avoid handling strong acids, such as Hydrochloric acid and sulfuric acid, which would require the use of a chemical hood (recommended also for Acetic Acid). Moreover, Citric Acid is more effective than acetic Acid since it is also a metal complexing agent. Indeed, Citric acid is available in the form of a salt allowing the direct preparation of the solutions without the dilution of concentrate acid solutions of which could be irritating to the respiratory tract, such as Hydrochloric and Acetic acid. Citric acid is commercially available at low costs. It is a tricarboxylic acid with formula $C_6H_8O_7$ (CAS Number 77-92-9). The solubility in water is very high, approx. 592 g/L at 20°C and the molar mass of 210.04 g/mol (as monohydrate salt). For the plastic cleaning a 150g/L water solution of Citric acid can be prepared: it proved to be a good acid descaler for cleaning ML plastic items. Plastic fragments can be left to soak for one or two days. Then, they should be rinsed thoroughly with tap water (demineralized water, if possible). After the rinse step, plastic items should be accurately dried before storing them for following analysis.

During such operations, it is important to wear protective glasses and protective gloves since Citric Acid is a skin and eye irritant, as clearly stated on the packaging.

2. Methods and instruments for classification and polymer identification applied to Plastic Marine Litter Samples (PMLS)

After cleaning, the selected samples can be subjected to the partition for single items and stored separately in a single bag. This must be labeled by assigning a unique identification code. This step can be performed simultaneously with the classification of the objects to be analyzed. This procedure should be applied if further analyses or cross-reports are planned between the data and the creation of a database.

2.1. Criteria for the classification, macroscopic description and labeling of waste items

2.1.1. Code assignment

The code assignment is important in the case of creation of a database, for multicriteria evaluations performed at different time, for repeated analysis with different instruments and in the case of historical specimen archive development. Within the ML-REPAIR project it was decided to assemble an identification number including geographic, temporal, macro-category information and PMLS of origin. According to this, a **Sampling Campaign Code** (**SCC**) was created (Tab. 1).

Data	Geographic				Time		Sampling Campaign Code (SCC)
ID	Nation ID		Location ID		Month (mm)	Year (yy)	Nat.ID/Loc.ID/mm/yy
Examples	IT	Italy	CH	Fishing Port (Chioggia, VE)	12	18	IT/CH/12/18
	HR	Croatia	G4	Croatian Fishing Zone (Hvar Channel)	01	19	HR/G4/01/19

Table 1: Examples of Sampling Campaign Code (SCC) for items collected during the FfL activities performed within the ML-REPAIR Project

Each single item has been labeled with its **specific SCC code**. The **PMLS** number means the Marine Litter bag sampled in the specific campaign. A **progressive number** for the **entire sampling campaign has been assigned to e**ach item, preceded by the abbreviation of previously defined **macro-categories (MCat)**, **F** for the **Relative to Fishing Item (RFI)** and **O** for the **Other (OI)** (See

2.2 Sampling methodology). In some cases the progressive campaign number can be followed by the acronym **SF** (**Special Features**), indicating the specific item section: letters with uppercase letters (A, B, C, etc.) indicate sections of objects consisting of an assembly of distinct elements (typical examples are bottles with caps and seals, or containers with connected lids), while for objects made of composite or multilayer materials (like packaging formed by superimposing different films), the individual fractions are indicated with lower case letters in italics reminding the initials of cardinal numbers (f (first), s (second), t (third), etc) (Tab. 2).

Data	Campaign	Item allocation		It. detail	Item Univocal Code (or part)
ID	**S.C.C.**	**PMLS N. (id-n)**	**MCat**	**ProgN**	**SF**	**S.C.C._id-n_MCat-ProgN(SF)**
Examples	**IT/CH/12/18**	**id-1**	**F**	**4**		**IT/CH/12/18_id-1_F-4**
	HR/G4/01/19	**id-1**	**O**	**5**		**HR/G4/01/19_id-1_O-5**
	IT/CH/06/18	**id-4**	**F**	**46**	**A**	**IT/CH/06/18_id-4_F-46A**
	HR/F2/02/19	**id-19**	**O**	**19**	**f**	**HR/F2/02/19_id-19_O-70f**

Table 2: Examples of Item Univocal Codes for items collected during the FfL activities performed within the ML-REPAIR Project

2.1.2. Waste classification and description

In order to characterize collected samples in terms of distribution of waste typology, based on the source and function of the original object, all items have been listed and classified according to the ***TSG_ML General- Code*** proposed by the ***MSFD Technical Subgroup on Marine Litter*** in the Annex 8.1 - Master List of Categories of Litter Items from the ***Guidance on Monitoring of Marine Litter in European Seas*** (Hanke et al., 2013). It may be preferable to use the list of codes proposed in the Guidance for the beach litter, in order to expand the number of waste classification options. If this option is used, it is important to note also the original size of some objects (e.g., fragments, sheets, bags etc.) before cutting the fragment to be analyzed.

Moreover, it is useful to report (as indicated in 3.1.1) also information related to items that are assembled or composite and multilayered.

Finally, it is basic to note in the database also the colors of the waste items; if more colors are present, these are annotated in order of covered extension, while for objects with different colors outside and inside, the outer surface should precede the inner one, if identifiable.

2.2. Polymer Characterization - Methods in Vibrational Spectroscopy

The identification of polymeric composition of marine litter plastics constitutes the core activity in advanced monitoring of plastic waste in the Marine Litter, especially if the aim of these actions is to provide a "sustainable fate" evaluation for the recovered waste, different from landfill disposal.

An effective support in the characterization of plastic polymer for the waste management needs methods and instruments without no time-consuming processes, reliable and offer the possibility to avoid further sample preparation and treatment before the analysis. Vibrational spectroscopy includes well established techniques applied also in the study of plastic polymers, offering a wide range of sub-techniques, such as non-destructive ones, which can be **applied directly to collected sample** even on-site and can **immediately identify the examined material**. Within the ML-REPAIR, it was decided to apply the following three techniques: **Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance** (FTIR-ATR), **Raman spectroscopy coupled to optical microscopy** (μ-Raman), and **Near InfraRed Spectroscopy** (NIR).

For each item or section, in the case of composite or assembled materials, identification data has been obtained by results of more measurements on the examined surface.

At least three analysis have been carried out **on different areas of collected items** (generally two main surfaces can be individuated) or different sections with **μ-Raman** and **FTIR-ATR**. Afterwards, acquired spectra have been used to identify and confirm the composition of investigated materials by using a **reference database** generated by **standard material characterization**. A rapid identification of material composition has been provided by using a handheld NIR spectrometer, which allows an automatic spectrum interpretation performed directly by instruments.

The adopted NIR allows a large spot covering a relevant area of item surface, and a correlation score about quality of the obtained analytical results is provided by the instrument. These features allow to limit the replication of analytical measurements.

2.3. Evaluation of potential "on-site" polymer identification.

In this last part of the protocol, the investigation carried out to compare results coming from the NIR handheld spectrometer with respect to FTIR-ATR spectroscopy identification of Marine Litter plastics is described in detail.

The commercial availability of portable and handheld vibrational spectroscopy instruments represents an interesting opportunity to develop more incisive supports to the waste management in the field, directly at disposal and treatment site. A Near Infrared Spectroscopy technique developed for application in industrial processes and stock material control, which allows also a rapid identification of plastic polymeric composition, was used. For this purpose, the assessment of the applicability of this technique to Marine Litter and the reliability of the results was tested using a Near Infrared (NIR) handheld spectrometer (Phazir TM 1624, Thermo Fisher Scientific Inc.; formerly Polychromix). Based on information supplied by the manufacturer, this instrument works in diffuse reflection mode in the 1600-2400nm spectral range, with an optical resolution of 11nm and the identification of synthetic polymers is carried out through the instrumental software chemometric method coupled to a spectral library. As for the recycling of plastics from urban waste, also ML polymers must be separated and selected for a proper following reuse as raw material. For example, in order to produce fuel by pyrolysis, it is necessary to use polyolefins with low contaminations by other thermoplastic polymers [Lopez et al., 2017; Buttler et al., 2011]. Among various spectroscopic instrumentations bearing technologies with a high level of miniaturization, those applying micro-electro-mechanical system (MEMS), such as the instrument used, seem more appealing, thanks to an electro-mechanical configurable chip changing the configuration of its pixels to act as a diffracting or reflecting element, allowing the selection of different infrared light wavelengths dispersed by sample radiation towards an InGaAs detector [Sorrak et al., 2012; Geller,2017]. In the last decades, these portable instruments have assumed an important role in the control of products of commercial interest such as pharmaceuticals, food and virgin or recycled thermoplastic resins. The main purposes of this assessment were: 1) to verify the applicability of this technique to the identification of plastic materials after environmental deterioration processes; 2) to compare obtained analytical results with those attainable by established laboratory techniques such as FTIR-ATR.

Data from the two techniques were obtained analyzing four groups of plastic items corresponding to samples of Marine Litter taken in Italy in 2018 and two in Croatia in 2019.

The information about sampling sites are reported in the Table 3; the heterogenicity of the used sample pool in relationship to the different marine environment, especially for the bathymetry is evidenced. The used ML plastics from different seafloors allowed to use waste samples which were exposed to various environmental processes, so with a potential influence on the degradative or deteriorative status of examined plastic polymers.

Each item involved in the trials was characterized by means of NIR and FTIR-ATR spectroscopy. A matrix in order to cross compare the results reached by means of both technics was created (table 4). Criteria to assess consistency between NIR and FTIR (Table 5) Have been assessed based on analytical results. Since FTIR-ATR represents a well-established vibrational technique for the characterization of plastic polymers, it was selected as reference for a comparison (Table 6 and Figure 1).

	Sample	Area of origin	Depth (m)
Italy, Northern Adriatic	IT/CH/06/18	Coastline in front of Po Delta	10-30
	IT/CH/12/18	Offshore in front of Venetian coast	20-35
Croatia, Central Adriatic	HR/G4/01/19	Between Hvar and Brač Islands	80
	HR/C1/02/19	Offshore in front of coast Sibenik	150

Table 3: Samples identification and sampling location of four pool of Marine Litter plastic items

NIR polymer identification

FTIR \ NIR	PE	PP	PET	PA	PVC	PS	PC	ABS	SAN	PE(PP)	TPV	coPE-PP	Ionomer	PMMA	Nylon-ABS	Cellulose	Methylcell.	Polyimide	N.I.
PE	167				1						1								30
PP		116									1								3
PET	4		64																8
PA	1			23															2
PVC					14									1		1			7
PS						6		1	1										2
PC							1												
ABS																			
SAN									2										
PE(PP)																			
TPV																			
coPE-PP	1										3	2							2
Ionomer																			
PMMA																			
Nylon-ABS																			
Cellulose																			1
Methylcell.																			
Polyimide																			1
N.I.														1					15

Table 4. Number of items polymer identification on the base of the cross-comparison between FTIR-ATR (red lines) and NIR (gray and white columns).

A total of 484 items or item components (for multilayered and assembled) with an amount of 968 spectroscopic data have been analyzed and pairwise compared; data produced are displayed in the two-entry matrix table (Table 4), horizontal entry for FTIR and vertical entry for NIR. In detail, the numbers indicated along the red lines correspond to the polymer-by-polymer identifications obtained using FTIR-ATR, while the gray and white columns show the identification results produced using NIR. Along the diagonal of the matrix the numbers of identification where both instruments produced coherent results are presented. Based on the consistency of achievements, evaluation criteria were formulated, whose definitions and explanations are described in Table 5.

Consistency Between NIR and FTIR spectroscopies results

Description of cross-comparison criteria	Acr.	NIR	FTIR
Consistency in the polymer identification	**YES**	V	V
No Consistency in the polymer identification	**NO**	V	V
Failure of the both spectroscopic techniques *(Unidentifiable material)*	**U.M.**	X	X
Failure of the NIR spectroscopy *(NIR Failure in Polymer Identification)*	**NIR Fail.**	X	V
NIR results not supported by FTIR spectroscopy data *(NIR Not confirmed Polymer Identification)*	**NIR N.C.**	V	X

Table 5: Criteria adopted for the interpretation of cross-comparison of the dataset related to NIR and FTIR results.

The criteria adopted to evaluate the results obtained in the cross comparison are based on the simple principle of the consistency of the outputs obtained by the two instrumental techniques used. These criteria are synthetically reported and explained in Table 5. When the polymer identification outputs, carried out on the same specimens, i.e. items used as reference to assess performance in material identification, resulted coherent, there is consistency in the results from the two techniques (indicated as YES, besides two green check marks, in Table 5 and in the aerogram in Figure 1). If polymers identified on the same specimens were different according to the two techniques, there is no consistency in the results (indicated as NO, besides two different check marks, in Table 5 and in the aerogram in Figure 1). In the remaining criteria, cases of non-identification by one technique (referred to as NIR Fail. for failure of NIR and success of FTIR and as NIR N.C. in the opposite situation) or both (U.M., non-identifiable material) are considered. The results reported in Table 4 were screened following criteria in Table 5, and the outputs of this classification process are displayed in figure 1 and Table 6.
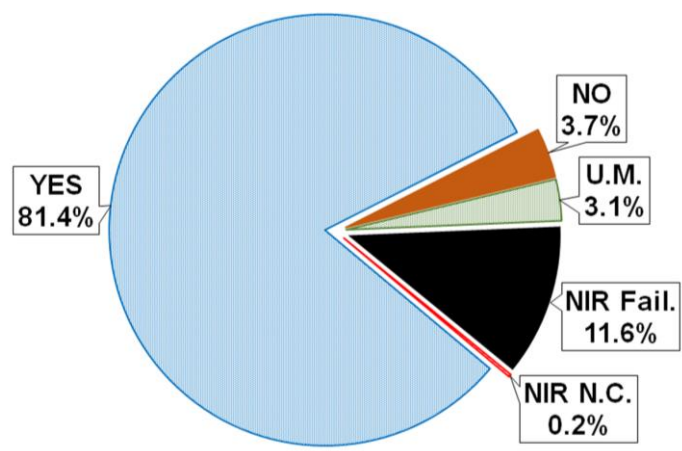
Figure 1: Aerograms with data distribution of cross-comparison using FTIR results as reference for plastic identification by NIR.

Polymer Identification by FTIR			Comparation with NIR identification results															
			Consistency			No Consistency			NIR identification failure			Unidentified Material			NIR results not supported by FTIR		
	n	%	n	%	Specific Polymer %	n	%	Specific Polymer %	n	%	Specific Polymer %	n	%	Not Identified %	n	%	Not Identified %
Total ident.	468	96.7	393			19			56								
Not Ident.	16	3.3										15		93.8	1		6.3
Overall data	484			81.2			3.9			11.6			3.1			0.2	
PE	199	41.1	167	34.5	83.9	2	0.4	1.0	30	6.2	15.1						
PP	120	24.8	116	24.0	96.7	1	0.2	0.8	3	0.6	2.5						
PET	76	15.7	64	13.2	84.2	4	0.8	5.3	8	1.7	10.5						
PA	26	5.4	23	4.8	88.5	1	0.2	3.8	2	0.4	7.7						
PVC	23	4.8	14	2.9	60.9	2	0.4	8.7	7	1.4	30.4						
PS	10	2.1	6	1.2	60.0	2	0.4	20.0	2	0.4	20.0						
PC	1	0.2	1	0.2	100.0												
SAN	2	0.4	2	0.4	100.0												
coPE-PP	8	1.7				6	1.2	75.0	2	0.4	25.0						
Cellulose	1	0.2							1	0.2	100.0						
Methylcell.	1	0.2				1	0.2	100.0									
Polyimide	1	0.2							1	0.2	100.0						

Table 6: Summary results cross-comparison using FTIR results as reference for identification by NIR.

The comparison with FTIR-ATR results allowed to estimate a good consistency in the identification of ML polymers, with an overall score of 81%. Considering the polymers with the major contribution to overall set (PE, PP and PET with 36%, 24% and 13%, respectively with an

overall contribution of 73%), the level of relative consistency, evaluated specifically for each polymer, ranged from 84% for PE to 97% for PP, showing a good agreement between results of both techniques. The No consistency was limited to 4%, while the number of failures in polymer identifications by NIR could be a source of concern (12%). A detailed analysis of obtained results (Figure 2) pointed out that the main issues arose from the presence of black or very dark colored materials, that accounted for 64% of total NIR failures (it should be noted that black and dark surfaces are critical for most spectroscopic techniques). Some analytical constrains were posed also by composite or multilayered materials, where closely associated polymeric materials could contribute to the generation of complex spectra not solvable by the NIR software (reference spectra refer only to pure polymers), especially when it was not possible to physically separate the composing layers.
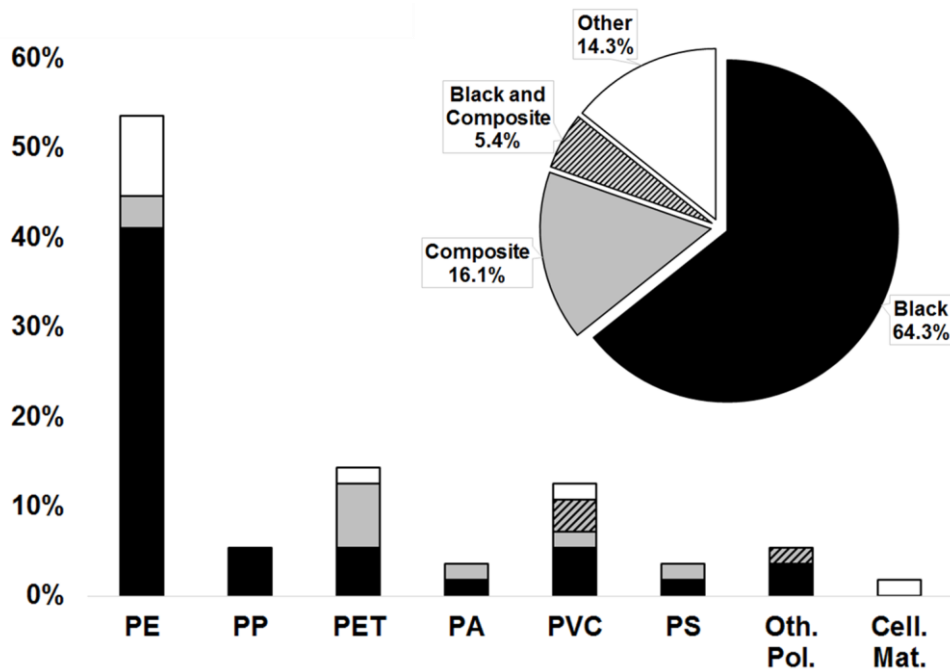

Figure 2: Analysis of NIR failure referred to material features.

In conclusion, given the relevant positive feedback in a significant dataset (484 plastic items), the portable NIR spectroscopy allowed a simple and reliable identification of most plastic marine litter samples. Failures in polymer identification by NIR represented, in comparison to FTIR-ATR

only 12%, and were prevalently due to difficulties in the identification of black or composite materials.

The performed investigation can constitute a "practical guideline or indicative track to be followed" when handheld or portable instruments as support to management of plastic waste from Marine Litter are engaged or planned.

3. References

- Hanke, G., Galgani, F., Werner, S., Oosterbaan, L., Nilsson, P., Fleet, D., Kinsey, S., Thompson, R., Palatinus, A., Van Franeker, J.A., Vlachogianni, T., Scoullos, M., Veiga, J.M., Matiddi, M., Alcaro, L., Maes, T., Korpinen, S., Budziak, A., Leslie, H., Gago, J., Liebezeit, G., 2013. Guidance on Monitoring of Marine Litter in European Seas (EUR - Scientific and Technical Research Reports). Publications Office of the European Union. https://doi.org/10.2788/99475 (pdf)
- Lopez G., Artetxe M., Amutio M., Bilbao J. and Olazar M., Renewable and Sustainable Energy Reviews, 2017, 73, 346
- Butler E., Devlin G. and McDonnell K., Waste and Biomass Valorisation, 2011, 2, 227.
- Sorak D., Heberholz L., Iwascek S., Altinpinar S., Pfeifer F. and Siesler H.W. Applied Spectroscopy Reviews, 2012, 47, 83.
- Geller Y., 2007, Proc. SPIE, 6466.