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## Transformations of crude oil into tar: a case study from a plastitar-contaminated site in NE Sicily, Italy (Western Mediterranean)

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### ABSTRACT

This study examines the aging of industrial crude oil to simulate the chemical transformations that occur when it is exposed to environmental conditions over time. It was triggered by the finding of plastitar — a mixture of tar and plastic waste — on the coast of Milazzo, Sicily. Research began with a chemical characterization of the tar component of plastitar, followed by aging experiments designed to simulate environmental conditions such as seawater, UV light and sunlight. Fourier transform infrared spectroscopy (FTIR) was used to analyze the chemical changes during the aging process and compare the results with local tar samples. The results showed significant chemical changes in the aged crude oil, including oxidation, degradation of hydrocarbons and the formation of oxygenated compounds. In particular, the FTIR spectra of the aged crude oil closely matched those of the local tar and provided valuable insights that could help address similar coastal pollution issues in other regions.

### 1. Introduction

Crude oil and most petroleum products are complex mixtures of hydrocarbons that differ in molecular weight and in their physical and chemical properties. When the oil enters the marine environment, it undergoes a series of processes that rapidly change its composition and disperse much of the oil along the coast. The properties of different oils and the processes that influence their fate in the sea are described in detail in the Good Practice Guide entitled Impacts of Oil Spills on Marine Ecology (IPIECA-IOGP, 2015). Over time, oil that remains on the sea surface usually becomes more viscous and less acutely toxic as it undergoes weathering. The conversion of crude oil to tar occurs through simultaneous processes such as photo-oxidation by solar radiation, weathering under UV radiation and chemical changes due to interactions with seawater. These processes change the original composition of the crude oil and lead to the formation of more persistent compounds that can have long-term effects on the environment (Warnock et al., 2015; Lelario et al., 2021).

Aging experiments in the laboratory are necessary to understand

these transformation mechanisms, as they allow researchers to simulate and study these processes under controlled conditions. Early studies have shown that tar balls can form in seawater within two weeks through combined evaporation, emulsion and oxidation processes (Warnock et al., 2015). Other studies conducted laboratory experiments on the degradation and weathering of crude oil and tar ball samples to evaluate different weathering processes (e.g. Albaigés and Cuberes, 1980). Itah and Essien (2005) studied microorganisms on stranded tar balls from the Nigerian coast and found that some microbes degrade tar more effectively. Savage and Ward (1984) successfully produced tar balls from different types of crude oil under controlled weathering conditions over a period of 4 months and achieved a chemical composition comparable to that of natural samples. Hayworth et al. (2011) investigated the fate and persistence of the oil spill associated with the Deepwater Horizon (DWH) incident in the Gulf of Mexico in April 2010. Their results showed that the tar mats weathered only minimally during this period. Mulabagal et al. (2013) analyzed tar balls and chocolate mousse that washed up on the Alabama coast in June 2010 in connection with the DWH incident to evaluate their weathering processes. Recent

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studies conducted using solar simulators and combined thermal/photo-oxidation protocols have provided valuable insights into crude oil degradation processes (Lelario et al., 2021; Abouelsaad and White, 2022). However, linking laboratory observations to real weathering processes remains a challenge due to the complexity of environmental conditions. These experimental approaches have helped to elucidate the formation mechanisms, although it remains a challenge to reproduce the full complexity of environmental weathering.

While previous studies have comprehensively investigated crude oil weathering and tar formation, several key gaps remain, particularly the lack of a systematic comparison between laboratory-aged samples and environmental tar samples. This study aims to address this gap by conducting aging experiments on tar samples from Milazzo in north-eastern Sicily. The tar used in these experiments is a component of plastitar, a newly identified tar-based pollutant found in the region. Plastitar, classified by Domínguez-Hernández et al. (2022), consists of weathered tar combined with plastic debris and forms aggregates on coastal rocks. It serves as an important indicator of weathering processes and represents a new environmental threat distinct from other formations such as plastiglomerates and pyroplastics (Turner et al., 2019; Gestoso et al., 2019; Ehlers and Ellrich, 2020; De LaTorre et al., 2024; Saliu et al., 2023a, 2023b). Ellrich et al. (2023) emphasize that plastitar is widespread in coastal systems worldwide, but is often overlooked. In Italy, it has been documented mainly in the Adriatic Sea, the Ligurian Sea and around Sardinia, indicating a need for further research, especially in the Tyrrhenian Sea.

The recent discovery of plastitar on the coast of north-eastern Sicily offers an opportunity to study the processes of tar transformation in detail. The strategic location of Milazzo, with its refinery operations and heavy shipping traffic, makes it an ideal site for studying the environmental factors that influence the weathering of crude oil and tar formation. In the laboratory, we simulate the aging of a crude oil sample by investigating the effects of three important environmental factors: natural solar radiation, UV radiation and interactions with seawater. These experiments aim to simulate the conditions under which industrial crude oil is converted into tar, so that a direct comparison with tar samples from the contaminated site in Milazzo is possible. The chemical changes of the functional groups are identified using Fourier transform infrared spectroscopy (FTIR), which allows a detailed analysis of the molecular transformations under different environmental conditions. By comparing the FTIR spectra of laboratory-aged crude oil with those of tar from the contaminated-site of Milazzo, this study provides new insights into the weathering processes that occur in coastal environments. These results are transferable to similar studies in other marine regions affected by the same type of pollution.

## 2. Materials and methods

Our methodological approach differs from previous studies by involving a direct comparison between artificially aged crude oil and environmental tar samples from the same geographical area. This approach enables a systematic investigation of three distinct weathering factors (UV, sunlight, seawater) under standardized conditions, while combining the analysis of tar from plastitar with crude oil aging experiments. Additionally, we have developed a reproducible experimental setup that facilitates a comprehensive characterization of the weathering processes at the contaminated site under investigation.

### 2.1. Study area

The Milazzo peninsula on the north-eastern coast of Sicily in southern Italy is a distinct geographical region belonging to the Peloritani Mountains and extending to the Tyrrhenian Sea. The geological composition of the peninsula reflects a complex interplay of tectonic, volcanic and sedimentary processes influenced by the interaction between the African and Eurasian tectonic plates. It consists mainly of

metamorphic rocks such as gneisses and schists of the Calabride complex, overlain by sedimentary formations, including Miocene sandstone conglomerates and marine deposits of Pliocene and Quaternary age (Dewey et al., 1989; Scicchitano et al., 2011).

The Milazzo peninsula has a varied terrain in which coastal and hilly landscapes intermingle. The coast is characterized by jagged cliffs with small bays and beaches formed by the erosion of metamorphic and sedimentary rocks. In contrast, the interior is hilly and extends from sea level to an altitude of around 500 m above sea level. It is crossed by numerous small streams and gullies that have carved valleys and gorges into the landscape. The drainage pattern is closely linked to the underlying geology and the prevailing climatic conditions. In the northern part of the peninsula lies Cape Milazzo, an imposing promontory of erosion-resistant metamorphic rock of the Calabride complex, surrounded by steep cliffs and rocky shores. The southern part, on the other hand, has a gentler topography with hills and coastal plains consisting of sedimentary rock that erodes more easily than the metamorphic rock to the north. The Milazzo Peninsula is a dynamic landscape with a variety of landforms and habitats shaped by a variety of geomorphologic processes, including coastal and fluvial erosion and mass wasting. Cape Milazzo offers a mixture of sandy and rocky beach stretches, each with unique geomorphological features that provide a habitat for different ecosystems, while the sheltered bays along the coast provide a calm environment protected from direct wave action (Scicchitano et al., 2011; Stagnitti and Musumeci, 2024).

### 2.2. Sampling

The pollutant plastitar was found in the intertidal zone of the Milazzo peninsula and served as the starting material for the development of aging experiments. To assess the extent of tar pollution in this area, we conducted detailed surveys and sampling in the wave-exposed rocky intertidal zones on the Milazzo peninsula, an area known for its prevalence of plastic pollution (Compa et al., 2019; Fossi et al., 2020; Stagnitti and Musumeci, 2024; Donato et al., 2024a, 2024b). Sampling was carried out on a wave-exposed beach facing the open sea, located about 1 km north of the nearest village of Milazzo, near the Marine Protected Area (MPA) of Cape Milazzo. We searched the entire intertidal zone at medium and high tide in the western part of the Milazzo peninsula (see Fig. 1c), which corresponds to a total length of 2500 m. Whenever a plastitar was identified, we carefully collected samples stranded in the outcropping rocks with a hammer and chisel (Fig. 2a-b-c-d) and stored them in cardboard boxes for transportation to the ECCSEL-NatLab laboratory on the island of Panarea (Italy), where chemical analyses and aging experiments were performed on selected samples (Fig. 2e-f-g-h).

A total of 25 plastitar samples were collected and later separated into plastic and tar components in the laboratory using metal tweezers. Chemical characterization by Fourier transform infrared spectroscopy (FTIR) was then performed on tar and crude oil used for the aging experiments (Permanyer et al., 2005; Abbas et al., 2006; White et al., 2016, 2020; White et al., 2018; Morrison et al., 2018; Veerasingam et al., 2020; Ellrich et al., 2023; Ma et al., 2023) and to define a general classification of the main types of plastic polymers contained in plastitar (Rajandas et al., 2012; De Monte et al., 2022; Phan et al., 2022; Sabatino et al., 2024).

### 2.3. Experimental setup

To investigate the changes in the chemical composition of crude oil during accelerated aging, we conducted laboratory experiments designed to simulate the environmental factors that influence the natural aging process of industrial crude oil. We chose FTIR as the analytical method because of its ability to identify functional groups and evaluate the chemical composition of solids. Therefore, FTIR is particularly well suited for characterizing tar and assessing the chemical transformations that occur during aging (Permanyer et al., 2005; Abbas

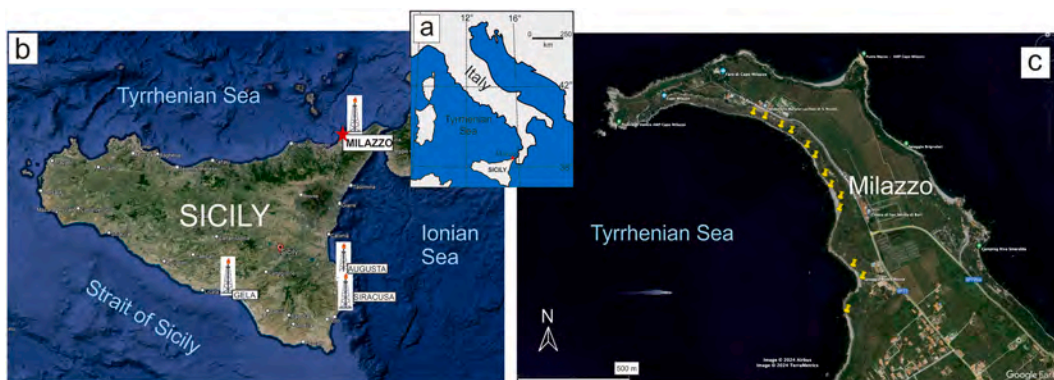


Fig. 1. a-b) Maps showing the location of Milazzo (marked with the red star) in northeastern Sicily in the Tyrrhenian Sea. In b) location of all oil refineries in Sicily; c) Map of the Milazzo peninsula, with the yellow marks representing the plastitar sampling locations in this study.

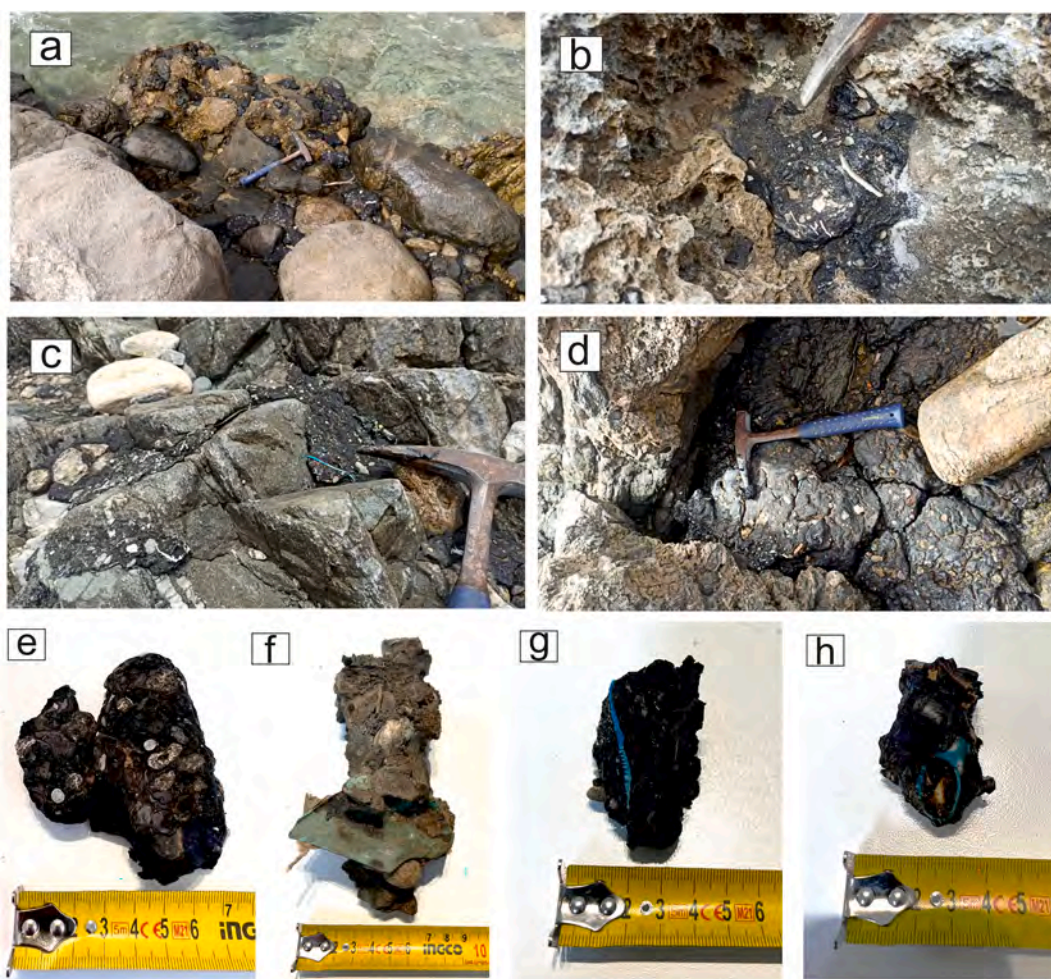


Fig. 2. a-b-c-d) Examples of tar stranded on the rocks of west coast of the Milazzo peninsula; e-f-g-h-i) representative samples of plastitar analyzed in the laboratory.

et al., 2006; Abdulkadir et al., 2016; White et al., 2016, 2020; White et al., 2018; Morrison et al., 2018; Wolak et al., 2020; Veerasingam et al., 2020; Nikita et al., 2023) and for the analysis of plastics containing plastitar (Rajandas et al., 2012; De Monte et al., 2022; Phan et al., 2022; Sabatino et al., 2024). First, we analyzed a sample of the industrial crude oil, followed by analyses of the tar and plastic components of the Milazzo plastitar samples. The repeatability of the FTIR analysis was evaluated by comparing the spectra of three replicates of each sample. Three experiments have been developed to simulate

different aging mechanisms:

1. UV light exposure - A layer of crude oil (with a surface area of approximately 6 cm<sup>2</sup> and a thickness of 1 mm) was applied to a glass slide and irradiated with UV light (315 to 400 nm) to simulate prolonged exposure to the long-wave UV portion of the solar spectrum. FTIR analysis was performed at 24-hour intervals to monitor the chemical changes. The experiment was conducted until the spectrum stabilized after 96 h.

- Sunlight exposure - A layer of crude oil (approximately 6 cm<sup>2</sup> in surface area and 1 mm in thickness) was applied to a glass slide, which was then placed in a Petri dish to prevent contamination. The sample was exposed to natural sunlight to induce photooxidation, and FTIR spectra were collected at regular intervals until the chemical composition stabilized.
- Seawater aging – Approximately 2 cm<sup>3</sup> of crude oil was added to a cone-shaped centrifuge tube containing seawater. FTIR measurements were taken at regular intervals throughout the experiment to track changes in the chemical composition over time.

The FTIR spectra of the aged crude oil samples were compared with those of untreated crude oil and with the spectra of the tar in the Milazzo plastitar samples. This comparative analysis provided insights into the chemical changes that occur in crude oil as it transitions into tar in coastal environments.

#### 2.4. FTIR analyses

Measurements were performed using an Agilent Cary 630 FT-IR spectrometer equipped with ATR sampling modules with a sampling press, single-reflection zinc selenide (ZnSe), and diamond. The spectra were collected in the 4000 and 650 cm<sup>-1</sup> ranges with a resolution of 4 cm<sup>-1</sup> after 50 scans. The FTIR spectra were baseline corrected and smoothed. This preprocessing was necessary to improve resolution and interpretation by reducing noise and background peaks.

Analyses of tar and crude oil were performed on untreated samples to better simulate a natural weathering process. The tar fragments extracted from the Milazzo plastitar were analyzed as a solid immediately after drying them in the oven. Before analysis, the solid tar was ground with a mortar and pestle to ensure sufficient contact with the crystals. The repeatability of the ATR-FTIR analysis was assessed by comparing the spectra of six replicate measurements for each sample fraction from the same sample.

#### 2.5. Sample preparation

The tar fragments extracted from the Milazzo plastitar were analyzed as a solid immediately after drying them in the oven. Before analysis, the solid tar was ground with a mortar and pestle to ensure sufficient contact with the crystals. The repeatability of the ATR-FTIR analysis was assessed by comparing the spectra of duplicate or repeated tar fractions from the same tar sample. Concerning plastic, prior to analysis, the fragments of plastic extracted from plastitar were cleaned in an ultrasonic bath with cyclohexane for 10 min to remove tar residues from the surface and ensure accurate identification of individual polymers (Saliu et al., 2023c). The library of polymers and polymer additives provided by AGILENT was used to verify the polymer types and analyze the scans. The AGILENT database of plastic polymers and additives was also used to determine the specific composition of polyethylene (low density polyethylene pellets, CAS 9002-88-4) and polypropylene (isotactic polypropylene pellets, CAS 9003-07-0) for each plastic pellet. The abbreviations for the polymers are as follows: PE for polyethylene and PP for polypropylene.

### 3. Results and discussion

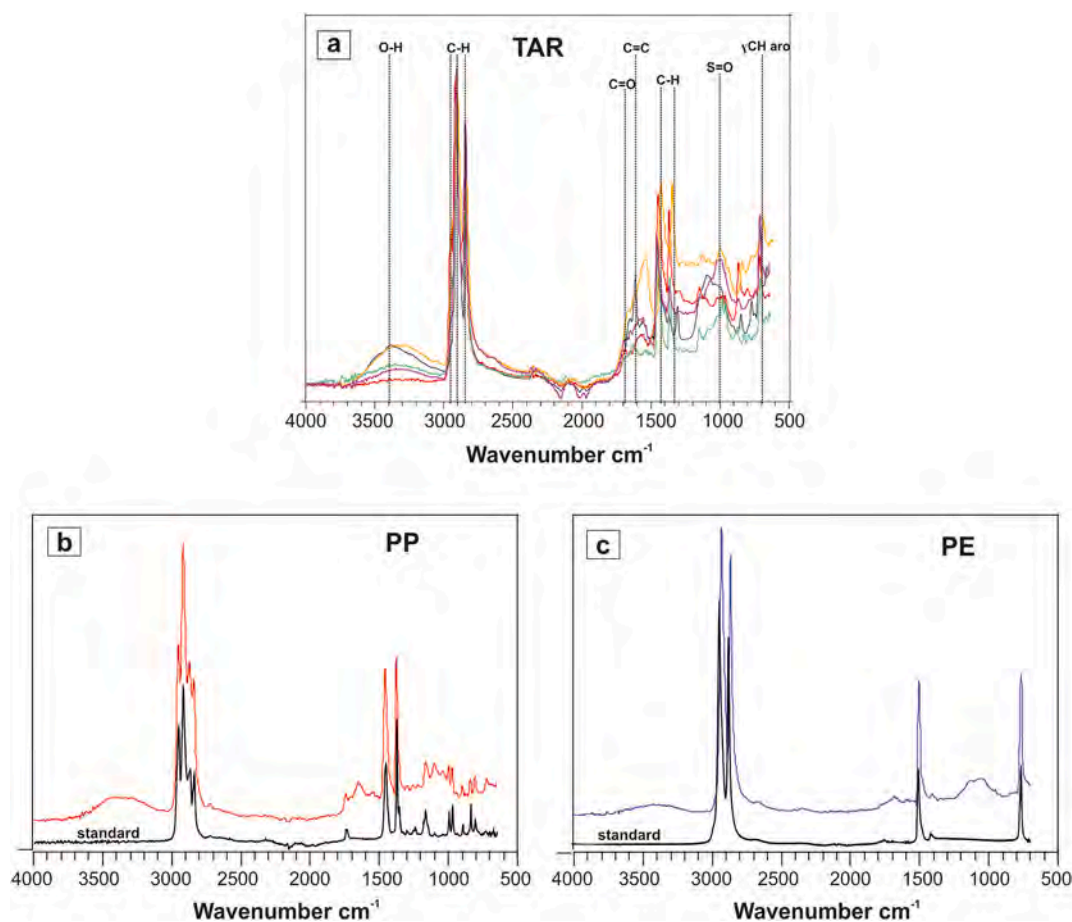
#### 3.1. Physical properties and FTIR characterization of the starting material plastitar

The field investigations carried out on the west coast of the Milazzo peninsula shed light on the complex morphological characteristics and the diverse appearances of the plastitar specimens in this area. These investigations revealed that plastitar exhibits a wide range of sizes and varying degrees of weathering, indicating a mixture of aged remnants of oil spills and smaller, fresher oil slicks. The appearance of the plastitar

indicates that it is weathered to varying degrees, with some samples even resembling asphalt surfaces (see Fig. 2a-i). Macroscopic examination of the plastitar samples collected from the beach revealed that this material can undergo a wide range of changes probably due to the various weathering factors at the coast. Smaller semi-solid oil stains were found on the rocks. In general, most of the samples collected had a solid dark matrix interspersed with plastic fragments of varying size and color, ranging from a few millimeters to several centimeters. These plastic fragments were irregularly shaped and ranged in color from translucent white to opaque black. Different types and different colored plastic waste, such as bags, bottles, lids, films, food packaging and pellets, were preserved and distributed in the black matrix in varying quantities. The overall appearance was homogeneous, with a smooth surface and firm texture, indicating minimal alteration probably due to shorter exposure times or less intense weathering conditions on the beach. In contrast, a smaller subset of samples exhibited a higher degree of alteration characterized by a less compact and more friable dark brown tar matrix. The plastic fragments in these samples showed clear signs of degradation, including rounded shapes, worn edges, and more opaque colors. These samples reflect plastitar that has undergone significant degradation, likely due to prolonged exposure to weathering elements such as UV radiation and chemical processes on the beach.

Before carrying out the aging experiments, in which crude oil is converted into tar, it was considered essential to first characterize the tar and provide information about the representative composition of the plastics contained in the tar matrix. As can be seen in Fig. 3a, the tar spectra show absorption bands in the single C—H bond stretching region (2800–3000 cm<sup>-1</sup>), indicating the presence of alkanes. However, differences in the relative intensities of these bands suggest possible variations in the proportions of methylene, -CH<sub>2</sub>- and methyl, -CH<sub>3</sub>, groups within the tar. In addition, the tar spectra are characterized by distinct absorption bands in the fingerprint region 1300–900 cm<sup>-1</sup> associated with aromatic compounds. Variations in the intensity and specific positions of these bands, indicate potential differences in the types and abundances of aromatic structures present in the tar. Absorption bands around 1700–1750 cm<sup>-1</sup> in the correspond to C=O stretching vibrations and indicate the presence of carbonyl-containing compounds such as carboxylic acids, aldehydes, or ketones, which are commonly found in weathered or degraded petroleum products such as tar (Fingas, 2016). Moreover, the FTIR spectrum of the tar sample shows a broad absorption band around 3400 cm<sup>-1</sup>, indicating the presence of O—H stretching vibrations. This feature indicates the presence of water or other hydroxyl-containing compounds that may have been incorporated into the tar during its formation or during the subsequent weathering process. In summary, the FTIR spectrum of the tar sample covers the presence of alkanes, aromatic compounds, potentially carbonyl-containing substances, and water or hydroxyl-containing compounds as previously reported in the literature (Permanyer et al., 2005; Fernández-Varela et al., 2006; Abbas et al., 2006; Fresco-Rivera et al., 2007; Asemami and Rabbani, 2016; Riley et al., 2016; White et al., 2016, 2020; Morrison et al., 2018; Yang et al., 2019; Vethamony et al., 2021). The characteristic ranges of the FTIR absorption peaks for the analyzed tar are shown in Table 1.

The chemical composition of the plastic inclusions in the tar pitch was determined by FTIR analysis. The plastic fragments were first extracted from the tar, and any residual tar was cleaned from the samples prior to analysis, to avoid contamination of the data. The results showed the presence of two types of polymers: polyethylene (PE) and polypropylene (PP). To compare and validate the findings, representative spectra of certified PE and PP (indicated by the black line on the spectrum) were plotted alongside the spectra obtained from the collected plastic polymers (indicated by the red or blue line on the spectrum). Of all the plastics analyzed, two representative spectra of PP and PE are shown in Fig. 3b-c (indicated by the red and blue lines in the spectrum, respectively). Most of the plastic analyzed exhibited characteristic infrared absorption bands at around 2900, 1450, and 700 cm<sup>-1</sup>,



**Fig. 3.** Representative ATR-FTIR composition of the tar matrix and plastic fragments found in plastitar. In: a) spectra of the tar matrix (colored lines); b) spectra of plastic fragments identified as PP (red) and of the spectral library (black); and c) spectra of a fragment identified as PE (blue) and of the spectral library (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

Characteristic FTIR absorption peaks for the analyzed tar.

Characteristic peaks (cm <sup>-1</sup> )	Assignment
3650–3150	O-H stretching vibration
3000–2850	=C-H stretching vibration
2953	C-H asymmetric stretching vibration in CH <sub>2</sub> (ν <sub>as</sub> CH <sub>2</sub> )
2860	C-H asymmetric stretching vibration in CH <sub>3</sub> (ν <sub>as</sub> CH <sub>3</sub> ) and C–H asymmetric stretching vibration in CH <sub>2</sub> (ν <sub>as</sub> CH <sub>2</sub> )
1650–1700–1750	C=O stretching vibration
1600	C=C stretching vibration aromatic compounds
1460	Methyl C–H (CH <sub>2</sub> and CH <sub>3</sub> ) asymmetric/symmetric bending vibrations
1376	C-H (CH <sub>3</sub> ) symmetric bending vibrations
1030	C-OH stretching vibrations
864, 810, 743	Out of plane bending vibrations of C–H in aromatic compounds
700	Out of plane bending vibrations of C–H in aromatic compounds and bending vibrations (rocking type) of C–H in CH <sub>2</sub>

which closely match the baseline FTIR spectrum of PE (Fig. 3c). The FTIR spectrum of PE is characterized by several prominent peaks, including the C–H stretching vibration around 2850–3000 cm<sup>-1</sup>, corresponding to the methylene (-CH<sub>2</sub>-) groups in the polymer chain. In addition, a significant feature is the presence of the C–H bending vibration, typically observed as a peak around 1375 cm<sup>-1</sup>, while the presence of peaks in the region of 1460–1470 cm<sup>-1</sup> indicates the presence of methylene groups, and the strong absorption band in the region

of 720–730 cm<sup>-1</sup> is known as the vibration of the CH<sub>2</sub> group. A smaller portion of the pellets showed specific wavelengths consistent with PP, with the most prominent peaks observed at wavenumbers of 971, 995, 1167, 1375, 1454, 2838, 2865, 2918, and 2953 cm<sup>-1</sup>. Distinctive functional groups in the FTIR spectrum of PP are peaks associated with methyl (-CH<sub>3</sub>) groups observed at around 1375 cm<sup>-1</sup> and 1450 cm<sup>-1</sup>, in addition to the absorption band in the region of 720–730 cm<sup>-1</sup> corresponding to the vibration of the CH<sub>2</sub> group (Fig. 3b). These results are consistent with previous studies conducted in the coastal areas of the western Mediterranean (Pedrotti et al., 2016; Caldwell et al., 2020; Piazzolla et al., 2023; Sabatino et al., 2024), which have reported on the composition and distribution of plastic pollution in different beach sites along the Ionian and Tyrrhenian coasts, mainly characterized by PE and PP polymers.

### 3.2. Aging experiments: from crude oil to tar

Research into the aging of crude oil is essential for both ecological and industrial purposes. Understanding how crude oil evolves over time is crucial for predicting its behavior during transportation and storage, assessing environmental impacts during spills, and optimizing refining techniques to enhance product yield and quality (Kowalewski et al., 2003; D'Auria et al., 2008; Juyal et al., 2011; Heidari, 2017; Lelario et al., 2021; Rohde-Brandenburger and Zsoldos, 2021; Sarathkumar et al., 2023). Other studies that employed a combination of laboratory experiments and observational methods were conducted to understand the behavior and transformation of crude oil and tar in marine environments (e.g. Keym and Dieckmann, 2006; Warnock et al., 2015;

Lelario et al., 2021; Abouelsaad and White, 2022). However, linking laboratory findings to real-world weathering remains challenging due to the complexity of environmental conditions. For example, Savage and Ward (1984) successfully created tar balls from various crude oils in controlled settings over four months, achieving chemical compositions like those found in nature.

In our experiments, we compared the representative FTIR spectrum of aged crude oil with those of the collected tar, aiming to evaluate the chemical changes and their environmental implications.

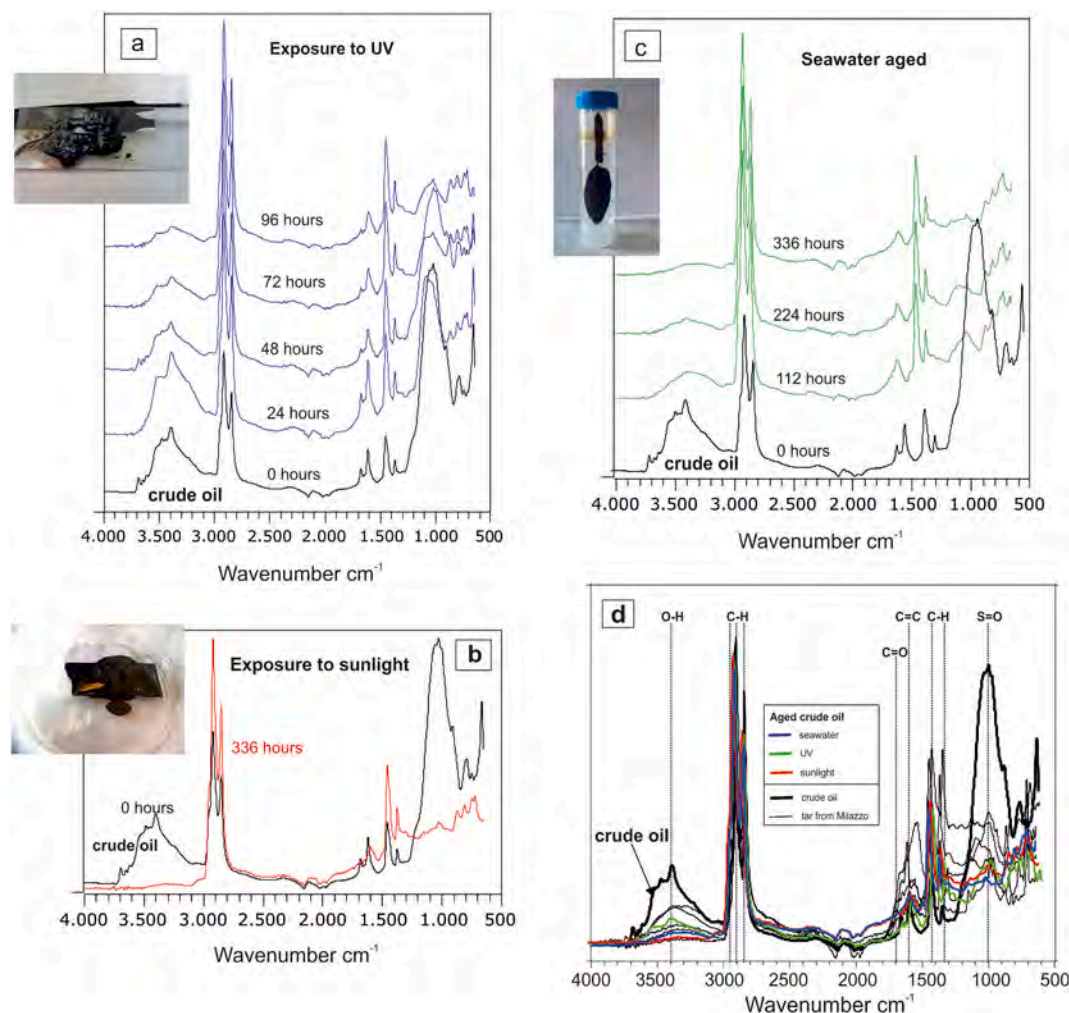
First, a sample of the industrial crude oil was analyzed with FTIR-ATR. The black spectrum (shown in Fig. 4a-c for comparison) shows strong absorption bands in the C—H stretching region  $2800\text{--}3000\text{ cm}^{-1}$ , indicating the presence of alkanes, the main constituents of crude oil. The peaks in this region indicate the existence of methylene ( $-\text{CH}_2-$ ) and methyl ( $-\text{CH}_3$ ) groups, which are typical of long-chain hydrocarbons. The spectrum also shows absorption bands in the fingerprint region  $1300\text{--}900\text{ cm}^{-1}$ , which are attributed to aromatic compounds such as benzene and its derivatives and originate from C—H bending and ring stretching vibrations. In addition, a broad absorption band around  $3400\text{ cm}^{-1}$  indicates O—H stretching vibrations, suggesting the presence of water or other hydroxyl-containing compounds in the original crude oil sample. Overall, the FTIR spectrum provides valuable insight into the chemical composition of the crude oil and confirms the presence of

alkanes, aromatic compounds and possibly traces of water or hydroxyl-containing substances. The following sub-sections present the results of the FTIR analyses performed on the crude oil samples.

### 3.2.1. Experiment 1: exposure to UV light

In this first experiment, at laboratory environmental conditions, the crude oil was irradiated with UV light to simulate prolonged exposure to long-wave UV of the solar spectrum. FTIR analysis was performed at 24-h intervals to monitor the chemical changes of the material. After 96 h of exposure, the spectra remained constant, indicating that the composition of the material had stabilized, and no further changes occurred. The changes that occurred in the FTIR spectra during UV irradiation (Fig. 4a) are as follows:

1. Decreased O—H stretching ( $3200\text{--}3600\text{ cm}^{-1}$ ): This broad peak indicates the formation of new oxidation products, like those observed in the seawater aging experiment.
2. Significant changes in C=O ( $1700\text{--}1750\text{ cm}^{-1}$ ) and S=O ( $1030\text{ cm}^{-1}$ ) stretching: This suggests substantial oxidation, leading to the generation of a variety of carbonyl compounds and degradation of sulfur compounds.



**Fig. 4.** FTIR-ATR spectra of aging experiments carried out on a sample of industrial crude oil (black spectrum) a) exposure to UV (blue spectra); b) exposure to sunlight (red spectrum), and c) aging in seawater (green spectrum). In d) comparison between the spectra of the Milazzo tar studied (thin black spectra), the spectrum of the original crude oil (thick black spectrum) and the representative spectra obtained for crude oil subjected to experiments with UV (blue – after 96 h), sunlight (red – after 336 h) and seawater (green – after 336 h). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

- Alterations in aromatic C—H out-of-plane bending (700–900  $\text{cm}^{-1}$ ): Changes in this region indicate modifications in the aromatic content of the crude oil, likely due to photodegradation.

These observations demonstrate that prolonged exposure to UV light can induce significant chemical changes in crude oil, including the formation of new oxidation products, the generation of carbonyl compounds, and alterations in the aromatic structure of the oil. Previous studies have shown that UV radiation can cause significant modifications to crude oil composition, including oxidation of double bonds and formation of oxygenated compounds (e.g. [Asemani and Rabbani, 2016](#); [Lelario et al., 2021](#)). These findings are consistent with the weathering processes that can occur when crude oil is exposed to sunlight in the marine environment.

### 3.2.2. Experiment 2: exposure to sunlight

The crude oil was exposed to sunlight to trigger photooxidation, a process that degrades the chemical composition of the oil. This degradation was monitored by analyzing changes in the oil's FTIR spectrum over time. The FTIR spectra were collected at regular intervals. The results showed that the chemical composition of the crude oil had changed significantly in the initial phase of exposure. However, after two weeks, the FTIR spectra showed that the oil had reached a stable state, and its chemical composition had not changed significantly. The changes that can be observed in the FTIR spectrum are the following ([Fig. 4b](#)):

- Increase in carbonyl groups: exposure to sunlight can lead to the formation of carbonyl groups, such as aldehydes and ketones, in the oil. These functional groups can be detected in the FTIR spectrum as characteristic peaks in the region of about 1700  $\text{cm}^{-1}$ .
- Changes in aromatic compounds: sunlight exposure can also cause changes in the aromatic compounds present in crude oil. This can be observed in the FTIR spectrum as shifts or changes in the intensity of peaks associated with aromatic C—H stretching vibrations.
- Alterations in functional groups: the FTIR spectrum may show changes in the intensity or position of peaks associated with various functional groups present in crude oil, such as alkanes, alkenes, and alkynes and sulfur compounds. These changes give an indication of the degree of degradation and oxidation of the oil.

It is important to note that the specific changes observed in the FTIR spectrum of sun-aged crude oil may vary depending on factors such as the composition of the oil, the duration of exposure to sunlight, and the environmental conditions.

### 3.2.3. Experiment 3: aging in seawater

In the last experiment, crude oil was aged in seawater to mimic realistic marine environmental conditions. In addition to this experiment, the researchers also evaluated the attainment of a threshold level, beyond which no further changes occurred. This threshold was reached after two weeks of aging. The FTIR spectra showed several changes ([Fig. 4c](#)):

- Alkane (2850–3000 and 1200–700  $\text{cm}^{-1}$ ) and alkene (1680–1620  $\text{cm}^{-1}$ ) functional groups: the peaks associated with these functional groups show significant changes as the crude oil ages in seawater. The intensity and shape of these peaks change, indicating that the aliphatic hydrocarbon components of the crude oil are being depleted or transformed by various weathering processes.
- Aromatic functional groups: the peaks corresponding to aromatic functional groups (C=C aromatic stretching and C—H out-of-plane bending modes) also show significant changes. The intensity and profile of these peaks vary, suggesting that the aromatic compounds in the crude oil are being affected by the weathering reactions in the seawater environment.

The important changes observed throughout the FTIR spectrum, with the appearance and disappearance of various peaks, reflect the complex chemical transformations that the crude oil undergoes when exposed to seawater. These changes are likely to be driven by processes such as evaporation, dissolution, oxidation, and biodegradation, as previously discussed.

### 3.3. Insights from the aging of crude oil

The FTIR spectra of tar samples collected in the rocky coastal region of Milazzo were compared with those from three aging experiments, showing consistent chemical transformations under all conditions. This comparison highlights the primary weathering processes affecting the Milazzo tar, which are discussed below.

When examining oxidation and compound formation during aging, the variations in peak values reflect a continuum of chemical transformations. Beginning in the 700–900  $\text{cm}^{-1}$  spectral range, peaks associated with out-of-plane aromatic C—H bending vibrations indicate the formation of aromatic hydrocarbons ([Asemani and Rabbani, 2016](#)). These compounds are much more stable and resistant to degradation than their aliphatic counterparts and mark an early stage of the aging process and the first structural changes as the material oxidizes. As we approach 1000  $\text{cm}^{-1}$ , we observe S=O stretching peaks related to sulfur compounds such as thiols, sulfides and sulfoxides. As aging increases, the intensity of these peaks decreases, indicating the degradation of these sulfur-containing species, largely due to oxidative processes and microbial activity. Previous studies indicate that sulfonic acids in crude oil are significantly degraded during natural weathering ([Fathalla and Andersson, 2011](#); [Filewood et al., 2022](#)), with these compounds being affected by photodegradation, biodegradation, dissolution and evaporation ([Ren et al., 2019](#)). Other experiments and analyses of oil spills show that sulfonic acids resulting from the oxidation of sulfur heterocycles decrease over time, especially lower molecular weight acids, while some higher molecular weight compounds are more resistant ([Filewood et al., 2022](#)). This decrease occurs through oxidation to sulfates, photochemical degradation and increased water solubility. Around 1700  $\text{cm}^{-1}$  there is an increase in C=O stretching peaks, indicating an increase in carbonyl compounds such as ketones, aldehydes and carboxylic acids. This shift emphasizes the incorporation of oxygen into the molecular structure and signals the progression of oxidative reactions ([Fathalla and Andersson, 2011](#); [Filewood et al., 2022](#)). The spectral region near 1800  $\text{cm}^{-1}$  may also show increased C=O stretching peaks, further emphasizing the formation of these oxygen-containing compounds. Another significant transformation involves the degradation of hydrocarbon chains, as evidenced by an increase in C—H stretching peaks in the 2800–3000  $\text{cm}^{-1}$  range. This increase in aliphatic C—H bonds indicates a fragmentation of the aliphatic hydrocarbons, which are the main components of the fresh tar. Degradation can occur through various abiotic and biotic processes, including photo-oxidation, hydrolysis and microbial biodegradation, resulting in the formation of smaller, polar compounds that are more easily dissolved and dispersed in the marine environment ([Gustitus and Clement, 2017](#); [Asemani and Rabbani, 2016](#); [Ma et al., 2023](#)). In the 3200–3500  $\text{cm}^{-1}$  range, a broad absorption band corresponds to the O—H and N—H stretching vibrations. A marked decrease in the intensity of these peaks indicates a loss of water and the presence of alcohols, phenols and amines as oxidation progresses ([Asemani and Rabbani, 2016](#)). This decrease reflects a transformation to more complex oxygenated compounds, further altering the chemical landscape of the material.

Overall, the variations in peak intensity and position illustrate the complex chemical transformations associated with the aging of crude oil. The initial stability of the aromatic structures is followed by the degradation of sulfur compounds and an increase in oxygen-containing functional groups. These changes have a significant impact on the physical and chemical properties of tar, affecting its solubility, reactivity, and potential ecotoxicological effects ([Garrett et al., 1998](#);



Asemiani and Rabbani, 2016; Mirwald et al., 2020; Aeppli et al., 2022; Ma et al., 2023; Gustitus and Clement, 2017). Significant oxidation indicates interactions between crude oil components and atmospheric oxygen, while degradation of hydrocarbon chains indicates a decrease in structural integrity over time. This degradation can lead to evaporation of lighter fractions, increased viscosity or conversion to other compounds (Garrett et al., 1998; Liu et al., 2020; Lelario et al., 2021; Aeppli et al., 2022; Gustitus and Clement, 2017; Ma et al., 2023). The formation of aromatic and oxygenated compounds during aging illustrates the complex weathering and chemical evolution of tar in marine and coastal environments and provides new insights into the mechanisms driving tar evolution in these environments. FTIR spectra of tar samples collected in the rocky coastal region of Milazzo were compared with those from three aging experiments (Fig. 4d) and revealed several consistent chemical transformations under all aging conditions. This comparison highlights the primary weathering processes affecting the Milazzo tar:

### 3.4. Implications and future research directions

The aging of tar in coastal environments triggers a series of chemical transformations that lead to the formation of more stable and durable compounds. Over time, the physical and chemical properties of tar change, making it more persistent in the environment. These changes can have profound long-term effects on the persistence of contaminants, environmental dynamics and the overall health of coastal ecosystems (Smith et al., 2017; Domínguez-Hernández et al., 2022; Mudumba et al., 2023). Our laboratory analyses of tar samples from the contaminated Milazzo site show how environmental factors drive these chemical changes. In particular, the oxidation of the crude oil components indicates their interaction with atmospheric oxygen, while the degradation of the hydrocarbon chains suggests that the tar loses structural integrity over time. This degradation process leads to the evaporation of lighter fractions, an increase in viscosity and the conversion of compounds into different chemical forms (Garrett et al., 1998; Liu et al., 2020; Lelario et al., 2021; Aeppli et al., 2022; Gustitus and Clement, 2017; Ma et al., 2023). The formation of aromatic and oxygenated compounds during aging highlights the complexity of the chemical evolution of tar and its gradual transformation in marine and coastal environments.

One of the most concerning aspects of this transformation is the presence of polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic sulfur hydrocarbons (PAHSS) in crude oil derivatives. These aromatic compounds are particularly resistant to weathering (Filewood et al., 2022), which means that they remain in the environment much longer than other components of crude oil. PAHs and PAHSS are persistent organic pollutants that can bioaccumulate in marine organisms, leading to a range of harmful effects. These include toxicity, endocrine disruption and potential carcinogenesis, which pose significant risks to marine life and therefore to human health through the consumption of contaminated seafood (Lammel et al., 2017; Zhang et al., 2020; Domínguez-Hernández et al., 2022; Wietzoreck et al., 2022; Faboya et al., 2023). In summary, it can be said that the chemical transformations of tar in the coastal and marine environment not only increase the stability and persistence of pollutants, but also contribute to the formation of harmful compounds such as PAHs and PASHS.

The plastitar found on the coast of Milazzo is a new pollutant that requires further investigation, especially on the interaction between plastics and hydrocarbon components. Given the likelihood that this problem affects many coastal regions worldwide, a comprehensive study is needed to understand the potential impacts (Domínguez-Hernández et al., 2022). Future research should address several critical areas, including the chemical interaction between crude oil/tar and plastic in plastitar, the rate of degradation under different environmental conditions, the ecological footprint, and the long-term effects of these pollutants.

Our preliminary FTIR analysis has identified polyethylene (PE) and

polypropylene (PP) as the main plastic constituents in the plastitars of Milazzo, which is consistent with the results of previous studies on plastic pollution in the Mediterranean (Galgani et al., 2013; Pedrotti et al., 2016, 2022; Caldwell et al., 2020; Piazzolla et al., 2023; Sabatino et al., 2024; Donato et al., 2024a, 2024b). On the west coast of Milazzo, the amount of plastic waste is increasing, influenced by coastal currents, winds, waves and river flooding (Stagnitti and Musumeci, 2024). Plastics migrate towards the coast and marine protected area (MPA) throughout the year, with significant seasonal fluctuations (Fig. 5a-c). A comprehensive analysis of the types and quantities of plastics, along with their chemical interactions with the hydrocarbon components in plastitars, will enhance our understanding of pollution in coastal and marine environments.

## 4. Conclusions

This study investigates the formation of the tar component in plastitar found along the rocky coast of the Milazzo peninsula using laboratory aging simulations of an industrial crude oil sample. The focus on this region of northeastern Sicily provides site-specific data that may be transferable to similar coastal environments, although local conditions may influence specific weathering patterns. Our laboratory experiments provide insights into the aging of crude oil under controlled conditions by simulating selected environmental factors such as solar and UV radiation and interactions with seawater. We observed chemical transformations during artificial weathering, although natural weathering may involve additional complexities not captured in our setup. FTIR analyses revealed oxidative interactions between crude oil components and atmospheric oxygen. Changes in the signatures of the hydrocarbon chains indicated degradation processes and the formation of polar compounds. Photooxidation produced alcohols, phenols and carbonyl compounds, which altered the solubility and reactivity of the tar. Fluctuations in the intensity and position of the peaks illustrated the complex changes associated with the aging of the tar. Our comparative analysis showed that the laboratory-aged crude oil exhibited FTIR spectral patterns very similar to those of tar samples from the Milazzo coast, particularly in the oxidation regions ( $1700\text{--}1750\text{ cm}^{-1}$ ) and aromatic transformation signatures. The degradation of sulfur compounds and the increase of oxygen-containing functional groups led to changes in the stability of the aromatic structures, which significantly affected the physical and chemical properties of the tar and its potential ecotoxicological impact. In summary, this study provides new insights into the chemical transformations of crude oil during aging as well as new data on tar formation and its chemical properties. These results contribute to the understanding of coastal pollution and may be useful for studies in regions with similar environmental problems.

### CRedit authorship contribution statement

**Marcella Di Bella:** Writing – original draft, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Giuseppe Sabatino:** Writing – original draft, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Giuseppe De Rosa:** Writing – original draft, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Cristina Leonelli:** Writing – review & editing, Validation, Investigation, Formal analysis. **Michela D'Alessandro:** Writing – review & editing, Validation, Investigation, Formal analysis. **Cinzia De Vittor:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization. **Valentina Esposito:** Writing – review & editing, Validation, Investigation, Formal analysis. **Marco Graziano:** Writing – review & editing, Validation, Investigation, Formal analysis. **Alessandro Tripodo:** Writing – review & editing, Validation, Investigation, Formal analysis. **Valentina Volpi:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization.



**Fig. 5.** a) Plastic litter in debris polluting the coast at the Cape of Milazzo in January 2024; b) Detail of the stranded plastic; c) Milazzo Cape coastline after a clean-up operation by local volunteers in May 2024.

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### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Data availability

Data will be made available on request.

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