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Micro(nano)plastics from synthetic oligomers persisting in Mediterranean seawater: Comprehensive NMR analysis, concerns and origins

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ABSTRACT

The presence in seawater of low-molecular-weight polyethylene (PE) and polydimethylsiloxane (PDMS), synthetic polymers with high chemical resistance, has been demonstrated in this study for the first time by developing a novel methodology for their recovery and quantification from surface seawater. These synthetic polymer debris (SPD) with very low molecular weights and sizes in the nano- and micro-metre range have escaped conventional analytical methods. SPD have been easily recovered from water samples (2 L) through filtration with a nitrocellulose membrane filter with a pore size of 0.45 µm. Dissolving the filter in acetone allowed the isolation of the particulates by centrifugation followed by drying. The isolated SPD were analysed by ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR), identifying PE and PDMS. These polymers are thus persisting on seawater because of their low density and the ponderal concentrations were quantified in mg/m^3. This method was used in an actual case study in which 120 surface seawater samples were collected during two sampling campaigns in the Mediterranean Sea (from the Gulf of Salerno to the Gulf of Policastro in South Italy). The developed analytical protocol allowed achieving unprecedented simplicity, rapidity and sensitivity. The ^{1}H and ^{13}C NMR structural analysis of the PE debris indicates the presence of oxidised polymer chains with very low molecular weights. Additionally, the origin of those low molecular weight polymers was investigated by analysing influents and effluents from a wastewater treatment plant (WWTP) in Salerno as a hot spot for the release of SPD: the analysis indicates the presence of low molecular weight polymers compatible with wax-PE, widely used for coating applications, food industry, cosmetics and detergents. Moreover, the origin of PDMS debris found in surface seawater can be ascribed to silicone-based antifoamers and emulsifiers.

Abbreviations: DOSY, Diffusion-ordered spectroscopy; EDX, energy-dispersive x-ray spectroscopy; OM, fluorescence microscopy; FTIR, Fourier-transform infrared spectroscopy; HDPE, high-density polyethylene; GC–MS, gas chromatography-mass spectrometry; LDIR, laser direct infrared imaging; LS, light scattering; LDPE, low-density polyethylene; MPs, microparticles; µ-FTIR, FTIR microscopy; µ-Raman, Raman microscopy; NPs, nanoparticles; NMR, nuclear magnetic resonance spectroscopy; OM, optical microscopy; Ps, plastics; PDMS, poly(dimethyl siloxane); PE, poly(ethylene); PP, poly(propylene); PS, poly(styrene); pyr-GC/MS, pyrolysis−gas chromatography-mass spectrometry; SEM, scanning electron microscopy; STEM, scanning transmission electron microscopy; SPs, synthetic polymers; SPD, synthetic polymer debris; TEM, transmission electron microscopy; TCE-d_2, 1, 1, 2, 2-tetrachloroethane-d$_2$; UNEP, United Nations Environment Programme; WWTP, wastewater treatment plant.

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1. Introduction

The invention and applications of synthetic polymers (SPs) for producing thermoplastic and thermoset materials have enormously and positively impacted human society. (Brydson et al., 1999) These materials have easily replaced, partially or almost wholly, several others such as wood, glass, ceramics, natural rubber and metals; they also have an uncountable variety of novel applications. On the other hand, their actual disposal or reuse at the end of their life cycle poses several challenges. A considerable amount of SPs, estimated between 4.8 and 12.7 million metric tons, according to a report by the United Nations Environment Programme (UNEP), (United Nations Environment Programme. Marine Plastic Debris and Microplastics: Global Lessons and Research to Inspire Action and Guide Policy Change., 2016) escapes yearly from the conventional recovery pathways, ending up in the seas. Jambeck and co-workers, in 2015, examined in detail the data from 192 coastal countries and estimated that 8 million metric tons of SPs enter the oceans each year. They also determined that the top 20 countries account for more than 80 % of the plastic waste that enters the sea. (Jambeck, 2015) These materials persist for a prolonged time in the marine environment, eventually in the form of small debris colonised by aquatic microorganisms that protect these organic substrates for decades from further mechanical, chemical and photophysical degradation. (Krause, 2020) SP debris observed in the marine environment are generally in the micrometre and also in the nanometre size range. These materials are currently improperly indicated as micro- and nanoplastics, although the term "*plastics*" technically does not cover viscoelastic materials (amorphous polymer materials with glass transition temperature below the room temperature) and thermoset materials (*i.e.*, crosslinked polymers such as cured resins and vulcanised elastomers as the rubber of automotive tyres). Considering this point, the term "*synthetic polymer debris (SPD)*" will be used herein.

Marine animals can ingest SPD, from tiny plankton to large fish, and accumulate in their digestive systems, potentially harming them, manifesting as decreased appetite, weight loss, oxidative stress, organ and tissue damage, inhibition of growth and movement and, finally, even the death. (Li, 2023; Khalid, 2021; Wright et al., 2013; Galloway and Lewis, 2016) As larger organisms consume these smaller ones, the SPD can accumulate and become more concentrated, potentially harming predators at the top of the food chain, including humans. (Kye, 2023; Mamun et al., 2023) This creates an additional pathway for transferring harmful chemicals and pollutants absorbed and accumulated in the polymer particles into the human food chain. (Kaur, 2022) Last but not least important factor, SPD can contribute to the overall degradation of marine environments, affecting their biodiversity and the ecosystem's functionality (Li, 2023; Roy et al., 2022).

Considering the complexity and variety of SPD and of the environments where they can be found (surface water, deep water, sediments, seawater, river water, soil, wastewater, biological tissues, etc.), standardising a uniformly applicable protocol for recovering and quantifying all types of SPD is not feasible. (Cai, 2021; Zhao et al., 2018; Ivleva, 2021) The current methods for isolation and quantifying SPD in seawater typically involve several steps, such as sampling, digestion, separation, identification and quantification. (Ivleva, 2021; Cutroneo, 2020; Prata et al., 2019) To collect seawater SPD samples, nets (for large particles) or micro-filtering (for MPs) systems are used for the *in-situ* recovery. (Karlsson et al., 2020; Wagner, 2017) *Ex-situ* recovery is also commonly employed, where the sample is collected and subsequently processed in a laboratory. In both cases, the water from diverse sea (or sediment) depths can be collected in order to separate different polymer materials depending on their densities. Common floating polymers found in seawater are polyethylene (PE, density = 0.94–0.95 g/cm^3), high-density polyethylene (HDPE, density = 0.94 g/cm^3), low-density polyethylene (LDPE, density = 0.92–0.93 g/cm^3), polypropylene (PP, density = 0.90–0.92 g/cm^3), expanded polystyrene (PS, density = 0.01–1.05 g/cm^3) and polydimethylsiloxane (PDMS, 0.96–0.97 g/cm^3). (Coyle et al., 2020; Auta et al., 2017; Choy, 2019; González-Fernández, 2021) The main applications of PE and PDMS are depicted in Fig. 1 and can be divided depending on the molecular weight of the commercialised polymers. PE (HDPE, PE and LDPE) polymers are largely used to produce consumer products such as containers for food or general storage, tubing, disposable bags and for packaging. PDMS found mainly applications for making sealers, gaskets and moulded items. Low-molecular weight PE and PDMS found both application for the production of detergents, cosmetics, lubricants and in industries such as textiles, leather manufacture, paper and wastewater treatment. Notably, PE waxes are used for coating applications in food industries (additive E914) (EFSA, 2015) and low molecular weight PDMS is used as an antifoaming agent in the food industry (additive E900).

Depending on the purpose of marine SPD analysis (qualitative, quantitative, morphological or resolution of the polymer microstructure; see Table 1), recovery, processing and analysis techniques must be carefully selected. A universal protocol that would yield all this information on marine MPs and NPs is still lacking. It won't be easy to draw up immediately with the currently available techniques for recovery and characterisation. The purpose of analysis addresses to the technique that must be employed for the characterisation of the marine particulate and, consequently, the sampling and the processing of the sample before the analysis. (Mariano et al., 2021).

For the purposes of *identification of polymer particles*, optical microscopy (OM) (Wang et al., 2017; Song, 2015; Ding, 2019) and fluorescence microscopy (FM) (El Hayany, 2020) can be used only for large particles or microparticles. Scanning electron microscopy (SEM), (Wagner, 2017; Wang et al., 2017; Girão et al., 2020; Fries, 2013; Shi, 2022) transmission electron microscopy (TEM) (Watteau et al., 2018) and scanning transmission electron microscopy (STEM) techniques coupled with energy-dispersive X-ray spectroscopy (EDX) (Gniadek and Dąbrowska, 2019) significantly extend the possibilities of identifying MPs and NPs when compared to OM and FM. (Mariano et al., 2021; Gniadek and Dąbrowska, 2019) As typical of all microscopy techniques, qualitative analysis of the whole sample is difficult due to the limited representativeness of the small sample portions that can be analysed with these techniques. Fourier transform infrared (FTIR) (Käppler, 2016) and Raman (Araujo et al., 2018; Sobhani, 2020; Schymanski et al., 2018) spectroscopies, although unable to discriminate between MPs and NPs, are powerful tools for identifying the overall plastics present in a sample. (Meyer et al., 2023) Microscopy techniques coupled with FTIR (μ-FTIR) (Primpke et al., 2018; Hufnagl, 2022) or Raman (μ-Raman) (Araujo et al., 2018; Schymanski et al., 2018) spectroscopy and, more recently, laser direct infrared imaging (LDIR) (Ourgaud, 2022), allow to identify MPs well, but those techniques cannot be used for NPs characterisation and suffer from overall analysis limitations of the samples typical of the microscopic methods above mentioned. Laser-based technologies, such as static or dynamic light scattering (LS) (Liu, 2021; Choobbari, 2022) and flow cytometry (FC) (Tse et al., 2022), are unsuitable for identifying MPs and NPs.

Computer-assisted identification of SPD, based on machine learning and artificial intelligence, coupled with conventional techniques, such as μ-FTIR, can be a promising tool for rapid and reliable analysis, but this approach requires further development. (Hufnagl, 2022).

The *morphological analysis* of SPD requires techniques such as SEM, TEM, STEM, μ-FTIR, μ-Raman or LS. Electron microscopies (SEM, TEM and STEM) are the most powerful in the morphological resolution of plastic particles, while LS-based techniques allow for obtaining in-depth and rapid information on the size distribution of plastic particles. (Choobbari, 2022) However, reliable separation of naturally occurring organic or inorganic particulates from SPD is critically important since their presence can alter the results.

For the *structural characterisation* of polymeric chains (referred to in polymer science as polymer microstructure), information concerning the degree of oxidation can be obtained by FTIR, Raman, and their combination with microscopy μ-FTIR and μ-Raman. Nuclear magnetic resonance (NMR) spectroscopy is the most powerful tool in this context because it allows a thorough resolution of the microstructure of the polymer chain.

Electron microscopies (SEM, TEM and STEM) and microscopy techniques coupled with infrared or Raman spectroscopy (µ-FTIR and µ-Raman) effectively quantify the number of MPs. TEM and STEM microscopies are also suitable for analysing nanometric particles; however, their extensive use for quantitative measurements on whole samples is often impractical due to the large number of acquisitions required to obtain a representative analysis for each sample. The LDIR (Ourgaud, 2022) and LS (Choobbari, 2022) techniques are helpful for getting particle numbers and size distribution information, respectively. Pyrolysis-gas chromatography-mass spectrometry (pyr-GC/MS) (Santos, 2023; Matsui, 2020; Matsueda, 2021), thermal extraction desorption-gas chromatography-mass spectrometry (TED-GC/MS) (Zhou et al., 2019; Sorolla-Rosario et al., 2023) and NMR (Corti, 2020; Peez and Imhof, 2020; Peez et al., 2019) techniques do not allow to discriminate between MPs and NPs, but these are powerful tools for identifying plastics by type and those overall present in a sample. These latest techniques are the only ones that allow determining the weight quantity of plastics in an aqueous sample. The applicability of NMR (Corti, 2020; Peez and Imhof, 2020; Peez et al., 2019; Peez, 2019) spectroscopy has been explored for the identification and quantification (Peez and Imhof, 2020; Peez et al., 2019; Peez, 2019) of SPD in lake sediments (Corti, 2020).

Sample pre-treatments for preconcentration and purification are often necessary in order to improve the limit of detection (LOD) and limit of quantification (LOQ) of the technique adopted for SPD quantification. Sedimentation, ultrafiltration, ultracentrifugation, (Jakobs, 2023) continuous flow centrifugation (Hildebrandt et al., 2019) or cloud point extraction (Zhou et al., 2019) or solvent extraction (Corti, 2020) are primarily used for preconcentration of SPD. In addition, digestion can be used to break down for SPD purification. (Pfeiffer and Fischer, 2020) This typically involves treating the sample with strong acids and oxidising agents or enzymes, which dissolve organic matter and leave the SPSs almost intact. These treatments preclude the isolation of low

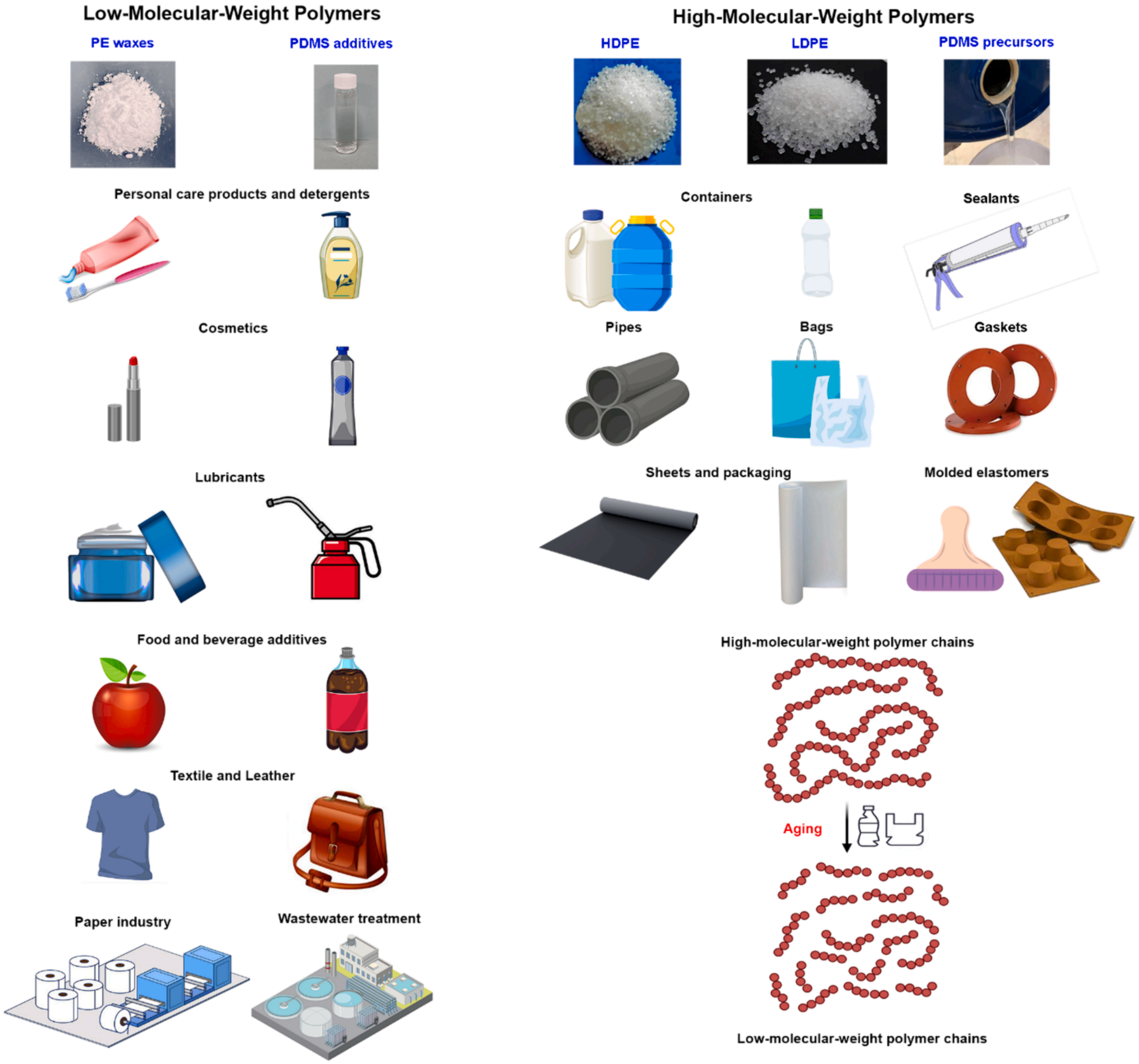

Fig. 1. Possible sources of synthetic polymer debris with low molecular weights floating on seawater.

molecular weight polymers sensible to the digestion process.

Each of the methods mentioned above has its advantages and limitations, and the choice of an SPD quantitation approach depends on the specific research questions, sample type, and available resources. Researchers often combine multiple analysis methods to get a complete picture of SPD contamination in a given environment.

In the current study, we demonstrate the application of NMR spectroscopy for the identification of SPD in marine surface water, their weight quantification and structural analysis (Fig. 2). Samples of surface seawater (1 2 0) obtained during two sampling campaigns in 2021 in the Mediterranean Sea, from the Gulf of Salerno to the Gulf of Policastro in South Italy, were investigated in this study. The SPD were recovered by filtration with a nitrocellulose microfilter with a pore size of 0.45 µm (see Fig. 2). The dissolution of the microfilter in acetone and the centrifugation of the sample allowed a direct recovery of the particulate matter present in the samples. The SPD isolated were directly analysed by solution high-resolution NMR spectroscopy, which allowed identifying PE, PDMS, and traces of PP. The quantitative PE and PDMS analysis were performed using mesitylene as an internal standard. Microstructure and molecular weights of the polymer chains were also determined by mono and two-dimensional NMR techniques, which were used to develop an in-depth picture of the polymers polluting surface seawater and to draw conclusions concerning the origin and the fate of synthetic polymers in marine environments. Actually, the analysis of influents and effluents from a wastewater treatment plant (WWTP) in Salerno was carried out to identify the source of the SPD identified, quantified and characterised in surface seawater.

2. Materials and methods

2.1. Seawater sampling

Four marine water sampling campaigns were conducted from June to December 2021. Each campaign consisted of sampling 30 samples of marine water, 15 taken at a distance of 2 nautical miles from the coast and 15 taken at a distance of 4 nautical miles from the coast. The cost investigated was between the Amalfi Coast and the Gulf of Policastro in southern Italy. Sampling activities were carried out by a Fishermen's Cooperative from Maiori on the Amalfi Coast of Italy. The fishermen were trained by the researchers to ensure the application of good practices for marine water sampling. The monitoring activities have been carried out during their night fishing activities. Marine water samples were taken on the marine surface to collect all the floating debris, including SPD. The samples were directly collected using the glass storage bottles of 2000 mL with an opening diameter of 3 cm. The seawater samples were taken positioning the bottle horizontally to take the floating materials inside a glass bottle. All samples taken were identified and labelled and were kept at a controlled temperature during storage and transport to the laboratory.

2.2. Recovery of synthetic polymer debris from surface seawater

2 L of sea water were filtered with a Buckner apparatus using a nitrocellulose filter (0.45 µm pore size and 50 mm diameter from Sartorius, Germany). The filter was removed and dried in air, preserved from external contamination with SPD between two Petri dishes. The filter was transferred into a 50 mL PP centrifuge tube filled with acetone (99.9 %, HPLC grade, Sigma-Aldrich – Merk Life Science, Italy). After

Table 1
Main techniques for qualitative, morphological, microstructural and quantitative analysis of marine synthetic polymer debris.

	Identification			Morphological		Structural	Quantification					Ref.
							Particle count			By weight		
	Per type		Total				Per type		Total	Per type	Total	
	MPs	NPs		MPs	NPs		MPs	NPs				
OM	🟡	🔴	🔴	🟢	🔴	🔴	⚫	🔴	🔴	🔴	🔴	(Wang et al., 2017; Song, 2015; Ding, 2019)
FM	🟡	🔴	🔴	🟢	🔴	🔴	🟡	🔴	🟡	🔴	🔴	(El Hayany, 2020)
SEM-EDX	🟡	🟡	🟡	🟢	🟢	🔴	🟢	🟡	🟡	🔴	🔴	(Wagner, 2017; Girão et al., 2020; Fries, 2013; Shi, 2022)
STEM-EDX	🟢	🟢	🟡	🟢	🟢	🔴	🟢	🟢	🟡	🔴	🔴	(Watteau et al., 2018; Gniadek and Dąbrowska, 2019)
FTIR	🔴	🔴	🟢	🔴	🔴	🟡	🔴	🔴	🔴	🔴	🔴	(Käppler, 2016)
Raman	🔴	🔴	🟢	🔴	🔴	🟡	🔴	🔴	🔴	🔴	🔴	(Araujo et al., 2018; Sobhani, 2020; Schymanski et al., 2018)
µ-FTIR	🟢	🟡	🟡	🟡	🔴	🟡	🟢	🟡	🟡	🔴	🔴	(Hufnagl, 2022)
µ-Raman	🟢	🟡	🟡	🟡	🔴	🟡	🟢	🟡	🟡	🔴	🔴	(Araujo et al., 2018; Schymanski et al., 2018)
LDIR	🟢	🟡	🟡	🟡	🔴	🟡	🟢	🟡	🟡	🔴	🔴	(Ourgaud, 2022)
LS	🔴	🔴	🔴	🟡	🟡	🔴	🟢	🟢	🟢	🔴	🔴	(Liu, 2021; Choobbari, 2022)
pyr-GC/MS	🔴	🔴	🟢	🔴	🔴	🔴	🔴	🔴	🔴	🟢	🟢	(Fries, 2013; Santos, 2023)
TED-GC/MS	🔴	🔴	🟢	🔴	🔴	🔴	🔴	🔴	🔴	🟢	🟢	(Zhou et al., 2019; Sorolla-Rosario et al., 2023)
NMR	🔴	🔴	🟢	🔴	🔴	🟢	🔴	🔴	🔴	🟢	🟢	(Corti, 2020; Peez and Imhof, 2020; Peez et al., 2019; Peez, 2019)

🟢: particularly effective; 🟡: effective; 🔴: not suitable.

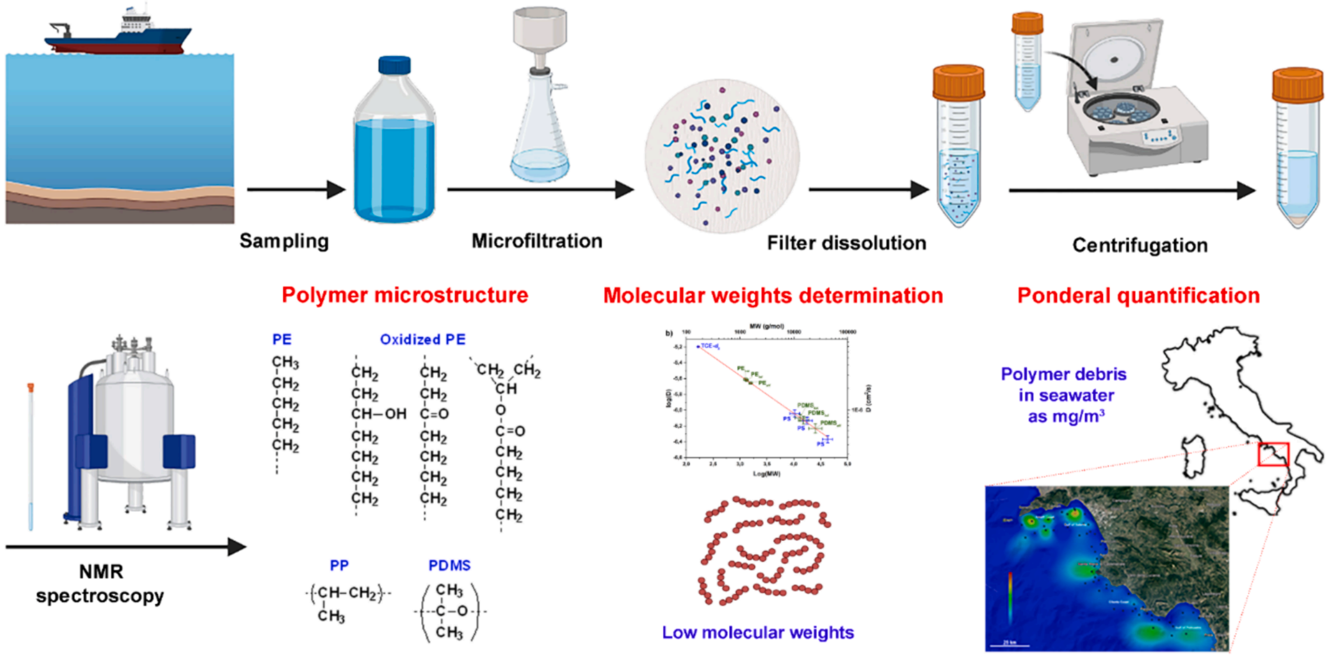

Fig. 2. Synoptical view for the analysis of seawater synthetic polymer debris.

the dissolution of the nitrocellulose in acetone at room temperature, the tube was centrifuged at 9500 rpm for 10 min, the surnatant solution was gently removed, and the SPD recovered at the bottom of the centrifuge tube. The tube was filled again with acetone, the eventual remaining nitrocellulose redissolved with a further 50 mL of acetone at room temperature, the tube was recentrifuged (9500 rpm for 10 min), the surnatant was gently removed, and the SPD collected again at the bottom of the centrifuge tube. The SPD were dried in air at room temperature in the centrifuge tube covered with blotting paper

2.3. *Recovery of synthetic polymer debris from wastewater treatment plants*

The samples from the influent and the effluent of the WWTP of Tavernola in Battipaglia, Salerno, Italy, were collected with an automatic sampler within 24 h. The Tavernola plant serves a region with 69,000 inhabitants, and the quantity of treated wastewater is 700–800 m^3/h. The samples were transferred to the laboratory with glass bottles. The sample (2 L) was transferred in a conical flask, disinfected with sodium hypochlorite, treated with 250 mL of a sodium chloride solution (2 M) and let to settle for 48 h. The surnatant was filtered with a Buckner apparatus using a nitrocellulose filter (0.45 μm pore size and 50 mm diameter from Sartorius, Germany). The filter was removed and dried in air, preserved from external contamination with SPD between two Petri dishes. The filter was transferred into a 50 mL PP centrifuge tube and filled with acetone (99.9 %, HPLC grade, Sigma-Aldrich – Merk Life Science, Italy). After the dissolution of the nitrocellulose in acetone at room temperature, the tube was centrifuged at 9500 rpm for 10 min, the surnatant solution was gently removed, and the SPD recovered at the bottom of the centrifuge tube. The tube was filled again with acetone, the eventual remaining nitrocellulose redissolved with a further 50 mL of acetone at room temperature, the tube was recentrifuged (9500 rpm for 10 min), the surnatant was gently removed, and the SPD collected again at the bottom of the centrifuge tube. The SPD were dried in air at room temperature in the centrifuge tube covered with blotting paper.

2.4. *Analytical methods*

NMR analyses of the SPD were carried out by dissolving the polymer particles in TCE-d_2 (≥99.5 %, Sigma-Aldrich – Merk Life Science, Italy) and using mesitylene (99.9 %, Sigma-Aldrich – Merk Life Science, Italy) added as internal standard. The SPD were transferred into a 4 mL vial and TCE-d_2 was added. The vial was equilibrated at 80 °C for 24 h to dissolve the TCE-d_2 soluble polymers. The solution was transferred into an NMR tube, a TCE-d_2 solution of mesitylene as an internal standard (0.1 M) was added and analysed. NMR spectra were recorded at 80 °C on a Bruker AVANCE 600 MHz spectrometer (for ^{1}H NMR experiments, the following instrumental parameters were used: d1 = 2.0 s; ns = 256) and all chemical shifts are reported in parts per million (ppm, δ). Chemical shifts are reported calibrating the residual solvent peak of TCE-d_2 at 5.80 ppm. ^{1}H DOSY experiments were performed at 80 °C (by using the following instrumental parameters: p30 = 600; d20 = 0.25 ms; ns = 16) by using PS standards supplied by Shoko Co., LTD (with M_w/M_n of 1.05; and M_w of 10.4, 17.9 and 42.6 kDa) as references. Polymer molecular weights were determined according to the procedures reported in the literature. (Li et al., 2012; Groves, 2017) The elaboration of the NMR spectra was performed with the software TopSpin (version 2.1) from Bruker or MestReNova (version 14.0) from Mestrelab Research.

The PE and PDMS concentrations ([PE] and [PDMS]) were determined respectively with the following equations:

$$[PE]\left(\frac{g_{PE}}{m_{sw}{}^{3}}\right)=\frac{\left(\frac{A_{CH_2PE}}{2}\right)n_{IS}\bullet MW_{CH_2}}{\left(\frac{A_{CH_{IS}}}{3}\right)V_{sw}} \tag{1}$$

$$[PDMS]\left(\frac{g_{PDMS}}{m_{sw}{}^{3}}\right)=\frac{\left(\frac{A_{CH_3PDMS}}{6}\right)n_{IS}\bullet MW_{(CH_3)_2SiO}}{\left(\frac{A_{CH_{IS}}}{3}\right)V_{sw}} \tag{2}$$

where $A_{CH_{2PE}}$ is the area of the ^{1}H NMR signal due to the methylene groups of the PE (signal at 1.12 ppm), $A_{CH_{IS}}$ is the area of the ^{1}H NMR signal due to the methine groups of the internal standard (mesitylene, signal at 6.63 ppm), $A_{CH_{3PDMSO}}$ is the area of the ^{1}H NMR signal due to the methyl groups of the PDMS (signal at 0.08 ppm), n_{IS} is the *mol* content of the internal standard, MW_{CH_2} is the molecular weight of the CH_2 group, $MW_{(CH_3)_2SiO}$ is the molecular weight of the dimethyl siloxane group

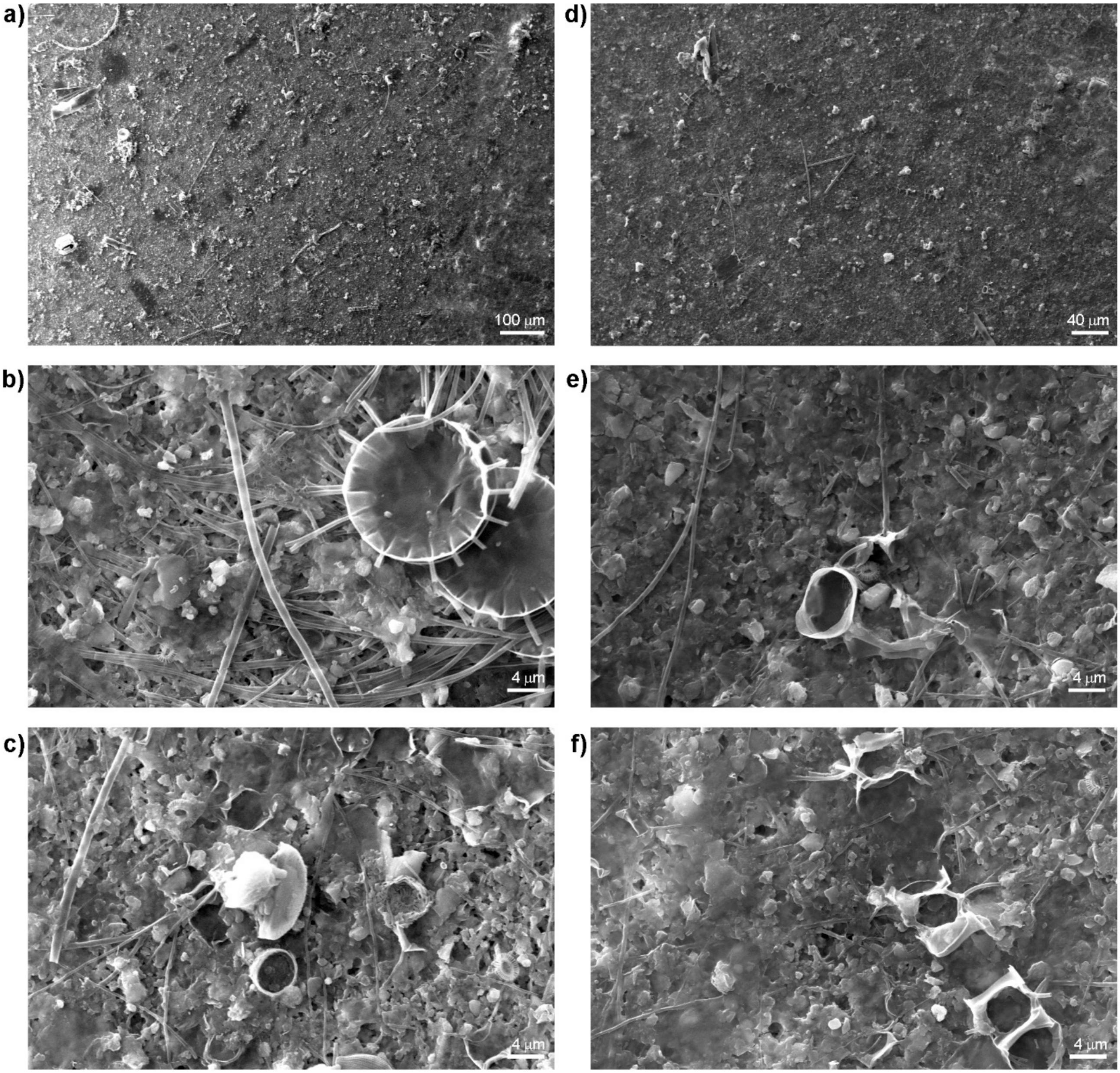

Fig. 3. ***Microscopy of*** the particulate in seawater recovered by microfiltration. SEM micrographs of two samples of microfiltered marine water (panels a and d, with corresponding magnification in b-c and e-f panels) showing organic, inorganic and microbiological particulates (each sample was obtained by filtration of 2 L of seawater through a 0.45 μm nitrocellulose microfilter).

($(CH_3)_2SiO$), V_{sw} is the volume of sampled and filtered seawater. The detailed derivation of the Equations (1) and (2) is reported in the Supporting Information. Figs. 6, 7, 8 and 9 have been generated using the Software OriginLab 2018 using the corresponding colour gradient reported generated from the polymer concentration data. As positive control experiments, the recovery efficiencies of PE and PDMS have been determined for 10 samples of deionised water (10 L) seeded with micronised PE (DEUREX E 0915 M, 50 μg; molecular weight of 1352 ± 95 Da determined by DOSY NMR, see Table S2) and PDMS (Food additive E900; 50 μg) applying the above-described procedure: in all the case the recovery efficiency for both the polymers was > 99 %. As negative control experiments, blank samples consisting of deionised water (2 L) were analysed according to the above-described procedure: the average NMR integral areas were negligible with respect to those of the analysed marine samples.

FTIR measurements were performed with a Vertex 70 spectrometer from Bruker, equipped with a deuterated triglycine sulphate detector and a Ge/KBr beam splitter. The spectra were collected performing 128 scans in the range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}. The samples were analysed in the form of KBr pellets.

A Phenom desktop scanning electron microscope from Thermo Fisher Scientific was used to analyse the particulate recovered by filtration of seawater (2 L) on nitrocellulose filters (pore size of 0.45 μm). The samples were gold-sputtered before the analysis.

3. Results

3.1. Recovery of synthetic polymer debris from surface seawater

Four sampling campaigns of surface seawater (each including 29–30 samples taken within a distance of 4 nautical miles from the coast) were carried out along the coastal area, including the Amalfi Coast and the Gulf of Salerno, in Italy, in the period 14/06 /2021–23/06/2021, repeated in the period 19/07/2021–28/07/2021, and along the coastal

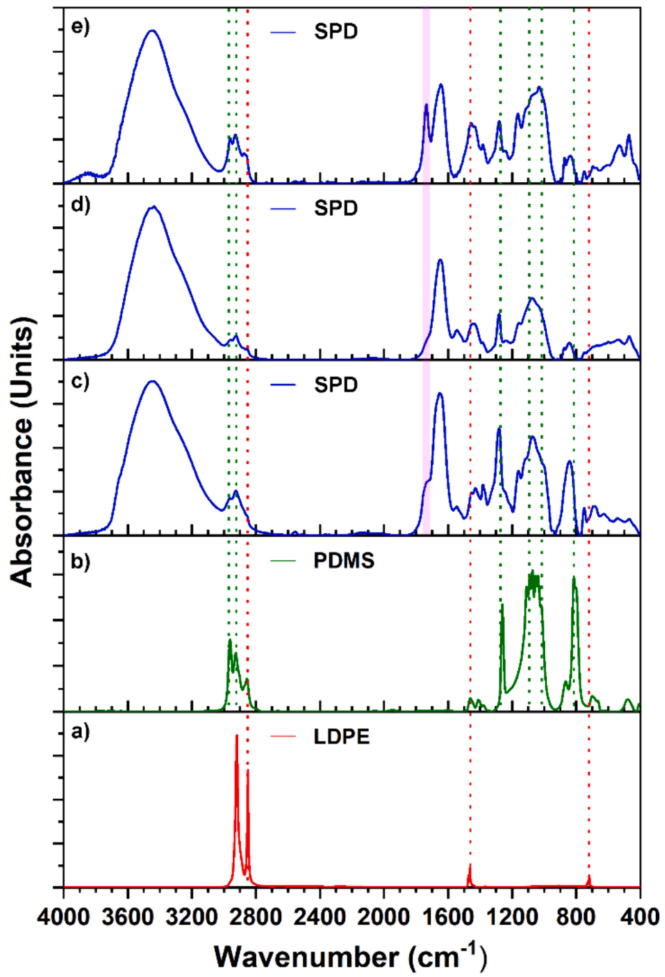

Fig. 4. ***FTIR analysis.*** Infrared spectra of: LDPE (a), PDMS (b) and representative SPD samples isolated from seawater (sample 16 of Table S4 and S6 (c); sample 17 of Table S5 and Table S7 (d); sample 19 of Table S5 and Table S7 (e)).

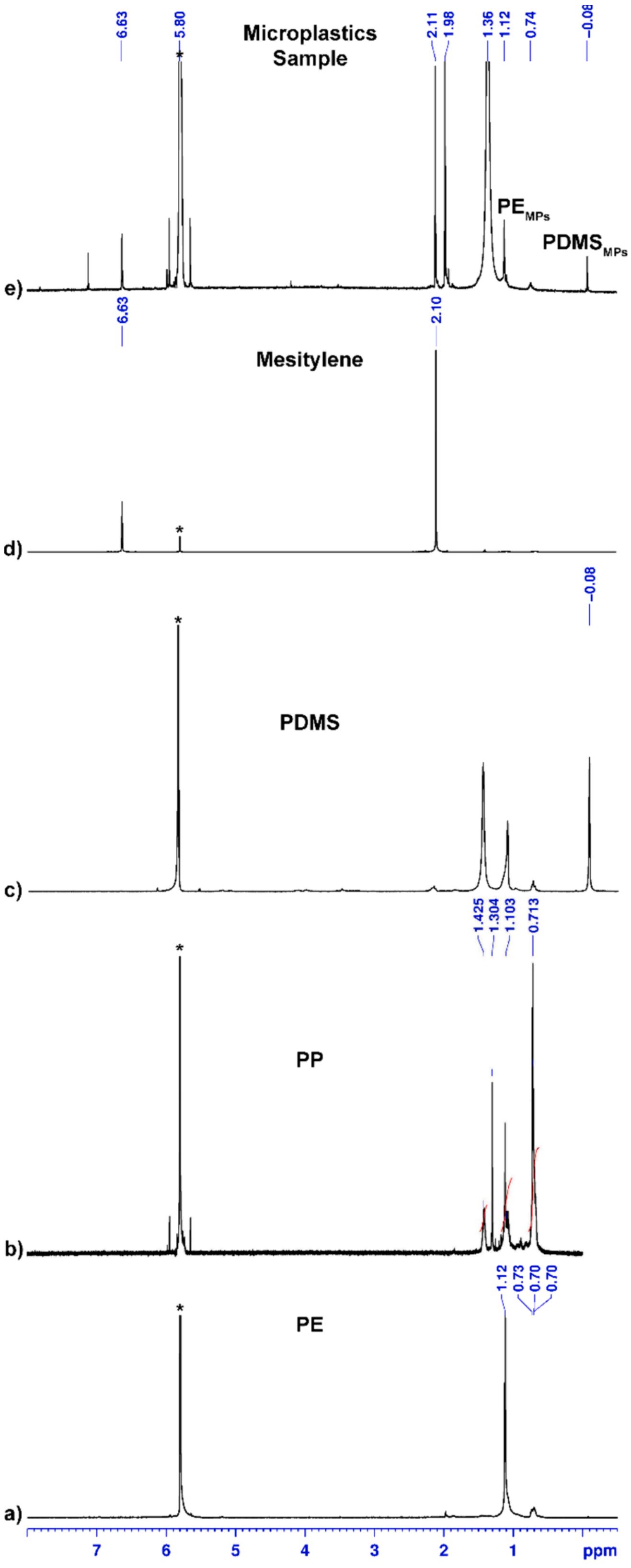

Fig. 5. ***NMR analysis.*** ^{1}H NMR spectra (600 MHz, TCE-d_2, 80 °C) of LDPE (a), PP (b), PDMS (c), mesitylene (d) and representative SPD isolated from seawater (e).

area including the Cilento Coast and the Gulf of Policastro, in Italy, in the period 27/10/2021–09 /11/2021, repeated in the period 22/11/2021––13/12/2021. Surface seawater (2 L) was collected in glass bottles and microfiltered with a stainless-steel Buchner-type apparatus using cellulose nitrate filters with a pore size of 0.45 μm. This apparatus ensures the filterability of over 2 L of surface seawater, quantitatively recovering the entire particulate matter with a size larger than 0.45 μm. Attempts with filters with porosity lower than 0.22 μm failed because of the heavy clogging with a consequent worsening of the analytical sensitivity for quantitative weight estimation of the SPD.

Fig. 3 shows the particulate recovered on the filters used to process two seawater samples obtained during the sampling campaigns. The figure demonstrates the presence on the filter of both inorganic and organic particulates, *i.e.*, crystallised sea salt, marine microorganisms and their exoskeletons. These micrographs show the challenge of identifying and quantifying SPD present in seawater through microscopic techniques. FTIR spectroscopy allows the qualitative identification of the types of plastics in the particulate recovered through microfiltration. Fig. 4 shows the FTIR spectra of three SPD samples recovered during the abovementioned sampling. The FTIR spectra allow for verifying the presence of PE and PDMS, which can be identified by comparison with the standard spectra of these two polymers. Additionally, the spectra show the presence of carbonyl functionalities (via the diagnostic absorption band centred at 1730 cm^{-1}), which, however, can be attributed to both oxidised SPD and organic and biological contaminants (vide

Fig. 6. ***PE concentrations.*** Coastal PE concentrations in Amalfi Coast-Gulf of Salerno (sampling period: 14/06/2021——23/06/2021) and Cilento Coast-Gulf of Policastro (sampling period: 27/10/2021——09/11/2021) in Italy (for punctual concentration values see additionally Table S4 of Supplementary information).

infra for the explanation of the presence of these functionalities in the SPD sample).

The SPD recovery procedure developed herein exploits the high solubility of nitrocellulose in acetone (Wilson et al., 1934). This allows the filter to be dissolved in this solvent and recover the insoluble particulate by centrifugation. The process was repeated twice to ensure the complete removal of the filter substrate and of lipid and hydrocarbons in acetone. The retained SPD and particulate matter have a higher density than that of acetone (0.784 g/cm^3). After centrifugation for 10 min at 9600 rpm speed, the SPD was recovered at the bottom of the centrifuge tube, dried and analysed by solution NMR spectroscopy.

The selective dissolution of the SPD allows the specific analysis by typology. Surface seawater is known to contain SPD with low specific weight and, therefore, able to float. These SPD include polyolefins (LDPE, PE, HDPE, PP and expanded PS) and polysiloxanes (PDMS). (Coyle et al., 2020) SPD with higher density, when covered by microbial biofilm, can also float or remain suspended in water before sinking and accumulating in marine sediments or being ingested by marine fauna. Polyolefins and polysiloxanes are hydrophobic and can be analysed by high-resolution NMR spectroscopy in solution, *i.e.*, after dissolution in a high-boiling solvent such as 1,2-dideutero-1,1,2,2-tetrachloroethane (TCE-d_2). The samples obtained in this study were thus dissolved in this solvent at 80 °C and analysed at the same temperature by one-dimensional (^{1}H and ^{13}C NMR) and two-dimensional (^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and ^{1}H DOSY) NMR techniques. This approach allowed identifying which SPD are present on the surface seawater, to estimate their occurrence quantitatively, analysing their microstructure, *i.e.*, the presence on the polymeric chain of functional groups due to thermal and photochemical oxidation and, finally, the determination of the molecular mass of the polymeric chains. The ^{1}H NMR spectrum in Fig. 5a shows the signals due to PE (signals at 1.12 and 0.74–0.70 ppm) and PDMS (signal at −0.08 ppm). The presence of PP in traces was also observed in some samples (see Figs. 5 and 10). The presence of other polymer types has been investigated by NMR analyses of the isolated polymer particles in other deuterated solvents different from the TCE-d_2 (helpful in dissolving hydrophobic apolar polymers) by using deuterated-dimethyl sulfoxide for polar polymers and deuterated-trifluoroacetic acid for polyesters and polyamides. Both these analyses indicated the absence of other polymers in the surface seawater we analysed. On the base of the polymer densities with respect to the seawater, we ascribed this evidence to the sinking of the polymers different from PE, PP and PDMS in the sea.

3.2. Quantification of weight concentrations of synthetic polymer debris in surface seawater

The weight analysis of the microplastic content was carried out by introducing a known quantity of mesitylene as an internal standard into the samples to be analysed by NMR, through which the microplastic content was determined using Equations (1) and (2) reported in the Methods section (the detailed derivatisation of these equations is reported in the Supplementary Information). Integration of the signals of the ^{1}H NMR signals PE methylene groups (1.12 ppm, Fig. 5 a and e) and the mesitylene methyl groups (2.10 ppm, 1.12 ppm, Fig. 5 d and e) allowed determining the PE concentrations as mg of the polymer per m^3 of seawater. The concentrations of PDMS were similarly determined from the corresponding methyl signals (−0.07 ppm, Fig. 5 c and e). Figs. 6, 7, 8 and 9 show the distribution of the concentrations of PE and

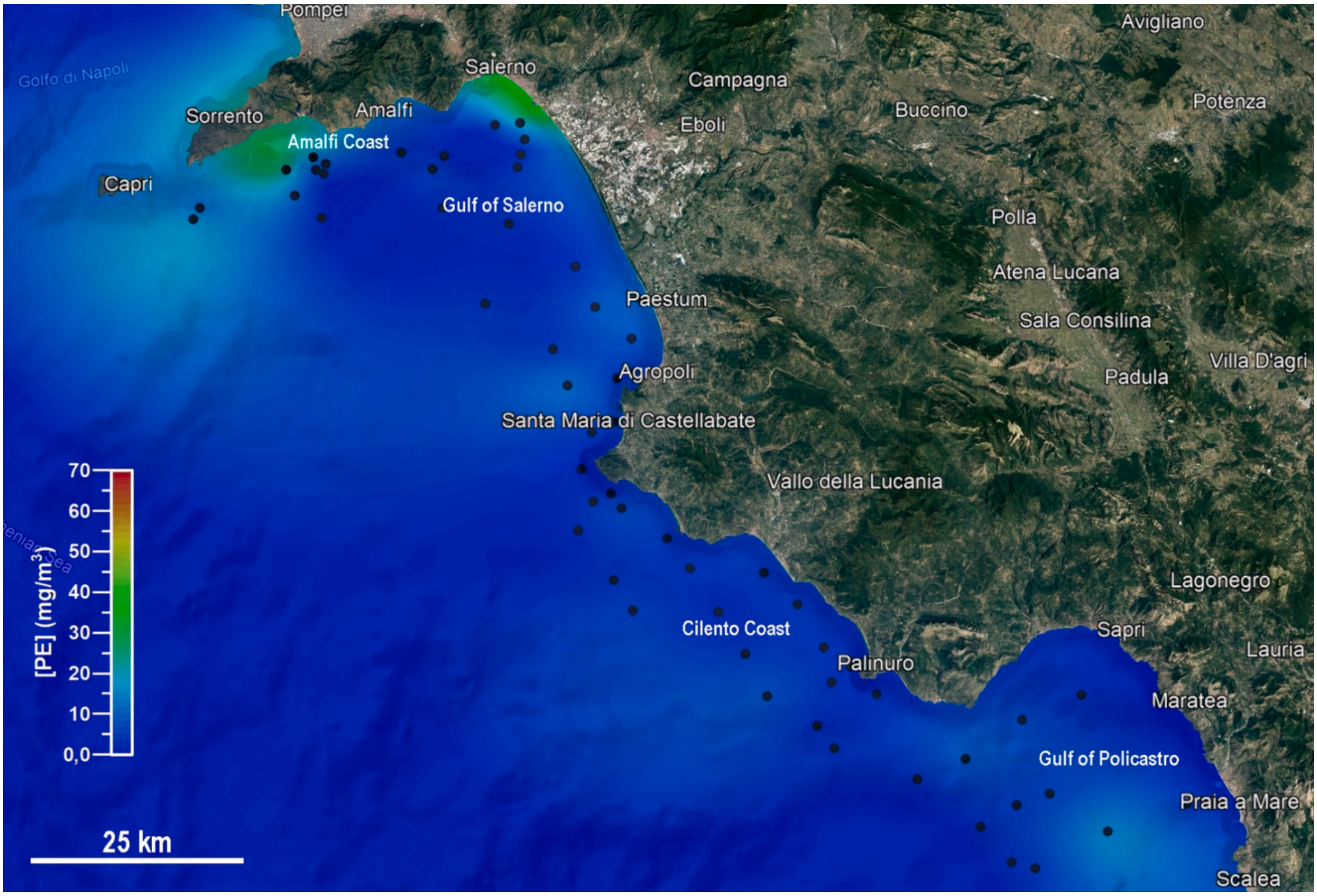

Fig. 7. ***PE concentrations.*** Coastal PE concentrations in Amalfi Coast-Gulf of Salerno (sampling period: 19/07/2021——28/07/2021) and Cilento Coast-Gulf of Policastro (sampling period: 22/11/2021——13/12/2021) in Italy (for punctual concentration values see additionally Table S5 of Supplementary information).

PDMS detected in the seawater in the investigated coastal areas of Amalfi Coast, Gulf of Salerno, Cilento Coast and Gulf of Policastro. Point-by-point values of the SPD concentrations are reported in Supplementary Information. The observed PE concentrations were in the range of 0.7–70 mg_{PE}/m^3, while those of PDMS were below 3.2 mg_{PDMS}/m^3. The lowest concentrations in terms of PDMS resulted consistent with the largest use of PE in different industrial sectors. The PE has been confirmed as the most abundant polymer in SPDs also by other studies. The short-lived plastics represent 69 % of the total plastic wastes. Considering that 68–81 % of SPDs (secondary MPs) derives from the fragmentation and/or deterioration of large SP products, the packaging, including bottles and recipients for food and detergent storage, may be regarded as the main source of SPDs. Consequently, the PE resulted as the most abundant polymer in SPDs, as confirmed in this study since, as expected from the extensive use of PE compared to that of PDMS, the concentrations of the polyolefin vastly exceeded those of the silicone polymer. The SPD concentration maps (Figs. 6, 7, 8 and 9) clearly show that coastal areas with higher population density, comprising wastewater treatment plants (WWTPs), port areas and rivers, are the hotspots for PE and PDMS debris emission. The PE concentration maps in Figs. 6 and 7 show that in both the sampling campaigns, the areas with the highest concentration of this are near the Amalfi Coast and the port of Salerno, with PE concentration peaks of 70 and 50 mg_{PE}/m^3, respectively (Tables S4 and S5 of Supporting information). The maximum values detected in the Cilento coastal area and near Sapri in the Gulf of Policastro were about 18 and 15 mg_{PE}/m^3, respectively (see Figs. 6 and 7 and additionally Tables S4 and S5 of Supplementary information). These areas coincide with those with a greater population density and with the presence of WWTPs whose treated effluents are discharged into rivers and finally into the sea and they are characterized by a greater number of environmental pressures. In particular, the presence of river mouth has been well established as driver of SPDs in marine environments coupled with human activities that produced plastic debris directly immitted in seawater. Moreover, the influence of human activities along coastal zone also concur to the presence of these materials in marine environments as also reported by Wang et al. (2020) in a study conducted in China (Nchimbi, 2022).

The PDMS concentrations found in the two sampling campaigns were very low and in a narrow range of 0–3.2 mg_{PDMS}/m^3 (Figs. 8 and 9 and additionally Tables S6 and S7 of Supplementary information). The maps in Figs. 8 and 9 seem to accentuate the concentration of these polymers, compared to the maps showing the distribution of PE concentrations; however, in this case, the different scales of SPD concentrations must be considered. In the case of the PDMS, it is also possible to observe that the areas with the highest concentration of PDMS match those of the PE. The Amalfi Coast and the port area of Salerno are again the areas with the highest concentration of these SPs. This outcome can be ascribable to the seasonal variability linked to the tourist vocation of the areas investigated. During the period of June-July, the number of people and the activity both terrestrial and in the aquatic systems are surely more intensive compared to those conducted during the autumn months of October and November. Consequently, the SPDs concentrations detected in the Amalfi Coast, Gulf of Salerno resulted higher than those detected in Cilento Coast and Gulf of Policastro.

The mechanisms of formation of SPD can be probably related mainly to the fragmentation and breakdown of larger plastics originating from land and transported by vehicles like rivers, storm drains and nearshore and alongshore currents where debris are subjected to further

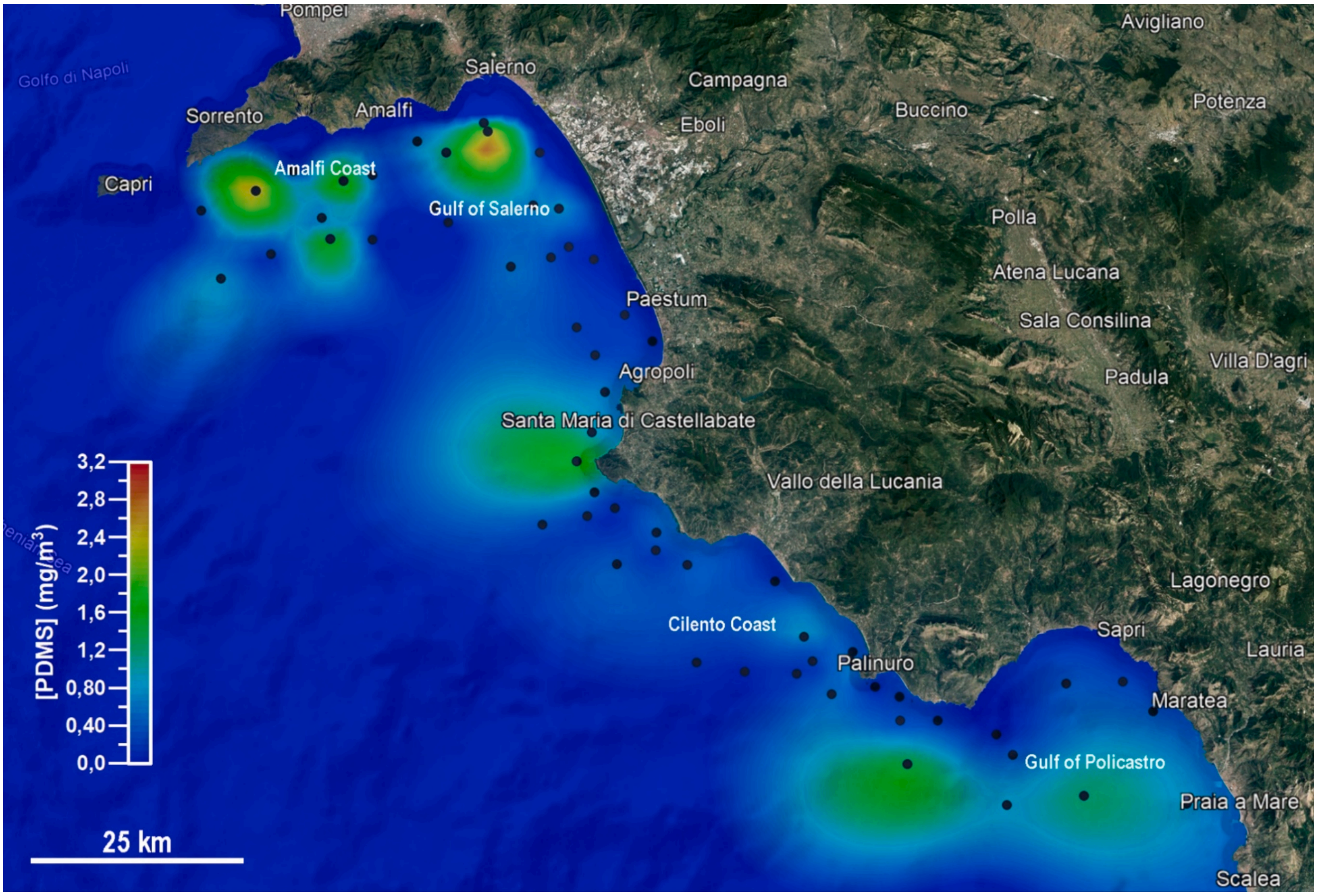

Fig. 8. ***PDMS concentrations.*** Coastal PDMS concentrations in Amalfi Coast-Gulf of Salerno (sampling period: 14/06/2021——23/06/2021) and Cilento Coast-Gulf of Policastro (sampling period: 27/10/2021——09/11/2021) in Italy (for punctual concentration values see additionally Table S6 of Supplementary information).

fragmentation. (Brandolini, 2000) It has been indeed demonstrated that more than 80 % of SPDs enter oceans from terrestrial sources. (Buonerba, 2013) Information about the origin and fate of SPDs can be retrieved also by their morphology since the high prevalence of films and foils may be related to single-use products while fibres may be originated from fishing activities along the coastal areas and from washing clothes activities from urban centres and from weathering and shredding of industrial fabrics (canvas, tarpaulins, fishing nets, and cables). (Buonerba, 2013; Buonerba et al., 2013) The investigation and identification of entry pathways is essential to reduce the introduction of such materials in ecosystems by designing control measures at the sources, as also suggested by other studies. (Capacchione, 2013; Buonerba, 2014; Buonerba, 2017).

The developed method of recovery, concentration and weight determination of the SPD occurrence is unprecedented, especially for the level of sensitivity achieved. The detection limit in the order, below 1 $mg_{SPD}/m^3_{seawater}$, is far below the previous methods.

3.3. Microstructural and morphological characterisation of synthetic polymer debris

NMR spectroscopy is a powerful tool for the structural analysis of organic and polymeric compounds. (Brandolini, 2000) The microstructure of polymer chains can be finely resolved by one- and two-dimensional NMR techniques. (Buonerba, 2013; Buonerba et al., 2013; Capacchione, 2013; Buonerba, 2014; Buonerba, 2017; Naddeo, 2017; Galdi et al., 2014) Thus, in addition to quantitative ^{1}H NMR, two samples of marine SPD (sample 8 of Table S4, Supplementary information) were analysed by ^{13}C NMR (Fig. 9) and two-dimensional ^{1}H–^{1}H COSY and ^{13}C–^{1}H HSQC (see Figs. 1-2 in Supplementary information) spectroscopy in order to determine the microstructure of the polymeric chains present in the recovered marine SPD.

Traces of PP were found in the analysed samples. This polymer was identified by ^{13}C NMR (Fig. 10), ^{1}H–^{1}H COSY (Fig. 1 in Supplementary information) and ^{13}C–^{1}H HSQC NMR (Fig. 2 in Supplementary information). The observed presence of PP in traces is consistent with the lower yearly production compared with that of PE. In addition, PP is more susceptible than PE to rapid environmental oxidative degradation. (Nakatani, 2023) In fact, the PP methyne groups are more reactive of the PE methylenes, resulting in an important reaction pathway of PP oxidation. On the other hand, the absence of bulk PS in the examined sample can be ascribed to the rapid sinking of this polymer to marine sediments (Coyle et al., 2020) or to the dissolution of the expanded PS in the acetone used in the extraction process of the SPD.

Fig. 10a-b shows the ^{13}C NMR spectra of the recovered SPD. The presence of PE and its oxidised derivatives enriched in the hydroxyl, carbonyl and carboxylate groups, as well as the presence of PP and PDMS, was confirmed by comparison of the chemical shifts of the NMR signals present in the spectra with the chemical shifts reported in the literature for these polymeric materials. (Cheng et al., 1976; Randall, 1989; Kuroki et al., 1983) This was confirmed further by two-dimensional ^{1}H–^{1}H COSY and ^{13}C–^{1}H HSQC analyses reported in Supplementary materials (Figs. 1-2 in Supplementary information).

An estimation of the molecular weights of the polymer chains was performed by ^{1}H diffusion-ordered spectroscopy (DOSY) NMR analysis. (Li et al., 2012; Groves, 2017) Fig. 11 shows the DOSY NMR analysis of the SPD from sample 8 of Table S4 of Supplementary information (panel a) carried out in the presence of three polystyrene standards with known

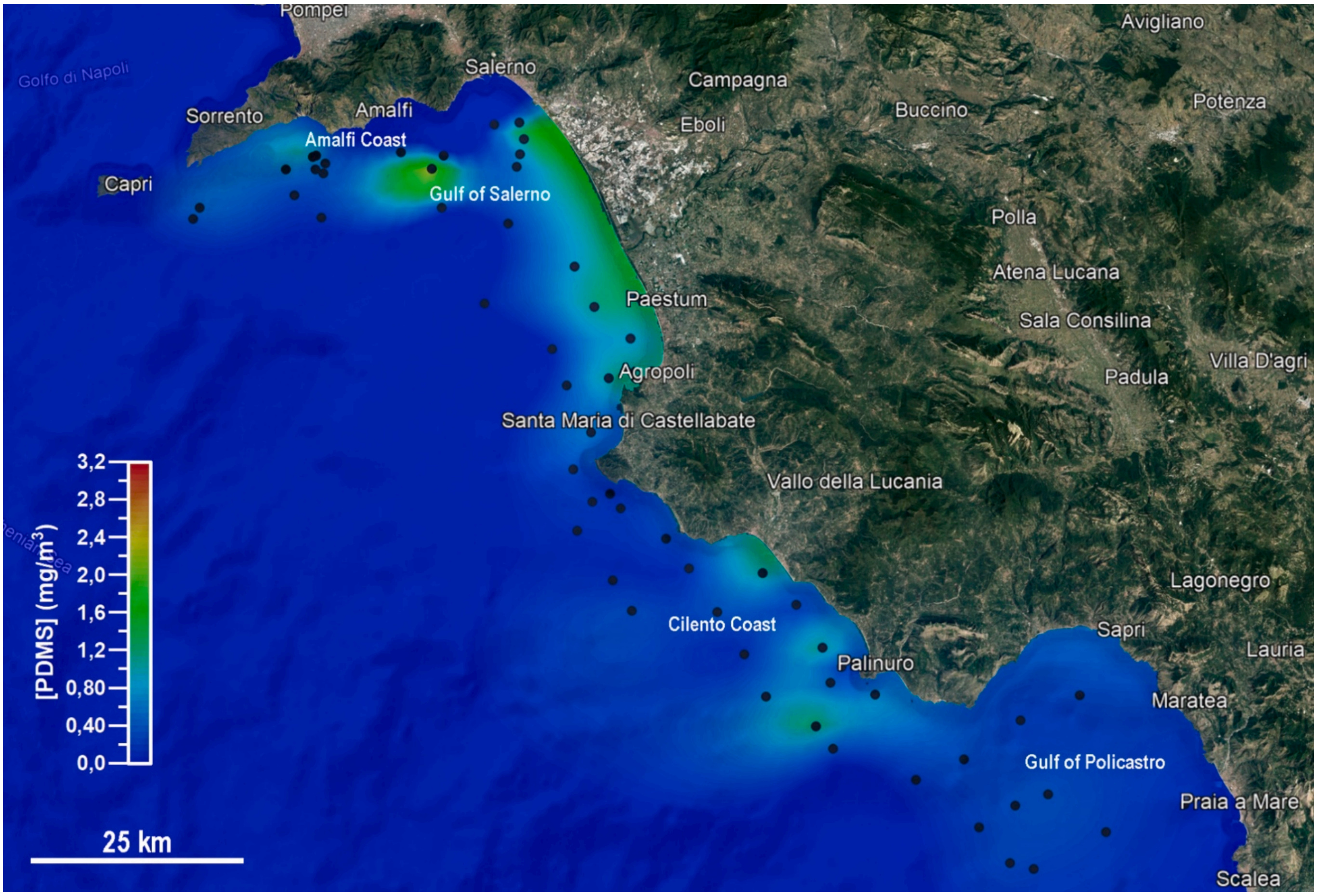

Fig. 9. ***PDMS concentrations.*** Coastal PDMS concentrations in Amalfi Coast-Gulf of Salerno (sampling period: 19/07/2021—–28/07/2021) and Cilento Coast-Gulf of Policastro (sampling period: 22/11/2021—–13/12/2021) in Italy (for punctual concentration values see additionally Table S7 of Supplementary information).

molecular weights of 10.4, 17.9 and 42.6 kDa and narrow dispersity index, M_w/M_n, with the value of 1.05. The molecular weight of the PE and PDMS determined using this calibration were 1266 ± 85 and 13518 ± 2783 Da, respectively (Fig. 11b; see additionally Tables S1 and S2 and Figure S3 of Supplementary information). The molecular weight of the PDMS was also very low: a value of 13518 ± 2783 Da was found for the polymer chain of this polymer (see Fig. 11b, and additionally Tables S1 and S2 and Figure S3 of Supplementary information).

The presence of the products of PE oxidation agrees with the results of a recent study on the deterioration of PE in a water environment under exposure to light radiation. (Menzel, 2022) Menzel and co-workers conducted long-term accelerated weathering experiments on LDPE, subjecting polymer specimens to simulated solar irradiation and water exposure. (Menzel, 2022) The cracking of the specimens into micro- and nano-plastics was observed, accompanied by polymer chain degradation and oxidation. The LDPE was oxidised to the corresponding hydroxyl, carbonylic, carboxylic and carboxylate derivatives, and the progressive reduction of the molecular weight of the polymer due to polymer chain breakage was also observed by the authors of this study. The molecular weight observed for the PE after accelerated weathering, studied by Menzel and co-workers, coincides with that we found for the PE in surface seawater (1 kDa circa).

In order to investigate the possible origin of these low molecular weight polymers, microstructural analysis of PE and PDMS in municipal wastewater from the WWTP of Battipaglia, Salerno, Italy, was carried out. The wastewater was treated with sodium hypochlorite for sterilisation and with sodium chloride for the sedimentation of the organic matter, according to previously reported procedures. (Bayo et al., 2020) The supernatant was then directly filtered with nitrocellulose filters and processed similarly to the seawater samples according to the procedure herein described. The NMR analysis showed the presence of low molecular mass polymers in influent and in treated wastewater (≈ 1.3 and 1.6 kDa, respectively; see Fig. 10c-d, Fig. 11, see additionally Table S1-S2 and Fig. S3 of Supplementary information). PE was found in the non-oxidised form both at the inlet and outlet of the WWTP (Fig. 10c-d). This result indicates that LDPE or HDPE were absent in the analysed wastewater samples. The PDMS from the wastewater samples also presents low molecular weights of ≈ 15–26 kDa. Non-oxidised PE and PDMS, both with low molecular weights identified in wastewater, can come respectively from PE waxes, used as additives in food processing, coating applications, cosmetics and detergents, and from PDMS antifoamers, also used for food applications.

4. Discussion

The conventional analyses of SPD after this filtration stage involve the removal of the particulate matter adhering to the filter, which could not be quantitative, and a mild digestion with inorganic acids and peroxides, or with enzymes to remove the biological component other than the SPD. (Pfeiffer and Fischer, 2020) SPD resist these treatments moderately; however, the exposure time to the digesting agents and their concentrations must be finely regulated. The results of the analyses depend on the skill of the operator in charge. The pre-treatments of the SPD are time-consuming, and the use of strong acids and peroxides could be dangerous for the personnel. The treatment is also necessary to remove the biofilm that could cover the SPD to prepare samples for particle counting via μ-FTIR or μ-Raman, as well as for the thermal decomposition analysis coupled to analysis GC–MS of the released gases

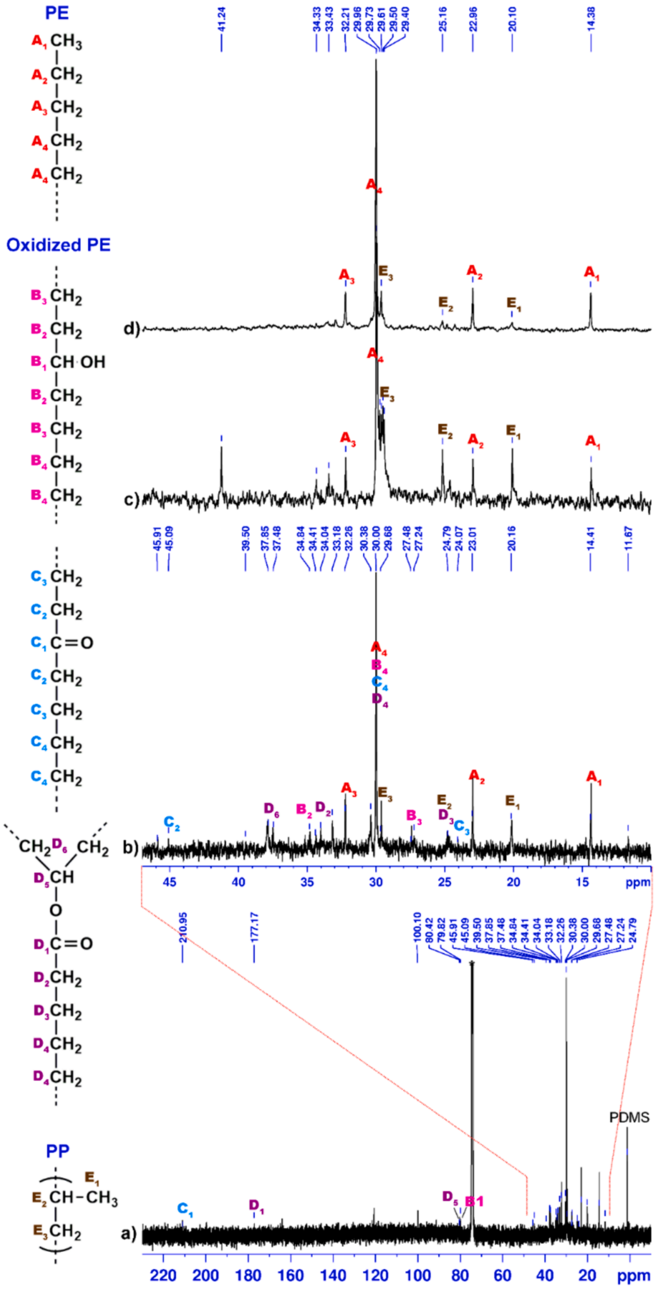

Fig. 10. ***^{13}C NMR analysis.*** ^{13}C NMR spectra (TCE-d_2, 80 °C) of: SPD from seawater (spectrum a with a magnification of the aliphatic spectral region in b) and SPD from influent (spectrum c) and effluent (spectrum d) of WWTP (from Battipaglia, Salerno, Italy).

(TED-GC/MS and py-GC/MS, respectively). This treatment is also necessary to avoid erroneous identification as SPD of other particulates (organic, inorganic and biological) present on the filter. Filtration with 0.45 μm nitrocellulose filters recovers a large part of the microorganisms present in marine samples, and only spores and viruses pass through these filters with this pore diameter.

The direct microfiltration of the surface seawater allowed the fine recovery of the organic, inorganic and above all of the synthetic particulate floating on the sea. The selective dissolution of the nitrocellulose filter allowed thus the isolation of the SPD recovered. Acetone also dissolves lipids and other hydrocarbons, bearing repeated methylene sequences, that could interfere with the NMR quantification based on the signal of this moiety. Biological macromolecules such as cutins and other hydrocarbons insoluble in acetone are typically crosslinked and, therefore, insoluble also in TCE-d_2 and require solid-state NMR. (Zlotnik-Mazori and Stark, 1988) The ^{13}C NMR signals are highly diagnostic for the identification of PE and its oxidised derivatives. Also in this case, the observation of a single signal for the methylene moiety in the DOSY NMR analysis confirms the exclusive presence of the PE with molecular weights around 1 kDa. The presence of other molecules bearing repeated methylene moieties with different molecular weights from those of PE would have resulted in several signals in the DOSY NMR spectrum. Thus, the NMR analysis allowed the identification of PE and PDMS. The ponderal quantification of these synthetic polymers, with an excellent LOD and LOQ in the order of the milligram per cubic metre of surface seawater (see paragraph: 4. Determination of NMR LOD and LOQ for PE in seawater in Supporting information), allowed the identification of the hot spots for the release of these polymers: the concentrations of these polymers in sea were higher in proximity of WWTPs, rivers and port areas and highly inhabited urban areas. The microstructural NMR analysis revealed PE bearing hydroxyl, and carbonyl groups, as an

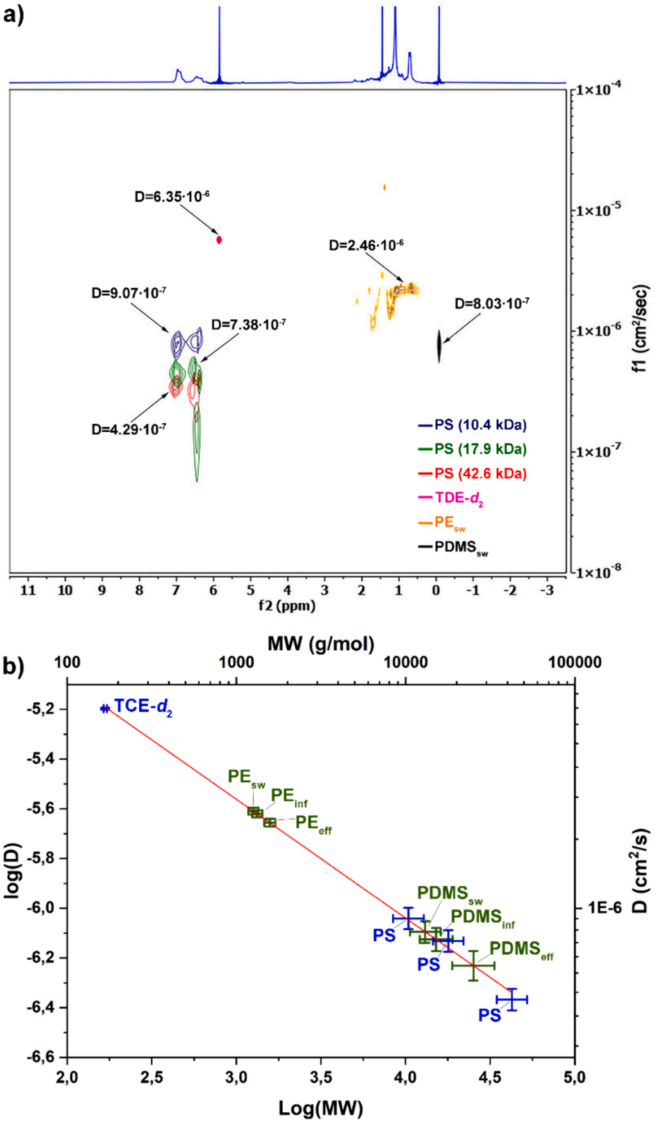

Fig. 11. ***Polymer molecular weights determination by DOSY NMR.*** ^{1}H DOSY NMR analysis of SPD (panel a; sample 8 of Table S4 of Supplementary information; 600 MHz, 80 °C, TCE-d_2) referenced to low polydispersity index PS standards (10.4, 17.9 and 42.6 kDa; M_w/M_n: 1.05), with the corresponding logarithmic plot of the diffusion coefficients as a function of the molecular weights (panel b; the red line is the calibration line; see additionally Table S1 and S2 and Fig. S3 in Supplementary information).

indication of the oxidation process in course for this polymer. The polymer molecular weights, determined by DOSY NMR, were very low for both PE and PDMS. Wastewater influents and effluents from WWTP were analysed in order to investigate the possible origin of the SPD polluting the seawater. PE and PMDS identified in the wastewater presented similar molecular weights to those found on seawater. However, PE found in wastewater was present in unoxidised form. The molecular weights distribution, in all the cases investigated was narrow.

Low-molecular-weight PE and PDMS floating on seawater can come from PE waxes and PDMS additives, yet present with low molecular weights, or can be originated from degradation of high-molecular-weights PE and PDMS (see Fig. 1).

5. Conclusion

A new approach for recovering, identifying and quantifying synthetic polymer debris in marine water is presented here. The procedure is based on the microfiltration of seawater, removal of the filter substrate by solvent dissolution, separation of the retained particulates by centrifugation, and the analysis of the isolated particulate matter by NMR spectroscopy. The described method is simple, quantitative and highly sensitive. The limit of quantification is below 1 mg of plastic per m^3 of seawater. The polymer materials identified were PE, PP and PDMS. The method was applied to multiple samples obtained during four sampling campaigns in the Mediterranean Sea between the Amalfi Coast and the Gulf of Policastro in Italy. The results allowed mapping the point concentrations of synthetic polymer debris in seawater. The results show that the highest concentration of PE and PDMS debris are present in the most populated coastal areas, where there are wastewater treatment plants and rivers. The microstructural NMR analysis of the polymer debris highlighted the presence of the oxidised forms of PE (bearing hydroxyl and carboxyl groups) with low molecular weights (≈1.3–1.6 kDa). Traces of PP were also found. The presence of oxidised low molecular weight PE is consistent with previous studies on the degradation of this polymer in an aqueous environment under simulated solar radiation. (Menzel, 2022) The microstructural analysis of PE present in influent and effluent waters from the urban wastewater treatment plant of Tavernola in Battipaglia, Salerno, Italy, discharging into the marine waters subjected to analysis in this study, also shows the presence of low molecular weight PE (≈ 1.6 kDa), however, in unoxidised form. The molecular weights and microstructures determined here are also compatible with those of polyethylene waxes, widely used in the food industry, cosmetics, detergents and in coating applications. The presence of low-molecular-weight PDMS can be indicative of the release into the environment of this polymer used in the food and cosmetics industries as an antifoam agent. PDMS debris presents enhanced chemical stability, and its accumulation in seawater could constitute an emerging concern for the environment, the aquatic fauna and the humans at the top of the food chain. Based on the results of the present work, the recovery of significant quantity of synthetic polymer debris (SPD) may be uneconomic, also considering the low quality of the materials potentially recovered. However, marine litters of bigger size, which can be directly collected without the need of a filtration phase, should be included in a virtuous context of circular economy by recovering polymers and energy [82], with mechanical recycling [83], chemical recycling [84], pyrolysis for fuels recovery [85] and combustion for energy recovery [86].

CRediT authorship contribution statement

Alessia Giannattasio: Writing – review & editing, Writing – original draft, Investigation, Data curation. **Veronica Iuliano:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Giuseppina Oliva:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Data curation. **Domenico Giaquinto:** Writing – review & editing, Supervision, Data curation. **Carmine Capacchione:** Writing – review & editing, Validation, Supervision, Investigation, Data curation. **Maria Teresa Cuomo:** Writing – review & editing, Validation, Supervision, Funding acquisition. **Shadi W. Hasan:** Writing – review & editing, Validation, Supervision. **Kwang-Ho Choo:** Writing – review & editing, Validation, Supervision. **Gregory V. Korshin:** . **Damià Barceló:** Writing – review & editing, Validation, Supervision, Formal analysis. **Vincenzo Belgiorno:** Writing – review & editing, Validation, Supervision, Formal analysis. **Alfonso Grassi:** Writing – review & editing, Writing – original draft, Validation, Supervision, Formal analysis, Data curation. **Vincenzo Naddeo:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization, Formal analysis. **Antonio Buonerba:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2024.108839.

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