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Microplastics in inland and offshore sediments in the Apulo-Lucanian region (Southern Italy)

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ABSTRACT

Inland and offshore sediments from Southern Italy were studied in order to evaluate the occurrence and nature of microplastics (MPs). Inland sediments were collected in the Bradano and Basento rivers (Apulo-Lucanian region, Southern Italy), while offshore sediments were collected on the continental shelf near Bari (Adriatic Sea) and Metaponto (Ionian Sea). MPs were detected and characterized using optical microscopy, micro-Fourier-Transform Infrared spectroscopy (μ-FTIR) and micro-Raman analyses. The number of MPs present varied between 144 and 1246 kg^{-1} of dry sediment (468.8 ± 410,7 MPs kg^{-1}) with a predominance of black fibers; no correlation emerged between MPs and sediment grain size. In river sediments, the occurrence of MPs is associated with local pollution, whereas the offshore occurrence of MPs depends on seasonal river flow and submarine canyons. Compositional analyses suggest that the main source of MPs in the studied sediments is sewage discharge from residential areas.

1. Introduction

Plastic pollution is among the most critical environmental issues; the rapidly growing production of single-use plastic products outstrips the global capacity to tackle the problem (GESAMP, 2015; Kershaw et al., 2019; Campanale et al., 2020a; Forleo and Romagnoli, 2021). Furthermore, limited recycling of plastics, coupled with the demand for plastic products used to combat the COVID-19 pandemic, have contributed to the accumulation of plastic waste in the environment (Rajmohan et al., 2019; Parashar and Hait, 2021; Fang et al., 2023). Generally, plastic pollution is divided into two categories of polymers: primary and secondary plastics (GESAMP, 2015; Kershaw et al., 2019). Primary plastics are polymers released directly into the environment without undergoing degradation, whereas secondary plastics are subjected to fragmentation and degradation by several agents, such as solar radiation, mechanical forces, and microbial action, thereby reducing plastic size (Lehtiniemi et al., 2018). Both primary and secondary plastics lead to the formation of small plastic debris referred to as macroplastics ($>$ 25 mm), mesoplastics (25–5 mm), microplastics ($<$ 5 mm) and nanoplastics ($<$ 0.1 μm) (Law and Thompson, 2014). Microplastics (MPs) can be distinguished into large microplastic particles (LMPs; 5–1 mm), and small microplastic particles (SMPs; $<$ 1 mm) (Andrady, 2011; Lambert and Wagner, 2016). MPs can also be classified into primary microplastics, represented by polymers not fragmented and deposited in their original form (Horton et al., 2017; Akdogan and Guven, 2019), and secondary microplastics, which originate from physical, chemical, and biological processes resulting in fragmentation of plastic debris (Thompson, 2006; Ryan et al., 2009). MPs include polymers designed to be lightweight, strong, and durable. They have a potentially higher negative impact on ecosystems than meso- and macroplastics because of their small size and high surface area (Hurley et al., 2018). MPs are ubiquitous in terrestrial and marine environments, are generally transported by rivers, runoff and groundwater flow (Phuong et al., 2016), and their properties can change due to physical, chemical and biological processes in the environment (Lenz et al., 2015). Consequently, distinct patterns of MPs accumulation have been observed across various portions of the water column, seafloor sediment, and biota (Horton et al., 2017; Naidu, 2019; Näkki et al., 2019;

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Kane et al., 2020). Recent studies have focused on the collection, identification and occurrence of MPs in seawater and in different sediment types, including lacustrine, riverine and marine sediments, as well as on the associated risks to the environment and human health (Cincinelli et al., 2019; Oliveira and Almeida, 2019; Prata et al., 2019; Wolff et al., 2019; Yao et al., 2019; Schmidt et al., 2020; Yang et al., 2020; Phuong et al., 2021). Significant attention has been devoted to marine MPs, whereas the extent of pollution due to MPs in continental environments (e.g. rivers, lakes, soil and aquifers) is poorly understood (Akdogan and Guven, 2019; Guerranti et al., 2020). In addition, a standardized approach for MPs evaluation in such environments, encompassing study design and methodologies, has yet to be fully developed. An international protocol has been proposed (Kvalvik, 2012) but its implementation is ongoing. Recently, Phuong et al. (2021) reviewed the protocols used for evaluating MPs in marine sediments based on seventy studies. Schmidt et al. (2020) also reviewed all available research on plastics and, specifically, marine litter affecting the Adriatic Sea, in order to provide a comprehensive overview of the findings available to date.

Previous studies of the Mediterranean area have mostly focused on MPs at the water surface (Cincinelli et al., 2019), followed by studies using biota such as invertebrates, fish and sea turtles (Santini et al., 2022). Investigations have also been conducted in Southern Italy concerning MPs in water and aquatic organisms (Campanale et al., 2020b; Furfaro et al., 2022; Dambrosio et al., 2023; Trani et al., 2023); however no previous studies have investigated MPs in sediments. Nevertheless, according to Zhang et al. (2021), plastics can persist in seabed sediments due to the combined effects of shelter from UV, low temperatures, low oxygen, and slow biodegradation. Nauendorf et al. (2016) showed that polyethylene (PE) carrier bags incubated in sediments from Eckernforde Bay showed no sign of biodegradation after 98 days. Further research on microplastics in sediments is therefore required. In the present study, the nature and abundance of MPs from sediments of the Bradano and Basento rivers in the Apulo-Lucanian region and of Adriatic and Ionian seas were investigated by combining geomorphological, sedimentological, spectroscopic and microscopic analyses. In particular, grain size analysis, optical microscopy, image analysis and μ-Fourier Transform Infrared spectroscopy (μ-FTIR) and micro-Raman were carried out. Quantification of MPs per kg^{-1} d.w. (dry weight) in sediments was performed and the correlation between the number of MPs stored in sediment and their transport paths have been investigated.

The Bradano and Basento rivers are affected by anthropogenic activity due to their locations at short distances from several urban centres and industrial areas; however, no previous studies have considered MPs pollutions in the river system of the Apulo-Lucanian region. On the other hand, the Adriatic and Ionian Sea have been identified as preferential areas for floating plastics accumulation (Gajšt et al., 2016; Ruiz-Orejón et al., 2016) and previous work has shown that floating MPs, transported by sea currents, can migrate from the sea surface to marine sediments (Alomar et al., 2016; Palatinus et al., 2019; Kane et al., 2020). Although studies of MPs in the water column and in aquatic organisms have been performed (Campanale et al., 2020a; Furfaro et al., 2022; Dambrosio et al., 2023; Trani et al., 2023), no data are available on the occurrence of MPs in Adriatic and Ionian sediments. To our knowledge, this is the first effort to quantify MPs in sediments from an area in Southern Italy and highlights a correlation between the storage of MPs in sediment and their transport.

2. Materials and methods

2.1. Geographic and geomorphological setting of the study area

The Basento and Bradano rivers originate in the northern Lucanian Apennines, from Mount Arioso (1715 m a.s.l.) and Pesole Lake (829 m a.s.l.), respectively. Their valleys are oriented SW–NE in the first mountainous section then, at Potenza, their direction changes to NW–SE, flowing into the Gulf of Taranto (Ionian Sea).

The Bradano is one of the largest rivers in Basilicata, with a catchment area of approximately 2765 km^2. It traverses the landscape in a northwest to southeast direction, spanning the provinces of Potenza and Matera, which are the two primary cities in the region. The river exhibits an average annual flow rate of approximately 7 m^3/s (Sole et al., 2007).

The Basento is the longest river in Basilicata and flows into the Ionian Sea. It flows predominantly from northwest to southeast. Although its catchment area is smaller than that of the Bradano (approximately 1530 km^2), its average annual flow is approximately double that of the Bradano, approximately 12.2 m^3/s (de Musso et al., 2020). The mouths of the Basento and Bradano rivers are influenced by both the sedimentary supply from inland sources and the meteo-marine regime of the Gulf of Taranto (Perrone et al., 2020; Dal Sasso et al., 2020; La Salandra et al., 2022). The sea-floor sediments of continental shelf of the Gulf of Taranto comprise Pleistocene and Holocene sandy clay deposits influenced by surface water currents (Grauel et al., 2013) and deep water mass transport (Teofilo et al., 2018; Artoni et al., 2019).

The Adriatic Sea is an elongated basin, extending up to 800 km from NW to SE between Italy and the Balkan regions. The average depth of the Adriatic ranges from approximately 35 m (the northern part) to 140 m (central part), reaching 260 m in the Pomo Depressions. This semi-enclosed basin, surrounded by Italy, Slovenia, Croatia, Bosnia and Herzegovina, Montenegro, Albania, and Greece, receives freshwater mainly from the Po River (Gajšt et al., 2016), the largest Italian river, but is also fed by numerous other rivers that drain the densely inhabited, industrialized and intensively cultivated areas of Northern and Central Italy (Sagratini et al., 2008). The southern area of the basin lacks substantial riverine inputs (Mistri et al., 2017).

Intense human activity along the coasts includes heavy marine traffic, intensive mussel aquaculture, fish farming, and seasonal tourism. These activities are fundamental economic sources for the countries bordering the basin but likely contribute to the dispersion of litter in the Adriatic Sea (Vlachogianni et al., 2018; Rizzo et al., 2021; Kolitari and Gjyli, 2022). It has been estimated that 40% of marine litter enters the Adriatic basin through rivers, an additional 40% through coastal urban populations, and the remaining 20% through shipping and fishing activities (Liubartseva et al., 2016). van der Wal et al. (2015) estimated that the Po River discharges 120 tons of litter and 7×10^{11} micro litter particles per year. Other studies have reported that land-based activities are a major input of marine litter in the Adriatic Sea (Vlachogianni et al., 2018), with an increasing number of cases of waste pollution.

2.2. Sampling strategy

Six sampling sites in the Apulo-Lucanian region were selected: two river and two marine sites for the Ionian Sea, and two marine sites for the Adriatic Sea (Fig. 1). For the Ionian coast, sediment samples from the Basento and Bradano rivers (identified as BAS1 and B1A, respectively) were collected, and two samples from the offshore areas of Gulf of Taranto (identified as 1BAS and 1BRA) were also considered. The BAS1 site is located adjacent to the industrialized area of Val Basento, and close to the industrial towns of Pisticci and Ferrandina; in contrast, the B1A site is located in a non-densely populated foothill area, with water flows coming mainly from the San Giuliano Regional Reserve and Montescaglioso, in the province of Matera. Marine samples, identified as 3BAB40 and 4BAB40, were collected in the Adriatic Sea facing the coastal area of Bari (BA), in the central part of the Apulian region.

River sampling was carried out on a middle-channel bar in the upper part of a sequence of coarsening upward sediments. Sediments were collected using a stainless steel spoon to fill a 1 L glass jar from an area of 30 cm^2 and a depth of 2–3 cm, at randomly chosen points along transects of approximately 10 m, to guarantee the accuracy of the sampling

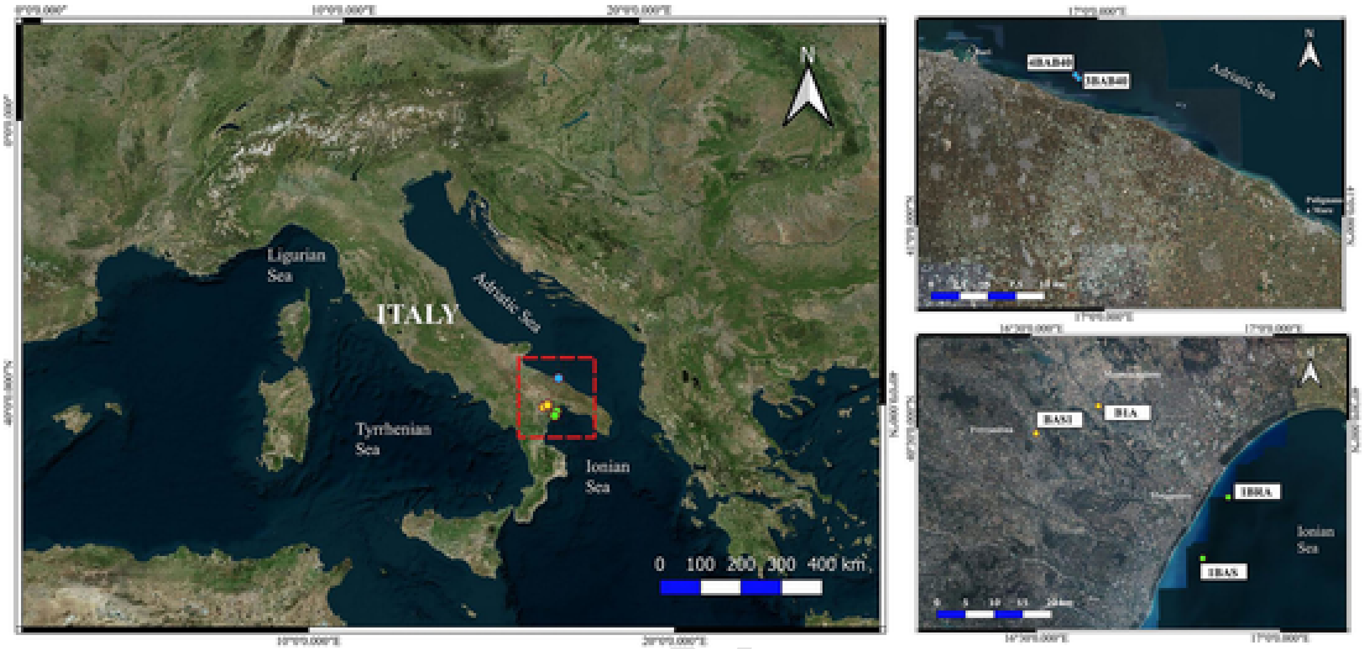

Fig. 1. Study area and sampling stations. Blue dots represent marine sampling in Adriatic area. Yellow dots represent river sampling and green dots represent marine sampling in Ionian area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

results (Klein et al., 2015; Horton et al., 2017). Particles larger than 10 mm were removed from the samples. The direction of the transects was chosen according to the morphology of the rivers, focusing on areas characterized by limited changes in the last 150 years (de Musso et al., 2020). Specifically, in the Basento river, transects were set perpendicular to the riverbank, whereas in the Bradano river, transects were set parallel to the riverbank. Sampling areas were chosen according to three factors: i) accessibility of the watercourse, density of vegetation and distance from the main communication routes; ii) lithological characteristics and slope gradient; and iii) proximity to urban and industrial areas.

The studied marine samples (1BAS, 1BRA, 3BAB40, and 4BAB40) were collected using a metal Van Veen Grab at 40 m depth during a joint operation carried out between July and September 2019 by the Department of Earth and Geoenvironmental Sciences of the University of Bari and Marina Militare Italiana. The survey campaign aimed to collect sediment samples from both the Ionian and Adriatic seas.

2.3. Quality assurance

To ensure any cross-contamination, strict laboratory procedures were executed. Procedures and laboratory analysis were conducted under laminar flow hood, using nitrile gloves and cotton lab coats. Only glass materials or stainless-stell materials were used. Petri dish and becker were always covered after analysis. A contamination control was monitored at each step through control Petri dishes and laboratory blanks (Simon-Sánchez et al., 2019; Angiolillo et al., 2021; Celine et al., 2023).

2.4. Grain size analysis

Grain size analyses were conducted using an aliquot of the collected sediment samples for each station of the study area. A combined procedure was used. The size fractions coarser than 3 ϕ (125 μm) were analyzed by mechanical sieving at an interval of 1 ϕ ($\phi = -\log_2 D$, where D is particle size in mm). The finer fractions, from 4 ϕ (63 μm) to 9 ϕ (2 μm), were analyzed using a Beckman Coulter Multisizer 4 (Mele et al., 2015).

2.5. Sample preparation and MP extraction

A weighted amount of collected sediment samples was dried at 50 °C for 3 days following the methods of Klein et al. (2015). This temperature was chosen so as to not alter the intrinsic shape of the selected particles, since it lies below the melting point of all common polymers (Kalpakjian and Schmid, 2008). Sediment fractions >0.063 mm were separated (Klein et al., 2015) and treated with 10% H_2O_2 solution for 24 h to remove organic matter. A low concentration of H_2O_2 was used to avoid changes in the polymers, such as transparency and size reduction, which have been identified when using 30% H_2O_2 (Karami et al., 2017). Density separation of plastic particles was performed using a $ZnCl_2$ solution (Nuelle et al., 2014; Horton et al., 2017), which was added to the sediment up to 1 cm from the top of the beaker. The suspension was mixed with a glass rod and left to settle for 24 h (Blair et al., 2019), whereupon more $ZnCl_2$ solution was gently added to the beaker in order to promote the overflow of the suspended particles. The overflow solution was filtered through 0.8 μm paper filters and the collected particles were dried at 50 °C, separated from the filter and placed in a clean petri dish to be analyzed (Firdaus et al., 2020).

2.6. Characterization and identification of MPs

MPs were initially photographed using a Nikon D300 SLR camera to enable particle identification and then subjected to optical observations to better define their shape and color. Observations were carried out following the criteria proposed by Hidalgo-Ruz et al. (2012): no cellular or organic structures are visible; fibers should be equally thick throughout their entire length; particles must present clear and homogeneous colors. MPs were then divided according to shape (fibre, fragment and film), size (LMPs and SMPs), and color (Vianello et al., 2013; Fastelli et al., 2016; Horton et al., 2017; Firdaus et al., 2020). Their concentration was calculated as the number of MPs (items) per kg using two methods: i) MPs in relation to the weight of the whole sample (hereafter MPs kg^{-1}), after Nel et al. (2018), and ii) normalizing MPs to the weight of the sample without the particle size fraction <0.063 mm (hereafter MPs kg^{-1} no 0.063 mm).

A random subsample of 22 MPs was selected to be analyzed by μ-FTIR and μ-Raman, following the approach used by Celine et al. (2023) and Simon-Sánchez et al. (2019). A Thermo Fisher Scientific μ-FTIR Nicolet iN10 MX, equipped with a mercury cadmium telluride (MCT) detector was used. In order to automatically select, analyze, identify and count the microplastics on the filter, the "Microparticle WIZARD function" of OMNIC Picta software was used. The first step of the analysis involved the acquisition of a visual mosaic image, constructed from many individual field views. Correct image contrast is crucial in this step because visible image is used to select particles and determine particle size. The software automatically detects the particle present on the filter using an image processing algorithm. The operator can select particle range. All particles down to 10 μm were analyzed. Finally, the software automatically collected one spectrum from each particle at a spectral resolution of 4 cm^{-1}, averaging 16 scans for each spectrum, i.e. 5.58 s per spectrum. The aperture dimensions for the spectral acquisition were automatically chosen by the software, which sets the correct value based on particle dimensions. The last step consists of the background subtraction; the software automatically collects a background for each aperture dimension and processes the data. All spectra are then analyzed using a library search algorithm. The proprietary library from Thermo Fisher Scientific was used to identify all the acquired spectra.

μ-Raman analyses of MPs were performed using a Thermo Fisher Scientific Nicolet DXR3TM Raman microscope, equipped with a 532 nm laser (Lenz et al., 2015; Wolff et al., 2019; Fang et al., 2023). In order to select, analyze, identify and count the MPs present on the filter, we used the Particle Analysis function of the OMNIC TM Atlus software. The process is very similar to that used for FTIR. First, the software acquires a visual mosaic image, constructed from many individual field of view, automatically recognizes particles, and acquires one spectrum from each. A library search algorithm based on the proprietary Thermo Fisher Scientific library is then used to identify all the acquired spectra. The power of the laser was set 10 mW on the sample and the exposure time was set at 3 s with three exposures. No apertures were used because the size of the spot on the sample is determined by the laser used and the magnifications of the microscope; in this case the spot was 2 μm, although spatial resolutions of 0.5 μm can be reached.

3. Results

3.1. Grain size distribution

The grain size results show differences between inland and offshore samples. Sample B1A, from the Bradano River, shows a unimodal and asymmetrical distribution, with a modal value of 0.5 mm (Fig. 2C). Grain sizes below 0.063 mm are not present at significant percentages in the sediment. Sample BAS1, from the Basento River, shows a polymodal distribution, containing three subpopulations with modes of 8 mm, 0.25 mm and 0.016, respectively (Fig. 2C). The offshore samples from the Ionian Sea, 1BRA and 1BAS, show a unimodal distribution with a mode corresponding to the 0.063 mm size (Fig. 2B). Samples 3BAB40 and 4BAB40 from the Adriatic Sea both show a unimodal and Gaussian distribution in which mode is shifted to the lower grain sizes (0.016 mm) (Fig. 2D).

3.2. Morphology and abundance of MPs in sediments

The total amount of MPs varied between 144 and 1246 kg^{-1} of dry sediment (mean ± SD; 468.8 ± 410.7 MPs kg^{-1}) (Fig. 2A). The lowest and highest values were found in the Ionian area, in Bradano river sediments (B1A site) and offshore at the mouth of the same river (1BRA site), respectively. MPs exhibit morphologies including fibers (98.3%), films (1.2%) and fragments (0.6%). These are mainly black in color (75.1%), although blue (10.8%), red (10.2%), transparent (3.5%) and

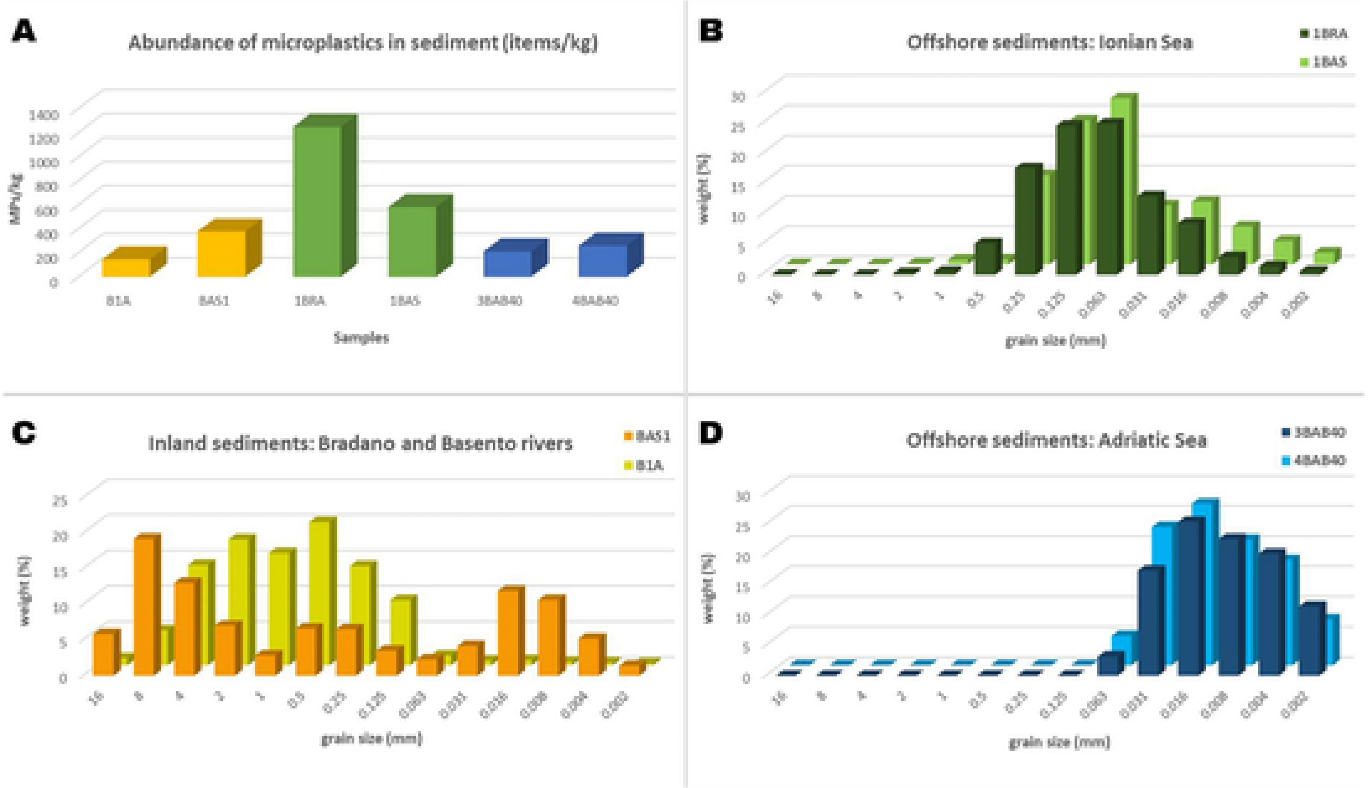

Fig. 2. A) Abundance of MPs in sediment samples, reported in MPs/kg, combined with particle size analysis of: B) offshore sediments from Ionian Sea (samples 1BRA and 1BAS); C) inland sediments from Bradano and Basento rivers (samples B1A and BAS1); D) offshore sediments from Adriatic Sea (samples 3BAB40 and 4BAB40).

white (0.4%) MPs were also detected. Similar concentrations of LMPs (52%) and SMPs (48%) were found (Table 1; Fig. 3).

In the Ionian area, MPs from the Bradano (B1A) and Basento (BAS1) rivers exhibit 144 and 376 MPs kg−1 d.w., respectively. These are mostly black fibers, although red and blue fibers were also found in minor quantities. Small particles predominate over LMP. Considering the values of "*MPs per kg−1 d.w. no 0.063 mm*", the river samples show values of 147 (B1A) and 563 (BAS1). In the offshore part of the Ionian area, the zone corresponding to the mouth of the Bradano river (1BRA) exhibits 1246 MPs kg−1 d.w., whereas the sediments from the mouth of the Basento river (1BAS) exhibit 581 MPs kg−1 d.w.; black fibers are most frequently observed, with a minor content of blue, red, and transparent fibers and an additional white fragment. Large microplastics are more abundant at the mouths of the Bradano and Basento rivers. Considering the "*MPs per kg−1 d.w no 0.063 mm*", 2262 (1BRA) and 1143 MPS kg−1 (1BAS) were identified.

In the Adriatic area, marine sediments exhibit 209 (3BAB40) and 257 (4BAB40) MPs kg−1 d.w., with a prevalence of black, red and blue fibers, but also films and fragments. The amount of SMP and LMP are approximately balanced, particularly in sample 3BAB40. Considering the values of "*MPs per kg−1 d.w. no 0.063 mm*", the samples 3BAB40 and 4BAB40 exhibit 6744 and 5350 MPs kg−1 d.w., respectively.

3.3. Polymer types

82% of all particles analyzed using μ-FTIR and μ-Raman were identified as MPs. The results of the μ-FTIR investigation of particles selected from the Ionian sediment showed that these consist of polystyrene (27%), poly (2-acrylamido-2-methylpropanesulfonic acid: styrene) (40%), polyester (13%) and poly (isodecyl methacrylate) (20%). Particles of methyl palmitate, protein and cellulose were also identified. Using μ-Raman, it was possible to identify a black rayon fibre, a polycarbonate fibre and a white fragment derived from printer starch (Fig. 4A).

Particles from the Adriatic sediment are dominated by fibers consisting of poly(ethylene: acrylic acid) (33.3%), poly(butyl methacrylate) (33.3%), and poly(acrylonitrile) (33.3%). A rounded particle of cellulose nitrate was also identified (Fig. 4B). μ-Raman measurements identified a blue fragment, which was found to be a *co*-polymer composed of polyethylene and nylon.

Table 1
Number of MPs and main characteristics for each sample.

	Number of MPs	Shape			Color					Size	
		Fibre	Fragment	Film	Black	Red	Blue	White	Transparent	SMP	LMP
B1A	60	60	0	0	51	4	5	0	0	34	26
BAS1	155	155	0	0	131	13	11	0	0	107	48
1BRA	81	80	1	0	41	11	20	1	8	11	70
1BAS	36	36	0	0	16	8	8	0	4	5	31
3BAB40	84	79	2	3	64	9	7	1	3	34	50
4BAB40	103	100	0	3	87	8	5	0	3	59	44

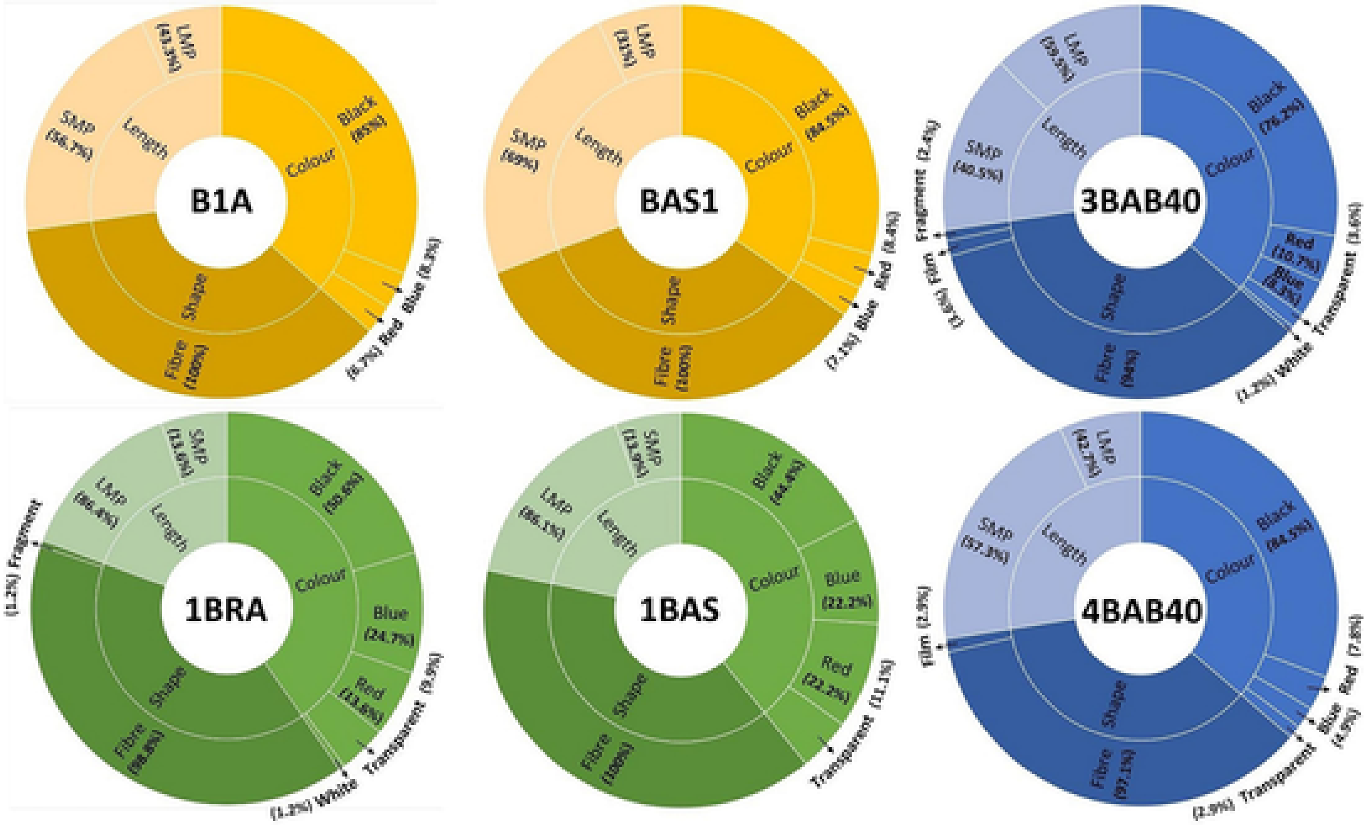

Fig. 3. Characterization of MPs by shape, color and size for each sediment sample.

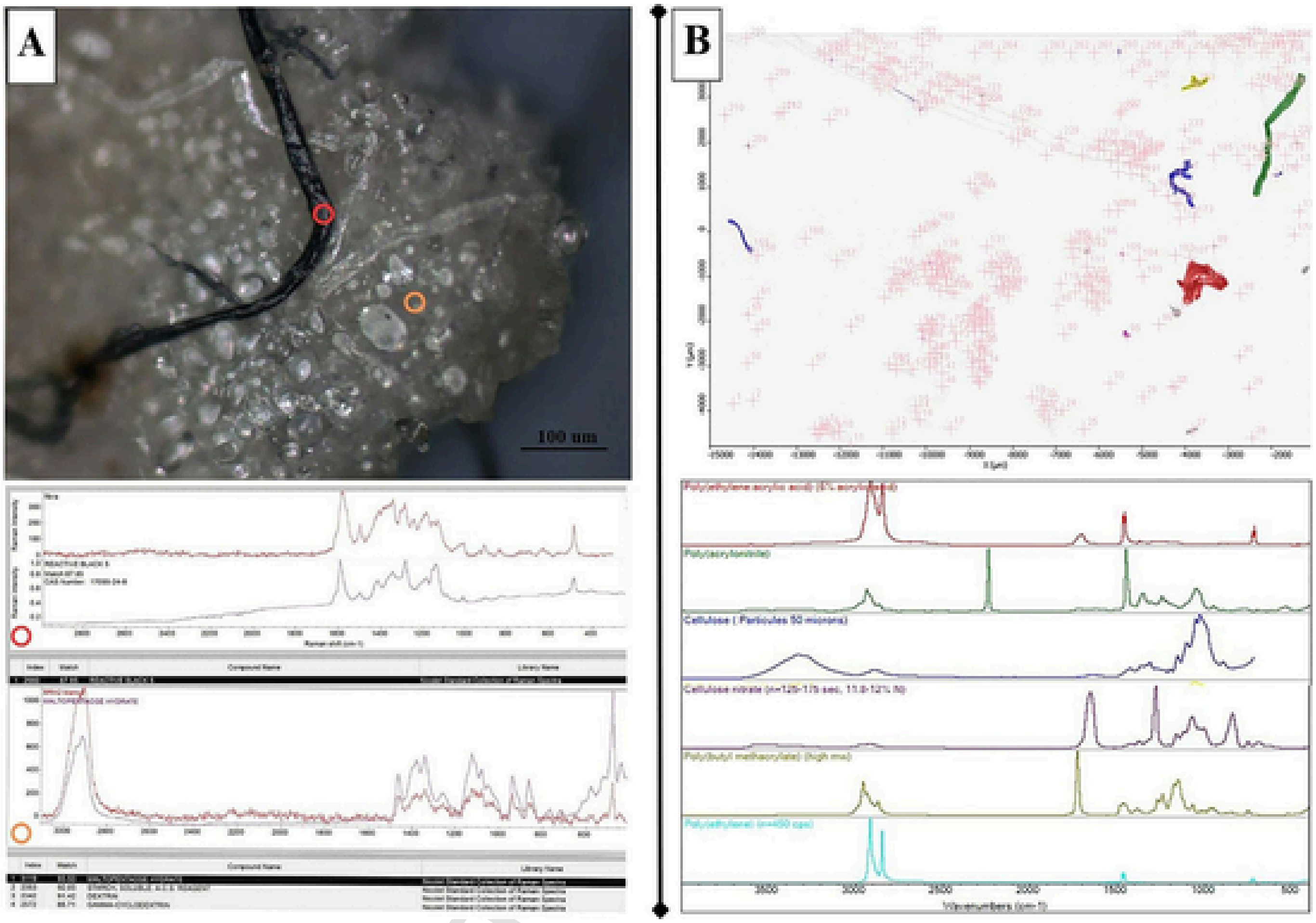

Fig. 4. µ-Raman spectra from a black polycarbonate fibre (red dot) and a printer starch (orange dot) relative to the BAS1 sample (A); µ-FTIR visual mosaic image of particles from the 4BAB40 sample (B) and relative spectra. Color of spectra is matching the color of identified particle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Discussion

MPs occurring in Ionian and Adriatic sediment fraction from 5 mm to 0.063 mm have been quantified and characterized. The concentration of MPs is generally expressed as MPs per kg^{-1} d.w., referring to either the weight of the entire sediment or of the sieved sediment. Higher amounts of MPs are expected to be present in sieved sediment fraction than in the entire sediment. This was found particularly in samples 3BAB40 and 4BAB40, where the fine grain size was predominant (Fig. 2). The concentrations of MPs in our samples were not found to be correlated to the grain size distribution of the sediments. Indeed, despite the different grain size distribution of the inland (B1A and BAS1) and Adriatic offshore (3BAB40 and 4BAB40) sediments, a similar MPs content was measured (Fig. 2A). This confirms the findings of other studies and suggests that sediment composition and grain size do not control MPs concentration (Harris, 2020) and Dodson et al., 2020). Most studied MPs exhibited fibrous morphologies, with subordinate fragments and films. Similar results were reported by Horton et al. (2017) for MPs in sediments from the River Thames. On the contrary, spheres and pellets (Klein et al., 2015), flakes, fibre clusters, single fibers and pieces (Pojar et al., 2021) were found in the Danube River. These differences probably reflect the source of pollution, which depends on the specific anthropogenic activities affecting the study area. Differences between MPs in inland and offshore sediments were also found. MPs in river sediments are composed entirely of black, blue and red fibers with a predominance of SMP. MPs in marine sediments show a higher presence of LMP, fragments and films, and other colors are visible.

MPs in Basento river sediments (376 MPs kg^{-1} d.w) are more abundant than those in Bradano river (144 MPs kg^{-1} d.w). This may reflect the fact that the Basento sampling site is located in a densely industrialized area. The highest numbers of MPs stored in the marine sediments sampled at the mouth of the rivers near the Bradano sampling site (1246 MPs kg^{-1} d.w) can be explained by considering the underwater landforms from bathymetry data. These data clearly show that the sampling locations of MPs in the Ionian offshore occur within an area influenced by submarine canyons (Fig. 5). According to Kane et al. (2020), low-intensity summer currents may induce the accumulation of MPs on the seabed. Previously deposited microplastics may have also be exhumed when shear stresses exceed the critical limit, due to more intense bottom currents in winter. The deep-sea marine sediments studied herein were sampled in summer, which this may explain their higher MP concentrations. Additionally, the flow rate of Bradano river, which is much lower than that of the Basento, may account for the higher accumulation observed.

The MPs concentrations values are lower in the Adriatic Sea than in samples collected at the same depth in the Ionian Sea. The lack of submarine canyons and major rivers associated with the Adriatic sampling locations suggests that MPs transport may have been influence by gravitational processes or deposition along the water column rather than by bottom currents.

The variety of MPs identified enables a tentative assessment of their different environmental sources. Cellulose is likely to result from the low hydrogen peroxide content used to prevent alteration of the artificial particles but was clearly detectable using optical microscopy. Poly-

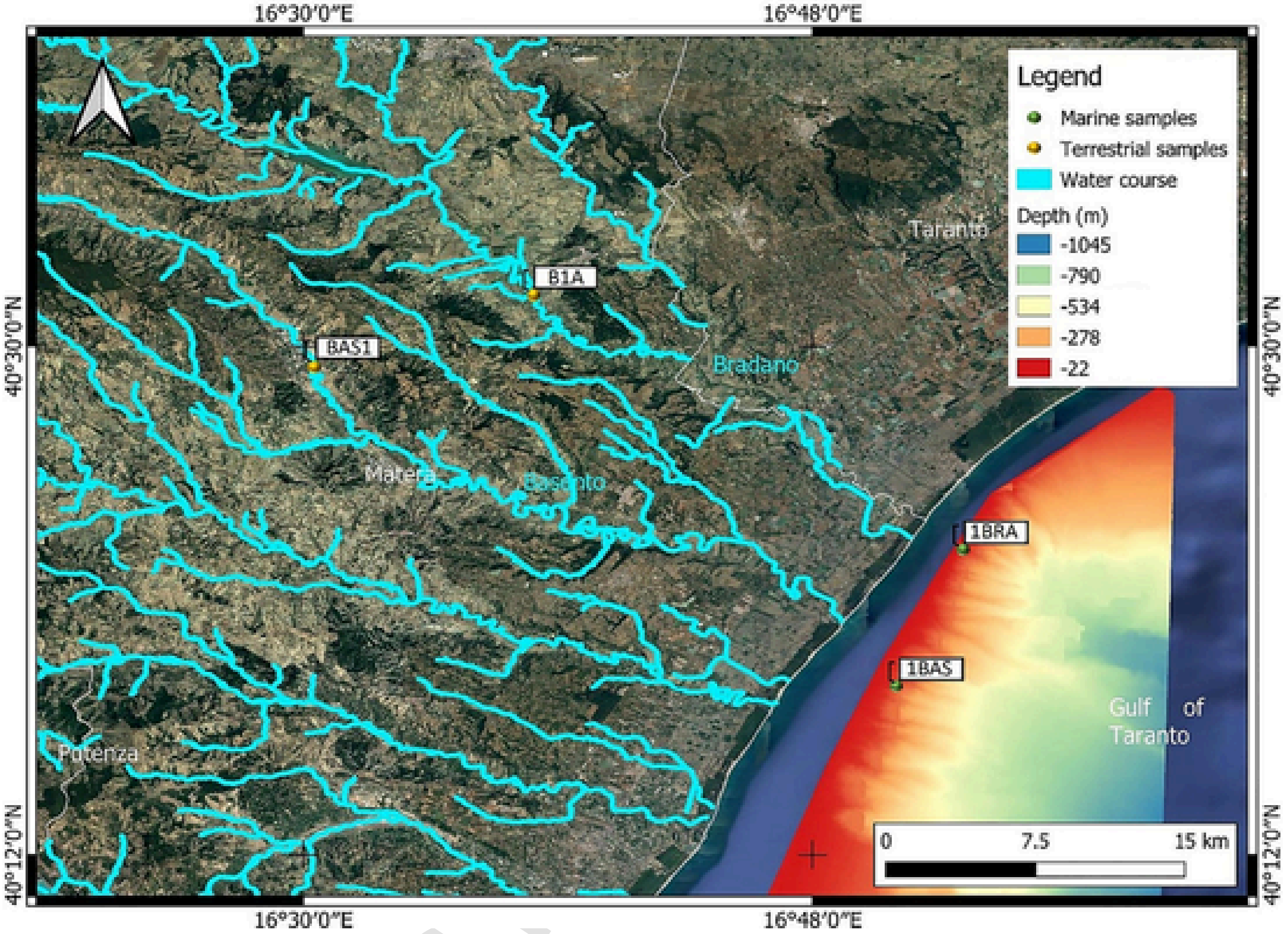

Fig. 5. Submerged landform of Ionian arc in proximity of Metaponto coast (from the Marine Geohazards Along the Italian Coasts project-MaGIC (Chiocci and Ridente, 2011)). Position of river and marine samples are highlighted with yellow and green dots respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

carbonate black fibre combined with printer starch likely originates from 3D printing equipment. However, it is generally difficult to determine specific sources of MPs due to complex scenarios of pollution including effluent discharges from production plants (Cousins et al., 2002; Klecka et al., 2009; Fu and Kawamura, 2010; Idowu et al., 2022), the degradation of used plastics, and influxes of leachate from landfill and waste dumpsites (Yamamoto et al., 2001; Flint et al., 2012; Idowu et al., 2022). Polycarbonate has also been found in river and marine sediments by Idowu et al. (2022) and Zhang et al. (2021), showing higher concentrations in sediments than in water samples. Rayon fibers, commonly used in clothing production, could have been introduced to marine environments through wastewater, one of the main input sources of which is presumed to be washing machines (Browne et al., 2011; Woodall et al., 2015). The presence of rayon in coastal and deep-sea sediments is in agreement with Frias et al. (2016) and Woodall et al. (2015). The large variety of MPs with a fibrous shape, such as polyester, polyacrylonitrile and rayon, suggests that textiles from wastewater discharge are a major cause of MPs pollution in inland and offshore sediments in the Apulo-Lucanian region.

The obtained results were compared with research conducted in the Mediterranean area using only sediment in order to provide a clearer comparison of MPs kg^{-1} in the sediment matrix. Thirty such studies have been conducted (excluding the present study; Table 2). Italy has the most studied country in terms of MPs investigations in sediment; indeed, 13 studies have been conducted (Supplementary Material, Fig. S1). However, this is the first research conducted in Southern Italy. The sediments most explored in the Mediterranean area are beach sediments (19 out of 30), exhibiting a slightly greater abundance of fibers than fragments. When fibers are more abundant than fragments, a black color predominates; when fragments are more abundant, a white color predominates. Other studies have explored regions from the shallow coast to the deep sea, observing, on average, a dominance of fibers. The single previous study performed on sediments (Romano et al., 2023) suggested that these represent a promising new sampling focus to interpret MPs behavior in environment. It is also important to note the limited availability of inland work. Excluding this study, only two rivers (in Italy and Spain) have been investigated. Guerranti et al. (2017) collected samples from three rivers in Maremma Regional Park, province of Grosseto (Italy), finding a prevalence of fibers with an average concentration of 222.6 MPs/kg d.w. and a predominantly black color. These data agree with the results found here, i.e., an average of 260 MPs/kg d.w. and a prevalence of black fibers. On the other hand, Simon-Sánchez et al. (2019) investigated the Ebro River, finding more colored fibers than black, with mean concentrations of one order of magnitude greater (2052 MPs/kg d.w.). This difference could be explained by either geographical differences or differences in the sampling strategies employed.

Unfortunately, the scarcity of research conducted in Mediterranean inland areas and the different extraction MP methods used prevent direct comparisons. In order to extract MPs, most authors use the density separation method with NaCl, while a limited number use $ZnCl_2$ (Kazour et al., 2019; Piehl et al., 2019; Angiolillo et al., 2021; Celine et

Table 2
Literature data on MPs in sediments in Mediterranean area to date.

ID	Country	Area	Number of station	Density separation	MPs identification	MPs/kg (d.w)		Shape (more aboundant)	Color	Author
						Min	Max			
1	Algeria	Beach	4	NaCl	FTIR	182.7	649.3	Fibers	White > black > other	Tata et al., 2020
2	Algeria	Beach	7	No	FTIR	1.9	123	Fragments	White > other	Grini et al., 2022
3	Croatia	Bay (−3 to −15 m)	10	NaCl	No	15	414	Fibers	Clear > white > other	Blašković et al., 2017
4	Egypt	Delta/beach	4	NaCl	FTIR	480	766	Fibers	Green > white > other	Sayed et al., 2021
5	France	Beach	2	NaCl	FTIR	12	798	Fibers	No	Constant et al., 2019
6	France/ Italy	Deep sea (−600 to −900 m)	16	NaCl	FTIR	186.4	3808.6	Fibers	Black > blue > other	Kane et al., 2020
7	Greece	Beach	3	NaCl	FTIR	4.8	86	Fragments	No	Piperagkas et al., 2019
8	Greece	Shallow coast (0 to −10 m)	1	NaCl	FTIR	1.1	37.2	Fragments	No	De Ruijter et al., 2019
9	Italy	Lagoon	10	NaCl	FTIR	672	2175	Fragments	No	Vianello et al., 2013
10	Italy	Continental shelf (−30 m)	7	NaCl	No	151	678.7	Fibers	Black > green > other	Fastelli et al., 2016
11	Italy	Beach	11	NaCl	No	42	1069	Fibers	Black > blue > other	Cannas et al., 2017
12	Italy	River Beach	8 6	NaCl	No	57 45	477 1069	Fibers Fibers	Black > white > other Black > white > other	Guerranti et al., 2017
13	Italy	Beach	5	No	FTIR	6	21.6	Fragments	No	Munari et al., 2017
14	Italy	Beach	6	NaCl	FTIR	72	191	Fragments	White > blue > other	Blašković et al., 2018
15	Italy	Beach to continental shelf (0 to −30 m)	3	NaCl	FTIR	81	438	Fibers	Black > clear > other	Renzi et al., 2018
16	Italy	Beach	3	$ZnCl_2$	FTIR	2.92	23.3	Fragments	No	Piehl et al., 2019
17	Italy	Beach	2	NaCl	FTIR	191	223	Fibers	Black > other	Scopetani et al., 2021
18	Italy/ France	Deep sea (−358 to −2194 m)	11	$ZnCl_2$	No	120	1040	Fibers	No	Angiolillo et al., 2021
19	Italy	Cave (−6.7 to −9.1 m)	4	NaCl	FTIR	10	27	Fragments	Blue > clear > other	Romano et al., 2023
20	Italy	River Continental shelf (−40 m)	2 4	$ZnCl_2$	FTIR + Raman	144 209	376 1246	Fibers Fibers	Black > blue > red Black > blue > other	This study
21	Lebanon	Beach	3	$ZnCl_2$	Raman	/	2433	Fragments	White > blue > other	Kazour et al., 2019
22	Lebanon	Beach to continental shelf (0 to −120 m)	10	$ZnCl_2$	Raman	/	4500	Fibers	No	Celine et al., 2023
23	Malta	Shallow coast (−4 to −22 m)	8	NaCl	No	/	12	Fragments	No	Romeo et al., 2015
24	Slovenia	Beach	6	NaCl	No	/	444.4	Fibers	No	Laglbauer et al., 2014
25	Slovenia	Beach	9	NaCl	FTIR	/	3.1	Fibers	White > other	Korez et al., 2019
26	Spain	Bay (−8/-10 m)	6	No	No	100.8	897.3	Fibers	Black > blue > other	Alomar et al., 2016
27	Spain	Continental shelf (−43 to −154 m)	10	NaCl	FTIR	45.9	280.3	Fibers	Transparent > blue > other	Filgueiras et al., 2019
28	Spain	River Delta/beach	3 5	NaCl	FTIR	1491 283	2899 557	Fibers Fibers	Colored > black > other Colored > black > other	Simon-Sánchez et al., 2019
29	Tunisia	Lagoon/beach	5	NaCl	FTIR	141.2	461.2	Fibers	Black > blue > other	Abidli et al., 2018
30	Tunisia	Lagoon/beach	8	$ZnCl_2$	FTIR + Raman	129	606	Fibers	No	Missawi et al., 2020
31	Turkey	Beach	4	NaCl	FTIR	593.3	2073.3	Fragments	White > blue > other	Yabanlı et al., 2019

al., 2023; this study). Considering that $ZnCl_2$ is environmentally hazardous, whereas NaCl cannot achieve the required density to extract all types of MPs (Harris, 2020; Lusher et al., 2020), new extraction processes must be developed. For this purpose, several studies have assessed the use of different natural oils, showing this to be an easy and inexpensive method with an average MPs recovery rate above 96% (Crichton et al., 2017; Mani et al., 2019; Scopetani et al., 2020). In order to identify polymer type, a large number of studies have used FTIR. Raman analysis has been used in only two instances (Kazour et al., 2019; Celine et al., 2023), while a further study coupled Raman and FTIR measurements (Missawi et al., 2020). The present study used both methods, noting that FTIR is a more rapid technique than Raman.

The amount of MPs kg^{-1} found in sediments varies from zero (Laglbauer et al., 2014; Romeo et al., 2015; Kazour et al., 2019; Korez

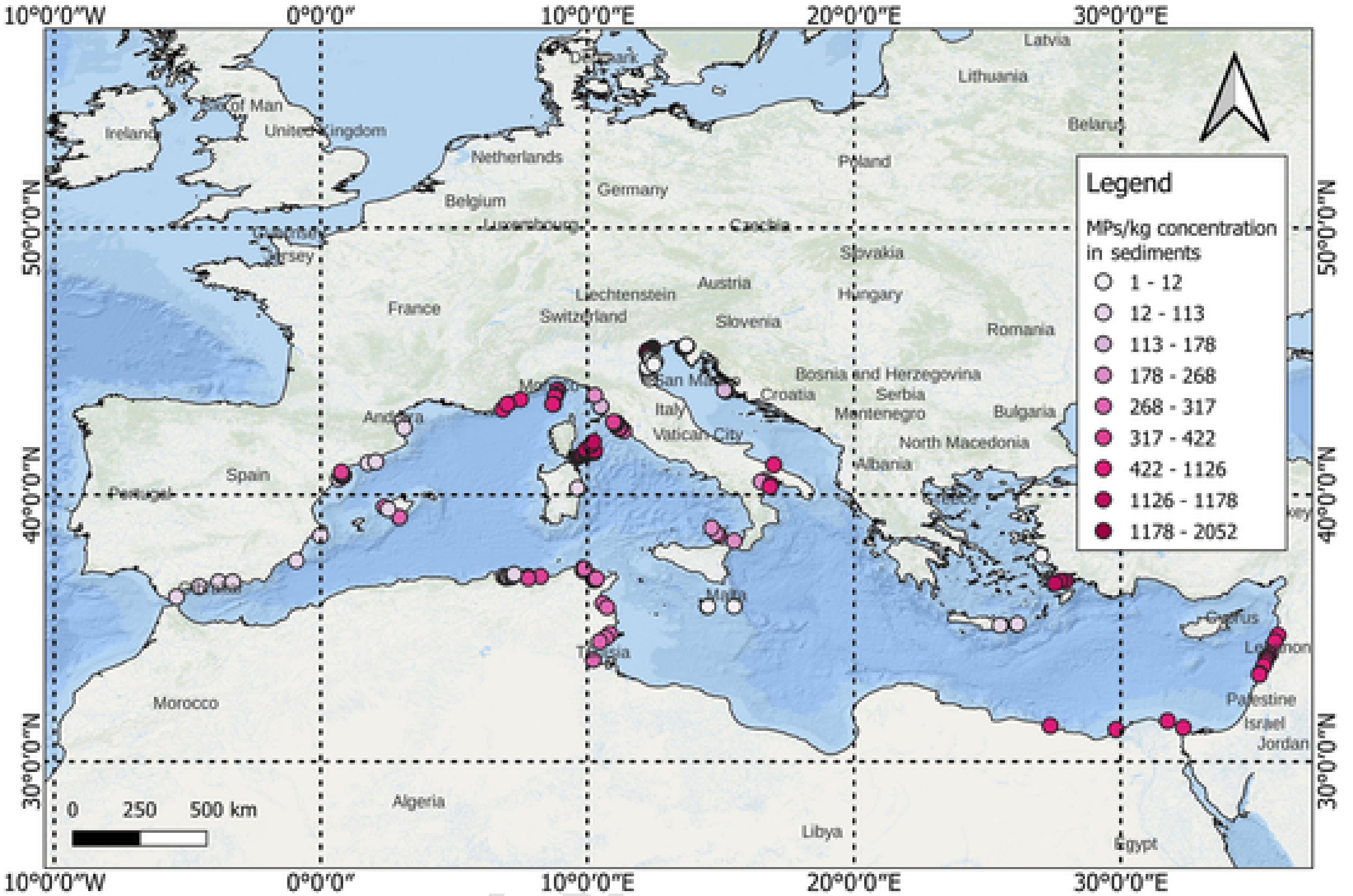

Fig. 6. Review of MPs/kg d.w concentration for each study conducted in Mediterranean area. The values represent the average obtained from each work in the same sediment matrices.

et al., 2019; Celine et al., 2023) to 4500 along the coast of Lebanon (Celine et al., 2023) (Fig. 6), with a total average corresponding to 403.6 ± 440.5 MPs kg^{-1} d.w. (Supplementary Material, Table S1). In this research, the resulting average is 468.8 ± 410.7 MPs kg^{-1} d.w., which is similar to the current average of MPs in Mediterranean sediments (Supplementary Material, Fig. S2).

5. Conclusion

This work represents the first study on MPs in both inland and offshore sediments from the Apulo-Lucanian region, Italy, while also addressing the paucity of MPs research in Mediterranean inland sediments. Comparing MPs/kg d.w. content and grain size in the different environments examined, no correlation was found between these two factors. The dominant factor determining MPs transport appears to be water currents. In river sediments, the concentration of MPs arises from local pollution. On the other hand, in offshore regimes, the concentrations of MPs in sediment are determined by river flow. Lower flow results in higher accumulation, especially in summer. In winter, sediments storing MPs may be relocated due to increased river discharge, mainly in offshore areas with canyons (Kane et al., 2020). If no rivers and canyons are present, MPs transport is influenced only by gravitational processes and/or deposition in the water column, resulting in minor accumulation in offshore sediments. It was also noted that a large proportion of MPs in sediment probably originates from textile fibers. According to De Falco et al. (2019), many microfibers of cellulosic composition are released during washing of clothes made with a blend of polyester and cellulose. At present, no legislation governs the control of this type of plastic in the Mediterranean area. Ongoing studies should be complemented by further research into the nature and distribution of MPs in marine sediments, with special attention to sediment dynamics on the seafloor, since currents may reactivate MPs and extend their lifetime in the environment. In addition, further studies should focus on microplastics in inland sediments, since most research carried out thus far has focused only on beach and marine sediments. Considering the total average values of MPs in Mediterranean Sea sediments, it is important to monitor whether these statistical data show an upward or downward trend over time.

CRediT authorship contribution statement

Cofano Vito: Conceptualization; Methodology; Sampling; Formal analysis; Investigation; Data Curation; Original Draft & Editing; Visualization. **Mele Daniela:** Methodology; Formal analysis; Investigation; Data Curation; Review & Editing. **Lacalamita Maria:** Methodology; Formal analysis; Investigation; Data Curation; Review & Editing. **Di Leo Paola:** Investigation; Data Curation; Review & Editing. **Scardino Giovanni:** Sampling; Investigation; Data Curation; Review & Editing. **Bravo Barbara:** Investigation; Data Curation; Review & Editing. **Cammarota Francesca:** Investigation; Data Curation. **Capolongo Domenico:** Supervision; Conceptualization; Methodology; Sampling; Data Curation; Review & Editing.

Uncited references

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.marpolbul.2023.115775.

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