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

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Marine Pollution Bulletin

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Object: paper submission

To the EDITOR of Marine Pollution Bulletin,

I am writing you to submit the paper titled “Microplastics in inland and offshore sediments in the Apulo-Lucanian region (Southern Italy)”. This paper takes into account microplastic analysis in Apulia and Basilicata region (Southern Italy). Results of our paper showed the first evidence of microplastics in marine and fluvial sediments detected in Southern Italy. Our results were compared with literature works of Mediterranean basin.

All authors of this work approved the final version and submission of the main text.

Material, figures, tables are original products made by co-authors.

No intentional or unintentional plagiarisms are presents in the main text.

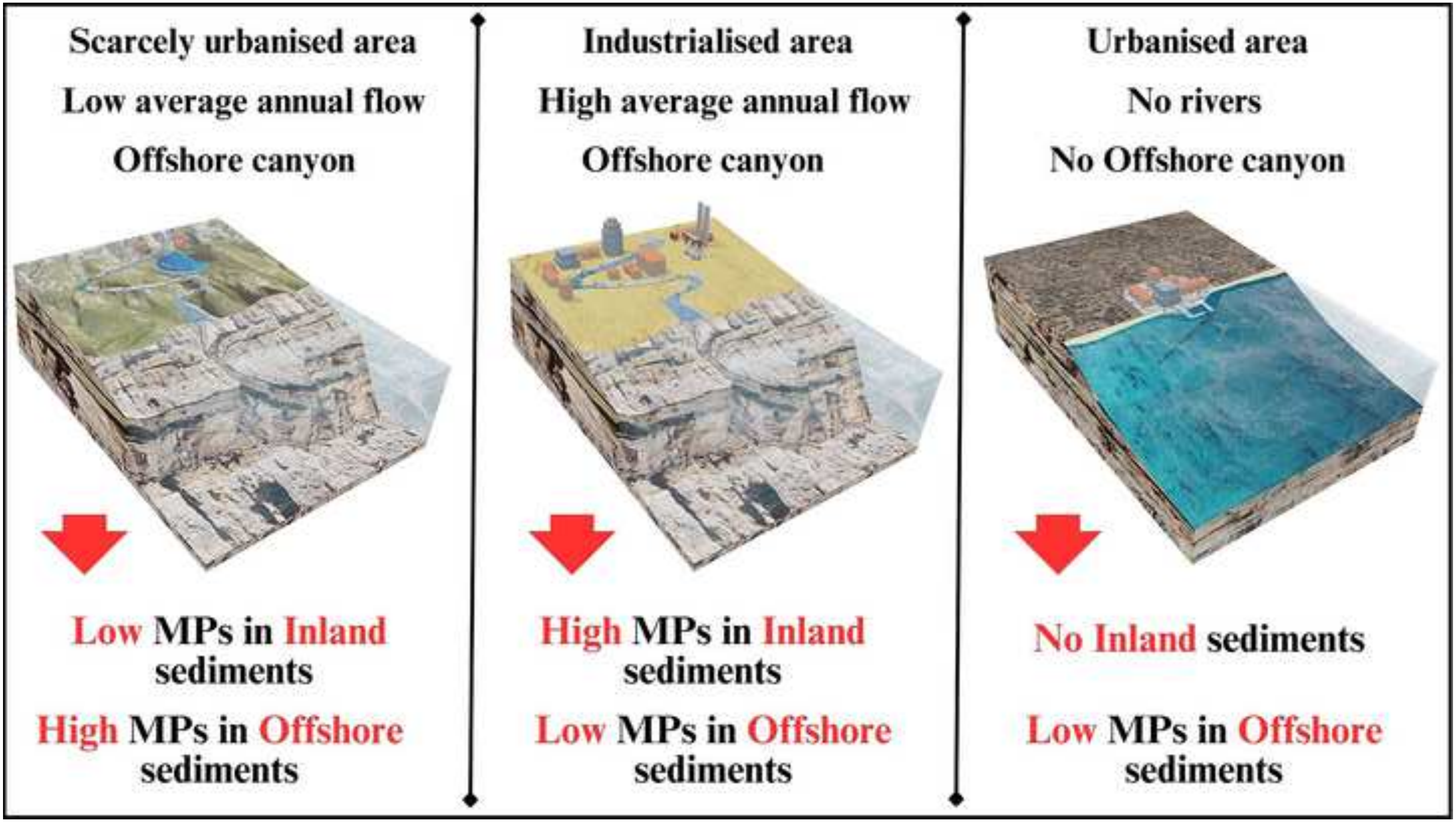
I hope that this argument could be of your interest and reliable for the publication on your journal.

Certain of your feedback.

Kind regards.

Dr. Vito Cofano

Graphical Abstract



Highlights

1. River sediments pollution is caused by urban and industrial areas
2. Offshore areas with canyons and submarine drifts are most polluted by microplastics
3. No relationship exists between particle size of sediment and microplastics
4. The principal microplastic source are synthetic clothes residues from wastewater

Research paper

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

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Synthetic clothes
Continental shelf
River
Mediterranean pollution

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Abstract

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

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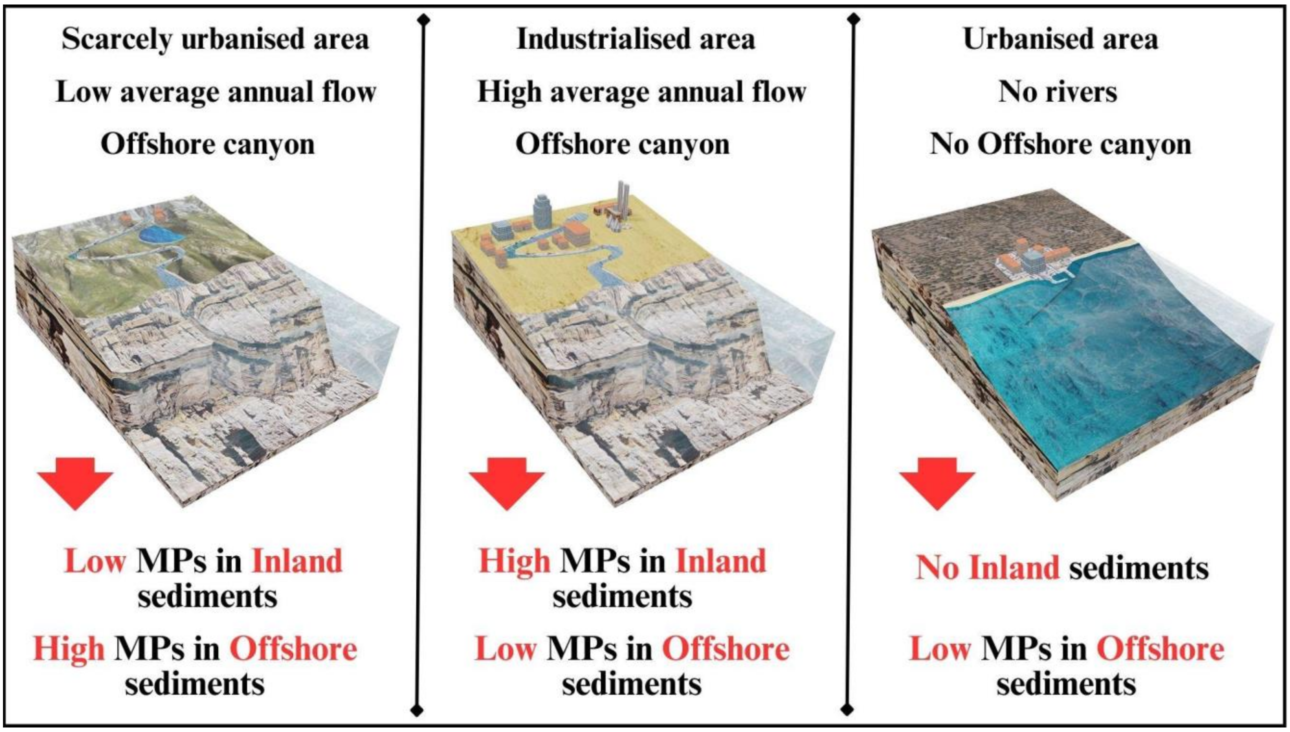

1. Introduction

Plastic pollution has become one of the most critical environmental issues, as the rapidly growing production of single-use plastic products outstrips the capacity to tackle the problem (GESAMP, 2015; Kershaw et al., 2019; Campanale et al., 2020; Forleo and Romagnoli, 2021). In addition, low recycling, as well as plastic products helping fight the COVID-19 pandemic, 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 has been referred to two categories of polymers: primary and secondary plastics (GESAMP, 2015; Kershaw et al., 2019). Primary plastic corresponds to polymers directly released into the environment without them undergoing degradation. Instead, secondary plastics polymers are subjected to fragmentation and degradation by several agents, such as solar radiation, mechanical forces, and microbial action, 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, when < 1 mm (Andrady 2011; Lambert and Wagner, 2016). MPs are considered polymers designed to be lightweight, strong, and durable. They have a potentially higher dangerous impact on the ecosystem than meso- and macroplastic because of their small size and high surface area (Hurley et al., 2018). MPs are ubiquitous in terrestrial and marine environments, generally, transported by rivers, runoff and groundwater flow (Phuong et al., 2016), and their properties can change in the environment if physical, chemical and biological processes alter the polymers (Lenz et al., 2015). Consequently, distinct patterns of microplastics accumulation were observed across various segments of the water column, seafloor sediment, and biota (Horton et al., 2016; Naidu, 2019; Näkki et al., 2019; Kane et al., 2020). Recent studies have focused on the collection, identification, and occurrence of MPs in seawater and in different sediment types, including lake, river, 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; Schmid et al., 2020; Yang et al., 2020; Phuong et al. 2021). Significant attention was devoted to marine microplastics, whereas the extent of microplastic pollution in continental environments (rivers, lakes, soil, 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, is still to be fully developed. An international protocol has been proposed (Kvalvik, 2012) but its implementation is still ongoing. Recently, Phoung et al. (2021) reviewed the protocols used for evaluating MPs in marine sediments based on 70 studies. Schmid et al. (2021) reviewed all the available research on plastic and, specifically, marine litter affecting the Adriatic Sea in order to provide a comprehensive overview of the findings available to date.

In the present study, the nature and abundance of MPs from sediments of Bradano and Basento rivers in the Apulo-Lucanian region and of Adriatic and Ionia Sea were investigated by combining geomorphological, sedimentological, spectroscopic and microscopic analyses. In particular, grain-size analysis, optical microscope, image analysis and µ-Fourier Transform Infrared Spectroscopy (µ-FTIR) and µ-Raman were carried out. Quantification of MPs per kg^{-1} d.w (dry weight) in sediments have been carried out in details and a correlation between number of MPs stored in sediment and their transport path have been stressed.

The Bradano and Basento rivers are affected by anthropogenic activity, being located at short distance from several urban centres and industrial areas. However, studies on the MPs pollutions in the river system from the Apulo-Lucanian region have been so far lacking. On the other hand, the Adriatic and Ionian Sea have been identified as preferential areas for floating plastics accumulation (Gajšt et al., 2016; Ruiz-Orejon et al., 2016). Floating MPs, transported by sea currents, can migrate from the sea surface to sea sediments (Alomar et al., 2016; Palatinus et al., 2019; Kane et al., 2020). Notwithstanding some studies on MPs in the water column and in aquatic organism were published (Campanale et al., 2020; Furfaro et al., 2022; Dambrosio et al., 2023; Trani et al., 2023), no data are available on the occurrence of MPs in the Adriatic and Ionian sediments. To our knowledge, this is the first research that quantifies MPs in sediments from an area in Southern Italy and highlights a correlation between number of MPs stored in sediment and transport.

2. Materials and methods

2.1 Geographic and geomorphological setting of the study area

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 in the SW–NE direction in the first mountainous section up to Potenza; then, its flow direction changes to the NW–SE direction, flowing into the Gulf of Taranto (Ionian Sea).

The Bradano is one of the large rivers in Basilicata, with a catchment area of about 2765 km^2. It traverses the landscape in a northwest to southeast direction, spanning across 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 (about 1530 km^2), it has an average annual flow of approximately double that of the Bradano, of about 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., 2019; Dal Sasso et al., 2020; Pizarro et al., 2020; La Salandra et al., 2022). The sea-floor sediments of continental shelf of the Gulf of Taranto are characterized by Pleistocene and Holocene sandy-clay deposits influenced by surface water currents (Grauel et al., 2013) and mass transport in deep water (Teofilo et al., 2018; Artoni et al., 2019).

The Adriatic Sea is an elongated basin, extending about 800 km from NW to SE between Italy and the Balkan regions. The average depth of the Adriatic ranges from about 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 (Gajst et al., 2016), the largest Italian river, but is also fed by numerous other rivers that drain the highly 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).

Human activity is intense along the coasts, with 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 the rivers, an additional 40% through coastal urban populations, and the remaining 20% through shipping and fishing activities (Liubartseva et al., 2016). Van der Wall et al., (2015) estimated that the Po River discharges 120 tons of litter and 7E+11 micro litter particles per year (Van der Wall et al., 2015). Others 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 side, and two marine sites for the Adriatic side (Fig. 1). In particular, in the Ionian area sediment samples from Basento and Bradano rivers (identified as BAS1 and B1A respectively) were collected, whereas two samples (identified as 1BAS and 1BRA) from the offshore areas of Gulf of Taranto were considered. The BAS1 site is located next to industrialized area of Val Basento, and close to the industrial towns of Pisticci and Ferrandina; however, the B1A site is located in a non-densely populated foothill area, with water flows coming mainly from San Giuliano Regional Reserve and Montescaglioso, in the province of Matera. Marine samples identified as 3BAB40 and 4BAB40, were collected in Adriatic Sea facing to the coastal area of Bari (BA), located in the central part of the Apulian region.

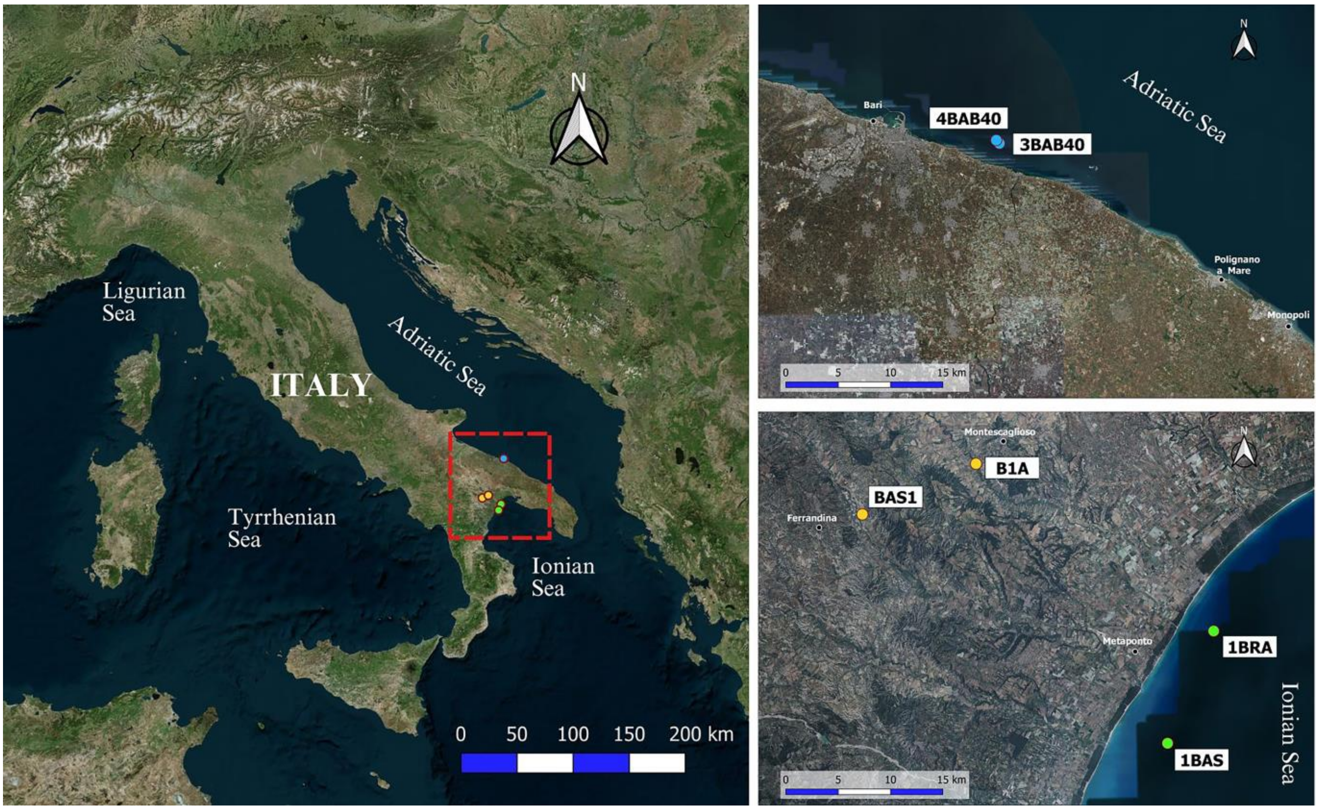

Fig. 1. Study area and sampling stations. Blue dots represent marine sampling in Adriatic area. Yellow dots represent river sampling and green dots represent marine sampling in Ionian area.

River sampling was carried out on the middle-channel bar in the upper part of the coarsening upward sediments. The sediments were collected using a stainless-steel spoon to fill a 1 L glass jar (Horton et al., 2016) in an area of 30 cm² and at a depth of 2-3 cm removing stones >10 mm (Klein et al., 2015), at randomly chosen points along transects of about 10 m, to guarantee the accuracy of the sampling results. The direction of the transects was chosen following the morphology pattern of the rivers, focusing on the areas characterized by low changes in the last 150 years (de Musso et al., 2020). Specifically, in the Basento river, transects were set perpendicular to the riverbank. On the contrary, in the Bradano river, transects were set parallel to the riverbank. Sampling areas were chosen according to: i) accessibility of the watercourse, density of vegetation and distance from the main communication routes; ii) lithological characteristics and slope gradient, iii) proximity to urban and industrial areas.

The studied marine samples (1BAS, 1BRA, 3BAB40, and 4BAB40) were collected through 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 in the Ionian and Adriatic Seas.

2.3 Grain-size analysis

The grain-size analyses were conducted on an aliquot of the collected samples. A combined procedure was used. The size fractions coarser than 3 ϕ (125 μm) were analyzed by mechanical sieving at 1 ϕ interval ($\phi = -\log_2 d$; d is the particle size in mm). The finer fractions, from 4 ϕ (63 μm) to 9 ϕ (2 μm), were analysed by means of a Beckman Coulter Multisizer 4 (Mele et al., 2015).

2.4 Sample preparation and MP extraction

A weighted amount of collected sediment samples was dry at 50°C for 3 days following Klein et al. (2015). This temperature does not alter the intrinsic shape of the selected particles, being below the melting point of all common polymers (Kalpakjian and Schmid, 2008). The sediment fractions > 0.063 μm was separated (Klein et al., 2015) and treated with 10% H_2O_2 solution for 24 hours to remove the organic matter. The H_2O_2 concentration was set low as changes in the polymers, such as transparency and size reduction, were identified if using a 30% H_2O_2 (Karami et al., 2017). Density separation of the plastic particles was performed using a $ZnCl_2$ solution (Nuelle et al., 2014; Horton et al., 2016), 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 hours (Blair et al., 2019). After this time, 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 then dried at 50°C. The resulting particles were separated from the filter and placed in a clean petri dish to be analyzed (Firdaus et al., 2020).

2.5 Characterization and identification of MPs

MPs were initially photographed using a Nikon D300 SLR camera to support particle identification and then subjected to optical observations to better define their shape and color. The 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., 2016; Fridaus et al., 2020). Their concentration was calculated as number of MPs (items) per kg^{-1} pursuing two methods: i) MPs in relation to the weight of the whole sample (hereafter MPs per kg^{-1}), according to Nel et al. (2018), and ii) normalizing MPs to the weight of the sample without the particle size fraction < 0.063 mm (here after MPs per 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 in Celine et al. (2023) and Simon-Sánchez et al. (2019). A Thermo Fisher Scientific µ-FTIR NicoletiN10MXTM, equipped with a MCT detector (mercury cadmium telluride detector) was used. In order to automatically select, analyze, identify, and count the microplastics on the filter, the "Microparticle WIZARDTM function" of the OMNIC PictaTM software was used. The first step of the analysis was the acquisition of a visual mosaic image, constructed from many individual field views. During this step, a correct image contrast is crucial 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. In this case all the particles have been analyzed, going down to 10 µm. Finally, the software automatically collects one spectrum from each particle. The spectral resolution was set at 4 cm^{-1}, and 16 scans have been acquired for each spectrum, that means 5.58 sec/spectrum. The dimensions of the apertures for the spectral acquisition have been automatically chosen by the software that automatically set the correct value based on the particle dimension. The last step consists in the background subtraction; the software automatically collects a background for each aperture dimension and process the data. All the spectra are then analyzed using a library search algorithm. Proprietary library from Thermo Fisher Scientific has been used to identify all the acquired spectra.

The µ-Raman analyses on MPs were carried out using the Thermo Fisher Scientific Nicolet DXR3TM Raman microscope, equipped whit an 532nm laser (Lenz et al, 2015; Wolff et al, 2019; Fang et al., 2023). In order to select, analyze, identify and count the microplastics present on the filter we have used the Particle Analysis function of the OMNIC TM Atlus software. The process is very similar as for FTIR. First the software acquires a visual mosaic image, constructed from many individual fields view. Then the software automatically recognizes the particles and acquire one spectrum from each particle. A library search algorithm based on a proprietary Thermo Fisher scientific library is finally used to identify all the acquired spectra. The power of the laser was set 10 mW measured on the sample; the exposure was set at 3 sec with 3 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 microns, although space resolutions of 0.5 microns can be reached.

3. Results

3.1 Grain size distribution

The grain size results show differences between inland and offshore samples (Fig. 2). Sample B1A, from Bradano River, shows a unimodal and asymmetrical distribution, with mode coinciding with the 0.5 mm size. Grain sizes below 0.063 mm are present with no significant percentage in the sediment. Sample BAS1, from Basento River, shows a polymodal distribution, with three evident subpopulations with the mode to 8 mm, 0.25 mm and 0.016, respectively. The offshore samples from the Ionian Sea, 1BRA and 1BAS, show a unimodal distribution with the mode corresponding to the 0.063 mm size. Samples 3BAB40 and 4BAB40 from Adriatic Sea show a unimodal and Gaussian distribution, which mode is shifted to the lower grain sizes (0.016 mm).

3.2 Morphology and abundance of MPs in sediments

The total amount of MPs varied between 144 to 1246 items kg^{-1} of dry sediment (mean ± SD; 468.8 ± 410.7 MPs kg^{-1}) (Fig. 2). The lowest and highest values were found in the Ionian area, located in Bradano river sediments (B1A site) and offshore at the mouth of the same river (1BRA site), respectively. MPs appear as are fibers (98.3%), films (1.2%) and fragments (0.6%). They are mainly black in color (75.1%), although blue (10.8%), red (10.2%), transparent (3.5%) and white (0.4%) MPs were also detected. Similar concentration of LMPs (51%) and SMPs (49%) was found (Fig. 3).

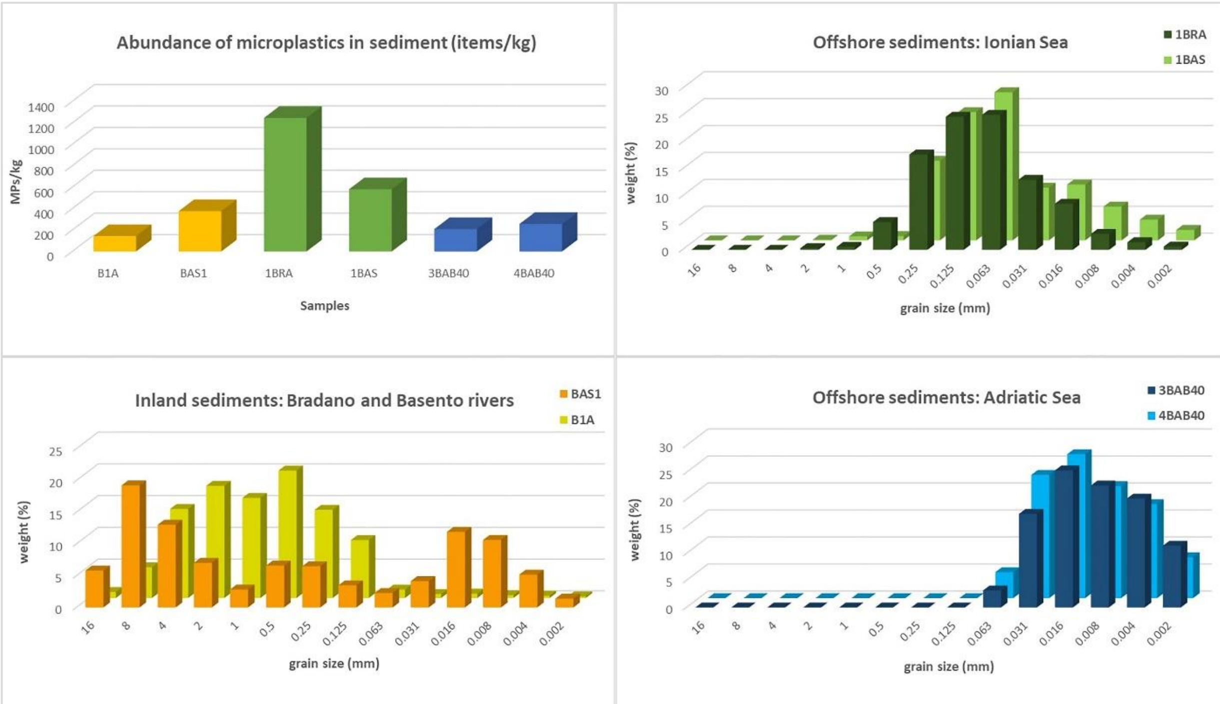

Fig. 2. MPs concentration in samples collected in Southern Italy, reported in MPs/kg, combined with particle size analysis

More specifically, in Ionian area MPs selected from Bradano (B1A) and Basento (BAS1) rivers exhibit 144 and 376 MPs kg^{-1} d.w, respectively. They are black fibres, although minor red and blue fibers were also found. Small particles predominate with respect to LMP. If looking at 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 Ionian area, the zone corresponding to the mouth of the Bradano river (1BRA) exhibits 1246 MPs kg^{-1} d.w, whereas the sediment from the mouth of the Basento river (1BAS) shows 581 MPs kg^{-1} d.w. The particles most frequently observed are black fibers, which include blue, red, and transparent fibers and an additional white fragment. In this context, large microplastics are more abundant. Considering the "*MPs per kg*$^{-1}$ *d.w no 0.063 mm*", 2262 (corresponding to 1BRA) and 1143 MPS kg^{-1} (corresponding to 1BAS) were identified.
Regarding the Adriatic area, marine sediments show 209 (3BAB40) and 257 MPs kg^{-1} d.w (4BAB40), with a prevalence of black, red and blue fibers, but also films and fragments were observed. The amount of SMP and LMP are approximately balanced, particularly in the 3BAB40

sample. If looking at the values of *"MPs per kg^{-1} d.w no 0.063 mm"*, the samples 3BAB40 and 4BAB40 exhibit values of 6744 and 5350 MPs per kg^{-1} d.w.

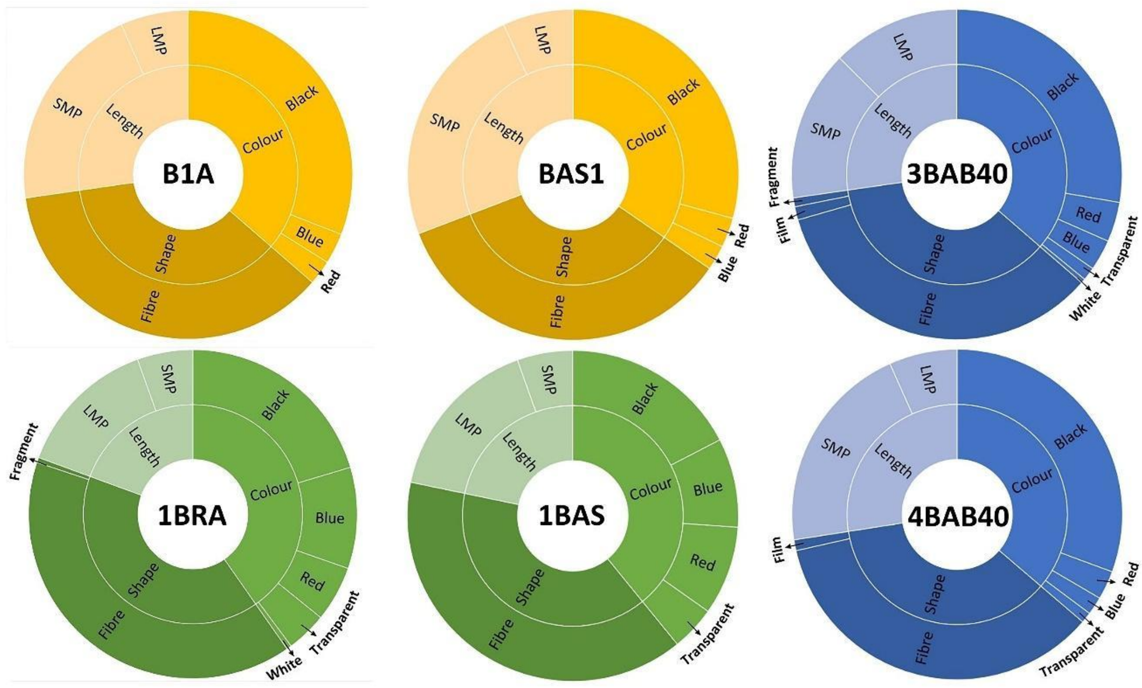

Fig. 3. Characterization of MPs by shape, color and size for each sediment sample acquired.

3.3 Polymer types

The 82% of all the particles analysed by µ-FTIR and µ-Raman were recognized as MPs. In detail, the results of the µ-FTIR investigation on particles selected from the Ionian sediment evidenced that they consist of polystyrene, poly (2-acrylamido-2-methylpropanesulfonic acid: styrene), polyester and poly (isodecyl methacrylate). Particles of methyl palmitate, protein and cellulose were also identified. Using µ-Raman technique, it was possible to identify a black rayon fibre, polycarbonate fibre and a white fragment proved to be a printer starch (Fig. 4A).

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

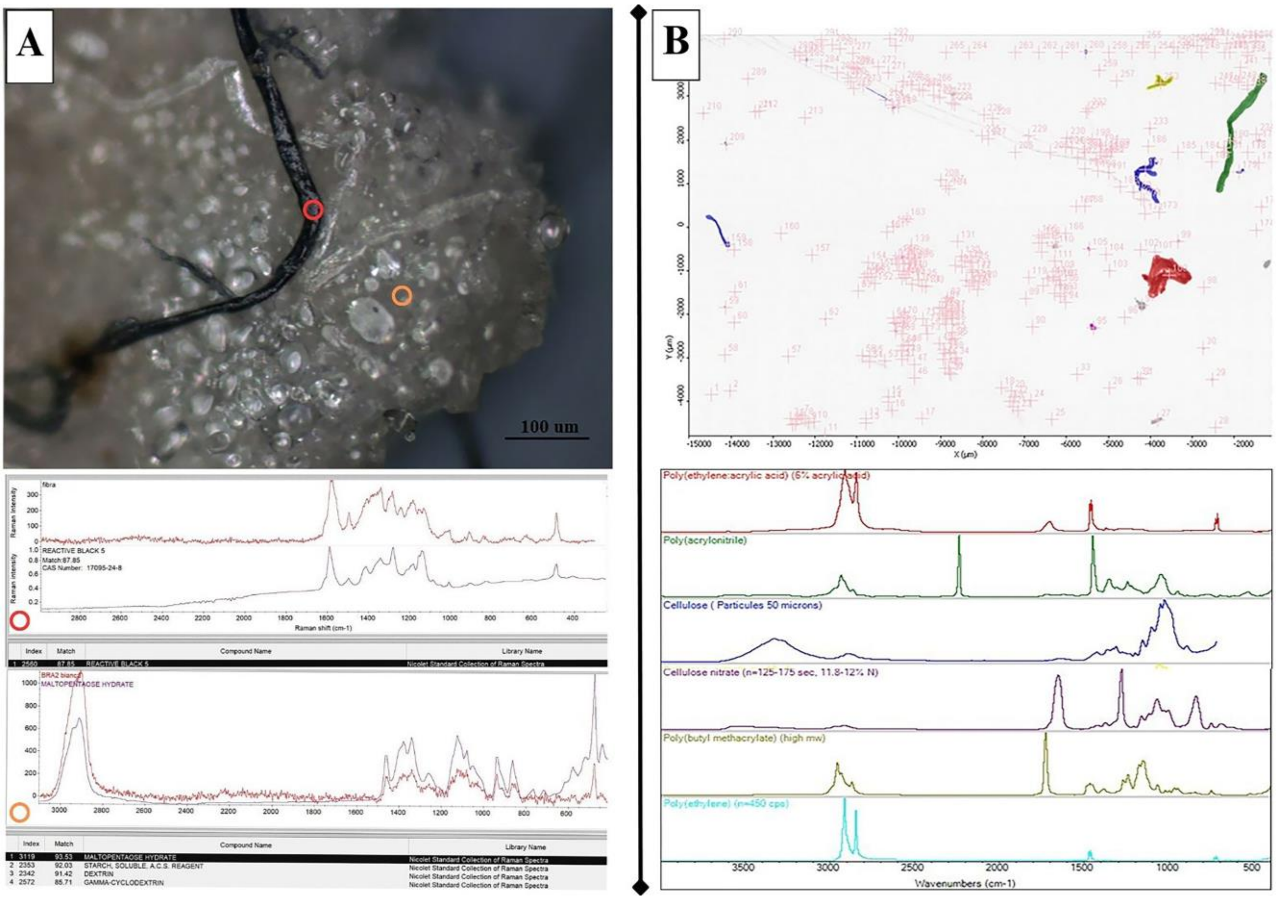

Fig. 4. μ-Raman spectra from a black polycarbonate fibre (red dot) and a printer starch (orange dot) relative to the BAS1 sample (A); μ-FTIR visual mosaic image of particles from the 4BAB40 sample (B) and relative spectra. Color of spectra is matching the color of identified particle.

4. Discussion

MPs occurring in Ionian and Adriatic sediment fraction from 5 mm to 0.063 mm have been quantified and characterized. The MPs concentration is generally expressed as MPs per kg^{-1} d.w. by referring to the weight of the entire sediment or of the sieved sediment. Higher amounts of MPs are expected to be present in sieved sediment than in entire sediment. This result was found particularly marked in the 3BAB40 and 4BAB40 samples where the fine grain size was predominant (Fig. 2). The MPs concentration in our samples is not correlated to the grain size distribution of the sediments. Indeed, despite the Inland (B1A and BAS1 samples) and the Adriatic offshore sediments (3BAB40 and 4BAB40 samples) have a different grain size distribution, a similar MPs content was measured (Fig. 2). This confirms the findings of other studies, that sediment composition and grain size do not control MPs (Harris, 2020) and Dodson et al. 2020). Regarding the morphology, the studied MPs appeared mainly as fibres and subordinately as fragments and films. Similar results were reported by Horton et al. (2016) for MPs in sediments from River Thames. On the contrary, spheres and pellets (Klein et al., 2015) or flakes, fibre clusters, single fibres and pieces (Pojar et al., 2021) were found in Danube River. These differences are probably ascribed to the source of pollution, which depends on the anthropogenic activities affecting the study area. Differences between MPs in inland and offshore sediments were 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 appear, and other MPs colors are visible.

MPs in Basento river sediments (376 MPs kg^{-1} d.w) are more abundant than those in the Bradano river (144 MPs kg^{-1} d.w). Being the Basento sampling site located in a densely industrialized area, this could account for the higher numbers of MPs detected. The highest numbers of MPs stored in the marine sediments sampled at the mouth of the rivers just in front of the Bradano sampling site (1246 MPs kg^{-1} d.w) can be explained by considering the underwater landforms as from bathymetry data. These data clearly unveil that the sampling locations of microplastics in the Ionian offshore occurred in an area affected by canyons (Fig. 5). According to Kane et al. (2020), the low-intensity summer currents may have induced MPs to accumulate on seabed. Previously deposited microplastics may have thus be exhumed when shear stresses exceed the critical limit, due to more intense bottom currents in winter. Being the marine sediment sampling performed in summer, this may justify the large number of MPs found in the deep-sea sediments. Besides, the flow rate of Bradano river, much lower than the Basento one, may account for the observed data as higher accumulation is to be expected.

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.

The MPs kg^{-1} 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 may have thus affected the MPs transport that could have been mainly influenced by gravitational processes or deposition along the water column rather than by bottom current.

As a variety of MPs were identified, it was tentatively assessed their different environmental sources. The cellulose found in the analyses is likely to be a consequence of the low hydrogen peroxide content used to prevent alteration of the artificial particles but was clearly detectable under optical microscope. Polycarbonate black fiber combined to printer starch, is supposed to be originate from a 3D printer. However, it is difficult to determine the source due to different scenarios such as: effluent discharges from production plants (Cousins et al., 2002; Klecka et al., 2009; Fu and Kawamura, 2010; Idowu et al., 2022), degradation of used plastics as well as leachate of 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 fiber, commonly used in clothing production, could have been introduced in marine environments through wastewater, and one of the main input sources is presumed to be washing machines (Browne et al., 2011; Woodall et al., 2014). The existence of rayon in coastal and deep-sea sediments is in accordance with Frias et al. (2016) and Woodall et al. (2014). The large variety of MPs, such as polyester and polyacrylonitrile in fiber shape, in addition to rayon, suggests that the major cause of MPs pollution in inland and offshore sediments in the Apulo-Lucanian region is caused by textiles from wastewater discharge.

4.1 MPs in Mediterranean sediments: comparison with other studies

MPs contamination of the environment is becoming an increasingly discussed issue. For this reason, several matrices and their pollution levels are being investigated. In the Mediterranean area, several studies have been conducted mostly on MPs in the water surface (Cincinelli et al. 2019), followed by studies in 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., 2020; Furfaro et al., 2022; Dambrosio et al., 2023; Trani et al., 2023), but MPs in sediments have not been investigated, until today. However, according to Zhang et al. (2021), plastics can persist on seabed sediments due to shelter from UV, low temperature, low oxygen, and slow biodegradation. Evidence was given by Nauendorf et al. (2016), showing that PE carrier bags stored in sediments from Eckernforde Bay showed no sign of biodegradation in 98 days. More research on microplastics in sediments is therefore desirable. As a consequence, this study summarized the research conducted in Mediterranean area on sediment exclusively in order to provide a clearer comparison of MPs kg^{-1} in the sediment matrix. The most relevant works, conducted in this area, are 30 (excluding this one) (Table 1). Italy has the most MPs investigations in sediment; in fact, no less than 13 research were implemented (Supplementary Material, Fig. S1). However, this is the first research conducted in Southern Italy. The sediments most explored in Mediterranean area, are beach sediments (19 out of 30), exhibiting fibers slightly more abundant than fragments. When fibers are more than fragments, black color predominates; in the opposite, white color prevails. Other studies explored from shallow coast to deep sea, observing an average prevalence of fibers. A single study was performed on sediments caves (Romano et al., 2023), a promising new sampling focus to interpret MPs behavior in environment. In contrast, it is important noting the limited availability of inland work. Excluding this study, only two rivers (in Italy and Spain) were investigated. Guerranti et al. (2017) collected samples from three rivers in Maremma Regional Park, province of Grosseto (Italy). The authors found a prevalence of fibers, predominantly black and an average of 222.6 MPs/kg d.w. This data agrees with the results found here, i.e., a prevalence of black fibers and an average of 260 MPs/kg d.w. On the other hand, Simon-Sànchez et al. (2019) investigated the Ebro River, finding more colored fibres than black, with mean values of one order of magnitude greater (2052 MPs/kg d.w). This difference could be explained by geographical differences or the sampling strategy closest to the Spanish coastline (Ebro River delta) than our river sampling area.

Unfortunately, the scarce research conducted in Mediterranean inland area and the different extraction MP methods prevent an exhaustive comparison. In order to extract MPs, most authors use the density separation method with NaCl, while just a limited number use $ZnCl_2$ (Angiolillo et al., 2019; Kazour et al., 2019; Piehl et al., 2019; Celine et al., 2023) adding also this study. Considering that $ZnCl_2$ is environmentally hazardous, while NaCl cannot achieve the required density to extract all types of MPs (Harris, 2020; Lusher et al., 2020), new extraction processes must be considered. To this purpose, several authors are assessing the use of different natural oils (Crichton et al., 2017; Mani et al., 2019), proving to be a method easy and inexpensive (Scopetani et al., 2020) with an average MPs recovery rate over 96% (Crichton et al., 2017; Mani et al., 2019; Scopetani et al., 2020). In order to identify polymer type, a large number of authors used the FTIR technique. Raman analysis was only used in two examinations (Kazour et al., 2019; Celine et al., 2023), while another author coupled it with FTIR (Missawi et al., 2020). This study used both methods, noting that FTIR is a faster technique than Raman.

The amount of MPs kg^{-1} found in sediments varies from zero (Laglbaur et al., 2014; Romeo et al., 2015; Kazour et al., 2019; Korez et al., 2019; Celine et al., 2023) to 4500 on Lebanon coast (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, a value in conformity with the current average of MPs in Mediterranean sediments (Supplementary Material, Fig. S2).

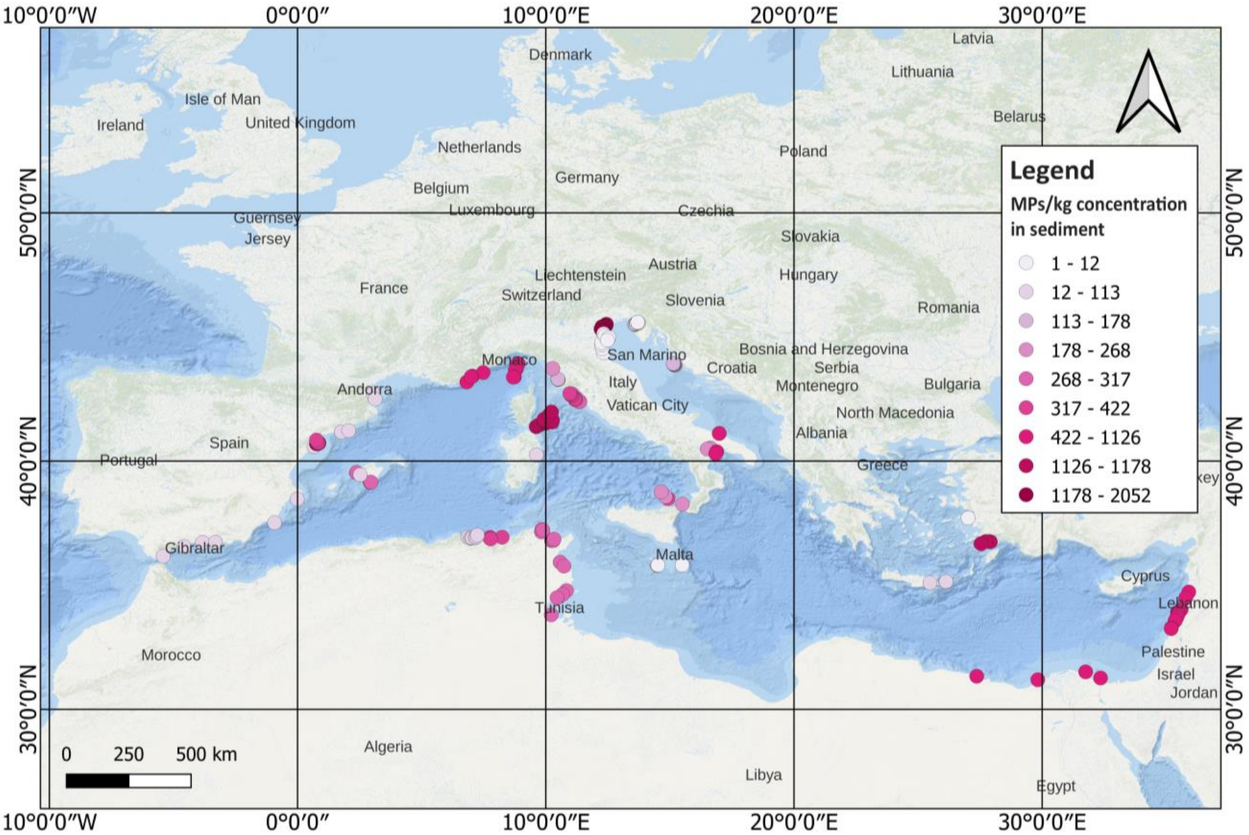

Fig. 6. Review of MPs/kg d.w concentration for each study conducted in Mediterranean area. The values represent the average obtained from each work in the same sediment matrices.

ID	COUNTRY	AREA	NUMBER OF STATION	DENSITY SEPARATION	MPs IDENTIFICATION	MPs/kg (D.W) min	max	SHAPE (more abundant)	COLOUR	AUTHOR
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	15.0	414.0	fibers	clear > white > black	Blašković et al., 2016
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	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	8	NaCl	no	57	477	fibers	black > white > other	Guerranti et al., 2017
		beach	6			45	1069	fibers	black > white > other	
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	2	$ZnCl_2$	FTIR + Raman	144	376	fibers	black > blue > red	This study
		continental shelf (-40 m)	4			209	1246	fibers	black > blue > other	
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	Laglbaur 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)	10	NaCl	FTIR	45.9	280.3	fibers	transparent > blue > other	Filgueiras et al., 2019
28	Spain	river	3	NaCl	FTIR	1491	2899	fibers	colored > black > other	Simon-Sànchez et al., 2019
		delta / beach	5			283	557	fibers	colored > black > other	
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	Yabanli et al., 2019

Table 1. Review of research conducted in sediments in Mediterranean area to date. Country, area of sampling, and number of stations are indicated. Extraction method and analysis technique for polymer identification are also specified. Finally, the number of minimum and maximum MPs/kg values, the most abundant shape and the colours are present.

5. Conclusion

This work represents the first study on MPs in both inland and offshore sediments in Apulo-Lucanian region, also enriching the paucity of MPs research in Mediterranean Inland sediments. Comparing MPs/kg d.w content and grain size in the different examined environments, no relevant 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 is due to local pollution. In offshore, on the other hand, the MP amount in sediment is determined by river flow. Lower flow determines higher accumulation, especially in summer. In winter, sediments storing MPs may be relocated due to an increase in river discharges, mainly in offshore areas with canyons (according to Kane et al., 2020). Moreover, if no rivers and canyons exist, MPs transport is only influenced by gravitational processes or deposition along the water column, determining minor accumulation in offshore sediments. It was also noted that a large part of MPs in sediment probably comes from textile fibers. According to De Falco et al. (2019), many microfibers of cellulosic nature were also released during washing of clothes made with a blend of polyester/cellulose. It must be mentioned that no legislation that governs this type of plastic in the entire Mediterranean area. Studies are continuing, but more research in MPs from marine sediments needs to be performed, with special attention to sediment dynamics on the sea bottom: currents may reactivate MPs and extend their lifetime in the environment. In addition, more studies should focus on microplastics in Inland sediments, being the research carried out so far mainly on beach/marine sediments. Considering the total average values of MPs in Mediterranean Sea sediments, it is important to monitor whether this statistical data shows 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.

Declaration of competing interest

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

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Table 1. Review of research conducted in sediments in Mediterranean area to date. Country, area of sampling, and number of stations are indicated. Extraction method and analysis technique for polymer identification are also specified. Finally, the number of minimum and maximum MPs/kg values, the most abundant shape and the colours are present.

ID	COUNTRY	AREA	NUMBER OF STATION	DENSITY SEPARATION	MPs IDENTIFICATION	MPs/kg (D.W) min	max	SHAPE (more abundant)	COLOUR	AUTHOR
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	15.0	414.0	fibers	clear > white > black	Blašković et al., 2016
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	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	8	NaCl	no	57	477	fibers	black > white > other	Guerranti et al., 2017
		beach	6			45	1069	fibers	black > white > other	
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	2	$ZnCl_2$	FTIR + Raman	144	376	fibers	black > blue > red	This study
		continental shelf (-40 m)	4			209	1246	fibers	black > blue > other	
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	Laglbaur 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)	10	NaCl	FTIR	45.9	280.3	fibers	transparent > blue > other	Filgueiras et al., 2019
28	Spain	river	3	NaCl	FTIR	1491	2899	fibers	colored > black > other	Simon-Sànchez et al., 2019
		delta / beach	5			283	557	fibers	colored > black > other	

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	Yabanli et al., 2019

Figure1

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Figure 2

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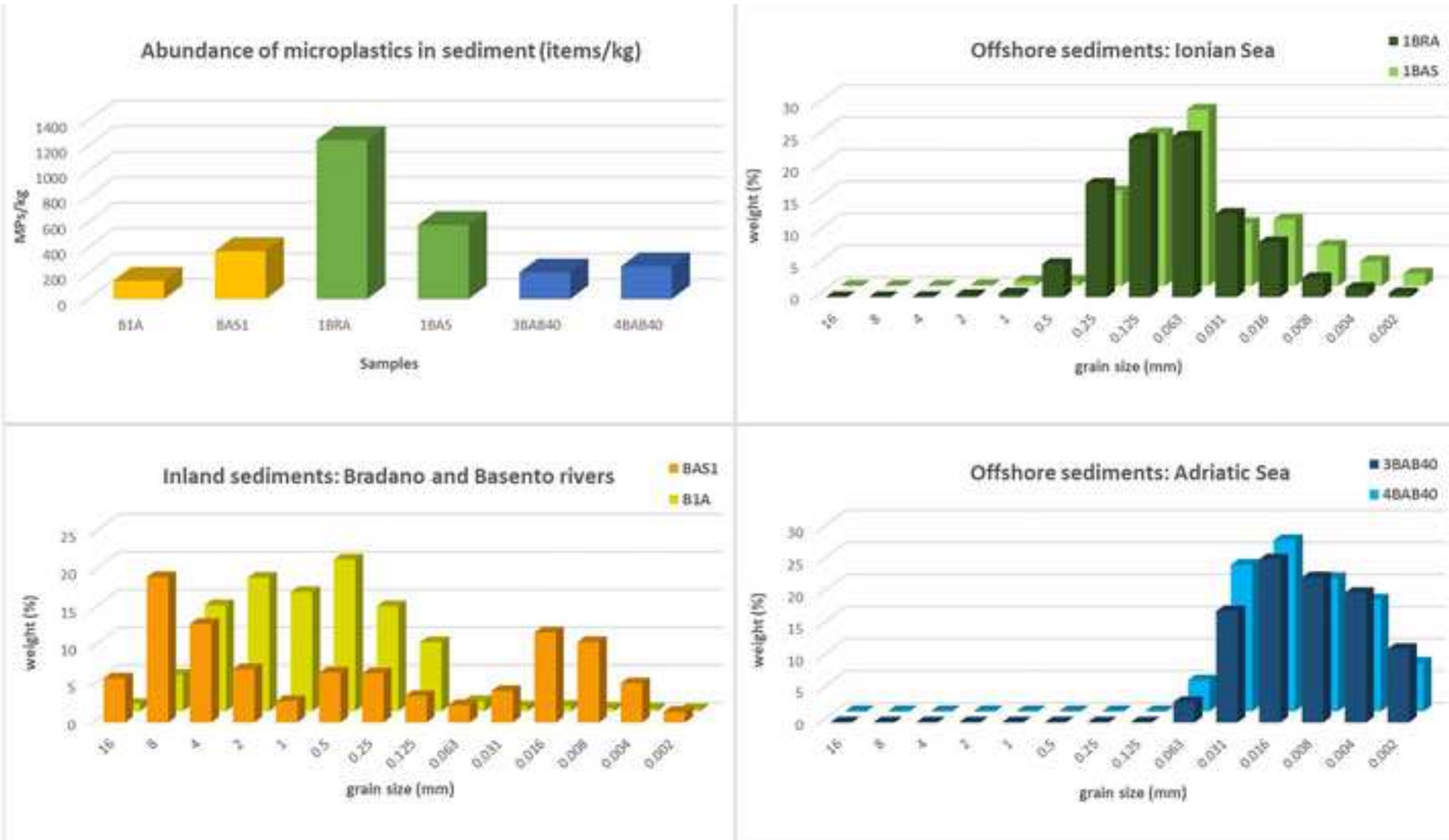


Figure 3

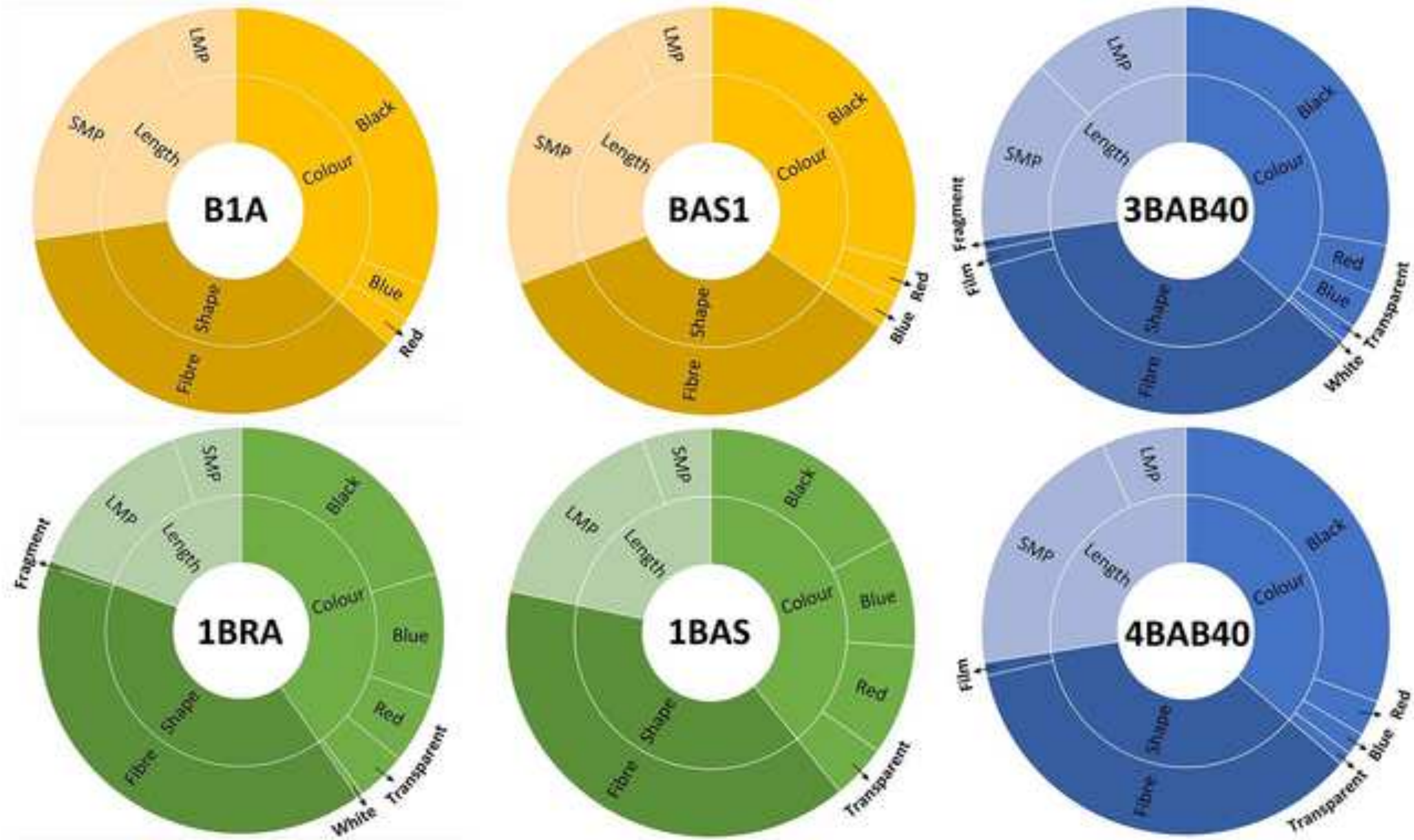

B1A
LMP
SMP
Length
Colour
Black
Blue
Red
Shape
Fibre
BAS1
LMP
SMP
Length
Colour
Black
Red
Blue
Shape
Fibre
3BAB40
LMP
SMP
Length
Colour
Black
Red
Blue
Transparent
White
Fragment
Film
Shape
Fibre
1BRA
SMP
LMP
Length
Fragment
Colour
Black
Blue
Red
Transparent
White
Shape
Fibre
1BAS
SMP
LMP
Length
Colour
Black
Blue
Red
Transparent
Shape
Fibre
4BAB40
LMP
SMP
Length
Colour
Black
Film
Red
Blue
Transparent
Shape
Fibre

Figure 4

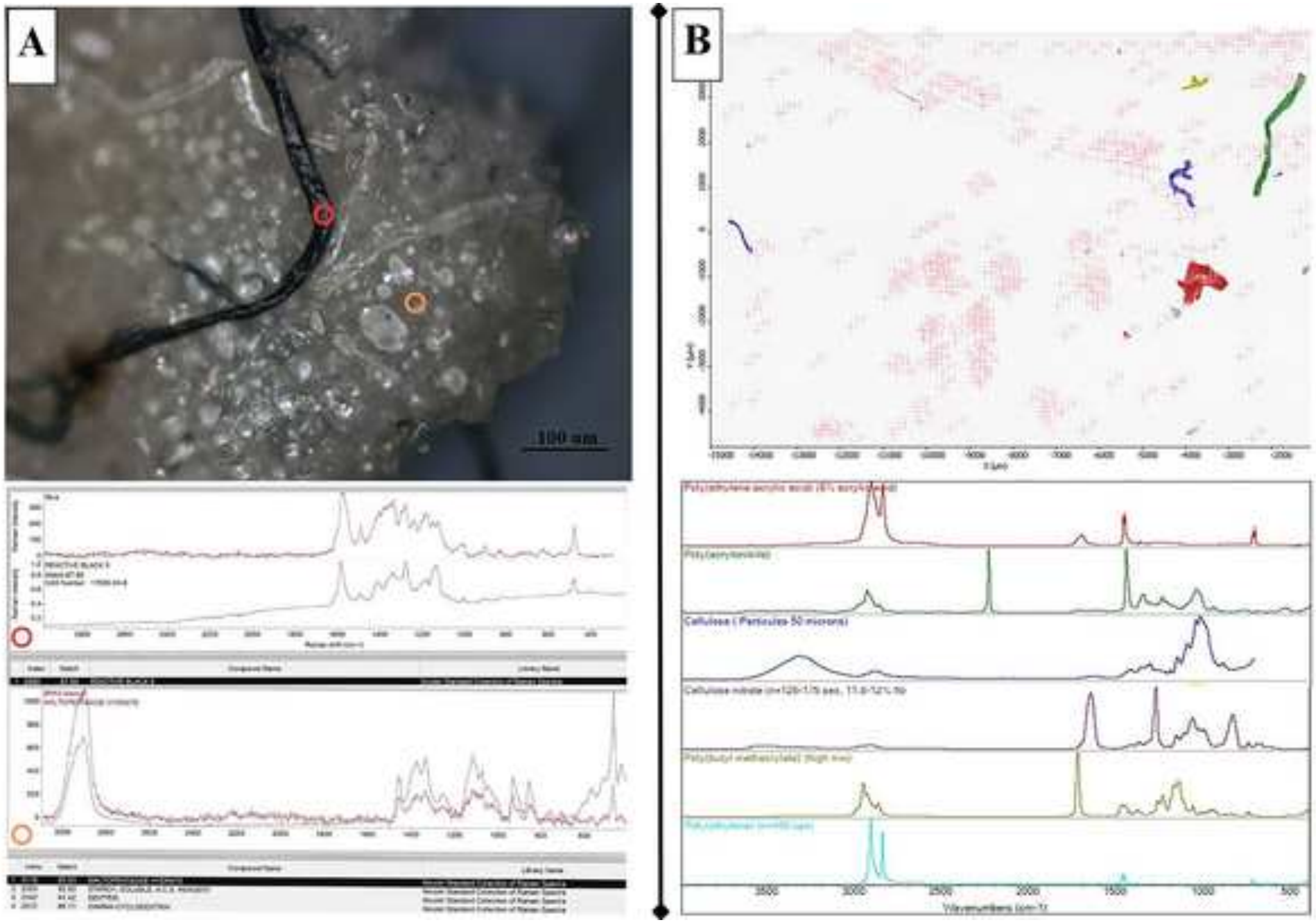


Figure 5

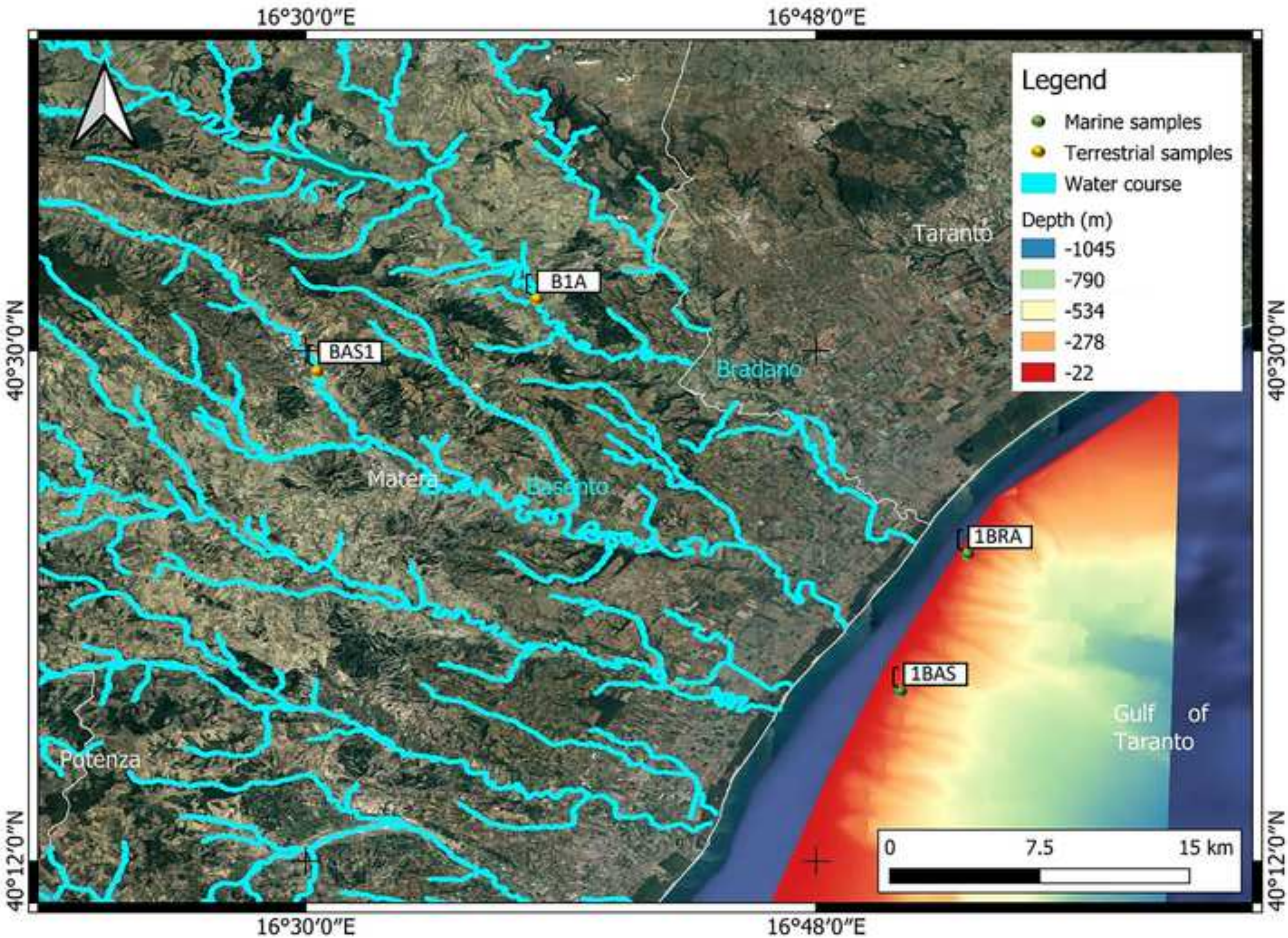
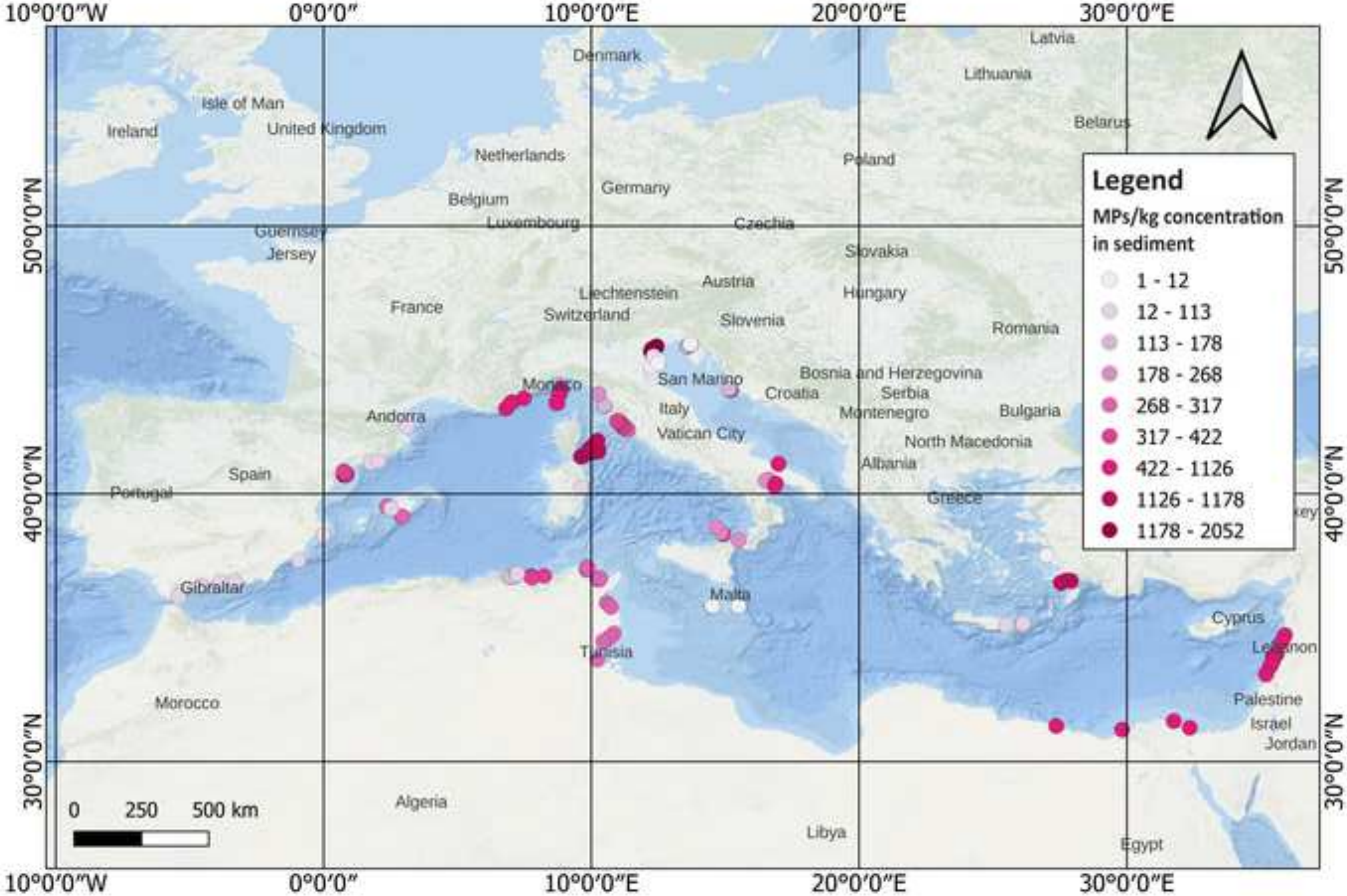

16°30′0″E
16°48′0″E
40°30′0″N
40°12′0″N
Legend
Marine samples
Terrestrial samples
Water course
Depth (m)
-1045
-790
-534
-278
-22
B1A
BAS1
Taranto
Bradano
Matera
Basento
1BRA
1BAS
Gulf of Taranto
Potenza
0
7.5
15 km

Figure 6

Click here to access/download;Figure(s);Fig. 6.jpg



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

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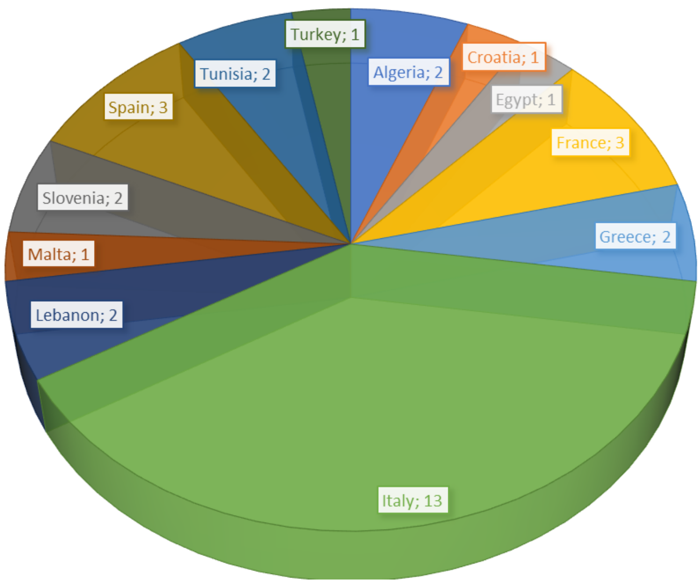

Fig. S1. Number of studies per country on MPs in sediments in the Mediterranean Sea.

ID	COUNTRY	AUTHOR	AVERAGE (MPs/kg d.w)
1	Algeria	Tata et al., 2020	405.0
2	Algeria	Grini et al., 2022	73.4
3	Croatia	Blašković et al., 2016	177.6
4	Egypt	Sayed et al., 2021	623.2
5	France	Constant et al., 2019	112
6	France / Italy	Kane et al., 2020	1177.7
7	Greece	Piperagkas et al., 2019	30.2
8	Greece	Ruijter et al., 2019	11.5
9	Italy	Vianello et al., 2013	1445.2
10	Italy	Fastelli et al., 2016	371.7
11	Italy	Cannas et al., 2017	316.8
12	Italy	Guerranti et al., 2017	269.0
13	Italy	Munari et al., 2017	12.1
14	Italy	Blašković et al., 2018	131.5
15	Italy	Renzi et al., 2018	258.0
16	Italy	Piehl et al., 2019	11.0
17	Italy	Scopetani et al., 2021	207.0
18	Italy / France	Angiolillo et al., 2021	450.0
19	Italy	Romano et al., 2023	17.3
20	Italy	This study	468.8
21	Lebanon	Kazour et al., 2019	1216.5
22	Lebanon	Celine et al., 2023	1126
23	Malta	Romeo et al., 2015	4.4
24	Slovenia	Laglbaur et al., 2014	177.8
25	Slovenia	Korez et al., 2019	1
26	Spain	Alomar et al., 2016	282.5
27	Spain	Filgueiras et al., 2019	113.2
28	Spain	Simon-Sànchez et al., 2019	1237
29	Tunisia	Abidli et al., 2018	316.03
30	Tunisia	Missawi et al., 2020	314.5
31	Turkey	Yabanli et al., 2019	1154.4
		Total average	**403.6**

Table S1. Average values of MPs per kg^{-1} d.w in sediment (and total average) divided by author and country.

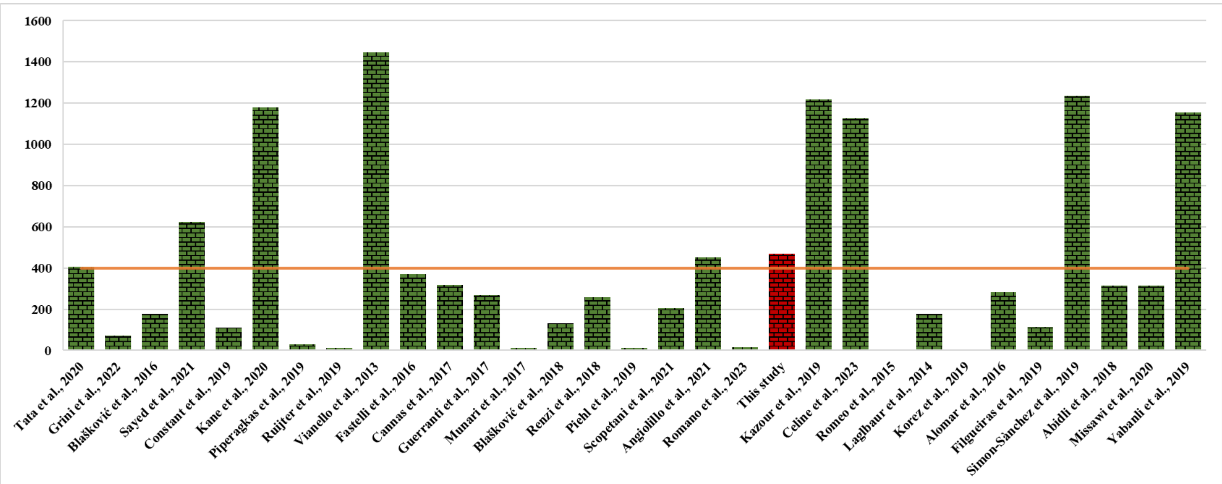

Fig. S2. Average MPs/kg in sediment by author. In red is highlighted this study while orange line represents the total average.

Declaration of interests

☒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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: