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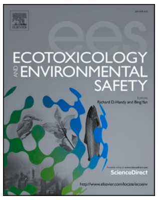

Survey on the presence of floating microplastics, trace metals and metalloids in seawater from Southern Italy to the United States of America

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ABSTRACT

The presence of microplastics (MPs), trace metals (TM) and metalloids (Ms) in surface seawater is a severe emerging issue of global concern. Information about the distribution of these pollutants is often lacking, and large-scale studies come with uncertainties because of difficult comparisons of results obtained using different methods to collect and process data. This study presents a comprehensive investigation of microplastics (MPs), trace metals (TM) and metalloids (Ms) in surface seawater during two transatlantic sampling campaigns, covering approximately 17,000 nautical miles. The results reveal the presence of MPs in all the samples analyzed and a broad variation in microplastic concentration (230–3320 MPs/L), with filaments or fibers being the most abundant shape. Coastal waters generally exhibit higher MPs, TM and Ms concentrations than open sea waters. The results showed high concentrations of MPs, particularly in the waters near the Faroe Islands, in the Sea of Magdalena department and in the Strait of Gibraltar. The order of the overall metals and metalloids concentrations was: As>Cr>Pb>Cd. High concentrations of Pb and Cr were recorded in the Mediterranean waters whereas high Arsenic (As) were found in the Southern coasts of United States, with values that exceeded the limits considered hazardous for aquatic life (81.55–101.12 μg/L). No significant correlations were found between microplastics, and the heavy metals examined. Here, we emphasize the need for sustainable environmental management actions and policies in a global context to monitoring the growing problem of pollutants in our oceans.

1. Introduction

Plastic wastes are mainly the most problematic pollutants among marine debris, due to their persistence and tendency to fragment into microplastics (MPs) which are plastic portions and particles having a diameter smaller than 5 mm; nanoplastics (NPs) are defined as plastic particles that are less than 100 nm, although plastic particles that are as big as 1000 nm have been considered as NPs by some authors (Barbosa et al., 2020). Microplastics are usually divided into primary and secondary, and both accumulate and remain in the environment. Primary MPs are plastics that are manufactured as microbeads and directly released into the environment as plastic particles. Cosmetics and cleaning products contain microbeads; these latter are dumped in the sea because of their micro dimension, which are only partially entrapped in the conventional wastewater plant (Cheung and Fok, 2016).

Additionally, primary MPs include pellets unintentionally leaked during manufacturing or transport of raw polymer materials (Belioka and Achilias, 2023; Loubet et al., 2022). Secondary MPs, on the other hand, are the result of a broken-down of larger plastic debris processes as biological, chemical, physical, and mechanical aging. Previous studies report that a relevant part of the sea MPs comes from laundry fibers produced by the abrasion and shading of synthetic textiles (Sun et al.,

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2019).

The main sources of MPs present in the seawater are related to the fishery, shipping activities, industrial agriculture, petrochemical, and other anthropical activities in coastal cities and ports (Alfaro-Núñez et al., 2021; Galloway et al., 2017). Eighty percent of plastics in the ocean are estimated to come from land-based sources, the largest illegally dumped in Asia rivers, and the remaining 20 percent comes from boats and other marine sources (Li et al., 2016; Zhang et al., 2022). Every year the global plastic production is about 400 million tons and according to the current growth trend, is forecasted to reach 1100 million tons by 2050, (Geyer, 2020) that is because pollution from MPs is a growing problem around the world, worsened by mobile and transborder nature of MPs waste (Nunes et al., 2023). Garbage patches, referring to large areas in the ocean where garbage and debris accumulate, represent a tangible symbol of the dramatic environmental crisis we are facing. Floating garbage in oceans is composed of various materials, mainly plastic, since 2020, an important new mass of debris like used face masks has been increased by the COVID-19 pandemic emergency (Peng et al., 2021).

Garbage patches are primarily located in oceanic areas to the principal gyres. There are six main influential gyres: the North Atlantic Gyre, the South Atlantic Gyre, the East Pacific Gyre, the North Pacific Gyre, the South Pacific Gyre, and the Indian Ocean Gyre. Garbage patches are inside these gyres (Lebreton, 2022; Zaman et al., 2020). The sizes of these patches vary, but the largest one, the Great Pacific Garbage Patch, spans waters from the West Coast of North America to Japan and contains 79,000 tons of floating plastic (Lebreton, 2022). These accumulations pose a growing threat to marine life and the marine environment. Microplastics can act as a vessel for toxic chemicals promoting their absorption into biological tissues and contaminating the food chain; so a recently emerging area of research focuses on the toxicological aspects of MPs (Mamun et al., 2023; Sönmez et al., 2023).

The most common pollutants in the seas, along with microplastics, are heavy metals and metalloids. High concentrations have been recorded in the environment because of their inert and non-degradable. Heavy metals are present in the environment from both natural and anthropogenic sources (Liu et al., 2021a). As widespread contaminants, heavy metals continuously enter water bodies due to their non-degradable nature, leading to their recycling and accumulation in aquatic environments. Heavy metals and metalloids such as Chromium (Cr), Arsenic (As), Cadmium (Cd), and Lead (Pb) are extremely dangerous for human health and the environment because of their high bioaccumulation, toxicity, persistence, and potentiality to affect the seafood chain (Cammilleri et al., 2020; Garai et al., 2021; Parrino et al., 2021; Tolkou et al., 2023; Tranchina et al., 2008). Human activities in particular, naval traffic (fishing, trading, transporting, and recreational), chemistry (pharmaceuticals, fertilizers, paints, dyes, pesticides, leather and textile), extraction activities (mining and oil and gas exploration), and sewage contribute to increasing the metal concentrations in the marine environment (Luo et al., 2022; Qasem et al., 2021). The presence of microplastics and heavy metals has been recorded in all types of marine environments, from coastal ecosystems to the deep sea (Caruso et al., 2011; Loughlin et al., 2021; Mitra et al., 2022). The simultaneous presence of the two pollutants is even more worrying and harmful, especially in the delicate marine environment. Some researchers supposed that MPs can act as carriers for heavy metals and their metal ions adsorption capacity increases with MPs aging and smaller MPs sizes (Liu et al., 2021a; Mao et al., 2020; Wang et al., 2020). The relationship between MPs and heavy metals can be attributed to physical and environmental factors. Recent reviews analyse the literature attempted to understand the complex mechanism of interactions between MPs and heavy metals in marine environments and to explore environmental factors that influence metal adsorption onto MPs (Bhaumik and Chakraborty, 2024; Narwal et al., 2024). Several studies have focused on the combined toxic effects of MPS and heavy metals and their bioaccumulation in the organism (Khalid et al., 2021; Cao et al., 2021; Chen et al., 2023). Microplastics can increase the bioavailability of heavy metals, making them more accessible to organisms and potentially increasing their toxic effects. This is especially significant in aquatic environments, where microplastics can carry heavy metals throughout the water column. (An et al., 2023; Li et al., 2020). Factors such as pH, dissolved organic matter (DOM), and salinity can affect the adsorption and desorption of heavy metals on microplastics. For instance, increased salinity can enhance the adsorption of heavy metals onto microplastics (Liu et al., 2022, 2021b). As carriers for heavy metals, MPs exhibit complex interactive effects, with interactions governed by mechanisms that remain poorly understood.

Monitoring and mapping are needful to evaluate the amount of toxics disposal that contaminates oceans and can be useful to study the risk assessment.

In this study, we have outlined an overview of the pollution status of microplastics in a portion of the Mediterranean Sea and two routes of the Atlantic Ocean. The sampling, to analyze MPs amount, was performed during two sampling campaigns from Palermo (Southern Italy) to New York (USA) and from Palermo to Los Angeles (USA). The sampling campaigns were conducted in 2019 and 2021–2022, covering about 7.000 nautical miles, being of interest due to the wide area examined.

Furthermore, seawater samples were also collected to assess heavy metals and metalloid levels during the sampling campaign from Palermo to Los Angeles. The concentration of Chromium (Cr), Arsenic (As), Cadmium (Cd), Lead (Pb) were also evaluated by the validation of an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method.

2. Materials and methods

2.1. Sampling plan

The study was divided into two sampling campaigns, including an area of over 17,000 nautical miles, from the Mediterranean Sea to the United States coast, as shown in Fig. 1. Thirty-four sampling sites for the TM and Ms analysis, and nearly sixty sampling sites for the MPs analysis were investigated, including Sicily, Sardinia, the Balearic Islands, southern Spain, the Atlantic coasts of Africa, the Canary Islands, Cape Verde, Suriname, Guyana, Venezuela, Colombia, Panama, Costa Rica, Nicaragua, El Salvador, Mexico, and Baja California up to Los Angeles. Additionally, Portugal, the United Kingdom, the Faroe Islands, Iceland, Greenland, Canada, and the United States up to New York were included in the study. The analysis process of microplastics, trace metals, and metalloids, involves different steps: sampling, pretreatment, analysis, and data elaboration in a period ranging from 2019 to 2022.

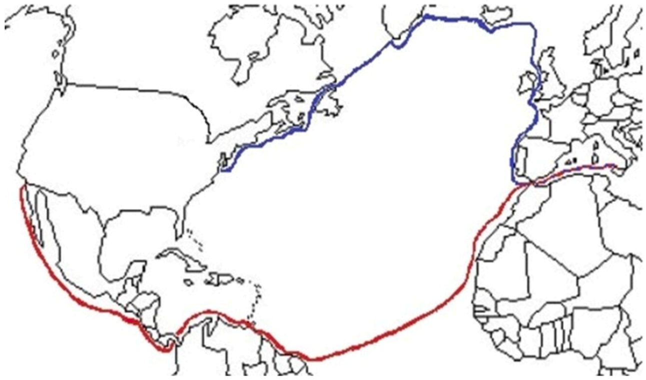

Fig. 1. Synoptic view of both routes taken during the two sampling campaigns: Ice RIB Challenge 2019 (blue line) and Ocean to Ocean RIB Adventure 2021–2022 (red line).

2.2. *Sample collection for MPs analysis*

Five dark glass bottles (1 L) of surface seawater were collected for each sampling site, with light wind conditions (under 5 knots), at 50 cm depth. The sampling position was determined by GPS by Simrad (Dordrecht, The Netherlands). Samples were stored at + 4 °C until analysis. The sampling procedure was developed considering the type of vessel used during the sampling, the numerous sampling sites, and the absence in the literature of a standard sampling method at that time.

2.3. *MPs analysis*

Preliminary validation of the microplastic treatment method was carried out using aluminum (Al), as a metal sample, and three kinds of most common plastic types: Polyethylene (PE), Polypropylene (PP), and Polyethylene terephthalate (PET). Tests were performed according to procedures reported in the literature with some appropriate modifications (Zobkov et al., 2019; Budimir et al., 2018). Samples were prepared adding 5 mg of plastic and 3 mg of metal in 100 ml of MilliQ water and 5 ml of 35 % hydrogen peroxide. The samples were digested overnight, at 25°C and 45 rpm. The mixtures were filtered in a vacuum Millipore system using a 47 mm gridded, 0.45 μm MCE (mixed cellulose esters) filter (Millipore).

The residues were then added with 100 ml of MIlliQ water and 5 ml of 37 % hydrochloric acid. After the digestion overnight at 25°C and 45 rpm, the mixture was again filtered as previously described. Filters were rinsed using MilliQ water. Recovery was 99 % by weight. Filters were analysed using optical microscopy: pictures of the samples before and after treatment were collected, even using polarized light. Results reveal that the procedure is suitable for the estimation of the number of microplastics since metals are efficiently dissolved and the polymers analysed are resistant to the treatments.

Accordingly, seawater samples (1 L) were at first filtered in a vacuum Millipore system using a 47 mm gridded, 0.45 μm MCE (mixed cellulose esters) filter (Millipore); residues were processed using the above procedure. The analysis were carried out at the ISO 9001:2015 certified laboratories of the Advanced Technologies Network Center (ATeN Center). The quality control (QC) and quality assurance (QA) were guaranteed according to the workflow and laboratory environments characteristics proposed by Richter et al. (2022).

Plastic fragments on the filters were sorted and counted using visual analysis by Dino-Lite Edge digital microscope equipped with polarized light (Manuscriptstraat, The Netherlands).

Optical stereo microscopy (OPTECA - magnification 10X to 90X) and SEM microscopy (Phenom Pro X, Thermo Scientific, Waltham, USA) analysis were performed for morphological characterization. The size range of analysed microplastic is 0,45 μm to 5 mm.

Before carrying out the reported analyses, training tests were conducted with polarized light microscopy and various types of known plastics to improve experiences. Moreover, Raman analyses were randomly carried out on analyzed samples for confirming the composition of the microplastics visualized by optical microscopy (data not reported). Raman spectra were acquired using Horiba LabRam HR Evolution equipment with a 633 nm laser line; laser power was reduced to 25 % of its nominal value (70 mW) to avoid sample degradation.

2.4. *Sample collection for metals and metalloids analysis*

2.4.1. *Reagents and gases*

Ultrapure deionized water was obtained by a Milli-Q® Integral water purification system (Millipore, Bedford, MA, USA). The multielement calibration solutions were obtained from VWR International LTD (Randon, Pennsylvania, USA). A tuning solution for ICP-MS (Ce, Co, Li, Mg, Tl, and Y 1 μg/l) was purchased from Agilent Technologies (Santa Monica, CA, USA). Ultrapure carrier (Ar, 99.9995 % pure) and dilution (He, 99.9995 % pure; H_2, 99.9995 % pure) gasses were purchased from SOL S.P.A. (Monza, Italy). Ultrapure nitric acid (60 % V/V) was obtained from Merck KgaA (Darmstadt, Germany).

2.5. *Seawater sampling for TM and Ms analysis*

Seawater samples were collected as described before (Munksgaard and Parry, 2001) with some modifications. The samples were collected using an all-plastic submersible in-line pump attached to a polyethylene pole, positioned at 50 cm depth, and directed upstream from the boat. The pump was connected to acid-washed PUR-ether tubing (Nalgene), and the samples were gathered in acid-washed 500 ml polyethylene bottles (Restek, Milan, Italy). Unfortunately, we did not have the possibility of having the in-line pump during the 2019 sampling campaign, this reason forced us to analyse the trace metals and metalloids only for the 2021 sampling campaign.

2.6. *Seawater pre-treatment and ICP-MS analysis*

The seawater samples were filtered with 0.45 μm acid-treated cellulose acetate filters (VWR, Randon, Pennsylvania, USA), then pH was adjusted at 2 with ultrapure nitric acid. Subsequent. The samples were diluted before the analysis according to Luo et al.(2022).

The trace metals and metalloids (Cr, As, Cd, Pb) concentrations were determined using a 7700x series ICP-MS (Agilent Technologies, Santa Monica CA, USA) with the following instrumental conditions: Carrier gas: 1.2 ml min^{-1}, Reflect power: 1100–1500 W, Plasma gas flow: 15 ml min^{-1}, Auxiliary gas flow: 0.9 ml min^{-1}, spray chamber temperature: + 2°C, lens voltage: 4.5 V.

A tuning solution was used daily to optimise these parameters, aiming to maximize the signal while minimizing interference effects from polyatomic ions and doubly charged ions. Residual standard deviation (RSD) values below 3 % were deemed acceptable for the resolution. The concentration was determined by the sum of the isotopes, with the signal intensity adjusted for matrix effects.

Matrix effect correction was achieved through the online determination of the Internal Standard (I.S.) associated with all the elements analyzed. The analyses were performed by introducing He and H_2 gases into the Dynamic Reaction Cell to mitigate interferences. The method was validated for instrumental/method detection and quantification limits, linearity, repeatability, and recovery according to previous works (Bacchi et al., 2022; Lo Dico et al., 2018; Table 2).

2.7. *Data collection and statistical analysis*

The microplastics concentrations were expressed as MPs/L whereas, the trace metals and metalloids concentrations were expressed as μg/L. A Principal Component Analysis (PCA) was carried out after autoscaling of the data to explore the dataset structure and to obtain more information on the variables that mainly influence the samples' similarities and differences. Before the PCA, Cd variable was excluded due to constant not detected values. The sampling sites (Mediterranean Sea, North Atlantic Ocean, Kourou River, Caribbean Sea, Miraflores Lake Panama, Gulf of Panama, North Pacific Ocean, All Saints Bay, Channel Islands of California) were considered categorical variables. A total of 3 PCs were selected after Kaiser-Harris criterion, Cattel Scree test and parallel analysis (n.iter=100) (Kabacoff, 2022). The total variance explained was 73.8 %. Correlations between trace elements and microplastics were tested with the Spearman's correlation method with Bonferroni correction. All the statistical analysis were conducted with R software (4.4.0).

3. Results and discussion

3.1. *Microplastic*

Distribution and accumulation data of marine debris can be influenced by environmental factors such as hydrography, flow rate, weather conditions, anthropogenic activities, intrinsic characteristics of the sampling sites, and chemical features of the materials themselves. Moreover, because there is no standardized methodology for sampling and laboratory protocol analysis, the microplastic concentration data originating from different approaches could be difficult to correlate or not always comparable across studies (Isobe et al., 2021; van Sebille et al., 2015; Kaandorp et al., 2023). Therefore, the results obtained in this work will not be combined with already published works.

In this study, analysing all the collected data for MPs, it comes out that concentrations show variability ranging from 230 M to 3320 MP items/liter seawater [MPs/L]. Table 1 shows details of the samples analysed. Fig. 2 shows the box and whisker plot for the two sets of data corresponding to the two-sampling campaigns.

Graphical representations of the MPs' concentration calculated using data from the first and the second sampling campaigns are reported in Fig. 3 and Fig. 4, respectively.

The graphical method displays a significant value variation between the sampling areas. In 2019 sampling from Palermo to New York most of the data, i.e., about 71 %, fall below the mean value while in the sampling carried out from Palermo to Los Angeles, the percentage showed a decrease of 57 %. Moreover, the 2022 sampling shows the upper whisker extending more from the box indicating more variability outside the upper quartiles. However, the outlier related to the 2019 journey is significantly higher than the outlier of the 2022 one. Surprisingly, the highest MP concentrations were recorded in the Faroe Island (Northeast Atlantic) near Torshavn, in the Sud of Streymoy, where the main industries are fishing and related activities.

Table 1

Details of the sampling sites sorted by sampling campaign and microplastic concentrations of the surface seawater samples.

Sampling campaign	Sample	Latitude	Longitude	sampling date	Microplastics / L
1	**Site 1**	38,1877778	13,2375	21/06/2019	420
	Site 2	38,9930556	9,144166667	21/06/2019	870
	Site 3	36,6769444	−2,516800833	26/06/2019	1120
	Site 4	42,3835456	−9,016782778	06/07/2019	540
	Site 5	46,0335125	−5,800235833	10/07/2019	600
	Site 6	49,8168206	−5,416667222	11/07/2019	540
	Site 7	61,9834883	−6,733500833	27/07/2019	3320
	Site 8	63,1833639	−19,76691667	01/08/2019	1290
	Site 9	64,1668786	−21,91670944	04/08/2019	780
	Site 10	65,2169311	−33,68353167	05/08/2019	290
	Site 11	65,1500089	−38,05004583	07/08/2019	1140
	Site 12	63,78359	−39,4167975	07/08/2019	860
	Site 13	60,5002364	−46,38358333	17/08/2019	750
	Site 14	51,350125	−55,55004167	27/08/2019	590
	Site 15	47,9167117	−59,51679694	04/09/2019	870
	Site 16	46,2501417	−60,16671111	06/09/2019	1050
	Site 17	45,0333708	−61,48360472	06/09/2019	610
	Site 18	44,6002333	−63,55021528	09/09/2019	800
	Site 19	41,2666833	−72,46671667	10/09/2019	970
	Site 20	40,8001028	−73,76676389	11/09/2019	580
	Site 21	40,5168028	−74,1167	12/09/2019	580
2	**Site 22**	38.83575	13.1501833	15/12/2021	1230
	Site 23	38.83575	8.81795	16/12/2021	1120
	Site 24	39.36785	3.24181666	17/12/2021	770
	Site 25	36.4486667	−3.5092666	20/12/2021	2180
	Site 26	35.8803667	−5.7849833	27/12/2021	1900
	Site 27	29.99085	−12.548483	28/12/2021	1190
	Site 28	28.81545	−13.923783	03/01/2022	890
	Site 29	27.7312667	−15.606116	03/01/2022	1290
	Site 30	23.6162833	−19.2804	22/01/2022	760
	Site 31	16.8583	−25.127783	04/02/2022	1140
	Site 32	13.9941167	−32.02485	06/02/2022	200
	Site 33	11.2627167	−38.626183	08/02/2022	440
	Site 34	9.6598333	−42.3987	09/02/2022	730
	Site 35	6.1112833	−50.666716	10/02/2022	560
	Site 36	5.1333167	−52.67965	13/02/2022	310
	Site 37	5.36755	−52.630166	20/02/2022	250
	Site 38	10.8165333	−61.785666	25/02/2022	1160
	Site 39	12.0010667	−68.553216	26/02/2022	460
	Site 40	12.4895333	−70.343233	28/02/2022	490
	Site 41	11.4210167	−74.014166	01/03/2022	2250
	Site 42	10.3475333	−75.679766	10/03/2022	970
	Site 43	9.0059667	−79.601733	18/03/2022	1360
	Site 44	8.5705167	−79.578866	22/03/2022	1070
	Site 45	7.6355833	−81.635966	22/03/2022	950
	Site 46	10.9334833	−87.018	31/03/2022	910
	Site 47	13.8908	−90.9662	03/04/2022	650
	Site 48	15.6578667	−96.224983	10/04/2022	570
	Site 49	16.14825	−98.405566	10/04/2022	700
	Site 50	17.5398	−101.82633	11/04/2022	750
	Site 51	18.88095	−104.14888	11/04/2022	410
	Site 52	23.385	−110.66443	26/04/2022	400
	Site 53	28.0316167	−115.07461	14/05/2022	230
	Site 54	31.8566167	−116.67881	19/05/2022	350
	Site 55	32.6418167	−117.24966	23/05/2022	280
	Site 56	33.6466833	−118.07585	23/05/2022	470

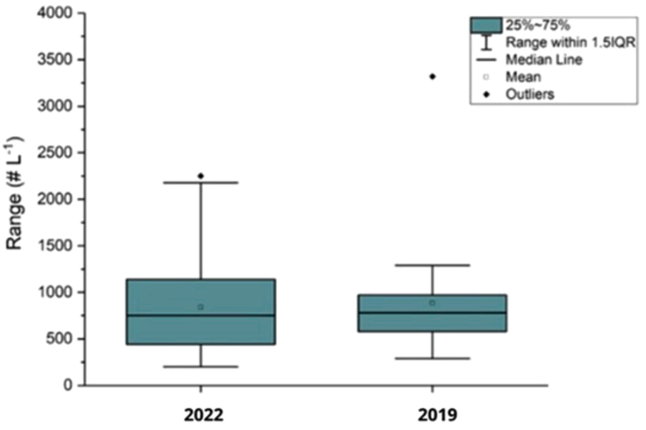

Fig. 2. Box-whisker plot of the microplastics data distribution (MPs/L), sorted by sampling campaign (on the right 2019 sampling campaign, on the left 2021–2022 sampling campaign).

The unexpected and alarming pollutant values recorded in Faroe Island may be related to upwelling phenomena and to the oceanic water circulations due to the merging of the warm Gulf Stream and the cold polar arctic waters (Våge et al., 2018). As known floating oceanic debris moves to accumulate at the center of gyres and on coastlines (Sebille et al., 2020). Anyway, it must be taken into account that ordinary and commercial fishing activity, existing in the area, is a source of microplastics deriving from the abrasion of the plastic ropes and wear and tear of fishing tools (Andrady, 2011; Syversen and Lilleng, 2022). The outlier related to the second journey is in the Sea of Magdalena department in Colombia; nevertheless, the recorded value is similar to the value recorded in other areas such as the Strait of Gibraltar. These findings suggest that anthropic impact is the key factor, and the contamination is a consequence of maritime traffic, direct discharge of domestic and industrial waste, toxic chemicals from agriculture and oil activities (Galindo Montero et al., 2023; Rodríguez-Grimón et al., 2021).

MPs were found in all the analyzed samples; in addition, the concentrations of microplastics, overall, are higher in coastal waters with respect to open sea water indicating a direct correlation between pollution and human production activities. Finally, a comparison in the same site area, i.e., from Palermo to the Strait of Gibraltar, from 2019 to 2022 seems to indicate that accumulation leads to an increase in the MP's amount, although different weather and sea conditions could have influenced these values.

Optical and SEM microscopy allow the characterization of MP in terms of size, shape, and morphology. Counted microplastics have been

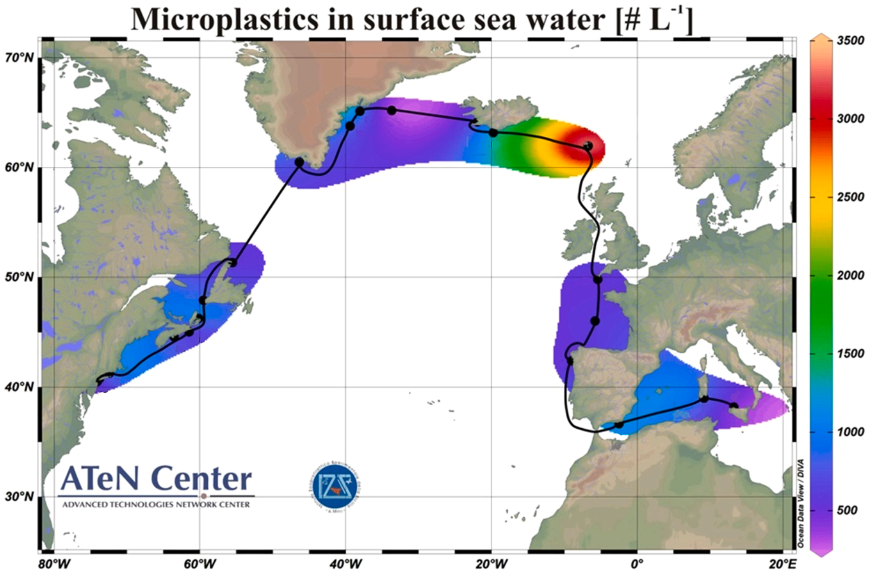

Fig. 3. Graphic representation of the microplastic concentration (MPs/L) of 2019 sampling, from Palermo to New York (Ice RIB Challenge), obtained using Ocean Data View software.

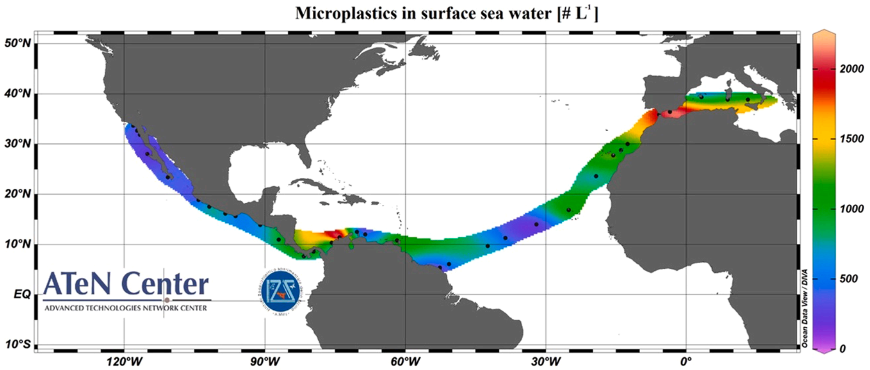

Fig. 4. Graphic representation of microplastic concentration (MPs/L) of 2021–2022 sampling, from Palermo to Los Angeles (Ocean to Ocean RIB Adventure), obtained using Ocean Data View software.

Table 2
Results of the validation of the ICP-MS method carried out.

Lead				
Concentration level (μg/L)	Repeatability (μg/L)	LOD (μg/L)	LOQ (μg/L)	Mean Recovery (%)
0.5	0.05	2.0	2.0	106.7
5	0.12			
50	0.52			
Cadmium				
Concentration level (μg/L)	Repeatability (μg/L)	LOD (μg/L)	LOQ (μg/L)	Mean Recovery (%)
0.5	0.01	0.5	0.5	100.6
5	0.10			
50	0.50			
Arsenic				
Concentration level (μg/L)	Repeatability (μg/L)	LOD (μg/L)	LOQ (μg/L)	Mean Recovery (%)
0.5	0.05	1.0	1.0	106.9
5	0.20			
50	1.30			
Chromium				
Concentration level (μg/L)	Repeatability (μg/L)	LOD (μg/L)	LOQ (μg/L)	Mean Recovery (%)
0.5	0.02	5.0	5.0	96.6
5	0.25			
50	1.12			

classified into three different types based on their shape: filaments, films or plane geometry, and granules or tridimensional fragments representing 95.2 %, 3.6 % and 1.2 % of the total, respectively.

The highest part of MP exhibits a filament shape (Fig. 5) so we can hypothesize that the main sources of marine pollution might be fishing, industrial production of textiles, and domestic and laundry waste; significant origins are fiber and microfibers from synthetic clothes because of washing (Mishra et al., 2019).

Films mainly originate from packaging, plastic bags, wrapping, and beverage bottles, while the source of granules and tridimensional fragments are almost microbeads from personal care products and secondary MPs coming from the degradation and breakdown of large plastic. Plastic, indeed, fragmentises into smaller pieces by aging. Photodegradation and/or oxidative stress make brittle plastics, so they are more easily reduced into microplastics (Dimassi et al., 2022). Besides, plastic fragments are usually smaller near the coast respect to offshore ones, probably due to marine organisms' activity and abrasion with waves, sand, and rocks. Representative pictures of MPs coming from optical analysis are also shown in Fig. 6.

Polarised light microscopy was used to improve the check of MPs (Sierra et al., 2020; Tong et al., 2021); the sample pretreatments allow us to analyse MPs in the filters without interference from other components in the sample that initially is likely to be present, such as impurities, biological materials, etc. Birefringence can occur in optically anisotropic polymeric materials and or stress-induced birefringent polymeric materials. Pictures obtained by Dino-Lite Edge digital microscope equipped with polarized light, of standard samples treated in preliminary validation analysis method, pre- and post-treatment respectively, are reported in Fig. 7.

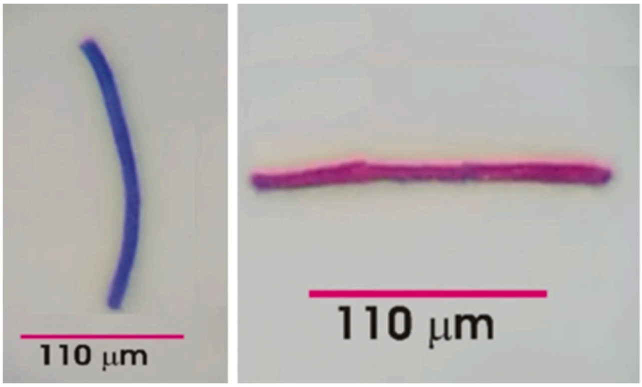

Fig. 5. Microplastic fibers obtained by optical microscope.

MPs exhibit brightness and color changes in cross-polarized light. It is important to underline that any impurities traces still present, exhibit different behavior from microplastic when exposed to conventional light or polarized light. SEM high-resolution images are reported in Fig. 8. The irregular morphology of MPs suggests a fragmentation of a larger plastic debris while, cracks on the surface and fraying of filament shape advise polymer aging. Smooth surfaces, indeed, are likely associated with manufactured fibers (Reisser et al., 2014; Wang et al., 2017).

3.2. *Trace metals and metalloids*

Accurate determination of trace metals and metalloids in seawater is important to explore the contamination in aquatic ecosystems. The trace metals and metalloid levels found in the samples examined are shown in Table 3.

Pb and Cr were highly variable at most sampling sites whereas As generally showed an intermediate degree of variation. No Cd levels were found in all the samples examined. Highest Pb values were found in the Mediterranean sampling sites, with a maximum of 17.675 μg/L in Sardinia coasts (Site 23), up to 68 times higher than what was found by Manfra and Accornero (2005) in central Mediterranean. Our results are surprising if we consider the legislation that limited the consumption of leaded petrol applied in European countries since the 1970s. However, a statistical simulation of the superficial and lower layers of the Mediterranean conducted at the end of the 1990s (Tian and Ruiz-Pino, 1995) predicted an increase in Pb concentrations in the entire basin, confirmed by the high concentrations of this element found in small pelagic fish and in other marine organisms (Cammilleri et al., 2020; Copat et al., 2012; Tigano et al., 2009). In particular, the levels found along the coasts of Sardinia are certainly subject to the oceanographic nature of the site. The vertical migration of Pb was collectively influenced by the impact of vertical water movement, input from sources, and water exchange. Additionally, the influence of marine currents on the vertical migration of Pb in the marine bay was noteworthy (Zhang et al., 2018). Significantly high Pb levels in South Sardinia were also found by Schintu et al. (2008). Schintu and Degetto (1999) found extremely high concentrations of Cd and Pb in the sediments of the harbour as a result of smelting activities, highlighting the risk of remobilisation of Cd and Pb into the marine environment.

Similarly, to Pb, the highest Cr levels were found in Mediterranean sites with a maximum of 52.15 μg/L in the North-western coasts of Sicily (Southern Italy). Regarding As, very high concentrations were found on the coasts of North America, near the San Diego Bay (USA, sites 54, 55 and 56). Previous studies on surface waters and Pacific oysters assumed that higher levels of total arsenic in this area might be partly attributed to groundwater seepage (Ford et al., 2008). Arsenic concentration varied widely ranging between 35.52 and 101.13 μg/L, up to 168 times higher than what was found in the literature (Lahijanzadeh et al., 2019; Luo et al., 2022; Raknuzzaman et al., 2016; Zhang et al., 2017, 2016). The general data of the present study reveal a greater presence of trace metals and metalloids in the sampling sites closer to the coasts compared to samples taken in the open sea because of the emissions from anthropogenic activities.

3.3. *Multivariate analysis and correlation between heavy metals, metalloids and microplastics*

The PC1 vs. PC2 score plot and loading plot reporting the seawater samples colored by sampling site are shown in Figs. 9 and 10. The PC1 opposes sites characterised by a high level of trace elements vs microplastic. In the score plot, PC1 separates sites such as 48, 51, 56, 55, 54

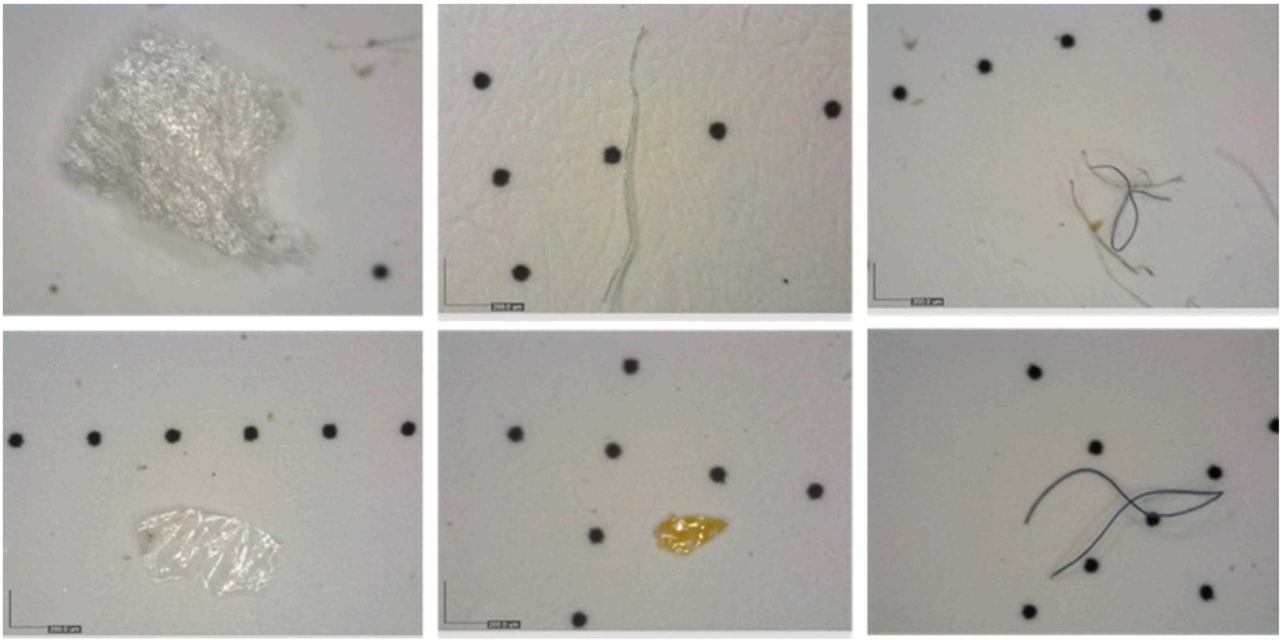

Fig. 6. Microplastics detected in the seawater samples examined obtained by Dino-lite microscope, using polarized light.

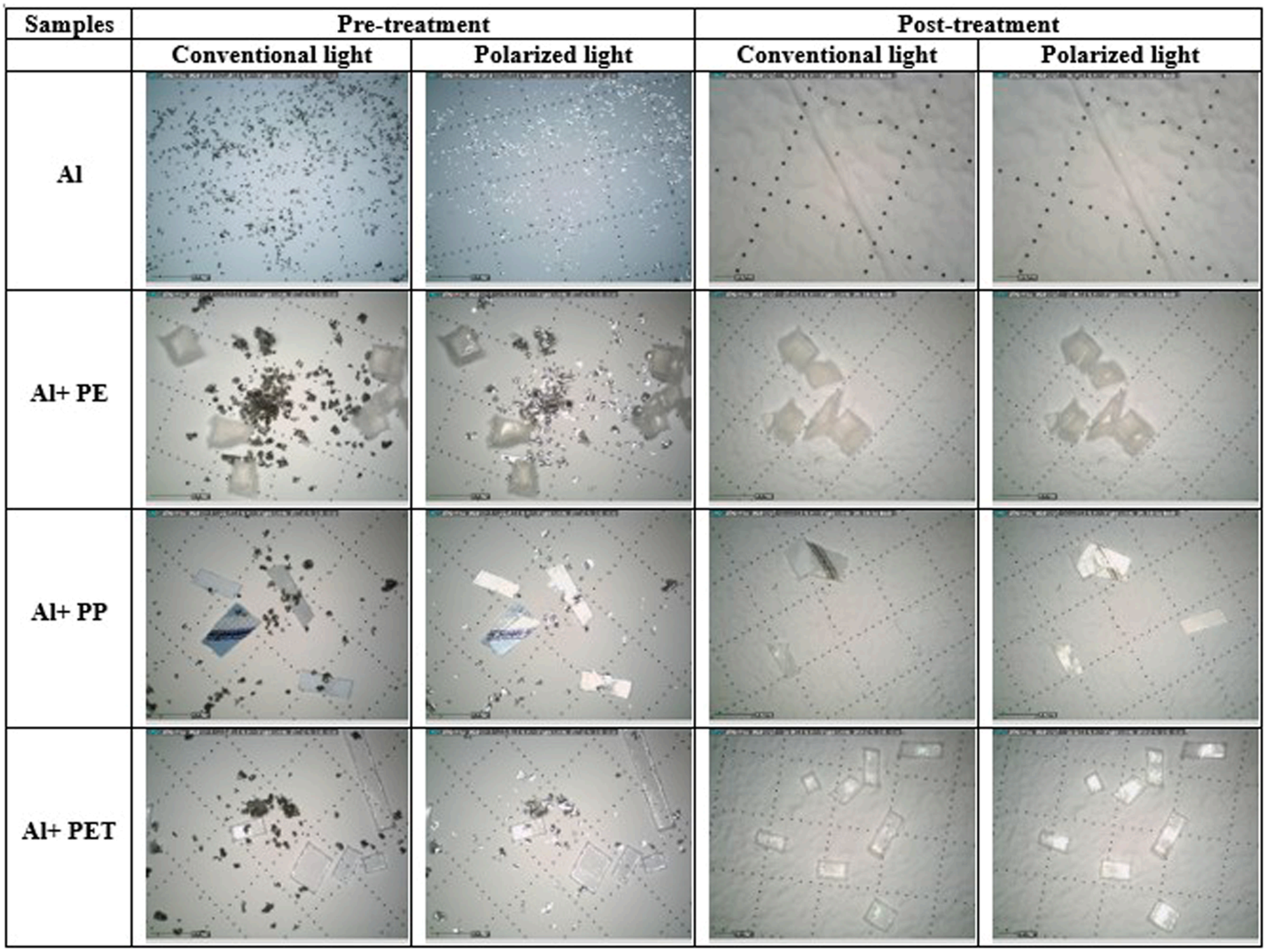

Fig. 7. Pictures of microplastics and aluminum standard samples using polarized light or conventional light, pre- and post-treatment.

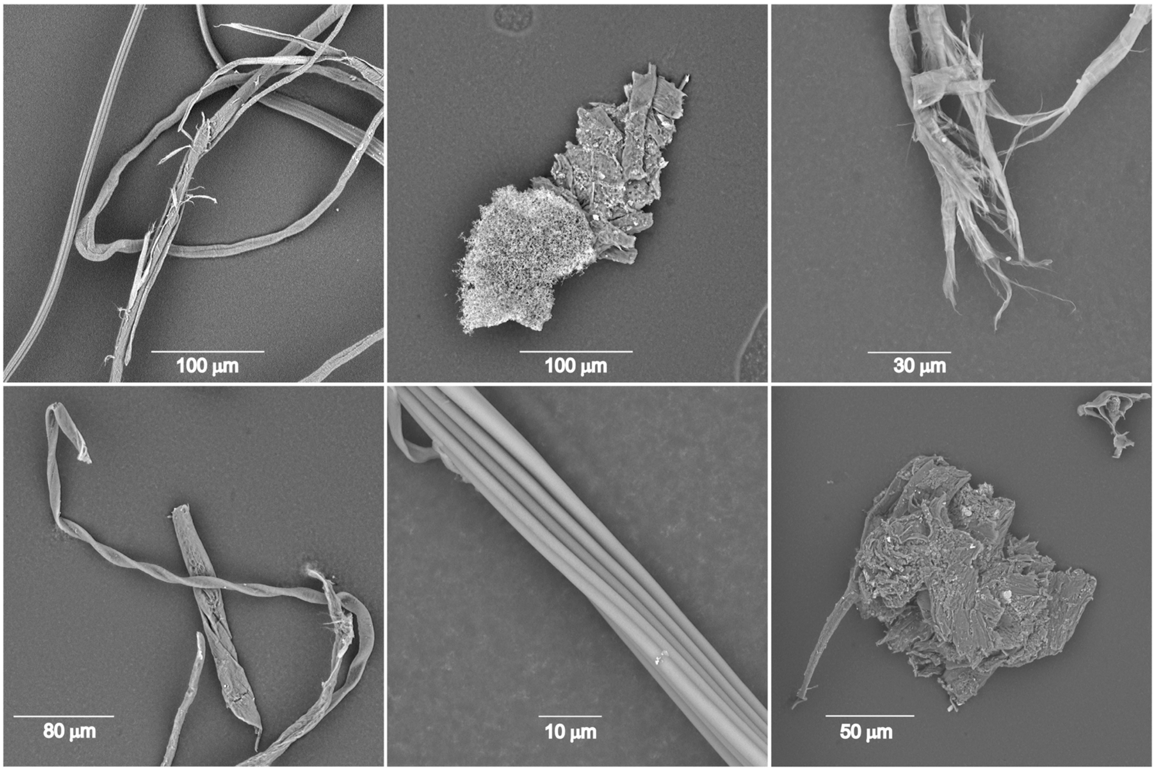

Fig. 8. SEM images of the microplastic examined at different magnitudes (from 790X to 4400X).

Table 3
Trace metals and metalloids concentrations (μg/L) of the seawater samples examined sorted by sampling site. n.d. = not detected.

	Cr	As	Cd	Pb
Site 22	52.15	66.77	n.d.	13.35
Site 23	29.52	55.7	n.d.	17.67
Site 24	25.42	64.12	n.d.	9.62
Site 25	16.52	67.67	n.d.	10.37
Site 26	23.97	38.72	n.d.	8.32
Site 27	16.7	66.15	n.d.	8.37
Site 28	21.82	72.22	n.d.	11.72
Site 29	21.87	75.85	n.d.	15.75
Site 30	10.57	69.32	n.d.	9.82
Site 31	19.35	35.52	n.d.	9.72
Site 32	35.12	76.52	n.d.	9.32
Site 33	4.92	68.4	n.d.	8.32
Site 34	7.27	58.9	n.d.	8.32
Site 35	23.92	68.15	n.d.	10.15
Site 36	18.95	67.67	n.d.	9.2
Site 37	13.55	57.15	n.d.	7.6
Site 38	21.02	73.35	n.d.	11.82
Site 39	21.52	67.4	n.d.	10.42
Site 40	18	80.02	n.d.	10.6
Site 41	10.42	67.45	n.d.	8.65
Site 42	16.27	59.5	n.d.	9.37
Site 43	33.65	59.15	n.d.	11.55
Site 44	18.52	73.2	n.d.	10.22
Site 45	15	63.67	n.d.	9.92
Site 46	26.4	70.2	n.d.	13
Site 47	24.77	65.7	n.d.	11.4
Site 48	28.65	78.42	n.d.	12.17
Site 49	21.72	70.05	n.d.	11.62
Site 50	22.57	62.02	n.d.	9.3
Site 51	31.4	77.42	n.d.	15.3
Site 52	6.45	64.67	n.d.	10.2
Site 53	40.12	81.55	n.d.	10.77
Site 54	8.45	97.7	n.d.	11.27
Site 55	11.87	101.12	n.d.	12.9
Site 56	32.72	89.57	n.d.	12.02

with positive coordinates, from sites 33, 34, 52, 37, with negative coordinates.

The former group shares high values of As and Pb and low values of microplastic, indicating significant trace elements presence, particularly in the Channel Islands of California. The latter group shows low values of Pb and Cr, indicative of lower trace elements contamination, as seen in the North Atlantic Ocean. The PC2, which accounts for 32.6 % of the variability, further distinguishes sites. PC2 separates sites 26, 43, 22, and 31, with positive coordinates, from sites 33, 34, 52, and 37, with negative coordinates.

The positive group has high values of microplastic and Cr and low values of As, highlighting significant microplastic and chromium presence, particularly in the Mediterranean Sea. The negative group shows low values of Pb and Cr, similar to the North Atlantic Ocean, indicating lower contamination levels. The loading plot shows that Pb and As have strong positive loadings on PC1, while microplastic has a strong negative loading. For PC2, Cr and microplastic have positive loadings, whereas As has a negative loading. This highlights the influence of these elements on the respective principal components.

The results of the Spearman's test revealed a significant positive correlation between Cr and Pb (Spearman correlation = 0.5, Bonferroni corrected p = 0.013; Fig. 11), and a significant positive correlation between As and Pb (Spearman correlation = 0.48, Bonferroni corrected p = 0.018). No significant correlations were found between trace elements and microplastics. We suppose these findings are due to environmental factors, different sources, or different chemical and physical properties among metals and MPs. As stated by Liu et al. (2021a) microorganisms play a crucial role in the interaction network involving heavy metals and microplastics in aquatic environments. Although many studies focus on microplastics and heavy metals, detailed explanations of the role of microorganisms in their interactions are still lacking. Furthermore, factors such as temperature pH, salinity, dissolved organic matter (DOM), polymer type and particle size influence the interactions between microplastics and heavy metals, impacting their bioavailability and, subsequently, their bioaccumulation potential in

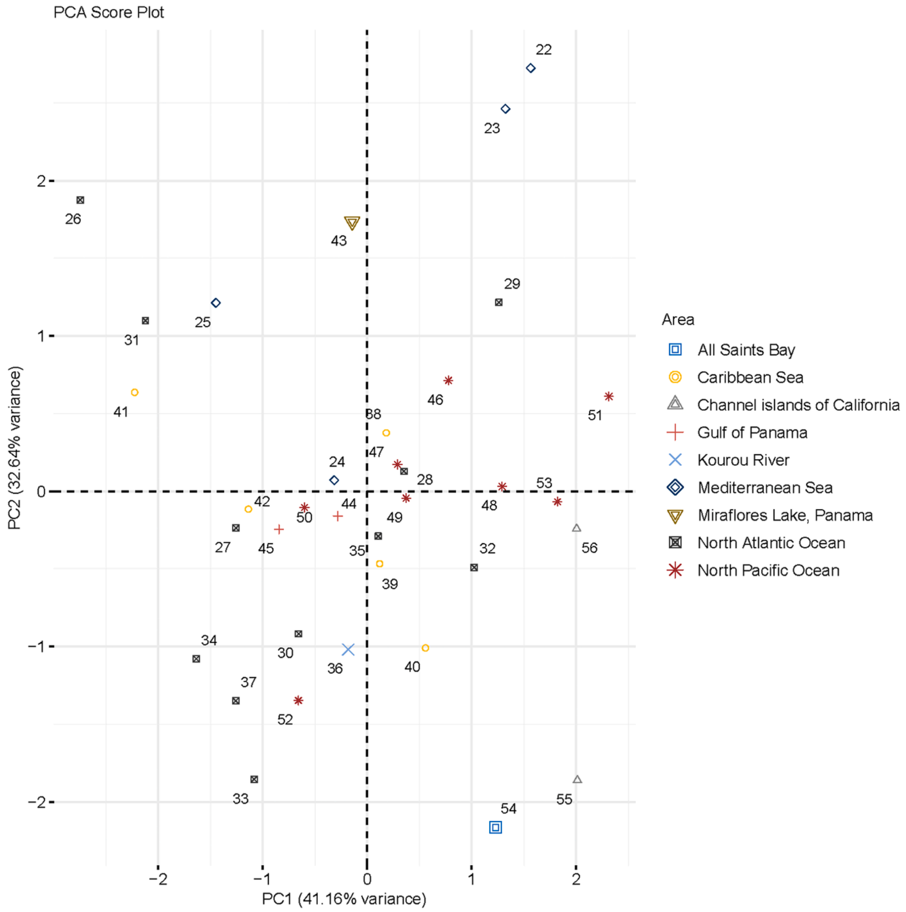

Fig. 9. PC1 vs PC2 score plot of microplastics, heavy metals and metalloids contents of the seawater samples, sorted by sampling site.

organisms (Ha et al., 2023). Only specific heavy metals (e.g., Cu, Ni) exhibit a positive correlation with the specific surface area of MPs, suggesting that interactions between heavy metals and MPs can vary. This variability may explain the absence of a consistent correlation (Liu et al., 2022a). Finally, heavy metals can desorb from MPs under different environmental conditions, such as temperature fluctuations or the presence of sediments, adding complexity to the relationship between MPs and heavy metals in seawater (Zhang et al., 2023). Therefore, the absence of correlation between microplastics and heavy metals can be attributed to the complex interactions influenced by various environmental factors and the sources of these pollutants. The ecological impact of their presence in sea water highlights the need for comprehensive methods that enable rapid and accurate sampling, characterisation, analysis, and evaluation of these composite pollutants and their combined risks.

4. Conclusions

The present study analyses a very extensive marine sea routes using a unique approach for sampling and evaluating MPs amounts, providing a global idea of the marine environment's status.

Data collected in this study, in terms of microplastics and heavy metals and metalloids concentration, suggest us that marine pollution is an issue of concern. Microplastics appear in all the analysed sites with different shapes and filaments are the most abundant. Unexpectedly higher value for MPs concentration was recorded near the Faroe Islands, in the North Atlantic Ocean, in the Sea of Magdalena department in Colombia, and the Strait of Gibraltar, while high Pb and Cr values were found in the Mediterranean Sea. Severe concentrations both for MPs and TM and Ms have been noted in coastal waters and are directly related to the intensity of human activities. Only in few locations in the open sea and near Greenland, the situation is not yet alarming. Besides, a trend to increase in the number of microplastics due to accumulation emerged. As noted by our results, analysing the correlation between MPs and metal species and/or combining the collected data with the analysis of factors influencing pollutant concentrations could be the topic of future work. The diversity of experimental approaches and materials used to analyse microplastics-metals interaction and lacking of conceptual models for hypothesis creation have hindered progresses in the ability of understanding and predicting the microplastics-trace element interaction process (Binda et al., 2021).

Environmental authorities and administrations must implement measures to reduce contamination from fishing, chemicals, textiles, and performing circular economy action plan. So, limitations in single-use plastic, precautions in fishing activities and in the fiber and textile manufactures like suitable treatment techniques, a total ban of microbeads from sunscreen and personal hygiene products, and conducting of environmental monitoring programs, are, for example, some of the measures that would be taken against ecological risk and to mitigate marine environmental damage.

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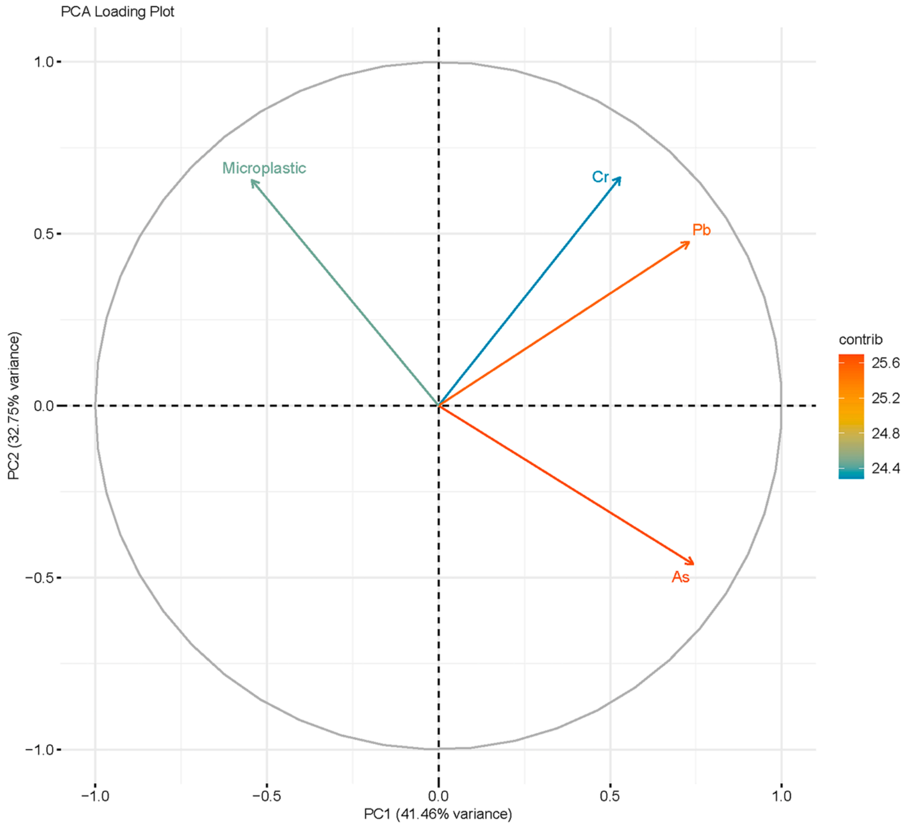

Fig. 10. PC1 vs PC2 loading plot of microplastics, heavy metals and metalloids contents of the seawater samples examined, sorted by sampling site.

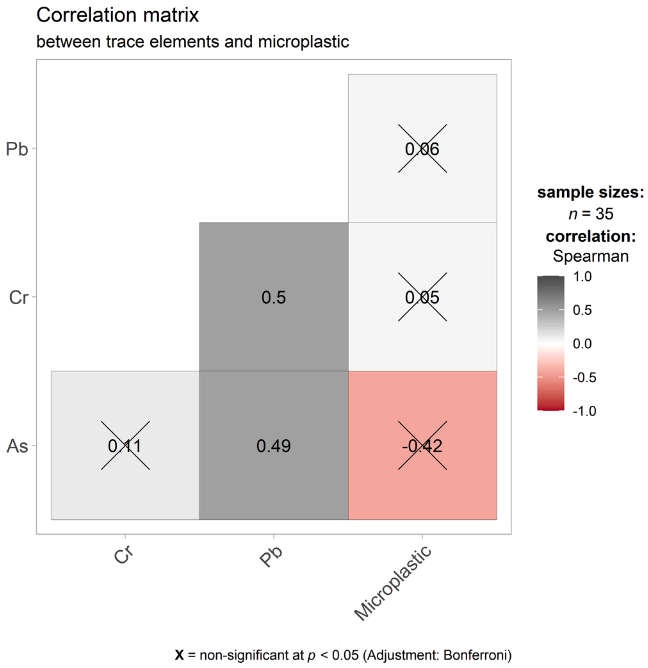

Fig. 11. Correlation plots between trace elements and microplastics of the seawater samples analysed.

CRediT authorship contribution statement

Elisabetta Morici: Writing – original draft, Visualization, Validation, Investigation, Conceptualization. **Vincenzo Monteverde:** Validation, Supervision, Resources. **Sergio Davì:** Resources, Project administration, Funding acquisition, Conceptualization. **Paola Galluzzo:** Methodology, Formal analysis. **Vincenzo Ferrantelli:** Visualization, Supervision, Project administration, Funding acquisition, Conceptualization. **Luigi Tranchina:** Software, Methodology, Data curation. **Francesca Terracina:** Visualization, Resources, Methodology, Investigation. **Sergio Scirè:** Software, Methodology, Formal analysis, Conceptualization. **Francesco Bonomo:** Software, Investigation, Formal analysis. **Salvatore Dara:** Writing – review & editing, Visualization, Supervision, Resources, Project administration. **Gaetano Cammilleri:** Writing – review & editing, Writing – original draft, Validation, Conceptualization. **Francesco Galluzzo:** Software, Data curation. **Mariano Licciardi:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gaetano Cammilleri reports administrative support, statistical analysis, and writing assistance were provided by Istituto Zooprofilattico Sperimentale della Sicilia. Gaetano Cammilleri reports a relationship with Istituto Zooprofilattico Sperimentale della Sicilia that includes: employment. If there are other authors, they 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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