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Examining Microplastics Along the Calabrian Coastline: Analysis of Key Characteristics and Metal Contamination

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Abstract: Plastic pollution is a major concern today. Microplastics (MPs), due to their small size, can enter the food chain and cause serious harm to living organisms. The Mediterranean Sea is the sixth largest accumulation area for plastic waste, including MPs, worldwide. In this study, we analyzed the distribution, shape, color, size, and polymer composition of MPs (having dimensions between 330 µm and 5 mm), collected from the water surface in six areas along the Calabrian coast, Italy. A prevalence of polyethylene was detected, with higher concentrations of MPs found in the Gioia Tauro and Cetraro areas. Additionally, heavy metals were identified within the MPs, suggesting that these particles could act as environmental carriers of such elements into the food chain.

Keywords: plastic pollution; microplastic polymeric composition; Mediterranean Sea; Calabrian coast; heavy metals

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1. Introduction

Today, plastic pollution represents one of the main environmental concerns worldwide due to its distribution (there is no area of the planet immune to this problem) and permanence in ecosystems; and it is estimated that at least 5.3 trillion plastic particles are currently floating in the seas [1]. The Mediterranean Sea is the sixth largest accumulation area of floating marine plastic waste, and this is due to its hydrodynamics. It is in fact a semi-closed convective basin and this structure determines not only the maintenance of local plastic pollution, but also the entry of floating waste from the Atlantic Ocean [2–4]. The main origin of these marine contaminants is recognized to be litter on beaches and coasts, fishing activities, and, most importantly, the contribution of rivers carrying municipal wastewater discharges [5–10]. The main problem is that the biodegradation of plastics in marine waters is extremely slow; this causes them to be transported over long distances, ensuring that plastic pollution reaches even the most remote areas of the planet. Furthermore, the salinity of the water, solar radiation, and mechanical degradation determine the reduction of plastic waste into increasingly smaller fragments, favoring interactions with the biota [11–14]. The continuous process of the fragmentation of plastic leads to the formation of very small particles called microplastics (MPs). This term defines particles with dimensions between 300 µm and 5 mm [15,16], although, currently, the range 1 µm–5 mm is accepted [17,18].

Precisely as a result of their small size and their resistance, these substances, together with all the toxic substances they contain, are easily ingested by aquatic and terrestrial organisms, thus entering the food chain, and reaching humans [19–22]. It must be taken into consideration that MPs are distributed at the level of surface waters, the water column, coastal sediments, and deep waters, and this compartmentalization depends on their polymeric composition, and, therefore, on their density. Consequently, they will have different interactions with aquatic organisms [23]. Many studies have highlighted how MPs have been found in various foods such as beer [24], honey [25], sea salt [26], canned sardines [27], mineral water [28], and tap water [29]. This obviously poses a risk to human health, both as a vehicle for accumulated toxic substances and for intrinsic additives.

Many studies have shown how plastics are able to absorb molecules derived from drugs and antibiotics [30] and heavy metals [31]. Plastics are carriers of metals, both those that are adsorbed from the surrounding environment and those that are used in the plastic-manufacturing process itself as plasticizers, stabilizers, color pigments, fillers and extenders, flame retardants, blowing agents, antioxidants, impact modifiers, lubricants, and antimicrobial agents [32,33]. Heavy metals are elements with a high density compared to that of water, and, since toxicity and density are related, they are capable of inducing toxicity at low levels of exposure. In recent years, the public health concern associated with environmental contamination by these metals has grown [34]. Humans are exposed to toxic metals that come from various industrial, agricultural, domestic, and technological processes. It has been observed that natural phenomena such as weathering and volcanic eruptions are sources of pollution, while metal processing in refineries, coal burning in power plants, oil combustion, nuclear power plants, microelectronics, the conservation of wood, and paper processing are some of the important industrial sources [35]. Some of these metals such as cobalt (Co), copper (Cu), chromium (as Cr(III)), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn) are essential for the biological functions of plants and animals; however, at high levels, they interfere with metabolic reactions in organism systems and are toxic. While other heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), chromium as Cr(IV), uranium (U), or arsenic (As) are not useful for living organisms and they are extremely toxic and are capable of reducing plant growth due to the reduced photosynthetic activity, reduced mineral nutrition, and reduced activity of essential enzymes. Furthermore, they could lead to cancer in humans; in fact, these toxic metals can accumulate in the body if consumed with contaminated foods through the food chain and become risky to health [36].

This study aimed to monitor the Calabrian (Italy) coastline to assess the quantity and characteristics of MPs, their composition, and heavy metals they may carry.

For this purpose, MPs (small and large microplastics) has been sampled in six areas on the Calabrian, more specifically, three stations on the Ionian coast and three stations on the Tyrrhenian coast. Microscopic observations made it possible to make a count of particles in each collected sample, as well as to identify the color, the shape and the size of each microplastic. Infrared spectroscopy allowed us to identify the polymeric composition, while, by means of electronic microscopy coupled with energy-dispersive spectrometry and inductively coupled plasma-mass spectrometry, it was possible to identify the presence of heavy metals carried by MPs.

2. Materials and Methods

2.1. Study Area

The microplastic samples analyzed were taken from the coasts of the Calabria Region, south of the Italian peninsula, and the sampling areas of the Operational Plan of the Marine Strategy of Calabria of the Regional Agency for Environmental Protection (ARPA) were used [37]. Sampling sites were chosen both on the Ionian Coast and on the Tyrrhenian Coast, for a total of 6 sites. The choice of areas was made based on certain factors, such as the distance from direct input sources, such as river mouths, port facilities, significant urban settlements, or accumulation areas for local hydrodynamic conditions. For each area, samples were taken from three distances from the coast, 0.5, 1.5, and 6 nautical miles (M). From north to south, the sampling areas are the following: Mouth of the Crati River (Cosenza), Mouth of the Neto River (Crotone), and Mouth of the Corace River (Catanzaro) for the Ionian Coast; and Cetraro (Cosenza), Vibo Marina (Vibo Valentia), and Gioia Tauro (Reggio Calabria) for the Tyrrhenian Coast (Figure 1). The sampled areas are part of the monitoring activities conducted since 2015 under the framework of the Community Directive 2008/56/EC Marine Strategy, carried out by the Marine Strategy Regional Center (CRSM) of ARPA Calabria.

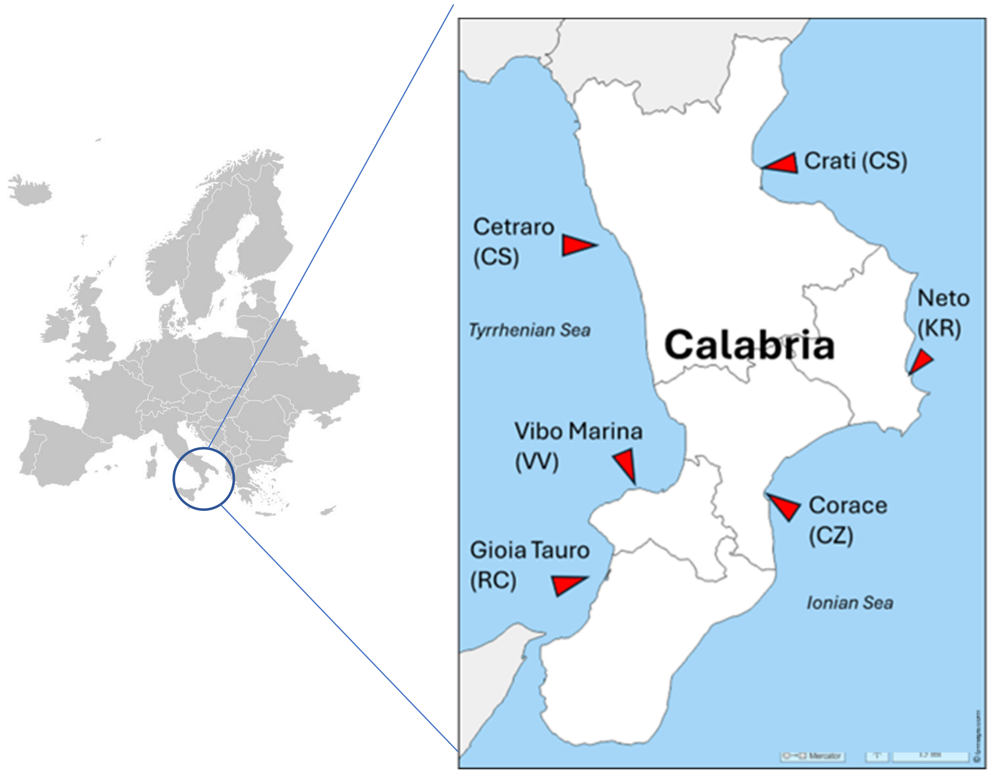

Figure 1. Sampling areas on the Ionian Coast (Crati, Neto, and Corace) and on the Tyrrhenian Coast (Cetraro, Vibo Marina, and Gioia Tauro).

2.2. Sampling

The MP sampling was carried out in March 2022 and June 2022 as described in [37]. MPs were sampled using a 2.5 m-long manta trawl with a mesh size of 333 µm with a rectangular frame opening of 25 × 50 cm. The manta ray was towed to the surface, against the current, for about 20 min from the ship's starboard side at an average speed of 2.5 knots. To avoid wake turbulence, all sampling was taken from the starboard side of the vessel, beyond the bow wave. After each haul, the net was rinsed with sea water, and, subsequently, the collected material was screened through two stacked stainless-steel sieves with a mesh void of 5 mm and the underlying one of 300 µm. The accumulated residues were transferred to a glass vial with 70% alcohol and stored at room temperature. For each area, 3 samples have been collected (one at 0.5 M, one at 1.5 M, and one at 6 M from the coast). The number of particles collected from each sampling has been divided by the surface area (distance towed x horizontal dimension of the frame) to obtain the abundance per square meter, and divided by the volume (distance towed × surface of the frame) to obtain the abundance per volume.

2.3. Characterization

The samples were visually inspected under a stereomicroscope (Zeiss Axiolab microscope equipped with a digital camera to acquire images), and, using laboratory tweezers, suspected MP particles were carefully collected, placed in a Petri dish, and washed with double-distilled water to separate them from other organic residues. The criteria taken into consideration to classify a potential MP particle are the following: (1) absence of cellular or organic structures; (2) a homogeneous thickness across the particles; and (3) homogeneous colors. Once isolated, potential MPs were counted and photographed, and their maximum length (mm) was recorded, considering the largest diameter, shape, and color. All samples were examined and double-checked by two different researchers to confirm that MP counts were consistent and conservative. In order to confirm the polymeric nature of the samples (suspected MPs) and to allow specific identification of the different types of plastic, samples were analyzed by FTIR investigations; for this purpose, a PerkinElmer Spectrum 100 spectrophotometer equipped with an attenuated total reflectance (ATR) accessory has been used. Infrared spectra were recorded in ATR mode, in the range of 500–4000 cm^{-1} with a resolution of 4 cm^{-1}. After background scans, 16 scans per particle were performed and CO_2 interference was removed for clarity. The obtained spectra were then compared with a library of standard polymer spectra and accepted with a similarity threshold greater than 70%. All MPs collected in the first sampling were analyzed by FTIR, while, regarding MPs from the second sampling, only 15 were analyzed for each transect (five for each of the three sampling distances from the coast). After confirming the polymeric nature of the samples, to detect the potential presence of metals on their surface, they were analyzed by scanning electron microscopy (SEM), using a Zeiss Crossbeam 350 microscope, equipped with an energy-dispersive spectrometer (EDS). We analyzed 60 MPs collected in March (10 for each transect), and 6 MPs collected in June (1 for each transect) by SEM-EDS.

All samples were grouped in Ionian and Tyrrhenian coast and analyzed by ICP-MS. The samples were subjected to acid digestion before analysis. Microwave-assisted digestion was performed using a One-Touch MARS6 (CEM Corporation, Charlotte, NC USA) with tetrafluormethaxyl (TFM) vessels. The operating conditions are reported in Table S1. For digestion, 50 mg of each sample was placed in the vessels with 2.3 mL of HNO_3 (65%) and 1 mL of H_2O_2 (30%). After the digestion program, the samples were diluted with ultrapure water obtained from a Milli-Q system (Millipore, Bellerica, MA, USA), then analyzed by ICP-MS. A Perkin Elmer Elan DRC-e mass spectrometer (Toronto, ON, Canada) was used. Instrumental parameters are described in Table S2. For statistical tests, IBM SPSS software has been used. The Shapiro–Wilk test was performed to evaluate the normality of the abundance data (H_0, null hypothesis: population is normally distributed). Since not all data were normally distributed, the Kruskal–Wallis non-parametric test was employed to assess the significance of variations among particle abundances (H_0, null hypothesis: particle abundances of each sample come from the same population). Additionally, results from the size, shape, color, and composition analysis were analyzed using the chi-square test (H_0, null hypothesis: size/shape/color/composition classes ratios are independent from the sampling site and/or sampling period).

3. Results and Discussions

3.1. Distribution of Microplastics

In Table 1, the results about the counting of the sampled MPs are summarized. Taking into account all samples, the average particle abundance is equal to 0.06 particles/m^2 (0.24 particles/m^2); it is worth noting that there is a great variability in this parameter ranging from 0.01 to 0.3 m^2. However, this value is lower than that obtained after the sampling campaign in 2021 in the same areas (0.13 particles/m^2) [38]. The abundances, calculated as an average of all results from each coast (Figure 2), suggest that there is not a significant difference in the number of MPs among the Tyrrhenian and Ionian coast in the two sampling periods; this is confirmed by a statistical test (Table S3). Looking at the abundance values in Table 1, it is quite evident that samples collected at Corace and Neto (Ionian side) showed a lower abundance in June with respect to March. Looking at the single values calculated for each area, abundances rarely exceed 0.10 particles/m^2, except for Cetraro (up to 0.16 particles m^2) and Gioia Tauro (up to 0.30 particles m^2). This could be explained by the fact that two important commercial ports are located in Cetraro and Gioia Tauro; it is a bit surprising that Vibo Valentia has a lower abundance, despite being located near another commercial port. This indicates that the presence of ports is not the only element that can justify the high presence of plastic; in fact, the surface circulation of the Mediterranean Sea must also be taken into consideration [39–44]. The Mediterranean Sea is a semi-enclosed basin, connected to the Atlantic Ocean through the Strait of Gibraltar and this hydrodynamic model determines the entry of plastic pollutants from the ocean [43,45]. This is a less saline current, which, once it enters the basin, is diverted to the right by the Coriolis Force, skirting all the coasts in an anti-clockwise direction. Added to this phenomenon are also the surface winds that blow towards the Tyrrhenian coast, contributing to the accumulation of material. Precisely for this reason, the largest accumulation areas are the Tyrrhenian coast, and, particularly, the Strait of Messina, which acts as a funnel for marine waste. On the Ionian coast, the opposite phenomenon is observed; that is, the winds and currents tend to move the waste towards the open sea. It is, therefore, normal to attribute the difference between its coasts to the marine and atmospheric circulation, which makes the Tyrrhenian Sea an area of accumulation of materials, both local and coming from distant places [46,47].

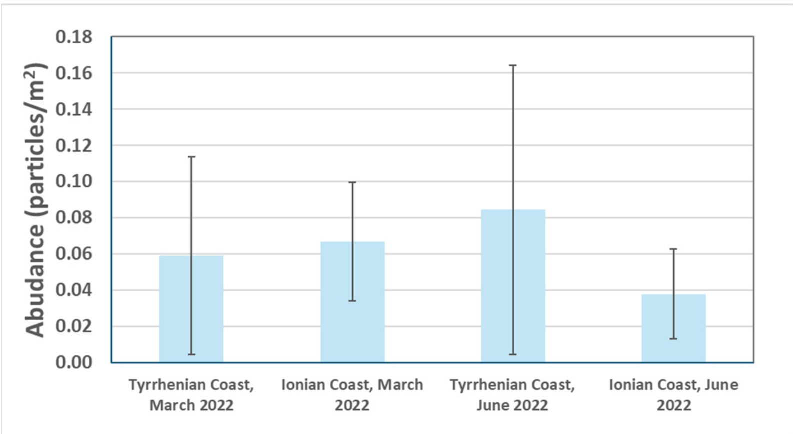

Figure 2. Differences among coasts and sampling periods.

The concentration of MPs on the Calabrian coasts, detected in the present study, is comparable with what was measured in other studies carried out in the Mediterranean Sea (Table 2). However, there appears to be a big difference regarding studies conducted in other areas of the world, in particular, the Atlantic Ocean and the Asian coasts. This difference, however, is obvious, because, globally, waste tends to accumulate in five "ocean garbage patches" located at the North Atlantic, South Atlantic, North Pacific, South Pacific, and Indian levels. The largest of these areas is the Great Pacific Garbage Patch, located between Hawaii and California. The highest percentage of plastic present in this region would derive from sources present in Asia and would reach there through the Kuroshio, also known as the "black current" [48].

Table 1. Quantity and origin of collected MPs.

Sampling Site	Location	Starting Coordinates		Distance from Seashore (Nautical Miles–M)	March 2022		June 2022	
		Latitude	Longitude		N° of Particles	Abundance (particles/m^2)	N° of Particles	Abundance (particles/m^2)
Cetraro	Tyrrhenian Coast	39.50683	15.934	0.5	42	0.04	17	0.02
		39.50083	15.9076	1.5	167	0.16	25	0.02
		39.45016	15.7566	6	29	0.03	40	0.04
Vibo Marina	Tyrrhenian Coast	38.733595	16.089434	0.5	12	0.01	40	0.03
		38.719219	16.099541	1.5	47	0.04	21	0.02
		38.797072	16.038261	6	79	0.07	17	0.01
Gioia Tauro	Tyrrhenian Coast	38.4344	15.87206	0.5	16	0.02	219	0.26
		38.44173	15.85291	1.5	26	0.02	319	0.30
		38.46905	15.76335	6	176	0.14	70	0.06
		Mean values of Tyrrhenian Coast				0.06 ± 0.05		0.08 ± 0.07
Crati River Mouth	Ionian Coast	39.727313	16.541585	0.5	31	0.04	40	0.05
		39.732025	16.561949	1.5	49	0.05	25	0.03
		39.756677	16.652299	6	64	0.10	30	0.04
Neto River Mouth	Ionian Coast	39.200117	17.157133	0.5	32	0.10	15	0.04
		39.202667	17.17865	1.5	41	0.10	18	0.05
		39.198202	17.273467	6	36	0.10	34	0.09
Corace River Mouth	Ionian Coast	38.811868	16.617133	0.5	22	0.02	21	0.02
		38.798977	16.637915	1.5	37	0.04	13	0.01
		38.76624	16.700495	6	51	0.05	12	0.01
		Mean values of Ionian Coast				0.07 ± 0.03		0.04 ± 0.02

Table 2. Microplastic concentrations in sea.

Study Area	MPs Range (mm)	Average Abundance (particles/m^2)	Ref.
Calabrian Coasts	0.33–5	0.06 particles/m^2	This study
Calabrian Coasts	0.33–5	0.13 particles/m^2	[38]
North Western Mediterranean Sea	0.30–5	0.12 particles/m^2	[49]
Western Mediterranean Sea	0.33–5	0.13 particles/m^2	[50]
Western Mediterranean Sea—Adriatic	0.20–20	0.40 particles/m^2	[51]
Mediterranean Sea—Corsica	0.20–2	0.06 particles/m^2	[52]
Central–Western Mediterranean Sea	0.33–5	0.15 particles/m^2	[53]
	MPs Range (mm)	**Main Abundance (particles/m^3)**	
Calabrian Coasts	0.33–5	0.24 particles/m^3	This study
Sardinian Sea	0.33–5	0.17 particles/m^3	[54]
Ligurian Sea	0.20–5	0.49 particles/m^3	[55]
Mediterranean Sea	0.20–5	0.24 particles/m^2	[56]
North Atlantic	0.33–4.75	1.70 particles/m^3	[57]
North-East Atlantic	0.25–5	2.46 particles/m^3	[58]
East Asian Sea	0.35–5	3.70 particles/m^3	[59]
Seto Inland Sea	0.30–5	0.39 particles/m^3	[60]
Arctic Polar Waters	0.30–5	0.34 particles/m^3	[61]
Bohai Sea	0.50–5	0.33 particles/m^3	[62]

3.2. Physical Characterization

The size of MPs is a determining factor for their interaction with marine organisms and for their ingestion. At sea, plastic waste is degraded into increasingly smaller fragments, increasing in number quantity as the size decreases [63].

The size of MPs is a determining factor for their interaction with marine organisms and for their ingestion. [63]. In Figure 3, distribution of the sizes of the identified MPs it is shown. It is clear that the dimension class 1–2 mm is the most abundant in all sampled areas. Such distributions are quite similar with that found by elaborating the 2021 data in the same areas, with the same sampling method [38], but also with other studies in other areas [59,63]. However, due to the sampling methods with a cutoff at 330 microns, there is no chance at all to detect particles smaller than that size. Regarding the upper limit of the distribution, for the sampling of MPs, filters with pores smaller than 5 mm are used; however, samples such as filaments, which have an elongated shape, still manage to pass through the pores even if they are larger in size and this is the reason why plastics were found larger in size. The presence of such sized particles is an alarming factor for ingestion by marine organisms, because, the smaller they are, the higher the probability that they enter the food chain; in fact, the number of particles in the various organisms increases as the dimensions decrease [64,65]. The distributions in Figure 3 have also been tested with the chi-square statistical tool, and the results are reported in Table S4. According to the result, the size classes' abundance depends on the sampling sites and on the period as well.

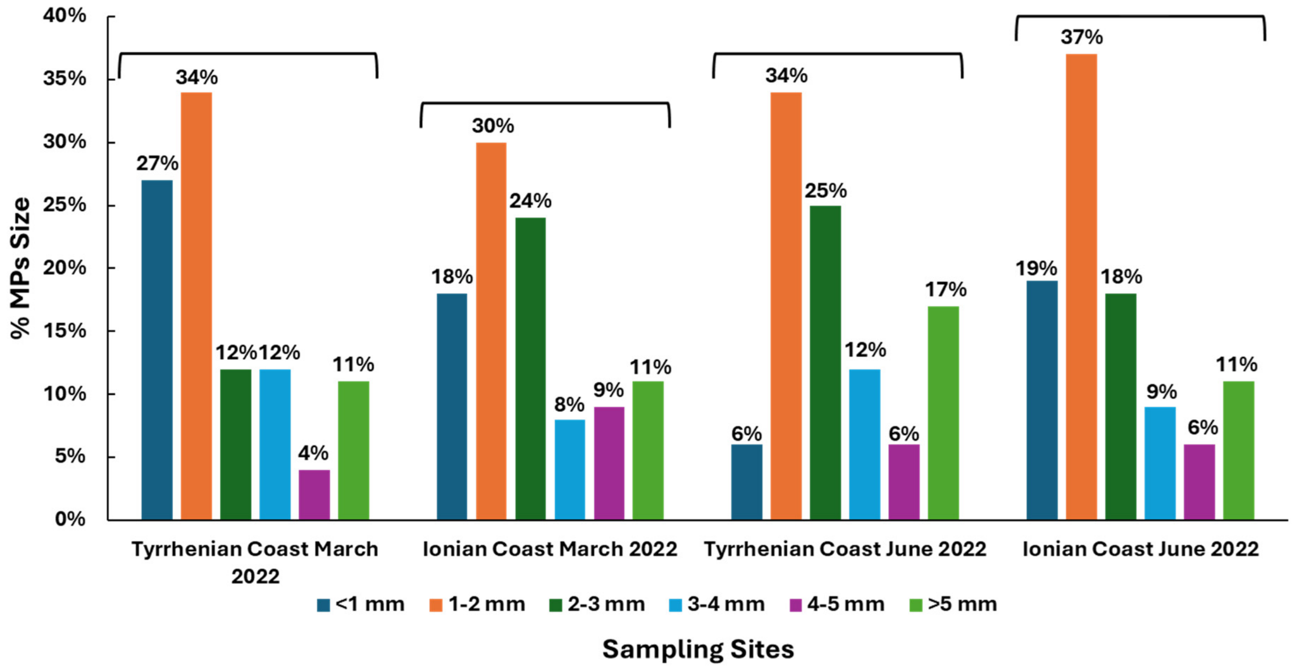

Figure 3. Summary of results of size analysis of MPs.

Another important factor for the classification of MPs is the shape, also implicated in the potentially harmful effects that these substances have. Based on their appearance they are classified into six different forms: fragment, sheet, filament, granule, foam, and pellet [38]. In Figure 4, a summary of the percentages of the shapes detected has been reported.

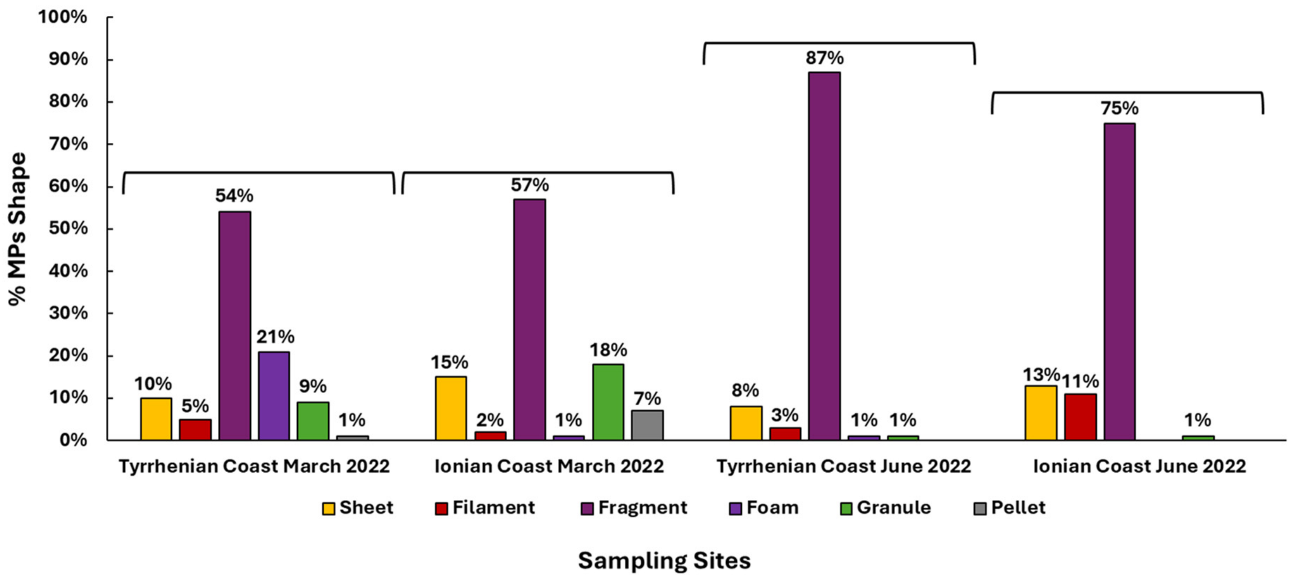

Figure 4. Summary of results of shape analysis of MPs.

The fragment shape is the most abundant in all sampled areas, ranging from 54 to 87%, whereas the sheet shape has an abundance between 8 and 15%. Despite the fragment prevalence, the Chi-square test revealed that such distribution profiles are dependent on the sampling site and on the period (Table S5). The filament shape reaches a maximum of 11% on the Tyrrhenian coast in March, while foam has been significantly found on the Ionian coast in March. Pellets and granules are considered primary MPs, while all the others are defined as secondary as they originate over time through photochemical, mechanical, and biological processes [66]. It could be hypothesized that the fragments derive from hard and packaging plastics, the sheets from plastic bags, and the filaments from fishing lines or textiles [67,68]. Filaments are rather insidious forms (or fragments), because, due to their structure, if they are ingested by aquatic organisms, they can seriously damage both the intestine and the gills with lethal consequences [65,69].

Although the percentage of fibers found is low, their presence could be much higher because they originate mainly from the fragmentation of fishing lines and textiles which, once they end up in the sea, tend to sink, while only a small part remains on the surface. Moreover, fibers also come from wastewater treatment plants effluent as textile residues; then, this source seems to not be the main contributor to the pollution in the area studied.

In Figure 5, the results about the color assessment have been reported. The white and transparent color are the most abundant. Red, blue, green, and other colors are found in relatively low percentages. A statistical test (Table S6) revealed that the color pattern depends on the sampling site and on the sampling period; then, the differences among the distribution are not only ascribable to statistical fluctuations. Colors have been observed that interfere with the ability of marine organisms to distinguish between plastic and natural food [70]. White and transparent MPs are most dangerous ones, because they are more easily mistaken for food by marine organisms and enter the food chain in greater quantities [71]. These latter types of MPs could derive from plastic bags that are used daily, but also from colored particles which, upon entering water and being subjected to various processes, lose their color. Indeed, many samples found had acquired a pale-yellow color and showed rounded corners, due to long environmental exposure. Black, on the other hand, represents one of the most used colors to produce plastics which, precisely because of their color, are very difficult to recycle. This pigment is usually made with carbon black and specific techniques are required for the disposal of plastic waste containing it [72].

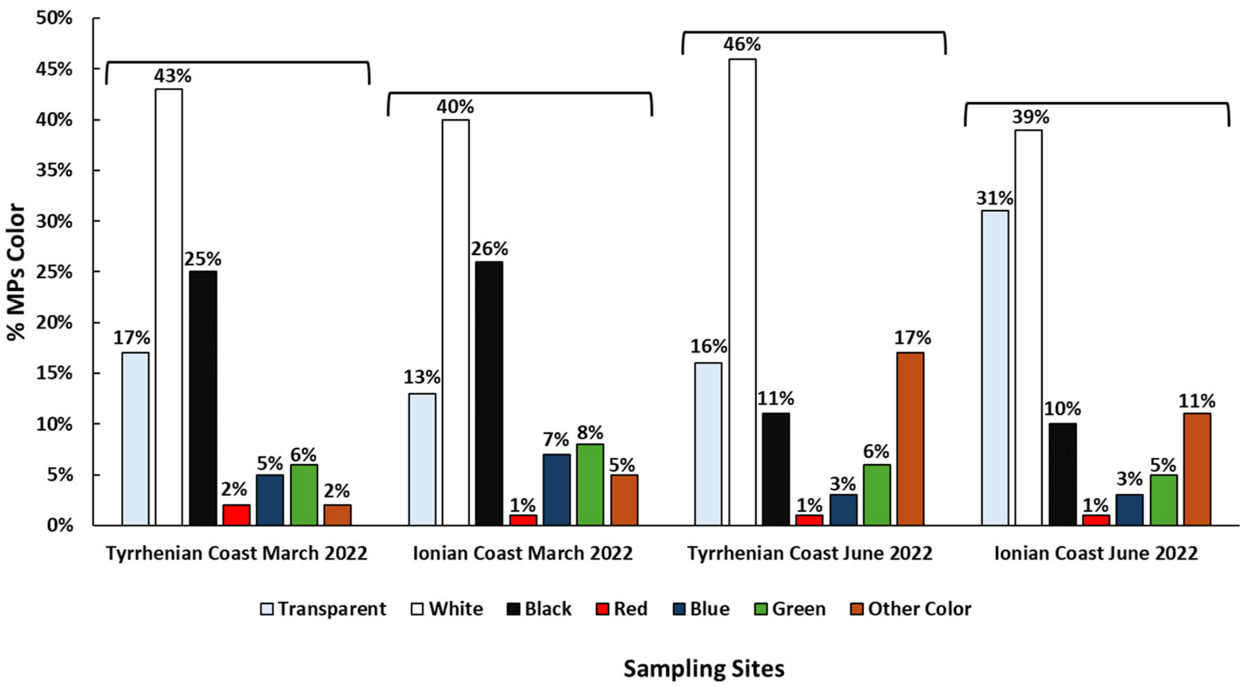

Figure 5. Summary of results of color analysis of MPs.

3.3. Compositional Features

The MP samples were analyzed by ATR FTIR to determine their polymeric composition. The results are summarized in Figure 6, and shows that polyethylene (PE) is the most abundant polymer (67–89%), followed by polypropylene (PP) (11–27%). Moreover, in this case, the chi-square test revealed a dependence of the pattern of polymers on the sampling site/period (Table S7). PE and PP are part of the polyolefin family, thermoplastic compounds produced through the polymerization process [73].

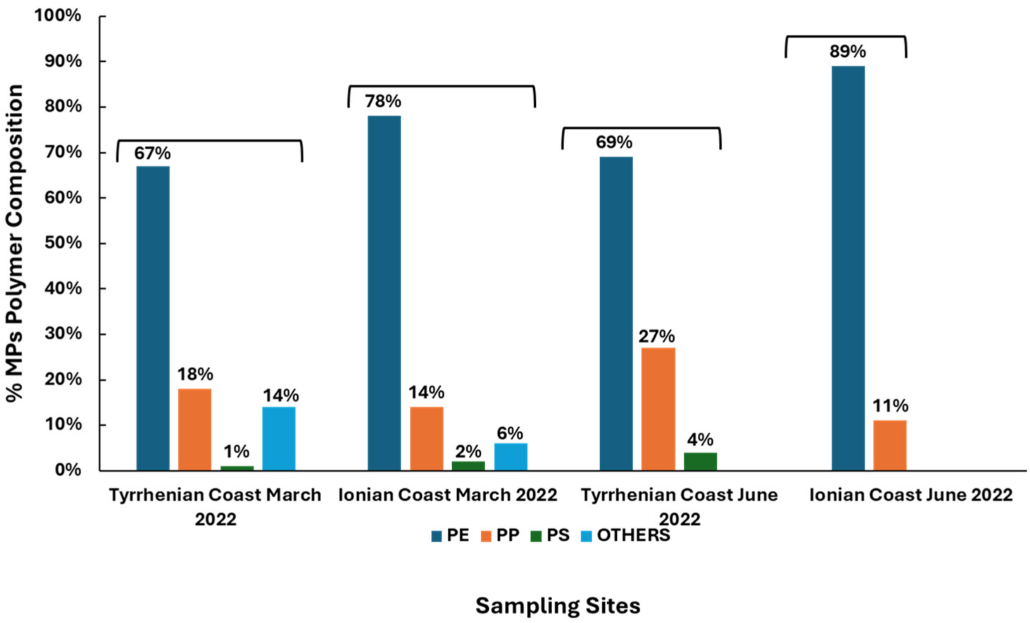

Figure 6. Summary of results of composition analysis of MPs. The term "others" includes the following: polyvinyl chloride, polyethylene terephthalate, polyurethane, acrylonitrile butadiene styrene, and polyamide.

Based on worldwide plastic production data starting from the 1990s [74], an estimation of the production percentages of each polymer has been carried out (Table 3).

Table 3. Estimation of the worldwide production of each polymer, expressed in percentage.

Polymer	%	% of Polymer Particles in This Research
Polyethylene (PE)	33	75
Polypropylene (PP)	20	17
Polyvinyl chloride (PVC)	17	8
Polystyrene (PS)	10	
Polyethylene terephthalate (PET)	7	
Others (i.e., polyurethane, acrylonitrile butadiene styrene, polyamide, and polycarbonate)	13	
Total	100	100

There is an accordance between the worldwide polymer production and the results of this research: in both cases, PE is the most diffused polymers. However, if we consider the percentages, the data do not fit each other, since, in our samples, PE seems to be overestimated with respect to the all-other polymers. To explain this, it must be considered that PE and PP have a lower density than that of water, so they can float on the surface of the water. PS, PET, and other substances have a higher density than that of water, so they tend to sink [75]; however, in this study, polymers with a density greater than that of water were also detected. This is due to the fact that the distribution of MPs in the sea is not determined only by the density, but also by other factors such as wind, temperature, salinity, and hydrodynamic conditions; these variables ensure that even polymers with a high density are able to rise to the surface [76]. Similarly, even a part of low-density polymers, such as PE and PP, can sink and, consequently, not be picked up during sampling. and, therefore, they are the most abundant in the samplings that are carried out [73–80]. In addition, looking at the percentages of PE and PP in Table 3, the ratios seem to be not comparable (PE/PP: 1.65 worldwide production; 4.4 in collected samples). The reason of this discordance is not clear; however, some aspects can be taken into account. PP is less resistant than PE to UV rays and oxidation processes; therefore, once it ends up in the sea, it ages very quickly and breaks down into very small particles, which form nanoplastics; consequently, the concentrations of PP could be underestimated compared to those of PE which is the most abundant substance. Another explanation can be related to the fact that PE is more used as packaging, which are the objects that can more easily be dispersed into environment [74–79].

3.4. Analysis of Metals

The microplastic samples were also analyzed by using a scanning electron microscope (SEM) coupled with an energy-dispersive spectrometer (EDS) to obtain information on micromorphological features and elemental composition. SEM observations highlighted the presence of brighter spots, which indicate heavier elements with respect to the bulk, in which C of the polymer is predominant (Figure 7). All bright spots highlighted on the analyzed side of MP have been analyzed by EDS analysis, and the results are summarized in Table S8; it reports the frequency of detection of each element (element detection limit = s/n > 10).

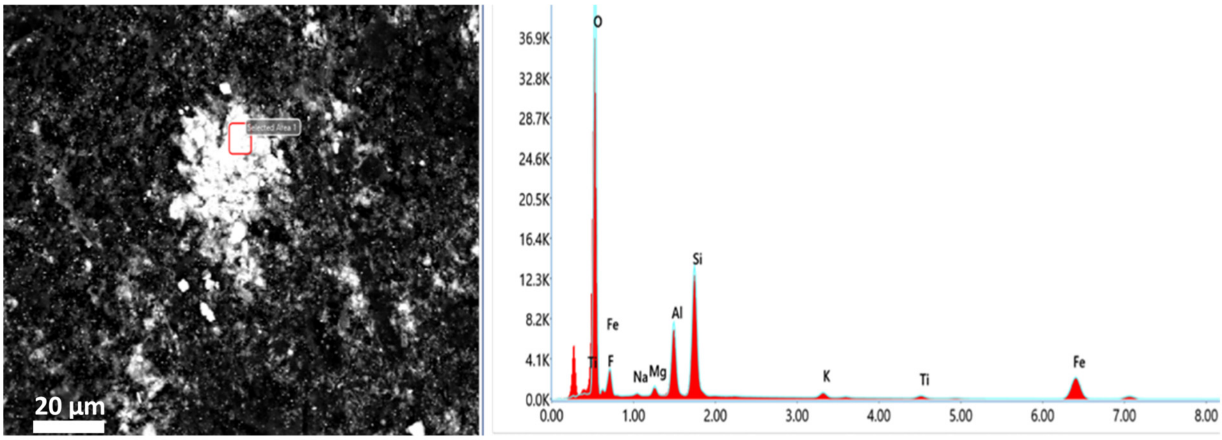

Figure 7. Example of image and related spectrum representing the elements detected during the SEM-EDS analysis.

The most frequent elements detected in all spots (Si, Na, K, Ca, Al, and Mg) suggest that most of the inorganic fraction detected on MPs is ascribable to natural sediments. However, the frequency of some heavier elements like Pb and Ba can also suggest the contribution of a certain level of pollution. From this type of analysis, it is hard to understand whether these elements are endogenous, i.e., used in the production processes of the plastic itself, or exogenous, i.e., if they were absorbed from the surrounding environment during the fragmentation process in the marine environment. However, some evidence can be collected; an element which has been found on bright spots, and was not present, or present with a significant lower EDS signal in the surrounding area, suggests that the element itself may be exogenous.

To confirm that point, some “virgin” polyethylene and polypropylene polymers, coming from common objects and not dispersed into the environment, were observed by the SEM microscope. In these plastics, the light spots (heavier elements with respect to elements of the bulk) are distributed uniformly over the entire surface (Figure S1a,b), while, in plastics sampled in the sea (Figure S1c,d), the light spots are not uniformly distributed and have very different sizes between them. All analyzed samples show a morphology attributable to Figure S1c,d; then, it is reasonable that the detected elements are mainly exogenous.

In order to obtain quantitative information about the amount of some metals in the sampled MPs, an ICP-MS analysis was performed on samples grouped in the Ionian and Tyrrhenian coasts. Among the elements determined (with the results shown in Table 4), lead is the most abundant, followed by chromium and zinc. It is worth noting that the concentration of lead is higher in MPs on the Ionian coast with respect to the Tyrrhenian coast (two to four times higher). Moreover, in the case of chromium, there is a higher amount of this metal in MPs from the Ionian coast. These results suggest that MPs in the Ionian Sea are more impacted by pollutants. In order to compare these metal contents with other results both from the MP analysis and also from marine sediments, some results are also reported in Table 4.

Comparing our results with those obtained from MPs of Indian coral reefs [81], MPs from the Calabrian coast are less contaminated by all metals considered in this research. In addition, there is a coherence between the lead content measured in sediments from nearby Mediterranean areas [82,83] and the lead measured in MPs in this research.

Table 4. Results of ICP-MS analysis performed on MPs sampled on Ionian and Tyrrhenian coast in March and June 2022. Some results of previous studies are also reported.

	Pb	Cd	Cr	As	Sb	Sn	Zn
				Concentration $\mu g \cdot g^{-1}$			
Ionian Coast, 03/2022	147 ± 3	10.3 ± 0.1	140 ± 1.1	0.53 ± 0.01	0.16 ± 0.05	0.31 ± 0.2	61.1 ± 0.1
Ionian Coast, 06/2022	205 ± 5	1.3 ± 0.03	153 ± 1.3	0.63 ± 0.02	0.016 ± 0.001	0.028 ± 0.016	47.9 ± 0.6
Tyrrhenian Coast, 03/2022	72 ± 1.4	1.3 ± 0.06	104 ± 3	0.446 ± 0.03	1.06 ± 0.15	0.464 ± 0.07	26.3 ± 0.7
Tyrrhenian Coast, 06/2022	53.3 ± 0.3	17.1 ± 0.3	98 ± 1.2	0.431 ± 0.03	0.079 ± 0.05	0.57 ± 0.05	46 ± 1
UK, PE pellets [84]	1.72	-	-	-	-	-	0.25
Indian coral reef, MPs [85]	218–3765	10–212	27 -191	0.03–1	11–653	1–2	2187–3076
Gulf of Lions and the Ligurian Sea, sediments, Tyrrhenian sea [86]	19–86	-	-	-	-	-	-
Mar Piccolo Taranto (Ionian sea), sediments [87]	44–111	0.6	-	-	-	1.9–5.6	165–241

These results confirm that MPs carry heavy metals, which are harmful even at low concentrations and persist in the aquatic environment. Commonly, “heavy metals” are defined as elements with a density of at least 5 g/cm^{-3}, which have an atomic mass greater than 23 or an atomic number greater than 20 [84–86]. Heavy metals present in the environment, both of natural and anthropogenic origin, can be affected by sorption processes on plastic waste, which depend on several factors [87–93]. However, the presence of heavy metals on MPs can derive from their production processes (endogenous); in fact, metals can be used as additives to improve the quality of the plastic product: dyes (zinc, lead, chromium, cobalt, and cadmium), heat- and flame-retardants (bromine and chlorine), or stabilizers (cadmium and tin) [94]. In our case, it is difficult to quantitatively distinguish the fraction of each exogenous and endogenous metal and this point has to be investigated in further research. Table 5 summarized the different uses of metals as polymer additives together with the potential effects on human health.

Table 5. Main heavy metals used as additives and their effects on human health.

Element	Polymer	Additives	Effects on Human Health	Ref.
Al	PET, PE, PVC	Stabilizer, inorganic pigments, and flame retardants	Metal-estrogen, breast cancer	[95–97]
Ti	PVC	Inorganic pigments, UV stabilizers	Cytotoxicity on human epithelial lung and colon cells	[95,98,99]
Cu	-	Biocides	Inducing DNA strand breaks and oxidation; formation of reactive oxygen species (ROS)	[86,95,96, 100]
Cr	PE, PP, PVC	Inorganic pigments	Severe cardiovascular, respiratory, hematological, gastrointestinal, renal, hepatic, and neurological effects; allergic reactions to the body; nasal septum ulcer; possibly death	[86,101]
Mn	-	Inorganic pigments	Neurodegenerative disorder	[95,102]
Ba	PVC	Inorganic pigments and UV stabilizers	Metal-estrogen, breast cancer; cardiovascular and kidney diseases; metabolic, neurological, and mental disorders	[95–97,103]

Table 5. *Cont.*

Element	Polymer	Additives	Effects on Human Health	Ref.
Pb	All types of plastics where red pigments are used	UV stabilizers; heat stabilizers and inorganic pigments	Anemia; hypertension; miscarriages; disruption of nervous systems; brain damage; infertility; oxidative stress and cell damage	[86,95–97,101,104]
Zn	PE, PP, PVC	Stabilizers, inorganic pigments, and flame retardants	-	[95,97]
Sn	PVC, Foam, PU	UV stabilizers and biocides	Metal-estrogen; breast cancer; skin rashes; stomach complaints; nausea; vomiting, diarrhea; abdominal pain; headache and palpitations; potential clastogen	[95–97,104]
Co	PET	Inorganic pigments	Formation of reactive oxygen species (ROS); neurological (e.g., hearing and visual impairment); cardiovascular and endocrine deficits	[86,96,105]
Cd	PVC	UV stabilizers, inorganic pigments, heat stabilizers	Changes in metabolism of calcium, phosphorus and bone; osteomalacia and bone fractures in postmenopausal women; lipid peroxidation and in the promotion of carcinogenesis; cellular apoptosis; DNA methylation	[86,96,106]
Hg	PU	Biocides	Mutagen or carcinogen; induction of the disruption of DNA molecular structure and brain damage	[86,96,107,108]
As	LDPE, PVC, Polyesters	Biocides	Congenital disabilities; carcinogen: lung, skin, liver, bladder, kidneys; gastrointestinal damage; death	[95,96,101]
Ba	PVC	Inorganic pigments and UV stabilizers	Metal–estrogen, breast cancer; cardiovascular and kidney diseases; metabolic, neurological, and mental disorders	[95–97,102]
Sb	Various plastics	Biocides and flame retardants	Metal–estrogen; breast cancer	[95–97]

In biological systems, heavy metals have been reported to exert an action on cellular components such as the cell membrane and cytoplasmic organelles, as well as on some enzymes involved in metabolism, detoxification, and damage repair [36,109].

The most frequent metals identified in MPs in this research and reported in Table 5 are as follows: Al, Cr, Cu, and Pb. Copper is an essential element for human survival, but, at high concentrations, it is harmful because it is responsible for DNA damage and the formation of ROS, as well as causing serious pathologies such as Wilson's Syndrome. Lead is considered an extremely toxic and carcinogenic element even at low concentrations.

4. Conclusions

In this study, we collected and analyzed microplastics (MPs) from six marine areas along the Calabrian coast. An average MP abundance of 0.06 particles/m^2 has been calculated. The results suggest that there is not a prevalence of MPs between the Tyrrhenian and Ionian Sea; however, in the areas of Cetraro and Gioa Tauro, greater abundance values have been highlighted, likely due to the presence of two important commercial ports. White/transparent fragments of polyethylene having sizes between 1 and 2 mm are the prevalent physical and chemical features of the samples analyzed. The variability in the size, color, shape, and polymeric composition of the MPs was found to depend on the sampling site and time period, suggesting that these characteristics are not consistent across time and space. The presence of exogenous materials' sorption on the MPs' surface has been observed by electron microscopy of the fragments collected. The analysis of such materials revealed the presence of several elements, including heavy metals such as Pb, which come from the surrounding environment, proving that MPs can act as carriers of heavy metals in the food chain. Further studies are needed to understand the ability of a living organism to absorb such elements.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/environments12010004/s1. Table S1. Temperature program for microwave-assisted digestion of polymers. Table S2. Instrumental parameters for ICP-MS measurements. Table S3. Abundance data used for Shapiro-Wilk test and Kruskal-Wallis tests, and test results. Table S4. χ^2 tests performed on results of size analysis, H_0, null hypothesis: size classes ratios are independent from the sampling site and/or sampling period. H_0 null hypothesis is rejected. Table S5. χ^2 tests performed on results of shape analysis. H_0, null hypothesis: shape classes ratios are independent from the sampling site and/or sampling period. H_0 null hypothesis is rejected. Table S6. χ^2 tests performed on results of color analysis. H_0, null hypothesis: color classes ratios are independent from the sampling site and/or sampling period. H_0 null hypothesis is rejected. Table S7. χ^2 tests performed on results of composition analysis. H_0, null hypothesis: composition classes ratios are independent from the sampling site and/or sampling period. H0 null hypothesis is rejected. Table S8. Elements detected in samples of Microplastics, Ionian Coast and Tyrrhenian Coast, March and June sampling. Analyzed by Scanning Electron Microscopy (SEM-EDS). Figure S1. Elements present on (a) "virgin" polyethylene sample (magnification 399X); (b) "virgin" polypropylene sample (magnification 963×); (c) sample of environmental polyethylene (magnification 516×); (d) sample of environmental polypropylene (magnification 532×). Analyzed by backscattered electrons (BSE).

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