Article

Characterization of Large Microplastic Debris in Beach Sediments in the Po Delta Area

Luca Cozzarini [1],*, Joana Buoninsegni [2], Corinne Corbau [2] and Vanni Lughi [1]

[1] Department of Engineering and Architecture, University of Trieste, Via Valerio 6A, I-34127 Trieste, Italy
[2] Department of Environmental Sciences and Prevention, University of Ferrara, Via Saragat 1, I-44122 Ferrara, Italy
* Correspondence: lcozzarini@units.it

Abstract: The use of single-use or disposable plastic objects has massively increased during the last few decades, and plastic has become the main type of litter found in marine environments. The Adriatic Sea is seriously prone to marine litter pollution, and it collects about one-third of all the freshwater flowing into the Mediterranean, mainly via the river Po. This study investigated the type and composition of large microplastic debris collected in different sites in the Po Delta area. Visual classification was performed by relevant criteria, while chemical composition was assessed by infrared spectroscopy. The main plastic fraction is composed of polyolefin (76%), followed by polystyrene (19%). This proportion roughly matches global plastic production, rescaled after excluding plastics with negative buoyancy: all the identified compounds have a specific gravity lower than that of the seawater. Fragments (irregularly shaped debris) represent the most abundant category fraction (85%), followed by pellets, which represent roughly 10% of the total. Overall, the results provided an insight into large microplastic pollution in beach sediments in the Po delta area.

1. Introduction

The use of plastics has massively increased during the last few decades and is nowadays widespread in everyday life, leading to a dramatic expansion in plastic production worldwide [1,2]. Since most of these objects are designed to be single-use or disposable parts, the increase in their use has inevitably been followed by a growth in the amount of generated plastic waste, which is leading to serious environmental consequences [3]. Due to this pattern, plastic has become the main type of litter affecting marine environments. The Mediterranean Sea is seriously subjected to marine litter pollution since it is heavily trafficked, it receives water from rivers from three continents and its coastlines are highly urbanized and used for industrial and tourist activities [4,5]. Moreover, the semienclosed geography of the Mediterranean basin inhibits litter dispersion to the other oceans [6]. As a consequence, the Mediterranean is considered one of the most polluted marine areas in the world regarding marine litter [7,8].

The Adriatic Sea, which is part of the Mediterranean Sea, is an elongated basin extending between Italy and the Balkan region for about 800 km from NW to SE. Among its peculiar characteristics, it has a high land-to-sea ratio and it collects about one-third of all the freshwater flowing into the Mediterranean (mainly via the river Po) [9–11]. In addition, the Adriatic Sea is considered the most polluted subregion of the Mediterranean Sea [12]. It has been estimated that about 40% of marine litter enters the Adriatic from rivers and an additional 40% derives from urban activities in coastal areas, while the remaining 20% is from fishing and shipping activities [13,14].

The greater portion of plastic waste derives from packaging, with the largest share composed of polyethylene (PE) and polypropylene (PP), followed by polyethylene terephthalate (PET) and with a minor contribution of polyvinyl chloride (PVC), polystyrene (PS) and polyamides (PA) [15–17]. A considerable amount of plastic debris has been observed on Adriatic beaches, with their main source being land-based activities, commercial fishing and recreational use by tourists [18–20]. This study was performed within the NET4mPLASTIC Project (European Programme CBC Interreg Italy-Croatia 2014–2020), which aims to develop new technologies for monitoring micro- and macroplastic in the Adriatic Sea in order to identify marine litter accumulation zones and quantify its presence in four areas. Under the NET4mPLASTIC project was developed a 3D hydrodynamical model of the Po river delta [21,22], which identifies some beaches as potential marine litter accumulation zones. In order to compare hydrodynamic modeling with in situ sample collections [23], this study investigated the type and composition of large microplastic (LMP) debris collected in different sites in the Po Delta area.

2. Materials and Methods

2.1. Study Area and Sampling Sites

The studied area is along the coast of Po Delta system in the northern Adriatic Sea (Figure 1). The Po Delta area lies on the Natura 2000 Italian network, which includes Sites of Community Importance (Habitat Directive, 92/43/CEE) and Special Protection Areas (79/409/CEE). The Po Delta has a triangular shape extending 30 km offshore and is divided into seven active branches delimited by a series of semienclosed lagoons (1000 km^2 [24]), which are separated from the sea by sandy spits. From a geomorphological point of view, these lagoons are generally classified as either "bar-built estuaries" [25] with a salinity gradient near the inlet similar to the estuary; according to Barnes [26] as "typical lagoons"; or according to Kjerfve [27] as "restricted lagoons" because they have a well-defined tidal circulation and are usually oriented shore-parallel. Tide is semidiurnal with a mean range of 60 cm (40 cm during neap tide and 120 cm during spring tide) [28]. There are eight main lagoons: four of them are located in the northern part of the delta (lagoons of Caleri, Vallona, Barbamarco and Burcio) and four in the southern portion of the Delta (lagoons of Basson, Canarin, Scardovari and di Goro), which are separated from the sea by spits.
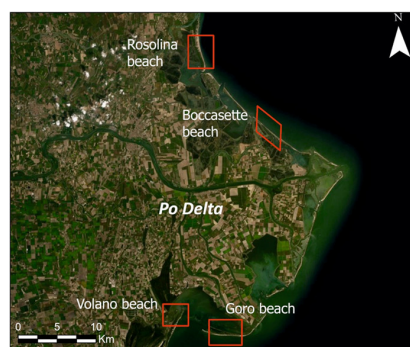

Figure 1. Location of sampling sites in the study area.

For this study, 2 pilot sites were selected on the northern Delta and 2 on the southern: Rosolina and Boccassette sandy spits (Rovigo); Goro spit and Volano beach (Ferrara). The spit of Rosolina, oriented N–S and 8 km long, is delimited to the north by the mouth of the Adige River and to the south by the Caleri inlet. The beach is gently sloping with a width ranging from 20 m to 210 m, generally composed by fine sand. The spit can be divided in three areas with different geomorphological characteristics [29]. The northern beach, about 2 km long, is very narrow (less than 10 m); the central part (3 km long) is characterized by a wide urbanized beach (reaching 200 m) and a discontinuous dune system; the southern part (3 km long) is characterized by a wide beach (100 m) and a well-

developed dune system. It should be noted that the central part is also characterized by an economy based mainly on tourism (1,100,000 visitors in 2016), while the southern part comprises major environmental areas, protected and designated as Natura 2000 sites [30].

The Barbamarco lagoon has a triangular shape and is separated from the sea by two spits and a barrier island. Our study focuses on the northern spit, which is locally called Scanno Bocassette (Bocassette spit). The two inlets are sediment sinks, trapping longshore moving sediment as a result of current and waves. The Boccasette spit (NW–SE orientation) is about 4 km long and the beach width ranges from less than 10 m northward to about 30 m southward. The dune system is generally continuous. Tourism activities are generally limited to the northern part, where touristic installations are present.

Southward, the Goro spit is about 7 km long (W–E orientation) and its width ranges from less than 100 m to more than 500 m. The morphology of the Goro spit beach is characterized by several gently sloped bars. Onshore, the dunes are widespread and present throughout, while the beaches, composed of fine-to-medium sand, are discontinuous (longshore) and variable in size, ranging from less than 10 m to more than 30 m. The coastline is generally complex in relation to the morphology of the barrier–lagoon system. Finally, it is important to note that tourism activities are not intense considering its position (not easily accessible) and touristic infrastructures are almost absent.

Finally, Volano beach has a NNE–SSW orientation and the beach, consisting of fine sand, presents a morphology characterized by well-developed single bar-trough system especially in northern part. This morphology is variable from south to north and the beach width ranges from few meters to more than 30 m. The backshore is occupied by a well-developed dune system that is well vegetated by a small pine forest. It should also be noted that in the southern part of the study area, bars and beach structures are present during the tourist season (June–September). Moreover, it should be noted that the pilot sites are part of a social context typical of rural areas, where fishing, aquaculture and hunting activities are well established.

2.2. Sampling and Separation of Plastic Particles

The samples were collected on the beach of Rosolina (45°6′36′′ N, 12°19′48′′ E), Boccasette (45°1′13′′ N, 12°25′51′′ E), Goro (44°47′24′′ N, 12°20′24′′ E) and Volano (44°47′60′′ N, 12°16′12′′ E) (Figure 1) following the method proposed by Palatinus et al. [31]. On the field, five replicate samples (5 m away from each other) were collected on the backshore (between the high-water mark and the dune). First, a 1 × 1 m wood square was placed on the sampling points. Successively, the sediment was sampled by collecting the top 5 cm of sand with a metal spoon or a small shovel and putting it in a 2 L glass beaker in order to record the volume of sediment sampled.

It is currently accepted [32–34] that plastic litter can be divided into the following size categories: macroplastics (>2500 mm); mesoplastics (5–2500 mm); large microplastics (1–5 mm); small microplastics (1 μm–1 mm); nanoplastics (1 nm–1 μm) [32,35,36]. Then, in the case of dry sand, the sediment was filtered in situ through 5 mm and 1 mm mesh metal sieves. In the case of wet sand, the collected sample was properly labeled in situ and then air-dried (for 2 or 3 days) and sieved in laboratory (in a controlled environment to avoid contamination). The mixed residual particles (LMPs with shells, sand and twigs) found between the two sieves (size between 1 and 5 mm) were stored in paper bags properly labeled. In the laboratory, the mixed particles were manually sorted to separate the LMP items from the others.

2.3. Visual Identification, Classification and Composition of the Particles

All the particles previously identified as LMPs (a total of 240 objects) were photographed and numbered (a unique identification number was assigned to every particle). Visual classification (size, type, color) and chemical assessment (polymer identification) were performed. Relevant criteria for the classification (size, category, color and composition) were those defined in technical documents and peer-reviewed literature [32–35,37].

Particle size (maximal and minimal extent) was measured directly on the pictures by means of image analysis software (GNU Image Manipulation Program—GIMP development team); aspect ratio was defined as the ratio between the maximal and minimal dimension. Particles were divided into size categories (mesoplastics, large microplastics and small microplastics) and object categories ("pellet", "fragment" or "filament"). Particles labeled as "pellets" were spherical or cylindrical in shape, and typically were small granules used as raw material in plastic production. Particles identified as "filaments" were thin and with a high aspect ratio. Irregular particles were categorized as "fragments": these are three-dimensional objects, not to be confused with "film", as items belonging to this category generally develop mostly in two dimensions: length and width, to the detriment of the third dimension (height). The color was attributed according to the best match to the following: black, blue, brown, green, grey, orange, pink, red, sky blue, transparent, white and yellow.

Sample composition was assessed via Fourier transform infrared spectroscopy (FT-IR). Spectra were acquired with a Thermo-Nicolet Nexus 470 spectrometer, equipped with an attenuated total reflectance (ATR) accessory, in the 4000–500 cm^{-1} spectral range. Different plastic materials were identified by comparison with known reference spectra of the most common polymers available in an internal database; the most important vibrational bands used as fingerprints for identification were those suggested by Jung et al. [38]. Other compounds (such as sand, calcium carbonate or cellulose) were identified by their characteristic vibrational bands [39–41]: strong peaks in the 1400–1440 cm^{-1} region ($CaCO_3$ vibrational mode 2) or in the 1100 cm^{-1} region (SiO_2), when superimposed to the polymer spectra, were related to the presence of sand (carbonate or siliceous origin) in the plastic debris. Spectra with only a broad, not well-defined vibrational band in the 1000–1050 cm^{-1} region (compatible with C-O-C stretch in polysaccharides) were identified, after visual examination of the sample, as fragments of algae or paper (cellulose). Samples with only $CaCO_3$ vibrational bands were identified as fragments of shells.

3. Results

3.1. Visual Sorting

A summary of debris category, size and aspect ratio is reported in Table 1. It is possible to notice that the majority of debris lies in the "large microplastics" (LMPs) category, between 1 and 5 mm (considering their greater measured size), and about ¾ of it has an aspect ratio below 2 (roughly round or roundish shape). About 5% of the collected objects are clearly elongated (aspect ratio > 10).

Table 1. Size, aspect ratio and category of the collected objects.

Size Range (Max Extent—mm)	
<1 mm	0.4%
1–5 mm	76.1%
5–10 mm	17.6%
10–20 mm	4.2%
>20 mm	1.7%
Aspect Ratio	
1	24.3%
1–2	49.0%
2–5	17.2%
5–10	4.6%
>10	5.0%
Object Category	
Filament	4.6%
Pellet	10.5%
Fragment	84.9%

One would expect that size of all the analyzed objects should fall in the LMP category (as a result of the sieving method). However, given the very elongated aspect ratio of some debris (filaments) it is possible that these, while measuring as much as 20 mm at the maximum length, were able to pass through the sieve in their minimum diameter. Conversely, objects smaller than 1 mm are likely to have originated from fragmentation of larger objects during transport. Therefore, 0.4% of the identified debris falls in the "small microplastic" category (smaller objects were not easily visible or recognized), and on the opposite far end, 1.7% can be categorized as "mesoplastics". The majority of the collected objects (84.9%) were labeled as "fragments" (irregular shape), 10.5% as "pellets" (cylindrical or spherical) and 4.6% as "filaments" (very elongated, thin sheets). A pie chart showing the color of identified debris is shown in Figure 2. Pictures of representative plastic debris are shown in Figure 3.
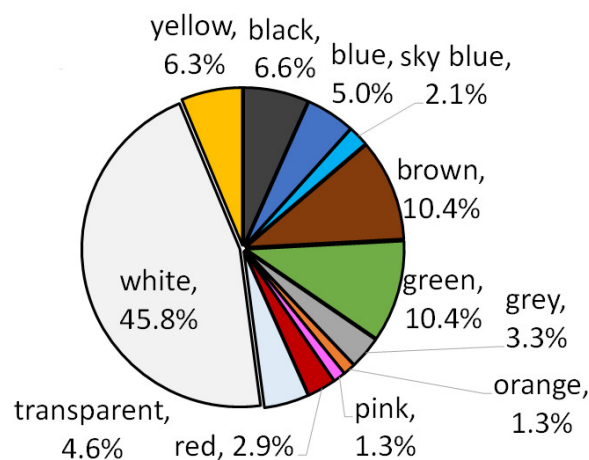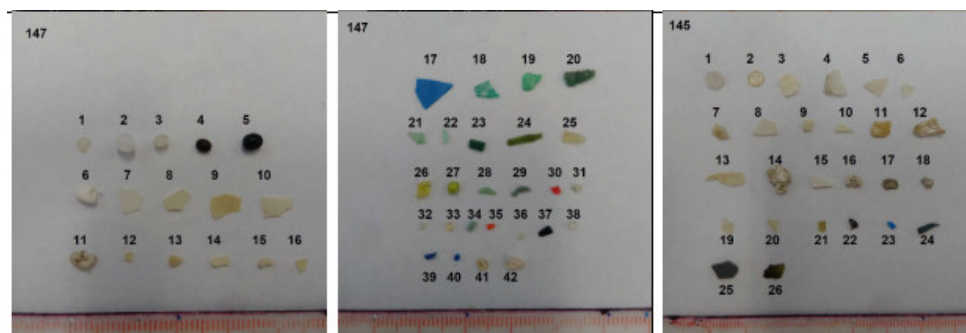

Figure 2. Color of the collected debris.

Figure 3. Representative picture of some of the analyzed plastic debris.

3.2. ATR-FTIR Analysis

About 5% (11 objects) of the analyzed debris comprised false positives (paper, algae or shells). The remaining 95% (229 objects) was recognized as "plastics" (artificial polymers). Representative FTIR spectra of most common polymers identified among the analyzed plastic debris are shown in Figure 4. A pie chart showing the composition of positively identified plastics is reported in Figure 5.
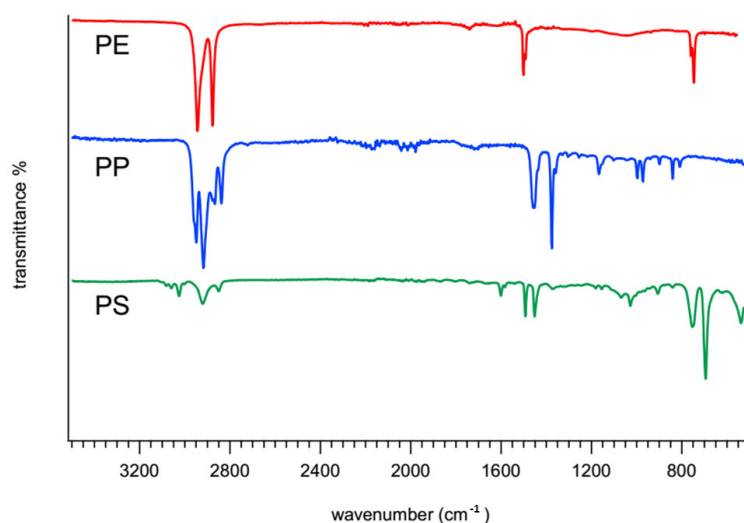
Figure 4. Representative FTIR spectra of most common polymers identified among the analyzed plastic debris: PE (red curve), PP (blue curve) and PS (green curve).
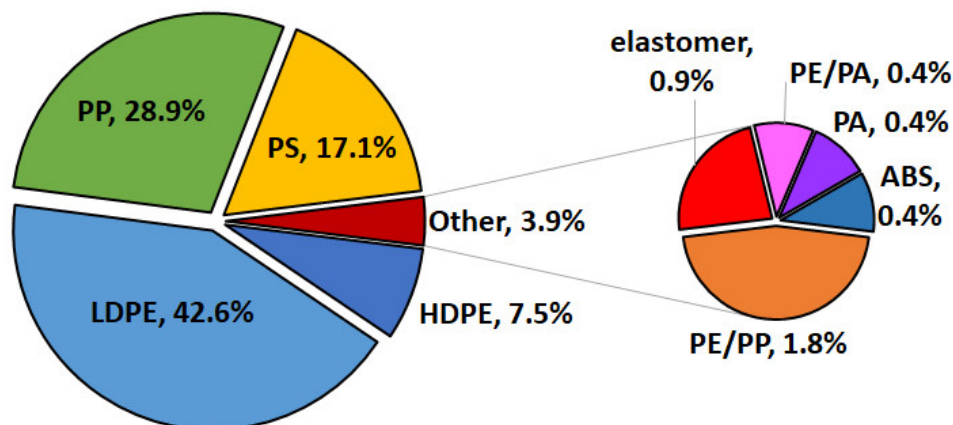

Figure 5. Composition of the analyzed plastics.

Polyethylene (PE) alone (sum of low density—LDPE and high density—HDPE) represents roughly half of the total collected plastic fragments. Polypropylene (PP) has the second-highest share (28.9%). The polyolefin fraction (LDPE + HDPE + PP) is nearly 80% of the collected plastics. About 17% of the collected objects are made of polystyrene (PS); given their softness, shape (round or roundish) and density (<1), most of this PS debris was recognized as granules of expanded polystyrene (EPS). Of the "other plastics" fraction (3.9% of the analyzed objects), most of them (about 80%) were, again, polyolefin-based blends or copolymers (PE/PP, PE/PA and elastomers). The other fractions are represented by acrylonitrile butadiene styrene (ABS) and polyamide (PA).

Debris categories, sizes and aspect ratios, divided by sample composition (the three most abundant polymers found) are reported in Table 2. It is possible to notice that PS debris belongs to the "fragment" category only (no PS pellets or filaments were found); this category also represents the most abundant one for PE (85%) and PP (70%). Pellets represent roughly 20% and 10% of PP and PE debris, respectively. A total of 10% of PP debris is filaments. It is worth noticing that the aspect ratio of nearly 65% PS debris is equal to 1 (round objects). Since no granules or pellets were identified among PS objects, these are likely expanded polystyrene (EPS) beads, resulting from disaggregation of EPS foam objects widely used in packaging. In 85.2% of this plastic debris it was possible to identify a clear signal related to the presence of SiO_2; in 42.2% of these, a $CaCO_3$ signal

was also noticeable. Given their sampling location, it is possible to speculate contamination of the samples with sand and/or shell fragments.

Table 2. Categories, sizes and aspect ratios of the collected plastics, organized by sample composition (three most abundant polymers found: PE, PP and PS).

Object Category	PE (HDPE + LDPE)	PP	PS
Filament	3.5%	10.6%	0.0%
Pellet	11.4%	18.2%	0.0%
Fragment	85.1%	71.2%	100.0%
Size Range (Max Extent—mm)	**PE (HDPE + LDPE)**	**PP**	**PS**
<1 mm	0.0%	0.0%	2.6%
1–5 mm	8.2%	24.2%	17.9%
5–10 mm	69.1%	56.1%	74.4%
10–20 mm	14.4%	12.1%	5.1%
>20 mm	6.2%	4.5%	0.0%
Aspect Ratio	**PE (HDPE + LDPE)**	**PP**	**PS**
1	16.7%	21.2%	64.1%
1–2	51.5%	45.5%	25.6%
2–5	18.2%	18.2%	10.3%
5–10	6.1%	4.5%	0.0%
>10	7.6%	10.6%	0.0%

4. Discussion

4.1. Identification and Possible Sources of Plastic Debris

Among the different polymers produced worldwide, the market is dominated by polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), polyurethane (PUR), polyethylene terephthalate (PET) and nylon (polyamide—PA) [42,43]. The density of polymers affects their distribution in the water column; low-density plastics such as PE, PP and expanded PS are predominant in sea surface samples as well as in beach samples [36,42,44]; their buoyancy allows this debris to be transported over long distances and finally settle in the beach sediments. The proportion of different polymers identified in this work roughly matches global plastic production [16,43], rescaled after excluding plastics with density >1. The polyolefin fraction is the most abundant, as already shown in other works [5,19,20,45]. Table 3 reports the common applications of these plastics and their specific gravity [16,42,43].

Table 3. Common plastics found in marine waste, their common application and specific gravity.

Plastic Type		Common Application	Specific Gravity
Low-density polyethylene	LDPE	Plastic bags, film, packaging	0.91–0.93
High-density polyethylene	HDPE	Bottle caps, storage containers	0.92–0.95
Polypropylene (PP)	PP	Ropes, storage containers, bottle caps	0.90–0.92
Polystyrene—expanded	EPS	Boxes, packaging	0.01–1.00
Polystyrene	PS	Utensils, cups	1.05–1.10
Polyvinyl chloride	PVC	Pipes, containers, insulators, films	1.20–1.30
Polyamide (Nylon)	PA	Ropes, fishing nets	1.15–1.20
Polyethylene terephthalate	PET	Bottles	1.35–1.40
Polyurethane	PU	Adhesives, foams	variable

All the identified plastics have a specific gravity lower than that of the seawater (which lies between 1.02–1.03 g cm^{-3}, depending on the temperature and salinity); therefore, they possess a positive buoyancy (floating objects). It is worth remembering that the

buoyancy of a plastic object also depends on other factors such as entrapped air, water currents and turbulence. This explains why drinks bottles made of PET (density 1.35–1.40 g cm^{-3}) can be found either floating in coastal waters or deposited on the seabed. However, in this study, no PET debris (negative buoyancy) was found among analyzed particles. Fragments and filaments are likely secondary microplastics (originating from the breakdown of larger plastic items), while pellets (which represent roughly 10% of the total) can be categorized as primary microplastics (originally and intentionally manufactured in that size). These pellets are preproduction plastic granules made of raw resin, which are usually melted and used in the manufacturing of everyday plastic items. They somehow entered the environment before the plastic objects' production stage (i.e., lost during transportation) and were subsequently found in areas of marine waste concentration.

The main plastic fraction that was identified is made of polyolefins (PE and PP); these secondary microplastics originated from plastic bags, packaging films, containers and bottle caps. Polyolefins (HDPE, LDPE, PP) are used throughout the world for several applications: bags, toys, containers and pipes (LDPE); housewares, wrapping and films, gas pipes (HDPE); battery cases, automotive parts and electrical components (PP) [46]. The PS fraction derives almost exclusively from EPS packaging and boxes, likely from fishing activities.

Considering the local sources of waste release into the environment (rivers, wastewater and human activities such as fishing, aquaculture and tourism), the results of the most represented LMP categories agree with the distribution defined by the hydrodynamic model.

4.2. Comparison with other Studies in Mediterranean Sea, Adriatic Coasts and Tributary Rivers

A large-scale survey of floating micro- and mesoplastic characterization in the Mediterranean sea is available in the work of Suaria et al. [5]. The polymer distribution reported only partially matches the one reported in this work. Furthermore, taking into account the overall Mediterranean data and removing the "no plastic" fraction (4.4%), only the PE fraction (54.4%) is quite similar, while the reported PP fraction (16.8%) is about ½ of ours (31%), and the PS fraction (2.9%) is substantially lower than what we found (18.5%). In our case, the influence of fishing activities in the sampling area is most likely responsible for this increase in the PS fraction (deriving almost exclusively from EPS packaging and boxes). Notably, they found also substantial fractions of paints (8.1%), PA (6.9), epoxy (5.2%) and PVC (2.7%). Paints were described as "paints chips from repair and maintenance of ships". All the "other plastics" (sum of paints, nylon, epoxy, PVC, PVA, PET and EVA) account for 25.9% of the total (while in our data they account for only 4.3%). These plastics have densities higher than water, but even so, they were collected by neuston nets.

Vlachogianni [19] in 2018 reported an assessment of abundance, identification and possible sources of marine litter in the Adriatic and Ionic Seas. Nonetheless, the objects were categorized only qualitatively (i.e., caps, lids, bags, etc.) and not by their composition. It is, however, possible to gather some useful information. For instance, the sum of "straws", "cups", "food containers" and "other polystyrene items" (all the items that we can speculate to be composed of PS) accounts for 18.6% of the total mesoplastic and microplastic items. Similarly, the sum of "cotton bud sticks", "packets, sweet wrappers", "plastic caps/lids" and "plastic rings", "shopping bags" and "sheet and industrial packaging" (items that are likely composed of PE or PP) accounts for 66.7%. Bottles (PET) represent 6.0%; nets (likely PA) 6.1%; and "strings and cords" 2.6%.

Moreover, results of other studies in the Adriatic basin, and more specifically in the Po Delta region, are available. Korez et al. [47] sampled and identified plastic particles on Slovenian beaches. They reported different polymer distributions for March (PE 10%, PP 23%, PS 10%, PET 23%, PA66 23%, others 11%) and August (PE 35%, PP 17.5%, PS 23.5%, PET 12.5%, PA66 5%, others 6.5%). Both distributions only partially match ours (even if the PE + PP fraction is again the prevalent one); it is worth noticing that they sampled only

26 pieces of debris (the statistical significance is limited). Similar studies are available for plastic debris on the Slovenian, Croatian and Montenegrin coasts [18,48,49]. Munari et al. [45] in 2021 characterized the floating plastic debris collected by manta trawl in the Po river, the largest contributor of freshwater to the Adriatic Sea. They found a relative abundance of PE and PP of 40.5% and 25.7%, respectively (slightly lower with respect to ours); their PS fraction (14.9%) is also lower. Moreover, they found PET, PVC and EVA debris (which are supposed to be nonfloating polymers).

It is worth noticing that all these datasets are generally difficult to compare, since no standardized protocol of collection, category sorting and chemical characterization is used among different studies.

5. Conclusions

The present study provided insight into large microplastic pollution in beach sediments in the Po delta area. Although the role of geomorphological and hydrodynamic factors on the distribution of marine litter of all size classes is reported in the literature, this study emphasizes the importance of local activities and waste management policies on the typologies of plastic litter distribution. About 95% of the analyzed sediments were positively identified as "plastics" (artificial polymers); the most abundant plastic types were polyethylene and polypropylene, followed by polystyrene. Fragments (irregularly shaped debris) represent the most abundant category fraction (85%), followed by pellets, which represent roughly 10% of the total. These pellets are preproduction plastic granules made of raw resin, which somehow entered the environment before the plastic production stage (i.e., lost during transportation) and are later found in areas of marine waste concentration. They can be categorized as "primary microplastics" (originally and intentionally manufactured in that size), different to fragments and filaments, which are categorized as "secondary microplastics". This relative abundance of primary microplastics and the way they are leaked into the environment is certainly a matter for further consideration.

Standardized characterization and monitoring protocols of plastic debris are needed to ascertain comparable results from different studies. Further evaluation and comparisons can be used to gain critical data for the management of macro- and microplastic debris in the Adriatic and Mediterranean regions.

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