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Chapter

From Macroplastic to Microplastic Litter: Occurrence, Composition, Source Identification and Interaction with Aquatic Organisms. Experiences from the Adriatic Sea

Alessio Gomiero, Pierluigi Strafella and Gianna Fabi

Abstract

Marine litter is human-created waste that has been discharged into the coastal or marine environment. “Marine debris” is defined as anthropogenic, manufactured, or processed solid material discarded, disposed of, or abandoned in the environment, including all materials discarded into the sea, on the shore, or brought indirectly to the sea by rivers, sewage, storm water, waves, or winds. A large fraction of marine debris is made up of plastic items. Plastic marine debris has become one of the most prevalent pollution related problems affecting the marine environment globally. The widespread challenge of managing marine litter is a useful illustration of the global and transboundary nature of many marine environmental problems. At a global level, plastic litter constitutes 83–87% of all marine litter. Land-based sources are estimated to be responsible for approximately 80% of marine litter. The largest portion of plastic associated with marine pollution is often linked to the contribution from terrestrial sources associated with accidental or deliberate spills as well as inefficient waste management systems in heavily anthropized coastal regions. This chapter is intended to serve as a catalyst for further discussion to explore the potential for developing a Mediterranean regional framework for addressing marine litter.

Keywords: plastic debris, Adriatic Sea, sediments, floating litter, sediments, distribution models

1. Introduction

We live in the “Plastic Age”. From its creation in the early 1870, plastic material has largely contributed to the society development making everyday life easier. Plastic material offer good advantages as it can be customized with specific shapes and chemical and physical properties i.e., elasticity, hardness, lightness, transparency and durability. Due to this, the production has dramatically boosted annual plastic production from 0.5 million tons in the 40s to 550 million tons in 2018 [1].
Plastics in the Environment

However, plastics sturdiness presents some negative implications as the increasing rate of plastic consumption worldwide its release in the environment associated with a low degradation rate is resulting in its accumulation in coastal and marine sediments, pelagic and benthic biota from coastal to open ocean areas at each latitude from the poles to the equator. Depending on sources and formation mechanisms plastic fragments are split into “primary” and “secondary”. Primary plastics are resulting from the direct input of freshly manmade emissions, adding new micronized size by-design plastic material to the environment. According to this definition, major sources primary plastics are: (A) polymers intentionally produced and used as such. In this group belong i.e., personal care consumer products, industrial or commercial products and other specialty chemicals with plastic microbeads; (B) inherent collateral products of other industrial activities or (C) plastic sourced as accidental or deliberate spillage i.e., pellets loss from plastic factories and transport. In contrast, secondary plastics are associated as secondary pollution sources where larger plastic items undergo degradation and subsequent fragmentation leads to the formation of smaller plastic pieces as they start to break down by photo-oxidative degradation followed by thermal and/or chemical degradation [2].

2. Sources, degradation processes, detection of plastic debris in marine environments

While addressing the comprehension of plastics degradation mechanisms in marine aquatic environments it is useful to divide them into plastics with a carbon-carbon backbone and plastics with heteroatoms in the main chain. Some of the most environmentally recurrent polymers like polyethylene, polypropylene, polystyrene and polyvinylchloride have a pure carbon-based backbone. On the contrary, polyethylene terephthalate and polyurethane plastics have heteroatoms in the main chain. Most packaging materials are made of plastics with a carbon-carbon backbone structure. As they are very often discarded after a short period of time, there is a high potential to observe significant loading in the environment. All these polymers are susceptible to photo-initiated oxidative degradation, which is believed to be their most important abiotic degradation pathway in aerobic outdoor environments. This degradation pathway consists of a complex sequential multi-step process where initially chemical bonds in the main polymer chain are broken down by light, by heat or by a combination of both to produce a free radical formation [3, 4]. Polymer radicals react with oxygen and form a peroxy-radical species. As a side effect, the co-occurring formation of hydroperoxides promotes a further complex pathway of radical reactions leading to significant autoxidation of the target polymer. These processes ultimately lead to chain scission, branching and creation of oxygen-containing functional groups. As the molecular weight of the polymers is reduced, the material becomes fragile and is more vulnerable to fragmentation, which makes a higher surface area reactive to further degradation. Nevertheless, anti-oxidants and stabilizers used as additives inhibit the degradation of the polymer. Thus, degradation rates depend strongly on used additives and plasticizers [4]. In most cases these are well-known toxic chemicals not covalently bonded to the polymer and therefore capable of leaching out from the plastic during the degradation process, and easily enters into the aquatic environment representing a further point of concern for eco-toxicologists. On the other hand, different degradation mechanisms cause degradation of plastics with heteroatoms in the main chain. They show an increased thermal stability compared to polymers with a simple carbon backbone. Under marine environmental conditions the degradation processes of plastics like polyethylene terephthalate (PET) or polyurethane (PU) are normally controlled by hydrolytic
cleavage. Similar to carbon-carbon backbone plastic polymers, PET can undergo photo-induced autoxidation via radical reactions leading to the ultimate formation of a carboxylic acid end groups, which show a promoting effect on thermo- as well as photo-oxidative degradation. Weathering of PET in the marine environment occurs mainly by photo-induced oxidation and secondly by hydrolytic degradation processes which cause the yellowing of the polymer. For thermo-oxidative degradation the consequences are an in the content of the some end groups i.e., carboxylic acid as well as a general decrease in molecular weight of the main polymer [4]. Hydrolysis also leads to a reduction in molecular weight and an increase in carboxylic acid end groups. PET is highly resistant to environmental biodegradation because of its compact structure [4]. On the other hand, polyurethane-like compounds show carbon, oxygen and nitrogen in the main chain demonstrating enhanced susceptibility to degradation via photo-oxidation, hydrolysis and biodegradation. Plastic floating on the ocean surface is exposed to moderate temperatures, solar radiation at wavelengths of 300 nm and longer, as well as oxidizing conditions. Since temperatures are moderate, the most important factors initiating abiotic degradation are oxygen and sunlight. According to recent studies, fragmentation patterns first occur at the plastic surface, which is exposed and available for chemical or photo-chemical attack. The process is more efficient with smaller plastic fragments as they show a higher surface to volume ratio [5]. Changes in color and crazing of the surface are the initial visual effects of polymer degradation. Surface cracking makes the inside of the plastic material available for further degradation, which eventually leads to embrittlement and disintegration. Furthermore, almost all commercial plastics include additives. These co-production chemicals embedded in the polymers can also leach into the aquatic environment, which is an additional point of concern. As these substances enhance plastics’ resistance to degradation, it becomes difficult to quantitatively estimate the fragmentation patterns since different plastic products can vary in their composition. On the other hand, additional factors can significantly influence degradation rates as floating plastic may develop biofilms that shield it from UV radiation. The formation of biofilm in plastic microliter collected from the marine aquatic environment has been previously documented worldwide [6–8]. Such phenomena could lead to a reduction in photo-initiated degradation. So far, there have been very few studies of degradation mechanisms for plastic polymers in the marine environment although some promising early findings have been reported by ongoing joint research initiatives (e.g., JPI-Weather Mic and JPI-PlasTox). The biofilm formation can also affect the vertical distribution of plastic fragments largely affecting their distribution in the water column or in the sedimentary environment. Most synthetic polymers are buoyant in water and substantial quantities of plastic debris that are buoyant enough to float in seawater are transported and potentially washed ashore. The polymers that are denser than seawater tend to settle near the point where they entered the environment; however, they can still be transported by underlying currents. Table 1 resumes the theoretical densities of the most recurring polymers found in the environment. Microbial films rapidly develop on submerged plastics and change their physico-chemical properties such as surface hydrophobicity and buoyancy [9, 10]. All in all, plastic debris is a mixture of molecules and chemicals, its size ranging from some meters to a few micrometers and probably nanometers. It is derived from a broad variety of origins, such as fishing gear, nets, bottles, bags, food packaging, taps, straws, cigarette butts and cosmetic microbeads and the associated fragmentation of all of these. Plastic debris has become ubiquitous in all environmental compartments of the marine ecosystem form sediments to sea surface. Thus, the observed loadings floating in the ocean represents only a limited portion of the total input. It has been previously reported that most plastic litter ends up on the seabed with a remaining fraction distributed on beaches or floating on the seawater surface leading one to
consider that merely quantifying floating plastic debris may lead to a significant underestimation of the actual amount of plastics in aquatic environments [11].

2.1 The interaction of plastic debris with aquatic life

Overall ecosystem health can be significantly affected by the accumulation of trash and plastics in our seas. Ingestion of and entanglement in marine debris directly impacts marine life. Laboratory studies provide a strong proof of evidence for the effects of microplastic ingestion observed in organisms collected from the natural environment. Indeed, in laboratories, under natural like conditions, microplastics have been shown to be ingested by amphipods, barnacles, lugworms and bivalves [12–14]. In the same organisms, the uptake of microplastics caused notable ultrastructural changes in the investigated tissues including histological changes as well as cell functioning impairments [15]. In field observations, the occurrence of MPs in the gastrointestinal tract and gills of pelagic and demersal fish and marine mammals has been documented [16, 17]. Past reports have shown that many marine organisms wrongly identify plastic debris for food. Ingestion of marine debris induce different deleterious effects such as pathological alteration, starvation and mechanical blockages of digestive processes. Furthermore, the interaction of plastic fragments, especially those at micrometric and nanometric scales, with organic pollutants are of importance in relation to environmental contamination and biological effects on organisms in the water column as well as in the sedimentary environment [18, 19]. Hydrophobic pollutants co-occurring in the aquatic environment may in fact adsorb onto MP debris. According to the different sizes, plastic fragments have the potential to transport contaminants more effectively through biological membranes and ultimately inside cells of aquatic organisms. The presence of organic pollutants on marine plastics has been illustrated for a wide range of chemicals in natural aquatic conditions [20, 21]. The exposure routes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbreviation</th>
<th>Density (g/cm³)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expanded polystyrene</td>
<td>EPS</td>
<td>0.01–0.04</td>
<td>Bait boxes, floats, cups</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>LDPE</td>
<td>0.89–0.93</td>
<td>Plastic bags, bottles, gear, cages</td>
</tr>
<tr>
<td>High density polyethylene</td>
<td>HDPE</td>
<td>0.94–0.98</td>
<td>Plastic bags, bottles, gear, cages</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>PP</td>
<td>0.83–0.82</td>
<td>Rope, bottle caps,</td>
</tr>
<tr>
<td>Polypropylene terephthalate</td>
<td>PET</td>
<td>0.96–1.45</td>
<td>Bottles, gear</td>
</tr>
<tr>
<td>Styrene butadiene rubber</td>
<td>SBR</td>
<td>0.94</td>
<td>Car tyre</td>
</tr>
<tr>
<td>Polyamide</td>
<td>PA</td>
<td>1.02–1.16</td>
<td>Gera, fish farm nets, rope</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>PS</td>
<td>1.04–1.10</td>
<td>Containers, packaging</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>PMMA</td>
<td>1.09–1.20</td>
<td>Insulation, packaging</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>PVC</td>
<td>1.16–1.58</td>
<td>Film, pipe, containers</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>PC</td>
<td>1.20–1.22</td>
<td>Textiles, leisure boats</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PU</td>
<td>1.20</td>
<td>Insulation, floats</td>
</tr>
<tr>
<td>Alkyd</td>
<td>ALK</td>
<td>1.24–2.10</td>
<td>Paints, packaging</td>
</tr>
<tr>
<td>Polyester</td>
<td>PES</td>
<td>1.24–2.3</td>
<td>Textiles,</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>PTFE</td>
<td>2.1–2.3</td>
<td>Personal care products</td>
</tr>
</tbody>
</table>

Table 1. Theoretical densities of the most recurring polymers found in the environment.
of organic pollutant-enriched MPs are varied, while the toxicity is largely inversely correlated to the size of the particles, as the smaller the particle the further into the organism it can penetrate releasing toxic chemicals under acidic gut conditions [22]. According to the properties of the adsorbed chemicals, several toxicity mechanisms are represented by increased oxidative stress, genotoxicity, depletion of immune competence, impairment of key cell functioning, loss in reproductive performance, disorders in energy metabolism, and changes in liver physiology [23–25].

2.2 Extracting microplastics from environmental matrices

Different methods have been developed for identifying plastics, including meso, micro and nanoplastics in water, sediments and biota as well as to a lesser extent in soil. The percentage of organic matter (OM) in general as well as some recurring specific macromolecules, such as fats and proteins may hamper the analysis, thus hiding plastic fragments in visual analyses and distort signals in Fourier transformed infrared (FT-IR) and Raman spectroscopy, two of the most frequently used methods for plastic identification [26, 27]. Hence, identifying and quantifying plastic materials in organic matter enriched samples may be a challenge. In sediments, several available protocols recommend a preliminary sorting of plastic size grounding and sieving. After sieving, the mineral phase of soils might be removed easily using density fractionation methods. Different density solutions have been used including NaCl, ZnCl₂, NaI and more recently 3Na₂WO₄ 9WO₃ H₂O to obtain dense floating solutions [28, 29]. However, it has been shown that simple density fractionations will not succeed in separating organic matter from plastic materials in sediments because most of the OM show densities between 1.0 and 1.4 g/cm³, similar to that of several environmentally recurring plastic types like PET, PP, PE and Nylon. Sufficient removal of OM without destroying small plastic polymers is challenging because large parts of OM are refractory. At the same time, polymers show strong sensitivity to acidic or strong oxidizing treatment conditions, which induce permanent modifications (e.g. yellowing), thus hampering their classification by microscope-oriented techniques. To efficiently remove OM, multistep extraction, purification processes based on alkaline treatments possibly combined with multi-enzymatic digestion steps have been suggested for the analyses of biota water or sediments. Enzymatic digestion has been promising for the removal of organic as well as other interferents, such as chitin, agar and lipid enriched samples [27]. Strong alkali digestions have been pointed out as being effective for sediments as well as biological samples, without altering the plastic itself [30]. While on the contrary and as previously mentioned, strong acidic conditions induce partial dissolution of polycarbonate as well as partial digestion of polyethylene and polypropylene [13]. Another largely exploited strategy to remove organic matter relies on the application of concentrated hydrogen peroxide [26]. However, its use must be critically evaluated in terms of digestion conditions as treatments with incubation exceeding 48 h with temperatures exceeding 50°C, which may degrade plastic polymers like polyethylene and polypropylene [31]. In this context, some authors have recently suggested an effective combined multistep method based on a sequence of enzymatic digestions followed by a short hydrogen peroxide treatment for the removal of organic matter from complex environmental matrices (e.g., wastewater samples). In summary, several promising methods have been tested for extracting, purifying and pre-concentrating plastic materials from sediments and marine biota, all of them having potential limitations. More research is needed to develop a standard protocol for isolating plastics from a range of different environmental matrices, ideally at low cost and without altering plastic properties.
2.3 Overview of the most applied detection and quantification methods

Once isolated, plastic fragments can be tracked and characterized by different analytical techniques. Some are defined as “surface oriented” methods like Raman spectroscopy, Fourier Transformed Infra-Red (FTIR), Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and environmental scanning electron microscope (ESEM) with an attached X-ray energy dispersive system (ESEM-EDS). Plastic fragments are visually sorted and analyzed coupled with microscopy. However, as discussed above, the use of strong oxidant/acidic agents applied during the extraction from sometimes complex environmental matrices (e.g., organic matter enriched marine sediments, or fat rich marine biota) may induce alteration in the plastic surface like partial dissolution, yellowing and polymer structure disruption leading to erroneous characterization of microparticles. Furthermore, some compounds of natural origin occurring in marine samples (e.g., chitin) have shown spectroscopic properties similar to those of the most recurrent plastic polymers leading to inaccurate polymer characterizations and overall abundance estimation. In addition, these microscopy-based techniques are time consuming and unable to process large numbers of samples. However, significant advances in the automatic and semi-automatic FTIR spectra recognition have been recently presented as promising time saving solutions (Jes recent paper). Alternatively, promising solutions include the Pyrolysis-gas chromatography in combination with mass spectrometry (Pyr-GC-MS) as well as the Thermogravimetric analysis coupled with mass spectrometry (TGA-MS). Pyr-GC-MS in particular can be used to assess the chemical composition of potential microplastic particles by analyzing their thermal degradation products. The polymer origin of particles is identified by comparing their characteristic combustion products with reference pyrograms of known virgin-polymer samples. Py-GC/MS had the advantage of being able to analyze the polymer type and OPA content in one run without using any solvents and with few background contaminations. Additionally, the Pyr-GC/MS method has an appropriate degree of sensitivity for analyzing plasticizers in microplastic particles with limited sample masses. However, although the pyrolysis-GC/MS approach allows for a good assignment of potential microplastics to polymer type it has the disadvantage of being a “destructive” technique as the sample is burned to obtain the pyrolytic products. Furthermore, due to limitations in the quantity of sample loaded in the pyrolysis cup only particles of a certain minimum size can be processed resulting in a lower size limitation of particles that can be analyzed. Each of these methods have their own limitations and advantages, therefore, their combined use, especially for the analysis of complex environmental samples, is a recommended strategy to reduce the effect of interferents in the analysis and obtain reliable results.

3. The Mediterranean and the Adriatic Sea

With some of the most significant amounts of solid waste generated annually per person (208–760 kg/year), the Mediterranean Sea is one of the world’s areas most affected by litter [32]. The estimated amount is 62 million of macrolitter items floating on the surface of the whole basin [33]. Litter enters the seas from land-based sources, ships and other infrastructure at sea and can travel long distances before being deposited on the seabed or along the coasts. Mean densities of floating microplastics in the Mediterranean Sea of more than 100,000 items/km² [34] indicate the importance of this threat for the basin. In this context, the Adriatic Sea represents a hot spot for plastic litter both because of peculiarities in its oceanographic
conditions as well as the high degree of anthropogenic pressure related to tourism, artisanal and industrial activities coexisting in a narrow area. The Adriatic Sea is an elongated basin, located in the central Mediterranean, between the Italian peninsula and the Balkans, with its major axis in the NW-SE direction. The northern area is very shallow, gently sloping, with an average depth of about 35 m, while the central part is on average 140 m deep, with the two Pomo depressions reaching 260 m. The northern and central parts of the basin are affected by a great number of rivers along the Italian coast, of which the Po river is the most relevant. River discharge and wind stress are the main drivers of the water circulation. West Adriatic Current (WAC), flowing SE along the western coast, and East Adriatic Current (EAC), flowing NE along the eastern coast are the main currents affecting the Adriatic circulation. There are two main cyclonic gyres, one in the northern part and the other in the south. The Bora wind (from NE) causes free sea surface to rise close to the coast enhancing the WAC and the Sirocco wind (from SE), which is the major wind affecting the Adriatic Sea, leads flood events in the shallow lagoons along the basin coast [35]. A vertical thermohaline front parallel to the coast and extending throughout the water mass, divides the coastal waters from the open sea. This retains the materials flowing from rivers and other water sources within the coastal area. A stratification characterizes the water column separating the warmer surface waters with lower salinity from deeper, colder and more saline ones during summer [35].

3.1 Marine sources of plastic pollution

3.1.1 Plastic products in aquaculture and fishery

Across the Mediterranean, but in the Adriatic Sea in particular, there is a continued demand to increase aquaculture production to fulfill the increasing market demand. Mussels, clams, sea bass and seabream production has become a significant source of regional income. Aquaculture was developed to support consumers’ demand for seafood and the methods of production have continued to expand with the growing consumer market. As the need for fish and mussel aquaculture has increased, the development and expansion of aquaculture facilities in coastal and open water locations has increased accordingly. The expansion of the industry and the diversity of materials used to build and maintain aquaculture systems have paralleled the development of synthetic polymers over recent decades. Synthetic fibers offer greater strength and durability than natural fiber ropes; they are cheap, durable and easier to handle compared to their natural counterparts. Most modern aquaculture activities use plastic-based lines, cages, or nets suspended from buoyant or submergible structures (in part made of plastic) and have nanotech plastic-based biofouling and paint applied. Today, tanks, pens, nets, floats, pontoons as well as the pipes of the fish feed supplying systems are made of plastic materials. All plastic material within an aquaculture site is maintained and controlled for chemical degradation, biofouling and corrosion, and is regularly inspected to ensure strength and stability. In the context of global plastic pollution to the oceans, aquaculture may be a contributor to this. However, the estimation of their contribution remains a knowledge gap and lost or derelict gear as well as other possible plastics emissions from aquaculture can be a locally important contributor especially in coastal areas with intensive activity. New reports also point out a potential micro and nanoplastic contamination in wild and cultured seafood products even if the extent of such phenomena is still unknown. There is also concern regarding fisheries as a source of microplastics to the marine environment because both sectors use plastics that may degrade/fragment into microplastics. The coastal areas of Emilia Romagna and the Croatian coast represent sites of intense mussel
and fish aquaculture production with hundreds of tons produced yearly. On the other hand, intense fishing activities coexist with a variety of fishing gear and methods being used in industrial and small-scale fisheries. Fishing gear for capture fisheries includes trawl nets, dredges, surrounding nets, lift nets, seine nets, traps, hook and lines. Nets and floats are made from a range of plastics including PP, PET, NyL, PVC, polyamide (PA) and PS.

3.1.2 Offshore oil and gas production activities

In oil and gas exploration, drilling fluids based on plastic microbeads were introduced a decade ago. Teflon strengthened particles have been largely applied for drilling purposes internationally. Despite the use of Teflon and other polymers with specific features being used extensively in production, waste treatment processes are not designed for, and give no mention of how to handle plastic particles, so this has clearly not been addressed as an issue in the past. Therefore, there is a substantial lack of information on potential loadings of microplastics used in this sector. To date, few fragmentary studies have addressed this topic. CEFAS’s report entitled, “The discharge of plastic materials during offshore oil and gas operations” suggests that 532 tons of plastics and 7475 tons of “possible plastics” have been released from the UK offshore oil sector. Although knowledge about microplastic from oil and gas extraction activities is limited, it is very likely they represent a potential contributor in the emissions of plastics in aquatic environments, including microplastic and fibers, emphasizing that it should certainly be considered in future source assessments. The mapping of the distribution of rigs and platforms in the Adriatic Sea where tens of oil fields with hundreds of medium sized oil rigs occur, may provide estimations about the geographic distribution of the potential input related to these industrial activities.

3.1.3 Decommissioning of ships and oil rigs

Ships and maritime installations contain many plastic items, like insulation, coating, electrical wiring, furniture and textiles. Ideally, installations should be stripped of all potentially hazardous materials before dismantling. However, plastics items are not identified in the list of harmful materials. Therefore, polymer-based coatings and several kinds of insulation and wiring are rarely stripped.

3.1.4 Transportation and logistics

The distribution of products can contribute to the release of plastics in the environment. Most transferring of stock will occur alongside the transport infrastructure network. However, even if recognized as an important source of pollution, the contribution from releases during transportation, and as is the case for shipping, a map of the main transportation network including roads and harbors is still lacking. Systematic mapping in the Adriatic context has been suggested to improve the understanding of the areas where potential inputs can occur, providing a proxy for the potential intensity for release. The Adriatic Ship Traffic Database also contains information on ports in the Adriatic Sea that could be used to gauge the intensity of port activity to identify which of the port areas could potentially be receiving the largest inputs. Furthermore, the cruise ship industry is pointed out as a significant contributor to the problem of plastic pollution in the Adriatic sea. However, very limited data are available and no specific regulations in place for their plastic waste management and/or assessment of their environmental impact [36].
3.2 Land-based sources

3.2.1 Waste management

At a global level, the major challenge to tackle the input of plastic debris from land into the ocean is the lack of adequate waste management in coastal regions with a high and growing population density. Due to a generally high population density in coastal areas of the Adriatic, the pressure resulting from land-based inputs should be relatively high overall. Given such levels of anthropogenic pressure, the lack of, or deficient local waste management systems may lead to locally high inputs linked to industrial or domestic waste management.

There are no studies looking specifically at the leakage and marine input of plastic debris linked to these waste management systems, but ongoing work to quantify and characterize beach litter here points toward potential input from inadequate waste management on the eastern shores of Croatia where the islands of the Quarnero natural park present high loadings of plastic fragments. The composition of the waste accumulated resembles the composition of surveys carried out in the mid-Adriatic region where influence from higher population densities along the coastline is being registered. In addition, a study looking into microplastics near Venice has detected exceptionally high concentrations of small plastic fragments and microplastics in a nearby sandy beach [52]. Though not specified in this report, this exceptionally high concentration of microplastics, including large amounts of plastic fibers and film, could be linked to this location being close to the harbor as well as the lack of waste management facilities. To gain further insight into the potential release of plastics associated with waste management, it would be useful to map the distribution of population density as well as the location of urban agglomerations and settlements as this information will provide an indication of potential localized points of release of plastic waste into the environment. This kind of information is readily available at a sufficient resolution to allow identification of the areas within the Adriatic Sea that need more attention to this potential source of plastic pollution.

3.2.2 Sewage treatment plants

A rough estimation predicts that 70–80% of marine litter, composed primarily of plastics, originate from inland sources, ending in rivers and oceans. However, inland deposition of MP has not been investigated thoroughly. Potential sources include sewage treatment plants (STPs) and runoff from urban, agricultural, tourist, and industrial areas. As the retention capacity of conventional wastewater treatment processes to MPs appears to be variable in both magnitude and specificity, a characterization of MP emission by STPs and other sources is needed to map major sources of freshwater and terrestrial MPs. A relevant input to the terrestrial ecosystem is by fertilizers obtained by processing sewage sludge, as it typically contains more MPs than liquid effluents. Such fertilizers are frequently used in agriculture, implying a potential accumulation of plastic particles in the soil with continued use, and a systematic examination and quantification has been addressed by several research groups around the world. However, due to runoff, deposited plastic items are most likely transported to rivers and other waterways and ultimately discharged into estuarine and marine environments.

3.2.3 Agricultural production

The north of Italy and Croatia represent areas of intense horticultural activities where the agricultural practice of plastic mulching is prevalent. Plastic sheets are
used to cover soil in order to preserve moisture, improve fertility and reduce weed infestation. Very often, fragments of plastic films are left behind after use and may accumulate in the soil, further fragmenting to produce nanometric particles. It has been estimated that 125–850 tons of microplastic per million inhabitants are added each year to agricultural soils in Europe, with an annual total of 63,000–430,000 tons of microplastic added to European farmlands. The northern part of Italy and Croatia is an area of significant agricultural and horticultural activities, therefore representing a potential hot spot for the release of plastic fragments in the terrestrial ecosystem. However, due to runoff phenomena these plastic items are most likely transported to rivers and other waterways and ultimately discharged into the estuarine and marine environments.

3.2.4 City dust and road wear

The first pilot studies of microplastic abundance in confined areas of heavily populated areas like the Oslo fjord noted that a large fraction of particles may be related to city dust (e.g. asphalt and car tires). City dust in urban runoff is known as a significant source of pollution to waterways. Plastics, such as styrene-butadiene, styrene-ethylene-butylene-styrene copolymer, are also used in road materials to make the asphalt more elastic [37]. Another potential contributor to the emissions of plastic fragments is road marking paint as these paints have a variable fraction (1–10%) of thermoplastic component (e.g. styrene-isoprene-styrene, ethylene-vinyl acetate, polyamide and acryl-monomer). On the other hand, the tread of car tires is largely based on styrene-butadiene rubber, a synthetic polymer formulation. Therefore, road dust entering the sea through air or storm water carries a significant fraction of microplastic from road materials, marking paint and car tires.

3.3 Pathways and distribution

The description and understanding of the pathways of the entry of marine plastic pollution into the Adriatic Sea is a central element in tracing the pollution back to its sources and developing effective plastic pollution preventing policies. A complete understanding of the input of plastic pollution into the aquatic environment needs to consider the source sectors and the mechanisms of transportation, distribution and partition through different environmental matrices. If the release occurs in the terrestrial environment, rivers and wind or atmospheric circulation constitute the logic pathways. When considering the presence of plastic debris and microplastics in a part of the global Mediterranean Sea there is a need to consider the transfer of marine plastic pollution into the relevant part of the large water bodies through the regional circulation pathway like the Adriatic Sea. The understanding of the input through these pathways is crucial in gauging the relative importance of local sea-based or coastal sources versus remote sources within the Arctic watershed or from other parts of the ocean.

3.3.1 Riverine input

The Adriatic Sea has a limited watershed. The largest rivers in the area are mostly located in the northern sector and include the Po, Adige, Tagliamento, and Arsa rivers. In terms of discharge, the Po River has the largest discharge with 1540 m³/s followed closely by the Adige River with 235 m³/s. The Po Basin is home to some 14 million people and extends over 24% of Italy's territory. The Po catchment is densely populated and subjected to high anthropogenic pressure heavily anthropized. Indeed, it represents the largest cultivated area in Italy and accounts for one third of national's
agricultural production. The area account also for one of the highest concentrations of economic activities. Such massive river discharges make terrestrial influences particularly strong in the Adriatic Sea. However, to date there is no monitoring of the flux of plastics from rivers into the Adriatic Sea and though it has been identified as a possible pathway, the contribution of riverine discharge to plastic input is expected to be high because these rivers flow through densely populated and anthropized watersheds.

3.3.2 Atmospheric input

It has been speculated that at the global level much less plastic debris is transported by wind than by rivers [38, 39]. However, wind transport of plastic debris may be significant, particularly in coastal areas dominated by strong periodic winds. Wind may be a significant contributor in lightweight debris distribution. During intense storms wind can mobilize debris that would not normally be available for transport and carry it directly into rivers and the sea. Wind-blown litter is likely to be considerable as the Adriatic Sea is characterized by periodically windy shorelines. Atmospheric circulation has been proven to provide an efficient pathway for the transportation of floating microfibers and small plastic particles in the Mediterranean Sea as well as in other areas [33, 40]. Furthermore, some preliminary transport models tailored to the Adriatic oceanographic conditions, considering the contribution of waves and wind in the surface plastic distribution, define the Adriatic Sea as a highly “dissipative” system with respect to floating plastics with a calculated half-life of floating condition of 43.1 days [41, 42]. The authors conclude by pointing out that by construction the Adriatic coastline may be responsible for the main sink of floating plastic debris.

3.3.3 Oceanic input

The contribution of inputs through the movement of marine water masses by currents also needs to be considered in the global distribution model. The Adriatic region is poorly connected to the Mediterranean through the southern edges of the Otranto strait and the Ionian Sea exchanging with the Mediterranean Sea. The exchange of water, and possibly any moving plastic pollution, from and to the Mediterranean Sea has recently been addressed by the modeling work of Liubartseva et al. [40] and partially by the results of Pasquini et al., [40] which pointed out the formation of an accumulation zone corresponding to the three well known gyres located northside, central and in the southern sector of the Adriatic Sea.

4. Occurrence of plastic litter in the Adriatic Sea

4.1 Levels of macro- and microlitter in beaches

Some key research projects have recently addressed the need of defining the baseline levels of litter (macro-, meso- and microplastics) in the intertidal areas of beaches within the Adriatic Sea. Blašković et al. [41] investigated the occurrence of plastic debris in several sites of the Natural Park of Telašćica (Croatia). In all analyzed sites, fibers were the most recurring shape (90%) within the identified plastic debris while films where the second most common plastic fragment observed (7%) followed by pellet, foams, granules and unrecognized plastic pieces. Most of the plastic debris belonged to the size fraction from 1 mm and 64 μm (88%) followed by the fraction between 1 and 2 mm (11%). These results confirm previous characterization efforts of Laglbauer et al. [43] in six Slovenian beaches located in the gulf...
of Trieste (North-East Adriatic Sea). Within this assessment the authors sorted out a total of 5870 macro-debris units, yielding a median density of 1.25 items/m$^2$. The detailed analyses of the processed samples revealed a dominant secondary micro-plastics source being fibers the 85% of the total observed plastics and a number of 155 particles m$^2$ in the infralittoral zone, and 133 particles m$^2$ on the shoreline. On the Adriatic beaches surveyed, plastic dominated in terms of abundance, followed by paper and other groups. The average density was 0.2 litter items m$^2$, but at one beach it raised to 0.57 items m$^2$. Among plastic, cigarette butts were the most frequently found type of litter, and other plastic items with the highest occurrence were: small fragments, bottles and bottle caps, cutlery, and mesh bags. Their presence is a good indicator of pollution from beach users [44]. Most of the beached marine litter are from land-based sources, but with different sources and contributors. The main source of litter was primarily touristic activities, accounting for 37.9% of found litter which is lower than the Mediterranean average (52%; [45, 46]). Filter cigarette were the second litter origin, but with a value (25.5%) lower than indicated for the Mediterranean (40%) [44]. The high percentages of in situ deposited litter found in the investigated sites are caused by the high number of visitors, more than 700,000 annually mainly during the touristic season (see i.e., http://statistica.regione.veneto.it; http://imprese.regione.emilia-romagna.it).

4.2 Levels of macro- and microlitter in surface waters

Few studies have addressed the occurrence of floating plastic debris in the surface water of the Adriatic Sea. Suaria et al. [33] reported by a larger study addressing the Mediterranean Sea and partially the Adriatic sector a clear prevalence of smaller particles. Quantitative estimations collected by a 400 μm net mesh pointed out values ranging from 0.4 ± 0.7 to 1.0 ± 1.8 items/m$^3$. The overall result the study pointed out that, within a total no. of 14,106 scored particles, 26% of all counted particles were smaller than 300 μm while 51% were smaller than 500 μm being the mean abundance of these meso-particles of 0.016 ± 0.028 particles/m$^2$. PE was the predominant form with an overall frequency of 52%, followed by PP (16%) and synthetic paints (7.7%). Polyamides (PA) accounted for 4.7% of all categorized particles which accounted alone for 2%, while PVC, PS and PVA represented equally contributed with 3% of the total. Other less frequent polymers (≤1%) included: PET, polysisoprene, poly(vinyl stearate) (PVS), ethylene-vinyl acetate (EVA) and cellulose acetate. Noteworthy the authors concluded that the composition of western Mediterranean samples was dominated by low-density polymers such as polyethylene and polypropylene while the processed Adriatic samples instead were more heterogeneous and rather characterized by a higher presence of paint chips, PS, PVC, PVA and PAs. Within the “Derelict Fishing Gear Management System project – “DeFishGear” project co-funded by IPA-Adriatic Cross-border Cooperation Programme and the European Union, 120 visuals transect surveys were conducted during three cruises, covering a total length of 922.2 km [47]. A total of 1364 macro marine debris objects were observed floating on the Adriatic. The densities of the recorded floating debris were 5.66 items/km$^2$. The authors estimated that the observed floating marine debris was mostly originated from coastal segments close the high-density population cities and major rivers and transported by cyclonic surface circulation until either stranding. They calculated an average time from source to the sighting point of 22.8 days. These outcomes support Carlson and co-workers [48] previous assessment where an average residence time of 22.9 days but with also an average transit times of 20–60 days from a coastal region in the northwest Adriatic to a coastal region in the southwest [47]. The transport pathways, residence times, and probable sources and sinks identified further
support with previous studies of the Adriatic Sea surface circulation and marine debris published by Liubartseva et al., [40].

4.3 Levels of macro- and microlitter in sediments

Data regarding macro- and mesolitter on the sea-floor in the Adriatic Sea are also available from the “SoleMon” Project (Solea Monitoring—Rapido trawl survey in the Northern Adriatic Sea), carried out since 2005 in the Northern and Central Adriatic Sea [49]. Plastic litter was divided by the authors in three sub-categories based on its source: fishing nets, mussel culture debris and other plastic e.g., bottles, plastic glasses, bags. Lost fishing nets and mussel culture debris accounted for 50% of the overall plastic litter collected over the investigated period. The remaining plastic comprised a wide range of objects such as garbage bags, shopping bags, cups, bottles, food packaging, dishes, other kitchen stuffs and industrial packaging [40, 48]. Results of this study indicated that the largest amount of mussel culture debris was found close to the coast and its distribution was constant over the years. These nets might have been accidentally lost/abandoned at sea during the collection and preparation of the product [50]. In the meantime, the fishing nets were found mainly close to the coast within 3 nm. This distribution was explained as fishing nets were mainly set-nets used by small scale fisheries that usually fish not further than 3 nm where there is not trawl fishing that can destroy these nets. A significant contribution of plastic litter found close to the coast was represented by food packaging, plastic bags, bottles and dishes or kitchen tools. The land origin is due to the municipal solid waste [48]. The authors concluded considering that the distribution varied among the years, but the occurrence was mostly related to both the close position of the sampling site to large cities along the coast, where the population density increases during the touristic season as well as the contribution of river [40, 50, 51]. As regards the microlitter in the sedimentary environment, a preliminary assessment of microplastics in marine sediments along a coast-offshore transect in the Central Adriatic was performed by Munari et al. [44]. Plastic fragments recollected from 64 samples were scored, weighted and identified by FTIR. Microplastics ranging 1–30 mm were found in all analyzed samples. The most recurring shapes were filaments-like (69.3%), followed by fragments-like (16.4%), and film-like (14.3%). In term of size distribution, plastic fragments in a range from 1 to 5 mm accounted for 65.1% of debris, while larger fragments (5–20 mm) contributed with the 30.3% of total amount, while larger fragments >20 mm represented the 4.6% of total. Six were the most recurring polymer types: nylon, polyethylene and ethylene vinyl alcohol copolymer. Furthermore, sediments from several sampling sites located in Italy, Slovenia, Croatia, and Greece were also analyzed for plastic debris content by the “DeFishGear” project. Plastic fragments in beach sediments were ranked into large sized particles (1–5 mm) and small microplastic particles (<1 mm). In general, microplastic from 1 to 5 mm ranged from 11 to 710 items/m². On the other hand, the fraction of smaller size scored from 70 to 6724 items/kg of dry sediments. The mean concentration for all Adriatic region was calculated as 113 ± 101 items/kg for the larger sized fragments and 1133 ± 1271 items/kg of dry sediments for the smaller ones. In detail, the selected Croatian beaches showed considerably greater presence of smaller microplastic per kg of sediment with value of approx. 227 items/kg of sediment while the larger sized fragments sored values approx. Ten times lower (17–28 items/kg of dry sediments). The composition of sorted fragments <1 mm showed the prevalence of plastic fragments as fragments represented approx. 70% of the total while filaments represented the left 29% of the total while a limited amount (1.8 and 0.9%) were film and foams. The chemical
characterization of microplastic of the larger particles was performed on foams, pellets, fragments and filaments, while filaments and films were analyzed among the smaller sized particles. Beside the PE and PP in a few percent also PA, PET, PES, PS, PO, nylon and acrylic fibers were present among larger particles, while among the smaller viscose was detected. In the Greek sector data were obtained from three sites: the Halikounas, Issos and Acharavi beaches. The mean concentration of 1–5 mm sized debris varied from 68 items/m² (Halikounas) to 58 items/m² (Acharavi) while the small sized fraction of Ø > 1 mm showed values from 19 to 7 items/m² respectively for Halikounas and Acharavi. The most abundant categories on Halikounas beach were fragments and foam, while on the contrary pellets were the most abundant in Issos and Acharavi beaches. Chemical characterization of fragments, for Halikounas beach were done being both PE and PP the most recurring polymers in the larger particles while PP was the most occurring polymer in the smaller size fraction. The same project also addressed the occurrence in the Italian sector. High amount of small microplastic particles (<1 mm), up to 2526 items/kg of sediment, was found in the Cesenatico area. In the meantime, a limited amount corresponding to 0.56–1.02 items/kg of large particles (1–5 mm) were reported. Overall, 73% of the small microplastic particles were characterized by fragments while the remaining 26% as filaments. On the other hand, the large microplastic particles had different amount of all categories; however, fragments resulted the most abundant category (44%). The chemical identification showed PE as the most abundant material, followed by PP, PO, PES, PS and PAN. In the Slovenian coastline the selected sampling site showed a higher abundance of small microplastic particles (615 items/kg) respect of large microplastic particles (516 items/kg). In detail, the analysis of the small size fraction reported filaments being the predominant type of the microplastic composition, with representation of approx., 76% of the total. The second most common type of microplastic category were fragments and the third were films, with occurrence high as 9.5%. The chemical identification pointed out PE as the most recurring polymer type in the analyzed sediment samples, by followed by PP, PET and PVC. Finally, Vianello and co-workers investigated the Venice Lagoon, a fragile estuarine ecosystem dominated by diversified anthropogenic activities, suspected to be a hot spot of plastic debris contamination [53]. Plastic debris of ≤1 mm or less was investigated in sediments collected from 10 sites chosen in shallow areas. Total abundances of plastic fragments varied from 2175 to 672 items/kg with higher concentrations generally found in the inner parts of the Lagoon. PE, PP, ethylene propylene (PEP), polyester (PEst), polycrylonitrile (PAN), PS, alkyd resin (Alkyd), PVC, polyvinyl alcohol (PVOH) and NyL were identified. PE and PP were the most recurring polymer in the investigated samples which accounted for more than 82% of the total detected plastic debris in the whole sampling area. Among all classified shapes, irregular fragments accounted of the 87% of the total while films (2%) and pellets/granules (1%) were only occasionally recognized [54].

4.4 Levels of microplastic in biota

The first report on the harmful effects of plastic debris ingestion on marine species in the Adriatic Sea was published in 1999 [55]. A dead dolphin S. coeruleoalba with the stomach occluded by different kinds of plastic materials was found near the island Krk, in the North Adriatic Sea. A following study on the logger head sea turtles, C. caretta, revealed a percentage of 35.2% of turtles sampled in the eastern Adriatic Sea were affected by plastic debris [55]. Occurrence of MPs in the gastrointestinal tract and gills of pelagic and demersal fish and marine mammals have been reported [56]. Few plastic debris accumulation studies have been performed in
the Adriatic Sea. Pellini et al. [57] aimed at characterizing the occurrence, amount, typology of microplastic litter in the gastrointestinal tract of a benthic fish, *S. solea*, in the northern and central Adriatic Sea. The digestive tract contents of over 500 individuals were collected from 60 sampling sites and examined for microplastics. These were recorded in 95% of sampled fish, with more than one microplastic item found in around 80% of the examined specimens. The most commonly found polymers were PVC, PP, PE, polyester (PES) and PA. In details, 72% of the total classified plastic debris were fragments and 28% were identified as fibers. The mean number of ingested microplastics was 1.6–1.7 items/fish. PVC and PA showed the highest densities in the northern Adriatic Sea, both inshore and off-shore while PE, PP and PET were more concentrated in coastal areas with the highest values offshore from the port of Rimini. These results confirm previous observations of Avio and co-workers [13] in various fish species collected along the Adriatic Sea.

FTIR analyses indicated PE as the predominant polymer (65%) in the stomach of fish. More than 100 fish representatives of five commercial species like *S. pilchardus*, *S. acanthias*, *M. merlucius*, *M. barbatus* and *C. lucernus* were collected from the Central and North Adriatic Sea. The mean number of ingested microplastics was 1.0–1.7 items/fish. In details, the shape of the plastic debris observed in the stomachs of the investigated samples was mostly fragments and line followed by film and pellet. The 18% of extracted microplastics exhibited the larger size class (from 5 to 1 mm), 43% was between 1 and 0.5 mm, 23% between 0.5 and 0.1 mm, and the 16% lower than 0.1 mm. The chemical characterization pointed out that approximately 65% of analyzed plastic fragments were PE, followed by PET, PS, PVC, Nylon and PP. These early findings suggest the possible accumulation of plastic debris through the food web. Despite of some recent findings point out that at the bottom of the food pyramid, filter feeders, such as mussels can ingest and incorporate MPs in their tissues [58], more research is needed to unveil the abundance, distribution and polymeric composition of plastic debris in marine organisms at different levels ecological web in areas like the Adriatic Sea were multiple anthropogenic activities coexist.

5. Conclusions

The few available studies in the area prove the ubiquity of plastic pollution in the Adriatic Sea. The peculiar oceanographic conditions as well as the high levels of plastic debris recorded in all investigated matrices tend to classify such enclosed area as a hot spot of plastic contamination. Despite the distribution and circulation models appear to accurately estimate fluxes and final fate of marine plastic debris, sinks, sources, fate and residence times of different polymers at sea are the knowledge gaps that need to be addressed in the future to provide concrete info to support concrete actions toward plastic contamination reduction and remediation solutions.

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Conflict of interest

The authors declare no conflict of interest.
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