Journal of
Marine Science and Engineering

MDPI

Review

Knowledge about Microplastic in Mediterranean Tributary River Ecosystems: Lack of Data and Research Needs on Such a Crucial Marine Pollution Source

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Received: 4 February 2020; Accepted: 19 March 2020; Published: 20 March 2020

Abstract: Plastic debris occurring in freshwater environments, which can either come from the surrounding terrestrial areas or transported from upstream, has been identified as one of the main sources and routes of plastic pollution in marine systems. The ocean is the final destination of land-based microplastic sources, but compared to marine environments, the occurrence and effects of microplastics in freshwater ecosystems remain largely unknown. A thorough examination of scientific literature on abundance, distribution patterns, and characteristics of microplastics in freshwater environments in Mediterranean tributary rivers has shown a substantial lack of information and the need to apply adequate and uniform measurement methods.

Keywords: plastic litter; freshwater ecosystems; sediments; floating microplastic; estuarine environments; marine litter

1. Introduction

Among environmental pollutants, microplastics (MPs) are currently receiving much attention as they have been found in all matrices of aqueous environments and their ingestion by animals has been widely observed [1–4]. The risks related to MPs derive from the multitude of chemical additives contained in the plastic raw materials and from all contaminants (such as chlorinated pesticides, polycyclic aromatic hydrocarbons, dioxins, metals etc.) [5] absorbed from surrounding media. MPs can act as a vector of pollutants and a source of exposure to wildlife, also leading to risks to human health [2,3].

Most of marine litter and MPs in the sea come from land: the rivers, in particular, are responsible for up to 80% of the plastic load floating on seas all over the world [6]. As for the Mediterranean, the highest amounts of MPs have been found at sites subjected to heavy riverine run-off and at lagoons [7,8]. Several studies have demonstrated the presence of MPs in freshwater environments, including beaches, surface waters, and sediments of rivers, lakes, and reservoirs [9–18] emphasizing the ubiquity of this form of pollution and the risks to freshwater ecosystems [19]. Studies also presented have shown that MPs are present in different layers of the river-bed and of the water column (e.g. [20] or [21]).

Classified according to the annual discharge, the ten largest Mediterranean tributary rivers are the Rhone, Po, Drin-Bojana, Nile, Neretva, Ebro, Tiber, Adige, Seyhan, and Ceyhan. These rivers account for half of the mean annual water discharge into the Mediterranean, with the Rhone and Po contributing a third [22,23]. The discharge into the Adriatic Sea, the North-western Basin, and the Aegean Sea represents 76% of the total, with the Adriatic accounting for about one third of the total [23]. Other rivers can be considered important, even if of relatively small dimensions, because they are characterized by the crossing of regions rich in civil or industrial settlements or densely populated, therefore of concern for many forms of pollution. Examples in this context are the Arno and Vjosa rivers [23].

Given this pattern of tributary rivers and the importance of what they convey in determining sea pollution levels, knowing the level of MP contamination of these rivers represents the starting point for assessing the status of the Mediterranean. This in turn generates important information on pollution sources and hotspots and provides significant data to territorial managers and decision makers on where to intervene in order to mitigate risks and damages and to begin restoration.

This review considers the current literature on the occurrence of MPs in the Mediterranean tributary rivers, considering parameters such as environmental matrices levels and patterns, organisms' exposure, as well as risks and evidencing information gaps.

2. Discussion

All data on MP contamination in river environments from different studies on Mediterranean tributaries are reported in Table 1. The data available are graphically reported in Figure 1.

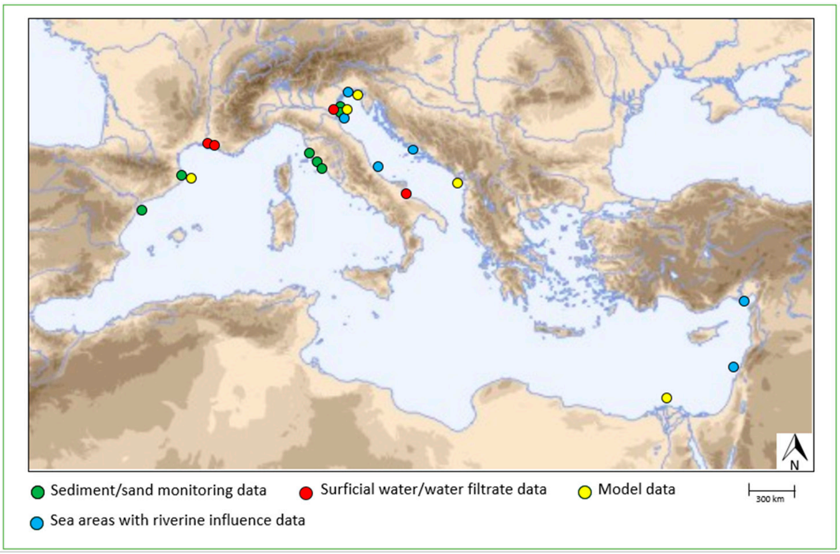

Figure 1. Map showing the geographical locations for data available on microplastic contamination in Mediterranean tributary rivers.

In the table, together with the name of the river, the geographical area, the drainage basin, the matrices analysed in the study, and the results in qualitative and quantitative terms, a summary of the analytical method is also taken into consideration. The latest updated information was necessary here, however this review did not focus on analytical methods, due to the considerable variety of analytical processes and ways of expressing the results, found in the compilation of the table itself. This aspect, which may seem pleonastic in a reasoned review of data on the presence of contamination in a large area, is recognized by many authors as one of the most critical [7,24–29].

Table 1. Field data and laboratory analytical methods for microplastics (MPs) in environments of Mediterranean Sea tributary rivers.

Drainage Basin	River Area	River	Matrices Analysed	MPs Level	Notes	Experimental Details	Reference
Thyrrenian Sea	Southern Tuscany (Italy)	Osa and Albegna	Surficial sediments from river rod, river mouths, and beaches	Mean levels items/kg dry sediment: Osa river 286 ± 37 Albegna river 453 ± 424		Decantation in NaCl solution, filtration; particles recovered on paper filter, examined under a light microscope and measured by graph paper. Smallest fraction considered: range 0.063–0.125 mm	[30]
	Southern Tuscany (Italy)	Ombrone, Osa	Surficial sediments from river rod, river mouths, and beaches	Ranges items/kg dry sediment: Ombrone river 75–188; Maremma Regional Park shores (Ombrone's mouth) 45–397; Osa river 134–312 Albinia shore (Giannella-Osa's mouth) 134–1069	Incorrect agricultural practices identified as potential source of plastic pollution	Decantation in NaCl solution, filtration; particles recovered on paper filter, examined under a light microscope and measured by graph paper. Smallest fraction considered: range 0.063–0.125 mm	[31]
	Central Tuscany (Italy)	Cecina	Surficial sediments from river rod, river mouths and beaches	Range items/kg dry sediment: 72–191	The highest values at Cecina river mouth (urban beach)	Decantation in NaCl solution, filtration; particles recovered on paper filter, examined under a light microscope and measured. Polymer identification on selected items by Fourier Transform Infrared Spectroscopy. Smallest fraction considered: range 0.063–0.125 mm	[32]
Northern Adriatic	Northern Italy	Po	Beach samples	Range items/kg dry sediment: 0.5–78.8	Various levels of river estuarine influence; mainly PE and PS found	Decantation in $ZnCl_2$ solution, filtration, rinse with 98% ethanol; particles recovered on glass Petri dish, examined under a stereomicroscope and measured. Polymer identification on selected items by Fourier Transform Infrared Spectroscopy	[33]
			Sandy beaches of the Po River Delta	Range items/kg dry sediment: 2.92 (±4.86 SD)–23.30 (±45.43 SD)	The accumulation of microplastics among drift lines showed no consistent pattern, besides expanded polystyrene tending to accumulate backshore	Decantation in ZnCl2 solution, filtration, rinse with 98% ethanol; particles recovered on glass Petri dish, examined under a stereomicroscope and measured. Polymer identification on selected items by Fourier Transform Infrared Spectroscopy	[34]

Table 1. *Cont.*

Drainage Basin	River Area	River	Matrices Analysed	MPs Level	Notes	Experimental Details	Reference
			Surficial water sampled in Ferrara	About 2 million MPs/km^2	Po river showed the highest levels, in comparison to other three European rivers	Manta trawl sampling (333 µm). Samples sieved, cleaned with filtered tap water rinsed with 70% ethanol and stored in the refrigerator. Microlitter removed from the samples using stereomicroscopes and micro tweezers; particles dried, weighted and photographed. Fragments and pellets analysed by near infrared spectroscopy; foams and fibres analysed by Fourier transform infrared spectroscopy in ATR mode.	[35]
Southern Adriatic	Southern Italy	Ofanto	River water filtrates	Range items/m^3: 0.9 ± 0.4–13 ± 5	Significant temporal and spatial variation in microplastic concentrations. The highest during wet periods indicating land-based attributed to agricultural waste Strong positive statistically significant correlation between the concentration of microplastics and the water level	Plankton nets (2.5 m long), mesh size of 333 µm and opening 55 x 55 cm Samples wet-sieved at 300 µm and a 5 mm, digested using 30 % hydrogen peroxide with iron (II) catalyst Decantation in NaCl solution, filtration through 1.2 µm glass microfiber filter Items extracted examined under a 40 X digital microscope	[36]
Gulf of Lion	Southwestern France	Tet	Beach samples	Mean value in the sampling area close to the river mouth up to 798 items/kg dry sediment	Area influenced also by Rhône river; mainly PE and PS found	Decantation in salt solution, filtration; particles recovered on paper filter, examined under stereomicroscope and measured by Fourier Transform Infrared Spectroscopy	[37]

Table 1. *Cont.*

Drainage Basin	River Area	River	Matrices Analysed	MPs Level	Notes	Experimental Details	Reference
	Swiss and Southern France	Rhône	River and sea surficial water filtrates	Range items/Km^2: 33–400 (mean 11) river plume 7–69 (mean 34) items river	Rhône River at Arles (France), 48 km from the river mouth Fibres not taken into account Estimations for daily microplastic transport by the Rhône range 0.20 to 21.32 kg	Plankton net size 0.50 m × 0.15 m, mesh size 780 µm Samples preserved with a buffered seawater formalin solution, sieved (mesh size 125 µm) and rinsed with ultrapure water Plastic debris picked out with tweezers under a dissecting microscope	[38]
			River surficial water filtrates	Range items/Km^2: 52–103	Rhône River at Chancy (Swiss); PE > PP > PS	Plankton net size 0.60 m × 0.18 m, mesh size 300 µm Samples, digested using 35% H_2O_2 with iron (II) catalyst Decantation in NaCl solution, filtration Items examined under a microscope and polymer identification by Fourier Transform Infrared Spectroscopy	[39]
North western Mediterranean	Catalonia, Spain	Ebro	Sandy beaches and benthic sediments	Mean items/kg dry sediment sandy beaches samples: 422 ± 119 sediment in the riverbed: 2052 ± 746	The Ebro surface water estimated to represents a yearly input of 2.14 × 10^9 MPs to the Mediterranean Sea	Sandy beaches samples: Decantation in NaCl solution, filtration; particles recovered on glass fibres filter Benthic sediments: extraction by NaCl an H_2O_2 solution; filtration; particles recovered on glass fibre filter Items extracted examined under a stereomicroscope	[40]

To the best of our knowledge, data reported in Table 1 indicates that, despite a large number of important freshwater inputs in the Mediterranean Sea, studies on the occurrence of MPs of tributary rivers are very limited, almost all are very recent, and mainly concern the final part of the rivers. This is probably attributable to the fact that MP monitoring is a relatively new topic compared, for example, to chemical contamination. In general, large rivers around the world have so far received relatively little attention, as noted by a review of scientific literature by Campanale and colleagues [36]. There are no systematic studies on entire rivers from the source to the mouth and especially for Mediterranean tributaries, considering the actual inputs. The monitoring data available (Table 1) are limited to the following Mediterranean tributary rivers: Osa, Ombrone, Albegna, Cecina, Po, Tet, Ebro, Ofanto, and Rhone. The levels reported are extremely variable: among the lowest values in beach and sediment samples, there are those measured in the Po [33,34], the highest ones refer to the Tet and Ebro [37,40], both flowing in the north-western Mediterranean. The available data regarding the values of MPs in water are scarce and, in general, poorly comparable. An example is the article by Schmidt and colleagues [38] in whose analysis microfibers were not quantified; an underestimation of real data should be taken into account when comparing these results, since fibres are often the most abundant form of MPs (for instance 40%–90% in Tet River [37] and 70% in the Ebro [40]). The level reported by Van der Wal et al. [35] for the Po River is the average maximum number detected in the study.

Some studies attribute to agricultural practices (even fraudulently) a large part of the load of plastics found in the water and river sediment samples [31,35]. The use of plastic pipes for irrigation and plastic sheets for the protection of crops, which were then abandoned in the fields, instead of being properly disposed of, found a correspondence among the levels and patterns of MPs in sediments and river water [28,32].

Concerning the studies of floating MPs reported in Table 1, several authors given the large variability in results from one sampling time to the other, emphasize the need of performing replicate sampling to gain a better understanding of spatial and temporal distribution patterns [33,36,37].

The Isonzo, Timavo, Rizâna, and Dragonja rivers, flowing in the northern Adriatic have not been directly monitored. Indirectly, however, the data on the presence of MPs reported for sediments collected in the Gulf of Trieste (133.3 items/kg dry sediment shoreline and 155.6 items/kg dry sediment infralittoral) provide an indication of the importance of the contribution of these rivers [41]. The same considerations, still relative to the Adriatic area, are valid for the Livenza and Lemene rivers, Adige, Reno, Lamone, Fiumi Uniti, Bevano, and Pescara, although not directly monitored, of which the order of magnitude of the contribution of MPs can be deduced from the values found in the sediments of marine areas subject to their influence [42–45]. In particular, very high levels of MPs were found in the sampling stations located between the mouth of the Livenza and Lemene rivers (700 items/kg dry sediment, [44]) and between the mouth of the United Rivers and the Bevano river, (1512 ± 187 items/kg dry sediment [43]. Other Mediterranean areas affected by rivers have been monitored for the presence of MPs, such as stretches of coastline in Turkey [46] and Lebanon [47].

As for the Nile River, one of the major tributaries of the Mediterranean, in recent literature no data on the actual MP contamination have been found. A global circulation model ranked this river fourth among those that, at a global level, contribute to the input of MPs in marine environments [48]. Other models have calculated the MPs that rivers export, focusing also on the Mediterranean area. The river export of MPs to coastal seas (calculated for the year 2000) showed a wide range that reflected the variation of socio-economic development and technologies applied in the sewage treatment [49]. MPs export to the Mediterranean Sea was by far the highest figure (5.6 kilotonnes), compared to those calculated for the Black Sea (4.1 kilotonnes), for the European part of the Atlantic Ocean 2.7 (kilotonnes), the North Sea (1.1 kilotonnes), and the Baltic Sea (0.9 kilotonnes). The study also estimates that the input attributable to the Rhone is 163 t MPs per year [49].

A further model [50] estimates water concentrations of MPs for the Po River equal to 0.0035 g/m^3: according to this estimate, the MPs concentrations of this Mediterranean tributary would be similar to other European rivers (Rhone, 0.0043 g/m^3, and Danube, 0.0041 g/m^3). The application of this model also confirms that river export of MPs to the oceans varies considerably among regions. Furthermore, in general, the study points out that the fragmentation of macroplastics is the main source of MPs in rivers and predicts that by the year 2050 export of MPs might increase by 50% unless adequate mitigating actions are applied [50].

As regards overall, the contribution to plastic litter pollution, an average of 208 t per year was estimated to enter the Mediterranean from the Rhone [51], 1349 t from the Po, 575 t by Buna/Bojana, 283 t by Neretva; and 191 t by Adige [52].

Data on organisms are even rarer than those on water and sediments; mainly these are related to exposure experiments [3,53–55] or, more recently, aimed to assess the risk in the case of organisms intended for human consumption [2]. Few studies consider the ecological effects of MPs in whole ecosystems, in their spatial complex, in the biotic and abiotic compartments and in what happens at the level of entire food chains [56–58]. The above statement is generally valid for knowledge concerning the spread and effects of MPs, but in particular for freshwater environments.

The contamination of a multitude of different marine organisms has been demonstrated by monitoring all over the world: for example in plankton [59], elasmobranchs [60,61], whales [1,62], teleosts [63,64], and molluscs [2,65–67].

On widening the horizons outside the Mediterranean tributaries, even at a global level, there are very few monitoring studies on river organisms. The occurrence of microplastics in the digestive tract of the gudgeons (*Gobio gobio*) was investigated in specimens from French rivers: freshwater fish ingest MPs, with 12% of collected fish found to be contaminated [68]. The occurrence of MPs was also studied in digestive tracts of fishes from the Amazon River estuary, finding particles in 14 out of 46 species considered [4,69].

Recently, Hamed et al. 2019 [55] exposed early juvenile Nile Tilapia (*Oreochromis niloticus*) to MPs, evidencing an accumulation in the whole body and effects like anaemia and perturbations in the biochemical parameters. This is the only example of an exposure experiment involving riverine fish, ecotoxicological experiments being mainly concerned with MP ingestion and the effects in various marine species (for example [3,53,54]). However, most experiments were conducted by exposing organisms to microspheres at high concentrations [70] for short periods; this situation does not reflect the reality of natural environments, since the microspheres represent a very small part of the MPs present [71].

3. Conclusions

Literature studies analysed show various critical issues regarding the assessment of MPs in freshwater environments in general and in Mediterranean tributary rivers in particular.

First of all, there are limited data on the presence of MPs in water or sediment of the largest Mediterranean tributary rivers (Rhone, Po, Drin-Bojana, Nile, Neretva, Ebro, Tiber, Adige, Seyhan, and Ceyhan). There are no data for other rivers, such as the Arno and Vjosa for example, characterized by crossing regions rich in civil or industrial settlements or densely populated. In any case, the available data are limited to a few sampling points, often close to the river mouth, and to single matrices or compartments. There are no systematic studies on the entire course of a river or involving various environmental compartments and biota, addressing different discharge conditions of the rivers. Making comparisons between results of studies made with such different approaches is difficult; however, it is possible to draw in-depth elements, such as, in some cases, the agricultural origin of plastic contamination.

Few studies address the problem of MPs from an ecological point of view, which is considering an entire environment, with its communities, food webs, and its balances, as a whole.

Other critical aspects emerged are represented by the need to:

(1) carry out sampling campaigns articulated in space and repeated over time, given the extreme variability reported by many studies and the emergence of the scarce significance of point-like monitoring. Long term monitoring has to be carried out on a regular basis to improve the data

on MP occurrence, in order to identify sources and contamination dynamics and to mitigate the effects.

(2) harmonize protocols for sampling, MP identification and expression of results, necessary to compare the results from different studies and integrate them to draw general conclusions. A standardized methodology for measuring the MPs should also address the different layers and harmonized sampling methods should be uniform net sizes and units (e.g. particles per volume, mass per volume, mass per second, etc.).

Once the MP pollution in Mediterranean tributary rivers has been better evaluated, the results can be the basis for strategies to manage and mitigate problems. Particular attention should be paid to the management of plastic materials in agriculture, a field in which information to operators on the management of plastic materials used in the fields and their correct disposal and control plans would be highly desirable.

Effective and complete monitoring data on rivers should be disseminated to the general population, which, erroneously, may be led to think that the problem of plastic pollution only affects the sea, given the greatest media attention. The general population could obtain an attitude of attention and protection, aimed at avoiding incorrect and harmful practices, being aware of the pollution levels of rivers and the associated risk for the balance of the ecosystem and for species.

Author Contributions: Conceptualization, C.G., T.M. and A.C.; Investigation, C.G., L.G. and G.P.; Writing–Original Draft Preparation, C.G.; Writing–Review and Editing, C.G., G.P., T.M., A.C., L.G.; Supervision, A.C., L.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: All the authors declare no conflict of interest.

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