

Microplastics in Mediterranean coastal area: toxicity and impact for the environment and human health

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ABSTRACT

The so-called marine litter, and in particular microplastics (MPs) and nanoplastics (NPs), are ubiquitously distributed and recognised as an emerging risk for the environment and human health. It is known that marine environments are one of the most impacted areas and among them; coastal zones are the most contaminated ones. They are subjected to population pressure, tourism, harbours, desalination plants, marine traffic and fish farms.

This review is focused on the Mediterranean Sea, currently considered one hot spot of microplastics pollution in the world, as a consequence of the high number of plastic marine litter generating activities and its characteristic morphology of semi-enclosed sea. MPs and NPs have been detected not only in surface water and water columns but also in sediments, deep seafloor, and biota including fish and seafood for human consumption. Because of this, different European legislation initiatives have been launched during the last years in order to prevent MPs and NPs contamination and to face derived problems. Finally, this review summarises the main problems and shortcomings associated to MPs and NPs analyses such as their identification and quantification or the necessity of standardised protocols.

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1. Introduction

In 1972, E. J. Carpenter and K. L. Smith presented the first publication alarming about the presence of plastic pellets on the surface of the North Atlantic Ocean [1]. However, it has not been until the last 10 years when a general increasing concern has raised, both in the research community and the society, about the impact of plastic-based pollution in the marine environment. The plastic pollution is one of the major environmental challenges generated by the unsustainable use and disposal of plastic products by human societies. Nowadays, it is recognised as a global complex, multidimensional and multi-sectorial problem with environmental, economic, public health, food safety and even cultural impacts.

In spite of the enormous number of works recently carried out, the knowledge about the quantities, sources and impacts of marine litter continue being limited. However, it is widely accepted that

both the levels and the rate of entry into the oceans are increasing. Moreover, the microplastics (MPs) and nanoplastics (NPs) themselves can be a source of pollutants to the environment, through the release of additives and plasticisers used in conjunction with the basic polymers. Plastics concentrate contaminants from the environment (air, water or particulate matter) which can be transferred to the marine environment [2]. Besides, they also can adsorb other contaminants present in the water column and marine sediments, accumulate and transfer them to the biota [3,4]. MPs have sizes similar to plankton, benthic protozoa and bacteria, and their presence in marine environment facilitates their ingestion by aquatic organisms, with particular reference to those with a relatively indiscriminate feeding strategy (e.g. planktonic suspension and filter feeders).

MPs are defined as plastic pieces below 5 mm and they include NPs. They have their origin in cosmetics and cleanser products (primary MPs) and in the fragmentation and erosion of plastics pieces and debris (secondary MPs) [5,6]. MPs and NPs generate another type of environmental problems compared to macro and meso-plastics pollution due to their size difference.

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Coastal areas are submitted to direct environmental pressures like the increasing population (10 % of the world's population live on the coast), the tourism, harbours, desalination plants, marine traffic and fish farms that contribute to the emission of complex mixtures of contaminants including plastic pollution. Besides, there are also indirect contributions through their release via fluvial discharges and atmospheric deposition. The estimated per capita emission of those plastics into rivers is 8.8 kg/cap/y for macro-plastics and between 0.0055 and 0.18 kg/cap/y for MPs coming from the fragmentation of macro-plastics as a significant contribution but also from personal care products, laundry fibres and tyre wear [7]. The recognition of the magnitude of the problem has given rise to a series of initiatives at the global level [8], such as those included in the European Marine Strategy Framework Directive (MSFD). The initial studies about MPs in the marine environment have been focused on plastic debris around 5-1 mm size, and the identification of MPs composition and characterisation. However, quantification is still challenging (as it is addressed in section 5. 1), and the current studies are mainly focused on (1) their presence in water and sandy and muddy sediments, (2) vertebrate and invertebrate ingestion, (3) leachates of other chemicals from their composition, and (4) co-contaminants interactions and (5) particulate and chemical toxicity.

Several reviews have discussed the presence of MPs in marine environments, with particular emphasis on plastic litter and the estimation of MPs in the oceans [9–12]. Besides, the occurrence of meso- and MPs is also gaining attention in freshwater ecosystems [13–15]. The accumulation in biota has been very much discussed in some cases, together with their toxicological aspects [16–20]. In relation to the accumulation in biota, the relevance of MPs for food safety is another hot topic nowadays [21–23] despite the fact that the risk of MPs in foodstuff is still mostly unknown and the risk derived from MPs associated contaminants is controversial. Other reviews have approached the different analytical methods available for the determination of MPs and NPs in complex samples [24,25]. Recently, some publications have assessed MPs in

different geographical areas, such as freshwater ecosystems in China [26], the North Pacific gyre [27], subtropical gyres [28], the Atlantic ocean [29,30], and the Antarctic marine systems [12,31,32]. However, some of these reviews should face up different data (weight of plastics or number of items), sampling protocols, and the data comparison is therefore difficult. Concerning the Mediterranean Sea, different authors have provided an overview of the abundance and composition of plastic debris in the sea surface and the water column with emphasis on hydrodynamic features [33,34]. The Mediterranean is a semi-closed sea with a substantial contribution of land pollution (80% of the total) as consequence of the high population density and industrial activities concentrated in its coasts. It is currently in a critical pollution situation, overexploitation and under the pressures of global warming and the European Union (EU) has highlighted the need to take measures for its preservation. In this regard, different projects have been funded during the last years (see Table 1), boosting the research of the occurrence, fate and behaviour of MPs and NPs in the different Mediterranean Sea compartments. The present review provides insight into the abundance of MPs in the Mediterranean Sea, levels of organic contaminants related to plastics formulation, impact on biota, and potential transfer along the food chain.

2. General problems of microplastic pollution in marine ecosystems

Some of the main problems associated with the presence of MPs in marine waters are eutrophication, their behaviour as transfer vectors for other co-contaminants and microorganisms, and its ecological function as sites for the colonization of microorganisms [35] and their introduction to the aquatic food web.

Another relevant problem associated with plastic litter in general and MPs in the aquatic environments is their role as a source of chemicals that can lixiviate from their composition. In addition, MPs act as transport vehicles for other toxic contaminants adsorbed on their surface [36–38] that can be eventually

Table 1
on-going European and national projects related to microplastics and plastics in Mediterranean Sea.

Title	Call	Execution period
On-going European projects within the H2020 [153]		
ATLAS: A Trans-Atlantic Assessment and deep-water ecosystem-based Spatial management plan for Europe (678760)	H2020-EU.3.5. H2020-EU.3.2.	1 May 2016 – 30 April 2020
CLAIM: Cleaning Litter by developing and Applying Innovative Methods in european seas (774586)	H2020-EU.3.2.5.	1 November 2017 – 31 October 2021
EnviroCaps: Enabling a future of safer laundry products and cleaner oceans (849456)	H2020-EU.3. H2020-EU.2.3. H2020-EU.2.1.	1 April 2019 - 31 March 2021
TOPIOS: Tracking Of Plastic In Our Seas	H2020-EU.1.1.	1 April 2017 - 31 March 2022
On-going Spanish national projects [154]		
PLAS-MED: Microplastics and microcontaminants in the Mediterranean coast: Toxicity and environmental and human health impacts (CTM2017-89701-C3)	Spanish Ministry of Science, Innovation and Universities	1 January 2018 – 31 December 2020
Derived plastics from aquaculture: impacts and effects in marine food web (CTM2017-88332-R)	Spanish Ministry of Science, Innovation and Universities	1 January 2018 – 31 December 2020
Impact and degradation of biomicroplastics in the environment (RTI2018-097860-J-I00)	Spanish Ministry of Science, Innovation and Universities	1 November 2019 – 30 October 2022
Microplastics in marine ecosystems from the northwestern Mediterranean: presence, origin and potential impact on organisms and ecosystems (RTI2018-094806-B-I00)	Spanish Ministry of Science, Innovation and Universities	September 2019 – August 2022
Use of fish and human cellular models to evaluate the toxicologic impact of nano/microplastics as vector transfers for flame retardants (RTI2018-096046-B-C22)	Spanish Ministry of Science, Innovation and Universities	September 2019 – August 2022
Mechanical recycling of polylactic acid (PLA): degradation of recycled plastic (CTM2017-88989-P)	Spanish Ministry of Science, Innovation and Universities	January 2018 – December 2020

released. It has been observed that the hydrophobicity of the contaminants is the most important factor that facilitates their concentration in the plastic and MPs litter [39]. For example, the adsorption of persistent organic pollutants (POPs) in plastics has been described for polychlorinated biphenyls (PCBs) [37], polychlorinated pesticides, polycyclic aromatic hydrocarbons (PAHs) [38], current-use pesticides (CUPs) and personal-care products (PCPs) [2,40], polybrominated diphenylethers (PBDEs) and organophosphate flame retardants [41] and perfluoroalkyl substances (PFASs) [42,43]. The latest data suggests that plastic concentrates hydrophobic co-contaminants in up to ten million times higher than their concentration in water [44]. Although it is an important increase, it can be considered negligible compared to the total mass of water that is approximately 10^{13} larger than that of plastic [44]. However, although the transport of hydrophobic contaminants by plastic debris is not relevant in terms of masses [44], under authors' point of view their capability to act as a Trojan Horse for these contaminants to living organisms cannot be underestimated. Hence, their toxicity may be caused by the plastic polymer itself, the additives that it contains, and/or by other chemicals associated to MPs that might be released to the aquatic media [45,46]. In fact, the highest contribution from beached plastics to seawater corresponded to the leaching of plastic additives (flame retardants and plasticizers) followed by PCPs, being also relevant that a significant proportion of less hydrophobic contaminants can be desorbed from plastics to seawater in the first 24 h [2,40]. There are 7 mechanisms that affect the role of MPs as carriers of co-contaminants summarized by Koelmans et al. [39] as follow: 1) absorption – ingestion-egestion of plastic, with chemical transferred from plastic to organism, 2) cleaning – ingestion-egestion of plastic, with an increase of chemical excreted from organism, 3) source – plastic acting as a source of co-contaminant in the environment, 4) sink – plastic accumulate co-contaminants from the seawater and organisms, 5) indirect source, dietary – desorption of chemical from plastic to natural food/prey followed by ingestion of prey [34], 6) dietary – uptake of chemical by ingestion of regular contaminated food (i.e., NPs), and 7) dermal – uptake of chemical from any medium other than plastic and natural prey. In addition to hydrophobic contaminants such as POPs [5,33], some authors investigated how MPs and plastic debris may also concentrate metals [47]. This is possible due to the oxidised form of the plastic surface that can carry functionalities that may bind metals [35]. This last finding was unexpected, and it emphasizes the necessity to further investigate the behaviour of MPs in the environment with special attention to ageing MPs.

MNPs due to their small size, similar to plankton, can be ingested by aquatic organisms, and therefore be introduced into marine food web [38,47,48]. Setälä et al. [49] observed that polystyrene (PS) microspheres can be transferred via planktonic organisms from one trophic level (mesozooplankton) to a higher one (macrozooplankton). The study also confirmed the ingestion of PS based MP by mysid shrimps, copepods, cladocerans, rotifers, polychaete larvae and ciliates although some of the species ejected the microspheres after 12 h of ingestion [49]. MPs and NPs may also pose a risk to human health due to their potential accumulation in seafood reaching the consumers. For example, mussel *Mytilus edulis* [38,39,50] have been reported as marine species able to ingest MPs. However, MPs and NPs can be retained in some organs, and they may be translocated in living tissues [50]. Furthermore, evidence of physical size alteration of microplastics by a planktonic crustacean has been recently demonstrated [51]. It is estimated that some of the plastics can reach concentration factors inside the organisms near to 1 million-fold increase [52].

3. Microplastics in the Mediterranean Sea

The occurrence of plastic and MPs along the coastline and particularly in beaches has been evidenced in many studies [2,40,53–55]. Koelmans et al. [44] have estimated that the average concentration of plastics in the ocean is around ~ 2 ng/L. Although the highest accumulation has been found in Atlantic beaches in the vicinity of industrial areas, urban areas and/or cargo/port facilities [53], the Mediterranean Sea could accumulate between 1,000 and 3,000 tons of floating plastic debris [56] and has recently been shown as one of the most affected marine environments with regards to marine litter [54].

The presence of plastic debris is related to the high human pressure combined with the hydrodynamics of its semi-enclosed basin where the outflow is mainly through a deep water layer [56]. Besides, this characteristic morphology makes it comparable with accumulation zones described for the five subtropical ocean gyres [56,57]. The major plastic contamination of Mediterranean surface waters' is dominated by millimetre-sized fragments [58–64] but with a high proportion of macro- and mesoplastics [56,65], while sediments [66–68] and fish [58] are dominated by MPs. However, the lack of quantitative analytical methods refrains the assessment of small size MPs and NPs and only estimation data are available.

Initially, the characteristics of MPs in aquatic systems depend on their composition; the type of polymers and the additives used to confer de final plastic characteristics. The main classes of polymers identified in marine MPs are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and polyamide (PA). Their environmental fate is also depending on their ageing features, which will depend on the physico-chemical properties of base polymers such as density, particles shape, and also the media characteristics. The media will influence the interactions between particles and organic material or organisms, which influence their buoyancy or sinking [69]. For example, biofouling increases the weight of particles, affecting resilience and accelerating their sinking on bottom sediments [39,70].

3.1. Floating plastic litter in the Mediterranean Sea

During the last years, several studies have evaluated the abundance, distribution and composition of floating macro and MPs in the Mediterranean Sea. Fig. 1 summarises some of the most recent works focused on the Mediterranean Sea among other worldwide areas (more information can be seen in Table S1).

Most of these studies have been based on sampling sea-surface using different versions of the neuston and manta trawl nets. After separation and cleaning of the particles, the most common methods for MPs identification used have been first the visual inspection of possible plastics particles on optical microscope [71]. Second the chemical analysis, of the polymeric composition using Fourier Transform Infrared Spectroscopy (FTIR), micro-FTIR, Raman, micro-Raman, and Scanning Electron Microscope (SEM) to avoid MPs overestimation due to the presence of non-plastic items and to identify the polymeric composition [71]. This type of procedure is used for macro, meso-plastics and MPs with size ranging from $10\ \mu\text{m}$ (for μ -Raman) to 5 mm in length (for the others). Samples with a size below $10\ \mu\text{m}$ are quite difficult to quantify. In the case of SEM, it is difficult to identify the polymer, but it is possible to differentiate plastic from other microparticles such as glass.

One of the first studies evaluating the floating particles in the Mediterranean Sea covered the central and western areas [72] during two sampling campaigns (2011 and 2013). Seventy-one samples were collected with a manta trawl. Floating plastic was found in all the sampled sites, with an average particle

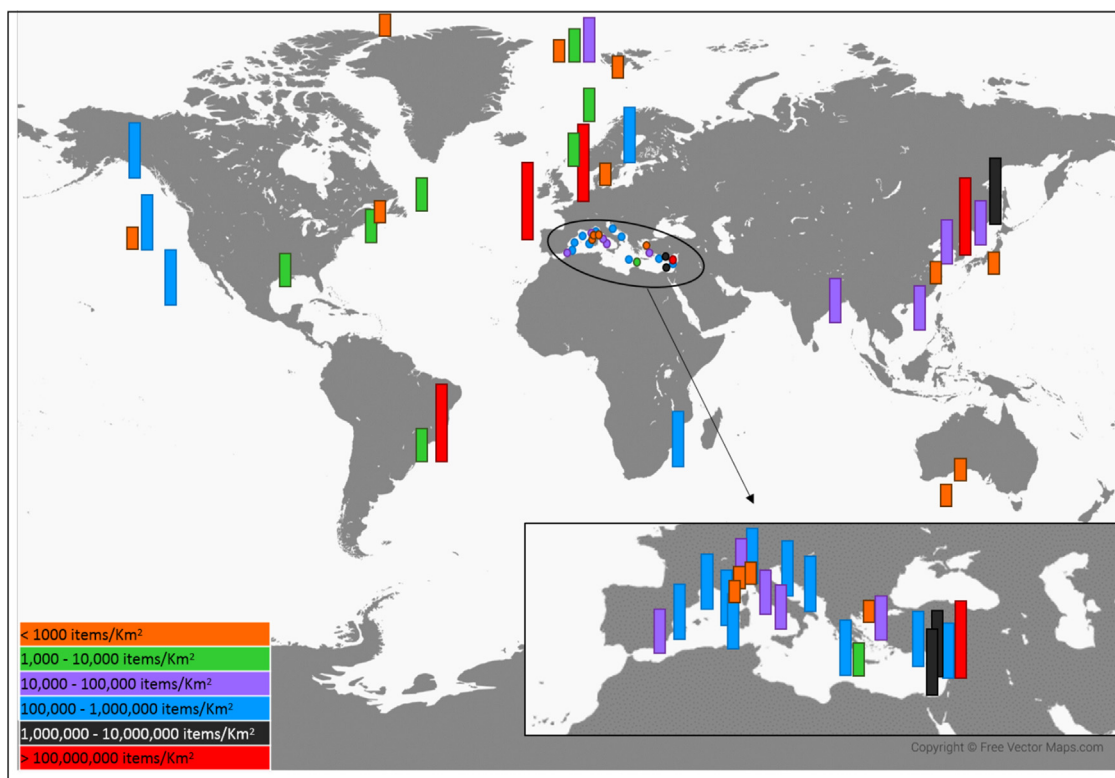


Fig. 1. average number of microplastics reported in the literature, expressed in items/Km² (see Table S1 for more details).

concentration of 147,500 items/km² and the maximum concentration was 1,164,403 items/km². MPs were present in all the samples. The most abundant particles had a surface area of approximately 1 mm² (the mesh size was 333 μm). These results were used to estimate the floating plastic in the entire Mediterranean region in a total value of 1455 tons of dry weight (DW). One of the best-studied areas of the Mediterranean Sea is the Adriatic Sea including studies regarding marine sediments [73] or the occurrence and distribution along Adriatic shorelines [74] among others. Gajst et al. [75] assessed MPs of sea-surface in the Slovenian part of the Trieste Bay in the Northern Adriatic Sea. During the 20 months that last this study, a high average concentration of 406,000 MPs particles up to 5 mm per km² were found, and over 80% of the particles were identified as PE. In another study [76], floating MPs were assessed in the north-western Adriatic Sea to evaluate the possible contribution of two significant potential sources: the lagoon of Venice and the Po River. MPs were found in all samples, albeit with high spatial and temporal variability. The peak concentrations were found at the offshore station of the Pellestrina transect (10,400,000 particles/km²) and the two landward stations off the Po Delta (2,100 and 4,300,000 particles/km²). These results highlighted the influence of river discharges, hydrodynamic and meteorological factors on short time scales. As in the previous study at the Adriatic Sea, PE was the polymer more frequently found, followed by PP, and most of the particles were secondary MPs (83.5%) [76]. In another study [77], the occurrence of macro and meso-plastics of 2.5–5 cm were determined in the Adriatic Sea following the MSFD TG10 protocol. The results showed an average macro-plastic density of 251 ± 601 items/km². Meso-plastics revealed an average abundance of 315,009 ± 568,578 items/km², with higher abundances in nearshore (≤4 km), and as in other studies, the dominant polymers were PE and PP [77]. In a more recent work, floating macro and MPs in the Central Adriatic Sea in front of Croatia coasts were assessed. The sampling was carried out using a manta net [78]. The particles

visually found under the microscope were chemically analysed with FTIR. The average concentration of floating macro-plastics was 175 items/km², and for the floating MPs was 127,000 particles/km², similar values as other published studies from the Mediterranean Sea. A statistically significant ($p < 0.01$) correlation between the MPs and macro-plastics concentrations was found for the channel waters. The assessment Ligurian and Tyrrhenian Seas showed that the composition of floating meso- and MPs average concentration was 28,376 ± 28,917 particles/km², and an average mass of 268.61 ± 421.18 g/km² [79]. The particle shape ratio was 65% fragments, 19% films, 10% lines, 4% foams, and 2% pellets. MPs particles comprised 65% of the sample. Analysis with attenuated total reflection (ATR)-FTIR showed that predominant polymer types were PE, PP, PS, and PA [79]. In another article [62], the eastern section of the Gulf of Lion was assessed. The selected stations were investigated between 2014 and 2016. MPs and meso-plastics were found in every station with highly variable concentrations and masses. Concentrations ranged from 6,000 items/km² to 1·10⁶ items/km² (with an average of 112,000 items/km²), and mass ranged from 0.30 g/km² to 1018 g/km² DW (mean 61.92 ± 178.03 g/km²). Particles < 1 mm² clearly dominated sampling stations in the Northern Current, the Rhône River and its plume (52, 53 and 61%, respectively). Items between 1 and 5 mm² in size were the most abundant in Marseille Bay (55%), which suggests coastal pollution sources. However, coastal pressures are as well influenced by hydrodynamic conditions. For example, 20 samples were collected in the Balearic Sea during summertime using a manta trawl net to examine the concentrations of floating plastic debris [80]. The higher particle concentration was 4,576,115 items/km² at the north of the Balearic Promontory. The particle size analysis showed the high prevalence of MPs, where particles of approximately 0.7 and 1 mm² were the most frequent. The high plastic concentration values in the coast of Ibiza and Mallorca in sparsely populated locations suggest that the plastic particle distribution was mostly influenced by the hydrodynamic

conditions. Another study along the Lebanese coast (Eastern Mediterranean Basin) [81] showed that water was highly contaminated in MPs with abundances of 6.7 MPs/m³. In the southern part of the Mediterranean Sea some floating MPs patch were found. Sea surface MPs were evaluated in 17 sites along the Israeli Mediterranean coast [82]. In this study, MPs between 0.3–5 mm were investigated and found in all samples, with a mean abundance of 7.68 ± 2.38 particles/m³ or 1,518,340 particles/km². In some cases, MPs particles were found floating in large patches. One of these patches contained an extraordinary number of plastic particles; 324 particles/m³ or 64,812,600 particles/km². Microplastic abundances mean values were 1–2 orders of magnitude higher than abundances reported in other parts of the world.

As can be seen, the comparison of the results of the different reports is not possible because of the high spatial and temporal variability of floating particles distribution due to the influence of land sources, river discharges, and hydrodynamic conditions. In addition, the different works present differences in sampling approaches, nets size, and analytical approaches used to examine particles. Overall, an extremely high spatial-temporal variability in sea-surface MP concentrations has been suggested for the Mediterranean Sea using model-based assessments, without any stable long-term accumulations, underlying the importance and convenience of MPs fluxes quantification (frequency) instead of individual MP concentration measurements [34].

3.2. MPs in coastal marine sediments and deep seafloor

Plastics materials with a density over the seawater (1.02 g/cm³) can be expected to sink and accumulate in the sediment, while low-density materials initially tend to float on the surface or be maintained in suspension in the water column [83]. Biofouling, the association between particles and organic materials and organisms produces density-modification favouring the sinking of plastic debris and MPs. However, flat fragments may stay motionless under certain conditions, being captured within viscous boundary layers. MPs have an extraordinary mobility in marine environment as a combined result of the properties of particles (e.g. density, chemical composition, shape) and external hydrodynamics, marine sedimentology, and physical oceanographic environmental conditions. Recent studies demonstrate that settling/re-suspension behaviour of MPs is highly dependent of the particle shape and considering biofouling, floating fibers and threads (“one-dimensional” (1-D) particles) are the first to begin sinking,

followed by 2-D films and flakes, and then 3-D fragments [83]. Sediments are presumed to be sinks for MPs and could have the potential to accumulate them. It has been proposed that beyond the shelf, the principal agents for MPs transport are: (i) gravity-driven transport in sediment-laden flows; (ii) settling, or conveyance through biological processes, of material that was formerly floating on the surface or suspended in the water column; (iii) transport by thermohaline currents, either during settling or by reworking of deposited microplastics [84].

The occurrence of MPs in sea sediments of the Mediterranean Sea has been characterised during the last years, some of these studies are summarised in Table 2. In contrast to macroplastics, MP concentrations are largely non associated with local sources of contamination. MPs in continental shelf sediment samples of the Western region from Algeciras to Barcelona were assessed [85]. The number of MPs per kg of DW ranged from 45.9 ± 23.9 MPs/kg DW in Palma de Mallorca to 280.3 ± 164.9 MPs/kg DW noted in Málaga, with an average value of 113.2 ± 88.9 MPs/kg DW. Another study carried out in the western region [66] addressed MPs quantification and morphological description of the spatial differences along an anthropogenic gradient of shallow coastal sediments. It also evaluated the potential preferential deposition of MPs in a given sediment grain fraction. In this study, it was shown that sediments from a Marine Protected Area of Cabrera in the Balearic Island, contained higher levels of MPs (up to 0.90 ± 0.10 MPs/g) than in the sediments from a highly populated and touristic area in Mallorca, also in the Balearic Islands. These results suggested the transfer of MPs from source areas to endpoint areas. However, no clear trend between sediment grain size and microplastic deposition in sediments was found, although MPs were always present in two-grain size fractions: $2 \text{ mm} > x > 1 \text{ mm}$ and $1 \text{ mm} > x > 0.5 \text{ mm}$.

In a parallel study [86], the levels and patterns of different plastic litter groups (macro-, meso-, and MPs) in sediments from a zone selected to be a new marine protected area in the Aeolian Archipelago in Italy were studied. Similar results as in the previous work were obtained. MPs were found in all the samples, and the levels in the area of study were similar to values recorded in harbour sites and lower than those reported in the Adriatic Sea, while macro-plastics levels were notably lower than in harbour sites. Sediment grain-size resulted not significant in determining levels and distribution of plastic debris [86]. Also, in another Marine Protected Area, the Natural Park of Telašćica bay (the Adriatic Sea, GSA n. 17) the levels of macro-, meso-, and MPs in

Table 2
occurrence of MPLs in sea sediments from the Mediterranean Sea.

	Average items/ Kg sediment DW \pm SD	Ref.	
Spanish Mediterranean Coast (Mediterranean W)	Algeciras	111.3 ± 15.9	[85]
	Málaga	280.3 ± 164.9	
	Castell de Ferro	81.4 ± 41.3	
	Almería	81.8 ± 20.2	
	Cartagena	133.4 ± 104.1	
	Benidorm	138.9 ± 54.7	
	Benicarló	94.8 ± 80.2	
	Vallcarca	74.5 ± 29.1	
	Barcelona	132.7 ± 67.8	
	Palma de Mallorca	45.9 ± 23.9	
	Balearic Islands (Mediterranean W)	From 100.0 ± 60 to 900 ± 100	
Aeolian Archipelago's islands, Tyrrhenian sea (NW Mediterranean)	From 151.0 ± 34.0 to 678.7 ± 345.8	[86]	
Natural Park of Telašćica bay (Adriatic Sea)	From 32.3 ± 20.2 to 377.8 ± 88.8	[87]	
Grand Harbour of Malta (Central Mediterranean)	From 4 to 12	[88]	
Venice (North Adriatic Sea)	From 672 ± 124 to 2175 ± 466	[89]	
Central Adriatic Sea	From $2.5 \pm 5 / \text{m}^2$ to $75 \pm 15 / \text{m}^2$	[90]	
Northern Tunisian coast	From 141.20 ± 25.98 to 461.25 ± 29.74	[67]	
Maremma Regional Park (Tyrrhenian Sea, Italy)	From 45 to 1069	[91]	
Ebro Delta (NW Mediterranean)	422 ± 119	[64]	
NW Mediterranean deep sea sediments	10 – 35 / 50 ml sediments	[92]	

sediments were evaluated [87]. No macro-plastics were found in the studied samples, while the MPs were 88.71% and meso-plastics the 11.29% of the total. From a comparison with other studies in the Mediterranean Sea, a medium to high range of contamination by MPs was evidenced. MPs levels were similar to values recorded in harbour sites in Malta [88], and less contaminated than those from Venice [89]. In fact, one of the first observations on the occurrence and spatial patterns of MPs investigated the sediments of the Venice Lagoon [89]. MPs of 1 mm or less were found in all the samples. Total abundances varied from 2175 to 672 MPs/kg DW. PE and PP were the most abundant polymers. The most frequent size was in the range of 30–500 μm . Besides, the total MPs content correlated with the finer sediment fraction and with the metal pollution index [89]. Another study was focused in the central Adriatic Sea [90], the results in sediments collected along 140 km-long transects showed that several types of plastic particles were observed in 100% of the stations. MPs (1–5 mm) accounted for 65.1% of debris, meso-plastics (5–20 mm) made up 30.3% of the total amount, while macro debris (> 20 mm) accounted for 4.6% of total plastics collected. Identification through FTIR spectroscopy evidenced the presence of 6 polymer types: the majority of plastic debris were nylon, PE and ethylene-vinyl alcohol copolymer. The sediments from 5 sites at the Northern Tunisian coast showed that MPs were extensively distributed [67]. Concentrations varied from 141.20 ± 25.98 to 461.25 ± 29.74 items/kg DW. MPs particles ranged from 0.1 to 5 mm in length and three polymer types were predominant PE, PP and PS. The investigation of plastic litter in sediments of the Maremma Regional Park in the Tyrrhennian Sea in Italy showed the influence of fluvial inputs and evidenced the impact of plastic materials derived from agricultural activities in the coastal areas [91]. The MPs values per kg of sediment and the common type of items mainly found varied between the investigated sites between 45 and 1069 items/kg DW, and contribution by the Ombrone river was identified as one of the more relevant sources [91].

As in the case of the Ombrone river, several studies demonstrated that the river discharges are one of the most prominent flows of plastic litter into the Mediterranean Sea. For example, recently, the MPs in estuarine benthic sediments of the northern edge of the delta Ebro showed levels of 422 ± 119 MPs/kg DW [64]. Fibres were found to be the largest class. In addition, it was estimated that the Ebro surface water represents an input of $2.14 \cdot 10^9$ MPs/y to the Mediterranean Sea [64].

Some studies also have shown that the deep-sea sediments are a likely sink for MPs. Woodall et al. [92] studied the occurrence of MPs in deep-sea sediments from the Atlantic Ocean, the Mediterranean Sea and the Indian Ocean. The results highlighted that MPs in the form of fibres was up to four orders of magnitude more abundant (per unit volume) in deep-sea sediments than in contaminated sea surface waters, evidence of a large and hither repository of MPs.

3.3. MPs in Mediterranean biota and seafood

MPs ingestion by biota is an emerging threat to marine ecosystems. In order to have enough information to assess the potential impact of MPs in marine ecosystems and human health it is of primary interest to monitor MPs contamination in marine biota and their potential entrance in the food chain. In vivo studies have demonstrated that nanoplastics can translocate to all organs [50]. Evidence is evolving regarding relationships between micro- and nanoplastic exposure, toxicology, and human health. Nowadays, MPs have been found in many species, including invertebrates, crustaceans, and fish from the Mediterranean Sea [93,94]. Among them, mussels are of special interest due to their filter-feeding behaviour and commercial interest. Although several

studies reported that filter-feeding organisms ingest and subsequently eliminate MPs, there are also evidences pointing that small MPs in digestive gland are slower processed and eliminated than larger ones, and that a translocation of small MPs occurs from the digestive system to the gills [95]. Evidences also suggest that they are more likely to consume smaller MPs instead of larger microfibers [95]. On the other hand, the potential effects at organ and tissue level remain unclear, especially considering exposure to different MPs sizes and concentrations. For example, the pathophysiological effects on the Mediterranean mussel (*Mytilus galloprovincialis*) exposed to spherical polystyrene MPs, under controlled conditions, showed that mussels can filter MPs regardless of their size. After ingestion, MPs were identified in the lumen of the gut and they were excreted through faeces without any evidence of histopathological damage in whole-body sections of exposed animals [96]. Nevertheless, the fact that the animals were able to translocate MPs to the gut reveals that filter-feeding organisms may indeed become a target of concern in the case of small size MPs and NPs. Moreover, the information regarding how long the ingested MPs are retained in their digestive tracts remains limited. In another study, the gut retention time (GRT90) and the long-term egestion time of three different sized PS microspheres (1, 10, and 90 μm) were studied in the Mediterranean mussel, showing significant differences in GRT90 with respect to MPs size [97]. Other recent study evidenced that mussels efficiently cleared MPs from water during exposure, and that MPs were accumulated in digestive gland and gills during depuration [98]. In digestive gland, the amount and size of the MPs accumulated decreased with time, indicating a slower processing and elimination of small MPs than of larger ones. However, MPs' burdens in gills increased with time, the MPs accumulated were the smallest ones, suggesting the translocation of small MPs from the digestive system to the gills. In fact, translocation of ingested MPs to the circulatory system of the mussel occurs [50].

Other works were mainly focused on the study of MPs in species directly collected from the environment. As example, MPs ingestion was evaluated in four highly commercial marine species from Greek waters in the Northern Ionian Sea [99]. MPs were confirmed in mussels (*Mytilus galloprovincialis*) and all three fish species (*Sardina pilchardus*, *Pagellus erythrinus*, and *Mullus barbatus*) examined. The frequency of occurrence of ingested MPs was 46.25% in mussels, while among fish species, *S. pilchardus* showed the highest frequency of ingestion (47.2%). FTIR indicated PE as the most common polymer type in mussels and the studied fish species. Higher rates of contamination by MPs were found in the stomach contents from *Sardinia pilchardus* and *Engraulis encrasicolus* from the Adriatic Sea [100]. These species selected are planktivores of great ecological and commercial importance in the Adriatic Sea. Over 90% of samples from both species contained marine litter. Sardines evidenced a higher number of MPs than those in anchovies. Moreover, in the case of anchovies, differences related to the sex of animals and the colour of the materials (prevalence for black and blue colours) were encountered [100]. The stomach of 18.8% of red mullets (*Mullus barbatus*) sampled in 5 areas from the Western Mediterranean showed MPs, mainly fibers, corresponding the highest abundance to Barcelona coast samples (33% of fishes) [101]. A new procedure [102] was optimized for extraction of MPs from marine organisms based on density gradient separation with a hypersaline solution, filtration and partial digestion of organic matter using 15% H_2O_2 that allows 90% recovery from complex samples. The analysis of polymers was performed with FTIR. The method was further validated on the fish mullet, *Mugil cephalus*, exposed to PS and PE particles under laboratory conditions. Moreover, translocation of particles was shown from stomach to liver of exposed fish. This approach was used to investigate MPs in various fish species collected along the

Adriatic Sea. FTIR analyses indicated PE as the predominant polymer (65%) in the stomach of fish [102]. In general, MPs had higher frequency of detection in benthic fish species with commercial interest [102]. In another study, in order to assess the impact of MPs in human health two important marine species used for human consumption were analysed: the European anchovy, *Engraulis encrasicolus*, and the spiny oysters, *Spondylus spinosus*. They were sampled in three different sites of the Lebanese littoral (Tripoli, Beirut and Sidon) [81]. The occurrence of MPs in anchovies was 83.4% and in spiny oysters 86.3% of the studied individuals of each species. Both anchovies and oysters from the Beirut region had the highest ingested MPs/individual (2.9 ± 1.9 and 8.3 ± 4.4 MPs/individual, respectively) [81]. Some commercial species can be as well used as relevant bioindicators of MPs contamination. This is the case of bogues (*Boops boops*) that has been proposed as bioindicator species in a recent article [103]. In this work, the gastrointestinal tracts of 102 bogues sampled from three areas off the Catalan coast (Spain), subjected to different degrees of industrialization, were analysed. MPs were detected in 46% of the samples. As expected, the abundance and frequency of MPs were higher in the samples collected from the most anthropized area of Barcelona. The majority of MPs were ranging 0.1–0.5 mm and the most common polymer type was PP [103]. Some of these species can be in addition a good indicator of deep-sea reservoirs. This is the case of two economically and ecologically key crustaceans of the Mediterranean Sea, the Norwegian lobster *Nephrops norvegicus* and the shrimp *Aristeus antennatus*, that were collected around Sardinia Island, at depths comprised between 270 and 660 m. In this study, 89 and 63 stomachs were analysed for *N. norvegicus* and *A. antennatus* respectively. The results obtained by using FTIR indicated that in *N. norvegicus* 83% of the individuals contained MPs, with an average abundance of 5.5 ± 0.8 MPs/individual, while *A. antennatus* showed a lower frequency of ingestion with only 67% of the specimens and a lower mean number of MPs ingested (1.66 ± 0.1 MPs/individual). Composition and size of particles differed significantly between the two species. The non-selective feeding strategy of *N. norvegicus* could explain the much higher numbers of MPs in its stomach compared to *A. antennatus*. The extremely high MPs abundance recorded for *N. norvegicus* is among the highest detected in Mediterranean species considering both fish and invertebrate species. This provide new insights on MPs bioavailability in the deep-sea habitats.

4. Legislation

In order to prevent MPs contamination several initiatives have been developed at global and regional levels. For example, the United Nations Environment Organization has launched a global campaign to eliminate primary sources of marine plastic litter such as MPs in cosmetics and to reduce the excessive usage of single-use plastic by 2022. In Europe, the member States must monitor MPs [14] and promote research initiatives through the Horizon 2020 programme [11] in order to reduce their environmental levels.

For protecting the marine environment, the European Union has implemented several legislations related to MPs in different relevant areas. For example, in fishing regulation through the Common Fisheries Policy (CFP) [104] and in the control of nutrients and chemical products that enter the aquatic system through the Water Framework Directive (WFD) [105]. However, although these legislations are necessary to protect the marine media, they contribute to marine protection from specific pressures but do not specify actions to mitigate MPs contamination. Because of this, EU has implemented two instruments: the EU recommendation about the Integrated Coastal Zone Management (ICZM) [106] and the Marine Strategy Framework Directive (MSFD) [107]. They offer a

global perspective and protection of all European coastal areas and marine waters. The MSFD (2008/56/CE) [107] establishes that all EU state members' must achieve the good marine and oceanic environmental state for 2020. The descriptor 10 of the MSFD establishes the properties and quantities of marine litter that do not cause harmful effects on marine media and coastal areas [107]. In addition, EU adopted on January 2018 the European Strategy for Plastics. It presents new strategies for life cycle economy and life cycle assessment for plastics, and it is focused on the way that plastic products are designed, used, produced and recycled in the EU [108]. Despite clean-up activities are being conducted for awareness campaigns and mitigation strategies, it must be stated that removing MPLs from the marine environment is not a realistic option because the plastic microparticles are widespread in all marine matrices. On the other hand, the adopted measurements are clearly insufficient to mitigate the quantity of MPs than daily enter in the Mediterranean Sea, which is currently expected to increase.

The EU has also highlighted the necessity to adopt measures to preserve the Mediterranean Sea, a partial-closed sea with high contribution of terrestrial contamination (80% of the total). The contamination in the Mediterranean Sea is critical, mainly due to overexploitation of the resources and the global warming. In 1975, the European Community implemented the first Mediterranean Action Plan (MAP) [109], followed by the Protocol on Integrated Coastal Zone Management in the Mediterranean [110] (Phase II of the MAP) adopted during the Barcelona Convention in 1995. Nowadays, the Barcelona Convention and the MAP are devoted to protect marine environment and coastal areas from the Mediterranean Sea. There are 22 countries involved and one of the main goals is to enforce regional and national initiatives in order to achieve the sustainable development of the Mediterranean [109].

5. Problems and shortcomings

5.1. Identification and quantification of MNPs

One of the main limitations faced in the investigation of MPs in aquatic environments, sediments and biota is the lack of quantitative analytical methods. There are not many analytical techniques available that combine quantitation and characterization of MPs [111]. The majority of the methodologies are based on the separation of fibres or particles of MPs, in most cases by manual procedures and visual inspection, followed by counting methods (Fig. 2). It is commonly extended the previous separation by means of density flotation/separation for waters and sediments [58,112]. Then, MPs are separated manually when it is possible, or by means of filtration. Subsequently, MPs from water or sediments are extracted from the rest of material by digestion, or directly digestion when is biota. This extraction is usually done by wet digestion of organic matter with H_2O_2 (either seawater, biota and sediments) [58,60,65,71,113,114], alkaline or acidic attack [65,113], and/or enzymatic digestion (specially for biota) [48]. Afterwards, another density flotation separation is necessary before the identification of MPs [65]. For MPs identification, most of the works published are based on visual identification (naked eye [56], or by optical microscopy or high-resolution microscopy combined with an image processing software [56,58–60,71,113,115]), followed by chemical characterization of the polymer type, and weight in some cases [56,71,115]. These techniques include Fourier Transform infrared spectroscopy ($(\mu-)$ FTIR) and $(\mu-)$ Raman spectroscopy [59,71,114], selected scanning microscopy (SEM) [114,116] and pyrolysis and/or thermal desorption gas chromatography coupled to mass spectrometry (Py-GC-MS [117,118] and TD-GC-MS [119,120], respectively). Although micro-FTIR and micro-Raman can work with little amount of sample (just one particle is

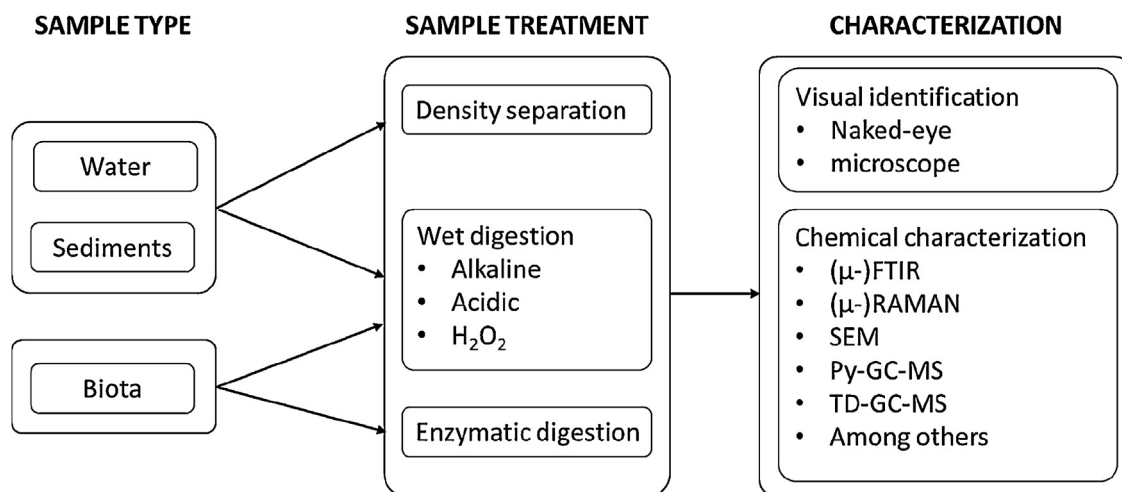


Fig. 2. Scheme of commonly used methods for the analysis of MPLs.

needed for identification), the other techniques have the main limitation that a big amount of sample is required to identify or count MPs. Besides, there are few quantitative methodologies and most of them are based on GC-MS techniques. In the case of analytical techniques, the FTIR [59] and RAMAN spectroscopies are techniques that can distinguish among different types of polymer and up to 1 μm particle size when they are combined with image techniques [116]. However, both techniques are time consuming. The work of Schirinizi et al. [61] that has been recently published explores the capabilities of size exclusion chromatography coupled to high resolution mass spectrometry (SEC-HRMS) for the identification and quantification of low molecular weights nano- and microplastics (between 500 – 3000 Da) in freshwater and seawater media. This methodology could be extended to other matrices offering the possibility of detecting the smallest size of plastic litters, which are the ones identified as the most problematic under an ecotoxicological point of view.

5.2. Standardized protocols for MNPs

Due to the wide variety of polymer-based MPs as well as additives, these contaminants can be distributed in different environmental compartments. For example, MNPs can be found at different depths of the water column and even reaching depth water sediments because of plastic differences in density and sinking [121]. In the same way, the analysis is not only sample dependant but also dependant on the physic and/or chemical characteristic that wants to be determined (i.e. plastic type, number of particles, particles size, morphology, quantification of total MPs, among others). In this context, it is necessary the development of suitable standardized strategies for sampling as well as analytical methodologies to correctly compare results. Currently there are different organisations working on this like, for example, the non-governmental International Organization for Standardization (ISO). For example, regarding the sampling and the analysis of biota, Hermsen et al. [122] proposed 10 criteria that needs to be defined/standardized based on Criteria for Reporting and Evaluating Ecotoxicity Data (CRED) [123] but that could be extended to other matrices. The criteria includes: 1) sampling method strategy, 2) sample size, 3) sample processing and storage, 4) laboratory preparation, 5) clean air conditions, 6) negative controls, 7) positive controls, 8) target component, 9) sample (pre) treatment, and 10) polymer identification [122]. Other strategies have been proposed for the sampling of seawater surface [124] or sediments [125]. On the other hand, it is important to evaluate the

reliability of the methodology for the analysis of MPs in different matrices. The best option is to participate in interlaboratory studies devoted to the analysis of MPs in prepared samples. Some examples are the comparison exercise for the determination of MPs in bottles to assess the consistency of their quantification across several laboratories [126], the exercise organized by QUASIMEME Laboratory Performance Studies devoted to the identification and quantification of MPs in different water samples [127] or the comparison exercises organised by the European Joint Research Centre (JRC). In this last example, JRC organises free of charge exercises which are available to all the scientific community and the results will be the basis to create a certified reference material (CRM) [128]. This CRM is really needed since the variability of analytical procedures do not allow to compare methods and to evaluate their robustness.

5.3. Toxicity

Recently, different reference organisms including Science Advice for Policy by European Academies consortium (SAPEA) [129] and European Commission by means of SAPEA recommendations among others [130], have published recommendations where they express the necessity of understanding the potential modes of toxicity for different sizes, shapes and types of NMP in human models but also for animals [129]. Currently, the research undertaken has been mainly focused in the investigation of any potential toxic effect related to the presence of MPs in the environment at metabolomics level and physiological changes. However, the concentrations tested are, in general, much higher than the ones detected in the environment.

Most of the research undertaken since the past decade has been focused in the investigation of any potential toxic effect related to the experimental exposure to MPs on sub-cellular level and physiological changes in marine organisms. Nowadays, scientific evidence pointing that microplastic ingestion or its associated chemicals pose a threat to marine organism from natural populations (from whales to corals) is mounting [131,132].

For example, toxicity studies based on mussels (*Mytilus edulis*) exposure to 15,000 individual PS microspheres (3 – 9.6 μm) where their ingestion have shown that these MPs are accumulated in gut and translocated into the circulatory system within 3 days, where they persisted for 48 days [50]. Moss et al. studied the uptake and effects of high density polyethylene (HDPE) particles ranging from 0 to 80 μm at dose of 2.5 g HDPE-fluff/L also in mussels [133]. The MPs were detected in gills, transported into the digestive glands

and accumulated in the lysosomal system after 3 h of exposure [133]. The authors combined metabolomics results with physiological effects like histological changes, and a strong inflammatory response by formation of granulocytomas and lysosomal membrane destabilization was observed [133]. Another study showed that, after ingesting microspheres, blue mussels experienced an immune response and the formation of granulomas [23,134]. Significant reduction in the food consumption rates over time in crabs feeding on food containing PP plastic microfibers (between 0 and 1 mg/L) cause a small but significant reduction in the available energy for growth [135]. Concerning fish, the ingestion of virgin polyethylene fragments (addition of 0.3 mg of PE per day in each tank containing 71 specimens) caused hepatic stress in the Japanese medaka (*Oryzias latipes*) [136], and the leachates of PS and PE (monomers and/or additives at concentrations of 10^3 , 10^4 and 10^5 microspheres/mL) caused higher toxicity on sea urchin gametes and embryos than virgin and aged materials themselves [137].

Other studies revealed that MP toxicity is particle size-dependent for some species, with smaller MPs more toxic than bigger ones. For example, the exposition of monogonont rotifer *Brachionus koreanus* to PS microbeads, ranging from 0.05 to 6 μm size at concentrations between 0.1 and 20 mg/L, showed a reduction on growth rate and fecundity, a decreased lifespan and longer reproduction times for the smallest sizes of plastic [138]. Size-dependant effects were also observed for zebrafish (*Danio rerio*), where 5 μm of PS was accumulated in gills, liver and gut, whereas 20 μm PS was accumulated in gills and gut but not in liver (at 20 mg/L both experiments) [139]. At metabolomics level the authors observed that MPs caused inflammation and lipid accumulation in fish liver. They also induced oxidative stress by significantly increasing the activities of superoxide dismutase and catalase [139].

There is a limited information regarding the contribution that MPs may have when co-contaminants sorbed to them are released inside of organisms, although some studies pointed out the necessity of investigating such interactions. For example, Garrido et al. [140] observed two different dose-response curves resulted from pesticide chlorpyrifos (CPF) bioassays with microalgae depending on the presence of PE (ranging from 0.5 to 25 mg/L), with lower percentages of inhibition when CPF was presented through PE. Thus, the adsorption of CPF onto PE surfaces modulates the toxicity of CPF on *Isochrysis galbana* growth through a reduction in its toxicity, as CPF is adsorbed onto MP surfaces which are less bio-available to the algal cells. On the other hand Paul-Pont et al. [141] researched the modulation of the toxicity of the PAH fluoranthene to mussels *Mytilus edulis* with the presence of PS based MPs at a daily dose of 32 μg in 30 L tanks. The results did not show different bioaccumulation pattern with or without MPs. However, MPs alone had effects at metabolomics level by increasing hemocyte mortality and modulating cellular oxidative balance due to an increase in reactive oxygen species production and enhancement of anti-oxidant and glutathione-related enzymes [141]. When mussels were exposed to the presence of MPs and fluoranthene simultaneously, the histological damage and effects observed at metabolomics, enzymatic and cellular level were higher than when mussels were exposed individually to them [141]. In contrast, dissimilar results were observed for *Mytilus galloprovincialis* exposed to low density polyethylene (LDPE) MP with benzo(a)pyrene (BaP) sorbed on its surface at approximately 15 μg BaP/g of LDPE [38]. The authors observed a modulation of immune responses and an increase of bioaccumulation in the digestive tissue of mussels when exposed at 10 mg/L of MP [38]. Similar results were observed for embryonic development of the sea urchin (*Lytechinus variegatus*) exposed to 2 ml of beached MPs of PE with co-contaminants sorbed on surface compared to

virgin MPs [142]. The authors observed a decrease on the embryonic development for the specimens exposed to virgin pellets compared to specimens exposed to pellets with sorbed co-contaminants possibly due to the high toxicity of additives present in the virgin pellets [142]. These two examples denoted the necessity to further investigate the interaction of MPs with co-contaminants in order to shed light upon this matter. There may be synergistic and/or antagonistic interactions that may occur in the real environment. In this sense it is also important to point out the necessity of considering not only organic co-contaminants but also inorganic ones, such as metals. Laboratory study has demonstrated that microplastics (up to 0.69 mg/L tested) increase mercury bioconcentration in gills and bioaccumulation in the liver, and cause oxidative stress and damage in *Dicentrarchus labrax* juveniles [143]. In fact a recent study has concluded that 2 mg/L of PE can be considered vectors of mercury in mussels in a similar way as other natural particles of the seston, as phytoplankton, but in a different order of magnitude due to the poor digestibility of plastic particles [144].

5.4. Weathering effects on MPs surface, size and properties

MPs can suffer some weathering effects once they reach the environment (aquatic media in most of the cases) [145]. Once there, the plastic surface is submitted to some physical and chemical natural processes such as waves in the ocean, salinity of the media, acidity or basicity of the media, UV radiation that can develop surface cracks [146] and particle fragmentation [147,148]. Certain microorganisms (e.g. *Micrococcus* sp.) can also slowly degrade plastic polymers [149]. Overall, the dominant cause of degradation is photodegradation that can facilitate oxidation reactions as in the case of polyethylene, polypropylene and polystyrene [145,150]. Furthermore, it is important to notice that MPs used nowadays have properties modified through the addition of selected additives in order to meet the product application [145]. For example, these additives stabilize the plastic versus the UV radiation, heat temperatures or antioxidants that markedly retard the chemical weathering of the plastic surface [145]. Then, weathered MPs could affect the media in a different mode than the virgin MPs. For example, by enhancing or decreasing the sorption capacities of other co-contaminants or by increasing or diminishing the related ecotoxicological effects on fauna. On the other hand, experimental conditions have demonstrated that cationic nanoplastic particles may acquire a protein corona when they are incubated in biological fluids (such as hemolymph serum or celomic fluid) that increase the MPs-related biological effects [151,152].

6. Future work

At this stage, it is necessary to evaluate the environmental and human health risks due to the presence of MPs associated to complex mixtures of co-contaminants and microorganisms. This requires increasing the knowledge on exposure levels and effects of MPs and its associated chemical and microbiological components. Concerning chemicals, the risk associated to MPs associated with other contaminants present in the same compartments are difficult to characterize due to at least five reasons. First, the scarcity of global studies; second, the toxicity of particle depends on their size and shape; third, the need of characterise the chemical composition of the particles in terms of polymeric composition and additives; fourth, their potential of bioaccumulation; and fifth, toxicological effects on the environment and human health through the diet. In this sense the identification of the most toxic additives or components is also crucial to limit their use in future plastic formulations, particularly for biodegradable

plastics which can be a faster potential source of these pollutants than current plastic polymers.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.teac.2020.e00090>.

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