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Microplastics in Aquatic Environments and Their Toxicological Implications for Fish

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Abstract

The intensive use of plastics and derivatives during the last century has increased the contamination of animal habitats. The breakdown of these primary plastics in the environment results in microplastics (MP), small fragments of plastic typically <1–5 mm in size. Apart from the potential negative effects of the MPs *per se*, it is generally assumed that microplastics may increase the exposure of marine aquatic organisms to chemicals associated with the plastics. In addition, to enhance the performance of plastics, additives are added during manufacture. Furthermore, they are active in absorbing other contaminants and be used as vectors of highly and well-documented persistent contaminants. Finally, these small MPs are easily ingested by animals and affect their physiology and behaviour. Thus, aquatic living organisms are continuously exposed to these MPs, and associated contaminants, and could suffer from its contamination but also introduce them into the food chain.

Keywords: Microplastics, toxicants, aquatic environment, fish

1. Introduction

The production of synthetic polymers has increased more than 100-fold since the middle of the twentieth century to reach the 280 million tonnes of plastics produced annually worldwide most of which is destined for disposable use [1]. High production coupled with the physical characteristics of most plastics, such as their chemical inertness and very slow biodegradation rates, results in an accumulation of plastic debris in the environment [2]. Routes of discharge such as improper waste disposal, insufficient waste management and urban run-offs [3] may

lead to significant amounts of these plastics entering the aquatic environment [4, 5]. It is a long-recognized fact that marine plastic debris contaminates the oceans and seas of all the world [3, 6, 7]. In the marine environment, plastics undergo a process of weathering and fragmentation that breaks down macrodebris into smaller micro- and nanodebris. This fragmentation of plastic is caused by a combination of mechanical forces, for example waves and/or photochemical processes triggered by sunlight. Some 'degradable' plastics are even designed to fragment quickly into small particles, although the resulting material does not necessarily biodegrade [8].

The terms 'microplastics' (MP) and 'microlitter' have been defined differently by various researchers. Gregory and Andrady [9] defined microlitter as the barely visible particles that pass through a 500- μm sieve but are retained by a 67- μm sieve ($\approx 0.06\text{--}0.5$ mm in diameter), while particles larger than this were called mesolitter. Others [10–12] defined the MPs as being in the size range <5 mm (recognizing 333 μm as a practical lower limit when neuston nets are used for sampling). Microplastic particles may further fragment into 'nanoplastics', a term that has not been defined uniformly in the literature, and may refer to $<100\text{-}\mu\text{m}$ particles of plastic [13].

Microplastics have been accumulating in the environment for nearly half a century and are found in oceans worldwide [3] including in the Antarctic [7]. Despite this worldwide dissemination of plastic fragments, the global load of plastics on the open ocean surface has been estimated to be far less than might be expected, but nevertheless increasing. Thus, the potential effects of microplastics on marine ecosystems are still far from being well understood [14]. It is believed that the virgin MP are not chemical contaminants to marine organism, but they can produce physical problems such as digestive congestion. However, they can be loaded with many substances to fit the virgin MP to industry and consumer demand (e.g. additives, preservatives, etc.). In addition, these MPs can also adsorb contaminants present in the environment and act as vectors. Therefore, in this chapter, we shall summarize some important aspects of the microplastics found in the marine environments and some of the effects described in fish biota.

2. Chemical nature

Plastics are usually synthesized from fossil fuels, but biomass can also be used as feedstock. The most commonly used plastic materials, the also called virgin plastics, are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET), which, together, represent approximately 90% of total world plastic production [15]. They are elements of high molecular weight and are non-biodegradable and therefore extremely persistent in the environment. PE, PP, PVC, PS, PET and polyurethane (PUR) are widely used resins (29, 19, 12, 8, 6, and 7% of global production, respectively) [16]. Plastics present many advantages since they are inexpensive, water- and corrosion-resistant, chemically inert, easily moulded and exhibit good thermal and electrical insulating properties. However, plastics also present many disadvantages, being non-renewable resources and

sources of contamination by additive compounds; they suffer embrittlement at low temperatures and deformation under loads; they need costly recycling processes and are highly resistant to degradation, etc. The behaviour of plastics in the environment will differ according to their chemical nature and physical properties. A reflection of this is the description of microplastics found in marine environments in different studies (**Table 1**).

Polymer type	% Studies (n)
Polyethylene (PE)	31 (33)
Polypropylene (PP)	25 (27)
Polystyrene (PS)	16 (17)
Polyamide (nylon) (PA)	6.0 (7)
Polyester (PES)	3.7 (4)
Acrylic (AC)	3.7 (4)
Polyoxymethylene (POM)	3.7 (4)
Polyvinyl alcohol (PVA)	2.8 (3)
Polyvinyl chloride (PVC)	1.8 (2)
Poly methylacrylate (PMA)	1.8 (2)
Polyethylene terephthalate (PET)	0.9 (1)
Alkyd (AKD)	0.9 (1)
Polyurethane (PU)	0.9 (1)

Table 1. Frequency of occurrence of different polymer types in microplastic debris sampled at sea or in marine sediments [17].

3. Sources

Microplastics comprise a very heterogeneous assemblage of particles that vary in size, shape, colour, chemical composition, density, and other characteristics. They can be subdivided according to their usage and source into (i) ‘primary’ MPs, produced either for indirect use as precursors (nurdles or virgin resin pellets), for the production of polymer consumer products or for direct use, for example in cosmetics, scrubs and abrasives and (ii) ‘secondary’ MPs, which result from the breakdown of larger plastic material into smaller fragments [18].

3.1. Primary: common consumer products

Microplastics (e.g. PE spheres) are used in personal care products such as toothpaste, facial and exfoliating creams, even though many consumers are not aware of this. In some cases, these MPs have replaced natural materials, such as seeds, shells or ground pumice ingredients. Usually, they are not filtered during wastewater treatment and are usually released directly

into the sea or other water bodies such as lakes and rivers. Microplastics are also found in synthetic textiles: wastewaters from washing synthetic clothes, such as shirts, contain more than 100 fibres per litre of water. According to a study by Browne et al. [19], on average, about 1900 MP fibres can be released in a single machine wash. Similar fibres have been observed in wastewater effluent and sludge near large urban centres.

3.2. Primary: industrial sources of microplastics

Plastic pellets are the raw material of plastic products. They are typically spherical or cylindrical in shape and millimetres in diameter. In addition, pellets are used in various industrial applications, including as ingredients of printing inks, paints spray, injection mouldings and abrasives [20]. A proportion of MPs used in these industrial applications enters the environment. The improvement in the management of operations in which plastic pellets are used could be a clear way to prevent them from entering the environment.

3.3. Secondary: plastic waste as a source of microplastics

Secondary microplastics are formed when larger plastic items are broken down. The rate at which fragmentation occurs is highly dependent on environmental conditions, especially temperature and the amount of UV light available [20]. Plastic debris can enter the ocean directly or can reach it through other water bodies or the atmosphere. The key to stopping plastic 'ocean trash' is to prevent such waste from entering the environment in the first place. Obviously, larger objects are easier to identify and control than smaller objects. About half of the world's population lives within 100 km of the coast, with an increasing population in that area. It is therefore highly likely that the amount of plastic waste entering the ocean from land-based sources will increase if significant changes are not made in the waste management on land.

4. Ecosystem distribution

The accuracy of MP emission estimates is currently hindered by lack of data. More specifically, information on MP transport efficiency in run-off and streams is missing. This is despite the large number of qualitative studies on microplastics in rivers and sediments [21–24]. Similarly, only limited assessments of MPs from sewage and canalizations, their retention by wastewater treatment plants and release by effluents are available [25, 26].

One of the most important factors affecting microplastic distribution in marine waters is the density of the materials (**Table 2**). Materials whose specific density is less than that of marine water (~ 1.02) may be located on the surface, while materials with a specific density greater than that of marine water may sink (**Table 2**). Thus, being buoyant in water, PE and PP float in seawater and mainly affect ocean surfaces and deposits ashore [27, 28], while PVC, which is denser than seawater, affects the seabed, often next to the source [27].

Categories	Common applications	Specific density*
Polyethylene (PE)	Plastic bags, six-pack rings	0.91–0.94
Polypropylene (PP)	Rope, bottle caps, netting	0.90–0.92
Foamed polystyrene (PS)	Cups, buoy	0.01–1.05
Polystyrene (PS)	Tools, packaging	1.04–1.09
Polyvinyl chloride (PVC)	Bags, tubes	1.16–1.30
Polyamide or nylon	Rope	1.13–1.15
Polyethylene terephthalate (PET)	Bottles	1.34–1.39
Polyester resin+fibreglass	Textiles	>1.35
Polycarbonate (PC)	Electronic compounds	1.20–1.22
Cellulose acetate	Filter cigarettes	1.22–1.24
Polytetrafluoroethylene	Teflon, tubes	2.1–2.3

*Specific density expressed in g/cm³. The density of plastics may change depending on additives and environmental processes. Based on References [5, 29, 30].

Table 2. Common applications and specific density of some plastics found in the marine environment.

Location	Microplastic concentrations	References
Pacific Ocean	27,000–448,000 particles per km ²	[33, 34]
	370,000 particles per km ²	[35]
	0.004–9200 particles per m ³	[36, 37]
Atlantic Ocean	2.5 particles per m ³	[38]
Indian Ocean	81.43 mg per kg*	[39]
Mediterranean Sea	0.16 particles per m ²	[40]
	0.62 particles per m ³	[41]

*Sediment samples.

Table 3. Microplastic concentrations observed in oceans of the world.

Moreover, the colonization of MPs by microalgae and other microorganisms increases plastic density, which has been shown to affect the vertical transport of MPs in an aquatic environment and their long-term distribution [31]. However, the chemical composition, particularly as a result of low amounts of additives, may partially explain the changes in microbiological colonization from one type of polymer to another. Also, for the same type of polymer, the chemical composition can vary considerably depending on chemical additives and the time passed in the environment. Hence, the distribution of MPs in the ecosystems may change according to these parameters, too. Long et al. [32] recently showed that MPs could be incorporated in microalgal homo-aggregates, demonstrating the existence of a pathway of vertical transport of MP from the surface layer to the floor of the ocean.

In addition, MP concentrations and/or quantities differ between sampling sites (**Table 3**). A significant variation between the microplastics sampled in different oceans is evident, but there are also differences between the areas of the same ocean or sea. Published works have detected different concentrations of MPs depending on the proximity to populated and/or contaminated areas.

5. Absorption of toxicants

To enhance the performance of plastics, additives are added during manufacture, such as reinforcing fibres, fillers, coupling agents, plasticizers, colorants, stabilizers (halogen stabilizers, antioxidants, ultraviolet absorbers and biological preservatives), adsorbed chemicals, and unreacted starting materials (monomers), processing aids (lubricants and flow control), flame retardants, peroxide, antistatic agent, and plasticizers [16, 42], which may leach out under conditions of use and accumulate in the environment [43]. Apart from the potential negative effects of the MPs *per se*, it is generally assumed that microplastics may increase the exposure of marine aquatic organisms to chemicals associated with the plastics, such as persistent organic pollutants (POPs) or plastic additives [44–47]. Thus, analytical study of marine MPs has revealed the composition of many toxicants adsorbed to them.

Additive	CAS	Log K_{ow}	Water solubility (mg/L)
<i>UV stabilizers</i>			
Benzophenone	119-61-9	3.18	None
Benzotriazol	95-14-7	1.44	1.98×10^4
<i>Antioxidants</i>			
Irganox 1024	32687-78-8	7.79	<1
Irganox 1098	23128-74-7	–	0.1
Irganox 1076	2082-79-3	<6	<0.01
Irganox 1010	6683-19-8	≈23	<0.01
Irganox 168	31570-04-4	>6	<0.005
<i>Plasticisers</i>			
Dimethyl phthalate	131-11-3	1.61	4.2×10^4
Diethyl phthalate	84-66-2	2.38	1.1×10^4
Di-n-butyl phthalate	84-74-2	4.45	112
Butylbenzyl phthalate	85-68-7	4.59	2.7
Bis(2-ethylhexyl) phthalate	17-81-7	7.5	0.003
Di-n-octyl phthalate	3-1307	8.06	0.02
<i>Lubricants</i>			

Additive	CAS	Log K_{ow}	Water solubility (mg/L)
n-Hexadecanoic acid	57-10-3	7.17	0.04
Oleic acid	112-80-1	7.64	None
Glycerol tricaprilate	538-23-8	9.20	0.40 (37°C)
Isopropyl myristate	110-27-0	7.17	2.44×10^{-2}
1-Eicosanol	629-96-9	8.70	1.5×10^{-3}
2-Hexyl-1-decanol	2425-77-6	6.66	0.1727
Octadecanamide	124-26-5	7.292	None
4-Methyl-benzenesulfonamide	70-55-3	0.82	3.16×10^3
Hexacosanol	506-52-5	11.65	1.438×10^6
Decanedioic acid, bis(2-ethylhexyl)	122-62-3	9.63	None
Fuel			
Pentadactyl ester trichloroacetic acid	74339-53-0	–	–
1,10-[2-methyl-2-(phenylthio)cyclopropenyldiene] bisbenzene	56728-02-0	–	–
2,4-dimethyl-4-octanol	568123	3.51	188.9
Hexadecyl ester trichloroacetic acid	74339-54-1	9.1	6.223×10^{-5}
Intermediates			
HEHA	59130-69-7	11.15	4.127×10^6
2,3-Dihydroxypropyl ester hexadecanoic acid	542-44-9	4.364	None
Hexadecanoic acid ethyl ester	628-97-7	7.74	3.71×10^3
Behenic alcohol	661-19-8	9.68	1.5×10^5
Nonanoic acid	112-05-0	3.42	284
Pimaric acid	127-27-5	6.60	9.232×10^2
3,5-Di-tert-butyl-4-hydroxy phenyl propionic acid	20170-32-5	4.48	12.93
Abietic acid	514-10-3	6.51	8.96×10^2
Dehydroabietic acid	1740-19-8	6.35	8.161×10^2
Monomers and oligomers			
Bisphenol A	80-05-7	3.32	300
4-Hydroxyacetophenone	99-93-4	1.42	2.32×10^4
4-Hydroxyacetophenone	99-96-7	1.58	5×10^3
Flame retards			
PCBs	1336-36-3	3.76–8.26	$2.7\text{--}1.5 \times 10^4$
PBBs	67774-32-7	6.5–9.4	–
PBDE		5.52–11.22	$5.6 \times 10^{-10}\text{--}0.13$
-tetraBDE	40088-47-9	5.87–6.16	1.1×10^{-2}

Additive	CAS	Log K_{OW}	Water solubility (mg/L)
-pentaBDE	32534-81-9	6.57	13.3×10^{-3}
-hexaBDE	36483-60-0	6.86–7.92	4.2×10^{-6}
-heptaBDE	68928-80-3	9.44	2.2×10^{-7}
-octaBDE	32536-52-0	6.29	5×10^{-4}
-nonaBDE	63936-56-1	11.22	5.6×10^{-10}
-decaBDE	1163-19-5	6.265	–
α -HBCD	134237-50-6	5.07	48.8
β -HBCD	134237-51-7	5.12	14.7
γ -HBCD	134237-52-8	5.47	2.1
TBBP-A	79-94-7	4.5	720
BTBPE	37853-59-1	7.88	19
DBDPE	84852-53-9	11.1	21
Anti-DP syn-DP	13560-89-9	9.3	250
<i>Others</i>			
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	3.59	15.5
Glycerol 1-palmitate	32899-41-5	6.17	0.1252
(Z)-13-docosenamide	112-84-5	5.3	0.2
Di-tert-dodecyl disulfide	27458-90-8	6.1	None
1-Hexadecanol	36653-82-4	6.83	4.1×10^{-2}
Oleic acid eicosyl ester	22393-88-0	13.609	–
Octadecanoic acid	57-11-4	8.23	0.568–0.597
Octadecanoic acid 4-hydroxy-methyl ester	2420-38-4	–	–
Tridecanoic acid 4,8,12-trimethyl-methyl ester	5129-58-8	–	–
Succinic acid	110-15-6	-0.59	8.32×10^4
Triclosan	3380-34-5	4.76	12

Table 4. Log K_{OW} and water solubility of main additives of microplastics. Based on References [53–62].

In recent model analyses, however, it was shown that the effects of plastic on the bioaccumulation of POPs may be small, due to a lack of gradient between POPs in plastic and biota lipids, and that a cleaning mechanism is likely to dominate at higher log K_{OW} (octanol/water partition coefficient) values [44, 48, 49] (Table 4). In the case of additives, monomers or oligomers, which are components of the plastics, this issue has hardly been addressed. Many substances such as plasticizers may have biological effects even at low concentrations in the ng/L or μ g/L range [50]. Although it has been argued that exposure to additives will probably be low because of the low diffusivities of the chemicals, bioaccumulation could increase the concentration in animal tissues. Moreover, POPs, like the bisphenols or nonylphenols found in plastics, have

been suggested to be a relevant environmental problem [51]. It has been reported that the concentrations of bisphenol A in wild freshwater fishes oscillated from undetected to 25.2 µg/kg biomass, while nonylphenol levels varied from 1.01 to 277 µg/kg [52]. So, the substances can enter and be accumulated by animals, and the log K_{OW} could give an idea of the behaviour of additives in aquatic environments and their solubility in water (Table 4).

5.1. Hydrocarbons

Hydrocarbons are organic compounds comprising only carbon and hydrogen atoms. The molecular structure comprises a frame of carbon and hydrogen atoms and grouped into saturated (straight, substituted and cyclic alkanes), unsaturated (alkenes with straight, branched and cyclic), halogenated and aromatic hydrocarbons. The hydrocarbons can be classified into two types—aliphatic and aromatic. Aliphatic hydrocarbons in turn can be classified into alkanes, alkenes and alkynes as link types that bind the carbon atoms. The general formulas of alkanes, alkenes and alkynes are C_nH_{2n+2} , C_nH_{2n} and C_nH_{2n-2} , respectively. Many alkanes with a chain length varying from C-11 to C-31 have been found in plastics from coastal debris [16]. These are other oligomers originating from polyolefins (polypropylene, polyethylene and poly(acetylene: styrene)) during recycling [63]. Octadecane ($n=20/43$), hexadecane ($n=19$), eicosane ($n=18$), tetradecane ($n=18$), heptacosane ($n=14$), heptadecane ($n=13$), pentadecane ($n=11$), tetracosane ($n=10$), docosane ($n=8$), dodecane ($n=7$), hexacosane ($n=7$), 2,6,10-trimethyl-tetradecane ($n=10$) and heptadecane, 3-methyl- ($n=6$) were the most frequently detected in the plastic debris from near the coasts [16].

Linear alkanes, together with iso-alkanes, originate from the paraffin wax that is used as an external lubricant in PVC and other polymers, where they help the polymers to slide over other surfaces. Alkanes are also used as solvents, such as hexane and heptane. Alkenes (squalene and others) and cycloalkenes are used as starting compounds for several additives and polymers and are formed as by-products during olefin polymerization.

Aromatic hydrocarbons, such as benzene and anthracene derivatives, have also been found in MP debris. Benzene is an important organic chemical compound used mainly as an intermediate to make other chemicals, mainly ethylbenzene, cumene, cyclohexane, nitrobenzene, and alkylbenzene. More than half of the entire benzene production is processed into ethylbenzene, a precursor of styrene, which is used to make polymers and plastics like polystyrene and expanded polystyrene. Around 20% of benzene production is used to manufacture cumene, which is needed to produce phenol and acetone for resins and adhesives. The plastics may also carry halogenated hydrocarbons, which have been considered as POPs and are of proven toxicity [64, 65].

5.2. UV stabilizers/absorbers

Benzophenone and its derivatives are used as photo-initiators in the UV curing of inks and as UV absorbers. These compounds absorb the harmful UV light that would eventually change the physical and optical properties of the polymer and make the material lose colour or fade. This substance can also be added to plastic packaging as a UV blocker to prevent photo-

degradation of the packaging polymers or contents. Its use allows manufacturers to package the product in clear glass or plastic [66] since, without the UV blocker, opaque or dark packaging would be required. These plastic additives are used in PP, PE (2–3%) and acrylonitrile, butadiene and styrene (ABS) copolymer products. Benzotriazole UV stabilizers (BUVS) are emerging contaminants that are mutagenic, toxic, pseudopersistent, bioaccumulated and show significant estrogenic activity [67–70]. Great amounts of BUVS have been detected in rivers from Japan and China coming from wastewater treatment plants [71–73]. Due to their common use, BUVS have been found in aquatic environments [69, 72, 74], organisms [71, 72, 74, 75], tap water and well water [76]. Recent findings in German rivers and previously reports suggest that BUVSs have a potential of long-range transport, similar to several POPs [74].

5.3. Antioxidants

Antioxidants are widely used in plastic polymers to delay oxidation and to improve polymer properties [77]. Several types of antioxidants can be used to prevent the aging of plastic, such as phenolic antioxidants, organophosphorus compounds and different amines. However, antioxidants can migrate from the plastics into the food and contaminate it during production or storage, potentially giving rise to food safety issues [78, 79]. Antioxidants are used in almost all commercial polymers in small amounts up to 2% (w/w) (20,000 mg/kg or ppm) [16]. The polymers can be oxidized during synthesis, processing, transfer or final use, resulting in loss of chemical, optical and mechanical properties, among others. Thermal oxidation results in the formation of free radicals that react with oxygen to form hydroperoxides. In order to inhibit the onset of thermal oxidation of polymers and/or slow down degradative processes, the antioxidant additives are added during manufacture, processing and/or during the manufacture of the products. In the specific case of the polypropylene, antioxidant additives are important because the chemical structure of this type of polyolefin tends to degrade easily. The plastic antioxidants identified in the literature are usually limited to the commonly used Irganox series (including Irganox 1010, Irganox 1076, Irganox 168) [80–84].

5.4. Plasticizers

Plastic as a material may contain a variety of chemicals, some potentially hazardous. Plasticizers, which are used to make the plastic soft and flexible, are mainly used in PVC, but they are detected in other polymer plastics. Several types of plasticizers are found in plastic debris, but phthalates predominate [85]. The phthalates found in plastics include dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DNOP) [86]. Their concentrations in different plastics vary widely; for example, in foodstuffs, the content of phthalates varies from 658 to 1610 ng/g fresh weight [87]. Phthalates are produced in large quantities around the world and are also widely used in cosmetics, plastics, carpets, building materials, toys, medical and cleaning products.

Several cross-sectional and case-control studies have reported an association between exposure to phthalates and the development of certain human allergies and respiratory diseases [88]. A recent systematic review based on less than ten relatively small ($N < 400$) studies found

that the findings from these studies are inconsistent, with both decreases in birthweight and null associations, and both longer and shorter gestational periods being recorded [89]. A prospective birth cohort study researched the association between butyl benzyl phthalate and an early-onset eczema, although not the late-onset eczema, finding that prenatal exposure to butylbenzyl phthalate may influence the risk of developing eczema in early childhood [90]. Three studies reported a positive relation between prenatal exposition and the risk of wheeze, asthma and respiratory infections in children aged 5–11 years [91–93], although, even here, there were inconsistencies concerning the phthalate congeners implicated [94].

On the other hand, phthalates have been related with hormone disorders [95], abortion [96], metabolic diseases [97], hormone disturbances, reprotoxicity or even suspected cancer [98–100]. Other plasticizers are often used as substitutes for phthalates, but their effects on the health are not always clear, usually because of the limited data available. Therefore, because the amount of plasticizers could increase the 50% of the total weight, and the possibility that these substances will leach when the plastics come into contact with seawater is greater [16], the substances called plasticizers should be considered in a hazard category and need be reviewed.

5.5. Lubricants

Usually, lubricants are used to minimize adhesion and viscosity of plastic polymers. Internal lubricants can facilitate the production process by providing lubrication at molecular level between the polymer chains [101]. Commonly, they are composed of an oil base accompanied by a variety of additives that confer desirable properties. Lubricants are based in one type of base oil, but in commercial requirements, it usually makes that a mixture are used [102]. n-Hexadecanoic acid, oleic acid, glycerol tricaprylate, isopropyl myristate, 1-eicosanol, 2-hexyl-1-decanol, octadecanamide, 4-methyl-benzenesulfonamide, 1-hexacosanol and decanedioic acid, bis(2-ethylhexyl) ester can be found in plastic debris [16]. The transfer of additives such as lubricants to the medium or to the substances which are in contact with the plastics has been reported previously [103].

5.6. Fuel

Chemicals like pentadactyl ester trichloroacetic acid, 1,10-[2-methyl-2-(phenylthio) cyclopropenylidene] bisbenzene and 2,4-dimethyl-4-octanol are often found in plastic debris [16]. These substances and others, like hexadecyl ester trichloroacetic acid, have been considered as fuel precursor based on plastic wastes additives, due to the large amount and variety of additives that plastics can contain [63]. Waste plastics are considered a promising source for fuel production because of their high combustion heat and their increasing availability in local communities [104].

5.7. Intermediates

In manufacture of plastics, it is normal to use stabilizers (DEHA or DEHP) and plasticizers that contain intermediate substances like hexanoic acid 2-ethyl-hexadecyl ester (HEHA), 2,3-

dihydroxypropyl ester hexadecanoic acid, hexadecanoic acid ethyl ester, behenic alcohol, nonanoic acid, pimaric acid, 3,5-di-tert-butyl-4-hydroxyphenyl propionic acid, abietic acid and dehydroabietic acid [16]. HEHA has been classified as belonging to reprotoxic category 3 by Council Directive 67/548/EEC [105].

5.8. Flame retardants

Flame retardants are a group of chemical compounds that are used in plastics with the aim of diminishing the flammability of combustible materials, like synthetic polymers and plastics. To make sure that flame retardants remain in the polymers, these compounds are designed to be stable for many years, which means they will remain in the environment long past the time when the material itself was used [106]. Thus, these compounds can enter aquatic environments via the atmospheric deposition of fine particles, direct discharges of municipal and industrial wastewater effluents, and through run-off and other human activities [107]. Flame retardants include α , β , γ -diastereoisomers of hexabromocyclododecane (HBCD), tetrabromobisphenol-A (TBBP-A), anti- and syn-isomers of dechlorane plus (DP) and two novel compounds, decabromodiphenylethane (DBDPE) and 2-bis(2,4,6-tribromophenoxy) ethane (BTBPE). Among the most widely used flame retardants are polybrominated diphenyl ethers, which have been in use since the late 1970s. Polybrominated diphenyl ethers are a class of brominated compounds widely used as flame retardants including in polymers such as low density polyethylene or silicone rubber [45, 108]. Polybrominated diphenyl ethers are very hydrophobic, with $\log K_{OW}$ above 5.5 and molecular weights (MW) in the range of 300–1000 g/mol which means that these compounds are likely to have diffusion coefficients significantly lower than those measured for polycyclic aromatic hydrocarbons and polychlorinated biphenyls. This implies that the polymer diffusion coefficients for these plastic additives used as flame retardants need to be taken into account when considering the risk posed by microplastic particle ingestion by marine organisms [109]. Many studies on polybrominated diphenyl ethers [110–118] have shown that these compounds are ubiquitous, toxic, persistent and bioaccumulated in the environment. As a result, some flame retardants have been prohibited in the USA and European Union [119, 120], such a penta- and octabrominated diphenyl ether. Nevertheless, new compounds have replaced the forbidden polybrominated diphenyl ethers, such as 1,2-bis(pentabromodiphenyl) ethane, which is used in solid plastics, wire, cable and electronics, high impact polystyrene and thermoplastics [121].

5.9. Monomers and oligomers

Bisphenol A (2,2-(4,4-dihydroxydiphenyl) propane) is used as a monomer in polycarbonate, for the production of polycarbonate plastics and epoxy resins. It has been found in samples of PE, PP and acrylate-styrene, where it is probably used as chain terminator, to finish the polymerization of polymers or as antioxidant for polymers or plasticizers [16]. Bisphenol A is also used to manufacture a great variety of products, including CDs, food can linings, thermal paper, safety helmets, plastic windows, car parts, adhesives, protective coatings, powder paints, and the sheathing of electrical and electronic parts [122]. As a result of its wide usage, bisphenol A is frequently detected in wastewaters [123].

Bisphenol A has been identified as an endocrine disruptor [124], and several studies have demonstrated reproductive, metabolic and neurodevelopmental problems in animals exposed to environmentally relevant levels of this substance [125–127]. In addition, an increased risk for cardiovascular disease, altered immune system activity, miscarriages, decreased birth-weight at term, metabolic problems and diabetes in adults, breast and prostate cancer, reproductive and sexual dysfunctions and cognitive and behavioural development in young children have been associated with the human exposure to bisphenol A [128–134].

It is known that plasticizers may have biological effects even at low concentrations in the ng/L range, especially for molluscs, crustaceans and amphibians [50]. Although it has been argued that one should expect levels of exposure to plastic additives to be low due to the low diffusivities of chemicals like bisphenol A or nonylphenol in plastics [51], as we said above, their bioaccumulation could play an important role, increasing physiological concentrations in the food chain. In an attempt to solve these problems, physicochemical processes for the removal of bisphenol A from wastewaters have been studied [135, 136]. However, possible solutions presented several problems related to the cost of chemicals, the generation of bisphenol A-containing sludge and the conditions necessary to optimize the bisphenol A elimination process. The most frequently detected metabolic products of the aerobic biodegradation pathway of bisphenol A include 4-hydroxyacetophenone and 4-hydroxybenzoic acid [137]. Both bisphenol A and 4-hydroxybenzoic acids have shown a certain degree of biodegradability [138], and these compounds are not expected to be persistent in an activated sludge system, although the information concerning 4-hydroxyacetophenone is scarce.

5.10. Others

Degradation products, antifogging, antiblocking, colouring, heat stabilizers, fatty acids and their derivatives have also been found in plastics debris [16]. This heterogeneous group includes 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione, glycerol 1-palmitate, (Z)-13-docosenamamide, 2,3-dichloro-1,10-biphenyl, trans-13-docosenamamide, di-tert-dodecyl disulfide, 1-hexadecanol, 2,4-bis [2-(4-methoxyphenyl-2-propyl)] methoxybenzene, oleic acid eicosyl ester, octadecanoic acid, octadecanoic acid 4-hydroxy-methyl ester, octadecanoic acid 2-hydroxy-1-(hydroxymethyl)ethyl ester, tridecanoic acid 4,8,12-trimethyl-methyl ester, heptanedioic acid 4-(ethoxycarbonylmethylene)-diethyl ester and succinic acid [16]. Fatty acids and their esters could originate from several kinds of oils, such as coconut oil (lauric acid) or palm oil (palmitic acid), acids which, along with their esters, are usually used as internal lubricants. Besides, metallic salts of fatty acids are normally used as stabilizers and plasticizers in the production of the plastics.

Other substances can stick or bind to plastics, such as disinfectants, aromatic compounds, soaps used to clean the plastics. In this respect, triclosan (5-chloro-2-[2,4-dichloro-phenoxy]-phenol) is an additive that has been reported to be toxic [139–141]. Triclosan is an antimicrobial that is effective against bacteria of the adult oral cavity and skin. It is currently used in antibacterial soaps, deodorants, skin creams, toothpastes and plastics. Triclosan is an ionizable chlorinated biphenyl ether of low water solubility, with a pK_a of 8.1, and a vapour pressure of 4×10^{-6} mm Hg [139]. Triclosan readily bioaccumulates within aquatic organisms and has been

found to be toxic to fish. In larval fishes, exposure to triclosan disrupts a variety of developmental processes, impairs hatching success, and causes pericardial oedema, having the potential to cause subtle cardiac toxicity [142]. Browne et al. [47] showed that triclosan added to MPs diminished the ability of worms to engineer sediments and caused mortality, each by >55%, while PVC alone made worms >30% more susceptible to oxidative stress. Triclosan persists in water and is difficult to eliminate from wastewaters [143, 144]. The ingestion of MPs by organisms can transfer pollutants and additives (such as triclosan) to their tissues at concentrations sufficient to disrupt ecophysiological functions linked to health and biodiversity. Biomarkers of endocrine disruption found in fish indicated long-term exposure to estrogenic chemicals in the wastewater [145].

6. Effects on marine fish

The accumulation of microplastic waste could affect the functioning of marine ecosystems. However, the mechanisms by which these effects will be manifested have not been identified. Impacts on biota and marine environmental quality are well documented [146], with damage for the global economy estimated to be in the range of \$13 billion per year [147].

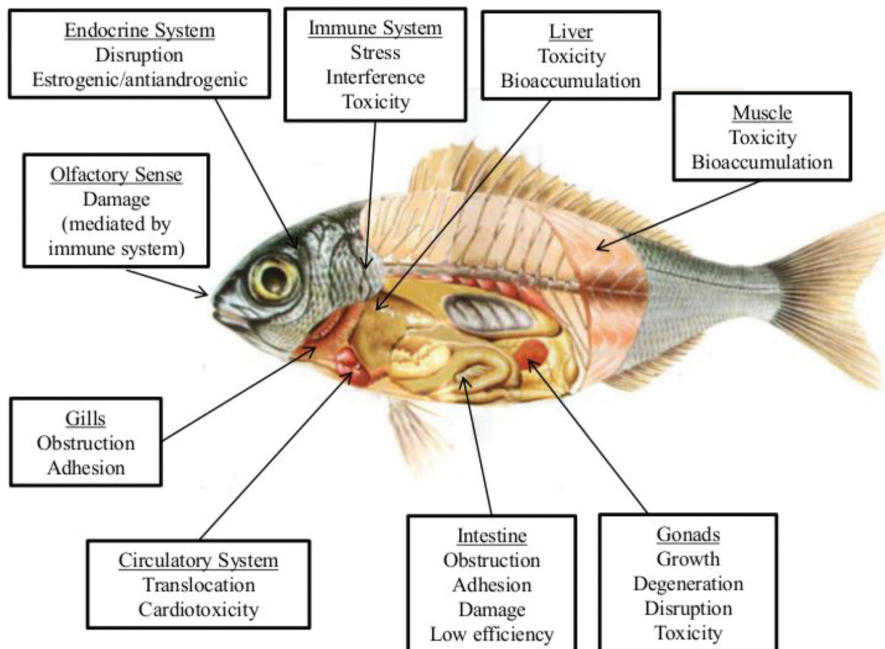


Figure 1. Principal effects of microplastics on fish.

Negative effects include entanglement in plastic wires or nets, or to ingestion, which has been reported in benthic invertebrates, birds, fish, mammals and turtles [148–151]. This is especially true for eggs, embryos and larvae of aquatic organisms, which are particularly vulnerable to water-borne pollutants owing to their limited ability to regulate their internal environment [152]. In particular, the early life stages of fishes are subjected to strong selection forces, driven by high rates of predator-induced mortality [153, 154]. So, it has been reported that there is a clear overlap between areas with high levels of microplastics pollution and the feeding grounds of fin whales in the Mediterranean Sea, which could mean that fin whales are subjected to a high level of exposure to MPs ingestion during feeding in the areas [155]. The bioaccumulation of MPs and the substances which they could carry seem to be an increasing problem due to MPs which has been detected from little fish species to the top of food web.

The ingestion of the MPs can influence marine animals in different ways (**Figure 1**). It can affect to the immune system, both chemically (caused by the substances that MPs might contain, absorb or release, which may be toxic) [156] and physically blocking the digestive organs and preventing the animals from feeding [157]. Ecology and behaviour could also be affected.

6.1. Immune system

Interactions between plastic microparticles and aquatic organisms have been reported, and several recent studies have addressed the effects of nanoplastic material on different organisms and their health status. This research suggests that nanoplastics can enter different organisms and may interact with the immune system [158–161].

In fish, cellular innate immunity effectors act as one of the first organ defences against various agents, which makes these effectors the possible target for interaction with nanoplastic particles. Neutrophil activation is critical for the host defences, and their function is a valuable tool to assess the health status of individuals and animal populations [162]. So, fish neutrophils can extravasate, migrate chemotactically, degranulate, release neutrophil extracellular traps and phagocytize particulate matter such as bacteria [163]. Hypotheses existed about the interactions between MPs or nanoplastics and the neutrophils until recently, it has been reported that polystyrene and polycarbonate nanoplastic can act as stressors to the innate immune response of fish [164]. Therefore, nanoplastic could potentially interfere with innate immune responses in fish populations by altering organismal defence mechanisms.

In addition, plastic fragments found in the marine habitat have been shown to absorb POPs, so effects on the immune system may be caused by particle toxicity, plastic-associated chemicals and absorbed environmental chemicals.

6.2. Disrupting effects

Evidence points to the potential role of microplastics as vectors of chemical pollutants, either used as additives during polymer synthesis, or adsorbed directly from seawater [27, 45, 165]. The hydrophobicity of organic xenobiotics and the surfaces of polymers facilitate the adsorption of the chemicals on MPs at concentrations with orders of magnitude higher than those usually detected in seawater [166].

Several of these plastic-associated chemicals have been linked to endocrine-disrupting effects in fish. Styrene [167], a monomer of several plastic types including polystyrene, rubber and acrylonitrile–butadiene–styrene, and bisphenol-A [168] a monomer of polycarbonate, can disrupt the endocrine system function, as mentioned above. In addition, there is evidence that UV stabilizers, phthalates and nonylphenol, additives to plastic, are estrogenic and/or antiandrogenic [169, 170]. Furthermore, chemicals historically known to promote adverse effects in the endocrine system functions, including heavy metals, organochlorine pesticides and petroleum hydrocarbons [171, 172], have been found attached to plastic debris around the world [173, 174].

The ingestion of plastic debris has been documented in fish [175, 176], which may introduce a ‘cocktail’ of endocrine-disrupting chemicals [47, 150, 177]. Significantly higher concentrations of several polybrominated diphenyl ethers, such as polychlorinated biphenyl congener (PCB#28) and the polycyclic aromatic hydrocarbon chrysene, have been recorded in Japanese medaka (*Oryzias latipes*) exposed to polyethylene that had been deployed in the marine environment compared to fish exposed to a virgin polyethylene and a control treatment [177].

Fish are useful as sensitive indicators of endocrine-disrupting chemicals in aquatic habitats, as exposure can result in changes in gonadal growth, gonadal degeneration, sex-specific gene protein and intersex induction [178]. Finally, recent research showed that ingestion of plastic debris at environmentally relevant concentrations may alter the endocrine system function in adults [179], where the presence of abnormal germ cell proliferation observed may be related to plastic. In this respect, ovary structure protein 1 (OSP1) gene has been proposed as a suitable indicator of the early stages of intersex development and suggested to be a more sensitive early-warning signal than histopathological observation [180].

6.3. Physiological

It has been shown in various marine organisms that ingestion of MPs occurs in animals with different feeding strategies and may negatively influence both the feeding activity and nutritional value, especially in species which cannot vary their food source [181, 182]. Different studies have pointed to the obstruction and damage of digestive tracts or even animals starving to death caused by stomachs filled with plastic [18]. In addition, MP ingestion by marine biota has been detected in benthic fish species [183, 184], and different sized plastic items were identified in the stomachs of three large pelagic fish in the Mediterranean Sea [185].

In a study made in Spanish coastal waters and which constitutes the first report of MPs ingestion by demersal fishes, red mullets (*Mullus barbatus*) from Barcelona presented the highest abundance of microplastics, followed by dogfish (*Scyliorhinus canicula*) from the Cantabrian coast and the Gulf of Cadiz, whereas dogfish from the Galician coast presented the lowest levels [186]. In agreement with previous studies, the detected MPs were mostly fibres (71%) [174, 184, 187], and the most frequent colour was black (51%) (Table 5).

Because of their small size, MPs may be ingested by marine organisms, regardless of their feeding mechanisms, and may enter their circulatory system and accumulate in different types of tissues, as has been proven in laboratory experiments [182]. These reported data, along with

the fact that MPs serve as dispersal vectors for invasive species [188] and the toxic and bioaccumulative substances bound to the plastics [149], together with the research that indicates that MPs may have the ability to enter and disseminate through the marine food web [189, 190], suggest grave ecological implications of microplastics across the food web.

Form	Percentage (%)
Fibre	71.0
Sphere	24.2
Film	3.2
Fragment	1.6

Table 5. Types of plastics found in fish and their relative abundance in Spanish coastal waters [188].

6.4. Behaviour

Behaviour is a crucial determinant for essential parameters such as overall health, growth, reproduction and survival [191]. During the life cycle of fish, a critical point is the early stage of development. Survival depends, in many cases, on the capacity of the organism to evade predators. An innate ability to detect and act accordingly is therefore vital [153, 154, 192].

In this regard, it has been suggested that olfactory sense in fish larvae could suffer damage mediated by an immunological response produced by the pollutant from microplastics. Lönnstedt and Eklöv [193] found that not only was crucial behaviour, such as activity and feeding, affected by microplastics, but that innate responses to olfactory threat cues were also impaired. Such a loss of predator avoidance behaviour greatly increased predator-induced mortality rates of larvae. Finally, survival of fishes could be seriously affected by the presence of MPs, with their significant impact on the life cycle of the fish.

7. Conclusion

Microplastics in the aquatic environment have been demonstrated to be a significant problem. The great amount of research on this topic, as well as the quantity of the results that describe the problem of MPs and their effects on fishes and aquatic life, have thrown some light on this issue. Among the effects that MPs have are stress, intestinal obstruction and the alteration of health, while further studies are in progress to ascertain the full potential risks of MPs in aquatic organisms with special attention paid to fish. A huge number of substances are added to plastics, which can bioaccumulate throughout the trophic chain. Besides the problems that MPs represent for marine life in general, the MPs could begin to act as disruptors of the welfare and health of fishes, both wild and cultivated. This is clearly a growing problem not only for the environment but also for human health. For these reasons, further efforts are needed to know the exact effects that microplastics, and their constitutive and adsorbed contaminants, may have on aquatic environments.

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