



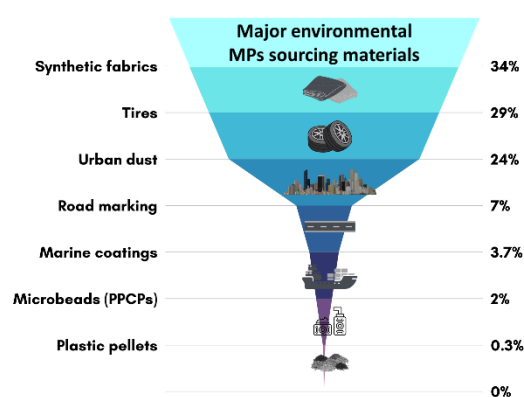
Microplastics in aquatic environments: a growing, unresolved concern

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ABSTRACT

The global rise in plastic demand and production, combined with the significant amount of plastics found in municipal solid waste, has led to the ubiquitous occurrence of microplastics (MPs) in the aquatic environment. This review examines the existing information on the origin, behaviour, fate, and effects of MPs on living organisms and the environment. In aquatic ecosystems, the reported high concentrations of MPs potential threat to the exposed organisms, causing blockage of the intestinal tract, alterations in feeding and digestive habits, injury, and death. Both fresh and aged MPs interact with different components of the aquatic ecosystem, leading to changes in their behaviour and bioavailability. Additionally, MPs often serve as vectors for sorbed pollutants and the chemicals leaching from their polymeric chains, enhancing the transportation of contaminants within the aquatic environment and to predators. With the current rate of plastic production and use coupled with the lack of proper waste management policies in many countries, the worries about environmental MPs have increased in recent years. Hence, a better understanding, continuous monitoring, and plastics management methods and waste control plans are crucial to address the issue of MPs in the environment.



HIGHLIGHTS

- MPs are composed of both homogeneous and heterogeneous plastics.
- MPs degrade via processes like mechanical, thermal, photo-oxidation, etc.
- The emergence of eco-coronation intensifies concerns regarding MPs.
- MPs are present in human organs, among other gangers.

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1. Introduction

The assurance of high-quality water for all organisms, including humans, has become a distant dream due to the enormous influx of unwanted and hazardous pollutants that pervade natural water ecosystems worldwide daily. Several thousands of pollutants, including microplastics (MPs), are currently monitored in environmental compartments due to their known and potential harm to the health of the environment and humans. The occurrence of MPs in the environments "stretches from the equator to the poles", and the problems associated with them are at the centre of scientific discussions and global concerns today [1, 2].

Although there is no definition widely accepted by the scientific community, MPs can generally be defined as solid particles with an effective diameter of less than 5 mm, composed of mixtures of polymers and functional additives, and found in various shapes.

They can persist in the environment and have been found in many aquatic ecosystems such as surface waters, beaches, oceans, and seas, as well as in aquatic organisms. Therefore, MPs are considered ubiquitous, and they have the potential to act as vectors of organic and inorganic environmental pollutants.

Environmental MPs are of both primary and second origin in terms of particles released and environmentally degraded MPs. MPs are mainly sourced from anthropogenic activities, and synthetic fabrics (34%), tires (29%), urban dust (24%), road markings/dust (7%), marine coatings (4%), microbeads (2%), and plastic pellets (0.3%) have been identified as significant sources of MPs [3-5]. They enter into the environment through various transport media, including sewage sludge, urban runoff and dust, and industrial, agricultural and municipal wastes [5].

With a wide range of physical and chemical properties that depend on the type of polymer and the production process, MPs may exhibit unique behaviour in the environment, affecting their interactions with other components, bioavailability, and potential

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impacts on organisms. In addition to the direct impacts of MPs on environmental organisms, they can adsorb and accumulate various types of contaminants and release some of them into freshwater and marine environments, which raises further concerns [6-8]. Furthermore, aquatic organisms that ingest MPs can become exposed to these harmful substances, resulting in a significant pathway for introducing pollutants into the tissues of aquatic organisms and the food chain [9]. The gastric fluid environment of organisms enhances the desorption of persistent organic pollutants from MPs, which is more pronounced than in aqueous solutions [10].

In general terms from studies, MPs are potentially harmful to wildlife, aquatic ecosystems and humans and other organisms. For instance, MPs have been detected in the tissues of marine animals, causing negative physiological effects [11]. They can act as vectors for the transfer of toxins and pollutants to higher trophic levels [12] and have the potential to accumulate in the tissues of aquatic animals, resulting in several consequences, including starvation, entanglement and economic ones, as they can affect the quality and marketability of seafood, among others [13].

The abundance and distribution of MPs in aquatic environments are not well understood, yet, making it difficult to assess the full extent of the problem [14]. This is a particular concern since MPs have also been found in remote areas, indicating widespread distribution and potential global impact [15, 16]. The lack of understanding about their prevalence and impacts in aquatic environments highlights the need for further research on this issue. Therefore, this study aims to review the sources, presence, fate, and potential harms of MPs. It will examine the potential impacts of MPs on aquatic ecosystems and human health, as well as their interactions with other pollutants in aquatic environments. The study will also consider the factors that influence adsorption strength in different aquatic ecosystems and biological fluids.

2. Physicochemical properties of some MPs

MPs may pose a significant threat to the environment due to their small size, persistence, absorbency, physical entanglement, chemical toxicity, bioaccumulation, and ability to transport invasive species. As more studies emerge, additional risks associated with MPs are coming to the limelight. The small size of MPs makes them easily ingestible by a wide range of organisms, and their persistence in the environment means they can cause harm to ecosystems for hundreds of years [25, 26]. The high surface area-to-volume ratio of MPs makes them highly absorbent of pollutants, increasing their toxicity and the risk of harm to organisms that ingest them [27]. Table 1 presents some physicochemical properties of commonly found MPs in aquatic ecosystems.

When polymers are exposed to sunlight, they undergo photo-oxidation, which causes the polymer chain to undergo homolytic scission and produce free radicals, ultimately leading to the formation of photo-oxidized products with low molecular weight and increased brittleness [28]. The weathering process of MPs in aquatic environments is influenced by the physicochemical properties of the plastic, such as structure, tensile strength, and crystallinity, as well as environmental factors, including oxygen, temperature, organic matter, light, and salinity [29]. For example (Figure 1), MPs made of polyethylene terephthalate (PET) are more challenging to biodegrade than other polyesters (like Polyurethane (PU) which is more open), primarily due to the limited mobility of the aromatic terephthalate units, resulting in a reduced hydrolysis rate of the backbone ester linkages by enzymes [30]. Similarly, resins containing tertiary hydrogens such as polystyrene (PS), polypropylene (PP), and polyvinyl chloride (PVC) have lower weathering resistance than those without tertiary hydrogens, like polyethylene (PE), which are more stable [29]. PU materials degrade in the aquatic environment mainly through photo-oxidation, hydrolysis, and biodegradation, with photo-induced oxidation occurring at the α -methylene position, followed by the hydrolysis of the ester bond, which is accelerated by acidic conditions, resulting in the formation of carboxylic acid end groups [31].

The properties of MPs can be modified by the presence of additives and environmental processes such as weathering and fouling, and environmental conditions, among others. This can lead to variations in the properties of aged MPs. Density is another key property that affects the rate of MPs degradation and fragmentation. Higher-density MPs tend to sink in water, reducing their exposure to sunlight and other weathering factors, and making them more likely to accumulate in sediment and persist in the environment. On the other hand, MPs with lower density MPs will have more buoyancy, being more susceptible to fragmentation and biodegradation [32].

3. Sources of MPs in the environment

MPs in aquatic ecosystems originate from primary or secondary sources in several tonnes. Primary microplastics (PMPs), including microbeads, pellets, etc., are manufactured at the micrometre scale and used as ingredients of many personal care products (PCPs), which can result in their release into the environment as micro-sized particles. PMPs serve a variety of functions in PCPs including their role as exfoliants, antimicrobial, antibacterial, viscosity regulators, emulsifiers, film formers, opacifying agents, liquid absorbents, binders, bulking agents, glitters, skin conditioning, abrasives, dental care, scent delivery, vitamins, oils, moisturizers, and preservation agents. After use,

Table 1. Physicochemical properties of commonly encountered MPs in aquatic ecosystems, [5, 17-24]

Property	PE	PP	PVC	PS	PET	PU
Glass transition temperature (T_g , °C)	-25	-20 – -10	75 –105	74 –105	70	-12 – -48
Melting point (°C)	90 – 130	168 – 175	115 – 245	240 – 270	245	130 – 160
Density (g/cm ³)	0.89 – 0.98	0.83 – 0.92	1.16 – 1.58	1.04 – 1.1	0.96 – 1.45	1.2
PZC	4.30	4.26	3.41	3.96	5.16	7.26
Crystallinity (%)	45 – 95	50 –80	5 –15	0	0 – 50	61.5
Tensile strength (MPa)	45 –90	31 –41	41 –52	36 – 52	48	2.62 – 5.80
Estimated lifespan (year)	10 –600	10 –600	50 –150	50 – 80	450	-

PE = polyethylene, PP = polypropylene, PET = polyethylene terephthalate, PS = polystyrene, PVC = polyvinylchloride, PU = polyurethane, PZC = point of zero charges, PZC = point of zero charge.

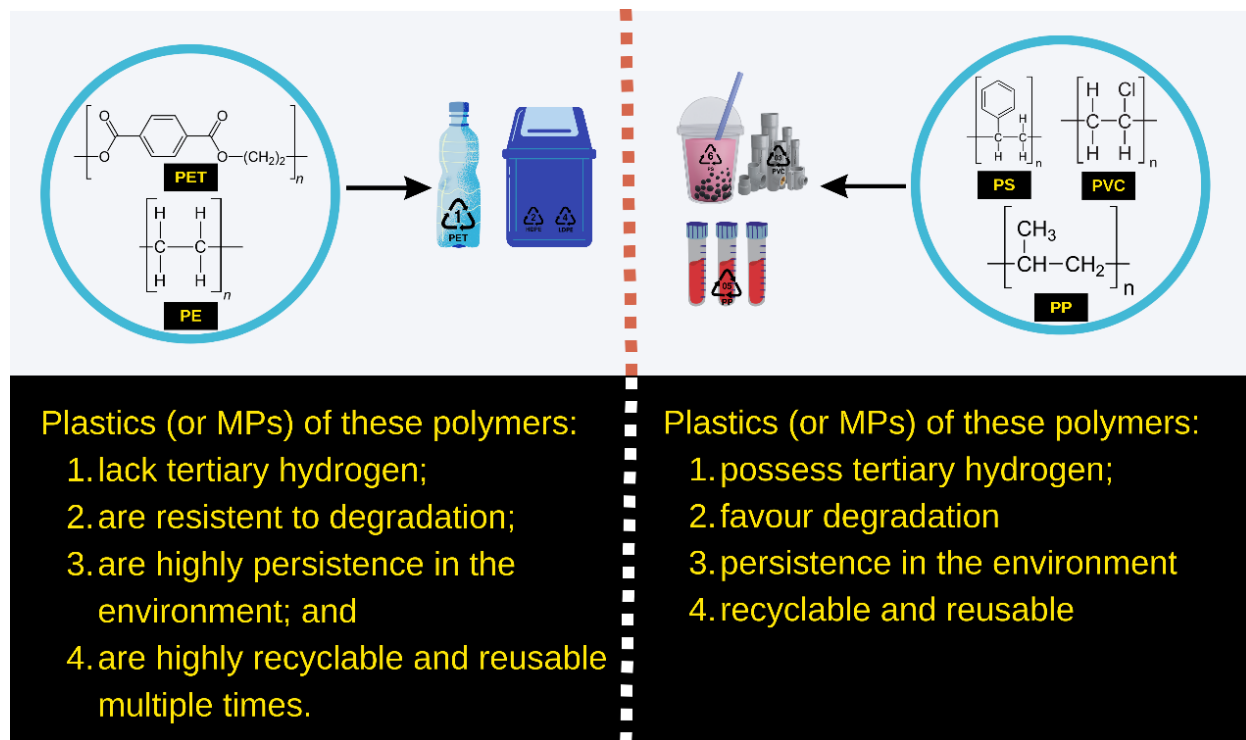


Figure 1. Some chemical properties of plastic polymers that predict their behaviour in aquatic environments

PMPs are typically released into waste streams, with around 95-99% of them being partitioned into biosolids or removed during wastewater treatment. They can also enter the environment through accidental spills and industrial abrasives [1, 33].

Plastic ingredients are present in a wide range of PCPs, including toothpaste, shower gel, shampoo, creams, eye shadow, deodorant, blush powders, make-up foundation, skin creams, hairspray, nail polish, liquid makeup, eye colour, mascara, shaving cream, baby products, facial cleansers, bubble bath, lotions, hair colouring, insect repellents, and sunscreen [34]. A wide range of goods incorporates plastic materials, with some containing only a fraction of a per cent, while others contain over 90% plastic. Throughout their life cycle, from polymer synthesis to the production and transportation of plastic items, pellets are inevitably released into the environment. It is estimated that around ten trillion plastic pellets enter streams each year, contributing to significant levels of plastic pollution in natural waters [35]. Figure 2 presents some of the sources of MPs in aquatic ecosystems.

The tiny solid particles resulting from the unintentional degradation of plastics due to weathering processes such as hydrolysis, UV photodegradation, mechanical abrasion, and biodegradation are known as secondary microplastics (SMPs). They are believed to be the main source of MPs in the aquatic environment. Plastic is a widely used, durable, lightweight, and cost-effective material used as a major or minor ingredient in many consumer and commercial products, including automobile tyres, domestic and industrial water tanks, bags, food and beverage packing, and more [36]. While plastic production has certainly been beneficial to mankind – so much so that approximately 373 million tons (MT) were produced in 2021 [37] – disposal of plastic waste is a significant challenge and often poorly managed. As a result, substantial quantities of plastic waste are introduced into the environment, particularly aquatic ecosystems, favouring the upsurge and proliferation of pollutants. The rapid increase in global population, economic development, and urbanization has led to a

surge in urban plastic waste generation [7]. Also, wastewater treatment plants (WWTPs) can release a massive quantity of SMPs into the environment, in addition to the large amounts of plastic debris present in aquatic environments. Microbeads from cosmetic products and polymer fibres from clothing have been detected in WWTP effluents [38].

4. Components of some MPs found in the environments

The chemical composition of a plastic product and its resulting MPs in the environment is determined by its manufacturing processes leading to the heterogeneous nature of MPs. Plastics are composed of polymers and additives, produced through the polymerization of various monomers in the presence of additives. These differences in composition can impact the types of pollutants released into the environment, their affinity for other pollutants, and the potential risks associated with them. The most commonly detected plastics in the environment include PE, PVC, PP, PET, and PS, while the most common types of MPs found in the aquatic environment include fibres, fragments, granules, films, and styrofoam particles [18, 33, 39, 40]. Although only 7.9% of PU is produced annually, it is frequently detected in the form of microplastics in marine environments, which is noteworthy compared to the more widely produced plastics such as PE, PP, and PVC [28]. Additives such as bisphenol A, triclosan, flame retardants, phthalates, Pb, Cr, Cd, and others are incorporated during plastic manufacturing. Some of these additives, which can leach from the plastic into the environment, are of significant concern due to their potential toxicity (e.g., endocrine disrupting, carcinogenic, and/or mutagenic properties) to living organisms. Phthalates and bisphenol A (BPA), commonly found in packaging materials predominantly made of PE and PP, while PVC can consist of up to 50% phthalates by weight, are environmentally ubiquitous pollutants [41]. The detection of high levels of MPs in

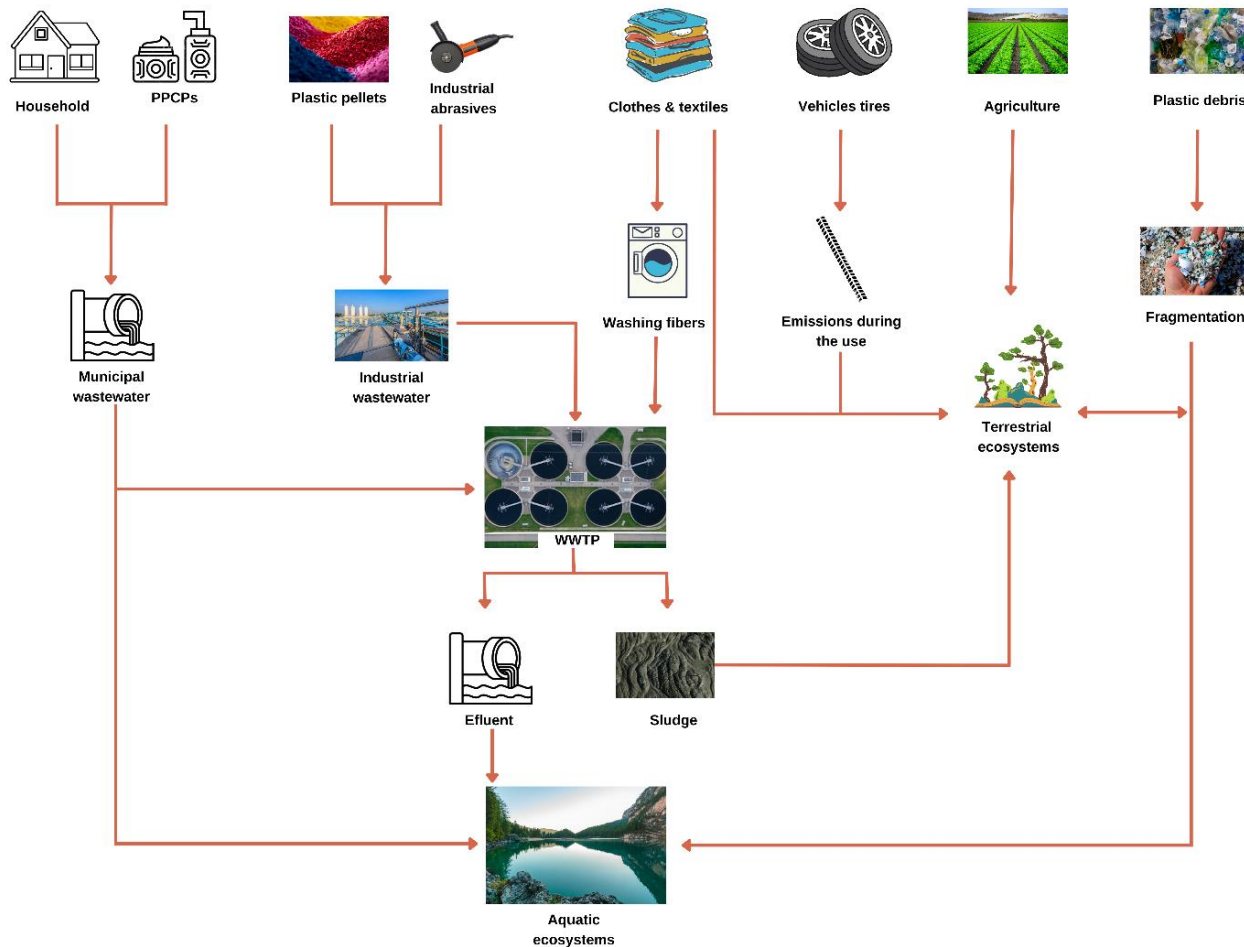


Figure 2. Some identified sources of MPs to the environment. Adapted from Miloloža et al. [5]

oceanic convergence zones has prompted further studies, resulting in the detection of MPs in oceans worldwide [18], although some areas are far less investigated.

A major concern regarding the presence of MPs in the environment is that plastics are composed of potentially health-threatening substances. PE is the most frequently detected polymer in the environment, either as high-density or low-density PE (HDPE and LDPE, respectively) (Table 2), especially because of its wide usage in packaging. While other resins used for making plastics tend to accumulate environmental contaminants, PVC is known for its relative resistance to such accumulation. On the

other hand, it should be noted that PVC is composed of a high content of phthalates, which are known carcinogens [33].

5. Fate of microplastics in the aquatic environments

MPs in aquatic ecosystems have become a global challenge as the demand and production of plastic materials are uninterruptedly increasing. Unfortunately, most plastics products are neither recycled nor properly disposed of, contributing to approximately 10-15% of total municipal solid waste (MSW) [6]. The presence of PMPs and SMPs has been confirmed in aquatic

Table 2. The major composition of Plastic Produced, Recycled, and Waste and their Resin Contents [42, 43]

Plastics	% Waste	Estimation of Resin in the waste (%)						
		HDPE	LDPE	PP	PU	PVC	PS	PET
Packaging	33.5	25.4	44.5	–	–	4.3	9.8	6.4
Building & Construction	24.8	5.3	–	–	4.2	42.9	4.3	–
Consumer Goods	11.1	13.6	12.7	16.7	–	7.0	29.3	7.1
Electricals & Electronics	6.1	5.3	13.8	9.4	4.6	17.1	10.6	–
Furniture & furnishings	4.9	–	–	42.5	30.0	12.5	–	–
Automobiles & Transportation	4.5	7.8	–	9.7	22.8	5.9	–	–

HDPE = high density polyethylene, LDPE = low density polyethylene, PP = polypropylene, PU = polyurethane, PVC = polyvinyl chloride, PS = polystyrene and PET = polyethylene terephthalate

ecosystems, and their fate, amount, and transportation depend on factors such as market demand, uses, and post-use management. MPs can enter natural waters through various pathways, including direct deposition, run-off, and wastewater discharges. The uncontrollable dumping of household waste, which varies among countries, cities, and towns, is particularly prevalent in low and middle-income countries. Residents in such areas often take advantage of the convenience of disposing of waste items on river banks, waterways, and open drains leading to increased marine litter. Plastic particles are the most commonly collected items during aquatic surveys [44]. The physical and chemical properties of plastics play a crucial role in determining the fate and transformation of MPs in aquatic environments worldwide. MPs with lower density tend to float on the surface of the water and be transported by currents, often reaching remote regions such as the Arctic and Antarctic [32]. The marine environment is primarily contaminated by continental waters, while sewage discharges, whether treated or untreated, have a more significant impact on rivers and lakes. WWTPs use different methods to remove contaminants of varying levels from wastewater, but there is only a limited number of studies available on the effectivity of WWTPs in removing MPs from wastewater and on the levels of such items in WWTP effluents and sludge. Mechanical treatment of wastewater sludge is a primary and one of the integral stage of the wastewater treatment process, where screens or sieves are used to remove suspended coarse or floating solids, including MPs.

There are limited reports available on the effectiveness of WWTP in removing MPs from wastewater and on the loading of MPs in WWTP effluents and sludge. Studies have shown that about 1-55 microplastics/litre (MPs/L) may be found in WWTP effluent [18, 45]. In an MPs removal efficiency study of a WWTP, approximately 200 MPs/L and 20 MPs/L have been found in WWTP influent and effluent of activated sludge, respectively, indicating a removal efficiency rate of about 90% [18, 46]. Similarly, a range of MPs with varying compositions, totalling about 0.08 to 8.9 MPs of <500 µm, were detected in WWTP effluent collected before filtration [18, 47]. The study also reported a removal efficiency of 93% and 98% for MPs with sizes >500 µm and <500 µm, respectively, in filtered effluents, with about 1041-24129 MPs/kg (dw) present in the sludge. Although the stabilization of sludge containing a relatively high number of MPs may affect their size and form, the disposal of the sludge can reintroduce MPs into the environment, as they may persist in the soil and be transported via surface runoff to aquatic ecosystems. Direct deposition of sewage sludge or sewage overflow during heavy rain also sourced MPs to aquatic environments [18, 48].

6. Levels of MPs in the aquatic environments

Studies have confirmed the presence of MPs in various environmental matrices, including soil, sediment, air, and water. Of these matrices, aquatic compartments are more heavily impacted, with waters from urbanized areas exhibiting higher levels of MPs compared to those from rural areas. This suggests a significant impact of anthropogenic activities on MP levels in the environment. Moreover, the detection of unexpectedly high levels of MPs in oceanic convergence zones triggers more investigations, leading to the discovery of MPs in ocean freshwaters worldwide [18]. In their study, Deng et al. [49] found MPs in surface water and sediment samples from an industrial area in China, with concentrations ranging from 2.1 to 71.0 items/L and 16.7 to 1323.3 items/kg, respectively, indicating the abundance of MPs in the sediment. In another study, on the transport media of MPs from freshwater and estuary to the oceanic environment, Luo et al. [50] found MPs in the range of 1.8 to 2.4 items/L and approximately 0.9

items/L, respectively, in the spatial distribution of MPs in the Yangtze Delta area of China. Low concentrations of MPs, ranging from 1.2 to 10.1 items/L in sea surface water, were reported by Zhu et al. [51], suggesting that MPs may enter the oceanic region through various routes.

It is important to note that issues associated with the prevalence of plastic pollution, including MPs, are not unique to a particular country, but is a global concern. However, the specific circumstances and challenges faced by each country may vary. It is estimated that about 89.7% of total waste generated in Brazil is collected and approximately 13.5% of them are plastic items, suggesting that part of the uncollected plastics end up in the aquatic environments. This pattern highlights a potential trend of plastic pollution on a global scale, further intensifying ecological degradation worldwide. In a study by Khan et al. [52], MPs were reported in tilapia and catfish collected from the River Nile in Egypt, the world's longest river, with an abundance of 75.9% and 78.6%, respectively. In the world's largest river by discharge volume of water, [53] found MPs contamination in sediments from Amazon rivers, with concentrations ranging from 0 to 8,178 items/kg (dw). In the beaches of Guanabara Bay, one of the most important embayments of the Brazilian coast, de Carvalho and Baptista Neto [54] have reported MPs concentrations ranging from 12-1,300 items/m². This is probably one of the most MPs polluted environments in the world. In her study, Alves [55] reported an average concentration of 2.59 items/m³ in Paranoá Lake, one of the most important urban lakes in Brazil that receives inputs from basins with different characteristics. In Nigeria, fragments of PE, PP, and PS have been abundantly detected in epipsammic sediments of the tropical Atlantic Ocean [56]. These findings suggest the urgent need for further studies to ensure the safety of both inhabitants and environments across the globe.

7. Behaviour of MPs in aquatic environments

The physical (size, shape, density, etc.) and the chemical (degradation, adsorption, surface charges, etc.) properties of MPs vary among their different types. These properties affect how MPs interact with aquatic biota and the environment. Some particles may float in the water column due to their low density, while others may sink to the bottom as a result of their high density. The settling of MPs is also influenced by many other factors, including their shapes and size, the presence of other particles in the water and the flow rate of the water. Smaller particles are generally more buoyant and are more likely to remain suspended in the water column, while larger particles are more likely to sink. The quantity of sorbed substances can also affect the settling of MPs, as particles with a greater amount of sorbed substances may be more likely to sink.

The adsorption capacity of MPs is affected by several factors, including the type of MP and ageing. Aged MPs tend to adsorb more pollutants from their surroundings than newer and more colourful MPs. The lighter the colour, the lower the molecular weight they adsorb, and the opposite is true for darker MPs and higher molecular weight hydrophobic compounds. The density of MPs is lower than that of water, and this influences their distribution and destination in aquatic environments [25, 43, 57].

The bioaccumulation of MPs in aquatic ecosystems tends to increase as the size of the MPs decreases. Weathering and degradation can cause the surfaces of MPs to become rough, and uneven, and develop cracks and cavities, surfaces of MPs, which can lead to the release of toxic monomers and additives. These processes can also enhance the dark colour and increase the adsorptive capacity of the MPs. Studies have shown that MPs

possess surface charges and selectively interact with natural organic matter (NOM) [25, 57, 58].

7.1. Degradation of plastics in the aquatic environment

To fully comprehend the impact of naturally modified MPs and organic contaminants on the environment, it is crucial to understand their behaviour and sorption mechanisms. MPs are exposed to natural effects in the aquatic environment that can lead to modifications such as increased surface oxidation and micro-cracks in aged plastic [59]. The plastic weathering layer in the aquatic environment increases the surface hydrophilicity, leading to enhanced microbial adhesion and mineralization rate [29]. MPs can also degrade through mechanical, photo-oxidation, thermal, chemical or biological processes [60]. Mechanical degradation, an important factor in the fate of plastic in the aquatic environment, is responsible for transforming as-disposed macroparticles into MPs through friction forces occurring during natural aquatic movement in different environmental habitats. Furthermore, the mechanical degradation does not stop if the particles are within the size range of MPs, i.e., the formation of even smaller particles, in the nano-scale, is also presumed. During the degradation process, polymers are converted into smaller molecular units such as oligomers, monomers, or chemically modified versions. The decrease in particle size leads to an increase in the surface area of the plastic particles, making them more reactive towards other forms of degradation.

In addition to mechanical degradation, molecular-scale degradation is often caused by photo-oxidation and photo-degradation processes induced by ultraviolet (UV) radiation from sunlight that breaks the C–C and the C–H bonds in plastics [29]. Photo-degradation is a rapid process, but the degradation rate also depends on the presence of additives in the plastic, which can help prevent oxidation processes. Studies have confirmed that exposure to UV light and mechanical abrasion can increase the number of MPs produced, resulting in even smaller particles [61]. The crystalline and amorphous structures of MPs significantly affect their susceptibility to photo-degradation. Crystalline MPs have ordered molecules that scatter and reflect light, reducing penetration and causing degradation mainly on the outer layer of MPs with a depth in the micrometre range. Amorphous MPs have disordered molecules, making them more susceptible to photo-degradation with increased light penetration and surface hydrophilicity. Since no 100% crystalline polymer is known, all are degradable and mostly within the amorphous regions [29].

The thermal degradation of MPs occurs when chemical bonds are broken due to increased temperature. It has been reported that soil surfaces with temperatures reaching 90 – 100 °C can cause thermal degradation of MPs [29]. A study has shown that a 3-month period of thermal weathering of PE strips at 80 °C is equivalent to 270 days of UV irradiation at 43 – 45 °C in terrestrial environments [62]. However, due to water's natural ability to dissipate heat and maintain lower temperatures, thermal degradation is generally less significant in aquatic environments [29]. Microbial degradation and biological ingestion and digestion are the primary pathways for the biological weathering of MPs. Many plastic-degrading microbial strains have been identified, with degradation efficiency ranging from 3.9% to 60% depending on the species and diversity of the microbial community [29]. In natural environments, interactions among microorganisms in bacterial consortia play a significant role in MP biodegradation. For example, toxic metabolites produced by one microorganism may be used as a substrate by another, reducing their impact on MP-degrading bacteria [63]. The biodegradation of MPs by bacteria, bacterial consortia, biofilm-forming bacteria, and fungi can be

much more efficient than that of a single bacterium, and it can be further improved by the ingestion of MPs by freshwater amphipods [64].

7.2. MPs Aggregation

MPs can associate with other solid constituents in aquatic environments such as algae, suspended solids, and colloids, through a process called aggregation, which involves two particles colliding and attaching (Zhang, 2014). When MPs come into contact with suspended matter, they can be physically trapped or adsorbed onto the surface of the particles, leading to the formation of larger aggregates that can be easily transported by water currents and settle more quickly to the bottom of the aquatic body. This aggregation can occur between the same type of MPs (homoaggregation) or different types of particles (heteroaggregation), with the latter being more common in natural waters and driving the floating, sedimentation, and resuspension processes of MPs [33, 65]. MPs surfaces contain hydrophobic functional groups which facilitate the adsorption of dissolved organic matter (DOM) and organisms, including algae and bacteria, and MP surfaces in natural waters often harbour microbial habitation and biofilm formation [66]. Additionally, organic matter, layered clay minerals, and nanoparticles can also aggregate with MPs, but studies on heteroaggregation of MPs are still limited due to the complexity of the system [65, 67].

The aggregation behaviour of MPs in natural waters has significant environmental implications, including changes in their particle sizes, specific surface areas, toxicity towards organisms, transformation, co-transport with other pollutants, and the formation of biofilm [68]. The aggregation of MPs can alter the buoyancy of MP and increase MPs concentration in the water column, thereby negatively impacting marine organisms [69]. Additionally, the transport of aggregated microplastics by water currents can increase their ingestion by marine organisms and accumulation in sediment [65].

The magnitudes of MP aggregates in natural waters can range from nanometers to centimetres or larger, leading to toxicity towards organisms in different layers of the water column. MPs that aggregate slightly can remain suspended on the water surface for months (up to 8 months), impacting zooplankton, planktivory, filter feeders, suspension-feeders and other aquatic species, while those with a large degree of aggregation settle quickly and accumulate in seabed sediments, leading to toxicity towards benthic organisms and deposit feeders [70]. Toxic pollutants may adhere to the surface of sinking plastic aggregates, which could have a detoxification effect on organisms inhabiting the water surface but could be detrimental to those living in the benthic region. [66, 71]. Conducting toxicity studies on organisms exposed to MPs in the laboratory can be a useful approach to assess regional variations in the biotoxicity of MPs, which is essential for a better understanding of the impacts of MPs on aquatic ecosystems.

7.3. MPs Eco-corona

Aquatic MPs have been reported to interact with co-existing natural organic matter (NOM) to form a "biofilm layer" or "eco-corona (EC)" through some complex interactions that are critical in determining the aggregation, mobility, fate, bioreactivity, and ecological impact of plastic particles in the ecosystem [72]. While the biofilm layer is a layer of microorganisms that adhere to the surface of MPs that make them more resistant to degradation and increasing their potential to transfer pollutants to marine organisms [59], EC is a layer of organic and inorganic substances that adsorb

to the surface of MPs in aquatic environments that alter their physical and chemical properties and potentially increase their toxicity [73]. Just like MPs, NOM is ubiquitously present in the aquatic body in the form of extracellular polymeric substances (DNA, proteins, carbohydrates, etc.) and humic substances (humic acid, fulvic acid and humin) released by organisms and degradation products of organic matter, respectively [74]. They comprise a convoluted matrix of organic complexes with varying properties, weights, and molecular sizes. They originate from different sources such as allochthonous, autochthonous, and anthropogenic, and possess unique physicochemical properties, including size, weight, surface charges, shape, and surface functionality. These features play an essential role in their interaction with MPs [75].

Allochthonous NOM, such as humic acid (HA), fulvic acid (FA), cellulose, and alginate, originate from the terrestrial environment and interact with MPs in the ambient to form environmentally persistent complexes EC or biofilms due to their unique chemical properties and functional groups, like $-OH$ and $-COOH$ among others. The surface properties of MPs and their modifications can affect the development of EC and biogenic aggregates, impacting their stability, transportation, dispersion behaviour, and environmental fate. The presence of allochthonous NOM can also affect the sorption and detachment of co-existing pollutants on MPs. The interaction between allochthonous NOM and plastic particles is influenced by environmental factors such as salinity, ionic strength, ionic valency, and medium acclimatization [76]. The physicochemical properties of NOM can also alter the release rates of plastic additives during the ageing of plastic particles, thus influencing the fate and mobility of plastic particles and the development of biogenic aggregates [74].

Autochthonous NOM is produced by various biological species like algae, fungi, and bacteria, and through the secretion of extracellular polymeric substances (EPS) [73]. These substances can interact with MPs in the environment, leading to the formation of protein layers, extracellular coatings, or biogenic aggregates. EPS in the form of proteins, released by organisms like *Daphnia magna* alters the size and identity of MPs after coating and acts as signalling agents to facilitate their interaction with cellular receptors [72].

Anthropogenic NOM, derived from industrial processes, domestic wastewater, and agricultural activities, among others, interact with plastic particles in the environment [76], and act as a transport medium for NOM and MPs, increasing their dispersion and persistence. The chemical composition and properties of anthropogenic NOM can vary depending on its source, which may include septic system, WWTP, industrial and agricultural discharge etc, and their treatment process.

Several studies have established NOM coating of MPs in aquatic ecosystems [72]. For example, MPs are reported to be more tolerant of NOM, microorganisms in particular, than other components of the exposed environment, producing a stronger interface in an aqueous environment [77]. Generally, eco-corona is an ongoing process that tends to decrease the surface hydrophobicity and buoyancy of plastic debris. As a result, the volume and density of MP may increase due to the embedding of suspended minerals in the water. It has been confirmed that NOM enhances the ability of MPs to adsorb POPs and facilitates the penetration of POPs into the interior of the MPs through their pores and cracks [77, 78].

7.4. Interactions of MPs with Environmental Pollutants

The physical and chemical properties of MPs can affect their ability to interact with other environmental pollutants such as

PBDEs, PAHs, PCBs, endocrine disruptor chemicals, and heavy metals. This is due to their increased surface area and hydrophilicity when they age, which enables them to adsorb contaminants and aggregate with other solid particles [29]. MPs can serve as carriers, enhancing bioaccumulation and toxicity of pollutants, or as a sink, reducing potential bioaccumulation in other cases [79]. The interactions between MPs and other pollutants can be synergistic, additive, or antagonistic, and the effects can vary based on the physicochemical properties of the MPs [2].

Studies investigating the combined effects of MPs and inorganic pollutants have mainly focused on heavy metals and metalloids. These studies have found that MPs can alter the bioaccumulation and toxicity of such elements [29]. Weathered MPs are capable of absorbing potentially toxic elements through ion complexation, hydrogen bonding, and electrostatic forces [80]. The increased surface area and hydrophilicity of aged MPs enhance their adsorption capacity for inorganic contaminants and aggregation with other solid constituents due to the numerous active sites, oxygen-containing functional groups, and increased electronegativity on their surfaces. Furthermore, biofilms on weathered MPs can serve as vectors for metal cations and change the mechanism of metal diffusion, thereby facilitating their adsorption [29].

Interactions such as hydrogen bonding, hydrophobic interaction, and electrostatic are predominant in the adsorption of organic pollutants on the MP surfaces. This is because MPs have increased oxygen-containing functional groups, high hydrophilicity, and electronegativity. Electrostatic interactions involve the attraction between opposite charges, hydrogen bonding can be considered a covalent bond between a hydrogen atom and a highly electronegative atom. Hydrophobic interaction is based on the differences in hydrophobicity of the interacting moieties. UV-aged MPs have demonstrated an increased adsorption capacity for hydrophilic organic pollutants but decreased adsorption capacity for hydrophobic organic contaminants due to lower hydrophobic interaction forces [59]. Other minor interactions, such as π - π interactions, cationic bridging, van der Waals interaction, partition, and pore-filling mechanisms have also been reported [29]. Attractive forces known as π - π interactions occur between cyclic molecules with conjugated double bonds. A cation bridge is formed when a negatively charged adsorbate interacts with an anionic surface of an adsorbent in the presence of divalent cations. Weak interactions, called van der Waals forces, occur between atoms or molecules. Pore-filling involves trapping small molecular-sized substances in nano-scale cracks and pores that develop on the aged surface of MPs [81]. All the mechanisms that drive the adsorption of pollutants onto the surface of MPs are considered reversible and weak compared to ionic and covalent bonds. Therefore, they can be influenced by various factors including pH, salinity, dissolved organic matter, and the physicochemical properties of both MPs and the contaminants. For example, interactions between ibuprofen and PP are driven by van der Waals forces, [82], while fluoroquinolones and PS are influenced by hydrogen bonding, [83], and copper and PE by electrostatic interaction [84]. Many other types of interactions have also been reported.

8. Effects of MPs on organisms and environments

There are several risks associated with the presence of MPs in aquatic ecosystems that can affect both the organisms living in these environments and the overall ecology. The relatively high

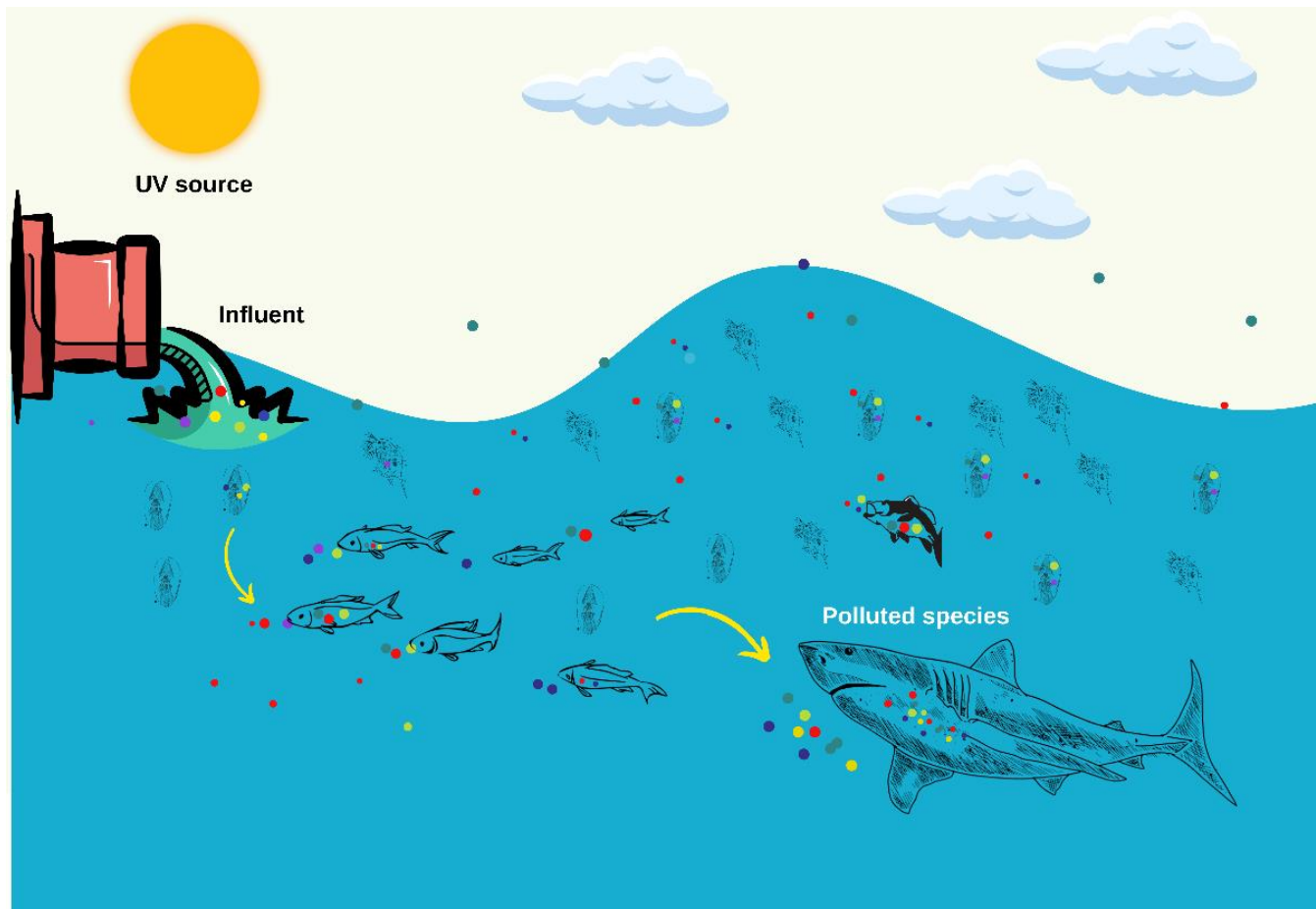


Figure 3. Demonstrations of MPs are in the aquatic environment and contaminated aquatic species

concentration of MPs, which can reach up to 100,000 items per cubic meter in surface waters and shorelines (Figure 3), poses a threat to a variety of organisms, including invertebrates and vertebrates, leading to unpredictable ecological consequences [1, 85]. This has caught the attention of some countries to take legislative measures as an important tool in the fight against MPs. For example, the use of microbeads in cosmetics has been banned in the US, and other countries, including the EU, are working to introduce legislation to manage MPs in their environments [86, 87].

Due to their small size and large surface area, MPs are often bioavailable to aquatic organisms, causing unwanted effects, not only to affected organisms only but to predators higher up in the food chain. MPs have been reported to be ingested by aquatic organisms in both freshwater and marine environments [18, 88]. Several studies have demonstrated the harmful effects of MPs on aquatic organisms at the individual, cellular, and molecular levels [2]. These effects are not uniform across species and ecosystems, and their interaction and ingestion have been documented in the past few years [89-91]. The effects include decreased survival, inhibited feeding, distorted digestive patterns; reduced energy reservation, and injury or death of organisms such as lugworms, copepods, jacobever, oysters, crabs, and diving beetles [92-98]. Additionally, MPs affect growth, development, and reproduction, leading to malformations and starvation [96, 99-101]. MPs may also transfer persistent bioaccumulative toxic substances (PBTs) and chemicals to organisms through trophic transfer across the food chain [102]. At the cellular level, MPs induce adverse effects and stress responses, leading to developmental defects, oxidative

damage, inflammatory responses, and neurotoxicity in organisms such as sea urchins, brine shrimp, zebrafish, rotifers, mussels, fish, and coral [103, 104]. At the molecular level, MPs alter the expression of genes related to stress response, detoxification, and the immune system in organisms such as seabream, nematodes, and Chinese mitten crabs [2].

In addition to their presence in the environment, MPs have also been detected in human breast milk, placentas, meconium, faeces, liver, lung, blood, and infant formula [105-108]. The potential health effects of MPs on humans are not fully understood, but they have been linked to hormonal disruption, immune system dysfunction, and gastrointestinal problems. Reports indicate that MPs can release co-existing and adsorbed pollutants in tissues and organs, such as the intestine, of organisms, which can then be translocated to their circulatory systems and other parts of their bodies [109]. It is important to note that the benefits of breastfeeding usually outweigh the potential risks of MPs in most cases.

Marine organisms often mistake plastic pellets for food because of their size and shape. This poses a significant risk to both wildlife and humans due to the transfer of hazardous substances into the marine food chain. To address this issue, the plastics industry has adopted best practices known as Operation Clean Sweep. These practices promote good housekeeping and pellet containment to achieve zero discharge of pellets, flakes, and powders into the environment. However, despite these efforts, the amount of pellets in the environment continues to increase [3, 110-112].

Table 3. Some known effects of microplastics on organisms and the environment

Category	Hazard	Effect
Physical harm	Ingestion	Marine organisms can ingest MPs, leading to blockages in their digestive system, physical damage to their internal organs, and a reduced ability to absorb nutrients.
	Entanglement	Marine animals can become entangled in MPs, restricting their movement, and causing physical injury, suffocation, and even death.
	Laceration	The sharp edges of MPs can shred the tissues of organisms, causing physical harm and increasing the risk of infection
	Impaired growth	The ingestion of MPs by marine life can have long-term effects on their growth and reproduction.
	Altered behaviour	MPs can alter the behaviour of marine animals, such as affecting their feeding and migration patterns.
Chemical toxicity	Leaching of additives	Chemical additives in plastics, such as plasticizers and flame retardants, can be released into the environment when MPs break down, potentially harming the health of marine organisms.
	Chemical transfer	MPs can absorb and transfer harmful chemicals and pollutants from the environment to organisms, resulting in toxicity. Many chemical interactions, as well as physisorption, have been reported elsewhere.
	Oxidative stress	The ingestion of MPs can cause oxidative stress in marine organisms, resulting in cellular and tissue damage.
	Endocrine disruption	Some studies suggest that MPs may disrupt the endocrine systems of marine organisms, affecting their growth, development, and reproductive health.
	Carbon cycle disruption	The accumulation of MPs in the environment can impact the ability of ecosystems to sequester and store carbon, potentially accelerating global warming and climate change
Biological effects	Direct impacts	MPs can physically harm organisms such as fish, birds, and marine mammals, leading to entanglement, ingestion, and internal damage. These effects can cause death or impair the organism's ability to survive and reproduce.
	Indirect impacts	The indirect impacts of MPs are far-reaching and occur throughout the food chain.
	Bioaccumulation	MPs can accumulate persistent chemicals from the surrounding environment and transfer them up the food chain, posing a risk to organisms at higher trophic levels, including humans.
	Reduced fertility	Exposure to MPs can damage the reproductive system of organisms, reducing their fertility.
	Spread of diseases	MPs can host pathogenic bacteria and viruses, potentially spreading diseases
Potential risks to humans and organisms	Detected in tissues and organs	MPs have been detected in n various tissues and organs of both humans and other organisms, including the gastrointestinal tract, liver, lungs, kidneys, blood, placenta, brain, and breast milk.
	Health risks	MPs have been associated with a range of health issues, including respiratory problems, allergies, developmental and reproductive problems, hormone function interference, inflammation, oxidative stress, and DNA damage. Ingestion of MPs has been shown to cause cellular and molecular damage, which may increase the risks of chronic diseases, such as cancer, asthma, and COPD.

COPD: chronic obstructive pulmonary disease

MPs have the potential to act as carriers for hydrophobic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and heavy metals, which they can transport over long distances to remote regions [113]. Additionally, MPs contribute to the overall amount of floating debris in aquatic environments and can provide a substrate for various organisms [114]. In addition to these impacts, the presence of MPs in aquatic environments can alter sediment properties and affect the balance of organisms and ecosystem processes within these environments [33, 58]. In summary, the presence of MPs can have complex and far-reaching effects on both the environment and the organisms that depend on it.

The interaction of MPs with other environmental pollutants can result in various impacts on bioaccumulation and toxicity [115]. The effects of such interactions can either enhance or inhibit each other individual effects, and may exhibit synergistic, additive, or antagonistic behaviour [116-118]. For instance, the presence of MPs may increase the bioaccumulation of other pollutants, resulting in a greater accumulation of harmful substances [119]. On the other hand, MPs may also reduce the accumulation of pollutants in organisms [120]. It is noteworthy that the combined effects of MPs and other pollutants are complex and may vary based on the specific pollutants involved and the organisms affected.

MPs have the potential to harm both the environment and humans, but the extent of these risks is not well understood [121]. Table 3 summarizes some of the reported effects of MPs on organisms and ecosystems. With the increasing research on the negative impacts of MPs and their co-pollutants on the environment and organisms, the list of their risks continues to expand.

9. Characterization and remediation of MPs

In recent years, numerous analytical methods have been developed for characterizing MPs in waters [87, 122-125]. However, the protocols involved during the entire analytical sequence, from sampling to MP identification, present several challenges due to the irregular sizes, shapes, weathering degree, and chemical composition of MPs. A sampling of water for MP analysis can be performed using nets, sieves, or pumps, while sediment sampling can be done using a grab sampler or box corers [87, 126]. MPs isolated in nets and sieves are typically transferred into glass bottles for further treatments, such as filtration using stainless steel sieves or glass fibre filters. Separation from NOM and other debris can be achieved through density separation and/or oxidation of NOM, or a combination of both techniques.

Identification of MPs could be achieved through methods including visual observation, optical or electron microscopes, and physicochemical assays such as heating at high temperature assisted by a series of physicochemical tests, using red Nile reagent or hot needle mouth to distinguish them from other artificial particles. Confirmation and quantification of MPs can be done through visual counting or instrumental analysis. Vibrational techniques, such as Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy, have been widely used for MP characterization due to their ability to identify chemical bonds and molecular structures. Other techniques, such as pyrolysis-gas chromatography coupled to mass spectroscopy (Pyr-GC-MS) and thermogravimetry coupled to differential scanning calorimetry, have shown promising results for quantifying and characterizing MPs.

9.1. The Challenges of Microplastic Measurement and Comparison

The study of MPs in aquatic ecosystems is a significant topic in environmental studies and has been ongoing for about a decade. However, a lack of standardization in the methods of measurement and units for expressing concentrations presents a challenge to accurately assess the distribution and impacts of MPs on organisms and the environment on a global scale, as well as establishing effective regulations and policies to address the risks [127]. It is essential to ensure informative experimental controls that account for various environmental and other factors that may affect the result of MPs measurement [128]. So far, three guidelines have been published by the European Commission, the National Oceanographic and Atmospheric Agency, and the UK Water Industry Research [127]. Nonetheless, without standardized methods and unified units of concentration, comparing results from different studies and accurately assessing the global distribution and impacts of MPs is challenging. Researchers may use different methods and protocols to extract, concentrate, and analyze MPs, leading to inconsistent and incomparable results, making it difficult to develop effective solutions and establish a clear understanding of the problem.

The lack of a standardized quantification protocol and unified unit of measurement of MPs in environmental samples has been

subject to scrutiny in recent years and has been labelled a "bandwagon" topic [128]. This has made it difficult to apply known concentrations of MPs to exposure studies and to accurately compare results from different studies. Different units such as particles per litre (ppl) or particles per cubic meter, mass per litre (mg/L) or mass per cubic meter (mg/m³), number of particles per organism (particles/organism), and mass per organism (mg/organism) have been used to measure MPs, but each unit has its limitations [29, 129]. For example, units such as ppl, or particles/organism indicate the number of MP particles present but do not account for the size or mass of the particles, while units such as mg/L, mg/m³, or mg/organism indicate the total mass of MPs present but do not account for the number of particles. Other units in the literature include microplastics/volume (items/L, items/mL, items/m³), and microplastics/weight (items/kg, items/g) [128]. Therefore, the development of a standardized method for quantifying and expressing the concentration of MPs is crucial for accurate assessment of the distribution and impacts of MPs on the environment and organisms.

10. Conclusion

Microplastics are potentially harmful to the environment and organisms, including humans, and some of the effects are still unknown. To mitigate the negative impact of MPs, it is essential to raise awareness, promote the use of eco-friendly and non-toxic alternatives, monitor their presence in aquatic environments, and regulate their use in consumer products through strategies and legislative measures that focus on source control, remediation, recycling and waste reduction programs and public awareness campaigns. There is a pressing need for further research to fully comprehend the prevalence, distribution, transport mode and rates, and their long-term impacts on aquatic ecosystems. This challenge requires action from all stakeholders to tackle this issue effectively.

CRediT authorship contribution statement

IMA: Conceptualization, Writing -original draft, Resources, Software, Data curation, Writing -review & editing. IOA: Software, Writing -review & editing. NUB: Writing -review & editing. FFS: Conceptualization, Writing -review & editing.

Declaration of competing interest

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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