CRITICAL REVIEW

Emerging investigator series: microplastic sources, fate, toxicity, detection, and interactions with micropollutants in aquatic ecosystems – a review of reviews†

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Hundreds of review studies have been published focusing on microplastics (MPs) and their environmental impacts. With the microbiota colonization of MPs being firmly established, MPs became an important carrier for contaminants to step inside the food web all the way up to humans. Thus, the continuous feed of MPs into the ecosystem has sparked a multitude of scientific concerns about their toxicity, characterization, and interactions with microorganisms and other contaminants. The reports of common subthemes have agreed about many findings and research gaps but also showed contradictions about others. To unravel these equivocal conflicts, we herein compile all the major findings and analyze the paramount discrepancies among these review papers. Furthermore, we systematically reviewed all the highlights, research gaps, concerns, and future needs. The covered focus areas of MPs' literature include the sources, occurrence, fate, existence, and removal in wastewater treatment plants (WWTPs), toxicity, interaction with microbiota, sampling, characterization, data quality, and interaction with other co-contaminants. This study reveals that many mechanisms of MPs' behavior in aquatic environments like degradation and interaction with microbiota are yet to be comprehended. Furthermore, we emphasize the critical need to standardize methods and parameters for MP characterization to improve the comparability and reproducibility of the incoming research.

Environmental significance

This first "review of reviews" critically evaluates all the paramount findings and discussions in published review studies on microplastics. The study covers the sources and environmental impacts, fate, toxicity, detection, and characterization of microplastics in freshwaters, wastewater treatment plants, and drinking water as well as the interactions between microplastics and other organic and inorganic contaminants.

1. Introduction

Plastics have become a mark of the inherited single-use consumer culture as they provide convenient, light, and cheap alternatives in versatile daily life activities. Despite the increasing concern about the inexorable environmental and

health hazards associated with plastics, millions of tons are still produced every year.[1] Plastic materials, which are formed from a wide range of synthetic or semi-synthetic organic polymers, are produced by the polymerization of monomers generally coming from oil, natural gas, or coal.[2,3] Plastics are subjected to successive breakdowns into smaller fragments in the natural aquatic and terrestrial environments.[4,5] Thus, the attention has been shifted from macroplastics to microplastics (MPs) and nanoplastics (NPs) over the last decade.[6,7] As depicted in Fig. 1, among all sizes of plastic fragments or particles, MPs are one of the potential threats in aquatic ecosystems with size ranging from 0.1 to 1000 μm. MPs are classified according to their origin, size, and chemical composition into primary and secondary MPs.[8] Primary MPs are produced industrially in the form of plastic-based fragments or pellets, which can be found as nurdles (small plastic pellets <1000 μm) in several industrial facilities, microbeads (1–1000 μm) in cosmetics, and

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microfibers (0.1–1000 μm) in textiles.[2,7,9,10] Secondary MPs are generated by the chemical and physical aging and degradation of macroplastics such as plastic bags, computer casing, disposable dishes, plastic bottles, fishing nets, and foam products.[11,12] According to the Mepex® report (Fig. S1†), MPs originate in the natural environments from various sources including car tires (56%), painting and maintenance of ships, leisure boats, buildings, constructions, and roads (24%), loss from plastic production (10%) and others (10%).[13]

Although >90% of large MPs can be removed in the wastewater treatment plants (WWTPs), the removal efficiency of the small size MPs (<500 μm) and NPs is very low.[14] Therefore, the discharge of MPs from WWTPs to surface waters is threatening aquatic life and human health.[15] The scientific community and media have been focusing on the accumulation of these non-visible plastics in the aquatic environment, after the rising of

unanswered issues about the degradability and toxicity of MPs, as well as the associated problem of plastic litter accretion in the oceans, which is far from being resolved.[2] In addition, most MPs have hydrophobic surfaces and abundance of functional groups, which interact with a variety of other substances in the aquatic environment including organic contaminants (OCs) and inorganic contaminants (ICs), especially those of hydrophobic nature and low solubility.[16] MPs can also be colonized by diverse microorganisms including bacteria and microalgae by developing biofilms on their surface.[1,17] Therefore, understanding the sorption and interactions between MPs and contaminants is another fundamental task for examining the impacts of MPs in water.

The impacts of MPs in the aquatic systems were of limited interest in the early 1970s,[18,19] however, they have been resurrected in the later decades. According to a recent bibliometric study, more than 3000 peer-reviewed research articles have reported the environmental impacts, fate, and toxicity of MPs in addition to the sorption of contaminants on MPs under various environmental conditions.[8] Among these studies, hundreds of review articles have been published over the past decade about MPs covering many research areas (Fig. S2†) with five major topics: (i) sources and environmental impacts, (ii) fate, (iii) toxicity, (iv) detection and characterization, and (v) sorption of contaminants on MPs under various environmental conditions. Most recent reviews have evaluated the occurrence, environmental effects, interactions with organisms, and detection and characterization of MPs.[20–27] In contrast, fewer review studies have examined the aggregation, biodegradation of MPs, and interactions with other contaminants.[11,28–30]

Herein, we provide a review of reviews by providing a critical overview of the aspects, advances, gaps, and doubts that have been raised about MPs. We compiled the current state of
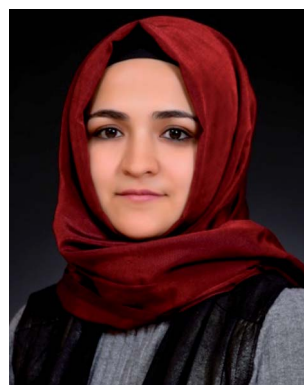
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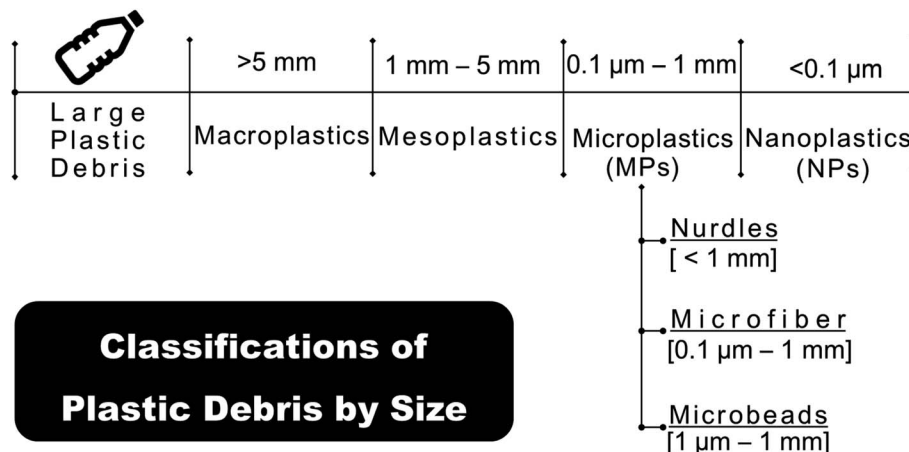
Classifications of Plastic Debris by Size

Fig. 1 Large plastic debris breaks down to small fragments under natural exposure conditions (*i.e.*, UV-radiation, wind, wave, ingestion of organisms, *etc.*) *Classifications and ranges are derived from Alimi *et al.*, 2018b;[7] Arthur *et al.*, 2009;[9] Blettler *et al.*, 2018; and Rochman *et al.*, 2014.

knowledge about the behavior and ecological impacts of MPs (*i.e.*, sources, fate, and toxicity) in aquatic systems and WWTPs reported in those review papers. Then, we critically assessed the existing quantification and characterization methods implying the limitations associated with the current sampling and pretreatment techniques. Moreover, we comprehensively evaluated the current reviews about the adsorption of contaminants on MPs and the influence of environmental parameters. Lastly, we identified the current gaps of knowledge and formulate perspectives for future research on MPs.

2. The sources and occurrence

2.1. MPs in solid wastes

More than 300 million tons of plastic waste annually enter water bodies. The major sources of MPs and their pathways are depicted in Fig. 2. Depending on the source of MPs, they can be divided into primary and secondary MP classes.[31] The sources of primary MPs include nurdles, microbeads, microfibers, and other forms that have been produced intentionally in this small size range.[32] These primary MPs are widely used in personal care products (*e.g.*, face scrubs, toothpastes, makeup products, sunscreens, bath and shower products), industrial cleaning products (*e.g.*, paint and rust scrubbers), and the pre-production of plastic (*e.g.*, nurdles and pellets).[33] The secondary MPs, however, are those coming from the breakdown of large plastic pieces by a number of mechanisms such as UV light irradiation or mechanical abrasion, biodegradation by microorganisms, thermo-oxidative degradation at low temperature, thermal degradation at high temperature, and hydrolysis in water.[34,35]

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Human activities can be used to predict the types of MPs.[36] For instance, raw plastics or fragments occurred in rivers, runoffs and streams that have plastic production sites adjacent to each other,[23] resin pellets and microbeads were most prevalent in industrial regions,[37] and secondary MP fragments in the lake shores suggested an origin from the breakdown of household items.[23] In marine environments, while commercial fishing nets contribute around 20% of the marine plastic,[38] the marine litter as a terrestrial source contributes to about 80% of the plastics.[21] Ocean and coastal activities, fishery resources, marine boats, and industries are all contributors to MPs that can reach aquatic habitats directly, threatening the biota as primary and secondary MPs after long-term deterioration.[39] As their raw materials, granules and small resin pellets, which are known as nibs, are a notable source of plastic debris from plastic manufacturing.[21,36] Polyethylene (PE), polypropylene (PP), and polystyrene (PS) are the dominant MP types in the marine environment.[23] In the freshwater ecosystem, however, tire wear particles generated from tire abrasion on roads account for 60% of MPs in urban areas.[24,40] Therefore, combining the storm water with sewage in WWTPs is associated with the increment of MP concentration, which is directly linked to the wearing of tires and sweeping of different particulates.[40] For these reasons, MPs are more prevalent in densely populated areas.[41]

2.2. MPs in WWTPs

MPs are found in the influent and effluent streams of WWTPs with wide variations in shapes, compositions, and concentrations,[42] depending on the location, industrial activities, average income, levels of tourism activities, and the linkage to storm drains.[27] Despite the scarcity of MP quantification in routine domestic wastewater characterization, current available data suggest that the concentration of MPs in the influents of WWTPs covers a wide range (1 to 10 044 piece per L).[43] Untreated fractions of MPs in WWTPs will be present in the effluent, while the removed fraction will end up in biosolids. Thus, WWTPs are considered to be the major sources of MPs in urban areas either by direct discharge of effluents to surface waters especially during rain events or by run-off from farms that apply biosolids from WWTPs as fertilizers.[25,33,34,44] The particle size distribution is another important parameter for the characterization of MPs and evaluation of their removal in the WWTPs. Enfrin et al. reviewed the size of MPs in the effluents of WWTPs, indicating that it ranges between 20 and 1000 μm.[45] In another review study, Hamidian et al. reported that particles with size >1 mm comprise 22%, 17%, 17%, 13%, and 31% of fibers, fragments, films, pellets/beads, and foams, respectively. It is worth noting that different procedures of sampling, pretreatment, and measurement have been used. For instance, the reviewed studies used different mesh sizes (0.7 to 300 μm) for retaining the enumerated particles, which unambiguously bias the comparison of different sources.[46]

The composition of MPs in WWTPs includes tens of identified polymers in addition to others with unknown chemical structures. Among the identified polymers, PE, polyamide (PA), polyethylene terephthalate (PET), polyvinyl chloride (PVC), PP, and polyester prevail in the influents.[46] Other polymers like polylactide, PS, polyurethane, acrylate, and polyvinyl alcohol were also detected with less dominance (≤5%).[43,47] The
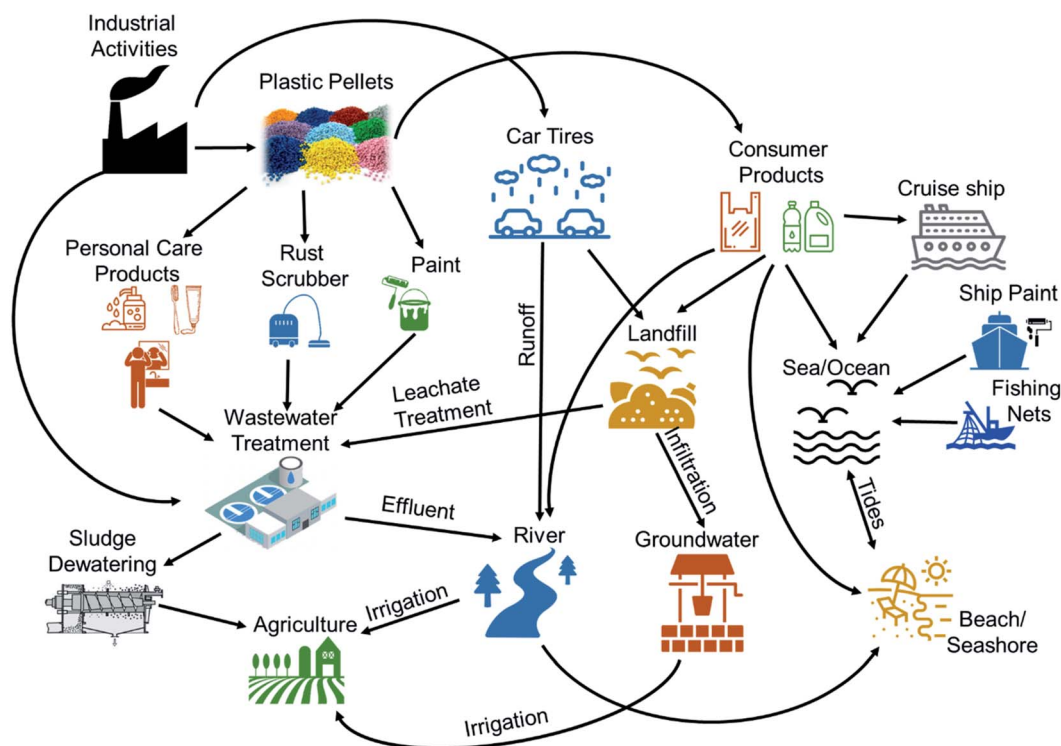

Fig. 2 The major sources of MPs and their pathways in the environment.

existence of MPs in WWTPs is also characterized by the prevalence of specific shapes. Most recently, Liu *et al.* reviewed the diverse shapes of MPs in the literature, reporting that nine shapes of MPs may exist in the influents or effluents of WWTPs with fibers, pellets, fragments, and films being the most prevalent.[14] Other shapes like foams, ellipses, lines, and flakes exist in the influents with lower abundance and are rarely detected in the effluents.[46] The dominance of fibers is attributed to their release from textiles in domestic washing machines, whereas the abundance of fragments and pellets is ascribed to the increasing consumption of personal care products like toothpaste, skin creams, and soaps.[48]

Another source of MPs is the transfer to the atmosphere *via* disintegration of agricultural PE foils, clothes dryer, and MP-containing biosolids employed as fertilizers.[22] Furthermore, industrial activities (*e.g.*, thermal cutting of PS foam) have been found to emit nano-size polymer particles that can be transferred by air.[7] Besides, the wide use of 3D printing for rapid prototyping and small-scale manufacturing has been considered as a source of ultrafine nanoparticles.[22] MPs exist in domestic and industrial solid wastes and hence, they can accumulate in landfills.[49] Thus, municipal landfill leachate is a huge reservoir of MPs. However, they may be resuspended turning airborne and spread in the terrestrial ecosystems by deposition into the soil.[50,51] Some species may also contribute to the development of secondary MPs by shredding that occurs during or after ingestion of big particles of plastic litter.[41] Indigestible foods are detoxified by storing them in the stomach for a long time until digestive processes and mechanical grinding are accomplished, with gastrointestinal muscles wearing down the particle size to a size small enough for expulsion.[52] In an example, fulmars, a type of seabird, are predicted to reshape and globally redistribute annually about 6 tons of MPs.[53] Overall, identifying all sources of MPs and the released amount from each source is a complex challenge despite current painstaking efforts to estimate emissions. Thus, these data are crucial in order to help the society protect its members from unknown exposures and preventing harmful and/or irreversible effects that might be discovered.

3. Fate of MPs

3.1. Removal of MPs in WWTPs

Typical WWTPs comprise primary, secondary, and sometimes tertiary stages, then the effluent water is released usually to surface waters and the sludge is used in agriculture as a fertilizer and/or for biogas production *via* anaerobic fermentation.[54,55] Current data suggest that the majority of MPs in domestic wastewaters are removed in WWTPs, however, the residual MPs and NPs are considered as major sources in aquatic environments.[44] A portion of MPs in wastewater could be removed in the primary stage by flotation, settling, coagulation, and filtration.[56] At this stage, the removal is usually attributed to the agglomeration of plastic particulates, which can occur naturally in settling and floatation tanks, or by chemical aids that reduce the electrostatic repulsive forces in favor of the prevalence of Van Der Waals attractive forces.[48] In

a recent review study, Iyare *et al.* (2020) reported that the average MP removal in the primary stage is 72%, however, it could reach 93% depending on the composition and characteristics of the MPs. Bigger anthropogenic plastics are usually removed in the grit and grease removal chambers, whereas smaller plastics like fibers and spherical particles are usually eliminated in sedimentation and flotation tanks.[57] Of note, removal by flotation and settling is mainly dependent on the polymer type. Some light-weight polymers like PE are likely to be buoyant in water, and hence they could be skimmed during the flotation, whereas other polymers tend to sink in sedimentation tanks.[43] The secondary treatment stage comprises a series of aerated (oxic) or non-aerated (anoxic or anaerobic) tanks, besides a final sedimentation tank for the collection of active biosolids (sludge).[58] During this stage of wastewater treatment, the organic contaminants in wastewater are being consumed (digested) by microorganisms to produce new cells.[59] According to this mechanism, the removal of non-biodegradable MPs by secondary treatment is very limited.[60] However, some strains of bacteria like *Rhodococcus* and *Ideonella sakaiensis* are capable of digesting some types of polymers but with low efficiency besides the need for a long solid retention time (SRT).[48] Furthermore, the toxic nature of some MP polymers may inhibit the metabolism of the microorganisms, which may result in lower growth of new cells and less removal of the biochemical oxygen demand (BOD).[44] In a recent review by Agathokleous *et al.* (2021), the potential interactions between polymers and particular bacteria strains suggested that PVC MPs can facilitate the propagation of some mobile genetic elements in the aerobic bacteria. These elements improve the antibiotic resistance genes leading to the production of antibiotic resistant bacteria in the next generations.[20]

On the other hand, the bacteria in the activated sludge system tend to accumulate on the surface of plastic debris, which may be entrapped in the form of sludge (Sun *et al.*, 2019 (ref. 43)). Even though a considerable number of MPs is eliminated with the sludge, there is a big concern about the fate of the removed MPs. MPs-containing sludge is usually digested and dried, then reintroduced to farms as biosolids. A recent critical review analyzed 76 published studies, however, the authors have suggested that the quantity and properties of MP emissions to the soil through biosolids are unclear.[61] Here again, the discrepancies between the sampling and analysis methodologies in the current literature are limiting us from obtaining an undoubted overview of the persistency of MPs during biosolid processing.[62]

Tertiary treatment methods include different processes that differ from one plant to another according to the location, available technologies, and costs. They usually include a disinfection step using chlorine, UV, or ozonation to kill the remaining pathogens.[45] Advanced WWTPs may include further effluent polishing like rapid sand filtration, dissolved air flotation, or membrane bioreactor (MBR).[57] The MPs in tertiary treatment stages usually have lower concentrations than in primary and secondary stages, and they axiomatically have smaller sizes allowing them to pass the previous stages.[63] Therefore, the removal during tertiary stages may not be high

regarding the original amount in the influent. However, the reported removal efficiencies by tertiary processes are of a wide range reliant on the type of process, MP characteristics, and analysis procedure.[14] We found notable differences in the ranges of removal reported in the recent review studies. For instance, Koutnik *et al.* (2021) found that the WWTPs with tertiary treatment have better average removal of 10% than those with only secondary treatment based on 76 previous studies.[61] Iyare *et al.* (2020) found that tertiary treatment improves the MP removal by 5% to 20%.[57] In contrast, Liu *et al.* (2021) reported that tertiary treatment achieves a limited reduction of MPs according to their analysis of the current literature.[48] On the other hand, Enfrin *et al.* (2019) raised a concern about the fragmentation of MPs into NPs during the tertiary treatment which may increase the uncounted plastic particles in the effluents of WWTPs.[45] This notable contradiction in the recent literature suggests the need for further investigation about the actual MP removal and sweeping mechanisms in each stage/process inside WWTPs.

3.2. Fate of MPs in natural waters

Due to the increasing release of MPs into the environment, the potentially adverse impact on the aquatic systems has become a priority concern for environmental and marine sciences.[64] When MPs enter the aquatic environment, they are exposed to natural factors (*i.e.*, UV radiation, oxidants, wave actions, or various weathering processes) as demonstrated in Fig. 3,[63] leading to different transformations on their surfaces and structures in short and long periods, as reported by others.[7,17,65,66] To date, several review studies have examined MPs' fate, but so far, the contaminants released from MPs (*e.g.*, additives, antioxidants, UV stabilizers) have not been well investigated from an environmental perspective.

3.2.1. Aggregation and deposition of MPs. MPs are subjected to aggregation and deposition in aquatic environments, which critically control their environmental fate and interactions with existing contaminants.[7] Nevertheless, the current literature lacks the investigation about the aggregation of naturally overwrought MPs whose properties are affected by the long interaction with the surrounding environment. Furthermore, only limited types of lab-prepared MPs were reported.[49,67] MPs–MPs, MPs–contaminants, and MPs–water interactions can all play a paramount role in controlling the aggregation and deposition behavior of MPs in water.[1,68] These interactions are usually driven by van der Waals and electrical double layer (EDL) forces, which are identified by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of stability.[69] However, non-DLVO forces like steric, magnetic, and hydration force interactions may also exiguously influence their aggregation and deposition stages.[7] Li *et al.* (2018) investigated the DLVO interaction energy profiles for PS based MPs as a function of the electrolytes with and without humic acids (HAs).[70] Their results indicated that the energy barriers decrease at high electrolyte concentrations, which increase MP aggregation. By adding HAs into negatively charged PS-based MP suspensions, NOM molecules induced highly negative zeta potentials, which led to the prevalence of electrostatic repulsive force and reduction of MP aggregation.[70] Since the aggregation of MPs is highly affected by pH, the aggregation/or dispersion of MPs in aquatic systems can be controlled by its point of zero charge (pH_{pzc}). When the pH value in aqueous water is higher than pH_{pzc} of MPs, the net charge on the MP surface is negative because of the deprotonation of carboxyl and hydroxyl groups and increasing electrostatic repulsion between HAs and MP surfaces. When the pH level was lower than pH_{pzc} of MPs, the net charge on the MP surface becomes positive, and thus reducing the electrostatic repulsion between each other and moving MPs towards the NOM molecules, which increased the MP aggregation. Moreover, the aggregation stage of MPs was greatly influenced by the water chemistry and sources (ionic strength, ions, organic matter, *etc.*). The results from Li *et al.* suggested that PS-based MPs can aggregate less in freshwaters
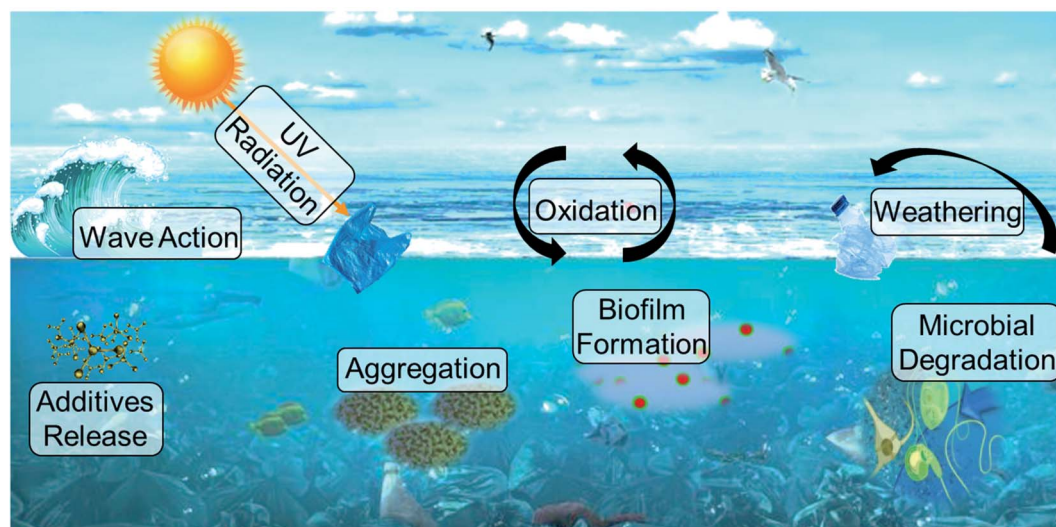

Fig. 3 The fate of MPs in the aquatic environment.

(*i.e.*, lakes and rivers), whereas they can aggregate more in seawaters (*i.e.*, estuaries). This might be attributed to the salts promoting outer-sphere surface complexation.[70]

In addition to the physiochemical properties of MPs and background water, environmental behavior such as weathering, wave actions, heat, UV radiation, oxidants, microorganisms, and a combination of these factors may also have an impact on the aggregation and deposition of MPs. As we further discuss in the following section (Section 3.2.2), both weathering processes and wave actions can cause several mechanical fragmentations of MPs. Such effects are accelerated at increased temperature according to the Arrhenius relationship.[71] It should be noted that laboratory based aging processes (*e.g.*, UV and ozone) for MPs can cause a much rougher surface and introduce hydroxyl, carbonyl, and carboxyl functional groups on the MPs' surface, when compared with virgin MPs.[5] On the other hand, in the presence of oxidants, the reactive oxygen species (*i.e.*, hydroxyl radical, singlet oxygen and/or superoxide radical) would initiate chain reactions, and thus degrade the polymeric structure and/or oxidize the surface of MPs.[66] Furthermore, microorganisms may also play important roles in the aggregation and deposition of MPs, and the utilization of the polymer matrix as an energy source. Since the aggregation mechanism is a key issue in understanding the environmental fate of MPs, the exact aggregation mechanism of MPs in natural sources depends on the properties of MPs (such as size, density, shape, chemical composition, surface charge, and coating), water chemistry, hydrodynamic conditions in natural water and environmental factors.[2,72] As a result, greater research into MP aggregation behavior in aquatic environments, particularly in drinking water supplies, is needed to determine their environmental fate and ecological concerns.

3.2.2. Degradation of MPs. Degradation is a series of reactions that break down the structures of MPs, which are categorized into photo-oxidative, thermal, chemical, and microbial mechanisms.[73] The degradation alters the physico-chemical properties of MPs (*i.e.*, shape, color, size, functional groups, crystallinity, and densities) depending on the mechanisms involved.[74] Although some MPs of higher molecular weight have a bio-recalcitrant nature, they may suffer from photo-oxidative degradation by sunlight, hydrolysis, and UV radiation, which can be followed by thermal and/or chemical degradation (such as mechanical fracture due to sand abrasion or water turbulence) in the marine environment.[17,75] The degraded products can be subjected to further microbial degradation (such as bio-assimilation) due to the changes in their molecular weight, amorphous, and crystalline forms.[66,76] The produced organic carbon has a significant potential for engaging with biotic systems, which affects carbon storage and interchange between aqueous, terrestrial, and atmospheric carbon stocks, as well as water chemistry (*e.g.*, pH). However, the influence of MPs and their decomposition byproduct carbon on existing stocks has yet to be assessed, but it is possible that plastic-derived carbon is turning up in total and dissolved organic carbon assessments (TOC and DOC).[77] In addition, standard methods are being used to evaluate MPs' degradation visually and by measuring the weight loss over time

to obtain some insight on the fragmentation rate. These laboratory-based methods employ the aerobic biodegradation of plastics and monitoring CO_2 production over time.[78]

Several review studies have recently focused on the MP degradation on a more global scale, addressing the degradation of several synthetic[29,30,65] and commercial MPs.[79] Their potential degradation pathways and products depend on the UV-radiation, oxygen, and MP type. Extensive oxidative fragmentation of larger MPs into small-sized particles mostly occurs in their amorphous regions because their crystalline areas have low oxygen permeability.[80] Thus, the amorphous regions of MPs are responsible for the fragmentation of MPs whereby the fracture starts.[76] On the other hand, the presence of additives in MP products enhances the tendency of photo-oxidative degradation.[35] Thus, the polymerization impurities of MPs and other surrounding factors, such as temperature, exposure to sunlight, and oxygen, can lead to different products of degradation in different proportions.[81]

To date, several studies have reviewed the degradation rates of MPs produced from plastic litter.[17,82,83] However, obtaining a universal criterion for the determination of MP degradation rates is still elusive due to their dependence on numerous environmental factors and MP materials (sizes, shapes, densities, and mechanical and chemical properties). Changes in the color of MPs after aging experiments were evaluated as an indication of the changes in the chemical structure of MPs. For instance, Cai *et al.* tested the UV degradation of three virgin plastic types (*i.e.*, PE, PP, and PS virgin plastic pellets) under several environmental conditions (*i.e.*, synthetic seawater, distilled and deionized water (DDW), and airborne). The level of chemical weathering of plastic pellets followed the order airborne environment > DDW > synthetic seawater.[84] Yet, there is no available systematic study that links the changes in MP characteristics to their sorption behavior. On the other hand, the chemical degradation of MPs by UV irradiation-induced oxidation occurs only in surface waters.[45] However, MP fragments may not be exposed to UV light in the case of the MP pieces traveling in pipes. Thus, further research is needed to understand other possible degradation mechanisms.

The recent literature mostly focused on the commercial MPs, since the lower molecular weight and faster surface structure changes of commercial MPs are most likely attributed to the degradation of chemical additives.[15,37] A reduction in the molecular weight of the MPs was also observed, especially at the first aging period, which can alter their environmental fate and toxicity. In general, the microbial degradation of conventional MPs is a very slow process.[65] Due to their high molecular weight, strong C–C bonds, and extremely hydrophobic surface, any enzymes can attach to MPs' surfaces. However, only one study demonstrated that brown rot fungi can attack polystyrol by hydroquinone-driven Fenton reactions.[85] *Gloeophyllum striatum* DSM 9592 and *Gloeophyllum trabeum* DSM 1398 induced significant depolymerization after 20 days of incubation, according to this study. The most aggressive Gloeophyllum strains resulted in molecular weight reductions of over 50%. The enzymes involved in the depolymerization step are yet be investigated for the degradation of high-molecular-weight

polymers. As previously stated, the breakdown of chemical additives may have accelerated weight loss. Therefore, the use of microbial enzymes to remove plastics from the ecosystem has recently gotten increased attention.[14,17,86] Nevertheless, the impact of MPs on microorganisms is still unclear and requires further research to understand the mechanisms and analyze the degradation byproducts. In our opinion, biodegradation is favored for the removal of MPs from the aqueous water, however, there is a lack of knowledge about the effect of some environmental parameters such as water matrix, contact time, temperature, properties of MPs, and effective bacteria availability. Filling these gaps could help to enhance the biodegradation of MPs in WWTPs.

4. Toxicity and ecological risks

4.1. Toxicity

Filter feeders in the open sea, spanning from nano-zooplanktons to baleen whales, interact with MPs on a regular basis.[35] As a result, there is growing concern about toxicological hazards associated with MP uptake by microorganisms, either directly (*i.e.*, misidentification or indiscriminate ingestion of MPs for nutrition) or indirectly (*i.e.*, trophical transmission along with the food chain).[87,88] The physicochemical characteristics of MP surface are essential determinants of their

biological impacts.[89] Some by-products from the fragmentary degradation of MPs, residual monomers from plastic production, and toxic additives used in the compounding of plastic may leach out of the ingested plastic and cause several risks of detrimental impacts on aquatic life.[87] Fig. 4 summarizes the highlighted toxicological risks of MPs in recent review studies. So far, several studies on the toxicity of MPs have been focusing on aquatic invertebrates and direct feedings or waterborne exposure at the individual level; however, there is less concern about the exposure to MPs through trophic transfer.[80,90,91] Therefore, more research is particularly needed to help understand the potential impact of MPs at the ecosystem level, such as how MPs can alter the natural habitat of organisms and impact ecosystem functioning and services.

The ingestion of MPs by different marine species was confirmed after detecting different types of polymer particles in their intestines and/or stomachs (*e.g.*, zooplanktons, shellfish, corals, fish, and marine mammals).[92] For instance, MPs were found to bioaccumulate and impact cells and tissues of shellfish including mussels. The health implications of their presence in animals are that they block their digestive system which obstructs their feeding habit and may lead to death.[93] However, the health impacts in humans have yet to be determined, although possible effects include lung inflammation and general and specific genotoxicity.[89] Furthermore, the interaction
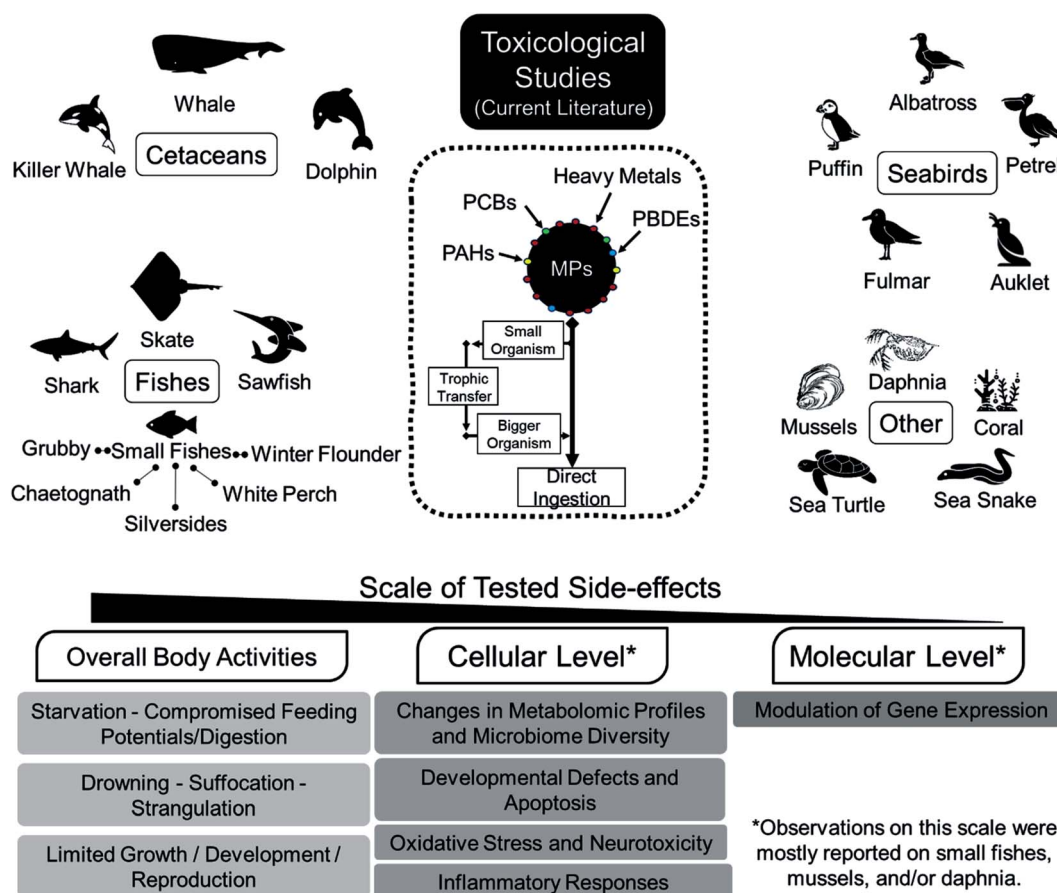

Fig. 4 The toxicological effects of MPs on aquatic organisms.

of MPs and NPs with the immunological system may result in immunotoxicity, and as a result, these modifying negative effects may result in unwanted issues such as immunosuppression, immunological activation, and aberrant inflammatory reactions.[94]

Some studies reported that MPs (*e.g.*, PS) can form free radicals and cause oxidative stress.[38] These free radicals originate from oxygen and/or nitrogen molecules, and act as reactive oxygen species. When these reactive oxygen species are over-generated, they alter the physiological homeostasis of cells *via* inhibiting the production of antioxidants. Furthermore, excessive generation of these species is usually associated with harm to cellular macromolecules (carbohydrates, lipids, proteins and nucleic acids).[95] Genome fragility, metabolic and pathophysiological changes, and carcinogenesis may all be linked to this detrimental damage.[88,94] Several studies highlighted that the evidence of MP ingestion by the microorganisms in freshwater is much more limited than in seawaters. Furthermore, there is little research on the mechanisms of MP bioaccumulation, translocation into organs, cellular transport routes, and elimination kinetics.

The other significant threat from MPs comes from the adsorbed toxic chemicals on MP surfaces including heavy metals, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers.[96] Some opinions claim that MPs can act as carriers of toxic pollutants, thereby enhancing their bioaccumulation and toxicity.[76] On the other hand, others state that MPs can act as a sink for contaminants and hence reduce their potential bioaccumulation.[95] More details on the adsorption of toxic chemicals on MPs are later discussed in Section 7. The bioaccumulation patterns of MPs and organic pollutants, as well as the mechanisms underlying the various influences on toxicity, are still unknown due to a lack of quantitative methodologies. Besides, field studies have demonstrated that secondary MPs are predominantly found in the environment, whereas bench-scale studies have focused on characterizing the toxicity of primary MPs.[90] Studying the toxicological effects of secondary MPs is of immediate need, since their compositions and characteristics that control all the above-mentioned factors are different from those of primary MPs and pure polymers. Furthermore, the threshold of toxicological concern of different MPs should be focused in future studies and compared with the MP amounts passed to humans through food chains.

4.2. Interaction with microbiota

One of the major concerns is about the harmful effects of MPs on microalgae as a principal component of the food web.[1] However, the interactions between plastic debris and microalgae in aquatic environments are rarely investigated in the literature. The accumulation of microalgae on MPs may change the particle buoyance leading to faster settling. Furthermore, MPs can change the photosynthesis and chlorophyll behaviors, which may deteriorate the functionability of some components and inhibit microalgae growth.[1] Apart from the growth inhibition, the accumulation of algae biofilms on plastic debris

reduces the ability of many grazers, such as zooplanktonic organisms, to discriminate between edible and nonedible particles subjecting the higher organisms in the food chain to the hazards of MPs.[97] Herein, we argue that the persistence of MPs in aquatic ecosystems can cause long term impacts. For instance, organisms might change their feeding behavior and might also evolve to coexist with plastic particles. Yet, no data are available on the movement of MPs within and between aquatic and terrestrial ecosystems *via* trophic transfer from aquatic insects to birds.

MPs can act as Trojan horses carrying bacteria, antibiotic resistance genes, and other pathogens inside the bodies of other organisms.[20] The inhalation of MPs by animals and other organisms may deliver diverse pathogens inside their guts that would never reach them without this route. However, this Trojan horse-like effect requires more experimental studies with relevant environment concentration to support this hypothesis which is still lacking in the current literature.[52] The interaction between MPs and microorganisms also includes chemical adsorption, degradation, ingestion, and colonization.[98] For instance, some species like gut bacteria and *Pseudomonas* can degrade PE MPs.[52] The adsorption was found to be responsible for the colonization of millimeter-sized marine plastic debris by different species of microorganisms, which turned out to be a new pelagic habitat for many of them.[99] Further research is needed for investigating to what extent MPs and NPs could be passed from a generation to another. Moreover, it is important to consider that natural MPs and NPs may behave different from those synthesized in laboratories.

5. Detection and characterization of MPs

Since 2011, several review studies have addressed the methodologies for the sampling, pretreatment, characterization, and quantification of MPs from the aquatic environment.[31,32,100–102] However, the detection, pretreatment, quantification, and characterization of MPs in aqueous water are still analytical challenges and lead to the study of unrealistic high concentrations in lab-scale experiments manifesting some misleading toxicological impacts under natural conditions.[103] On the other hand, it is difficult to compare the data obtained in the field studies because of the lack of standard methods for sampling techniques towards the identification and quantification of MPs. This section evaluates the sampling, pretreatment, characterization, quantification, existent protocols, and analytical challenges of MPs in the current review studies. A summary of the current procedures is depicted in Fig. 5.

5.1. Sampling and pretreatment of MPs

Due to the low density of MPs, some of them tend to float on the water surface. These floating MPs can be collected with a trawl, vessel, surface microlayer, or hand-net from the surface water level, as shown in Fig. 5. Among all sampling methods, the benefit of using a trawl is that it can provide a smaller sample volume while covering large sampling areas.[50] Typically, 333–
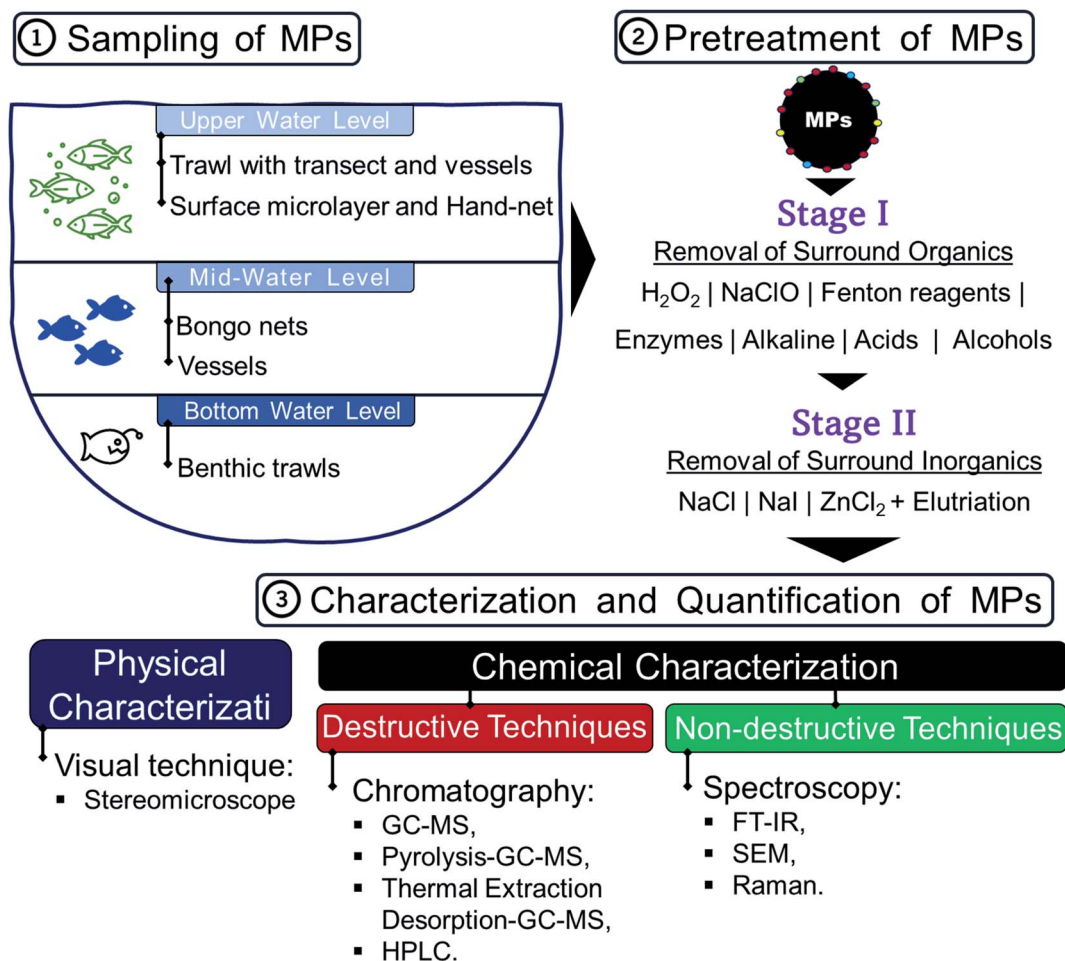
Fig. 5 Methodologies for the sampling/pretreatment/characterization and quantification of MPs.

335 μm meshes are commonly used for the net. The mesh size of the trawl highly affects the amount and size of the collected MPs. The variation of the mesh size used in the literature leads to misleading information when comparing the characteristics of MPs at different locations.

The MPs located in the mid and/or bottom levels of water bodies can be collected with stainless-steel spoons or spatula, box-corer, core, bongo net, benthic, or bottom trawls.[50] However, according to our review, there is still a lack of specific universal sampling protocols for the collection of MPs in water bodies.

The separation of MPs from water bodies has also been examined by density separation, filtration, sieving, and visual sorting. Among all, visual sorting was the commonly used method for the identification of MPs (i.e., type, size, shape, degradation stage, and color).[50] However, this technique may not provide accurate information about the abundance of MPs in the presence of clay and algae. Besides, other extracted organic and inorganic particles, and MPs have similar sizes and shapes making the differentiation a very tedious step, especially when the collected samples are not pre-treated or tiny MPs are present.[104] To overcome these limitations, more reliable methods should be used for the identification of MPs instead of

relying on visual observation that would introduce large variations in the results.[105]

Since MP samples are obtained from aquatic water, they may be surrounded by biofilm, organic and inorganic particles, and thus various approaches are applied to extract MPs from their original matrix.[106] These processes also facilitate the characterization and quantification of MPs. Pretreatment by oxidation is commonly employed for the removal of organics in water samples. H_2O_2, NaClO, Fenton reagents, enzymes, alkalies, acids, and alcohols are frequently used for oxidizing organic matter.[43,107] These oxidation methods are widely used to pretreat MP samples collected from seawater, freshwater, wastewater, sediments, and organisms.[83,91] On the other hand, for the removal of inorganics from MPs, elutriation, and salts like NaCl, NaI, and $ZnCl_2$ are generally preferred while employing density separation techniques.[23] The reagent salts are, in general, mixed with the samples and shaken, however the efficiency of each salt depends on its characteristics. When compared with NaI, $ZnCl_2$ is less expensive and more effective due to its higher density (1.6–1.8 g cm^{-3}).[108] Since $ZnCl_2$ is highly toxic, corrosive and requires large amounts of the sample,[109] its disposal and reuse techniques must be improved in the near future. So far, the reuse process of NaI solution has

been widely investigated since there is a lack of information about the $ZnCl_2$ reagent for the density separation methodology.[110] Therefore, among all salts, the saturated NaCl solution is generally used because of the low cost, non-toxicity and very high density ($1200\ g\ L^{-1}$) of NaCl. However, it should be noticed that these pretreatment techniques may also alter MP structures and characteristics. The structural changes of MPs due to the pretreatment steps may be quite different and depend on the involved mechanisms, properties of MPs themselves (*i.e.*, age, color, size, shape, aggregation, *etc.*), and water matrix.[111] Therefore, further research is required to examine the characteristic changes of MPs under different pretreatment methods.

5.2. Characterization and quantification of MPs

The identification of the origin of MPs is very tedious due to their small size, fragment nature, and wide range of possible sources. The analysis of MPs can be categorized into physical and chemical characterizations. Physical characterization refers to characterizing their size distribution, shape, texture, and colors.[112] Stereomicroscopy is a visual method and can be straightforwardly used to measure the size, characterize the morphological structure, and enumerate the MP count.[43] A relatively large number of MPs can be quickly identified by this microscopic counting method which provides overall images of MP abundance at low cost. However, stereomicroscopy cannot determine the nature of the MPs (*i.e.*, polymer types) and is a time-consuming process since automatization is not possible.[113] Besides, visual counting methods are subjected to bias, due to their limited size and relatively low magnification factor, so the results may strongly depend on the operator.[31] Accordingly, high error rates can be observed, and they usually increase with smaller MP size reaching 70%.[43,114]

Chemical characterization aims to explore the composition and structure of MPs. The current chemical analysis methods are conducted using destructive techniques (gas chromatography coupled with mass spectrometry (GC-MS), pyrolysis-GC-MS, thermal extraction desorption-GC-MS, and liquid chromatography (LC)) and non-destructive spectroscopic techniques (Fourier transform infrared (FTIR), Raman, and scanning electron spectroscopy).[82,113] Among all these techniques, we noticed that non-destructive spectroscopic techniques are most extensively used to analyze MPs in environmental samples.

For the characterization of the chemical composition of MPs, among all non-destructive techniques, FTIR spectroscopy is the most reliable method.[115] Three different operating modes are employed with an FTIR analyzer, namely transmission, reflection, and attenuated total-reflectance (ATR) modes. These modes depend on MP particle sizes. For example, larger MP samples (>500 mm) can be analyzed by ATR-FTIR, while smaller MPs can be measured by micro-FTIR spectroscopy for simultaneous visualization, mapping, and collection of spectra.[111] However, micro-FTIR spectroscopy needs plenty of time and effort to find the appropriate particles for the analytical procedure.[100] Besides, the contact of the crystal with the inorganic particles can cause several instrumentation damages. On the other hand, for more reliable MP analysis, a focal plan array

(FPA) based FTIR analyzer was used with several detectors placed in a grid pattern.[116] This method offers detailed and unbiased high-throughput screening of total MPs on the entire filter paper. Moreover, several thousands of spectra in a targeted area within a single measurement can be recorded simultaneously, and thus chemical images can be captured for the whole filter paper. However, two limitations of these methods have been reported so far: (i) the detection is affected by the environmental matrix such as biofilm formation on MPs, and thus it may create difficulty in data interpretation unless the sample is pretreated to eliminate IR active water;[106] (ii) it is difficult to analyze non-transparent, irregular shaped MPs and NPs by FTIR. Furthermore, spectral interpretation of FTIR (*i.e.*, comparison of diagnostic signals) and interrogation (*i.e.*, comparison of overall spectra) are crucial to assign the chemical type of MPs.[107]

As a surface analytical technique, Raman spectroscopy can be used for the identification of large and visually sorted MPs.[117] Theoretically, micro-Raman microscopy combined with the Raman spectra imaging technique can afford the spectral analysis of entire filters at a spatial resolution (<1 mm).[107,118] Since lasers with a single wavelength are applied to excite molecules, Raman spectroscopy can throw light on the polarizability of the chemical bond, which mainly identifies the aromatic bonds, C–H and C=C double bonds of MPs. Compared to FTIR spectroscopy, Raman techniques have a better spatial resolution (<1 mm) (Araujo *et al.*, 2018 (ref. 82)) and higher sensitivity to non-polar functional groups, but less sensitivity towards disturbing signals of air and aqueous water.[107] However, Raman spectroscopy is highly ineffective in the case of fluorescent samples, which are highly excited by laser.[113] Furthermore, the biological, organic, and inorganic residuals in the MP sample can interfere with the spectra which may present some misleading signals. Accordingly, the samples must be pretreated carefully to avoid any undesirable modification.[111] Alternatively, fluorescent dyes (*i.e.*, Nile Red) have been employed in recent studies to enhance the Raman analysis of hydrophobic MP samples.[46] Nile Red can quickly bind to the MPs, so the dye-stained MPs can be detected by fluorescence spectra.

The surface morphology of MPs can also be assessed by scanning electron microscopy (SEM).[7] The conventional SEM shows images of MPs by scanning their surface with intensified electron beams (Nguyen *et al.*, 2019 (ref. 112)). Besides, SEM-energy dispersive X-ray spectroscopy (SEM-EDS) and environmental scanning electron microscopy-EDS (ESEM-EDS) have been utilized for both evaluating the morphologies of MPs and elemental analysis of polymers.[89,102]

In addition to the non-destructive spectroscopic techniques, GC-MS and LC-based technologies may be employed for the quick characterization of MPs in the aqueous water.[43] Both procedures can test polymer types, and with adequate calibration, quantitative findings can be achieved, simplifying the assessment of MP pollution.[31] In general, GC-MS is frequently associated with thermo-analytical technologies (*i.e.*, pyrolysis-GC-MS and TGA-MS). In a nutshell, MP samples are first thermally destroyed, then the resulting compounds are transported

to a mass spectrometer for examination. To get sample information such as identification and concentration, the obtained data are compared with ref. 119. The processes, however, place a limit on the size of the plastic objects. Samples less than 500 μm are difficult to manage because they cannot be placed in the tube. Furthermore, the approach is less suitable for combinations of high impurity concentrations.[120] Duemichen *et al.*, (2014) used another thermo-analytical method for direct analysis of MPs from the field samples. For this thermogravimetric analysis method, solid-phase extraction (TGA-SPE) was combined with thermal desorption GC-MS (TDS-GC/MS).[121] So far, only PE-based MPs have been characterized by the thermogravimetric analysis method. Furthermore, Hintersteiner *et al.* (2015) and Elert *et al.* (2017) used LC for the quantification of MPs and found that MPs with different solubilities can be quantified by this method if appropriate solvents are used to dissolve different types of MPs (such as tetrahydrofuran solvent for PS based MPs and hexafluoroisopropanol solvent for PET-based MPs).[122,123] After MP extraction, the samples can be directly analyzed by HPLC coupled with size exclusion systems. Although the particle size of MPs cannot be determined with this method, the HPLC analyzer shows high recoveries and can quantify the concentration of MPs. However, this method has only been applied to synthetic water samples.[31] Therefore, further research is required to verify this method for MP samples in other water matrices. Overall, for the chemical assignment, the lack of standard procedures using spectroscopy makes comparisons across different studies very tedious.

5.3. Data quality

The rising concern about the existence and fate of MPs in natural waters and WWTPs has resulted in a massive inventory of data but without standardized approaches or methods for sample collection, pretreatment, extraction, or analysis.[124,125] Only a handful of research studies have approached the optimization of these methods in a quest for obtaining a developed procedure that possesses the strengths and avoids the limitations of the reported methods.[126,127] Koelmans *et al.* (2019) developed a quantitative quality assessment method to assess the quality of the occurrence data in drinking and surface waters reported in fifty studies according to the sampling and analysis procedures.[27] To build their indicator, they used nine crucial criteria based on the method reproducibility, precision, and sensitivity. The criteria included sampling method, sample size, sample processing and storage, lab preparation, clean air condition, negative controls, positive controls, sample treatment, and polymer identification. For each criterion, a score from zero to 2 was given according to the reliability (non-reliable = zero; middle reliability = 1; reliable = 2), so a total maximum score of 18 points was obtained for each study.[27] It is worth noting that only four of the fifty studies got positive scores for all the evaluated quality criteria. Furthermore, the average, median, maximum, and minimum scores were 8.41, 8, 15, and 3 points, respectively. These findings imply the considerable uncertainty of the current MPs data in the literature and the need for standardized procedures. Using the same quality assessment methodology,

Hermsen *et al.* (2018) evaluated the data of 35 studies that report the ingestion of MPs by aquatic biota. For a total maximum score of 20 points, the average, median, maximum, and minimum scores were 8.0, 9.5, 15, and zero points, respectively.[128] Likewise, Praveena and Laohaprapanon (2021) evaluated the quality of the detection and characterization methods of MPs in bottled water. With the low abundance of reports about MPs in bottled water, only twelve studies were assessed.[129] Again, the average of total scores implied the limited quality of the current characterization methods. Of note, in our opinion, it is worthwhile to assign different weights for each criterion in such quality assessment studies to obtain better representative evaluation. In another critical review study, Lee *et al.* (2021) investigated the variability and uncertainty of the data describing the existence of MPs in table salt according to the analytical methods.[69] They found that the most serious variability comes from the methods associated with minimum cut-off size, which may cause variations of 10–600 times especially by visual observation, followed by FTIR and Raman methods to a lesser extent.

Recently, a group of 23 scientists around the world collaborated to present guidelines for MP sampling and characterization.[126] They suggested a typical framework that comprises practices for reporting, quality assurance and control, data processing, sampling, extraction, identification, categorization, quantification, and considerations for toxicity assessment. This framework was successfully translated into a quick use detailed document, a checklist, and a mind map to be used as reference guidelines for future studies. In another study, Primpke *et al.* (2020) developed free programmed software for fast and harmonized MP characterization based on the outputs of FTIR analysis. The software can assign the FTIR signals to different types of polymers based on a database.[127] Further developments and verifications of such initiative trials could be a great step toward obtaining a standardized tool for MP identification with minimal uncertainty.

6. Interaction with other contaminants

Several review articles have recently addressed the adsorption of contaminants onto MPs under various environmental conditions.[44,130] However, only a limited number of reviews considered addressing the adsorption mechanisms of contaminants onto MPs under different background water chemistries.[73,76,131] Hence, in this section, we investigate the contributions of individual mechanisms such as hydrophobic, π–π, π–π electron donor–acceptor (π–π EDA), van der Waals forces, electrostatic (Coulomb force), Lewis acid–base, and hydrogen bonding interactions. The adsorption mechanisms are briefly summarized in Fig. 6. The interactions between MPs and contaminants in single solute systems are dependent on the molecular structures of MPs and contaminants. Thus, these interactions are a challenging task for understanding the transfer of contaminants from MPs to aquatic systems.[117]

Adsorption of several organic contaminants (OCs) and inorganic contaminants (ICs) to date has been recently reviewed
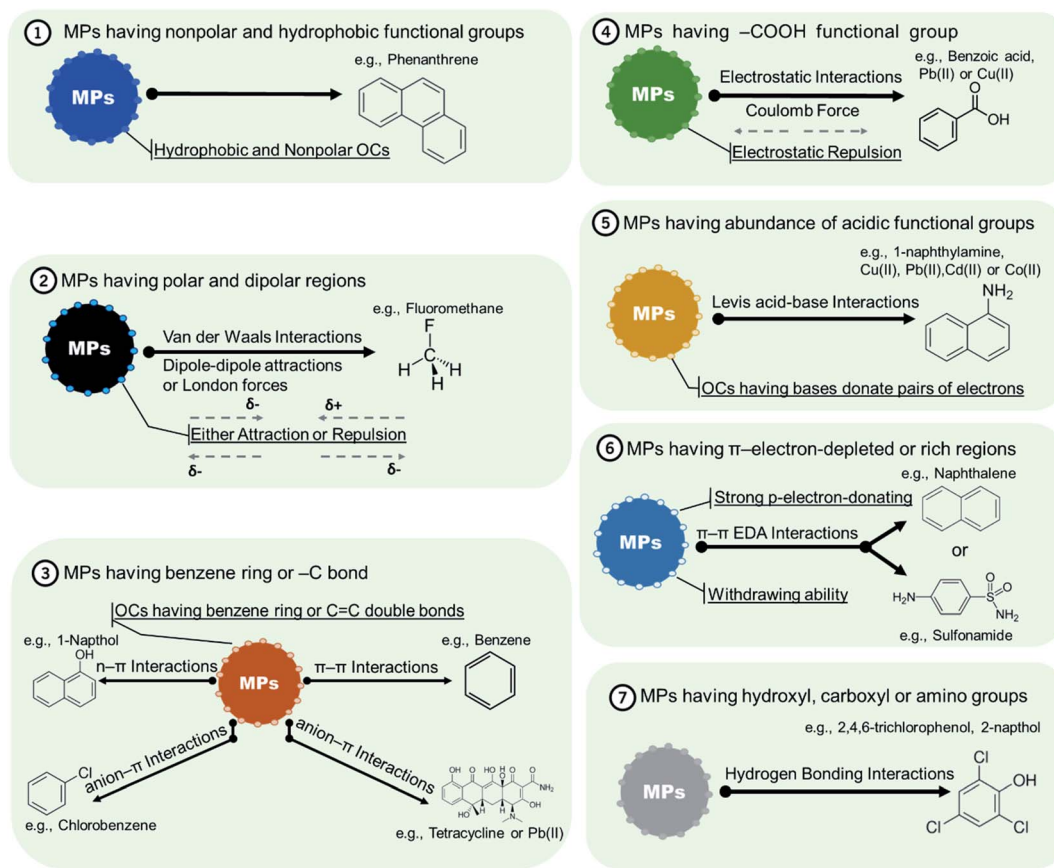
Fig. 6 Molecular–level interactions for the adsorption of OCs and heavy metals by MPs in a single solute system.
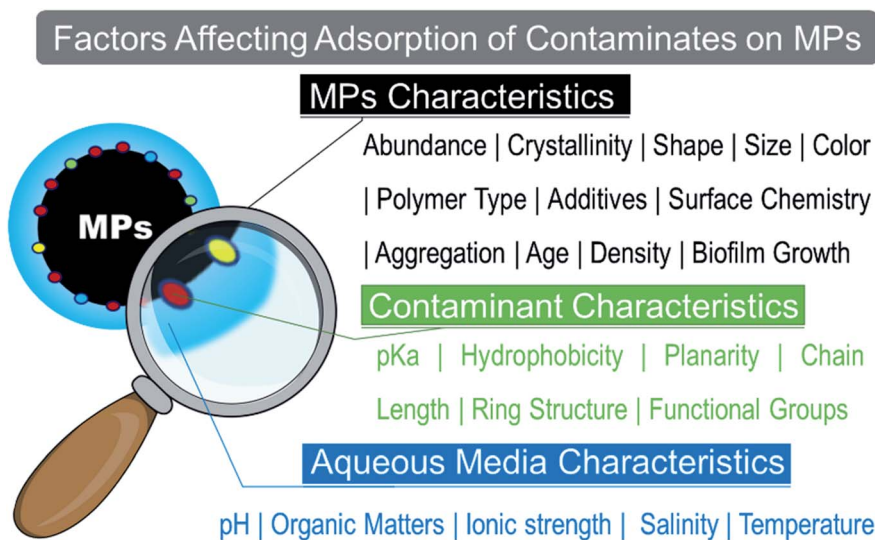

Fig. 7 Factors affecting adsorption of contaminants onto MPs.

in the literature.[132–135] OCs include polycyclic aromatic hydro-carbons (PAHs), per- and polyfluoroalkyl substances (PFAS), halogenated aliphatic, pharmaceuticals and personal care products (PPCPs), dichloro-diphenyl-trichloroethane (DDT), [poly]chlorinated biphenyls (PCBs), and poly-brominated

diphenyl ethers, whereas ICs include different heavy metals. The adsorption of contaminants on MPs is greatly influenced by the water matrices such as DDW, synthetic sea water, sea water, and freshwater. As briefly demonstrated in Fig. 7, the physico-chemical properties of MPs, the contaminants' characteristics,

and the aqueous media characteristics can affect the sorption behavior. Accordingly, all adsorption mechanisms and factors affecting the sorption of MPs are briefly reviewed in the next subsections.

6.1. Impact of the physicochemical properties of MPs on adsorption

The adsorption of contaminants on MPs is highly dependent on physicochemical properties such as polymer types, specific surface area, polarity, degree of crystallinity, and pore size distribution as illustrated in Fig. 7. So far, many researchers have emphasized that the material types, polarity, abundance of the rubbery type, and degree of crystallinity have a great influence on the adsorption capacities of OCs and heavy metals.[132]

The major types of polymers in MPs are classified as conventional polymers (*e.g.*, PS, PE, PVC, PP, PA, PET, high-density polyethylene [HDPE], low-density polyethylene [LDPE], medium-density polyethylene [MDPE], polystyrene carboxylate [PS-COOH]), consumer MPs (*i.e.*, drinking water containers, water, drug and soda bottles, disposable foam dishes, computer casing, carpets, vinyl flooring, formica sheet), and biodegradable MPs (butylene adipate-*co*-terephthalate [PBAT]).[132] To date, more than 70 conventional, 20 consumer, and only one biodegradable MPs have been investigated for the adsorption of OCs or heavy metals. During the last decade, researchers specifically focused on the adsorption of OCs and heavy metals by different types of commercial MPs. Among all commercial MPs, PS, PE, and PVC-based MPs were widely examined for the adsorption of OCs and heavy metals due to their high prevalence. The main limitation in the current literature is that the studies of commercial MPs did not shed light on the uptake of contaminants onto consumer MPs in the case of environmental purposes (*i.e.*, UV radiation, oxidation, weathering, wind, wave action, biofilm formation, microbial degradation, additives, *etc.*).[7,136] On the other hand, as an alternative to conventional MPs, biodegradable MPs are increasingly used but their interactions with OCs and heavy metals are still unknown.[137] However, it is stated that the decomposition of biodegradable plastics in natural water is similar to that of conventional plastics, and hence they produce similar amounts of MPs.[138] In addition, some eco-toxicological studies also argued that biodegradable and conventional MPs had a similar toxic impact on marine organisms.[137] Therefore, it is reasonable to be concerned about the adsorption of different contaminants on biodegradable MPs as much as non-biodegradable MPs.

MPs exist in different chemical and physical forms such as crystalline *versus* amorphous, rubbery *versus* glassy, and cross-linked *versus* non-cross-linked.[139] Amorphous polymers are categorized based on the glass transition temperature (T_g) into glass-like MPs (used below their T_g) and rubber-like MPs (used above their T_g).[7] The abundance of crystalline domains, molecular chain arrays, and rubbery-based MPs have become more important due to their influence on the adsorption of contaminants. In addition, the diverse monomeric compositions and molecular structures of MPs may also cause different molecular interactions.[83,134] Therefore, the uptake level of

contaminants onto each type of MPs can probably be varied because of their structural diversity. Rubbery PE-based MPs exhibited higher linearity in the adsorption isotherm of OCs than glassier PP, PS, and PVC based MPs, with a higher Freundlich nonlinear index n value ($n > 1$).[139] Adsorption onto the surface of rubbery MPs probably played a minor role compared to partitioning into the bulk polymer.[140] In contrast, the Freundlich n values of glassy PS-based MPs were generally lower ($n < 0.85$), indicating that the heterogeneity of the surface and that sorption were probably more dominant onto the polymer surface.[141] Similar findings also linked the polymer crystallinity with the sorption linearity of MPs.[12]

On the other hand, only a few studies have examined the effect of particle size of MPs on the sorption of contaminants onto commercial MPs[140,141] and PS based microbeads.[98] The adsorption coefficients were reduced with decreasing particle size for micron- and submicron-sized PS-based MPs.[68] For instance, when the nano-sized PS-based MPs (50 nm) were compared to submicron-sized ones (235 nm), the adsorption coefficients of nano-sized PS-based MPs were significantly lower due to the size exclusion effects.[142] Besides, the sequences of adsorption capacity of contaminants were the same as their specific surface areas, indicating that the specific surface area of MPs plays an important role in the adsorption of OCs on MPs.[143] In contrast, some researchers demonstrated that the uptake of OCs is not affected by the surface area of MPs.[144] Therefore, the order of adsorption capacities of aromatic OCs onto MPs may be linked with their particle size and surface area depending on the properties of OCs. However, it is worth noting that all the other factors (*i.e.*, surface charge, chemistry, and additives) also influence the adsorption mechanisms for the different types of MPs (Fig. 7) and probably have a major effect on these interactions. In addition, diverse monomeric compositions and structures of MPs can lead to different molecular interactions with contaminants (Fig. 6). For instance, PE and PP based MPs can directly interact with OCs *via* van der Waals forces due to their non-specific functional groups, whereas PS based MPs possess strong π–π interactions with OCs due to the substitution by benzene rings, which increases the aromaticity.[140,141] Furthermore, PE, PP and PS based MPs are known as non-polar polymers, but their presence in the form of MPs can increase the polarity, and hence improve the adsorption capacity *via* polar interactions.[132] However, more research is required to examine the impacts of the surface chemistry of consumer and biodegradable MPs on the sorption mechanisms under natural environmental conditions.

The short-term and long-term transformations of MPs are inevitable under environmental conditions whether due to aging (degradation) or physical and chemical abrasion (*i.e.*, color, size, shape, density, *etc.*), which consequently influence the adsorption behavior of other existing contaminants on their surface.[7,50] Until now, there is a lack of information about how the aging of MPs influences their adsorption behaviors. Since aging naturally occurs by exposure to the sun, UV radiation, or other weathering processes the changes of the surface topography over time can change the adsorption behavior.[133,134] The impacts of MP aging by UV radiation on the uptake of OCs[145,146]

and by natural solar light on the heavy metals[147] on MPs have been investigated. Interestingly, one of these studies argued that the adsorption behavior of MPs was not affected by aging due to the increasing crystallinity of MPs after the aging process.[146] Other studies demonstrated that uptakes of PAHs, PCBs, and DDTs on darker and aged plastic pellets were much higher than those on lighter colored ones.[28,148] Besides, weathering can accelerate the adsorption of cationic metals onto aged MPs since it may increase the surface area and hence creates additional oxygen functional groups on MPs.[147] Due to the weathering by photodegradation, the oxidation of MPs can enhance their surface polarity, which consequently reduces the adsorption of heavy metals. The charged or polar regions of the MP surface can interact with bivalent cations (*i.e.*, Cu^{2+}, Cd^{2+}, Pb^{2+}) or oxoanions (*i.e.*, $Cr_2O_7^{4-}$) due to the non-specific interactions between neutral metal–organic complexes and the hydrophobic surface of the MPs.[149] On the other hand, when the aged commercial MPs were compared with aged biodegradable MPs, the uptake of estrogenic compounds onto aged PVC was higher than that of heavy metals in seawater, whereas no estrogenic activity was detected for PET-based MPs due to the low weakening of their surface.[11] The interactions between MPs, additives, and contaminants during aging in the marine environment remain less understood and the potential toxicity of MPs after these interactions urgently needs to be explained because it may have serious adverse effects on wildlife and human health. It is worth mentioning that numerous laboratory studies have examined the adsorption of contaminants onto natural colloids, pellets, and fragments in aquatic environments,[11,135] however, there are no data on how the environmental conditions affect the adsorption of various classes of contaminants.

6.2. Impact of contaminants' characteristics

The interactions between MPs and different types of contaminants such as legacy persistent OCs, endocrine disrupting compounds (EDC), antibiotics, herbicides, and heavy metals have been investigated in the literature.[10,11,146,149] The interaction and adsorption of these contaminants on MPs are highly dependent on the hydrophobicity, aromaticity, polarity, substituent groups, and molecular configuration (*e.g.*, size, planarity, and chain length or ring structure) as depicted in Fig. 7.

To date, most studies have focused on the adsorption of hydrophobic OCs, which are usually nonpolar and non-ionizable, whereas only a few studies investigated the adsorption of polar and ionizable OCs on MPs.[132–134] According to the latest review studies, the adsorption affinities of different OCs on MPs correlated with the hydrophobicity of the OCs.[132,133] In general, the adsorption of OCs by MPs is better in the case of relatively higher hydrophobicity and aromaticity or low solubility. Therefore, log K_{ow} of the OCs can play an important role in determining the sorption extent of hydrophobic OCs onto MPs, including non-polar OCs and PPCPs.[107,141] Besides, the strong adsorption behavior of highly aromatic OCs to aromatic polymer-based MPs is due to a combination of hydrophobic and

π–π-interactions at the aromatic sites of MPs (Velzeboer *et al.*, 2014 (ref. 140)). Moreover, the adsorption capacity of PAHs on aromatic PS-based MPs was higher than on other nonaromatic PE, PP and PVC based MPs, and thus it enhanced their adsorption capacity *via* π–π-interactions.[10]

The uptake of OCs on MPs may also be affected by electrostatic interactions (Fig. 7), which are dependent on the pH_{pzc} of MPs, pK_a of OCs and pH value of water.[132] If the pH at the pH_{pzc} of the MPs was lower than the pH of the solution, MPs can carry negative surface charges. Thus, the adsorption of positively charged OC is enhanced.[144] In contrast, the electric repulsion forces reduce the sorption of negatively charged OC on MPs.[133] Consequently, the relationship between the pK_a of the OCs, the pH of the background water, and the pH_{pzc} of the MPs can determine the electrostatic attraction/repulsion interactions and may directly influence the adsorption process between OCs and MPs. In addition, hydrophobic and electrostatic interactions are two main mechanisms for the adsorption of perfluoroalkyl acids (PFAAs) on sediments, which could be quite similar to the adsorption mechanisms on MPs.[150] It was also reported that the sorption of PFAS on MPs is highly dependent on the functional groups. For instance, the adsorption of perfluoro-sulfonates and sulfonamides on high-density PE was notably higher than that of carboxylic acids.[151] Furthermore, planar molecules of relatively similar hydrophobicity such as PCBs and PAHs are more likely to be adsorbed on MPs.[16]

Since polar OCs have a strong adsorption capacity to polar MPs *via* polar–polar interactions, the polarity of MPs is expected to greatly influence the adsorption of polar OCs.[142] For instance, the different polarities of perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA) affect their adsorption on PE-based MPs. FOSA is more polar than PFOS, so the adsorption of FOSA on nonpolar PE-based MPs was higher than that of PFOS due to the polar–polar interaction between FOSA and PE-based MPs.[152] However, when the adsorption capacities of different types of polar MPs were compared, only polar PE-based MPs had a notably higher capacity for antibiotics.[70] These findings indicate that the polarity of MPs alone is not sufficient for explaining the differences in adsorption capacities. In the current literature, several studies have only evaluated the roles of hydrophobicity, chemical composition, and polarity of OCs in their adsorption.[132] Although the structure of OCs can also dominantly control the adsorption behavior, we cannot find any comprehensive study investigating the roles of molecular configuration (*e.g.*, size, planarity, and chain length or ring structure) in the adsorption onto MPs.

On the other hand, the interactions between heavy metals and MPs triggered a big splash after the sorption of metals to MPs became a frequently reported problem during sample storage or in experiments involving the metal standards.[153] However, a few review studies have focused on the adsorption of different trace metals (Al, Fe, Mn, Cu, Zn, Pb, Ag, Cd, Co, Sr, Mo, Sb, Sn, and Ni) by MPs.[7,44,87] The adsorption of heavy metals to MPs is dependent on the physicochemical properties and modifications of each metal on MPs (*i.e.*, surface area, hydrophobicity, polarity, ageing, fouling, *etc.*) (Cao *et al.*, 2021 (ref. 153)). Accordingly, further research is required to fully

understand the mechanism and effective factors. Furthermore, the long-term interactions between heavy metals and MPs under real environmental conditions should be fully elucidated.

6.3. Impact of aqueous media characteristics

Due to the complexity of the aquatic environment, the physicochemical properties (i.e., hydrophobicity, specific surface area, and particle size) of MPs are not only changed, but also their chemical compositions are subjected to alteration due to the abrasion, fouling, degradation, and surface modification.[33] Hence, the physicochemical changes of MPs may affect the adsorption behavior of contaminants, and consequently influence their transfer, release, and the associated risks to the aquatic environment (Fig. 7). Therefore, it is worthwhile to evaluate the effect of background water characteristics on adsorption behavior of different contaminants on MPs.

The pH of water highly influences the adsorption of contaminants on MPs depending on the pK_a values of contaminants and pH_{pzc} of MPs.[154] Therefore, recent review studies have demonstrated the paramount importance of the solution pH in the adsorption of OCs onto MPs.[132,134] These effects are related to the ionizability and EDA ability of contaminants, in addition to the protonation/deprotonation of the functional groups on the active sites of MPs.[144] Wang et al. (2015) found that raising the pH of the background water enhanced the dissociation of ionizable OCs which increased their hydrophilicity and consequently reduced the adsorption on MPs.[152] In contrast, more anionic PFOS molecules could easily interact with PE and PS-based MP surface due to the positive MP surface at lower pH.[152] However, at acidic pH, the adsorption of PFOS on MPs was dependent on the polymeric type of MPs. Differently, the sorption of FOSA on MPs was not affected by decreasing the pH because the sulfonamide functional groups in FOSA molecules make them nonionic in an aqueous solution. Some contaminants have several pK_a values and their adsorption on the MPs was also found to be strongly dependent on the pH of background solutions and pH_{pzc} of MPs.[132] Apart from OCs, the impact of pH on the adsorption of heavy metals was less investigated in the literature. Holmes et al. (2014) found that the adsorption of Cd, Co, Ni, and Pb on PE-based pellets in a river was improved by raising the pH due to the interactions of divalent cations with the functional groups of natural organic matter. In contrast, the adsorption of Cr(VI) was reduced by raising the water pH due to the weak coulombic interaction between positively charged pellets and the oxyanionic form of Cr ($HCrO_4^-$ and CrO_4^{2-}).[155] With the limited number of studies focusing on the adsorption of heavy metals on MPs, further research is required to elucidate the adsorption mechanism at different water pH values.

Ionic strength (salinity) also plays a paramount role in the adsorption of contaminants on MPs and significantly affects their fate and transport in the marine environment.[92,156] Ionic salts are involved in a variety of adsorption mechanisms, particularly those interactions with contaminants in aqueous water and on the MP surface, besides their effects on MP surface charge.[157] Hitherto, two distinctive impacts have been studied to characterize ionic strength in the adsorption of contaminants from adsorbents: (i) the impact of ionic salts on the adsorption capacity depends on the physicochemical properties of the selected contaminants (such as electrostatic nature, molecular configuration, and activity coefficient), which can reduce the solubility of weakly polar OCs (known as "salting out"), and hence improves the adsorption on MPs;[7] (ii) the increase in salt ions may cause a "squeeze-out" impact on the adsorbent reducing the adsorption of contaminants.[158] Ions may permeate the diffuse MP surface and reject contact between the MPs, facilitating the development (or squeezing out) of a more compacted aggregate structure.[7] Salt cations may also neutralize the negatively charged MPs and pollutants, reducing the repulsive force and causing MPs to migrate toward pollutants.[70] For instance, the adsorption of PFOS, carbamazepine, 17a-ethinyl estradiol, and 4-methylbenzylidene camphor on MPs was increased by increasing NaCl or $CaCl_2$ concentration due to the salting-out effect.[152] However, Na^+ ions may compete with the contaminant ions, and hence reduce the sorption capacities of contaminant ions on MPs. Another study also reported that the adsorption of tetracycline on MPs slightly decreased at higher ionic strengths of aging solutions.[115] In addition, the adsorbability of MPs at different concentrations of NaCl (0.01, 0.1, and 1.0 M) was also found to be similar, indicating that MPs whether aged in sea or fresh water will not affect the adsorption of OCs.[159] Another study reported that increasing the salinity slightly decreased the adsorption of DDT on PE and PVC based MPs.[160] When different salts (viz., NaCl, $CaCl_2$ or Na_2SO_4) existed during the adsorption of oxytetracycline on MPs, higher capacity was observed in the presence of $CaCl_2$.[115] The sorption is better in the presence of multivalent cations (such as Ca^{2+}) than monovalent cations (like Na^{1+}) because monovalent cations may strongly compete for cationic exchange sites (i.e., carboxyl groups) on the MP surfaces.[70] Apart from OCs, only one study has investigated salinity effects on heavy metals sorption on MPs,[155] and it reported that the adsorption of heavy metals (except Cu^{2+} and Cr^{2+}) on PE based MPs was influenced by salinity. Overall, due to the limited number of studies and contradictory reports, the impacts of salinity on the adsorption of OCs and heavy metals on MPs require further investigation.

Natural organic matter (NOM) includes diverse functional groups, which can interact with sediments or other contaminants, and therefore impact their fate and transport in aquatic environments.[161] Similar interactions between NOM and MPs are anticipated in aqueous water, and hence NOM can alter the adsorption behavior of other contaminants on MPs. NOM can suppress the adsorption of contaminants onto different adsorbents.[162,163] Two possible factors can affect the adsorption in the presence of NOM: (i) the accessible surface area of the MPs may be enhanced by better dispersion,[70] (ii) the sorption uptake may decline due to the competition by NOM with other contaminants on the active sites causing rapid pore/interstice blockage.[7,137] Since NOM carries negative charges at pH range from 4 to 8,[164] the accumulated NOM on PS-based MPs could cause electrostatic repulsion between MP particulates and thereby improve the dispersion.[45] Furthermore, the adsorption

of OCs was more enhanced in the presence of HAs than fulvic acids (FAs) due to the π–π conjugation between the HAs and MP surface which also led to enhanced electrostatic attraction for OCs.[115] On the other hand, molecular sieving and pore blockage could primarily dominate in the MP sorption process. Briefly, NOM molecules are larger than most contaminant molecules, therefore they can preferably enter or block the pores of MPs and prevent other contaminants from subsequently reaching the active sites.[137] A recent study indicated that there is no considerable interaction between the dissolved organic matter (DOM) and PS-based MPs, whereas considerable interaction with PS-based NPs was observed due to the π–π conjugation.[115] It may be imputed to the fact that when MPs are fragmented or degraded into NPs, the NOM molecules have less access to the inner regions of the NPs due to the reduced hindrance faced by the contaminant molecules in reaching the active sites on NPs. Such explanations increase the complexity of the interactions between contaminants and NPs. The influence of dissolved organic carbon (DOC) concentration – as an indication of DOC – on the adsorption of contaminants onto the MPs has been evaluated.[137,159] In general, the adsorption of contaminants onto MPs decreases at higher DOC concentrations, but it is also dependent on the MP type.[154] Consequently, the impact of NOM on OC adsorption solutions has been found to be dependent on several factors such as NOM composition (HAs *versus* FAs) and DOC concentration, in addition to the charge, size and polarity of contaminants, and the pore structure and surface chemistry of MPs.[137,154,156] However, the impacts of MP aggregation and stability on the adsorption of contaminants (especially heavy metals) in the presence of NOM and other organic matter (such as algal and effluent organic matter) are yet to be investigated. Therefore, further research is needed to present a comprehensive understanding of the impacts of organic matter characteristics (*i.e.*, hydrophobic, *vs.* hydrophilic, isolated *vs.* reservoir water, aromatic content, species of algae *etc.*) on MP aggregation and stability and their consequent influence on the adsorption of OCs and heavy metals.

The temperature of the water also affects the adsorption of contaminants on MPs.[7] The glass transition temperature (T_g) which indicates the temperature at which MPs change from rubbery to glassy is the paramount factor that influences the adsorption at different temperatures because it directly changes the crystallinity of MPs.[132] Apart from the crystallinity of MPs, the adsorption of OCs could be improved at lower temperatures due to the increase of surface tension and the reduction of solubility.[132]

7. Future suggestions

This review compiles all the paramount findings and highlights in the current review studies on MPs. The study covers the sources and environmental impacts, fate, toxicity, detection, and characterization of MPs in freshwaters, wastewater treatment plants, and drinking water. Besides, the adsorption mechanisms of OCs and ICs by commercial, consumer, and biodegradable MPs under various environmental conditions were comprehensively discussed.

The fate of MPs requires further investigation to be fully understood so that the potential environmental repercussions of MPs could be substantively investigated. The fate of MPs is dependent on their physical and chemical characteristics (*i.e.*, size, color, density, shape, chemical composition, surface charge, and coating), water types (*i.e.*, seawater, freshwater, algal impacted water or wastewater effluent), and hydrodynamics. The elucidation of the aggregation and deposition mechanisms, and behaviors in aquatic environments needs to consider all the aforementioned factors. Furthermore, the fate of MPs should also be correlated with substantive experimental results for commercial, consumer, and biodegradable MPs. Although the chemical structures and crystalline forms of commercial and consumer MPs may directly change their degradability, their effects on the degradation rate are yet to be fully discovered. For instance, biodegradation is the most prevalent degradation mechanism in water, however, there is a lack of knowledge about the effects of environmental parameters (*i.e.*, water chemistry, temperature), properties of MPs, and bacteria strains.

MPs in the natural environment have different chemical and physical characteristics inherited from their pristine polymers that can also influence their environmental fate and toxicity. Briefly, these characteristics are dependent on two main factors; (i) MPs undergo various modifications in the environment (*i.e.*, UV irradiation, fractionation to different sizes, water temperature, and salinity), and (ii) MP products contain constituents other than the plastic polymers (*i.e.*, binders, pigments, fillers, extenders, solvents, or additives). Not only the environmental conditions but also mixing MPs with additives and fillers is important for understanding the impact of these constituents on the fate of MPs. Fillers from different sources (*e.g.*, calcium carbonate, talc, graphene) can be critical for controlling the degradation of MPs in accelerated aging experiments. Furthermore, they also increase the sorption capacity of aged MPs (when compared to their precursor particles). This increase might also be linked to the changes in their surface morphology which increase the surface area by the introduction of surface cracks and pores. Accordingly, these hypotheses may be an area worthy of further investigation.

The detection and characterization of MPs in aqueous water are still big challenges for both lab-scale experiments and field studies. There is a lack of universally agreed sampling protocols and standardized methodologies for the identification and quantification of MPs. Therefore, further research needs to consider sampling design (*i.e.*, replicates, field area, collecting methods [*i.e.*, type of net and vessels for aquatic samples]), pretreatment methods for removal of organics and inorganics, and characterization and quantification of MPs. To date, researchers have used different pretreatment techniques to facilitate the characterization and quantification of MPs. However, these pretreatment techniques may alter MP structures, which consequently may change the characteristics of MPs (*i.e.*, aging, color, size, shape, aggregation, *etc.*) and background water chemistry. Therefore, the scientific society and environmental agencies should unify and develop standard

methods for the pretreatment and characterization protocols of MPs.

The adsorption of OCs and ICs on MPs is dependent on the physicochemical properties of both adsorbates and MPs in addition to the background water chemistries. The effective physicochemical properties of contaminants include the molecular size, geometrical configuration, hydrophobicity, and substituent groups. On the other hand, the characteristics and modifications of MPs such as surface area, surface charge, color, shape, and age are the most important parameters that could improve or suppress the adsorption. The adsorption uptake rates are also dependent on the background water characteristics (*i.e.*, pH, ionic strength, temperature, NOM, and competition ions). Most of the studies in the literature focus on the adsorption of OCs, whereas the adsorption of ICs such as heavy metals has been rarely investigated. More research is needed to understand the adsorption of different OC and IC classes (*i.e.*, aromatic *vs.* aliphatic, ionic *vs.* nonionic) onto MPs under varying environmental conditions. Moreover, understanding the impacts and role of each adsorption mechanism needs further investigation. All these interactions may be influenced by the molecular configuration of contaminants and MP type (*i.e.*, consumer, conventional and biodegradable) and are all possible contributors to the adsorption of contaminants by MPs. More research is needed to learn more about the adsorption affinity of different classes of pollutants on various types of MPs.

Acronyms

ATR	Attenuated total-reflectance
BOD	Biochemical oxygen demand
DDT	Dichloro-diphenyl-trichloroethane
DDW	Distillated and deionized water
DLVO	Derjaguin–Landau–Verwey–Overbeek
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EDA	Electron donor–acceptor
EDCs	Endocrine disrupting compounds
EDL	Electrical double layer
EDS	Energy-dispersive X-ray spectroscopy
FOSA	Perfluorooctanesulfonamides
FPA	Focal plane array
FTIR	Fourier transform infrared
GC	Gas chromatography
HAs	Humic acids
HDPE	High-density polyethylene
ICs	Inorganic contaminants
LC	Liquid chromatography
LDPE	Low-density polyethylene
MBR	Membrane bioreactor
MDPE	Medium-density polyethylene
MPs	Microplastics
MS	Mass spectrometry
NOM	Natural organic matter
OCs	Organic contaminants
WWTPs	Wastewater treatment plants

PA	Polyamide
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PE	Polyethylene
PET	Polyethylene terephthalate
PFAAs	Perfluoroalkyl acids
PFAS	Per- and polyfluoroalkyl substances
PFOS	Perfluorooctanesulfonate
pH_{pzc}	The pH at the point of zero charge
PP	Polypropylene
PPCPs	Pharmaceuticals and personal care products
PS	Polystyrene
PVC	Polyvinylchloride
ROS	Reactive oxygen species
SEM	Scanning electron microscopy
SRT	Solid retention time
T_g	Glass transition temperature
TOC	Total organic carbon

Disclaimer

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Conflicts of interest

Authors have no conflict of interest to report.

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