

Edited by Xinxing Zhang

Microplastics in the Environment

From Formation to Remediation



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Editor

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Preface

Plastics are indispensable in modern society due to their high performance, low cost, and easy processing, with a wide range of applications from packaging to aerospace. However, their environmental impact has raised increasing concerns, particularly microplastics (<5 mm) that are fragments of plastics. Microplastics have a large specific surface area, making them prone to carrying environmental pollutants and posing severe toxicological risks. Microplastics have been reported to exist in oceans, soils, and even polar permafrost. Furthermore, microplastics might transfer and accumulate through the food chain, leading to amplified harm. Current microplastic remediation technologies face numerous challenges, such as low efficiency, high costs, and difficulties in large-scale implementation.

This book provides a systematic and comprehensive description of microplastics from formation to remediation in the environment. The book consists of four sections, including microplastic formation process, transport mechanisms, toxicological effects, and potential solutions. The first chapter discusses the generation behavior of secondary microplastics of different polymeric product forms (plastic, rubber, fiber, and foam), combining aging factors, mechanical wear, and biological action. The second chapter reviews the distribution characteristics and the biotic and abiotic transport of microplastics in water, soil, and atmosphere. The third chapter involves the toxic effects of microplastics on estuarine and marine organisms, freshwater organisms, soil organisms, and human health, focusing on the enrichment of microplastics in organisms and the toxic mechanisms. The fourth chapter overviews the solutions to microplastic pollution, including the reduction in the usage of plastics, the development of substitutable plastics, the recycling of waste plastics, and the remediation strategies for existing microplastics in the environment.

This book may serve as an essential resource for understanding the lifecycle, risks, and solutions associated with microplastics, offering valuable insights for researchers, policymakers, and environmental practitioners.

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Microplastics Formation

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1.1 Definition of Microplastics

Over the last few decades, plastic contamination has become a major cause of concern among scientists, politicians, and the public. The world production of plastic surpassed the 320 million tons mark in 2016, most of which is intended for packaging, i.e. for immediate disposal. Consequently, these materials significantly contribute to waste generation, and it is estimated that between 5 and 13 million tons leak into the world's oceans every year [1]. When inappropriately dumped or mismanaged, plastic waste can accumulate in both terrestrial and marine environments, and once released, it may be subjected to degradation by several agents or routes, such as solar radiation, mechanical forces, and microbial action. This leads to fragmentation and breakdown of larger materials into plastic debris and eventually nanoplastics (NPs), though the latter has only been recently identified as potentially deleterious toward the environment, and research is currently underway. In addition, these particles can be intentionally produced with micro- and nano-sizes and disposed of directly into the environment [2]. Microplastics (MPs) are defined as debris smaller than 5 mm. Mesoplastics are defined as plastic debris within the 5 mm–20 cm range, while MPs are defined to be less than 5 mm in size, according to the National Oceanic and Atmospheric Administration (NOAA) workshop consensus definition. However, as far as the authors are aware, the lower limit for defining MPs remained undefined for a long time. Recently, two categories have been proposed: large MPs in the 1–5 mm range and small MPs defined as micrometric particles, that is, below 1 mm [3]. These categories were confirmed by Galgani et al. [4] and suggested for adoption by the European Marine Strategy Framework Directive (MSFD) (precisely, large MPs were defined by the range 1–5 mm and small MPs by the range 20 μm –1 mm). Nanosized plastic particles are referred to as NPs (1–1000 nm size range) [5]. In 2008, Klaine et al. defined NPs as particles with at least two-dimensional diameters between 1 and 100 nm [6]. However, some studies defined NPs as plastics with particle sizes between 1 and

1000 nm [7, 8]. Although there are some controversies about the definition of NPs, the definition of NPs with a particle size of 1–1000 nm is generally accepted by researchers. Here, MPs are defined as debris smaller than 5 mm, and our book defines NPs as plastics with particle sizes between 1 and 1000 nm.

When discussed in detail, MPs in the environment are usually categorized as primary or secondary MPs (PMPs or SMPs) depending on their source [9]. PMPs are MPs produced without aging, whose primary source is particulates specifically manufactured for commercial applications such as personal care products and cosmetics [10, 11]. In general, they include plastic pellets used as raw polymer materials, cosmetic microbeads, and sandblasted plastic microbeads [9]. SMP are smaller fragments formed from larger plastic products (e.g. fishing nets, plastic bottles, and films) that have been broken up through the effects of aging processes, biological action, and mechanical wear [12, 13]. Notably, SMPs are being generated in an increasing number of obsolete consumer products, and many studies have shown that SMPs account for the majority of MPs in the environment, including oceans, rivers, mountains, landfills, and even drinking water [14–19].

Due to the small particle size, high specific surface area, remote migration, and contaminant adsorption capacity, these particles can be ingested by several species, leading to direct physical damage and potential toxicity effects [2]. MPs may also leach plastic additives, including persistent organic pollutants (POPs) and potentially toxic elements that are adsorbed in higher concentrations than those found in the surrounding environment. These pollutants may transfer and accumulate in different tissues of organisms, possibly undergoing biomagnification along the food chain. Hence, the consumption of contaminated seafood poses a route for human exposure to MPs, POPs, and potentially toxic elements [20]. POPs, including polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), have also been shown to accumulate on MPs, thus enhancing their potential toxic effect in the environment [21–23]. Recently, Jovanović reported potential negative effects of the ingestion of MPs and NPs by fish, including possible translocation of MPs to the liver and intestinal blockage, yielding not only physical damage but also histopathological alterations in the intestines and modification in lipid metabolism [24]. Hence, it is of urgent and significant importance to clarify formation mechanisms, transport processes, toxicity of composite pollutants, and control technologies, which can provide meaningful guidance for production and use of plastics and thus prevent MP pollution.

1.2 Types of Microplastics

Many studies have given information about the most widespread species of MPs in terms of the distribution of plastic debris in systems such as soil, freshwater, and oceans. It reveals that polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyester, polyamide (PA), and polylactic acid (PLA) are found in a variety of locations, and the majority of environmental MPs are concentrated in the top five, which are also the most common types of plastic products

[25–29]. Plastics with simple composition are basically composed of polymers without any additives. Some types require only small amounts of additives, such as PE and PP. However, most plastics are multicomponent systems that contain a wide range of additives, in addition to the basic polymer component (generally 40–100% polymer). The most important additives can be divided into four types: lubricants to help with processing; fillers, enhancers, impact modifiers, plasticizers, etc., to improve the mechanical properties of the material; flame retardants to provide the flame resistance; and various stabilizers to improve the aging resistance during use. Understanding the composition of plastics is essential for the study of MP formation mechanisms, generation behavior, and even toxicological effects.

1.2.1 Polyethylene

PE has sufficient sources of raw materials and has excellent chemical corrosion resistance, low-temperature resistance, and good processing fluidity. Therefore, the production of PE and its products has developed very rapidly. Since 1966, the production of PE has been the first in the world in terms of plastic production. Due to the simple molecular structure of PE and its good flowability at high temperatures, only small amounts of plasticizers need to be added during the molding process. Excellent processing properties and low cost are the advantages of PE being used in a wide range of film products.

1.2.2 Polypropylene

PP and PE are both polyolefins with similar properties and use. Compared to PE, the molecular chain of PP is less flexible and more rigid, so PP is stronger and harder than PE, presenting a more rigid performance. Another characteristic of PP plastic in performance is its low density, which is the lightest of the commonly used plastics and can float on water. The heat resistance of PP is also better, with a long-term use temperature of 100–110 °C. Even PP does not deform when heated to 150 °C without external forces.

The biggest disadvantage of PP films is the poor aging resistance than PE, mainly owing to the fact that PP has many methyl groups on its main chain, and the hydrogen on the tertiary carbon atoms connected to the methyl groups is easily attacked by oxygen [30]. Therefore, PP plastics are usually subject to the addition of antioxidants and UV absorbers, which greatly affect the generation behavior of PP MPs. For example, variable-valent metal ions such as copper and manganese ions accelerate the oxidative aging process of PP. Metal ion inhibitors are a class of additives that can complex with the variable-valent metal ions to reduce the catalytic oxidative activity of these metal ions. Some of the commonly used ion inhibitors are aldehydes and diamine condensates, oxamide compounds, hydrazide compounds, and so on. Light shielding agents, such as titanium dioxide, are also frequently added to PP to protect the polymer, which will directly reflect light or absorb specific light waves and then convert light energy into heat to scatter. The introduction of metal ion inhibitors and titanium dioxide will greatly slow down the photo-aging process of PP plastic products in nature and reduce the generation of PP MPs.

1.2.3 Polystyrene

The main chain of PS is a saturated alkane chain, and its side groups are benzene rings with large spatial positional resistance. The irregularity of the molecular structure increases the site resistance while affecting the orderly arrangement of molecules; thus, PS has large rigidity but is not easy to crystallize, which is a typical linear amorphous polymer. PS plastic is a transparent hard solid at room temperature, whose light transmission rate (88–92%) is second only to Plexiglas. The extremely small water absorption is the distinguishing feature of PS, which hardly absorbs water at room temperature. In addition, due to the absence of polar groups in the molecular structure, PS has excellent corrosion resistance and electrical properties. PS plastics obtain better mechanical strength due to the presence of benzene rings but also face poor impact strength and brittle cracking due to the lack of flexibility of the chain segments caused by the benzene rings. There is another noteworthy aspect of PS plastics related to the generation of MPs. Although PS is one of the most radiation-resistant polymers, it becomes brittle when cross-linked at high doses of radiation. These brittle qualities are potentially important reasons for the breakage of PS into plastic fragments and the generation of MPs. PS plastic is now widely used in industrial decoration, lighting indication, and electrical insulation materials, as well as optical instrument parts, transparent models, toys, and daily necessities. According to the different usage requirements of PS plastic products, coloring agents, plasticizers, light stabilizers, flame retardants, anti-static agents, and other additives will be added in appropriate amounts.

1.2.4 Polyvinyl Chloride

PVC, in terms of molecular structure, has polar chlorine atoms in the molecular chain, which increases the intermolecular force. The chlorine atom on the side group hinders the rotation within the single chain, and thus compared to PE, the flexibility of the molecular chain decreases while the rigidity increases, resulting in high compressive strength, surface hardness, and good rigidity but low elongation of PVC products. When the operating temperature is lower than 0 °C, the products will easily become hard and brittle, and PVC MPs will be generated in large quantities. PVC is divided into rigid PVC and soft PVC according to the requirements of usage performance, which is controlled by the different amounts of plasticizer added during processing and molding. Most commonly used plasticizers are esters synthesized from fatty alcohols with carbon atoms of 6 to 11 and phthalic acid, which are utilized to reduce the intermolecular forces of PVC, thus having the effect of lowering the molding temperature of the polymer, as well as reducing the modulus, rigidity, and brittleness of the product. Industrial plasticizers used in PVC processing are the most major ones, accounting for about 80% of plasticizer usage. Rigid PVC plastic can be made when a small amount of plasticizer is added to the production. It has high mechanical strength and is resistant to acid and alkali corrosion, so it can be used to replace some valuable stainless steel and other corrosion-resistant materials to manufacture various downpipes and joints. It is widely used in agricultural drainage and irrigation, urban downpipes, and exhaust pipes. When plasticizer is added at 30–40%, soft PVC is produced. Although the tensile strength and bending

strength are lower than those of rigid PVC, the elongation is high, and the products are soft. The main disadvantages of rigid PVC plastics are poor processability, thermal stability, and impact resistance. On the other hand, soft PVC plastics are susceptible to plasticizer volatility, migration, and extraction during use. Another significant characteristic of PVC is its very poor thermal stability. In air above 150 °C, PVC degrades and emits HCl, which acts as an autocatalyst and promotes degradation. Macroscopically, the color of the product turns yellow and, finally, black. Therefore, a large number of heat stabilizers must be added to PVC plastics. Organotin compounds are the most common heat stabilizers for PVC products, while others include metal salt compounds. The abovementioned plasticizers and heat stabilizers are generally toxic and can cause adverse effects on living organisms.

1.2.5 Polyester

Polyester mainly refers to PE terephthalate, which is primarily used as the fiber. Polyester is a linear macromolecule with a symmetrical benzene-ring structure and neat arrangement of functional groups on the molecular chain, so it has high density, softening point (230 °C), melting point (250–260 °C), heat resistance, and light resistance. The presence of a benzene ring hinders the internal rotation of the molecular chain, making its macromolecular backbone rigid and resistant to deformation, with high initial modulus and excellent recoverability. In addition, the structure of polyester also contains methylene, so it has a certain degree of flexibility, which endows the fiber with good elasticity. It is worth noting that the ester bond of polyester will be oxidized during the long-term use of the fiber, thus leading to oxidative cleavage of the molecular chain and the generation of carboxyl groups. The result is decreased molecular weight, reduced strength, yellowing of the color, and even the generation of MPs. Particularly, the ester group will undergo hydrolysis or alcoholysis with water and alcohol at high temperatures, which will damage the fiber as well. Due to the regularity of the molecular chain, polyester has the ability to form crystals by the orderly arrangement in three-dimensional space. Although the trait is limited by the benzene ring, the crystals are more stable once polyester has been stretched to form them. Therefore, polyester has a high degree of crystallinity overall, which is also closely related to the formation of MPs. Besides fibers, polyesters are also widely used in the preparation of films and hollow plastic bottles. However, the main drawback of polyester is its poor processability, which is due to its low crystallization rate. Nucleating agents and other additives are now needed to increase polyester crystallization speed to improve molding processability.

1.3 Generation of Microplastics

Due to their small sizes, MPs are easily introduced into the body by organisms through nutrient intake, causing a range of physical effects and toxicological reactions [31, 32]. In addition, the high surface area of MPs tends to complex and enrich with various contaminants such as PCBs, PAHs, antibiotics, heavy metals, and organochlorine pesticides. These adsorbed chemical pollution complexes have been proven in numerous studies to be highly toxic and harmful to marine

organisms, soil microorganisms, and plants [12, 33–38]. Therefore, a detailed and extensive discussion of the degradation processes, formation mechanisms, and generation behaviors of secondary MPs is a very important and urgent task, which is essential to improve our understanding of the threat of environmentally relevant MPs to ecosystems and the biosphere.

1.3.1 Primary Microplastics

Due to the many benefits of plastic, its use has increased, but improper waste management has led to the entry of these materials into the environment. One of the emerging contaminants of plastics is MPs, which are plastic particles smaller than 5 mm. MPs can be present in the environment as manufactured MPs (known as primary MPs) or resulting from the continuous weathering of plastic litter, which yields progressively smaller plastic fragments (known as secondary MPs) [39]. Categorizing MPs into primary and secondary particles is beneficial to help identify their sources and a solution to reduce their entry into the environment.

MPs are released into the environment from both primary and secondary sources [19]. Primary MPs often refer to pellets and personal care and cosmetics products (PCCPs), which are produced and enter the environment with small sizes [9]. However, some studies have proposed a broader range of primary MPs [40, 41]. They proposed that primary MPs include not only intentionally created MPs (e.g. PCCPs) but also by-products during the use of related plastic products (such as microfibers detached from clothing, tire dust from running cars, and MPs discharged from artificial turfs and paints), as well as unintentionally released ones (e.g. pelleted raw materials) [42]. They considered that primary MPs are those as adding new plastic materials of micro size to the environment [43].

Primary MPs are mostly produced as part of the daily plastic product use. The emission process is often invisible but poses potential ecological hazards. Primary MPs are inherently small in size, including resin pellets, micrometer pellets in personal care products, industrial scrubbers used in cleaning materials, and plastic powders used for molding, which contain PE, as well as PP and PS. Furthermore, primary MPs are at least less than 10 μm in size, and their average size is between 150 and 330 μm [39]. On the other hand, primary MPs are generated from the breaking of larger plastic particles. For example, up to 700 000 synthetic fibers can enter the water in a washing process, which falls into this category. These textiles are mainly composed of polyester (78%), followed by PA (9%), PP (7%), and acrylic (5%) [44].

Based on the relevant literature, we identified the main sources of primary MPs [45, 46]. The finalized list generated for this study included the following: (i) synthetic fibers produced during the laundry process and present in household/indoor dust, (ii) microbeads produced in the use of PCCPs, (iii) marine coatings (shedding of paint during the use of the ship or removal of old paint during maintenance), (iv) vehicle paint (flaking and chipping of the paint in original equipment manufacturer (OEM) or paint emissions during refinishing), (v) road markings, (vi) architectural coatings (such as paint falling off during the process of painting buildings), and (vii) plastic dust (pellets) from raw material production or generated during transport [44]. Given the known use of MPs and in view of desired product properties,

consumer product categories containing primary MPs are determined. Synthetic fibers (i) and microbeads (ii) are primary MPs released from consumer products, and others are from industrial processes.

1.3.1.1 Industrial

Primary MPs may be added to coating products to achieve specific functional requirements such as weight reduction, scratch and abrasion resistance, and elasticity. Plastic particles, such as (hollow) microspheres (5 to 80 μm) and microfibers (0.5 to 50 μm) that are artificially incorporated or present in the design in the size range of 1 nm to 5 mm can be added to coatings [47]. These microspheres can reduce the mass of the coating, improve the application function of the coating, allow thicker coatings and provide unique coating film properties such as elasticity and scratch resistance. Microfibers can improve the toughness of coatings, act as a joint in cracks and joints in walls or ceilings and increase the thixotropy of undried coatings. Water-based coatings contain “polymer dispersions in water,” which are considered virgin-grade MPs and consist of dispersed polymer particles. They act as a binder in the cured coating but are still the main MPs when the coating is not handled properly; for example, when fluids are poured down the drain [48]. Possible sources of coating-related virgin MPs include the following applications: (i) paints: architectural, industrial, automotive, wood, marine (including antifouling), etc.; (ii) road marking paints; (iii) sandblasting of old coatings using plastic materials [49].

Primary MPs can be released by draining waste waterborne paint down the drain and rinsing brushes and rollers under the tap. This release of polymer particles and intentionally added microspheres/microfibers from liquid waste paint occurs from time to time. It is important to note that the MPs will enter the sewage system and eventually the publicly owned treatment works (POTW), and a proportion of them will enter and be present in the sludge of the sewage treatment plant [50]. In recent years, environmental pressure to control volatile organic chemicals (VOCs) has led to the rapid development of waterborne coatings, and changes in the composition of waterborne coatings have led to changes in other characteristics of the coating products. Waterborne coatings contain MPs (emulsions containing dispersed solid polymer particles), whereas solvent-based coatings do not contain MPs (dissolved polymers) [51]. The change from solvent-based to water-based paints may result in increased environmental releases of primary MPs through the disposal of waste water-based paints in drains.

The main components of coatings are fillers, film-forming resins, additives, and dispersing media. Many natural resins and synthetic polymer resins can be used as film-forming resins in coating products. The film-forming resins used in coatings are usually based on carbon-chain polymers such as alkyd, polyester, acrylic, polyurethane (PU), and epoxy resins, which form a solid coating after the coating has been applied. The chemical properties of the coating MPs will, therefore, depend on the main components chosen for the coating product. In addition, coatings are complex mixtures of many compounds, some of which are associated with potential health effects in biological organisms (e.g. biocides in antifouling coatings) [9]. Whereas solvent-borne paint polymers are dissolved in the paint system, water-borne paints are essentially emulsion systems in which polymer particles are

dispersed. The size of the polymer particles has a different effect on the performance of aqueous coatings, with the fine particles enhancing the film formation and pigment adhesion of the coating, as well as increasing the viscosity of the coating. Polymer particles in aqueous coatings generally range from 80 to 1000 nm [52].

The shapes of primary grade MPs added to marine coatings include microspheres/beads, but most coating formulations do not contain microspheres as a component. Acrylic polymers range from 5 to 80 μm (0.005 to 0.8 mm), and acrylic polymer nanoparticles are used as binders ranging from 50 to 200 nm (0.000 05 to 0.000 2 mm). The polymer particles in aqueous coatings range from 80 to 1000 nm (0.000 08 to 0.001 mm). The particle size of microspheres added to coatings ranges from 5 to 80 μm (0.005 to 0.08 mm) [53]. It has also been reported that the size of microspheres added to coatings can range from “a few to several hundred microns” and that microbeads for reflective purposes can have diameters of up to several millimeters. The size of microfibers added to coatings ranges from 0.5 to 50 mm. PA or polyacrylonitrile fibers are 4 to 50 mm long and have a diameter of 10 μm (0.01 mm). MP coating particles are denser than MPs of the same size. Theoretically, paint particles of the same size and shape as MPs are easier to deposit and less mobile in aquatic systems [54].

Reflective glass spheres collected from San Francisco Bay, US, are part of road marking coatings ranging from 0.25 to 1 mm. In addition to the polymer binder, most coatings usually include fillers (glass beads) that provide abrasion resistance and increase tire grip as well as light reflectivity. Road marking paint granules are “irregularly shaped” chips and road marking paint granules are “colored, rounded and with a rough surface.” Road marking paint particles and road dust are also described as fibrous [55]. The density of the MPs associated with road marking paint is approximately greater than 1.2 g cm^{-3} .

Air blasting and industrial abrasive technology are special procedures in which compressed air generates pneumatic velocity for the abrasive material to be pushed to the surface through nozzles. Industrial abrasive technology and air blasting are commonly utilized to wipe out rust, color, and other contaminants from steel surfaces, such as ship hulls, machines, engines, and walls before new coatings are added through the media blasting process. MPs as abrasive media (including acrylic and polyester) are the best media for mold washing. Popular sectors that use air blasting technology include automobile, aircraft, boating, telecommunication, and manufacturing industries. Waldschläger et al. [56] reported that the MP particle size used as abrasive media is around 0.2–2 mm, which can be considered a primary source of MP pollution. This issue is a major concern in harbors and ports because huge tankers are stripped of paint, and the untreated wastewater is released directly into the sea. According to the data, the plastic particles used for sandblasting are in the range of 0.15 to 2.5 mm. In contrast, at the lower limit of the statistical values, the range of plastic media used for sandblasting materials for stripping coatings is 0.012 to 2.03 mm. Microbeads have been used for sandblasting materials. The relative density of sandblasted particles is generally greater than 1000 kg m^{-3} , indicating that they do not float and drift [57]. Similarly, European Chemicals Agency (ECHA) states that the particle size of sandblasted materials “typically ranges from 0.15 to 2.5 mm with

a relative density greater than 1000 kg m^{-3} , indicating that the particles will not float on water.”

1.3.1.2 Consumer

Primary fiber MPs are synthetic fibers less than 5 mm in length that are released or shed from the fiber material during the production and processing process. There are two forms of shedding, from the surface of the fabric and the cut edges of the fabric [36]. The two types of shedding coexist during the production of the fabric, and the surface shedding is predominant during daily use due to the hemming design of the fabric. In the first stage of washing, most of the shedding is in the form of floating fibers in the fabric. The amount of fiber MPs release depends to a large extent on the fibers, the yarn, and the processing of the fabric. Fiber MPs that do not leave the fabric in time for the production phase cannot be ignored.

Fiber MPs are produced and spread to the environment at all stages of the textile life cycle. The carding, drafting, and finishing of fibers in the yarn formation and weaving process cause damage to the fibers/yarns and form fiber MPs. Textile mills have special ventilation and dust removal systems that allow fibers and dust to enter the air through ducts. The garment care process also generates a certain amount of fiber MPs, and drying fabrics using a drying cycle increases the release of fiber MPs by a factor of 3.5. Washing one garment in a washing machine makes 100 to 1000 fiber MPs being shed and an increase in fiber MP release during washing. The Norwegian Environment Agency reports that household laundry discharges 600 t of effluent per year, and fibers shed in textile washing are bound to be of concern as an important source of fiber MPs in the water environment [58].

The type of fiber affects the formation of fiber MPs, and it has been found that washing a 660 g polyester fabric can shed between 220 and 260 mg of fiber, while cotton fabrics shed even more fiber during washing. Francesca et al. found that the amount of natural fibers in air and water was 97% and 80%, respectively, mainly because polyester is highly crystalline and does not swell and break significantly in water [59].

The shorter the fiber length, the higher the likelihood of fiber migration to the yarn surface and the greater the release of fiber MPs during the washing process. Polyester filament woven fabrics are made from continuous filaments. As the twist increases, the resistance to fiber migration and elasticity within the yarn increases, resulting in a more compact yarn structure, whereas cotton yarns are short fiber yarns with large length irregularities and a higher number of fiber slips, which leads to more hairiness on the surface of the yarn, which can be stretched to varying degrees during the washing process, resulting in fiber shedding [60]. At the molecular level, the macromolecules in the amorphous zone are stretched, the bond lengths and angles become larger, other molecules are broken or even pulled out, and eventually, the macromolecules are unevenly stretched and slip off until they break.

Fabric structure is also an important factor in the shedding of fibrous MPs. Woven fabrics are more compact than knitted fabrics and produce less fiber MPs. Plain fabrics are less susceptible to abstraction at higher warp and weft densities because of the relatively high number of interweaving points, the strong attachment of fibers

to the fabric, and the narrow inter-fiber spaces; satin fabrics also release the least amount of fibers into the atmosphere at higher warp and weft densities, but are more likely to produce fiber MPs than plain fabrics; twill fabrics shed the least fibers at moderate warp and weft densities [61]. Because the fabric structure affects the flatness and feel of the fabric and the amount of friction that exists during washing is influenced by the flatness of the surface, fabrics with low abrasion resistance, high hairiness, and low yarn breakage strength have a higher tendency to pile up and release fiber MPs during mechanical washing, with the broken fibers forming a short layer of fuzz on the surface of the fabric, which is subjected to various mechanical forces during washing and becomes less able to adhere to the fabric and eventually falls off. Eventually, they fall off. The production of fiber MPs in knitted fabrics is also very closely related to the tissue, and the basic rules are the same as for woven fabrics.

The yarns are bent and stretched by external forces in the course of use, resulting in damage and the formation of hair feathers on the yarn surface that break off and produce fiber MPs. During daily wear and use, loose fibers protrude from the surface of the textile and are then subjected to mechanical forces such as friction between the fabric and the laundry, between the laundry and the cylinder wall, between the laundry and the water, and the force of the water flow [62]. In a domestic drum washing machine, when the laundry is placed in the drum, the inertia causes the laundry to move slowly, increasing the contact area between the laundry and the water, and the laundry is deformed by the difference in speed between the laundry and the water flow, resulting in bending and elongation of the fibers and eventual damage and breakage [62]. The friction between the clothes causes relative movement between the clothes and the stains, which promotes the removal of dirt from the surface of the clothes, while the microplastic fibers fall off under mechanical action.

Friction between garments causes the most wear and tear, and damage caused by friction can be divided into two types: superficial damage and decolorization damage. Superficial damage is caused by the frictional force of washing, resulting in the surface of the clothing in the yarn of the fibers disperse into extremely fine hair-like feathers, which fall off. If not removed these fibers will form small balls, and under the action of mechanics, this process will extract a certain amount of hair feathers, and friction is very easy to make it break, thus accelerating the formation of fiber microplastic, mainly in the softer fine fabrics. The damage occurs on garments that have been washed over a long period of time, where the surface is white or even worn, and where the fibers are easily dislodged [63]. The ability of the fibers to shed MPs is therefore largely dependent on the formation of lint and the ease with which these fibers can be broken off by external forces in the washing machine before forming a hairball.

As primary MPs have a high surface-to-volume ratio (which increases with the decreasing linear dimension); their role in ecological impact is crucial, especially as vectors for pollutants and viruses or substrates for biofilm. One can classify them further as those originating from industrial dust, washed-out from synthetic textiles, transferred to waters as a spillage of nurdles, or being an ingredient added to cause surface abrasion (in cosmetics or detergents). Particles originating from those sources are persistent and ubiquitous, freely passing the wastewater treatment

plants (WWTP) [64]. One can estimate the number of microbeads added to domestic sewage in a single use is >200 000. Primary MPs dominate environmental samples filtered from waters, soils, or airborne. The MPs from cosmetics, comprising >90% PE and also PP, PET, polymethyl methacrylate (PMMA), and nylon, were already studied locally in many research studies [42]. According to the European Cosmetic Ingredient Database, currently added abrasive agents in cosmetics include, among others, the following: PE, PLA, hydrogenated poly (c6–20 olefin), ethylene/propylene copolymer, ammonium acryloyldimethyltaurate/laureth-7 methacrylate copolymer, and 1,4-butanediol/succinic acid/adipic acid copolymer. Research conducted in the UK estimated the number of microbeads released in a single use to be between 4594 and 94 500 particles. This considerable amount of particles varies in size, shape, roughness, and sorptive properties comparable with the transport potential. Primary MPs are potential vectors for hydrophobic pollutants with a considerable affinity to dichlorodiphenyltrichloroethane (DDT) [65]. The transfer of hydrophobic substances (PAHs, PCBs, and PBDEs) from plastic to biota was already proved. Fortunately, the increasing awareness of the problem caused the systematic reduction in primary MPs on the market. The EU has reduced primary MPs in cosmetics from 4360 tonnes in 2012 to 793 tonnes in 2015. From 2020, MPs as exfoliating agents in cosmetics are entirely forbidden. The bans in the US and UK prohibit the use of MPs microbeads in rinse-off cosmetics. However, there is still a need to extend these strategies and policies [66].

Singers, celebrities, models, performing artists, and not to mention many ordinary people use makeup materials, clothing, and objects extensively containing glitters to achieve a more attractive look [67]. These products are promoted, advertised, and sold with the help of beauty, makeup, and shopping websites, as well as influencers using their social media accounts and bloggers. To boot, many childrens movies entail animations with characters composed almost completely of glitter. That is why this shiny material's popularity increases each day, leading to increased use of an expanding range of products.

Shows, fashion events, celebrations, marches, and festivals take days and even weeks (Mardi Gras – United States, Coachella Valley Music and Arts Festival – United States, Rio Carnival – Brazil, Carnival of Venice – Italy, Halloween, etc.) see excessive use of glitters. For example, in 2011, nearly 70 kg of glitter was used in the Toronto Santa Claus Parade alone. Between 1989 and 2009, more than 4.5 million kg (10 million lbs) of glitter were purchased in the United States [68].

People do not content themselves with the use of glitters on themselves alone but apply them to animals as well. For instance, there are a number of firms applying various patterns and figures using glitters on the bodies of horses, including their eyes, trunk, legs, hooves, mane, and tail. At times, glitter madness reaches extreme levels, and some people cover their whole body with glitter, from head to toe (even their tongues). It is obvious that a person who covers their hair and whole body with glitter would be shedding millions of MP particles all around, as well as into the sewer system during a shower. Therefore, “MP litter” could be an apt description for glitter.

Glitters are used not only in makeup and cosmetics products but also in kindergarten, preschool settings, and primary schools for various art class purposes.

Thinking that these activities are guided by otherwise educated and informed teachers is a true source of pessimism. Glitters are used as a coating material for new puzzles, ornaments, metal objects, masks, ethylene-vinyl acetate (EVA) stickers, various toys, doll hair, crayons, and much more [69]. Moreover, play-dough, a material hitherto reported to be swallowed by children, and materials marketed as kinetic sand can also contain excessive amounts of glitter. It is widely known that children younger than the age of 3 are inclined to put into their mouths and swallow whatever they can put their hands on, including various objects, paints, and articles. Indeed, today, kindergartens are at the stage of excessive use of glitters along with similar ornamental materials, craft, and do it yourself (DIY) materials such as flakes and beads, which had hitherto been popular items in these activities [69]. Today, these materials are almost universally made of plastic. Products such as Slime, which are favorites among children and known to contain borax – widely considered a health hazard – are also characterized by the involvement of plastic glitters, not to mention other types and forms of plastic polymers (PET, PE, PP, PS foam [Styrofoam]). Yet the dangers of MPs in these products are almost completely ignored.

Glitter is not a basic need. In a psychological hierarchy of needs, the need to use glitters can arise in the sixth stage (esthetic needs) and above of the extended hierarchy of Maslow. Based on Maslow's beliefs, it is stated in the hierarchy that humans need beautiful imagery or something new and esthetically pleasing to continue up toward self-actualization. Humans need to refresh themselves in the presence and beauty of nature while carefully absorbing and observing their surroundings to extract the beauty that the world has to offer. Glitters are pleasing to human beings as they allow one to stand out among the crowds of ordinary people and thus see extensive use [70]. Maybe its sparkle reminds us of water resources or sunlight. Shiny objects have hitherto been associated with spiritual powers. Glitter symbolizes vividness, joy, and hope. Shiny materials can attract people and even animals. There is a rough consensus that human beings love to stand out with a shiny look and play with shiny things, likely because glitters are associated with wealth and status or a glittering of nature.

In recent years, the increasing use of glitters can be observed in many products, including textiles, shoes, bags, ornaments, and more. Manufacturers apply glitter-coated patterns even on children's clothing made of 100% cotton, 100% organic materials, and not to mention other textile products. To make the matters worse, such glittery and shiny products attract substantial consumer interest. As these clothes are washed a few times, the glitters are shed into the water and eventually find their way into sewer systems. In addition, the microfibers shed by synthetic textile products, which are produced by thousands of tons each year, are also an undeniable source of MPs.

On top of all these, nowadays, most haberdashery products such as sequins, beads, and buttons are made of plastics such as PET, recycled PET, PVC, nylon, polyester, and melamine. The fact that some of these are made of recycled PET, is a small consolation from an environment perspective. Sequins are used widely on various evening dresses for special occasions such as proms, weddings, and other ceremonies, as well as on other goods. They even find their way into daily clothing items

produced for children in the form of patches ornamented with sequins or sequined fabrics (e.g. multicolored reversible sequins) [71]. It should be evident by now that plastic glitters and similar small particle materials such as sequins and beads, used in excessive quantities in the textile industry, are almost always produced from plastic polymers, and the use thereof pose major sources of plastic litters, which can affect land-based and aquatic ecosystems (biotopes and biocenosis) for centuries to come.

The term glitter refers to an assortment of small, flat, and reflective particles. Glitter is made of a plastic polymer known as Mylar™, which refers to a specific type of polyester film known as Biaxially oriented polyethylene terephthalate (BoPET). BoPET is a polyester made from stretched PET and is used for various purposes. The glitter (PET) particles have a true density of 1.38 g cm^{-3} and a melting point of 260°C . They are also insoluble in water. The particles are coated with metal (aluminum-coated PET glitter) in order to obtain high reflectivity.

Plastic glitters can be found in all colors, including gold and silver. They can even exhibit holographic qualities. The glitters can be produced in different shapes (in precision-cut pieces of uniform size, sometimes with notches): the most common shapes are hexagonal, including square, triangle, stripe, heart, star, crescent moons, diamond/rhombus, flower, snowflake, butterfly, irregular, and so on. Indeed, on e-commerce sites, suppliers often talk about providing 10 000 combinations of glitter colors, shapes, sizes, and materials. In the case of polyester glitters, $200 \mu\text{m}$ ($0.008''$) standard glitter flake size is the most popular and versatile one. As glitters are produced on a commercial scale using PET films, with marketed sizes below $< 5 \text{ mm}$, they can indeed be categorized as MPs.

Used widely in cosmetics products and household applications, glitters are known to be messy and easy to spill away. Thus, they are often sold in boxes with holes punched at the top. As soon as they are applied, the glitters shine, not only on the body, clothing, or objects they were applied on but also all over the place and often “on the ground” as well. Indeed, upon mere contact, they may be transferred from one carrier to another. It is found that glitters can effectively serve as forensic evidence, which can freely circulate in the environment and which is capable of contamination through contact with someone or something.

Regular glitters are manufactured from PET polymer. There are also varieties made of acrylic, PMMA, PVC plastic epoxy resin mixture, or melamine and phenolic resin mixture. However, renewable plant-based raw materials such as soluble seaweed, regenerated cellulose (sourced mainly from Eucalyptus trees), and glycerin (plant-derived) are also produced as alternatives to glitters [72]. Biodegradable glitters made of plant-derived materials and painted with mineral pigments are rather limited in terms of color and shape options, compared to what is on offer in the case of plastic ones, and are approximately 35% softer compared to the latter group. The plastic glitters, in turn, can be subjected to toxic finishes.

It is true that different types of natural phlogopite and synthetic fluorophlogopite mica glitters for cosmetic uses (shimmers) and edible glitters (mixtures of sugar, gum arabic, and cornstarch for food and cake decorations) also exist.

A large number of studies show that the source of primary MPs are microbeads from personal care products, followed by the spillage of preproduction pellets from

industrial operations. The first element that one thinks of in the context of MPs in cosmetic products is microbeads. Their use in cosmetic products is currently prohibited. Yet, there is another major source of MPs, comparable to microbeads in the sense that they are also composed of primary MPs, albeit receiving only a muted interest. These are glitters, which are used often in all kinds of cosmetic and textile products, not to mention craft activities [73]. Commanding a very low price, glitters start to get into the environment directly or indirectly (discharge into sewage systems following washing/cleaning activities) from the time of their first use. Had each and every glitter particle that found its way into the environment were self-luminous or phosphorescent, enabling the ability to trace them (such as radiotracers or thermal cameras), their prevalence in the environment would have been obvious.

A glance at the life cycle of glitters could start with their manufacturing from petroleum-derived polyesters, followed by their shipping to suppliers, to find their way eventually to consumers in a wide range of products (such as textiles, craft and DIY materials, EVA stickers, jewelry, shoes, and bags). Once they start to be used by the consumers, they are often prone to shedding away from the objects they are attached to. If not, they would still be transferred to landfills, where they can continue to contaminate the air, water, and clean soil, where they would remain intact for years. If they had been initially used in makeup materials applied to the face and body, they would, sooner rather than later, be washed with water and reach wastewater treatment plants through sewer systems. If the treatment plant applies secondary treatment processes, a portion of the glitters could be kept in the sludge. Yet, the remaining would still be released into natural sources of water, and affecting living organisms.

Even though there are some studies aimed at understanding the level of microbeads contamination in water sources and to assess the amount of microbeads ingested by organisms, comparable studies on glitters are just starting to take off and are few in number. The figures presented in three new and distinct studies on the analysis of MPs from different cities of Iran suggest the presence of hexagonal film-like MPs in the samples and presume these to be probably from a primary source.

Paints and coatings generally contain polymers. The binder in waterborne emulsion paints (latex paints) may consist of (nanosized) MPs. Different polymeric binders are used. Waterborne emulsion paints (latex) may contain dispersed micro-sized polymers as a binder for pigments. In solvent-borne paints (e.g. lacquer), the binder polymers are dissolved and, after hardening, form polymer films. Waterborne emulsion paints have replaced many solvent-based paints [41]. In the Netherlands in 2008, five times as much waterborne as that of non-waterborne acryl or vinyl polymer paints were produced; in 2013, this ratio increased to six times as much [41]. MP contents in paint have been reported to be 14–30% [37]. Wall paints are reported to have binder content up to 30% [42]. The various scenarios are calculated with plastic content of 14, 20, and 30%. Exact numbers on the market penetration of MP-containing paints are unknown. Based on the scattered product information available, the minimal scenario uses a market penetration of 9%, the average at 13%, and the maximum at 17%.