Microplastic generation, distribution, and removal from the environment: a review

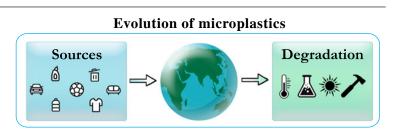
Yulia V. Ioni,^a Muneeb Farooq,^b Diana Roshka,^b Amit K. Pal,^b Dmitry V. Krasnikov,^b* Albert G. Nasibulin^{b, c}* ^(D)

^a Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Science, 119991 Moscow, Russia

^b Skolkovo Institute of Science and Technology, 121205 Moscow, Russia

^c Kemerovo State University, 650043 Kemerovo, Russia

The presence of microplastics (MPs) in the environment is a highly relevant and aggravating environmental problem, which is a concern not only for specialists in various fields but also for everyone who cares about the future of our Planet. The ever-increasing production of polymers and the expanding use of plastic products escalates MP concentrations in the Earth's ecosystem. The need to control the accumulation and spread of MPs is caused by the current crisis, in which no microplastic-



free areas have remained on the Earth. The number of studies dealing with the existing and potential threat to living organisms from the accumulation and consumption of MPs is increasing every year. The aim of this review is to systematize the available information on the occurrence of MPs in the environment and briefly describe the main types of polymer materials acting as MP sources and mechanisms of MP formation and transport in the environment. The hazardous behaviour of MPs is analyzed by considering their impact on the physiology of aquatic and soil organisms. Special emphasis is on demonstrating the adverse environmental effects of the emissions from 3D printing with polymer materials. An overview of various methods for MP capture is given to facilitate the analysis and development of more reliable methods for MP removal and disposal. As a result of the review, we assess the long-term environmental and human health consequences of MP exposure. Understanding the mechanisms of MP formation, lifecycle in the environment, and ways of interaction with living organisms will facilitate the development of methods for controlling the spread of MPs and the design and implementation of effective techniques for environmental remediation to prevent adverse ecological consequences.

The bibliography includes 244 references.

Keywords: microplastics, environmental pollution, photodegradation, 3D printing, aerosols.

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Yu.V.Ioni. PhD in Chemistry, Researcher.

Current research interests: carbon nanomaterials, functionalization of E-mail: acidladj@mail.ru nanomaterials, CO₂ capture. Current research interests: synthesis and study of carbon D.V.Krasnikov. PhD in Chemistry, Senior Lecturer. E-mail: d.krasnikov@skol.tech nanomaterials, graphene oxide, adsorption of harmful and toxic substances, microplastics, environmental protection. Current research interests: carbon nanomaterials, kinetics, catalysis, M.Farooq. PhD Student. additive technologies, composites. E-mail: muneeb.farooq@skoltech.ru A.G.Nasibulin. Dr. in Engineering, Professor of RAS, Laboratory Current research interests: additive technologies, non-linear optics, Head. semiconductor devices. E-mail: a.nasibulin@skol.tech D.Roshka. PhD Student. Current research interests: carbon nanomaterials, synthesis of E-mail: diana.roshka@skoltech.ru nanomaterials, growth mechanism studies, applications, microplastics, Current research interests: microplastic pollution, waste recycling. aerosols. A.K.Pal. PhD Student. E-mail: amit.pal@skoltech.ru Translation: Z.P.Svitanko

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1. Introduction

Microplastics (MPs) are particles of polymer materials of various chemical compositions with a size of less than 5 mm in any dimension.^{1,2} The MP particles can be formed as a result of degradation of plastic products or directly as wastes of the plastic industry.³ In recent years, research into MPs has been intensified because of their wide occurrence and adverse effects on the environment and human life.⁴ Currently, it is obvious that microparticles resulting from cosmetic products, food packaging, clothing, medicines, children's goods, and manufacturing processes can pollute natural ecosystems.^{5–11}

The level of MPs in the environment is alarmingly increasing.¹²⁻¹⁴ In particular, the COVID-19 pandemic dramatically increased the use of N95 respirators, face masks, disposable gloves, gowns, and other products to prevent the spread of SARS-CoV-2. According to various estimates, nearly seven billion face masks, or 21000 tonnes of synthetic polymer, were used during the pandemic worldwide. Microplastics can be formed as a result of mechanical abrasion and degradation of polymer materials in the environment or upon condensation of molecules on heating or burning of plastics.^{15,16} The latter process can give rise to toxic particles of various morphology and chemical composition, which can cause immunosuppression, carcinogenesis, and even activate inflammatory reactions and disruption of physiological functions.¹⁷⁻²⁰ The active development of additive technologies results in the generation of micro- and nanometre-scale plastic particles, in particular, from the feedstock used in powder or jet 3D printers.21,22

Most microplastics are derivatives of common types of polymers such as polyethylene (**PE**), polypropylene (**PP**), polystyrene (**PS**), polyethylene terephthalate (**PET**), polyurethane (**PU**), polyamide (**PA**), *etc*. The polymers may also contain additional chemicals such as phthalates, polybrominated diphenyl ethers (**PBDEs**), and tetrabromobisphenol A [2,2-bis(3,5-dibromo-4-hydrxyphenyl)propane, **TBBPA**], which are easily leached out of the plastic matrices under certain conditions.^{4,23,24}

A variety of factors should be taken into account for the description of MPs, e.g., chemical composition, size, shape, origin, and even colour.^{1,2,25,26} However, the most common classification is based on the origin of MPs and includes two main categories: primary and secondary MPs. Examples of primary MPs are crushed plastic granules, flakes, microbeads, and microfibres with a size of up to a few mm, being directly released into the environment.^{27,28} They are actively utilized as components of cosmetics (lipsticks, toothpastes, creams, scrubs, etc.), textiles, baby products, and other products.^{10,29,30} A primary MP can adsorb antibiotics that have been discharged into water and store the drugs on the particle surface for a long period, which leads to undesirable consequences for the nature and humans.^{31,32} The secondary microplastics are formed upon the gradual decomposition of larger plastic products under environmental factors.33 Plastic waste can degrade to µm or even to nm sizes under long-term physical, chemical, and biological processes.³⁴ This is confirmed by the frequent detection of irregularly shaped MP particles. The secondary MPs can arise from water bottles, plastic bags, plastic containers, tea bags, food packaging, car tyres, etc. (Fig. 1).^{33,35,36}

Data on the exact contribution of each source of MP pollution are rather ambiguous and depend on the region. Generally, according to the report of the International Union for Conservation of Nature,³⁸ 35% of the whole MP amount appeared from textile waste, 28% formed by tyre degradation, 24% — from city dust, 7% — due to road markings, and so on.³⁷ Other sources provide a different distribution,³⁹ however, in all cases, most of the MP spread is due to tyre wear, road mapping, and textiles.^{40,41}

Both primary and secondary MPs are widespread, especially in water environments. Indeed, synthetic materials based on polyesters, **PU**, or **PA** degrade over time when washed, treated, and cleaned to produce MPs.^{6,42} Microplastics can also be concentrated in soil and air.^{43–45} Municipal landfills and spontaneous dumps are hotspots for accumulating household plastic waste,^{46–48} which decomposes upon regular exposure to light, elevated temperature, and mechanical stress to release

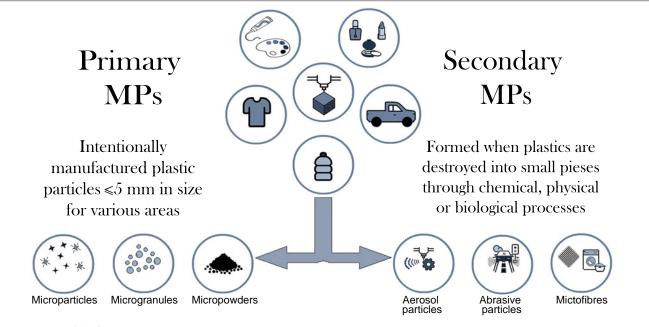


Figure 1. Classification of MPs.

MPs. The quantitative content of MPs is expressed as their mass concentration in the environment, which are thus treated as dispersion systems. The content of MPs can be described as the number of MP particles per unit area or volume.

The first studies dealing with MPs were published back in 2004. Since then, the number of publications on this subject has increased exponentially. In this review, we analyze the most relevant papers published within the last 5-7 years and data from UN reports, which have focused on the problem of MPs more and more often since 2018. A large number of publications are concerned with the spread of MPs in local territories or water areas of various countries. However, in Russia and former Soviet Union republics, where the MP problem is also highly relevant, only a few research groups are engaged in these studies. The purpose of this review is to demonstrate the integrated nature of the possible influence of MPs on living organisms and the prevalence of MPs in various parts of the global ecosystem: in soil, water, and air. The data on the evolution of MPs are summarized for the first time, starting from the chemical composition, production methods, and production outputs for polymers used most commonly in the human vital activity, which are the main source of MPs, and ending with the methods of capture and removal of particles in the environment. We analyzed the key mechanisms of generation and spread of primary and secondary MPs in nature. Unlike other reviews, here we demonstrate that the use of tobacco products is an significant source of MP contamination, and a single cigarette may contain various types of MPs. Also, we consider in detail the 3D printing as a source of atmospheric emission of microand nanoplastics and its effect on human health. In addition, we pay attention to the presence of MPs in the drinking bottles. It should be noted that, here, we intentionally avoided considering the problem of disposal of collected MPs, as this is a separate and large-scale subject matter, which will be addressed in future studies, since the processes for effective MP neutralization without harm to the living organisms are still at the stage of conceptual discussion. The review is designed, first of all, for

the scientists specializing in Materials Science, Polymer Chemistry, Biology, and Ecology, but it would be also useful for university and secondary school students, who intend to be engaged in Science and specialize in the development of methods for investigation of MP occurrence and influence on the environmental situation. Thus, this review demonstrates the degree and amount of damage brought about by the spread of MPs in nature and is expected to inspire researchers, including

2. Chemical sources of microplastics

the environment and their disposal.

In 2020, the global plastic production exceeded 367 million tonnes per year.⁴⁹ If the current trend continues, one can eventually expect an increase in the production of up to 30 billion tonnes per year.⁵⁰ Long-life polymer products used in aircraft manufacturing, mechanical engineering, construction, light and food industry, agriculture, health care, and so on can become MP sources during production, use, and disposal.

the authors, to explore new ways for the removal of MPs from

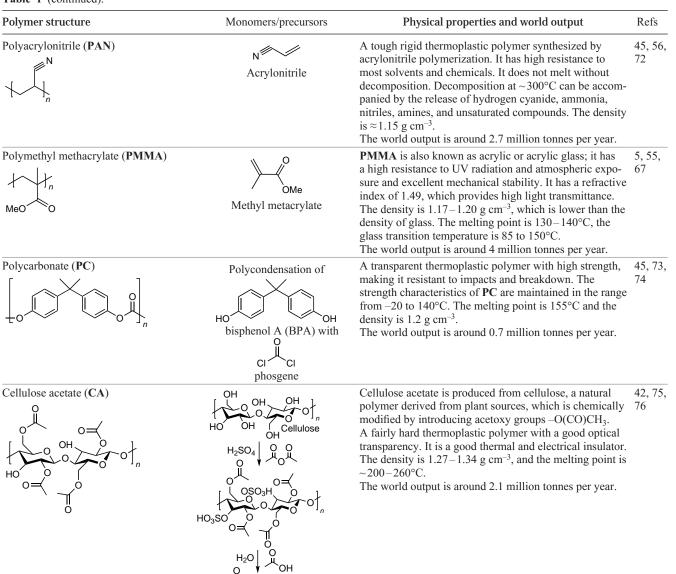
The polymer types used most commonly for the fabrication of non-specific products are PE, PP, PS, polyvinyl chloride (PVC), and PET. They form the basis for tens of thousands of various brands and sorts of plastics.⁵¹ Products made of polymethyl methacrylate (PMMA), polycarbonate (PC), polyacrylonitrile (PAN), PA, and cellulose acetate (CA) are also often mentioned as sources of MPs. Table 1 summarizes the information on the polymers that act most often as sources of MP spread, including the chemical structure of the polymers and monomer units, and the polymer properties and key applications. It is worth mentioning that composite plastics such as the acrylonitrile-butadiene-styrene (ABS) terpolymer used for manufacturing 3D printing filaments, which also contribute to MP spread in the environment, are not included in the table. Furthermore, the table does not contain plastics that have a special 'O' (meaning 'other') marking on the polymer products, because of their complex chemical structure.

Table 1. Most common polymers: structure, monomers, physical properties, world output, and references to publications indicating these polymers as MP sources.

Polymer structure	Monomers/precursors	Physical properties and world output	Refs
Polyethylene (PE) $\downarrow \frown \downarrow_n$	Ethylene	The most commonly produced plastic with the world output of approximately 135 million tonnes per year. There are several PE types (given below) differing in the structure and production process.	3, 5, 10, 15, 29, 34, 44, 45, 52–59
High-density polyethylene (HDPE) (1)	Ethylene	A flexible, translucent, and weather-resistant plastic. The HDPE melting point is $120-140^{\circ}$ C and the density is $0.93-0.97$ g cm ⁻³ .	24, 34, 60–62
Low-density polyethylene (LDPE) $\left[\begin{array}{c} R^{1}\\ R^{2}\end{array}\right]_{n}$ $R^{1}, R^{2} = Et,$ $Bu^{n}, Hex^{n} \text{ or more}$ complex groups	Sopolimeri- Ethylene zation with 1-butene 1-hexene 1-octene	A semi-rigid polymer with low crystallinity consisting of $4000-40000$ carbon atoms with numerous short branches. The LDPE melting point is $105-115^{\circ}$ C and the density is $0.91-0.94$ g cm ⁻³ .	5, 10, 24, 34, 61
Linear low-density polyethylene (LLDPE) $\left[\begin{array}{c} R \\ R \end{array} \right]_{n}^{R} = Et, Pr \text{ or } Bu^{n}$	Ethylene	A highly flexible polymer with high impact strength and good barrier properties to water vapour and alco- hols. The melting point is $117-130^{\circ}$ C and the density is 0.92-0.93 g cm ⁻³ .	5, 10, 24, 34, 61

Polymer structure	Monomers/precursors	Physical properties and world output	Refs
Polypropylene (PP) \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow	Propene	A semi-rigid and translucent thermoplastic polymer possessing high dielectric strength and a decent resistance to chemicals, stains, impacts, heating, and freezing. It is not susceptible to stress cracking and provides good electrical and chemical resistance at elevated temperatures. Depending on the production method and, correspondingly, the structure, polypropylene can exhibit opposite properties, being hard or soft, opaque or transparent, lightweight or heavy, <i>etc.</i> The density varies between 0.895 and 0.92 g cm ⁻³ . The melting point is in the range of $160-165^{\circ}$ C for homopolymers and $135-159^{\circ}$ C for copolymers. The world output is about 100 million tonnes per year.	3, 11, 13, 30, 44, 45, 55–57, 63–65
Polyvinyl chloride (PVC) $\downarrow \qquad \qquad$	Vinyl chloride	A white high-strength thermoplastic material. PVC polymers are widely available in two main forms: flex- ible (density of $1.1-1.35$ g cm ⁻³) and rigid (density of $1.3-1.45$ g cm ⁻³). The melting temperature varies from 150 to 220°C. The world output is 40 million tonnes per year.	10, 19, 24, 30, 44, 45, 55, 61, 66–68
Polystyrene (PS) $\left[\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	Styrene	A rigid, lightweight and transparent polymer. Like PP , it may be atactic, isotactic, or syndiotactic. The general properties of polystyrene include low weight, moisture resistance, good thermal and sound insulation, easy processing and moulding, and high rigidity and structural stability. The density is $0.96-1.05$ g cm ⁻³ and the melting temperature is ~217°C. The output is around 16 million tonnes per year.	19, 30, 35, 45, 52, 55, 56, 60, 62–64, 67 69
Polyethylene terephthalate (PET) H = 0 $O = 0$	Polyesterification of O O dimethyl terephthalate with OH OH OH OH OH	A versatile semi-crystalline linear thermoplastic polymer. The polymer is mechanically, thermally, and chemically stable, and resistant to moisture or solvents. It exhibits good shape retention properties and excellent electrical insulating properties. The melting point is $240-270$ °C. The density depends on the crystallization degree: 1.37 g cm ⁻³ for the amorphous phase and 1.46 g cm ⁻³ for the crystalline phase. The world output is 35 million tonnes per year.	5, 13, 15, 24, 33, 44, 45, 54–57 61–64, 67 70, 71
	or polycondensation of O HO		
Polyamide (PA) $\left[\begin{array}{c} H \\ \neg \\ \neg \\ Polyamide 6 (Nylon 6) \end{array}\right]_{n}$ $\left[\begin{array}{c} \circ \\ \neg \\ \neg \\ Polyamide 66 (Nylon 66) \end{array}\right]$	Ring-opening polymerization of $H \to 0$ caprolactam; Polycondensation of $H_2N \longrightarrow NH_2$ hexamethylene-diamine and $HO \longrightarrow OH$ adipic acid	Nylons are the most common artificially produced poly- amides. Nylon 6 and Nylon 66 possess high strength in a wide temperature range and good abrasion and wear re- sistance. They also have high water uptake and electrical insulating properties. Nylon 66 has better wear resistance and heat resistance than Nylon 6. The melting points of Nylon 6 and Nylon 66 are 223°C and 255°C, respectively. The density of the polymers is quite similar 1.13 and 1.14 g cm ⁻³ . The world output is 6 million tonnes per year.	5, 30, 35, 42, 44, 45, 52, 55, 59, 62

Table 1 (continued).



TI Cellulose acetate

A representative of polyolefins, **PE**, is prepared by radical polymerization of ethylene. Other possible synthesis methods are the Ziegler–Natta polymerization and metallocene catalysis.^{77,78} There is a large number of various commercial polyethylene products including high-density (**HDPE**), low-density (**LDPE**), and linear low-density (**LLDPE**) polyethylenes, and other. The classification is based on the polymer density. Polyethylene is widely used for the production of plastic products for agriculture, household goods, laboratory equipment, mulch films, *etc.*^{79,80}

High-density polyethylene is produced at low temperatures $(70-300^{\circ}C)$ in the pressure range from 10 to 80 bar. It has a high degree of crystallinity and consists of linear chains that are tightly packed together and has a very low content of short-chain branching.^{18,81} **HDPE** has good resistance to alcohols, dilute acids, alkalis, and most solvents; it is moderately resistant to oils and lubricants and poorly resistant to aliphatic, aromatic, and

halogenated hydrocarbons. It is used in a range of packaging products including boxes, trays, milk and fruit juice bottles, food packaging lids, canisters, drums, industrial bulk containers, *etc*. In addition, the polymer is a popular material for the production of various consumer products such as fibres and textiles, ropes, fishing and sports nets, pipes, fittings, and telecommunication cables. The main disadvantages of **HDPE** are susceptibility to stress cracking and low UV and heat resistance.

LDPE and **LLDPE** are produced at higher pressures (1000–3000 bar) by free-radical polymerization.⁸² **LDPE** and **LLDPE** have more branches than **HDPE**;¹⁸ this decreases the intermolecular interactions and, therefore, the tensile strength of the polymers.^{53,83} The use of **LDPE** is mainly related to the production of containers, dispensing bottles, wash bottles, test tubes, and various moulded laboratory equipment. The most popular application of **LDPE** is for plastic bags and films used for agricultural and food packaging and cable insulation jackets.

Polypropylene is also a type of polyolefin slightly harder than **PE**.⁸⁴ The production methods are similar to those used to synthesize **PE**. Polypropylene is one of the lightest polymers among all commercial plastics;^{85,86} therefore, it is often used to produce goods for which low weight is a critical issue: packaging films, automotive interiors, household and consumer goods, textiles, and medical devices. In addition, PP is highly resistant to environmental impacts, except for UV irradiation and impact load.^{87,88} It has good resistance to dilute and concentrated acids, alcohols, and alkalis, as well as to most of the common organic solvents.

A comparison of the environmental impacts of **PE** and **PP** generally shows better characteristics for the latter, which has a shorter degradation time (20 to 30 years vs. 1000 years for **PE**) and better recyclability. Although both polymers are derived from non-renewable resources and contribute to MP pollution, the amount of greenhouse gas emissions is lower during the production of PP. Polypropylene is often erroneously considered to be more environmentally benign due to its better recyclability and shorter degradation time.

Polyvinyl chloride is the third most widely produced synthetic polymer in the world after PE and PP; it is synthesized by polymerization of the vinyl chloride monomer.⁸⁹ Plasticized (flexible) PVC is formed by adding compatible plasticizers, causing the plastic to become more transparent and flexible. Unplasticized (rigid) PVC has a high resistance to impacts, water, weather conditions, chemicals, and harsh environments; PVC is temperature-sensitive and has a narrow processing temperature range.90 Fillers are often added to PVC compounds to form composites with increased rigidity and strength and to improve the impact strength, conductivity, colour, etc.⁹¹ The key applications of PVC are based on its key properties such as high dielectric constant; durability; resistance to weather conditions, corrosion, impacts, and abrasion; flame retardancy (the oxidation index is \geq 45); excellent mechanical properties; and chemical resistance to many inorganic chemicals and aliphatic hydrocarbons. This polymer is widely used in the construction industry for the manufacture of door and window profiles, drinking and waste water pipes, wire and cable insulation, medical devices, etc.^{66,92} The production of PVC causes considerable environmental problems, since toxic chemicals, including dioxins and phthalates, are released into the environment. The disposal of the PVC waste is particularly problematic, since it is not biodegradable and can persist in landfills for centuries and burning PVC releases harmful chlorine-based chemicals into the atmosphere.

Polystyrene is an extremely versatile material, which makes it applicable in various fields and industries and suitable for the production of household goods along with **PP**.⁹³ The most popular applications include packaging materials and heat and sound insulation (most often, as polystyrene foam). Also, **PS** can be mixed with additives, blended with other polymers, or chemically modified to improve the desired properties of the material.⁹⁴ This polymer poses significant environmental challenges as its decomposition in landfills may take up to 500 years. It is especially harmful, as it can absorb and concentrate toxic chemicals from the environment.

Polyethylene terephthalate belongs to the family of aliphatic polyesters and has a semi-crystalline structure.⁷⁰ It is obtained as a result of the polycondensation reaction between terephthalic acid and ethylene glycol or the transesterification reaction between ethylene glycol and dimethyl terephthalate.⁹⁵ Depending on the production method, the polymers can be semi-rigid or rigid. **PET** has a wide range of application temperatures

from –60 to 130°C, good gas (in relation to oxygen and carbon dioxide) and moisture barrier properties; it is resistant to impacts and to the action of alcohols and solvents; however, the amorphous structure of PET is easily destroyed on treatment with boiling water or alkalis. Furthermore, under the action of ketones, aromatic and chlorinated hydrocarbons, and dilute acids and bases, the polymer can be destroyed at temperatures above $60^{\circ}C$.⁹⁶ Meanwhile, **PET** is recyclable. The polymer is used in the production of packaging and in the textile industry, while **PET** films are often used for moulding of automobile parts, electronic devices, *etc.* Although **PET** degrades faster in natural environments due to hydrolysis and photolysis, its overall degradation remains very slow. This leads to decades of accumulation when littered or mismanaged. The natural weathering destroys **PET** to give MP particles.

Polyamides are polymers containing repeating amide bonds (-CO-NH-). The names PA and nylon are often used interchangeably, but there are some differences between them. Polyamides are aliphatic or aromatic, natural or synthetic polymers, less resistant to water than nylon, and possessing slightly hydrophobic properties.⁹⁷ Nylons belong to the aliphatic subgroup of polyamides and are purely synthetic; they have good resistance to moisture. The digit after the word 'nylon' refers to the number of carbon atoms contained in the repeating unit of the polymer, for example, Nylon 12 is made of laurolactam, and Nylon 46 is prepared from 1,4-diaminobutane and adipic acid.98 One of the most widely used PAs known as Nylon 6 or polycaprolactam⁹⁹ is synthesized using a ringopening polymerization reaction of caprolactam. PA66 (Nylon 66) is a popular engineering thermoplastic. It is mainly used as a substitute for metals in various applications. Nylon 66 is synthesized by the polycondensation of hexamethylenediamine and adipic acid. All PA polymers can be processed by conventional melt processing methods such as injection moulding and extrusion. Due to the high PA sensitivity to moisture, an intensive drying process is required, since insufficient drying deteriorates the mechanical properties of the polymer products.¹⁰⁰ The use of **PA**/nylon has several environmental consequences. The production of these materials is accompanied by greenhouse gas emissions and requires a lot of water and energy, while PA products can degrade in landfills for hundreds of years, thus producing long-term environmental pollution, in particular with MPs.

Polyacrylonitrile is an acrylic thermoplastic polymer with high strength and thermal stability,¹⁰¹ produced as film, fibres, or foam.⁷² Due to the presence of nitrile groups in the polymer molecules, PAN polymers are resistant to most organic solvents. In addition, they are resistant to alcohols, organic acids (except for formic acid), hydrocarbons, ketones, and esters but are soluble in concentrated sulfuric acid, dimethylformamides, and dimethyl sulfoxide. PAN is strong, lightweight, and resistant to UV radiation; it has low gas permeability and is used for the production of ultrafiltration membranes for water treatment.¹⁰² Generally, the polymer has a variety of applications ranging from clothing materials to high-tech carbon fibres. The manufacturing process of PAN involves toxic chemicals and generates significant greenhouse gas emissions, while the material itself is non-biodegradable and can persist in the environment for hundreds of years.

Polymethyl methacrylate is a transparent and rigid thermoplastic polymer.¹⁰³ This high-strength plastic can be easily moulded and is widely employed as a replacement for glass. It is used to manufacture automobile windows, lenses, smartphone screens, terrariums, *etc.* Compared with other

transparent polymers, it has good abrasion resistance. PMMA is chemically resistant to aqueous solutions of most laboratory chemicals (diluted inorganic acids, alkalis, and aliphatic hydrocarbons). However, it is unstable to strong acids or alkalis, chlorinated or aromatic hydrocarbons, esters, or ketones; it cannot be sterilized by heating, which is important for food and medical applications. The polymer has unlimited colouring possibilities. Often, special additives are used during the PMMA synthesis for modification, e.g., comonomers, plasticizers, fillers, and dyes.¹⁰⁴ PMMA is naturally compatible with human tissues and used for dentures and bone replacement.¹⁰⁵ The limitations for PMMA application are poor impact strength and limited heat resistance (up to 80°C). The use of PMMA poses environmental concerns, primarily because of its nonbiodegradable nature, which results in the persistence in the environment for hundreds of years. Although PMMA can be recycled, most of the material ends up in landfills or oceans, thus contributing to plastic pollution. Meanwhile, PMMA exhibits exceptional resistance to UV radiation and weathering, which makes it highly strong and durable for outdoor applications. The production process involves harmful chemicals and generates greenhouse gas emissions, though it generally has a lower environmental impact compared to some other plastics.

Polycarbonates are composed of aromatic monomers linked together by carbonate groups (-O-(C=O)-O-). They are produced by polycondensation of bisphenol A and phosgene. They have good chemical resistance to dilute acids, aliphatic hydrocarbons, and alcohols, but are easily attacked by dilute alkalis, as well as aromatic and halogenated hydrocarbons. The properties of PC are similar to those of PMMA: it is a highperformance, durable, amorphous, and transparent thermoplastic polymer.¹⁰⁶ It is lightweight and a great alternative to glass, as it is easily moulded at a high temperature and pressure. PCs are used as an engineering plastic due to high impact strength and good electrical properties. The introduction of additives can improve the flame retardancy, heat resistance, ultraviolet resistance, and colour stability.¹⁰⁷ The polymer can be used to block UV radiation, providing up to 100% absorption of UV rays. The common applications include the production of compact discs, safety helmets, bulletproof glasses, car headlight lenses, baby feeding bottles, roofing, glazing, etc. Polycarbonate is used for 3D printing with a print bed temperature of 90°C or higher. PCs have a substantial adverse effect on the environment due to their slow breakdown, which can take hundreds of years, while bisphenol A used in the synthesis can leach into soil and water, thus generating potential threats to ecosystems.

Cellulose is one of the main structural polymers in plants (especially wood or cotton). These natural fibres are treated with acetic anhydride or acetic acid in the presence of a catalyst to produce cellulose acetate (CA). In this reaction, the hydroxyl groups of cellulose are replaced with $-O(CO)CH_3$ groups. Controlled synthesis provides the desired degree of substitution. Owing to its structure, CA has a low susceptibility to stress cracking. It has excellent water absorption properties, but poor resistance to concentrated acids, alkalis, and other chemicals. The polymer is soluble in a wide range of solvents, including acetone, ethyl acetate, and chloroform. Owing to its versatile properties, CA finds applications in various industries,¹⁰⁸ including the manufacturing of blister packs, covers for automotive parts, writing pens, various types of packaging, toys, brushes, cosmetic containers, tool handles, eyeglass frames, etc. Cigarette filters are also produced from CA. The low-viscosity polymer is used for the production of textiles and printing inks, while high-viscosity CA serves for manufacturing protective and electrical insulating films. Furthermore, **CA** has antistatic properties. However, the polymer is virtually not resistant to UV radiation and polymer degradation under natural conditions requires up to 15 years.¹⁰⁹

It is evident that the problem of accumulation and spread of MPs arises as early as during the production of polymers and polymer products. As can be seen from the above data, the overall production output and the range of applications of polymers are enormous. There is no human activity without polymers capable of MP generation. The overview of various polymers showed their unique chemical structures, properties, and applications. In view of this fact, it is important to study the chemistry of each polymer separately, which obviously complicates the solution of MP formation and accumulation problems. The unique structures of polymers determine not only their properties but also degradation mechanisms in the environment and also determine their effects on the health of living organisms. This emphasizes the importance of a thorough, separate investigation of each type of polymer to fully understand the long-term effects of polymer use and the necessity to develop guidelines for their responsible production, application, and disposal.

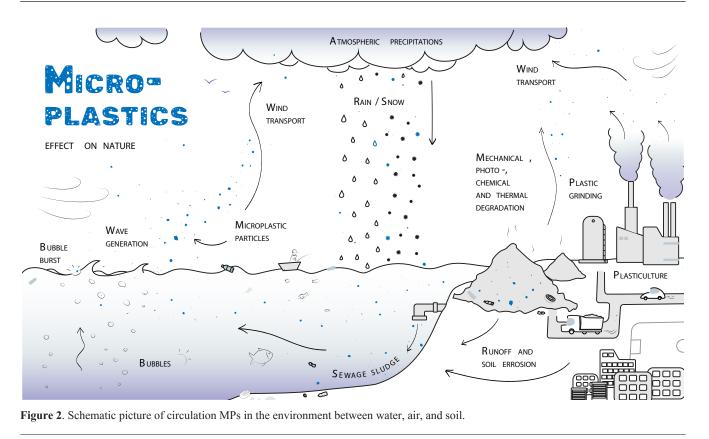
3. Microplastics in the environment

Currently, scientific journals contain a large number of studies on the detection and identification of MPs in food, air, soil, and water.54,55,61,63,110-112 Microplastics have been found at the bottom of the deep ocean and in polar ice,^{64,113–115} in the human intestinal tract, lungs, blood, and placenta.56,65,67,69,73,116 Not only the widespread occurrence of MPs is dangerous, but also their easy transfer from one environment to another.117 Figure 2 schematically depicts the MP circulation in nature. The complex and unstable balance between the air, soil, and water-based on numerous processes such as the water cycle (hydrological cycle), transfer by wind and sewage, etc. facilitates the spread of MPs throughout the world. Interestingly, most of the early studies focused on the effect of MPs on water bodies in general, as it was rather difficult to establish the effect on particular microorganisms due to the diversity of life forms. Currently, in view of the major role of vehicle and road emissions, the problem of aerosol spreading of MPs becomes more and more important. Nevertheless, some cycles in nature that facilitate MP spreading cannot be controlled; therefore, a detailed analysis of the MP transport and hotspots for MP accumulation in nature is of primary concern.

The lifecycle of MPs often begins with the extraction of raw materials (*e.g.*, oil, natural gas) and the subsequent chemical processing to obtain monomers for the production of plastics. As a result of waste disposal, burial in landfills, and uncontrolled industrial emissions, MPs enter the atmosphere, rivers, and seas. Over time, MPs can be converted to aerosols and dispersed by air flows. The MP particles that get into water are captured by air bubbles, rise to the surface under the action of waves, and again become available for wind transport. Subsequently, these particles get into soil or water through precipitation.

3.1. Microplastics in soils

The presence of MPs in soils and groundwater has been proven.^{59,62,79} Soils appear to be a considerable storage container of MPs, because landfills hold up to 80% of the world plastic trash. MPs get into soil *via* landfills,^{55,118} soil reclamation,^{119,120} sewage sludge and wastewater treatment,¹²¹ the use of compost



and organic fertilizers,^{57,122} residues of agricultural mulching films,^{3,123} tyre wear,¹²⁴ atmospheric precipitation,⁵⁹ *etc.* Moreover, the biological activities of soil organisms, such as feeding, digestion, and excretion, can lead to plastic trash fragmentation into MPs.¹²⁵ The presence of MPs greatly reduces soil quality ^{62,126,127} and, along with the transportation of heavily contaminated soils, creates significant risks for sustainable agriculture and ecosystems in general.

Microplastic contamination in soils has detrimental effects on soil quality and function. Earthworms, an important component of the soil ecosystem, accidentally ingest MPs. This leads to their death and thus decreases the soil productivity.^{68,119,128} Primary MPs can also influence the transport of contaminants into deep soil layers through ground cracks and change the soil water cycle.¹²⁹ In addition, MPs reduce the mobility of soil organisms by sticking to their outer surface. Another important factor is that animals mistake MPs for food. The false satiation caused by swallowing MPs can reduce the rate of carbon biomass utilization. The ingestion of MPs by soil organisms can generally lead to energy depletion, stunted growth, and even mortality. MPs may cause intestinal obstruction, impaired fertility, mechanical damage to the oesophagus, decreased immunological response, metabolic disorders, and other biochemical reactions.68,119,130 А histopathological damage to earthworms was observed after their exposure to MPs for 28 days.¹¹⁹ Similar studies⁷¹ have revealed a considerable damage to the villi of the gastrointestinal wall of snails (Achatina fulica). After four weeks of exposure to PET microfibres, their average food intake decreased, and a general deterioration of the digestive and excretory systems was observed. A close contact with MPs can cause a disruption of the hepatic lipid metabolism in mice, decrease the secretion of intestinal mucin, and reduce the mRNA expression of some important genes that regulate lipogenesis and hepatic triglyceride synthesis in the liver and epididymal fat.^{131,132} These findings indicate that ingestion of MPs by living organisms can impair critical physiological processes that regulate biodiversity, in general, and living health, in particular. As a result of the large surface area of MP contamination, heavy metals, antibiotics, and other toxicants can be adsorbed on MP surface and transported and stored by MPs, thus increasing the risks to humans and living organisms, in addition to the hazards associated with the direct ingestion of plastic particles.

3.2. Microplastics in water

Due to durability and floating characteristics, plastics and MPs are widely spread in the aquatic environment by ocean currents;^{64,133} MP accumulation sites have been already identified throughout the ocean, from the surface to the deep sea, including the Arctic zone.^{64,134} The increasing levels of detected MPs raise concerns about the pollution of the water ecosystem. MPs released from cosmetics³⁰ or household chemicals¹³⁵ pass through a water-filtering system and enter the global ocean, since the filters employed in wastewater treatment plants cannot completely capture small particles.¹³⁶ This has adverse consequences for the marine environment.

Microplastics are often found in deep waters, deep-sea sediments, sandy beaches, and surface waters.^{137–139} Soil and sand particles, shells, dead tissues of plants, algae, or other living organisms brought to the oceans and rivers by wind can also bring MPs. Natural factors such as winds and surface ocean currents influence the distribution of MPs in the marine environment. Today, artificial intelligence (AI) can be used to monitor the migration of tiny plastic wastes. A three-dimensional numerical particle-tracking model (PTM) coupled with a hydrodynamic model for simulating the MP transport in rivers, lakes, estuaries, and coastal waters has been developed.¹⁴⁰ The hydrodynamic PTM is suitable for simulating the MP transport in aquatic environments with irregular geometries and complex

hydrodynamics. The study also proposed further improvements of PTM to enhance the accuracy, in particular, considering physical and chemical processes (*e.g.*, degradation, weathering) and adding back-tracing capabilities, which may help to identify the potential hotspots of MP accumulation and to track MP pollution dynamics.

Currently, it can be stated that there are no microplasticfree areas in the Earth. A well-known publication describes almost a hundred plastic fragments from a dozen different types of polymers found in Antarctic Sea ice.141 Moreover, plastic and MP accumulations are still being detected in the Antarctic environment.^{113,142} A large number of full articles and brief reports on MP pollution in local water areas are published annually. According to an early detailed investigation,143 which was carried out for Lake Huron bottom sediments, the MP concentration in water samples is approximately 37.8 plastic fragments m⁻². Somewhat later, it was found that the MP concentration in the Great Lakes is approximately ~40 000 particles km⁻².¹⁴⁴ The later investigation of the Lake Winnipeg, located not far from the Great Lakes, showed a surface MP concentration of 193 420 particles km⁻².¹⁴⁵ Most MP particles are tiny fibres resulting from the destruction of larger plastic pieces and synthetic textiles. Australian researchers who studied coastal samples along the Brisbane River over a year registered MP concentrations ranging from 0.18 to $129.20 \text{ mg kg}^{-1}$ (10 to 520 MP particles per kg).¹⁴⁶ The value strongly depended on the season and was minimal during the drought period. The MP samples mainly consisted of PE, PA, PP, and PET particles of <3 mm in size (Fig. 3). The sandy Moroccan beaches along the Tetouan coast are regularly plagued by widespread MP pollution due to tourism, fishing, and uncontrolled accumulation of waste.147 Samples of bottom sediments in the San Francisco Bay contained 2.1 to 11.9 MP particles g⁻¹ (dry weight), with particle size ranging from 25 µm to 5 mm.148 Thus, geographically, MPs are distributed throughout all water areas of the Earth, with the highest MP concentration being found in the highest human activity areas (industrial, logistic, and tourism areas and large coastal cities).

The MP accumulation influences the feeding, growth, spawning, and survival of living organisms present in all aquatic ecosystems.¹⁴⁹ The spread of plastics gives rise to serious problems for shipping, trawling, and fish farming. Owing to their flotation and sorption properties, MPs act as additional marine contaminants by transporting and spreading harmful and toxic compounds.^{31,32} Since primary and secondary MP particles have a small size, they are bioavailable at any level of the food chain. MPs are ingested by various aquatic animals, disrupt their physiological processes, and subsequently move up the food chain, thus affecting the human health. Some marine organisms quickly absorb plastic particles, fibres, and flakes and also quickly excrete them.¹⁵⁰ However, MP ingestion still causes behavioural changes, growth problems, and changes in the feeding behaviour. It was shown¹⁵¹ that the accumulation of MPs had already negatively affected ~700 aquatic species worldwide, including some sea turtles, penguins, and various crustaceans. However, as the majority of victims remain undetected in the vast waters, the problems caused by MPs are actually more global than it may seem.¹⁵² Indeed, plastic pollution of the environment is primarily the result of negligent human behaviour and uncontrolled discharge from waste treatment plants or textile industry: due to improper waste disposal, plastics and MPs end up in global water systems.

What is even more important, hazardous organic compounds, such as dioxins, chlorobenzene derivatives, polybrominated diphenyl ethers, and other additives used in production processes can be accumulated on MPs and released to the aquatic environment. Several studies 153-157 have demonstrated the effects of MPs on a variety of marine creatures, including oysters, plankton, and mussels. The harm from MPs varies depending on the type and concentration of the plastic and particular living species. For example, polystyrene MPs were shown¹⁵⁷ to have a detrimental effect on the reproduction and feeding of oysters. Polystyrene microparticles of up to 6 µm in size ingested by a group of oysters were later found in the oyster faeces. The fertilization of oysters takes place directly in the sea where they release eggs and spermotozoa. The animals that ingested MPs produced fewer eggs and had lower-quality oocytes and spermotozoa. The micropolystyrene particles in the

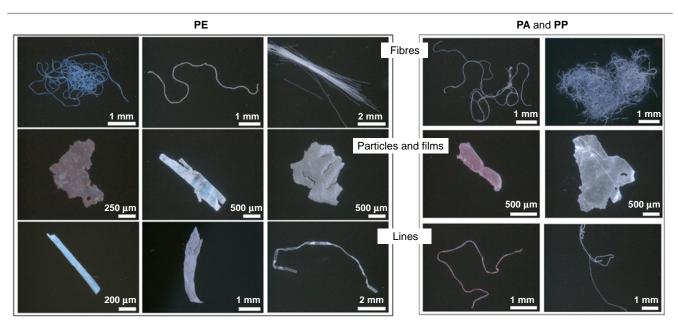


Figure 3. Bright-field optical microscopy images of various types of MPs found in the bottom sediments of the Brisbane River (Australia).¹⁴⁶

oyster's body decreased the sperm motility and thus prevented fertilization. The fertility of oysters and the growth of the offspring derived from oysters exposed to microplastics decreased by 41% and 18%, respectively.

Microplastics have been detected in various drinking water sources, including water bottles.^{158,159} This fact cannot be ignored because of the possible severe consequences for the environment and human health.¹⁶⁰⁻¹⁶³ The bottled drinking water may contain small particles, fibres, flakes, and even granules.^{61,161,164,165} Plastic bottles themselves are also sources of plastic and MP pollution as a result of mechanical damage to their surface.¹⁶⁶ A study of repeated opening and closing of bottles showed a marked increase in the number of MP particles on the surface of PET bottlenecks and HDPE caps. Moreover, pronounced differences between the degrees of cap abrasion were found for bottles from different manufacturers. Even if there were no microplastic particles inside the bottles, mechanical stress increased the probability that MP would be ingested by humans through the bottleneck. Similar results were obtained in another study carried out by fluorescence microscopy:¹⁶⁷ opening and closing of the bottle repeated many times increases the content of MPs in water by a large factor. The drinking fountains installed in public places are also becoming hotspots for MP contamination. Analysis of water from drinking fountains located in more than 40 metro stations in Mexico revealed the presence of MPs in all examined samples.¹⁶⁸ The main sources of pollution in the drinking fountains are sewage leaks and atmospheric precipitation.

Thirsty people consume not only pure bottled water but also various soft drinks. The content of MPs was determined in 50 packaged soft drinks sold in Hong Kong (tea, sparkling water, and energyetic drinks).¹⁶⁹ The results were provocative, as it was shown that all beverage samples, regardless of packaging (aluminium, carton, plastic, or glass), contained **PS**, **PP**, **PT**, **PET**, and **PMMA** particles with a size of approximately 150 µm. Thus, residents of large cities can swallow about 6 000 MP particles annually. The sources of these MPs include atmospheric precipitations, packaging materials that were subjected to mechanical stress during the production and transportation of drinks, and external contamination of containers after reuse.

Our study of the MP amount in a disposable bottle confirmed the influence of the number of openings and closings of the bottle on the dynamics of water pollution with MPs. Optical microscopic examination showed the presence of microplastic particles in water samples inside a disposable drinking bottle (Fig. 4a). Using Fourier transform IR spectroscopy in combination with optical microscopy, we found that the detected MPs were **PET** particles from which the disposable bottle was made (Fig. 4b). An increase in the amount of MPs in bottled water samples was observed after repeated opening and closing cycles (Fig. 4c). For statistical validation of the results, six samples were taken during each cycle. After the 100th cycle, noticeable microcracks were found on the inner surface of the PET bottle, which served as a secondary source of MP release into the water. The formation of microdamages is also caused by mechanical stress, drops, and impacts of the bottle against various surfaces during the use.^{166,170}

In many offices and households, replacement bottles for drinking water dispensers are an alternative to installing tap water filtration systems. According to statistical analysis, drinking water in a 19-litre bottle can contain up to 8 MP particles cm⁻² (for a 0.1 mL drop on a microscope slide) with a median value of 4.3 MP particles cm⁻² (Fig. 4*d*). A

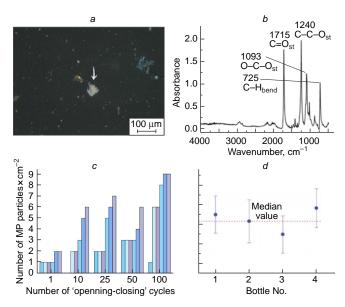


Figure 4. Bright-field optical microscopy image of MP particles found in a disposable bottle (*a*), IR spectra of ~100 μ m **PET** microparticle (*b*), dependence of the number of MP particles on the number of bottle opening–closing cycles (*c*), statistics on the MP amount in drinking water dispenser bottles (*d*).[†]

possible source of MPs is an impact load on the bottle during transportation, damage to the bottleneck during installation in the dispenser, and external sources.

3.3. Microplastics in air

The widespread occurrence of MPs affects the air as well as the marine and coastal environments. The accumulation and distribution of MPs in the atmosphere is associated with complex processes. In recent years, the importance of air transport of MPs has increased; as a result, they can settle in water or on the land.^{171,172} This mobility considerably influences the dynamics of plastic pollution in various ecosystems. The review¹⁷³ presents the results of investigations of urban air, road dust, and indoor and outdoor air in cities of China, Iran, Europe, Japan, and other countries, in which MPs were detected in all of the samples. A combination of transmission electronic microscopy and infrared spectroscopy was used to examine polymer particles found on the streets of São Paulo (Brazil).¹⁷⁴ It was shown that the polluted air mainly contained polymer microfibres composed of **PE, PP, PET, PA**, and **PAN**.

The manufacture and use of synthetic clothes, tyre erosion, plastic household items, burning of garbage, production and application of building materials, sewage sludge accumulation, and 3D printing may be potential sources of MP released into the atmosphere.¹⁷⁵ In the textile industry, exceptionally thin fibres $(1-5 \,\mu\text{m}$ in diameter) are used more and more often. Fragments of **PA**, **PAN**, **PE**, and **PP** fibres may form aerosols and pollute the air. The fibre particles can be inhaled and enter the human lungs or ingested after the hand contact with the surface polluted with MPs.¹⁷⁶ One more source of atmospheric pollution is household washing, drying, and treatment of clothes and shoes.^{39,177} A single garment typically releases about

[†] The data in the Figure are the results of author's studies being prepared for publication.

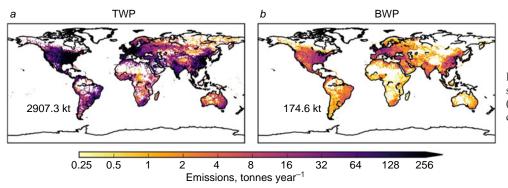


Figure 5. Global annual emissions of tyre wear particles (TWPs) (*a*) and brake wear particles (BWPs) (*b*).¹⁷⁸

1900 microfibres per wash.⁴⁴ A significant contribution to the release of MP dust into the air is made by mechanical cutting and grinding of polymer products. Yet another major source of MP emissions into the air environment is tyre and brake abrasion.^{38,45} In a global investigation of air, enhanced concentrations of MPs were detected in the regions with a high vehicle density: east of the USA, Northern Europe, eastern China, the Middle East, and Latin America.¹⁷⁸ Throughout the world, the annual total emissions of tyre wear particles (TWPs) and brake wear particles (BWPs) were 2907 and 175 kt year⁻¹, respectively (Fig. 5). In urban areas, MPs are concentrated in soil and road dust. The wind and vehicle traffic easily suspend and re-suspend lightweight polymer materials in the air currents.

The inhalation of MP particles can be harmful to human health. These particles can become lodged deep in the lungs and cause long-term inflammation, formation of scar tissue (fibrosis), and even consolidation (granulomas).^{56,174} The extent of tissue damage usually depends on the cumulative inhaled dose. According to studies, inflammation can occur in two ways. First, the particles or fibres can directly stimulate cell growth in lung tissue. Second, the interaction between the lung cells and MP particles/fibres can cause inflammation, cell proliferation, and DNA damage (genotoxicity) due to the continuous formation of reactive oxygen species (ROS).¹⁷⁴ Overproduction of ROS causes oxidative stress, thus inducing chronic inflammation and promoting further lung disease pathogenesis. The aspect ratio of the fibres affects both the fibre uptake by alveolar macrophages and the rate of mucociliary clearance, that is, a nonspecific mechanism that provides local protection of respiratory mucosa from external impacts or infections. Long and thin fibres are typically more physiologically active than short ones and are usually phagocytized only partially. These stable particles can penetrate the epithelial layers and cause either short-term or long-term inflammatory responses. A few studies have been conducted to elucidate the hazard of micro- and nanoplastics for human lungs. The effect of polystyrene nanoparticles (25-70 nm) on a lung cancer cell line (A549) was investigated.¹⁷⁹ The authors found that these particles substantially decrease the cell viability, increase the production of proapoptotic proteins such as caspase-3, caspase-8, caspase-9, and cytochrome and disrupt the proteins that regulate cell growth and cell death.

The 3D printing technology is another possible source of MPs in the atmosphere. Thermoplastic filament materials such as **PLA**, **PA**, and **PET** are often used in 3D printing by fused deposition modelling. In the fused filament fabrication (**FFF**) technology, the plastic filaments are melted and are deposited layer-by-layer.¹⁸⁰ The printing is accompanied by the unintentional release of nano- or ultrathin particles. The ejection of aerosol particles is due to the open architecture of most 3D printers. This problem is aggravated by the ever-growing

popularity of indoor 3D printing stations within the living area. It was found that a 3D printer using ABS filament releases a high concentration of tiny particles during printing inside an enclosed indoor space.¹⁸¹ According to experiments, up to 10⁶ particles cm⁻³ could occur in air, most of them were between 20 and 40 nm in size, and they could easily agglomerate with one another. The higher the temperature required to melt the filament, the greater the amount of emissions. As a result, PLAbased filaments, which melt at a lower temperature, produce less emissions than ABS-based filaments, which require higher temperatures. Both ABS and PLA particles have adverse effects on cell viability.¹⁸² According to toxicity testing results, PLA particles are more hazardous than ABS particles, but since ABS is much more commonly used for printing, the harm of these two types of plastics is comparable.182 Meanwhile, ABS filaments may have even more complex effects than PLA, since a higher temperature of the nozzle naturally increases the number of released particles. The complex processes that cause the formation of aerosols during FFF 3D printing have not yet been thoroughly studied. Researchers measured the concentrations and size distributions of the particles emitted by a 3D printer under various conditions.¹⁸³ The authors showed that near the extruder nozzle, a heated filament generates particles that are then dispersed in the air in the form of an aerosol (Fig. 6). The technical details of the printing process such as the filament feed rate are also important.¹⁸⁴ Compared to a slow feed rate of 30 mm s⁻¹, a medium feed rate of 60 mm s⁻¹

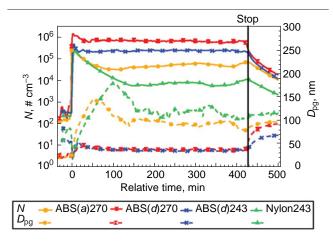


Figure 6. Time evolution of the total number concentrations (*N*) and geometric mean diameters (D_{pg}) of MP particles measured in chamber experiments. The zero time in the *x*-axis indicates the beginning of the print run, and the vertical line indicates the the end of printing. The filament type and brand and the extruder temperature are given in the bottom frame.¹⁸³

results in more particle emissions. However, owing to faster heat dissipation from the nozzle and less pronounced thermal disintegration of the filament, fast feed rate results in the lowest concentration of the emitted plastic particles. Thus, to reduce the MP particle emission, it is possible to change the feed rate, although this may affect the printing quality.¹⁸⁵

The plastic particle emissions from laser printing or powder coating in indoor workplaces have a significant impact on human health.²² The study¹⁸⁶ describes characteristics of particle emissions from 110 laser printers produced by different manufacturers. The emission intensity and particle size distributions were assessed by measuring the total concentration of particles emitted by the printers placed in an experimental chamber. In terms of the number, surface area, and weight of particles, the emission rates varied from 3.39×10^8 to 1.61×10^{12} particles min⁻¹, from 1.06 to 1.46×10^3 mm² min⁻¹, and from $\tilde{1}.2 \times 10^{-1}$ to $1.23 \times 10^2 \ \mu g \ min^{-1},$ respectively. The diameter of particles detected for the investigated laser printers was from 10.8 to 124.1 nm, with a median value of 34 nm. The parameters determined in this study are not lethal to the human body. However, when plastic nanoparticles are continuously inhaled, they are highly toxic and can be detrimental to human health.187,188

Here the question may arise of whether it is appropriate to classify nanoparticles emitted during 3D printing as MPs.^{189–191} Or should they be identified only as nanoplastics and be the subject of another review? No unambiguous answer has yet been given in the scientific literature. In principle, in most studies, scientists do not differentiate between the damages caused to a living organism by nanoplastic or microplastic particles.^{20,160,192–194} Among other reasons, this is due to the difficulty of separating particles by size, especially in complex matrices such as biological tissues.^{195–197} Another possible reason may be related to the ability of unstable nanoscale plastic

particles to agglomerate and aggregate into MPs.^{198,199} Accurate determination of plastic particle size is achieved by using highprecision methods such as scanning electron microscopy, Raman spectroscopy, and other physical techniques.^{198,200-203} Routine characterization and quantification of micro- and nanoplastics in biological and environmental samples will require simultaneous application of a few analytical methods. A multicentre observational study of patients undergoing carotid endarterectomy for asymptomatic carotid artery disease has been reported.²⁰⁴ The samples of carotid plaques examined by chromatographic methods in combination with isotope analysis and electron microscopy showed the presence of plastic micro and nanoparticles. These patients had a higher rate of myocardial infarction and stroke compared to the patients whose blood vessels showed no evidence of micro- and nanoplastics. Using Fourier transform IR spectroscopy, forty types of MPs were detected in the samples of human lung tissue.⁵⁶ Microplastic particles were found in all parts of the lungs, with the maximum concentration being present in the lower parts. The results of these studies indicate that the inhalation of MPs leads to disastrous consequences for living organisms.

Thus, micro- and nanoplastics affect all the existing systems: hydrosphere, atmosphere, lithosphere, and biosphere. A broad range of their sources (in combination with the easy transport possibility by all the existing environmental mechanisms) gives rise to a grim situation of total and ever-growing pollution of the Earth. The damage brought by MPs to living organisms is enormous.

4. Degradation mechanisms of plastics

Plastic materials are aged under the action of natural environmental factors such as solar radiation, waves, and wind,

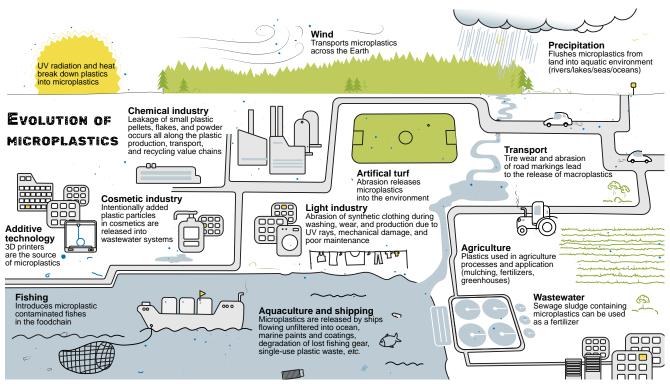


Figure 7. Evolution of MPs: formation, transport, and accumulation.

mechanical abrasion, thermal oxidation, and biodegradation. Furthermore, UV radiation, acidity and salinity of the medium, and temperature influence the degradation and fragmentation of plastics and the formation of MPs.¹¹⁷ Solar radiation is a major cause for the aging of plastics: UV radiation causes rupture of polymer chains, which leads to plastic degradation to give primary and secondary MPs.²⁰⁵ Figure 7 shows the evolution of MPs, namely, how they are formed, transported, and accumulated in various media.

4.1. Mechanical degradation

The mechanical formation of MPs is caused by the physical degradation of plastics under the influence of external forces: friction, weathering, or washing out by waves.^{206,207} In addition, the mechanical degradation of polymers can be caused by freezing and heating of plastics.^{15,16} The mechanical degradation due to abrasive wear is a result of the scratching and cutting of softer surfaces by harder particles. The harder material is either one of the mating surfaces or abrasive particles that happen to get between the mating surfaces from the outside²⁰⁸ or have formed as a result of wear. When an abrasive particle cuts a film, the crumbled material is removed as thin plastic chips (Fig. 8).

The mechanical degradation is most common in synthetic fibres (polyester, polyolefin, acrylates, and polyamide), which account for more than 60% of global fibre consumption. As has already been shown, household laundry and processes in the textile industry may be major sources of MP fibres due to the shear, abrasion, and impact stresses, which accompany the above processes.^{7,42} Wearing clothes may lead to MP release into the surrounding air.6 The mechanical wear also takes place for tyres, brakes, and the road surface. The stress generated upon abrasion of the road surface can be as high as the ultimate strength of the material, resulting in micro-cuts or scratches in the tyres. In chemical laboratories and in industrial plants, polymeric materials are being more and more often used instead of laboratory glass, and samples are kept in Eppendorf tubes. The ultrasonic treatment employed in the synthesis and research and to wash laboratory glassware also induces the mechanical degradation of polymers. Ultrasonic waves that pass through a plastic induce the breakdown of polymer chains and a change in the polymer molecular weight, which results in the mechanical formation of MP fragments.²⁰⁹

The polymer chain breaks that arise during photo, thermal, and chemical degradation influence the mechanical properties of the plastics, especially their elongation at break and tensile modulus. The long-term degradation in the environment increases the lifetime of materials, which results in the mechanical fragmentation of plastics and formation of MPs.²¹⁰

4.2. Photodegradation

The photodegradation is considered to be a major cause for aging of polymer molecules in the environment under the action of external factors that initiate the degradation of plastic products.²¹¹ Unlike mechanical degradation, which represents the direct conversion of plastics to MPs, photodegradation usually involves free radical reactions initiated by solar radiation. This process is mainly driven by high-energy UV-B radiation medium-energy UV-A (290 - 315 nm)and radiation (315-400 nm). The latter has a more pronounced effect because it is less absorbed by the atmosphere.²¹² The effect of UV radiation on polymers varies depending on the environmental conditions.²¹³ The photodegradation and oxidation of PE are minimized in an aqueous salt solution and are enhanced in air.²¹⁴ The refractive index of water increases due to the presence of salts, minerals, and lower temperatures, which reduces the light intensity. This results in a lower degree of oxidation and degradation. Accordingly, the largest MP particles are formed when the material undergoes photodegradation in air.²¹³

The studies addressing the plastic degradation rate under UV irradiation help to reveal the risks associated with MP contamination. According to experimental studies,^{215,216} the polystyrene coffee lids and polypropylene food wrappers can produce MP particles at a high fragmentation rate, along with plastic (PET) bottles, bags (LDPE), and cigarette filters (CA). The cigarette residues, which represent hazardous unsorted waste, contain cigarette ends made of plasticized cellulose acetate.²¹⁷ It was found²¹⁶ that cigarette filters peel off approximately <0.2 mm-thick 100 microfibres per day. The degradation of cellulose acetate is accelerated on exposure by UV radiation. Thus, up to 0.3 million tonnes of MPs can enter the aquatic environment annually. New varieties of cigarettes often contain flavoured filters with one or more 'buttons'. Technically, buttons in the cigarettes are capsules filled with a chemical flavouring agent that are embedded in the filter. Since flavoured cigarettes are considered to be more attractive to consumers (although no less harmful; in some countries, there are even projects to prohibit them), the amount of waste from the use of these cigarettes is increasing. As a result, not only CA microfibres but also residues of poorly soluble polymer capsules enter the environment (Fig. 9).

Most plasticized polymers (such as **PC**, **PET**, and **PE**) that are widely used in the food industry begin to slowly degrade when exposed to UV radiation and heat. Therefore, it is important to choose appropriate storage conditions.⁸ The photodegradation makes a contribution to plastic degradation; however, there are areas where sunlight has a negligible effect such as the ocean bottom or tropical forests. The degradation of a number of polymers was studied by simulating the tropical conditions:²¹⁸ eight hours of UV exposure followed by four

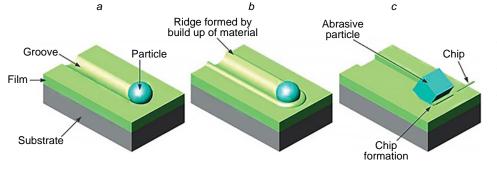


Figure 8. Mechanical degradation of polymer material: (*a*) plastic compression of the material under the slider in the formed groove, (*b*) ploughing in which the material is pushed aside to form ridges, and (*c*) abrasion in which all the displaced material is removed as a chip.²⁰⁸

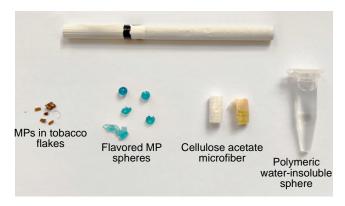


Figure 9. Microplastics from cigarette residues: tobacco dust, polymer capsules, cigarette filters.

hours of humidity. Extrapolation of the time required for complete loss of weight of the original polymer sample under accelerated weathering conditions showed that **PP** could degrade within one year, while **PET** remains stable for up to 1179 years.²¹⁸ However, the results correspond to a model laboratory experiment, while under more drastic real environmental conditions, plastics degrade much faster. Furthermore, none of the samples, except for **PP**, contained antioxidant additives, which accelerate the weight loss when present in the polymer.

On exposure to UV and visible light, polymers undergo chain cleavage with the formation of double bonds. Gradual yellowing of plastic materials attests to aging and degradation. PET and PE are completely transparent and highly resistant to photodegradation. Chemical additives, plasticizers, initiator remainders, chemophores, and structural defects present during plastic manufacturing can alter the way in which UV and visible light is absorbed and reflected.²¹⁹ The degradation of PE is accompanied by the Norrish reaction, resulting in the formation of free radicals, terminal vinyl and ketone groups, and backbone cleavage. Free radicals are combined with oxygen to form peroxides and peroxy radicals. The decomposition of peroxides can produce alcohols, carboxylic acids, ketones, aldehydes, or esters, which also break the polymer chain.^{220,221} **PP** is less stable than **PE** because it has a tertiary carbon atom, which is less resistant to oxidation. However, in general, the photodegradation mechanisms of PP and PE are similar. Commercial PP often contains added chromophores that promote the formation of free radicals on exposure to UV radiation. The subsequent radical reactions result in random chain cleavage and cross-linking and in the formation of lower molecular weight degradation products. On exposure to UV radiation, PVC also undergoes rapid dehydrochlorination, resulting in the formation of short fragments of polymer chains with double C=C bonds. Unsaturated carbon bonds are more susceptible to photodegradation.²²² Consequently, polymers lose molecular weight and become more brittle, which facilitates the subsequent degradation to MPs.

4.3. Thermal degradation

Heat treatment can also lead to the decomposition of polymer molecules. The chemical reactions involved in the thermal degradation are comparable to those occurring during photodegradation. At elevated temperatures, macromolecules can break to give free radicals. The thermal degradation can either decrease or increase the weights of the molecules as a result of polymer chain cleavage and formation of a new chain. The process can continue until the energy supply stops or until the recombination of two radicals occurs.

Exothermic oxidation is unlikely because of high temperature. However, slow thermal oxidation of plastics can occur through photodegradation, especially on beaches or open sidewalks exposed to direct sunlight. Both high temperature and UV radiation can accelerate oxidation reactions and degradation of plastics.²¹⁰

The degradation of plastics can also be induced by cooling and freezing. Plastic materials are characterized by a ductileto-brittle transition temperature (DBTT) at which the plastic becomes brittle and breaks, especially upon high-speed impacts. DBTT varies depending on the chemical composition of the plastic. As a rule, aging of plastics is accompanied by a decrease in their strength, and as materials are cooled from room temperature to cryogenic temperatures, they become increasingly brittle in response to mechanical stress. Cooling down plastics to temperatures below 0°C significantly increases the probability of plastic breakdown and the formation of MP particles.^{223,224}

4.4. Chemical degradation

In the atmosphere, there are various chemically reactive substances: ozone (O₃), sulfur dioxide (SO₂), nitrogen dioxide (NO₂), volatile organic compounds (VOCs), etc. The action of these chemicals induces fast or gradual degradation of plastics. Ozone is formed in minor amounts from atmospheric oxygen under the action of UV radiation and electric discharge. However, the concentration of ground-level O₃ increases due to environmental pollution. Plastics are greatly degraded on contact with ozone molecules: even at low concentrations, ozone reacts with unsaturated C=C double bonds to release free radicals, which induces polymer chain cleavage. Saturated polymers react with ozone in a similar way, but at a somewhat lower rate. When exposed to solar radiation, SO₂ becomes reactive by forming singlet or triplet states; thus, it can react directly with unsaturated double bonds in the polymers or induce photochemical reactions with O₂ to form O₃. The unsaturated double bonds in polymers can be attacked by NO₂. Furthermore, ozone can be generated by photochemical reactions between NO₂ and O₂.^{210,225}

The rate of chemical degradation of plastics to MPs depends on the type of polymer, the presence of additives, and the environmental conditions. The most important factors for the degradation of plastics are pH and salinity of water. Thus, the chemical degradation is faster in seawater than in freshwater. High concentrations of hydrogen ions (H⁺) in acid media or hydroxide ions (OH⁻) in alkaline media can accelerate the degradation of **PA** due to hydrolysis.²²⁶ The chemical degradation is often a catalytic reaction and occurs on the surface of the plastic. This is manifested as external defects, cracks, and a colour change; for example, excessive oxidation of phenolic compounds contained in polymers leads to yellowing or discoloration of plastics.²⁰⁵

Thus, although plastics are commonly considered to be inert, they can degrade to MP particles under the action of various factors ranging from mechanical load to reactions with chemical oxidants. Additional environmental risks are generated by advanced technologies or nanotechnologies and additive manufacturing processes, which promote the release of plastic nanoparticles into the environment as aerosols.

5. Capture of microplastics

Microplastics are transported across the environment in a variety of ways, in particular by rivers, coastlines, and air currents. There are two major pathways for MPs to get on the Earth's surface from the atmosphere. The first pathway is wet: suspended microplastics are deposited together with atmospheric precipitation, and rainwater containing MP particles migrates into the ground and ends up in freshwater lakes, seas, and oceans.^{54,227} The second pathway is the transfer of MPs by wind, waves, currents, and tides. Monitoring of air circulation may help to identify the sites of plastic and MP accumulation. Coastlines, mountains, and natural/artificial structures can greatly influence the distribution of MPs and create conditions for MP accumulation.²²⁸ One more possible way of MP spreading can be provided by movement of all transport vehicles (aircrafts, ships, and cars).

A variety of methods can be used to capture MPs, depending on the location and type of pollution. Figure 10 depicts the modern mechanisms of MP capturing: water and air filtration, adhesive-coated beads, and the design and use of microrobots. Actually, the capture and removal of pollutants from the environment is not limited to the methods presented here; the number of relevant studies is permanently increasing.^{133,229–231}

Trawl nets with various mesh sizes (100 to 500 μ m) are used to capture and remove MPs from water. The finer the mesh, the smaller the collected MP fibres may be.²³² Nano- and microrobots can also be used to capture MPs from contaminated water. They represent modified devices fabricated from microand nano-sized materials capable of collecting energy from the environment and converting it into motion. For example, this may be photocatalytic micromotors based on TiO₂ deposited on magnetic (Fe₃O₄) microspheres, which are collected in a magnetic field and move under the action of light.²³³ The systems can be supplemented by ion exchange resins or porous materials to improve the adsorption properties. These miniature devices operate on local chemical fuels (*e.g.*, hydrogen peroxide), light energy, or magnetic fields or use self-propelled biological components (algae, plankton). The tunable surface charge makes it possible to attract MP particles to microrobots. Light energy is used to move and remove pollutants from water, while an applied magnetic field enables easy collection of the contaminants after the treatment even from locations difficult to access, *e.g.*, inside pipelines.

Adhesive coatings can be used to capture MPs. For example, zirconium silicate or stainless-steel beads coated with poly(2ethylhexyl acrylate) can be effective for removing MPs from aqueous mixtures. Adhesives are suitable for capturing both polar and non-polar MPs, since their surface charges are identical and markedly differ from the charge of water.^{234,235} Aerosol MPs emitted from various sources are involved in many dynamic processes, including diffusion, convection, agglomeration, and settling; therefore, the MP lifetime substantially depends on the concentration and size of particles. A simple estimation of the settling rate of aerosol MP particles in room air shows that deposition of 5-µm particles can occur within a few minutes, and larger particles will settle even faster.²³⁶ Table 2 summarizes data on settling of spherical aerosol particles of various sizes. For effective capturing of MPs and air cleaning, it is possible to use air filters based on

Table 2. Settling velocity of aerosol MPs particles of various sizes in room air at $20^{\circ}C.^{236}$

Particle size, µm	Settling velocity, $\mu m \ s^{-1}$	Distance settled in 1 s, mm
0.2	1.2	0.072
0.5	7.5	0.5
1	30	1.8
2	119	7.2
5	746	44.8
10	2985	180
20	11942	717

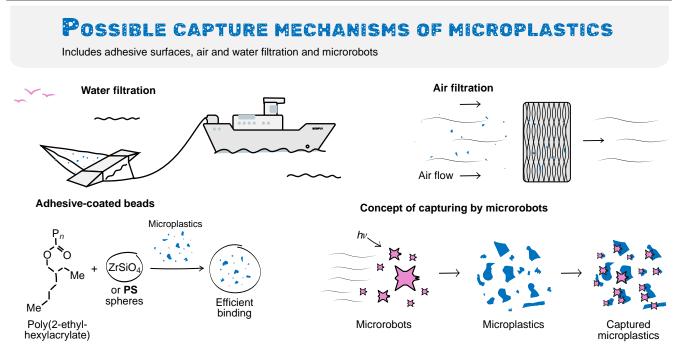


Figure 10. Major mechanisms of MP capturing: water and air filtration, adhesive-coated beads, microrobot concept.

multi-walled (MWCNT) and single-walled (SWCNT) carbon nanotubes. $^{\rm 237-239}$

Microparticles contained in air and water are eventually deposited on a solid surface. There are a few ways to detect MPs in soil and remove them from soil and sediments. The most commonly used approach is based on the density difference between MPs and the polluted soil. The procedure consists of three stages: (1) mixing of a water or soil sample with the flotation solution; (2) continuous flotation and settling of the system; and (3) filtration or sieving of the supernatant.²⁴⁰ In addition, the removal of MPs from soil and water can be accomplished by targeted oxidation and photocatalysis to give volatile organic compounds, CO₂, and H₂O and forced biodegradation of MPs by various microorganisms.^{209,241–244}

Development of the techniques for efficient capture and removal of MPs is becoming an important and a necessary tool for achieving the sustainable development of the ecosystem. This will require a major investment of time and resources from the global scientific community in the near future. The present review only briefly touched upon the methods of MP degradation, since this issue requires more in-depth and detailed consideration. The complete withdrawal of MPs from the environment implies two general approaches. First, it is necessary to comprehensively prevent the emergence, accumulation, and spread of MPs. The second approach requires the invention of the ways for chemical and physical destruction immediately after the collection. The most evident ways for controlling MPs according to the first approach is prevention and elimination of spontaneous dumping and landfills, decrease in the quantity and use of plastic products, and replacement of polymers by biodegradable materials. Even now there are stringent regulations on the consumption of tobacco products, which cause irreparable damage to both human health and the environment as a whole (accumulation of garbage, which further turns into MPs). These measures may be initiated by the governments, local authorities, and the public. The second, more advanced approach implies the use of hightemperature pyrolysis for the processing of MPs into fuel or carbon nanomaterials, which can then serve for various applications. Studies of this type are in progress, but currently they are at an early stage of development. However, it should be mentioned once again that despite numerous studies on the detection, spreading, and capture of MPs and active discussion of the problem at international scientific events, researchers and participants have not yet proposed a global and rational approach to the capture and destruction of MPs. The authors hope that solution of the problem of accumulation and disposal of MPs is only a matter of time, and effective approaches and techniques will certainly appear.

6. Conclusion

For over a century, people have been using plastics instead of materials based on non-renewable resources (metals, wood, paper), believing plastics to be harmless. However, due to the ever-increasing variety of polymer production as well as the addition of plasticizers and complex chemicals to polymers, plastic products are no longer considered to be only beneficial. Apart from the enormous amount of plastic garbage generated after household use of plastic products, polymer materials are converted to microplastics (MPs) through various mechanisms: photodegradation, weathering, and thermal or mechanical degradation. Due to the abundance of transportation pathways, in the future MPs may become predominant pollutants in soil, water, and air, in addition to radioactive and highly toxic chemicals. MPs affect soil organisms and tremendously alter the marine environment. They have already been found inside the human body, and the number of studies reporting these facts is increasing every day. By changing the methods of plastic production and disposal, we can significantly reduce the harm to the Earth and to the health of people and all living beings. For instance, polymers that degrade at higher temperatures may be used for 3D printing, and this would reduce the emission of MP aerosols. However, it is obvious that due to the diversity of MP types and transportation mechanisms, an ensemble of methods is required to reduce the damage to the environment. Therefore, a complex and comprehensive study of the MP formation, lifecycle in the environment, and capture and MP decomposition routes will provide for the development of integrated methods to prevent possible environmental disasters.

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7. List of acronyms

- ABS acrylonitrile-butadiene-styrene;
- AI artificial intelligence;

ATR FTIR — attenuated total reflectance Fourier-transform infrared spectroscopy;

- CA cellulose acetate;
- FFF fused filament fabrication;
- HDPE high-density polyethylene;
- LDPE low-density polyethylene;
- LLDPE linear low-density polyethylene;
- MP microplastic;
- MWCNT multi-walled carbon nanotube;
- PA polyamide;
- PAN polyacrylonitrile;
- PBDE polybrominated diphenyl ether;
- PC polycarbonate;
- PE polyethylene;
- PET polyethylene terephthalate;
- PLA polylactic acid;
- PMMA polymethyl methacrylate;
- PP polypropylene;
- PS polystyrene;
- PTM particle-tracking model;
- PU polyurethane;
- PVA polyvinyl alcohol;
- PVC polyvinyl chloride;
- ROS reactive oxygen species;

SWCNT — single-walled carbon nanotube;

- TBBPA tetrabromobisphenol A;
- US ultrasound;
- UV ultraviolet.

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