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Review

Degradation of Microplastics and Nanoplastics: An Underexplored Pathway Contributing to Atmospheric Pollutants

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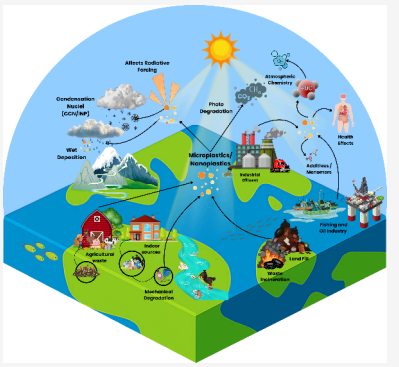
ABSTRACT: Microplastics (MPs) and nanoplastics (NPs) are widespread pollutants present across all environmental matrices, including the atmosphere. They originate anthropogenically from primary sources, like microbeads, glitters, industrial abrasives, etc., and from secondary sources through degradation of larger plastic products, textile fibers, tire wear, waste incineration, etc. Degradation processes, such as mechanical, photochemical, chemical, and microbial degradation, break down plastics into smaller particles and gaseous byproducts. Atmospheric degradation processes of MPs/NPs enhance their area/volume ratio and introduce oxygenated functional groups at the surface, which increases their hydrophilicity and interactions with other pollutants in the surroundings. Thus, MPs/NPs also act as great vectors for toxic substances, including heavy metals, polycyclic aromatic hydrocarbons, and persistent organic pollutants, amplifying their environmental and health risks. MPs/NPs have been detected in various human tissues and fluids. Being bio-inert, they cannot be metabolized and leave the body only through excretory routes. They not only interact with the human organs directly but also indirectly via releasing additives and adsorbed/absorbed pollutants and, thus, can exhibit higher toxicity compared to other atmospheric aerosols. Furthermore, atmospheric MPs/NPs influence radiative forcing and cloud formation, and their photodegradation also releases greenhouse gases, like CO_2, CH_4, and volatile organic compounds (precursors of ozone), linking plastic pollution to climate change. Despite their growing recognition, the study of atmospheric MPs and NPs remains in its infancy, with numerous uncertainties surrounding their behavior, fate, and effects. This review aims to highlight underexplored degradation pathways of atmospheric MPs/NPs that may be enhancing their environmental, health, and climatic implications. It also proposes the future directions for atmospheric MP/NP research.



KEYWORDS: *greenhouse gases, climate change, particulate matter, health effects, organic aerosols*

1. INTRODUCTION

Plastics are synthetic organic polymers derived primarily from products of fossil fuels and are extensively used in industrial and commercial sectors due to their flexibility, durability, and cost-effectiveness.[1,2] According to the United Nations Environment Programme (UNEP), global plastic production reached approximately 460 million metric tons (Mt) in 2019 and is projected to increase to 1480 million Mt by 2050.[3] An estimated 20 million Mt of plastic waste enters the environment annually, and this figure is anticipated to rise significantly in the coming decades.[2,3] Improper disposal and inadequate waste management practices have led to plastics being detected in nearly every corner of the planet, from the depths of the Mariana Trench to the summit of Mount Everest, and from the polar regions of the Arctic and Antarctic to more temperate and tropical zones. Plastics are now pervasive in diverse environmental compartments, including terrestrial soils,[4] freshwater systems,[5] the atmosphere,[6] and marine environments.[7,8] Among these, oceans serve as the ultimate sink for most plastic debris due to hydrodynamic and atmospheric transport mechanisms.[9]

Plastic pollution is a direct result of anthropogenic activities, predominantly originating from single-use items such as bottles, straws, caps, cups, and carry bags. This form of pollution contributes significantly to biodiversity loss and the degradation of ecosystems. Once introduced into the environment, plastics undergo various degradation mechanisms, including mechanical, photochemical, chemical, and microbial processes, leading to the formation of smaller plastic particles and gaseous byproducts.[10−12] Over time, these processes transform macroplastics into microplastics (MPs) and nanoplastics (NPs). MPs are typically defined as plastic particles ranging in size from 5 mm down to 1 μm, while NPs refer to particles smaller than 1 μm.[13,14]

MPs and NPs have emerged as pervasive contaminants across all environmental matrices, including the atmos-

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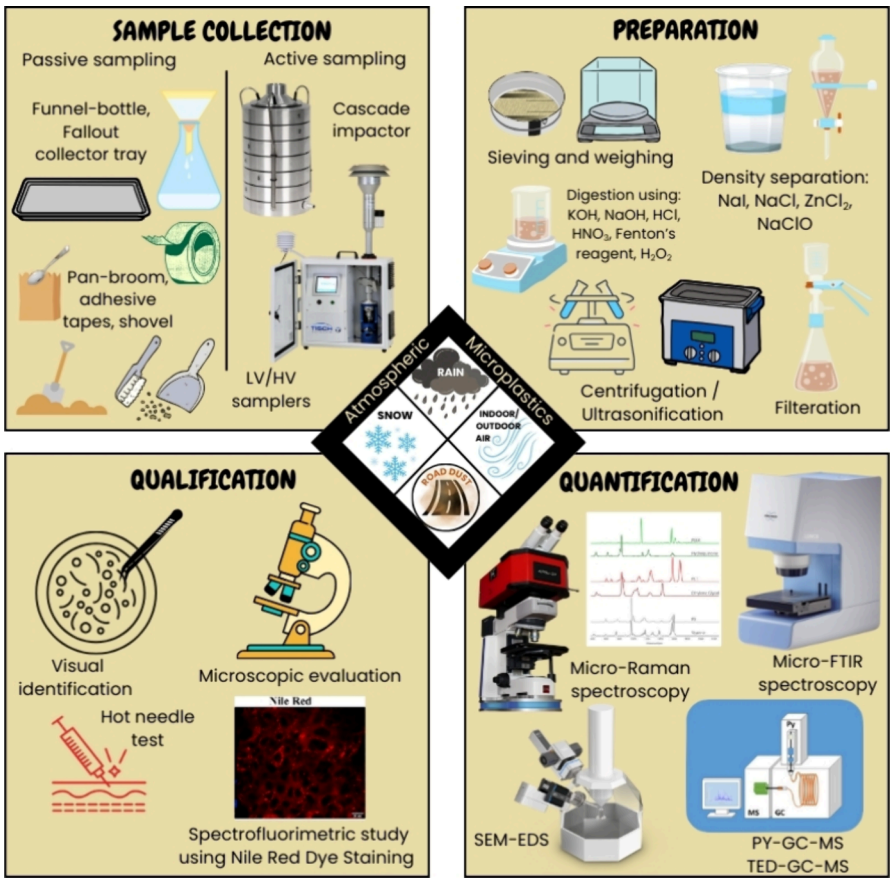

Figure 1. Overview of sample collection, preparation, and instrumentation techniques used for studying atmospheric MPs.

phere.[15,16] While considerable research has been conducted on MPs in aquatic and terrestrial environments,[17−24] the study of atmospheric MPs/NPs is yet in the initial stages, with a limited but growing number of investigations.[25−29] Atmospheric MPs/NPs have been detected in diverse settings, including urban centers, remote regions, and even polar environments, underscoring their capacity for widespread dispersion and long-range atmospheric transport.[25,30−35] Due to their bio-inert nature and persistent presence, these plastic fragments pose significant risks to human health, especially when airborne. Their small size facilitates inhalation and potential translocation within biological systems, raising concerns about long-term exposure and toxicity.[36,37] Emerging evidence links MPs and NPs to various adverse human health effects, including cancer risk, endocrine disruption, respiratory dysfunction, and disturbances in gut microbiota.[38−46] MPs/NPs cannot be metabolized in biological systems and thus, they are eliminated from the body primarily through excretory pathways.[36] They have been detected in human breast milk, urine, and feces, indicating systemic exposure.[47−52] Moreover, their contact with living tissues within the body can trigger inflammation and abnormal cellular activity.

Environmental weathering and surface oxidation of MPs over time lead to the formation of reactive oxygen species (ROS) and the development of bioactive functional groups.[53,54] These transformations not only increase the toxicity of MPs/NPs but also enhance their ability to absorb, adsorb, and transport harmful substances. In addition, MPs and NPs can serve as carriers for pathogenic microorganisms and antibiotic-resistant bacteria, further exacerbating their threat to environmental and public health.[55,56]

MPs and NPs undergo various physical and chemical aging and degradation processes, which have important implications for climate dynamics and environmental sustainability.[57,58] Existing literature includes several reviews on the photodegradation of MPs in marine, terrestrial, and aquatic environments.[59−62] Additionally, studies have examined the degradation of MPs and associated greenhouse gas (GHG) emissions in soil and aquatic systems,[63,64] as well as GHG emissions from plastics during the production stage.[65] It was estimated that about 4.5% of global GHG emissions were from plastics in 2015.[66] GHGs are emitted into the atmosphere throughout the plastic lifecycle, from extraction to disposal. Other reviews have explored the impact of plastic pollution on soil microbial diversity and its broader implications for the carbon cycle.[67,68] However, despite the growing concern over airborne MPs and NPs, the role of these particles in the atmospheric environment, particularly in relation to degradation pathways, GHG emissions, and interactions with climate processes, remains largely unaddressed. Some reviews have addressed the sampling, detection, occurrence, abundance, sources, and health effects of MPs in the atmospheric environment.[69,70] Recently, a review discussed MPs aging and its impacts on various spheres of the atmosphere.[71]

The present review article critically evaluates the current state of knowledge on atmospheric MPs/NPs by addressing four key aspects: (a) sources and atmospheric abundances, (b) atmospheric degradation mechanisms, (c) accumulation mechanisms of pollutants on MP/NP surfaces, and (d) their

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Table 1. Technique Used in the Identification of Atmospheric MPs/NPs

technique	principle	size limit	advantages	limitations
μFTIR	absorption of IR by the chemical bonds	>20 μm	non-destructive, minimal sample preparation is required	cannot detect black particles, and spectra overlapping can cause misidentification
μRaman	laser scattering identifies molecular structure	>1 μm	non-destructive, high spatial resolution, and can detect MPs of different colors	fluorescence interference in aged MPs and expensive
Py−GC/MS	thermal decomposition + chemical analysis	no limit	specific and quantitative detection of polymer mass	destructive, lacks size and shape information
optical microscope	using magnification	>50 μm	inexpensive and quick detection	polymer type cannot be confirmed
SEM−EDS	electron beam interaction with the sample	100 nm	very useful in fiber detection, particle morphology, and elemental composition	polymer type cannot be identified and expensive

potential impacts on human health and climate. It also proposes the future directions for atmospheric MP/NP research.

2. SOURCES AND ABUNDANCE OF MPs/NPs IN THE ATMOSPHERE

In order to study the sources and abundances of atmospheric MPs/NPs, samples are collected and analyzed using various methods. Their atmospheric abundances are often expressed as the number of particles per unit volume of air. Abundances of MPs/NPs in road dust are described as the number of particles per unit mass of dust or per unit of area of sampling surface. As of now, there are no uniform criteria for studying atmospheric MPs/NPs, and thus, the comparison of reported values may be biased.

2.1. Sampling and Analysis. Numerous active and passive sampling techniques are available to measure and report atmospheric MPs (Figure 1), but they are not standardized. Researchers across the globe often use aerosol or particulate matter (PM) active sampling measurement techniques to estimate and report airborne MPs.[6] Depending on the aerosol composition to be analyzed, PM is usually collected using a high- or low-volume (HV/LV) air sampler with various filter substrates. Dust or resuspended dust on roadside and kerbs, indoor dust, snow, and rainfall samples are collected using passive sampling techniques (Figure 1). A recent study reported that MPs are also deposited on plant leaves,[72] suggesting their potential for assessing atmospheric MPs pollution.

In the case of dry deposition and road dust samples, the samples are first sieved to remove coarse debris and irrelevant large particles. The sieved material is then subjected to organic matter digestion using either H_2O_2 or Fenton's reagent (a mixture of H_2O_2 and Fe^{2+} catalyst) to break down residual biological material. This step is essential to eliminate organic interference during spectral measurements using μFTIR (Fourier transform infrared spectroscopy) or Raman spectroscopy. Following digestion, samples undergo density separation using high-density salt solutions such as sodium iodide (NaI), zinc chloride ($ZnCl_2$), or sodium chloride (NaCl) to isolate microplastic particles based on their buoyancy.[34,73,74] The floating fraction is then recovered via vacuum filtration for subsequent analysis (Figure 1).

Atmospheric MPs can be identified and quantified commonly using microscopy, spectroscopy, and mass spectrometry techniques.[75,76] After sample processing (if needed), optical microscopy is used initially to determine the size, shape, and color of the larger MPs; however, this technique may have a bias in measurement.[77] Atmospheric MPs/NPs are generally fine fractions mixed with other aerosol particles and are not easily detectable using scanning electron microscope (SEM) and transmission electron microscopy (TEM) due to the limited availability of information on their chemical characteristics. Nile red staining for fluorescence microscopy also faced challenges due to the lengthy workflow and limitations in optical quantification.[6] Vibrational spectroscopy techniques such as infrared (IR) and Raman, attached to a microscope, help obtain chemical information, polymer characterization, and visual identification.[13] These techniques can differentiate MPs from other aerosols in the atmosphere. Multiple techniques used for identification, along with their advantages and disadvantages, are presented in Table 1.

Extensive libraries of vibrational spectroscopy used in the polymer industry help identify the polymer in complex mixtures of aerosols with distinctive spectra (Figure 1). However, the microspectroscopy technique has its limitations in particle detection, leading to increased analysis time.[13] Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM−EDS) is highly effective for detecting MP fibers, and analyzing their surface morphology and elemental composition.[78] However, it cannot identify the polymer type, as it lacks functional group specificity. The alternative method for microspectroscopy to identify MPs is mass spectrometry, which can identify complex mixtures of aerosols in the nanometre size range. Pyrolysis gas chromatography and mass spectrometry (Py−GC/MS) is an offline technique which is destructive and requires sufficient processed samples.[79] High-resolution time-of-flight mass spectrometry (HR-ToF-AMS) is an online technique,[80] that has recently been shown to be helpful for identifying specific types of MPs/NPs.[81,82] Further, emerging techniques such as laser-directed infrared (LDIR)[83] and time-domain nuclear magnetic resonance (TD-NMR)[84] are also helpful in identifying MPs/NPs.

2.2. Primary and Secondary Sources. MPs and NPs are emitted into the atmosphere from primary and secondary sources. The primary sources are manufactured MPs for industrial applications, such as microbeads, pellets, glitters, industrial abrasives, etc.[85] Microbeads are primarily used in personal care products. Cosmetic industries or personal care products manufacturers use microbeads in toothpaste, facial scrubs, and creams. About 4594 to 94 500 microbeads are released into the atmosphere in a single wash from cosmetic products.[85,86]

In contrast, secondary MPs/NPs are formed in the atmosphere mainly through photo and chemical degradation of plastics present in the environment, such as the breakdown of plastic bottles and carry bags due to UV radiation and oxidation. Secondary MPs/NPs are most abundant in the atmosphere. Synthetic fibers, textiles, fragments, and wear and

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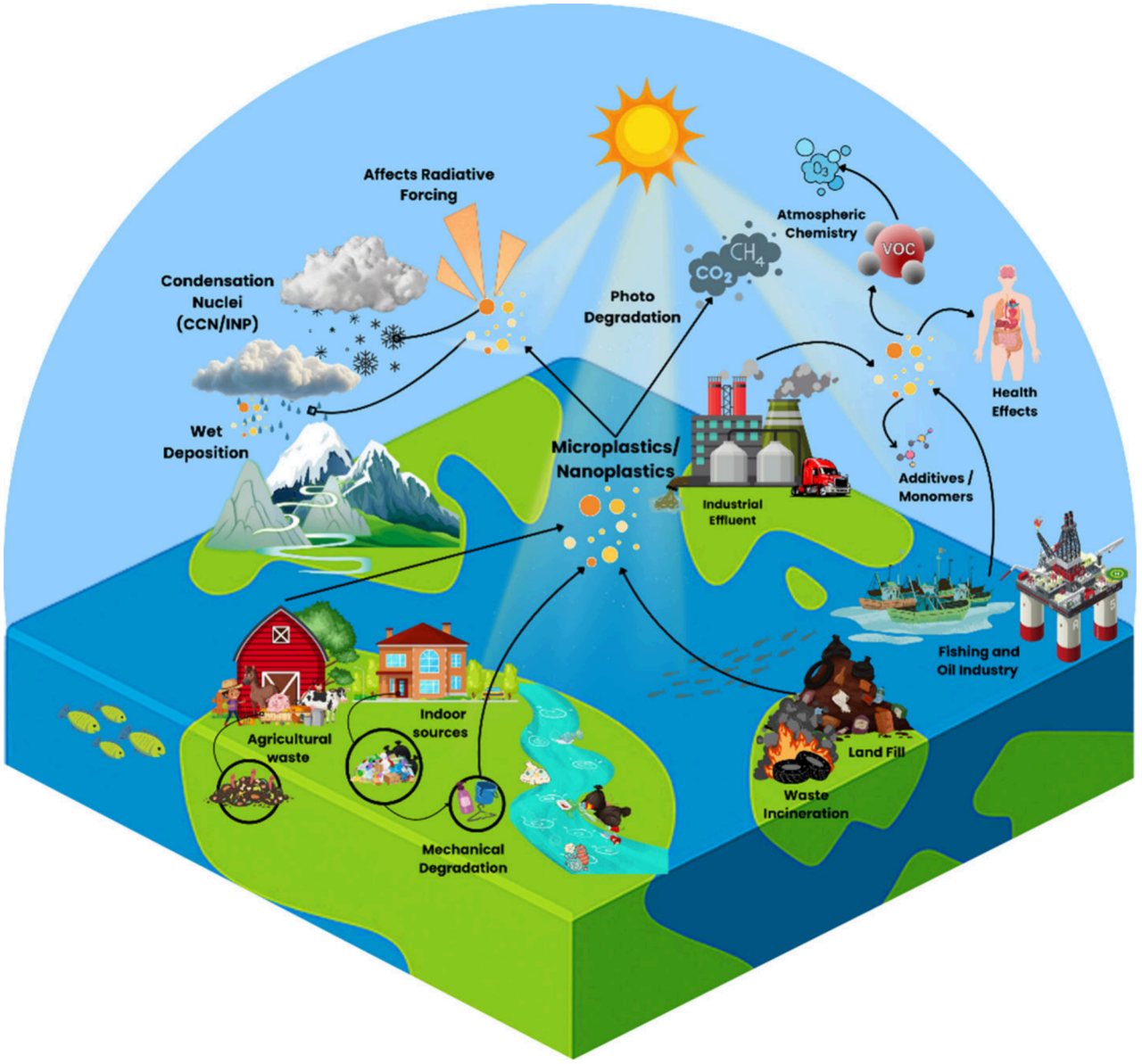

Figure 2. Schematic representation of sources, transport, degradation, and removal of atmospheric MPs/NPs and their possible effects.

tear of tires are the major secondary sources.[87] MPs/NPs present in a fibrous form in the atmosphere come predominantly from textiles and clothes. These fibers are usually artificial and made up of polyamides (PA) and polyesters (PES). Non-exhaust emissions, tire wear debris, and road dust primarily emit particles through the abrasion of tires [generally comprising polymer styrene−butadiene rubber (SBR)], generating airborne MPs.[73,74]

Further, landfills, solid waste generation, and domestic and industrial wastes can act as sources of MPs/NPs in the atmosphere (Figure 2). About 79% of manufactured plastics are in landfills and natural environments.[2] Solid waste sent to landfill sites produces leachates that affect the groundwater and the surrounding environment in the region, further resulting in atmospheric MPs (Figure 2). The waste management activities, such as loading, unloading, sorting, recycling, composting, and landfill incineration, also contribute to MPs/NPs in the atmosphere.[88] Open dumping and burning of plastic waste are important source of atmospheric MPs/NPs.[89,90] Laundry and textile washing are the most common sources of domestic fiber MPs. The indirect release also happens through chemical and mechanical wear and stress of garments and upholstery during washing.[91] Effluents from washing reach the wastewater treatment plants (WWTP) and contain significant amounts of MPs/NPs in the environment (Figure 2), and NPs are emitted from sewer pipe repairs.[92] Both primary and secondary sources of MPs are present in the treatment plants.[93]

Water disposed of from the domestic and industrial environment, either with or without treatment, reaches the canals and rivers in the region (Figure 2). These effluents from domestic and industrial waste contain MPs that travel to the estuaries and finally reach the ocean. The ocean is believed to act as a major sink and a minor source for airborne MPs; however, it is debatable.[9] The bubble burst ejection from the sea surface is the expected way plastics (mostly NPs) enter the atmosphere from the ocean. Earlier studies through inverse modeling suggested that the ocean was a significant source of MPs. On the contrary, a recent study on the global distribution of MPs with the help of chemical transport models proved

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minimal emission from the ocean.[9] Moreover, studies have established that soil acts as both a sink and source for atmospheric MPs through particle deposition and aerosol emission.[94] Fertilizers, wastewater irrigation, and plastic mulching are the common sources of MPs in agricultural soil.[95]

2.3. Atmospheric Transport and Deposition. Regional and global meteorology plays a vital role in the distribution of atmospheric MPs/NPs via long-range transport and deposition.[96] The MPs/NPs lifted into the atmosphere could be transported over long ranges like mineral dust and other aerosols (Figure 2). This is evident from detecting MPs in remote environments, poles, and snow environments.[97] MPs have also been detected in uninhabited environments such as Antarctica, implying their global presence through atmospheric circulation.[31] MPs present in snow or ice could darken the surface (lower albedo). This could lead to faster melting, especially in polar and alpine regions. Accelerated melt contributes to sea level rise and feedback loops in climate systems.[31,32] Airborne MPs undergo complex transport, transformation, and deposition processes influenced by weather, particle surface properties, and various human activities. Atmospheric transport facilitates the release of MPs/NPs pollutants into the environment.[98] The finer particles have a large surface area, thus degrading faster and acting as better vectors to carry other pollutants in the atmosphere,[99] along with enhancing particle-to-gas conversion of inorganic and volatile organic compounds (VOCs) present as monomers in MPs/NPs.

The transported MPs get settled through wet and dry deposition (Figure 2). Wet deposition occurs through rain and snow,[100] while dry deposition occurs under gravity, turbulence, impaction, and interception. The larger the particle size, the faster the settling velocity of MPs.[101] Fine MPs/NPs generally remain suspended in the tropospheric air for about a week, as they take more time to settle from the atmosphere. Higher deposition has been observed in urban and coastal areas.[34,102] As plants and forests can trap the MPs/NPs from the atmosphere, they act like a sink.[72]

2.4. Abundance of MPs in the Atmosphere. As discussed earlier, airborne MPs have been detected virtually in every environment, ranging from densely populated urban centers to remote polar regions, highlighting their pervasive nature and potential for long-range atmospheric transport. Their abundance varies significantly with the proximity of sources, geographic location, meteorological conditions, and the intensity of human activities. Moreover, concentrations of MPs differ considerably between indoor and outdoor environments, with indoor air generally exhibiting higher levels due to continuous shedding from textiles and other household sources.[26] Table 2 summarizes a few global studies reporting the size, shape, types of polymers, and relative abundance of airborne MPs, illustrating regional variability in their characteristics and environmental presence.

The most commonly identified polymers in airborne MPs are polyesters (PES) and polyamide (PA), primarily originating from synthetic textiles, followed by polyethylene (PE) and polypropylene (PP), typically associated with packaging materials, containers, and carry bags. Polystyrene (PS), often derived from foam and food containers, has also been frequently reported.[103] Morphologically, fibers dominate the shape profile, accounting for approximately 60−90% of airborne MPs, followed by fragments and granules (10−30%) (Table 2). However, it is important to note that most of the

Table 2. Abundance of MPs in the Atmosphere Observed from a Few Recent Studies across the Globe

country/region	sampling location	mean abundance	shapes	colors	types of polymers	reference
China	Harbin	1.76 number of particles/m^3	fiber (59.01%), fragmented (30.18%), and granular (10.18%)	transparent (62.39%), black (13.74%), red (7.43%), white (6.53%), blue (6.31%), and yellow (3.6%)	PP (26.13%), PET (24.1%), PE (23.87%), PS (13.51%), and PVC (12.39%)	104
	Jiaozhou Bay, the Yellow Sea	708 ± 21.316 items/m^2/day	fragments (61.9%), fibers (25.6%), and granules (10.5%)		PET (23.8%), PE (31.6%), and cellulose (34.9%)	105
Iran	Tehran	1165 ± 147.64 items/m^2/day	fragment and fiber	black (38−43%), red (17−19%), gold (13−14%), brown (12%), blue (7−10%), yellow (3−5%), and green (2−5%)	PP (28.7%), PET (18.7%), PS (15%), PA (12.5%), PE and PVC (11.2%)	106
Taiwan	Taipei	6.39 ± 10.8 particles/m^3	fragment and fiber	gray, black, and translucent	PS (42.3%), PE (22.5%), and PP (21.6%)	108
	Taichung	2.2 ± 2.97; 1.92 ± 2.35 particles/m^3	fragment (40%; 46%) and film (41%; 33%)		PTFE and PA	107
India	Goa	1.46 ± 0.12 n/m^3	fibers (40%), fragments (35%), and films (25%)		PVC and PMMA (50.5%), polyester (15%), SBMA (11%), and polyacetal (9%)	109
	Ranchi	465 ± 27 particles/m^2/day	fibers (36%) and fragments (61%)	white and transparent	PE, PP, PS, and PVC	28
New Zealand	Aotearoa	65 ± 6 ng/m^3	fibers and fragments		PET, PS, PP, PE, PVC, PMMA, and nylon	110

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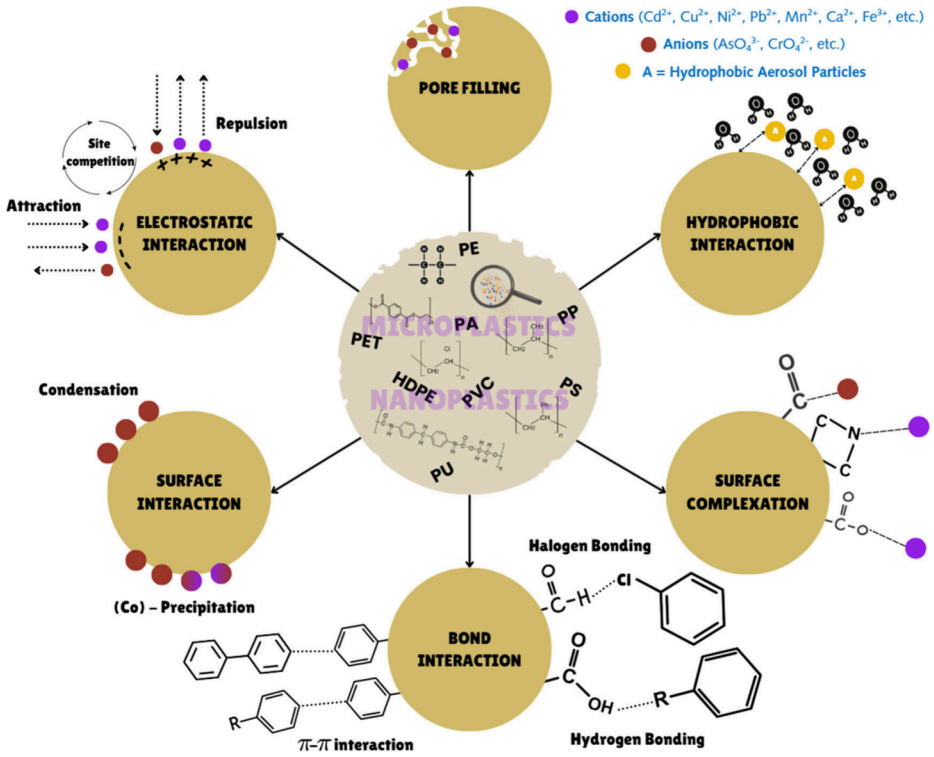

Figure 3. Adsorption and absorption mechanisms and interaction of organic and inorganic pollutants at the surface of MPs/NPs.

reported studies might have underestimated the abundance of NPs due to limitations in their detection and characterization methods.

Recent regional studies further highlight this variability (Table 2). In China, Harbin recorded 1.76 n/m^3 (number of particles/m^3) MPs, primarily fibers and transparent in color, with PP, polyethylene terephthalate (PET), and PE as major constituents.[104] Coastal sampling from Jiaozhou Bay showed higher deposition (46.7 items/m^2/day), with cellulose, PE, and PET dominating.[105] In Tehran, Iran, atmospheric MPs reached 1165 items/m^2/day, mainly black-colored fragments and fibers, with PP being the most abundant polymer.[106] In Taiwan, Taipei and Taichung reported varying concentrations (~6.4 and 2 particles/m^3), with PS, PE, and polytetrafluoroethylene (PTFE) identified.[107,108] India's Goa and Ranchi showed distinct profiles. Goa recorded 1.46 n/m^3, with high levels of PVC and poly(methyl methacrylate) (PMMA), while Ranchi had 465 particles/m^2/day dominated by PE, PP, and PS.[28,109]

In New Zealand, Aotearoa reported 65 ng/m^3, identifying multiple polymers including PET, nylon, and PMMA.[110]

These findings underscore the need for standardized methodologies in airborne MPs monitoring to enable meaningful comparison and improved understanding of their environmental and health implications.

3. ATMOSPHERIC DEGRADATION OF MPs/NPs

Polymers are of two types, namely hydrocarbon polymers and heterochain polymers, where the latter may contain oxygen/nitrogen/sulfur/chloride, etc., along with hydrocarbons.[111,112] Depending upon the target products, these plastic polymers often blended with chemical additives like hardeners [e.g., bisphenol A (BPA) and bisphenol S (BPS)],[113] plasticizers (e.g., phthalate esters), ultraviolet filters (e.g., oxybenzone), antimicrobials (e.g., isothiazolinones), and flame retardants (e.g., brominated organic compounds) in varying proportions to make them suitable for the targeted use.[114−116] Plastics made from these polymers may undergo various environmental degradation, resulting in the formation of fragments of lower molecular weight along with the release of additives.

3.1. Degradation Mechanism. Plastic or MPs degradation in the environment occurs mainly via four processes: photodegradation, chemical degradation, biodegradation, and mechanical degradation.[117] However, the degradation of MPs in the atmosphere is a complex process driven primarily by photochemical and mechanical degradation. Environmental parameters such as temperature, oxidants, and chemical interactions influence the degradation processes, while biological degradation is likely to play a minor role in the atmosphere. Although photodegradation is primary,[61] the other phenomena involved are chemical degradation caused by oxidation and hydrolysis, and mechanical (physical) degradation by embrittlement and cracking.[118]

Photodegradation is the degradation of plastics through sunlight (Figure 2). Atmospheric MPs undergo weathering in the ambient environment due to sunlight and moisture in the air. Weathering oxidizes the surface of the MPs, and the product may form carboxylic functional groups at the surface.[119] This carboxylic group induces a negative charge on the surface of the MPs, thus increasing their hydrophilicity, even though the pristine plastics are hydrophobic.[120,121] Chemical degradation occurs when the MPs/NPs break down in the atmosphere due to reactions with oxidizing agents such as ozone (O_3), hydroxyl radical ($^{\bullet}OH$), and singlet oxygen ($^1O_2$).[122−124] The oxidation reaction can happen with or without sunlight if oxidants are present, a key difference from photodegradation, which requires sunlight, especially UV-B and UV-C.[125] The degradation results in surface cracking, chemical oxidation, and loss of mechanical integrity, resulting in emissions of hydrocarbons, VOCs, fragmented MPs,

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carbonyl compounds, oligomers, and monomers of MPs and GHGs (Figure 2).[126−128]

Physical degradation of MPs in air involves fragmentation, embrittlement, and changes in surface texture and mechanical integrity, primarily driven by environmental factors like UV radiation, wind, and temperature fluctuations.[129] Airborne MPs originating from both outdoor and indoor sources undergo continual physical weathering. These transformations often lead to a reduction in their size, eventually forming NPs. Evidence of this was observed in studies characterizing MPs in ambient air, where a range of particle sizes suggested physical breakdown through environmental exposure.[29] Thermal degradation occurs at high atmospheric temperatures, especially in urban heat islands or wildfires. It can accelerate breakdown, leading to volatilization of low molecular weight fragments and the generation of toxic fumes such as dioxins and furans from PVC.[130]

GHG emission over time may act as slow but persistent climate forcers, especially in urban or high-UV environments. The release of monomers (various hydrocarbons/VOCs) may affect atmospheric O_3 and secondary organic aerosols (Figure 2).[131] Further, plastics contain chemical additives used in manufacturing to enhance their properties. These additives can leach out during degradation and pose a significant environmental threat. They may also cause severe health impacts such as cancer risk, inflammation, and oxidative stress,[3,132−134] as discussed in later sections.

3.2. Atmospheric MPs/NPs as Vectors. Atmospheric MPs/NPs are part of the atmospheric aerosols. MPs/NPs are more toxic than other aerosol particles because they not only cause serious health effects directly but also through acting as a vector of other pollutants. As they are anthropogenic organic polymers, they contribute directly to the atmospheric organic aerosols abundances, but their fractional contribution is not yet known. As they undergo fragmentation, MPs break down into NPs, further enhancing their contribution to atmospheric effects. Smaller MPs and NPs have a higher surface area to volume ratio, enhancing adsorption capacity.[135] Atmospheric degradation processes, including photochemical oxidation and mechanical weathering, can significantly alter their surface properties, increasing their reactivity and affinity for environmental pollutants. Aged MPs/NPs can act as better vectors by adsorbing/absorbing a wide range of toxic substances such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), phthalates, dioxins, and polychlorinated biphenyls (PCBs), thereby concentrating the levels of toxic species in aerosols (Figure 3).[121,135,136] After deposition, these sorbed contaminants can later be released back into the ambient environment (air, soil, water, or human body), posing additional and enhanced risks to human health and ecological systems.

The adsorption behavior of MPs and NPs in the atmosphere is governed by a complex interplay of environmental factors such as temperature, pH, and coexisting organic aerosols, which can either facilitate or hinder the adsorption of pollutants onto plastic surfaces. The specific adsorption mechanisms are primarily determined by the physicochemical characteristics of both the polymers and the interacting contaminants (Figure 3).

Hydrophobic interactions are predominant when nonpolar organic pollutants, such as PAHs and PCBs, interact with hydrophobic polymers like PE and PP, driven by the mutual exclusion of water. Electrostatic interactions occur between ionic pollutants and the charged surfaces of MPs and NPs. The charge at the surface may be acquired due to environmental aging or atmospheric ion deposition. Hydrogen bonding is another key mechanism, involving interactions between hydrogen donors (e.g., −OH and $-NH_2$) and acceptors (e.g., C═O, O, and halogens) found on either the pollutants or the plastic surface, particularly relevant in aged plastics enriched with oxygen-containing functional groups.[137]

Additionally, $\pi-\pi$ interactions play a role when aromatic polymers such as PS or PET interact with aromatic pollutants, resulting in the stacking of π-electron systems.[137,138] Other mechanisms contributing to the adsorption of organic pollutants include van der Waals forces, halogen bonding, and surface complexation, further enhancing the affinity of MPs for a wide range of contaminants.[138,139] Likewise, the adsorption of inorganic pollutants, particularly heavy metals, primarily involves electrostatic interactions, hydrophobic forces, and surface complexation[140−142] (Figure 3). These physicochemical properties enable MPs to act as vectors for various atmospheric pollutants, potentially prolonging the atmospheric residence time of certain compounds, altering their chemical reactivity, and indirectly influencing climate-related processes.

Further, coexisting atmospheric pollutants such as nitrogen oxides (NO_x), sulfur dioxide (SO_2), and VOCs can interact with MPs, influencing their environmental fate and reactivity. Earlier studies primarily focused on the interaction between MPs and hydrophobic organic pollutants, such as pesticides, due to their mutual nonpolar nature and affinity.[143] However, environmental aging significantly alters the surface chemistry of MPs, affecting their degradation kinetics and interaction potential. Photochemical and oxidative weathering introduce oxygen-containing functional groups onto the MPs surface, increasing surface polarity, porosity, and hydrophilicity.[143,144] Overall, the degradation mechanisms at the surface of MPs and NPs are highly dependent on the polymer type, surface chemistry, and the surrounding atmospheric conditions. As a result, recent research has increasingly shifted toward investigating interactions between aged MPs and inorganic pollutants, particularly heavy metals.[145,146]

4. CLIMATE AND HEALTH IMPACTS

4.1. Climate Effects via GHG Emissions. The GHG emission during the various stages of the lifecycle of plastics is a recurring process.[65] The warming effect of different GHGs is measured in CO_2 equivalent. A study estimated GHG emissions from all lifecycle stages as 1.79 billion tonnes of CO_2 equivalent, and the end-of-life of plastic emitted as 193.12 million tonnes of CO_2 equivalent, which was calculated using the existing scientific data.[147,148] Studies have estimated that fossil fuel extraction and transportation alone emit approximately 1.5 to 12.5 million Mt of GHGs into the atmosphere annually. These emissions are further amplified during the refining and manufacturing stages, which contribute an additional 184 to 213 million Mt of GHGs per year.[149−151] Collectively, these upstream processes represent a significant share of the total carbon footprint associated with fossil fuel-based energy systems, as up to 98% of the plastics produced are from fossil fuels, and only 2% are bioplastics. About 2.24 billion Mt of CO_2 equivalent was emitted into the atmosphere from plastic production, which accounts for about 5.3% of total GHG emissions.[152] The next stage is plastic usage, in which emissions are released in negligible amounts, and the final

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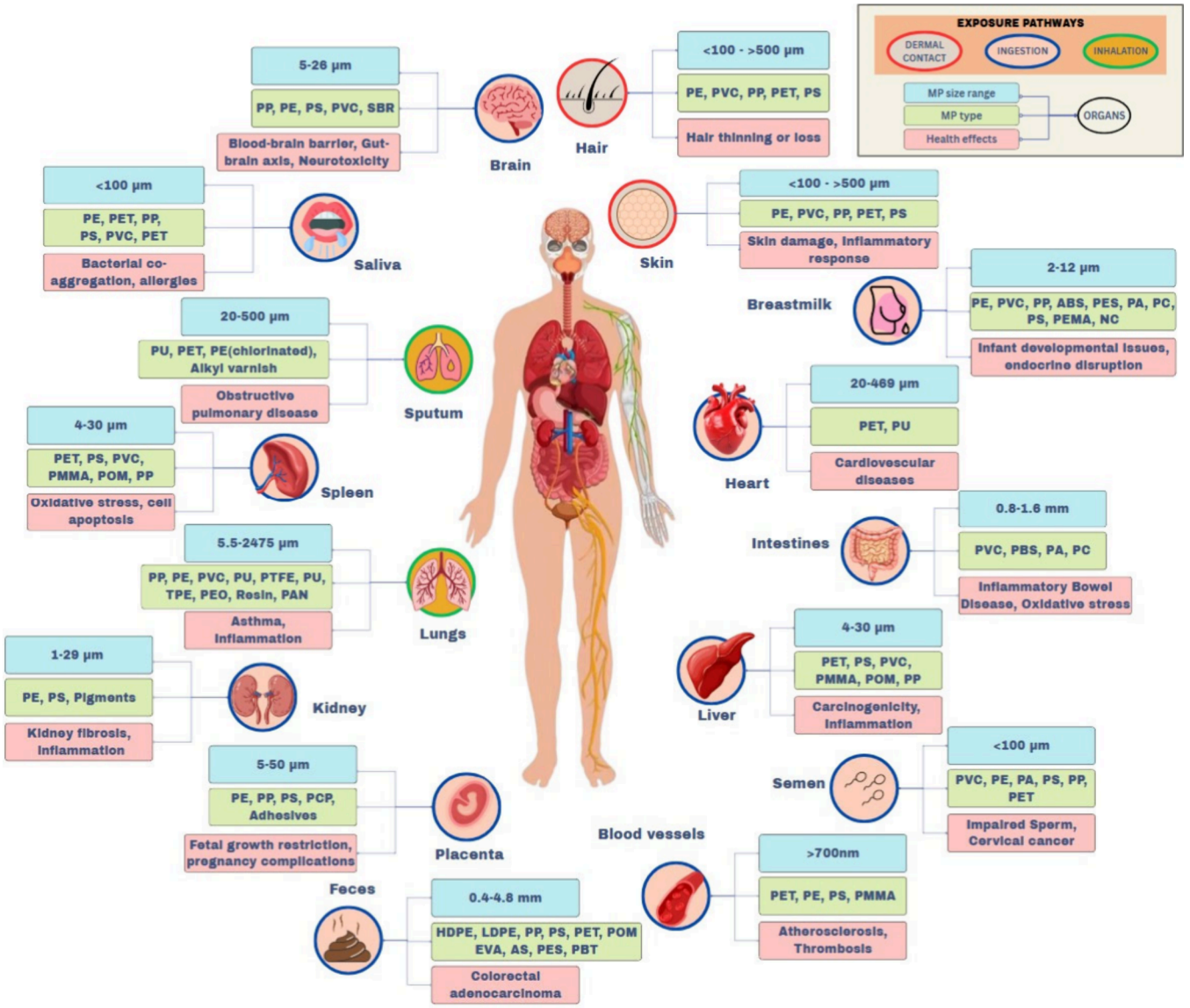

Figure 4. Compilation of reported MPs found in multiple organs in the human body, along with polymer types, size, and proposed health effects (POM, polyoxymethylene; PU, polyurethane; PC, polycarbonate; PBT, polybutylene terephthalate; and NC, nitrocellulose).

phase is the end of the cycle of plastic or disposal in different environments.

Global atmospheric emission of MPs stands at 9.6 ± 3.6 Tg/year.[153] The present review tries to have a rough estimate of GHG emissions from atmospheric MPs based on the reported research,[128,154] which demonstrated that various commonly used plastics emit GHGs at different rates when exposed to sunlight under ambient conditions. PE, one of the most widely used and discarded polymers, emits higher levels of GHGs during degradation compared to PP.[154] MPs with larger surface areas can further accelerate the release of hydrocarbon gases into the atmosphere.[154] Coarse and fine fractions of low-density polyethylene (LDPE) pieces were investigated for the release of CO_2 and CH_4 gases due to photodegradation under ambient light conditions.[131] It was also observed that the release of gases from fine fractions was twice that of coarse.[128] Moreover, CH_4 has an 85 times higher warming potential than CO_2 in a short period (less than 20 years), but after 100 years, it is only about 25 times as per the Intergovernmental Panel on Climate Change (IPCC) Assessment Report (AR5).[155] Hence, emission was calculated using the CO_2 equivalent. GHG emission from MPs degradation of LDPE alone was estimated to be 2.9 kilotons (kt) of CO_2 equivalent per year for CH_4, and CO_2 was 51.6 kt per year. A detailed calculation has been provided in Supplement Text S1 of the Supporting Information. However, it is relevant to state that these estimates have limitations which can be reduced by further studies. The estimate does not account for the varying intensity of sunlight at the poles and tropics or the average number of days of sunlight received. The degradation also depends upon the environment and region of the study. It also does not consider the role of additives and catalysts used in polymers while calculating GHG emissions. However, the Organization for Economic Cooperation and Development (OECD)[156] reported that the GHG emissions from the end-of-life plastics were 180.9 million tonnes of CO_2 and 10.21 million tonnes of CH_4.[147] The OECD report shows that the ratio of CO_2 to CH_4 emissions as 17.71, and in our estimate for the CO_2 and CH_4 emissions from LDPE, this ratio was 17.64, which validates the our estimates. Despite some limitations in the estimates, the

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exponential growth of plastic in the environment and its role in GHG emissions and climate change compels the need for research into MPs degradation for the same.

4.2. Direct and Indirect Effects. The ability of MPs/NPs to scatter and/or absorb solar radiation is the direct effect, which is quantified as effective radiative forcing (ERF). ERF of MPs, which does not include aerosol cloud interactions, and calculated with the assumption of 1 MP m^{-3} for an altitude of 10 Km, was 0.044 ± 0.399 milliwatts per square meter.[157] However, the estimate may have large uncertainties as it does not consider the spatial and vertical distribution of MPs, as well as their size and color. In addition, the rapid increase in plastic production and usage is expected to increase the abundance of MPs in the atmosphere and thus increase the estimate.

MPs present in clouds affect the cloud formation process, which is an indirect effect. MPs/NPs (especially aged particles) in the atmosphere can act as a cloud condensation nucleus (CCN) and ice nucleating particles (INP).[158,159] Surface adsorption, absorption, and photochemical degradation during the aging can make MPs/NPs a better CCN and thus alter the cloud albedo, lifetime, reflectivity, and precipitation.[158] Weathering of MPs/NPs dictates the ice-nucleating activities.[159] Recently, lab-based studies estimated the potential of MPs/NPs of four polymers as INP in both immersion and deposition freezing regimes.[159−162] Among them, PVC increased the ice nucleating activity more compared to PP, PET, and LDPE, and these studied MPs proved to be non-negligible sources of INP.[162] Further, an increase in pH increased the particle density and ice nucleation efficiency.[160]

A study modeled and accounted for 40% of MPs emitted from road traffic, which contributed to ice nucleation compared to dust and sea spray aerosols.[163] A field study conducted at Mount Tai in eastern China reported MPs concentrations as high as 463 particles per liter in cloudwater samples, with the majority (60%) comprising particles smaller than 100 μm. The study further demonstrated that aged MPs exhibited greater adsorption capacity and served as carriers for toxic heavy metals, emphasizing their potential role in pollutant transport within the atmospheric system.[164] Studies have shown MPs can influence albedo and thermal absorption similar to black carbon, though at a smaller scale.[165,166] This can have regional climate effects, especially in heavily polluted urban atmospheres.

4.3. Health Effects. Plastics pose a significant threat to human health by contributing to ambient PM and serving as a carrier for emerging pollutants, as well as by releasing additives into the atmosphere.[167,168] MPs and NPs can enter the human body through three primary exposure pathways: ingestion, inhalation, and dermal contact.[169] These bio-inert or bio-persistent particles have been detected in various human tissues and fluids at different concentration levels, polymer types, and size ranges (Figure 4). Once inside the body, these bio-inert MPs and NPs cannot be metabolized, and leave the body primarily through excretory routes. Notably, infants are particularly vulnerable to MP exposure, with high levels reported from ingestion via PP feeding bottles.[170]

Laboratory studies on rodents have demonstrated the detrimental effects of MPs and NPs on multiple organ systems, including the lungs, liver, intestines, reproductive organs, and nervous system.[171] Recent studies have also detected MPs and NPs in human hair,[172,173] brain,[174,175] skin,[172,174] saliva,[36,176] breastmilk,[36,177] sputum,[36,174] spleen,[172,178] heart, intestines,[36,172,174,179] lungs,[172,180] liver,[172,181] kidney,[36,182] semen,[36,174] blood vessels,[172,174] placenta,[172,179] and feces,[172,174] indicating their systemic exposure[183] (Figure 4). Many MPs and NPs contain additives such as phthalates, BPA, and polybrominated diphenyl ethers (PBDEs), which have endocrine-disrupting properties and are associated with developmental toxicity, diabetes, cardiovascular disease, reproductive dysfunction, and neurotoxicity.[184,185]

It is estimated that tens of thousands of MPs and NPs are inhaled by humans daily,[186] with indoor environments showing higher concentrations than outdoor settings, thereby increasing exposure duration.[26] Once inhaled or ingested, these particles may translocate across biological barriers, leading to local or systemic inflammation.[187] NPs, due to their ultrafine size, can enter the bloodstream and thus, any part of the body.[188] Their interactions with biomolecules such as proteins, lipids, and carbohydrates can potentially alter biological functions.[189] Preliminary findings suggest that irregularly shaped fragments may be more harmful than spherical particles due to their increased surface area and reactivity.[190]

In particular, additives such as phthalates and BPA have been shown to cross the placental barrier, potentially disrupting embryonic and fetal development.[191] BPA has been linked to metabolic disorders, cardiovascular diseases, and an increased risk of miscarriage.[184,185] PBDEs used as flame retardants in plastics are known to be neurotoxic and have been associated with reduced sperm count and adverse effects on female reproductive health, including oxidative stress, inflammation, and menstrual irregularities.[192,193]

Given these emerging concerns, the potential health risks posed by MPs, NPs, and associated additives are of growing importance for public health policies and exposure mitigation strategies. However, the field remains in its early stages, and more robust, in-depth studies, including in vitro and in vivo models, are needed to conclusively assess human health impacts of MPs/NPs and form regulatory frameworks.[194]

5. FUTURE RESEARCH

To better understand the implications of MPs/NPs for environmental and climate systems, future research should address the following critical knowledge gaps:

Emission Inventories: There is a pressing need for comprehensive emission inventories identifying both primary and secondary sources of atmospheric MPs and NPs. Detailed emission profiles based on polymer types are essential for source apportionment and atmospheric modeling.

Standardization of Methods: The development of consistent, sensitive, and reproducible techniques for sampling, measurement, and characterization of atmospheric MPs/NPs remains a major challenge. Harmonized methodologies are crucial for interstudy comparability and reliable global assessments.

Degradation Kinetics and Aging: Understanding the degradation rates and byproducts of different polymers under varying environmental conditions is essential. Particular focus is needed on photodegradation mechanisms, estimating degradation times under sunlight exposure, and determining the influence of polymer type and environmental factors (e.g., temperature, humidity, and UV intensity) on degradation rates.

Greenhouse Gas Emissions: The release mechanisms and pathways of CO_2, CH_4, and other gaseous species from degrading MPs/NPs require detailed investigations. The roles of additives, binders, and coexisting pollutants in facilitating or

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inhibiting degradation and gas emission processes should also be elucidated.

Radiative Forcing: Atmospheric MPs/NPs interact with solar radiation similar to traditional aerosols. Depending on their size, color, and polymer composition, they may scatter light (leading to a cooling effect) or absorb it (causing a warming effect). Better estimates of radiative forcing due to MPs/NPs are needed.

Hygroscopic Properties: Investigations into the hygroscopicity and microphysical behavior of MPs/NPs in the atmosphere are necessary to understand their role in CCN activity, as well as in cloud and ice nuclei formation under different atmospheric conditions.

Health Effects: As MPs/NPs are bio-inert as well as vectors of contaminants, they may affect health in various ways after entering the human body. It is important to assess the effects of MPs/NPs and related additives/binders on human health.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.5c00210.

Calculation details for the estimation of greenhouse gases emitted from microplastics (PDF)

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Notes

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