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Review

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Understanding the leaching of plastic additives and subsequent risks to ecosystems

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Abstract

Plastic pollutants have emerged as one of the biggest environmental concerns in recent times. The potential hazards arise from the presence of additives within microplastics (MPs), which can leach into the environment. These additives serve a multitude of purposes, resulting in a diverse range of compounds used in plastic formulation. These elements are commonly integrated into plastic molding processes to enhance usability, optimize material performance, and reduce costs. Throughout the lifespan of plastics, there exists a potential for the release of unpolymerized monomers (sometimes more toxic) and additives that are not chemically bound to polymers; these elements pose risks to the environment and, ultimately, human well-being. Assessing the potential impact of MPs on life requires determining the precise chemical composition and the level of exposure to these additives. Phthalates and chemical flame retardants are currently the focus of extensive examination due to their widespread presence in the environment. Following closely behind are stabilizers and antioxidants, which are also undergoing evaluation. Chemical compounds like hexabromocyclododecanes (HBCDs) and polybrominated diphenyl ethers (PBDEs) possess characteristics such as persistence, bioaccumulation, and toxicity. The understanding of the ecotoxicological implications of plastic additives and their discharge from primary plastic materials remains limited at present. The current state of issues concerning the regulations and transparency regarding plastic additive chemicals is marked by a significant lack of openness and clarity. It is paramount to

thoroughly comprehend and assess the risks that ecosystems face due to the leaching, degradation, bioaccumulation, and eventual fate of additive compounds when plastics are released into the environment.

Keywords: Plastic leaching, plastic additives, ecotoxicology, microplastics

INTRODUCTION

The use of plastics, a revolutionary invention, has significantly increased in the 20th and 21st centuries. In 2021, global plastic production was estimated at 390.7 million metric tons. This surge in production stems from the manifold economic and social benefits of plastics, which have been instrumental in enhancing the quality of life[1,2]. Synthetic and semi-synthetic materials are part of plastic. Plastics comprise two categories, i.e., thermosets and thermoplastics. Thermoplastics represent a class of plastics that can be easily modified under high-temperature conditions. This category includes polycarbonate (PC), polystyrene (PS), polypropylene (PP), polyarylsulfone (PAS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyamides (PA), and thermoplastic elastomers, all of which are commonly found in the environment. Conversely, thermosets denote plastics that retain their form even when subjected to heat, such as vinyl ester, polyurethane, acrylic resin, silicone, melamine resin, phenolic resins, and phenol-formaldehyde[3-7].

Numerous international policies have been established to address the improper disposal of plastic waste; however, mismanagement often leads to the release of such waste, causing detrimental effects on the ecosystem[8,9]. Plastic undergoes degradation via chemical and physical weathering processes, breaking down into smaller fragments known as MPs. These particles come in various sizes, with those measuring < 5 mm categorized as MPs and those smaller than < 1 μm termed nanoplastics[10,11]. Apart from the degradation of large plastics, MPs can also be produced through anthropogenic activities such as in the manufacturing of clothing, cosmetics, nurdles, industrial processes, and wastewater treatment[12].

MPs pose a significant challenge to marine ecosystems globally[13]. Their impact extends beyond the marine environment, as they are increasingly recognized as pollutants across various environmental compartments[14]. Due to their ubiquitous nature and bioavailability, MPs are found extensively in terrestrial environments, marine ecosystems, and plant tissues[4,7,12,15]. This widespread presence potentially amplifies the concentration of contaminants in the environment and burdens biological organisms that inadvertently consume microplastic particles[16]. The interaction between toxic pollutants and MPs presents a considerable environmental concern, impacting the ecosystem and its biota[17,18]. Various toxic chemicals, such as persistent organic pollutants (POPs), also known as hydrophobic organic contaminants (HOCs), include organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polyaromatic hydrocarbons (PAHs), as well as heavy metals such as lead, copper, zinc, silver, manganese, iron, and aluminum. These contaminants attach to the pitted surfaces of floating MPs in water, facilitated by their wide distribution in water.

Besides contaminants that adsorb onto MPs, additives are another agent that intensifies their ecotoxicity. Approximately 7% of additive compounds are used during the plastic manufacturing process to shape the material and provide specific functions[19,20]. These additives fall into distinct categories such as plasticizers, flame retardants, stabilizers, and antioxidants. Among plasticizers, examples include terephthalates, DEHT, di-2-ethylhexl terephthalate, TOTM, tris-2-ethylhexyl trimellitate, 1,2-cyclohexane dicarboxylic acid, diisononyl ester, and adipates[21]. Beyond their incorporation into MPs, additives find applications in manufacturing biocides, UV protection materials, dye agents, clothing, and formaldehyde-releasing chemicals[22]. Plastic contains a diverse range of additives, monomers, and oligomers. Most of these

substances are not chemically bound to the plastic, causing them to leach out and migrate into various matrices (soil, air, water, food, and even human body), leading to harmful consequences[23,24]. For example, the plasticizer di (2 ethyhexyl) phthalate (DEHP) disrupts the endocrine systems of humans and animals. Studies by Tanaka *et al.* demonstrated the accumulation of additives in seabird tissues, revealing the leaching of these substances from plastics, particularly facilitated by the oil components in the digestive tract[25,26]. Moreover, exposure to DEHP for 15-30 days in Carassius auratus (goldfish) resulted in reduced sperm production and diminished motility[27,28].

The existing literature on the leaching of additives from plastic pollution is limited, showcasing a variety of experimental methodologies used in previous studies. Plastic leaching is a widely recognized phenomenon extensively studied in the assessment of potential risks posed by leached additives to various ecosystems. This study aims to investigate the transfer of plastic leachate to organisms in order to address the existing uncertainty and debates surrounding its potential hazards. This paper provides a comprehensive analysis of the distinctive features that differentiate MP additives from other toxic pollutants. Moreover, it investigates the process of additive leaching from MPs and its subsequent dispersion into the environment. Furthermore, it evaluates the environmental impact of MP additives on various ecosystems, including marine, freshwater, and terrestrial environments. Specifically, this study aims to scrutinize the release of these MP additives and their detrimental effects from an environmental perspective.

CO-CONTAMINANTS OF PLASTICS

Microplastics, due to their large surface area, act as transporters of hazardous contaminants in the environment and within organisms. Various pollutants, such as POPs and heavy metals, adhere to the expansive surface area of MPs. According to Maršić-Lučić *et al.*, MPs have the ability to accumulate heavy metals from water, which can then be taken up and consumed by various species[29]. The presence of MPs in the natural environment significantly affects the global transport of detrimental pollutants[30]. In some instances, contaminants may detach from MPs while organisms ingest them.

POPs

POPs, such as PCBs and OCPs, remain in the environment for long periods. Verla *et al.* explained that POPs resist photolytic and biochemical breakdown processes, making them easily transportable and prone to binding with various objects. Due to their poor solubility, organic contaminants tend to adhere to MPs in the environment[31]. Pascall *et al.* demonstrated the presence of 113 chlorinated chemicals among a total of 200 comprising polychlorinated biphenyls, also known as PCBs, in the environment[32]. The first observation of PCB adsorption on polystyrene MPs dates back to 1972[33]. Studies investigating microplastic distribution on New Zealand beaches and in sediments revealed high PCB adsorption on PP microplastic pellets[34]. Subsequent research indicates an increasing adsorption concentration of up to 18,700 ng/g over time[35]. Samples of resin PP pellets were collected from four coastal areas in Japan, revealing polychlorinated chemicals in concentrations ranging from 97 to 117 ng/g. Among 55 polypropylene pellets, a significant quantity of PCBs was detected, indicated by regional differences and discoloration of pellets[36]. Additionally, MPs collected from two beaches in Portugal exhibited concentrations of PCBs ranging from 0.02 to 15.56 ng/g[37]. PAHs, another organic molecule, were found attached to MPs in the North Pacific Gyre, ranging from 39 to 1,200 ng/g in concentration. Researchers noted that when the concentration of connected PAHs increased from 6,100 to 12,000 ng/g, the color of the plastic faded, turning yellow[38].

Heavy metals

Heavy metals refer to metals with a higher density, typically around 5 g/cm^3. Recent studies by several authors have provided evidence supporting the attachment of heavy metals to MPs. In a comprehensive 12-

month investigation conducted by Rochman *et al.*, the attachment of heavy metals to newly manufactured MPs, such as PP, LDPE, PVC, HDPE, and PET collected from three different sites in San Diego Bay, USA, was examined. The final data yielded at the end of 12 months indicated that Zn, Cd, and Pb were found attached to MPs at concentrations of 4.16 μg/g, Cd 3.8 μg/g, and 0.8 μg/g, respectively[39]. Another study focused on eight farms in China, six of which were culture ponds, while two were open area farms for sea cucumber culturing. This study identified the presence of eight heavy metals, including arsenic, cadmium, lead, zinc, manganese, nickel, copper, and chromium, attached to MPs at varying concentrations across these farms[40].

ATTACHMENT AND DETACHMENT MECHANISM OF TOXIC POLLUTANTS ONTO PLASTIC

Attachment mechanism

The attachment of different pollutants to MPs relies significantly on factors like surface structure, affinities towards pollutants, and the types of polymers involved, such as polyethylene (PE), PS, and PP. Toxic chemical pollutants generally become embedded within the pitted surface of MPs[41]. Several key elements of plastics - like surface area, surface chemistry, and size - influence the interaction between MPs and environmental pollutants. For instance, polychlorinated organic pollutants exhibit a higher tendency to be adsorbed by PE pellets than PP pellets, as demonstrated in an *in situ* experiment by[36]. According to Wu *et al.*, alkyl benzenes show higher adsorption onto PVC than onto PE-MPS[42]. This consistent adsorption pattern of MPs towards heavy metals has been observed in numerous studies[43]. For example, when exposed to Zn, PS showed greater adsorption than PVC. Conversely, PVC exhibited higher adsorption when exposed to copper. Moreover, PVC demonstrated increased adsorption after exposure to Cu. Aging also plays a crucial role, potentially affecting the interaction between metal ions and MPs. For instance, in a NaCl solution, the ultraviolet irradiation aging process inhibits the assembly of PS-NPs. Natural organic matter present in natural waters is likely to adhere to plastic surfaces, thereby influencing the properties of plastic particles[44,45]. Ali *et al.* reported that natural organic matter forms a protein layer on the surface of MPs[46]. However, humic acid improves the aggregation of PE-MPs, while sodium alginate enhances the assembly of PS-MPs[47,48].

There are two mechanisms by which MPs attach to various toxic chemical pollutants: (1) attachment of pollutants onto MPs hydrophobically; and (2) incorporation into the biofilm matrix.

Hydrophobic attachment of pollutants

MPs exhibit low surface polarity, rendering them more hydrophobic, facilitating increased adsorption of hydrophobic pollutants. Due to their lower density compared to water, MPs commonly accumulate in the microlayer of seawater. POPs, such as organochlorine (DDT), PAHs, and PCBs, are all lipophilic and typically remain in the upper layer of seawater, where they undergo hydrophobic adsorption with MPs. The combination of the low polarity and a relatively lower pH than most environmental PHs creates favorable conditions for MPs and aqueous metal ions on their surfaces. The pH of the medium, particularly when nearing 0, significantly promotes the electrostatic interaction between polymers and oppositely charged organic compounds. Micelle shaped structures are formed by the attachment of positively charged aqueous ions to the negatively charged surface of MPs. Upon adsorption, the charge is neutralized. In a natural environment, the adsorption or attachment of toxic pollutants onto MPS is a lengthier process compared to artificial laboratory experiments[49]. Research on the degradation of MPs has indicated an increased generation of oxygen groups during the process, altering the surface charge and enhancing polarity, thereby making the plastic surface more reactive. Consequently, it takes longer to reach equilibrium[50,51]. However, laboratory experiments often reach equilibrium more rapidly. For example, Holmes *et al.* performed a lab study exposing virgin PE pellets to six heavy metals: Cr, Cu, Co, Ni, Pb, and Cd, demonstrating a rapid

equilibrium[52].

Van der Waal forces: These are the weak intermolecular electric forces between molecules. Polyvinyl chloride and polyethylene microplastic adhere to toxic pollutants through Van der Waal interactions[53,54].

The Pi-Pi (Electron-Donor-Acceptor) interaction: this type of sorption behavior observed in polymers that incorporate benzene rings within their structure. This interaction is non-covalent, involving both electron donation and acceptance. Both the polymer and contaminant types act as electron donors and acceptors. The sorption capacity of polystyrene, polyvinyl chloride, and polyethylene was observed with aromatic organic compounds. Among all phenyl groups, polystyrene plastic shows higher sorption towards organic compounds[55]. PS plastic and tetracycline (TC) demonstrate more sorption via Pi-Pi interaction than polyethylene and polypropylene due to the presence of benzene rings in both PS and TC[56].

Incorporation into biofilm matrix

A phenomenon known as quorum sensing plays a pivotal role in the formation of biofilms. Initially, microbes attach to the surface of MPs, forming micro colonies that eventually mature into biofilms. In addition, biofilms may absorb toxic chemicals due to their unique structure. When virgin MPs come into contact with the bacteria in water, the initiation of biofilm formation within the water can occur in a matter of seconds[57,58]. Temperature and light are essential factors for the formation of biofilm[59,60]. Quorum sensing controls the gene expression of diverse microorganisms that produce extracellular polymeric substances by adhering to each other on non-living or living objects. Studies have shown that biofilms can be present wherever water exists, attaching themselves to hard surfaces or floating freely within the water[61,62]. Extracellular polymeric substances (EPS) govern the distribution and mobility of metals in aquatic environments, either by chelating the metals or by integrating them into their cellular structure[63]. In biofilms, microorganisms create pits on the surface of MPs, thereby increasing the available surface area of MPs available for the sorption of different types of heavy metals. Additionally, this process significantly enhances the hydrophobicity of MPs[63,64].

Detachment mechanism of pollutants

Toxic pollutants may readily attach themselves to MPs via non-covalent bonds, enabling the contaminants attached to plastic surfaces to detach easily [Figure 1]. Goss and Schwarzenbach demonstrated that the forces that hold atoms together include weak van der Waals forces, hydrogen bonds, and the creation of cavities. During the desorption process, pollutants initially travel from their original location to the plastic surface and are then subsequently released into various mediums, such as sediment, water, human or animal bodies, or dirt. The specific desorption mechanisms vary based on the adsorption sites. Moreover, several factors impact desorption, including the type of polymer, the pH of the medium, the salinity of the medium, and the presence of inorganic and organic ligands in the medium[65]. Research by Violante and Pigna revealed that when contaminants discharge into soil or sediment, they tend to adsorb trace elements, humic compounds, inorganic components, and carbonates. Once hazardous pollutants are released from the plastic into an unpolluted environment, the situation is considered resolved[66]. Pollutants, along with organisms in the medium (soil or sediment), also adsorb on the organic and inorganic ligands in the medium[67]. In aqueous environments, the desorption process is largely influenced by medium salinity. According to research by Awet *et al.*, the adsorption of the contaminant DDT onto plastic reduces as the salinity of the solution rises[68].

PLASTIC ADDITIVES

Plastic not only comprises polymers but also contains some other substances known as additives. These

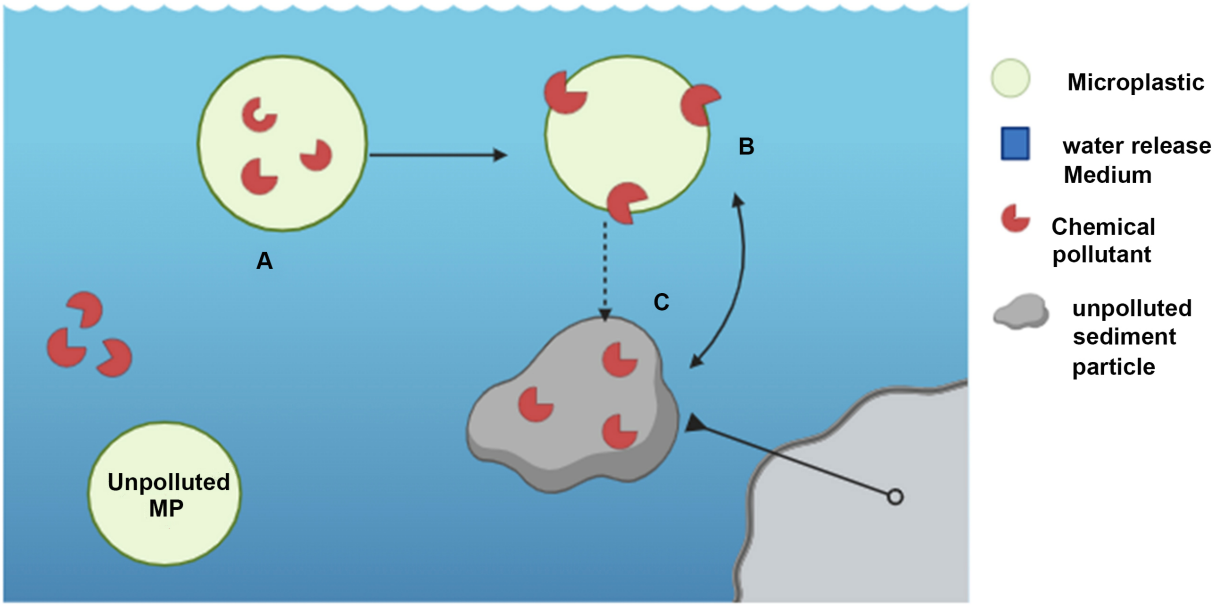

Figure 1. Unpolluted MPs come into contact with chemical pollutants (heavy metals, organic compounds) adsorbed onto MPs (A). When all the organic matter on MPs is used up by pollutants, they slowly move to the outer surface of MPs (B) and migrate to the unpolluted sediment particle that is rich in humic and fulvic acid (C). MPs: Microplastics.

additives serve the purpose of modifying the physical and chemical properties of plastic. The selection of additives significantly influences both the cost and production of plastic materials[69]. The ecotoxicity of MPs is not only affected by their shape and size but also by the concentration, composition, and sheer quantity of additives. The concentration of additive chemicals in MPs surpasses that of toxic anthropogenic pollutants in the environment[20,24]. The specific type of additives plays a crucial role in determining the physicochemical properties of MPs and their behaviors and interactions within the environment[70].

In 2021, the global plastic additives market witnessed substantial growth, reaching 48.41 billion USD with a growth rate of approximately 6%, and is expected to be 51.04 billion dollars by 2026 and 75.29 billion dollars by 2028 (Fortune, plastic additives market size, growth, and forecast report 2022). The manufacturing of plastic involves around 6,000 chemical classes of additives. Along with that, light stabilizers are incorporated to slow down chemical degradation, while added pigments contribute to creating different colors, thereby enhancing the appeal of plastic products.

Identification of MPs-derived pollutants

The current presence of microplastics in the environment can be identified by the chemical additives they contain, such as phthalates, nonylphenol, polybrominated diphenyl ethers, and Bisphenol A (BPA)[47,70]. These pollutants derived from microplastics have been identified through electrochemical oxidation on electrodes. Carbon nanomaterials, including graphene oxides (Gr), carbon nanotube (CNTs), boron-doped diamond (BDD), carbon quantum dots (CQDs), and grapheme oxides (GO), are employed for monitoring and identifying EPS. They are chosen due to their rich surface chemistry, low cost, high conductivity, electrochemical property, chemical stability, and large surface area[71,72]. Jiang *et al.* reported that boron-doped diamond glassy carbon electrode shows a higher detection ability towards bisphenol A than for hydroquinone and 1,2-dihydroxybenzene in urban wastewater[73]. Molecularly imprinted polymers (MIPs) act as synthetic polymeric receptors for dibutyl phthalate and bisphenol A[74,75]. MIPs demonstrate selective identification even in the presence of interfering EPS. For the detection of EPS, carbon materials modify the

structure of MIPs, such as QDs, MWCNTs, and CdTe, providing abundant active sites with high stability and surface area, good electrical conductivity, and high sensitivity for bisphenol A analysis[76]. Metal/covalent-organic frameworks (MOFs/COFs) have emerged as excellent electrodes for electrochemical identification of MPs-derived pollutants. When MOFs are modified with CTAB (cetyltrimethylammonium bromide), the response for bisphenol A detection is enhanced threefold compared to MOFs.

The classification of additives is divided into: plasticizers, antioxidants, flame retardants, and monomers, as described in Table 1.

Plasticizers are added to enhance the flexibility and softness of plastics. They encompass substances like phthalates, epoxides, *etc.* On the other hand, antioxidants are incorporated to mitigate the degradation of plastic caused by chemicals, light, or heat.

Antioxidants, including phenols, arylamines, *etc.*, are introduced into plastics to impede oxidation and prevent aging[94]. Similar to other plastic additives, antioxidants sometimes leach out and enter the environment. Particularly in food packaging, antioxidants from containers can migrate into food, posing a threat to food safety.

Flame retardants are used in plastic to meet fire safety standards, rendering the plastic materials resistant to fire or the spread of flames. Various flame retardants are employed, such as halogens and bromine compounds. For instance, BPA is an additive monomer.

MECHANISM OF LEACHING OF PLASTIC ADDITIVES

Since these additives are either loosely attached or not chemically bonded to plastic, they can escape from the plastic during use or after disposal. Once they leach out, they may degrade and form other toxic chemical pollutants, persisting in the environment and accumulating in living organisms[95]. The presence of additives in the environment or MPs largely depends on their origins[96]. However, pinpointing the source can be challenging, as some additives are not exclusively used in plastic but also in various other products. For instance, bisphenol A is used not only in plastic bottle production but also in food can lining and thermal paper manufacturing. Perfluorinated compounds (PFCs), employed in textiles and food packaging, exhibit persistent qualities, remaining in sediment, soil, water, and biota[97].

The leaching of additives from plastic is influenced by various factors, including solubility, volatility, additive size, pH, physical or chemical properties of media, temperature, permeability of the polymer matrix, and gaps between polymer molecules allowing migration [Figure 2]. Additive chemicals possess the ability to migrate from plastic materials to external matrices, such as water, soil, and food, as well as internally within plastic to its surface[20]. In many cases, the unintended and uncontrolled leaching of additives from plastic has significant consequences for the environment and human health. For example, a flame retardant, polybrominated diphenyl ethers (PBDEs), is ubiquitous, environmentally persistent, and accumulates within organisms. It has been banned in the European Union since 2004[98]. However, there are instances where the intentional and controlled migration of additives is beneficial, such as the release of mold agents on the surface to prevent silver oxidation and enhance mechanical, optical, and antistatic properties, thereby improving food preservation[99,100].

The process of leaching/migration of additives from plastics can be categorized into four steps:
1. Diffusion leads to the additive moving towards the surface of polymer.
2. Desorption occurs as the additive separates from polymer surface.

Table 1. Polymers and their additive compounds with different classifications

Polymer type	Additive compound	Classification of additive	Ref.
PS, PP, PA, PE, PVA, HDPE	DEP	Plasticizers	[77,78]
ABS	BHT	Antioxidant	[79]
PC	BPA	Monomers	[80]
PE, PS, PP, PVC	PBDEs	Flame retardants	[81]
PP, PE	Tris (2,4-di-tert-butylphenyl) phosphite	Antioxidant	[82]
PVC, PE	BBP	Plasticizer	[83,84]
Modified PS, PVC, ABS, PS	ATBC	Plasticizer	[85]
PP, PE, PA, PS	2,4-Di-tert-butylphenol	Antioxidant	[77,86]
PVA	Acetic acid	Monomer	[87]
PET, PS, PVC, ABS	TBBPA	Flame retardants	[88,89]
PVC, PET, PS, ABS	TCEP	Flame retardants	[90]
PVA	Diisobutyl phthalate	Plasticizer	[91]
PP, LDPE	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	Antioxidants	[92]
PVC, PE	DINP	Plasticizer	[83]
PE, PBT	Calcium bis (ethyl 3,5-di-tert-butyl-1-44-hydroxybenzylphosphonate	Antioxidant	[93]

PS: Polystyrene; PP: polypropylene; PA: polyamides; PE: polyethylene; PVA: polyvinyl alcohol; DEP: diethyl phthalate; ABS: acrylonitrile butadiene styrene; BHT: butylated hydroxytoluene; PC: polycarbonate; BPA: bisphenol A; PVC: polyvinyl chloride; PBDEs: polybromodiphenyl ethers; BBP: butyl benzyl phthalate; ATBC: acetyl tributylcitrate; PET: polyethylene terephthalate; TBBPA: tetrabromobisphenol A; TCEP: tris(2-chloroethyl) phosphate; DINP: di-isononyl phthalate; PBT: polybutylene terephthalate.

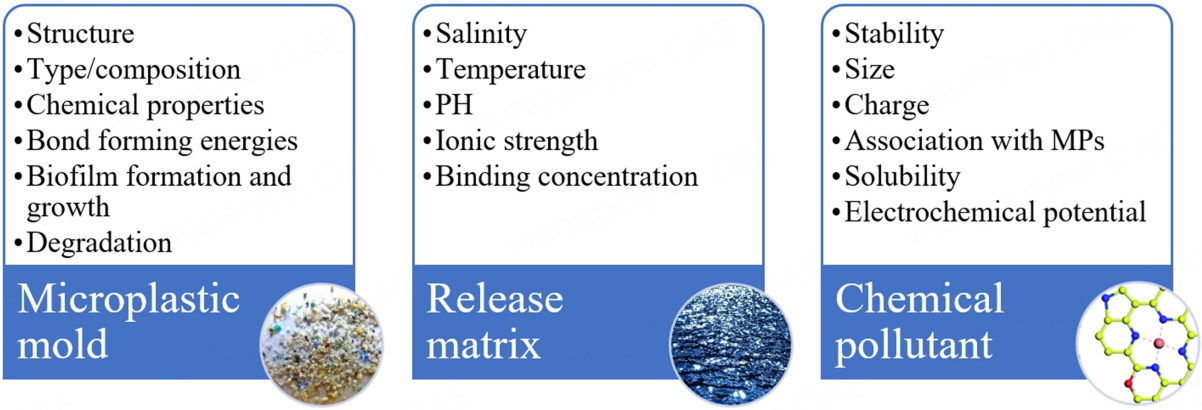

Figure 2. Factors affecting the migration of pollutants from MPs into the medium[18]. MPs: Microplastics.

3. Sorption takes place as the additive becomes absorbed within the plastic matrix in the surrounding medium.
4. Dispersion and absorption occur within the matrix.

Moreover, the leaching or migration of additive chemicals is directly related to the particle size. Smaller particles are more easily and quickly removed. For example, monomers with low boiling points tend to escape even at room temperature. According to Hahladakis *et al.*, these monomers include ethylene, vinyl chloride, butadiene, and formaldehyde. Once released, the additive chemicals become absorbed into a matrix consisting of two phases: a solid phase represented by the polymer, and a liquid phase represented by either water or air[20]. Both adsorption and absorption are part of the sorption concept. During adsorption, the chemical remains at the interface between the solid phase and the fluid phases, while in absorption, additive compounds are embedded and penetrate the layer of the solid phase as polymers[101].

RISK OF LEACHED ADDITIVES ON THE ECOSYSTEM

In recent years, there has been growing evidence indicating the harmful effects of plastics and their constituent substances. This heightened awareness has emerged due to both direct and indirect sources of exposure. According to Wright *et al.*, the intake of plastic particles results in direct poisoning. On the other hand, indirect toxicity occurs when plastic breaks down and releases dangerous chemical components into the environment[102]. This is primarily because most additive components are physically rather than chemically bonded to the plastic.

Effects on marine organisms

The natural compartments of the marine ecosystem serve as reservoirs for all the impurities released by anthropogenic discharges. Across the global marine environment, significant quantities of chemical plastic additives have been identified[103,104]. In a field study, six types of phthalates were detected in sediments, with DEHP accounting for 95% of the total. Additionally, plastic additive compounds have been linked to heavy metals such as Cu, Mn, Ni, Cd, Co, Pb, and Fe. This association has been observed to potentially impact the reproductive and immune systems of *H. diversicolor*[105]. In Osaka Bay, Japan, the plastic additive compounds BPA, NP, and octylphenol (OP) have exhibited bioaccumulation and caused endocrine disruption in *Paraprionospio sp.* (Polychaete)[106]. Furthermore, exposure to leached additives from seven commercially used recyclable plastics has been linked to increased mortality among larvae of *Amphibalanus amphitrite* due to toxicity[47]. Leachates from polypropylene pellets encountered during the embryonic developmental stage of *Perna perna* (mussels) exhibited increased toxicity, inhibiting the growth of the embryos of mussels across all samples[107].

Data were obtained from various marine invertebrate species, including *D. magna*, *Lytechinus variegatus*, *A. amphitrite*, *N. spinipes*, and *P. perna*. The effects of leached additives from three different plastic types on these invertebrate species were observed. It was indicated that additives leached from PVC are more toxic towards species, while PP and PE are less toxic or, in some cases, not toxic towards these diverse species[47,107-109] [Figure 3].

Another study investigated the toxicity and bioaccumulation of PBDEs, a flame retardant, when exposed to *Capitella sp* during the larval settlement stage. Tests were conducted under both hypoxic and normoxic conditions. Under hypoxia, larva settlement was observed[110]. The presence of additives, including flame retardant, had adverse effects on polychaetes, leading to reduced growth and various other biological effects. Moreover, these effects were significantly exacerbated when additional stressors, such as PVC contaminants, were introduced in conjunction with hypoxia conditions and additives, amplifying the impacts on the organisms' immune systems. Table 2 presents an overview of recent studies conducted on the effects of additives found in MPs on various marine species.

Effects on freshwater biota

Wastewater treatment plant effluents often contain various additives of plastics released by industries, dust, sewage sludge, municipal waste, and domestic waste when discharged into freshwater. Another significant contributor to these additives in freshwater is the wear and tear of tire rubber (CTR), which enters freshwater through surface runoff. In their study, Capolupo *et al.* investigated the adverse effects of additives released from tire wear and MPs of PP, PVC, PS, and PET on the freshwater microalga *Raphidocelis subcapitata*. Among the most notable additives detected were cobalt, zinc, and benzothiazole from car tire rubber; antimony and cobalt from PET; acetophenone and lead from PP; and phthalide and zinc from PVC. The quantities of these additives extracted from MPs varied in freshwater, with the highest counts recorded as 19 (PP), 17 (CTR), 9 (PS), 9 (PVC), and 1 (PET). PET, in its purest form, did not exhibit

Table 2. Recent studies on exposure of MP additives to different marine species and the end results

Additives compound	Microplastic type	Species	Exposure time	End results	Ref.
Phthalate; bisphenol A; nonylphenol; brominated flame retardant; boric acid; tris(2-chloroethyl) phosphate	Polystyrene microbeads	*Marenzelleria spp*	1 day	Ingestion by organism	[111]
Phthalate; bisphenol A; nonylphenol; brominated flame retardant; boric acid; tris(2-chloroethyl) phosphate	Polyvinyl chloride, polypropylene, PET	*Nitroca sinipes*	96 h	Leads to mortality	[108]
Polybrominated diphenyl ethers (BDE-47)	Polyethylene	*Laeonereis acuta*	14 days	Bioaccumulation of MPs	[112]
Brominated flame retardant; boric acid	High-density polyethylene, polypropylene, polyvinyl chloride, epoxy resins	*Daphnia magna*	24-48 h	Leads to mortality	[113]
BPA	Polypropylene	*Perinereis aibuhitensis*	4-14 days	Change in the expression of Pa Ga gene	[114]
Polybrominated diphenyl ethers (BDE-47)	Polyethylene	*Pseudochromis fridmani*	2 days	Mortality happens	[115]
Phthalate; bisphenol A; brominated flame retardants; boric acid	Polyvinyl chloride, polyactic acid, high-density polyethylene.	*Arenicola marina*	31 days	Biomass survivorship	[116]
Bisphenol A; nonylphenol; brominated flame retardant; boric acid; tris(2-chloroethyl) phosphate	Polystyrene, polypropylene, polycarbonate, low-density polyethylene	*Amphibalanus amphiteite*	24-96 h	Settlement	[47]
Dibutyl phthalate	Polystyrene	*Galeolaria caespitosa*	15 min - 2.5 h	Toxicity in embryo	[117]
Phthalate; bisphenol A; nonylphenol	Polyvinyl fragments	*Hediste diversicolor*	10-28 days	Organism survived	[118]
Dibutyl phthalate; PA 6,6; PA 11; PA 12; PA 4,6	Polystyrene and polyamide fragments	*Arenicola marina*	106-240 days	Survival of organisms	[119]
Polybrominated diphenyl	Polyethylene	*Capitella sp. I*	1 day	Settlement of larva occurs	[110]
Brominated flame retardant; boric acid; tris(2-chloroethyl) phosphate	Polyurethane, Polymethyl Methacrylate	*Daphina magna*	24 and 48 h	Mortality occurs	[109]
Polybromodiphenyl ethers; PCBs	Polystyrene, polyethylene	*Nereis virens*	28 days	Bioaccumulation of MPs	[120]

MP: Microplastic; PET: polyethylene terephthalate; BPA: bisphenol A; PA: polyamides; PCBs: polychlorinated biphenyls.

any inhibitory effects on the growth of *R. subcapitata* even at 100% leachate concentration. However, the leachates from CTR, PP, PS, and PVC microplastic materials showed full toxicity and resulted in reduced growth of the microalgae[121].

Phthalate compounds, commonly found in polyvinyl chloride plastics, are not chemically bound, allowing them to quickly leach into the environment[122]. These phthalates serve various purposes across multiple products, including medical devices, building materials, electrical cables, food packaging, and toys. Due to their widespread use, these compounds have permeated ecosystems, accumulating in organisms. The presence of MPs, including phthalates, poses a severe threat to freshwater biota, notably keystone species like *D. magna*. This pollution endangers biodiversity and destabilizes entire food systems. *D. magna*, a filter feeder with a diet encompassing particles ranging from 1-70 μm, inadvertently consumes MPs in aquatic ecosystems[123]. Upon ingestion, the chemicals from these microplastics leach into the organisms' gastrointestinal tracts. Particularly, polystyrene carboxylated MPs sized between 20-1,000 nm can permeate the epithelium of *D. magna*, resulting in adverse effects on reproduction, organism growth, and mortality. Recognized as an essential indicator species for environmental pollution, *Daphnia magna* plays a crucial role in detecting contaminants in aquatic ecosystems[124].

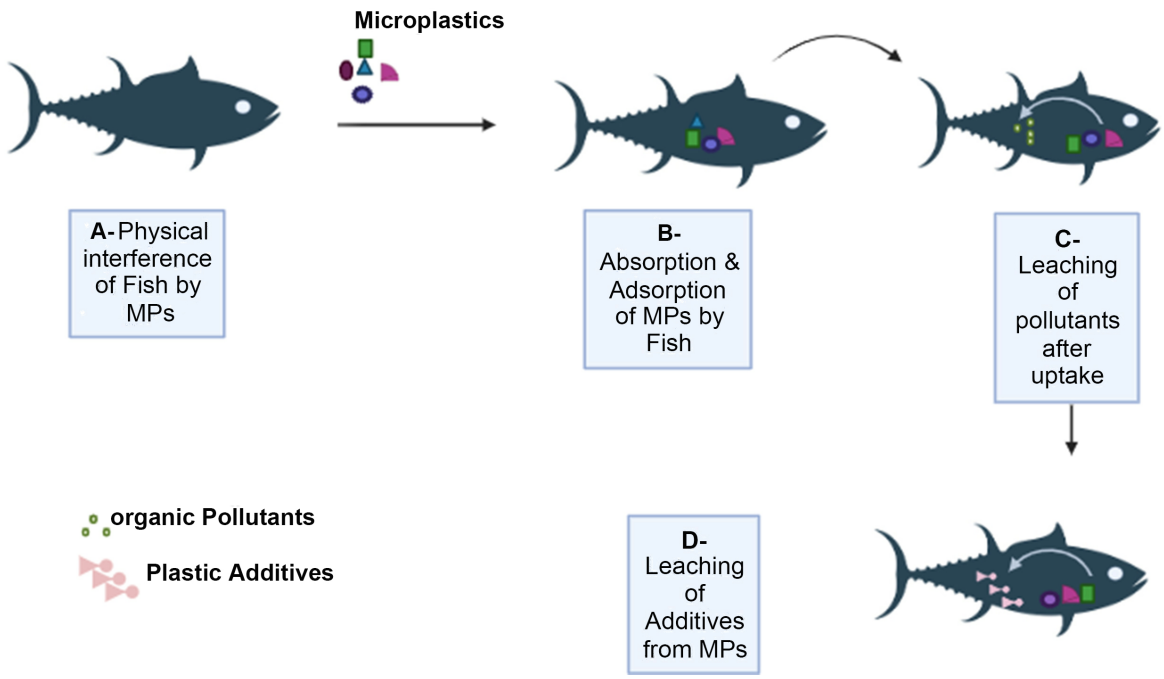

Figure 3. Physical obstruction occurs through different types of MPs encountered by fish in water. A-Sorption occurs after interaction. B-Firstly, pollutants such as chemicals, ions, and C- organic compounds leach from MPs, and then D- additives from plastic released into the fish body. MPs: Microplastics.

Daphnia magna was exposed to three different types of phthalates - DEHP, dibutyl phthalate (DBP), and DEP - ranging from 1-10 µm in concentration. After 14 days of exposure, no significant impact on reproduction or hatching was observed. However, an unexpected outcome emerged: DEHP increased reproduction at a concentration of 1 µm. On the other hand, growth and development were reduced by all the three phthalates, whereas the lipid content of Daphnia increased upon exposure to these substances. Negative effects on the lifespan of *D. magna* were observed with DBP at both 1 and 10 µm concentrations, and with DEP at 10 µm[125]. Blinova *et al.* demonstrated in a laboratory assay the negative impacts of 1-Hydroxycyclohexyl phenyl ketone (1-HCHPK) on two planktonic organisms, *Thamnocephalus platyurus*, *Daphnia magna*, and the benthic organism *Heterocypris incongruens*. 1-HCHPK is a chemical additive used in plastic construction, coating materials, and 3D printing UV-radiation-curable technologies such as 3D printing. This compound enters freshwater systems through consumer waste flows. After 6 days of exposure to 1 HCHPK (25 mg/L), *H. incongruens* exhibited a visible reduction in body size (1.3-1.8-fold) compared to the control[126]. By contrast, Murugan *et al.* found that in *T. platyurus*, hatching was promoted by the introduction of medium calcium into embryonic cells[127]. Zhang *et al.* demonstrate the capacity for biodegradation of dimethyl phthalate (DMP) by three species of freshwater unicellular cyanobacteria, i.e., *Synechocystis sp.*, *Synechococcus sp.*, and a diazotrophic *Cyanothece sp.* Low concentrations of DMP were found to enhance the growth of cyanobacteria, but increased concentrations resulted in reduced growth. At pH 9 and a temperature of 30 °C, degradation of dimethyl phthalate occurred. Cyanothece cyanobacteria exhibited the highest rate of phthalate degradation compared to the other two species. Phthalic acid was identified as an intermediate product of dimethyl phthalate after degradation[128].

Effects on terrestrial ecosystem

Plastic additives have been discovered not only in marine and freshwater ecosystems but also in terrestrial ecosystems, accumulating in the soil and posing risks to human health. A small number of studies have

indicated their presence in soil[129]; however, major additives and plasticizers have not been detected yet. One prominent plasticizer found in soil is phthalate, primarily originating from agricultural plastic use[130,131]. Recently, terrestrial ecosystems have been recognized as major receptors of plastic in the environment[132]. MPs in soil degrade into smaller particles through diffusion, the leaching of plasticizers onto their surface, and subsequent release into the soil[129]. The leaching potential of plasticizers depends on the polymer type and physical state of the plastic. Plasticizer content varies in every plastic type; for instance, PE contains minimal plasticizer, while PVC comprises over 80% plasticizers[133].

Billings *et al.* performed a field study in central and southern England (UK), aiming to assess microplastic and leached plasticizer concentrations in UK soil. They collected 19 samples from different sites, including woodlands (7 samples), urban roadsides (3 samples), urban parklands (3 samples), and landfill areas (6 samples). These samples comprised both soil and surface plastic collections. Varying quantities of microplastic items were evident across different land uses. The highest count was found in landfills, registering 42 items per 25 m^2 of soil, followed by urban roadsides with 21 items per 25 m^2, parkland exhibiting 1.3 items per 25 m^2 of, and the lowest amount in woodland, measuring 0.1 items per 25 m^2. Notably, woodlands exhibited the lowest account due to their historical tree cover dating back to 1,600 CE (Natural England, 2021). The high counts in landfills and roadsides are attributed to the widespread disposal of waste by humans[134]. Upon microplastic deposition in soil, additive compounds are released through fragmentation or degradation. Phthalate, for example, is 25 times higher in concentration in urban roadside soil than in landfills (2.3 times), parklands (1.6 times). In deciduous woodlands, the substantial presence of organic matter accelerates plasticizer biodegradation by bacteria[129].

The detrimental impact of phthalates, widely regarded as one of the most hazardous chemicals in plastic, on human health has been well-established. Phthalates enter the human body through dermal contact, eye contact, ingestion, and inhalation. They are present in numerous everyday items, such as personal care and consumer products[135,136]. Additionally, infants are exposed to and ingest phthalates through various sources such as infant formula milk, breast milk, food packaging, or cow milk[137]. Recent studies have revealed the presence of phthalates in cord blood, human breast milk, and other pregnancy specimens[135,138,139]. Colon *et al.* documented the presence of mono-(2ethylhexyl) phthalate (MEHP) and DEHP in 41 Puerto Rican girls, associating it with endocrinal disruption. Moreover, other effects such as damage to the pulmonary system, asthmatic reactions, rhinitis, direct toxicity, and allergies have been observed[140]. In Sweden, a study involving 198 children with asthmatic symptoms and 202 without symptoms, aged between 3 and 8 years, found that asthmatic symptoms were relate to exposure to air with dust containing butyl benzyl phthalate (BBzP)[141].

BPA, an additive compound, finds use in various products such as food can linings, epoxy resins, polycarbonate, polyester-styrene plastics used in containers and other baby bottles, as well as some dental sealants, protective coatings, adhesives, and water storage and supply pipes[142-146]. Many findings have detected the presence of BPA in both animal and human bodies, indicating its effects on thyroid function[147]. Research indicates that women experiencing miscarriages tend to exhibit higher BPA serum levels compared to those who are not parents[148]. A major concern in females is the prevalence of PCOS (polycystic ovary syndrome). It has been evidenced that females facing PCOS issues have a higher level of bisphenol A in their bodies compared to those without PCOS[149,150]. PBDEs are a flame-retardant present in a variety of products, including mattresses, upholstered furniture, televisions, computers, and textiles[151]. A study on humans has shown that exposure to PBDEs causes thyroid hormone level disruption[152].

Urban wastewater serves as a significant source and repository for NPs and MPs. After entering the urban wastewater system, these particles can either travel with the water flow or accumulate within sediment deposits. Notably, NPs have more prominent effects on wastewater treatment processes than MPs. Specifically, PS-NPs (100 nm) impede the removal of nitrogen in activated sludge systems due to their release or induction of reactive oxygen species (ROS) and lactate dehydrogenase (LDH), which cause acute toxicity in activated sludge, consequently suppressing the nitrification and denitrification genes through the reduction of denitrifies and nitrifies[153]. Lee *et al.* also reported the inhibitory effect of nitrification by PS-NPs, which causes disruption of cells membrane potential. Furthermore, NPs show significant effects on the production of hydrogen and methane in anaerobic digestion processes[154].

CONCLUSION AND FUTURE PROSPECTIVE

MPs and plastic additives are both emerging contaminants that have garnered considerable attention from researchers. MPs, together with naturally occurring microorganisms and synthetic chemicals, significantly impact the environment due to the continuous release of chemical pollutants, including heavy metals and organic compounds resulting from human activities. These anthropogenic pollutants have detrimental effects on the environmental matrix. Along with MPs, another major concern is additive compounds constituting the structure of plastic. Additives and plasticizers enhance the stability, shape, and properties of plastic. However, the non-covalent bonding of additives with the polymer often leads to their migration or leaching from plastics. Additives serve as antioxidants to prevent aging and as flame retardants to ensure safety against fire hazards. It is clear that aquatic ecosystems bear a substantial brunt of this pollution. Additionally, terrestrial ecosystems are grappling with issues arising from these additives. Consequently, organisms are exposed to MPs through water, soil, and food ingestion, where these pollutants and additives are retained after physical obstruction. Firstly, pollutants are released from MPs, followed by the detachment of additives due to loss of binding. This results in various dangerous effects on organisms, damaging their endocrine systems and reproductive stages, and ultimately increasing mortality rates.

Currently, there is a significant lack of comprehensive understanding regarding MPs and their leaching into the environment. This knowledge gap spans multiple areas, underscoring the imperative for future research to bridge these limitations. Despite extensive studies on the effects of leached plastic additives on marine and freshwater organisms, there remains a notable scarcity of literature concerning their impact on terrestrial organisms. Terrestrial environments significantly contribute to the accessibility and utilization of MPs from an ecological perspective. Therefore, expanding the experimental investigation of plastic additives to encompass diverse ecosystems, particularly soil, holds significant importance. Further research should prioritize investigating the ecotoxicological impacts of plastic additives on animals, insects, and plants in terrestrial environments. The feasibility of removing MPs from marine water or rivers faces limitations due to their widespread presence and ongoing fragmentation into smaller particles. It is imperative to extensively study methods for removing or converting MPs, assessing their toxicity, and monitoring their presence. Another field that needs to be explored is the potential conversion of these MPs into valuable products as a means of mitigating ecosystem contamination. Efforts targeting the control of MP pollution, particularly focusing on wastewater discharges and leachates, should prioritize transforming MPs into valuable products. Investigating the origins and destinations of MPs and their associated additives in various urban settings is crucial. The development of new technologies and methods is necessary to effectively control MPs in both wastewater treatment plants (WWTPs) and waterways to halt the continued spread of MPs and their subsequent leachates in terrestrial ecosystems.

Moreover, there is a gap in comprehensive research concerning the adsorption of contaminants onto MPs in landfill settings. Understanding the degradation process of MPs and the mechanisms involved in

contaminant adsorption in landfills is crucial for the development of an efficient treatment methodology. This significance arises from the fact that leachates within landfills often contain heightened levels of MPs, which may be associated with bound contaminants that can hinder the effectiveness of biological treatment phases. Therefore, acquiring knowledge about MP degradation and contaminant adsorption in landfills is crucial in order to establish an effective treatment strategy. Further investigation is warranted in the area of biological process development. An essential aspect of the study pertains to characterizing microbes, functional enzymes, and their respective genes concerning the degradation of synthetic plastics. Such an understanding not only helps in curbing MP pollution but also aids in mitigating their toxic effects on various organisms.

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All authors declare that there are no conflicts of interest.

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