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*Review*

# The Interaction between Microplastics and Polycyclic Aromatic Hydrocarbons: Mechanisms and Ecosystem Consequences

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## Abstract

This review systematically examines the interactions between microplastics (MPs) and polycyclic aromatic hydrocarbons (PAHs) in environmental systems, with a focus on the factors governing their co-behavior and combined ecological effects. The influence of MP properties, including polymer type, particle size, and aging characteristics, on the adsorption, transport, and bioavailability of PAHs across soil, aquatic, and atmospheric media is analyzed. Key mechanisms such as hydrophobic partitioning, π–π interactions, and surface adsorption are discussed in relation to environmental conditions such as salinity, pH, and organic matter content. Evidence on the combined toxicological effects of MP-PAH complexes on organisms is further synthesized. These interactions can lead to either synergistic or antagonistic outcomes across different species and exposure pathways. Based on identified research gaps, several critical directions for future studies are proposed, including the need for more realistic long-term exposures, advanced degradation techniques, and a better understanding of mixed pollutant dynamics. This review aims to provide a theoretical foundation for ecological risk assessment of coexisting MPs and PAHs and support the development of integrated strategies for environmental pollution prevention and control.

**Keywords:** microplastics, polycyclic aromatic hydrocarbons, adsorption mechanism, toxicological effects

## Introduction

Plastics, valued for their malleability, durability, and low cost, have significantly driven socioeconomic development and are considered a hallmark of the "Anthropocene" [1]. With a production history spanning over a century, plastics are ubiquitous in applications ranging from food packaging and industrial and agricultural production to commerce and healthcare. Since the early 20th century, global plastic output has surged dramatically, reaching a cumulative total of approximately 10 billion tons [2], with annual demand increasing by about 245 million tons per year [3]. Projections suggest that global plastic production can reach 33 billion tons by 2050 [4]. Despite growing awareness of plastic pollution, an estimated 31.9 million

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tons of plastic waste still leak into the environment annually [5]. These plastics are transported through water [6], air [7], and organisms [8], leading to widespread contamination.

Due to their strong resistance to degradation, plastics can fragment into microplastics (MPs) particles smaller than 5 mm under the influence of high temperature, UV radiation, mechanical forces, biological activity, and chemical reactions [9-11]. These MPs persist in the Earth's surface systems for extended periods. Researches have shown that MPs have extensively infiltrated the atmosphere, hydrosphere, pedosphere, biosphere, and even the lithosphere, influencing elemental cycles and greenhouse gas emissions [12, 13], thereby posing a threat to ecosystems and human health.

MPs carry 16,325 chemical substances, including bisphenol-A, phthalates, and brominated flame retardants, over 4,219 of which are toxic [14]. These substances accumulate in living organisms through skin contact, inhalation, and dietary intake, triggering inflammatory and oxidative stress responses, disrupting metabolic processes, inducing apoptosis, and even exhibiting genotoxicity [15]. While some MPs are excreted from the human body via urine and feces [16], others migrate into various tissues. To date, MPs have been detected in more than a dozen human tissues and fluids, including blood, the uterus, placenta, lungs, liver, spleen, kidneys, testes, semen, heart, arteries, bones, skeletal muscle, and cerebrospinal fluid [17-21]. Moreover, MPs act as effective carriers for other pollutants, such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), per- and polyfluoroalkyl substances (PFAS), and antibiotic resistance genes [22-25].

Polycyclic aromatic hydrocarbons (PAHs) are persistent toxic organic pollutants composed of two or more fused benzene rings, with many exhibiting carcinogenic, mutagenic, and teratogenic effects [26, 27]. According to Han et al. [28], incomplete fuel combustion in China alone released approximately 32,700 tons of PAHs in 2016. PAHs are widely distributed across environmental media. Owing to their strong hydrophobicity and lipophilicity, they persist in the environment and accumulate through the food chain, posing significant risks to organisms and human health and attracting extensive research attention [29-31]. Furthermore, PAHs can form complex mixtures with other pollutants, such as heavy metals, enhancing their overall toxicity [32]. They also adsorb onto environmental substrates, altering their transport and fate. In this context, ubiquitous MPs serve as both "carpooling" vehicles for PAH migration and environmental "reservoirs" [33-36].

The interaction between MPs and PAHs influences the occurrence, transport, and bioavailability of both pollutants. Studies indicate that these interactions are governed by intrinsic properties, such as MP composition [37], structure [38], particle size [39], and surface characteristics [40], as well as the hydrophobicity of the PAHs [41] and external environmental conditions, including water salinity [42], dissolved organic matter [43], temperature [44], and pH [45]. However, previous research has largely focused on the mechanisms of individual factors affecting either MPs or PAHs, and a systematic analysis of how environmental conditions influence their co-behavior remains limited. Moreover, consensus is lacking regarding the toxicological effects of MP–PAH complexes on organisms. In some cases, PAHs desorbed from MPs are absorbed by organisms, enhancing toxicity through synergistic effects. In contrast, when MPs strongly adsorb PAHs, they may reduce bioavailability and toxicity, leading to antagonistic effects [46]. It is important to note that desorption in environmental systems is not simply the reverse of adsorption. Due to hysteresis, the bioavailability of PAHs does not necessarily correlate with desorbed concentrations [47]. Additionally, the aging of MPs in the environment further influences the bioavailability of associated PAHs [48]. Therefore, a systematic understanding of the impacts of co-exposure to MPs and PAHs is critical for assessing ecosystem safety [49].

Several recent reviews have addressed aspects of MP-organic pollutant interactions. Ali et al. [34] surveyed MP-PAH co-occurrence in marine ecosystems; Conesa [36] reviewed PAH and PCDD/PCDF adsorption isotherms; and Goveas [33] discussed environmental mechanisms of MP-PAH interactions. While these reviews have advanced the understanding of MP-PAH interactions, three gaps merit further attention. First, they focus predominantly on marine systems, and less attention has been given to soil and atmospheric compartments. Second, they tend to provide descriptive summaries of individual studies, and quantitative data synthesis across studies, such as systematic comparison of $K_d$ values across polymer types or environmental conditions, remains limited. Third, the factors that determine whether combined MP-PAH effects on organisms are synergistic or antagonistic have not been examined in a systematic and critical manner. In light of these gaps, the present review seeks to contribute to the literature through the following aspects. First, a quantitative compilation of adsorption and toxicity data is presented in structured tables (Tables 1 and 2) to facilitate cross-study comparison. Second, a systematic, factor-by-factor analysis of the determinants of MP-PAH co-behavior is conducted, with the aim of identifying the conditions under which MPs may serve as significant versus negligible PAH vectors. Third, soil, aquatic, and atmospheric systems are given comparable treatment within a unified framework. Fourth, specific recommendations for experimental standardization, risk assessment framework development, and future research prioritization are offered for consideration.

Table 1. Summary of PAH sorption onto MPs across environmental factors.

| Location | PAHs | MPs | Concentration ($\mu g \cdot g^{-1}$)* | Refs. |
|---|---|---|---|---|
| Costa Rica | 16 priority PAHs | PE, PP | 1–284 | [50] |
| Baiyangdian Lake, China | 16 priority PAHs | PA6, PP, PE, PET | 39.4–99.8 | [41] |
| Bohai and Huanghai Seas, China | 16 priority PAHs | PS, PE | 3400–120,000 | [51] |
| Xiamen coastal area, China | 13 PAHs including 3 or 4-ring PAHs and alkylated PAHs | PE, PP, PES, PU, cellophane | 18.1–248 | [52] |
| Mediterranean beaches, Spain | PHE, ANA | PE, PP, PS, PET, PVC | ~195 | [53] |
| Feilaixia Reservoir surface water, China | CHR, BghiP, PHE | PE, PP, PS, PVC, PET | 25.6–89.6 | [54] |
| North Atlantic gyre, USA | 15 PAHs | PE, PET | 58–142 | [55] |
| Cilacap coast, Indonesia | NAP | PP, PE | 552 $ng \cdot g^{-1}$ | |
| Canary Islands, Spain | ANA, ANT, BkF, BaP, BghiP, CHR, FLT, FLU, INP, NAP, PHE, PYR | PE, PP | 35–17,024 | [56] |
| Southwestern coast of Taiwan, China | ANY, ANA, FLU, PHE, ANT, FLT, PYR, BaA, CHR, BbF, BkF, BaP, DBahA, INP, BghiP | PE, PP, PA, PVC, PS | 104–3595 | [57] |
| Nigeria maritime zone, Nigeria | NAP, 2-MNaP, ANY, ANA, FLU, PHE, FLT, PYR, BaA, BkF, BbF, DahA, BghiP | PEP, PP, PS, PU, PEVA, PET, PA | ~320 | [58] |
| Alqueva Reservoir surface water, Portugal | NAP, ANY, FLU, PHE, FLT, PYR, BaA, CHR, BkF | PS, PP, PE, PA, PET, PVC | 45.5±8.5 | [59] |
| Surface water from canals, Vietnam | ANA, ANY, FLU, PHE, ANT, FLT, PYR, BaA, CHR, BbF, BkF, BaP, DBahA, INP, BghiP | PE, PP, PS, PET, PC, Nylon | 30.94–8940.99 | [60] |
| Water from Saigon River, Vietnam | | | 432.95–3267.88 | |
| Water from Can Gio Sea, Vietnam | | | 232.71–6448.66 | |
| Beach sediments, Brazil | 14 PAHs | Styrofoam | 0.25–71.60 | [61] |
| Marine organisms from Sanggou Bay, China | 16 priority PAHs | PE, PP, PS, PET, cellulose, cellophane | 6.98±0.45 to 15.07±1.25 $\mu g \cdot kg^{-1}$ | [62] |
| Surface water and sediment from the Prahova and Ialomita, Romania | NAP, PHE, PYR, CHR, BkF, BaP, FLU, BaA, BghiP | PE, PVC, PP, PET | < LOQ–0.0187 $\mu g \cdot L^{-1}$ for surface waters; < LOQ–875 $\mu g \cdot kg^{-1}$ for sediment | [63] |
| Experimental research | NAP, PHE, PYR | PT, PU, UF | $6.71 \times 10^4$–$7.93 \times 10^4$ | [64] |
| Experimental research | CHR, BaP, INP | MPs from e-waste recycling site | 46–236 | [4] |
| Experimental research | PHE, PYR | PBS, PCL, PU, PS | PHE = $1.06 \times 10^4$ $mg \cdot kg^{-1}$; PYR = $5.87 \times 10^3$ $mg \cdot kg^{-1}$ | [65] |
| Experimental research | Nitro-PAHs | PE, PS, PP | 587–744 | [66] |
| Experimental research | NAP, PHE, PYR | PLA, PE | 140–2688 $mg \cdot kg^{-1}$ | [67] |

Note: phenanthrene (PHE), acenaphthene (ANA), chrysene (CHR), benzo[g,h,i]perylene (BghiP), naphthalene (NAP), anthracene (ANT), benzo(k)fluoranthene (BkF), benzo[a]pyrene (BaP), fluoranthene (FLT), fluorene (FLU), indeno[1,2,3-cd]pyrene (INP), pyrene (PYR), acenaphthylene (ANY), benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo(a)pyrene (BaP), dibenz[a,h] anthracene (DBahA), 2-methyl naphthalene (2-MNaP), dibenzo[a,h]anthracene (DahA), polyamide 6 (PA6), polyethersulfone (PES), polyurethane (PU), ethylene vinyl acetate copolymer (PEVA), polyamide (PA), polytetrafluoroethylene (PT), urea-formaldehyde (UF), resinpoly(1,4-butylene succinate) (PBS), polycaprolactone (PCL), polylactic acid (PLA).* All units not specified in the data are expressed in $\mu g \cdot g^{-1}$.

Table 2. Combined toxicological effects of MPs and PAHs on various organisms.

| Test Organism | PAHs | Main MPs | Major Conclusion | Refs. |
|---|---|---|---|---|
| *C. gigas*, *P. fangi*, *M. yessoensis*, *H. discus hannai*, *C. japonica*, *H. otakii*, *S. schlegelii* | 16 EPA priority PAHs | PE, PP, PS, PET | Human health risk depends on MP characteristics (type, size, color); Bioaccumulation of PAHs varies with MP type and organism feeding habits. | [62] |
| Human | NAP, PHE, PYR, CHR, BkF, BaP, FLT, BaA, BghiP | PE, PVC, PP, PET | Health risk modeling revealed that while adult exposure remained within safe margins, children exhibited a higher non-carcinogenic risk. | [63] |
| Human | CHR, BaP, INP | PC | MPs could transfer hazardous pollutants to seafood (e.g., fish and prawns), leading to cancer risk in humans. | [4] |
| *Mytilus galloprovincialis* | PHE, PYR | PBS, PCL, PU, PS | PS MPs downregulated gill NF-κB mRNA and reduced uptake/toxicity of B[a]P, likely due to PS adsorption and strong affinity lowering bioavailable concentrations. | [65] |
| Copepod | PHE, FLT | PE, PS | MP-sorbed PAHs were not bioavailable to copepods; MPs reduce toxicity by sequestering PAHs, with no size effect (10 vs 100 μm), and reduce lethality and bioaccumulation. | [37] |
| Blood clam (*Tegillarca granosa*) | 16 priority PAHs | PS | Total haemocyte count decreased, phagocytosis inhibited, ROS increased, causing LPO and DNA damage, viability reduced, signaling disrupted, and co-exposure showed synergistic effects greater than single pollutants. | [113] |
| Seaworm *Hediste diversicolor* | BaP | MPs | Environmental MPs and BaP induced oxidative stress, genotoxic effects, and cytotoxic effects under environmentally relevant exposure concentrations. | [114] |
| Aquatic organisms | 16 priority PAHs | PA6, PP, PE, PET | MPs increased risk of PAHs to aquatic organisms by altering exchange fluxes at environmental interfaces. | [41] |
| Red seabream gastric, Mummichog agastric | PHE, PYR, CHR | PE | Ingestion of PAH-laden MPs causes PAH uptake via gut desorption, but this vector effect is much lower than uptake from seawater through gills. | [115] |
| Marine diatom (*Skeletonema costatum*) | PYR,1-Methylpyrene,1-Hydroxypyrene, 1-Aminopyrene, 1-Pyrenecarboxylic acid | PS | Toxicity ranks P-$CH_3$, P-OH, P-$NH_2$ > pyrene > P-COOH. Micro-PS alone has no growth effect, but combined antagonism reduces toxicity and raises DEGs. Endpoints are growth inhibition, photosynthesis, SOD, and MDA. | [116] |
| Adult zebrafish (*Danio rerio*) | BaP, NAP, ACN, ANA, FLU, PHE, FLT, PYR, CHR, Triphenylene, BeP, ANT | PS | Contaminated MPs did not increase PAH levels in zebrafish, but size-dependent effects highlight the need for urgent ecotoxicological studies on real NPs and MPs. | [117] |
| Fish, mollusks, crustaceans, rotifers, annelids, echinoderms | PAHs | Multiple MPs | MP vector effects enhance bioaccumulation and synergistic toxicity (oxidative, neuro, genotoxic, fitness loss), but competing pathways, low levels, and desorption variability pose challenges, and contextual factors leave the real effects unclear. | [118] |

Note: naphthalene (NAP), phenanthrene (PHE), pyrene (PYR), chrysene (CHR), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), fluoranthene (FLT), benz[a]anthracene (BaA), benzo[g,h,i]perylene (BghiP), indeno[1,2,3-cd]pyrene (INP), acenaphthylene (ACN), acenaphthene (ANA), benzo(e)pyrene (BeP), anthracene (ANT), polycarbonate (PC), resin poly(1,4-butylenesuccinate) (PBS), polycaprolactone (PCL), polyurethane (PU), polyamide 6 (PA6)

## Results and Discussion

### Environmental Occurrence of PAHs on MPs

In the natural environment, the high hydrophobicity and lipophilicity of PAHs promote their tendency to associate with solid phases such as sediments, MPs, and soil. Among these, MPs are considered particularly important "carriers" for PAHs, often playing a greater role in adsorption than water or soil media [34, 36]. Most types of MPs readily accumulate PAHs under environmental conditions.

A synthesis of the available adsorption data reveals several consistent patterns (Table 1). Firstly, the partition coefficient (log $K_d$) of PAHs onto polyethylene (PE) typically exceeds that onto polystyrene (PS) by 0.5-1.0 log units for three-ring PAHs such as phenanthrene, reflecting the dominance of bulk partitioning in the amorphous regions of PE. Secondly, the adsorption affinity increases with PAH hydrophobicity. Across all MP types, log $K_d$ values for pyrene (log $K_{ow}$ = 5.18) are consistently 0.5-1.5 log units higher than those for naphthalene (log $K_{ow}$ = 3.37). Thirdly, UV aging exerts divergent effects depending on polymer type. It generally reduces adsorption on aromatic polymers such as PS due to surface oxidation and increased hydrophilicity, while enhancing adsorption on polyolefins (PE, PP) through surface roughening and increased specific surface area. However, direct quantitative comparisons are hampered by substantial methodological heterogeneity across studies, including differences in particle sizes (30 nm to 5 mm), experimental durations (24 h to 180 d), and solution chemistry. This underscores the urgent need for standardized adsorption protocols.

Significant variations exist in the abundance of PAHs adsorbed onto MPs across different environmental conditions. For instance, Mato et al. [68] reported that the concentrations of organic pollutants adsorbed onto plastics can be up to six orders of magnitude higher than those found in the surrounding seawater. In oceanic environments, PAHs have been detected in approximately 80% of plastic samples, with concentrations reaching as high as 14,459 ng·g$^{-1}$ [69]. On beaches in California, USA, PAH concentrations in polypropylene (PP) MPs ranged from 1,400 to 6,200 ng·g$^{-1}$ [70]. In China's Feilai Reservoir surface water, the total concentration of 16 priority PAHs carried by MPs ranged between 282.4 and 427.3 ng·g$^{-1}$ [54]. A broader analysis indicated that PAH concentrations on MPs from the high seas, remote beaches, and urban beaches span from 1 to 9,300 ng·g$^{-1}$ [50]. Along the Portuguese coastline, plastic fragments contained PAH concentrations between 53 and 44,800 ng·g$^{-1}$, with the most severe pollution observed near industrial areas and port facilities, and higher levels typically associated with aged and black plastic particles [71]. Studies on plastic resin pellets from Zhengming Temple Beach and Dongshan Beach in China reported total PAH concentrations of 136.3-1,586.9 ng·g$^{-1}$ and 397.6-2,384.2 ng·g$^{-1}$, respectively [72]. In soil environments in China, PAHs adsorbed onto PE and PS reached concentrations as high as 9,363.95 ng·g$^{-1}$ and 13,259.73 ng·g$^{-1}$, respectively [73].

The interaction mechanisms between MPs and PAHs have been extensively investigated [47, 56, 74, 75]. MPs exert complex influences on the behavior of organic pollutants in soil, potentially either enhancing their mobility or increasing their retention. For example, Li et al. [76] observed that the introduction of MPs into soil reduced the soil-water partition coefficient of pollutants and decreased their adsorption to soil, potentially facilitating the migration and release of organic contaminants. Conversely, one study reported that adding polyethylene, polypropylene, and polyvinyl chloride to seawater sediment samples significantly increased the concentration of phenanthrene in the sediments [77]. Similarly, the presence of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) MP particles in water can enhance the adsorption and retention capacity for organic pollutants [78]. Given that the adsorption behavior of MPs toward PAHs varies across environments, a comprehensive analysis of the influencing factors and underlying mechanisms is essential.

### Adsorption Mechanisms and Influencing Factors

#### *Adsorption Mechanism*

MPs adsorb persistent organic pollutants through multiple mechanisms, including hydrophobic partitioning [79], electrostatic interactions [80], hydrogen bonding, π–π interactions [81, 82], van der Waals forces, and pore filling [83, 84]. As a major category of traditional organic pollutants, PAHs interact with MPs via a combination of these mechanisms, with the relative contribution and dominance of each depending on the intrinsic properties of both the MPs and the PAHs, as well as ambient environmental conditions (Fig. 1).

#### *MP Properties Affecting Adsorption*

The extent to which MPs serve as vectors for PAHs in environmental matrices is governed primarily by three intrinsic properties: polymer composition, particle size, and aging state. These are examined below in order of their influence on sorptive capacity.

(1) Types of MPs

The adsorption affinity of MPs for PAHs varies substantially across polymer types, driven by differences in functional groups, crystallinity, and hydrophobicity. Common environmental MPs include PE, PP, PS, polyvinyl chloride (PVC), and polyethylene terephthalate (PET). In soil environments, the adsorption capacity for phenanthrene follows the order PE>PP>PVC, attributable to the hydrophobic surfaces of polyolefins [85, 86]. Aromatic polymers such as PS

exhibit a distinct advantage through π–π electron donor–acceptor interactions between their benzene rings and the conjugated ring systems of PAHs [87]. In marine environments, this structural effect is pronounced. PAH concentrations on PS surfaces have been reported to be 8 to 200 times higher than those on HDPE, PVC, LDPE, and PP [88].

Crystallinity further modulates adsorption behavior. Rubbery, low-crystallinity polymers such as LDPE permit bulk partitioning of PAHs into the amorphous polymer matrix, whereas glassy, high-crystallinity polymers such as PS and PP primarily support surface adsorption [88, 89]. This mechanistic distinction explains why LDPE exhibits adsorption rates for naphthalene, anthracene, and pyrene that are 4 to 10 times faster than those of PS and PP [89]. A systematic comparison by Wang and Wang [90] established the overall adsorption affinity order for phenanthrene as PE>PS>PVC>natural sediment, demonstrating that polymer type and its dominant sorption mechanism (partitioning versus surface adsorption) are the primary determinants of sorptive capacity.

(2) Particle Size

For spherical MPs, specific surface area increases as particle size decreases, theoretically providing more adsorption sites for PAHs. Studies on phenanthrene adsorption onto PS particles ranging from 30 μm down to 235 nm confirm that adsorption capacity generally increases with decreasing particle size [91]. However, this relationship is non-monotonic. Below approximately 50 nm, further size reduction paradoxically decreases adsorption capacity due to aggregation of nanoscale particles, which reduces the effective specific surface area [91, 92]. This implies a size threshold effect. Above ~50 nm, smaller particles adsorb more PAHs; below it, aggregation dominates and adsorption declines.

Comparisons between micro- and nanoscale plastics further illustrate this dual mechanism. Nanoplastics exhibit adsorption rates one to two orders of magnitude higher than their micron-scale counterparts, yet their strong aggregation tendency in environmental media substantially reduces the surface area accessible to PAHs [93]. Consequently, particle size effects and aggregation propensity must be evaluated jointly when predicting MP–PAH interactions in natural systems.

(3) Aging Effects

Environmental aging driven by UV radiation, mechanical abrasion, chemical oxidation, and biological activity profoundly alters the surface morphology, functional group composition, and porosity of MPs [94, 95]. These changes exert opposing influences on PAH adsorption. On one hand, aging increases specific surface area and porosity through surface roughening and crack formation, enhancing physical adsorption capacity [95, 96]. On the other hand, aging introduces oxygen-containing functional groups (e.g., –OH, C–O,

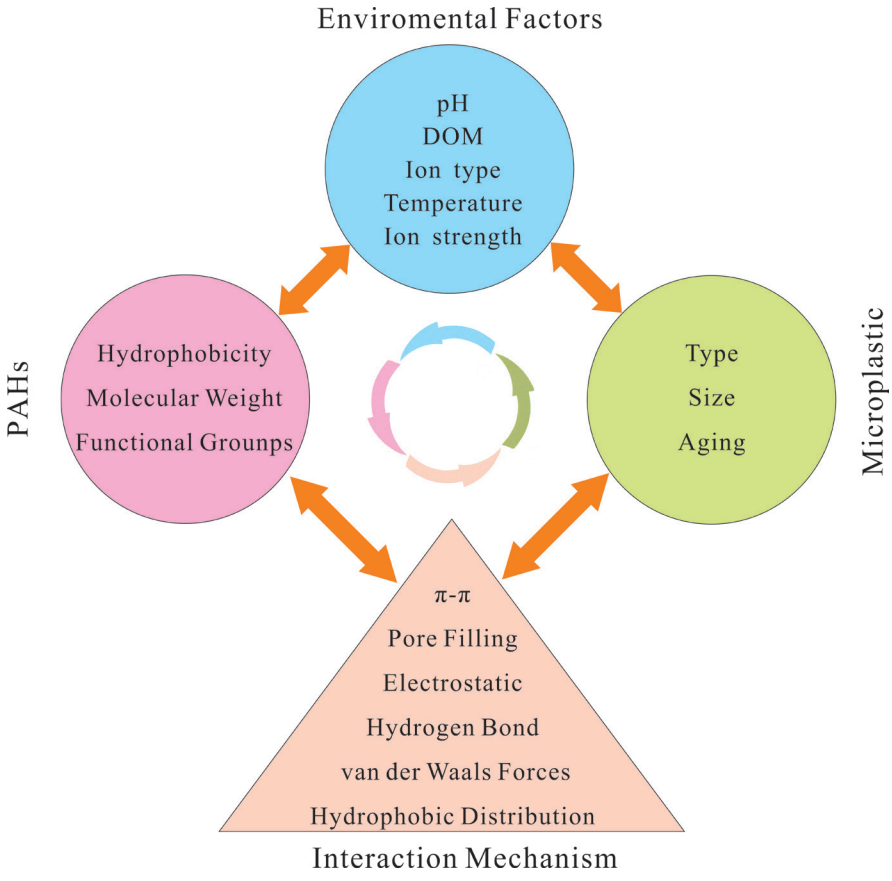



Fig. 1. The mechanism and influencing factors of MPs and PAHs.

C–OH) that increase surface hydrophilicity, thereby reducing the affinity of MPs for hydrophobic PAHs [97, 98].

The net effect of aging is strongly polymer-dependent. For rubbery polymers (PE, PP), surface roughening and increased porosity typically outweigh the countervailing effect of increased hydrophilicity, resulting in enhanced PAH adsorption after aging [95]. For glassy, aromatic polymers (PS), the introduction of oxygen-containing groups on the benzene-ring-rich surface substantially increases hydrophilicity, often reducing PAH adsorption by up to an order of magnitude relative to pristine particles [98]. UV-aged micro- and nanoplastics have consistently shown decreased adsorption of naphthalene and phenanthrene [99]. Additionally, photoaging can generate persistent free radicals (PFRs) through covalent bond cleavage, introducing emerging contaminants that further complicate the environmental behavior of aged MPs [94]. In summary, aging does not produce a unidirectional effect on MP–PAH interactions; the outcome is jointly determined by polymer type, aging mode, and aging duration, with rubbery and glassy polymers responding in opposite directions.

### *PAH Properties Affecting Adsorption*

When MPs coexist with multiple pollutants in the environment, their interaction mechanisms differ from those under single-pollutant conditions. This can be attributed to competitive adsorption at MP surface sites or to the intrinsic physicochemical properties of the pollutants, such as hydrophobicity, molecular structure, and functional groups. Wang and Wang [90] observed that as the initial concentration of pyrene increased, the adsorption of phenanthrene onto MPs decreased. PS showed a stronger adsorption capacity for pyrene than for phenanthrene and naphthalene, indicating that pollutant hydrophobicity plays a significant role in adsorption behavior [97]. The adsorption rate constants of LDPE for naphthalene, anthracene, and pyrene were reported as 0.5, 2.0, and 2.2 $h^{-1}$, respectively. Short-term adsorption followed first-order kinetics, with rate constants proportional to the hydrophobicity of the PAHs [89]. Furthermore, the aromatic structure of PS enables π–π interactions with pollutants containing double bonds or benzene rings, enhancing its affinity for such compounds [100, 101].

### *Environmental Factors*

The interactions between MPs and PAHs across different environmental media are influenced by a range of factors, including particulate matter, ion concentration, pH, dissolved organic matter, salinity, and temperature.

Salinity, in particular, plays a significant role in modulating the adsorption of PAHs onto MPs. In general, higher salinity promotes adsorption, which is often attributed to the salting-out effect that reduces the solubility of organic pollutants and enhances their partitioning to MP surfaces [93, 102]. This effect may be compounded by a multilayer adsorption mechanism involving both physical and chemical processes. Salt ions can strengthen the distribution capacity of MPs for hydrophobic organic contaminants, further facilitating adsorption [64]. However, some studies report contrasting behavior. As salinity increases, cations such as $Na^+$ and $Ca^{2+}$ may adsorb onto MP surfaces via electrostatic interactions, blocking available adsorption sites. Additionally, $Na^+$ can disrupt hydrogen bonding by displacing hydrogen atoms in acidic functional groups on the plastic surface, thereby reducing PAH adsorption [103]. While moderate salinity can enhance MP adsorption of PAHs, the presence of competing agents such as humic acid (HA) may suppress uptake, as observed in the reduced adsorption of phenanthrene in HA-containing systems [104]. Other studies note that phenanthrene adsorption is primarily governed by its initial concentration, with salinity playing a minor role [82]. For example, increasing NaCl concentration had no significant effect on the distribution coefficients of phenanthrene between PE or PVC [105]. Thus, the exact influence of salinity on MP–PAH interactions remains complex and warrants further systematic investigation.

Soil composition also significantly affects the behavior of MPs and organic pollutants. Soil organic carbon (SOC) plays a critical role in the adsorption, accumulation, and distribution of contaminants. For instance, pyrene exhibits higher adsorption capacity and faster adsorption rates in soils with elevated SOC content [106], while desorption rates are generally lower in such soils [107]. Soil organic matter often competes with MPs for the adsorption of organic pollutants [108]. Interestingly, the introduction of humic acid can inhibit PAH adsorption onto PE but enhance it on PS [72]. Dissolved organic matter (DOM) in aqueous environments also influences PAH–MP interactions: on one hand, DOM enhances the solubility of PAHs in water, introducing competition with MPs for sorption; on the other hand, it affects the colloidal stability and dispersion of smaller MPs in solution, indirectly altering their adsorption behavior. In summary, the adsorption of PAHs onto MPs in various environmental settings is a highly complex process, governed by multiple overlapping mechanisms rather than a consistent, universal pattern. The dominant mechanism in a given environment determines the overall adsorption outcome. Further research is needed to systematically disentangle these influencing factors and clarify their combined roles in MP–PAH co-behavior.

## Combined Toxicological Effects of MP-PAH Complexes

### *General Toxicological Mechanisms*

MPs not only release exogenous pollutants (e.g., PAHs, antibiotics, and heavy metals) into the

environment but also leach endogenous additives such as plasticizers and adhesives. These processes alter the environmental concentration and bioavailability of contaminants, leading to combined toxic effects on organisms and humans. The bioavailability of organic pollutants associated with MPs is influenced by several factors, including the match between the particle size of MPs and the feeding preferences of organisms, the hydrophobicity of the pollutant, desorption hysteresis, and the degradation of adsorbed compounds [109].

MPs can significantly modify the internal distribution of pollutants in organisms, facilitating the uptake and accumulation of such contaminants. This interaction often increases bioavailability and enhances biomagnification through trophic transfer [110-112]. The elevated bioavailability of PAHs in the presence of MPs may be attributed to two main mechanisms: (1) MPs act as a medium that promotes the release of PAHs into the environment, increasing dissolved or accessible concentrations; and (2) MPs themselves serve as vectors, transporting PAHs directly into organisms where the contaminants can be released. The combined MP–PAH system exerts toxicological effects on organisms primarily through exposure routes involving soil, water, and atmospheric pathways (Fig. 2).

The compiled toxicity data reveal that combined MP-PAH effects are predominantly synergistic, yet antagonistic and additive outcomes are also documented (Table 2). A critical analysis reveals that the direction of the combined effect depends on three key variables. First, particle size. Nanoscale MPs (<1 μm) almost universally enhance PAH toxicity via cellular internalization, whereas microscale MPs may sequester PAHs and reduce bioavailability. Second, polymer type. Rubbery polymers (e.g.PE) tend to release PAHs more readily in organism guts than glassy polymers (e.g.PS, PVC), promoting the 'Trojan horse' effect. Third, exposure duration. Short-term exposures often show antagonism due to incomplete desorption kinetics, while chronic exposures allow PAHs to reach equilibrium in organism tissues, shifting toward synergy. These patterns, however, are based on a limited number of studies and require validation through systematic, multi-species, multi-endpoint experiments.

*Soil Ecosystems*

When MPs carrying PAHs enter the soil, they can be transported to deeper layers by soil fauna such as earthworms and nematodes. This process can modify the physical structure and chemical properties of the soil, including water retention capacity, microbial community composition, soil pore structure, and aggregate formation [119], and may also lower soil pH [120]. MPs and associated PAHs can be taken up by plants together with water and nutrients, entering roots, stems, leaves, and flowers, thereby influencing plant growth and development. These pollutants can also be transferred through the food chain, affecting animal digestion, metabolism, enzyme activity, and genetic integrity, eventually accumulating in human tissues and organs. Such accumulation poses serious risks to human health, including an increased cancer risk [4].

The presence of MPs alters the behavior and effects of PAHs on plants. For example, due to the adsorption of phenanthrene onto MPs, uptake and accumulation of phenanthrene in wheat roots gradually increase [121]. PS can combine with phenanthrene and enter soybean plants through the roots, exerting combined toxicity. Notably, nanoscale PS exhibits lower toxicity to plants than micrometer-sized PS, as smaller PS particles reduce rhizosphere activity, thereby decreasing phenanthrene uptake in soybean roots and leaves [122]. However, some studies indicate that co-exposure to MPs and PAHs can

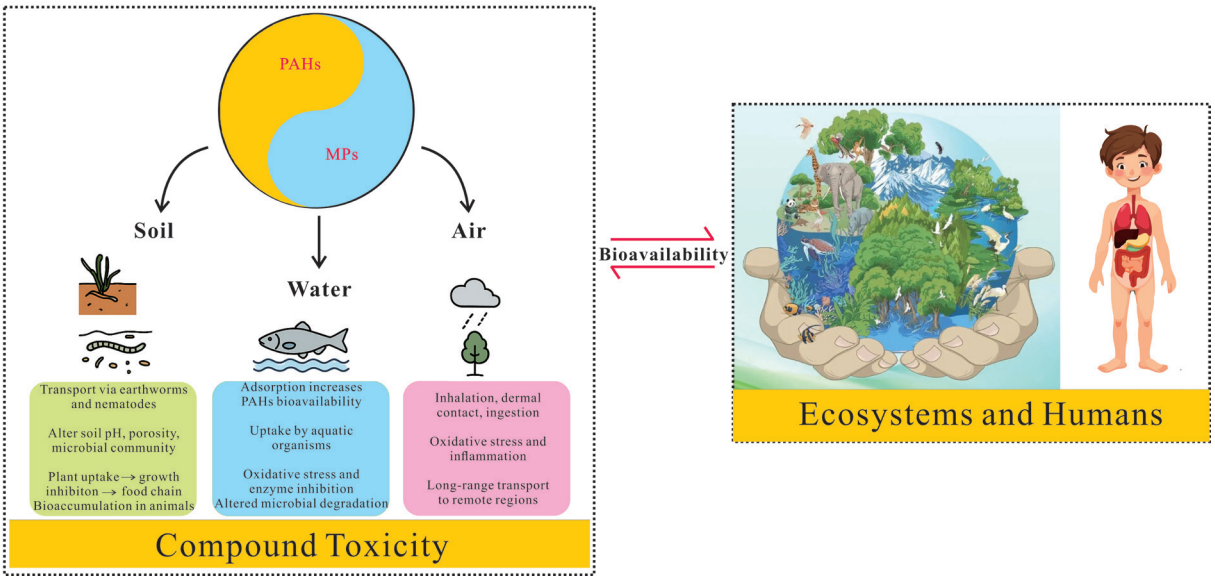



Fig. 2. Combined toxicity of MPs and PAHs.

mitigate the phytotoxicity of PAHs. For instance, PS has been shown to reduce the adverse effects of PAHs on wheat growth [123]. While naphthalene alone inhibits leaf growth and impairs photosynthetic capacity, combined exposure with PS nanoparticles alleviates such damage by enhancing energy metabolism and photosynthesis and modulating hormone signaling and carbon fixation pathways [34].

Earthworms contribute to the vertical transport of MPs into deeper soil through feeding, burrowing, excretion, and physical attachment, with micro- and nanoplastics capable of reaching even greater depths [124, 125]. Other soil animals, including ants and hamsters, also facilitate the migration of MPs within soil [126]. Teuten et al. [77] reported that PE, PVC, and PP increased phenanthrene concentrations in lugworms, enhancing its in vivo toxicity. Conversely, Xu et al. [126] observed that nano-PS significantly inhibited the activity of phenanthrene-degrading bacteria in earthworms, leading to higher residual phenanthrene concentrations. In some cases, the presence of MPs promotes the adsorption of PAHs in soil, reducing their bioavailability and thus potentially mitigating harm to plants and animals. In contrast, exposure to fluorene combined with PS showed the greatest impact on earthworms, while PE and PVC exhibited higher subacute toxicity [127]. Under certain conditions, PE and PS have been found to reduce PAH accumulation in *Eisenia fetida*. This may be attributed to the strong adsorption capacity of soil particles for organic pollutants, the limited amount of PAHs carried by MPs into the earthworm gut, or the shorter intestinal retention time of MP-adsorbed PAHs [39].

### *Aquatic Ecosystems*

When MPs carrying PAHs enter aquatic environments, they can be directly ingested by aquatic animals or adhere to their body surfaces. The mechanisms and toxic effects of such combined exposures differ from those of PAHs alone. MPs can modulate the bioavailability of co-occurring pollutants through adsorption [128]. For instance, PE and PS have been shown to enhance the bioavailability and toxicity of pyrene in mussels via adsorption [129]. Pyrene can be internalized by *Daphnia* through PS particles via endocytosis [130], while surface contact has been identified as the primary pathway for transferring PAHs from contaminated MPs to larvae [131].

The presence of MPs may synergistically increase the uptake of PAHs by organisms, elevating bioavailability and posing potential threats to aquatic life and human health. For example, MPs can inhibit the dispersion and transformation of phenanthrene and promote its bioaccumulation in *Daphnia* [132]. Nanoplastics have been found to facilitate the transport and uptake of phenanthrene, increasing its bioavailability and potential toxicity to zebrafish embryos [133]. Liu et al. [134] reported the highest apoptosis rate in the haemocytes of Manila clams (*Ruditapes philippinarum*) under combined exposure to PE-MPs and pyrene, with the toxic effect of co-exposure exceeding that of single-contaminant exposure. MPs loaded with PAHs can induce oxidative stress in mussels, manifesting as increased catalase activity in the digestive gland and decreased superoxide dismutase activity in the mantle [135]. Karami et al. [136] observed that MPs interact with phenanthrene by altering its bioavailability, thereby modulating biomarker responses in catfish. In mudskippers, combined exposure to MPs and pyrene significantly decreased acetylcholinesterase and isocitrate dehydrogenase activities and increased mortality [137]. Co-exposure to MPs and phenanthrene may also cause gill tissue damage and impair osmoregulatory function [138].

Such combined pollution can further reduce key physiological functions, compromise immune responses, diminish feeding capacity, and weaken the ability of organisms to tolerate other environmental stressors. For instance, PE significantly suppressed the activity of acetylcholinesterase and isocitrate dehydrogenase, negatively affecting growth, reproduction, and survival [139]. Combined exposure to nonylphenol, phenanthrene, and PVC reduced the survival rate, feeding amount, and immunity of lugworms [140]. Beyond altering the adsorption–desorption dynamics of PAHs, MPs may also influence PAH biodegradation by shaping microbial community structure and composition. Biofilms formed on MP surfaces can adsorb benzo[a] pyrene (BaP), and such combined pollution modifies the adsorption and release behavior of BaP, ultimately affecting its bioavailability and toxicological expression [141]. On the other hand, some studies indicate that MP–PAH interactions have limited impacts on aquatic organisms and may even exhibit antagonistic effects. For example, the presence of PVC significantly reduced the bioavailability of phenanthrene in zebrafish larvae, as analyzed through biomarker genes [142]. The adsorption and aggregation of MPs with naphthalene can reduce their contact probability with *Chlorella vulgaris* cells, leading to a joint toxic effect that is less pronounced than single-exposure toxicity, demonstrating an antagonistic interaction [143]. In summary, there is no clear consensus regarding the impact of micro/nanoplastics co-occurring with PAHs on the bioavailability and toxic effects in aquatic environments. Further systematic research is needed to clarify these complex interactions.

### *Atmospheric Exposure*

When MPs carrying PAHs enter the atmosphere, they can be directly taken up by animals, plants, microorganisms, and humans through inhalation, dermal contact, or ingestion. They can also settle onto the ground and be redistributed via precipitation and surface runoff, eventually exerting toxic effects on terrestrial and aquatic organisms. Airflow is a key factor influencing the spatiotemporal distribution of airborne

MPs and contributes to their dispersion into remote regions [144]. For example, Dris et al. [145] detected MPs in the atmosphere near Paris, while Zhou et al. [146] first reported an atmospheric deposition rate of approximately $1.5\times10^5$ particles·$m^{-2}$·$year^{-1}$ in coastal cities of China. In Shanghai, atmospheric MP concentrations ranged from 0 to 4.18 particles·$m^{-3}$, primarily comprising PET, PE, and polyacrylonitrile [147]. In Dongguan, Guangdong, the daily MP deposition was measured at 36±7 particles·$m^{-2}$, dominated by synthetic fibers [148].

Atmospheric transport is considered a major pathway for MP pollution and its spread across regions [149, 150]. For instance, MPs detected in remote lakes and glaciers on the Qinghai Tibet Plateau are likely attributable to long-range atmospheric transport [150]. In an urban environment in Guangzhou, Huang et al. [151] found that the atmospheric deposition flux of MPs ranged from 51 to 178 particles·$m^{-2}$·$day^{-1}$, with an average of 114±40 particles·$m^{-2}$·$day^{-1}$. Due to their small size, airborne MPs can be directly inhaled by humans, posing particular health risks, especially to industrial workers [152]. When MPs co-occur with other pollutants such as PAHs, their impact on the bioaccumulation and toxicity of these contaminants becomes highly complex. This complexity arises from multiple uncertain factors, including the properties, types, and concentrations of both PAHs and MPs, the duration of organism exposure, and the adsorption-desorption dynamics of pollutants on MP surfaces.

## Knowledge Gaps and Future Research Priorities

Despite recent advances, fundamental questions regarding MP–PAH co-behavior remain unresolved. Four priority areas that must be addressed to move the field from descriptive observation toward mechanistic prediction and evidence-based risk management are identified below.

(1) Methodological Standardization and Integrated Risk Assessment. The single greatest barrier to cross-study synthesis is methodological fragmentation: no two laboratories employ identical MP preparations, particle size distributions, aging protocols, or exposure matrices. We propose that the research community adopt a consensus minimum reporting framework encompassing four domains: MP characterization (polymer identity, size distribution, specific surface area, crystallinity), adsorption protocols (equilibration time $\geq$ 7 d, standardized background electrolyte, temperature control), toxicity testing (environmentally relevant concentrations, MP-only and PAH-only controls, $\geq$ 3 biological replicates), and data archiving (raw isotherms and kinetic curves in open-access repositories). An international ring-test program, analogous to OECD inter-laboratory initiatives for conventional chemicals, would accelerate protocol harmonization. Parallel advances in risk assessment are equally urgent. Current frameworks treat MPs and PAHs independently, potentially mischaracterizing risks when they co-occur. Three advances are advocated. First, a "vector enhancement factor" should be incorporated into equilibrium partitioning models to quantify MP-mediated bioavailability changes. Second, probabilistic approaches that account for joint MP–PAH concentration distributions should be adopted. Third, mixture-specific species sensitivity distribution curves should be developed.

(2) Long-Term, Multi-Compartment Field Studies with Ecological Realism. Current mechanistic understanding derives almost entirely from short-term (< 30 d) batch experiments using pristine MPs and single-species assays. Whether laboratory-derived adsorption coefficients and toxicity thresholds extrapolate to field conditions remains largely unknown. In field settings, MPs are weathered, PAHs exist as complex mixtures, and organisms face chronic, multi-generational exposure. Three priorities for field-based research are identified. First, Long-Term Ecological Research (LTER) sites with coordinated MP–PAH monitoring across soil, water, and atmospheric compartments should be established. Second, passive samplers should be deployed alongside MP traps to distinguish freely dissolved from MP-bound PAH fractions under in situ conditions. Third, dated sediment and ice cores should be used to reconstruct historical co-deposition trends. Particular urgency attaches to soil ecosystems, which annually receive an estimated 4-23 times more plastic input than oceans yet account for less than 10% of published MP–PAH studies. Future experimental designs should systematically extend exposure durations, incorporate environmentally weathered MPs, and include multi-trophic endpoints to better capture real-world ecological consequences.

(3) Multi-Contaminant Interactions Beyond Binary MP–PAH Systems. The vast majority of laboratory studies examine MP–PAH interactions in binary systems. Environmental realism, however, demands consideration of scenarios where MPs simultaneously carry PAHs, heavy metals (e.g., $Cu^{2+}$, $Cd^{2+}$), per- and polyfluoroalkyl substances (PFAS), and other co-occurring pollutants. Recent evidence indicates that the co-presence of cationic metals can modify MP surface charge and aggregation state, thereby altering PAH adsorption capacity; that PFAS compounds may form mixed adlayers with PAHs on MP surfaces, creating more complex desorption behavior in biological fluids; and that these multi-contaminant interactions may produce toxic effects that are not predictable from single-pollutant or binary data. A systematic research agenda is needed to (i) map competitive adsorption isotherms of PAHs versus other priority pollutants on major MP types under environmentally relevant conditions, (ii) determine whether multi-contaminant-loaded MPs exhibit synergistic, antagonistic, or independent toxic effects in model organisms representing different trophic levels, and (iii) assess whether current single-pollutant risk assessment frameworks are adequate. The development and validation of quantitative structure–activity relationship (QSAR) models capable of

predicting multi-sorbate competition on heterogeneous, aged MP surfaces should be prioritized.

(4) Mechanistic Understanding of Aging Effects and Development of Targeted Remediation Strategies. The contradictory literature on whether MP aging increases or decreases PAH adsorption reflects a deeper gap. A predictive framework that links aging mechanisms (UV photo-oxidation, mechanical abrasion, biofilming) to specific changes in adsorption contributions (hydrophobic partitioning, π–π interactions, hydrogen bonding, pore filling) for different polymer types is currently lacking. Systematic experiments that independently vary aging mode (UV, chemical oxidation, mechanical), aging duration, and polymer type are urgently needed. These experiments should quantify the relative contribution of each adsorption mechanism before and after aging. On the remediation front, photocatalytic, Fenton-based, and biodegradation approaches have shown laboratory promise. Yet three barriers preclude field deployment. These include reliance on pristine rather than environmentally weathered MPs, poorly characterized degradation byproducts that may exceed parent-compound toxicity, and absent life-cycle or techno-economic assessments. Future work should prioritize testing on field-collected, multi-contaminant-loaded MPs, comprehensive byproduct toxicity screening, and net-benefit verification through life-cycle assessment and techno-economic analysis. Additionally, against the backdrop of global carbon neutrality goals, research exploring how MPs influence carbon cycling through effects on $CO_2$ assimilation by primary producers and through MPs' own contribution to carbon emissions represents an emerging frontier warranting systematic investigation.

## Conclusions

This review concludes that MPs are significant but conditional vectors for PAHs, and their net environmental role cannot be captured by any single generalization. Three lines of evidence converge on this conclusion. First, the adsorption data compiled in Table 1 demonstrate that the vector function is substantial only when three conditions coincide. These are rubbery, low-crystallinity polymers (LDPE>PS>PVC) that permit bulk partitioning, submicron particle sizes with controlled aggregation, and saline, low-DOM aqueous environments that promote salting-out while minimizing competitive sorption. Under opposing conditions, particularly organic-rich soils (≥2% SOC), MPs are estimated to account for less than 5% of total PAH sorption capacity, with natural organic matter dominating partitioning. Second, the toxicity data in Table 2 reveal a predominantly synergistic pattern of MP–PAH co-exposure. However, this trend warrants cautious interpretation. Roughly two-thirds of published studies rely on PS nanoparticles and phenanthrene or pyrene as model systems, and the apparent prevalence of synergy may partly reflect publication bias rather than environmental reality. Third, a systematic geographic asymmetry undermines generalizability. Marine studies constitute approximately 65% of the literature, whereas soil ecosystems, which annually receive an estimated 4 to 23 times more plastic input than oceans, account for approximately 10%, leaving the rhizosphere as the most critically understudied compartment. Fundamentally, the inability of the field to resolve even basic mechanistic questions reflects a deeper problem of methodological fragmentation. The question of whether aging increases or decreases PAH adsorption exemplifies this challenge. Reliable meta-analysis, quantitative risk assessment, and evidence-based policy therefore depend, first and foremost, on the adoption of consensus experimental protocols and a standardized minimum reporting framework.

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## Conflict of Interest

The authors declare no conflict of interest.

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