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BIOFILM-MEDIATED INTERACTIONS BETWEEN MICROPLASTICS AND TRACE METALS IN AQUATIC ENVIRONMENTS: FROM SORPTION AND REMOBILIZATION TO ECOLOGICAL RISK

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ABSTRACT
Microplastics (MPs) are widespread contaminants in aquatic environments and can interact with trace metals through physicochemical processes occurring at their surfaces. Following environmental exposure, MPs are rapidly colonized by microorganisms and covered by biofilms, which substantially modify their surface properties and consequently influence their interactions with metals. This review critically synthesizes current knowledge on biofilm-mediated interactions between MPs and trace metals, with particular emphasis on sorption mechanisms, environmental controls, desorption and remobilization, bioavailability, and ecological consequences. Biofilm development and environmental aging can increase surface roughness, alter surface charge, and introduce extracellular polymeric substances and functional groups capable of binding metal ions through electrostatic attraction, ion exchange, and surface complexation. However, biofilm-coated MPs should not be regarded solely as sinks for trace metals. Changes in environmental conditions, biofilm degradation or detachment, and gastrointestinal conditions following ingestion may promote metal desorption and remobilization, potentially altering metal bioaccessibility and exposure. Available evidence further indicates that co-exposure to MPs and metals can produce synergistic, additive, or antagonistic biological effects rather than a universally enhanced toxic response. Major knowledge gaps remain regarding environmentally aged particles, complex contaminant mixtures, long-term field conditions, biofilm dynamics, metal remobilization, and trophic transfer. Future studies should therefore move beyond pristine MPs and single-metal laboratory systems toward environmentally realistic approaches integrating surface chemistry, biofilm processes, metal speciation, bioavailability, and biological responses. Such an integrated perspective is necessary to better evaluate the role of biofilm-coated MPs in the transport and ecological risk of trace metals in aquatic ecosystems.

KEYWORDS: Microplastics; Biofilm; Trace metals; Sorption; Remobilization; Bioavailability; Ecological risk

1. INTRODUCTION

Microplastic (MP) pollution has become an increasing environmental concern because of its widespread occurrence and persistence in aquatic ecosystems. MPs have been detected in water columns, river and lake sediments, and diverse aquatic habitats, with sediments acting as both repositories and potential sources of remobilized particles under changing hydrodynamic and environmental conditions [7,25,26,30,40]. Once released into the environment, MPs do not remain in a pristine state but undergo weathering, abrasion, oxidation, interactions with organic and mineral matter, and microbial colonization [1,21,22,27]. These processes modify surface roughness, area, charge, hydrophobicity, and functional-group composition, thereby influencing particle transport and interactions with co-occurring contaminants [1,11,20,21,44].

Of particular concern is the capacity of MPs to interact with trace metals. Pb, Cd, Cu, Zn, Cr, Ni, and other trace elements have been associated with various MPs in both experimental systems and environmental samples [1,5,10,12,13,21,33,37,44]. Metal sorption may involve electrostatic interactions, ion exchange, surface complexation, hydrogen bonding, and interactions with functional groups on particle surfaces [1,10,15,21]. However, metal binding is not determined by polymer chemistry alone. Metal identity, particle size, contaminant concentration, pH, salinity, ionic strength, dissolved organic matter (DOM), and MP aging can substantially modify sorption behavior [10,15,21,33,44].
Environmental aging is particularly important because it can transform relatively unreactive polymer surfaces into more chemically heterogeneous sorption interfaces. Oxidation and weathering can increase surface roughness and introduce oxygen-containing groups such as hydroxyl and carboxyl groups, while accumulated organic matter can

provide additional metal-binding sites [1,11,21,41]. Fu et al. [11], for example, reported greater Pb(II) sorption by naturally aged than pristine MPs and demonstrated an important contribution of carboxyl and hydroxyl groups in the surface organic film. Such evidence indicates that experiments based exclusively on pristine MPs may not adequately represent the properties and behavior of environmentally aged particles [1,11,18,21].

In parallel with abiotic aging, MPs in aquatic environments rapidly provide substrates for microbial attachment and biofilm development, forming communities commonly referred to as the plastisphere [8,21,23,27,31,42]. Colonization is influenced by polymer properties, particle size, exposure duration, seasonality, environmental conditions, and the surrounding microbial community [8,23,31,36,42,43]. Biofilm development can further alter MP surface roughness, charge, hydrophobicity, density, and transport behavior [17,21,23,27,39]. A key component of these biofilms is extracellular polymeric substances (EPS), comprising polysaccharides, proteins, extracellular DNA, and other organic constituents [27,34,39]. EPS contains metal-binding functional groups, including carboxyl, hydroxyl, phosphate/phosphoric, amino, sulfhydryl, and phenolic groups [21,27,34]. Consequently, biofilm formation can transform MPs into complex biogeochemical interfaces with more diverse binding sites than pristine polymer surfaces [12,21,27,34]. Experimental and field evidence indicates that biofilms can modify trace-metal sorption kinetics and contribute to metal enrichment on environmental MPs [9,12,19,37]. MP–metal interactions in natural waters should therefore be considered at the MP–biofilm–metal interface, rather than solely as direct interactions between polymers and dissolved metal ions [12,21,27].

However, enhanced sorption does not necessarily imply permanent immobilization. Biofilm-coated MPs may act as sinks by retaining metals, but they may also function as carriers/vectors or secondary sources when environmental conditions promote transport or metal release [16,17,20,21]. Kalčíková et al. [16] showed that aged/biofilm-coated MPs sorbed more Ag than pristine particles but could subsequently release a substantial fraction of the associated metal. Similarly, decomposition or detachment of organic coatings from naturally aged MPs may promote metal release [41]. Metal association with biofilm-coated MPs should therefore be regarded as a dynamic sequence of sorption–retention–desorption–remobilization, rather than as irreversible sequestration [5,16,17,20].

This dynamic behavior becomes particularly relevant after metal-bearing MPs are ingested by aquatic organisms. Total metal loading on MPs does not necessarily represent the fraction available for biological uptake. Gastrointestinal conditions, including changes in pH, ionic composition, and digestive constituents, can shift sorption–desorption equilibria and remobilize MP-associated metals [14,18,20,29]. Simulated digestion experiments have demonstrated the release of some sorbed metals into gastrointestinal fluids [14]. Accordingly, total metal loading, bioaccessible fraction, and bioavailable fraction should be distinguished when evaluating MPs as potential vectors of metal exposure [5,14,18,20,29].

Ecotoxicological evidence further indicates that MP–metal co-exposure does not produce a uniform biological response. Depending on polymer and metal characteristics, concentration, surface state, biofilm development, exposure duration, and organism physiology, MPs may enhance, reduce, or have little effect on metal toxicity [1,6,16,18,20,24,27]. Reported endpoints include oxidative stress, lipid peroxidation, immune dysfunction, altered feeding and growth, tissue damage, and other physiological responses [6,16,18,24,45]. MPs may increase metal transport or bioavailability under some conditions, whereas sorption may reduce dissolved metal concentrations and temporarily decrease biological exposure under others [17,18,20]. The proposed “Trojan horse” effect should therefore not be regarded as a universal mechanism but as a context-dependent outcome [13,17,18].

Despite rapid growth in research on MPs, biofilms, and metals, important knowledge gaps remain. Many experiments still rely on pristine MPs, single polymers, single-metal systems, and simplified laboratory conditions, whereas environmental MPs simultaneously undergo aging, biofilm colonization, and exposure to contaminant mixtures [1,15,18,21,44]. Research has also focused more extensively on adsorption than on desorption, remobilization, and bioavailability, despite the direct relevance of these processes to actual biological exposure [1,14,17,20]. Competitive or facilitating interactions in multi-metal systems further limit extrapolation from single-metal experiments [10,15]. Moreover, direct evidence for trophic transfer of the integrated MP–biofilm–metal system, long-term changes in metal loading during biofilm development, and transitions between sink and source functions remains limited [17,18,21,27]. Bridging the gap between short-term laboratory experiments and environmentally realistic field conditions therefore remains a major challenge [18,19,43].

Previous reviews have primarily addressed MP–metal interactions from the perspectives of sorption mechanisms, contaminant transport, and combined toxicity, while the role of biofilm has often been considered as one of several factors modifying MP surface properties. Comparatively less attention has been given to how biofilm development regulates the dynamic transition of MPs between metal retention and release. This review therefore adopts a biofilm-centered perspective and integrates sorption, desorption, remobilization, and biological exposure within a unified framework in which biofilm-coated MPs may function as sinks, carriers/vectors, or secondary sources of trace metals.

Accordingly, this review critically synthesizes current evidence on biofilm-mediated interactions between MPs and trace metals in aquatic environments, extending beyond sorption to consider desorption, remobilization, bioaccessibility, bioavailability, and ecological consequences. Specifically, it examines: (i) biofilm development and associated MP surface transformations; (ii) mechanisms governing metal binding at the MP–biofilm interface; (iii) the roles of polymer properties and environmental conditions; (iv) metal desorption, remobilization, and

bioavailability; and (v) the ecological implications of MP–metal co-exposure. Finally, major knowledge gaps and research priorities are identified to support more environmentally realistic assessments of the role of biofilm-coated MPs in trace-metal transport, transformation, and ecological risk.

2. REVIEW METHODOLOGY

Relevant literature on interactions among microplastics (MPs), biofilms, and trace metals in aquatic environments was searched using Scopus, PubMed, ScienceDirect, and Google Scholar. The literature search was conducted up to August 2026, with priority given to peer-reviewed English-language studies published between 2018 and 2026. Earlier publications were included when they provided relevant foundational or mechanistic evidence. Search terms included combinations of "microplastics", "biofilm", "plastisphere", "trace metals", "heavy metals", "metal sorption", "desorption", "remobilization", "bioavailability", "bioaccessibility", "environmental aging", "combined toxicity", and "trophic transfer". Reference lists of relevant original studies and review articles were also screened to identify additional publications.

Studies were included when they addressed one or more of the following topics: biofilm development on MPs; environmental aging and surface transformation; MP–metal interactions; environmental controls on metal sorption and desorption; metal bioaccessibility, bioavailability, or biological uptake; and ecological effects of MP–metal co-exposure. Peer-reviewed experimental studies were prioritized for mechanistic evidence, whereas review articles were used primarily to establish broader trends and identify knowledge gaps. Studies conducted in freshwater, estuarine, and marine environments were considered. Duplicate records and studies outside the aquatic scope or without direct relevance to MP–biofilm–metal interactions were excluded. Non-peer-reviewed sources were excluded when equivalent peer-reviewed evidence was available.

Given the substantial heterogeneity among studies in terms of polymer type, particle characteristics, aging status, biofilm properties, metal identity, exposure conditions, and biological endpoints, a quantitative meta-analysis was not performed. Instead, the evidence was evaluated using a narrative and critical synthesis framework. Evidence was organized around the progression from environmental aging and biofilm development to surface modification, metal sorption and desorption, bioavailability, and ecological effects. Both consistent and contrasting findings were considered to identify the conditions under which biofilm-coated MPs may function as sinks, carriers/vectors, or secondary sources of trace metals.

3. Biofilm Development and Surface Transformation of Microplastics

3.1. Biofilm Colonization and Development on Microplastics

Once introduced into aquatic environments, microplastics (MPs) rapidly interact with organic, inorganic, and biological constituents in the surrounding water. Adsorption of dissolved and organic compounds can form a conditioning layer that facilitates microbial attachment and subsequent colonization [21,27,39,42]. Attached microorganisms then proliferate and produce extracellular polymeric substances (EPS), leading to increasingly complex biofilm communities collectively referred to as the plastisphere [8,23,27,31,42].

Biofilm development is a dynamic process involving attachment, growth, community succession, maturation, and detachment, all of which vary over time and with environmental conditions [17,27,36,43]. Polymer type, particle size and morphology, surface roughness, aging status, temperature, nutrient availability, and water chemistry can influence microbial colonization and biofilm community structure [8,23,31,36,39,43]. Consequently, even MPs composed of the same polymer may develop substantially different biofilms depending on their environmental history.

EPS is particularly relevant to subsequent contaminant interactions because its polysaccharides, proteins, and other organic constituents contain functional groups including carboxyl, hydroxyl, phosphoric, sulfhydryl, and phenolic groups [21,27,34]. Following colonization, the reactive surface of MPs therefore evolves from a relatively simple polymer surface into a heterogeneous interface comprising the polymer, accumulated organic matter, microorganisms, and EPS [12,21,27].

3.2. Biofilm- and Aging-Induced Surface Transformation

Biofilm development commonly occurs alongside environmental aging of MPs. Weathering, abrasion, oxidation, mineral deposition, and biological colonization can modify particle roughness, surface charge, surface area, and functional-group composition [1,11,21,44]. Naturally aged MPs may therefore differ substantially from the pristine particles commonly used in laboratory experiments.

Organic conditioning and biofilm formation further modify these surfaces by introducing biologically derived functional groups and heterogeneous surface coatings [11,12,21]. Experimental observations confirm that these transformations are relevant to contaminant interactions: naturally aged MPs can exhibit different metal-binding behavior from pristine particles [11], while biofilm development can influence both contaminant association and subsequent release [16]. Organic coatings and biofilms therefore represent active components of environmentally transformed MP surfaces rather than passive surface layers [12,21,41].

Collectively, environmental aging and biofilm development transform MPs into dynamic biogeochemical interfaces whose physicochemical and biological properties continue to evolve over time [12,21]. The consequences of these transformations for trace-metal sorption and retention are examined below.

4. Trace-Metal Sorption at the Biofilm–Microplastic Interface

4.1. From Pristine Microplastics to Biofilm-Modified Sorption Surfaces

Microplastics can interact with trace metals even before biofilm formation. In their pristine state, metal sorption is influenced by polymer properties including chemical structure, surface charge, hydrophobicity, crystallinity, and available surface area [1,10,20,21,44]. Metal affinity also varies among ions; for example, sorption in some PS-based systems has been reported in the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$ [20,21]. Findings from individual polymer–metal combinations therefore cannot be generalized directly to other systems.

The surface transformations described in Section 3 can substantially modify this baseline sorption behavior. A particularly clear example was reported by Fu et al. [11], who found greater Pb(II) sorption by naturally aged MPs than by pristine particles, with a maximum sorption capacity of approximately 13.60 mg g^{-1} under the experimental conditions. Removal of the organic surface film reduced Pb sorption, demonstrating that enhanced binding was associated not only with polymer weathering but also with accumulated surface material [11]. Biofilm-derived EPS can further expand the range of potential metal-binding sites [12,21,27,34].

These findings highlight an important methodological limitation: commercially available pristine MPs may not adequately represent the metal-binding behavior of particles that have undergone prolonged environmental aging and biological colonizat**ion [1,11,12,21].**

4.2. Metal-Binding Mechanisms at the MP–Biofilm Interface

Metal retention by biofilm-coated MPs can involve several mechanisms operating simultaneously [1,12,21,34]. Electrostatic attraction occurs between metal ions and charged sites on MP or biofilm surfaces and is strongly influenced by the pH-dependent protonation of surface functional groups [1,21,33]. Ion exchange may occur when metal ions compete with or replace ions associated with active sites on the particle surface or within the EPS matrix [1,21].

Surface complexation is particularly relevant to aged and biofilm-colonized MPs. Carboxyl and hydroxyl groups in organic surface coatings contribute to Pb binding on naturally aged MPs [11], while phosphoric, sulfhydryl, phenolic, and other functional groups within EPS provide additional coordination sites for metal ions [21,34]. Mineral deposits and inorganic phases associated with environmentally aged MPs may further contribute through additional sorption sites, precipitation, or mineral-associated retention [12,21].

These mechanisms operate within a chemically heterogeneous interface rather than independently. Their relative importance depends on polymer properties, biofilm composition and maturity, metal speciation, pH, salinity, dissolved organic matter, and competition among ions [10,15,21,33,44]. Consequently, enhanced sorption following aging or biofilm formation is not universal, and metal retention under environmental conditions should be regarded as an emergent property of the entire MP–biofilm–water interface rather than being attributed solely to the polymer or EPS.

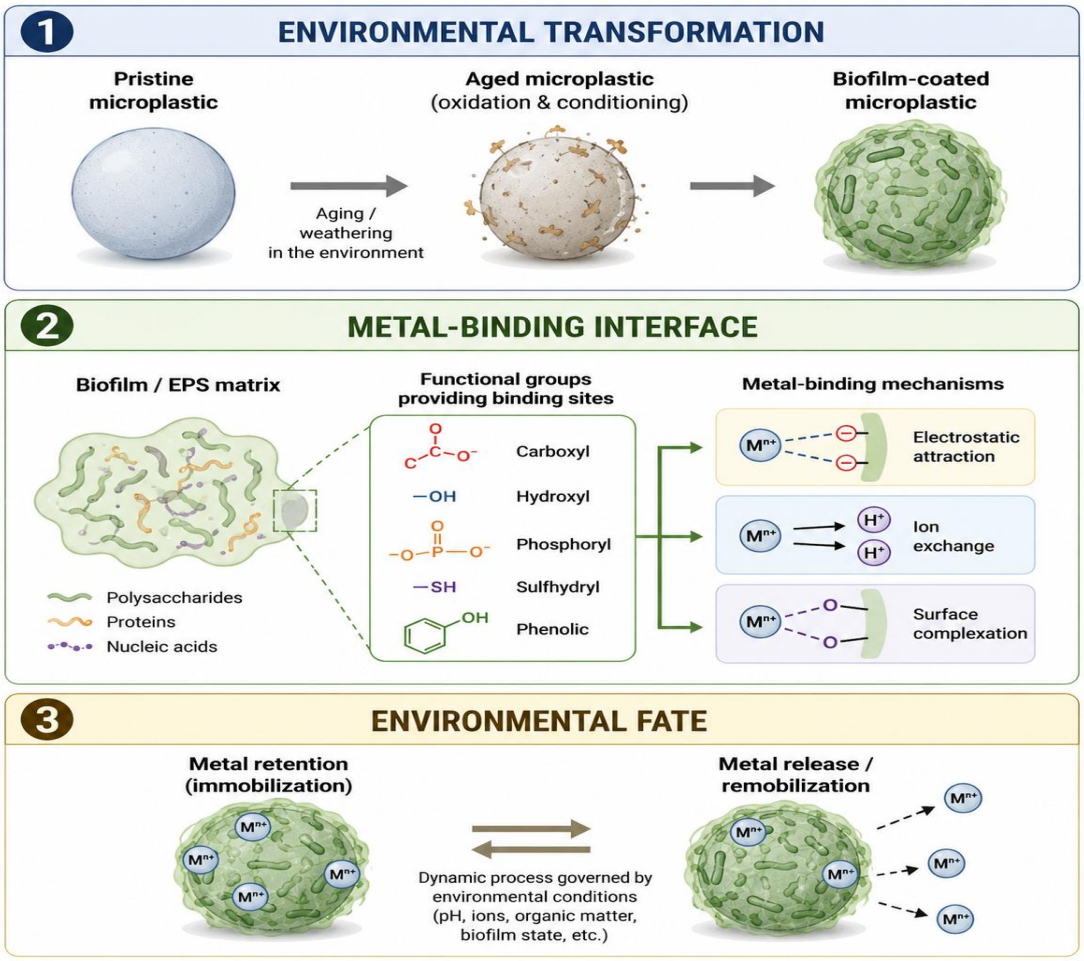

Figure 2. Major mechanisms governing trace-metal sorption at the biofilm–microplastic interface.

5. Environmental controls on biofilm–microplastic–metal interactions

5.1. pH, salinity and ionic strength

Metal retention and release by biofilm-coated microplastics (MPs) are dynamic processes strongly influenced by water chemistry. Among the major controlling factors, pH, salinity, and ionic strength can simultaneously affect surface charge, protonation of functional groups, and metal speciation, thereby shifting the equilibrium between dissolved and MP-associated metals [1,20,21,33,44].

pH is particularly important for functional groups such as carboxyl and hydroxyl groups. Under acidic conditions, protonation can reduce the availability of negatively charged binding sites for metal cations, whereas increasing pH may promote deprotonation and enhance sorption of some metals [20,21,44]. However, because pH also affects metal speciation, changes in sorption cannot be attributed solely to surface charge [20,21].

Salinity and ionic strength further influence metal sorption through ion competition and charge screening. Major ions in natural waters may compete with trace metals for binding sites or weaken electrostatic interactions at the MP–biofilm interface [20,21,33]. These processes are particularly relevant in estuaries, where MPs are transported across strong freshwater-to-seawater gradients. Biofilm communities may also shift along salinity gradients [36], indicating that river-to-sea transport can simultaneously alter both the biological characteristics of the particle surface and its metal-binding environment.

Overall, metal partitioning between the dissolved phase and biofilm-coated MPs should therefore be considered a dynamic equilibrium that may shift as particles move across aquatic environments with contrasting physicochemical conditions.

5.2. Dissolved organic matter and environmental variability

Dissolved organic matter (DOM) adds further complexity to MP–biofilm–metal interactions because it can interact with MP surfaces, biofilms, and dissolved metal ions. Its effects may operate in opposing directions: DOM may compete with metals for sorption sites or form aqueous metal complexes that reduce sorption, whereas organic coatings accumulated on MPs may introduce additional functional groups and metal-binding sites [11,20,21,33].

Rapljenović et al. [33] demonstrated that organic matter and metal speciation significantly influence the adsorption of multiple trace metals onto MPs under marine conditions. Similarly, naturally aged MPs bearing organic surface films exhibited greater Pb binding, whereas removal of these films reduced sorption [11]. Thus, DOM cannot be characterized simply as enhancing or suppressing metal sorption; its net effect depends on organic matter composition, metal identity, particle surface properties, and surrounding water chemistry [11,20,33].

Other environmental variables, including temperature, nutrient availability, seasonality, and hydrodynamic conditions, may indirectly affect metal interactions by altering biofilm growth, composition, and maturity [9,23,36,43]. Seasonal changes in MP-associated biofilms have been documented under varying environmental conditions [43]. Consequently, temporal variation in metal loading on environmental MPs is likely to reflect the combined influence of multiple environmental drivers rather than temperature alone.

5.3. Particle properties, aging and metal-specific responses

Particle characteristics remain important determinants of metal sorption even after biofilm development. Polymer type, particle size, morphology, surface roughness, and aging status influence available surface area, microbial colonization, and the development of metal-binding sites [1,10,21,44]. Weathering further modifies surface morphology and chemistry, while organic coatings, biofilms, and mineral deposition increase the heterogeneity of environmentally aged MPs relative to pristine particles [11,12,21].

These effects are also metal-specific. Multi-metal studies have shown that a given polymer can exhibit different affinities for Pb, Cu, Cd, and Zn, while the simultaneous presence of multiple ions may result in competitive sorption [10,15]. Evidence across different polymers and metals similarly indicates that sorption is jointly controlled by MP properties, metal identity, and environmental conditions [44]. Accordingly, there is no single "microplastic effect" that can be generalized across all polymer–metal combinations.

Environmental aging further modifies these interactions. Naturally aged MPs have been reported to exhibit greater Pb sorption than pristine particles [11], while aged/biofilm-coated MPs can similarly show enhanced Ag sorption [16]. Importantly, greater sorption does not necessarily imply permanent immobilization, because associated metals may subsequently be released as environmental conditions or biofilm characteristics change [16,17].

Metal fate on MPs should therefore be interpreted as the outcome of interacting particle properties, aging history, biofilm state, metal identity, and environmental chemistry. This context dependence also limits direct extrapolation from pristine, single-polymer and single-metal laboratory systems to environmentally exposed MPs [1,10,15,21,44].

Table 1. Representative experimental evidence on trace-metal interactions with pristine, aged and biofilm-coated microplastics

No.	Study	MP / polymer	Metal(s)	Surface condition	Experimental context	Quantitative outcome	Main implication
1	**Fu et al. [11]**	Environmentally collected MPs	Pb(II)	Naturally aged; organic surface film	Aqueous adsorption; pristine vs naturally aged MPs	Maximum Pb(II) adsorption capacity ≈ 13.60 mg g^{-1} for naturally aged MPs	Organic films and oxygen-containing groups, particularly carboxyl and hydroxyl groups, substantially contribute to Pb binding
2	**Kalčíková et al. [16]**	PE	Ag	Aged/biofilm-coated vs pristine	MPs aged under aquatic conditions and subsequently loaded with Ag	≈71% of adsorbed Ag was released from biofilm-coated MPs vs ≈30% from pristine MPs	Biofilm can enhance contaminant association but also facilitate subsequent remobilization; stronger sorption does not imply permanent

							immobilization
3	**Qi et al. [49]**	PP, PE, nylon, polyester microfibers	Pb	Naturally aged/biofilm-covered vs virgin	Environmentally relevant contaminant concentrations	Pb adsorption was 4–25% higher on aged/biofilm-covered microfibers	Biofilm-associated biomass and altered surface properties increase the contaminant-vector potential of microfibers
4	**Biofilm-colonized PBS study [51]**	PBS	Pb(II)	Virgin vs biodegraded/biofilm-colonized	Pb adsorption during biodegradation and biofilm colonization	647.09 μg g^{-1} vs 64.13 μg g^{-1}, approximately 10-fold higher on biofilm-colonized biodegraded PBS	Biofilm colonization, degradation and EPS substantially increase Pb retention
5	**Xiao et al. [50]**	PP, PET, PLA	Cd, Cu	Biofilm-developed vs virgin	35-day biofilm cultivation followed by metal adsorption	Cd adsorption on PP increased by up to 101.34%; intestinal Cd accumulation in zebrafish increased by 95.43%	Links biofilm-enhanced metal sorption with increased biological exposure
6	**[Authors] (2025) [new ref.]**	PA, PLA	Cu(II)	Chemical aging and biofilm development	Laboratory adsorption experiments comparing pristine, $K_2S_2O_8$-aged, and biofilm-covered PA and PLA MPs; effects of pH and fulvic acid were also evaluated	Cu(II) adsorption capacities reached 1.536 and 0.946 mg g^{-1} for chemically aged and biofilm-covered PA, respectively, and 1.163 and 0.812 mg g^{-1} for chemically aged and biofilm-covered	Both chemical aging and biofilm development altered MP surface properties and enhanced Cu(II) sorption, although the magnitude depended on polymer type and aging condition

						PLA, respectively	

6. ECOLOGICAL IMPLICATIONS OF MICROPLASTIC–METAL CO-EXPOSURE

The ecological relevance of metal sorption, transport, and release by microplastics (MPs) ultimately depends on whether these processes alter biological exposure. MPs can be ingested by diverse aquatic organisms, while particle-associated metals may remain bound or become released following ingestion [14,18,20,24,29,45]. Consequently, the ecological effects of MP–metal co-exposure cannot be predicted solely from the individual toxicity of MPs or metals but should be evaluated across the processes linking sorption, ingestion, desorption, bioavailability, and biological responses [1,5,18,20].

6.1. Uptake, Bioaccessibility and Bioaccumulation

Ingestion represents a major pathway by which MPs enter aquatic organisms. Following ingestion, particles may remain temporarily within the gastrointestinal tract before elimination, while associated contaminants may be released under digestive conditions [14,18,24,29]. It is therefore important to distinguish between the presence or accumulation of MPs themselves and the uptake of metals associated with those particles.

Available evidence indicates that gastrointestinal conditions can remobilize some MP-associated metals [14,29], supporting a potential exposure pathway following ingestion. However, the contribution of MPs to metal exposure depends on metal loading and binding strength, gastrointestinal chemistry, and particle residence time. If metals remain strongly bound and MPs are rapidly eliminated, their contribution to the overall metal dose may be limited [14,18,20].

Importantly, the co-occurrence of MPs and metals within an organism does not demonstrate that MPs enhance metal bioaccumulation. Establishing a vector-mediated increase in bioaccumulation requires direct evidence linking metal sorption onto MPs, ingestion of metal-bearing particles, gastrointestinal desorption, and subsequent uptake into tissues. This distinction is critical because total metal loading on MPs does not necessarily correspond to the bioaccessible or bioavailable fraction [5,14,20,29].

6.2. Combined Toxicity: Synergistic, Additive and Antagonistic Effects

MP–metal co-exposure has been associated with multiple biological responses, including oxidative stress, lipid peroxidation, immune disturbance, and cellular or tissue damage [1,6,18,20,24]. In a specific experimental system, Chen et al. [6] reported oxidative stress, histopathological damage, and immune dysfunction in Mytilus coruscus co-exposed to MPs and Pb. However, such findings should not be generalized across MP–metal combinations because the direction and magnitude of combined effects depend on polymer and metal properties, concentration, surface state, exposure duration, environmental conditions, and organism physiology [1,18,20].

Available evidence indicates that MP–metal interactions may produce synergistic, additive, or antagonistic effects [1,18,20]. Synergistic responses may occur when MPs increase metal transport or bioavailability while simultaneously imposing particle-related stress. Conversely, antagonistic responses may occur when sorption reduces the freely dissolved metal fraction and thereby decreases immediate biological exposure [18,20]. Thus, MPs do not consistently enhance metal toxicity.

Sorption capacity alone is therefore insufficient to predict combined toxicity. Strong sorption may initially reduce dissolved-metal exposure while facilitating particle-associated transport, whereas subsequent release under gastrointestinal or altered environmental conditions may increase exposure [14,16,17,20]. Biofilm-coated MPs may therefore shift between metal-retaining and exposure-enhancing roles, although the conditions governing such transitions remain incompletely resolved. Combined toxicity should consequently be regarded as a context-dependent outcome of interactions among particle properties, metal characteristics, environmental conditions, and organism physiology rather than as a universal consequence of MPs acting as metal vectors [1,13,18,20].

6.3. Trophic Transfer and Broader Ecological Implications

Trophic transfer represents a potentially important exposure pathway. Experimental evidence has demonstrated the transfer of MPs through prey–predator interactions [46], while separate evidence indicates that MP-associated metals can become bioaccessible under gastrointestinal conditions [14,29]. These findings, however, demonstrate individual components of the proposed pathway rather than the complete trophic transfer of biofilm-associated MP–metal complexes.

Direct evidence linking ingestion of metal-loaded biofilm-coated MPs by prey, trophic transfer to predators, metal desorption, and subsequent tissue accumulation remains limited [18,20,27]. Trophic transfer of trace metals mediated specifically by biofilm-coated MPs should therefore currently be regarded as a mechanistically plausible but insufficiently validated exposure pathway, rather than an established ecological outcome.

Similarly, experimentally observed individual-level responses, including oxidative stress, immune dysfunction, and tissue damage, should not be directly extrapolated to population- or ecosystem-level risk [18,24]. Higher-level ecological consequences depend on environmentally relevant exposure concentrations and durations, organism life histories and recovery capacity, and the propagation of effects through food webs. The gap between short-term laboratory observations and environmentally realistic exposure scenarios therefore remains an important source of uncertainty [1,18,24].

Overall, current evidence supports a framework in which the ecological significance of metal-bearing MPs depends not simply on sorption capacity but on the subsequent processes of transport, ingestion, desorption, bioavailability, biological uptake, and biological effects. Because these processes can be modified by biofilm development, aging, and environmental conditions, ecological risk should be evaluated across the MP–biofilm–metal continuum rather than inferred from metal loading or any single biological endpoint [1,17,18,20].

7. KNOWLEDGE GAPS AND FUTURE RESEARCH PRIORITIES

Despite substantial advances in understanding interactions among microplastics (MPs), biofilms, and trace metals, a considerable gap remains between simplified experimental systems and the behavior of MPs under natural environmental conditions [1,18,20,21]. Variability in polymer type, aging status, biofilm development, metal composition, and water chemistry limits cross-study comparability and complicates the translation of sorption and toxicity data into reliable ecological risk assessments [1,20,44].

7.1. Toward Environmentally Realistic MP–Biofilm–Metal Systems

A major limitation of the current literature is the widespread use of pristine MPs and single-polymer/single-metal systems in laboratory experiments [1,18,20,21]. Environmental MPs, in contrast, undergo UV exposure, oxidation, abrasion, organic conditioning, mineral deposition, and microbial colonization, all of which can alter particle morphology, surface chemistry, and metal-binding behavior [11,12,21]. Experimental evidence indicates that naturally aged MPs can exhibit greater metal sorption than pristine particles, while aging and biofilm development can influence both metal retention and subsequent release [11,16]. However, the magnitude and direction of these effects are likely to depend on the specific polymer–metal–environment combination.

Environmental MPs are also exposed to complex contaminant mixtures rather than isolated metals. Competition among metal ions has been demonstrated in experimental systems [10,15], while dissolved organic matter and metal speciation can further modify sorption behavior [33]. Consequently, adsorption capacities derived from single-metal experiments should be extrapolated to natural waters with caution [10,15,33,44].

Future studies should therefore prioritize naturally weathered or environmentally realistic aged and biofilm-coated MPs, environmentally relevant metal mixtures, and representative water chemistry. Where artificial aging is used, protocols should reproduce, as closely as practicable, the physical, chemical, and biological transformations occurring under environmental conditions [11,12,21].

7.2. From Static Adsorption to Dynamic Fate and Biological Exposure

A particularly important knowledge gap is the imbalance between the extensive literature on metal adsorption and the more limited understanding of desorption, remobilization, and subsequent bioavailability [1,17,20]. Available evidence demonstrates that high sorption capacity does not necessarily imply permanent immobilization, because associated metals can be released under altered environmental or gastrointestinal conditions [14,16,20]. Changes in organic or biofilm layers may further modify metal retention, although the long-term consequences of biofilm degradation and detachment remain insufficiently characterized [17,41].

Biofilms should likewise not be treated simply as a binary present/absent variable. Biofilm development involves colonization, maturation, community succession, and detachment, with community composition varying across environmental conditions and exposure periods [23,36,43]. However, the extent to which temporal changes in biofilm biomass, EPS composition, and community structure directly regulate metal sorption and remobilization remains incompletely resolved. These properties should therefore be quantitatively characterized in future MP–metal studies.

Experimental designs should also extend beyond adsorption equilibrium to follow the subsequent fate of particle-associated metals under changing environmental and biological conditions. This is particularly important for trophic exposure. Experimental evidence supports trophic transfer of MPs [46], while separate studies demonstrate that some MP-associated metals can become bioaccessible under gastrointestinal conditions [14,29]. However, direct evidence connecting these individual processes into the complete pathway from metal-loaded biofilm-coated MPs to trophic transfer, metal desorption, and subsequent tissue accumulation remains limited. Future trophic studies should therefore simultaneously quantify MP burden, metal concentration and speciation, tissue accumulation, and relevant biological endpoints.

7.3. Field Validation, Methodological Harmonization and Integrated Analysis

Laboratory experiments remain essential for identifying mechanisms, but their results cannot necessarily be extrapolated directly to natural systems. Biofilm development and metal loading have been shown to vary with environmental context, including spatial and temporal conditions, salinity, and seasonality [9,19,36,43]. Greater emphasis should therefore be placed on in situ exposure experiments, seasonal monitoring, and long-term field studies that simultaneously characterize MPs, biofilms, and associated metals within the same particle populations.

Cross-study comparison is further constrained by differences in polymer type, particle size, aging procedures, metal concentrations, exposure duration, and analytical methods [1,20,21,44]. More consistent reporting of particle characteristics, surface chemistry, biofilm status, water chemistry, and metal speciation would improve data comparability and facilitate future quantitative synthesis.

A further priority is to establish whether physicochemical changes at the MP–biofilm interface translate into meaningful changes in biological exposure. Integrating microscopic and high-resolution surface characterization with chemical analyses, quantitative biofilm characterization, and biological endpoints could help establish links between surface transformation → metal retention/release → bioavailability → biological response. Molecular and multi-omics approaches may provide complementary information on microbial- and organism-level responses, but their value will depend on their application to clearly defined mechanistic questions.

Ultimately, progress in this field requires moving beyond the well-supported observation that MPs can bind trace metals toward resolving a more ecologically relevant but still insufficiently answered question: under what environmental and biological conditions do biofilm-coated MPs meaningfully alter metal transport, bioavailability, and ecological risk?

Table 2. Major knowledge gaps and future research priorities for biofilm-mediated microplastic–trace metal interactions in aquatic environments

Knowledge gap	Current limitation	Recommended research direction
Environmental realism	Pristine MPs and simplified laboratory conditions are still widely used [1,11,21]	Use naturally aged/biofilm-coated MPs and environmentally relevant exposure conditions
Complex contaminant mixtures	Most experiments investigate single metals under controlled conditions [10,15,44]	Examine multi-metal systems together with DOM, salinity, minerals and other co-contaminants
Sorption–desorption dynamics	Research emphasizes metal adsorption more than subsequent release [16,17,20]	Couple adsorption with desorption, remobilization and simulated gastrointestinal experiments
Biofilm dynamics	Biofilm is often treated as a static coating rather than a developing community [23,36,43]	Investigate colonization, maturation, succession, EPS composition, degradation and detachment over time
Field validation	Short-term laboratory experiments dominate current evidence [1,18,21]	Conduct long-term, seasonal and in situ studies under realistic aquatic conditions
Trophic transfer and bioavailability	Direct evidence linking metal-loaded biofilm MPs to tissue metal accumulation across food webs remains limited [14,18,29,46]	Track MPs, metal desorption, tissue accumulation and biological responses simultaneously in controlled prey–predator systems

Abbreviations: MPs, microplastics; DOM, dissolved organic matter; EPS, extracellular polymeric substances.

8. CONCLUSION

Microplastics (MPs) in aquatic environments do not remain as pristine, relatively inert polymer particles. Environmental aging, weathering, and particularly biofilm formation progressively transform their surfaces into complex biogeochemical interfaces enriched with organic matter, microorganisms, and extracellular polymeric substances (EPS) [11,12,21,27]. These transformations introduce additional functional groups and binding sites that can substantially alter trace-metal sorption compared with pristine MPs [11,12,21].

However, enhanced sorption does not necessarily imply permanent metal immobilization. Metals associated with biofilm-coated MPs may subsequently undergo desorption and remobilization in response to changes in environmental conditions, biofilm state, or gastrointestinal conditions following ingestion [14,16,17,29]. Biofilm-coated MPs may therefore function as sinks, carriers/vectors, or secondary sources of trace metals depending on particle properties, biofilm characteristics, metal identity, and surrounding water chemistry.

From an ecological perspective, greater metal loading on MPs does not necessarily translate into greater biological risk. Ecological outcomes depend on the interconnected processes of metal sorption, transport, desorption and remobilization, bioaccessibility, biological uptake, and subsequent biological effects. Measurements of total MP-associated metal concentrations alone are therefore insufficient to determine their contribution to biological exposure and ecological risk [5,14,18,20].

Future research should move beyond simplified pristine MP–single-metal systems toward environmentally realistic scenarios incorporating aged and biofilm-colonized MPs, contaminant mixtures, variable water chemistry, and longer exposure periods [1,10,15,21,44]. Particular attention should be given to biofilm dynamics,

sorption–desorption processes, metal remobilization and bioavailability, together with direct experimental evidence linking metal-loaded biofilm-coated MPs to trophic transfer and tissue accumulation.

Overall, biofilm-coated MPs should be regarded as dynamic biogeochemical interfaces rather than passive carriers of trace metals. Integrating particle properties, biofilm development, environmental chemistry, sorption–desorption dynamics, and biological availability will be essential for determining when MPs act as sinks, vectors, or secondary sources of trace metals and for improving ecological risk assessment in aquatic ecosystems.

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