



# Influence of Microplastics on the Mobility, Bioavailability, and Toxicity of Heavy Metals: A Review

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## Abstract

Microplastics (MPs) can pose ecological risk to the environment and have the potential to negatively affect human health, raising serious public concerns. It is recognized that MPs could act as a vector for various environmental pollutants including heavy metals and potentially influencing their mobility, fate, and bioavailability in the environment. However, knowledge on the mechanisms underpinning the interaction processes between MPs and heavy metals is far from clear. This review discusses the effects of MPs on the adsorption/desorption, speciation and bioavailability, and toxicity of various heavy metals. The present review also systematically identifies the environmental factors (e.g., pH, ionic strength, and organic matters) that could affect their interaction processes. This work aims to establish a meaningful perspective for a comprehensive understanding of the indirect ecological risks of MPs as vectors for contaminants. The work also provides a reference for the development of better regulatory strategies in mitigating the negative effects caused by the co-existence of MPs and heavy metals.

**Keywords** Microplastics · Heavy metals · Sorption · Bioavailability · Toxicity

## Abbreviations

PE	Polyethylene
PLA	Polylactic acid
PS	Polystyrene
PVC	Polyvinyl chloride
PET	Polyethylene terephthalate
HDPE	High-density polyethylene
HPE	High crystallinity polyethylene
LPE	Low crystallinity polyethylene
CPE	Chlorinated polyethylene

The favorable properties of plastics, including lightweight, durability, and low price, make them an inevitable part of our modern life, leading to an exponential increase in their production in the past decades. Generally, plastics with

particle size smaller than 5 mm are defined as microplastics (MPs) (Alimi et al. 2018; Strungaru et al. 2019). Compared with larger plastics, MPs (including nanoplastics, NPs) are more difficult to be intercepted by specialized filter organs such as gastric filters. As a result, MPs and NPs are much easier to pass through epithelial tissues via transformation and be accumulated in the biological systems (e.g., circulatory system in mussels, gills and gut) once they are ingested by organisms (Lu et al. 2016; Kim et al. 2021). Therefore, MPs or NPs with smaller size and larger specific surface area have higher potential to induce toxicity. In addition, several MPs have been shown to exhibit significant adsorption capacity for various contaminants, primarily due to their large specific surface area (Abbasi et al. 2020; Abdolapur Monikh et al. 2020; Dong et al. 2020). The interactions between MPs and contaminants may alter their environmental behaviors such as chemical speciation, bioavailability, and toxicity, potentially generating new undefined risks to animals and ecosystem health. Recently, related studies have mainly focused on the interactions between hydrophobic organic contaminants and MPs because of their similar physicochemical properties (Fries and Zarfl 2012; Koelmans et al. 2013). However, relatively little information has been known about the influences of MPs on inorganic pollutants such as heavy metals.

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Environmental behaviors and ecological risks of heavy metals could be affected by MPs from direct or indirect pathways. On one hand, MPs can directly alter physicochemical properties such as adsorption and desorption processes of heavy metals, resulting in changes to the bioaccumulation and toxic effects on organisms (Godoy et al. 2019; Lee et al. 2019; Lian et al. 2020; Liao and Yang 2020; Lu et al. 2020; Wakkaf et al. 2020; Zhou et al. 2020). On the other hand, environmental factors such as pH and dissolved organic matter can affect MP-metal interactions, resulting in changes in the speciation and bioavailability of metals (Yu et al. 2020, 2021). These physiochemical changes would likely affect the environmental risks of MPs as well as metals. However, the interaction processes of different heavy metals to distinct MPs could be heterogeneous and complex, and the parameters governing MP-metal interactions have remained largely unknown. Currently, available reviews have mainly focused on analytical methods, ecotoxicological effects, microbial/chemical degradation, and detection and removal of MPs (Dey et al. 2021; Gao et al. 2020; Huang et al. 2021; Li et al. 2020a; Othman et al. 2021). However, reviews on the effects of MPs on the environmental behaviors of heavy metals is limited. Improving our understanding on MP-metal interactions is important for reducing the uncertainty in ecological risk assessment, particularly where elevated MPs and heavy metals co-exist in the environment.

Under this context, the present work aims to (1) provide a critical review of the influence of MPs on the adsorption, desorption, speciation, bioavailability, accumulation, and toxicity of heavy metals; (2) summarize the environmental parameters that could affect the abovementioned processes; and (3) critically assess the possible mechanisms that may govern their interactions in aquatic or terrestrial environments. The significance of this review is to provide a reference toward the development of better mitigation methods for the negative impacts of these contaminants.

## Effects of MPs on the Environmental Behaviors of Heavy Metals

The unique physicochemical properties of MPs make them strong adsorbents/vectors for heavy metals, which can significantly alter the bioavailability and toxicity of metals (Table 1).

### Adsorption and Desorption of Heavy Metals

MPs can accumulate diverse heavy metals such as lead (Pb), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), zinc (Zn) etc., while adsorbed/additive heavy metals can also be released from the surface or inside of MPs (Godoy et al. 2019; Abbasi et al. 2020; Kern et al. 2021; Liao and Yang

2020). These processes can therefore change the environmental concentrations of metals. In fact, several studies have shown that concentrations of heavy metals have a positive or negative significant correlation with the amount of MPs in sediment/organisms (Akhbarizadeh et al. 2017, 2018; Yazdani Foshtomi et al. 2019; Zhu et al. 2020). In addition, MPs show different adsorption and desorption capacities for various heavy metals (Godoy et al. 2019; Wang et al. 2020c). For instance, the sorption strength of PS MPs with metals was found to follow the order of  $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$  (Yuan et al. 2020). Additionally, the release of Cr from MPs was found to be faster than Pb under the same conditions (Godoy et al. 2020). This may be attributed to the differences of distinct hydrated ionic radii and complexing capabilities/affinities of the divalent cations (Zou et al. 2020). The adsorption, release, and diffusion behavior of heavy metals can also be affected by the composition of MPs, primarily owing to the distinct properties of various MPs (e.g., specific surface area, porosity, morphology, surface charge and/or surface degradation). The experimental medium as well as the various characteristics of heavy metals may also contribute to the differences in the adsorption properties of metals onto MPs (Godoy et al. 2019; Li et al. 2019; Guo et al. 2020b; Liao and Yang 2020).

### Speciation and Bioavailability of Heavy Metals

The existence of MPs can alter metal speciation in the environment. For instance, MPs increase the organic-bound fractions of heavy metals by direct adsorption and subsequently changing the soil physicochemical and biogeochemical properties such as dissolved organic carbon (DOC) and pH (Yu et al. 2020, 2021). Additionally, the presence of MPs in the soil can decrease the exchangeable, carbonate-bound, and Fe-Mn oxide-bound fractions of Cu, Cr, and Ni (Yu et al. 2020). On the other hand, a study showed that soil diethylenetriaminepentaacetic acid (DTPA)-extractable Cd concentrations increased due to the presence of HDPE, PE, PLA, and PS (Wang et al. 2020a, b). Speciation changes may ultimately alter the bioavailability of metals or metalloids in environmental matrices. For example, the presence of MPs in the soil was found to decrease Arsenic (As, metalloid) bioavailability due to As adsorption by MPs (Dong et al. 2021). In contrast, Cd bioaccessibility to earthworms was shown to increase in MP-contaminated soil (Zhou et al. 2020). In addition, it has been demonstrated that Cd exhibited a higher bioavailability when PLA is present in soil-plant systems, when compared to PE (Wang et al. 2020b). Collectively, these studies showed that the influence of MPs on metal speciation and bioavailability can be modified by a variety of factors, such as the types of MPs, soil chemistry, and environmental conditions (e.g., incubation time,

**Table 1** Influence of MP properties on MP-metal interaction and effects of MP/metal co-exposure on biological responses

Physical/biological properties	Metals	MP polymer type <sup>a</sup>	Purpose of study	Findings	Sampling condition	References
Adsorption/desorption	Cd, Co, Cr, Cu, Ni, Pb, Zn	PE, PET, PP, PS, PVC	Role of polymer type and characteristic (surface area, porosity, shape) on metal adsorption	Surface area and morphology of MPs affect their capacity to bind to various metals	Field	Godoy et al. (2019)
	Pb, Cd, Zn	PET	Adsorption/desorption capacity of Pb, Cd, Zn onto PET-MPs; transport of metal-MP in roots of wheat plants	Pb, Cd, and Zn adsorb onto PET-MP particles; PET particles transport metals into rhizosphere	Laboratory	Abbasi et al. (2020)
	Cu, Ni	PP	Diffusion coefficient of Cu or Ni onto water-soaked or dry PP	Cu ion diffuses faster than Ni onto dry PP, whereas wet Cu has slower diffusion than dry Cu	Laboratory	Kern et al. (2021)
	Hg, Zn, Cr, Mn, Fe, As, Cu, Se, V, Ni, Pb	NA	MP-metal content in fish muscles in benthic and pelagic fish	Fish in benthic zone have higher MP content in muscles; Fish length and MP content have positive correlation	Laboratory	Akbharizadeh et al. (2018)
	Zn, Mo, Pb, Cu, Cd, As, Mn	NA	MP-metal concentration in Iranian oil-terminal	Positive correlation between MP amount and metal concentration	Field	Akbharizadeh et al. (2017)
	Cu, Zn	PET	Adsorption capacity of microplastics subjected to UV radiation	Cu and Zn sorption increase with PET; Adsorption capacity for Cu > Zn; UV radiation increases PET surface area and therefore increasing metal adsorption	Laboratory	Wang et al. (2020c)
	Cr, Cd, Pb	PES, CP	Accumulation of metals and MP in Pacific oysters ( <i>Crassostrea gigas</i> )	MP accumulates in gill and mantle of organism; Evidence of metal precipitation on the surface of MPs in oysters	Field	Zhu et al. (2020)
	Cu, Cr, Ni	NA	Effects of MP on metal speciation in soil	MP affects chemical fractionation of Cu, Cr, and Ni; MP alters metal speciation, reducing bio-availability of metals; soil properties change with MP-metal interaction	Field	Yu et al. (2020)

**Table 1** (continued)

Physical/biological properties	Metals	MP polymer type <sup>a</sup>	Purpose of study	Findings	Sampling condition	References
Speciation/bioavailability	As	PSMP, PTFE	Role of MP and arsenic on nutrient properties in rhizosphere soil	MP addition reduces arsenic in soil; Metal-MP interaction reduces enzyme activities and microorganism abundance, thus decreasing availability of nitrogen and phosphorus	Field	Dong et al. (2021)
	Cd	NA	Effects of MP and MP/Cd exposure on earthworm <i>Eisenia foetida</i>	Earthworm growth rate reduces with MP or MP/Cd co-exposure. Increases in mortality with higher MP exposure; bioavailability of Cd increases with MP exposure	Laboratory	Zhou et al. (2020)
	Cr	PE, PP, PVC, PS, PLA (biodegradable)	Role of degradable and non-degradable MP on Cr in <i>in-vitro</i> human digestive system	Degradable MP exhibits higher bioaccessibility of Cr than nondegradable MP	Laboratory	Liao and Yang (2020)
	Cd	PE, PLA	Role of MP and Cd on plant growth ( <i>Zea mays</i> L)	PLA addition in soil leads to higher Cd bioavailability compared to PE addition	Field	Wang et al. (2020a)
	Au	PS	Bioaccumulation of PS plastics alone or with Au in zebrafish embryos ( <i>Danio rerio</i> )	PS alone slightly perturbs development of embryos; Zebrafish development and mortality are significantly impacted by the co-exposure of PS and Au	Laboratory	Lee et al. (2019)

Table 1 (continued)

Physical/biological properties	Metals	MP polymer type <sup>a</sup>	Purpose of study	Findings	Sampling condition	References
Bioaccumulation	Ag	PS, PE	Effect of nanoscale plastic debris (NPD) and Ag <sup>+</sup> on <i>Daphnia magna</i>	Toxic effects are higher when NPD is combined with Ag <sup>+</sup> exposure; PS-NPD has higher Ag <sup>+</sup> sorption than PE-NPD	Laboratory	Abdollahpur et al. (2020)
	Cd	PE	Effect of Cd and MP exposure (combined or alone) on the common carp ( <i>Cyprinus carpio</i> L.)	Cd and MP have additive negative effects on immunological responses	Laboratory	Banaee et al. (2019)
	Cd	PS	The role of PS on Cd accumulation in adult zebrafish; the role of chronic co-exposure on health	Cd and PS co-exposure results in highest accumulation in gills; chronic exposure leads to oxidative damage and inflammation	Laboratory	Lu et al. (2018)
	Cu, Pb, Cd	HDPE	Effect of MP and heavy metal exposure on growth of yellow seahorse ( <i>Hippocampus kuda</i> )	Co-exposure of MP and metals result in a stronger negative impact on growth of seahorse, compared to MP alone or metal exposure alone	Laboratory	Sun et al. (2019)
	Hg	NA	Short-term effect of Hg and MP exposure on young seabass ( <i>Dicentrarchus labrax</i> )	MP exposure influences accession of Hg in brain and muscle tissues; combined exposure leads to neurotoxicity	Laboratory	Barboza et al. (2018)
	Hg	HDPE	Effect of MP on the uptake/accumulation of Hg in mussel ( <i>Mytilus galloprovincialis</i> )	MP exposure leads to higher accumulation of Hg in mussel and subsequently results in increased Hg elimination	Laboratory	Fernández et al. (2020)
	Cu	PS-COOH NPs	Effect of combined exposure of Cu and PS-COOH NPs on freshwater alga <i>Raphidocelis subcapitata</i>	MPs do not inhibit algal growth after the co-exposure with Cu	Laboratory	Bellingeri et al. (2019)

<sup>a</sup>MP polymer types include: Polyethylene terephthalate (PET), Polyethylene (PE), Polyester (PES), Polypropylene (PP), Cellophane (CP), Polystyrene (PS/PSMP), Polyvinyl chloride (PVC), Polylactic acid (PLA), Polytetrafluoroethylene (PTFE), High density polyethylene (HDPE), Carboxylated polystyrene nanoparticles (PS-COOH NPs), Hexabromocyclododecane-polystyrene (HBCD-PS), Polystyrene nanoparticles (PSNPs), Chlorinated polyethylene (CPE), Polyamide (PA)

experimental mediums, etc.) (Liao and Yang 2020; Yu et al. 2020, 2021).

## Changes in the Accumulation and Toxicity of Heavy Metals by MPs

The interactions between MPs and heavy metals may modify their bioaccumulation and toxicity. For example, the adverse effects of MPs and/or heavy metals on organisms could be synergistically exacerbated in a dose- or size-dependent manner when these two pollutants coexist (Lee et al. 2019; Wang et al. 2020a). There is no toxicity of  $1 \text{ mg L}^{-1}$  PS nanoscale plastic debris or  $1 \mu\text{g L}^{-1}$   $\text{Ag}^+$  to *Daphnia magna*; however, toxicity was observed when the organisms were exposed to a mixture of these two contaminants (Abdolapur Monikh et al. 2020). Another example is that of growth inhibition in animals, which has been observed in yellow seahorse and earthworms with higher accumulations of Cd (Lu et al. 2018; Banaee et al. 2019; Sun et al. 2019; Yan et al. 2020; Zhou et al. 2020; Wang et al. 2021). This may be attributed to the oxidative damage and the inflammatory responses caused by the coexistence of these two contaminants (Lu et al. 2018; Wen et al. 2018; Lee et al. 2019). Interestingly, several studies have also demonstrated some opposite phenomenon, i.e., organisms may be protected by the interactions between Cd and chelating MPs. For example, PVC was found to reduce the toxicity of Cd to nematodes, possibly due to the high chelating capacity of PVC and its polymers (Wakkaf et al. 2020). Moreover, the presence of MPs partially reduced Cd contents in leaves of *Triticum aestivum L.*, and decreased the mercury (Hg) and Cd accumulation by *Dicentrarchus labrax* and *Symphysodon aequifasciatus*, respectively (Barboza et al. 2018; Wen et al. 2018; Lian et al. 2020). Furthermore, Hg elimination in the mussel, *Mytilus galloprovincialis* was promoted when MPs were present (Fernández et al. 2020). In addition, MPs were not found to enhance Cd bioconcentrations in plant tissues nor inhibit algal growth after the combined exposure with Cu (Bellingeri et al. 2019; Wang et al. 2020a, b). Moreover, results showed that the presence of organisms such as fish also influenced concentration of Hg in solution and the interaction processes between MPs and heavy metals (Barboza et al. 2018). These modifications would in turn affect the toxicity and bioaccumulation of metals in organisms.

## Influence of Environmental Factors and Possible Mechanisms

Various environmental factors such as water pH, ionic strength, and organic matters can directly (adsorption, complexation effects) or indirectly influence the chemical

speciation, transport, and fate of heavy metals on MPs (Table 2).

### pH

pH can alter the zeta potential of MPs, or the precipitation of heavy metals, thus increasing or decreasing the adsorption amounts of some metals. In general, the MPs zeta potentials decrease with increasing pH value. If the point of zero charge of MPs is lower than water pH, the charge of MPs becomes negative; this would increase the electrostatic attraction between polymers and metals (i.e., cations). On the other hand, the precipitation of some metals is very likely to occur in environments when  $\text{pH} > 7$ . A study showed that the adsorption of some heavy metals on MPs is pH-dependent (Godoy et al. 2019), and the increase in pH value was found to enhance the adsorption amounts of Pb, Cd, Co, Ni, Cu, and Zn onto MPs (Holmes et al. 2014; Guo et al. 2020b; Lin et al. 2021a, b; Purwiyanto et al. 2020; Tang et al. 2020; Wang et al. 2020c; Zou et al. 2020). These increases were likely attributed to the increase of charged sites on MPs. In contrast,  $\text{Cr}^{6+}$  adsorption onto MPs was found to reduce as the pH was increased, possibly due to the relatively weak coulombic interactions between the oxyanionic form of  $\text{Cr}^{6+}$  and the MPs with reduced positive charge in their surface (Holmes et al. 2014). On the other hand, pH was shown to have no influence on Cu adsorption (Holmes et al. 2014). Overall, pH appears to affect the adsorption of heavy metals on MPs by modifying the electrostatic properties on the MP surface (Guo et al. 2020b; Lin et al. 2021a).

### Ionic Strength

The surface charge, sorption site, aggregation of MPs, and activity of heavy metals, can be modified by ionic strength. This will in turn affect the adsorption behaviors between heavy metals and MPs. In contrast to the observation with pH, the adsorption of heavy metals (Cd, Cu, Co, Ni, and Pb etc.) on MPs is inhibited by increasing ionic strength (Holmes et al. 2014; Guo et al. 2020b; Lian et al. 2020; Tang et al. 2020; Lin et al. 2021a, b). This is because high ionic strength can increase the competition of heavy metals on the sorption sites of MPs while simultaneously decreasing the activity of heavy metals in solution (Zou et al. 2020). However, high ionic strength was shown to increase  $\text{Cr}^{6+}$  adsorption due to a reduction in the negative-negative (surface-chromate) repulsion between MP and  $\text{Cr}^{6+}$  (Holmes et al. 2014). On the other hand, because of the strong complexation of  $\text{Cu}^{2+}$  with CPE, the effect of increasing ionic strength on  $\text{Cu}^{2+}$  sorption to CPE is minimal (Zou et al. 2020). A few studies have demonstrated that salinity has no significant effects on MPs adsorption of Cu and Pb (Holmes et al. 2014; Purwiyanto et al. 2020).

**Table 2** Effects of environmental factors on metal-MP interaction

Environmental factor	Metals	MP polymer type <sup>a</sup>	Findings	Sampling condition	References
pH	Cd, Co, Cr, Cu, Ni, Pb	PTFE	Increase in water pH leads to increased adsorption for Cd, Co, Ni, Pb, decreased adsorption for Cr, and no effect on Cu	Field	Holmes et al. (2014)
	Pb, Cu	PP, PE, PES, PVC, nylon	Metal adsorption on MP increases as water pH increases	Field	Purwiyanto et al. (2020)
	Pb(II)	Nylon	Pb(II) amounts increase as pH increases	Field	Tang et al. (2020)
	Cd	PE, PP, PS, PVC	Surface area and charge of ion affect sorption process; sorption capacity increases as pH of solution increases	Laboratory	Guo et al. (2020a)
	Pb(II)	HBCD-PS	Increasing water pH leads to higher adsorption of organic matter and Pb(II) onto HBCD-PS	Laboratory	Lin et al. (2021a)
Ionic strength	Cd	PSNPs	Increases in ionic strength weakens adsorption of Cd to PSNPs	Laboratory	Lian et al. (2020)
	Pb(II)	PVC, PE, PS	Metal sorption onto MP increases with decreasing ionic strength	Laboratory	Lin et al. (2021b)
	Pb(II)	Nylon	Increases in ionic strength decreases Pb(II) sorption to MPs	Laboratory	Tang et al. (2020)
	Cu, Cd, Pb	CPE, PVC, PE	Dissociation constant ( $K_D$ ) for metal sorption reduces with increasing ionic strength	Laboratory	Zou et al. (2020)
	Cd	PE, PP, PS, PVC	Surface area and pH affect sorption process; increasing salinity reduces Cd sorption to MPs	Laboratory	Guo et al. (2020a)

**Table 2** (continued)

Environmental factor	Metals	MP polymer type <sup>a</sup>	Findings	Sampling condition	References
Organic matters	Cd, Pb, Co, Ni, Zn, Cu	PA, PE, PP, PVC, PS	MPs with sewage sludge exhibit higher sorption capacity to metals than virgin MPs	Field	Li et al. (2019)
	Cu	PS	Different sizes of MP particles display differential accumulation properties in different tissues; exposure of natural organic matter and MP increases accumulation of Cu in tissues	Laboratory	Qiao et al. (2019)
	Cu	PET, HDPE, PP	Modified microbeads placed in soil (with dissolved organic matter) adsorb more Cu compared to non-modified, pure microbeads	Laboratory	Wijesekara et al. (2018)
	Cd, Co, Cr, Cu, Ni, Pb, Zn	PE	Older, weathered plastics collected from beaches exhibit a greater metal sorption than new plastics, likely due to interaction with dissolved organic matter	Field	Holmes et al. (2012)

<sup>a</sup>MP polymer types include: Polyethylene terephthalate (PET), Polyethylene (PE), Polyester (PES), Polypropylene (PP), Cellophane (CP), Polystyrene (PS/PSMP), Polyvinyl chloride (PVC), Polylactic acid (PLA), Polytetrafluorethylene (PTFE), High density polyethylene (HDPE), Carboxylated polystyrene nanoparticles (PS-COOH NPs), Hexabromocyclododecane-polystyrene (HBCD-PS), Polystyrene nanoparticles (PSNPs), Chlorinated polyethylene (CPE), Polyamide (PA)

## Organic Matters

The presence of organic matter can alter the adsorption/desorption capacities, bioaccumulation, and toxicity of heavy metals via interfering with the interaction processes between MPs and heavy metals. The attachment of natural organic matter to the functionalized surfaces of MPs may facilitate their binding with heavy metals (Bradney et al. 2019; Li et al. 2019). For example, Cd sorption on MPs was found to increase with increasing humic acid levels (Guo et al. 2020b). The sorption of Ag, Pb, Cr, and Cu onto MPs was also found to be enhanced by organic matters (Godoy et al. 2019; Qiao et al. 2019; Abdolapur Monikh et al. 2020). These enhancements may be ascribed to the increased adsorption sites and the abundance of functional groups on the MP surfaces. Moreover, the bioaccumulation and toxicity of Cu in fish was found to be elevated by the coexistence of MPs and natural organic matters, likely because of Cu-ion transport inhibition in hepatocytes and oxidative stress enhancement (Qiao et al. 2019). Additionally, organic matter can compete with metals for the adsorption

sites on the MPs, which reduces the available heavy metals for MPs sorption, resulting in the desorption of heavy metals (Abbasi et al. 2020). For example, Pb<sup>2+</sup> adsorption is reduced with increased fulvic acid concentration, possibly due to the increased complexation between Pb<sup>2+</sup> and fulvic acid (Tang et al. 2020). Moreover, the addition of dissolved organic matter inhibited the combined toxicity of Ag<sup>+</sup> and nanoscale plastic debris to *Daphnia magna* (Abdolapur Monikh et al. 2020). These results indicated the modulatory role of organic matters on the adsorption/desorption, accumulation, and toxicity of heavy metals in relation to MPs.

## The Existence of Other Contaminants

In the study of the behaviors of heavy metals in relation to MPs, antagonistic or synergistic effects are observed when other elements or organic pollutants coexist with metals. For example, when Cd, Zn, or Pb was presented individually, increased adsorption of Cd on PET was observed (Abbasi et al. 2020). In contrast, PET was found to adsorb higher amounts of Zn when the above mentioned heavy metals



all co-existed in the testing solutions (Abbasi et al. 2020). Notably, desorption of metals occurs more easily when multiple heavy metals are present (Abbasi et al. 2020). This is because of the saturation of the adsorption sites on the MP surfaces; different affinities between heavy metals and MPs and the competition between different heavy metals may affect the adsorption process. In addition, the co-existence of organic contaminants can affect adsorption of heavy metals onto MPs (Lin et al. 2021a). For example, prothioconazole (fungicide) was shown to have no effect on Sn adsorption but could reduce the adsorption of Cr, As, Pb, and Ba onto MPs (Li et al. 2020b). In contrast, prothioconazole was found to enhance Cu adsorption onto MPs (Li et al. 2020b). The increased adsorption of Cu by prothioconazole could be due to the formation of triazole thiolates with Cu. In summary, the presence of other contaminants, the speciation of metal ions, and their relative concentrations, could modify the adsorption and the release of heavy metals from MPs (Gao et al. 2019; Li et al. 2020b; Tang et al. 2021).

### Physiochemical Characteristics of MPs

Adsorption of heavy metals onto MPs is a spontaneous process governed by the various characteristics of MPs, such as sizes and composition, aging degree, and degradability (Bayo et al. 2017; Gao et al. 2019; Abdolapur Monikh et al. 2020; Lu et al. 2020; Naqash et al. 2020; Tang et al. 2020). For instance, the extent of  $\text{Ag}^+$  sorption onto nanoscale plastic debris was found to follow: 600 nm PS > 300 nm PS > 300 nm PE (Abdolapur Monikh et al. 2020). Similarly,  $\text{Cd}^{2+}$  release and sorption were also found to be dependent on the sizes and types of MPs (Qiao et al. 2019; Liu et al. 2020; Guo et al. 2020b). In addition, different MPs exhibit different affinities to heavy metals (Godoy et al. 2019). For example, compared to PS, PVC showed a higher affinity to  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  because of its higher surface area and higher polarity (Brennecke et al. 2016; Lin et al. 2021b). Furthermore, the sorption affinity of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  to MPs was shown to follow the order of CPE > PVC > HPE > LPE, likely owing to the differences in chemical structure and electronegativity of the MPs (Zou et al. 2020). On the other hand, the adsorption of As, Ti, Ni, and Cd was enhanced by the increasing degree of aging, oxidation, and biodegradability of plastics (Lee et al. 2019; Li et al. 2020b; Wang et al. 2020c). Compared with original/newly generated MPs, aged/weathered MPs have higher adsorption capacities for heavy metals (Vedolin et al. 2018; Lee et al. 2019; Gao et al. 2020; Lu et al. 2020; Mao et al. 2020; Tang et al. 2020; Wang et al. 2020c; Aghilinasrollahabadi et al. 2021). This could be ascribed to the increased surface area and the diverse functional groups (e.g., oxygen containing function groups) present on the surface of aged MPs (Guo et al. 2020b; Tang et al. 2020, 2021). Furthermore, degradable

MPs exhibit a higher oral bioaccessibility and greater release of  $\text{Cr}^{6+}$  than nondegradable MPs in the whole digestive system *in-vitro* method, primarily due to possible destruction of surface chemical structures in degradable MPs (Liao and Yang 2020). Overall, the distinct physicochemical properties of MPs (e.g., composition, size, aging degree, polarity, and degradability) are key factors influencing MP-metals interactions in the environment.

### Possible Mechanisms on the Interactions Between MPs and Heavy Metals

#### The Mechanisms Associated with the Physiochemical Characteristics of MPs or Heavy Metals

The physiochemical characteristics of MPs and heavy metals determine their interaction mechanisms [e.g., physisorption (simple process and weak bonds) and chemisorption (electrostatic interaction, surface complexation, and intra-particle diffusion etc.)] which ultimately affect their sorption processes (Bayo et al. 2017; Godoy et al. 2019; Guo et al. 2020a; Lin et al. 2021a, b; Purwiyanto et al. 2020; Zou et al. 2020; Tang et al. 2020, 2021). For instance, the oxygen-containing functional groups such as the carboxyl group on the surface of nylon MPs were identified to promote the adsorption processes of metal ions, which facilitated the surface complexation mechanism (Tang et al. 2020, 2021). On the other hand, the mechanism of electrostatic interaction could be related to the hydrated ionic radius of heavy metals. For example,  $\text{Pb}^{2+}$  was demonstrated to exhibit a remarkable higher sorption than  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , which was suggested to be owing to a lower hydrated ionic radius of  $\text{Pb}^{2+}$  and the larger electrostatic interaction between  $\text{Pb}^{2+}$  and MPs (Zou et al. 2020).

#### Other Potential Mechanisms

The effect of salinity on the adsorption process of  $\text{Pb}^{2+}$  onto hexabromocyclododecane-PS MPs demonstrated that electrostatic interaction could be the predominant adsorption mechanism (Lin et al. 2021a). However, mechanisms involved in the adsorption process of metals and plastics, which are likely to be varied and complex, remain largely unknown. Other potential or related mechanisms dominated the interactions should be further explored under different environmental conditions (Brennecke et al. 2016). At present, some studies simply adopted several kinds of models (e.g., Langmuir model and Freundlich model) to assess the mechanisms between heavy metals and MPs (Godoy et al. 2019; Purwiyanto et al. 2020). This could inevitably cause some limitations such as results uncertainty, variability and incomparability, thus hindering our understanding of their environmental fate. Further development in analytical technologies or new characterization methods could be

considered to unveil the complex interaction mechanisms between MPs and heavy metals.

## Conclusions and Perspectives

In conclusion, there is increasing evidence for the effects of MPs on the mobility, bioavailability, and toxicity of heavy metals. The physicochemical properties of MPs and heavy metals, as well as various environmental factors, have been shown to influence their interaction processes. As a result, assessment of the ecological risks of MPs should take environmental parameters and the presence of metals (as well as other contaminants) into account. In a real world setting, complex environmental factors and variations, and the presence of different contaminants, would affect the fate, transport, and bioavailability of metals. Further investigation is required to understand the mechanisms of these interactions and to elucidate how their interactions modulate the effects of MPs and metals on animal and ecosystem health.

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