

Interaction of Microplastics and Heavy Metals: Toxicity, Mechanisms, and Environmental Implications



Xiaofeng Jiang and Mei Li

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Abstract With the wide use of plastic products in all aspects of life, more and more plastic ends up in the environment. Such plastic waste will gradually decompose, break up, and form smaller fragments through a series of physicochemical and biological processes. Among them, plastic fragments with particle size less than 5 mm are defined as microplastics (MPs). MPs have been reported to be widely distributed and to have the potential to adsorb other pollutants. Therefore, it is particularly important to evaluate the toxic effects of MPs in combination with other pollutants like metals. So far, studies on microplastic and metal toxicity have mainly focused on aquatic environments, while their impact on terrestrial ecosystems has been studied to a much lesser extent. In order to help our understanding of

X. Jiang and M. Li (✉)

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, China

e-mail: meili@nju.edu.cn

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the ecological risk of MP on soil ecosystems, this chapter reviewed the interaction of MPs and metals on soil organisms.

Keywords Combined exposure, Metals, MPs, Soil ecosystem, Toxic effects

1 Introduction

Microplastics can be divided into primary and secondary MPs. Primary MPs are plastic fragments or particles whose initial particle size is less than 5 mm when they are manufactured, mainly in textiles, drugs, and personal care products [1, 2]. The secondary MPs are plastic fragments shaped by environmental forces to a particle size less than 5 mm [3]. Up to now, most studies dealing with MPs and their toxicity have focused on the marine environment. Although freshwater and terrestrial environments have been considered the origin and transport route of plastics to the sea, there is still lack of research of MPs in these environments, especially in the soil environment.

In recent years, it has been found that MPs are widely detected in the soil environment. Fuller and Gautam have investigated the concentrations of MPs in industrial soils in Sydney, Australia, and found that it varies greatly among different sites, with a minimum concentration of 300 mg/kg, and the highest concentration of 6.75×10^4 mg/kg [4]. Scheurer and Bigalke reported the MP abundance of 26 flood-plain sites in Switzerland. Their investigations showed that the highest MPs concentration could reach 55.5 mg/kg [5]. In addition, the toxicity of MPs to terrestrial organisms, such as earthworms, mice, and other, has also been conducted. It has been confirmed that MPs with particle size less than 1 mm are easily ingested by soil organisms [6]. Lwanga et al. found that MP exposure could affect the growth and movement of earthworm *Lumbricus terrestris* (*L. terrestris*). The results showed that microorganisms in the earthworm gut significantly decreased low density polyethylene (LDPE) particle size [7, 8]. Other studies have also shown the toxic effects of various MPs on other soil organisms [9, 10]. Furthermore, particle size is one of the most important characteristics of MPs toxicity [1]. For example, 1 μm is the most common size of filter food organ interception in crustaceans, so crustaceans prefer to ingest MPs with particle size less than 1 μm . Smaller particles have a greater possibility of biological intake than larger size particles, which may enter the cells through endocytosis. Although it has been assumed that the toxicity of MPs is significantly related to its particle size, there is no unified view on what kind of particle size MPs is more toxic. The toxic effects of 0.05 μm , 0.5 μm , and 6 μm MPs on rotifer *Brachionus koreanus* were compared, and it was concluded that small particle size MPs had more significant toxic effects. The antioxidant enzyme activity and mitogen-activated protein kinase (MAPK) signaling pathway in rotifer changed with different particle size of MPs [11, 12]. Likewise, another study found that MPs

with particle size larger than 50 μm had no significant toxic effect on Grass shrimp (*Palaemonetes pugio*), while the fatality rate of acute toxicity test was higher when the size less than 50 μm . It was indicated that MPs have size-dependent effects on the same species [13].

The interaction between MPs and other pollutants is present in the environment. Therefore, in order to evaluate the ecological risk of MPs, the interaction between MPs and other pollutants should be considered, and the toxic effects of combined exposure on various organisms should be addressed. However, there is still lack of research on the toxic effects of MPs in combination with other pollutants, especially MPs and heavy metals [14–17]. There are only a few articles published that deal with the combined toxic effects of MPs and heavy metals. Combined exposure of Cr^{6+} and MPs enhanced the toxicity of the juveniles of common goby – *Pomatoschistus microps* and caused strong lipid peroxidation damage in larvae [18]. By contrast, another study has shown that the combined exposure of 1 μm MPs and Cu to microalgae did not show any toxicity [19]. These studies showed that the combined exposure of MPs and heavy metals is affected not only by the particle size but also by the selected biological species. Moreover, MPs can also interact with heavy metals in the soil environment [20, 21]. Hodson et al. studied the adsorption behavior of high density polyethylene (HDPE) on Zn^{2+} in soil. They found that HDPE had stronger adsorption capacity for Zn^{2+} in soil with more abundant organic matter. The adsorption behavior was in accordance with Langmuir and Freundlich equation [20]. The aged MPs in soil also had a significant effect on the adsorption of heavy metals. Nicole et al. exposed HDPE, polyvinyl chloride (PVC), and polystyrene to artificial aging conditions (2000 h, photo-oxidation and thermal oxidation) to simulate their aging process using a column percolation test. Their results showed that the aged MPs not only significantly increased the adsorption of TOC, Cl, Ca, Cu, and Zn but also weakened the desorption and release of heavy metals, which indicated that the aged MPs had stronger fixation ability to heavy metals [21]. In addition, the functional groups in the soil are adsorbed to the surface of the MPs and may change the adsorption capacity of heavy metals. Kim et al. investigated the adsorption of Ni by the functional group-coated polystyrene. Results showed that the functional groups change the surface hydrophobicity of the polystyrene microplastic and heavy metal and then alter the adsorption of the heavy metal [22]. Turner et al. also studied the adsorption properties of polyethylene microplastics (PE-MPs) for heavy metal ions (Ag, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn) [23]. The adsorption kinetics experiments showed that the adsorption efficiency of aged PE-MPs in river water was higher than that of original PE-MPs, which may be due to the change of the surface structure of aged PE-MPs to reach surface charge equilibrium. Holmes et al. also found that the adsorption capacity of aged polyethylene in seawater for heavy metals was stronger than that of the original polyethylene [24]. Therefore, once the MPs in the soil are weathered and aged, they can be effective carriers of heavy metal in the soil environment what can cause even greater damage to the health of the soil ecosystem.

2 Effects of Microplastics on Organisms

2.1 Individual Effects of Microplastics on Organisms

The ecotoxicity of MPs is mainly focused on smaller organisms. Organisms can directly ingest most MPs that can then cause physical damage, clog or wear ingestion organs and digestive tract, or reduce ingesting rate of organisms. Furthermore, sharp MPs can also cause damage to gills or intestinal tissues [25]. Mussel (*Mytilus edulis*) and herbivorous crab (*Carcinus maenas*) could ingest polyethylene (<80 µm) and polystyrene microspheres (10 µm) and ingested MPs could damage the intestinal tract [26, 27]. In addition, after organisms ingest MPs, they might cause the wrong sense of satiety, reduce the intake of food and act on the digestion process, resulting in energy loss, reduce growth as well as reproductive capacity, and ultimately lead to hunger and death [28].

MPs affect the individual growth, reproduction, and diversity of soil animals. Once MPs are taken up or accumulated by soil animals, in addition to causing physical damage, such as tearing of organs and tissues, the animal will also have an inflammatory response to invasive heterogenic substances [29]. In addition, the ingestion of MPs can also cause insufficient supply of nutrients and energy to soil organisms. Furthermore, the toxic substances released by MPs and the toxic effects of adsorbed pollutants can have varying degrees of adverse impacts on individual and species diversity [20, 30, 31].

The toxic effects of MPs on soil animals are related to particle size and concentration. Rillig showed that MPs with particle size less than 1 mm can be easily eaten by soil animals. After soil animals are fed with MPs, they can also remain in the body [32]. Another investigation showed that MPs are not only more likely to remain in the intestine than other ingested substances but can also pass through the intestinal wall and be transported to other tissues [33]. MPs with a particle size >1 mm remains in the intestinal tract or with the excreta while the small particles are more easily transferred, and can be accumulated by cells. It may relate to the limited space of intracellular phagocytosis of corpuscles [34]. Lwanga et al. studied the effects of different concentrations of MPs (polyethylene <150 µm) on the earthworm *Lumbricus terrestris*. It was found that the mortality rate was highest along with a negative growth rate, when the concentration of polyethylene reached 60% w/w [7, 35].

2.2 Combined Effects of Microplastics and Heavy Metals on Organisms

Heavy metals are widely distributed pollutants in the natural environment. Their toxic effects on aquatic organisms have been widely studied and they are considered to be high-risk pollutants. Heavy metals exist in various ion forms in the water

environment. It has been reported that heavy metals can be enriched by aquatic organisms and have an adverse impact on the whole ecosystem [36, 37]. MPs have the potential to act as vectors for heavy metals and may change the toxicity of other contaminants [38, 39]. Therefore, it is of great significance to explore the interaction between MPs and heavy metals for the complete evaluation of the ecological effects. Barboza et al. found that MPs could absorb mercury from surrounding water and subsequently affect the accumulation of mercury in the European seabass (*Dicentrarchus labrax*) [40]. Khan et al. reported that exposure to aged MPs could increase the bioaccumulation of Ag in the intestine tissue of zebrafish (*Danio rerio*) [41]. Luís et al. found that MP exposure could affect the toxic effects of Cr (VI) on juvenile *P. microps* [18]. Lu et al. reported that exposure to MPs and Cd resulted in increase of Cd bioaccumulation in the zebrafish (*D. rerio*) tissues and showed increased toxic effects compared to exposure to Cd alone [42]. Wen et al. investigated the single and combined toxic effects between polystyrene MPs (0, 50 or 500 mg L⁻¹) and two concentrations of Cd (0 or 50 mg L⁻¹) on the discus fish (*Symphysodon aequifasciatus*) for 30 days. The results showed that there are no obvious effects on the survival and growth of juvenile *S. aequifasciatus*, indicating that the decreasing toxicity may be due to the antagonistic effects of Cd and MPs. However, co-exposure to high concentration of MPs (500 mg L⁻¹) and Cd led to elevated protein carboxyl content, suggesting a synergistic effect of MPs and Cd on the accumulation of protein oxidation products [43]. Lu et al. investigated the biochemical markers, histopathological changes, and functional gene expression of zebrafish (*D. rerio*), showing that the presence of 5 µm polystyrene microspheres enhanced the toxicity of Cd²⁺ to zebrafish and its combined exposure with Cd²⁺ could lead to oxidative damage and inflammation of zebrafish [25]. Nevertheless, the reports regarding combined effects of MPs and heavy metals on soil organisms are still limited. Hodson et al. studied the interactions between HPDE MPs particles and zinc (Zn) to understand the effect of MPs on earthworms' metal bioavailability. Their results showed that MPs could increase Zn bioavailability; however, Zn accumulation, mortality, or earthworms weight have not changed significantly [20].

Wang et al. exposed PVC MPs to earthworm *Metaphire californica* with arsenic (As (V)), for 28 days. The total arsenic concentration and arsenic species in the soil, the gut microbiome, and the tissues of earthworm were analyzed. The findings illustrated that arsenic could be bioaccumulated in the earthworm gut and tissues. Nevertheless, total arsenic concentrations in the earthworm gut and tissues were significantly decreased when earthworms were exposed to the combination of As (V) and MPs, which may explain that MPs can alleviate the adverse effect of arsenic on the gut microbiome due to MPs possibly by inhibiting the reduction of As (V) [44].

3 Potential Mechanism of Microplastics Toxicity

3.1 Uptake, Translocation, and Accumulation of Microplastics in Organisms

Microplastic particles will be transferred to higher organisms through the food chain [45, 46]. Lwanga et al. performed one study on the trophic transfer of MPs in the terrestrial food chain, in which the concentrations of MPs in gardening soil, earthworm casts, and chicken (*Gallus gallus domesticus*) feces were analyzed. The concentrations increased along the trophic levels, and the highest concentration of MP was confirmed in chicken feces. In particular, chicken gizzards also contained MPs, and this indicated that the evidence of transfer of MPs to humans is through food because gizzards are used for human consumption [35]. Maaß et al. used two collembolan species, *Folsomia candida* and *Proisotoma minuta*, and observed the transport of urea-formaldehyde particles (200–400 µm). The transport of particles was strongly dependent on the type of particle, size of particles, and size of organisms. Nevertheless, the authors confirmed the horizontal transport of plastic particles by soil microarthropods [47]. Rillig et al. also studied the transport of PE-MP by soil organisms *L. terrestris*, which were cultured in 2.5 kg of soils covered with 750 mg of various sizes of PE-MPs particles. After 21 days of exposure, MPs were detected in the middle and bottom layers of soils, and the smallest particles (710–850 µm) reached the deepest layers of the soil. The mechanisms of plastic transport in soil were not demonstrated, but they suggested that MPs might be transported through the activities of earthworms such as ingestion/egestion, burrowing, adherence, and casts making [48].

So far, despite their ecological importance, the exposure of soil filter feeders such as nematodes, rotifers, and ciliates to MPs and nanoplastics has not yet been determined. Filter feeders in marine ecosystems have been shown to ingest micro-particles [30, 49], while filter feeders in freshwater ecosystems, *Daphnia magna* and *Thamnocephalus platyurus*, have been shown to be sensitive to nanoplastics [50]. Organisms with other feeding modes are also susceptible to microplastic ingestion. Taylor et al. found synthetic microfibers on and inside six out of nine deep-sea organisms that belong to the phyla Cnidaria, Echinodermata and Arthropoda with predatory and feeding mechanisms [51]. As such, woodlice, snails, caecilians, and other soil organisms with similar feeding mechanisms would be subjects of interest in agroecosystems. Information about the bioavailability and bioaccumulation of MPs in soil organisms is generally lacking. We know that nanoplastics can enter cells, as fluorescent nanoplastic polymers have been used as molecular probes for a wide range of biological studies with mammalian cells, for example, to measure blood flow in tissue and as tracers for phagocytic processes [34]. The translocation of a range of microparticles by mammalian gut into the lymphatic system has been demonstrated in rabbits, dogs, and rodents. There is no experimental evidence of nanoplastics being transferred from invertebrates to vertebrates. However, there is evidence of the transfer of MPs from contaminated land to vertebrates and potentially from earthworm to chicken [35].

3.2 *Molecular-Level Response*

So far, there have been published only a few papers that focused on the molecular-level response of organisms to MPs exposure [10, 52, 53]. Prendergast-Miller et al. used metallothionein (*mt-2*), heat shock protein (*hsp70*), and superoxide dismutase (*SOD-1*) as the biomarker responses to evaluate the molecular-level response in *L. terrestris* exposed to polyester-derived microfiber (MF) with 0, 0.1, and 1.0%w/w for a period of 35 days [53]. Their results showed that *hsp70* expression was downregulated at the high MF exposure, which indicated that downregulation of *hsp70* is an index of stress when *L. terrestris* is exposed to MF. However, the activity of *mt* is not completely understood. It can be explained by the shortage of metal transcription factor (*MTF-1*) in *L. terrestris* compared to other higher organisms. Therefore it is necessary to determine the transcriptional response of the earthworm's response to MF [53]. Rodriguez-Seijo et al. also studied molecular changes of earthworms (*Eisenia andrei*) exposed to PE-MPs. They concluded that multiple stress-response mechanisms of the immune system of earthworms led to, involving a wide range of molecules/enzymes, the increased content in proteins, lipids, and polysaccharides [10]. In addition, the alterations of saturation fatty acid have also been considered as a biomarker for the response of soil organisms to stress [54]. The increase in saturated fatty acids makes membranes more viscous and less permeable, while saturation reduces the susceptibility of fatty acids to free radicals [55].

4 Environmental Implications and Future Prospective

4.1 *Challenges About Toxicity Research Methodologies of Microplastics and Heavy Metals*

MPs can act as a carrier of metals and combined they can cause toxicity to various organisms. However, it is difficult to determine the contribution of MPs and metals to overall toxic activity. Furthermore, contaminants carried by MPs may be transported along the food chain [56]. Among the chemical substances present in MPs are those added during their manufacture (additives) and those present in water that are adsorbed on the surface of MPs, such as persistent organic pollutants, pharmaceuticals, pesticides or herbicides. Among pollutants that MPs can absorb, metals have been widely studied [29, 33, 56]. In addition, some metals are frequently added as catalysts, pigments, and stabilizers during plastic manufacturing [57]. The toxicity of MPs and heavy metals should not be generalized by synergistic, antagonistic, additive or independent effect. Therefore, it is important that relevant standards and rules for toxicity research on MPs should be first determined so that data from different researches can be comparable and reliable.

4.2 *Considerations for Assessing Ecological Risks of Microplastics and Heavy Metals*

The widespread distribution and accumulation of MPs in the global environment has attracted attention on its sources, migration distribution, and ecotoxicological effects. The size, quantity, and shape of MPs entering the environment are uncertain, and the related research methods and classification criteria are not unified, what causes lack of consistency in the study of environmental behavior of MPs. There is also a lack of systematic analysis of the bioaccumulation and the transfer of MPs in the food chain. In addition, the interaction mechanism of micro-plastics and heavy metals, as well as the role of the MPs in their combined toxicity needs further study.

5 Summary

This chapter reviewed the interaction of MPs and heavy metals: toxicity, mechanisms, and environmental implications. However, most of the toxicity experiments of MPs are carried out in the laboratory on single species, the exposure time is short, and the dose is higher than the environmental concentrations. Therefore, it is necessary to provide comprehensive evaluation of the MP toxic effects according to the environmental conditions. Furthermore, new molecular biological techniques such as relevant omics should also be applied to study the toxic effects of MPs. The toxic mechanism of MPs and heavy metals on organisms, as well as the toxic effects on biodiversity, community structure, and ecosystem function, also need more detailed approach, which can provide basic data support for the determination of MPs in the environment and the establishment of standards.

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