DOCTORAL THESIS

Occurrence, determination and environmental fate of microplastics in aquatic system

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ABSTRACT

The current period of human history is considered to be the plastics age due to its versatile characteristics, especially the lightweight, durability and low production cost. Plastics can be manufactured to suit multifarious functions, for example, for personal care products, food/drink storage and medical purposes. Thus, the use of plastics is unavoidable now, finally contributing to the severe pollution worldwide. In 2018 alone, the global plastics production amount has exceeded 359 million tons, around 10% of which ultimately become waste persisting in the environment. When plastic wastes exposed to the sun's radiation, climate change and mechanic abrasion, degradation and fragmentation may occur. Once the size of the fragmentation products is less than 5 mm, they are commonly defined as microplastics (MPs) by the National Oceanographic and Atmospheric Administration. Currently, microplastics have been regarded as the most pervasive environmental pollution problems, not only because of their physical hazards but also due to their interactions with other pollutants in the environment. Pollution can be attributed by the release of additives from MPs, as well as the MPs with adsorbed toxic contaminants. Moreover, MPs additives together with adsorbed chemicals can be easily uptaken by animals, which may cause further propagated effects on the ambient ecosystem. Through the bioaccumulation and biomagnification effect, MPs can even be accumulated in the organisms from different trophic levels and cause serious impacts on aquatic ecology and human health. Despite growing number of evidences that have confirmed the presence and consequential effects of microplastics, researches on microplastic pollution are still lacking. Investigations on occurrence, determination and

environmental fate of MPs in aquatic systems are clearly needed. Therefore, the major objective of this study is to elucidate the distribution of MPs in natural environment, to develop novel determination methods to characterize the micro-(nano-)plastics (MNPs), and to study the interactions of MPs with other contaminants in different conditions, as well as their consequential fate in different matrices (e.g. freshwater, cold-blooded intestine, and warm-blooded intestine).

The spatial-temporal distribution of the MPs along the Maozhou River was investigated for both the surface water and sediments from 17 sites. Results showed that MPs were widely and unevenly distributed along the river. The MP abundances in dry season ranged from 4.0 ± 1.0 to 25.5 ± 3.5 items·L^{-1} in water and 35 ± 15 to 560 ± 70 item·kg^{-1} in sediments, which were relatively higher than those observed in wet season (water: 3.5 ± 1.0 to 10.5 ± 2.5 items·L^{-1}; sediments: 25 ± 5 to 360 ± 90 item·kg^{-1}; p value < 0.05). The dominant types of MPs were identified as: polyethylene (PE, water: 45.0%, sediments: 42.0%), polypropylene (PP, water and sediments: 12.5%), polystyrene (PS, water: 34.5%; sediments 14.5%) and polyvinyl chloride (PVC, water: 2.0%; sediments: 15%). Moreover, metals such as Al, Si, Ca were discovered on the rough surface of the MPs, indicating the interactions between the MPs and the aquatic environment. After obtaining the occurrence of the MPs in the aquatic systems, we proposed an accurate method for MNPs identification and quantification with the employment of the matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS). By optimizing the conditions (e.g. the laser energy, matrix, analyte, cationization

agent and their ratio), the peaks of PS and polyethylene terephthalate (PET) were successfully identified. A quantitative correlation was built between the normalized signal intensity and ln[polymer concentration], with a correlation coefficient above 0.96 for low-molecular-weight (LM-) polymers and 0.98 for high-molecular-weight (HM-) polymers. Furthermore, two types of environmental MPs samples were prepared, including the particles of an aviation cup as the fresh plastics and the aged MPs extracted from river sediment. By using MALDI-TOF MS, the PS-related micro-(nano-)plastics (in both aviation cup and sediment) consisted of C_8H_8 and $C_{16}H_{16}O$ oligomers, while the PET-related MNPs (only found in sediment) were identified with compositions of $C_{10}H_8O_4$ and $C_{12}H_{12}O_4$. The contents of PS and PET MNPs in sediment were quantified as 8.56 ± 0.04 and 28.71 ± 0.20 $mg \cdot kg^{-1}$, respectively. Also, the interaction between MPs and bisphenols was investigated. PVC was selected as the representative target because it is comparatively easy to decompose into MPs with the release of additives, especially the bisphenols. The released bisphenols may then be readsorbed by the PVC MPs and cause consequential pollution to the ecosystem. To elaborate on the interactions mechanism, a systematic study was carried out to determine the adsorption mechanisms of five bisphenol analogues (BPA, BPS, BPF, BPB, and BPAF) on PVC MPs. The equilibrium adsorption numbers of the bisphenols on PVC MPs are 0.19 ± 0.02 mg/g (BPA), 0.15 ± 0.01 mg/g (BPS), 0.16 ± 0.01 mg/g (BPF), 0.22 ± 0.01 (BPB), 0.24 ± 0.02 mg/g (BPAF), respectively. Intraparticle diffusion modeling (kinetics) divided the adsorption process into three stages: external mass transport, intraparticle

diffusion and dynamic equilibrium. The isotherm results showed a better fit of the adsorption to the Freundlich model. Furthermore, the adsorption mechanisms of the five bisphenol analogues were explored intensively, with respect to hydrophobic interaction, electrostatic force and noncovalent bonds. Besides the adsorption process, the transfer and release behaviors of contaminated MPs are of critically importance in the exploration of their role as culprits and/or vectors for the aforementioned toxicity. Therefore, experiments were performed to examine desorption behaviors and cytotoxicity performance of contaminated MPs in aquatic surroundings and intestinal environment after ingestion by organisms (cold-/warm-blooded). The kinetic study showed that the rate of desorption for bisphenols could be enhanced threefold under simulated warm intestinal conditions. The Freundlich isotherms indicated multiple-layer desorption of the bisphenols on the heterogeneous surfaces of PVC MPs. Hysteresis was detected in the adsorption/desorption of bisphenols in a water environment, but no adsorption/desorption hysteresis was observed in the simulated intestinal conditions of warm-blooded organisms. Due to the enhanced bioaccessibility, the desorption results implied that the environmental risk of contaminated PVC MPs might be significantly increased after ingestion at a high bisphenols dosage. Although with different IC_{50}, the five bisphenols released under the intestinal conditions of warm-blooded organisms can cause higher proliferation reduction in fish and human cell lines than the bisphenols released in water.

In summary, this study elucidated the spatial-temporal distribution behaviors of MPs, developed effective determination methods for MNPs revealed the interactions mechanisms of MPs with other contaminants, and explored their consequential fate in different environments. The obtained results are helpful of better understanding on the land-based input of MPs from the intensively affected inland waters, realizing the role of microplastics as both source and carrier for emerging organic pollutants, and providing a novel alternative for MPs determination in future studies.

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