DOCTORAL THESIS

Joint Effects of Microplastic Associated with Multiple Environmental Contaminants

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Abstract

In recent years, the severity of microplastic pollution continues to increase and has reached worldwide proportions. Of particular concern are the increasing reports of their occurrence and adverse effects in various environmental compartments and biota, including species with critical ecological roles and those intended for human consumption. As described in the literature, microplastics (MPs) do not represent a threat to the environments solely in isolation due to their propensity to accumulate various waterborne contaminants and biological materials in the surrounding media. It is therefore proposed that MPs can be vectors for delivering harmful substances from different environmental matrices into ingested biota. Nonetheless, a consensus on the vector role of MPs has not been reached in the literature as their environmental relevance remains controversial.

Despite numerous reports on the MPs' sorption with anthropogenic pollutants, studies exploring the complexity of interaction between MPs and other aqueous constituents in multi-solute environments are nearly nonexistent. Thus, the effects of multi-contaminant interactions on the vector role of MPs were firstly elucidated. In most cases, the coexistence of other UV filters appeared to have an antagonistic effect on the sorption of primary solute, which was consistent with trends found in previous studies. Nonetheless, it was found that the formation of solute multilayers

among multiple UV filters on MP surface is possible, as evidenced by the enhanced sorption of 4-methylbenzylidene camphor (4-MBC) by polystyrene (PS) with other UV filter(s). Moreover, the subsequent desorption experiments also discovered that the bioaccessibility of primary solutes trapped in the form of solute multilayers on MPs was significantly higher, even though competitive sorption was occurred in the multi-solute media. These results highlight that the vector potential of MPs has been vastly underestimated in single-solute systems that are typically used in many of the earlier MP studies.

The surface characteristics, and hence the sorption behavior of MP particles is continuously changed by various weathering and biofouling processes that occurred in the environment. In order to have a realistic, accurate understanding of how MPs are affecting the natural environment, the combined effects of multi-contaminant interactions and natural attenuation processes on the vector role of MPs were then investigated. The results of structure characterization revealed that oxygen surface functionalities were introduced in all the weathered PSMPs, thus exhibiting lower surface hydrophobicity as compared to the pristine particles. Such surface alteration apparently changed the dominant interactions of PSMPs with different properties of UV filters, and eventually the composition and overall toxicity of adhered solute multilayers on the PSMPs. Specifically, the formation of surface multilayers among

hydrophobic UV filters on the PSMPs was drastically inhibited after UV irradiation because of intensified competition for hydrophobic sorption sites. On the contrary, hydrophilic UV filters contributed to solute multilayer sorption with 4-MBC on the UV-irradiated PSMPs, rather than on the pristine particles. It is also worth noting that these solute multilayers on PSMPs induced more deleterious effects on algal growth as compared to their individual constituents. Hence, these findings disclose a novel ecological risk of MPs in which they can serve as platforms for facile formation of unknown solute complexes with joint toxicity in actual environments.

With the increasing application of engineered nanoparticles (ENPs), it becomes more likely that ENPs will coexist with MPs in natural environments. Similarly, it is expected that the interaction of ENPs and MPs can be altered by other aqueous constituents in aquatic systems. Among these, heavy metals (HMs) are most likely to interfere such interactions via charge neutralization or even charge inversion after bindings to these particles. As such, it is imperative to comprehend the role of HMs on the uptake and subsequent release of ENPs by MPs. The results illustrated that PSMP particles exhibited substantially higher sorption affinity for isotropic charged ENPs when HMs were presented. This enhanced affinity was due to the formation of MP-HM-ENP complexes in multi-solute media. In addition, the bioaccessibility of MP-adhered ENPs and HMs differed significantly between aquatic media and

various simulated digestive fluids, verifying the vital role of MPs for ENP transfer from the environments into biota via ingestion of MPs and trophic transfer. Hence, these results disclose the enhanced potential for MPs to accumulate and to transport ENPs when metallic contaminants are present.

Overall, these thesis works reveal the importance and uniqueness of the vector role of MPs, which is ascribed to the facile formation of unknown solute complexes among multiple environmental contaminants on their particle surfaces. This is of particular importance as natural environments are highly heterogeneous systems composed of various anthropogenic pollutants.

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