

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.

Table of Contents

DECLARATION	i
Abstract.....	ii
Acknowledgements.....	vi
Table of Contents	viii
List of Tables.....	xii
List of Figures.....	xiv
List of Abbreviations and Symbol	xvii
Chapter 1. Microplastic Contamination in the Environments	1
1.1. Background	1
1.2. Sources of Microplastics in the Aquatic Environment.....	3
1.2.1. Primary Microplastics.....	3
1.2.2. Secondary Microplastics.....	4
1.3. Fate of Microplastics in the Aquatic Environment	5
1.3.1. Horizontal and Vertical Distribution of Microplastics	5
1.3.2. Natural Weathering Processes of Microplastic.....	7
1.4. Adverse Effects of Microplastics in the Aquatic Environment.....	9
1.4.1. Uptake of Microplastics by Marine Biota.....	9
1.4.2. Microplastic-Mediated Chemical Exposure	10
1.4.3. Biofilm Formation on the Microplastics.....	11
1.5. Aims of Thesis Work.....	13
1.6. References	15
Chapter 2. Materials and Methods.....	20
2.1. Chemicals and Reagents	20
2.2. Preparation of Pristine and Weathered Microplastic Particles	24
2.2.1. Pristine Microplastic Particles	24
2.2.2. UV-irradiated Microplastic Particles	24
2.2.3. Microbially Degraded Microplastic Particles	25
2.3. Structural Characterization.....	28

2.3.1.	Surface Characteristics of Microplastic Particles and Nanoceria....	28
2.3.2.	Total Biomass Quantification	29
2.4.	Batch Sorption and Desorption Experiments.....	31
2.4.1.	Sorption Experiments of Organic UV Filters	31
2.4.2.	Sorption Experiments of Nanoceria and Heavy Metals.....	31
2.4.3.	Desorption Experiments of Organic UV Filters and Nanoceria	32
2.5.	Algal Toxicity Tests.....	34
2.6.	Analytical Methods	36
2.6.1.	Analytical Procedures for Organic UV Filters.....	36
2.6.2.	Microwave-assisted Acid Digestion for Nanoceria and Heavy Metals	36
2.7.	Instrumentation	38
2.7.1.	UPLC-MS/MS and UHPLC-MS/MS for Organic UV Filters.....	38
2.7.2.	ICP-MS/MS for Nanoceria and Heavy Metals	41
2.8.	References	42
Chapter 3. Sorption and Desorption of Organic UV Filters onto Microplastics in Single and Multi-Solute Systems.....		44
3.1.	Introduction.....	44
3.2.	Materials and Methods.....	47
3.2.1.	Recovery of Organic UV Filters in Each Phase.....	47
3.2.2.	Sorption Equilibrium of Organic UV Filters on MPs.....	47
3.2.3.	Data Analysis	49
3.3.	Results and Discussion.....	50
3.3.1.	Characterization of the Microplastic Particles.....	50
3.3.2.	Single-solute Sorption Isotherms of Organic UV Filter by MPs.....	51
3.3.3.	Evaluation of Cosolute Effects of Multiple Organic UV Filters on MPs	55
3.3.4.	Elucidation of the Mechanisms of Multilayer Sorption on MPs	60
3.3.4.1.	Polymer Type and Cosolute Concentration.....	60
3.3.4.2.	Hydrophobicity of Cosolute.....	61

3.3.4.3. Hydrophobicity of Primary Solute	62
3.3.5. Bioaccessibility of MP-sorbed UV Filters in Simulated Digestive Fluid	65
3.4. Chapter Summary.....	69
3.5. References	71
Chapter 4. Effects of Weathering on the Sorption Behavior and Toxicity of Polystyrene Microplastics in Multi-solute Systems	74
4.1. Introduction	74
4.2. Materials and Methods	77
4.2.1. Sorption Equilibrium of Organic UV filters on Pristine and Weathered PSMPs	77
4.2.2. Data Analysis	81
4.3. Results and Discussion.....	82
4.3.1. Morphological and Surface Properties of Pristine and Weathered PSMPs	82
4.3.2. Role of Cosolute Properties in the Formation of Solute Multilayers by PSMPs.....	91
4.3.2.1. Effects of Hydrophobic Cosolutes	91
4.3.2.2. Effects of Hydrophilic Cosolutes	99
4.3.3. Toxicological Effects of Solute Multilayers on the Algal Cell Growth	101
4.4. Chapter Summary.....	107
4.5. References	109
Chapter 5. The Crucial Role of Heavy Metals on the Interaction of Engineered Nanoparticles with Polystyrene Microplastics.....	113
5.1. Introduction.....	113
5.2. Materials and Methods.....	116
5.2.1. Sorption Equilibrium for CeNPs and Heavy Metals on PSMPs....	116
5.2.2. Data Analysis	117
5.3. Results and Discussion	118
5.3.1. Sorption of CeNPs on PSMPs with Monovalent and Divalent Metal Ions	118

5.3.2.	Exploration of Complexation Mechanisms for PSMP-Pb(II)-CeNP...	123
5.3.3.	Environmental Factors affecting the CeNP Sorption on PSMPs with Metal Cations	126
5.3.3.1.	Effects of Ionic Strength	126
5.3.3.2.	Effects of Divalent Metal Cations	128
5.3.4.	Bioaccessibility of MP-sorbed CeNPs and HMs in Various Simulated Digestive Fluids	131
5.4.	Chapter Summary	134
5.5.	References	136
Chapter 6. Conclusion and Future Perspectives		140
6.1.	Thesis Summary	140
6.2.	Current Challenges and Outlook	143
6.2.1.	Quantification of the Ecocorona Components on Microplastics	143
6.2.2.	Overall Toxicity of MP-adhered Solute Complexes	144
6.2.3.	Biodistribution of Microplastics and Associated Contaminants	145
6.3.	References	146
	Outputs of Thesis Work	147
CURRICULUM VITAE		149

List of Tables

Table 2.1	Chemical structures with selected properties of the model UV filters.	22
Table 2.2	Measured UV intensity at the surface of exposure media and under natural sunlight.	27
Table 2.3	Conditions used in different types of <i>in vitro</i> digestion models.	33
Table 2.4	Operational parameters for the microwave digestion system.	37
Table 2.5	Instrumental parameters of UPLC-MS/MS.	39
Table 2.6	MRM conditions used in UPLC-MS/MS for model UV filters.	39
Table 2.7	Instrumental parameters of UHPLC-MS/MS.	40
Table 2.8	MRM conditions used in UHPLC-MS/MS for model UV filters.	40
Table 2.9	Instrumental parameters of ICP-MS/MS for nanoceria and selected heavy metals.	41
Table 3.1	Recovery of model UV filters in each phase of sorption experiments.	47
Table 3.2	Physicochemical properties of LDPE and PS used in this study.	50
Table 3.3	Isotherm parameters for sorption of a specific organic UV filter to the two types of MPs.	54
Table 3.4	Detailed conditions and results of multilayer sorption of organic UV filters on MPs.	58
Table 3.5	The n_F values of model UV filters derived from single and multi-solute media.	59
Table 3.6	Measured mass of sorbed UV filters on the two MPs in a multi-solute system.	68

Table 3.7	The bioaccessibility of MP-sorbed cosolute UV filters in simulated digestive fluid.	68
Table 4.1	Surface functionalities, elemental composition and properties of the pristine and weathered PSMPs.	89
Table 4.2	Biofilm biomass adhered on surface of the microbially-degraded PSMPs.	90
Table 4.3	Conditions and results of multi-solute sorption experiments on the pristine and weathered PSMPs.	98
Table 4.4	Measured mass of cosolute UV filters sorbed on the pristine and weathered PSMPs.	98
Table 4.5	Conditions of each bioassay group used in the algal toxicity tests.	104
Table 4.6	Measured mass of the sorbed UV filters on the PSMPs after modified sorption experiments.	105
Table 4.7	Toxicological effects of PSMPs with or without sorbed UV filters on the <i>C. vulgaris</i> .	106
Table 4.8	Bioabsorption of PSMP-sorbed UV filters by the <i>C. vulgaris</i> .	106
Table 5.1	Aggregation profile and sorption capacity of CeNPs and Pb(II) by PSMPs.	123
Table 5.2	Elemental composition of PSMPs after sorption experiment with CeNPs and Pb(II).	125
Table 5.3	Characteristic of the divalent metal cations.	130

List of Figures

Figure 1.1	Plastic accumulation zones in surface waters of the five oceans.	6
Figure 1.2	Simplified scheme illustrating adverse effects of MPs on the marine ecosystem.	10
Figure 2.1	The custom-made weathering chamber equipped with a ventilation system and a medium-pressure UV lamp.	26
Figure 2.2	Top and front views of PSMP suspension before UV irradiation.	26
Figure 2.3	Natural UV intensity measured at the Ho Sin Hang Campus of the Hong Kong Baptist University in the period of August to October 2019.	27
Figure 3.1	Sorption kinetics of model hydrophobic UV filters by LDPE.	48
Figure 3.2	Sorption kinetics of model hydrophobic UV filters by PS.	48
Figure 3.3	FE-SEM images of (a) LDPE and (b) PS.	50
Figure 3.4	Effects of other UV filters on the sorption of the primary solutes (BP-3 or 4-MBC) by the two MPs (LDPE or PS).	58
Figure 3.5	Effects of other UV filter(s) on the sorption of 4-MBC (as primary solute) by PS.	64
Figure 3.6	Relationship between solute hydrophobicity and sorption coefficient of primary solute in the multi-solute environment.	64
Figure 3.7	Cosolute effects on the sorption and subsequent desorption of primary solutes by LDPE and PS in multi-solute media.	67
Figure 4.1	Sorption kinetics of model hydrophobic and/or hydrophilic UV filters by NPS.	77

Figure 4.2	Sorption kinetics of model hydrophobic and/or hydrophilic UV filters by UV-PS.	78
Figure 4.3	Sorption kinetics of model hydrophobic and/or hydrophilic UV filters by MD-NPS.	79
Figure 4.4	Sorption kinetics of model hydrophobic and/or hydrophilic UV filters by MD-UV-PS.	80
Figure 4.5	Surface morphology of the pristine and weathered PSMPs: (a) NPS; (b) UV-PS; (c) MD-NPS; (d) MD-UV-PS; (e) DMD-UV-PS.	85
Figure 4.6	ATR-FTIR spectra of the pristine and weathered PSMPs: (a) NPS & UV-PS; (b) NPS & MD-NPS; (c) UV-PS & MD-UV-PS; (d) MD-UV-PS & DMD-UV-PS.	87
Figure 4.7	XPS wide-scan and C1s spectra of the pristine and weathered PSMPs: (a) NPS; (b) UV-PS; (c) MD-NPS; (d) MD-UV-PS; (e) DMD-UV-PS.	88
Figure 4.8	Effects of (a) hydrophobic and (b) hydrophilic UV filters on the uptake of 4-MBC by the pristine and weathered PSMPs.	96
Figure 4.9	Measured mass of sorbed hydrophobic UV filters (EHMC and OC) on the pristine and weathered PSMPs in multi-solute sorption experiments.	96
Figure 4.10	Effects of hydrophobic UV filters (EHMC and OC) on the uptake of 4-MBC by MD-UV-PS with or without chemical disinfection.	97
Figure 4.11	Measured mass of sorbed hydrophobic UV filters (EHMC and OC) on the MD-UV-PS with or without chemical disinfection.	97

Figure 4.12	Measured mass of sorbed hydrophilic UV filters on the pristine and weathered PSMPs in multi-solute sorption experiments.	100
Figure 4.13	Toxicological effects of (a) NPS and (b) UV-PS with or without sorbed UV filters on the growth of <i>C. vulgaris</i> after 96 h of exposure.	104
Figure 5.1	Sorption kinetics of CeNPs with a mixture of 50 mg/L Ag(I) and Pb(II) by PSMPs.	116
Figure 5.2	Percentage of CeNPs (200 µg/L) sorbed by NPS and UVPS.	121
Figure 5.3	Aggregation profile and sorption capacity of CeNPs and Ag(I) by the NPS (a – c) and UVPS (d – f) in a multi-solute system.	122
Figure 5.4	Aggregation profile and sorption capacity of CeNPs and Pb(II) by the NPS (a – c) and UVPS (d – f) in a multi-solute system.	122
Figure 5.5	FE-SEM images of (a) NPS and (b) UVPS after sorption experiment with a mixture of CeNPs and Pb(II).	125
Figure 5.6	Effects of ionic strength (in terms of NaCl) on the aggregation profile and sorption capacity of CeNPs and Pb(II) by the NPS (a – c) and UVPS (d – f) in a multi-solute system.	128
Figure 5.7	Effects of divalent metal cations (Co, Cd and Pb) on the aggregation profile and sorption capacity of CeNPs and metal ions by the NPS (a – c) and UVPS (d – f) in a multi-solute system.	130
Figure 5.8	Bioaccessibility of MP-sorbed CeNPs and Pb(II) from the NPS (a – b) and UVPS (c – d) in simulated digestive fluids.	133