

## DOCTORAL THESIS

### Exposure and risk assessment of organic UV filters: from environmental occurrence to human biomonitoring study

Huang, Yanran

*Date of Award:*  
2020

[Link to publication](#)

#### General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

## **Abstract**

In recent years, the studies of emerging contaminants have received growing concerns due to their ambiguous fate and unclear effect to the water environment, aquatic organisms or even human. With the development of the analytical techniques, the increase detection rate of emerging contaminants is at a rapid pace that many of their fates and influence are still pending investigation.

In this work, a group of organic UV filters, which is one of the vital categories of emerging contaminants are monitored. Organic UV filters, used as the major components in not only sunscreens but also other cosmetics products, have a widespread usage and large production volume for more than 80 years, causing the massive input towards the aquatic environment. To first investigate their environmental behaviours and impacts, the regional distribution of total nine commonly used organic UV filters was monitored along the southeast coastline of Shenzhen, which is the most rapid developing city in China with large population with the consideration of seasonal variation. In addition, the Shenzhen reservoirs, as the major sources of drinking water in Shenzhen, was also monitored together with the city tap water. The results indicated the extensive distribution of certain kinds of UV filters with obvious seasonal pattern, which may cause medium to high risk to aquatic organisms. And the incomplete removal of them in drinking water supply system resulting trace amount of UV filters to be detected in city tap water,

may cause a general exposure of these UV filters towards all populations. Therefore, a quantitative analytical method for simultaneous detecting multiple classes UV filters in human urine samples has been developed and applied on more than 100 real samples for determining internal exposure. Similar UV filters were also detected in human urine samples compared with surface water while one of the most commonly used organic UV filters, Ethylhexyl methoxycinnamate exhibited much lower detection rate and concentration in human urine.

Then, biotransformation of Ethylhexyl methoxycinnamate was examined in rats for the purpose of selecting suitable metabolites as exposure biomarkers. Several metabolites have been identified in urine and plasma by UHPLC-QTOF-MS. Two of its metabolites, 4-methoxycinnamic acid and 4'-methoxyacetophenone, were unambiguously identified by comparing with commercial standard. Excretion trend of Ethylhexyl methoxycinnamate and its two metabolites confirmed that most of the parent compound were quickly metabolized and excreted through urine samples. Herein, these three targeted compounds were further evaluated in two populations – female university students and school-aged children. Although Ethylhexyl methoxycinnamate was not detected in 49 female university students, significant internal correlations were discovered among these three analytes in school-aged students and extensive detection of metabolites instead of parent compound was also confirmed.

The third part of this thesis is to comprehensively monitor the internal exposure of UV filters and their metabolites, and also discover their potential adverse health impacts – obesity in Shanghai children and adolescents. Urinary concentration of certain kinds of UV filters were significantly higher in girls than in boys. However, further associations have been found with urinary Ethylhexyl methoxycinnamate concentration and reduced adiposity outcomes only in boys, indicating it may have the potential to influence the metabolism in male population during growing stage.

In short, a complete study of organic UV filters is presented in this thesis, from their environmental occurrence to metabolism in animal models, and finally to human exposure and potential health impacts. The widespread exposure and significant associations with adiposity outcomes can form a solid base for future comprehensive risk assessment of UV filters towards human health.

assistance. The support of postgraduate studentship from the University Grants Council is also gratefully acknowledged.

Last but not the least, I would like to express my endless thanks to my parents and my boyfriend Dr. Charles Z. Huang. It is their unlimited love and encourage that support me walking through the toughest moment during my study.

# Table of Contents

DECLARATION .....	i
Abstract .....	ii
Acknowledgements .....	v
Table of Contents.....	vii
List of Tables .....	xi
List of Figures .....	xiv
List of Abbreviations and Symbols .....	xvii
<b>Chapter 1 – Introduction .....</b>	<b>1</b>
1.1. Background .....	1
1.2. Release pathways .....	6
1.3. Environmental occurrence.....	7
1.3.1. Natural water .....	7
1.3.2. Wastewater and sludge .....	11
1.3.3. Sediments and soils .....	15
1.3.4. Aquatic organisms .....	18
1.4. Ecotoxicity.....	19
1.5. Human biomonitoring .....	20
1.6. Aims of thesis work.....	22
1.7. References .....	24
<b>Chapter 2 – Materials and methods.....</b>	<b>30</b>
2.1. Chemicals and reagents .....	30
2.2. Sampling.....	36
2.3. Analytical methods .....	36
2.3.1. Non-targeted analysis .....	36
2.3.1.1. Rats plasma .....	36
2.3.1.2. Rats urine .....	37
2.3.1.3. Rats feces .....	37

2.3.2. Quantitative analysis .....	40
2.3.2.1. Aquatic samples.....	40
2.3.2.2. Human urine samples .....	41
2.3.2.3. Rats samples.....	41
2.4. Instrumentation.....	44
2.4.1. UHPLC-QQQ-MS.....	44
2.4.1.1. General information .....	44
2.4.1.2. Columns and mobile phase.....	46
2.4.2. UHPLC-QTOF-MS .....	46
2.5. Bioluminescent Microtox bioassay – <i>Vibrio fischeri</i> .....	48
2.6. References .....	49
<b>Chapter 3 – Occurrence of organic UV filters in Shenzhen marine surface water and implication for human exposure .....</b>	<b>50</b>
3.1. Introduction .....	50
3.2. Materials and Methods .....	52
3.2.1. Sampling.....	52
3.2.1.1. Aquatic samples.....	52
3.2.1.2. Human urine samples .....	56
3.2.2. Statistical analysis .....	56
3.3. Results and discussion.....	58
3.3.1. Environmental occurrence of multiple classes of UV filters in Shenzhen ..	58
3.3.1.1. Method performance .....	58
3.3.1.2. Occurrence and composition of organic UV filters.....	59
3.3.1.3. Seasonal pattern of UV filters .....	67
3.3.1.4. Spatial distribution and possible sources.....	69
3.3.1.5. Ecological risk assessment .....	72
3.3.1.6. Implication for human exposure.....	77
3.3.2. Development of an analytical method for simultaneous determining multiple	

classes UV filters in human urine samples using SPE .....	78
3.3.2.1. Optimization of SPE cartridge and pH.....	78
3.3.2.2. Method validation .....	81
3.3.2.3. Application to human urine samples .....	84
3.4. Chapter summary .....	87
3.5. References .....	89
<b>Chapter 4 – Fate of EHMC in rat model and human urine .....</b>	<b>92</b>
4.1. Introduction .....	92
4.2. Materials and Methods .....	95
4.2.1. Tested animals .....	95
4.2.2. Human urine samples .....	96
4.2.2.1. Female University Students.....	96
4.2.2.2. School aged students .....	96
4.2.3. Metabolites identification.....	97
4.2.4. Statistical analysis .....	97
4.3. Results and discussion.....	99
4.3.1. Metabolites identification in rat plasma, urine and feces .....	99
4.3.1.1. Assigned metabolites.....	99
4.3.1.2. Unassigned metabolites.....	108
4.3.1.3. Metabolic pathway and confidence level .....	109
4.3.2. Formation and excretion trends of EHMC and its metabolites .....	111
4.3.2.1. Method development and validation .....	111
4.3.2.2. Quantitative analyses of EHMC and its metabolites in rat plasma and urine .....	116
4.3.3. Monitoring EHMC and its metabolites in human urine samples .....	121
4.3.3.1. Method validation .....	121
4.3.3.2. Female university students .....	123
4.3.3.3. School age students.....	126



4.4. Chapter summary .....	140
4.5. References .....	142
<b>Chapter 5 – Associations between urinary UV filters and adiposity in Chinese children and adolescents .....</b>	<b>146</b>
5.1. Introduction .....	146
5.2. Materials and Methods .....	148
5.2.1. Study population.....	148
5.2.2. Urine sample collection.....	151
5.2.3. Anthropometric measurements.....	151
5.2.4. Statistical analysis .....	151
5.3. Results and discussion.....	153
5.3.1. Method performance .....	153
5.3.2. General exposure level and gender difference.....	153
5.3.3. Correlations among UV filters .....	158
5.3.4. Relationships with adiposity outcomes .....	161
5.3.4.1. Characteristics of selected population.....	161
5.3.4.2. Longitudinal analyses.....	164
5.3.4.3. Cross-sectional analyses.....	167
5.3.4.4. Discussion .....	172
5.4. Chapter summary .....	175
5.5. References .....	176
<b>Chapter 6 – Conclusion and outlook.....</b>	<b>179</b>
6.1. Thesis summary.....	179
6.2. Current challenges and outlook.....	181
Outputs of Thesis Work.....	184
<b>CURRICULUM VITAE.....</b>	<b>186</b>