

## DOCTORAL THESIS

### Characterization and cytotoxicity of POPs and heavy metals in TSP and PM<sub>2.5</sub> from an electronic waste recycling site, compared with five urban sites in SE China

Deng, Wenjing

*Date of Award:*  
2007

[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

**Characterization and Cytotoxicity of POPs and Heavy  
Metals in TSP and PM<sub>2.5</sub> from an Electronic Waste  
Recycling Site, Compared with Five Urban Sites in SE  
China**

**DENG Wen Jing**

**A thesis submitted in partial fulfillment of the requirements**

**for the degree of**

**Doctor of Philosophy**

**Principal Supervisor: Prof. WONG Ming Hung**

**Hong Kong Baptist University**

**July 2007**

## ABSTRACT

This study aims to investigate characteristics of elements, heavy metals / metalloids (Cd, Cr, Cu, Pb, Zn, Mn, Ni, As), persistent organic pollutants (PAHs, PBDEs, PCDD/Fs) in the air from an electronic-waste recycling site and other five urban sites of Guangzhou and Hong Kong in South China, and also the cytotoxicity of air particles on human health.

Air samples of total suspended particles (TSP), and particles with aerodynamic diameter smaller than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) were collected simultaneously at Guiyu (an e-waste recycling site), two urban sites in Guangzhou (Li Wan, Tian He) and three urban sites in Hong Kong (Yuen Long, Tsuen Wan, Hok Tsui) in summer (from 16 August to 17 September 2004) and winter (from 1 February to 7 March 2005). The total concentration of  $\text{PM}_{2.5}$  ranked in the order of two urban sites in Guangzhou (LW and TH) ( $52.8\text{-}76.6 \mu\text{g m}^{-3}$ ) > e-waste site (GY) ( $50.5 \mu\text{g m}^{-3}$ ) > two urban sites in Hong Kong (YL and TW) ( $44.0\text{-}49.6 \mu\text{g m}^{-3}$ ) > the background site in Hong Kong (HT) ( $31.5 \mu\text{g m}^{-3}$ ). The same order was found for TSP concentrations.

In terms of elemental species in the  $\text{PM}_{2.5}$ , Guiyu contained high S ( $3204 \text{ ng m}^{-3}$ ), Cl ( $1175 \text{ ng m}^{-3}$ ), Guangzhou contained high S ( $5434\text{-}7522 \text{ ng m}^{-3}$ ), K ( $1038\text{-}1555 \text{ ng m}^{-3}$ ), and Si ( $696\text{-}935 \text{ ng m}^{-3}$ ), while Hong Kong contained high S ( $4463\text{-}5086 \text{ ng m}^{-3}$ ).

Concentrations of Cr, Cu and Zn (especially Cr and Zn) in Guiyu in  $\text{PM}_{2.5}$  were 4-33 times higher than other Asian metropolitan cities, such as Tokyo, Shanghai, Ho Chi Ming, Taichung and Seoul. In general, the concentrations of heavy metals in both TSP and  $\text{PM}_{2.5}$  followed the order of  $[\text{Cr}] > [\text{Zn}] > [\text{Pb}] \approx [\text{Cu}] > [\text{Mn}] > [\text{Cd}] \approx [\text{Ni}] \approx [\text{As}]$ . There were

significant correlations between Cd, Cr, Cu, Pb, Zn, Mn concentrations in TSP and those in PM<sub>2.5</sub>, except Ni and As. In general, there were significant correlations between concentrations of individual contaminants in TSP with PM<sub>2.5</sub> (i.e. PAHs, Cd, Cr, Cu, Pb, Zn, Mn except Ni and As).

The total sum of 16 USEPA priority polycyclic aromatic hydrocarbons (PAHs) associated with TSP and PM<sub>2.5</sub> in Guiyu ranged from 40.0 to 347 and 22.7 to 263 ng m<sup>-3</sup>, respectively. Five-ring and six-ring PAHs accounted for 73% of total PAHs. The average concentration of BaP in Guiyu (8.85 in PM<sub>2.5</sub>, 15.4 ng m<sup>-3</sup> in TSP) was 2-20 times higher than other Asian cities, such as Guangzhou (1.89 ng m<sup>-3</sup> in TSP) and Hong Kong (0.59 ng m<sup>-3</sup> in TSP), Tehran (4.02 ng m<sup>-3</sup>), Delhi (4.99-9.56 ng m<sup>-3</sup>), Bombay (5.6 ng m<sup>-3</sup>), Tokyo (2.0-2.9 ng m<sup>-3</sup>), and Singapore.

Twenty-two polybrominated diphenyl ethers (PBDE) congeners (BDE-3, -7, -15, -17, -28, -49, -71, -47, -66, -77, -100, -119, -99, -85, -126, -154, -153, -138, -156, -184, -183, -191) in TSP and PM<sub>2.5</sub> were selected. The results showed that the monthly concentrations of the sum of 22 BDE congeners contained in TSP and PM<sub>2.5</sub> at Guiyu were 21.5 and 16.6 ng m<sup>-3</sup>, with 74.5 and 84.3%, contributed by nine congeners (BDE-28, -47, -66, -100, -99, -154, -153, -183 and -191 respectively). The two urban sites of Guangzhou and Tsuen Wan of Hong Kong had a similar congener pattern, but not Yuen Long and Hok Tsui of Hong Kong. The results also showed that mono-penta brominated congeners, which are more toxic, accounted for 79.4-95.6% of  $\Sigma_{22}$ PBDEs from all sites. All congeners tested in Guiyu were up to 58-691 times higher than the studied urban sites of the present study and more than 100 times higher than elsewhere (the continent of Europe and Asia, Canadian Arctic and Siberia).

Ambient air concentrations of the 17 polychlorinated dibenzo-p-dioxins /dibenzofurans (PCDD/Fs) which sampled simultaneously on September 10<sup>th</sup> 2004 in Guiyu, Guangzhou and Hong Kong were measured. The concentration of PCDD/Fs in Guiyu was 6521 fg/m<sup>3</sup>, which was 1.5 times of Guangzhou and 3.1 times of Hong Kong. Total TEQ of Guiyu, Guangzhou and Hong Kong air samples were 590, 202 and 137 fg I-TEQ/m<sup>3</sup>, respectively. The concentration of 2,3,7,8-TCDD in Guiyu was up to 54 fg/m<sup>3</sup>, which exceeded the whole year standard (30 fg/m<sup>3</sup>) of USA (Indiana, Kansas and Washington).

Thus Guiyu was ranked as the most polluted site in terms of PBDEs, PCDD/Fs, PAHs and heavy metals contents in TSP and PM<sub>2.5</sub> among all the studied sites of the present study. Cytotoxicity of the extract of TSP and PM<sub>2.5</sub> (ten 24 h samples collected ) against human promonocytic leukemia cell line U937 (ATCC 1593.2) was determined by MTT (3-(4,5-dimethylthiazol-2-yl) -2,5-diphenyltetrazolium bromide) cytotoxicity assay. The results showed that under the same concentrations of extract, PM<sub>2.5</sub> cytotoxicity was 2-4 times higher than TSP.

The higher concentrations of heavy metals and POPs in the air of Guiyu were due to heating or opening burning of electronic waste, while the air of other urban sites in Southeast China contained relatively high concentrations of heavy metals and POPs, resulted in high cytotoxicity.

# TABLE OF CONTENTS

<b>DECLARATION.....</b>	<b>i</b>
<b>ABSTRACT.....</b>	<b>ii</b>
<b>ACKNOWLEDGEMENTS .....</b>	<b>v</b>
<b>TABLE OF CONTENTS .....</b>	<b>vi</b>
<b>LIST OF TABLES .....</b>	<b>xi</b>
<b>LIST OF FIGURES .....</b>	<b>xiv</b>
<b>ABBREVIATIONS AND ACRONYMS.....</b>	<b>xvi</b>
<b>Chapter 1 General introduction .....</b>	<b>1</b>
1.1 E-waste.....	1
1.1.1 Environmental effects.....	3
1.1.2 Human health effects .....	4
1.2 Aerosol, TSP and PM <sub>2.5</sub> .....	4
1.2.1 Research of TSP and PM <sub>2.5</sub> .....	4
1.2.2 Sources of aerosols .....	5
1.2.3 Standards of TSP and PM.....	5
1.2.4 Aerosols and climate.....	6
1.2.5 Aerosols and human health effects .....	7
1.2.6 Toxicity tests and health risk assessments .....	9
1.3 Air pollution in Pearl River Delta Region (PRD), especially Guangzhou and Hong Kong.....	10
1.3.1 Air pollution in PRD.....	10
1.3.2 Air pollution in Hong Kong.....	12
1.4 Persistent Organic Pollutants (POPs).....	13
1.4.1 Information of POPs .....	13
1.4.2 Polycyclic aromatic hydrocarbons (PAHs).....	14

1.4.3 Polybrominated diphenyl ethers (PBDEs).....	17
1.4.4 Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) .....	19
1.5 Heavy metals.....	20
1.6 Objectives of this study.....	24
1.7 Contribution and significance of the present research .....	26
1.8 Framework .....	27

## **Chapter 2 Mass concentrations of TSP and PM<sub>2.5</sub> and characteristics of carbonaceous aerosol at Guiyu, Guangzhou and Hong Kong 29**

2.1 Introduction.....	29
2.2 Materials and Methods.....	31
2.2.1 Sampling sites .....	31
2.2.2 Sample collection.....	40
2.2.3 Filter measurements and quality control.....	40
2.2.4 OC/EC analytical procedure and quality control.....	42
2.3 Results and Discussion .....	43
2.3.1 Spatial variations of 24-h average concentration of TSP and PM <sub>2.5</sub> .....	43
2.3.2 Meteorological factors .....	56
2.3.3 Comparison of values obtained by Anderson hi-vol. samplers and Partisol 2000 samplers in Hong Kong.....	57
2.3.4 Elemental carbon (EC) and organic carbon (OC) in PM <sub>2.5</sub> at Guangzhou and Hong Kong .....	60
2.4 Conclusions.....	63

## **Chapter 3 Characterization of atmospheric elements in PM<sub>2.5</sub> generated from an e-waste recycling site and urban sites in South China 64**

3.1 Introduction.....	64
3.2 Sampling and experimental procedures .....	66
3.2.1 Sampling sites .....	66
3.2.2 Sample collection.....	66
3.2.3 Gravimetric analysis .....	69
3.2.4 Elemental analysis .....	69
3.3 Results and discussion .....	70

3.3.1 PM <sub>2.5</sub> concentrations .....	70
3.3.2 Element concentrations .....	74
3.3.3 Sources of elements .....	76
3.3.3.1 Enrichment factor .....	76
3.3.3.2 Factor analysis .....	80
3.4 Conclusions .....	83

**Chapter 4 Characterization of atmospheric heavy metals in TSP and PM<sub>2.5</sub> generated from an e-waste recycling site and urban environment in South China ..... 84**

4.1 Introduction .....	84
4.1 Method and Materials .....	86
4.2.1 Sample sites .....	86
4.2.2 Digestion and analysis of heavy metals .....	86
4.3 Results and discussions .....	87
4.3.1 Heavy metals/metalloid in Guiyu .....	87
4.3.2 Heavy metals in Guangzhou and Hong Kong .....	92
4.4 Conclusion .....	95

**Chapter 5 Particulate associated PAHs in Guiyu and five urban environments of Guangzhou and Hong Kong ..... 96**

5.1 Introduction .....	96
5.2 Materials and methods .....	99
5.2.1 Sampling sites .....	99
5.2.2 Extraction and analysis of PAHs .....	99
5.3 Results and discussions .....	101
5.3.1 Size distributions in PAHs concentrations in aerosols .....	101
5.3.2 Spatial and seasonal variations of PAHs in aerosols at five sites of Guangzhou and Hong Kong .....	109
5.3.3 Benzo(a)pyrene (BaP) .....	114
5.3.4 Potential sources of PAHs .....	116
5.4 Conclusions .....	120



**Chapter 6 Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China ..... 121**

6.1 Introduction.....	121
6.2 Methods.....	124
6.2.1 Sampling sites.....	124
6.2.2 Extraction, clean-up and GC/MS analysis.....	124
6.3 Results and discussion .....	126
6.3.1 Concentrations of PBDEs in the air of Guiyu, Hong Kong and Guangzhou .....	126
6.3.2 Congener distribution patterns of PBDEs in air of Guiyu, Hong Kong and Guangzhou .....	129
6.3.3 Comparison of congener distribution patterns and concentrations of PBDEs in TSP and PM <sub>2.5</sub> between Guiyu and other studies.....	130
6.3.4 Implications for human exposure via inhalation.....	136
6.4 Conclusions.....	138

**Chapter 7 Study of PCDD/Fs in the atmosphere of South China..... 139**

7.1 Introduction.....	139
7.2 Methodology.....	142
7.2.1 Sampling.....	142
7.2.2 Laboratory analysis and QA/QC.....	144
7.2.3 Calculation of toxic equivalents (TEQs) .....	145
7.3 Results and discussions.....	148
7.3.1 Spatial variation of PCDD/Fs in South China .....	148
7.3.2 Seasonal variation of PCDD/Fs in Guangzhou and Hong Kong.....	149
7.3.3 Profiles of PCDD/PCDFs homologues in air .....	153
7.4.5 Health impact assessment based on PCDD/Fs in the air of south China	160
7.4 Conclusions.....	162

**Chapter 8 Cytotoxicity of PM<sub>2.5</sub> and TSP ambient air pollutants assessed by MTT and Comet assays ..... 163**

8.1 Introduction.....	163
-----------------------	-----

8.2 Experimental .....	165
8.2.1 Aerosol sample collection and preparation.....	165
8.2.2 Sample preparation .....	165
8.2.3 Cell lines and culture conditions.....	166
8.2.4 MTT cell proliferation assay.....	166
8.2.5 Comet assay .....	167
8.3 Results and discussion .....	168
8.3.1 Comparison of cytotoxicity of DMSO fractions of TSP and PM <sub>2.5</sub> in U937 cells assessed by MTT assay.....	168
8.3.2 DNA-damage potential of the SEOC in TSP and PM <sub>2.5</sub> .....	177
8.4 Conclusions.....	178
<b>Chapter 9 General discussion and conclusions.....</b>	<b>180</b>
9.1 Guiyu – the electronic waste site .....	180
9.2 Concentrations and distribution of elements, heavy metals/ metalloid, PBDEs, PCDD/Fs and PAHs in the air of Guiyu .....	181
9.2.1 Forty common elements.....	182
9.2.2 Eight toxic heavy metals/metalloid.....	182
9.2.3 Air PAHs.....	183
9.2.4 Air PBDEs .....	184
9.2.5 Air PCDD/Fs.....	185
9.3 Cytotoxicity.....	185
9.4 Conclusions.....	186
9.5 Limitations of the research.....	187
9.6 Future work.....	189
9.6.1 Aerosol modelling and multimedia multiple pathway exposure assessment .....	189
9.6.2 Cell line models to investigate toxicities due to inhalation exposure of contaminated air .....	190
<b>REFERENCES.....</b>	<b>191</b>
<b>CURRICULUM VITAE.....</b>	<b>225</b>