

DOCTORAL THESIS

Assessment of persistent toxic substances in China and Hong Kong with emphasis on uncontrolled recycling of e-waste

Leung, Anna Oi Wah

Date of Award:
2006

[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

**Assessment of Persistent Toxic Substances
in China and Hong Kong
with Emphasis on Uncontrolled Recycling of E-Waste**

LEUNG Oi Wah, Anna

**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

August 2006

ABSTRACT

This study involved the participation in a global initiative “Regionally Based Assessment of Persistent Toxic Substances” (RBA PTS) implemented by the United Nations Environment Programme (UNEP) focusing on the identification of sources, fates and impacts of persistent toxic substances (PTS) on environment and human health. For the Central and North East Asia Region, PCDD/Fs, PCBs, PAHs, DDTs and HCH were identified as high priority in terms of sources, especially PCDD/Fs and PAHs which are released into the environment as unintentional byproducts of manufacturing and combustion processes. The open burning of waste, in particular uncontrolled recycling activities involving e-waste, became a clear concern in contributing toxic PTS into the environment. This issue led to the investigation of the concentrations and distribution of PTS and heavy metals in the environment of Guiyu, a small town in northeast Guangdong Province, China, intensely involved in the recycling of electronic waste.

Combusted residue and soil samples collected from Guiyu revealed that PBDE levels were highest in combusted residue of plastic cables and wires and plastic chips nearby a residential area (30000-97400 ng/g, dry wt), soils at an acid leaching site (2720-4250 ng/g, dry wt.), a printer roller dump site (593-2890 ng/g, dry wt.) and at a duck pond (263-604 ng/g, dry wt.). BDE-209 was the most dominant congener and accounted for 35-82% of the total PBDE concentrations among the study sites. The average concentration at the acid leaching site was approximately 638 times higher than the highest reported background concentration (i.e. 5.6 ng/g, UK woodland soil). PCDD/Fs concentrations were also highest at the acid leaching site (12500-89800 pg/g, 203-1096 pg WHO-TEQ/g, dry wt.) and in combusted residue (13500-25300 pg/g, 84.3-174 pg WHO-TEQ/g, dry wt.). The average 2,3,7,8-TCDD equivalent concentration at acid leaching site (506 pg WHO-TEQ/g) exceeded the Canadian soil guidelines by 127 times and the US EPA Region 9

risk-based criteria for the protection of humans by approximately three times. In general, there appeared to be relatively mild contamination by PAHs (<2 mg/kg) in Guiyu with higher levels at open burn sites (11 – 19 mg/kg).

A human health risk assessment using exposure factors based on US EPA's Exposure Factors Handbook indicated that of the three possible exposure pathways to PBDEs, PCDD/Fs and PAHs, namely soil ingestion, dermal absorption and inhalation of fugitive dust from soil, soil ingestion would account for 73-93% of the average daily intake. The maximum potential average dose of PCDD/Fs by a child via soil ingestion at the acid leaching site was calculated to exceed the upper bound of the WHO 1998 advisory for tolerable daily intake by 3.5 times, an indicated a high noncancer toxic health risk. Cancer risk for a child was estimated to be moderate (a 180 in a million chance of getting cancer if the lifetime average intake of PCDD/Fs from soil ingestion was 1.20 pg TEQ/kg-bw/day). Noncancer and cancer risks for adult were found to be low. Calculated hazard indices for the ingestion pathway of penta-, octa- and deca-BDEs and PAH compounds indicated minimal health risks.

Lead concentrations (average 110000 mg/kg) in dust from printed circuit board recycling workshops were 269-2426 times higher than the New Dutch List optimum value. The calculated hazard quotients (HQ) for child scenario dust ingestion exceeded the "safe" reference dose level by 753. For an adult, the HQ was 40.3; 19 times lower than that predicted for a child. Copper, Ni and Zn concentrations in dust also exceeded the New Dutch List optimum values by 31-994, 2-228, and 7-73 times, respectively.

The results of this study indicated that soil in some selected land uses were contaminated with PCDD/Fs, PBDEs and to a lesser extent to PAHs and that the open burning of e-waste was a hotspot for PCDD/Fs and PAHs. Exposure to PCDD/Fs via soil ingestion by children may cause toxic noncancer health effects. Dust from printed circuit

board workshops and from streets in the the printed circuit board recycling district of Guiyu contained highly elevated concentrations of heavy metals, in particular Pb and Cu, and have the potential to pose serious environmental and human health risks.

TABLE OF CONTENTS

Declaration	i
Abstract.....	ii
Acknowledgements	v
Table of Contents	vi
List of Tables	xv
List of Figures.....	xx
Abbreviations and Acronyms	xv

PART I GENERAL BACKGROUND

CHAPTER 1 GENERAL INTRODUCTION	1
1.1 What is E-Waste?.....	1
1.2 Problems and Concerns of E-Waste	1
1.3 Regulations Concerning E-Waste.....	4
1.3.1 Basel Convention - International Treaty on the Control of Export of Hazardous Wastes	4
1.3.2 New Directives on Electrical and Electronic Equipment	6
1.4 Persistent Toxic Substances.....	7
1.5 Global Initiatives to Control Persistent Toxic Substances.....	10
1.5.1 Stockholm Convention	10
1.5.2 Regionally Based Assessment of Persistent Toxic Substances (RBA PTS).....	10
1.6 Description of Selected PTS	12

1.6.1	Polychlorinated Dibenzo- <i>p</i> -dioxins and Dibenzofurans.....	12
1.6.2	Polychlorinated Biphenyls (PCBs)	13
1.6.3	Polycyclic Aromatic Hydrocarbons (PAHs).....	14
1.6.4	Polybrominated Diphenyl Ethers (PBDEs)	15
1.7	Heavy Metals	17
1.8	The Environmental Problems Derived by E-Waste Recycling Industries at Guiyu - a Case Study in China.....	21
1.9	Previous Studies of Guiyu	25
1.10	Human Exposure and Health Concerns	27
1.11	Risk Assessment	28
1.11.1	Average Daily Dose.....	30
1.11.2	Noncancer Toxic Risk	31
1.11.3	Cancer Risk.....	32
1.11.4	Qualitative Descriptions for Health Risks	33
1.11.5	Exposure Factors.....	33
1.12	Objectives of This Study.....	37
1.13	Contribution and Significance of the Present Research.....	38
1.14	Framework.....	39
CHAPTER 2 REGIONALLY BASED ASSESSMENT OF PERSISTENT TOXIC		
SUBSTANCES IN THE CENTRAL AND NORTH EAST ASIA REGION,		
WITH EMPHASIS ON CHINA AND HONG KONG.....41		
2.1	Introduction.....	41
2.2	Materials and Methods.....	43
2.2.1	Study Area	43
2.2.2	Data Collection and Processing	45

2.3	Results and Discussion	48
2.3.1	Prioritising PTS.....	48
2.3.2	Priority PTS in China and Hong Kong	56
2.3.2.1	PCDD/Fs.....	57
2.3.2.2	PAHs.....	61
2.3.3	Difficulties, Needs and Follow-Up Work.....	63
2.3.4	Capacity Building	64
2.3.5	Recommendation and Future Activities	65
2.5	Conclusions.....	66
CHAPTER 3 PRELIMINARY ECOLOGICAL SURVEY OF GUIYU		68
3.1	Introduction.....	68
3.2	Materials and Methods.....	69
3.2.1	The Study Area	69
3.2.2	Sample Collection and Sample Preparation.....	70
3.2.3	Sample Analyses.....	70
3.2.3.1	PAHs.....	70
3.2.3.2	PCBs.....	74
3.2.3.3	PBDEs.....	74
3.2.3.4	Heavy Metals.....	75
3.3	Results and Discussion	75
3.3.1	PAHs.....	75
3.3.1.1	Sediment	75
3.3.1.2	Soil.....	79
3.3.2	PCBs	82

3.3.2.1	Sediment.....	85
3.3.2.2	Soil.....	86
3.3.3	PBDEs.....	87
3.3.4	Correlation Analyses.....	90
3.3.5	Heavy Metals	90
3.4	Conclusion	92

PART II SPATIAL DISTRIBUTION OF PTS IN DIFFERENT ENVIRONMENTAL COMPARTMENTS AND RISK ASSESSMENT

CHAPTER 4	SPATIAL DISTRIBUTION OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN SOIL AND COMBUSTED RESIDUE AND RISK ASSESSMENT.....	93
4.1	Introduction.....	93
4.2	Materials and Methods.....	95
4.2.1	The Study Area	95
4.2.2	Sample Collection and Sample Preparation.....	98
4.2.3	Measurement of PBDEs.....	98
4.2.4	Risk Assessment	99
4.3	Results and Discussion	99
4.3.1	Total PBDE Concentrations in Soil and Combusted Residue	99
4.3.2	Homologue and Individual PBDE Congener Concentrations	100
4.3.3	Investigation of Commercial/Technical Formulation Profiles at E-Waste Sites	104
4.3.4	Global Comparison of PBDE Levels in Soil and Combusted Residue.....	109
4.3.4.1	Background Levels and Non E-Waste Sites.....	109

4.3.4.2	E-Waste Sites.....	110
4.3.5	Risk Assessment.....	113
4.3.5.1	Soil Ingestion.....	115
4.3.5.2	Dermal Exposure.....	119
4.3.5.3	Inhalation.....	120
4.4	Conclusion.....	120
CHAPTER 5 SPATIAL DISTRIBUTION OF POLYCHLORINATED DIBENZO-<i>P</i>-		
DIOXINS AND DIBENZOFURANS (PCDD/Fs) IN SOIL AND		
COMBUSTED RESIDUE AND RISK ASSESSMENT122		
5.1	Introduction.....	122
5.2	Materials and Methods.....	125
5.2.1	The Study Area.....	125
5.2.2	Sample Collection and Sample Preparation.....	125
5.2.3	Measurement of PCDD/Fs.....	125
5.2.4	Risk Assessment.....	126
5.3	Results and Discussion.....	126
5.3.1	Total PCDD/F Concentrations in Soil and Combusted Residue	126
5.3.2	Ratio of PCDFs to PCDDs.....	129
5.3.3	Homologue Profiles.....	130
5.3.4	Relative Extent of Contamination by PCDD/Fs at Sampling Sites	
	134
5.3.5	Risk Assessment.....	136
5.3.5.1	Soil Ingestion.....	136
5.3.5.2	Dermal Exposure.....	140
5.3.5.3	Inhalation.....	142

5.4 Conclusion	143
----------------------	-----

**CHAPTER 6 SPATIAL DISTRIBUTION OF POLYCYCLIC AROMATIC
HYDROCARBONS (PAHs) IN SOIL, SEDIMENT AND COMBUSTED
RESIDUE AND RISK ASSESSMENT144**

6.1 Introduction.....	144
6.2 Materials and Methods.....	147
6.2.1 The Study Area	147
6.2.2 Sample Collection and Sample Preparation.....	147
6.2.3 Chemical Analyses	151
6.2.4 Risk Assessment	151
6.3 Results and Discussion	153
6.3.1 Total level of PAHs	153
6.3.1.1 Soil and Combusted Residue.....	153
6.3.1.2 Sediment.....	159
6.3.2 Carcinogenic PAHs.....	160
6.3.2.1 Soil and Combusted Residue.....	160
6.3.2.2 Sediment.....	163
6.3.3 PAH Profiles	163
6.3.3.1 Soil and Combusted Residue.....	163
6.3.3.2 Sediment.....	167
6.3.4 Sources of PAHs in Soil and Sediment	167
6.3.5 Risk Assessment	174
6.4 Conclusion	177

**PART III DETAILED ANALYSES OF DUST GENERATED FROM
PRINTED CIRCUIT BOARD RECYCLING WORKSHOPS AND RISK
ASSESSMENT**

**CHAPTER 7 PHYSIO-CHEMICAL ANALYSES OF DUST FROM PRINTED CIRCUIT
BOARD RECYCLING WORKSHOPS AND STREETS AND RISK
ASSESSMENT.....179**

7.1 Introduction..... 179

7.2 Materials and Methods..... 183

 7.2.1 The Study Area 183

 7.2.2 Sample Collection and Sample Preparation..... 188

 7.2.3 Analyses..... 188

 7.2.3.1 Laser Particle Size Analyses.....188

 7.2.3.2 Morphology of Dust Particles.....189

 7.2.3.3 *In Situ* Chemical Analyses of Dust.....189

 7.2.3.4 Analyses of Metals in Dust.....190

 7.2.3.5 Risk Assessment..... 190

7.3 Results and Discussion 191

 7.3.1 Laser Particle Size Analyses..... 191

 7.3.2 Morphology of Dust Particles..... 194

 7.3.3 *In Situ* Chemical Analyses of Dust..... 194

 7.3.4 Heavy Metal Concentrations in Dust..... 196

 7.3.4.1 Initial Study.....196

 7.3.4.2 Intensive Study.....202

 7.3.4.3 Correlations Between Heavy Metals in Dust.....214

 7.3.5 Risk Assessment 214

 7.3.5.1 Noncancer Toxic Risk.....217

7.3.5.2 Lifetime Cancer Risk.....	224
-----------------------------------	-----

PART IV GENERAL DISCUSSION AND CONCLUSIONS

CHAPTER 8 GENERAL DISCUSSION AND CONCLUSIONS	226
8.1 Introduction.....	226
8.2 Persistent Toxic Substances in Central and North East Asia.....	228
8.3 E-Waste.....	230
8.4 Concentrations and Distribution of PBDE, PCDD/Fs and PAHs in Environmental Media	231
8.5 Heavy Metals in Dust	233
8.6 Human Health Risk Assessment.....	233
8.6.1 Persistent Toxic Substances in Soil, Sediment and Combusted Residue.....	233
8.6.1.1 Average Daily Doses.....	234
8.6.1.2 Estimation of Toxic (Noncancer) Risk and Cancer Risk.....	237
8.6.2 Heavy Metals in Dust Resulting from Desoldering of Printed Circuit Boards	239
8.6.2.1 Estimation of Toxic (Noncancer) Risk and Cancer Risk.....	239
8.7 Exposure Pathways from E-Waste Pollution Sources to Human Receptors.....	243
8.8 Conclusions.....	245
8.9 Limitations of the Research	250
8.10 Future Work.....	251

8.10.1 Chemical Partitioning of Heavy Metals in Dust to Investigate Fate and Ecological Toxicity	251
8.10.2 Cell Line Models to Investigate Toxicities Due to Ingestion, Dermal and Inhalation Exposure of Contaminated Dust	252
8.10.3 Use of Mathematical Models to Conduct Multimedia Multiple Pathway Exposure Assessment.....	253
References.....	255
Appendix.....	282
Publications	284
Curriculum Vitae.....	287